

**Novel Bonding Motifs in
Low-valent Nickel Complexes:**
Dewar, Chatt, and Duncanson revisited

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Abstract

The classic Dewar-Chatt-Duncanson (DCD) model describes the bonding in transition metal-olefin complexes. In this framework, electron density can be bidirectionally relocated through binary frontier orbital interactions: σ donation and π back donation. Modern spectroscopic and theoretical methods have allowed us to probe the boundary of the framework of this bonding pattern, indicative of the existence of unique DCD model metal complex derivatives.

The introduction of this thesis is developed in Chapters 1 & 2, illustrating both the historical context for the development of the DCD model, and its utility in investigating catalyst transfer polycondensation with Ni(0) catalysts in polymer science.

Chapter 3 & 4 describe our initial studies using advanced synchrotron-based X-ray absorption spectroscopic methods to comprehensively re-examine this classic electronic structure and provide a framework for the interpretation of synchrotron spectroscopy of nickel complexes. These studies reveal the importance of ancillary ligands to enable strong metal-olefin bonding *via* ligand-induced backbonding.

Insights from these systematic studies afforded the opportunity to examine its relevance in catalytically-relevant systems. Chapter 5 reveals how these insights could be leveraged to stabilize previously elusive analogs of the previously proposed Ni(0) π intermediate in catalyst transfer polycondensation of polythiophenes. The dynamic behaviour of these π -intermediates along the delocalized polymer backbone, i.e. so-called ring-walking along the polymer chain, is explored both via experimental and computational methods.

An additional example of DCD-like bonding with unique properties is explored in Chapter 6, where a unique agostic interaction is identified and explained in some low-valent linear Ni(I) complexes, whose electronic structure provides a previously unreported mode of agostic bonding.

The application of advanced physical methods to classic problems in organometallic chemistry has afforded new insights into such systems, and revealed new motifs for metal-ligand bonding. These findings provide new opportunities to exploit these bonding motifs in

the design of novel organometallic species for catalysis and materials development.

Lay Summary

Understanding fundamental chemical bonding has always been an essential task of physical inorganic chemists, which dramatically helps elaborate the critical role that each chemical fragment plays in a complex. The Classic Dewar-Chat-Duncanson model is a successful strategy of addressing how a transition metal interacts with a pair of bonding electron and is also widely adopted in explaining numerous catalysts' electronic structures. This thesis expands its definition and unveils new motifs for chemical bonds, enabling us to predict the existence of more unique chemical structures, and rationally design and understand crucial catalysts' performance in chemical reactions.

Preface

Chapter 2 contains material that as a Review Article in *Dalton Transaction* (invited manuscript). All Schemes have been modified from the publishing version. I assembled the manuscript, with subsequent edits from Prof. Pierre Kennepohl.

Chapter 3 contains material that has been published as a peer-reviewed article in *Chemistry-A European Journal (Chem - A Eur J. 2019;25(20):5259-5268)*. The Ni(dtbpe) olefin complexes 3.1-3.12 were initially prepared by Dr. Addison Desnoyer, a previous graduate student in our collaborator Love group, who has synthesised all the experimental chemicals with the help of Weiling Chiu, another graduate student from Love group. All other experimental works, including the data collection and analysis of X-ray absorption Spectroscopy, performance of theoretical calculation were performed by me. Addison and I wrote the first draft for the manuscripts in this chapter, with subsequent edits being made by Prof. Pierre Kennepohl and Prof. Jennifer Love.

The spectroscopic work in Chapter 4 was an extension work of Chapter 3, which was fully accomplished by me. This work is published in *Faraday Discuss., 2019,220, 133-143*. This published manuscript was written in collaboration with my supervisor Pierre. Kennepohl. All the work in this chapter, including sample preparation, the XAS data collection and analysis were done by me. I wrote the first draft for the manuscripts in this chapter, with subsequent edits being made by Prof. Pierre Kennepohl.

The chemistry in Chapter 5 contains material that has been published in *Nat Commun. 2018;9(1):3866*. which was developed by me independently. Dr. Brian O. Patrick, the X-ray crystallographer in UBC Chemistry, performed the X-ray diffraction analyses and refined the structural data. All the rest experimental work, including chemical synthesis, characterisation, X-ray absorption spectrum collection and analysis, and DFT calculations were performed by me. I wrote the first draft for both manuscripts in this Chapter, with subsequent edits being made in collaboration with my supervisor Pierre Kennepohl.

The part on the experimental and theoretical work of Ni catalyst long-distance ring transfer is to be submitted. Two former undergrad volunteers Yao Zhang, Viola Kustario in the Kennepohl

group helped the synthetical work in this part. The experimental design and all related computational work were conducted by me. I wrote the draft for the part in this chapter, with subsequent edits being made by Prof. Pierre Kennepohl.

Chapter 6 reflects a collaboration with Dr. Dawson D. Beattie, a previous graduate student co-supervised by Prof. Jennifer Love and Prof. Laurel Schafer. This Chapter contains material that is to be submitted. The four Ni complex samples used in this Chapter were provided by Dr. Beattie. This work is designed and developed by my supervisor Prof. Kennepohl and me. All other experimental works, including the data collection and analysis of X-ray absorption Spectroscopy, performance of theoretical calculation were performed by me. I wrote the first draft for the manuscripts in this chapter, with subsequent edits being made by Prof. Pierre Kennepohl.

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List of Abbreviations

Å	angstrom (10^{-10} m)
AIM/QTAIM	(Quantum Theory of) Atoms in Molecules
AO	Atomic Orbital
COD	cyclooctadiene
CTP	Catalyst transfer polycondensation
Cy	cyclohexyl
d	doublet
D	deuterium
d ¹⁰	10 d orbital electron electronic configuration
DCD	Dewar-Chart-Duncanson
Dcpe	1,2-Bis(dicyclohexylphosphino)ethane
depe	1,2-Bis(diethylphosphino)ethane
DFT	Density Functional Theory
Dippe	1,2-Bis(diisopropylphosphino)ethane
Dmpe	1,2-Bis(dimethylphosphino)ethane
Dppe	1,2-Bis(diphenylphosphino)ethane
Edisp	Disproportionation Energy
IR	Infra-red
Jpp	NMR P, P coupling constants
kJ	kilojoule
MO	Molecular Orbital
NBO	Natural Bonding Orbitals
NHC	N-heterocyclic carbene
$Ni_{3d \leftarrow 1s}$	1s to 3d electronic transition
NMLO	Natural localized molecular orbitals
NMR	Nuclear Magnetic Resonance
OA	Oxidative Addition
RE	Reductive elimination
RW	Ring Walking
TD-DFT	Time-Dependant Density Functional Theory
TM	Transmetalation
XAS	X-ray absorption spectrum
XES	X-ray emission spectrum

XPS	X-ray photoelectron spectroscopy
δ	chemical shift
$\Delta G^\ddagger$	Gibbs free energy of activation
π^*	π antibonding orbital
∇^2	Laplacian of the DFT-derived electron density

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Dedication

To Liam. S. Sklar,

Nice to meet you, the girl makes joys and thrill knock on my door.

有你生活变得更有趣。

Weiqing He

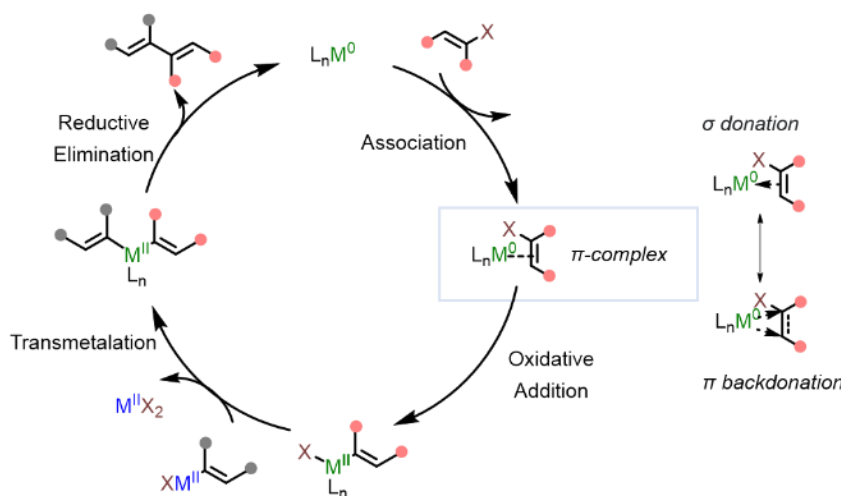
Chapter 1: Introduction (First Part) - Bond activation from low valent d¹⁰ metal complexes

1.1 Scientific Interests of depicting d¹⁰ transition metal σ and π complexes with DCD model

C-C bond established the most basic skeleton of organic chemistry, which directly contributes to the development of biochemistry, medicine and pharmacy science. The cross-coupling reaction is an efficient method of connecting two carbon atoms from two isolated organic compounds that has been in use for over a century.¹ When browsing the most successful catalysts for such reactions, we observe that d¹⁰ transition metals such as Pd⁰, Pt⁰, Ni⁰, and Cu^I are the most popular catalyst candidates in numerous cross-coupling reactions.^{2,3} From the early Cu(I)-catalyzed Cadiot-Chodkiewicz reaction⁴ to the Nobel prized Heck⁵, Negishi⁶, and Suzuki⁷ reactions, electron-rich low valent d¹⁰ metal in cross-coupling reaction can proceed the reaction in much milder conditions. A critical element for their success is the ability to perform both efficient reductive elimination (from the oxidized form) and oxidative addition (from the reduced form) with a reasonable balance between the energetics of these two processes. The nuanced electron density transfer between substrate and metal centre is a crucial necessity of achieving the rapid and smooth alteration between oxidation addition and reductive elimination in a cross-coupling cycle.⁸ The electron density transfer with molecular framework highly depends on the internal covalent interaction, which is the key topic in this Chapter.

Iterative cross-coupling reactions catalyzed by d¹⁰ metal complexes with large turnover numbers such as Kumada, Negishi, Stille and Suzuki cross-coupling⁹ have been widely applied into assembling π monomers into conjugated aromatic polymers which are widely used for photosensitive materials, semiconductor and organic sensor.¹⁰⁻¹² Late transition metals have also been shown to cleave stronger single bonds including dihydrogen bond and other carbon-heteroatom bonds (including C-H, C-S, C-O, C-N¹³). Studies have provided significant support for a generalized mechanistic model for sp²-sp² cross-coupling reaction, as shown in Scheme 1.1, that typically involves the initial binding of the π ligand to the metal centre. The resulting π complex

then rearranges to allow for oxidative addition. The bonding in these π complexes is normally discussed within the context of the Dewar-Chatt-Duncanson (DCD) model, which focuses on two interactions as the primary factors in the metal-ligand bond (Scheme 1.1). First, the π electron cloud can be used to form a σ bonding interaction with an appropriate (empty) orbital on the metal. Second, π backdonation can occur from a filled metal orbital into the ligand π^* orbital. This model successfully explains the formation of this unique bonding pattern and the electron transfer process, which are manifesting a profound chemical meaning of designing new catalysts by adjusting the relative capacity of bonding cleavage through late transition metal, mostly, d^{10} transition metal.



Scheme 1.1 A general mechanism of cross-coupling reaction with the involvement of a π -complex intermediate.

Reactive rates can be improved by enhancing the cleavage capacity by tuning the ancillary ligand.¹⁴ Stable reaction intermediates can be observed to reveal more reaction mechanism details when the cleavage process is decelerated.¹⁵ Most importantly, when a targeting carbon-heteroatom bond cleavage process gets dramatically promoted over others in a multiple carbon-heteroatom bond system, regioselective chemical transformation can be achieved¹⁶. Therefore, this thesis will focus on discussing some new knowledge of DCD model through modern theoretical and spectroscopic approaches, and its connection with related chemical transformation.

1.2 Origin of current bonding models for π complexes

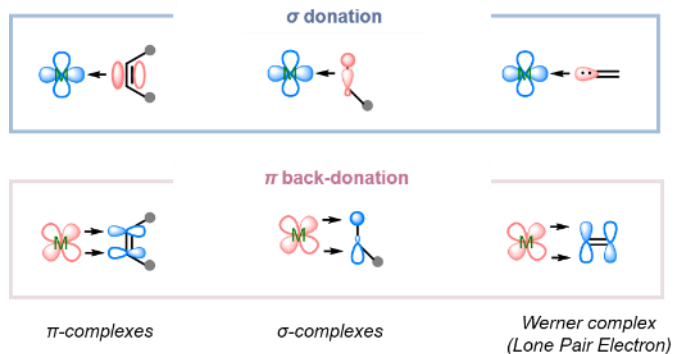
The first transition metal – olefin π -complex $K[PtCl_3(C_2H_4)] \cdot H_2O$ was found and named *Zeise salt* in 1831.¹⁷ Lewis theory claimed that a dative bond was formed through the donation of nonbonding lone pair electron from ligand to the metal at 1920. *Chatt* and *Duncanson* and their coworkers applied this idea into the π electrons of unsaturated ligands to give the first valence bond description of the electronic structure of this metal – olefin π -complex. Meanwhile, *Dewar* developed the first molecular orbital model based on a $Ag(I)$ -ethylene complex to show how the frontier orbitals of metal and ethylene with same symmetry interact. This metal olefin π -complex model is, therefore, established as the prototype of the standard DCD model we learn today. Transition metal olefin π -complexes were later ubiquitously found as intermediates in numerous indispensable chemical transformations such as hydroformylation¹⁸, olefin metathesis¹⁹, and polymerization of olefins²⁰. Very quickly, structural determined organometallic metal π -olefin complexes supported the tenets of the DCD model. Each of these complexes can all be described with similar electronic patterns having σ donation from the $C=C$ alkene π bonding orbital to an empty transition metal d orbital with correct symmetry, and π -back donation from an occupied metal d orbital to the empty antibonding $\pi^*(C=C)$ orbital. This binary bonding pattern is, therefore, treated as the most significant feature of the DCD model.

Complementary to the prevalent π complexes, the first σ complex, wherein a σ -bonding electron pair is involved as the donor, was identified in 1979 from dihydrogen binding to a metal.²¹ Prior to this discovery, σ complexes had been postulated as unstable intermediates with very short lifetimes or transition states. By analogy to what was proposed in π complexes, σ complexes were predicted to show similar binary interaction pattern by donating its σ bonding electron pair to the empty metal orbital and accepting the metal d electron by its σ^* antibonding orbital. Later, people realized that independent σ -bonding electron pair could only activate the single bond without an ultimate cleavage, indicative of that π back donation is the decisive force to break a bond completely.^{21,22} Many stable complexes with σ bond interactions are therefore structurally reported, including several stable η^2-M-H_2 complexes that were mistakenly diagnosed before. There are two major categories of σ bond interactions: *σ complex* and *agostic interactions*. Complexes with an external ligand-binding solely through a σ bond to the metal are defined as *σ complexes*^{21,22} (mostly

metal-dihydrogen bond). Intramolecular σ bond interactions from a ligand already tethered to the metal are known as agostic complexes.²³ The agostic interaction electron donor is often the electron pair of covalent σ bond such as C-H, Si-H, B-H bond(etc.).

Many recent electronic investigations suggested the coordinate bonding of Werner complexes with small π acceptor molecule ligands such as CO, N_2 are also best described in a similar way to the DCD model.^{24,25} These small molecules can bind to the metal in an end-on form. Lone pair electron at either terminal of the small molecule can function as σ donor, and their π^* antibonding orbitals are accessible for accepting the π back-donation electrons from the metal. The robust multiple bonds of small molecules can, therefore, be activated through the π back-donation and further reduced into valuable small molecules (CH_3OH , NH_3) for industrial application.^{26,27}

π -complexes, σ -complexes and lone pair electron complexes (Werner complex) are distinguished by the electron pair source of σ donation from the ligand (Scheme 1.2). They are all capable of receiving π back-donation by using empty antibonding orbitals with appropriate symmetry as π acceptors. Therefore, it is possible to extend the definition of DCD model to include a broader range of complexes beyond the narrow prototype of metal-olefin interactions originally defined by Dewar, Chatt and Duncanson, to include any covalent bonding system with the involvement of coexisting σ donation and π back donation. Based on this generalized definition, more unique derivatives have been explored, and their electronic and structural variation are well-explained within the framework of the DCD model.

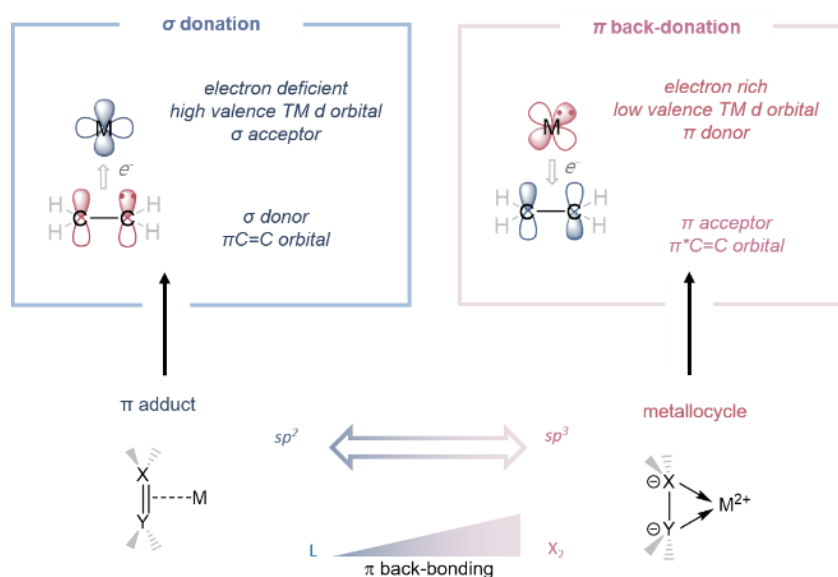


Scheme 1.2 Three categories of DCD model: π -complexes, σ -complexes and lone pair electron complexes (Werner complex).

1.3 Unique DCD Model derivatives in d^{10} π complexes

As discussed above, the DCD model was first introduced to explain the electronic and structural change of a π substrate when it is side-on bound to a transition metal. Within this context, the electron density is transferred through both ligand-to-metal σ donation and metal-to-ligand π back-donation. These interactions should weaken the π bond of the π substrate both from loss of electron density from $\pi(\text{C}=\text{C})$ bonding orbital through σ donation and an increase of electron density in $\pi^*(\text{C}=\text{C})$ antibonding orbital. A weakening of the $\text{C}=\text{C}$ bond leads to concurrent lengthening of the bond and an increase in the formal p -character in the carbon atom ($sp^2 \rightarrow sp^3$).

Depending on the weights of either interaction, π complexes can be described as either π -adducts or metallacycles (Scheme 1.3). Late metal π complexes are expected to typically behave as π -adducts due to the greater electronegativity of the metal leading to greater σ donation character relative to π back-donation. By contrast, early transition metals are can more easily donate electron density via π back-donation, leading to a metallacycle form. However, these general guidelines also strongly depend on the oxidation state of the metal involved. For example, - π complexes of electron-rich low valent late d^{10} transition metal no longer provide a suitable low-lying σ acceptor orbital. In addition, the d^{10} metal centre is poised for is now much easier to be transferred to the substrate through π back-donation.



Scheme 1.3 The binary bonding interaction motif of DCD model and the two extreme electronic structures π adduct and metallocycle.

In the last decades, a wide range of π complexes have been synthesized, isolated, and characterized – leading for broad diversity in the types of complexes to be explored and electronically studied. They are all following the general concept that chemical binding is driven by *some combination of σ donation and π back-donation*. Still, the final electronic structures can be described quite differently. A focus is placed on d^{10} metal complexes given that these are commonly used in a range of important chemical reactions.

1.3.1 Inorganic olefin complexes

The first example of unique derivatives of the DCD model is non-symmetric isoelectronic inorganic analogs of alkene d^{10} metal complexes, which were expected to have similar properties to the alkene parent complexes. In 2012, Bourissou and coworkers confirmed this assumption by the discovery of a side-on type coordination bond between Platinum and σ -phosphinoboranes $R_2PB(C_6F_5)_2$.²⁸ DFT calculations support a bonding scheme similar to the traditional DCD model. However, pronounced bonding asymmetry is observed through a substantial σ donation from electron-rich

A. Bourissou's work 2012

$R = \text{Cy, } t\text{-Bu}$

B. Dries' work 2019

$E = \text{N, P, As}$

1.3.2 CC triple and BB triple bond π complexes

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substrate has been reported by the Jones group.³⁰ Based on symmetry, a second *out-of-plane* empty π^* orbital is available in the alkyne substrate, which could allow for δ -type backdonation. Similarly, the Pt(0)-diborane complexes isolated by Braunschweig group in 2013 also exhibits the possibility of additional bonding, yet is much more fascinating.³¹ As before, both σ donation and π backdonation are possible – each of these interactions serving to weaken the B=B bond. However, an empty out-of-plane π bonding orbital is available, allowing for backdonation into this B=B π bonding orbital, which strengthens the B=B bond. Thus, a second π bond is formed due to the electron donation from the metal centre, leading a stronger interaction between two boron atoms.

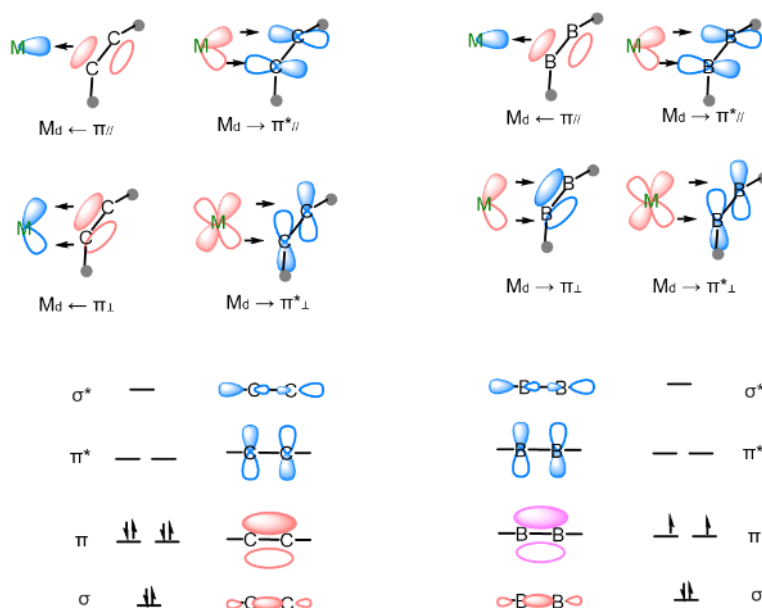


Figure 1.2 Valence-bond descriptions of π -alkyne and π diborene complexes.

1.4 Characterization of bonding in these systems

For many years, molecular vibrational spectroscopy was the most reliable option to probe electronic changes resulting from metal-ligand binding in π complexes if structural data were unavailable.³² Both σ

donation and π backdonation lead to the weakening of the π bond in the substrate; thus, an observable lowering of the vibrational frequency of the double bond (e.g. C=C) can be detected through either infrared (IR) or Raman spectroscopy. This shift correlates with a strengthening of the metal-ligand bond.³³ Vibrational spectroscopy is, therefore, a powerful indirect probe of bonding and electron delocalization in such complexes.

Nuclear magnetic resonance spectroscopy is another classic technique sensitive to the electronic properties in these complexes. The attached NMR active nuclear spins such as ^1H ³⁴ and ^{31}P nucleus³⁵ on the π substrate or ^{31}P nucleus⁹¹ on the ancillary ligand have been shown to be quite sensitive to differences in bonding, showing systematic variation in both chemical shifts and/or coupling constants when the electronic environment is altered. Solid-state NMR can also be used to probe magnetic anisotropy along the bonding direction in three-dimensional space, which has been used to probe the direct influence from the π backdonation.³⁸

However, IR and NMR provide indirect measures of changes in bonding and mostly reflect changes in the substrates upon binding. With the rapid development of computational methods, theoretical models have been used extensively to visualize the electronic structure of π complexes in an approachable manner. The Density-functional theory (DFT) is a computational quantum mechanical modelling method that helps investigate the electronic structure of many-atoms chemical system.³⁸ Within DFT theory, the electron density of each atom in the chemical system are described by its space-correlated functionals and modified with electronic interaction items.

Natural localized orbital methods including natural bond orbitals (NBO),³⁹ and natural localized molecular orbitals²⁴ (NLMO) allow for simple visualization of bonding interactions within the valence bond (VB) and molecular orbital (MO) frameworks. These localized molecular orbital theories reframe electron density localized on each atom and within each chemical bond, in a way that matches the intuitive bonding in natural Lewis structures for each molecular fragment. These natural localized orbital methods are distinguished in term of the weight of the localized electron density, trying to present a close description of the σ donation and π back donation between metal and π substrate based on Lewis Theory.

The growth of topological analysis on the total charge density as proposed by Bader and his powerful Atoms In Molecules (AIM) methodology⁴⁰ offers a different perspective on bonding contributions

in such complexes as exemplified by Sirsch and his coworker's work on Ni-ethylene by using AIM in 2006.⁴¹ Bond critical points (BCPs) are representing bonding paths between two adjacent atoms and thus were used to precisely identify covalent π backbonding. A ring critical point was also identified that corresponds with the σ donation from π bonding orbital to metal. There is, therefore, a good correlation between orbital methods and electron density distributions regarding the nature of chemical bonding within DCD model framework.

The frontier orbitals' interactions contribute the most to the covalent bonding and contribute to the formation of molecular orbitals, so does DCD model. X-ray based spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS),⁴² X-ray emission spectroscopy (XES),⁴³ and X-ray absorption spectroscopy (XAS)⁴⁴ all directly reflect the nature of the electronic behaviour, i.e. chemical bonding, by revealing the relative atomic contributions to their contributing molecular orbitals. These methods have been used to provide a more direct method of probing bonding interactions between metal surfaces and π absorbents in recent material science⁴². With assistance from Time-Dependent Density Functional Theory (TD-DFT),⁴⁴ a direct relationship between excited state spectroscopic data and computational results can be obtained.

1.5 Thesis Aims

The core of this thesis is presenting the application of a classic inorganic bonding concept, the Dewar-Chat-Duncanson model, in relatively complex systems – and evaluating its contributions in organometallic chemistry, polymer science and inorganic materials. The DCD model is a fundamental framework for describing metal-ligand bonding relationship for decades and is highly successful in describing numerous chemistry scenarios. However, its basic tenets can still be challenged with the development of more advanced spectroscopic methods, providing more detailed information than previously available. This thesis seeks to explore the validity and strength of some basic assumptions in organometallic chemistry while expanding our understanding of bonding in molecules that are of importance in a wide range of applications.

The aim of the thesis is three-fold:

1. To establish the use of XAS as a probe of metal pi complexes and related systems. In chapter 3 & 4, I provide evidence that the DCD model can be expanded and proved using advanced X-ray absorption spectroscopic methods. Indicative of that a new understanding of traditional inorganic concept needs positive support from physical and analytic techniques.
2. To provide evidence that details of bonding can be used to solve complicated catalytic questions. In Chapter 5, the synthesis and characterization of previously elusive Ni- π thiophene are described. The results provide a simple explanation for the possibility of living polymerization in Ni-catalyzed thiophene polymerization. This realization also shows the importance of dynamics in these Ni- π intermediates' and the possibility of "molecular walking" across a polymer chain is described and investigated.
3. To expand the classic definition of the DCD model. The basic tenets of the DCD bonding model are shown to be relevant in an unusual situation: for the description of bis-agostic complexes of Ni(I). In these complexes, an unusual agostic interaction is described where empty Ni 4p orbitals are responsible for σ acceptor and π acceptor for the first time in Chapter 7.

Chapter 2: Introduction (Second Part) - Ni(0) Catalyzed Catalyst Transfer Polymerization

2.1 Overview

Iterative Nickel-catalyzed cross-coupling reactions have inspired the development of an efficient and popular approach to the synthesis of aromatic polymers, which have increasing industrial applications. Catalyst transfer polycondensation (CTP) is a living chain growth method that is efficient for the synthesis of polythiophenes, among others. It has long been postulated that the mechanism for CTP involved the formation of Nickel- π polymer intermediates that could migrate across the polymer chain. Importantly, these proposed π complexes would need to form strong enough bonds to prevent dissociation from the polymer backbone, yet weak enough to allow migration across the π system to continue the polymerization process. The exact nature of these essential π intermediates had, as yet, not been determined. However, many indirect experimental and theoretical studies have indicated that they were feasible and that they could perform long-distance “*ring walking*” through the entire polymer. Via being educated with the electronic structure of a stable Ni-thiophene polymer analogy, polymer scientists realize sophisticated control over the living chain polymerization process to synthesize desired aromatic polymer is accessible. More importantly, the increasing curiosity of this catalyst’s “*ring walking*” is enlightening us to explore the possibility of designing a novel artificial molecule walker. The details of the catalytic process - and the predicted mobility of the Nickel along the polymer chain - suggest that a detailed understanding of the mechanism is required to improve the development of efficient methods for polymer synthesis using CTP. The fundamentals of CTP are described below, with a specific focus on the relevance and importance of Ni- π polymer complexes for efficient polymer control.

2.2 Introduction

Polymer materials play an indispensable role in our modern society. Numerous artificial and natural polymers pervade our lives from simple commodities such as plastic bags⁴⁵ to the most advanced

materials such as biomedical tissues,⁴⁶ reinforced aerospace materials,⁴⁷ and optoelectronic devices.⁴⁸ The development and application of polymer science have a considerable impact on ongoing developments in technology and improved quality of life. Polymers are well-organized assemblies of repeating chemical units, which manifest unique physical and chemical properties that differ from the discrete monomers from which they are made.⁴⁹ These properties can be highly dependent on the length of the polymer chains. The successful synthesis of polymers, therefore, requires the addition of repeating chemical units in a very systematic and controlled manner. Achieving this control depends strongly on the mechanism(s) of polymerization.⁵⁰

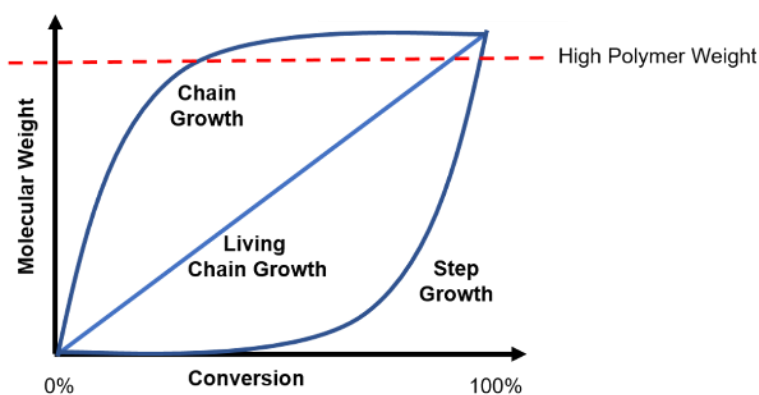


Figure 2.1 degree of polymerization as a function of monomer conversion for three different polymerization process

Fundamental discoveries in organic⁵¹ and organometallic⁵² chemical reactions stimulate the development of novel polymerization strategies. Chain-growth and step-growth are the most well-known mechanisms of polymerization.⁵³ Step-growth polymerization occurs when several different chemical reactions allow for the addition of either monomers or oligomer fragments of various lengths to a growing polymer chain. In such a situation, the reaction proceeds until the propagating species are quenched. Monomers exist through the entire reaction process of step-growth. However, a large amount of them is consumed at an early stage, leading a rapid reaction rate at the beginning but a slow increase of molecular weight of each polymer.

Chain-growth polymerization only allows the addition of one monomer length to the starting initiator through each propagation step, which offers a steady control over the increase of molecular weights. The reaction speed highly depends on initiators' concentration at the beginning and the initiation energy barrier (Figure. 2.2). However, due to accidental termination and chain transfer (The activity of growing polymer is transferred to another polymer chain), the conversion rate drops during chain growth. It needs a long reaction time to a high degree of conversion.¹⁰ Desirable polymer length and dispersity are the two factors of evaluating the final polymer products' quality. Dispersity in polymer science is a measure of the heterogeneity of length of polymers in a mixture. By comparing the polymerisation mechanism, the chain growth method offers a relatively tighter control of a narrow dispersity. However, chain growth's descending conversion rate makes it much harder to reach very high polymer length and maintain a narrow dispersity.

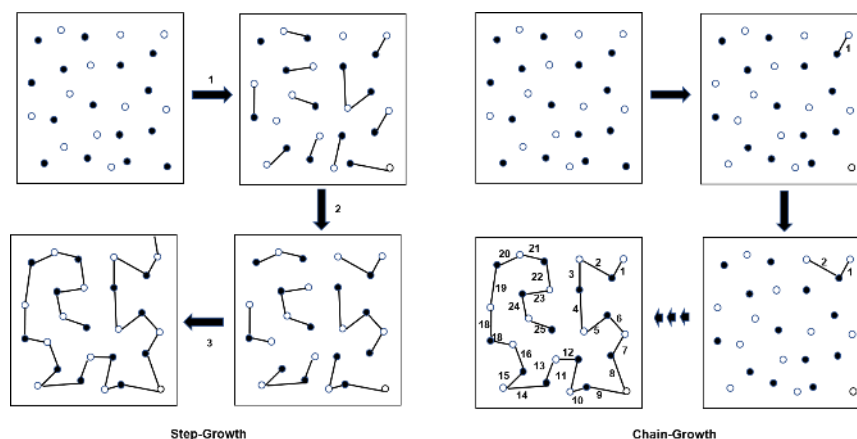


Figure 2.2 Illustration of the mechanistic difference between step-growth polymerization and chain-growth polymerization.

Living chain-growth polymerization is a form of chain growth polymerization where a growing polymer chain cannot terminate on its own. By prohibiting the unwanted chain termination and chain transfer reaction and increasing the chain initiation rate, the living chain growth could guarantee that the polymer chains grow at a constant rate. Living chain-growth provides complete control over the polymerization process, containing the three steps of chain growth-

initiation, propagation and termination. In this situation, the number of growing polymer chains is defined by the initial number of initiating species, and the only process that can occur is an extension of these chains. In this manner, the emerging polymer chain remains “active” or “living” even when monomers are no longer available to extend the polymer chain. In a truly living system, adding more monomers will allow the polymer to continue growing. This strategy guarantees that scientists control the conversion of the individual polymer by the catalyst to monomer ratio and reaction time.⁵⁵ Living chain growth has been observed with d¹⁰ transition metal catalysts (Ni, Pd, Pt) in CTP. The term “catalyst transfer” denotes the fact that the metal catalyst must migrate (or transfer) along the polymer backbone during propagation to the next reactive site. So far, CTP is the most efficient strategy to synthesize aromatic polymers made of benzene and/or other aromatic heterocycles (thiophene,⁵⁶ furan⁵⁷, and selenophene⁵⁸). These polymers, especially the polythiophenes, are incredibly applicable in the uprising industrial needs of organic photosensitive materials⁵⁹ due to its thermal stability, rigid conformation, and controllable conductivity.^{10–12}

2.3 Proposed mechanism for CTP

Inspired by the d¹⁰ transition metal such as Ni, Pd, and Pt catalyzed sp²-sp² cross-coupling reactions (e.g., *Kumada*⁶⁰, *Stille*,⁶¹ *Suzuki*,⁶² *Negishi*⁶³ and *Heck*⁶⁴ couplings), the first attempts to synthesize polythiophenes using Ni catalysts and halo/Grignard monomers goes back to the work of Yamamoto⁶⁵ and Lin⁶⁶ in 1980. This polymerization strategy was long treated as a step-growth reaction until Yokozawa^{67–69} and McCullough⁷⁰ groups showed evidence that the polymerization shows linear correlations between the number-average molecular weight (Mn) and monomer conversion, a hallmark for living polymerization. Both groups proposed that CTP is composed of continuous iterative cross-coupling reaction cycles connected by a migratory “non-diffusive associated pair” of Ni(0) catalyst⁷¹ and polymer through propagation. There is significant support for this theory, including that (i) the growth of polymer chain is controlled by the monomer/catalyst ratio, (ii) the monomer will be unidirectionally added based on its sequence, and (iii) simple copolymers can be synthesized depending on monomer addition sequence.^{67–70} The most currently accepted CTP proposed mechanism results primarily from

the work of the McNeil group. The different stages of the proposed mechanism are discussed below using polythiophene synthesis as the example(Figure 2.3).

2.3.1 Initiation:

A Ni(II)X₂ complex (X= halide) coordinated with an ancillary ligand (usually a bisphosphine or NHC ligand) is converted into a Ni(II)di(thiophen-2-yl) complex via transmetallation of two monomers onto the metal centre, which can then undergo reductive elimination. The resulting Ni(0) species, described as a π -complex, is formed after the reductive elimination and remains bonded to the emerging organic π aromatic polymer. The Ni(0) fragment migrates to the more electron-deficient binding site adjacent to the C-X bond through isomerization, via “ring-walking”, followed by the cleavage of C-X bond through oxidative addition to generating an active polymer-metal(II)-halide intermediate.

2.3.2 Propagation:

The propagation step of CTP occurs through a complete catalytic cycle constituted by transmetalation (TM), reductive elimination (RE), ring walking (RW), and oxidative addition (OA). The existence of a π -complex ensures that the catalyst cannot dissociate from the polymer chain and start growing new chains. The mechanism illustrated an ideal situation where the loading catalyst amount is strictly controlling the average length of each polymer chain, as the number of growing polymers should be equal to the amount of catalyst, and all of CTP proceed simultaneously from the beginning.

2.3.3 Termination:

The Ni(II) polymer halide species are the crucial intermediates after oxidation addition in the catalytic circle when no more monomer is supplied in the solution. This complete polymerization can, therefore, be terminated with a quenching agent such as a strong acid to protonate the polymer, or a nucleophile can be used to replace the Ni(II) halide for terminal functionalization.

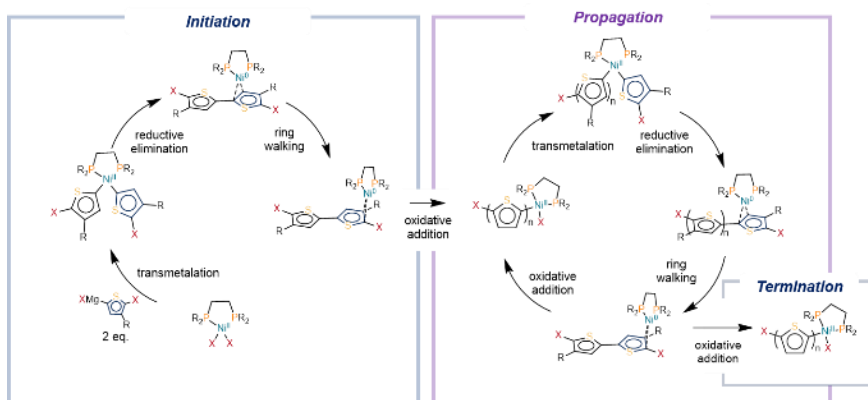


Figure 2.3 The state-of-the-art Ni-catalyzed catalyst transfer polycondensation mechanism proposed by McNeil and her coworkers. A diphosphine ligand is used as the ancillary ligand in this scheme.

2.3.4 Issues with the proposed mechanism

The overall proposed mechanism is appealing and provides a clear connection between polymerization and typical Ni-catalyzed sp^2 - sp^2 cross-coupling reactions. In principle, each of the necessary Ni(II) intermediates in cross-coupling correspond to resting states in Ni-catalyzed CTP⁷². The biggest assumption is the critical requirement for a strongly-bound Ni(0) π intermediate. This assumption has been quite controversial with very little evidence for such species in the literature.

It was argued that weak binding in such an intermediate would lead to dissociation and early termination to form shorter polymer chains. The unstable Ni(0) species might also perform chain transfer to start new polymer chains or even disturb other ongoing polymerization. Given that relevant species had not been observed, the specific bonding pattern of the proposed π -complex was also contested. Other forms of Ni coordination motif such as sulfur coordination⁶⁹ or stable Ni(II) inserted intermediate⁷³ could also serve as short-lived transient species between reductive elimination and oxidative addition. All of these concerns levied against the idealised CTP mechanism have found support to varying degrees from experimental findings. However, none of these potential alternatives could fully negate the possibility of stable π complexes as intermediates in CTP. As it turns out, appropriate selection of ancillary ligands and monomers can be used to show that these alternative options can be minimized as discussed in section 2.6.

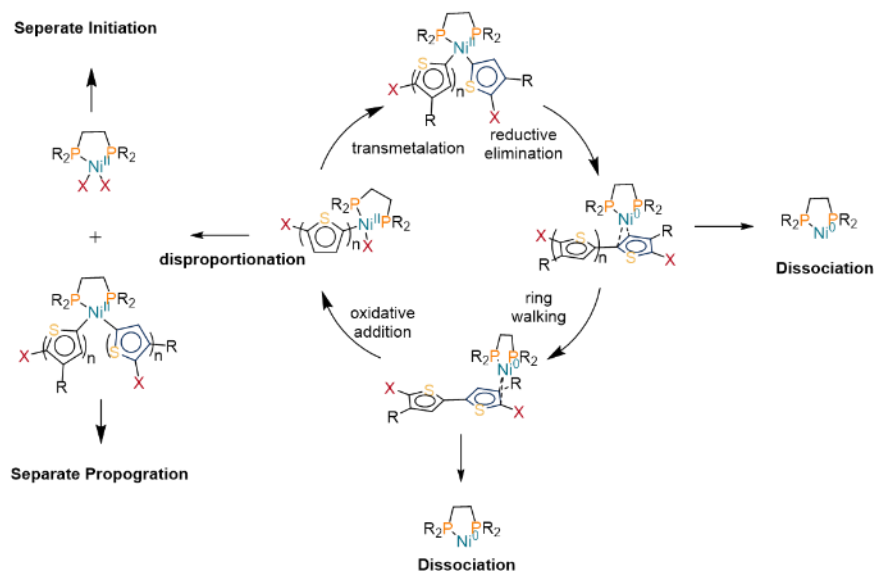


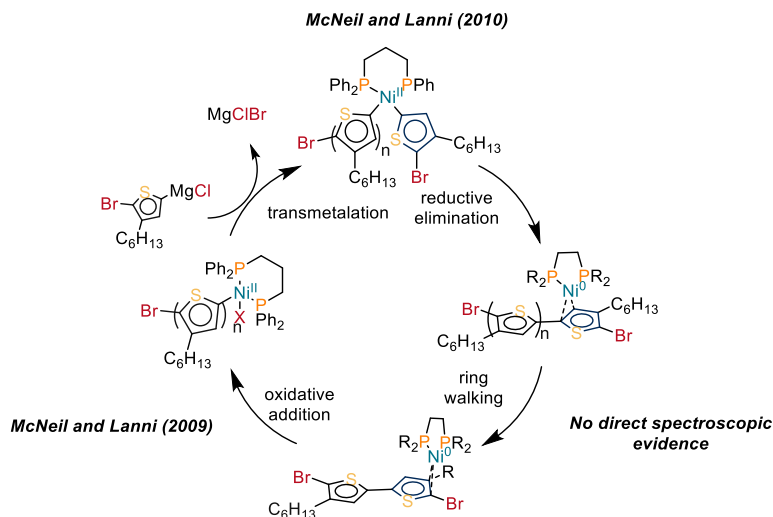
Figure 2.4 Controversial side reactions related to the proposed state-of-the-art Ni-catalyzed catalyst transfer polycondensation mechanism. Polymer termination routes by catalyst dissociation and chain disproportionation are indicated as off-cycle processes.

One last concern with regards to the postulated mechanism is the possibility of disproportionation when (aryl)Ni(II)X species are produced during initiation and propagation. Two (aryl)Ni(II)X species can exchange ligands through the disproportionation process, releasing a free Ni(II) dihalide complex into the solution.⁷⁴ This potential side reaction would lead to increase polydispersities as each of the newly produced Ni(II) species can initiate the formation of a new polymer chain.

2.4 Evidence of proposed Ni(II) Resting states.

Since 2009, McNeil group launched a series of attempts of identifying the crucial resting states related to Ni-catalyzed cross-coupling in the initiation, propagation, and termination during an undergoing Ni-catalyzed CTP of polythiophene. In 2009, McNeil and

Lanni provided evidence for Ni(II)-biaryl and Ni(II)-di(thiophen-2-yl) complexes as the resting states during polymerization of polyarene and polythiophene by ^{31}P NMR spectroscopy.⁷⁵ In 2011, they observed formation of Ni(II)-di(thiophen-2-yl) species after initiation, (polythiophen-2-yl)Ni(II)(thiophen-2-yl) species during propagation and the terminal species of (polythiophen-2-yl)Ni(II)Br.⁷⁶ The assignment of $^2J_{\text{PP}}$ coupling constant from the ancillary diphosphine ligand in ^{31}P NMR to different Ni(II) intermediates proved that a similar cross-coupling circle occurs during the initiation and propagation process of Ni-catalyzed CTP of polythiophene. Hitherto, Ni-catalyzed CTP is evidently supported as an iterative cross-coupling reaction. However, the remaining question of how each cross-coupling is continuously linked through the proposed Ni- π intermediate to guarantee a living chain process was still unresolved.⁵⁶ McNeil and Lanni suggested that an η^2 Ni-thiophene π complex must be formed upon reductive elimination based on the observation of analogous η^2 Ni-arene complexes.⁷⁷ This π complex could quickly migrate to the nearby reactive C-halogen site to proceed following oxidative addition⁷⁵. However, McNeil and her coworkers could not observe any Ni(0) π complexes due to their short lifetimes. McNeil and Bryan later added competitive agents in the reaction medium to show that the Ni catalyst successfully avoided loss from the ongoing polymer in 2013,⁷⁸ showing the importance of the intermediate without providing for evidence of its specific geometric or electronic structure. They further realized that slowing down oxidative addition would help in the observation of Ni(0) π complexes, and so they worked diligently to improve control over the rate-determining steps.^{72,79}



Scheme 2.1 Previous spectroscopic work conducted by McNeil group to confirm each Ni(II) species resting states.

2.5 Evidence of Ni π intermediate.

In addition to the pioneering work of McNeil and coworkers, additional evidence of the critical importance of the unidentified π intermediate was building. Several different research groups tackled this issue as well that importance of controlled ring-walking as the key for living chain growth in polythiophene synthesis.

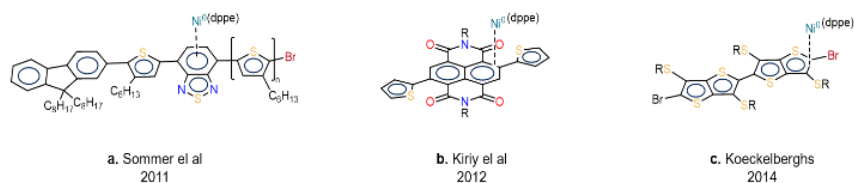
2.5.1 Small Molecule Studies isomerism in Ni thiophene complexes

Experimental evidence for Ni thiophene complexes came from the pioneering work of Jones and coworkers, whose studies focused on C-S bond cleavage for hydrodesulfurization of thiophenes and thiols in petroleum with late transition metals.⁸⁰ As early as 1999, they identified the propensity of d^{10} transition metals to cleave C-S bonds and reported on the specifics of the interactions of thiophene and its derivatives with both Ni(0) and Pt(0). They successfully synthesized a range of Ni and Pd catalyst precursors supported with diphosphine ligands such as $[(\text{dippe})\text{NiH}]_2$ ^{15,81} and $(\text{dippe})\text{Pd}(\text{alkyne})$ ⁸² which form active Ni(0)/Pd(0) catalysts for C-S bond cleavage with thiophenic

substrates. In 2008, DFT studies were used to propose that Pt(diphosphine) complexes can coordinate thiophene in an η^2 form similar to typical d^{10} transition metal olefin complexes through DFT calculation approach.⁸³ This same binding motif was also proposed for Ni(0) via DFT studies of a Ni-catalyzed isomerization. The Ni catalyst was found to migrate through an asymmetrical cyanothiophene substrate from C-S inserted κ^2 -S,C Ni(II) structure to the other side for a C-C bond cleavage. Both the η^2 and κ^1 S coordinate Ni(0) structures were proposed at this time. These computational results were used to assign various intermediates observed under low-temperature ^{31}P NMR by the Jones group, including the Ni- η^2 -thiophene. However, they also observed a more stable κ^2 -S,C Ni(II) intermediate, which supported McCullough's proposal that the formation of stable Ni(II) intermediates was preferred over potential Ni(0) π complexes.⁷³ Importantly, this C-S insertion has only been observed in a small molecule or the terminal thiophene unit of polythiophene with much less steric repulsion.

2.5.2 Trapped Ni(0) catalyst

Soon after the McNeil group postulated the existence of a π intermediate, Sommer and coworkers observed that Kumada-type polycondensation from the addition of 2-chloromagnesio-5-bromo-3-hexylthiophene to thiophene-benzothiadiazole-thiophene (TBT) terminated only after few reactive cycles. A Ni(0) catalyst was estimated still attached to the polymer with MALDI-mass and located at the starting TBT fragment with NMR study (Scheme 2.2a).⁸⁴ Kiriy *et al* also showed that a Ni catalyst could be trapped on an unreactive anion-radical naphthalene diimide monomers in 2012 (Scheme 2.2b). This Ni catalyst was confirmed as a reduced Ni(0) species by ^{31}P NMR and analyzed to be attached to the benzene ring supported by DFT calculation.⁸⁵ In 2014, Koeckelberghs and his coworker unsuccessfully attempted the polymerization of thieno[3,2-b]thiophene with Ni catalysts, yet were successful using Pd.⁸⁶ A Ni(0) π intermediate was observed in the crude reaction mixture with a large $^2J_{PP}$ coupling constant (62 Hz) in the in situ ^{31}P NMR measurement, indicative of that Ni catalyst was trapped on the thieno[3,2-b]thiophene (Scheme 2.2c). Each of these observations of trapped Ni(0) species with electron-deficient monomers were observed exclusively by NMR, without any additional information regarding the nature of the species.



Scheme 2.2 Previous reports of trapped Ni(0) catalyst during a proceeding CTP process.

2.5.3 Structural determined Ni(0) thiophene

Significant effort was placed on identifying and isolating well-defined transition metal -thiophene complexes in the quest for better understanding of hydrodesulfurization.⁸⁷ A large number of different structural motifs were observed for many transition metals, although no advances were made for d^{10} transition metal (Ni, Pd, Pt)⁸⁸ (Figure 2.5). The exact nature of Ni-thiophene π complexes thus remained a mystery until very recently. In Chapter 5 of this thesis, we report the successful isolation and characterization of η^2 -Ni(0)(bisphosphine)-thiophene complexes via careful steric and electronic control to prevent C-S insertion. The bonding in the η^2 -Ni(0)(bisphosphine) thiophene is best described as a 3c-4e bond (Figure 2.6), which allows major electron density donation directly from the electron-rich ancillary ligand to the π substrate. This electronic structure explicitly explained that an electron-rich ancillary ligand donor and electron-deficient monomer pair would help the formation of a stronger π interaction between Ni catalyst and the polymer.

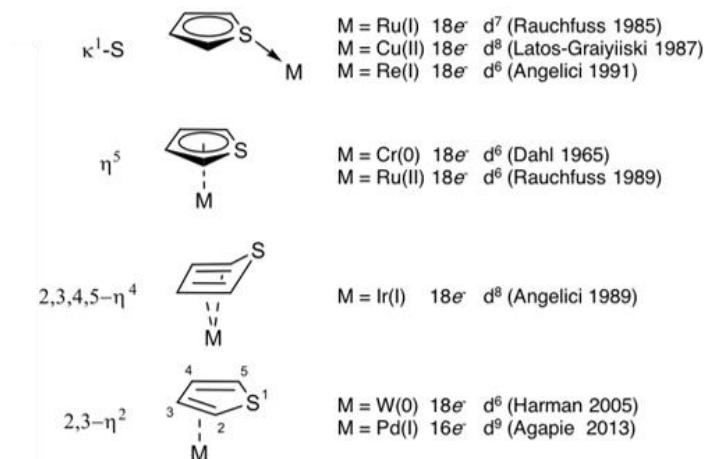


Figure 2.5 Selected examples of various transition metal-thiophene binding motifs (referred to Figure 5.1)

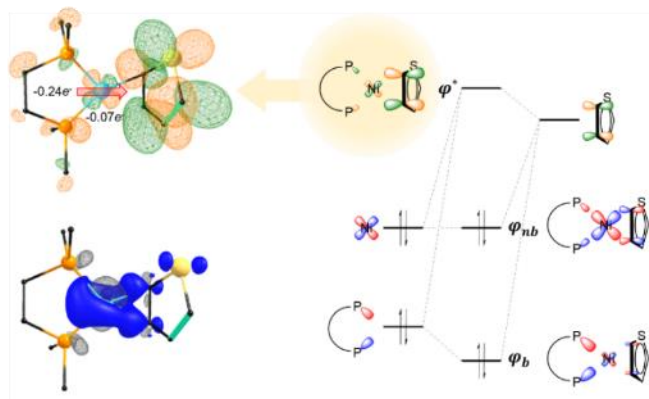
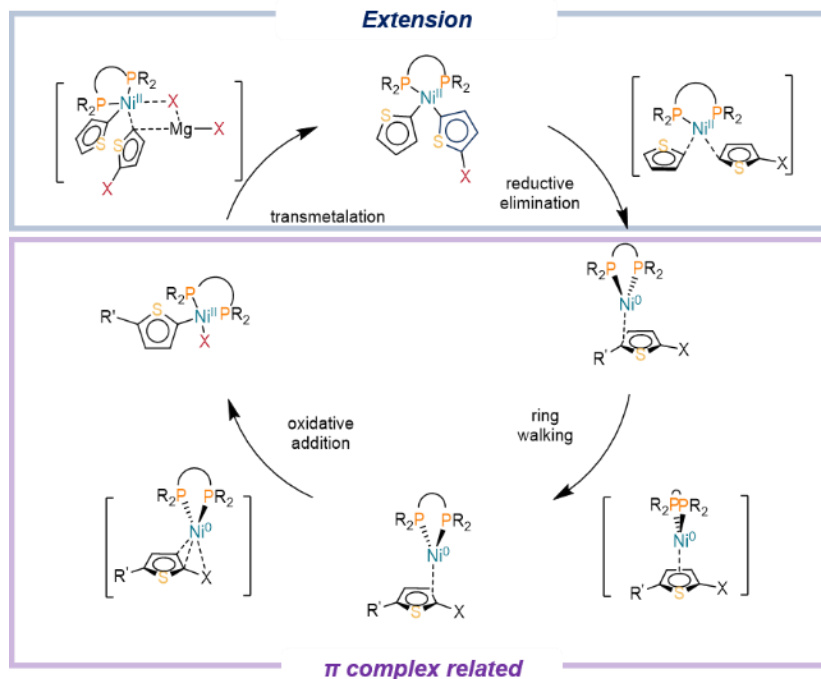


Figure 2.6 Dominant π -backbonding interaction between metal bisphosphine fragment and the thiophene ligand. The interaction is formally a three-centre four-electron interaction between the three molecular fragments: the diphosphine ligand, the metal centre, and the thiophene ligand (Referred to Figure 5.5).

2.5.4 Theoretical Study.

The $\text{Ni(0)}\text{-}\pi$ complex intermediate has an extremely short life during the initiation and propagation process due to a quick following

oxidation addition. Restricted by the acquisition time of ^{31}P NMR, a functioning π intermediate could not be captured during an undergoing CTP process and get structurally determined.⁸⁹ The structure information of Ni-thiophene π complex analogy was also not available until the Kennepohl group successfully synthesized the first Ni- π thiophene complexes at 2018. Therefore, more attention was placed in the theoretical calculation of understanding how the migratory process occurs at an early stage. η^2 Ni π complexes analogous to Ni arene π complexes^{77,90} or bonded to the S atom⁹¹ have been widely used as a reasonable model for building the theoretical geometry of Ni thiophene π complexes in DFT calculation.⁷³ The initial calculation was focusing on simulating the missing migratory process by depicting that a η^2 Ni(0) thiophene π intermediate was formed right after reductive elimination. The Ni(0) catalyst can jump across the thiophene through a η^4 bond transition state^{92,93} with low energy barrier, and this migration/ring walking was driven by the induction of a more electron-deficient binding site near the C-X group. The further calculation was conducted by Seferos group¹⁴ and the team of Mikami, Yokozawa and Uchiyama⁹⁴. Both of them reproduced a complete propagation catalytic cycle by successfully locating the transition states of a four-member ring transmetalation and oxidative addition,¹⁴ which enlightened more theoretical discussions on controlling the rate-determining step in the propagation process.



Scheme 2.3 Summary of previous theoretically structurally determined intermediates and transition states in a complete CTP propagation catalytic circle.

2.6 Considerations of CTP mechanism.

A major concern in the acceptance of the proposed CTP mechanism by McNeil is the stability of each intermediate during the catalyst transfer. Unstable Ni(II) species and Ni(0)- π intermediate can lead to uncontrolled chain transfer or chain termination, driving the catalytic process out of the track of living polymerization and produce polymers with large dispersity. The stability of these intermediates is, therefore, incredibly crucial in guaranteeing reliable control over the polymerization. Herein, we summarized the previous reports on avoiding unwanted chain transfer processes by keeping all the intermediates in reasonable stability through electronic and steric modification of ancillary ligand, monomers and metal centre.

2.6.1 Stability of Ni(II) species:

A major reason for the loss of Ni(II) species during CTP track is the propensity for Ni(II)(polymer)halide species to disproportionate into Ni(II)dihalides and Ni(II)di(polymer) complexes. Ni(II)dihalides can reenter the catalytic cycle by reinitiation, but control of polymer length is compromised. Therefore, these side reactions add polymer fragments of unpredictable length due to uncontrollable chain-coupling or separate chain growth, leading eventually to step-growth polymerization. Attempts to minimize disproportionation influence have focused on making the disproportion product either kinetically or thermodynamically unfavourable.

Disproportionation kinetically competes with rate-determining transmetalation or reductive elimination depending on the electronic environment of the catalyst⁹⁵ in the cross-coupling cycle. Numerous experiments have shown that alternation of metal-halide/halide in the monomer could dramatically speed up both initiation and transmetalation steps^{76,91,96}, outpacing the subsequent disproportionation. Similarly, a formation of highly reactive “turbo-Grignard” could also lower the transmetalation step's energy barrier to exclude disproportionation products.⁹⁷ On the other hand, Miyakoshi *et al.* showed that a low-temperature environment had a larger impact on reducing the activity of disproportionation than the transmetalation process, making the disproportionation no longer competitive.⁹⁸

In 2012, Lockin *et al.* calculated the relative thermodynamic energy cost of disproportionation E_{disp} with selected bisphosphine ligands with differing steric hindrance.⁷⁴ This study indicated that the computed E_{disp} could screen ancillary ligands which would increase the possibility of disproportionation. Although they confirmed that disproportionation could be avoided by a wise choice of bisphosphine ligands and guided by the ligands' electronic and steric properties, they failed to correlate the disproportionation energy cost to the steric hindrance of bisphosphine ligands represented by their cone angle and bite angle.

2.6.2 Stability of Ni(0)- π intermediate:

After determining that popular ancillary ligands such as 1,2-Bis(diphenylphosphino)ethane(dppe), and 1,2-Bis(dicyclohexylphosphino)ethane(dcpe) disfavoured

disproportionation⁷⁴, polymer scientists have shifted their attention to the stability of Ni(0)- π intermediates and their role in enabling living polymerization. These intermediates turn out to be essential to efficient CTP processes without loss of catalyst, and a controllable pace of polymer conversion based on the catalyst/monomer ratio.⁹⁹ In principle, the Ni(0) metal centre need only migrate one monomer unit distance to the adjacent C-X reactive site to enable rapid oxidative addition. Assumptions have been made based on two extreme scenarios: Ni (0) catalyst can either bind to the polymer strongly enough to make the competitive oxidative addition step no longer accessible or freely dissociate from the polymer's undergoing reactive side chain. Either of these extreme cases of Ni(0) species in terms of their stability will inevitably jeopardize the fluency of CTP.

Based on the recently elucidated electronic description of stable η^2 -Ni(0)(bisphosphine)-thiophene complexes (see Chapter 3), an electron-donating ancillary ligand and electron-deficient monomer pair would increase the affinity between the catalyst and the polymer through strong π -backbonding. This is consistent with the experimental fact that polymerization of electron-deficient monomers is extremely difficult,⁸⁴ as the Ni(0) catalyst would get trapped *via* strong affinity with the polymer and thus temper further reactivity. Another potential concern for trapping catalyst is the possibility of competitive reactive sites other than the C-X bond in the adjacent monomer unit that might compete with, and even quench the whole polymerization. Examples include C-S bonds, C-X bonds in other polymer locations, and any other potential electron-deficient functional groups along the polymer chain. Steric repulsion will limit C-S insertion of Ni catalysts from occurring within the polymer chain. However, the remote terminal C-S bond is sterically more accessible, making it significantly more vulnerable to insertion.^{15,82} Similar concerns exist from the equivalent C-X bond at the other terminus of the polymer as typical CTP strategies necessarily create an active C-X bond at each terminus. Therefore, if the catalyst has the potential of performing a long-distance migration without dissociating from the polymer, both C-S and C-X bonds could compete with the programmed oxidative addition step. This long-distance migration of Ni(0) catalyst – “ring walking” is further discussed in section 2.7.

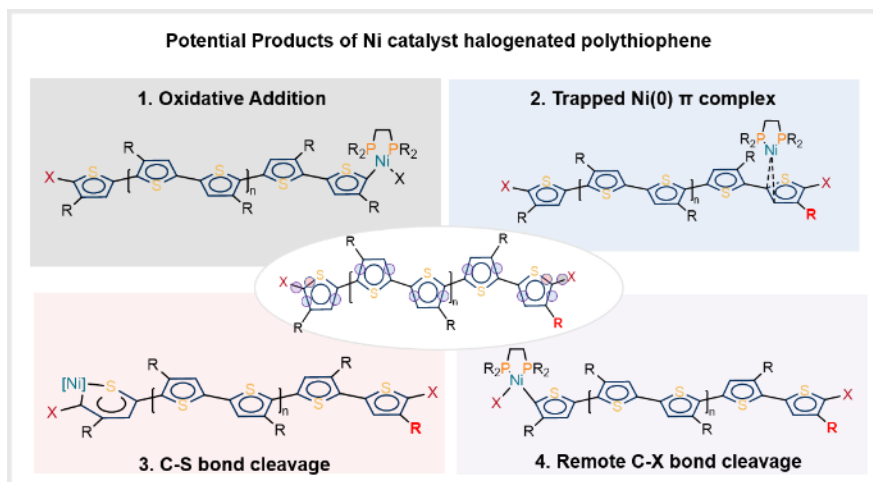
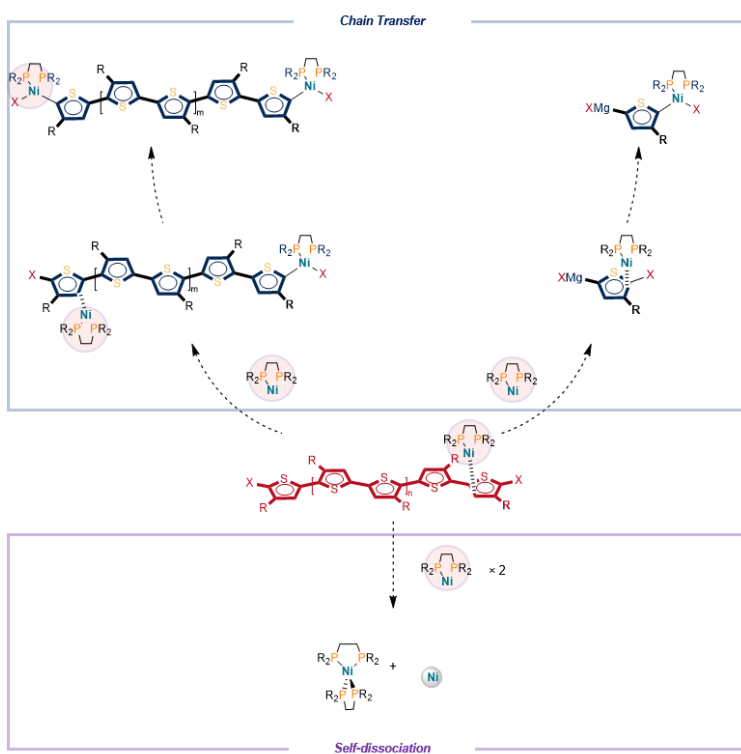


Figure 2.7 Potential side-reactions which will compete with the oxidative addition for cleaving the adjacent C-X bond (grey background), the branch alkyl-substituted of target activate unit is labelled in red.

Long-distance ring transfer increased explosion of vulnerable Ni(0) species and the risk of self-dissociation, which is another concern of the current CTP mechanism. The entropically favourable dissociation of the Ni(0) fragment must be counteracted by a comparable enthalpic stabilization provided by stronger affinity tuned by ancillary bisphosphine ligand. Self-dissociated Ni(0) fragment would entropically favour the following decomposition into tetraphosphine Ni(0) complexes coordinated two bis-phosphine ligands¹⁰⁰, which needs be avoided by large steric repulsion of bis-phosphine ligands. Therefore, a bulky electron-rich bis-phosphine ancillary ligand would be the top choice of maintaining the reactivity of Ni(0) intermediate. The biggest concern of a labile Ni(0) fragment would be its ability to jump from one polymer chain to another (or another monomer), thus allowing for chain transfer, intermolecular oxidative addition, and polymer control loss. Generally, two types of species could react with a free Ni(0) diphosphine complex: (i) unreacted Grignard/Halogen monomer, and/or an active polymer chain with an existing active Ni catalyst. The McNeil group has added highly concentrated competitive reactive oligomer or scavenger reagents to intercept such possible chain transfer processes. Besides, the nature of isolated Ni(0)-thiophene dimers indicate that the affinity of the second Ni(0) fragment is largely weakened by the other Ni catalyst.

Altogether, these studies clearly indicate that the kinetic behaviour of Ni(0) intermediates are tightly aligned with their electronic structure, which is controlled both by the details of the ancillary ligand and the nature of the monomer. The Dewar-Chatt-Duncanson model used to describe a transition metal - π complexes and carbon-heteroatom bond cleavage is particularly relevant for understanding the factors that affect reactivity which is relevant for the screening and design of effective Ni catalysts.



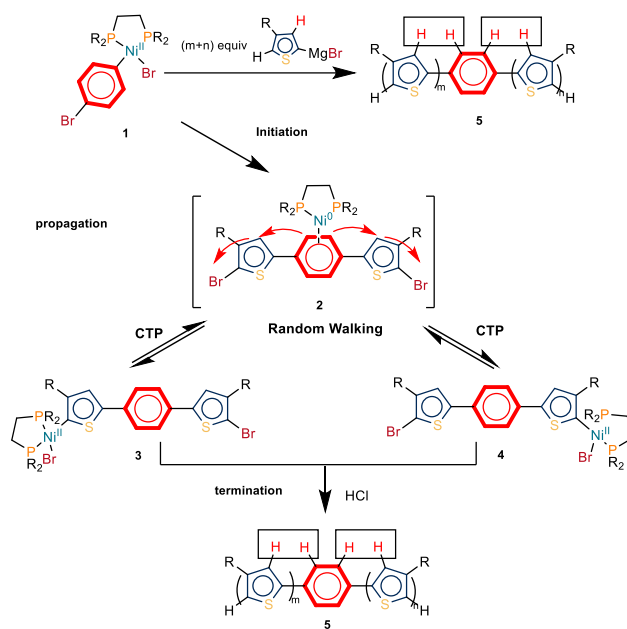
Scheme 2.4 Chain transfer and self-dissociation problem of an unstable Ni(0) fragment on polythiophene.

2.7 Ring Walking/Chain Walking

Traditionally, CTP processes are often initiated with a Ni(II)X₂ (X = Cl, Br, I) precursor⁹ that produces two coexisting active C-X bonds in one growing polymer chain. Immediately following the initial discovery of Ni-catalyzed CTP, McCullough and coworkers proposed

that the catalyst could allow for a long-distance ring walking/chain walking process based on an unusual observation. They found that regular Grignard reagents would difunctionalize both terminal C-X bonds when excess Grignard was added. McCullough group found that using unsaturated alkenyl and alkynyl Grignard reagents could monofunctional the terminal group to produce monocapped polythiophene, while phenyl Grignard reagents would difunctionalize both terminals of polythiophene. Therefore, a reduced Ni(0) catalyst was proposed to remain associated with the π polymer after the first functionalization. A long-distance ring walking was followed to activate the other remote terminal's C-X bond. However, unsaturated alkenyl and alkynyl could form a stable Ni(0) π complexes to trap the Ni(0) catalyst at one site (Scheme 2.4). This initial observation launched a journey of exploring the long-distance ring transfer despite a short ring transfer would much favour the unidirectional polymerization and guarantee the ideal CTP mechanism.

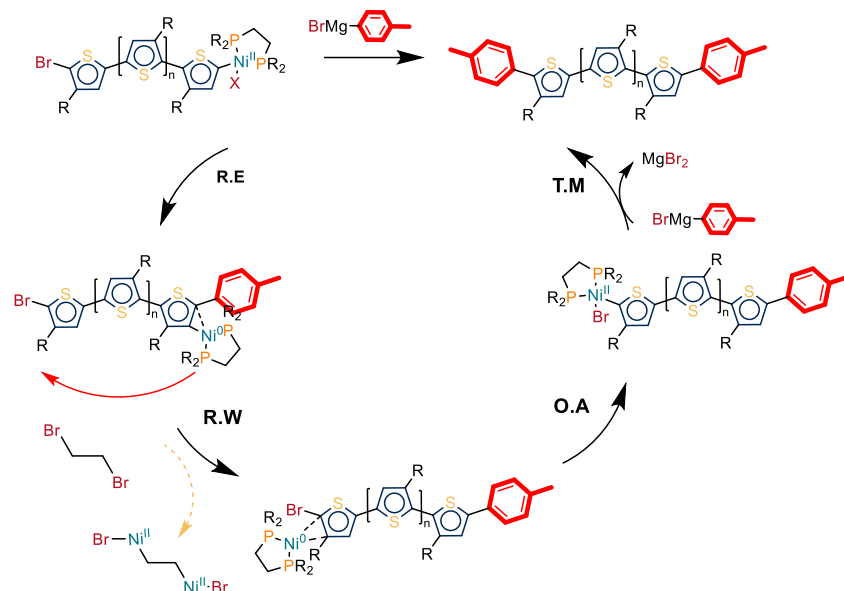
monomers' sequential addition would produce simple triblock copolymers. However, the walking time spent on the polymer backbone also varies along with the polymer's length, which decreases the rate of polymerization. A long polymer chain would also potentially increase the risk of losing an active catalyst due to self-dissociation or trapping.



Scheme 2.6 Proposed Mechanism for the bidirectional walking experiment by Kirly group.

The most recent evidence for long-distance ring transfer was the work performed by McNeil group in 2018.¹⁰² They started a polymerization process with NiCl_2 precatalyst, therefore, an unfinished polymer with one ongoing thiophenyl- NiCl species terminal and an unreacted C-X at the other side. The NiCl side was reduced with the Grignard reagent to produce $\text{Ni}(0)$ species that could attach to the polymer. The $\text{Ni}(0)$ was assumed to activate the remote side C-X bond after a long-distance ring transfer or a free-diffusion, a large amount of Dibromide ethylene was used as a scavenger to exclude the chances of free $\text{Ni}(0)$ catalysts in the solution. Therefore, decapping occurs at both termini of the polymer with the Grignard reagent *p*-tolylmagnesium

bromide would confirm a long-distance ring transfer though ~40-50 unit of thiophene.



Scheme 2.7 Proposed Mechanism for the End-Capping Reaction in McNeil group work.

2.8 Perspective

Ring and chain walking have been observed in Ni-catalyzed CTP and represent both a challenge and an opportunity within polymer synthesis and functionalization.¹⁰³ The thermodynamic driving force from a remote chemical bond cleavage or formation (often a C-C or C-heteroatom bond) enable transport of a specific chemical fragment via site discrimination between multiple remote reaction sites. In the specific case of CTP, the Ni(0) intermediate can provide sufficient kinetic lability to allow for transport, without decomplexation, depending on the ancillary ligand's nature (often bisphosphine or NHC ligand). In principle, control of ring and chain walking events can be modulated and tuned via both the ancillary ligands' electronic and steric features. The design of molecular machines with defined motion across such a backbone is challenging. Yet, the features required for

such machines already exist in nickel-catalyzed CTP but has not been exploited.

In search of new strategies for molecular machines of this type, people have noticed the promising potential of utilizing divergent remote functionalization.¹⁰⁴ However, despite the relative maturity of CTP as a polymerization strategy, it has not been significantly explored in the design of “molecular walkers”.¹⁰⁵ This result is primarily attributed to limitations in current physical techniques (mostly isotope labelling with NMR), which have been unsuccessful in capturing and characterizing the short-lived chemical intermediates in the ring and chain walking processes. Preliminary attempts at designing such a molecular walker based on Ni- π thiophene complexes are explored in Chapter 5.

Chapter 3: The importance of ligand-induced backdonation in the stabilization of square planar d^{10} Nickel π -complexes

3.1 Introduction

Over the last two decades, renewed interest in the redox non-innocence of ligands has led to their proliferation in inorganic chemistry.^{106,107} The use of these ligands as electron reservoirs enables two-electron processes from complexes which typically exhibit single-electron chemistry, particularly first-row transition metals.¹⁰⁸ In a pioneering example, Chirik and co-workers demonstrated that $(PDI)Fe(N_2)_2$ ($PDI = 2,6-(2,6\text{-}iPr_2C_6H_3NCR)_2C_5H_3N$, $R = Me$ or Ph) catalyses the formal [2+2] cyclization of diolefins to form cyclobutane rings.¹⁰⁹ Notably, the iron centre stays in the $Fe(II)$ oxidation state throughout the catalytic cycle, with the PDI ligand acting as a two-electron reservoir. More recently, the Tsurugi, Arnold, and Mashima groups reported that both the geometric and electronic non-innocence of α -diimine ligands plays a key role in niobium-catalysed chlorination of olefins, where the metal centre stays in the $Nb(V)$ oxidation state and redox events occur on the diimine ligand.¹¹⁰

In contrast to these open-shell systems, closed-shell systems that rely on the ligand accepting and/or donating electron pairs are less common. A notable example of this type of reactivity is the zirconium system reported by Heyduk, which allows for a putative “oxidative addition” reaction to occur at a $Zr(IV)$, d^0 metal centre.¹¹¹ In another example, we have recently shown that the oxidation of $(TPA)Rh$ olefin complexes ($TPA = \text{tris}(2\text{-pyridylmethyl})\text{amine}$) with H_2O_2 to form 2-rhodaioxetanes¹¹² is more accurately described as a ligand-centred¹¹³ rather than metal-centred oxidation.¹¹⁴ In this case, the π -ligand acts as a two-electron redox centre.

We have recently become interested in exploring the fundamental organometallic chemistry of earth-abundant, first-row transition metals. For example, we are exploring the organometallic chemistry of nickel,¹¹⁵⁻¹¹⁹ which has undergone a renaissance in recent years.¹²⁰⁻¹²⁶ Our focus has been the structure and reactivity of nickel π -complexes, which have been reported in a wide range of catalytic processes, including the coupling of CO_2 and ethylene,^{110,127,136,137,128 - 135} intermolecular Tischenko coupling,^{138 - 140} benzoxasilole

synthesis,^{141,142} the aldol reaction,¹⁴³ allylic alkylation,¹⁴⁴ allylic amination,¹⁴⁵ allylic amidation,¹⁴⁶ epoxide functionalization,¹⁴⁷ and Suzuki-Miyaura coupling.¹⁴⁸ Nickel π -complexes of heteroarenes have also been identified as key intermediates in nickel-catalysed catalyst transfer polycondensation to form polythiophenes.^{71,72,149-151,75,76,78,79,84,86,89,101} Given the importance of nickel π -complexes, detailed exploration of their structure and reactivity is needed. Herein, we report the electronic structures of a series of nickel π -complexes relevant to catalysis. Additionally, we identify the impact of ancillary ligands in inducing and supporting π -backbonding, even in cases where metal contributions are limited. In previous work, we noted that the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data of a number of (dtbpe)Ni (dtbpe = 1,2-bis(di-*tert*-butyl)phosphino)ethane) π -complexes were consistent with typical d^{10} Ni(0) complexes (Table 3.1).^{115,116,152} In contrast, we also noted that the distorted square planar geometry with significant elongation of the π -bond were most consistent with a d^8 Ni(II) formulation, in keeping with the metallaeopoxide extreme of the Dewar-Chatt-Duncanson (DCD) model of bonding (Scheme 3.1). In addition, preliminary density functional theory (DFT) calculations (*vide infra*) revealed *prohibitively* high barriers to rotation of the π -ligand (*i.e.* 80-100 kJ/mol), demonstrating that these complexes have a strong preference for the square planar geometry despite steric constraints. Experimentally, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3.1 up to 110 $^\circ\text{C}$ reveals no dynamical processes, indicating that the barrier to carbonyl rotation is *greater than* 70 kJ/mol. We have previously reported similar high barriers to rotation with a rhodium-olefin system.¹¹³ Indeed, the metallaeopoxide electrophile of related nickel complexes have recently been invoked by the groups of Doyle¹⁴⁷ and Ogoshi¹⁴² based on reactivity studies, and is also shown explicitly in Group 4 complexes that display similar structural parameters to the nickel species discussed here.¹⁵³⁻¹⁵⁸

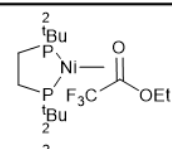
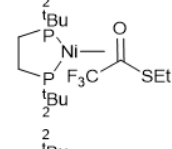
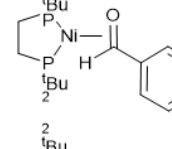
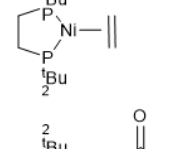
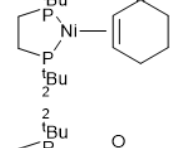
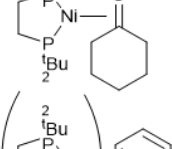
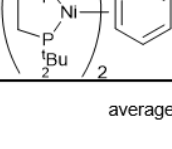
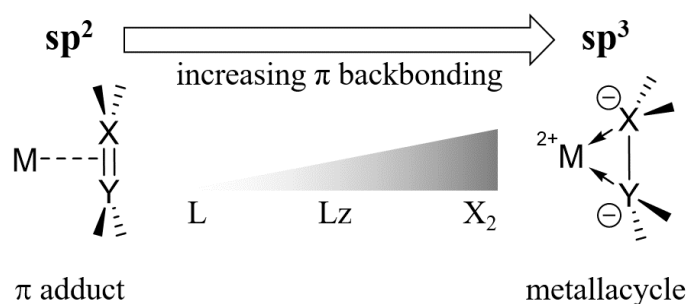
Distorted Square Planar Complexes						
	τ_4	$\Sigma \angle_{Ni}$	$\Sigma \angle_C$	r_{Co} (pm)	$J_{P,P}$ (Hz)	
3.1 	0.37	360.1°	341.7°	131.7	63	
3.2 	0.39	359.8°	345.4°	134.7	48	
3.3 	0.37	360.3°	351.7°	133.4	71	
3.4 	0.36	360.1°	352.6° 353.3°	141.9	-	
3.5 	0.39	359.2°	352.3° 348.3°	141.6	61	
3.6 	0.36	360.0°	344.7°	135.4	79	
3.7 	0.38	360.4°	355.4° 357.1°	142.1	-	
average	0.37	360.0°	350.3°	137.3	64	

Table 3.1 List of π -complexes considered in this study identified by their compound number (bold), τ_4 value, sums of the angles about the metal centre ($\Sigma \angle_{Ni}$) and carbons in the π -ligand ($\Sigma \angle_C$), C=X bond distance of the π -ligand (r_{CX}), and NMR P,P coupling constants (J_{PP}).

Ambiguity in the electronic structure of these nickel π -complexes hinders the effort towards rational design of nickel-catalysed processes. We thus set out to investigate the bonding and electronic

structure of a family of (dtbpe)Ni complexes by utilizing a combination of spectroscopic and computational techniques. This study is also relevant to the ongoing discussion about the value of formal oxidation states.¹⁵⁹⁻¹⁶¹ Overall, we have found that these systems are dominated by π -backbonding with minimal σ -donation from the π -acidic ligand; the degree of backbonding reflects the π acidity of the ligand as well as the ability of the ancillary diphosphine ligands to induce π -backbonding mediated through the nickel 3d orbitals. We believe that this insight will prove beneficial to both the logical improvement of known catalytic reactions with nickel and to the rational design of new transformations.



Scheme 3.1 Continuum of possible electronic configurations for binding of a π -system to a redox-active metal centre. On the left, is the limiting case of simple π -adduct formation, where M-L binding occurs via σ donation from the π -system. As π -backbonding increases, the X=Y π bond weakens and, in the limit, a metallacycle is formed with loss of the π bond and formal 2e- oxidation at the metal centre.

3.2 Results

3.2.1 Solid-state molecular structures

We selected a variety of (dtbpe)Ni complexes, ranging from well-defined nickel(II) complexes to π -complexes of organic molecules (Charts 3.1-3.3). The complexes were split into two categories based on the dihedral angles observed in the solid-state structures: (i) those with near planar geometries (3.1-3.12, where $\varphi_{dih} \sim 0^\circ$ and $\sum \angle_{Ni} \sim 360^\circ$) and those with pseudo-tetrahedral geometries at the

nickel centre (3.13-3.15, where $\varphi_{dih} \sim 90^\circ$ and $\sum \angle_{Ni} \sim 440^\circ$). Alternatively, differences in the geometry of four-coordinate complexes can be evaluated using τ_4 values, which range from $\tau_4^{(D_{4h})} = 0$ to $\tau_4^{(T_d)} = 1$.¹⁶² The coordinate complex is approaching square planar (D_{4h}) when τ_4 is closer to 0, or prone to be tetrahedral (T_d) when τ_4 is closer to 1. This approach confirms the *pseudo*-tetrahedral ($\sim T_d$) geometry of 3.13-3.15 (Table 3.3), but suggests that the more planar complexes split into a set of highly symmetrical square planar complexes (Table 3.2) and a set of complexes that deviate more strongly from idealized D_{4h} symmetry (Table 3.1). The latter complexes are all π -complexes where the deviation from an idealized geometry results from the extremely small bite angle formed by the π -ligand (when considered as an η^2 ligand), even while maintaining planarity. The planar geometry at the metal centre implies that 3.1-3.7 exhibit a large degree of backbonding, which would typically be ascribed to the formation of square planar Ni(II) d^8 complexes (*i.e.*, a metallacyclic electronic configuration as depicted in Scheme 3.1).

The structure of the π -ligand itself has also frequently been used to estimate the degree of backbonding: electron donation into the ligand π^* orbital *via* backbonding should lead to bond elongation. For example, Zeise's salt $[KPtCl_3(C_2H_4)]$ and Cramer's dimer $[Rh(C_2H_4)_2Cl]_2$, both commonly used organometallic starting materials, feature short C=C ethylene bond distances of 137.5 pm¹⁶³ and 139.5 pm¹⁶⁴, respectively. In contrast, (MeTPA)Rh(C_2H_4)(BPh₄) (MeTPA = N-(6-methyl-2-pyridyl)methyl-N,N-di(2-pyridylmethyl)amine), features a much longer C=C bond distance of 145 pm,¹⁶⁵ which corresponds to the metallacyclopropane end of the DCD spectrum. However, this method is generally qualitative, with many examples that fall in the middle of the spectrum being simply described as hybrids of the two resonance forms.^{166,167} Indeed, the C=O bond lengths of the η^2 -carbonyl complexes examined here (complexes 3.1, 3.2, 3.3 and 3.6) all fall between 131.7-135.4 pm.¹⁶⁸⁻¹⁷⁰ This range is unfortunately ambiguous, as it is in the middle of the typical bond lengths of ~ 122 pm and ~ 143 pm for C=O double bonds and C-O single bonds, respectively. Similarly, information about the degree of backbonding can be gleaned from the sum of the bond angles about the carbon atom of the π -unit ($\sum \angle_C$, Chart 1). However, these results are again inconclusive, as the observed $\sum \angle_C (= 341 - 352^\circ)$ are intermediate between those expected for planar sp^2 -hybridized and pyramidal sp^3 -hybridized carbon atoms. This approach also suffers from the fact that many π -

ligands bear hydrogen substituents, which can be difficult to locate using traditional X-ray diffraction (XRD)¹⁷¹ and occasionally require neutron diffraction experiments to accurately ascertain their positions.

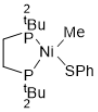
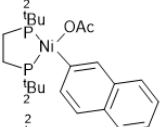
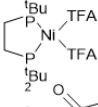
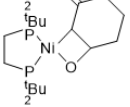
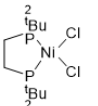
Square Planar Complexes					
	τ_4	$\Sigma\Delta_{Ni}$	$\Sigma\Delta_C$	r_{CO} (pm)	$J_{P,P}$ (Hz)
3.8 	0.08	360.9°	-	-	4
3.9 	0.11	360.6°	-	-	-
3.10 	0.04	360.1°	-	-	-
3.11 	0.13	359.8°	-	-	6
3.12 	0.11	361.1°	-	-	-
average	0.09	360.5°	-	-	5

Table 3.2 List of reference Ni(II) square planar complexes, which exhibit both small $^2J_{PP}$ coupling constants (where available) and τ_4 values.

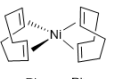
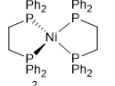
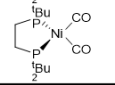
Tetrahedral Complexes					
	τ_4	$\Sigma\Delta_{Ni}$	$\Sigma\Delta_C$	r_{CO} (pm)	$J_{P,P}$ (Hz)
3.13 	0.89	411.4°	-	-	-
3.14 	0.81	424.8°	-	-	-
3.15 	0.93	429.7°	-	-	-
average	0.88	422.0°	-	-	-

Table 3.3 List of reference pseudo-tetrahedral Ni(0) complexes, with large τ_4 values and $\sum \angle_{Ni} > 400^\circ$.

3.2.2 Nuclear magnetic resonance spectroscopy

A common approach for evaluating the oxidation state of metals in diphosphine complexes involves using the magnitude of P,P-scalar coupling constants ($^2J_{P,P}$). In nickel chemistry, it is generally observed that small $^2J_{P,P}$ (i.e. 2-30 Hz) correspond to nickel(II) complexes whereas larger $^2J_{P,P}$ (i.e. 45-80 Hz) correspond to nickel(0) complexes.^{115,116,179,127,172-178} However, exceptions to this trend have been reported by ourselves¹¹⁵ and others.^{178,180} Moreover, this approach is limited to asymmetric species as $^2J_{P,P}$ cannot be observed in complexes such as 3.4 and 3.7 due to symmetry.

Others have noted similar results with infrared (IR) spectroscopy of nickel carbonyl complexes¹⁶⁸ as we have found from XRD and NMR, i.e. that electron donation from the metal to the ligand does reduce the C=O bond, but to the extent that is ambiguously between a single and double bond. Importantly, none of these traditionally-used methods *directly* provides information about the electron density at the metal centre. We thus turned to X-ray absorption spectroscopy (XAS) for an independent evaluation of the electronic structure and spectroscopic oxidation states at the metal. We sought to probe how a more direct measurement of Z_{eff} at the metal centre correlates to the above-discussed methods, in particular NMR spectroscopy. To the best of our knowledge, a study relating the magnitude of the NMR data (especially ^{31}P coupling constants) and how they correlate with alternate spectroscopic approaches has not been performed.

3.2.3 Ni K-edge X-ray absorption spectroscopy

In principle, the spectroscopic oxidation state of the metal ion can be accurately assigned *via* the energy of either the ionization edge and/or the low-energy pre-edge features in the metal K-edge near-edge spectrum.¹⁸¹⁻¹⁸⁷ Ni K-edge XAS can therefore be used to explore the spectroscopic oxidation state of a wide range of nickel-containing species.¹⁸⁸⁻¹⁹²

Ni K-edge XAS data were obtained for several Ni π -complexes, in addition to several reference complexes from Chart 1. Near-edge spectra for ‘classic’ Ni(II) complexes, such as that for complex 3.12,

have well-resolved pre-edge features: a weak feature at ~ 8333 eV and a more intense feature at ~ 8336 eV.^{193,194} The weaker feature results from the electric-quadrupole allowed Ni $1s \rightarrow 3d$ transition, whereas the more intense feature in such complexes has previously been ascribed to a dipole-allowed Ni $1s \rightarrow 4p$ transition.^{195,196} By contrast, Ni π -complexes (such as 3.1, 3.2, 3.4, and 3.7) have a markedly different edge profile and only one clearly resolvable intense pre-edge feature ranging from 8333-8336 eV. Similar spectroscopic behaviour has previously been observed in copper(I)-derived π -complexes.¹⁸² As expected, the energy of the Ni $1s \rightarrow 4p$ feature correlates with the oxidation state of the metal centre. The weaker pre-edge feature is not directly resolvable in most complexes, although in complexes 3.1 & 3.2 a weak low-energy shoulder is observed in the 2nd derivative of the spectra (see Figure 3.1).

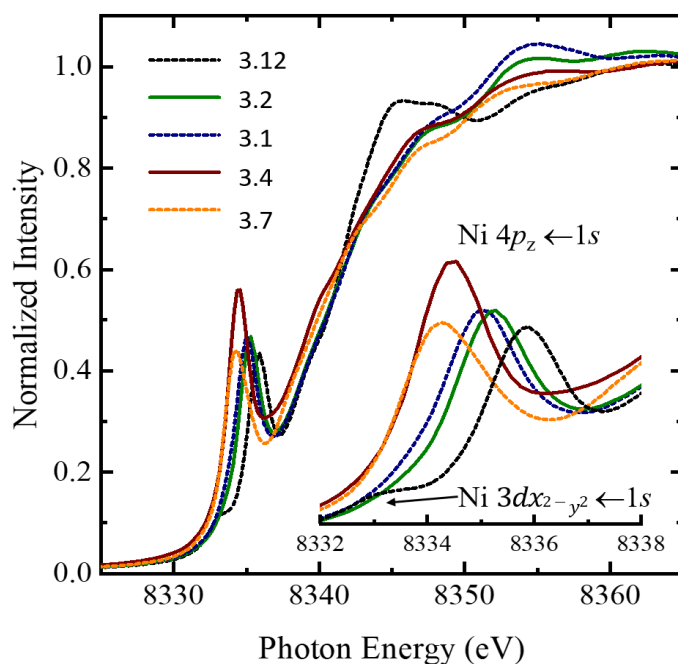


Figure 3.1 Normalized Ni K-edge PFY XANES edge spectra for Ni(dtbpe)Cl₂ (3.12), [Ni(dtbpe)]₂(benzene) (3.7), Ni(dtbpe)(ethylene) (4), Ni(dtbpe)CF₃COOEt (3.1), and Ni(dtbpe)CF₃COSEt (3.2). The pre-edge region for each of the spectra is shown in the inset with assignments for the observed features.

3.2.4 Computational Studies - Density Functional Theory

Full electronic DFT calculations were performed by using ORCA packages on each of the species in Table 3.1 using simplified diphosphine ligands (Appendix A.11). Molecular structures derived from B3LYP/def₂-TZVP calculations of the dtbpe complexes, as well as those using a simplified diphosphine ligand (dmpe = 1,2-bis(dimethylphosphino) ethane), yield good agreement with solid-state molecular structures of 3.1-3.12.^{115,116,127,152,197,198} The effect of decreasing the steric bulk and electron donation in the supporting diphosphine ligand does not affect the general structural trends and conclusions, which are consistent with those observed in the experimental data. Furthermore, the spectroscopic features observed in the Ni K-edge XAS data are well reproduced using TD-DFT analysis. Although qualitative results were consistent across a broad range of functionals, results from B3LYP provided the best agreement with experimental pre-edge features. Basis set effects were observed to be minimal beyond TZVP. The strong agreement with experimental data suggests that our DFT results should provide a reasonable description of bonding in these species.

The Ni K-edge pre-edge features are extremely sensitive to electron distribution (Figure 3.2). The more intense, higher energy (*Ni 4p_z ← 1s*) transition increases with greater oxidation at the metal centre and reproduces the trend observed in the experimental data. The weaker, low energy transition (*Ni 3d ← 1s*) shifts in the opposite direction, such that the energy difference between the two features (ΔE_{dp}) increases with increasing oxidation at the metal centre. The weak low-energy 3d feature should eventually be unresolvable from the higher intensity 4p feature, as observed in the experimental data.

The nature of the two pre-edge final states is consistent across the series of π -complexes. The intense feature results from a transition to the *non-bonding* Ni 4p_z orbital, whose energy directly reflects Z_{eff} at the metal centre. The weaker feature corresponds to a transition to the formally *ligand-based antibonding* π^* orbital, which gains electric quadrupole character by mixing with the Ni 3d_{x²-y²} orbital through π -back bonding. In principle, the intensity of these features should therefore reflect the degree of M-L π -backbonding. However, the intensity of this pre-edge feature also depends on the degree of Ni d-p mixing, which varies across the series. This contribution, in addition to

the difficulty of resolving weak pre-edge shoulder, makes it challenging to quantify the degree of back bonding from the experimental data.

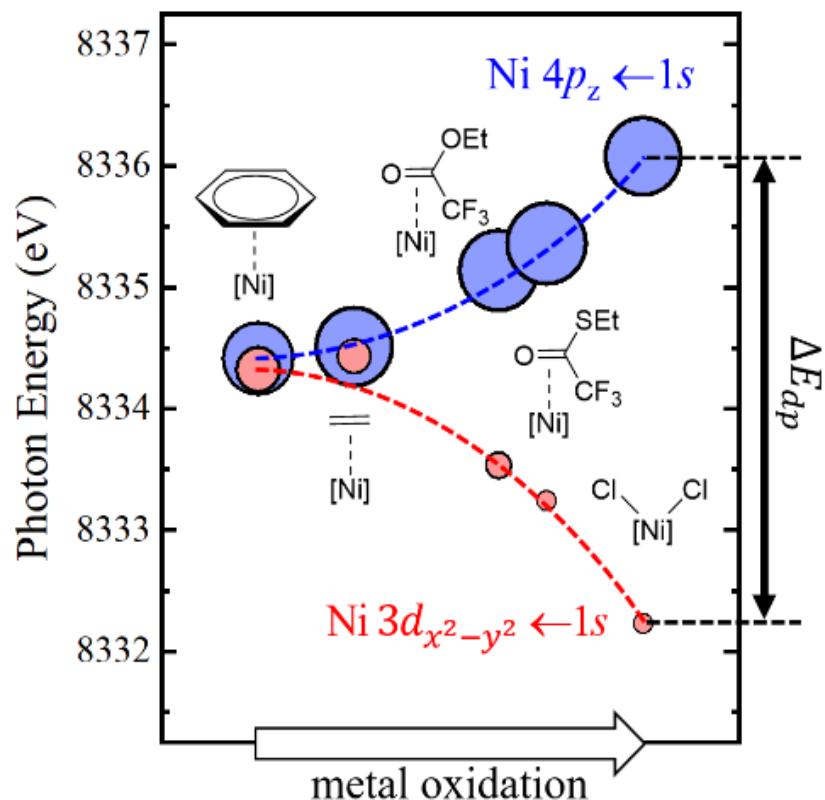


Figure 3.2 Calculated Ni K-edge XANES TD-DFT results for pre-edge region of the spectrum. Each complex is represented by a blue circle ($\text{Ni } 4p_z \leftarrow 1s$) and a red circle ($\text{Ni } 3d_{x^2-y^2} \leftarrow 1s$). The area of the of each circle is proportional to the calculated oscillator strength (f_{osc}) for each transition. All calculated TD-DFT energies at the Ni K-edge were shifted by -98.55 eV. [Ni] = Ni(dmpe).

To further explore the electron distribution in the ground state of these π -systems, we applied charge decomposition (CDA),^{199,200} natural bond orbital (NBO),²⁰¹ and the quantum theory of atoms-in-molecules (QTAIM)²⁰² analyses. Together, these provide a comprehensive view of the electronic properties of these systems. In all cases, the predominant interactions between the metal ion and the π -ligand can be well described using the basic interactions defined within the DCD bonding model.

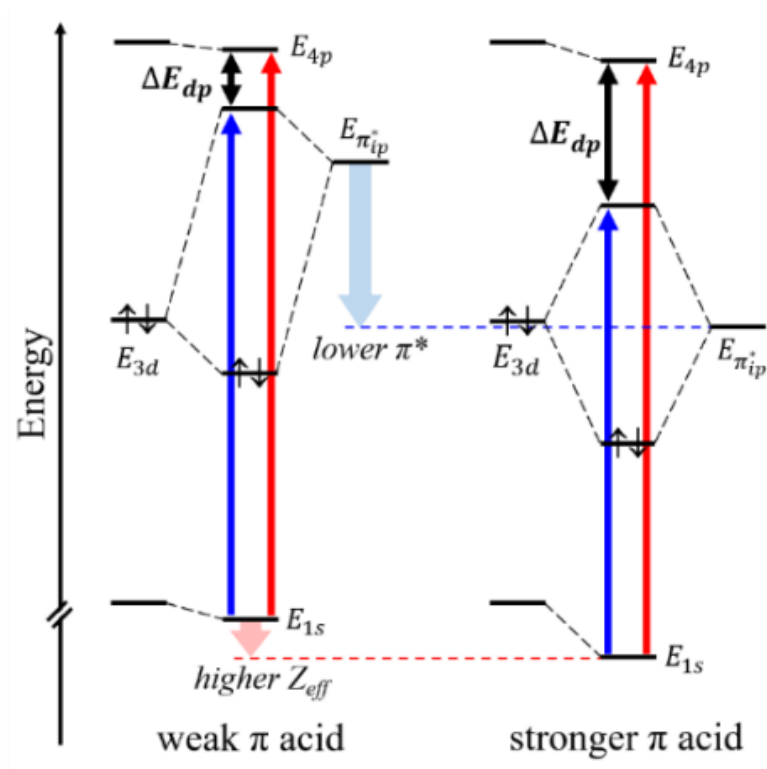


Figure 3.3 Simplified MO diagram depicting differences between weaker (left, *e.g.* ethylene in 4) and stronger π -acidic ligands (right, *e.g.* cyclohexanone in 6). Greater π -acidity leads to a much lower π_{ip}^* and thus greater π -backbonding. Decreased electron density at the metal centre (i.e. increased Z_{eff}) also lowers the energy of the Ni $1s$ orbital. These two effects lead to a simultaneous increase in energy of the Ni $1s \rightarrow 4p$ transition (red arrow) and decrease in energy of the Ni $1s \rightarrow \pi^*$ (blue arrow) and therefore an increase in the splitting of the two acceptor orbitals (ΔE_{dp}). Quantitative results are given in Appendix A.39.

Most notably, π -backbonding is the dominant contribution to bonding in these systems. The electron rich metal centre does not

accept significant electron density through σ donation from the π_b ligand orbital with only minimal charge donation into the higher lying empty Ni 4s/p orbitals. The π -backbonding interaction involves overlap between the Ni 3d_{x²-y²} and the in-plane ligand π^* (π_{ip}^*). As expected, the overall degree of charge transfer correlates directly with the relative energies of these contributing fragment orbitals (Appendix A.35). Given that the Ni(dtbpe) fragment is identical in all cases, differences within the series result primarily from changes in the energy of the ligand π_{ip}^* orbital. As summarized in Figure 3.3, poorer π -acids such as olefins have a higher energy $E_{\pi_{ip}^*}$ and thus should exhibit a small ΔE_{dp} , whereas $E_{\pi_{ip}^*}$ is lower in energy for stronger π -acids (such as carbonyls), increasing backbonding and a larger ΔE_{dp} . This interaction leads to a surprisingly large barrier for ligand rotation, even for those where backbonding is least important: barriers of ~ 100 kJ/mol are obtained for both symmetric (4) and asymmetric (3) π -ligands.

Wiberg Indices				$\nabla^2(\rho_{DFT})$		
	Ni-C	Ni-X	bcp _{NiC}	bcp _{NiX}	rcp _{NiCO}	
C=C	3.7'	0.362	0.357	0.217	0.224	0.309
	3.5'	0.495	0.403	0.213	0.261	0.353
	3.4'	0.486	0.487	0.235	0.238	0.359
C=O	3.3'	0.516	0.487	0.524	0.248	-
	3.1'	0.556	0.468	0.550	0.219	-
	3.2'	0.552	0.502	0.537	0.243	-
	3.6'	0.523	0.494	0.536	0.232	-

Table 3.4 Wiberg bond indices for Ni-C, Ni-X (X=O or most electron-rich C), and QTAIM $\nabla^2(\rho_{DFT})$ for optimized complexes at B3LYP/def2-TZVP level of theory.

Although the above analysis is valid for all species investigated, there is one additional factor that contributes to the nature of the bonding in these systems. The significant electronegativity difference between carbon and oxygen in the carbonyl π -ligands leads to

asymmetry in the orbitals involved in bonding. Indeed, this bonding difference between olefins and carbonyls was identified by Eisenstein and Hoffmann nearly four decades ago.¹⁶⁸ The nature of bonding in these asymmetric systems is therefore more complex and deviates somewhat from the simple DCD model as σ donation becomes more localized from the terminal oxygen atom and π -backbonding localizes onto the electron deficient carbonyl carbon atom. This localization is also consistent with π -backbonding (to C) being stronger than σ -donation (from O), as observed from bond strength parameters in Table 3.4.

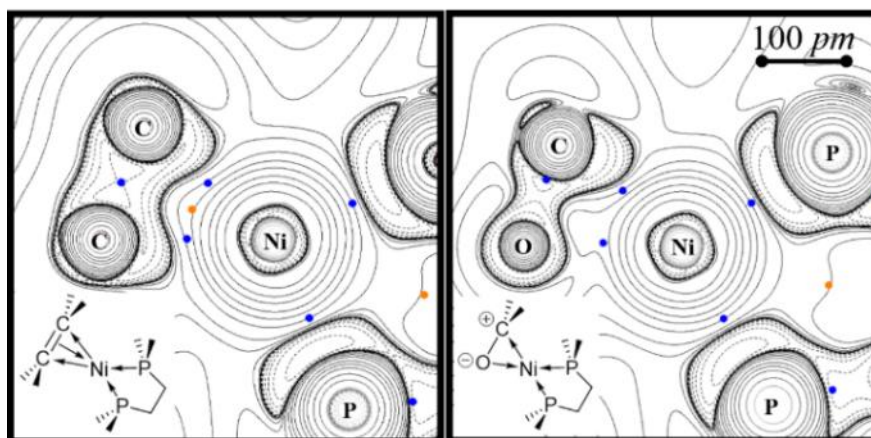


Figure 3.4 QTAIM topological analysis for complexes 3.4' (left) and 3.1' (right). Contour maps of $\nabla^2(\rho_{DFT})$ in the NiCX plane (X=C, O). Dotted contours refer to positive values of $\nabla^2(\rho_{DFT})$ and solid lines to negative values of $\nabla^2(\rho_{DFT})$. Bond critical points are shown in blue and ring critical points are shown in red. A simplified representation of these bonding interactions is shown on the bottom left for each of the complexes.

The effect of π -ligand asymmetry is also clearly observed in the QTAIM analysis: Figure 3.4 shows a comparison of the Laplacian of the DFT-derived electron density ($\nabla^2(\rho_{DFT})$) for 3.4' and 3.1'. In the olefinic π -complex, the electron density within the Ni-C-C trigonal core reveals two Ni-C bond critical points (bcp) and one ring critical point (rcp) that connects all three atoms. The rcp correlates with a σ donor interaction due to π_{CC} donation in the Ni $3d_{xy}$ orbital and the two Ni-C bcp's correspond to π -backbonding from the Ni $3d_{x^2-y^2}$ and the ligand π_{ip}^* . By contrast, $\nabla^2(\rho_{DFT})$ for 3.1' is highly asymmetric with two bcp's (Ni-O and Ni-C) but no discernible rcp in this case.

3.3 Discussion

Our studies of a series of nickel π -complexes reveal interesting electronic structure features that can be rationalized within the context of the DCD bonding model. The spectroscopic characteristics of these species are highly sensitive to the nature of bonding to the π -ligand, more specifically the properties of the species are intimately linked to the degree of π -backbonding from the electron-rich metal centre. Taken together, our studies allow for a more concrete evaluation of the factors that control this bonding and their implications.

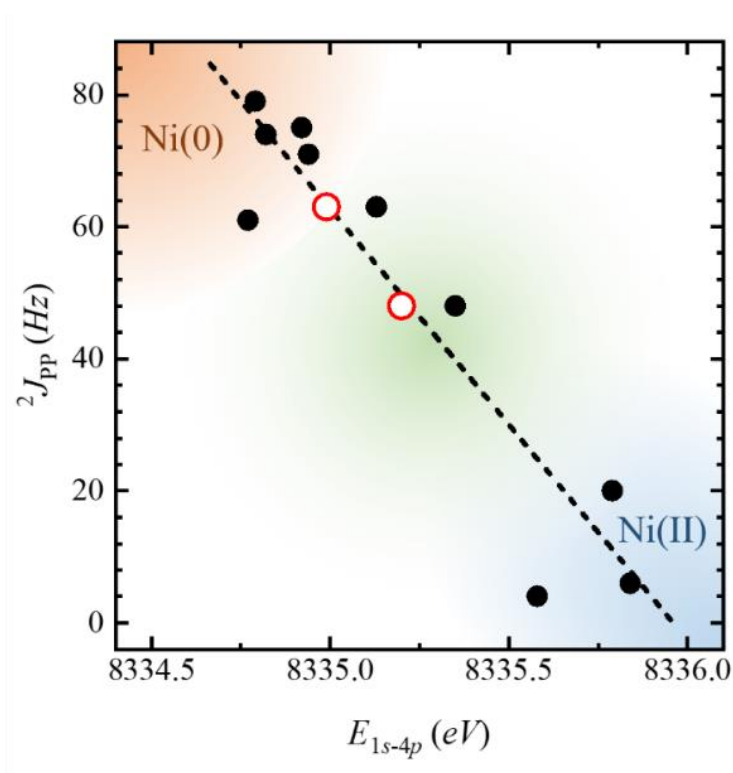


Figure 3.5 Correlation between Ni 1s→4p transition energies and $2J_{PP}$ NMR coupling constants. Data points in black circles are from TDDFT calculations whereas those in red circles are from experimental Ni K-edge XAS data. All TD-DFT calculated transition energies were linearly shifted by -98.55 eV. The dashed line represents a linear correlation fit ($R^2 = 0.87$); see Appendix A.3

As noted previously, oxidation states of nickel diphosphines are often evaluated *via* the magnitude of $^2J_{P,P}$ in unsymmetrical complexes. In principle, differences reflect electron density at the bridging metal centre,²⁰³ although limitations include the requirement for inequivalent P atoms and a diamagnetic ground state.^{118,175} XAS offers the advantage of providing an independent experimental probe of oxidation states without the limitations of $^2J_{P,P}$ values. The XAS data of formally square planar complexes yield distinctive pre-edge features that track with oxidation of the metal centre. The NMR spectroscopy coupling constants and XAS pre-edge energies correlate extremely well (Figure 3.5), providing good support that $^2J_{P,P}$ (where available) are useful in defining electron density at the metal centre.

The fact that the two pre-edge features in the Ni K-edge XAS data respond so differently to changes in the electronic structure implies that they are sensitive to different aspects of the electronic structure of the metal centre. The Ni 4p_z orbital is out-of-plane from the most important ligand field interactions in pseudo square planar geometries and thus reports directly on Z_{eff} of the metal centre. In contrast, the weak pre-edge feature is a predominantly in-plane ligand-based final state with some metal $3d_{x^2-y^2}$ character. The two features therefore behave very differently with the former reporting on Z_{eff} of the metal centre and the latter on differences in the ligand field.

The DCD model is a simple yet powerful approach for explaining the behaviour of π -complexes in transition metal chemistry. Its limitations have recently been explored in copper dioxygen and related systems by invoking the important contributions of static correlation, specifically by allowing for multi-determinant solutions.¹⁸² Since the electron density of these systems are well described from DFT calculations, we approached this same issue by applying natural resonance theory²⁰⁴⁻²⁰⁶ (NRT) to expose different contributions to the overall electronic description (Table 3.5).¹¹³ In all cases, the Ni(II) metallacycle contributes little to the overall electronic structure. The Ni(0) π -adduct and Ni(I) intermediate resonance structures account for >80% of the electronic structure in all cases. Indeed, we find that the Ni(0) π -adduct is the largest contributor for all the structures examined, although Ni(I) contributions are non-negligible.

		Ni(0)	Ni(I)	Ni(II)
	3.7'	67%	33%	0%
C=C	3.5'	56%	37%	7%
	3.4'	54%	36%	10%
	3.3'	57%	38%	5%
C=O	3.1'	48%	48%	4%
	3.2'	46%	43%	11%

Table 3.5 Summary of NRT analyses for complexes with either olefin or carbonyl π -ligands.

The high barrier to rotation for π -ligands in these complexes implies a surprisingly strong preference for a planar geometry even though a closed-shell Ni(0) π -adduct should not behave in this way. Even more surprisingly, the barrier to rotation does *not* correlate strongly with the degree of Ni(I) character from our NRT analysis. This effect points to the importance of the *trans*-diphosphine ligand in enabling and supporting π -backbonding. In principle, π -backbonding in a d^{10} Ni(0) occurs in any geometry of the π -ligand because of availability of filled Ni $3d_{xz,yz}$ orbitals that could also support backbonding. However, the C=C bond distance (r_{CC}) decreases significantly upon ligand rotation (from 147 to 139 pm), indicating that backbonding is not well supported in alternate geometries. The electronic changes that occur upon rotation of the π -ligand are an indicator of the importance of the diphosphine ligand.

Charge donation from the P_2Ni fragment to the π -ligand decreases substantially when the diphosphine ligand is perpendicular to the Ni $3d_{x^2-y^2}$ donor orbital (Figure 6A). This suggests that the metal centre in these complexes mediates charge donation from the electron rich diphosphine to the ethylene π^* . The orbital contributions that allow for π -backbonding are reminiscent of a classical 3c-4e bond; in this situation the three contributing orbitals are the antisymmetric combination of the phosphine σ -donor orbitals (P_{σ}^- , 2 valence electrons), the Ni $3d_{x^2-y^2}$ (2 valence electrons), and the ligand π_{ip}^* orbital (Figure 3.6B). In this geometry, the two sets of ligands generate a cooperative “push-pull” system mediated by the metal centre in a manner similar to that which has been observed in cytochrome

P450s.²⁰⁷ This $\sigma \rightarrow \pi$ cooperative interaction mediation by the metal centre is only possible in specific geometries and is essentially identical to mixed σ/π interactions observed in trigonal systems.²⁰⁸ This would preclude similar effects with ancillary ligands that enforce a linear geometry in Ni(0) complexes, such as N-heterocyclic carbenes (NHCs). It is noteworthy that Itami²⁰⁹ and Liu²¹⁰ have identified striking reactivity differences in the catalytic activity of monodentate phosphines versus their bidentate analogues, with additional computational studies performed by Houk.²¹⁰

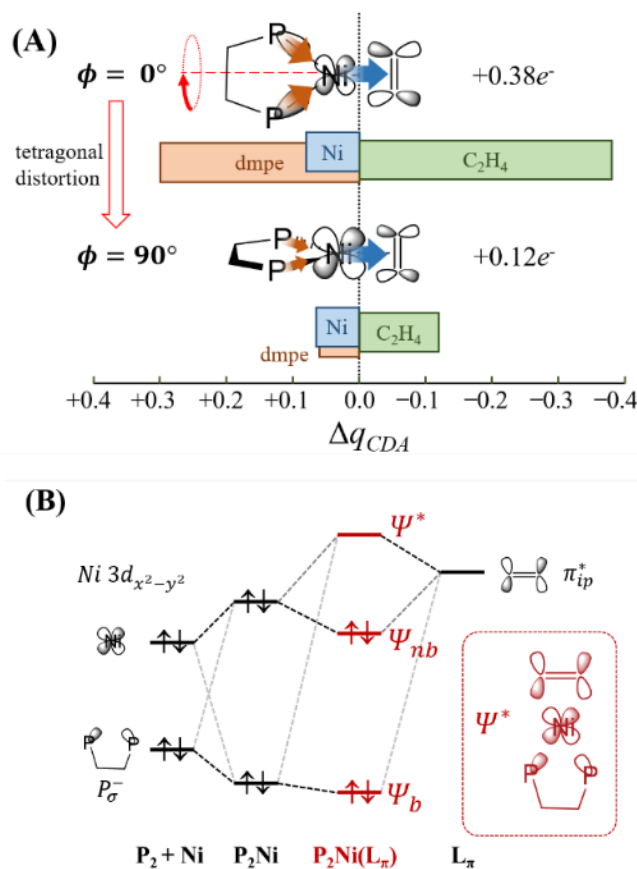


Figure 3.6 (A) DFT-calculated charge donation from CDA analysis for ethylene complex with dmpe ligand (4') for ground state geometry ($\phi = 0^\circ$) and after tetragonal distortion (rotation of NiCC plane relative to NiPP plane, $\phi = 90^\circ$). Backbonding decreases substantially due to large drop in phosphine σ donation into the Ni 3d_{x²-y²}. (B) Qualitative molecular orbital

representation of the 3c4e bonding that connects P_{σ}^- with π_{ip}^* via the Ni $3d_{x^2-y^2}$ orbital.

Although all of the olefin complexes investigated are best described as Ni(0) complexes, highly electron poor carbonyl complexes have significantly more oxidized metal centres. Complexes 3.1 and 3.2 represent intriguing examples of intermediate cases that are shifting towards a “Ni(I)”-type description. The CF₃ substituent at the carbonyl carbon increases their π -acidity substantially. However, the ester ligand in 3.1 is less π -acidic than the equivalent thioester in 3.2 due to better delocalization of the ligand π -system, which simultaneously decreases overlap of the π^* with the Ni $3d_{x^2-y^2}$ and increases its energy. In 3.2, poor π -overlap between the larger atomic orbitals on sulphur and the carbonyl π^* allows for significant backbonding in this case. These differences should lead to concomitant differences in reactivity.

Indeed, 3.1 and 3.2 display fundamentally different reactivity. In refluxing benzene, 3.2 slowly thermolyses over two days, resulting in complex 3.15, free ligand, and thioester, as determined by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. In contrast, complex 3.1 is stable for up to a week under the same conditions with no sign of decomposition. Complex 3.1 does not react with MeLi, even upon prolonged reflux in benzene, but under the same conditions, complex 3.2 reacts with MeLi to form trace amounts of EtSSEt. In addition, complex 3.2 is susceptible to cross-coupling with phenylboronic acid, forming PhSEt in moderate (35%) yield.¹¹⁶ No such cross-coupling reactivity was observed with complex 3.1. Lastly, complexes 3.1 and 3.2 react differently with MeI. Upon refluxing in benzene for 12 hours, 3.1 forms (dtbpe)Ni(Me)(I),²¹¹ which was verified by ^{31}P NMR spectroscopy, and liberates the free ester, whereas complex 3.2 does not react with MeI at all under the same conditions.^[B] Such behaviour is consistent with reduced π -donation of the ester in 3.1, allowing for its displacement by MeI.

3.4 Summary

Our spectroscopic and computational studies on a series of Ni π -complexes shed light on an intriguing effect whereby σ -donor ancillary ligands are instrumental in stabilizing a square-planar geometry in formally d^{10} nickel(0) complexes. In the case of olefinic complexes, the evidence shows that these are best described as Ni(0) π -adducts with strong π -backbonding coupled to in-plane σ donation from the

supporting electron rich diphosphine bidentate ligand. The formation of this 3c-4e interaction generates ligand σ -to- π ($L\sigma \rightarrow L\pi$) charge transfer. This ligand-induced (push-pull) π -backbonding is responsible for the large observed rotational barrier about the π -ligand even with relatively poor π -acidic ligands such as ethylene. This unique electronic structure can play an important role in the reactivity of such species. The situation is more complex in situations with highly electron poor π -systems, where metal-centred backbonding increases and leads to Ni(I) character becoming significantly more important. The implication here for catalyst design is the specific importance of the ancillary ligands in backdonation to the reactive π -acidic ligand. We anticipate that the tuning of both electron-donating diphosphine and the electron-accepting π -ligand will allow for an additional handle in the design of subsequent catalysts for a wide range of processes that involve similar intermediates, and that more detailed studies of ancillary ligand effects in such systems are warranted.

3.5 Methods

3.5.1 General Considerations

Unless stated otherwise, all reactions were performed in a glovebox or on a Schlenk line under an atmosphere of pure N_2 using standard Schlenk techniques. Anhydrous pentanes, toluene, diethyl ether, and tetrahydrofuran were purchased from Aldrich, sparged with N_2 , and dried further by passage through towers containing activated alumina and molecular sieves. C_6H_6 and C_6D_6 were purchased from Aldrich and dried over sodium/benzophenone before being distilled and degassed by three freeze-pump-thaw cycles. CD_2Cl_2 was purchased from Aldrich and dried over CaH_2 before being distilled and degassed by three freeze-pump-thaw cycles. $Ni(COD)_2$ (13) was purchased from Strem and used as received. Compounds 3.1-3.2,¹¹⁶ 3.3,¹⁵² 3.4,¹⁹⁷ 3.5-3.6,²¹² 3.7,²¹³ 3.8-3.10,¹¹⁶ 3.11,²¹² 3.12,²¹¹ 3.14,²¹⁴ and 3.15¹⁹⁷ were prepared according to literature procedures. All other chemicals were purchased from commercial suppliers and used as received.

3.5.2 X-ray Absorption Spectroscopy

All the XAS samples were analysed as solids under anaerobic conditions and diluted in boron nitride (20-50% by weight). XAS Ni K-

edges were acquired at the SSRL beamline 7-3, which is equipped with a Si(220) $\phi = 90^\circ$ double crystal monochromator, a 9 keV cutoff mirror, and a He cryostat (at 20 K). Data were collected using a Canberra 30-element Ge solid-state detector with a 3mm Co filter. Data averaging and energy calibration were performed using SixPack²¹⁵ and the AUTOBK algorithm available in the Athena software package²¹⁶ was employed for data reduction and normalization. Independent fitting was also performed using BlueprintXAS.^{217,218}

3.5.3 Computational methods

Initial geometries for all molecules were obtained from crystallographic coordinates (where available) or constructed from standard models. Geometry optimizations and numerical frequency calculations were performed using version 3.0.3 of the ORCA computational chemistry package. Molecular geometries were optimized using the B3LYP functional in combination with the Ahlrichs triple- ζ basis set with valence polarization (def2-TZVP) for all atoms. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional. All calculations were performed with integration grid 4. Reported thermochemical energies are given in kJ/mol and correspond to Gibbs free energies (ΔG^0) with zero-point vibrational energy corrections (ZPVE). NBO results were obtained using Gaussian 09; AIM and CDA calculation were performed in Multiwfn software from NBO outputs. All calculations were run on either the Abacus (UBC Chemistry) or GREX (Westgrid) computing clusters.

Chapter 4: Direct experimental evaluation of ligand-induced backbonding in Nickel metallacyclic complexes

4.1 Introduction

Transition metal catalyzed processes involving unsaturated organic substrates (e.g. alkenes, ketones, and other related species) often involves substrate activation via interactions between the metal centre and the π system. Bonding in such π adducts is commonly described using the framework first established by Dewar, Chatt, and Duncanson^{219,220}. The DCD model focuses on the direct overlap of available π -type orbitals on the unsaturated ligand (π_b and π^*) and valence metal d orbitals of appropriate symmetry (Figure 4.1), generating two primary interactions that contribute to bonding in such π adducts. One of these interactions involves σ donation from the ligand in an empty valence orbital on the metal ($Mnd \leftarrow L\pi_b$). The second interaction, commonly known as π -backbonding, involves π -type donation from the metal into an empty π^* orbital on the ligand ($Mnd \rightarrow L\pi^*$). The degree of π -backbonding is critical in defining the nature of the resultant organometallic complex. Two conceptual limiting cases can be defined based on the degree of backbonding (Figure 4.1): in the weakly backbonding limit, a weakly bound π -adduct is formed (M^nL), whereas, in the strongly backbonding limit, the π bond in the ligand is broken via formal two-electron transfer from the metal to the ligand to form an $M^{n+2}X_2$ -type metallacycle. Such π -type ligands are, therefore, redox-active two-electron reservoirs modulated and controlled by interactions with the metal centre.¹¹³

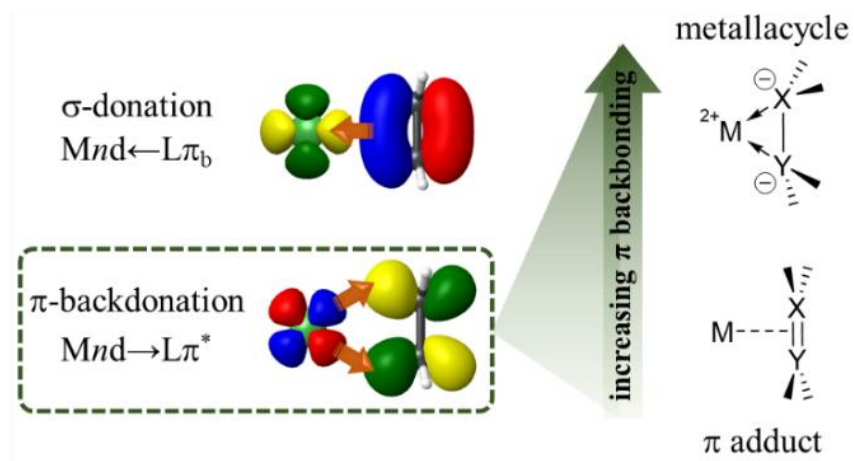


Figure 4.1 Fundamental metal-ligand interactions as defined in the classic Dewar-Chatt-Duncanson (DCD) model describing the bonding of alkenes with transition metal ions (left) and resulting limiting structures obtained based on the degree of backbonding (right).

Given the broad interest in nickel-catalyzed cross-coupling strategies, and the proposed intermediacy of nickel π adducts in many such processes,^{135,139,144,147} we recently probed the bonding in a series of nickel π adducts with diphosphine ancillary ligands, whose reactivity had been explored.^{152,212,221} The x-ray spectroscopic studies discussed in *Chapter 3* uncovered an intriguing scenario wherein weakly π acidic ligands such as alkenes and arenes are highly activated through backbonding whilst the metal centre is still extremely electron rich. In principle, these complexes defy the generalized predictions of the DCD bonding model by yielding Ni(0) metallacycles: the π bond in the alkene is essentially broken without concomitant oxidation of the metal centre. By contrast, more π acidic ligands show significant charge depletion at the metal centre leading to more Ni(I) character at the metal centre. This discovery was supported by complementary density functional theory (DFT) calculations, which provided a plausible rationale for our observations: activation of the π ligand was driven by donation from the ancillary diphosphine ligands via σ -donation through the formation of a formal 3-centre-4-electron (3c-4e) bond across the equatorial plane of these planar complexes (Figure 4.2). The metal centre therefore mediates ligand-to-ligand charge donation the phosphines to the π ligand, a scenario which we have termed *ligand-induced backbonding*²²². The specifics of this bonding

model, albeit consistent with available experimental data, could not be directly probed with available spectroscopic measurements. For example, Ni K-edge x-ray absorption spectroscopy (XAS) is very effective as an experimental probe of the overall electron density at the metal centre in square planar nickel complexes given that the dominant (electric dipole allowed) pre-edge transition is dominated by Ni $4p_z \leftarrow 1s$ character; given the nonbonding character of this transition, it effectively reports on the overall charge at the metal centre. To evaluate the specifics of bonding in these complexes, contributions from $3d$ states must be probed. Unfortunately, $3d \leftarrow 1s$ transitions are electric dipole forbidden ($\Delta l = 2$) and thus extremely weak in metal K-edge spectra.^{223,224} Ni $K_{\beta 1,3}$ x-ray emission spectroscopy (XES) involves core Ni $3p \rightarrow 1s$ transitions and is also somewhat insensitive to the specifics of bonding.²²⁵

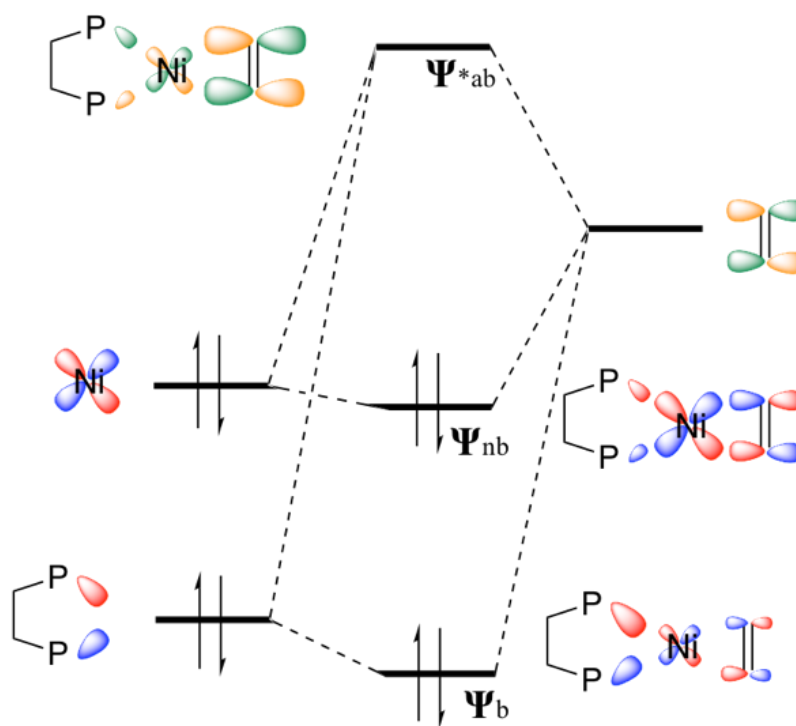
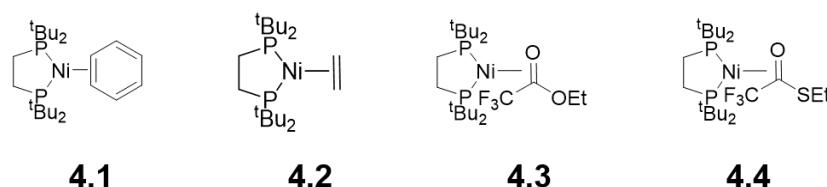


Figure 4.2 Molecular orbital representation of the 3c-4e bonding proposed for square planar Ni(0) diphosphine complexes with alkenes and other π ligands.

Herein, we explore the details of bonding in representative nickel π complexes (Scheme 4.1) using Ni L-edge XAS to directly probe the occupancy of the Ni 3d orbitals and thus directly evaluate the Ni 3d orbital contributions to backbonding in such species. L-edge XAS of first-row transition metal complexes provides the opportunity to quantitatively evaluate the degree of covalency in metal-ligand bonds.²²⁶ Such analyses have been most commonly utilized in the investigation of copper^{227,228}, and iron^{229–232} complexes but the overall principles are applicable to any first-row transition metal complex, including nickel organometallics²³³. Our analysis provides direct experimental support for the importance of ligand-induced backbonding in these complexes.



Scheme 4.1 Nickel complexes (4.1-4.4) investigated in this study. Previous investigations have suggested that 4.1 & 4.2 are best described as Ni(0) metallacycles, whereas 4.3 & 4.4 involve greater metal contributions to backdonation leading to greater Ni(I) character.

4.2 Results

4.2.1 Ni L-edge X-ray absorption spectroscopy

Experimental Ni $L_{3,2}$ -edge XAS spectra for the ethylene (4.1) and arene (4.2) complexes (Figure 3A,B) exhibit very weak features in the near-edge region yet are more feature-rich than typically observed for d^{10} species.²³⁴ Three features are clearly observable at the L_3 edge. The data for the more π acidic ester (4.3) and thioester (4.4) complexes (Figure 4.3C,D) show similar edge features shifted to higher energies (by ~ 1 eV) as well as an additional prominent shoulder at low energy. In all cases, the features observed at the L_2 -edge are similar to those at the L_3 -edge but are weaker and broader, as expected.²³⁵

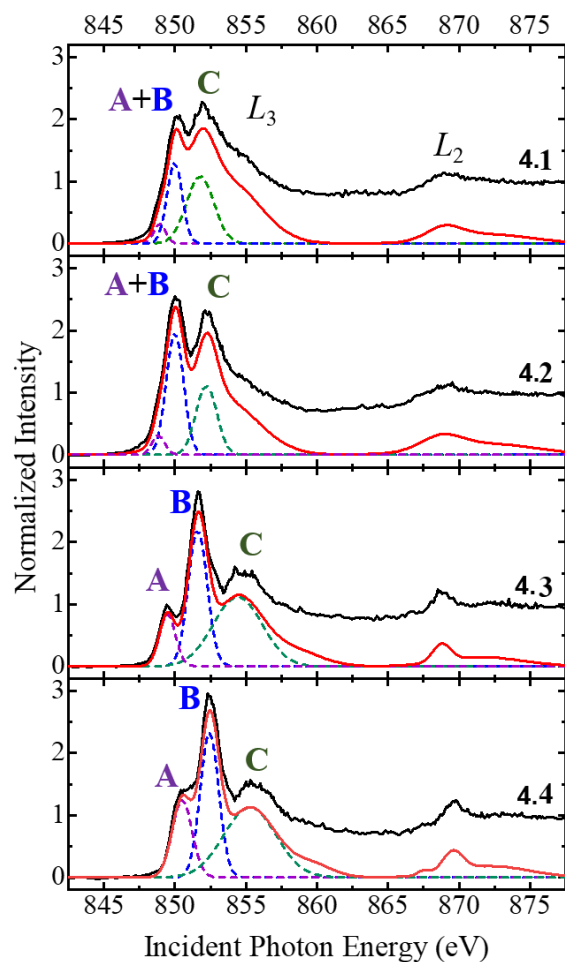


Figure 4.3 Normalized Ni L_{3,2}-edge XAS spectra for 4.1-4.4. Experimental data are shown in black and the simulated spectra are shown in red (background removed for clarity).

The energies of first-row transition metal L₃-edge features correlate very well with oxidation states^{236,237}. The literature on Ni L-edges is somewhat sparse, but Cramer and coworkers have demonstrated this relationship for Ni(I), Ni(II), and Ni(III) species^{238,239}. Linear extrapolation of these data suggests that L₃-edge spectra of molecular Ni(0) species should centre at ~851.5 eV, in good agreement with our experimental data for 4.1 & 4.2. The shift to higher energy for the main

features of 4.3 & 4.4 by ~ 1 eV is consistent with a spectroscopic oxidation state of Ni(I) based on this correlation (see Figure 4.4).

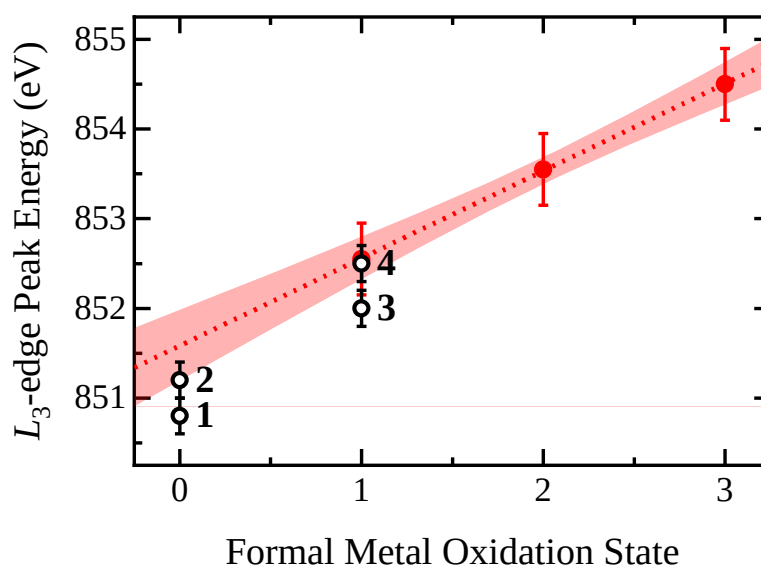


Figure 4.4 Intensity-weighted average energy of Ni L_3 -edge spectroscopic features as a function of formal oxidation state. Reference data are taken from previous studies by Cramer and coworkers²⁹. The red shaded area represents the 95% confidence interval from the Cramer data. Also plotted are the intensity-weighted average energies of the L_3 -edge features for complexes 4.1-4.4 in this work.

4.2.2 TD-DFT calculation

The high d occupancy in these species dramatically simplifies analysis of the L-edge spectra and allows for reasonable modelling of the final states without invoking atomic multiplets from multielectron configurational states^{231,240}. Time-dependent DFT (TD-DFT) calculations are therefore useful for evaluating the most important contributions to the spectra²³⁴. TD-DFT simulations of the Ni L-edges using B3LYP/def2-TZVP with zero-order relativistic corrections as implemented in ORCA 4.0 are shown in Figure 4.5; these results qualitatively mirror those of the experimental Ni L_3 -edges. A summary of the relevant TD-DFT calculated final states for each of the complexes are given in Table 4.1.

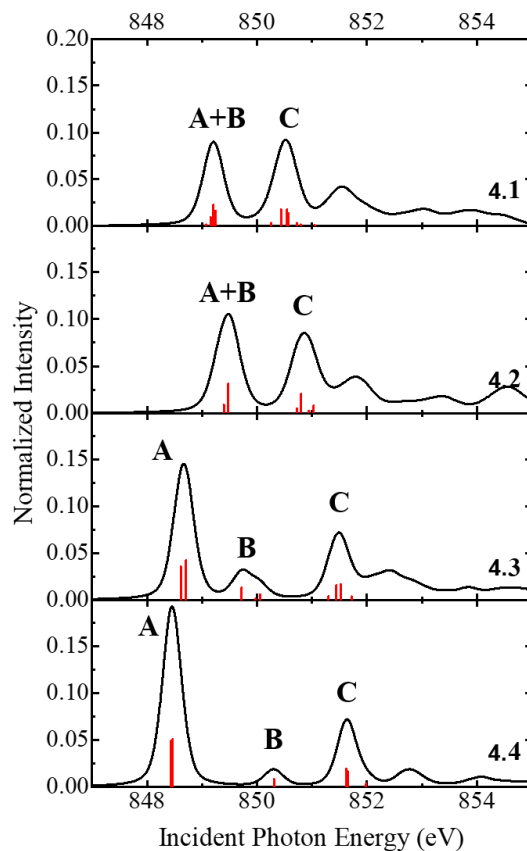


Figure 4.5 TD-DFT calculated Ni L-edge XAS spectrum for 4.1-4.4. Overall simulated spectra are obtained by including an arbitrary isotropic broadening (FWHM = 0.05 eV) to the sum of all individual contributing final states. Drop lines (red) indicate the dominant contributing final states to the overall simulated spectrum. The details of each of these final states is given in Table 4.1.

The nature of the final states listed in Table 4.1 is similar to that obtained for Ni K-edges, although relative contributions from each of these final states is very different due to differences in the initial state. Simulated spectra for 4.1 & 4.2 predict two important features - in good agreement with the experimental data. The lowest energy feature results from two contributions: (i) the ligand acceptor π^* orbital involved in backbonding ($L\pi^* \leftarrow Ni2p$), and (ii) a Ni $4p_z$ final state with

significant diphosphine ligand character ($\text{Ni}4p + \text{LMCT} \leftarrow \text{Ni}2p$). The $\text{Ni } 4p_z$ final state gains intensity from mixing with dipole-allowed $\text{Ni } 3d$ orbital character. The total intensity of this feature represents the overall depletion of electron density from the $3d$ manifold both to higher lying metal states (via hybridization) and backdonation to the ligands. By contrast, the intensity of the higher energy feature is dominated by $\text{Ni } 4s$ contributions in ligand-based final states; this dipole-allowed $\text{Ni } 4s \leftarrow \text{Ni } 2p$ ($|\Delta l| = 1$) feature is not observed in the corresponding Ni K-edge spectra as they correspond to an electric dipole forbidden $\text{Ni } 4s \leftarrow \text{Ni } 1s$ ($|\Delta l| = 0$). This feature includes only minor $\text{Ni } 3d$ contributions and therefore the intensity of this feature does not reflect $3d$ electron depletion. A broad shoulder at higher energy is also observed and is attributed to more ill-defined Rydberg final states²⁴¹. The shifts to higher energy and the appearance of a low energy shoulder in the experimental spectra of 4.3 & 4.4 (relative to 4.1 & 4.2) also occur in the simulated spectra of these species. The simulations indicate similar transitions as those observed in 4.1 & 4.2 but with systematic changes as summarized in Figure 6. Final states with significant $\text{Ni } 4s$ and $4p$ contributions (C & B, respectively) shift to higher energy, in accordance with a decrease in the electron density at the metal centre. The energy of the $L\pi^*$ final states (A), *i.e.*, those involved in backbonding, are lower in energy for these species because of the inherently greater π acidity of the ligands in these complexes. The intensity of the feature A increases as a function of the π acidity of the ligand, which reflects an increase in the contribution from the $\text{Ni } 3d$ manifold in these $L\pi^*$ final states. The change is substantial on going from alkene/arene ligands ($\sim 10\%$ for 1/2) to the electron poor ester/thioester ($\sim 25\%$ for 4.3/4.4).

Complex	Peak	E_{avg}	I_{tot}	% Ni (3d)	% L	% dtpe	final state
4.1	A	849.2	0.039	20 (14)	39	41	$L\pi^* + 3d_{x^2-y^2}$
	B	849.1	0.011	31 (6)	24	45	dtpe + Ni $4p_z$
	C	850.5	0.053	10 (2)	15	75	dtpe + Ni $4s$
4.2	A	849.5	0.056	7 (5)	31	63	$L\pi^* + 3d_{x^2-y^2}$
	B	849.4	0.009	13 (3)	5	82	dtpe + Ni $4pd$
	C	850.9	0.036	5 (1)	5	90	dtpe + Ni $4s$
4.3	A	848.7	0.078	28 (26)	33	38	$L\pi^* + 3d_{x^2-y^2}$
	B	849.8	0.021	43 (7)	17	40	dtpe + Ni $4p_z$
	C	851.5	0.041	8 (2)	4	88	dtpe + Ni $4s$
4.4	A	848.5	0.100	34 (25)	31	35	$L\pi^* + 3d_{x^2-y^2}$
	B	851.4	0.045	20 (8)	6	74	dtpe + Ni $4p_z$
	C	852.0	0.003	6 (1)	0	94	dtpe + Ni $4s$

Table 4.1 Summary of TD-DFT calculated Ni L-edge XAS data for 4.1-4.4. Each row represents a family of transitions (with an average energy, E_{avg} , and a total intensity, I_{tot}). Each of these families of transitions are ascribed to particular features in the Ni L_3 -edge spectra (A, B, and C in Figures 4.3 & 4.5). The averaged distribution of the final state acceptor orbitals is also broken down between the metal (Ni, metal $3d$ contributions given in parentheses), the π ligand (L), and the diphosphine ligand (dtpe). A detailed breakdown of all relevant TD-DFT calculated transitions are given in Appendix B.9-B.20.

The experimental and simulated L -edges are in agreement with the conclusion that Ni $3d$ charge depletion is small in both 4.1 and 4.2 even though the π ligands are strongly activated through significant backbonding. This observation supports the predominance of *ligand-induced backbonding*, which allows for π backbonding from the ancillary diphosphine ligand to the π ligand with only minimal contributions from the metal. Although quantitative evaluation of covalency has been performed for other transition metals such as copper and iron, appropriate validated references are not currently available for nickel complexes. However, the relative intensities of the contributing features in the L-edge spectra may be used to evaluate the

changes in the metal contributions to backbonding in each of the complexes.

4.3 Discussion

As noted previously, there are two mechanisms for Ni 3d contributions to bonding in these species; each of these is reflected in the Ni L_3 -edge spectra. Peak A derives intensity from direct Ni 3d contributions to backbonding, whereas the intensity of peak B reflects Ni 3d/4p mixing. We note that the overall Ni 3d contributions to bonding correlate very well with the energy of the Ni $4p \leftarrow 1s$ transition (see Appendix B.21), which reflects spectroscopic oxidation states. For both the alkene and arene complexes, Ni 3d contributions are relatively small such that 4.1 & 4.2 are best described as *Ni(0) metallacycles*. This formulation is a typical within the DCD bonding model, which envisages the formation of metallacycles with concomitant two-electron oxidation of the metal centre (i.e., a Ni(II) metallacycle). Formal cleavage of the C=C π bond is achieved primarily through charge donation from the diphosphine ligands rather than the metal centre. In more π acidic systems such as 4.3 & 4.4, the metal contribution to backbonding increases relative to that of the diphosphine (Figure 4.6), resulting in formal metal oxidation. These complexes have a more Ni(I)-like electronic configuration via increased covalency. Although ligand contributions are still extremely important in such species, metal donation is significant. We anticipate that the reactivity of complexes with dominant *ligand-induced backbonding* such as 4.1 & 4.2, where metal contributions are very small, will differ markedly from those with more classical metal-based backbonding. We postulate that this may be an important factor in reactivity differences between Nickel and its noble metal analogs, palladium and platinum, for whom metal-based backbonding is known to be very important.²⁴²

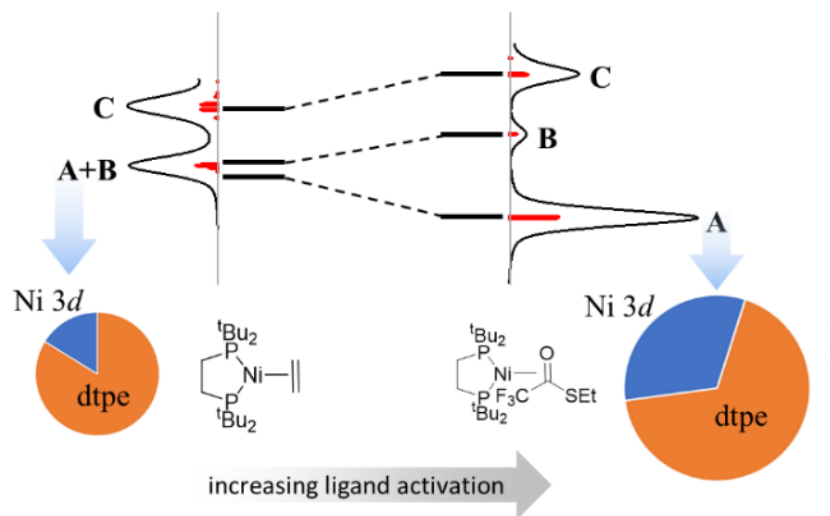


Figure 4.6 Schematic representation of changes in final states between 4.2 (left) and 4.4 (right). Most final states (B, C - see Table 4.1 for details) increase in energy due to charge depletion at the metal centre except for $L\pi^*$ states (A), which decreases in energy and increases in intensity. These changes occur because of increased charge donation from the metal centre in response to greater π acidity in the ligand. Each pie chart represents the changes in Ni and dtbpe charge donation from to the π ligand for each of the complexes. The Ni 3d contribution to backbonding increases from under 20% to $\sim 35\%$ between the two complexes.

4.4 Summary

Nickel $L_{3,2}$ -edge spectroscopic data on a series of well defined nickel diphosphine π complexes to provide support for the critical role of *ligand-induced backbonding* in bond formation and ligand activation. The data and supporting computational data indicate two major sources of Ni 3d contributions to bonding and a direct correlation between the degree of Ni 3d charge depletion and the spectroscopic oxidation state of the metal. In weakly π acidic complexes, Ni 3d contributions are very small even though the π ligand is strongly activated. With more strongly π acidic ligands, contributions from the metal increase leading to partial oxidation of the metal centre. These results support a direct involvement of ancillary ligands in π backbonding. The implications for reactivity are still being elucidated.

4.5 Methods

4.5.1 Experimental Sample Preparation

Selected (dtbpe)Ni (dtbpe = 1,2-bis(di-*tert*-butyl)phosphino)ethane) π -complexes were prepared as previously described.^{152,212,221}

4.5.2 Spectroscopic Measurements

XAS spectra were recorded at beamline 10-1 at the Stanford Synchrotron Radiation Lightsource (SSRL). An array of transition-edge-sensor (TES) detectors were used to obtain high energy resolution partial fluorescence yield (PFY) data. The TES array consists of 220 operational detectors spanning a total active area of 1.9 mm². While the monochromator was scanned across the intended energy region (e.g., 840–960 eV), the total electron yield from the samples was measured using a channeltron electron multiplier. The incident beam intensity was monitored via a gold grid and used as I_0 to normalize the total electron yield signal I_1 . For comparison, the normalized (I_1/I_0) spectra were renormalized to each other's maximum. The scans were recorded with a step size of 0.3 eV and an integration time of 1 s/pt. The energy resolution of the incident radiation is ~ 0.3 eV. Each final spectrum was the sum of five scans from different sample spots. Energy calibration was performed using NiF₂, with an L₃-edge feature at 852.7 eV.²⁴³ To minimize self-absorption in the fluorescence data, the incident angle was set at 55° with respect to the sample surface. All samples were measured at room temperature. To minimize radiation damage, a defocused beam (about 1×1 mm²) was used.

4.5.3 Computational methods

Initial geometries for all molecules were obtained from crystallographic coordinates (where available) or constructed from standard models. Geometry optimizations and numerical frequency calculations were performed using version 4.0 of the ORCA computational chemistry package²⁴⁴. Molecular geometries were optimized using the B3LYP functional in combination with the Ahlrichs triple- ζ basis set with valence polarization (def2-TZVP) for all atoms. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional²²⁸. All calculations

were performed with integration grid 4. Reported thermochemical energies are given in kJ/mol and correspond to Gibbs free energies (ΔG^0) with zero-point vibrational energy corrections (ZPVE). All calculations were run on either the Abacus (UBC Chemistry) or GREX (Westgrid) computing clusters.

Chapter 5: The structure of η^2 Ni(0) thiophene complexes, and its ring walking behaviour.

5.1 Introduction

The much-anticipated revolution from bulk to molecular electronics hinges upon efficient and controlled exploitation of appropriate molecular transistors, diodes, integrated circuits, and optoelectronic devices^{245–247}. Polythiophenes have been widely explored as building blocks in both electronic and optical molecular devices due to their efficient electronic and thermal conductivity as well as their high quantum efficiencies^{10–12}. Amongst current strategies for polythiophene synthesis, nickel-catalyzed *catalyst transfer polycondensation* (CTP) has proven particularly effective in the production of polythiophenes with high molecular weights, regioregularity, low polydispersities, and end-group control.^{69,248,249} The mechanism of thiophene CTP has attracted significant attention since it was first shown that it proceeded via *living* chain-growth polymerization^{9,71,74,250}, which requires that the metal catalyst must remain attached to the nascent polymer chain *throughout the process* (Figure 5.1a)¹⁰¹. Although stable Ni(II) intermediates have been characterized (I & II)^{70,251}, the identity of the postulated Ni(0) intermediate (III) has remained elusive.

McNeil and coworkers have postulated that such Ni(0)-thiophene intermediates could, by analogy to known Ni(0)-arene complexes, be formulated as $C,C\text{-}\eta^2$ Ni(0) structures²⁵². Such structures are consistent with computational⁹⁴ and experimental^{15,253} data but conclusive structural evidence is lacking. However, computational studies indicate the feasibility of alternative Ni-thiophene isomers and the available spectroscopic data are not inconsistent with other potential structures. In fact, there exist several reasonable bonding modes in metal thiophenes (see Figure 5.1b), including sulfur coordination ($\eta^1\text{-S}$)^{254–256} and a variety of π adducts (η^2 , η^4 , or η^5).^{257–260} A direct analogy between arene and thiophene binding modes is therefore potentially problematic as has been noted previously^{256,261}. Only two structurally-characterized complexes are known to adopt the proposed $C,C\text{-}\eta^2$ binding motif in thiophene complexes: the Harman group identified a saturated $18e^-$ tungsten complex with a weakly bound $C,C\text{-}\eta^2$ thiophene ligand²⁶² and Agapie and coworkers isolated a unique palladium(I)

dimer with a *bridging cis- μ - η^2 : η^2 thiophene*²⁶³. Although these two reports demonstrate the feasibility of *C,C- η^2* binding for thiophene, they differ both structurally and electronically from the proposed CTP intermediates and thus cannot directly address whether such bonding may be achieved in a low valent d^{10} system. For these reasons, elucidation of the geometric and electronic structure of species such as III remain an unsolved challenge until now^{55,250,264}. Herein we report the structure and properties of species that are directly relevant to the CTP process, providing an opportunity to evaluate the factors that allow for *living* polymerization of thiophenes.

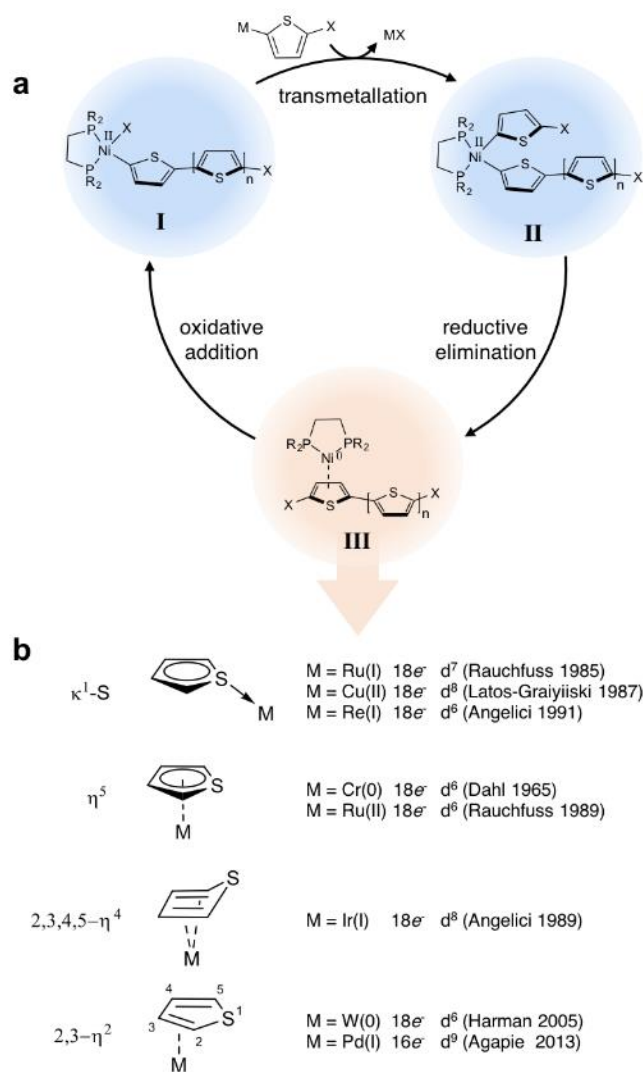


Figure 5.1. (a) Generally accepted mechanism for Ni-catalysed CTP. The Ni(II) species highlighted in blue (I, II) have been previously identified and characterized. By contrast, the putative Ni(0) species in red (III) has no precedent in the literature. (b) Structurally characterized thiophene binding modes from crystallographically-defined metal-thiophene complexes.

5.2 Results

5.2.1 Factors relevant to isolating relevant intermediates

We anticipated that a major challenge to successful isolation of Ni(0) thiophene π complexes would be to limit oxidative addition via cleavage of the C-X bond or the internal thiophene C-S bonds as shown in Figure 5.2.^{80,265} C-Br insertion can be avoided by choosing unsubstituted thiophene ligands and we anticipated that removing the bromine substituent would have a relatively minor effect on the electronic properties of the thiophenic ligand. This is supported by computational data (*vide infra*). Preventing C-S insertion, however, is a somewhat greater challenge. Given the more restricted geometry of the predicted C-S insertion product, we rationalized that increasing steric bulk near the metal centre could assist in minimizing C-S insertion. DFT calculations on the relative energies of the π complex relative to the C-S insertion product indicated a decreasing preference for C-S insertion on going from thiophene, bithiophene, and trithiophene (see Figure 5.3, A-D-C). The overall effect, however, is relatively small and ΔG_{ins}^{DFT} remains significantly exergonic even with the trithiophene ligand ($\Delta G_{ins}^{B3LYP} < -30 \text{ kJ/mol}$) at room temperature. By contrast, steric bulk in the ancillary diphosphine ligand is calculated to have a surprisingly large effect on the overall energetics of this equilibrium (Fig. 3, A-D-E); *t*-butyl substitution leading to a significant decrease in the preference for C-S insertion ($\Delta G_{ins}^{B3LYP} > -10 \text{ kJ/mol}$).

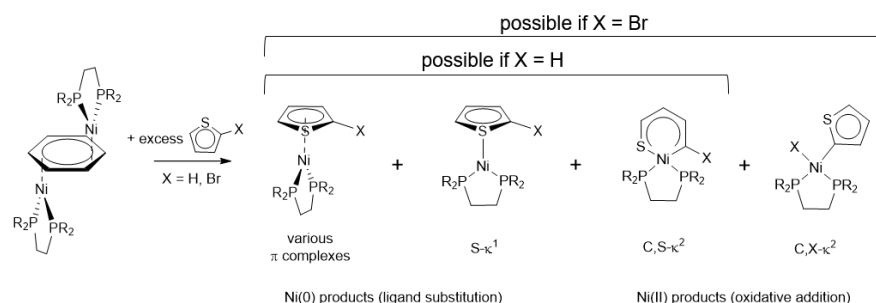


Figure 5.2 Possible products from reaction of Ni(0) arene precursor with excess thiophene reactants. In order to minimize the formation of unwanted oxidative addition products, thiophenes without a reactive 2-bromo substituent were chosen, leaving C-S insertion as the only other viable pathway for oxidative addition. Note that although the $S-\kappa^1$ isomer is shown,

it is not observed. Only one representative species of many possible isomers is shown for each of the possible outcomes.

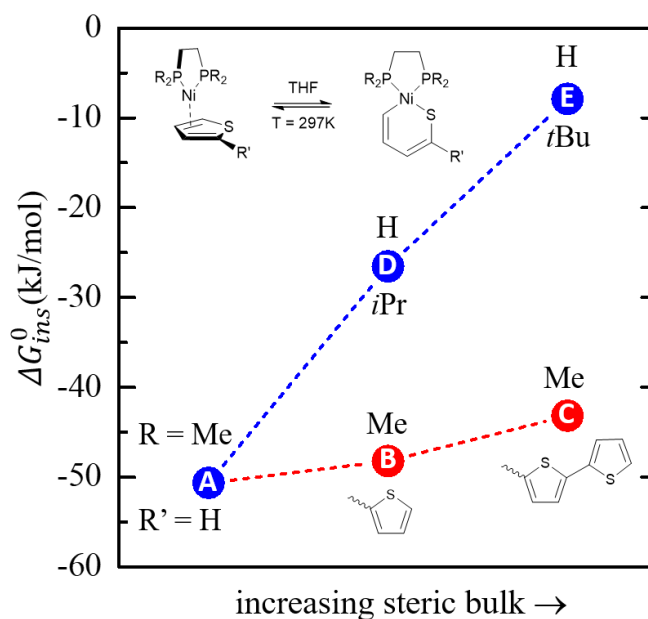


Figure 5.3 DFT-derived thermodynamics for C-S insertion from the exo- π adduct based on the B3LYP functional. Results obtained for the M06 and BP86 functionals yield the same trends as those shown here (see C11). Increasing the steric bulk at the thiophene ligand (R') results in a modest decrease in the preference for C-S insertion (A→B→C), whereas the effect is substantial when steric bulk is increased in the diphosphine ligand (R). The x-axis is a generic axis representing increasing steric bulk but it is not quantitative. Additional information is provided in Appendix C.11 & C.12.

5.2.2 Solution characterization of relevant species

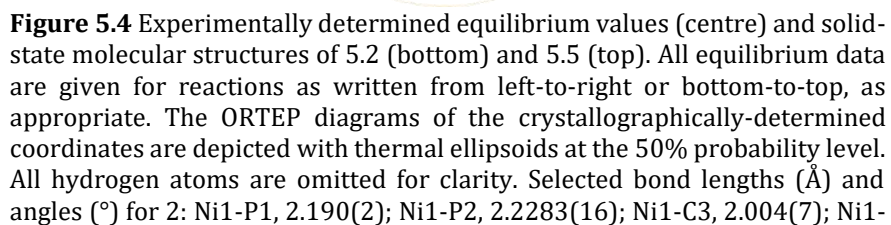
Inspired by Love and coworkers' approach to the synthesis of Ni(0) π complexes²¹², we used a bulky diphosphine Ni(0) benzene dimer $[(dtbpe)Ni]_2(\mu-\eta^2:\eta^2-C_6H_6)$ (3.1, dtbpe = 1,2-bis(di-*tert*-butyl)phosphinoethane) as a precursor from which to explore the formation of thiophene complexes in pentane at low temperature (~ 245 K). In the presence of a large excess of thiophene, an orange solid is obtained after *in vacuo* removal of solvent. The solid-state molecular structure of the recrystallized product (5.2, $[(dtbpe)Ni]_2(trans-\mu-\eta^2:\eta^2\text{-thiophene})$)

indicates formation of a nickel(0) dimer with a bridging $\mu\text{-}\eta^2\text{:}\eta^2$ thiophene ligand (Figure 4, top), which is structurally analogous to the precursor benzene dimer. Solution NMR data of 5.2 are consistent with the solid-state molecular structure; notably, a large primary coupling between the inequivalent ^{31}P nuclei ($\sim 87\text{Hz}$) implies a Ni(0) ground state configuration and additional splitting of the ^{31}P signals are consistent with weaker J_{PP} coupling across the bridging thiophene ligand (5–8Hz, see Appendix C.24). Seeking to generate the target *monomeric* thiophene complex, we added a further excess of thiophene to 5.2 in THF at $\sim 245\text{K}$. Under these conditions, an equilibrium mixture of the presumed mononuclear thiophene complex (3, (dtbpe)Ni(η^2 -thiophene)) and the C-S insertion side-product (5.4, (dtbpe)Ni(S,C- κ^2 -thiophene)) is obtained (see Appendix C 28). The ^{31}P NMR data for 5.3 are similar to that of 5.2 although the observed J_{PP} is slightly lower in 5.3 ($\sim 82\text{Hz}$), which is consistent with stronger binding to the π ligand in the monomeric species. We have been unsuccessful in isolating and/or crystallizing 5.3, presumably due to a significant enthalpic preference for 5.4 (See Appendix C.1-3).

Our DFT calculations indicate that C-S insertion should be less favoured in oligothiophenes as opposed to monothiophenes (Figure 5.3) and thus we postulated that switching to bithiophene as a ligand might provide a better opportunity to isolate and characterize an analogous mononuclear complex (5.5, bithiophene) and suppress formation of the insertion product 5.6 (Figure 5.4). This approach worked beautifully, allowing us to obtain diffraction quality single crystals of 5 and obtain its solid-state molecular structure (Figure 5.4, bottom). This species is the only structurally characterized d^{10} metal thiophene complex and exhibits an *exo-C,C- η^2* binding geometry. Importantly, the metal complex exhibits a *square planar geometry*, suggesting that π -backbonding plays a critical role in its stability³⁶. As with the monothiophene complexes in solution, the 5.5 = 5.6 equilibrium can be followed by $^{31}\text{P}\{^1\text{H}\}$ NMR. As predicted from DFT, the preference for C-S insertion is decreased slightly in the bithiophene equilibrium (5.5-5.6) relative to the monothiophene. We attribute this to a modest enthalpic preference for the π complex in the bithiophene system as predicted computationally (Appendix C.11 & C.12); available experimental data are also consistent with this hypothesis (Appendix C.1).

5.2.3 Geometric and electronic structure of intermediate species.

The isolation and characterization of 5.5 provide an opportunity to directly probe the nature of a very close structural analog to nickel(0) CTP intermediates. The metric parameters for 5.5 indicate strong similarities to other Ni(0) π complexes. In addition, the metric and electronic properties of the complex are in good agreement with a DFT-optimized analog (RMSD $\sim$ 8pm, see Appendix C.4-7). We have recently studied a broad range of well-defined nickel π complexes that are best described as *square planar* d^{10} complexes; this unusual bonding scheme derives from the dominance of backbonding from the metal to the π ligand through the same metal orbital (dx^2-y^2) that can receive electron density from the diphosphine ligand as shown in Figure 5.5. This situation formally creates a three-centre-four-electron (3c-4e)^{266,267} bond involving σ donation from the phosphines through to the η^2 thiophene ligand via π backbonding from the nickel centre. Computationally, we estimate that almost 75% of the backdonation comes from the *trans*-phosphine ligands indicating a large cooperative binding effect through this 3c-4e interaction. The nature of this backbonding interaction was confirmed using Ni K-edge X-ray absorption spectroscopy (Appendix 18), which confirms that the metal centre remains electron-rich and very Ni(0)-like. By comparison with other Ni π complexes, we note that the π acidity of the thiophene ligand is similar to that of ethylene in the analogous Ni(dtbpe)ethylene complex. The delocalized 3c-4e interaction necessitates a nearly square planar geometry about the metal centre. It also points to the importance of a sterically-encumbered but electron-rich diphosphine ligand, which provides significant charge donation to strengthen the metal-thiophene bond. This “*push-pull*” effect is similar to that which has been observed as a key factor in the mechanism of Cytochrome P450 enzymes²⁶⁸, where a thiolate ligand provides charge donation across the metal centre to increase activation of a dioxygen-derived ligand. In this case, however, the push-pull effect leads to stabilization of the Ni(0) intermediates, which should affect ligand dissociation during catalysis. We, therefore, suggest that this effect is critical in ensuring living polymerization of thiophenes with nickel diphosphine catalysts.



C4, 1.953(5); C3-C4, 1.432(15); Ni1-Ni1i, 4.764(7) P1-Ni1-P2, 91.16(8); C3-Ni1-P1, 111.7(5); C3-Ni1-P2, 157.0(4); C4-Ni1-P1, 150.78(17); C4-Ni1-P2, 116.12(18); Selected bond lengths (Å) and angles (°) for 5 : Ni-P1, 2.1831(5); Ni1-P2, 2.1970(5); Ni1-C7, 1.9985(18); Ni1-C8, 1.9570(18); C7-C8, 1.447(3); C5-C6, 1.338(6); C1-C2, 1.345(3); C3-C4, 1.380(6); P1-Ni1-P2, 92.612(19); C7-Ni1-P1, 151.09(6); C7-Ni1-P2, 114.51(6); C8-Ni1-P1, 110.60(6); C8-Ni1-P2, 156.78(6); C8-Ni1-C7, 42.89(8). Structures have been deposited to the CCDC (CCDC1587316 for 5.2, and CCDC1587317 for 5.5). There is disorder observed in both the thiophene and bithiophene complexes, which does not affect the overall structural features of the complexes, see SI for refinement and details, Appendix C4.

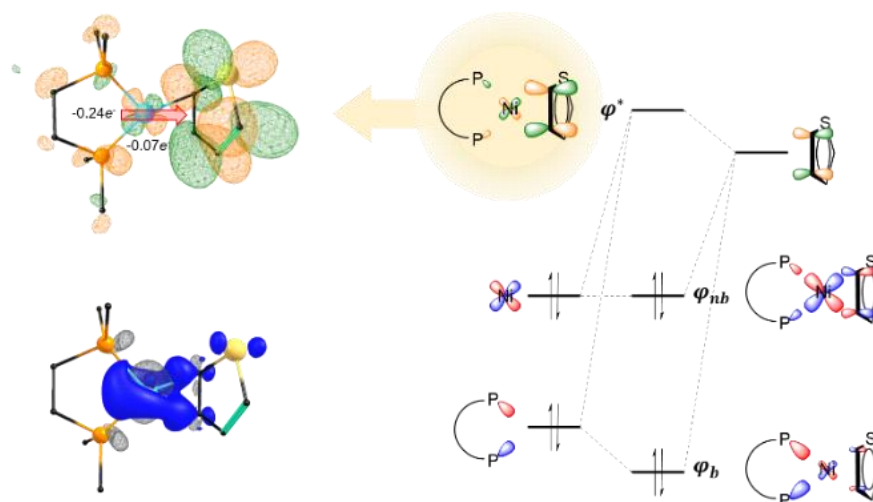


Figure 5.5 Dominant π -backbonding interaction between metal *bis*-phosphine fragment and the thiophene ligand. The interaction is formally a three-centre four-electron interaction between the three molecular fragments: the diphosphine ligand, the metal centre, and the thiophene ligand. This cooperative bonding interaction is most easily represented by looking at the formally antibonding orbital (-0.38eV), which shows the degree of charge donation from both the metal centre ($0.07e^-$) and the diphosphine ligand ($0.24e^-$). An Atoms-in-Molecules (AIM) fragment analysis (bottom) additionally shows the overall charge redistribution from the diphosphine ligand and metal centre into the thiophene ligand (grey = decreased electron density, blue = increasing electron density), see more details in and Appendix C.15 & 16.

The nature of bonding in the Ni(0) π complex is critical to the overall CTP mechanism as it represents the intermediate that is most weakly

bound and thus most likely to release the polythiophene chain during turnover. Previous studies have indicated that the bond must be strong enough to prevent loss of the ligand but labile enough to allow for chain walking along the polythiophene backbone.¹⁰¹ Intriguingly, At 200K, we observe an additional species in solution (5.7) in equilibrium with the dominant 5.5 and 5.6 (see Figure. 5.4, middle). This species has similar spectroscopic properties to 5.5 and we assign this species to the *endo* η^2_{CC} isomer. This is supported by computational results, where 5.5 is enthalpically favoured over 5.7 due to additional steric constraints in the *endo* configuration ($\Delta H_{DFT}^0 = 6.3 \text{ kJ/mol}$, see Appendix C.9 & C.10). Based on available NMR data, we estimate $K_{eq} = 20 \sim 40$ at $T = 200\text{K}$, suggesting a similar preference of $5\text{-}6 \text{ kJ/mol}$ for the *exo* isomer. Furthermore, we observe kinetic trapping of 5.7 during synthesis of 5.5 at very low temperatures ($<200 \text{ K}$). We are currently exploring the isomerization kinetics to provide insights into the dynamics of [Ni] walking along the polymer chain.

5.2.4 Exploration of Short-Distance Ring Transfer

Our results demonstrate the viability of specific structural motifs as intermediates in the catalytic mechanism for CTP. Importantly, our results provide validation of DFT-derived geometric and electronic structure models for such species and increases confidence in the computational models. We therefore expanded our computational studies to include the catalytically relevant 2-bromo-substituted bithiophene complexes to explore the impact of halide substitution on the nature of the intermediates. In computational models, we find only minor differences upon inclusion of a 2-bromo substituent. As summarized in Table 1, the metric parameters about the metal centre are nearly identical in both cases (5.3H vs. 5.3Br_X). Notably, the 5.3Br complex may adopt two different *C,C*- η^2 isomers depending on whether the metal binds adjacent to (3Br_X; *C2,C3*- η^2 binding) or remote to (5.3Br_H; *C4,C5*- η^2 binding) the bromo substituent, these isomers are easily interconverted via a symmetric *C,C,C,C*- η^4 transition state (TS5.2Br in Figure 5.6).¹⁸ The calculated structure for 5.3Br_H is very similar to 5.3H, indicating that the bromo substituent has only a marginal impact over longer distances. The largest effect observed in 5.3Br_X is a shift of the metal centre slightly towards the most electron deficient carbon (C2); this reflects greater asymmetry in the acceptor π^* orbital of the 2-bromothiophene ligand. In addition, there is a very

modest concomitant increase in the C=C bond distance, which is consistent with greater π backbonding in 5.3Br_X due to bromo substitution.

Given that the computational method is robust for the ground state species, we expanded our investigation of the 2-bromosubstituted nickel complex to evaluate the overall energy profile for all possible isomers of this species. The resulting energy landscape for Ni(dmpe) binding to 2-bromothiophene is shown in Figure 6. These data are in good agreement with experimental data that show that the *C*, *C*- η^2 (5.8Br_H) and *C*, *S*- κ^2 (5.4Br_H) species are in equilibrium, and that other possible isomers such as *C*, *S*- η^2 isomers (5.8Br_H & 5.8Br_X) are much higher in energy (by >40 kJ/mol). Calculated barriers for isomerization are quite large due to the strong π -backbonding in the *C*, *C*- η^2 structure. The barrier for C-Br oxidative addition (to form 5.9Br) is similar to that for chain walking and also significantly larger than that for C-S oxidative addition near the bromo substituent (to form 5.4Br_X). We note that 5.4Br_X is both the lowest energy species in the isomerization landscape (excluding formation of 5.9Br) and that with the lowest barrier to the formation. We, therefore, suggest that 5.4Br_X and similar species formed during polymerisation may serve as off-cycle intermediates during turnover. Such species are clearly important in hydrodesulfurization^{80,265,269}.

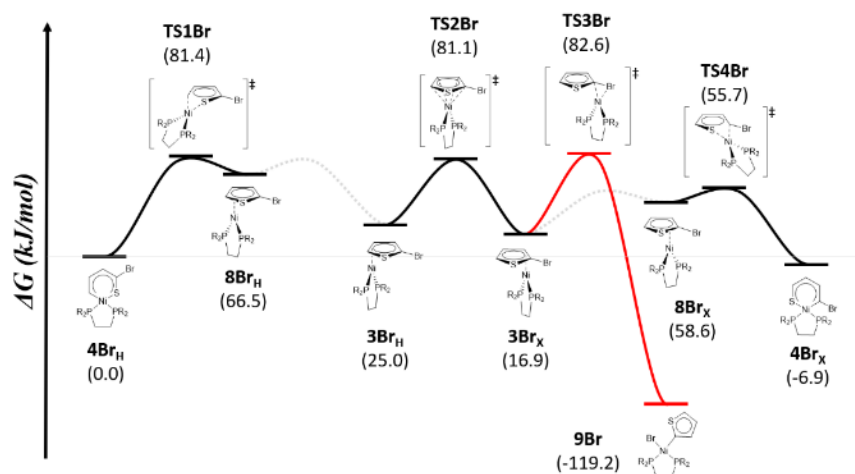


Figure 5.6 DFT calculated free energy of (dmpe)Ni(2-bromothiophene) ring transfer and oxidation addition in the gas phase (R = Me). Transition states connecting 3Br_X to 8Br_X and 3Br_H to 8Br_H have not been observed but coordinate scans indicate that these structural changes are associated with very low barriers.

The minor differences observed in our computational studies of the unsubstituted and 2-bromosubstituted Ni(0) $C,C\text{-}\eta^2$ thiophene complexes is strong evidence that 5.5 is highly relevant as a model for the actual intermediates in nickel-catalyzed CTP. In addition, our work supports the proposal that both the higher energy *endo* isomer (identified by NMR) and the *exo-C,S- κ^2* isomer (from DFT) are also relevant to the catalytic reaction mechanism. In fact, these results strongly support the idea that catalysis must proceed through *both* Ni(0) species as has been previously proposed^{250,252}. $C_{sp^2}\text{-}C_{sp^2}$ coupling via reductive elimination necessarily generates an *endo- η^2_{CC}* species (III, Figure 5.7), which must undergo ring walking to the more stable *exo- η^2_{CC}* species (IV, Figure 5.7). The relative energies of these isomers provides a bias towards the catalytically competent *exo- η^2_{CC}* . We further propose that the off-cycle $C,S\text{-}\kappa^2$ species may be important in the overall process by providing an off-cycle resting state prior to turnover limiting C-Br oxidative addition.

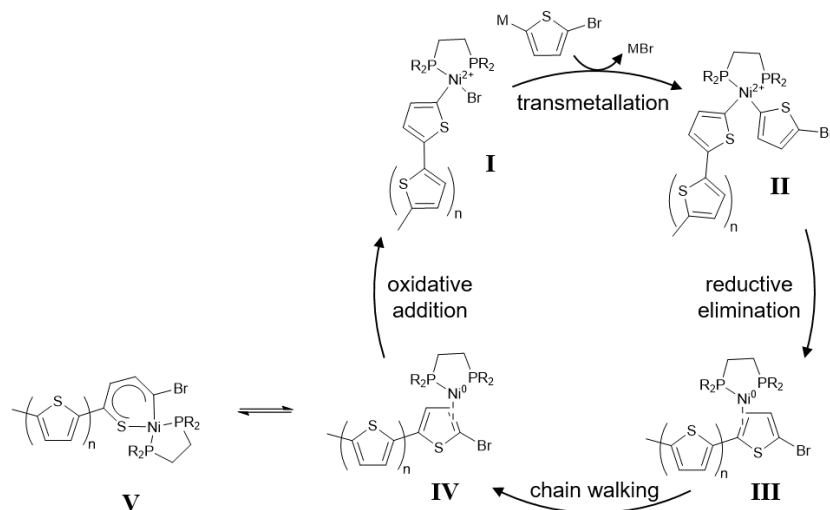
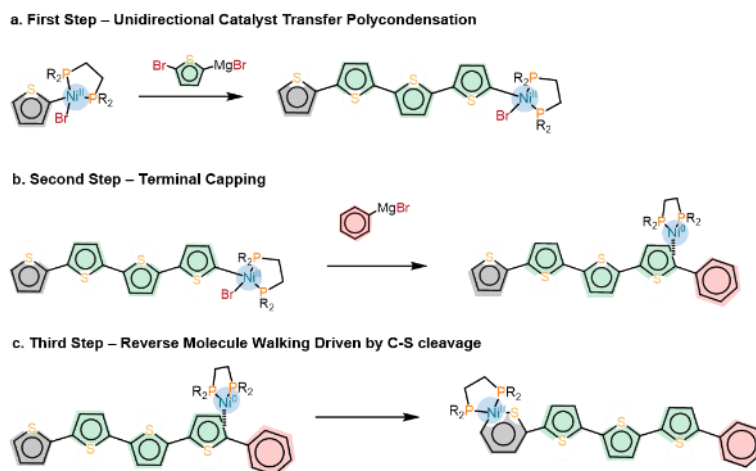


Figure 5.7 Proposed mechanism for CTP as supported by crystallographic and NMR spectroscopic evidence from this work. A close analog 5.7 to III is observed by low-temperature $^{31}\text{P}\{\text{H}\}$ NMR, and 5.5 is a model for IV has characterized via crystallographic and spectroscopic data. Preliminary

computational data suggest the potential relevance of species such as V as off-cycle resting states.

5.2.5 Exploration of Long-Distance Ring Transfer

With the findings that off-cycle C-S insertion could provide a significant driving force for migration of the Ni(0) intermediate across one thiophene unit to form *exo-C*, *S*- κ^2 isomers in the absence of a C-Br bond, we explored the use of Ni(thiophen-2-yl)Br supported with bisphosphine ancillary ligand as a precatalyst to enable *unidirectional* catalyst transfer polymerization. An open C-S bond at the starting thiophen-2-yl substitute could be maintained to allow Ni(0) catalyst to move reversibly after being capped by the Grignard reagent phenylmagnesium bromide. (Scheme 5.1)



Scheme 5.1 a. First Step: Unidirectional Catalyst Transfer Polycondensation. b. Second step: terminal Capping. c. Third step: Reverse Walking Molecule Walking Driven by C-S cleavage.

Previous reports have indicated that less sterically-hindered disphosphine ligands could lead to detrimental dissociation of the Ni catalyst from the π substrate and formation of a four coordinated tetraphosphine Ni(0) dead-end complex.¹⁰⁰ Therefore, a series of calculations comparing the binding dissociation energy (BDE) of different Ni(0)bisphosphine fragments with either thiophene or a

second bisphosphine ligand were conducted. Five bisphosphine ligands were selected and their Ni(0) fragment BDEs have been calculated. The BDE^{TH} (for thiophene dissociation) are only mildly affected by the size of bisphosphine ligand with a relatively constant value of 36 ± 12 kJ/mol. However, the BDE for the tetraphosphine complex (BDE^{BisP}) is highly sensitive to the steric constraints of the bisphosphine ligand; a staggering range of greater than 250 kJ/mol is observed from dmpe to dcpe. Negative values of $\Delta DBE^{BisP-TH}$ for both dcpe and dippe indicate a preference for thiophene binding as compared to formation of the unwanted four-coordinate Ni di(bisphosphine) complexes.

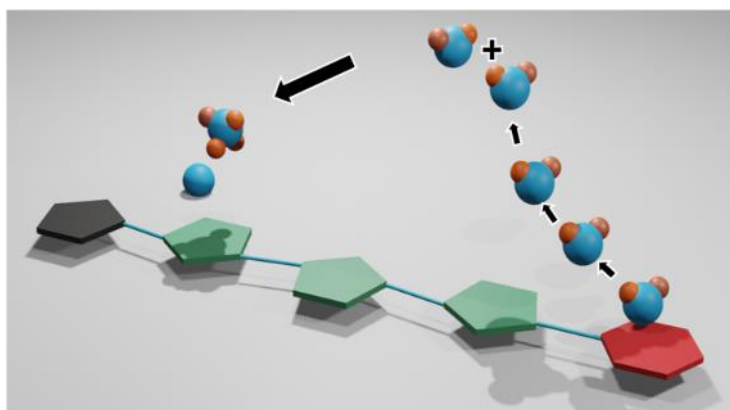
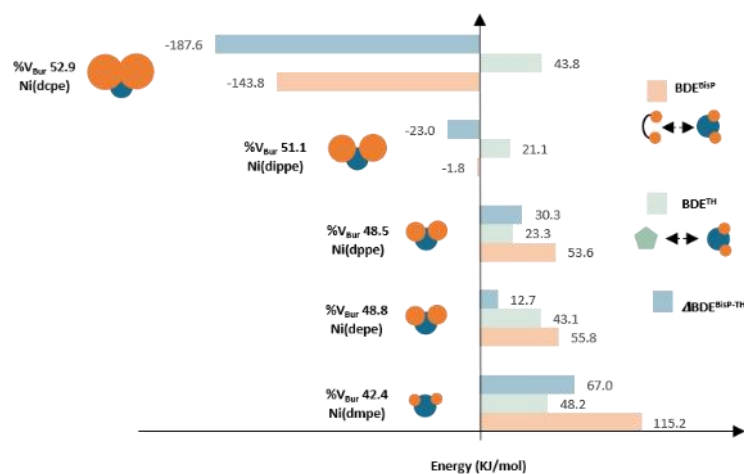


Figure 5.8 Top: The bonding dissociation energy profile of the interaction of Ni(bisphosphine) fragment and thiophene substrate (BDE^{TH} , column in light blue), the interaction of Ni(bisphosphine) and a second bisphosphine ligand (BDE^{BisP} , column in light orange), and their energy discrepancy (column in black). Bottom: The schematic diagram of postulated dissociation process from Ni catalyst ring walking due.

Based on these results, the commercially-available dcpe ligand was chosen for subsequent long-distance ring walking experiments. Pre-catalyst 5.10 (dcpe)Ni(thiophen-2-yl)Br (dcpe = 1,2-Bis(dicyclohexylphosphino)ethane) was prepared to evaluate unidirectional catalyst transfer polymerization in d_8 -THF. The reaction progress was monitored by ^{31}P NMR. The (polythiophen-2-yl)Ni(II)Br intermediates of varying lengths have characteristic $^2J_{pp}$ coupling constants (~ 30 Hz), but differ in their chemical shifts, allowing for identification of different species (See Figure 5.8). $C,S-\kappa^2$ species are observed upon addition of Grignard reagents; they are distinguished by their lower $^2J_{pp}$ coupling constants (~ 20 Hz). This result showed that the Ni(0) catalyst migrated through the entire newly synthesized oligomer back to the C-S bond at starting thiophene unit.

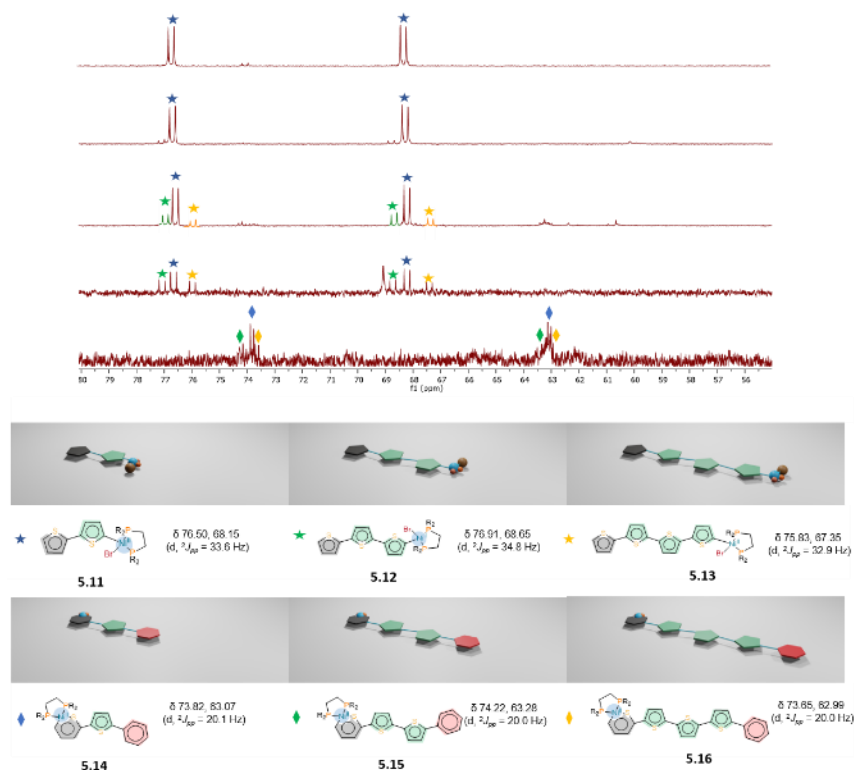


Figure 5.9 NMR spectrum of the unidirectional Ni-catalyzed CTP, each of the polymerization Ni(thiophen-2-yl)Br resting states are labelled and assigned based on $^2J_{\text{PP}}$ coupling constant. *C*, *S*- κ^2 species are formed after being reduced with phenylmagnesium bromide, and assigned by their characteristic $^2J_{\text{PP}}$ ($\sim 20\text{Hz}$)

^{31}P NMR was applied to monitor the reversible ring walking from (thiophene-2-yl)Ni(II)Cl to exo *C*, *S*- κ^2 species after being reduced with phenylmagnesium bromide. Two Ni(0)- π thiophene intermediates were observed and assigned based on its $^2J_{\text{PP}}$ coupling constant ($\sim 70\text{Hz}$) and matched the two *C*, *C*- η^2 π intermediates determined in the calculation work in Section 5.2.5. The major product is exo *C*, *S*- κ^2 species 5.14 ($^2J_{\text{PP}} = 19.7$ Hz). A sharp single impurity peak ($\delta 43.75\text{ppm}$, 2.1%) was found as Ni(dcpe) $_2$. A (phenylthiophene-yl)Ni(II)Br complex was also reduced with Grignard reagent phenylmagnesium bromide, and a Ni(0)-diphenylthiophene π complex was observed ($^2J_{\text{PP}} = 79.6$ Hz) under equilibrium with Ni(dcpe) $_2$ ($K_{\text{eq}} = 0.003$). (Figure 5.10) Thus, a large steric ancillary ligand such as dcpe could well refrain the

catalyst from self-dissociation. Also, due to the steric hindrance from *endo* C-S active sites, only the *exo* C-S bond can function as the driving force to proceed this reversible “ring walking” through multiple stable Ni(0)(dcpe)-thiophene intermediates and form a *exo* C, S- κ^2 species.

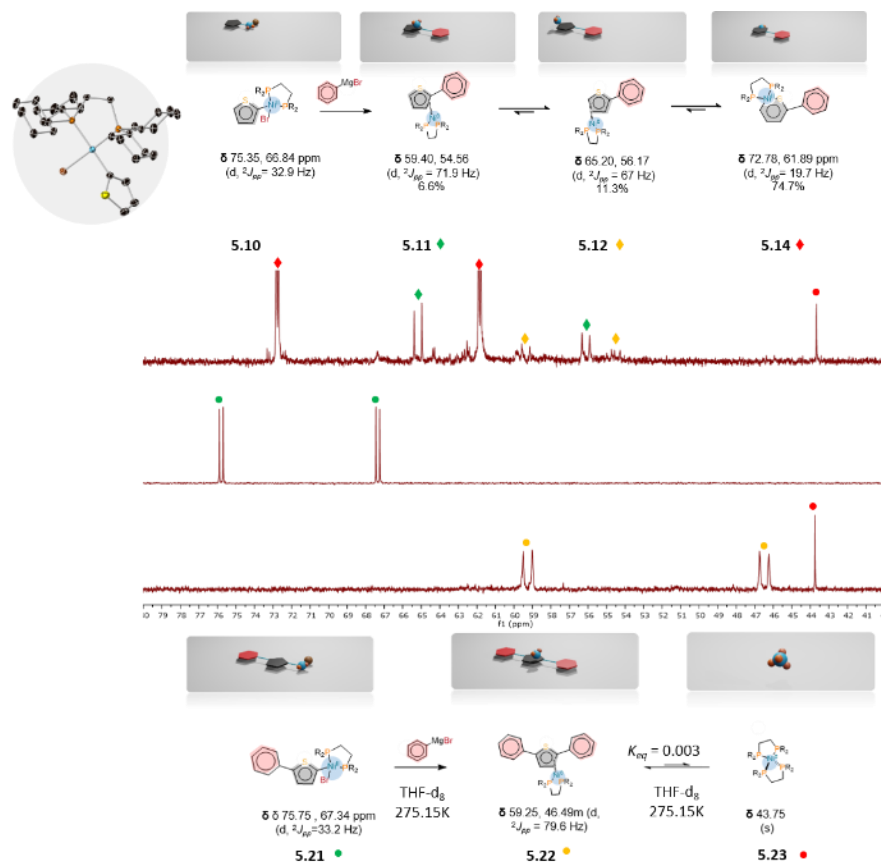


Figure 5.10 NMR spectrum of the capping reaction with the Grignard reagent phenylmagnesium bromide in both open (thiophen-2-yl)Ni(II)Br and pre-capped (phenylthiophene-2-yl)Ni(II)Br. The crystal structure of the pre-catalyst 5.10 is also provided.

Results with the less sterically-hindered dppe ligand were also evaluated; the commercially available dppe ligand is widely used in CTP reactions²⁵². We anticipated that a more electron-deficient cyanothiopen-yl could increase the stability of the Ni(dppe) π intermediate, such that a Ni(dppe) thiophene species might be

observed. However, reduction with Grignard reagent phenylmagnesium bromide leads to rapid formation of the undesirable $\text{Ni}(\text{dppe})_2$ complex, which can be isolated and crystallographically characterized (Figure 5.11).

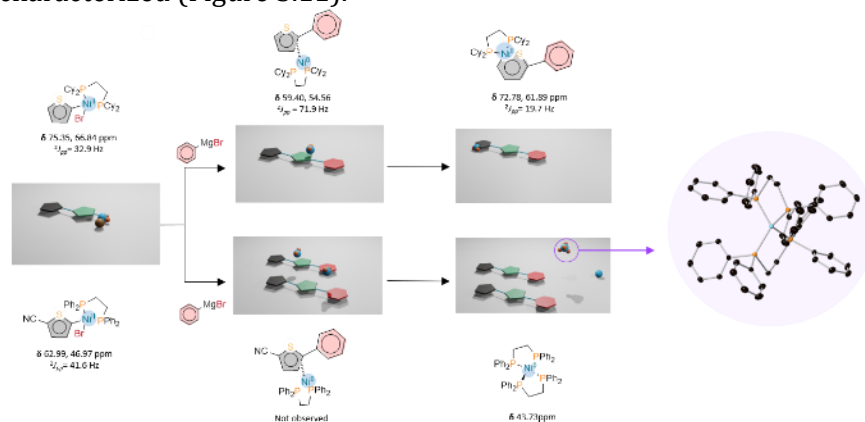


Figure 5.11 Comparison of the capping reaction of $(\text{dcpe})\text{Ni}(\text{thiophen-2-yl})\text{Br}$ and $(\text{dmpe})\text{Ni}(\text{cyanothiophene-2-yl})$. The $\text{Ni}(\text{dmpe})_2$ crystal structure was provided. All the observed species were characterized by ^{31}P NMR.

5.2.6 Computational Demonstration of Long-Distance Ring Walking.

Given the available data, direct observation of ring walking by ^{31}P NMR via $\text{Ni}(0)\text{-}\pi$ intermediates is largely restricted by NMR acquisition times and is thus unfeasible. Only intermediates in equilibrium with final stable isomers can be observed; and kinetics could not be adequately evaluated. Further computational studies by using orca packages, however, were performed to gain additional insights into potential long-distance ring walking processes. A simplified $\text{Ni}(\text{dmpe})\text{bithiophene}$ computational complex was constructed to mimic one of many repetitive “ring walking” motions, including catalyst transfer (i) *within* a single thiophene unit and (ii) between two connected thiophene units. All the important transition states were located through a rotation relaxed scan of Ni catalyst along the polymer surface.

We first compared two different paths of ring walking within one thiophene unit (Path 1-1 and Path 1-2). Low activation energies of $\sim 60\text{kJ/mol}$ were needed for both reaction paths. In Path 1-1, the one-step jump through a $\text{C,C,C,C-}\eta^4$ transition state (TS_{1-6}) connecting two

nonsymmetrical C,C- η^2 isomers is the rate-determining step (1 $\rightarrow$ TS₁₋₆, $\Delta G^\ddagger$ 57.9 kJ·mol⁻¹). However, we discovered a new multiple-step Path 1-2, that allows the Ni catalyst to rotate along with the sulfur atom through a S- κ^1 intermediate 3 (Figure 5.12). This path creates a much faster rate-determining step (3 $\rightarrow$ TS₃₋₄, $\Delta G^\ddagger$ 41.7 kJ·mol⁻¹). The rotation Path 1-2 along S atom gave much more flexibility of disorder from Ni catalyst fragment (3 $\rightarrow$ TS₃₋₄, $\Delta S^\ddagger$ 15.75 J·mol⁻¹·K⁻¹) than Path 1-1 (3 $\rightarrow$ TS₃₋₄, $\Delta S^\ddagger$ -28.07 J·mol⁻¹·K⁻¹).

Pathways allowing for transfer of the metal centre between two connected thiophene units are more complex. Three distinct walking paths (2-1, 2-2, 2-3) were located through relaxed rotation scan. In Path 2-1, a crucial intermediate 8 was found which allows a direct jump of Ni fragment between two adjacent C,C- η^2 binding sites. Also, the polythiophene plain was twisted by $\sim 20^\circ$ for lowering the transfer energy barrier. In both Path 2-2 and Path 2-3, the walking between two thiophene unit was linked by the intermediate 4, which allows a jump of Ni catalyst from adjacent C,C- η^2 and C,S- η^2 binding sites without twisting polythiophene chain.

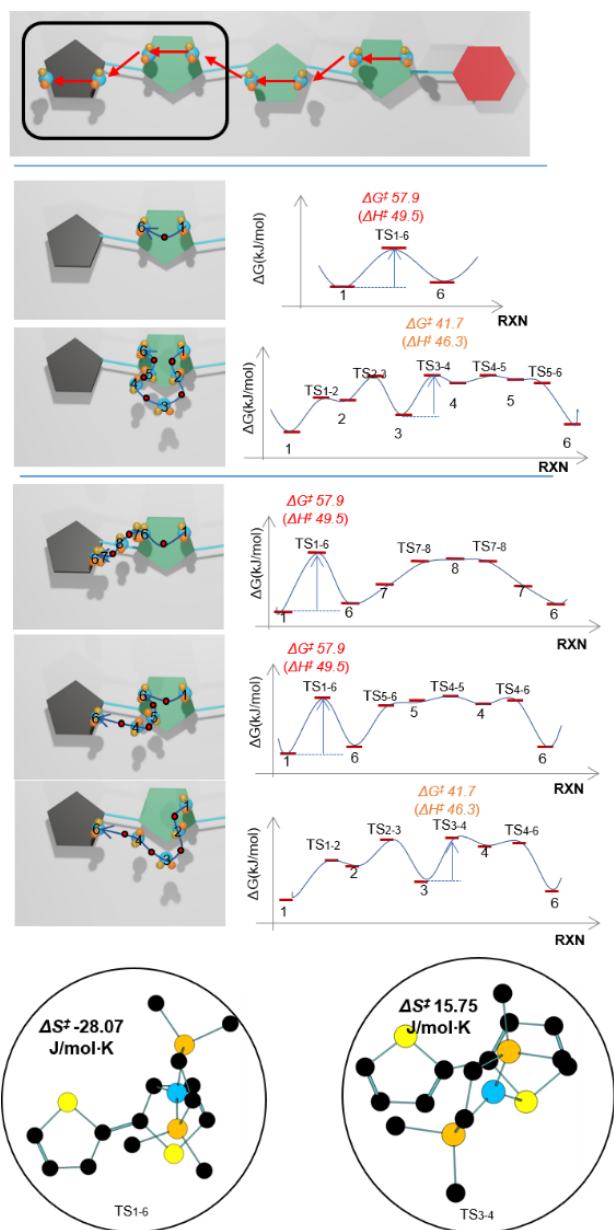


Figure 5.12 Energy profiles of two paths for ring walking within one single thiophene units and three paths for ring walking between two connected thiophene units. The rate-determining step lies in the motion within a thiophene unit. The details of theoretical level were discussed in Appendix C. 19-21

Finally, the termination process (terminal C-S bond cleavage $2 \rightarrow \text{TS}_{2-9} \rightarrow 9$) was also evaluated in concert with the ring transfer process. Two long distance ring walking mechanisms were plotted as Figure 5.13. The formation of *exo-C*, $S\text{-}\kappa^2$ species release 48.2 kJ/mol energy to provide a driving force for the Ni(0) fragment to proceed a long distance ring walking process. The individual transition states across the overall energy landscape are relatively similar, although trapped states correlate with Ni(0) π complexes localized on a single thiophene ring and C-S bond cleavage is non-rate limiting.

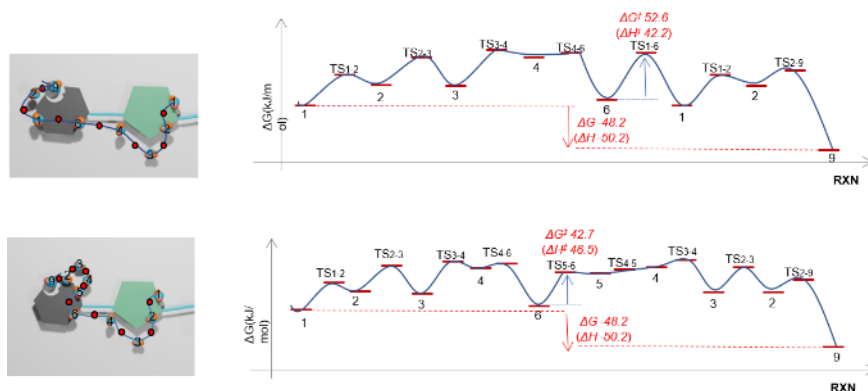


Figure 5.13 Energy profiles of two paths for ring walking within one single thiophene units and three paths for ring walking between two connected thiophene units. The rate-determining step lies in the motion within a thiophene unit.

5.3 Conclusion

Our studies on the unsupported η^2_{CC} -bound Ni(0) thiophene complex confirm the overall structure of previously proposed intermediates in CTP and yield new insights into the mechanism of action and the importance of the diphosphine ligand in ensuring strong metal-thiophene bonding via a dominant *push-pull* π -backbonding interaction. Living polymerization conditions may occur due to this surprisingly strong bond between the d^{10} metal centre and the growing polymer chain. A preference for the catalytically-competent *exo*- η^2_{CC} isomer is also observed. These conclusions provide clarity into the mechanism of catalyst transfer polycondensation and hence provide the basis for further work on improving catalyst performance in the

efficient synthesis of an important building block for molecular electronics.

5.4 Methods

5.4.1 Synthetic Methods

Unless stated otherwise, all reactions were performed in a glovebox under an atmosphere of pure nitrogen using standard Schlenk techniques. Anhydrous pentanes, toluene, diethyl ether, and tetrahydrofuran were purchased from Aldrich, sparged with dinitrogen, and dried further by passage through towers containing activated alumina and molecular sieves. THF- d_6 , C_6D_6 and toluene- d_8 were purchased from Aldrich and dried over sodium/benzophenone before being distilled and degassed by three freeze-pump-thaw cycles. Thiophene was purchased from Aldrich, were dried over activated 4 Å molecular sieves, distilled and degassed by three freeze-pump-thaw cycles. Bithiophene was purchased from Matrix and degassed by vacuum. Complex 3.1 was prepared according to the literature procedures. NMR spectra were recorded on 300, 400 MHz spectrometers and are referenced to residual protic solvent (7.16 ppm for C_6D_5H , 2.08 ppm for the methyl resonance of toluene- d_8 , 5.32 ppm for $CDHCl_2$) for 1H NMR spectroscopy, solvent peaks (128.06 ppm for C_6D_6 , 53.84 ppm for CD_2Cl_2 , 20.43 ppm for the methyl resonance of toluene- d_8) for ^{13}C NMR spectroscopy. ^{31}P NMR spectra were referenced to 85 % H_3PO_4 at 0 ppm. Mass spectra and elemental analyses were performed by the microanalytic services at the Department of Chemistry of the University of British Columbia. Details of specific synthetic procedures are included in Appendix C.1; relevant NMR characterization of complexes is given in Appendix C.5.

5.4.2 Crystallographic Methods

All measurements were made on a Bruker APEX DUO diffractometer with a TRIUMPH curved-crystal monochromator with Mo- $K\alpha$ radiation. The data were collected at a temperature of -183.0 $\pm$ 0.1 °C. Data were collected in a ϕ and ω 0.5° oscillations using 20.0-second exposures. The crystal-to-detector distance was 40.14 mm. Data were collected and integrated using the Bruker SAINT software package. Data were corrected for absorption effects using the

multi-scan technique (SADABS). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. In refinement of structure 5, the Ni-thiophene-Ni fragment is disordered and was modelled in two orientations with equal proportions. in refinement of structure 5, The material crystallizes with the bis-thiophene disorder in two orientations. The two orientations are related by a 180 degree rotation about an axis parallel to the C4-C5 bond. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The weighting scheme was based on counting statistics. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc} ; the values for f' and f'' were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbell. All refinements were performed using the SHELXL-2016 via the OLEX2 interface.

Chapter 6: Unusually Strong bis(C-H) Agostic Interactions in Linear Ni(I) complexes

6.1 Introduction

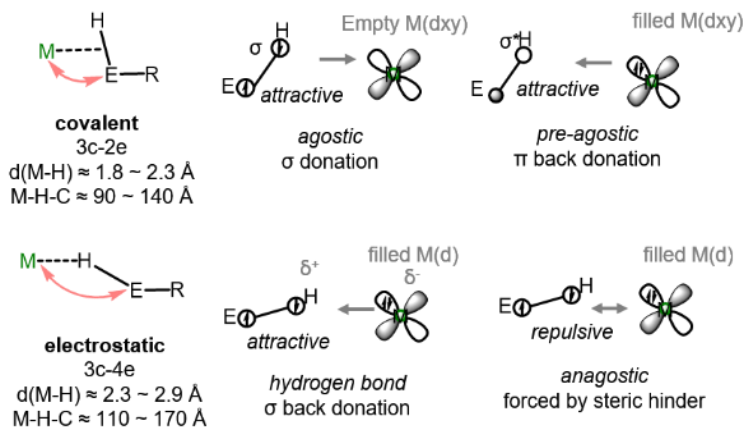
Metal-mediated activation and functionalization of C-H bonds is a powerful emerging strategy for the synthesis of high-value products and materials in many instances, C-H bond activation proceeds through the formation of direct interaction between the metal ion and the C-H functionality. The formation of a σ complex, where a CH moiety acts as a donor towards a metal, is thus often a prerequisite for bond activation and functionalization^{270,271}. Intramolecular σ interactions of this type are often termed *agostic interactions*; these are more commonly observed due to the significantly lower entropic penalty for bond formation (chelating effect)²⁷². Studies of agostic complexes have dramatically increased our understanding of σ complexes even though most untethered σ complexes are transient species that are very difficult to trap and investigate. Only recently have untethered σ complexes been structurally characterized via crystal-to-crystal diffusion of substrates by Weller, MacGregor and coworkers²⁷³.

Our understanding of the fundamental nature of M---HC interactions continues to evolve, but it has become clear that the degree and directionality of charge redistribution upon bond formation plays a critical role in defining their reactivity.²⁷⁴ If the CH moiety acts as a donor towards an electron-deficient metal centre (acting as a σ donor), the interaction is defined as a σ_{CH} interaction.²⁷⁵⁻²⁷⁷ Such a bond is often formally described as $M_d \leftarrow \sigma_{CH}$ donation, reflecting the fact that empty metal d-type orbitals act as acceptors.²⁷⁶ Such interactions lead to the weakening of the σ_{CH} bond, which therefore activates it for further reactivity, such as in olefin metathesis,²⁷⁸ olefin polymerization,^{279,280} cross-coupling,^{281,282} and hydrogenation.²⁸³ In contrast, a metal centre may also form a hydrogen bond (M---H—C) via electrostatic attraction between an electron-rich metal centre and the electron-deficient hydrogen. In this 3c-4e M---H-C interaction,²⁸⁴ the metal centre plays the role as the hydrogen bond acceptor for better stabilization of molecular motif.²⁸⁵ The specifics of these different interactions result in different geometric preferences (see Scheme 1A): the M-H-C angle is more acute for σ complexes than

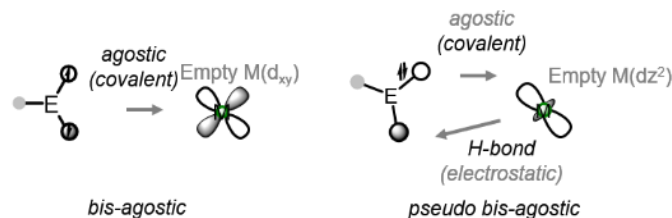
for hydrogen bonds.²³ Such interactions have been observed with other E-H moieties, such as boranes and silanes.²⁸⁶⁻²⁸⁸

Certain agostic complexes include more unusual bonding motifs - these are sometimes termed *non-classical* agostic complexes. For example, steric constraints often enforce a geometry where two adjacent E-H bonds (e.g. in a methyl group) are necessarily in close proximity to the metal centre (Scheme 1B). Symmetric *bis*-agostic complexes have been observed where a delocalized H-E-H (E = B, Si, C) fragment orbital interacts with a single empty metal d orbital;²⁸⁹⁻²⁹¹ formally, this represents a single 4 centre-2 electron bond equally delocalized over both E-H bonds. In other cases, an asymmetric bonding geometry is observed leading to the possibility of a *pseudo-bis-agostic* scenario where a classical agostic interaction dominates and a secondary hydrogen bond is also present.^{289,292} Some of us previously reported the structure of linear nickel(I) complexes with pairs of nearly symmetric δ -bis(C-H) contacts from pendant methyl groups that seemed appropriate examples of pseudo-bis-agostic complexes.^{118,293} More detailed investigations using x-ray spectroscopy have now revealed that these complexes exhibit an unusually strong bonding interaction driven by both σ and π charge donation primarily from the carbon into empty Ni 4p states with only minor contributions from Ni 3d states.

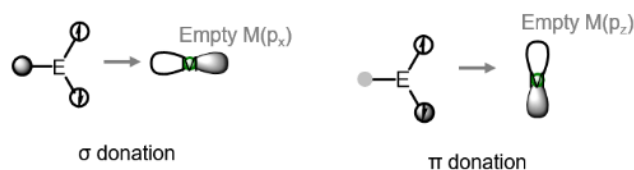
A Various type of single M···H-E interaction (E=C, Si, B).



B Summary of orbital interaction scheme for previous bis M···H-E interaction (E=C, Si, B).



C This work: p orbital type bis-agostic interaction (E=C)



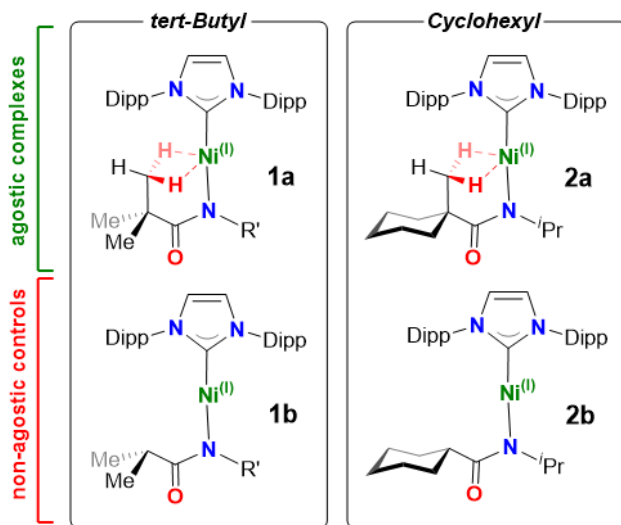
Scheme 6.1 a) geometrical definition of agostic interaction and hydrogen bond;¹⁴ b) previous reported modes for bis-agostic interaction; c) New modes found in this work.

6.2 Results

6.2.1 X-ray absorption spectroscopy

The first indication that these complexes were somewhat unusual came from the comparison of the experimental Nickel K-edge

X-ray absorption near edge structure (XANES) spectra for complexes 6.1-6.2a,6.1-6.2b (Figure 6.1).^{118,293} We had incorrectly anticipated that the spectra of linear Ni(I) complexes with a nearly symmetric bis-agostic interaction (6.1a, 6.2a) would be very similar to analogues without the agostic interaction (6.1b, 6.2b). As shown in Figure 6.1, significant differences in the pre-edge spectra are observed. The spectra are generally consistent with previously reported Ni K-edge spectra of Ni(I) complexes;^{294 - 296} in each case, a weak electric-quadrupole allowed Ni 3d←1s transition is observed at 8330-8332 eV in addition to an intense dipole-allowed Ni 4p←1s feature at ~8337 eV. However, we note large differences in the Ni 4p←1s feature depending on the presence of the agostic interaction. The non-agostic complexes 6.1b and 6.2b exhibit a broad complex feature peak comprising three major components (as observed from the second derivative of the data, see insets in Figure 6.1); these features sharpen into only two distinct features in 6.1a and 6.2a. Based on the 2nd derivatives and relative intensities of these features, the simplest explanation is that the two higher energy features merge in complexes where agostic interactions are present.



Scheme 6.2 List of agostic complexes (1a,2a) and the non-agostic complexes (6.1b,6.2b) as the control group considered in this study identified by their number (bold). Dipp = 2,6-diisopropylphenyl

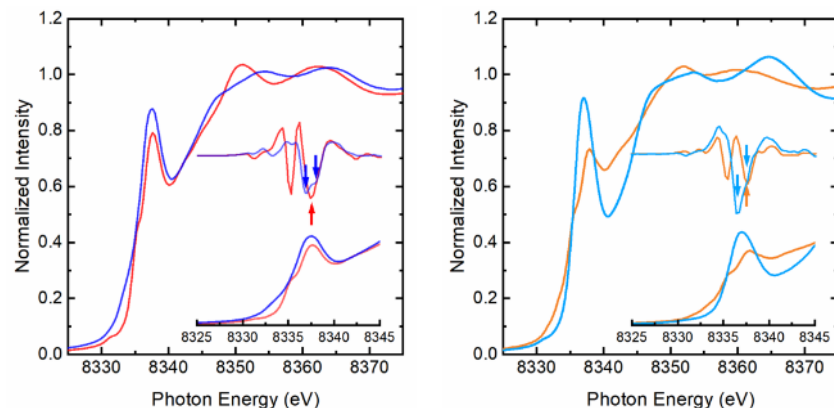


Figure 6.1 Normalized Ni K-edge PFY XANES edge spectra for agostic complexes (6.1a), (6.2a) and their control group complexes non-agostic complexes (6.1b), (6.2b). The pre-edge region of the spectra is shown in the inset with their second derivative spectra used for searching a local maximum of spectrum features. Due to the limitation of Ni K-edge pre-edge resolution,²⁹⁷ we need locate the $4p \leftarrow 1s$ feature splitting in non-agostic complexes 6.1b and 6.2b in second derivative spectrum and confirmed with XAS pre-edge simulation (See Appendix – D.1-D.4)

6.2.2 TD-DFT calculation

To understand the origins of the observed differences in the Ni K-edge spectra, we employed time-dependent density functional theory (TD-DFT) calculations to simulate the spectra. DFT-optimized structures for each of the complexes are in good agreement with experimentally-determined solid-state molecular structures (see SI). Furthermore, TD-DFT simulations of the Ni K edge XANES (see Figure 6.2) reproduce the trends observed in the experimental data.

Differences in the calculated spectra are more dramatic in the higher energy pre-edge features, which reflect strong Ni 4p contributions. These features predominantly reflect contributions from the Ni $4p_x$ (C) and $4p_z$ (D) orbitals (see Table 6.1 for detailed assignments). In the non-agostic complexes, we observe a large splitting between C and D, which reflects a significant x-z anisotropy in complexes 1b and 2b, whose origin is not immediately apparent. The large splitting (~ 0.9 eV) reflects the anisotropic π bonding in these complexes. The Ni $4p_x$ is perpendicular to these π interactions and is unaffected. By contrast, the Ni $4p_z$ contributes to the π_{CNiN} interactions

via $3d_{yz}/4p_z$ mixing, which leads to mixing of features B and D. This mixing causes splitting of the $4p_{x,z}$ orbitals and thus an observed large splitting between C and D.

Code	1a				1b			
Transition	Exp	TD-DFT			Exp	TD-DFT		
Assignment	Energy	Energy	Ni 3d	Ni 4p	Energy	Energy	Ni 3d	Ni 4p
$3dx^2-y^2 \leftarrow 1s$	8331.26	8330.35	80.10%	5.05%	8330.99	8330.059	80.63%	0.28%
$3d_{yz}(\pi^*)/4p_z \leftarrow 1s$	8335.2	8335.14	30.90%	68.63%	8335.37	8335.208	30.84%	69.16%
$4p_x \leftarrow 1s$	8337.28	8337.71	7.70%	85.19%	8336.68	8336.99	3.13%	94.29%
$4p_y \leftarrow 1s$	8337.61	8337.98	8.90%	75.78%	8337.59	8337.94	10.29%	87.32%
$\Delta E_{4p_z-4p_x}$	0.33	0.27			0.91	0.95		

Code	2a				2b			
Transition	Exp	TD-DFT			Exp	TD-DFT		
Assignment	Energy	Energy	Ni 3d	Ni 4p	Energy	Energy	Ni 3d	Ni 4p
$3dx^2-y^2 \leftarrow 1s$	8331.57	8330.3	77.91%	6.87%	8330.99	8330	78.13%	0.00%
$3d_{yz}(\pi^*)/4p_z \leftarrow 1s$	8335.52	8335.08	34.87%	65.13%	8335.2	8335.12	36.04%	63.96%
$4p_x \leftarrow 1s$	8337.61	8337.25	26.35%	42.79%	8336.41	8336.97	2.29%	96.88%
$4p_z \leftarrow 1s$	8338.21	8337.79	4.31%	85.26%	8337.9	8337.94	2.15%	97.50%
$\Delta E_{4p_z-4p_x}$	0.6	0.54			1.49	0.97		

Table 6.1 Four Lorentzian curves were implemented to simulate the experimental Ni K-edge spectra for comparing the transition energy in TD-DFT calculated Ni K-edge XAS spectra of complexes 1-2a,1-2b. The normalized metal character contribution was also provided. (See the details of simulated spectrum and the acceptor MO contribution in Appendix D.5-D.12) All the TD-DFT calculated transition energy was shifted by 180.06 eV for a better comparison with experimental data.

The C/D splitting decreases substantially in the presence of the additional agostic interaction in 1a and 2a (relative to 1b, 2b). More specifically, the energy of feature C is at much higher energy in the agostic complexes, which implies that the Ni $4p_x$ final states are strongly affected by the agostic interactions. From the calculated spectra, we observe that C occurs at much higher energy ($\sim +0.6$ eV), whereas D increases only slightly ($+0.1$ eV) in the agostic complexes. Qualitatively, the effect is the same in both pairs of complexes, albeit the decrease in C/D splitting is more pronounced in 1a than in 2a. Experimentally, features B, C, and D contribute to a broad multi-

component feature centred at $\sim 8337\text{eV}$ in 1b; the effect of the agostic interaction in 1a shifts C to higher energy and exposes B more clearly.

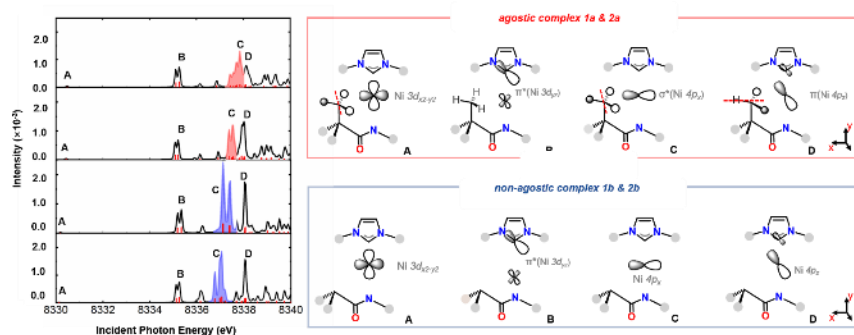


Figure 6.2 The TD-DFT calculated Ni K-edge XAS spectra of complexes 1-2a, 1-2b. Four isolated pre-edge features are labelled with A-D, the difference of $4p_x \leftarrow 1s$ transition (feature C) between agostic complexes and non-agostic complexes are highlighted in red and blue.

The observed changes in the $4p_{x,z}$ final states can be explained as shown in Figure 3. In the x,z plane the Ni 3d orbitals are completely filled and therefore cannot act as acceptors in bond formation. However, the empty $4p_{x,z}$ orbitals have the correct symmetry to interact with appropriate donors. The pendant methyl group has the correct orientation to interact with these empty states and thus generate donor-acceptor interactions between the methyl group and empty nickel 4p orbitals. The dominant σ -type interaction reflects a C $2p \rightarrow$ Ni $4p_x$ donor interaction which yields an increase in the energy of the Ni $4p_x$ orbitals by $>0.5\text{eV}$. The symmetry-allowed π interaction is extremely weak, due to both poor overlap and the strong involvement in the $4p_z$ orbital in π bonding with the NHC and amido ligands.

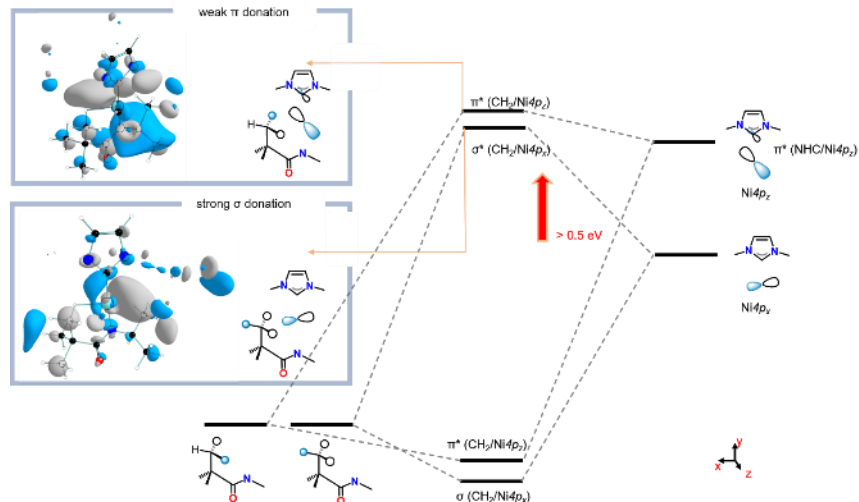


Figure 6.3 Molecular orbital representation of the agostic interaction contributed by the frontier Ni 4px/z orbital and the ligand group orbital of three C-H σ bonding orbital. The inset antibonding orbitals are representing σ donation and π donation through agostic interactions. 2,6-diisopropylphenyl(Dipp) substitutes in the MO graph are omitted for a better view of the frontier orbital interaction.

6.3 Discussion

The influence of the agostic interaction can be estimated by the observed increase in energy of C relative to the non-agostic analogue. From this, we estimate that the orbital contribution to the agostic interaction is larger in 1a (~ 65 kJ/mol) than in 2a (~ 50 kJ/mol). This difference can be explained from differences in steric repulsion of the substituent in each case. The cyclohexyl substituent exhibits a larger steric clash with the NHC ligand substituent (see Figure 6.4), which causes a distortion of the $\text{CH}_2\cdots\text{Ni}$ agostic interaction (See Appendix D.13). To probe the sensitivity of the Ni $4p_{x,z}$ final states to details of the agostic interaction, a relaxed surface scan was performed on 1b (see Figure 6.5) starting from its ground state geometry and scanning about the N-C-C-H dihedral angle (d_{CNNH}). Energetically, the formation of the agostic interaction ($100^\circ < d_{\text{CNNH}} < 120^\circ$) is not energetically favourable due to steric repulsion by forcing the methyl group towards the metal centre. Electronically, the effect of the agostic interaction has

a large impact on the Ni 4p_x final states. These are virtually unchanged across a large dihedral range ($0^\circ < d_{\text{CNNH}} < 95^\circ$), where the agostic interaction cannot form, yet once direct C→Ni orbital overlap is feasible ($100^\circ < d_{\text{CNNH}} < 120^\circ$), the Ni 4p_{x,z} splitting decreases as anticipated. The Ni 4p final states are therefore highly sensitive to the location and orientation of the methyl group and thus reflects the nature of agostic interaction. The 4p_x final states can, therefore, provide a zeroth-order estimate of the energetic stabilization that results from this interaction; we estimate *orbital contributions* to the agostic interaction at ~65 kJ/mol, which is surprisingly strong.

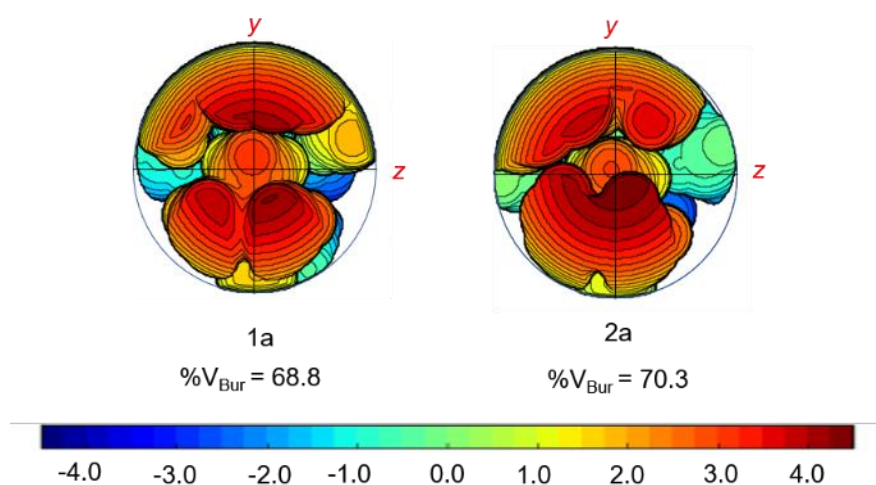


Figure 6.4 Topographic steric maps of agostic complexes 1a and 2a. Steric maps based on the density functional theory (DFT)-optimized structures of agostic Ni(I) complexes 1a, 2b. The steric maps are viewed down the x-axis (shown in yz plane), showing the protrusion of bulk into the metal coordination sphere (defined with a radius of 4.5 Å); The isocontour scheme, in Å, is shown at the bottom. The red and blue zones indicate the more- and less-hindered zones, respectively. %V_{Bur}, percentage of buried volume.

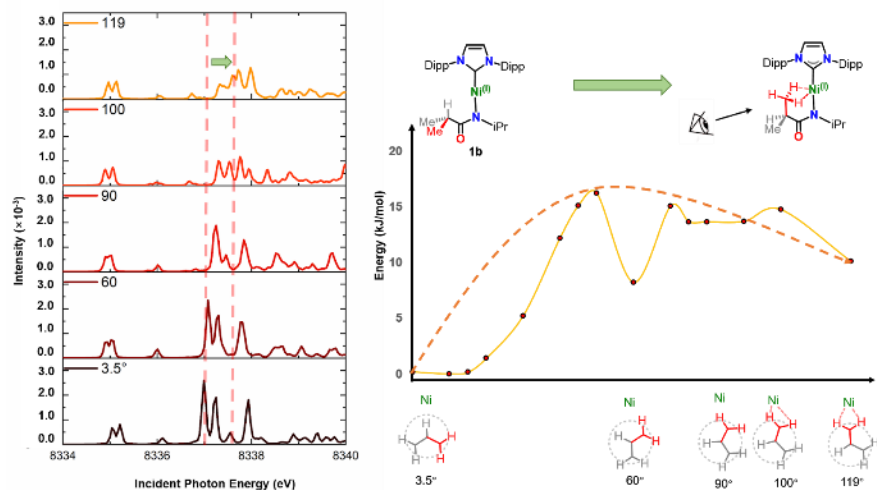


Figure 6.5 Rotational relaxed scan of 1b along Ni-N-C-H. TD-DFT calculated Ni K-edge XAS spectra of important structures were calculated

In the above-mentioned calculations, we noted that the specific geometry of agostic interaction was highly dependent on the steric constraints imposed by the pendant substituents of the NHC. A simplified model was therefore constructed to avoid these issues and focus exclusively on the electronic preferences of the σ_{CH} interaction. Electron density analysis of the simplified model (see Figure 6.6) reveals a single bond critical point that connects the carbon atom from the methyl group and the metal ion. The electron density value (0.0299) and bond energy (-41.2 kJ/mol) are in good agreement with a previous AIM analysis on 1a¹¹⁸. In the full complex, the orientation of the methyl group is slightly twisted with small energy cost (0.08 kJ/mol), which leads to a slight deviation in the agostic bcp (See Figure 6.6a). In both cases, the results differ markedly from that of other bis-agostic complexes, where two distinct bcp are observed.^{32,298} The presence of a single bond critical point connecting the methyl group to the metal highlights the unique character of these electron-rich Ni(I) species, which cannot make use of 3d states to accept electron density in forming the agostic bond.

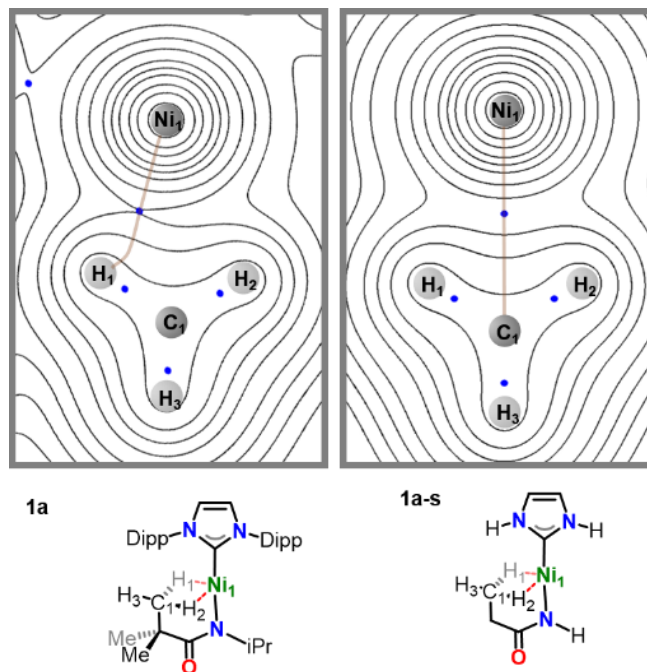


Figure 6.6 AIM contour map of the electron density in the H-Ni-H plane of complex 1a and its simplified version 1a-s showing bcps as blue dots and bond paths as brown lines. All possible steric substitutes in a simplified 1a-s structure including 2,6-diisopropylphenyl (Dipp) from NHC ligand, methyl (Me) and isopropyl (iPr) from amide ligand were replaced with hydrogen.

To evaluate the proposal that Ni 3d states were only minimally involved in the formation of the C-Ni bond, Ni L-edge XAS spectra were obtained for complexes 1a,b. In these spectra, transitions to Ni 3d final states are electric dipole allowed and thus differences between the two complexes from to Ni 3d contributions should be clearly observable.

Four Gaussian curves were applied for a good simulation of L-edge spectra of 1a and 1b (Appendix D.14), only the first curve lies in the energy region of 3d states (848~849 eV). From the spectrum difference of complexes 1a and 1b, the pre-edge 3d←2p transition was trivially lifted by 0.24 eV (from 1b 848.49 eV to 1a 848.73 eV) due to a weak Pauli repulsion between half-occupied Ni SOMO 3d_{x²-y²} and σ bonding orbital CH₂ in the pendant methyl group. A TD-DFT calculation was also indicating a 0.32 eV energy shift (from 844.39 eV (6.1b, non-agostic) to 844.71 eV (6.1a, agostic)). The p orbital involved agostic interactions are reducing metal centre through sigma and π donation

(See electron density difference map), which is supposed to lead a lower energy shift of features. However, the half occupied SOMO $d_{x^2-y^2}$ orbital energy is lifted up due to the Pauli repulsion. This also indicated that the only orbital stabilization energy was contributed by the p orbital involved agostic interaction.

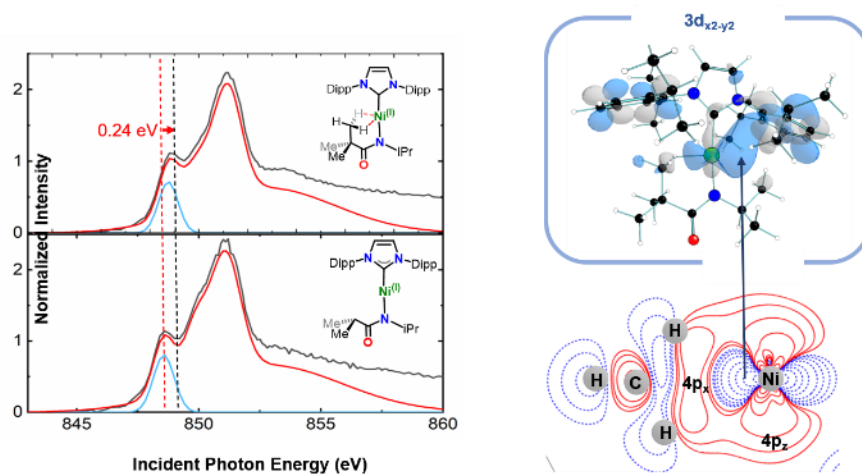


Figure 6.7 a) Normalized Ni L-edge PFY XANES edge spectra of agostic complex (1) and non-agostic complex (3). Three gaussian equations were used to simulate the pre-edge L3 edge feature. b) The TD-DFT calculated Ni L-edge XAS spectra of complexes 1a and 1b. The pronounced $3d \leftarrow 1s$ transition is labelled in the graphics.

6.4 Conclusion

Herein, we find a fundamentally new form of bis-agostic interaction where, due to the completely filled 3d manifold, only the empty 4p orbitals are available as electron acceptors, which is quite different from the standard picture for conventional agostic interactions. The characteristics of the 4p acceptors also limits options from the donor and enables a direct carbon-metal interaction rather than greater contributions from the hydrogen atoms. This agostic interaction has a large observable impact on the energy of the 4p orbitals and thus is clearly observable via X-ray spectroscopy. The recognition of new bonding modes in agostic interactions – and sigma complexes more generally – creates potentially new opportunities for sigma-bond

activation and provides an impetus to explore the reactivity of these species in greater detail.

6.5 Methods

6.5.1 X-ray Absorption Spectroscopy

All the XAS samples were analysed as solids under anaerobic conditions and diluted in boron nitride (20-50% by weight). XAS Ni K-edges were acquired at the SSRL beamline 7-3, which is equipped with a Si(220) $\phi = 90^\circ$ double crystal monochromator, a 9 keV cutoff mirror, and a He cryostat (at 20 K). Data were collected using a Canberra 30-element Ge solid-state detector with a 3mm Co filter. Data averaging and energy calibration were performed using SixPack²¹⁵ and the AUTOBK algorithm available in the Athena software package²¹⁶ was employed for data reduction and normalization. Independent fitting was also performed using BlueprintXAS.^{217,218}

6.5.2 Spectroscopic Measurements

XAS spectra were recorded at beamline 10-1 at the Stanford Synchrotron Radiation Lightsource (SSRL). An array of transition-edge-sensor (TES) detectors were used to obtain high energy resolution partial fluorescence yield (PFY) data. The TES array consists of 220 operational detectors spanning a total active area of 1.9 mm². While the monochromator was scanned across the intended energy region (e.g., 840–960 eV), the total electron yield from the samples was measured using a channeltron electron multiplier. The incident beam intensity was monitored via a gold grid and used as I_0 to normalize the total electron yield signal I_1 . For comparison, the normalized (I_1/I_0) spectra were renormalized to each other's maximum. The scans were recorded with a step size of 0.3 eV and an integration time of 1 s/pt. The energy resolution of the incident radiation is ~ 0.3 eV. Each final spectrum was the sum of five scans from different sample spots. Energy calibration was performed using NiF₂, with an L₃-edge feature at 852.7 eV.²⁴³ To minimize self-absorption in the fluorescence data, the incident angle was set at 55° with respect to the sample surface. All samples were measured at room temperature. To minimize radiation damage, a defocused beam (about 1×1 mm²) was used.

6.5.3 Computational methods

Initial geometries for all molecules were obtained from crystallographic coordinates (where available) or constructed from standard models. Geometry optimizations and numerical frequency calculations were performed using version 4.0 of the ORCA computational chemistry package²⁴⁴. Molecular geometries were optimized using the B3LYP functional in combination with the Ahlrichs triple- ζ basis set with valence polarization (def2-TZVP) for all atoms. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional²²⁸. All calculations were performed with integration grid 4. Reported thermochemical energies are given in kJ/mol and correspond to Gibbs free energies (ΔG^0) with zero-point vibrational energy corrections (ZPVE). All calculations were run on either the Abacus (UBC Chemistry) or GREX (Westgrid) computing clusters.

Chapter 7: Overview and Future Work

7.1 Overview

The significance of this doctoral work lies in providing cogent evidence that can inform the design and creation of novel complexes to improve catalysis and material synthesis. The Dewar-Chatt-Duncanson bonding model is a classic “textbook model” that powerfully describes the interaction between transition metals and various olefin π substrates. It helps us understand the electronic properties of numerous metal π intermediates in catalytic reactions, but has also inadvertently served to restrict the discussion of such systems. However, the alteration of electronic properties of the ancillary ligand, metal centre, the π substrates and the combination of the assembling patterns are forcing us to envisage its diverse derivatives and keep expanding the boundaries of its traditional definition.

To illustrate the connection between an electron structure described by DCD model and the molecular geometry, XAS and computational approaches were first applied to give a detailed description of the electronic structure of d^{10} Ni olefin complexes within the framework of DCD model in Chapter 3. Nickel- π complexes have been found as a crucial intermediate in numerous Ni(0) catalyzed sp^2 - sp^2 cross-coupling reactions. A series of stable Ni(0)- π olefin complexes cross-coupling reaction related have been synthesized and structurally determined. Four-coordinated Ni complexes' geometry is often tightly connected to its oxidation state, revealing an outcome of square planar Ni(II) species and tetrahedral Ni(0). However, these DCD model described Ni-olefin complexes had been well assigned with the $^2J_{PP}$ coupling constant from ^{31}P NMR as Ni(0), but performing an unusual square planar geometry. Ni XAS K edge spectrum work as core-shell electronic absorption spectroscopic technique, which is super sensitive to the electronic environment of targeting atom and its bonding character with the assistance of TD-DFT calculations. Therefore, it has been applied to quantitatively assign the electron density and analyze the DCD bonding covalency. These complexes are best described as square planar d^{10} complexes with π -backbonding acting as the dominant contributor to M-L bonding to the π -ligand. The degree of backbonding correlates with $^2J_{PP}$ from NMR and the energy of the Ni $1s \rightarrow 4p_z$ pre-edge in the Ni K-edge XAS data, and is determined by the energy of the π^*_{ip} ligand acceptor orbital. Thus,

unactivated olefinic ligands tend to be poor π -acids, whereas ketones, aldehydes, and esters allow for greater backbonding. However, backbonding is still significant even in cases where metal contributions are minor. In such cases, backbonding is dominated by charge donation from the diphosphine, which allows for strong backdonation even though the metal centre retains a formal d^{10} electronic configuration. This *ligand-induced backbonding* can be formally described as a 3-centre-4-electron (3c-4e) interaction where the nickel centre mediates charge transfer from the phosphine σ -donors to the π^*_{ip} ligand acceptor orbital.

Chapter 4 is the extension of the application of X-ray absorption technique in understanding the electronic structure of DCD model derivatives. The Ni K edge spectra were not able to provide any direct information to the frontier orbitals (Ni 3d orbitals) due to its dipole transition forbidden. $3d \leftarrow 2p$ dipole allowed Ni L edge spectroscopy helped us solve the issue. The details of ligand-induced backbonding in nickel diphosphine π complexes are explored using nickel L-edge ($3d \leftarrow 2p$) x-ray absorption spectroscopy as a means of quantifying the degree of backbonding derived from direct Ni 3d donation into the π ligand. It is observed that backbonding into weakly π acidic ligands such as alkenes and arenes is dominated by contributions from the diphosphine ligand via σ -donation, leading to activated metallacycles with a Ni(0) d^{10} metal centre. With more strongly π acidic ligands, however, metal contributions to backbonding increase substantially leading to a more electron-deficient metal centre that is best described as having a Ni(I) spectroscopic oxidation state.

In Chapter 5, we reinforce that top-down strategy by presenting a concrete example of solving a catalytic problem with knowledge from previous studies. Nickel-catalysed catalyst transfer polycondensation (CTP) of thiophenes is an efficient strategy for the controlled synthesis of polythiophenes. However, a detailed view of its reaction mechanism has remained elusive with unresolved questions regarding the geometry and bonding of critical Ni(0) thiophene intermediates. Herein, we provide experimental and computational evidence of structurally characterised square planar η^2 -Ni(0)-thiophene species and their relevance to the mechanism of CTP. These results confirm the viability of $C,C\text{-}\eta^2$ bound intermediates in CTP of thiophenes, provides an electronic rationale for the stability of such species, and thus that such processes can proceed as *living* polymerisations. We further show that $C,S\text{-}\kappa^2$ species may also be relevant in nickel-catalysed CTP of thiophenes, providing new avenues for exploitation and optimization.

A further investigation of using the formation of $C,S-\kappa^2$ species as a final driving force to programme a long-distance “ring walking” proceeded through the $\eta^2-Ni(0)$ -thiophene species was also proved with the assistance of computational investigation.

In Chapter 6, we expand the boundaries of the existing DCD model framework by providing a unique electronic structure example. Agostic interactions are critical in various transition metal-catalyzed C-H activation processes, resulting from the charge transfer from C-H σ bond into metal's empty d orbital acceptor. This σ -bonding interaction with late transition metal is also one of the DCD model categories. Here, a linear electron-rich d^9 Ni(I) complexes with a bis(C-H) agostic interaction of a pseudo-Cs-symmetry was electronically examined by Ni K-edge XAS and Ni L-edge XAS. The experimental results are supported by DFT calculations to reveal a perfect example of unconventional covalent agostic interaction with the involvement of metal 4p orbitals out of the traditional DCD model definition. It allows symmetric σ and π charge donation from two mirroring C-H bonds into the 4p orbitals of the metal centre through a four centre 2 electron system. This weak interaction primarily affected the ligand field splitting of 4p orbitals of the metal centre.

7.2 Future Work

Based on the conclusive findings through the entire thesis, we can see three main pillars of the research approach. 1. *New Techniques*: Using advanced physical techniques (e.g. XAS) can assist in obtaining a deeper understanding of fundamental bonding (e.g. the DCD model) (Chapter 3&4). 2. *New Applications*: Refinement of traditional concepts can help in the development of practical catalytic processes (e.g. CTP mechanism) and inorganic materials and molecular machines (e.g. Molecular walker) (Chapter 5). 3. *New Molecules*: Predicting and design novel molecules will help enrich the definition of the original concept (e.g. DCD model) (Chapter 6). Therefore, a complete loop of self-development of traditional knowledge could be achieved.

1. To apply more sophisticated x-ray methods: Benefiting from the power of synchrotron-based X-ray absorption spectroscopy, we could probe the bonding information through a core-shell electronic transition. These techniques are susceptible to the chemical environment and have atom-

specificity. One limitation of the XAS methods applied in this thesis is that the pre-edge features that directly reflect covalency are dipole-forbidden (and thus weak) and broadened by short excited-state lifetimes. These limitations can be circumvented by using resonant inelastic x-ray scattering (RIXS) to explore the electronic structure of these systems. The RIXS is an X-ray spectroscopy method that maps out the energy difference between a photon-in (absorption) and photon-out (emission) process, the first core to shell excitation will temporarily generate an electron-hole in the core-shell, which allows the succeeding valence-to-core emission. The principle of RIXS can be simply treated as a 2D spectrum mixed with both XAS and XES, which provides a detour to avoid the rigid dipole selection rule. A direct electronic dipole absorption transition, for instance, $3d \leftarrow 1s$ is forbidden. Its transition energy details can be deduced by the energy difference between electronic dipole allowed $4p \leftarrow 1s$ absorption and $4p \rightarrow 3d$ emission.

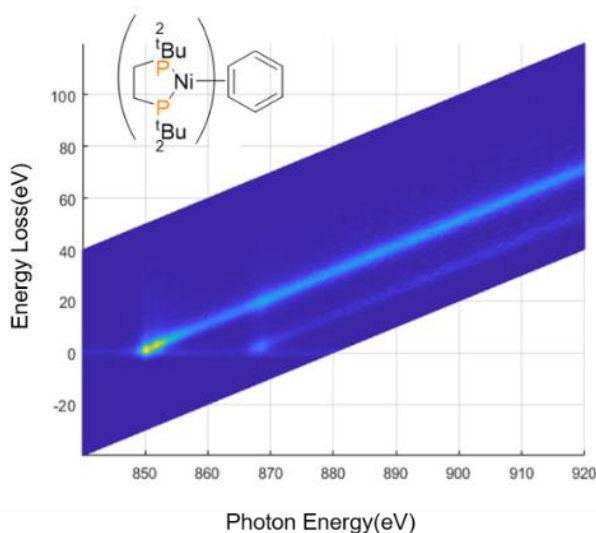


Figure 7.1 example Ni 2p3d RIXS spectrum of complex 3.7, the Photon energy is the absorption energy, the energy loss is the energy difference between absorption and emission.

2. To explore more applications of the Ni(0) studies: A meaningful extension of the work we have conducted in Chapter 5, would include further development of the long-distance ring walking system. Ni(0)-thiophene intermediates can walk across the surface of the polythiophene chain and controlled via application of an asymmetric driving force in the polymer substrate. This electronic asymmetry could also be created with an external electron current pulse. A stable Ni(0) fragment can attach to a rigid aromatic polymer chain supported by a conductor material. The external electrical field charged by the electrode can temporarily create an asymmetric electronic environment, which would enable Ni(0) reversible migration. The ancillary ligand and polymer chain would require tuning to ensure an appropriate balance between stability and mobility of the metal centre.

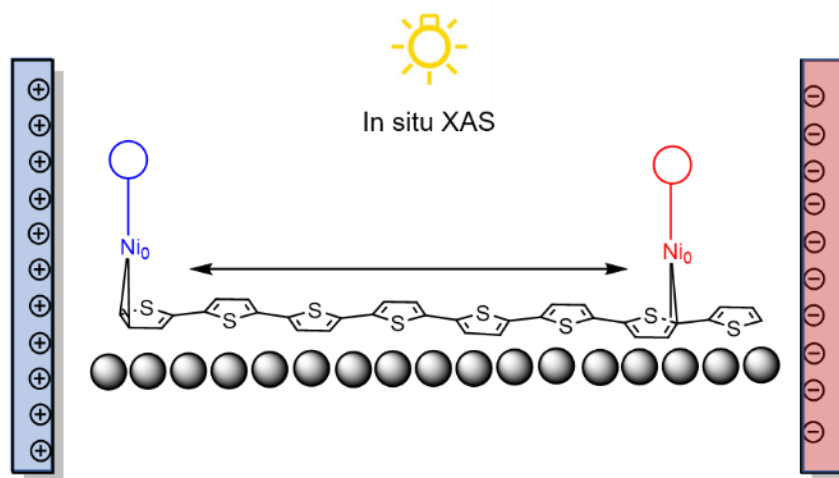


Figure 7.2 The scheme of electric drive translational motor based on Ni(0) thiophene model.

3. To design more unique DCD model derivatives: Alteration of the combination of ancillary ligands and π substrate could always provide unique electronic structures. Two out of the most exciting targets I would love to explore would be the

expansion of the DCD model framework on d^{10} -metal- π inorganic benzene and dinuclear d^{10} metal- π complexes (see Figure 7.3). Some preliminary calculations indicate that the asymmetric electronic distribution in an inorganic benzene ring would lead to different bonding modes, including η^2 and the unusual η^3 modes (Figure 7.3a). Binuclear Ni(0)-diphosphine complexes are forming a bent shape configuration, led by a formation of 4c-2e bridge. In contrast, a binuclear d^9 -Cu₂^{II}-O₂²⁻ are presenting a planar geometry. The definition of DCD model could be largely expanded by exploring some of these outstanding derivatives.

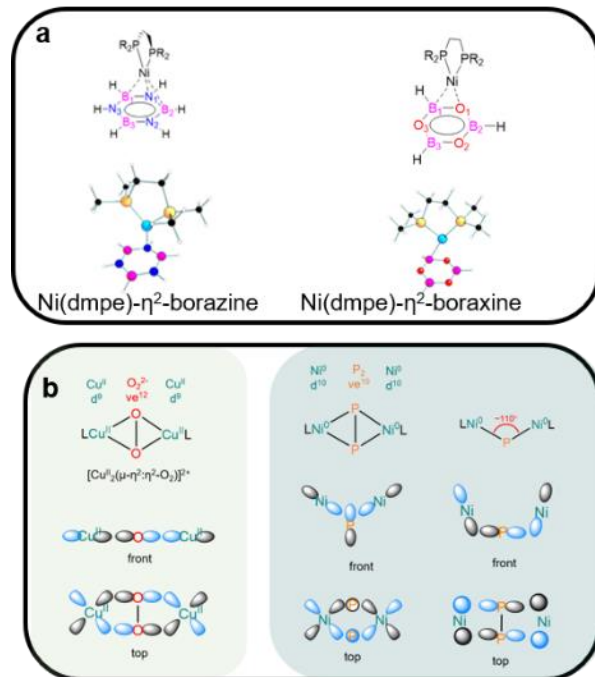


Figure 7.3 a. preliminary calculation results of η^2 and η^3 motifs of $\text{Ni}(\text{dmpe})\text{-}\eta^3\text{-borazine}$ and $\text{Ni}(\text{dmpe})\text{-}\eta^2\text{-boraxine}$; b. comparison of planar $\text{Cu}(\text{II})\text{-O}_2^{2-}\text{-Cu}(\text{II})$ motif and bent $\text{Ni}(\text{0})\text{-P}_2\text{-Ni}(\text{0})$ motif.

7.3 Conclusion

The global picture of fully investigating the electronic structure of small molecules and explore their novel derivatives in this thesis provides an example which clearly demonstrates that improved understanding of chemical bonding can lead to improved applications as in polymer synthesis, metal-organic frameworks (MOF), and solid-state material. There is still a broad range of unexplored chemical space within the basic framework of the DCD model, and its derivatives and the use of advanced characterization tools should continue to improve our understanding of such systems. Continued work in spectroscopic characterization, synthetic exploration, and applications development in transition metal complexes will certainly continue to lead to unique and unexpected results and correspondingly exciting advances.

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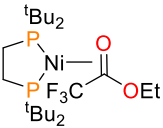
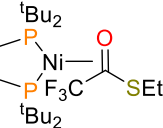
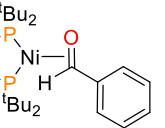
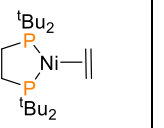
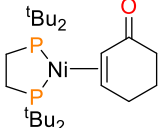
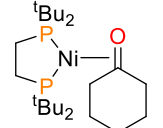
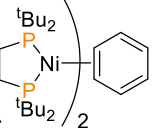
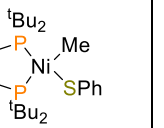
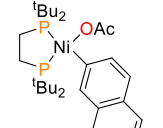
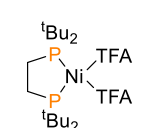
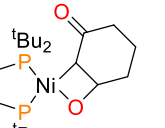
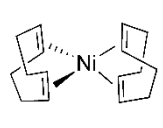
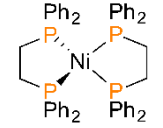
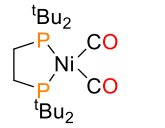
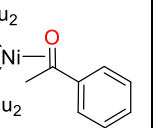
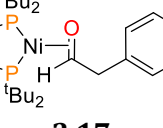
Appendices

Appendix A Experimental Data for Chapter 3

A.1 Synthetic Methods

General Considerations

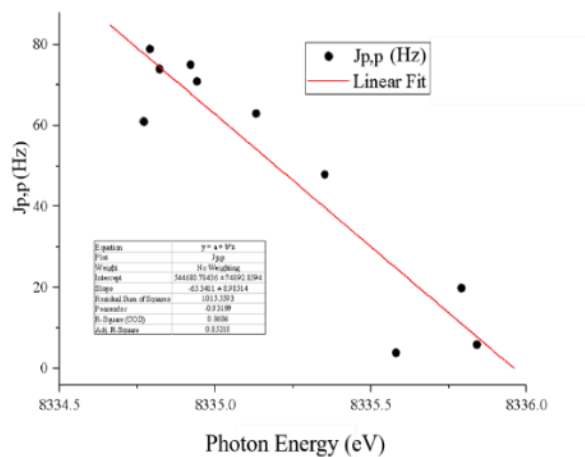
Ni(COD)₂ (3.13) was purchased from Strem and used as received. Compounds 3.1-3.12 and 3.14-3.15 were prepared according to literature procedures as listed in the experimental section of the manuscript. Compounds 3.16-3.17 were also synthesized according to ref 14 in the manuscript. All other chemicals were purchased from commercial suppliers and used as received.

			
3.1	3.2	3.3	3.4
			
3.5	3.6	3.7	3.8
			
3.9	3.10	3.11	3.12
			
3.13	3.14	3.15	3.16
			
3.17			

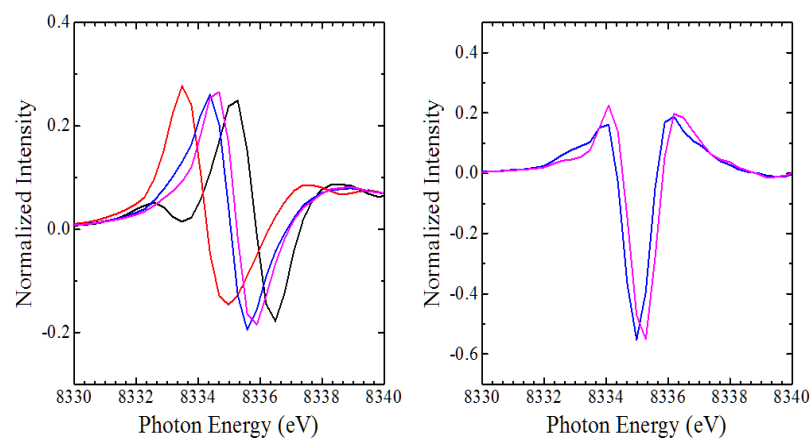
Appendix A.1 Complete list of complexes considered in this study.

³¹ P NMR				
#	δ1 (ppm)	δ2 (ppm)	Δδ (ppm)	J _{P,P} (Hz)
3.1	92.4	82.4	10	63
3.2	93.1	90.1	3	48
3.3	90	88.2	1.8	71
3.4	92.7	N/A	N/A	N/A
3.5	85.7	79.5	6.2	61
3.6	91.4	82.6	8.8	79
3.7	78.1	N/A	N/A	N/A
3.8	78.3	70.3	8	4
3.9	72.2	69.8	2.4	ND
3.10	85.3	N/A	N/A	N/A
3.11	72.7	71.5	1.2	6
3.12	N/A	N/A	N/A	N/A
3.13	N/A	N/A	N/A	N/A
3.14	44.7	N/A	N/A	N/A
3.15	95.6	N/A	N/A	N/A
3.16	94.6	83.9	10.7	74
3.17	87.1	85.9	1.2	75

Appendix A.2 List of ³¹P{H} NMR experimental chemical shift and P,P coupling constants.



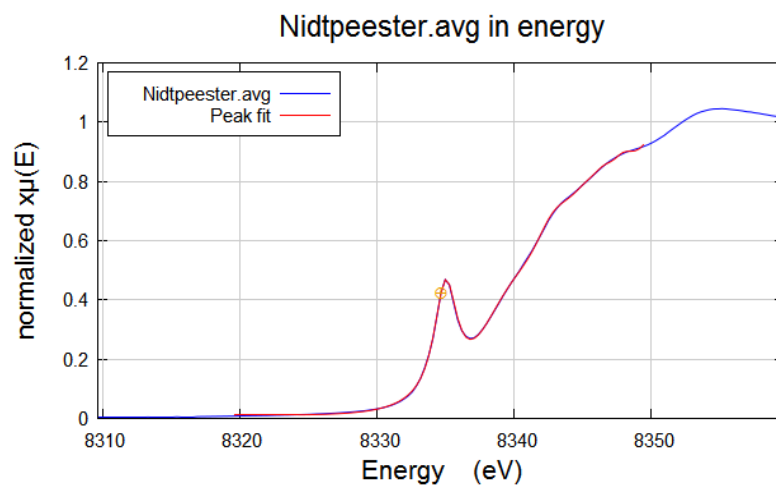
Appendix A.3 Correlation between TD-DFT calculated 1s→4p transition energy and P,P coupling constant.



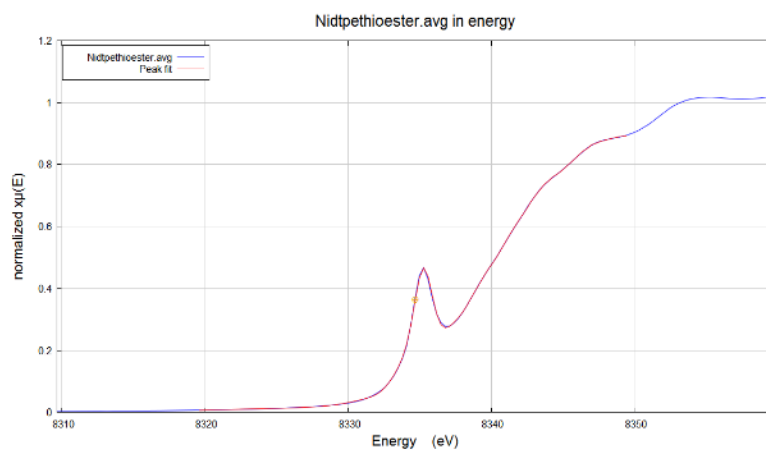
Appendix A.4 First and second-derivative plots of the Ni K-edge XANES pre-edge spectra of 3.12 (—), 3.7 (—), 3.1 (—), and 3.2 (—). The data show a weak low-energy shoulder in the spectra for the ester and thioester.

#	E(Ni 1s→3d) (eV)	E(Ni 1s→4p) (eV)
3.7	-	8334.2
3.4	-	8334.3
3.1	-	8335.0
3.2	-	8335.2
3.12	8333.1	8335.8

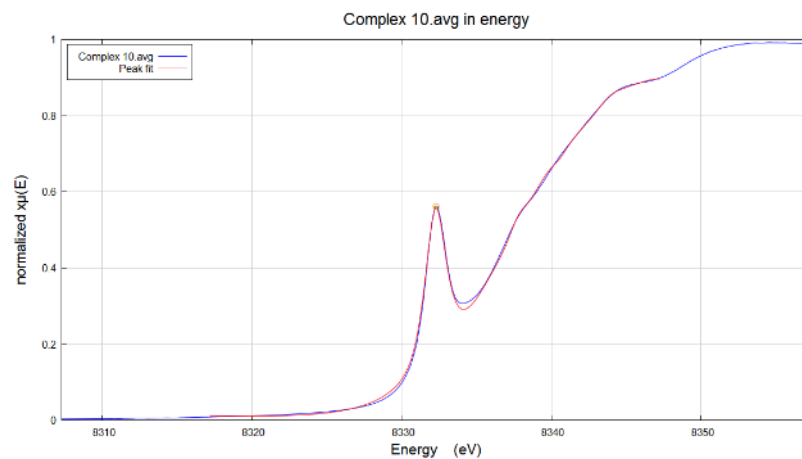
Appendix A.5 Pre-edge feature transition energy results from experimental spectrum simulation. Only those features that can be clearly observed are listed in this table.



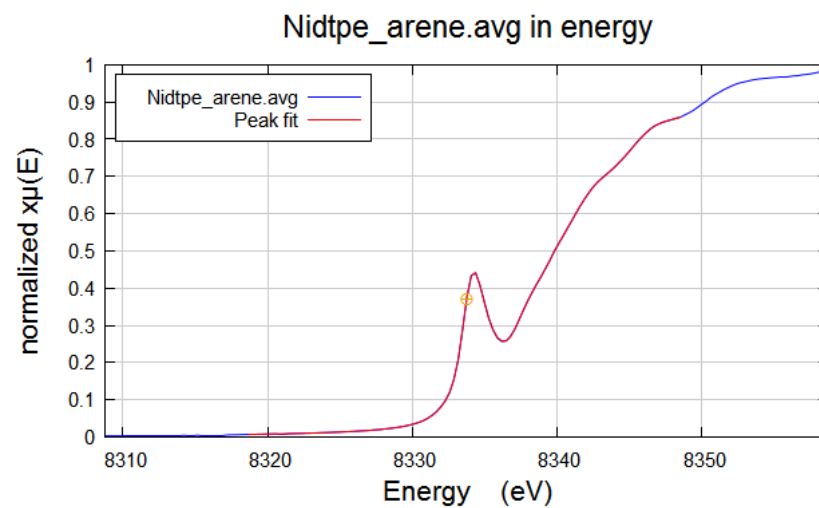
Appendix A.6 Peak fitting for Ni K-edge XANES edge spectra for 3.1.



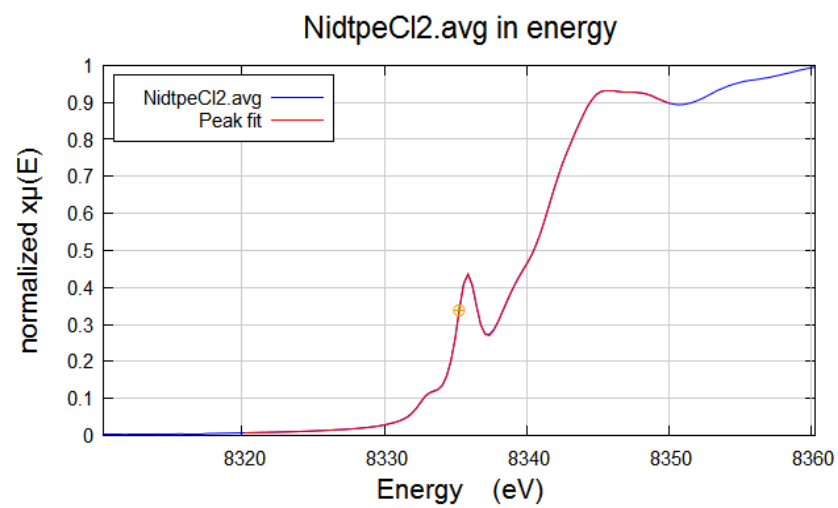
Appendix A.7 Peak fitting for Ni K-edge XANES edge spectra for 3.2.



Appendix A.8 Peak fitting for Ni K-edge XANES edge spectra for 3.4.

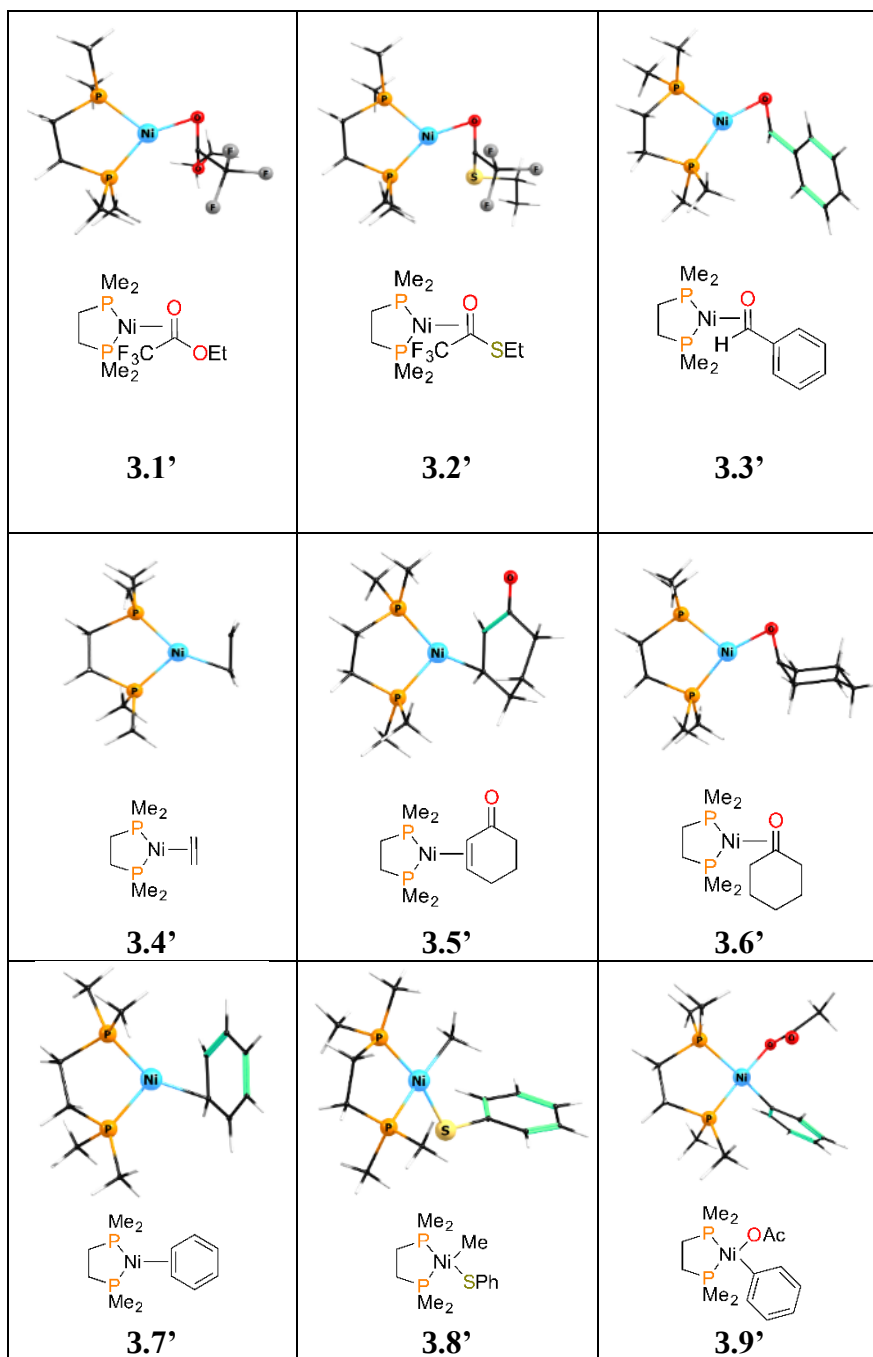


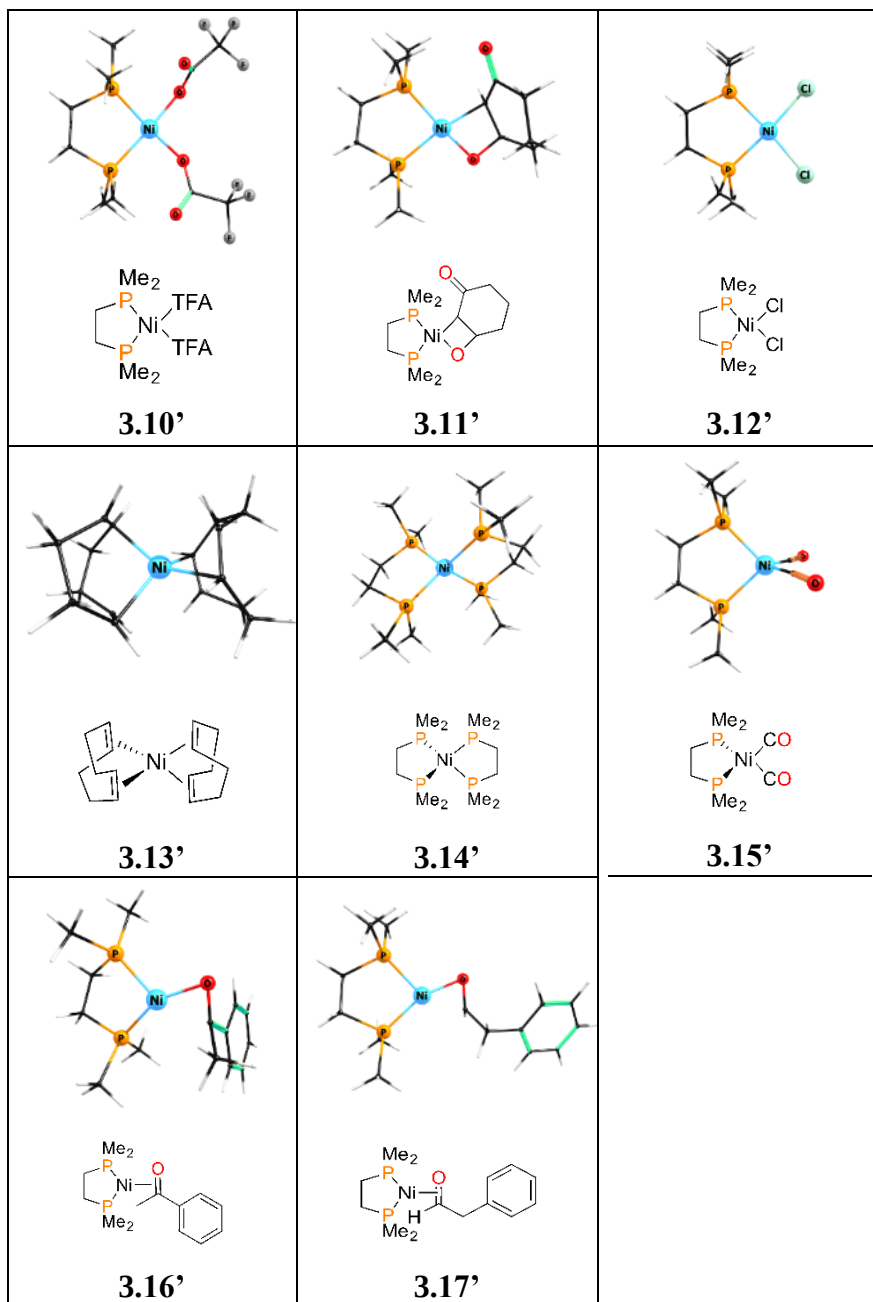
Appendix A.9 Peak fitting for Ni K-edge XANES edge spectra for 3.7.



Appendix A.10 Peak fitting for Ni K-edge XANES edge spectra for 3.12.

A.1 Density Functional Calculations

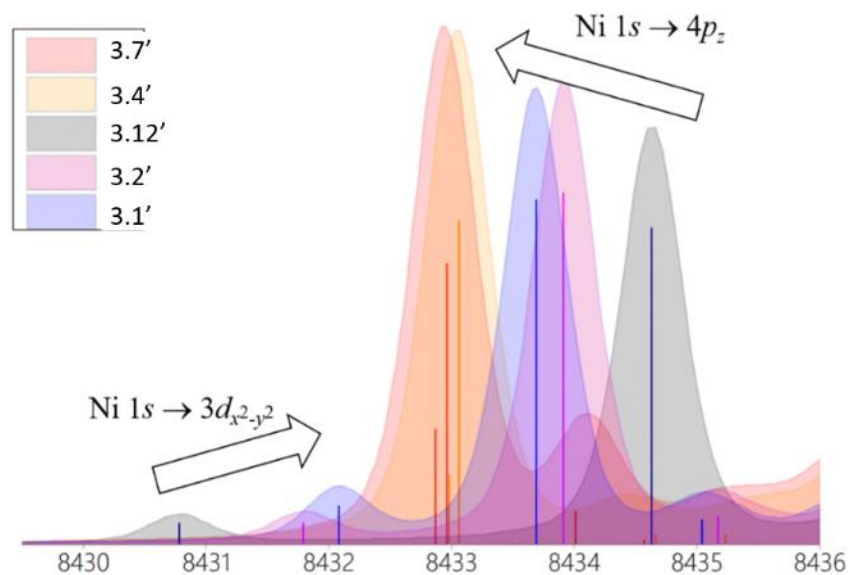




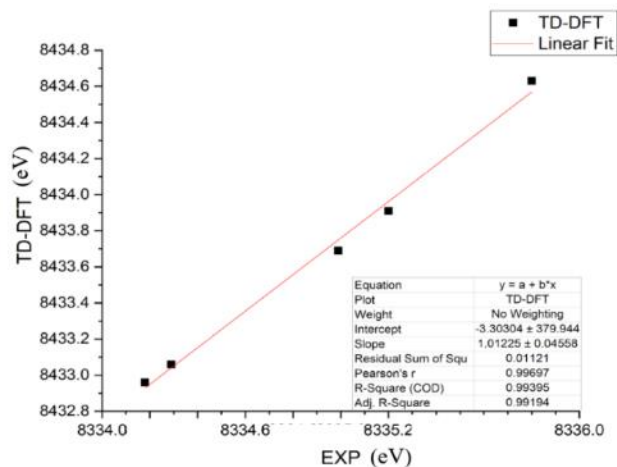
Appendix A.11 DFT optimized geometries for truncated diphosphine complexes (3.1'-3.17').

	α_1	α_2	β_3	β_4 (bite angle)	$\sum \angle_{Ni}$	$r_{M\pi}$	α	β	τ_4
3.1'	108.53	120.00	39.61	91.47	359.62	1.29	148.12	158.80	0.38
3.2'	110.84	118.59	40.08	90.50	360.00	1.31	150.92	158.63	0.36
3.3'	113.11	116.65	39.64	90.76	360.16	1.31	152.55	155.96	0.37
3.4'	113.52	113.89	25.48	91.25	344.14	1.41	154.72	155.16	0.36
3.5'	112.73	113.56	41.85	91.47	359.61	1.43	155.36	153.99	0.36
3.6'	116.30	112.98	39.85	90.75	359.87	2.66	156.14	152.61	0.36
3.7'	113.29	113.60	40.91	92.05	359.85	1.43	154.48	152.98	0.37
3.8'	87.66	91.41	96.18	87.14	275.25	3.14	169.15	165.48	0.18
3.9'	94.06	88.09	89.51	88.38	360.04	2.73	177.19	176.07	0.05
3.1 0'	97.24	91.53	83.76	87.17	359.69	2.54	176.57	172.87	0.07
3.1 1'	102.19	95.35	73.85	88.54	359.92	2.30	175.92	168.53	0.11
3.1 2'	86.93	85.86	98.71	88.90	360.39	3.38	173.85	172.52	0.10
3.1 3'	93.70	92.04	37.13	83.56	306.43	1.38	124.83	125.22	0.78
3.1 4'	111.58	109.30	90.07	90.13	401.08	3.13	136.30	123.71	0.71
3.1 5'	111.30	119.81	42.87	87.97	361.95	1.38	117.10	106.76	0.97
3.1 6'	111.49	117.25	39.75	90.75	359.24	1.31	156.49	150.89	0.37
3.1 7'	115.01	113.88	39.69	91.17	359.75	1.31	153.49	154.51	0.37

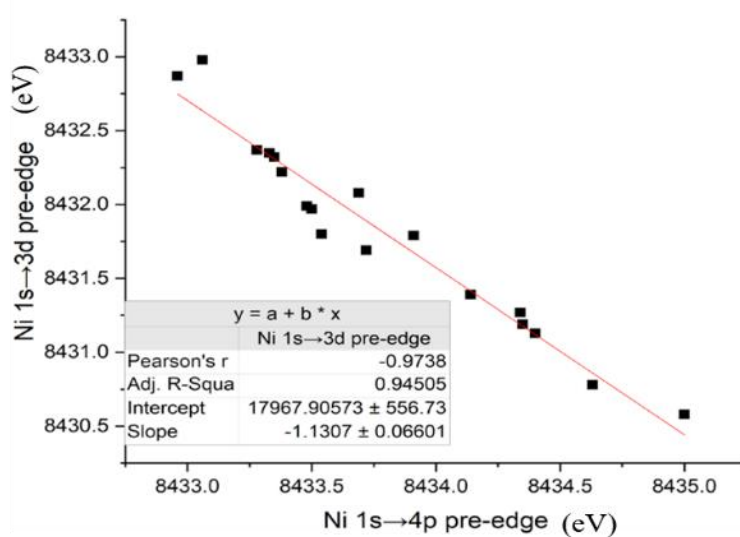
Appendix A.12 Tabulation of relevant geometric parameters from DFT optimization using B3LYP/def2-TZVP.



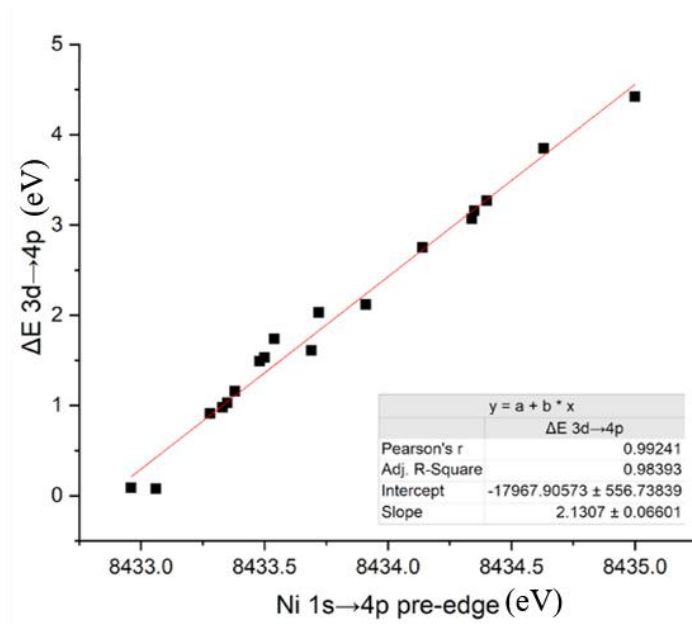
Appendix A.13 Calculated Ni K-edge XANES TD-DFT results for pre-edge region of complexes 3.1', 3.2', 3.4', 3.7', 3.12'. All calculated TD-DFT energies are the Ni K-edge were shifted by -98.55eV to provide a good match to experimental Ni 1s – 4p edge feature.



Appendix A.14 Correlation between experimental 1s→4p transition energy and TD-DFT calculated 1s→4p transition energy at B3LYP/def2-TZVP level.



Appendix A.15 Correlation between TD-DFT 1s→4p transition energy and TD-DFT calculated 1s→3d transition energy at B3LYP/def2-TZVP level.



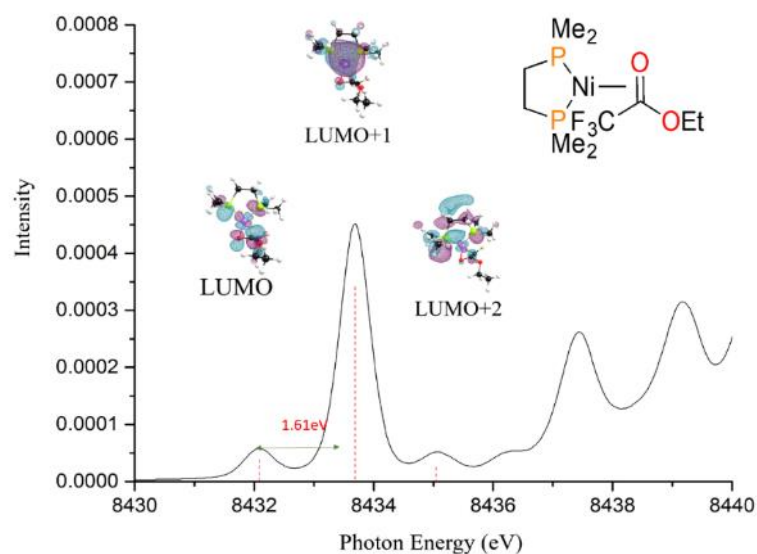
Appendix A.16 Linear correlation between TD-DFT 1s→4p transition energy and TD-DFT calculated transition energy gap 3d→4p at B3LYP/def2-TZVP level.

#	E Ni 1s→4p (eV)	E Ni 1s→3d (eV)	ΔE 3d→4p
3.1 0'	8435.00	8430.58	4.42
3.1 2'	8434.63	8430.78	3.85
3.1 1'	8434.40	8431.13	3.27
3.1 6'	8434.35	8431.19	3.16
3.9'	8434.34	8431.27	3.07
3.8'	8434.14	8431.39	2.75
3.2'	8433.91	8431.79	2.12
3.1 5'	8433.54	8431.80	1.74
3.3'	8433.50	8431.97	1.53
3.1 7'	8433.48	8431.99	1.49
3.1'	8433.69	8432.08	1.61
3.7'	8433.35	8432.32	1.03
3.5'	8433.33	8432.35	0.98
3.6'	8432.96	8432.87	0.09
3.4'	8433.06	8432.98	0.08

Appendix A.17 Summary of calculated Ni K-edge XANES TD-DFT energies (uncorrected) for pre-edge region of complexes. The complexes are listed in decreasing degree of oxidation as determined by the energy of the Ni 1s-4p transition energy.

#	1s→4p	TD-DFT 1s→4p			
	EXP	B3LYP	BP86	CAM-B3LYP	wB97XD
3.7'	8334.18	8432.96	8587.95	8624.29	8623.96
3.1'	8335.01	8433.69	8588.6	8625.29	8624.95
3.2'	8335.211	8433.91	8588.81	8625.54	8625.21
3.12'	8335.84	8434.63	8589.27	8626.41	8626.11
Max-Min	1.66	1.67	1.32	2.12	2.15

Appendix A.18 TD-DFT calculated Ni K-edge Ni 1s→4p pre-edge transition energy at selected functional theory level, def2-TZVP basis set is applied to all theory test. Note that results at theory level B3LYP/def2-TZVP are the closest to experimental results.

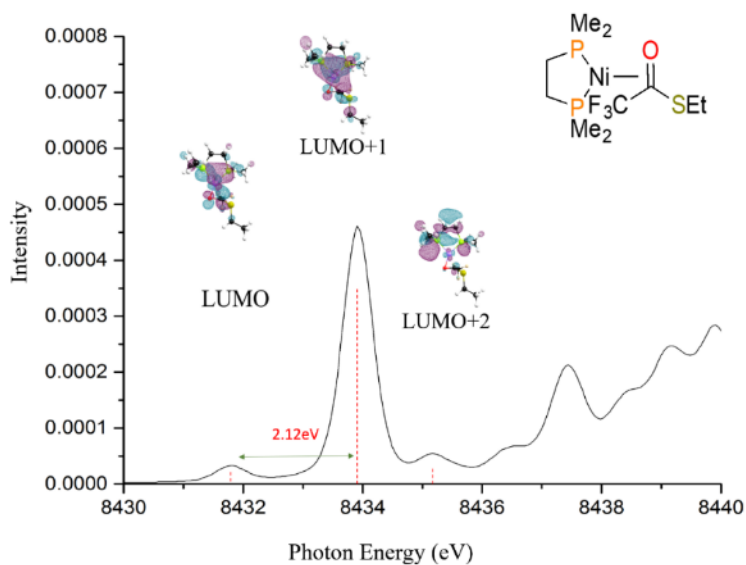


MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	92	0.896	8432.08	3.80E-05
LUMO+1	91	0.946	8433.69	3.41E-04

Note: LUMO stands for Lowest unoccupied orbital, the contribution of each orbital character (s,p,d orbital) are listed in the table below.

3.1'	Ni				P					O		C	
Orb	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	s %	p%
92	32	0.4	2.6	29	10.7	1.9	4.9	3.9	30	0.4	13.4	1.3	14.9
91	36.7	0	30.7	6	29.2	0	11	18.2	2.6	0	2	0	0.6

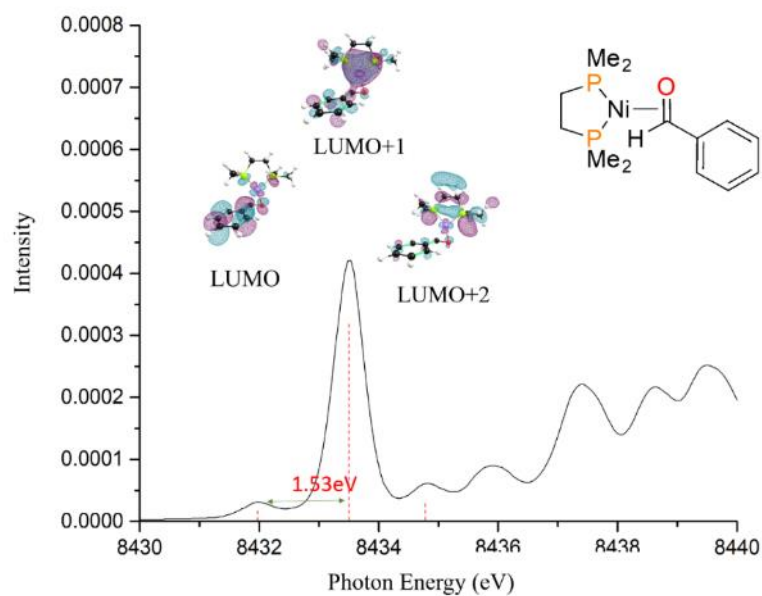
Appendix A.19 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.1'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	96	0.639	8431.79	2.10E-05
LUMO+1	95	0.661	8433.91	3.48E-04

3.2'	Ni				P					O		C	
Orb	Tot.%	s.%	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	s %	p%
96	33.9	0.1	9.6	24.2	15.5	2	6.6	6.9	20	0.2	10.3	0.4	9.1
95	34.3	0	20.9	13.4	25.5	0.3	10	15.2	10.8	0.1	5.8	0.3	4.6

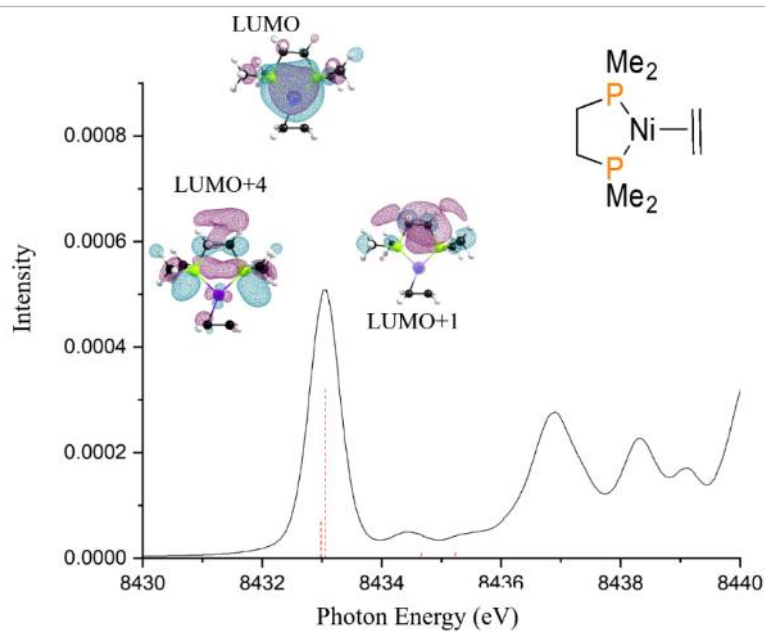
Appendix A.20 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.2'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	83	0.740	8431.97	1.70E-05
LUMO+1	84	0.849	8433.50	3.18E-04

3.3'	Ni				P					O		C	
Orb	Tot.%	s.%	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	s %	p%
83	19.1	0.1	0.8	18.2	6	1	3.2	1.8	15	0.1	7.7	0.2	7
84	36.2	0	30.1	6.1	23.8	0.4	8.9	14.5	2.5	0	1.7	0	0.8

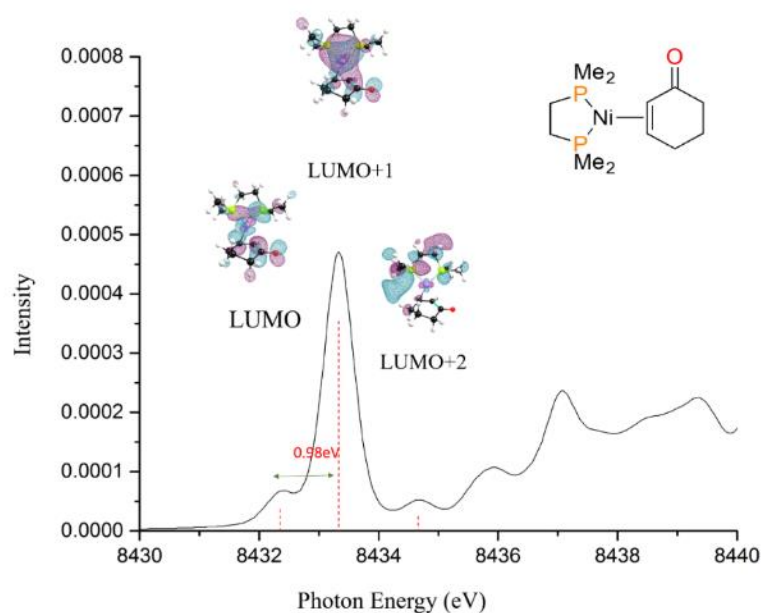
Appendix A.21 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.3'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	63	0.903	8433.06	3.20E-04
LUMO+4	67	0.782	8432.98	6.87E-05

3.4'	Ni				P				C		
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p %	d %	Tot.	s %	p %
63	42.3	0	36.9	5.4	26.6	0	10.2	16.4	1	0	1
67	23.5	0.1	3.1	20.3	9.6	3.1	3.4	3.1	36.1	0.9	35.2

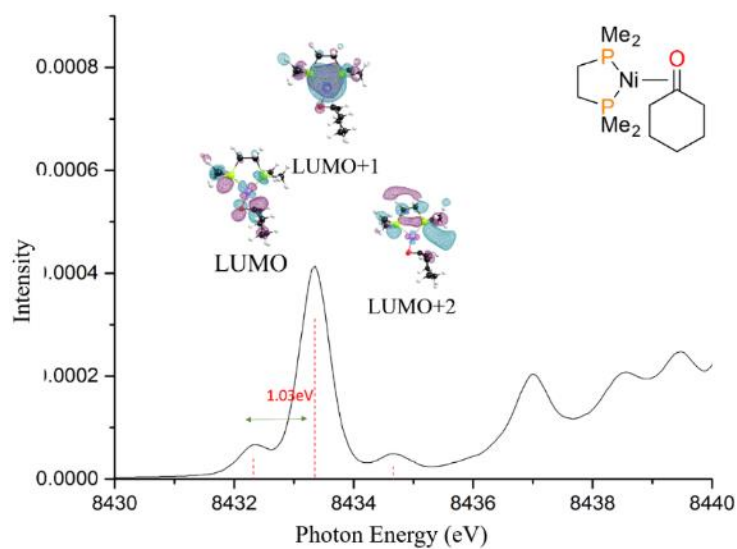
Appendix A.22 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.4'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	82	0.640	8432.35	3.65E-05
LUMO+1	81	0.724	8433.33	3.54E-04

3.5'	Ni				P				C		
Orb.	Tot.%	s.%	p %	d %	Tot.	s %	p %	d %	Tot. %	s %	p %
82	22.9	0.3	6.2	16.4	11.1	0.9	4.9	5.3	15	0.5	14.5
81	33.5	0	27.9	5.6	22.2	0.5	8.4	13.3	2.6	0	2.6

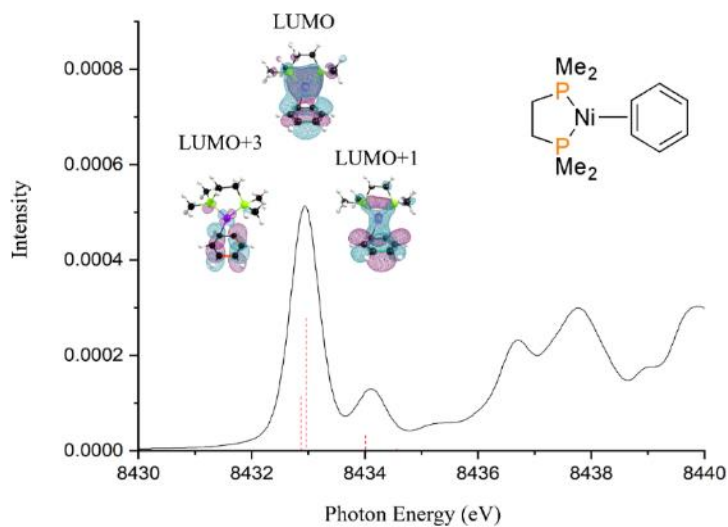
Appendix A.23 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.5'.



MO	Orb	Cont.	Trans. E (eV)	Intensity
LUMO	84	0.685	8432.32	3.89E-05
LUMO+1	82	0.964	8433.35	3.11E-04

3.6'	Ni				P				O			C	
Orb	Tot. %	s. %	p %	d %	Tot. %	s %	p%	d %	Tot. %	s %	p%	s %	p%
84	23.5	1.4	2.6	19.5	7.4	1.4	3	3	25.3	0.4	11.6	0.7	12.6
82	38.5	0.1	32.1	6.3	27.7	0	10.6	17.1	2.3	0	2.1	0	0.2

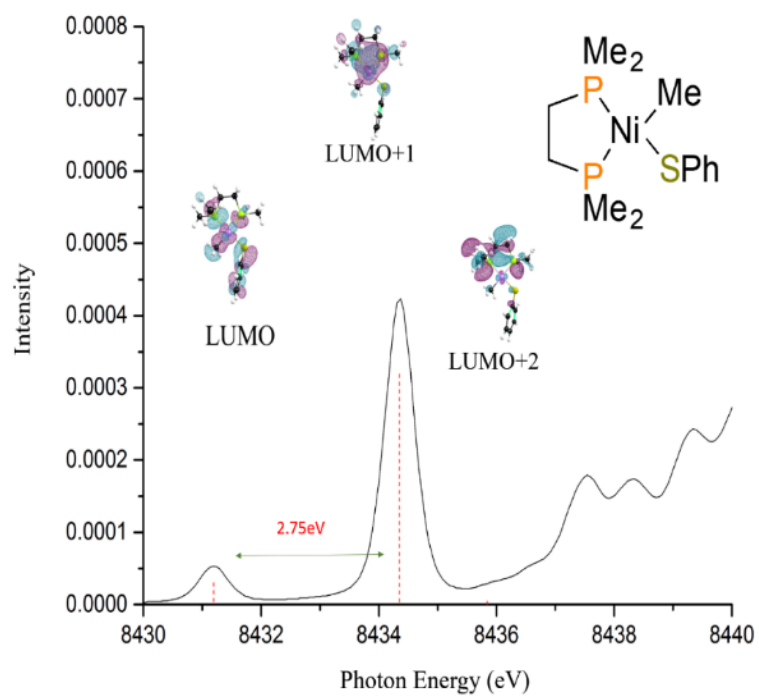
Appendix A.24 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.6'.



MO	Cont.	Trans. E (eV)	f
LUMO	76 0.688	8432.96	2.78E-04
LUMO+3	79 0.668	8432.87	1.14E-04

3.7'	Ni				P				C		
Orb.	Tot. %	s %	p %	d %	Tot.	s %	p %	d %	Tot. %	s %	p %
76	35	0.8	31	3.2	20	0.1	7.5	12.4	2.6	0	2.6
79	15.6	0.1	0.8	14.7	4.2	1.2	1.7	1.3	24.5	0.6	23.9

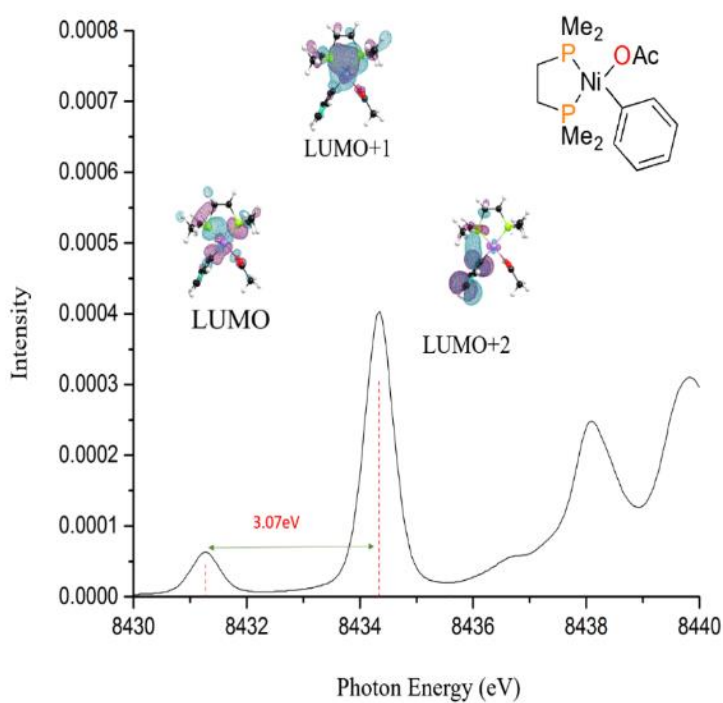
Appendix A.25 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.7'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	88	0.828	8431.39	4.96E-05
LUMO+1	89	0.890	8434.14	2.00E-04

3.8'	Ni				P					S				C	
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p %	d %	s %	p%	
88	36.5	0.6	4.9	31	13.9	3.4	7.5	3	21.1	0.8	6.3	1.7	1.5	10.8	
89	29	0.1	20.2	8.7	31	0.1	11.8	19.1	6.5	0.4	2.9	0.7	0.5	2	

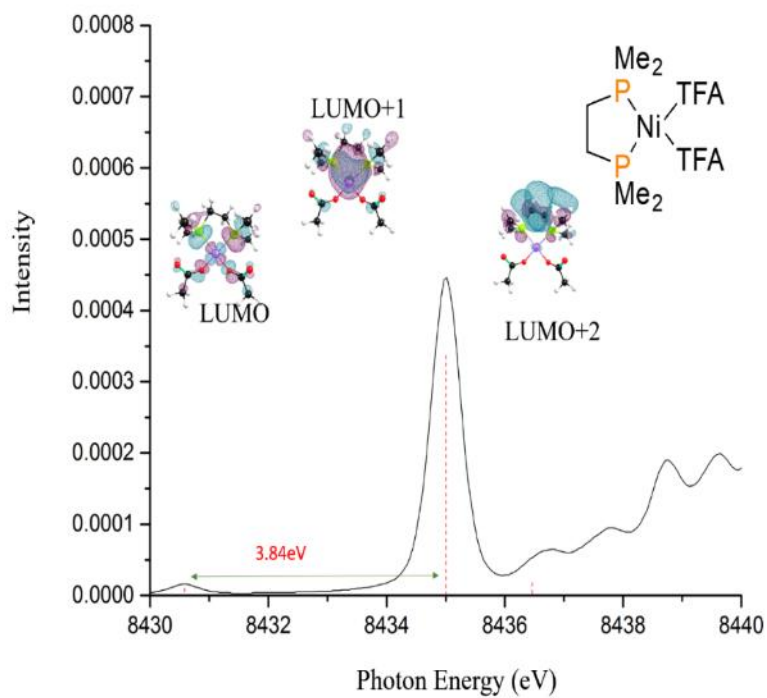
Appendix A.26 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.8'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	91	0.761	8431.27	4.58E-05
LUMO+1	92	0.763	8434.34	3.04E-04

3.9'	Ni				P					O			C	
Orb	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	s %	p%	
91	42.7	0.5	8.1	34.1	20.4	2.5	10	7.9	12.6	0.9	3.8	1.4	6.5	
92	32.8	0.3	18.8	13.7	29.8	1.6	11.2	17	4.1	0	1.4	0.5	2.2	

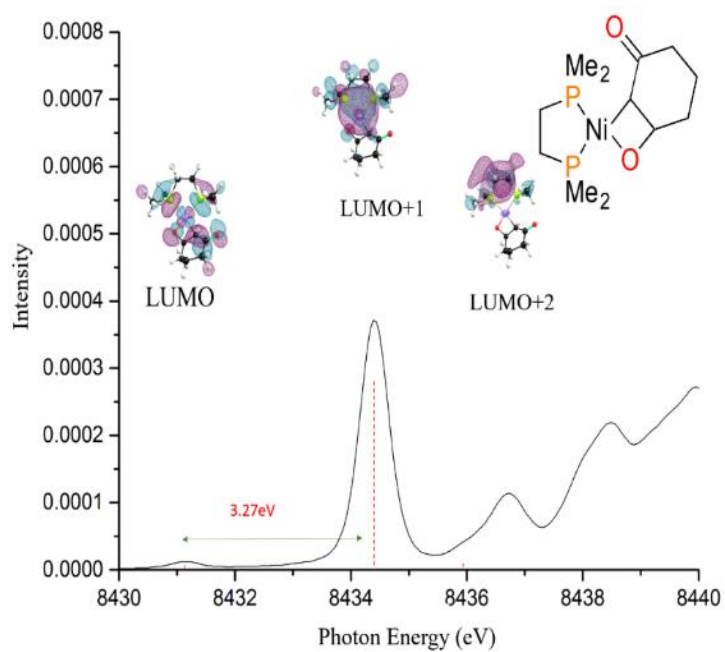
Appendix A.27 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.9'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	86	0.977	8430.58	1.03E-05
LUMO+1	87	0.971	8435.00	3.37E-04

3.10'	Ni				P				O		
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p %	d %	Tot.	s %	p %
86	52.1	0	0.8	51.3	18.5	4.3	12.6	1.6	12.1	1.1	11
87	33.4	0.3	29	4.1	32.1	0.1	11	21	0.7	0.2	0.5

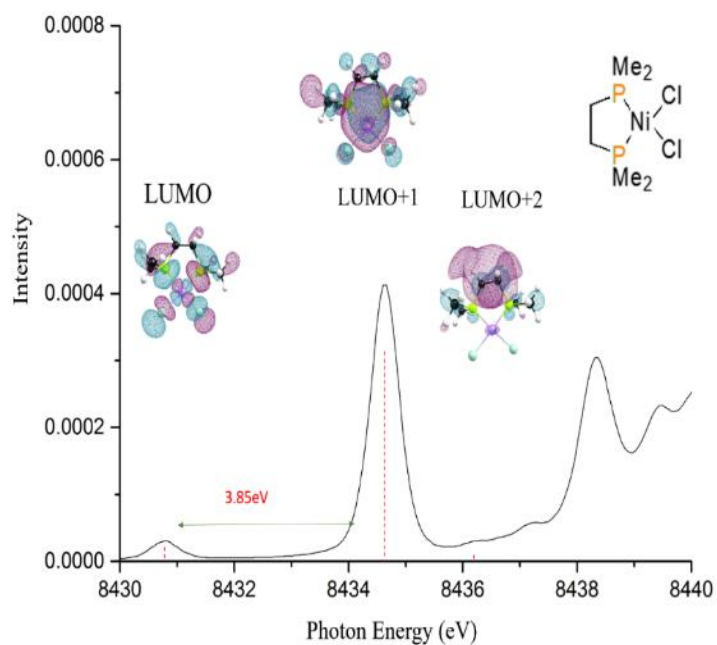
Appendix A.28 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.10'.



MO	Orb	Cont.	Trans. E (eV)	Intensity
LUMO	85	0.896	8431.13	7.24E-06
LUMO+1	86	0.946	8434.40	2.80E-04

3.11'	Ni				P				O			C	
Orb.	Tot.%	s %	p %	d %	Tot.	s %	p %	d %	Tot.	s %	p %	s %	p %
85	40	0.1	1.5	38.4	11.7	2.3	7.3	2.1	14.7	0.7	8.9	0.6	4.5
86	33.6	0	27	6.6	30.8	0.4	11.3	19.1	4.4	0	3.3	0	1.1

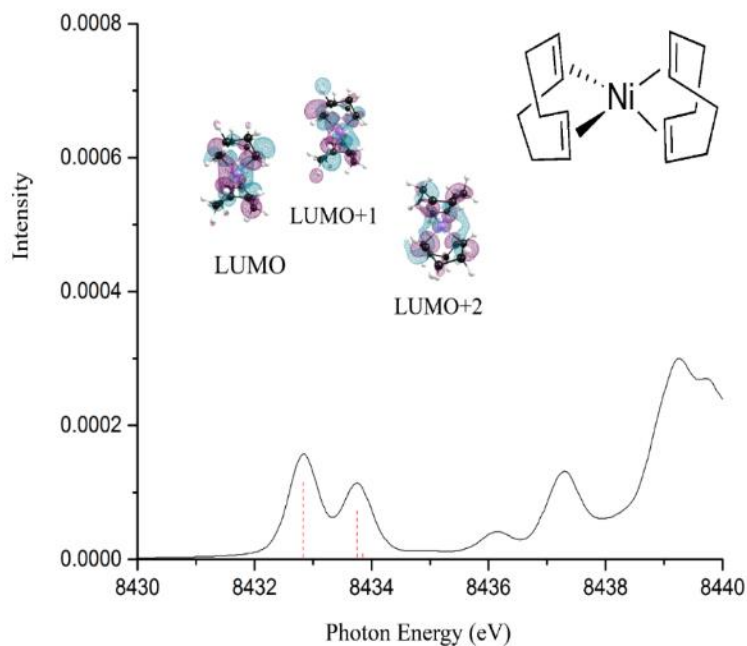
Appendix A.29 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.11'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	72	0.968	8430.78	2.10E-05
LUMO+1	73	0.966	8434.63	3.13E-04

3.12 ,	Ni				Cl				P			
Orb	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	d %
72	46.8	0	1.8	45	20.2	1	17.8	1.4	20.1	4.6	13.7	1.8
73	29.1	0	22.7	6.4	4.8	0	4.3	0.5	36.1	0.4	12.9	22.8

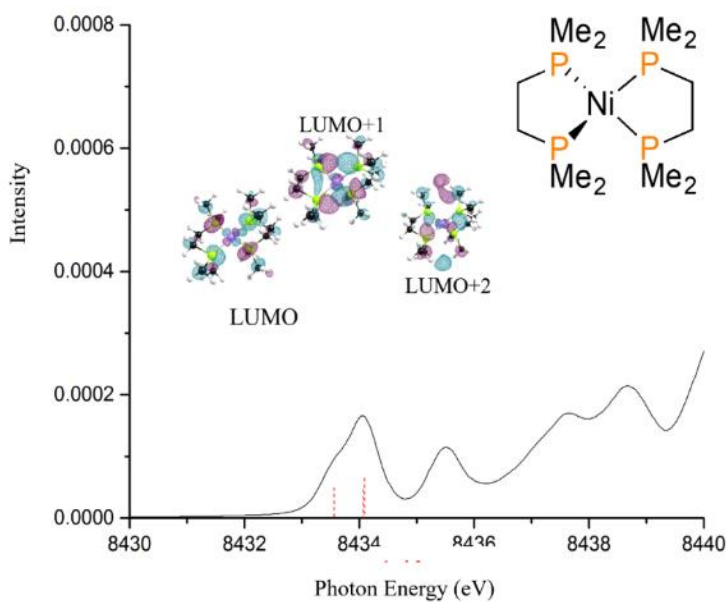
Appendix A.30 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.12'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	74	74.000	8432.83	1.15E-04
LUMO+1	77	77.000	8433.75	7.24E-05

3.13'	Ni				C			C		
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p %	Tot.	s %	p %
74	25.2	0	4.8	20.4	20.2	0.8	19.4	20.5	0.8	19.7
77	18.4	0	2.5	15.9	17	0.7	16.3	27.4	1	26.4

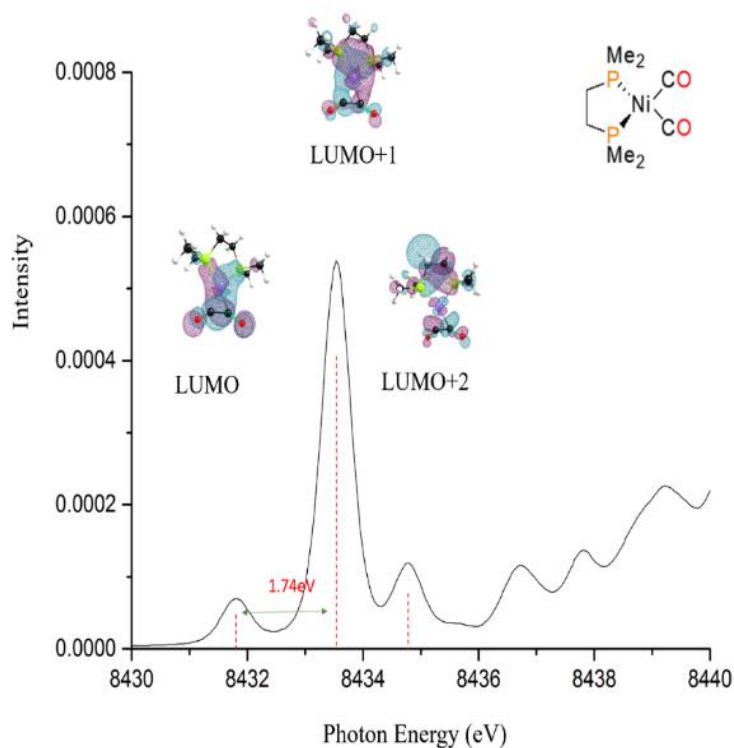
Appendix A.31 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.13'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	97	97.000	8433.56	5.00E-05
LUMO+1	99	98.000	8434.06	4.65E-05
LUMO+2	98	99.000	8434.09	6.49E-05

Orb	Ni				P				P			
	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	d %
97	25.3	0.1	16	9.2	9.4	2.1	3.8	3.5	9.8	2.5	3.8	3.5
99	14.8	0	9.1	5.7	7.7	0.7	3.4	3.6	9.1	0.6	4.1	4.4
98	13.2	0	6.8	6.4	14.7	1.2	5.9	7.6	13.5	1.4	5.4	6.7

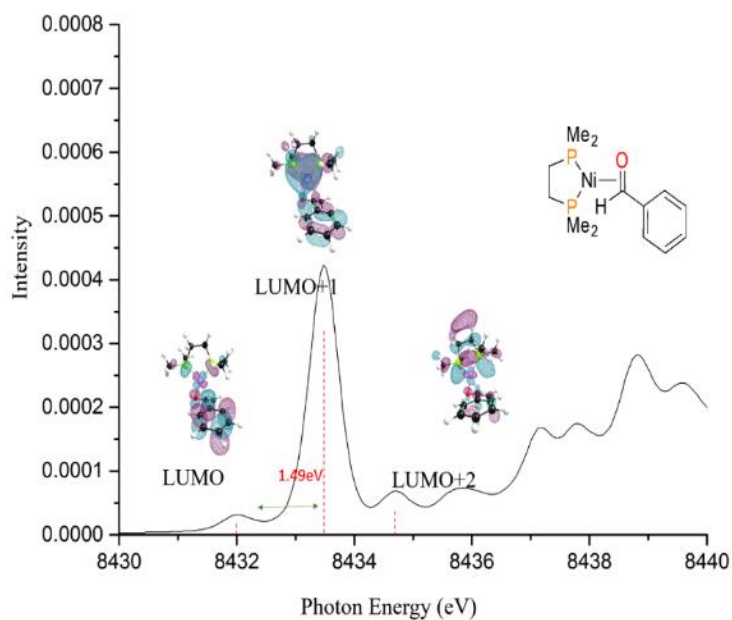
Appendix A.32 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.14'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	69	0.744	8431.80	4.69E-05
LUMO+1	70	0.544	8433.54	4.06E-04

	Ni				P				C		
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p %	d %	Tot.	s %	p %
69	21.9	0	11.7	10.2	8.1	0.5	3	4.6	25.1	0	25.1
70	33.1	0	21.1	12	24.1	0.3	9.4	14.4	11.5	1.9	9.6

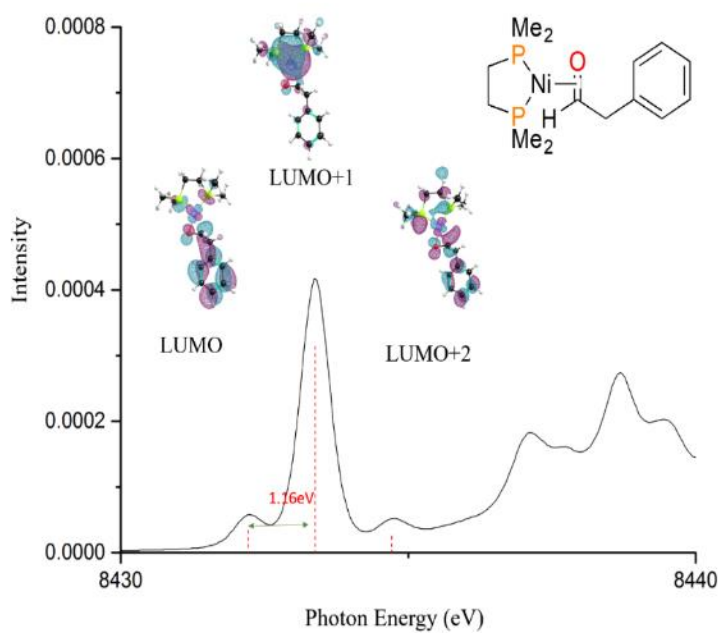
Appendix A.33 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.15'.



MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	87	0.619	8431.99	1.69E-05
LUMO+1	88	0.727	8433.48	3.19E-04

3.16'	Ni				P					O		C	
Orb	Tot. %	s. %	p %	d %	Tot.	s %	p %	d %	Tot.	s %	p %	s %	p %
87	21.2	0.2	6.4	14.6	8.7	0.6	3.9	4.2	12.2	0.1	6.5	0.2	5.4
88	32.5	0	23.7	8.8	21.2	0.7	8	12.5	4.2	0	2.6	0.1	1.5

Appendix A.34 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.16'.

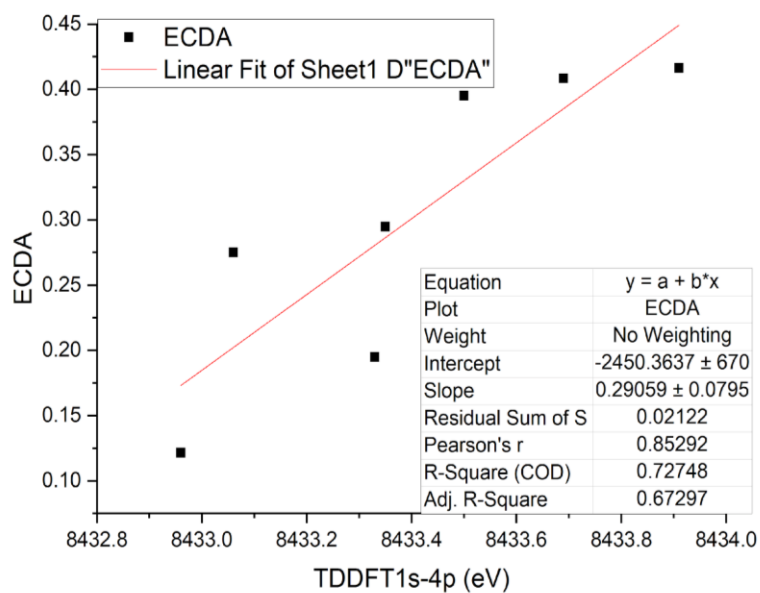


MO	Orb.	Cont.	Trans. E (eV)	Intensity
LUMO	88	0.919	8432.22	3.41E-05
LUMO+1	87	0.430	8433.38	3.14E-04

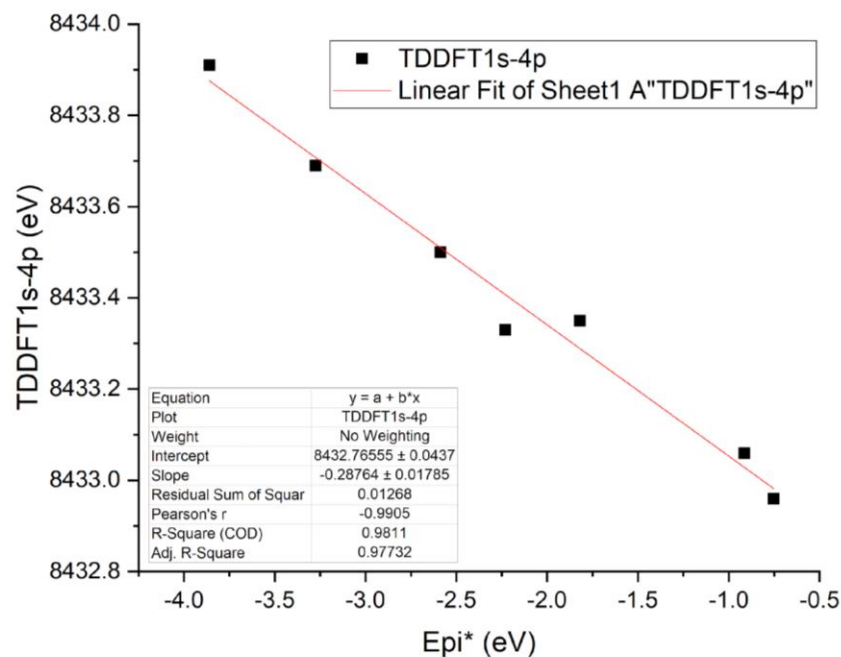
3.17'	Ni				P					O		C	
Orb.	Tot. %	s. %	p %	d %	Tot.	s %	p%	d %	Tot.	s %	p%	s %	p%
88	12.7	0	1.6	11.1	4.1	0.6	1.8	1.7	13.3	0.1	5.4	1.2	6.6
87	39.3	0.3	32.7	6.3	26.5	0	10.2	16.3	2.8	0	1.9	0	0.9

Appendix A.35 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 3.17'.

A.3 Molecular Orbital and Charge Density Analyses



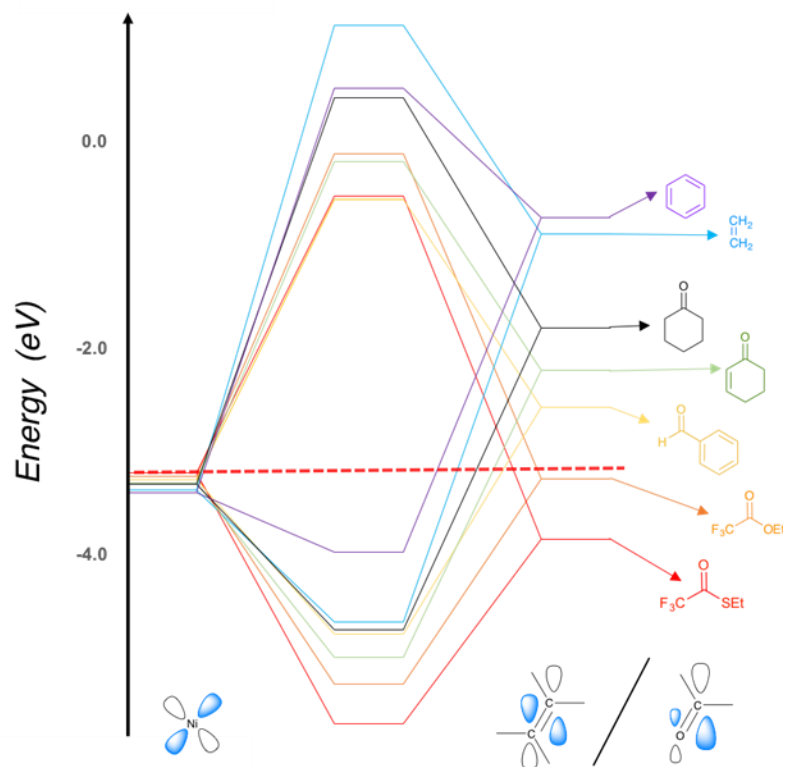
Appendix A.36 Correlation between ECDA Charge transfer from Ni(dmpe) fragment to π ligand and TD-DFT calculated XAS 1s $\rightarrow$ 4p transition energy.



Appendix A.37 Correlation between TD-DFT calculated XAS 1s→4p transition energy and π^* antibonding orbital energy of π ligands. See details of plots of each point and their TD-DFT results in Appendix 38.

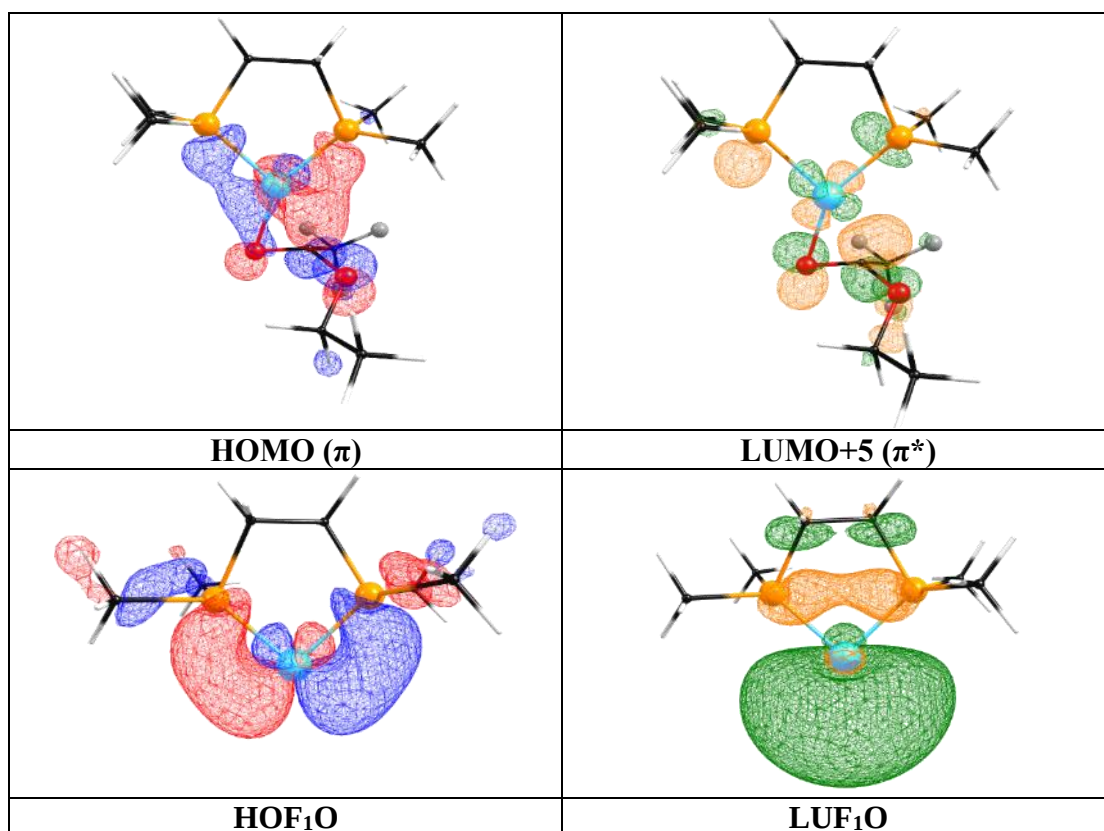
Comp	ENi _{d2-y2} (eV)	E π^* _{ip} (eV)	Energy Gap(eV)	ECDA	TD-FT 1s→4p(eV)
3.1'	-3.253	-3.276	0.02	0.408	8433.69
3.2'	-3.222	-3.860	0.64	0.416	8433.91
3.3'	-3.289	-2.587	-0.70	0.395	8433.5
3.4'	-3.385	-0.914	-2.47	0.275	8433.06
3.5'	-3.320	-2.230	-1.09	0.195	8433.33
3.6'	-3.327	-1.820	-1.51	0.295	8433.35
3.7'	-3.411	-0.753	-2.66	0.122	8432.96

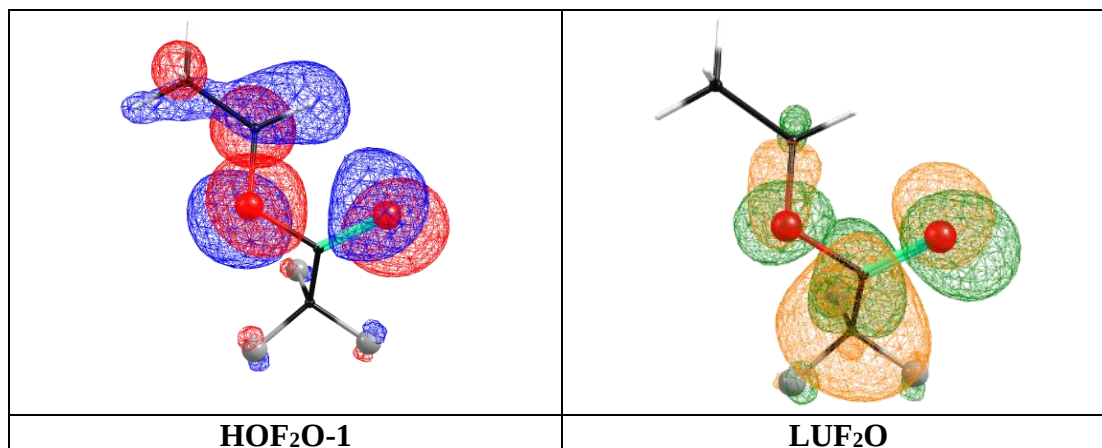
Appendix A.38 Calculated frontier molecular fragment orbital energy results, and ECDA results of charge transfer from Ni(dmpe) fragment to π ligand.



Appendix A.39 Molecular orbital decomposition analysis, the frontier fragment orbitals involved in forming π back-bonding are presented.

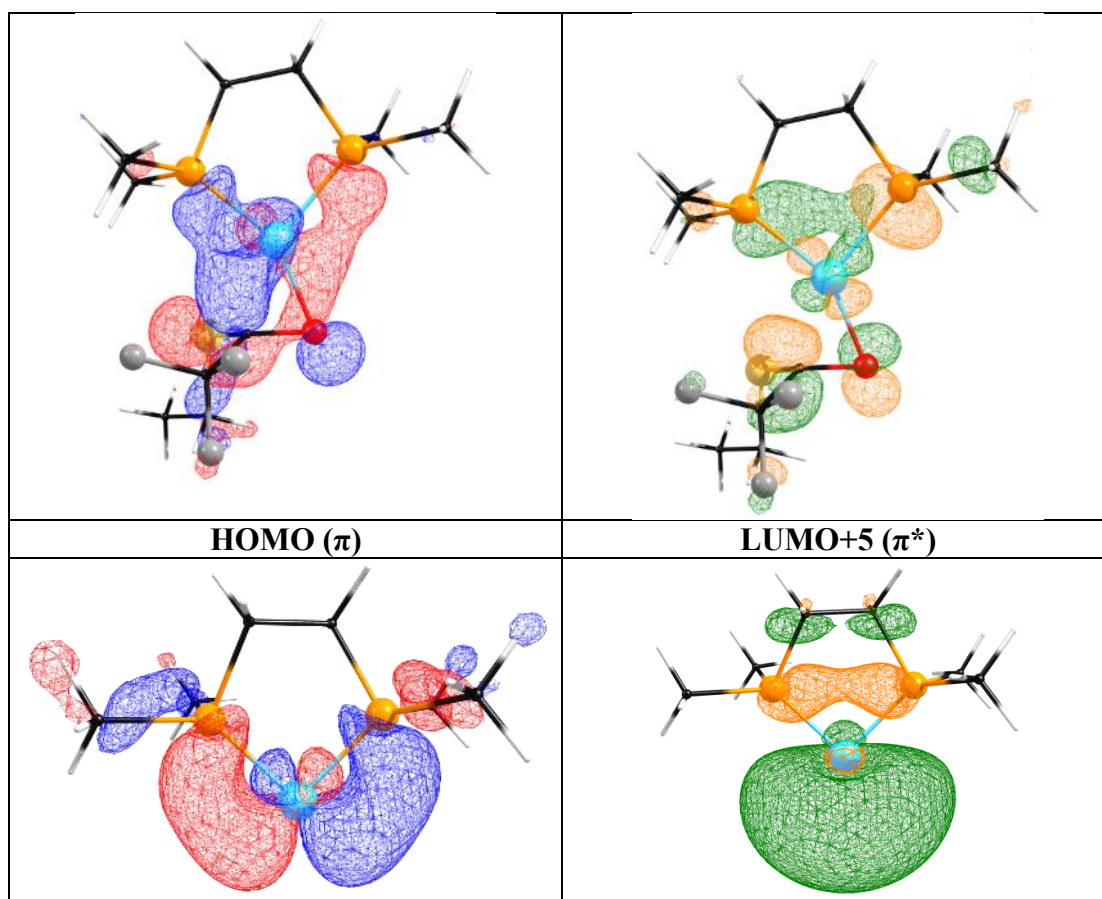
Comp.	Bond	Frag1 ^a			Frag2 ^b			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3.1'	π	HOF ₁ O	-3.25	40.18%	LUF ₂ O	-3.28	26.93%	HOMO	-5.26
	π^*	HOF ₁ O	-3.25	30.63%	LUF ₂ O	-3.28	46.09%	LUMO+1	-0.14
	n	LUF ₁ O	-0.68	1.00%	HOF ₂ O-1	-10.13	76.24%	HOMO-9	-8.85

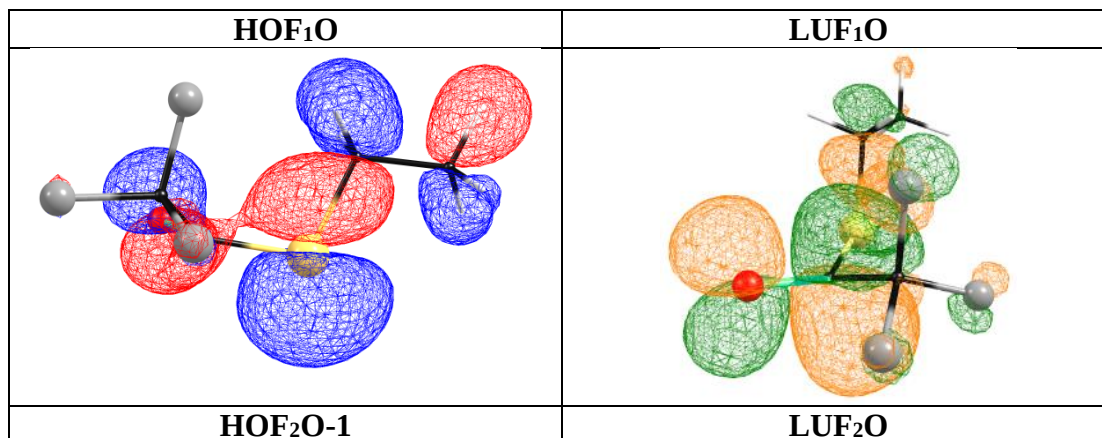




Appendix A.40 decomposition analysis with frontier fragment orbitals of complex 1'. The molecular orbitals corresponding π backbonding (π and π^*) contributed by Ni(dmpe) fragmenta highest occupied orbital (HOF_O) and π ligand fragmentb lowest unoccupied orbital (LUF_O), and a nonbonding orbital n contributed by the Ni(dmpe) lowest unoccupied orbital and π ligand fragment highest occupied orbital are listed with their character contribution in the table below. The occupied orbitals' negative and positive phases are labeled in blue and red, the unoccupied orbitals' negative and positive phases are labeled in green and orange. The Orbital contour value was set as 0.002.

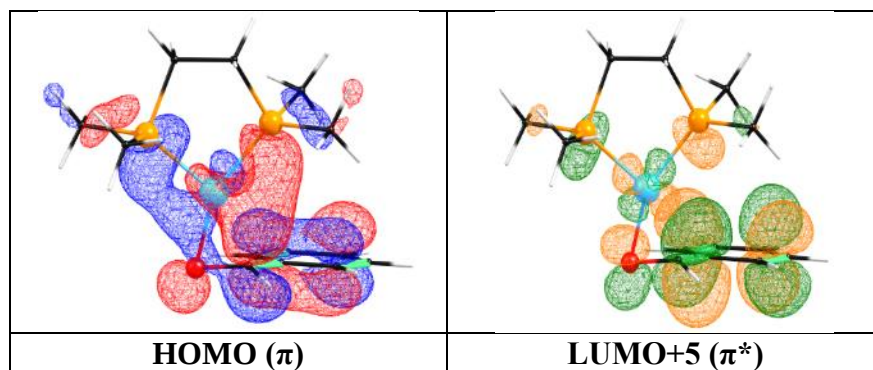
Comp.	Bond	Frag1			Frag2			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3.2'	π	HOF ₁ O	-3.22	36.47%	LUF ₂ O	-3.86	28.23%	HOMO-1	-5.65
	π^*	HOF ₁ O	-3.22	22.99%	LUF ₂ O	-3.86	27.59%	LUMO+2	-0.54
	n	LUF ₁ O	-0.68	1.52%	HOF ₂ O	-9.63	72.25%	HOMO-9	-8.56

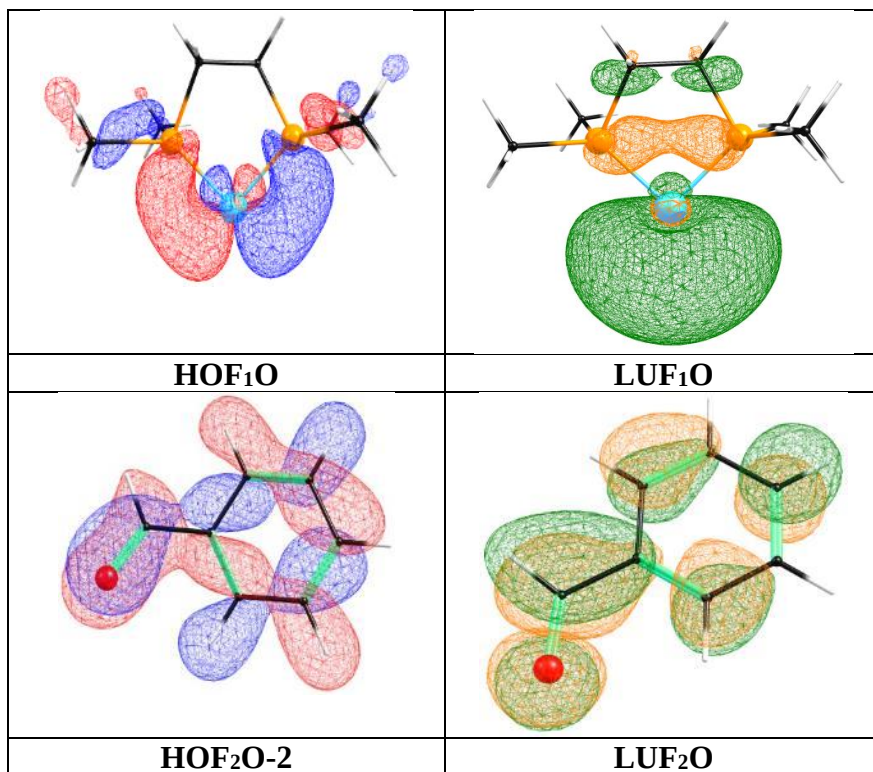




Appendix A.41 MO decomposition analysis with frontier fragment orbitals of complex 3.2'.

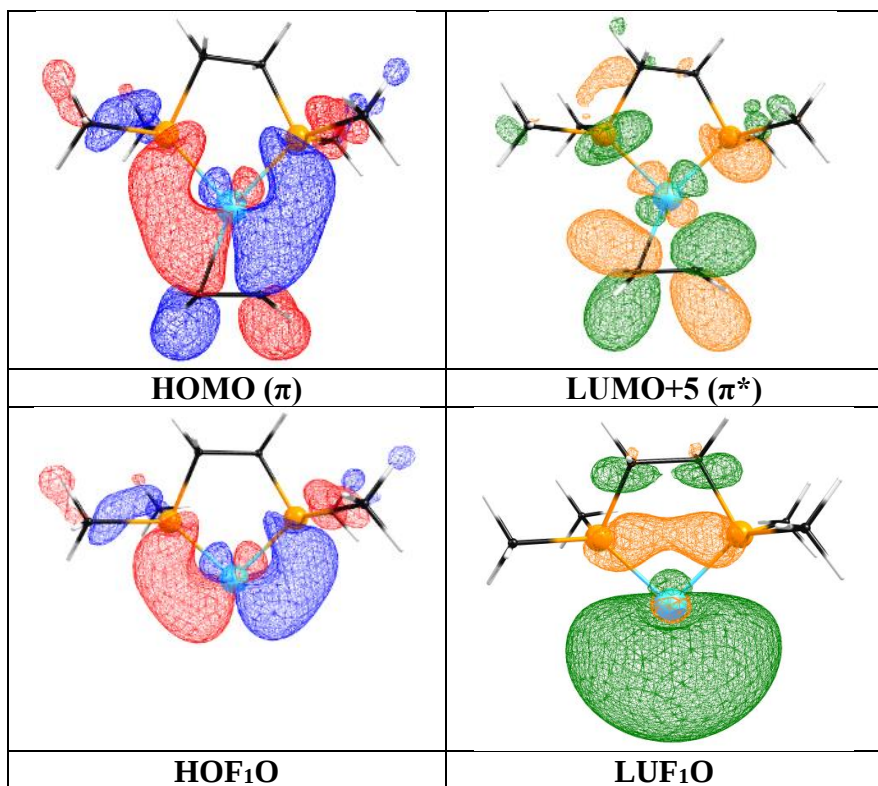
Comp	Bond	Frag1 Orb	E(eV)	Cont.	Frag2 Orb.	(eV)	Cont.	MO Orb.	E(eV)
3.3'	π	55	-3.29	46.43%	LUF2O	-2.59	28.50%	HOMO	-4.78
	π^*	55	-3.29	22.78%	LUF2O	-2.59	59.89%	LUMO	-0.58
	n	56	-0.72	<1%	HOF2O-3	-7.25	40.00%	HOMO-10	-6.74

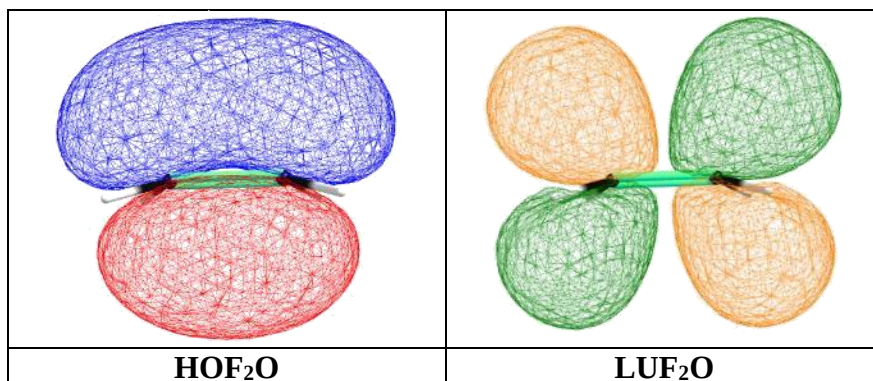




Appendix A.42 MO decomposition analysis with frontier fragment orbitals of complex 3.3'.

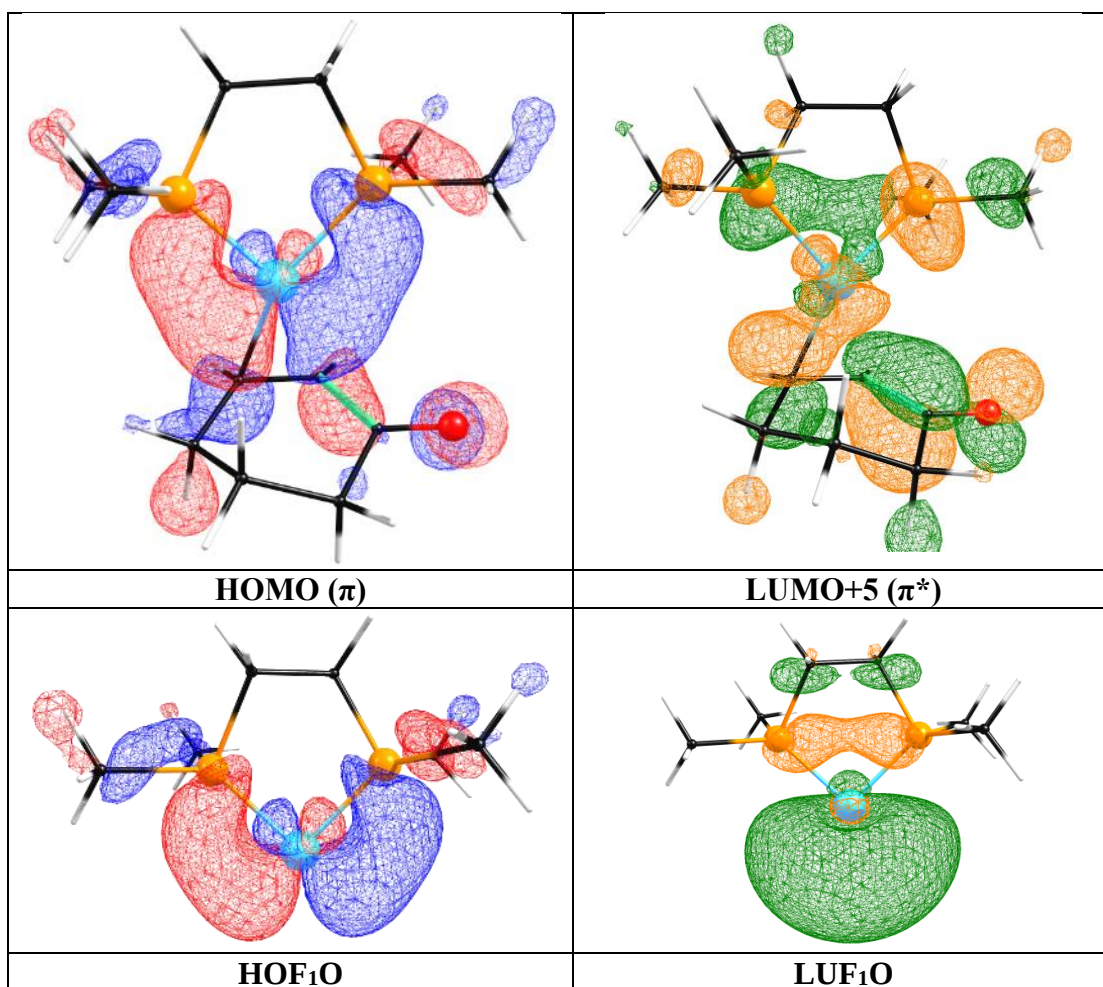
Comp.	Bond	Frag1			Frag2			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3.4'	π	HOF ₁ O	-3.39	66.54%	LUF ₂ O	-0.91	29.84%	HOMO	-4.66
	π^*	HOF ₁ O	-3.39	27.50%	LUF ₂ O	-0.91	72.36%	LUMO+5	1.11
	n	LUF ₁ O	-0.74	6.98%	HOF ₂ O	-7.37	59.29%	HOMO-5	-6.72

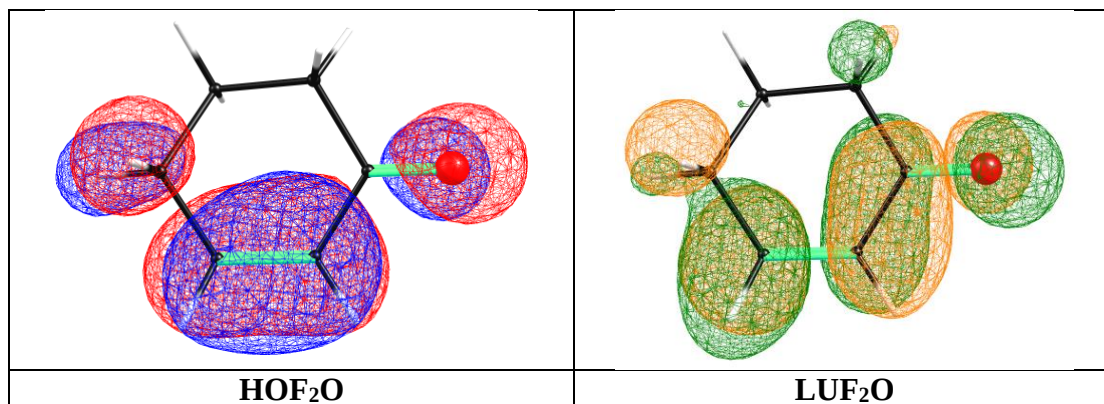




Appendix A.43 MO decomposition analysis with frontier fragment orbitals of complex 3.4'.

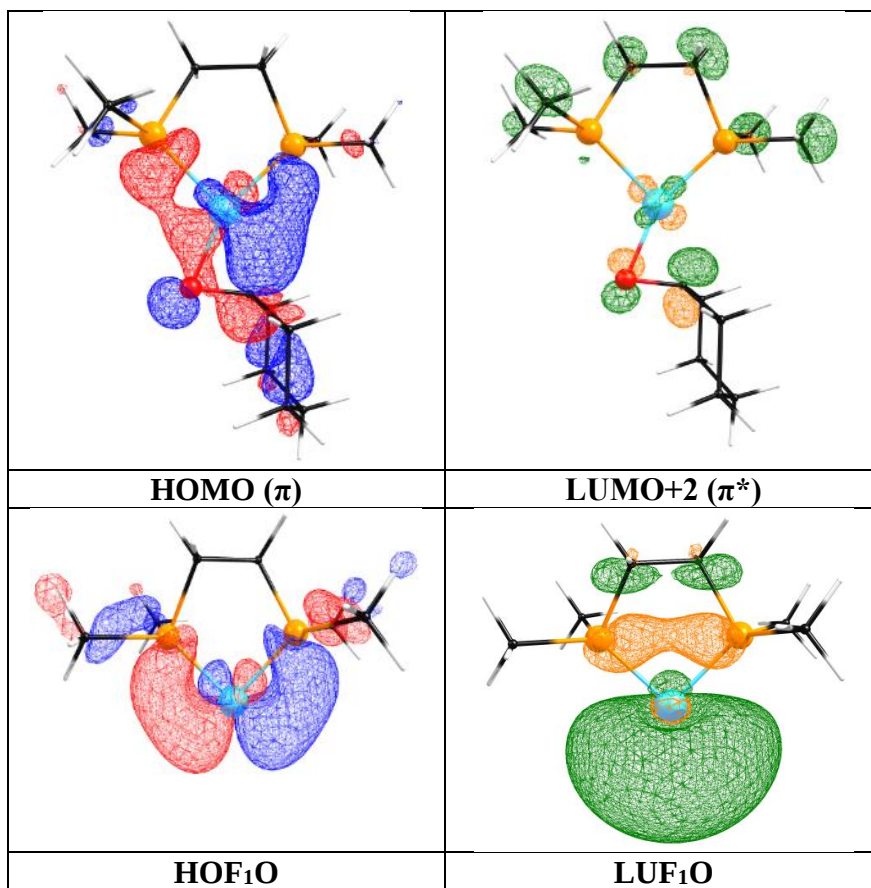
Comp	Bond	Frag1			Frag2			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3,5'	π	55	-3.320	63.10%	27	-2.23	26.26%	HOMO	-5.00
	π^*	55	-3.320	19.32%	27	-2.23	48.81%	LUMO	-0.21
	n	56	-0.70	4.37%	25	-7.45	60.67%	HOMO-6	-6.87

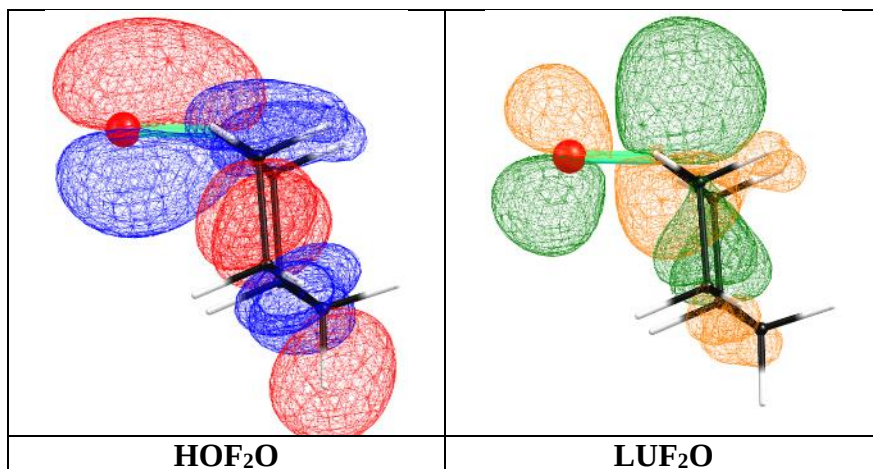




Appendix A.44 MO decomposition analysis with frontier fragment orbitals of complex 3.5'.

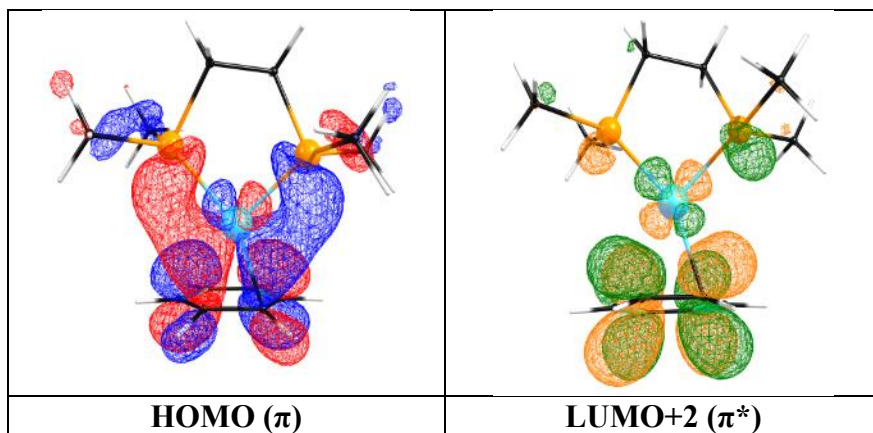
Comp.	Bond	Frag1			Frag2			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3.6'	π	HOF ₁ O	-3.33	54.34 %	LUF ₂ O	-1.82	29.44%	HOMO	-4.74
	π^*	HOF ₁ O	-3.33	20.32 %	LUF ₂ O	-1.82	34.49%	LUMO+2	0.41
	n	LUF ₁ O	-0.73	<1%	HOF ₂ O	-0.25	63.73%	HOMO-5	-6.32

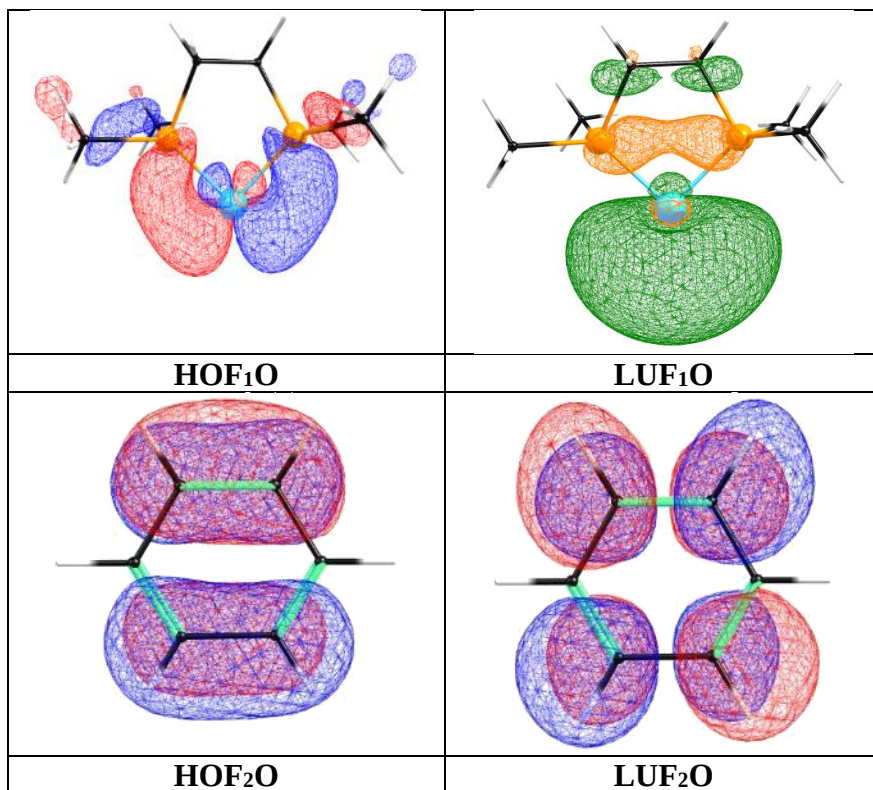




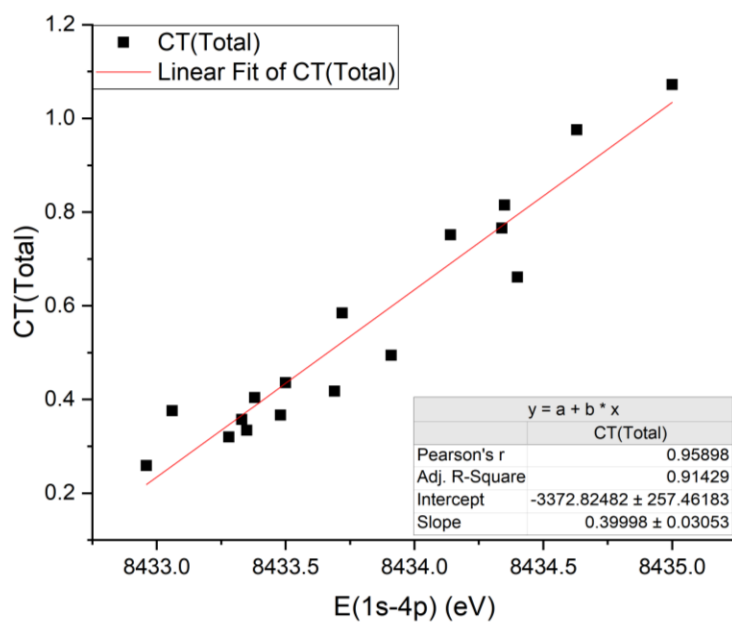
Appendix A.45 MO decomposition analysis with frontier fragment orbitals of complex 3.6'.

Comp.	Bond	Frag1			Frag2			MO	
		Orb.	E(eV)	Cont.	Orb.	(eV)	Cont.	Orb.	E(eV)
3.7'	π	HOF ₁ O	-3.41	63.40%	LUF ₂ O	-0.75	20.06%	HOMO	-3.99
	π^*	HOF ₁ O	-3.41	21.27%	LUF ₂ O	-0.75	72.87%	LUMO+4	0.50
	n	LUF ₁ O	-0.71	2.93%	HOF ₂ O	-6.93	72.65%	HOMO-5	-6.61





Appendix A.46 MO decomposition analysis with frontier fragment orbitals of complex 3.7'.



Appendix A.47 Correlation between DFT calculated charge donation from Mulliken charge distribution for simplified complexes with dmpe ligand of ground state geometry and oxidation state based on TD-DFT calculated X-ray absorption 1s-4p transition energies.

complexes	Mulliken Charge				
	Phosphine		Ni		CT(Total)
3.1'	0.291	69.55%	0.127	30.45%	0.418
3.2'	0.336	67.93%	0.159	32.07%	0.494
3.3'	0.303	69.57%	0.133	30.43%	0.436
3.4'	0.296	78.76%	0.080	21.24%	0.376
3.5'	0.373	104.36%	-0.016	-4.36%	0.357
3.6'	0.217	83.82%	0.042	16.18%	0.259
3.7'	0.207	61.82%	0.128	38.18%	0.334
3.8'	0.566	75.32%	0.185	24.68%	0.751
3.9'	0.507	66.15%	0.259	33.85%	0.766
3.10'	0.725	67.63%	0.347	32.37%	1.072
3.11'	0.535	80.85%	0.127	19.15%	0.661
3.12'	0.807	82.72%	0.169	17.28%	0.976
3.12O	0.628	77.01%	0.187	22.99%	0.815
3.1O	0.247	67.25%	0.120	32.75%	0.367
3.2O	0.277	68.51%	0.127	31.49%	0.404
3.6O	0.319	99.74%	0.001	0.26%	0.320
3.7O	0.469	80.23%	0.116	19.77%	0.585

Appendix A.48 DFT-calculated charge transfer (CT) from Mulliken charge distribution. Charge donation is divided into between phosphine (dmpe) and Ni metal contributions.

Complex 3.3'					
$\Phi=0^\circ$			$\Phi=90^\circ$		
At #	Element	q_{Mul}	At #	Element	q_{Mul}
2	Ni	0.135	2	Ni	0.121
Nickel Center		0.135	Nickel Center		0.121
1	P	0.218	1	P	0.144
3	P	0.235	3	P	0.216
7	C	-0.223	7	C	-0.214
8	C	-0.351	8	C	-0.355
9	C	-0.359	9	C	-0.352
10	C	-0.363	10	C	-0.367
11	C	-0.359	11	C	-0.349
12	C	-0.213	12	C	-0.229
14	H	0.095	14	H	0.089
15	H	0.099	15	H	0.097
16	H	0.094	16	H	0.087
17	H	0.099	17	H	0.098
28	H	0.135	28	H	0.115
29	H	0.096	29	H	0.094
30	H	0.109	30	H	0.115
31	H	0.100	31	H	0.090
32	H	0.117	32	H	0.116
33	H	0.109	33	H	0.103
34	H	0.097	34	H	0.098
35	H	0.108	35	H	0.112
36	H	0.125	36	H	0.111
37	H	0.108	37	H	0.105
38	H	0.097	38	H	0.087
39	H	0.124	39	H	0.107
Phosphine Ligand		0.300	Phosphine Ligand		0.120
4	O	-0.454	4	O	-0.390
5	C	0.054	5	C	0.124
6	H	0.080	6	H	0.084
13	C	0.074	13	C	0.043
18	C	-0.182	18	C	-0.191
19	C	-0.222	19	C	-0.162
20	H	0.129	20	H	0.137
21	C	-0.110	21	C	-0.113

22	C	-0.109	22	C	-0.125
23	H	0.102	23	H	0.110
24	H	0.118	24	H	0.124
25	C	-0.149	25	C	-0.130
26	H	0.116	26	H	0.122
27	H	0.117	27	H	0.124
benzaldehyde		-0.435	benzaldehyde	-0.242	

Appendix A.49 DFT calculated charge donation from Mulliken charge distribution for each element of complex 3.3' with tetrahedral dihedral angle $\Phi=0^\circ$ and $\Phi=90^\circ$.

Complex 3.4'					
$\Phi=0^\circ$			$\Phi=90^\circ$		
At #	Element	q _{Mul}	At #	Element	q _{Mul}
1	Ni	0.080	1	Ni	0.065
Nickel Center		0.080	Nickel Center		0.065
2	P	0.259	2	P	0.207
3	P	0.276	3	P	0.155
6	C	-0.360	6	C	-0.365
7	C	-0.355	7	C	-0.350
8	C	-0.228	8	C	-0.236
9	C	-0.207	9	C	-0.201
10	C	-0.357	10	C	-0.355
11	C	-0.359	11	C	-0.354
12	H	0.098	12	H	0.088
13	H	0.090	13	H	0.093
14	H	0.093	14	H	0.095
15	H	0.088	15	H	0.082
16	H	0.113	16	H	0.108
17	H	0.097	17	H	0.096
18	H	0.106	18	H	0.110
19	H	0.114	19	H	0.098
20	H	0.108	20	H	0.099
21	H	0.093	21	H	0.090
26	H	0.094	26	H	0.092
27	H	0.106	27	H	0.107

28	H	0.113	28	H	0.103
29	H	0.093	29	H	0.090
30	H	0.113	30	H	0.106
31	H	0.109	31	H	0.104
Phosphine Ligand		0.296	Phosphine Ligand		0.063
4	C	-0.347	4	C	-0.267
5	C	-0.344	5	C	-0.290
22	H	0.079	22	H	0.105
23	H	0.078	23	H	0.111
24	H	0.079	24	H	0.105
25	H	0.078	25	H	0.108
Ethylene		-0.376	Ethylene		-0.127

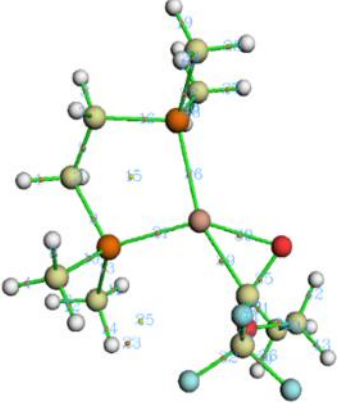
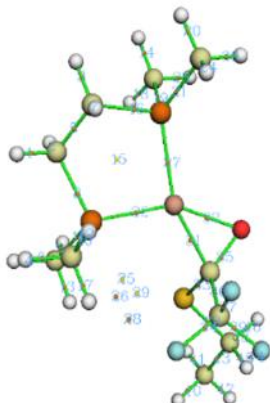
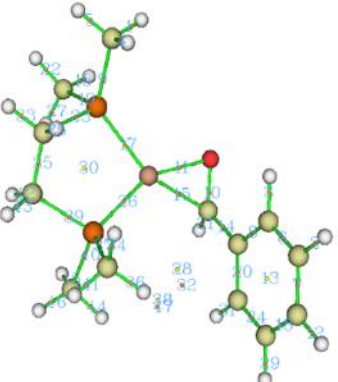
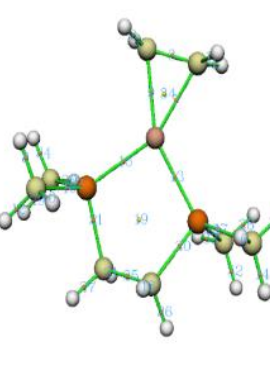
Appendix A.50 DFT calculated charge donation from Mulliken charge distribution for each element of complex 3.4' with tetrahedral dihedral angle $\Phi=0^\circ$ and $\Phi=90^\circ$.

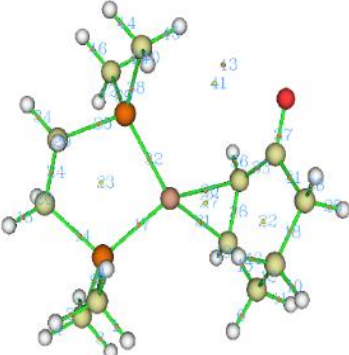
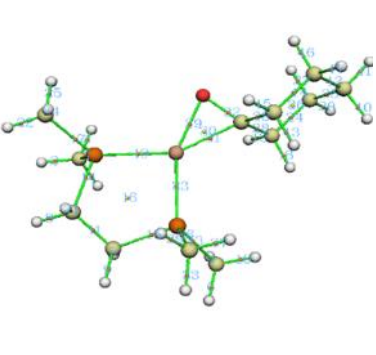
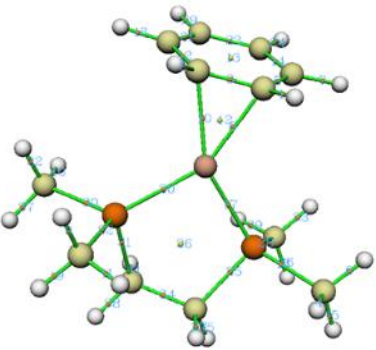
Ni _{3dx2-y2} → π^*			π →Ni _{4p}			
	E(2)	E(j)-E(i)	F(i,j)	E(2)	E(j)-E(i)	F(i,j)
	kcal/mol	a.u.	a.u.	kcal/mol	a.u.	a.u.
7'	58.65	0.19	0.099	44.58	0.52	0.142
4'	70.35	0.22	0.113	83.83	0.55	0.193

Appendix A.51. Key Second Order Interactions from NBO analysis, only fully symmetrical system σ donation from $\pi_{C=C}$ to Ni_{4p} and backdonation from Ni_{3dx2-y2} to $\pi^*_{C=C}$ could be found.

Complex	Critical Point(cp)	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	G(r)	K(r)	V(r)
3.1'	bcp _{NiC} -29	-0.052	0.219	-0.052	0.107	0.052	-0.159
	bcp _{NiO} -30	-0.027	0.550	-0.027	0.165	0.027	-0.192
3.2'	bcp _{NiC} -31	-0.049	0.243	-0.049	0.110	0.049	-0.159
	bcp _{NiO} -32	-0.029	0.537	-0.029	0.164	0.029	-0.193
3.3'	bcp _{NiC} -15	-0.037	0.248	-0.037	0.099	0.037	-0.136
	bcp _{NiO} -11	-0.031	0.524	-0.031	0.162	0.031	-0.193
3.4'	rcp _{NiCC} -34	-0.024	0.359	-0.024	0.114	0.024	-0.138
	bcp _{NiC} -7	-0.035	0.235	-0.035	0.093	0.035	-0.128
3.5'	bcp _{NiC} -9	-0.034	0.238	-0.034	0.094	0.034	-0.128
	rcp _{NiCC} -27	-0.025	0.353	-0.025	0.113	0.025	-0.137
3.6'	bcp _{NiC} -21	-0.038	0.213	-0.038	0.091	0.038	-0.130
	bcp _{NiC} -30	-0.032	0.261	-0.032	0.098	0.032	-0.130
3.7'	rcp _{NiCO} -30	-0.028	0.449	-0.028	0.140	0.028	-0.168
	bcp _{NiC} -31	-0.037	0.232	-0.037	0.095	0.037	-0.133
3.7''	bcp _{NiO} -29	-0.033	0.536	-0.277	0.043	0.277	-0.320
	rcp _{NiCC} -42	-0.018	0.309	-0.018	0.095	0.018	-0.113
3.7''	bcp _{NiC} -10	-0.026	0.217	-0.026	0.080	0.026	-0.107
	bcp _{NiC} -8	-0.025	0.224	-0.025	0.081	0.025	-0.105

Appendix A.52 DFT calculated AIM (Atoms in Molecules) results; $\rho(r)$ is Electron density; $\nabla^2\rho(r)$ is Laplacian of the electron density; H(r) is the Total energy density; G(r) is the Kinetic energy density; K(r) is Hamiltonian kinetic energy density; V(r) is the Potential energy density.

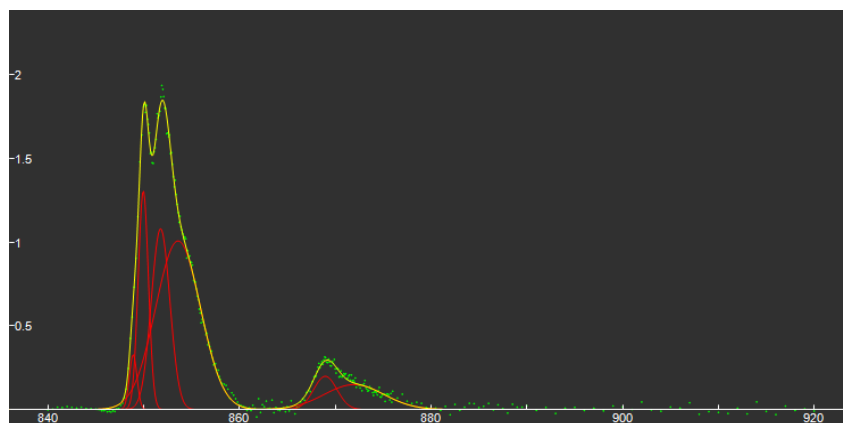
	
3.1'	3.2'
bcp_{NiC}-29, bcp_{NiO}-30	bcp_{NiC}-31, bcp_{NiO}-32
	
3.3'	3.4'
bcp_{NiC}-15, bcp_{NiO}-11	rcp_{NiCO}-34, bcp_{NiC}-7, bcp_{NiO}-9

	
3.5'	3.6'
rcp_{NiCC}-27, bcp_{NiC}-21, bcp_{NiO}-30	rcp_{NiCO}-30, bcp_{NiC}-31, bcp_{NiO}-29
	
3.7'	
rcp_{NiCC}-42, bcp_{NiC}-10, bcp_{NiO}-8	

Appendix A.53 All rcp(ring critical points) and bcp(bond critical points) of complexes 1'-7' from Topology analysis in AIM calculation

Appendix B Experimental Data for Chapter 4

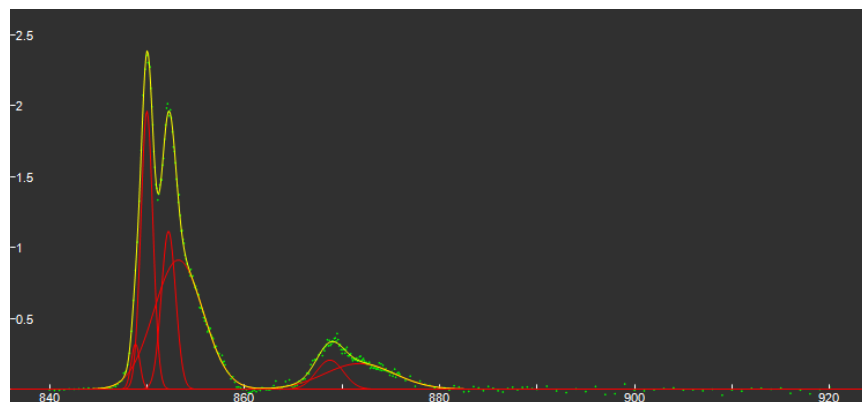
B.1 Spectrum Simulation



Appendix B.1 Simulated Ni L edge spectrum of 4.1, spectra are normalized with Athena and its background subtracted with Fityk.

complex 1	gaussian	height	center	hwhm	area	FWHM
L ₃ edge	1	0.328	848.909	0.464	0.324	0.927
	2	1.309	849.965	0.624	1.739	1.248
	3	1.082	851.768	1.136	2.618	2.272
	4	1.008	853.595	2.747	5.897	5.494
L ₂ edge	5	0.199	868.965	1.430	0.605	2.860
	6	0.149	871.974	3.667	1.165	7.334

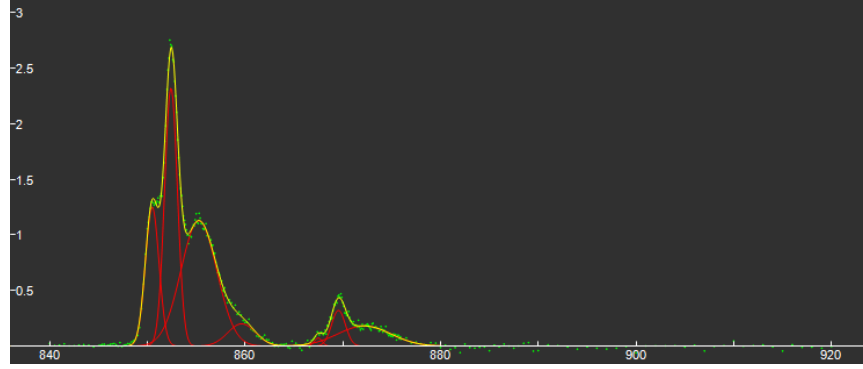
Appendix B.2 Ni L edge pre-edge fit results for 4.1.



Appendix B.3 Simulated Ni L edge spectrum of 4.2, spectra are normalized with Athena and its background subtracted with Fityk.

complex 2	gaussian	height	center	hwhm	area	FWHM
L ₃ edge	1	0.321	848.820	0.514	0.352	1.028
	2	1.963	849.985	0.723	3.020	1.445
	3	1.116	852.201	0.863	2.050	1.725
	4	0.912	853.217	2.965	5.754	5.930
L ₂ edge	5	0.206	868.762	1.631	0.714	3.261
	6	0.181	871.797	4.215	1.626	8.429

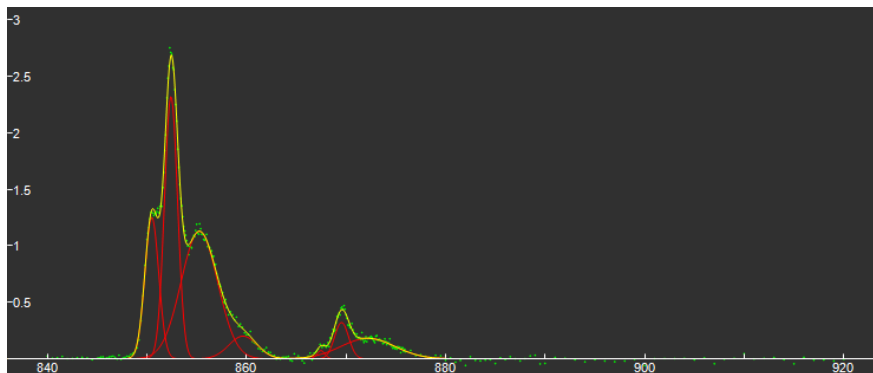
Appendix B.4 L edge pre-edge fit results for 4.2.



Appendix B.5 Simulated Ni L edge spectrum of 4.3, spectra are normalized with Athena and its background subtracted with Fityk.

complex 3	Gaussian	height	center	hwhm	area	FWHM
L ₃ edge	1	0.8401	849.4603	0.6646	1.1887	1.3293
	2	2.1918	851.5932	0.7861	3.6679	1.5721
	3	1.1171	854.4134	2.0235	4.8125	4.0471
	4	0.2488	858.3416	2.2268	1.1797	4.4536
L ₂ edge	5	0.2836	868.7728	0.7438	0.4490	1.4876
	6	0.1448	871.7257	3.2767	1.0101	6.5535
	7	0.0623	866.6410	0.2594	0.0344	0.5188

Appendix B.6. Ni L edge pre-edge fit results for 4.3.



Appendix B.7 Simulated Ni L edge spectrum of 4.4, spectra are normalized with Athena and its background subtracted with Fityk.

complex 4	Gaussian	height	center	hwhm	area	FWHM
L ₃ edge	1	1.251	850.495	0.818	2.178	1.636
	2	2.323	852.422	0.772	3.820	1.545
	3	1.128	855.271	2.154	5.172	4.308
	4	0.201	859.659	1.673	0.716	3.346
L ₂ edge	5	0.073	867.482	0.468	0.072	0.936
	6	0.322	869.557	0.829	0.568	1.657
	7	0.181	872.205	3.195	1.233	6.390

Appendix B.8 Ni L edge pre-edge fit results for 4.4.

B.2 Time-Dependent Density Functional Calculations

Complex 1			Ni character			Normalized Ni character		
Orbital	Energy	Total	s	p	d	s	p	d
76	-0.0106	34.90%	0.80%	30.90%	3.20%	2.29%	88.54%	9.17%
77	0.00891	10.70%	1.30%	7.20%	2.20%	12.15%	67.29%	20.56%
78	0.01894	6.60%	4.30%	1.20%	1.10%	65.15%	18.18%	16.67%
79	0.02251	15.80%	0.00%	0.90%	14.90%	0.00%	5.70%	94.30%
80	0.03369	16.00%	0.10%	12.50%	3.40%	0.63%	78.13%	21.25%
81	0.03514	12.90%	0.50%	7.20%	5.20%	3.88%	55.81%	40.31%
82	0.05266	15.60%	4.50%	8.80%	2.30%	28.85%	56.41%	14.74%

Appendix B.9 Molecular orbital descriptions for complex 4.1 from ground state DFT calculations.

Transition Energy	Contribution from MO acceptors				
849.078	MO #	76	77	79	
	Contribution	76.08%	6.70%	5.69%	
849.157	MO #	76	79	77	
	Contribution	64.69%	16.94%	5.16%	
849.208	MO #	79	76	80	
	Contribution	59.53%	12.32%	7.14%	
849.248	MO #	79	76	80	
	Contribution	56.74%	21.06%	6.75%	
850.26	MO #	77	76		
	Contribution	81.34%	8.76%		
850.574	MO #	78	81	80	82
	Contribution	57.78%	17.48%	5.07%	4.80%
850.726	MO #	78	82	77	81
	Contribution	69.97%	10.52%	5.12%	4.55%
850.803	MO #	78	82	77	
	Contribution	79.82%	7.74%	4.93%	
851.052	MO #	80	81	79	
	Contribution	65.70%	19.12%	9.76%	
850.439	MO #	81	80	78	
	Contribution	52.99%	15.00%	11.78%	

	MO #	81	78	80	77
850.55	Contribution	40.06%	20.89%	10.89%	4.54%

Appendix B.10 Acceptor orbital descriptions from L-edge TD-DFT calculation for complex 4.1.

Photon E	Intensity	Weighted Average			Renormalized		
		Ni	pi ligand	Phosphine	Ni	pi ligand	Phosphine
849.157	0.00948	25.80%	22.28%	38.70%	29.73%	25.67%	44.60%
849.078	0.00131	28.17%	19.57%	40.73%	31.84%	22.12%	46.04%
849.208	0.0225	14.85%	32.17%	31.97%	18.80%	40.73%	40.47%
849.248	0.0163	17.40%	32.33%	34.83%	20.57%	38.23%	41.19%
850.26	0.00302	11.76%	40.20%	38.14%	13.05%	44.62%	42.33%
850.439	0.0174	10.01%	10.43%	59.31%	12.55%	13.08%	74.37%
850.55	0.0175	12.03%	17.04%	68.19%	12.37%	17.52%	70.11%
850.574	0.0135	7.63%	11.32%	66.18%	8.96%	13.30%	77.74%
850.726	0.00308	7.39%	14.39%	68.39%	8.20%	15.95%	75.84%
850.803	0.00163	7.00%	14.16%	71.33%	7.57%	15.31%	77.12%
851.052	0.0011	14.52%	16.26%	63.80%	15.35%	17.19%	67.46%

Appendix B.11 Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for 4.1. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.

Complex 2			Ni character			Normalized Ni character		
Orbital	Energy	Total	s	p	d	s	p	d
63	-0.00606	42.60%	0.00%	36.90%	5.70%	0.00%	0.87%	0.13%
64	0.01785	6.40%	5.60%	0.00%	0.80%	0.88%	0.00%	0.13%
65	0.03339	16.40%	0.00%	16.30%	0.10%	0.00%	0.99%	0.01%
66	0.03785	14.60%	1.30%	6.70%	6.60%	0.09%	0.46%	0.45%
67	0.04489	23.70%	0.10%	3.20%	20.40%	0.00%	0.14%	0.86%
68	0.05371	11.30%	0.50%	7.80%	3.00%	0.04%	0.69%	0.27%
69	0.05634	22.50%	12.00%	7.60%	2.90%	0.53%	0.34%	0.13%

Appendix B.12 Molecular orbital descriptions for complex 4.2 from ground state DFT calculations.

Orbital	Contribution from MO acceptors					
849.399	MO #	63	67			
	Contribution	86.78%	8.21%			
850.725	MO #	64	69			
	Contribution	90.17%	6.08%			
850.947	MO #	64	69			
	Contribution	85.66%	9.68%			
851.032	MO #	64	66			
	Contribution	82.10%	9.84%			
850.808	MO #	66	67			
	Contribution	78.47%	4.25%			
849.474	MO #	67	68	66		
	Contribution	70.25%	7.73%	4.81%		
849.481	MO #	67	63	68	66	63
	Contribution	62.09%	11.24%	6.24%	5.02%	4.88%

Appendix B.13 Acceptor orbital descriptions from L-edge TD-DFT calculation for complex 2.

Photon E	Intensity	Weighted Average			Normalized		
		Ni	pi ligand	Phosphine	Ni	pi ligand	Phosphine
849.399	0.00911	12.32%	4.90%	77.77%	12.97%	5.15%	81.88%
849.474	0.0247	4.97%	27.83%	49.98%	6.01%	33.62%	60.38%
849.481	0.0313	6.65%	24.95%	57.87%	7.43%	27.89%	64.68%
850.725	0.00495	1.41%	3.46%	91.37%	1.47%	3.60%	94.93%
850.808	0.0204	10.42%	7.76%	64.55%	12.60%	9.38%	78.02%
850.947	0.00246	1.67%	4.01%	89.66%	1.75%	4.20%	94.04%
851.032	0.00829	2.10%	2.90%	86.94%	2.28%	3.16%	94.56%

Appendix B.14 Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for 4.2. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.

Complex 3			Ni character			Normalized Ni character		
Orbital	Energy	Total	s	p	d	s	p	d
91	-0.01633	37.10%	0.00%	31.00%	6.10%	0.00%	83.56%	16.44%
92	-0.00012	32.40%	0.40%	2.50%	29.50%	1.23%	7.72%	91.05%
93	0.00779	6.50%	3.90%	2.00%	0.60%	60.00%	30.77%	9.23%
94	0.02601	15.20%	0.80%	8.40%	6.00%	5.26%	55.26%	39.47%
95	0.03266	5.50%	0.30%	3.60%	1.60%	5.45%	65.45%	29.09%

Appendix B.15 Molecular orbital descriptions for complex 4.3 from ground state DFT calculations.

Orbital	Contribution from MO acceptors		
	MO #	91	
849.722	Contribution	90.96%	
	MO #	91	
849.97	Contribution	93.40%	
	MO #	91	
850.056	Contribution	93.17%	
	MO #	92	
848.614	Contribution	86.17%	
	MO #	92	
848.712	Contribution	88.24%	
	MO #	93	
851.305	Contribution	90.41%	
	MO #	93	94
851.727	Contribution	82.99%	6.77%
	MO #	94	95
851.446	Contribution	69.51%	14.63%
	MO #	94	95
851.525	Contribution	6.11%	64.66%

Appendix B.16 Acceptor orbital descriptions from L-edge TD-DFT calculation for complex 4.3.

Photon E	Intensity	Weighted Average			Normalized		
		Ni	pi ligand	Phosphine	Ni	pi ligand	Phosphine
848.614	0.0356	27.92%	32.83%	54.22%	24.28%	28.56%	47.16%
848.712	0.0423	28.59%	33.62%	25.42%	32.63%	38.37%	29.01%
849.722	0.0135	34.65%	4.39%	54.36%	37.10%	4.70%	58.20%
849.97	0.00138	50.22%	39.66%	3.52%	53.77%	42.46%	3.77%
850.056	0.00605	34.56%	4.38%	54.22%	37.10%	4.70%	58.20%
851.305	0.00387	5.88%	2.53%	82.00%	6.50%	2.80%	90.70%
851.446	0.0158	11.37%	4.50%	68.27%	13.51%	5.34%	81.14%
851.525	0.0168	5.38%	3.70%	75.49%	6.36%	4.37%	89.26%
851.727	0.00406	6.42%	2.70%	80.64%	7.16%	3.00%	89.84%

Appendix B.17 Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for 4.3. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.

Complex 4		Ni character				Normalized Ni character		
Orbital	Energy	Total	s	p	d	s	p	d
95	-0.01776	34.70%	0.00%	25.10%	9.60%	0.00%	72.33%	27.67%
96	-0.01219	34.30%	0.10%	5.60%	28.60%	0.29%	16.33%	83.38%
97	0.00781	5.40%	3.30%	1.60%	0.50%	61.11%	29.63%	9.26%
98	0.02325	12.90%	0.70%	6.60%	5.60%	5.43%	51.16%	43.41%
99	0.03099	5.40%	0.20%	4.00%	1.20%	3.70%	74.07%	22.22%

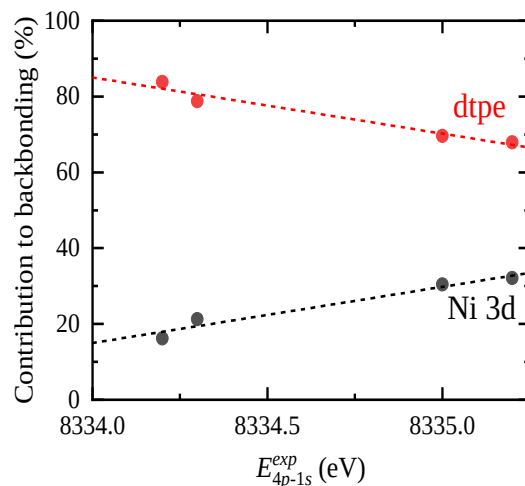
Appendix B.18 Complexes 4.4 TD-DFT calculation transitions final state acceptor Ni character contribution in MO, and normalized Ni character contribution are also provided.

Orbital	Contribution from MO acceptors		
850.307	MO #	95	96
	Contribution	77.86%	17.20%
848.442	MO #	95	96
	Contribution	15.97%	76.35%
848.471	MO #	95	96
	Contribution	15.82%	76.40%
851.986	MO #	97	98
	Contribution	85.86%	7.05%
851.624	MO #	98	99
	Contribution	80.14%	9.54%
851.649	MO #	98	99
	Contribution	75.31%	9.20%

Appendix B.19 Acceptor orbital descriptions from L-edge TD-DFT calculation for complex 4.4.

Photon E	Intensity	Weighted Average			Normalized		
		Ni	pi ligand	Phosphine	Ni	pi ligand	Phosphine
848.442	0.0492	31.73%	28.39%	32.20%	34.37%	30.75%	34.88%
848.471	0.051	31.69%	28.39%	32.13%	34.37%	30.79%	34.84%
850.307	0.00884	32.92%	13.45%	48.69%	34.63%	14.15%	51.22%
851.624	0.0196	10.85%	2.17%	76.65%	12.10%	2.42%	85.48%
851.649	0.0169	10.21%	2.05%	72.25%	12.08%	2.42%	85.49%
851.986	0.00329	5.55%	0.34%	87.03%	5.97%	0.37%	93.66%

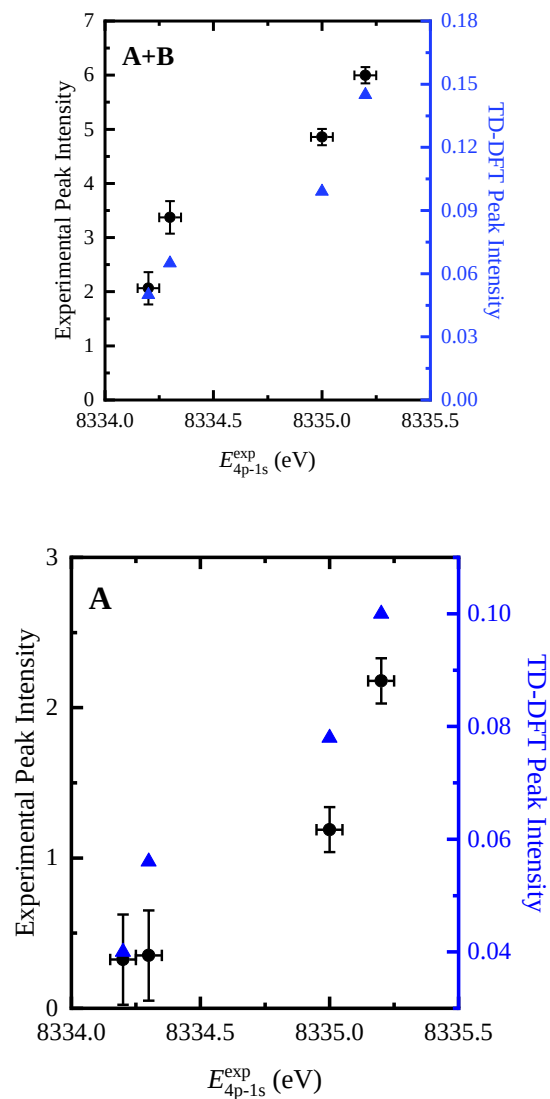
Appendix B.20 SI 20. Weighted averaged contributions of orbital contributions to each final state from TD-DFT calculations for 4.4. Since only contributors with >4% are included in the analysis, the total contribution does not equal 100%. Renormalized distributions (sum = 100%) are also included.



Appendix B.21 Total contributions to backbonding from charge decomposition analysis (CDA). An increase in π acidity in the π ligand causes an overall increase in charge donation from both the metal centre and the diphosphine ligand, but the Ni 3d contribution is significantly greater with more π acidic ligands (such as in 4.3, 4.4).

EXP _{4p←1s} (eV)	dtpe	Ni	Total	Ni 3d %	dtpe%
8334.2	0.217	0.042	0.2588	16.2	83.8
8334.3	0.296	0.080	0.37588	21.3	78.8
8335	0.291	0.127	0.41797	30.4	69.6
8335.2	0.336	0.159	0.49426	32.1	67.9

Appendix B.22 Calculated CDA-based charge donation from both the metal centre and the diphosphine ligand to π acidic ligands.



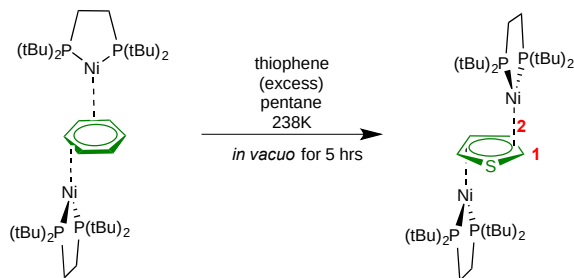
Appendix B.23 Correlation of Ni L-edge peak intensities (experimental in black and TD-DFT in blue) with the energy of the Ni 4p←1s transition from Ni K-edge XAS. Top: contributions from direct Ni 3d backbonding (Peak A). Bottom: contributions including 3d/4p mixing (sum of peaks A & B) are shown on the right.

Appendix C Experimental Data for Chapter 5

C.1 Synthesis

Synthesis and Isolation of 5.2

In a nitrogen-filled dry glovebox, a solution of 4.1 (38 mg, 0.0459mmol) in pentane was treated with thiophene (10 mg, 0.1189mmol) and reacted for 10 mins at -35 °C, resulting in a

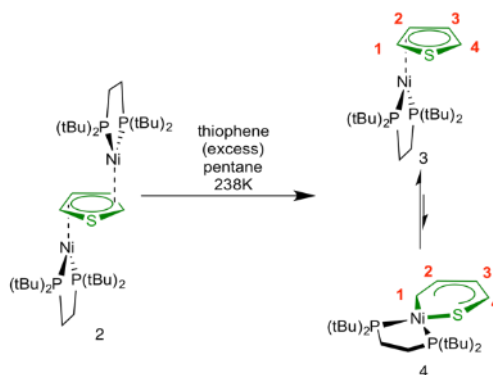


colour change of the solution to orange. The solvent was evaporated in vacuo for 5 hours and the crude product was extracted with cool pentanes stored at -35 °C, filtered through glass fiber to give an orange filtrate and stored at -35 °C. Yield 33.8mg (0.04051 mmol, 88.3 %), X-ray quality orange crystals of 2 were grown by slow evaporation of a saturated Et₂O/pentanes (1:1 ratio) solution in an open 1 dram vial sealed in a 5 dram vial over 2 days. Analytical data for 2. ¹H NMR (400 MHz, THF-d₈, -65 °C) δ 4.12 (t, J = 7.8, 6.1 Hz, 2H, H1), δ 3.56 (dd, J = 13.4, 5.3 Hz, 2H, H2), δ 1.95 – 1.79 (m, 8H, PCH₂CH₂P), δ 1.50 – 1.39 (m, 8H, PCH₂CH₂P), δ 1.30 (dd, J = 11.4, 6.8 Hz, 18H, C(CH₃)₃), δ 1.22 (dd, J = 24.3, 10.8 Hz, 18H, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, THF-d₈, -50 °C) δ 84.36 (d[AB], ddd, ²J_{P,P} = 87.1, ⁵J_{P,P} = 10.1, 6.3 Hz), 77.17 (d[AB], ddd, ²J_{P,P} = 87.1, ⁵J_{P,P} = 10.1, 6.3 Hz). ³¹P{¹H} NMR (162 MHz, THF-d₈, 25 °C) δ 86.60 – 83.25 (m), δ 80.24 – 77.17 (m). ¹³C{¹H} NMR (101 MHz, THF-d₈, -50 °C) δ 64.59 (d, J_{C,P} = 18.0 Hz, C1), δ 50.30 (d, J_{C,P} = 25.3 Hz, C2), δ 34.70 – 34.36 (m, C(CH₃)₃), δ 34.07 – 33.70 (m, C(CH₃)₃), δ 30.53 (d, J = 7.5 Hz, C(CH₃)₃), δ 30.14 (dd, J = 17.4, 6.5 Hz, C(CH₃)₃), δ 29.66 (d, J = 6.9 Hz, C(CH₃)₃), 22.88 (dd, J = 21.1, 12.1 Hz, PCH₂CH₂P). Anal. Calcd for C₃₉H₈₂Ni₂P₄S(%): C, 56.82; H, 10.03. Found: C, 56.03; H, 10.36. LRMS (MALDI) 838.6 [M⁺].

Formation of 5.3

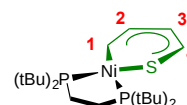
In a nitrogen-filled dry glovebox, A solution of 2 (20mg, 0.0435mmol) in 1.5 mL THF- d_8 was treated with thiophene (30 mg, 0.35mmol); the resulting orange solution was placed in a J-Young NMR tube at RT. The sample was placed in an NMR probe and cooled to -65 °C degree. Analytical data for complex 3. ^1H NMR (400

MHz, THF- d_8 , -65 °C) δ 6.35 (br, s, 1H, H4), δ 5.89 (br, s, 1H, H3), 4.52 (br, s, 1H, H2), 4.22 (br, s, 1H, H1), δ 1.39 – 1.16 (m, overlapped peaks of $\text{C}(\text{CH}_3)_3$ and $\text{PCH}_2\text{CH}_2\text{P}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF- d_8 -60 °C) δ 79.33 (d[AB] d, $J_{\text{P,P}} = 82.8$ Hz), 76.52 (d[AB] d, $J_{\text{P,P}} = 82.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , -50 °C) δ 126.70 (s, C4), δ 125.07 (s, C3), δ 65.61 (s, C2), δ 64.58 (s, C2), δ 35.88 – 35.28 (m, $\text{C}(\text{CH}_3)_3$), δ 35.05 (d, $J = 8.4$ Hz, $\text{C}(\text{CH}_3)_3$), δ 31.23 – 30.75 (m, $\text{C}(\text{CH}_3)_3$), δ 29.09 (d, $J = 13.6$ Hz, $\text{C}(\text{CH}_3)_3$), δ 23.33 – 22.43 (overlapped with other peaks, $\text{PCH}_2\text{CH}_2\text{P}$).

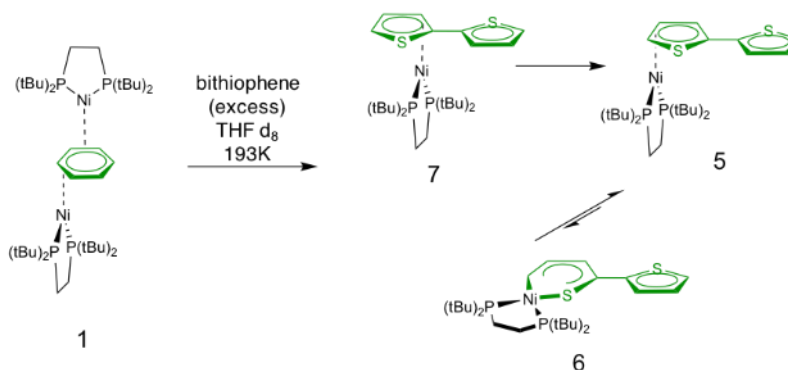


Formation of 5.4

Analytical data for 5.4. Clear and sharp peaks of 5.4 were found at -30 °C by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, where in a 2:5 ratio over 5.3, and the amount of 5.4 got increased as the temperature went lower. The equilibrium has been confirmed as the ratio hasn't changed over 70mins. Analytical data for 5.4. ^1H NMR (400 MHz, THF- d_8 , -65 °C) δ 8.02 (td, $J = 37.2, 9.8$ Hz, 1H, H1), δ 6.72 (dd, $J = 12.1, 10.5$ Hz, 10H), δ 6.61 (m, $J = 17.2, 7.9$ Hz, 1H), δ 6.53 (dd, $J = 15.0, 7.6$ Hz, 1H), δ 2.12 (dd, $J = 16.3, 7.8$ Hz, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), δ 1.94 (dd, $J = 8.2, 7.7$ Hz, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), δ 1.47 (dd, $J = 11.8, 7.6$ Hz, 36H, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF- d_8 -60 °C) δ 73.44 (d[AB] d, $^2J_{\text{P,P}} = 5.4$ Hz), δ 67.03 (d[AB] d, $^2J_{\text{P,P}} = 5.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , -50 °C) δ 128.78 (s, C1), δ 128.18 (s, C2), δ 128.05 (s, C4), δ 125.18 (s, C3), δ 34.86 – 34.68 (m, $\text{C}(\text{CH}_3)_3$), δ 29.17 – 28.99 (m, $\text{C}(\text{CH}_3)_3$), δ 23.33 – 22.43 (overlapped with other peaks, $\text{PCH}_2\text{CH}_2\text{P}$).



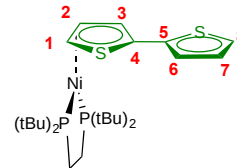
Formation of 5.7



Complex 4.1 (20 mg, 0.0239 mmol) was dissolved in 1 mL of THF-d₈. This red-orange solution was transferred to a screw-cap NMR tube and frozen in liquid nitrogen. To the top of this frozen solution was added a solution of bithiophene (8 mg, 0.0481 mmol, 2 equiv) in THF-d₈ (0.2 mL). The tube was then frozen in liquid nitrogen before being quickly placed in an NMR spectrometer pre-cooled to -80 °C. sample was only analyzed by ³¹P NMR spectrum, due to a short time existence of a small amount of 5.7. ³¹P{¹H} NMR (162 MHz, THF-d₈ -60 °C) δ 80.84 (d[AB] d, J = 82.5 Hz), δ 77.83 (d[AB], overlapped with other peaks).

Synthesis and Isolation of 5.5

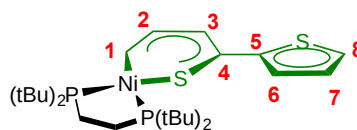
In a nitrogen-filled dry glovebox, a solution of 4.1 (10mg, 0.0119 mmol) in cool pentanes (-35 °C) was treated with a solution of bithiophene (8 mg, 0.0481 mmol) in cool pentanes (-35 °C) and reacted for 1h at -35 °C, resulting in a color change from fresh red into carrot orange. Saturated pentanes solution was placed in an open 1 dram vial sealed in a 5 dram vial and stored at -35 °C. After evaporating extra pentanes in vacuo. X-ray quality carrot orange crystals of 3 could be collected over several days. Analytical data for monomer-bithiophene-S3. ¹H NMR (400 MHz, THF-d₈ , -45 °C), δ 7.09 (d, J = 4.1 Hz, 1H, H₆), δ 6.86 (t, J = 4.2 Hz, 1H, H₇), δ 6.74 (d, J = 3.1 Hz, 1H, H₈), δ 6.64 (br, s, 1H, H₃), δ 4.42 (dd, J = 13.8, 4.4 Hz, 1H, H₂), δ 4.35 – 4.26 (m, 1H, H₁), δ 1.85 (dd, J = 21.2, 6.6 Hz, 2H, PCH₂CH₂P), δ 1.63 – 1.56 (m, 2H, PCH₂CH₂P), δ 1.32 (d, J = 5.3 Hz, 9H, C(CH₃)₃), δ 1.29 (d, J = 4.7 Hz, 9H, C(CH₃)₃), δ 1.25 (d, J = 10.5 Hz, 9H, C(CH₃)₃), δ 1.17 (d, J = 11.5 Hz,



9H, C(CH₃)₃). ¹³C NMR (101 MHz, THF-d₈, -50 °C) δ 140.65 (d, J = 3.1 Hz, C₅), δ 127.11 (s, C₆), δ 122.40 (s, C₇), δ 120.63 (s, C₈), δ 120.62 (d, J = 20.2 Hz, C₄), δ 115.91 (s, C₃), δ 59.60 (m, J = 16.8 Hz, C₂), δ 50.89 (m, J = 24.2 Hz, C₁), δ 35.86 – 35.50 (m, C(CH₃)₃), δ 35.34 (t, J = 6.1 Hz, C(CH₃)₃), δ 34.79 (dd, J = 8.3, 3.6 Hz, C(CH₃)₃), δ 33.94 – 33.40 (m, C(CH₃)₃), δ 30.18 (t, J = 7.2 Hz, C(CH₃)₃), δ 29.78 – 29.26 (m, PCH₂CH₂P). ³¹P{¹H} NMR (162 MHz, THF-d₈ -70 °C) δ 81.66 (d[AB] d, ²J_{P,P} = 78.4 Hz) δ 78.98 (d[AB] d, ²J_{P,P} = 78.5 Hz). Anal. Calcd for C₂₆H₄₆NiP₂S₂(%): C, 57.47; H, 8.53. Found: C: 56.80; H: 9.11. LRMS (MALDI) 543.3 [M⁺].

Formation of 5.6

5.6 was found at -35 °C by ³¹P{¹H} NMR spectroscopy, where in a 1:4 ratio over 5.6. The equilibrium has been confirmed as the ratio hasn't



changed over 70mins. ¹H NMR (400 MHz, THF-d₈, -45 °C), δ 7.99 (dt, J = 36.0, 9.6 Hz, 1H), δ 7.30 (d, J = 3.1 Hz, 1H), δ 7.15 (d, J = 5.0 Hz, 1H), δ 7.07 (d, J = 3.7 Hz, 1H), δ 6.98 (d, J = 6.8 Hz, 1H), δ 6.93 (t, J = 4.3, 3.0 Hz, 1H), δ 2.15 (dq, J = 16.4, 8.1, 7.5 Hz, 2 H, PCH₂CH₂P), δ 2.05 – 1.94 (m, 2 H, PCH₂CH₂P), δ 1.50 (dd, J = 18.9, 11.9 Hz, 36H, C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, THF-d₈, -60 °C), δ 75.29 (d[AB] d, ²J_{P,P} = 5.0 Hz), 68.88 (d[AB], d, ²J_{P,P} = 4.8 Hz). ¹³C{¹H} NMR (101 MHz, THF-d₈, -70 °C), δ 149.92(s), δ 135.79(s), δ 129.01 – 128.74 (m), 127.85 – 127.47 (m), 128.17 (s), 124.25 (s), 123.76 (s), 122.61 (dt, J = 8.5, 4.8 Hz), 35.81 (d, J = 3.9 Hz, C(CH₃)₃), 35.04 – 34.62 (m, C(CH₃)₃), δ 33.86 – 33.55 (m, C(CH₃)₃), δ 30.23 (d, J = 7.4 Hz, C(CH₃)₃, overlapped with peaks of 6), δ 23.09 (s, PCH₂CH₂P).

C.2 Variable-Temperature NMR Experiment

Equation 1 (an adaption of the Van't Hoff equation) allows for determination of ΔH⁰_{INS} and ΔS⁰_{INS} by plotting experimental data for the equilibrium Ni(dppe)-thiophene π adduct concentration [M]_{add} and insertion product [M]_{ins} in THF-d₈ at various temperatures (T). As the insertion equilibrium constant between two isomers of Ni-thiophene/ Ni-bithiophene complexes directly equals to the intensity ratio of two complexes' ³¹P NMR peak integrity (K_{eq} = [M]_{ins} / [M]_{add} = n_{ins} / n_{add}, the volume of the solution has no effect),

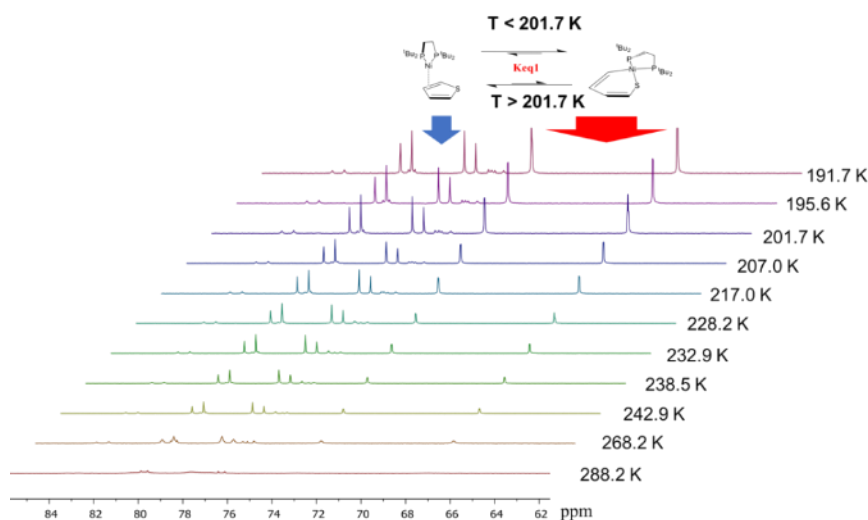
$$\ln[K_{eq}] = \frac{\Delta H_{INS}^0}{RT} - \frac{\Delta S_{INS}^0}{R} \quad (1)$$

we can obtain experimental ΔH⁰_{INS} and ΔS⁰_{INS} via integration of ³¹P signals assigned to the Ni π adduct and C-S insertion complexes,

respectively. The formation of dimeric species was suppressed by addition of a large excess of the thiophene ligand. This large excess does not affect the monomer equilibrium.

$$T_{\text{eq}} = T_{(K_{\text{eq}}=1)} = \frac{\Delta H_{\text{INS}}^0}{\Delta S_{\text{INS}}^0} \quad (2)$$

In binary equilibrium systems where the enthalpy (ΔH) and entropy (ΔS) have the same sign, there exists a temperature where $K_{\text{eq}} = 1$. This temperature is easily defined as shown in equation 2. This value is particularly relevant in this case as it represents the temperature at which the equilibrium shifts from preferring reactants to products (in an analogous fashion to an equilibrium constant. T_{eq} is easily obtained from a Van't Hoff analysis (equation 1).



Appendix C.1 ^{31}P NMR spectra (400 MHz, THF-d_8 , 191.7K-288.15K) that show the effect of temperature on the equilibrium between the Ni(dtbpe)thiophene π adduct complex and the C-S insertion product. Within the equilibrium mixture, the insertion product is favoured at lower temperatures

	ΔH_{INS}^0	ΔS_{INS}^0	T_{eq}
Thiophene (5.3=5.4)	-8.8 ± 0.7 kJ/mol	-44 ± 3 J/(mol K)	202 ± 5 K
Bithiophene (5.5=5.6)	-6.2 ± 0.8 kJ/mol	-38 ± 4 J/(mol K)	173 ± 5 K

Appendix C.2 Experimentally determined thermodynamic parameters for the C-S cleavage process in Ni(dtpbe)thiophene (5.3 $\rightarrow$ 5.4) and Ni(dtpbe)bithiophene (5.5 $\rightarrow$ 5.6).

5.3 $\rightarrow$ 5.4				5.5 $\rightarrow$ 5.6			
T(K)	1/T(1/K)	Ln(K _{ins})	STDEV.S	T(K)	1/T(1/K)	Ln(K _{ins})	STDEV.S
242.86	0.0041176	-1.045344	0.141053	238.47	0.0041934	-1.420016	0.1474273
238.47	0.0041934	-0.796343	0.0227102	232.85	0.0042946	-1.333583	0.1702991
232.85	0.0042946	-0.552353	0.0672726	228.16	0.0043829	-1.189128	0.1809951
228.16	0.0043829	-0.531983	0.0502451	222.53	0.0044938	-1.208677	0.1672291
217.01	0.0046081	-0.46294	0.066883	217.01	0.0046081	-1.27286	0.1174897
206.96	0.0048319	-0.085911	0.0518812	212.29	0.0047105	-1.220385	0.1454121
201.74	0.0049569	0.0002931	0.0660025	206.96	0.0048319	-0.956522	0.0453005
195.59	0.0051127	0.135611	0.051926	195.59	0.0051127	-0.742808	0.0362195
191.7	0.0052165	0.2775597	0.0430438	191.7	0.0052165	-0.605227	0.0267185

Appendix C.3 VT NMR experiment temperature (T), reciprocal temperature (1/T), average of insertion process from π adduct to S-C insertion product equilibrium constant (K_{ins}) calculated using the ^{31}P { ^1H } peaks intensity.

C.3 X-ray diffraction of Complex 5.2.

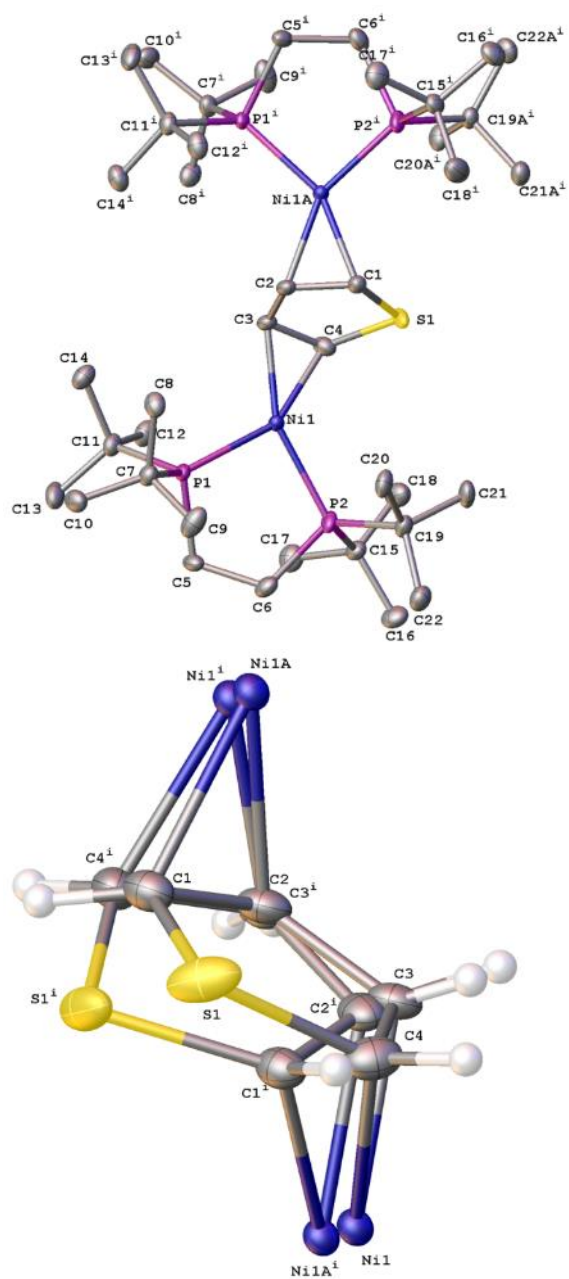
An orange irregular crystal of $\text{C}_{40}\text{H}_{84}\text{Ni}_2\text{P}_4\text{S}$ having approximate dimensions of 0.06 x 0.10 x 0.13 mm was mounted on a cryo-loop. All measurements were made on a Bruker APEX DUO diffractometer with a TRIUMPH curved-crystal monochromator with Mo-K α radiation. The data were collected at a temperature of $-183.0 \pm 0.1^\circ\text{C}$ to a maximum 2θ value of 52.8° . Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 20.0-second exposures. The crystal-to-detector distance was 40.14 mm. Of the 39334 reflections that were collected, 4651 were unique ($R_{int} = 0.062$); equivalent reflections were merged. Data were collected and

integrated using the Bruker SAINT² software package. The linear absorption coefficient, μ , for Mo-K radiation is 10.46 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS³), with minimum and maximum transmission coefficients of 0.807 and 0.939, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods⁴. The material crystallizes with one half-molecule in the asymmetric unit, residing on a two-fold rotation axis. The Ni-thiophene-Ni fragment is disordered and was modeled in two orientations with equal proportions. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement⁵ on F^2 was based on 4651 reflections and 284 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 (I > 2.00 (I)) = \|F_o\| - \|F_c\| / \|F_o\| = 0.033$$

$$wR2 (\text{all data}) = [\sum (w(F_o^2 - F_c^2))^2 / \sum w(F_o^2)^2]^{1/2} = 0.075$$

The standard deviation of an observation of unit weight⁶ was 1.05. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and -0.36 e-/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁷. Anomalous dispersion effects were included in F_{calc} ⁸; the values for f'' and f' were those of Creagh and McAuley⁹. The values for the mass attenuation coefficients are those of Creagh and Hubbell¹⁰. All refinements were performed using the SHELXL-2016¹¹ via the OLEX2¹² interface.



Complex 5.2 – CCDC #1587316

Appendix C.4 ORTEP representation of 2 and 5, depicting thermal ellipsoids at the 50% probability level. The relative orientations of the two Ni-

thiophene-Ni disordered fragments of complex 2 are presented on the top right.

X-ray diffraction of Complex 5.5

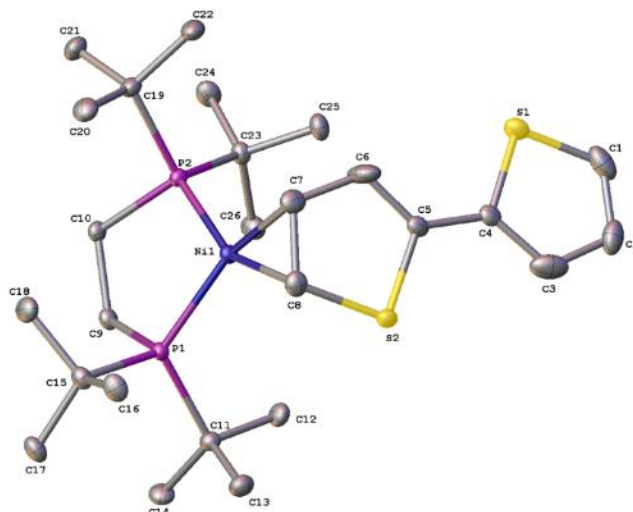
An orange irregular crystal of $C_{26}H_{46}NiP_2S_2$ having approximate dimensions of 0.05 x 0.11 x 0.24 mm was mounted on a cryo-loop. All measurements were made on a Bruker APEX DUO diffractometer with a TRIUMPH curved-crystal monochromator with Mo-K α radiation. The data were collected at a temperature of $-183.0 \pm 0.1^\circ\text{C}$ to a maximum 2θ value of 61.1° . Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 10.0-second exposures. The crystal-to-detector distance was 40.15 mm. Of the 36594 reflections that were collected, 8427 were unique ($R_{\text{int}} = 0.051$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT² software package. The linear absorption coefficient, μ , for Mo-K radiation is 9.81 cm^{-1} . Data were corrected for absorption effects using the multi-scan technique (SADABS³), with minimum and maximum transmission coefficients of 0.844 and 0.953, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods⁴. The material crystallizes with the bis-thiophene disorder in two orientations. The two orientations are related by a 180 degree rotation about an axis parallel to the C₄-C₅ bond. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement⁵ on F^2 was based on 8427 reflections and 318 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 (I > 2.00 (I)) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.036$$

$$wR2 (\text{all data}) = \left[\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2 \right]^{1/2} = 0.085$$

The standard deviation of an observation of unit weight⁶ was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.59 and $-0.58\text{ e}/\text{\AA}^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁷. Anomalous dispersion effects were included in F_{calc} ⁸; the values for f' and f'' were those of Creagh and McAuley⁹. The values for the mass attenuation coefficients are those of Creagh and Hubbell¹⁰. All

refinements were performed using the SHELXL-2016¹¹ via the OLEX2¹² interface.



Complex 5.5 – CCDC #1587317

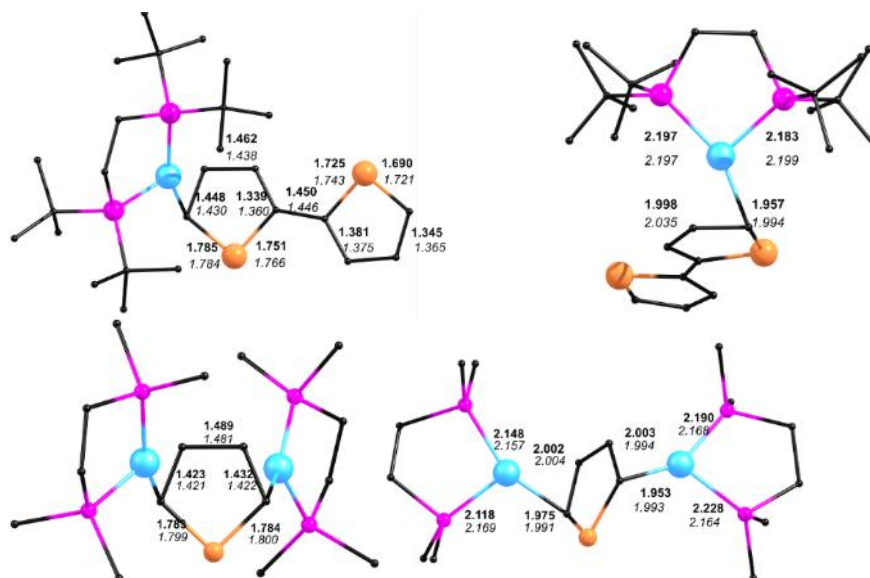
Appendix C.5 ORTEP representation of 2 and 5, depicting thermal ellipsoids at the 50% probability level. The relative orientations of the two Ni-thiophene-Ni disordered fragments of complex 2 are presented on the top right.

Compound Number	5.2 [Ni(dtpe)] ₂ thiophene	5.5 Ni(dtpe)bithiophene
Empirical Formula	C ₄₀ H ₈₄ Ni ₂ P ₄ S	C ₂₆ H ₄₆ NiP ₂ S ₂
Formula Weight	838.43	543.40
Crystal Colour, Habit	orange, irregular	orange, irregular
Crystal Dimensions	0.06 x 0.10 x 0.13 mm	0.05 x 0.11 x 0.24 mm
Crystal System	monoclinic	monoclinic
Space Group	C 2/c (#15)	P 2 ₁ /n (#14)
Lattice Type	C-centered	Primitive
a, Å	26.060(2)	9.2022(11)
b, Å	11.4151(9)	17.143(2)
c, Å	15.3575(11)	17.634(2)
α, °	90	90

β , °	98.329(2)	96.401(3)
γ , °	90	90
V, Å ³	4520.4(6)	2764.5(6)
Z value	4	4
D _{calc} , g/cm ³	1.23	1.31
F ₀₀₀	1824.00	1168.00
μ (Mo-K α), cm ⁻¹	10.46	9.81
Data Images (no., t/s)	1964, 20	1078, 10
2 θ max, °	52.80	61.10
Reflections measrd	39334	36594
Unique reflcn, R _{int}	4651, 0.062	8427, 0.051
Absorption, T _{min} , T _{max}	0.807, 0.939	0.844, 0.953
Observed data (I>2.00 σ (I))	3604	6700
No. parameters	284	318
R1, wR2 (F ² , all data)	0.054, 0.075	0.054, 0.085
R1, wR2 (F, I>2.00 σ (I))	0.033; 0.067	0.036, 0.079
Goodness of Fit	1.05	1.03
Max, Min peak, e-/Å ³	0.43, -036	1.59, -0.58

Appendix C.6. Crystallographic data for complex 5.2 and 5.5.

C.4 Computational Data

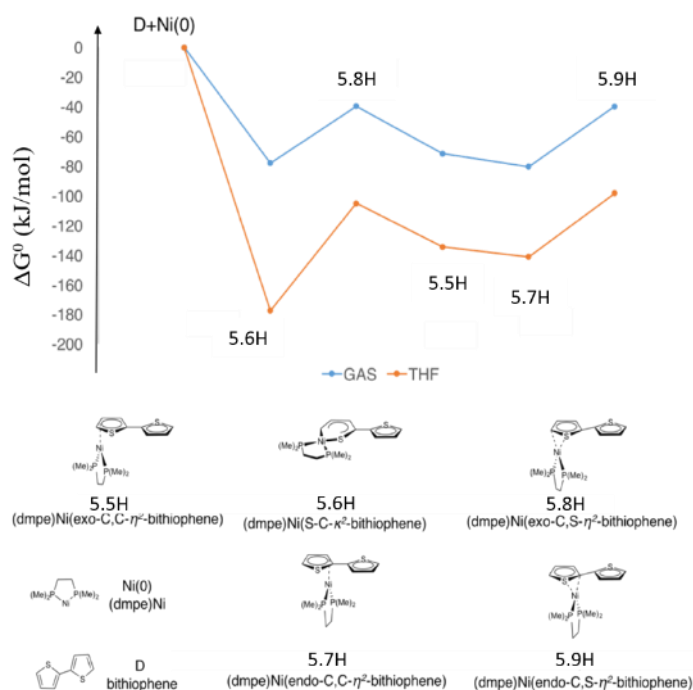


Appendix C.7 Experimental (bold) and calculated (italics) geometrical parameters for 5.5H-Ni(dtbpe)bithiophene and 5.2H-[Ni(dtbpe)]₂thiophene). Bond distances in Å, calculations were performed at the B3LYP¹⁴/Def2-TZVP¹⁵ level of theory using ORCA 3.03 package¹³. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional¹⁹

5.5H	P1-Ni1	P2-Ni1	Ni-C7	Ni-C8	C7-C8	S2-C8	S2-C5
XRD	2.197	2.183	1.998	1.957	1.447	1.785	1.751
Level A	2.176	2.172	2.037	1.971	1.429	1.791	1.77
Level B	2.197	2.199	2.035	1.994	1.43	1.784	1.766
σ_A	0.96%	0.50%	1.91%	0.74%	1.21%	0.33%	1.05%
σ_B	0.01%	0.75%	1.80%	1.86%	1.20%	0.03%	0.85%
δ_A	0.021	0.011	-0.039	-0.014	0.018	-0.006	-0.019
δ_B	0.000	-0.016	-0.037	-0.037	0.017	0.001	-0.015
5.5H	C5-C6	C6-C7	C1-C2	C2-C3	C3-C4	C1-S1	C4-S1
XRD	1.339	1.462	1.345	1.405	1.381	1.69	1.725
Level A	1.359	1.435	1.363	1.419	1.375	1.724	1.746
Level B	1.36	1.438	1.365	1.419	1.375	1.721	1.743
σ_A	1.53%	1.85%	1.28%	0.99%	0.41%	1.97%	1.17%
σ_B	1.57%	1.65%	1.45%	0.97%	0.44%	1.79%	1.04%
δ_A	-0.020	0.027	-0.018	-0.014	0.006	-0.034	-0.021
δ_B	-0.021	0.024	-0.020	-0.014	0.006	-0.031	-0.018

5.2H	P1-Ni1	P2-Ni1	Ni1-C3	Ni-C4	C3-C4	C1-C2
XRD	2.19	2.228	2.003	1.953	1.432	1.423
Level A	2.168	2.164	1.994	1.993	1.422	1.421
Level B	2.18	2.182	2.017	2.013	1.417	1.417
σ_A	1.03%	2.91%	0.46%	2.04%	0.63%	0.18%
σ_B	0.48%	2.09%	0.69%	3.04%	1.04%	0.42%
δ_A	0.022	0.064	0.009	-0.040	0.010	0.002
δ_B	0.010	0.046	-0.014	-0.060	0.015	0.006

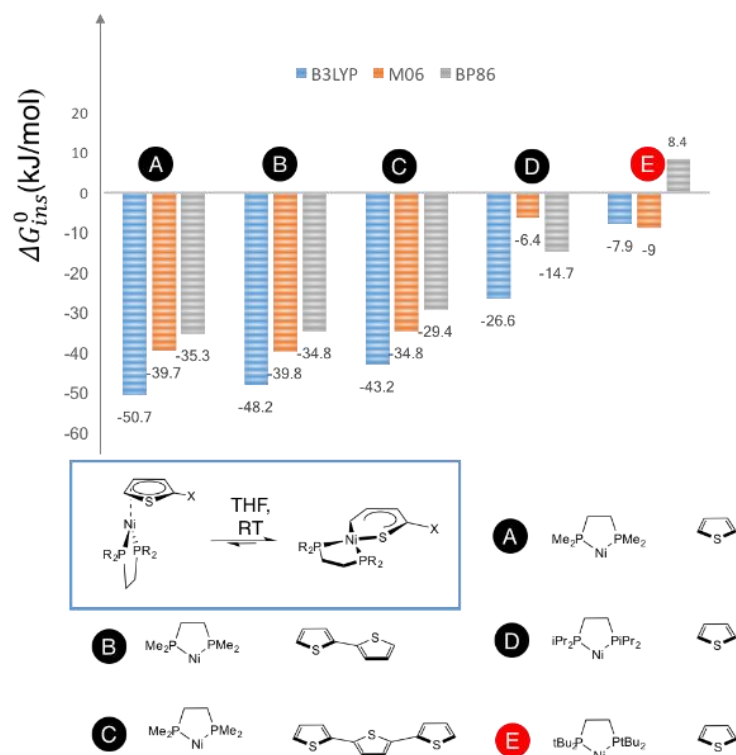
Appendix C.8 Comparison of selected bond distances for 5.5 and 5.2, and their corresponding simplified DFT-calculated distances for 5H and 2H. Bond distances are listed in Å, calculations of geometry optimizations were carried out in the gas phase using ORCA 3.03 program at B3LYP/ def₂¹⁸-TZVP level. Available experimental crystal structures were compared to results from two theoretical levels: A = B3LYP/def₂-TZVP ZORA²⁰ (Grid6) and B = B3LYP/def₂-TZVP(Grid4). σ_A and σ_B are % deviation from XRD. δ_A and δ_B are standard deviations relative to XRD. (Root mean square deviation (RMSD) value: $\delta A_{5.5H}$ 0.079, $\delta B_{5.5H}$ 0.080, δA_{2H} 0.080 $\delta B_{5.2H}$ 0.079).



Appendix C.9 Gibbs free energy profile of possible products. Optimizations were calculated at the B3LYP/def₂-TZVP level of theory. Gibbs free energies were derived in gas phased and THF solvent (298.15K) at the M06/def₂-TZVP ZORA and M06-SMD¹⁶/def₂-TZVP ZORA level, respectively. Gibbs Free Energy of isolated Ni(dmpe) fragment (Ni(0)) and bithiophene (D) arbitrarily set to 0 kJ/mol. Detail results are listed in Appendix C.10.

Code	M06 ¹⁷ , GAS (kJ/mol)		M06-SMD(THF) (kJ/mol)	
	ΔH^0_{ins}	ΔG^0_{ins}	ΔH^0_{ins}	ΔG^0_{ins}
D+Ni ₀	0.0	0.0	0.00	0.0
5.6H	-144.0	-78.2	-175.6	-177.7
5.8H	-101.9	-39.9	-107.3	-105.3
5.5H	-135.8	-71.9	-135.7	-134.7
5.7H	-142.7	-80.7	-143.5	-141.5
5.9H	-101.0	-40.0	-101.2	-98.6

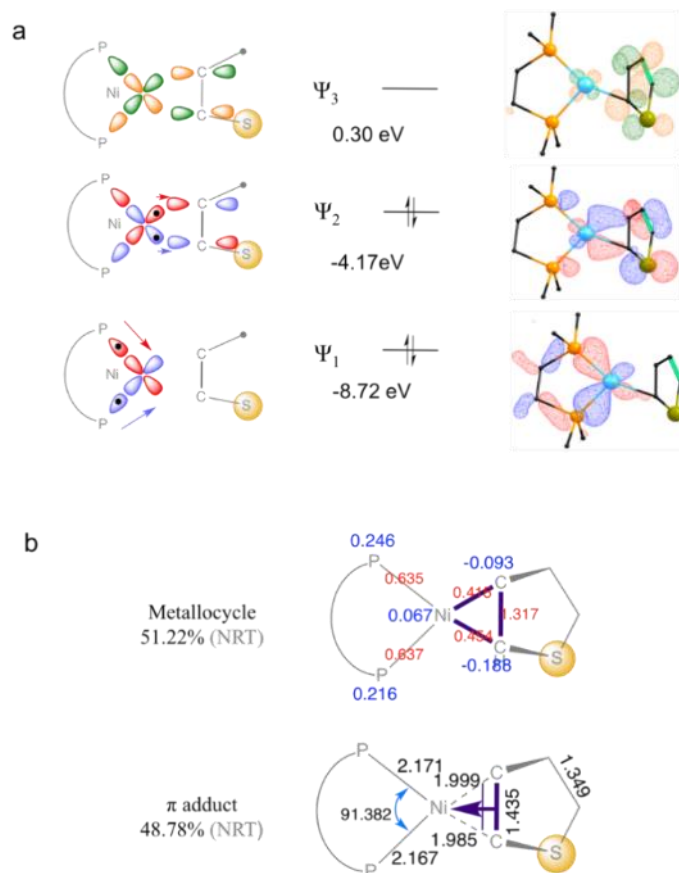
Appendix C.10 Entropy and Gibbs Free Energy results of DFT calculation of Ni(dmpe)bithiophene system. Gibbs free energy of isolated Ni(dmpe) fragment and bithiophene arbitrarily set to 0 kJ/mol. Related complex structures can be found in Appendix C.9. (SMD THF Solvnt parameters, dielectric constant ϵ 7.43, Refractive index 1.407, Surface Tension 26.59 mN/m, Abraham's hydrogen bond basicity parameter 0.48, Abraham's hydrogen bond basicity parameter 0.00).



Appendix C.11 Gibbs Energy difference between insertion product and π -adduct product ($\Delta\Delta G_{\pi-ins}$). Geometry optimization was calculated at the B3LYP/def2-TZVP level of theory. Gibbs free energies were derived in at the B3LYP/def2-TZVP ZORA, M06/def2-TZVP ZORA and M06-SMD/def2-TZVP ZORA level, respectively.

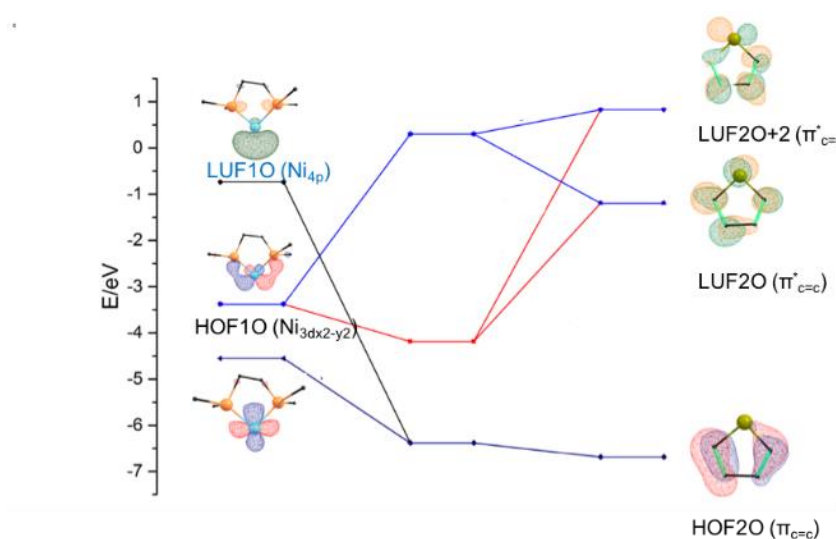
Code	ligand		B3LYP-SMD		M06-SMD		BP86-SMD	
			ΔH_i^0	ΔG_i^0	ΔH_i^0	ΔG_i^0	ΔH_i^0	ΔG_i^0
	R	X						
A	Me	H	ns	ns	ns	ns	ns	ns
B	Me	TH	-58.9	-50.7	-35.2	-39.7	-39.8	-35.3
C	Me	Bi	-53.4	-48.2	-37.9	-39.8	-36.7	-34.8
D	iPr	TH	-50.8	-43.2	-28.3	-34.8	-36.0	-29.4
E	tBu	H	-31.4	-26.6	-4.8	-6.4	-13.1	-14.7
			-19.5	-7.9	-14.6	-9.0	2.7	8.4

Appendix C.12 For structures of these ligands, see SI appendix. Zero-point energies, thermal corrections, and entropies are calculated at the B3LYP/B3LYP level. Energies are in kJ/mol. Gibbs free energies and Enthalpy in the energy profile are calculated at 298 K at the B3LYP//M06//BP86-SMD. Combination of thiophene(TH), bithiophene(TH-TH), terthiophene(TH-BiTH) and dmpe, dippe, dtbpe phosphine ligands are used to evaluate the steric effects.



Appendix C.13 DFT results for Ni(dmpe)thiophene. (a) the MO energy diagram involved in three center four electron charge transfer model of square planar Ni(phosphine)thiophene complexes. (b) NRT results and

Mulliken charge distribution (blue) and Bond order Index (red), calculated geometry bond distance and angle (black). NRT (natural resonance theory) calculation shows metallocycle resonance structure is slightly more populated than π adduct resonance structure.



Appendix C.14 Molecular Orbital Decomposition analysis of important frontier orbitals in Ni(dmpe)thiophene complex 5.3H system.

Code	Bonding	MO		Ni(dmpe)			thiophenic ligand		
		Orb.	E(eV)	Orb.	E(eV)	Cont.	Orb.	E(eV)	Cont.
5.3H	π	HOMO	-4.19	HOF1O	-3.38	51.1%	LUF2O	-1.2	22.2%
							LUF2O+ ₂	0.83	2.4%
	π^*	LUMO+ ₁	0.3	HOF1O	-3.38	14.9%	LUF2O	-1.2	54.3%
							LUF2O+ ₂	0.83	4.7%
	n	HOMO- ₅	-6.38	LUF1O	-0.74	3.1%	HOF2O	-6.69	58.8%
5.5H	π	HOMO	4.19	HOF1O	-3.41	50.3%	LUF2O	-1.84	14.2%
							LUF2O+ ₁	-0.43	7.0%
	π^*	LUMO	-0.94	HOF1O	-3.41	6.9%	LUF2O	-1.84	76.7%
							LUF2O+ ₁	-0.43	13.4%
	π^*	LUMO+ ₃	0.55	HOF1O	-3.41	11.7%	LUF2O	-1.84	3.3%
							LUF2O+ ₁	-0.43	58.1%
	n	N/A	N/A	LUF1O	-0.76	<1.00%	HOF2O	-5.85	<1.00%
5.2H	π	HOMO- ₁	-3.99	HOF1O	-3.42	31.4%	LUF2O	-0.5	7.6%
							LUF2O+ ₁	-0.19	5.2%
	π	HOMO	-3.72	HOF1O	-3.42	15.9%	LUF2O	-0.5	4.3%
							LUF2O+ ₁	-0.19	2.6%
	π^*	LUMO+ ₅	0.89	HOF1O	-3.42	12.7%	LUF2O	-0.5	17.4%
							LUF2O+ ₁	-0.19	34.0%
	n	N/A	N/A	LUF1O	-0.75	<1.00%	HOF2O	-4.28	<1.00%

Ni(dmpe)→thiophenic ligand Charge transfer (CDA)			
Code	π_{CT}	Total CT	% π_{CT}
5.3H	0.14	0.15	93.9
5.5H	0.12	0.15	75.1
5.2H	0.08	0.13	92.3

Appendix C.15 Molecular Orbital Decomposition Analysis (top) and Charge Decomposition Analysis (CDA) (bottom) results of important frontier fragment orbitals (FO) in Ni(dmpe)thiophene complex systems. Note: π_{CT} is electron donation from Ni(dmpe) to the π ligand that occurs specifically through π backbonding involving the Ni $3d_{x^2-y^2}$ orbital. Total CT includes contributions from all MO interactions. The MO analysis indicates that there is strong π backbonding but very little (if any) σ donation from thiophene π_b electrons to the nickel centre. This is supported by the observation that the 3c-4e π interaction described in the manuscript contributes a very large fraction of the total charge redistribution between the Ni(dmpe) and thiophene fragments (see % π_{CT}).

Ni(dmpe)BT 5.3H	Atom	Mulliken Charge	NPA Charge
1	Ni	0.056	-0.309
2	P	0.211	1.037
3	P	0.238	1.040
4	C	-0.363	-0.914
5	H	0.111	0.229
6	H	0.129	0.239
7	H	0.095	0.214
8	C	-0.357	-0.918
9	H	0.114	0.234
10	H	0.096	0.215
11	H	0.105	0.228
12	C	-0.357	-0.916
13	H	0.107	0.229
14	H	0.110	0.231
15	H	0.095	0.214
16	C	-0.359	-0.913
17	H	0.111	0.230
18	H	0.096	0.213
19	H	0.111	0.229
20	C	-0.218	-0.694
21	C	-0.218	-0.693
22	H	0.090	0.216
23	H	0.098	0.218
24	H	0.098	0.218
25	H	0.092	0.217
dmpe fragment		0.237	0.605

26	S	-0.102	0.335
27	C	-0.084	-0.477
28	C	-0.171	-0.349
29	C	-0.205	-0.199
30	C	0.067	-0.234
31	C	0.004	-0.216
32	S	0.004	0.421
33	C	-0.162	-0.424
34	C	-0.150	-0.246
35	C	-0.179	-0.256
36	H	0.112	0.229
37	H	0.109	0.235
38	H	0.103	0.214
39	H	0.120	0.229
40	H	0.122	0.218
41	H	0.120	0.223
bithiophene fragment		-0.293	-0.295
Ni(dmpe)TH 5.5H	Atom	Mulliken Charge	NPA Charge
2	Ni	0.067	-0.296
1	P	0.246	1.042
3	P	0.216	1.052
4	C	-0.356	-0.918
5	C	-0.360	-0.916
6	C	-0.220	-0.691
7	C	-0.218	-0.696
8	C	-0.365	-0.915
9	C	-0.347	-0.918
10	H	0.099	0.218
11	H	0.089	0.215
12	H	0.096	0.216
13	H	0.093	0.218
14	H	0.108	0.231
15	H	0.097	0.214
16	H	0.113	0.232
17	H	0.109	0.227
18	H	0.096	0.214
19	H	0.112	0.231
20	H	0.097	0.214
21	H	0.103	0.226
22	H	0.114	0.232
23	H	0.094	0.212
24	H	0.118	0.240
25	H	0.111	0.231
dmpe fragment		0.244	0.611
26	S	-0.079	0.309

27	C	-0.108	-0.412
28	C	-0.251	-0.232
29	H	0.103	0.221
30	H	0.097	0.211
31	H	0.102	0.228
32	H	0.105	0.231
33	C	-0.093	-0.374
34	C	-0.188	-0.498
thiophene Fragment		-0.312	-0.316

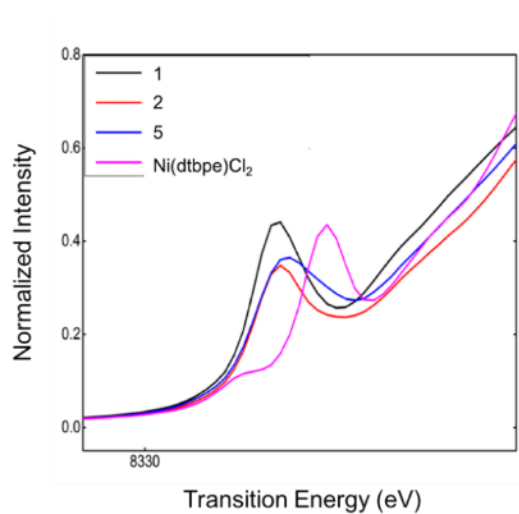
Appendix C.16 NBO charge distribution calculation results in Mulliken charge and Natural Population Analysis (NPA) charge. NBO²¹ calculations were calculated with Gaussian 09 program package²²

Code	Transitions	Trans. E (eV)	intensity	acceptor orbital	contr.	ΔE_{4p-3d} (eV)
5.5H	1s-3d	8623.95	7.38E-05	98	45.6%	0.92
				99	19.4%	
				101	18.7%	
	1s-4p	8624.87	3.15E-04	99	76.5%	
				98	15.3%	
5.3H	1s-3d	8624.73	3.45E-04	77	91.2%	0.35
	1s-4p	8624.38	4.70E-05	78	45.6%	
				79	22.1%	
				1s-3d	8624.53	
	133	13.0%				
137	11.5%					
5.2H	1s-4p	8624.58	1.44E-04	132	35.4%	-0.05
				137	26.3%	
				138	14.4%	

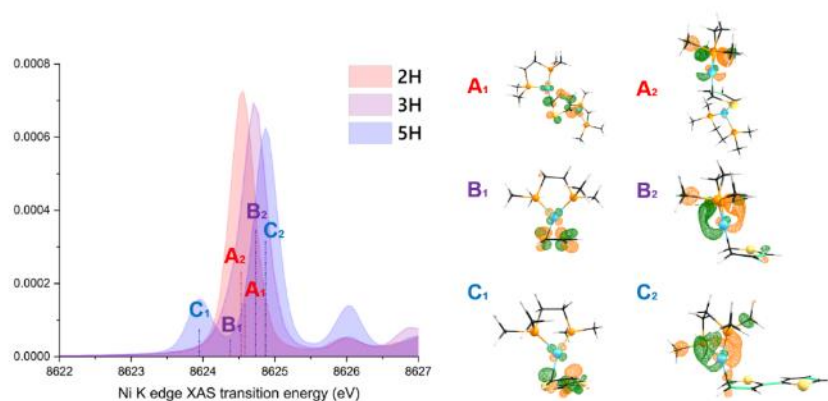
Code		Nickel				Phosphine (P atoms)				Thiophene (C atoms)		
		Ni				P				C		
		Total (%)	s	p	d	Total (%)	s	p	d	Total (%)	s	p
5.5H	98	6.5	0.4	0.8	5.3	2.2	0.4	1.2	0.6	3.7	0.2	3.5
	99	36.8	0.1	31.5	5.2	25.3	0.4	9.3	15.6	4.4	0.2	4.2
	101	12.5	0	4	8.5	3.9	0.2	1.5	2.2	15.5	1.1	14.4
	99	36.8	0.1	31.5	5.2	25.3	0.4	9.3	15.6	4.4	0.2	4.2
	98	6.5	0.4	0.8	5.3	2.2	0.4	1.2	0.6	3.7	0.2	3.5
5.3H	77	39.8	0.3	35.5	4	25.1	0.1	9.2	15.8	1.5	0.1	1.4

	78	10.8	1.2	0.7	8.9	3.7	1	1.4	1.3	10.1	0.6	9.5
	79	9.7	3.5	1.1	5.1	4.4	0.9	1.6	1.9	7.2	0.6	6.6
5.2H	132	36.7	0	32.1	4.6	24.3	0	9.3	15	1	0	1
	133	3.9	0.1	2.6	1.2	2.8	0.1	1.2	1.5	0.7	0.2	0.5
	137	10.3	0	2.6	7.7	2.6	0.6	0.9	1.1	12.1	1.4	10.7
	132	36.7	0	32.1	4.6	24.3	0	9.3	15	1	0	1
	137	10.3	0	2.6	7.7	2.6	0.6	0.9	1.1	12.1	1.4	10.7
	138	9.9	0.3	4.1	5.5	10	1.2	4.2	4.6	5.7	0.3	5.4

Appendix C.17 Ni K-edge TD-DFT results at B3LYP/dev2-TZVP level. Important pre-edge transitions with details of transition energy, intensity, acceptor molecular orbital and the orbital contributions (top). MO contributions for important valence orbitals are also listed (bottom).

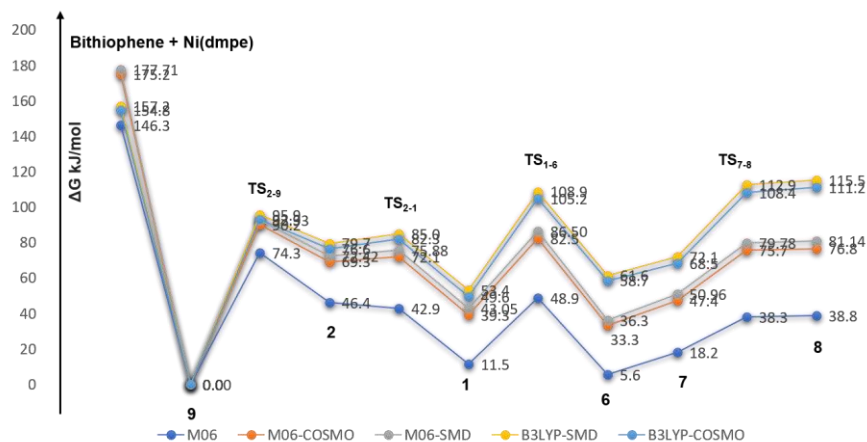


code		1	2	5	Ni(dtbpe)Cl ₂
1s→4p	transition Energy (eV)	8334.18	8334.32	8335.37	8335.84

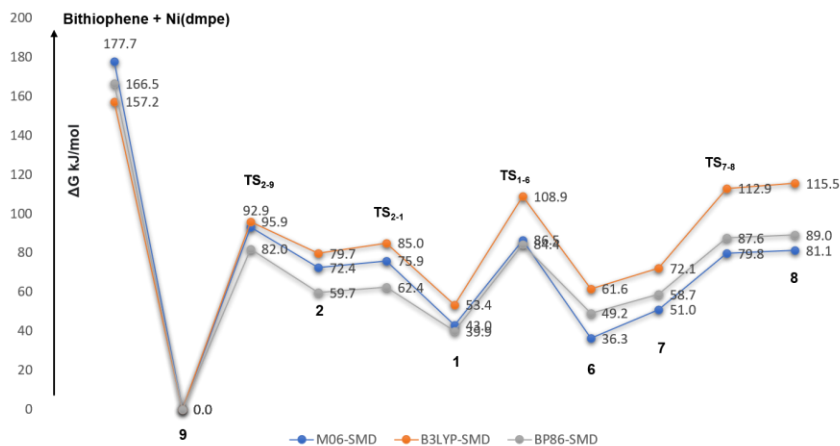


Appendix C.18 Ni K-edge XAS data. (top) experimental spectrum with 1s – 4p transition energy results obtained by fitting. (bottom) TD-DFT Ni K-edge pre-edge calculated spectra. π backbonding orbitals with Ni 3d character allows 1s-3d Ni K edge transition are presented as A₁, B₁, C₁, Ni 4p orbital allows 1s-4p Ni K edge transition are visualized as A₂, B₂, C₂. Calculation details can be found in Table S10.

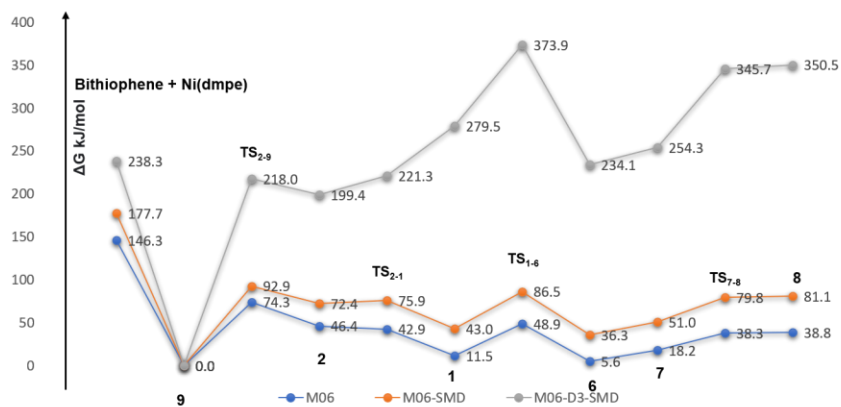
The 1s-3d pre-edge feature reflects the degree of electron depletion in the 3d_{x²-y²} orbital through π backbonding. In theory, the intensity of the feature therefore reflects the degree of metal backbonding although even small mixing of 4p character has a very large influence on the final intensity of this feature. The intense pre-edge 1s-4p_z transition feature correspond to a localized atomic transition where the energy of this transition directly reflects electron density at the metal centre.



Appendix C.19 Energy profiles were calculated at the M06//M06-COSMO(THF)//M06-SMD(THF)//B3LYP-SMD(THF)//B3LYP-COSMO(THF)/Def2-TZVPlevel of theory. Energy of D-S1 arbitrarily set to 0 kJ/mol. The trend of each energy profile under selected theory level of gas phase and THF solvent condition are consistent.

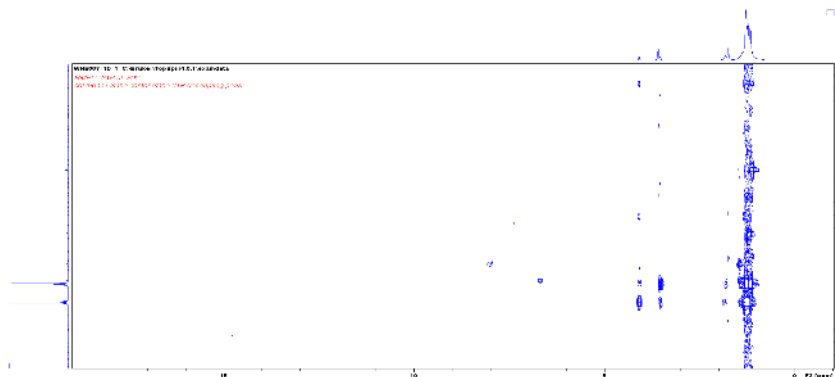


Appendix C.20 Energy profiles were calculated at the M06-SMD(THF)//B3LYP-SMD(THF)//BP86-SMD(THF)/Def2-TZVPlevel of theory. Energy of D-S1 arbitrarily set to 0 kJ/mol. The trend of each energy profile under selected theory level of functional are consistent.



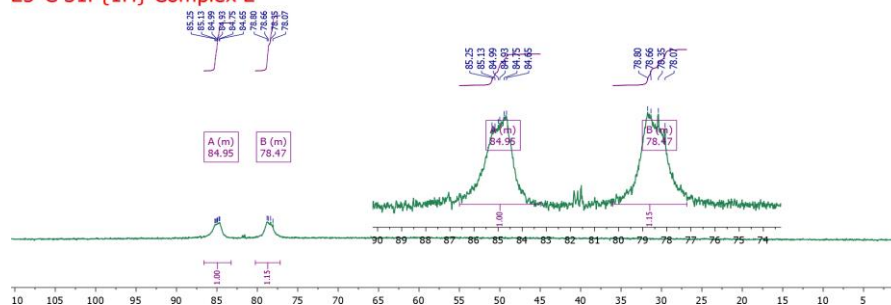
Appendix C.21 Energy profiles were calculated at the M06/M06(THF)/M06-D3-SMD(THF)/Def2-TZVP level of theory. Energy of D-S1 arbitrarily set to 0 kJ/mol. Theory Level with dispersion item largely exaggerate the electronic repulsion between Ni(dmpe) fragment and thiophene ligand.

C.5 NMR spectrum



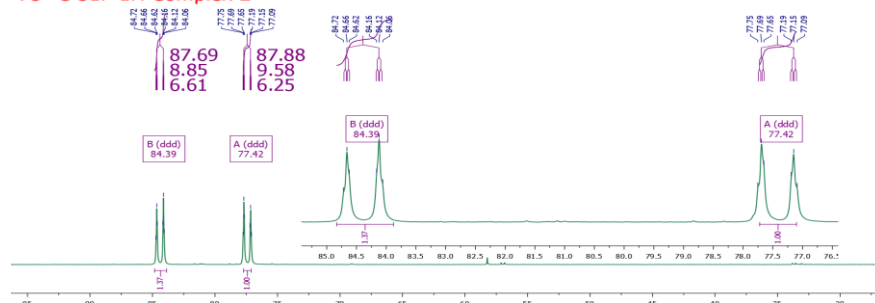
Appendix C.22 2D HSQC NMR of Complex 5.2. Strong coupling between P and H_(TH) were found.

25°C $^{31}\text{P}\{^1\text{H}\}$ Complex 2

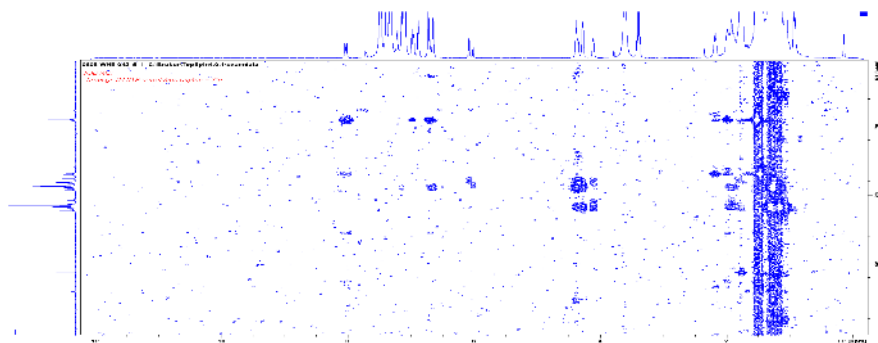


Appendix C.23 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 298K THF- d_8) of 5.2. Inset shows long distance $^5\text{J}_{\text{P,P}}$ coupling.

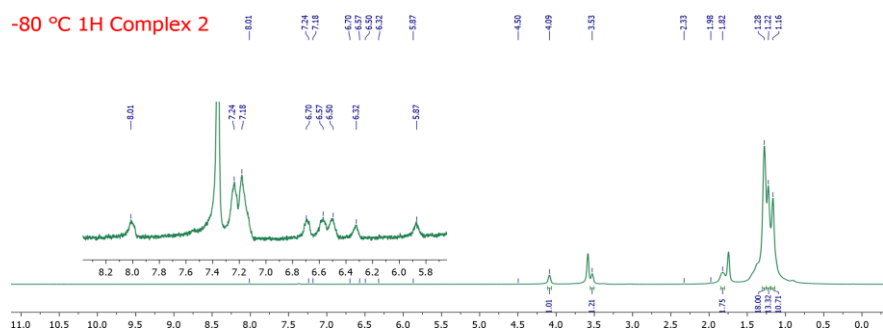
-75 °C ^{31}P 1H Complex 2



Appendix C.24 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 298K & 208K, THF- d_8) of 5.2. Inset shows long distance $^5\text{J}_{\text{P,P}}$ coupling.



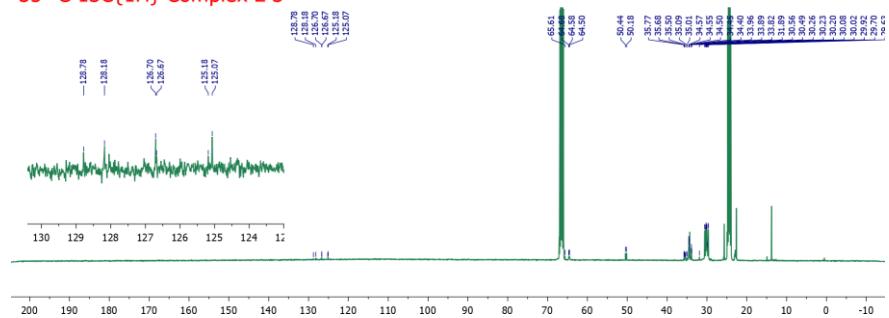
Appendix C.25 2D HSQC NMR of Complex 5.3 & 5.4. Strong coupling between P and H_(TH) were found in both π adduct species and insertion side product, which allows for assignment of the proton signals.



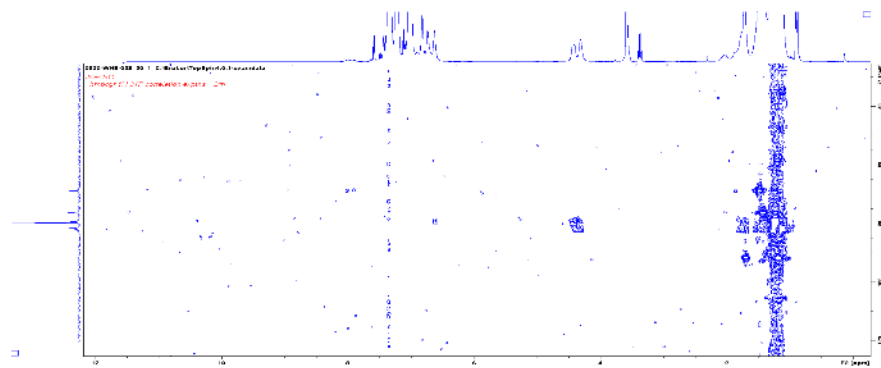
Appendix C.26 ¹H NMR (400 MHz, 298K & 208K, THF-d₈) of 5.2.

Appendix C.29 ^1H NMR (400 MHz, 218K, THF- d_8) of 5.3 & 5.4.

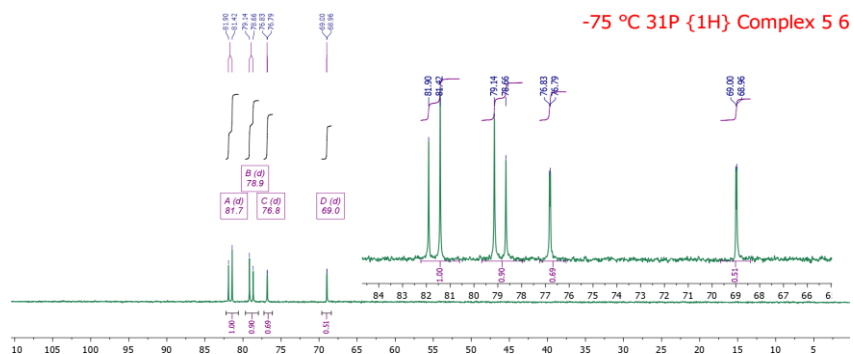
-35 °C $^{13}\text{C}\{^1\text{H}\}$ Complex 2 3



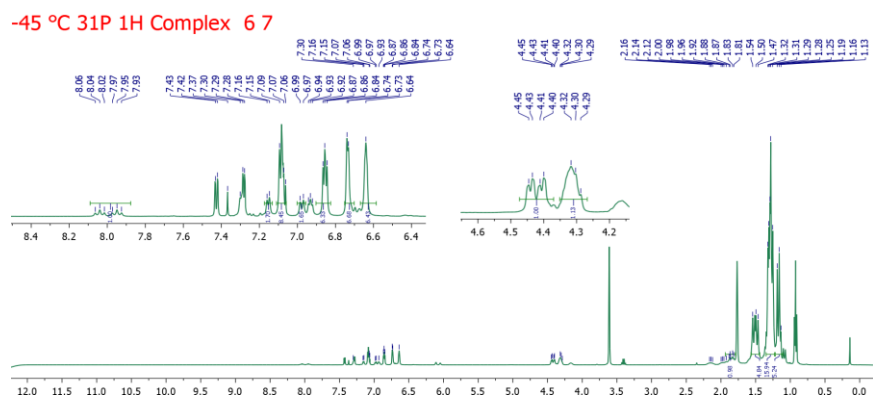
Appendix C.30 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (162 MHz, 238K, THF- d_8) of 5.3 & 5.4.



Appendix C.31 2D NMR of Complex 5.5 & 5.6. Strong coupling between P and $\text{H}_{(\text{TH})}$ were found.



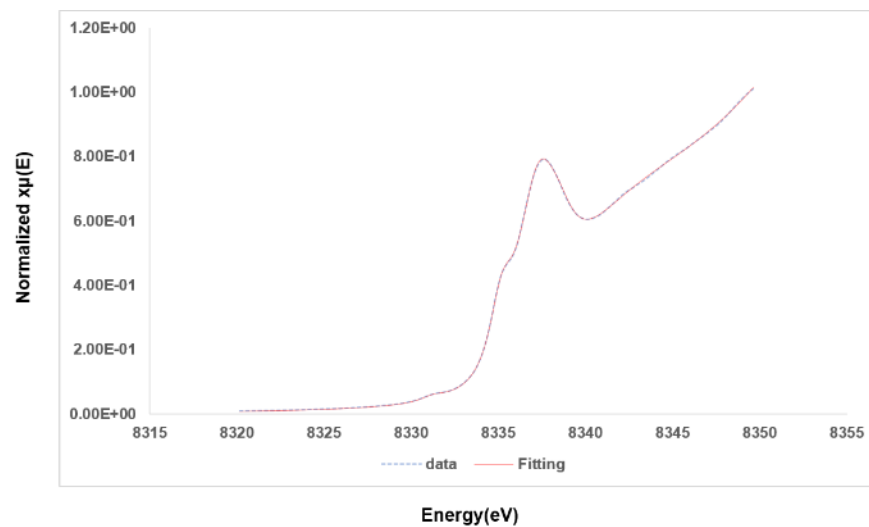
Appendix C.32 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, 198K, THF- d_8) of 5.5 & 5.6. Inset shows distance $^5J_{\text{P,P}}$ coupling.



Appendix C.33 ^1H NMR (400 MHz, 218K, THF- d_8) of 5.5 & 5.6.

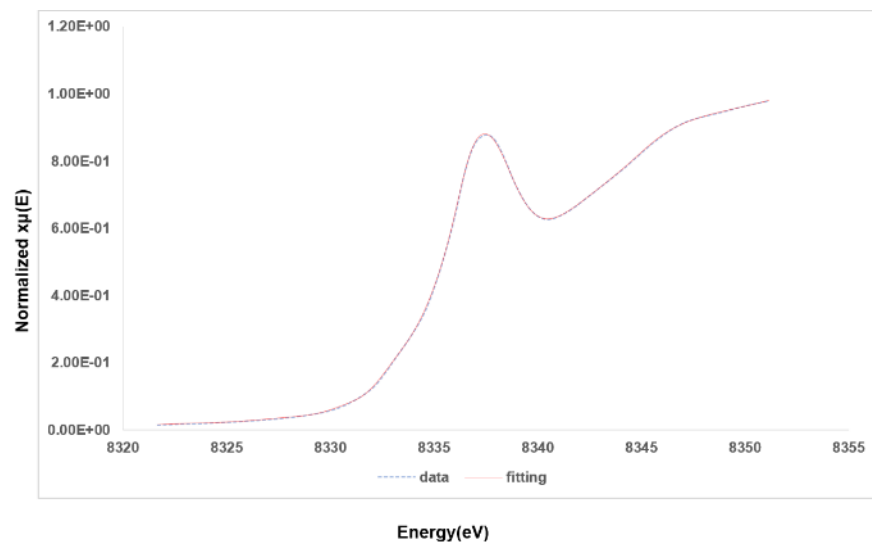
Appendix D Experimental Data for Chapter 6

D.1 Ni K edge XAS Simulation



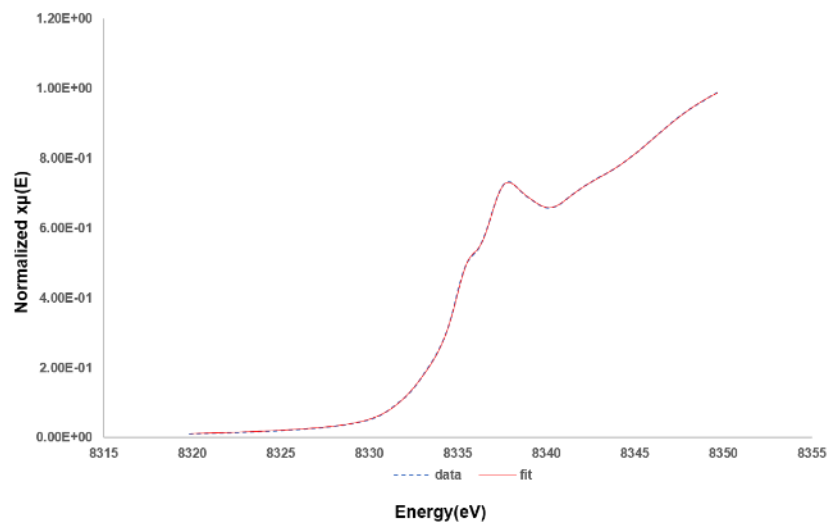
6.1a	Fitting R-factor	0.0000922	# lineshapes	6
	χ^2	0.00263	# measurements	18.563
	Reduced χ^2	0.0000299	Data points	100
Lorentzian	height	center	σ	area
1	0.035(0.035)	8331.26(5.40)	1.648(0.910)	0.035
2	0.610(0.069)	8335.20(0.12)	1.768(0.086)	0.61
3	3.146(0.416)	8337.28(0.08)	3.259(0.145)	3.146
4	0.319(0.057)	8338.53(0.30)	2.209(0.219)	0.32

Appendix D.1 Peak fitting for Ni K-edge XANES edge spectra for 6.1a.



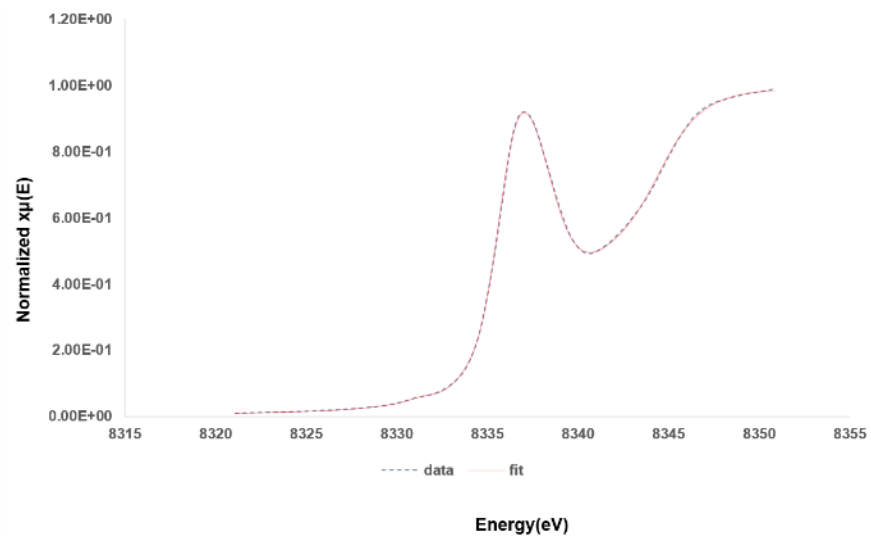
1b	Fitting R-factor	0.000005	# lineshapes	11
	χ^2	0.00018	# measurements	18.563
	Reduced χ^2	0.0000025	Data points	100
Lorentzian	height	center	σ	area
1	6.860(5.985)	8330.99(1.73)	5.380(0.773)	6.86
2	12.925(32.027)	8335.37(0.92)	5.376(2.127)	12.925
3	1.028(0.862)	8336.68(0.61)	2.606(0.539)	1.028
4	10.640(9.239)	8337.59(0.26)	4.928(0.691)	10.64

Appendix D.2 Peak fitting for Ni K-edge XANES edge spectra for 6.1b.



2a	Fitting R-factor	0.0000922	# lineshapes	6
	χ^2	0.00263	# measurements	18.563
	Reduced χ^2	0.0000299	Data points	100
Lorentzian	height	center	σ	area
1	-2.500(11.695)	8331.57(6.61)	5.242(4.461)	-2.5
2	1.083(0.314)	8335.52(0.11)	2.339(0.150)	1.083
3	-139.599(495.263)	8338.21(0.35)	7.300(3.620)	-139.599
4	154.706(668.701)	8337.61(1.12)	9.049(3.792)	154.71

Appendix D.3 Peak fitting for Ni K-edge XANES edge spectra for 6.2a.



6.2b	Fitting R-factor	0.0000922	# lineshapes	6
	χ^2	0.00263	# measurements	18.563
	Reduced χ^2	0.0000299	Data points	100
Lorentzian	height	center	σ	area
1	-29.524(635.037)	8330.99(10.32)	6.108(5.298)	-29.524
2	4.621(40.366)	8337.90(0.89)	4.398(5.864)	4.621
3	-125.886(724.789)	8335.20(0.84)	7.916(53.887)	-125.886
4	23.861(234.826)	8336.41(0.43)	4.960(3.850)	23.86

Appendix D.4 Peak fitting for Ni K-edge XANES edge spectra for 6.2b.

D.2 TD-DFT Calculations of Ni K edge XAS

complex 6.1a										
	Energy	Intensity	M01	Contribution	M01	Contribution	M02	Contribution	M02	Contribution
A	8330.35	6.36E-06	159b	52.42%	163b	18.42%	162b	13.03%		
B	8334.99	8.25E-05	164b	56.81%	161b	26.71%	160b	11.84%		
	8335.14	9.27E-05	164a	50.83%	162a	27.44%	160a	17.16%		
	8336.73	2.89E-05	166a	45.16%	176a	5.92%				
	8337.31	5.41E-05	166a	38.91%	176a	12.91%	170a	11.19%	167a	10.30%
	8337.42	2.87E-05	167b	71.43%	174b	12.68%				
	8337.45	2.28E-05	167a	65.64%						
C	8337.47	1.07E-05	166b	28.01%	172b	21.01%	176b	2.66%		
	8337.55	5.31E-05	168a	64.13%	174a	5.06%	176a	5.42%		
	8337.59	6.70E-05	168b	69.74%	174b	4.21%	176b	6.98%		
	8337.71	8.84E-05	174a	32.49%	169a	25.79%	167a	19.02%		
	8337.71	5.73E-05	174b	30.04%	169b	24.76%	167b	16.25%		
	8337.80	2.20E-05	169a	56.88%	174a	16.36%				
	8337.92	3.36E-05	170a	28.60%	172a	23.66%	168a	16.56%	174a	4.66%
D	8337.98	4.26E-05	170a	43.99%	176a	16.80%	168a	11.10%		
	8338.11	1.06E-05	171b	64.63%	174b	1.38%	176b	11.69%		
	8338.18	1.65E-05	173b	76.62%	176b	5.43%				

Appendix D.5 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 6.1a.

complex 6.1b										
	Energy	Intensity	M01	Contribution	M01	Contribution	M02	Contribution	M02	Contribution
A	8330.06	3.33E-06	155b	81.76%						
	8335.05	8.66E-05	160b	54.29%	156b	18.21%				
B	8335.21	9.90E-05	160a	47.84%	156a	23.54%	157a	17.06%	158a	9.54%
	8336.99	3.20E-04	164a	33.30%	170a	24.10%	167a	13.73%		
	8337.23	2.53E-04	164b	31.48%	170b	31.02%	167b	9.77%		
C	8337.56	2.24E-05	163a	74.33%	172a	9.38%				
	8337.92	8.42E-05	172a	35.24%	163a	16.43%	169a	14.46%		
	8337.93	2.61E-05	164a	50.24%	167a	16.16%	166a	10.30%		
	8337.93	3.25E-05	164b	51.67%	170b	14.79%	166b	11.77%	167b	10.28%
	8337.94	9.87E-05	172b	37.14%	169b	19.55%	163b	10.47%		
D	8338.10	1.26E-05	166b	54.57%	167b	11.22%	172b	8.87%		
	8338.20	1.17E-05	167a	41.74%	170a	26.82%	168a	16.02%		
	8338.20	1.38E-05	167b	58.49%	170b	17.83%				

Appendix D.6 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 6.1b.

complex 2a									
A	8150.24	5.47E-06	170b	55.60%	174b	11.80%			
B	8154.90	7.31E-05	175b	45.81%	172b	30.88%	171b	10.06%	170b 9.56%
	8155.02	8.25E-05	175a	41.45%	171a	40.12%	172a	11.44%	
	8155.96	1.40E-05	177a	49.45%	185a	8.09%	183a	6.42%	
	8156.73	3.42E-05	177a	49.45%	185a	8.09%			
C	8157.19	1.21E-04	177a	35.75%	179a	10.79%	185a	9.45%	
	8157.31	5.28E-05	178b	33.65%	179b	23.53%	180b	10.92%	177b 8.79%
	8157.33	1.07E-05	178a	78.59%	179a	7.60%			
	8157.36	9.41E-05	178b	52.50%	179b	7.72%	186b	7.64%	
	8157.43	3.32E-05	179a	42.65%	184a	12.61%	177a	8.57%	
	8157.62	1.83E-05	180a	63.30%	181a	8.87%	179a	8.72%	
	8157.64	2.50E-05	180b	50.40%	181b	13.04%	179b	7.38%	
	8157.73	6.26E-05	179a	24.19%	184a	19.13%	181a	9.69%	
	8157.82	2.30E-05	181b	26.81%	180b	18.15%	187b	15.78%	
	8157.83	5.06E-05	181a	30.87%	180a	14.68%	187a	11.78%	
D	8157.85	3.70E-05	185a	34.98%	181a	26.58%	184a	10.04%	187a 9.09%
	8157.86	4.72E-05	185b	24.93%	184b	23.07%	181b	21.85%	

Appendix D.7 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 6.2a.

complex 2b										
A	8330.00	2.00E-06	166b	82.35%						
B	8334.99	7.93E-05	171b	47.30%	167b	42.24%				
	8335.12	9.21E-05	167a	44.79%	171a	42.79%				
	8336.02	2.95E-05	169a	49.94%	170a	25.29%	171a	15.75%		
	8336.66	1.26E-04	174a	20.88%	172a	19.95%	173a	14.43%	179a	9.68%
	8336.88	1.59E-04	174a	26.08%	173a	16.21%	178a	10.53%		
C	8336.97	2.00E-04	175b	23.16%	176b	11.19%	178b	10.68%	174b	10.13%
	8337.11	4.58E-05	173b	48.67%						
	8337.54	2.17E-05	174b	69.27%						
	8337.55	2.40E-05	175a	51.48%	174a	21.66%				
	8337.75	1.35E-05	175b	42.62%	176b	40.52%				
D	8337.90	7.67E-05	182a	32.00%	176a	18.10%	177a	11.26%		
	8337.94	1.52E-05	177a	56.19%	174a	15.38%				
	8337.94	7.93E-05	181b	24.80%	177b	22.75%	180b	11.20%	174b	10.43%
	8338.04	1.07E-05	178b	38.30%	177b	31.60%	180b	9.70%	176b	9.26%

Appendix D.8 Calculated Ni K-edge TD-DFT results for pre-edge region of complex 6.2b.

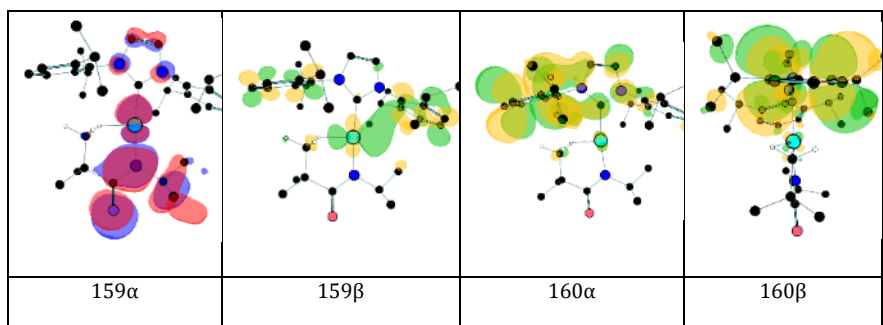
D.3 Density Functional Calculations

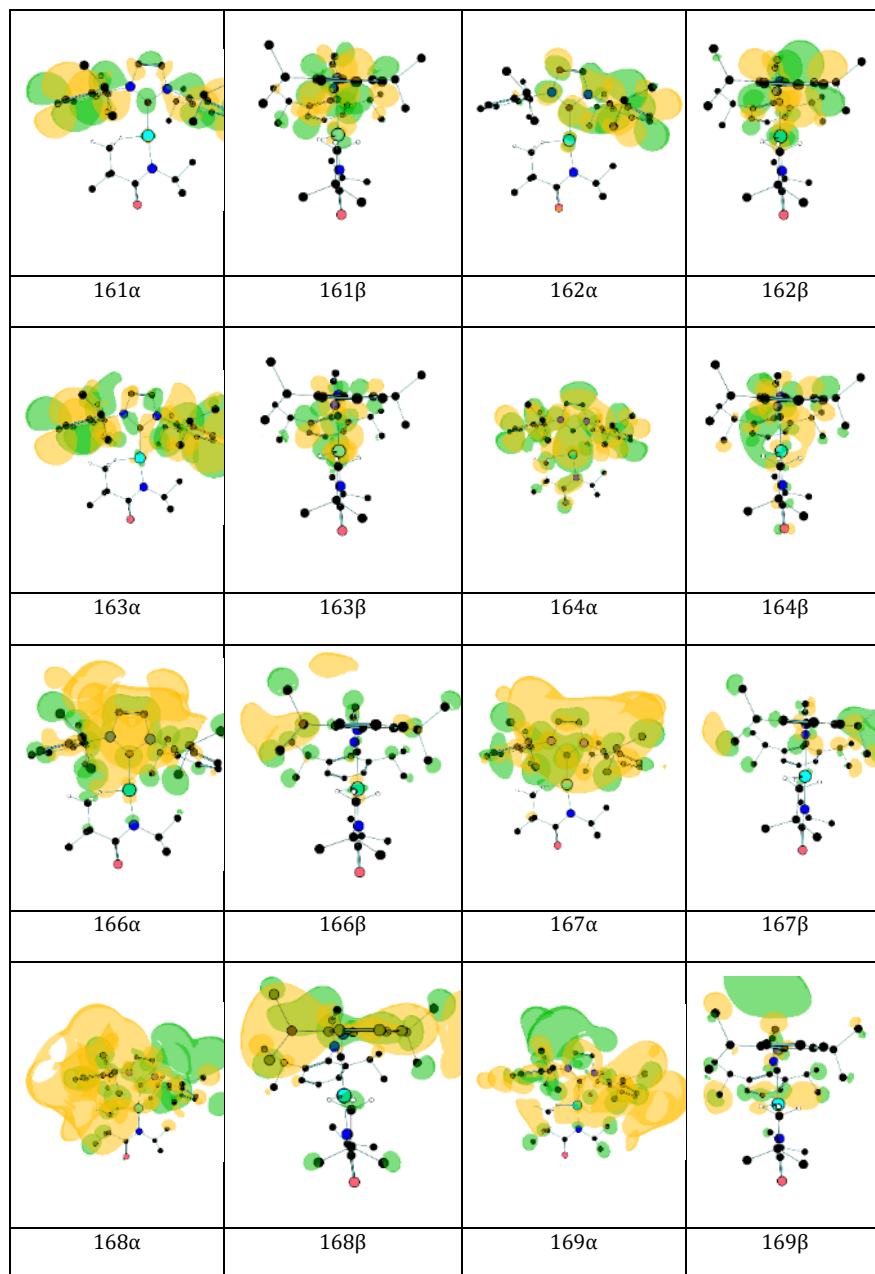
complex 1a		Nickel Center					amidate ligand					
Orbital	Energy	Total	Ni			Total	O		N		C	
			s (%)	p (%)	d (%)		s (%)	p (%)	s (%)	p (%)	s (%)	p (%)
159,a	-0.17683	23.4	0	2	21.4	52.8	0	20.1	0	31.4	0	1.3
160,a	-0.03246	1.4	0	0.9	0.5	0	0	0	0	0	0	0
161,a	-0.03136	0.2	0	0.1	0.1	0	0	0	0	0	0	0
162,a	-0.02943	2.9	0	2	0.9	0.3	0	0.1	0	0.1	0	0.1
163,a	-0.02523	0.2	0	0.2	0	0	0	0	0	0	0	0
164,a	-0.01489	11.3	0.1	7.9	3.3	1.1	0	0.4	0	0.3	0	0.4
166,a	0.01188	1.7	0.7	0.3	0.7	0	0	0	0	0	0	0
167,a	0.02623	1.6	0	1.3	0.3	0	0	0	0	0	0	0
168,a	0.03052	2.1	0.1	2	0	0	0	0	0	0	0	0
169,a	0.03302	1.5	0.3	1.1	0.1	0.2	0	0	0.1	0.1	0	0
170,a	0.03986	1.8	0.4	1.2	0.2	0.3	0	0	0.1	0.2	0	0
171,a	0.04408	3.1	1.1	1.3	0.7	0.4	0	0	0.2	0.2	0	0
172,a	0.04536	5.9	1.8	3.1	1	0.6	0	0	0.4	0.2	0	0
173,a	0.04731	0.1	0	0.1	0	0	0	0	0	0	0	0
174,a	0.05495	19.4	0.2	18.8	0.4	4.8	0	0.9	0	0.6	0	3.3
176,a	0.06061	12.1	0.5	10.5	1.1	2.5	0	0.6	0.3	0.9	0	0.7
159,b	-0.03801	44.3	6.8	2.4	35.1	0.8	0	0	0.1	0.7	0	0
160,b	-0.03232	1	0	0.5	0.5	0	0	0	0	0	0	0
161,b	-0.02918	4.8	0.3	1.8	2.7	0.3	0	0.1	0	0.1	0	0.1
162,b	-0.0283	12.2	1.7	0.9	9.6	0.2	0	0	0	0.2	0	0
163,b	-0.02282	17.1	2.4	0.4	14.3	0.2	0	0	0	0.2	0	0
164,b	-0.01376	13.4	0.1	7.8	5.5	1.5	0	0.5	0	0.4	0	0.6
166,b	0.01331	2.8	0.3	0.3	2.2	0.1	0	0	0	0.1	0	0
167,b	0.02631	1.5	0	1.2	0.3	0	0	0	0	0	0	0
168,b	0.03069	1.8	0.1	1.7	0	0	0	0	0	0	0	0
169,b	0.03331	1.2	0.1	0.8	0.3	0	0	0	0	0	0	0

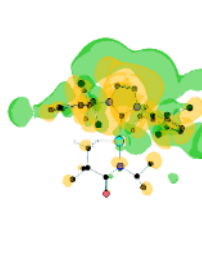
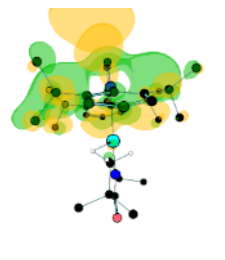
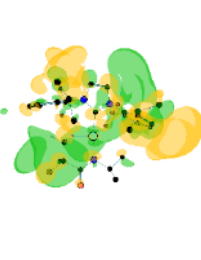
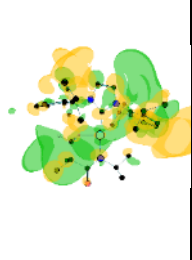
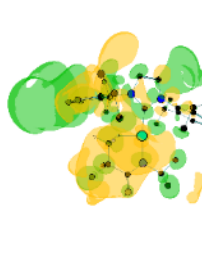
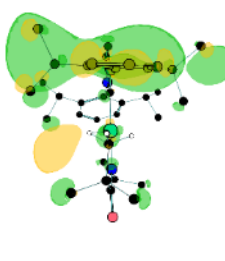
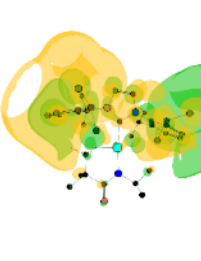
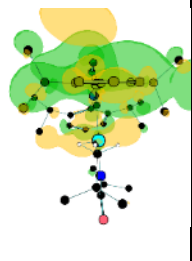
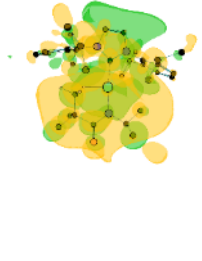
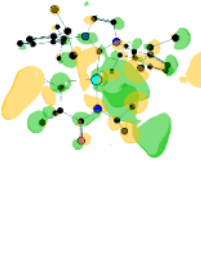
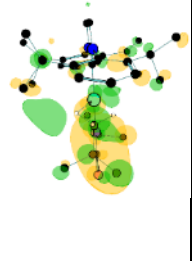
170,b	0.04026	0.9	0.1	0.7	0.1	0	0	0	0	0	0	0
171,b	0.04468	0.1	0	0	0.1	0	0	0	0	0	0	0
172,b	0.04673	7.9	1.5	4.6	1.8	0.7	0.1	0	0.3	0.2	0	0.1
173,b	0.04749	1.3	0.2	0.6	0.5	0.2	0	0	0.1	0.1	0	0
174,b	0.05542	18.7	0.1	18.1	0.5	4.3	0	0.7	0	0.6	0	3
176,b	0.06404	7.9	0	6.4	1.5	2.5	0	0.7	0.1	0.6	0	1.1

complex 1a			NHC ligand				CH3				
			N		C		C			H	
Orbita l	Energy (Ha)	Tota l	s (%)	p (%)	s (%)	p (%)	Tota l	s (%)	p (%)	s (%)	p (%)
159,a	- 0.17683	1.6	0	1.5	0	0.1	0.2	0	0.2	0	0
160,a	- 0.03246	4.3	0	2.3	0	2	0.6	0	0.4	0.2	0
161,a	- 0.03136	1.4	0	0.3	0.6	0.5	0	0	0	0	0
162,a	- 0.02943	7.7	0	3.7	0	4	0.1	0	0.1	0	0
163,a	- 0.02523	1.3	0	0.5	0	0.8	0	0	0	0	0
164,a	- 0.01489	35.3	0	13.3	0	22	1	0.1	0.5	0.3	0.1
166,a	0.01188	1.4	0	0.4	0.3	0.7	0.9	0.2	0.1	0.5	0.1
167,a	0.02623	5	0	1.4	0	3.6	0.2	0	0.1	0.1	0
168,a	0.03052	0.7	0.2	0.3	0	0.2	2.1	0.5	0.3	1	0.3
169,a	0.03302	0.9	0.4	0.4	0	0.1	0.1	0	0.1	0	0
170,a	0.03986	1.2	0.1	0.4	0	0.7	0.5	0.1	0.1	0.3	0
171,a	0.04408	1	0.1	0.5	0.1	0.3	1.3	0.3	0.2	0.5	0.3
172,a	0.04536	0.9	0	0.3	0.2	0.4	3.2	0.8	0.5	1.1	0.8
173,a	0.04731	0.6	0	0.5	0	0.1	0.3	0	0.2	0.1	0
174,a	0.05495	5.4	0	1.5	0	3.9	3.1	0	1.9	0.7	0.5
176,a	0.06061	2.2	0.5	0.2	0	1.5	5.5	1.5	0.8	2.2	1

159,b	- 0.0380 1	3	0	0.4	0.7	1.9	1.9	0.3	0.7	0.8	0.1
160,b	- 0.0323 2	3	0	1.7	0	1.3	0.3	0	0.2	0.1	0
161,b	- 0.0291 8	6.7	0	3	0	3.7	0.3	0	0.2	0.1	0
162,b	-0.0283	1.7	0	0.8	0.2	0.7	0.4	0.1	0.1	0.2	0
163,b	- 0.0228 2	1.4	0	0.3	0.2	0.9	0.8	0.2	0.4	0.2	0
164,b	- 0.0137 6	35.9	0	13. 4	0	22. 5	1.1	0.1	0.6	0.3	0.1
166,b	0.0133 1	1.3	0	0.4	0.2	0.7	0.5	0.1	0.1	0.3	0
167,b	0.0263 1	5	0	1.4	0	3.6	0.4	0	0.3	0.1	0
168,b	0.0306 9	0.6	0.2	0.2	0	0.2	2.1	0.5	0.3	1	0.3
169,b	0.0333 1	0.8	0.3	0.4	0	0.1	0.1	0	0.1	0	0
170,b	0.0402 6	1.2	0.2	0.4	0	0.6	0.2	0	0.1	0.1	0
171,b	0.0446 8	0.8	0.1	0.7	0	0	0.2	0	0.1	0.1	0
172,b	0.0467 3	1	0	0.3	0	0.7	3.6	0.9	0.6	1.3	0.8
173,b	0.0474 9	0.3	0	0.3	0	0	0.9	0.2	0.2	0.4	0.1
174,b	0.0554 2	4.7	0	1.2	0	3.5	3.1	0	1.8	0.8	0.5
176,b	0.0640 4	0.9	0.2	0.2	0	0.5	5.9	1.4	0.8	2.7	1





			
170α (Nip _x)	170β (Nip _x)	171α	171β
			
172α	172β	173α	173β
			
174α (Nip _y)	174β (Nip _y)	176α	176β

Appendix D.9 Molecular Orbital Characters and 3d graphics of complex 6.1a. The occupied orbitals' negative and positive phases are labeled in blue and red, the unoccupied orbitals' negative and positive phases are labeled in green and orange. The Orbital contour value was set as 0.002.

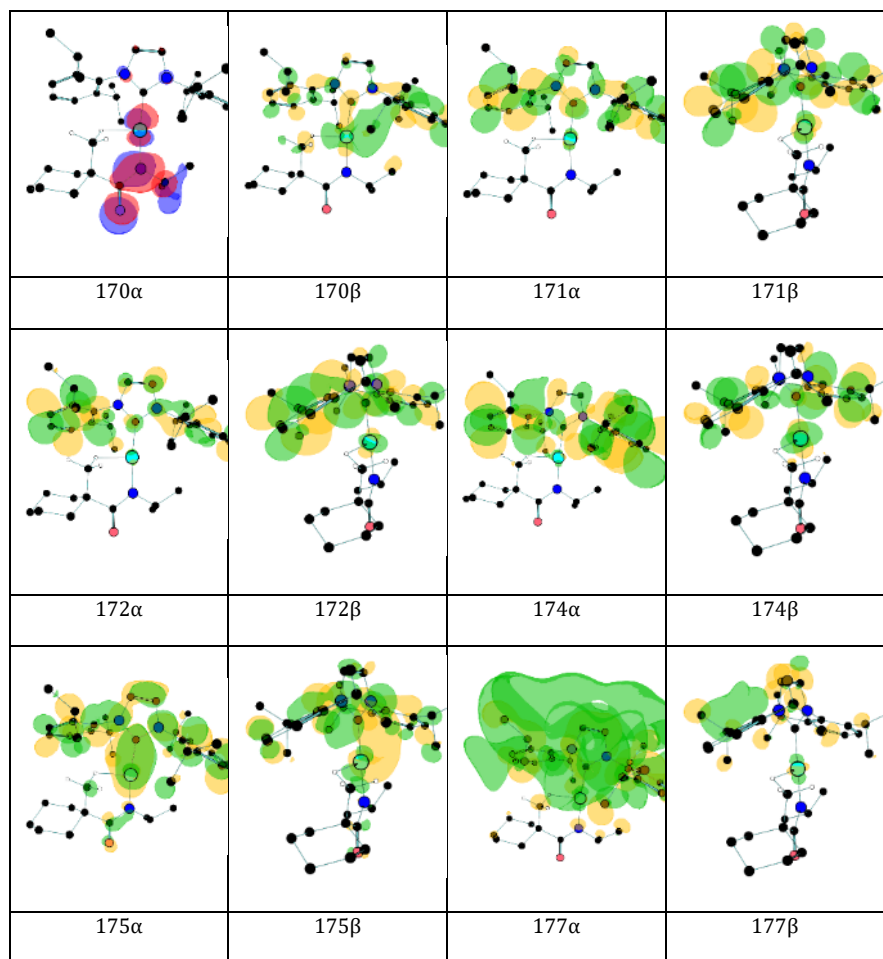
Complex 2a- K-MO

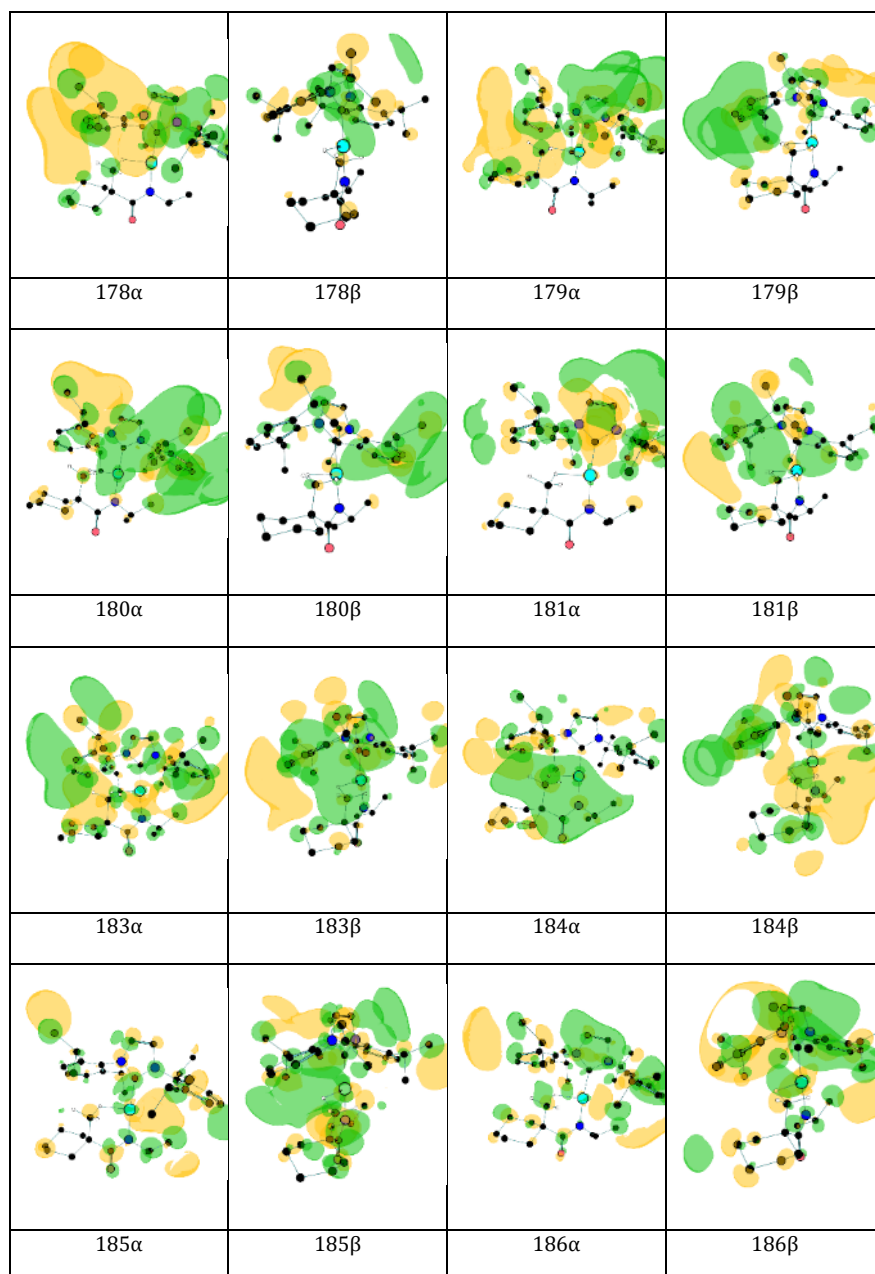
complex 2a		Nickel Center					amidate ligand					
Orbital	Energy	Total	Ni			Total	O		N		C	
			s (%)	p (%)	d (%)		s (%)	p (%)	s (%)	p (%)	s (%)	p (%)
170,a	- 0.17666	23.4	0	1.7	21.7	52.5	0	20.3	0	30.9	0	1.3
171,a	- 0.03312	2.9	0	1.8	1.1	0.4	0	0.1	0	0.2	0	0.1
172,a	- 0.03108	1.4	0	0.9	0.5	0	0	0	0	0	0	0
174,a	- 0.02558	0.1	0	0	0.1	0	0	0	0	0	0	0
175,a	- 0.01262	10.1	0	6.9	3.2	1	0	0.3	0	0.2	0	0.5
177,a	0.01219	1.3	0.6	0.2	0.5	0	0	0	0	0	0	0
178,a	0.02489	1.7	0.1	1.4	0.2	0	0	0	0	0	0	0
179,a	0.02847	1.6	0	1.6	0	0	0	0	0	0	0	0
180,a	0.03194	2	0.2	1.6	0.2	0.2	0	0	0.1	0.1	0	0
181,a	0.03898	1.4	0.2	1.1	0.1	0.1	0	0	0	0.1	0	0
183,a	0.04497	2.7	0.8	1.4	0.5	0.6	0	0.1	0.2	0.1	0	0.2
184,a	0.04805	6	1.3	4.2	0.5	1	0	0.2	0.3	0.2	0	0.3
185,a	0.05217	8.5	0.7	6.9	0.9	2	0	0.4	0.1	0.4	0	1.1
186,a	0.0564	5	0	4.7	0.3	1.3	0	0.3	0	0.2	0	0.8
187,a	0.05953	11.3	0.1	11.1	0.1	4.3	0	1	0	0.2	0	3.1
170,b	- 0.03889	48.5	7.5	3.5	37.5	1.1	0	0.1	0	0.8	0	0.2
171,b	- 0.03141	5.8	0.7	0.3	4.8	0.1	0	0	0	0.1	0	0
172,b	- 0.03072	4.8	0.3	1.6	2.9	0.3	0	0.1	0	0.1	0	0.1
174,b	- 0.02394	11.4	1.6	0.6	9.2	0.1	0	0	0	0.1	0	0
175,b	- 0.01078	13.3	0.3	6	7	1.3	0	0.5	0	0.2	0	0.6
177,b	0.01354	2.4	0.2	0.3	1.9	0	0	0	0	0	0	0
178,b	0.025	2	0.1	1.5	0.4	0	0	0	0	0	0	0
179,b	0.02866	1.6	0	1.3	0.3	0	0	0	0	0	0	0
180,b	0.03232	1.8	0.1	1.4	0.3	0.1	0	0	0	0.1	0	0
181,b	0.03936	0.9	0.1	0.6	0.2	0	0	0	0	0	0	0

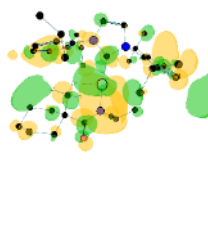
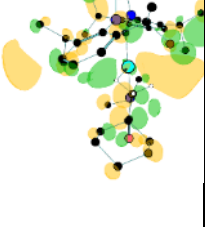
183,b	0.04559	0.9	0.1	0.4	0.4	0.3	0	0	0.1	0.1	0	0.1
184,b	0.0488	7.8	0.9	6.1	0.8	0.9	0	0.1	0.3	0.2	0	0.3
185,b	0.05459	4.4	0.5	2.5	1.4	2.9	0	0.7	0.1	0.2	0	1.9
186,b	0.05749	5.2	0.1	4.1	1	0.3	0	0	0	0.2	0	0.1
187,b	0.06005	11.2	0.1	10.9	0.2	4.4	0	1	0	0.2	0	3.2

complex 2a		NHC ligand						CH3			
Orbital	Energy	Total	N		C		Total	C		H	
			s (%)	p (%)	s (%)	p (%)		s (%)	p (%)	s (%)	p (%)
170,a	- 0.17666	1.4	0	1.2	0	0.2	0.2	0	0.2	0	0
171,a	- 0.03312	9.9	0	3.9	0.3	5.7	0.1	0	0.1	0	0
172,a	- 0.03108	3.5	0	1.8	0	1.7	0.5	0	0.2	0.3	0
174,a	- 0.02558	1.7	0	0.5	0	1.2	0.3	0	0.1	0.2	0
175,a	- 0.01262	35.3	0	13.5	0	21.8	0.3	0.1	0.2	0	0
177,a	0.01219	0.6	0	0.2	0.3	0.1	0.5	0.1	0.1	0.3	0
178,a	0.02489	3.7	0	1	0	2.7	1.9	0.3	0.4	0.8	0.4
179,a	0.02847	1.7	0	0.4	0.1	1.2	1.2	0.1	0.2	0.7	0.2
180,a	0.03194	0.7	0.3	0.2	0	0.2	0.6	0	0.5	0.1	0
181,a	0.03898	1.2	0	0.6	0	0.6	0.3	0	0.1	0.2	0
183,a	0.04497	0.6	0	0.3	0	0.3	1.1	0	0.4	0.5	0.2
184,a	0.04805	0.4	0	0.2	0.1	0.1	4	1.3	1.1	0.9	0.7
185,a	0.05217	2.3	0.2	0.5	0.2	1.4	2.1	0.5	0.2	0.8	0.6
186,a	0.0564	1.9	0.2	0.8	0	0.9	0.7	0.1	0.4	0.1	0.1
187,a	0.05953	3	0.2	0.3	0	2.5	3.8	0	1.8	1.2	0.8
170,b	- 0.03889	5.8	0	1.5	0.8	3.5	2.6	0.3	1	0.9	0.4
171,b	- 0.03141	3	0	1.3	0	1.7	0.6	0.1	0.1	0.4	0
172,b	- 0.03072	7.1	0	2.8	0	4.3	0.3	0	0.2	0.1	0
174,b	- 0.02394	2.1	0	0.3	0.1	1.7	0.3	0.1	0.2	0	0
175,b	- 0.01078	35.4	0	13.4	0	22	1	0.2	0.5	0.3	0
177,b	0.01354	0.6	0	0.2	0.2	0.2	0.4	0.1	0	0.3	0
178,b	0.025	3.8	0	1	0	2.8	1.9	0.3	0.4	0.8	0.4
179,b	0.02866	1.6	0	0.4	0	1.2	1.3	0.2	0.2	0.7	0.2

180,b	0.03232	0.4	0.2	0	0	0.2	0.6	0	0.5	0.1	0
181,b	0.03936	0.8	0	0.5	0	0.3	0.3	0	0.1	0.2	0
183,b	0.04559	0.2	0	0.2	0	0	1	0	0.3	0.5	0.2
184,b	0.0488	0.1	0	0.1	0	0	4.4	1.4	1.1	1	0.9
185,b	0.05459	1.1	0	0.6	0	0.5	1.1	0.1	0.2	0.6	0.2
186,b	0.05749	1.2	0.2	0.4	0	0.6	1.6	0.2	0.4	0.6	0.4
187,b	0.06005	3	0.2	0.3	0	2.5	3.5	0	1.8	1.2	0.5



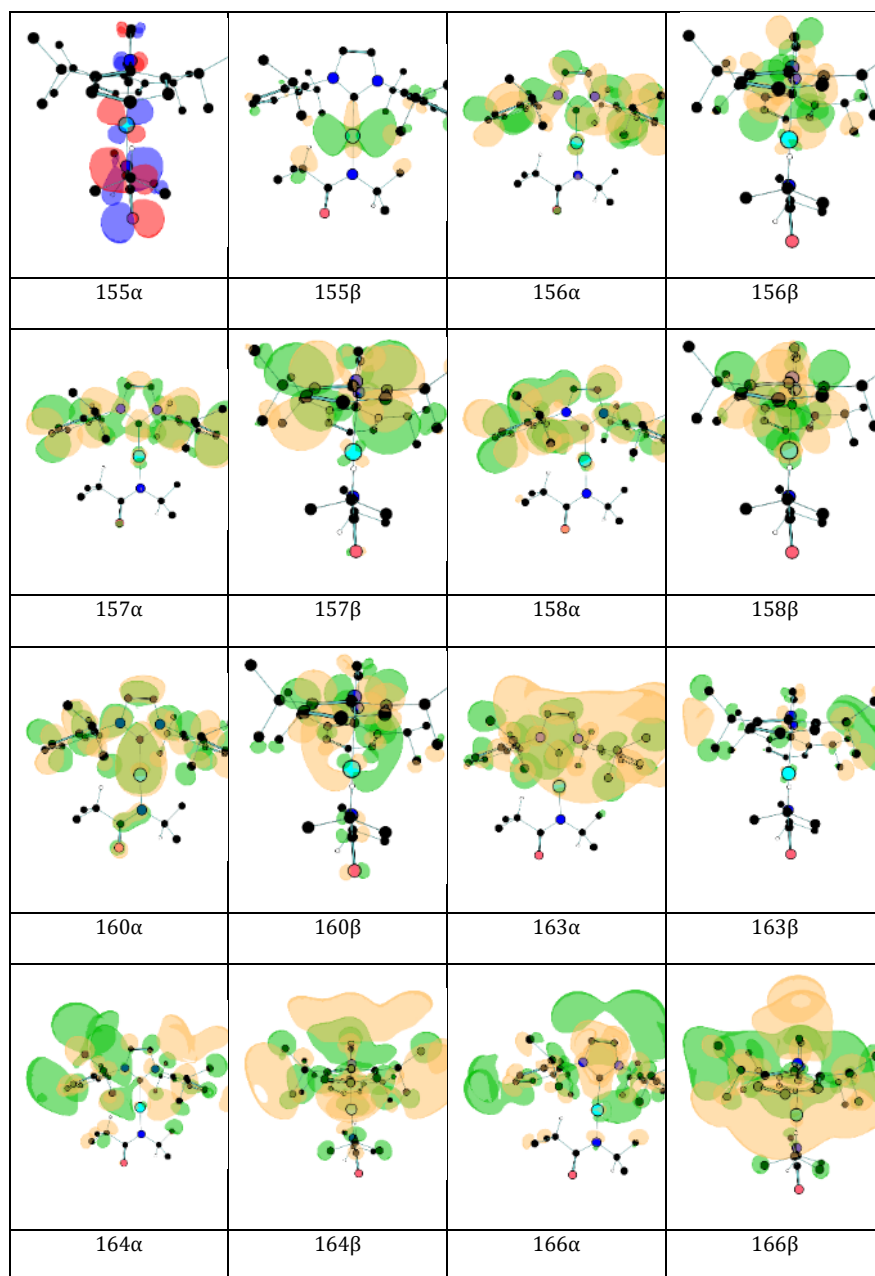


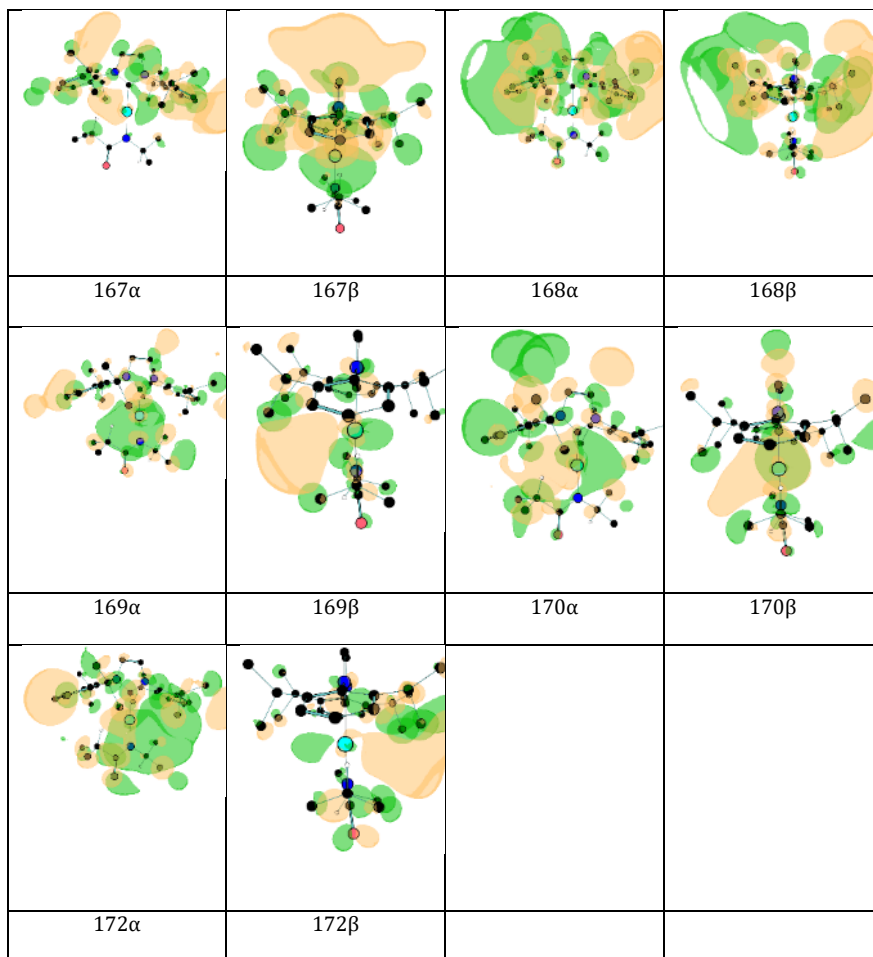
			
187 α	187 β		

Appendix D.10 Molecular Orbital Characters and 3d graphics of complex 6.2a. The occupied orbitals' negative and positive phases are labeled in blue and red, the unoccupied orbitals' negative and positive phases are labeled in green and orange. The Orbital contour value was set as 0.002.

complex 1b		Nickel Center					amidate ligand					
Orbital	Energy	Total	Ni			Total	O		N		C	
			s (%)	p (%)	d (%)		s (%)	p (%)	s (%)	p (%)	s (%)	p (%)
155,a	-0.17887	26.6	0.1	2.5	24	49.2	0	17.9	0	30	0	1.3
156,a	-0.03119	2.6	0	1.8	0.8	0.3	0	0.1	0	0.1	0	0.1
157,a	-0.03048	2	0	1.4	0.6	0.2	0	0.1	0	0	0	0.1
158,a	-0.02992	1.3	0	0.8	0.5	0	0	0	0	0	0	0
160,a	-0.01367	11.8	0	8.3	3.5	1.4	0	0.5	0	0.4	0	0.5
163,a	0.02749	2.1	0	1.8	0.3	0	0	0	0	0	0	0
164,a	0.02914	7.6	0	7.5	0.1	0	0	0	0	0	0	0
166,a	0.04026	3.9	0.5	3.1	0.3	0.3	0	0	0.1	0.2	0	0
167,a	0.04212	6	0.2	5.5	0.3	0	0	0	0	0	0	0
168,a	0.04749	1.6	0.1	1.4	0.1	0.7	0	0.3	0	0.1	0	0.3
169,a	0.04982	14.9	2	11.5	1.4	2.3	0	0.2	0.5	0.9	0.1	0.6
170,a	0.05131	17.5	1	15.7	0.8	1.1	0	0.1	0.2	0.4	0.1	0.3
172,a	0.06043	12.5	0.3	11.7	0.5	10	0	2.7	0.1	0.5	0.1	6.6
155,b	-0.05215	70.2	13.4	0.2	56.6	1.6	0	0	0.1	1.2	0	0.3
156,b	-0.03066	2.4	0	1.3	1.1	0.3	0	0.1	0	0.1	0	0.1
157,b	-0.02974	3.3	0	1.9	1.4	0.5	0	0.2	0	0.1	0	0.2
158,b	-0.0289	5.2	0.9	0	4.3	0	0	0	0	0	0	0
160,b	-0.01256	14	0.1	8.3	5.6	1.6	0	0.5	0	0.4	0	0.7
163,b	0.02759	1.7	0	1.3	0.4	0	0	0	0	0	0	0
164,b	0.03005	4.6	0	4.6	0	0	0	0	0	0	0	0
166,b	0.0411	1.8	0.1	1.3	0.4	0	0	0	0	0	0	0
167,b	0.04305	2.8	0	2.7	0.1	0	0	0	0	0	0	0
168,b	0.04774	0.5	0	0.4	0.1	0.7	0	0.2	0	0.1	0	0.4
169,b	0.05286	17.6	0.9	14.6	2.1	2.2	0	0.2	0.3	0.8	0.1	0.8
170,b	0.05556	20.2	0.4	18.8	1	1.2	0	0.2	0.1	0.3	0.1	0.5
172,b	0.06121	12.3	0.2	11.4	0.7	8.6	0	2.2	0.1	0.4	0.1	5.8

complex 1b			NHC ligand			
Orbital	Energy	Total	N		C	
			s (%)	p (%)	s (%)	p (%)
155,a	- 0.17887	2	0	1.8	0	0.2
156,a	- 0.03119	5.8	0	2.7	0.3	2.8
157,a	- 0.03048	4.6	0	1.9	0.3	2.4
158,a	- 0.02992	3.4	0	2	0.1	1.3
160,a	- 0.01367	34.8	0	13.1	0	21.7
163,a	0.02749	4.7	0	1.2	0.1	3.4
164,a	0.02914	1.6	0.2	0.6	0	0.8
166,a	0.04026	1.6	0.2	0.7	0	0.7
167,a	0.04212	1.8	0.4	0.5	0	0.9
168,a	0.04749	0.6	0	0.4	0	0.2
169,a	0.04982	3.2	0.1	0.6	0.3	2.2
170,a	0.05131	3.3	0.6	0.3	0.2	2.2
172,a	0.06043	3.5	0	0.5	0	3
155,b	- 0.05215	3.9	0	0.1	0.8	3
156,b	- 0.03066	4.4	0	2.2	0	2.2
157,b	- 0.02974	6.2	0	3	0	3.2
158,b	-0.0289	0.7	0	0.2	0.4	0.1
160,b	- 0.01256	35.6	0	13.2	0	22.4
163,b	0.02759	4.9	0	1.2	0	3.7
164,b	0.03005	0.8	0.2	0.3	0	0.3
166,b	0.0411	0.9	0	0.5	0	0.4
167,b	0.04305	1.2	0.3	0.5	0	0.4
168,b	0.04774	0.6	0	0.5	0	0.1
169,b	0.05286	3.2	0.1	0.7	0.1	2.3
170,b	0.05556	3.6	0.7	0.4	0.1	2.4
172,b	0.06121	3.1	0	0.5	0	2.6





Appendix D.11 Molecular Orbital Characters and 3d graphics of complex 6.2a. The occupied orbitals' negative and positive phases are labeled in blue and red, the unoccupied orbitals' negative and positive phases are labeled in green and orange. The Orbital contour value was set as 0.002.

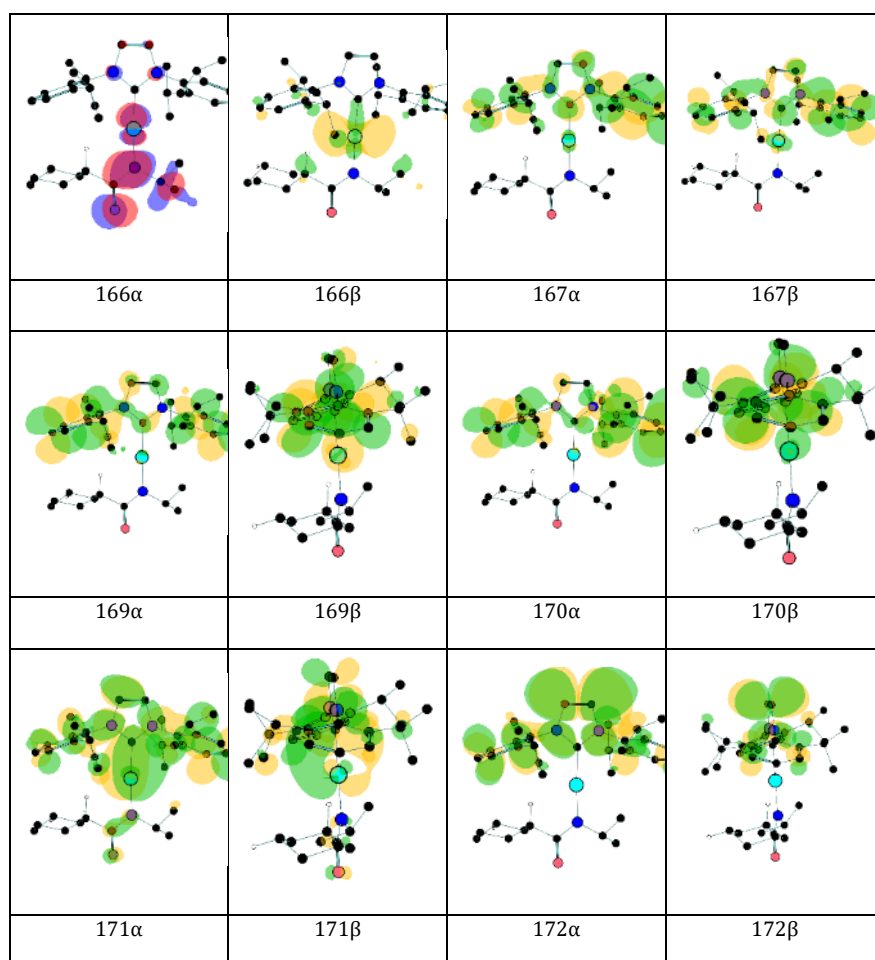
Complex 2b - MO

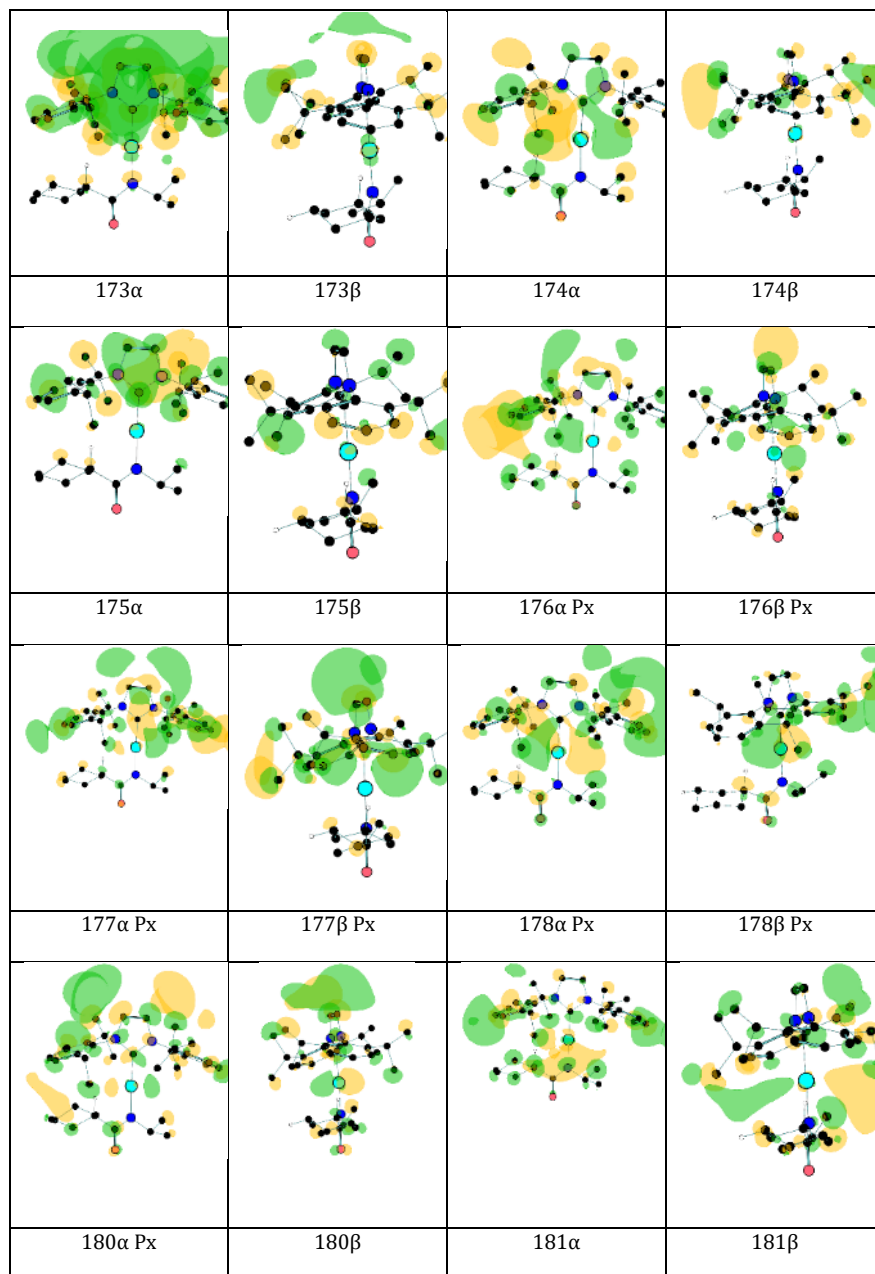
complex 2b		Nickel Center					amidate ligand					
Orbital	Energy	Total	Ni			Total	O		N		C	
			s (%)	p (%)	d (%)		s (%)	p (%)	s (%)	p (%)	s (%)	p (%)
166,a	-0.1797	24.9	0	2.3	22.6	51.2	0	19.2	0	30.8	0	1.2
167,a	- 0.03587	3.2	0	1.8	1.4	0.3	0	0.1	0	0.1	0	0.1
169,a	- 0.02709	1.1	0	0.8	0.3	0	0	0	0	0	0	0
170,a	- 0.02576	0.6	0	0.5	0.1	0	0	0	0	0	0	0
171,a	- 0.01461	11.8	0	8.5	3.3	1	0	0.3	0	0.3	0	0.4
173,a	0.0147	1.5	0.8	0.2	0.5	0.1	0	0	0	0.1	0	0
174,a	0.02546	15.6	0	15.5	0.1	1.2	0	0.3	0	0.1	0	0.8
175,a	0.02716	2.7	0	2.5	0.2	0.1	0	0	0	0	0	0.1
176,a	0.0318	4.8	0.1	4.7	0	0.4	0	0.1	0	0	0	0.3
177,a	0.0392	4	0	4	0	0.4	0	0.1	0	0	0	0.3
178,a	0.04239	6.9	0.2	6.6	0.1	0.9	0	0.3	0	0	0	0.6
179,a	0.04445	6.5	2.2	2.9	1.4	1.5	0	0.1	0.6	0.6	0	0.2
180,a	0.04901	3.4	0	3.4	0	1.1	0	0.3	0	0.1	0	0.7
181,a	0.05313	5.4	1.6	2.8	1	0.9	0	0	0.4	0.4	0	0.1
182,a	0.05369	10.4	0	10.2	0.2	1.4	0	0.1	0	0.3	0	1
166,b	- 0.05526	71.8	15.7	0	56.1	1.9	0	0	0.2	1.4	0	0.3
167,b	- 0.03515	4.3	0.2	1.5	2.6	0.3	0	0.1	0	0.1	0	0.1
169,b	- 0.02678	1.6	0.1	0.7	0.8	0.1	0	0.1	0	0	0	0
170,b	-0.0256	0.7	0	0.4	0.3	0	0	0	0	0	0	0
171,b	- 0.01276	14.1	0.1	8.1	5.9	1.4	0	0.5	0	0.3	0	0.6
173,b	0.01636	2.1	0.2	0.2	1.7	0	0	0	0	0	0	0
174,b	0.02664	3.8	0	3.5	0.3	0.1	0	0	0	0	0	0.1
175,b	0.02786	6.7	0	6.6	0.1	0.5	0	0.1	0	0	0	0.4
176,b	0.03256	5.2	0.1	5.1	0	0.4	0	0.1	0	0	0	0.3
177,b	0.03981	2.1	0	2.1	0	0.3	0	0.1	0	0	0	0.2

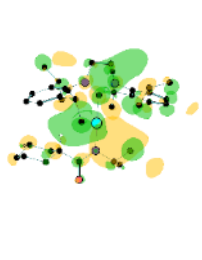
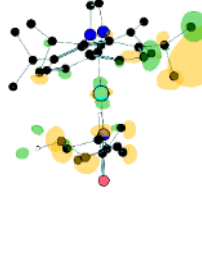
178,b	0.04407	8.9	0.2	8.6	0.1	1.1	0	0.3	0	0	0	0.8
179,b	0.04667	3.1	0.3	1.7	1.1	0.4	0	0	0.2	0.1	0	0.1
180,b	0.04973	5.9	0	5.8	0.1	1.8	0	0.5	0	0.1	0	1.2
181,b	0.05421	10.4	0.1	10.1	0.2	1.1	0	0.1	0	0.3	0	0.7
182,b	0.05569	6.3	0.6	4.2	1.5	0.8	0	0.1	0.3	0.2	0	0.2

complex 2b			NHC ligand			
Orbital	Energy	Total	N		C	
			s (%)	p (%)	s (%)	p (%)
166,a	-0.1797	1.6	0	1.4	0	0.2
167,a	- 0.03587	9.7	0	3.5	0.3	5.9
169,a	- 0.02709	2.8	0	1.2	0	1.6
170,a	- 0.02576	0.8	0	0.3	0	0.5
171,a	- 0.01461	34.2	0	13.6	0	20.6
173,a	0.0147	0.5	0	0.1	0.3	0.1
174,a	0.02546	2	0.2	0.5	0	1.3
175,a	0.02716	3.5	0	1.2	0	2.3
176,a	0.0318	1	0.4	0.2	0	0.4
177,a	0.0392	1.2	0.2	0.4	0	0.6
178,a	0.04239	1.2	0.3	0.3	0	0.6
179,a	0.04445	1.4	0.1	0.4	0.1	0.8
180,a	0.04901	1.5	0.1	0.7	0	0.7
181,a	0.05313	0.9	0	0.2	0.2	0.5
182,a	0.05369	2.8	0.1	0.9	0	1.8
166,b	- 0.05526	4.6	0	0.2	0.8	3.6
167,b	- 0.03515	9.4	0	3.4	0.2	5.8
169,b	- 0.02678	2.6	0	1.1	0	1.5
170,b	-0.0256	0.7	0	0.3	0	0.4
171,b	- 0.01276	34.7	0	13.6	0	21.1
173,b	0.01636	0.4	0	0.2	0.1	0.1
174,b	0.02664	3.7	0	1	0	2.7
175,b	0.02786	1	0.1	0.3	0	0.6
176,b	0.03256	0.9	0.4	0.2	0	0.3

177,b	0.03981	1	0.1	0.5	0	0.4
178,b	0.04407	1.4	0.4	0.3	0	0.7
179,b	0.04667	0.4	0.1	0.2	0	0.1
180,b	0.04973	1.6	0.2	0.5	0	0.9
181,b	0.05421	2.1	0.1	0.5	0	1.5
182,b	0.05569	0.5	0.1	0.1	0	0.3





			
182 α	182 β		

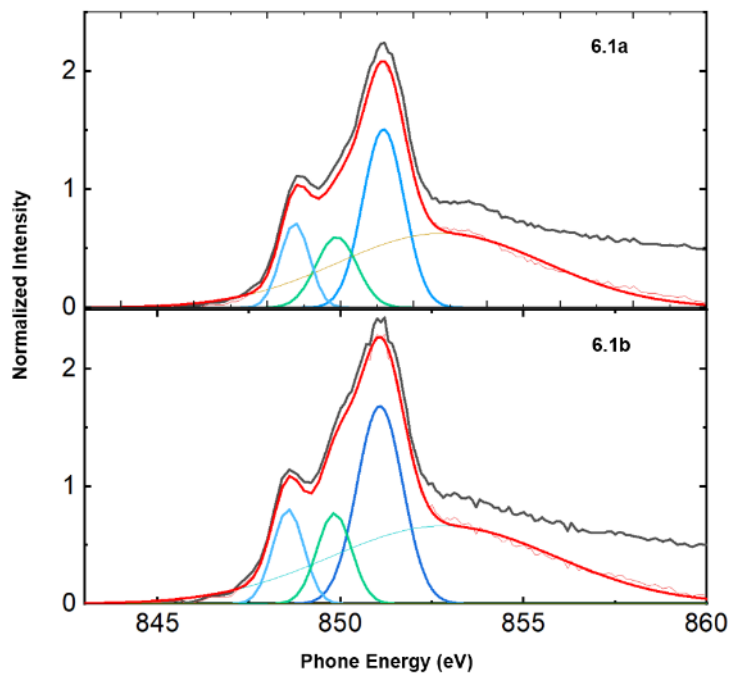
Appendix D.12 Molecular Orbital Characters and 3d graphics of complex 6.2b. The occupied orbitals' negative and positive phases are labeled in blue and red, the unoccupied orbitals' negative and positive phases are labeled in green and orange. The Orbital contour value was set as 0.002.

D.4 DFT Geometry VS XRD

complex	Ni1-H1 (Å)	N1-H2 (Å)	Ni1-C1 (Å)	Ni1-H1-C1 (°)	Ni1-H2-C1 (°)	Δ Ni-H (Å)	Δ Ni-H-C (°)
6.1a(XRD)	2.159(15)	2.024(15)	2.4476(10)	101.8(10)	94.3(10)	7.5	-0.135
6.2a(XRD)	1.94(2)	2.15(2)	2.4007(2)	106.18(3)	92.60(8)	13.575	0.21
6.1a(DFT)	1.98	2.133	2.394	97.384	89.488	7.896	0.152
6.2a(DFT)	1.97	2.263	2.461	102.276	86.734	15.542	0.294

Appendix D.13 The comparison of Distances and Angles of agnostic complexes 6.1a-6.2a in XRD and DFT structures.

D.5 Ni L edge XAS Simulation



complex 1a						
agostic	gaussian	height	center	hwhm	area	FWHM
L3 edge	1	0.503	848.733	0.486	0.521	0.973
	2	0.518	850.137	0.885	0.976	1.769
	3	0.932	851.245	0.596	1.183	1.193
	4	0.504	852.404	2.932	3.145	5.864
	5	0.061	857.706	1.657	0.215	3.313
L2 edge	1	0.182	866.176	0.905	0.352	1.810
	2	0.522	868.029	0.694	0.771	1.388
	3	0.331	868.390	1.210	0.854	2.419
	4	0.117	871.139	1.916	0.479	3.832

complex 1b						
non-agostic	gaussian	height	center	hwhm	area	FWHM
L3 edge	1	0.438	848.491	0.450	0.419	0.900
	2	0.784	850.441	1.133	1.892	2.267
	3	0.524	851.255	0.525	0.586	1.050
	4	0.391	852.530	3.276	0.586	1.050
L2 edge	1	0.078	865.915	0.506	0.084	1.011
	2	0.624	868.068	1.031	1.370	2.062
	3	0.148	868.300	0.419	0.132	0.838
	4	0.152	871.198	2.914	0.942	5.829

Appendix D.14 Peak fitting for Ni L-edge XANES edge spectra for 6.1a and 6.1b.