THE CHARACTERISTIC CHEMISTRY OF SOME ORGANOMETALLIC NITROSYL COMPLEXES

Ву

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ABSTRACT

Treatment of a CH₂Cl₂ solution of $(\eta^5 - C_5H_5)W(NO)_2Cl$ with an equimolar amount of AgBF, results in the rapid formation of a precipitate of AgCl and a bright green solution of $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$. This organometallic complex is а thermally unstable, air- and moisture-sensitve species whose characteristic chemistry is dominated by its electrophilic nature. Hence, it readily forms adducts of the type $[(\eta^5 - C_5 H_5)W(NO)_2 L]BF_4$ with Lewis bases, L, capable of good donation such as PPh₃ or P(OPh)₃. In an analogous manner, the novel complex $[(\eta^5 - C_5H_5)W(NO)_2(\eta^2 - C_8H_{14})]BF_4$ results when $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ is exposed to an exċess of cyclooctene. Other olefins, however, either do not react Allylbenzene) or undergo dimerization (e.q. (e.q. 1,1-diphenylethene) or isomerization (e.g. 2,3-dimethyl-1-butene), the latter transformations probably occurring via the formation of incipient carbocations. Phenylethyne is either polymerized or condensed with other unsaturated substrates (e.g. 2,3-dimethyl-2-butene). The electrophile also organometallic reacts with dichloromethane-soluble anionic nucleophiles, X^{-} to form $(\eta^{5}-C_{5}H_{5})W(NO)_{2}X$ (X = H or Br) products. Of greater interest

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is the fact that $(\eta^5 - C_5 H_5)W(NO)_2 BF_4$ is sufficiently electrophilic to cleave the M-C linkages in organic derivatives of the main group elements (e.g. B, Al or Sn) and so produce some new $(\eta^5 - C_5 H_5)W(NO)_2 R$ (R = C₂H₅, CH₂Ph or Ph) complexes. This chemistry has also been extended to encompass some of the pentamethylcyclopentadienyl analogues derivable from $(\eta^5 - C_5 Me_5)W(NO)_2 BF_4$.

Treatment of $(\eta^5-C_5H_5)M(NO)_2CH_3$ (M = Cr or Mo) with electrophiles such as HgCl₂, Ph₃C⁺, Ph₂CH⁺ and AlCl₃ results in rapid cleavage of the metal-methyl bond. Contrastingly, $(\eta^5-C_5H_5)MO(CO)_3CH_3$ reacts much less readily with these reagents. These results point to a fundamental difference between the reactivity of these alkylnitrosyl complexes and their isoelectronic carbonyl analogues.

Treatment of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ with an equimolar amount of HBF₄.O(CH₃)₂ in CH₂Cl₂ results in the clean formation of $[{(\eta^5-C_5H_5)Fe(CO)_2}_2H]BF_4$ which may be isolated in good yield. In contrast, 2 equivalents of the acid are required to consume completely $[(\eta^5-C_5H_5)Cr(NO)_2]_2$, the principal organometallic product being $(\eta^5-C_5H_5)Cr(NO)_2BF_4$. This latter complex is not isolable, but it may be characterized spectroscopically and by its derivative chemistry. The propensities of the $[(\eta^5-C_5H_5)M(LO)_2]_2$ (M = Cr or Fe; L = N or C) dimers to undergo protonation or oxidative cleavage when treated with H⁺ are rationalized in terms of the initially formed $[(\eta^5-C_5H_5)M(LO)_2]_2H^+$ adducts.

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Table of Abbreviations

In general the abbreviations and symbols used in this thesis are those recommended in the "Handbook for Authors of Papers in American Chemical Society Publications". In addition, the following are also used:

0	degrees Celcius
dec	decomposed
E(pa)	aniodic peak potential
E(1/2)	half wave potential
η 2	dihapto
THF	tetrahydrofuran
PPN	bis(triphenylphosphoranediyl)nitrogen(1+)
R	organic alkyl group
SCE	saturated calomel electrode
FT	Fourier transform

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Kekule dreams the Great Serpent holding its own tail in its mouth, the dreaming Serpent which surrounds the World. But the meanness, the cynicism with which this dream is to used. The Serpent that announces, "The World is a closed be thing, cyclical, resonant, eternally-returning," is to be delivered into a system whose only aim is to violate the Taking and not - Cycle. giving back, demanding that "productivity" and "earnings" keep on increasing with time, the System removing from the rest of the World these vast quantities of energy to keep its own tiny desperate fraction showing a profit: and not only most of humanity- most of the World, animal, vegetable and mineral, is laid to waste in the process. The System may or may not understand that it is only buying time. And that time is an artificial resource to begin with, of no value to anyone or anything but the System, which sooner or later must crash to its death, when its addiction to energy has become more than the rest of the World can supply, dragging with it innocent souls all along the chain of life. Living inside the System is like riding across the country in a bus driven by a maniac bent on suicide . . .

Thomas Pynchon in "Gravity's Rainbow"

CHAPTER ONE

1

GENERAL INTRODUCTION

A chemical characteristic of the transition metals is their ability to form complexes with a wide variety of neutral molecules such as carbon monoxide, isocyanides, substituted phosphines, arsines, stibines or sulfides, nitric oxide and various molecules with delocalized π -orbitals such as pyridine [1]. In many of these complexes the metal atoms are in low-positive, zero or negative formal oxidation states. The stability of these complexes is а result of the ligands possessing vacant π -orbitals as well These vacant orbitals accept as lone pairs of electrons. electron density from the filled metal orbitals to form a type of π -bonding that complements the σ -bonding arising from the lone-pair donation. Thus, the high electron density on the metal atom can be delocalized onto the ligands. The most important π -acid ligand is carbon monoxide. Examples of compounds with at least one carbonyl ligand are known for all of the transition metals. Moreover, many of these compounds are of considerable structural interest or are important in industrial, catalytic and other reactions.

Although the first carbonyl complex was prepared in 1868, [2] metal nitrosyl complexes have been known for several centuries [3]. However, the amount of literature published on metal carbonyl complexes far exceeds that of metal nitrosyl complexes. This can be attributed to two main Firstly, nitric oxide, unlike carbon monoxide, is reasons. not a potential building block of the chemical industry. If anything, attention has been concentrated on efficient methods to destroy NO [4]. Secondly, the synthesis of nitrosyl complexes has been problematic [5,6,7,8]. Although some metal nitrosyls are formed from the action of nitric oxide gas, this is not a generally applicable route. Consequently, as the major reviews of the metal nitrosyl literature indicate, most of the research into the chemistry of nitric oxide complexes can be divided into the two main areas of synthesis [5,6,7,8] or structure and bonding [9,10]. Although some attempt has been made to exploit the reactivity of coordinated nitric oxide [3,11,12,13,14], the effect of a nitrosyl ligand on the reactivity of other groups in the metal's coordination sphere has not been fully investigated [15].

When attempting to predict the reactivity of metal nitrosyl complexes, it is important to avoid any arguments that depend on the formal oxidation state of the metal. For a linear nitrosyl ligand, the most common formalism regards

nitrosonium (NO⁺) ion. For example, NO as а in the well-studied nitroprusside ion, [Fe(CN),NO]²⁻, the metal is assigned an oxidation number of +2. While this is an attractive formalism, Mossbauer and other physical data [16] indicate that the effective oxidation state is closer to +3. This is the value obtained if NO is considered to interact as a neutral ligand. The idea that that NO first transfers its π^* electron in order to become NO⁺, that this cation serves as an electron donor, and that finally $d\pi$ electron density is then returned to the same π^* orbital from which an electron was initially dislodged is overly complicated. Its only usefulness is that, in some cases, it leads to an intuitively satisfactory oxidation number for the metal. However, there are many cases where this is not true. For example, in Fe(CO)₂(NO)₂, Co(NO)₃ or Cr(NO)₄ unsatisfactory oxidation numbers of -2, -3 and -4 are obtained. Of course, the only thing that is physically and chemically important actual electronic distribution. In essentially is the covalent bonding situations, assignment of oxidation numbers is best avoided.

A comparison of the chemistry of nitrosyl complexes with their more extensively studied carbonyl analogues requires an understanding of the relative π -acidities of CO and NO. A "spectrochemical series" for π -bonding ligands has been established [17] (Table I) and NO is generally believed to be the strongest π -acid. The relative electron accepting

Table I. "Spectrochemical Series" for π -Acid Ligands

NO	PBr ₂ CH ₃	AsPh ₃
со	As(OCH ₃) ₃	PPh ₃
PF ₃	$PC1(OC_4H_9)_2$	SPh ₂
SbCl ₃	As(OPh) ₃	As(C_2H_5) ₃
AsCl ₃	PClPh ₂	P(CH ₃) ₃
PCl ₃	p-CH ₃ OC ₆ H ₄ NC	P(C ₂ H ₅) ₃
$PCl_2(OC_4H_9)$	P(OCH ₃) ₃	o-C ₆ H ₄ [P(C ₂ H ₅) ₂] ₂
PCl ₂ Ph	$As(NC_5H_{10})_3$	P(NC ₅ H ₁₀) ₃

abilities of CO and NO have been established using the disubstituted derivatives of $Co(CO)_3NO$ in which the CO and NO ligands compete directly for electron density in an otherwise identical environment. Using a comparison of the fractional changes in CO and NO stretching frequencies for the set of compounds tabulated below it was concluded that

 $\begin{array}{cccccc}
\nu(CO) & \Delta & \nu(NO) & \Delta \\
Co(CO)(NO)(PCl_3)_2 & 2044.5 & cm^{-1} & 1793.2 & cm^{-1} \\
& & 4.29\% & 4.24\% \\
Co(CO)(NO)(PPh_3)_2 & 1956.7 & 1717.0 \\
& & 2.40\% & 3.43\% \\
Co(CO)(NO)(o-phen) & 1909.8 & 1658.1 \\
\end{array}$

in situations of low electron density CO and NO are almost identical in their electron accepting power while at higher charge densities the NO group is slightly stronger. However, it must be remembered that there is no theoretical basis for assuming that infrared stretching frequencies (or force constants) directly measure bond strength [18]. Support for the relative ordering of the π -acidities of CO and NO has been derived from X-ray photoelectron spectroscopic studies. The measurement of C 1s, N 1s, and O 1s binding energies of the series of compounds Ni(CO)₄, Co(CO)₃NO, Fe(CO)₂(NO)₂, Mn(CO)(NO)₃ and Cr(NO)₄ provided data consistent with NO groups being much stronger π -acceptors than CO groups [19].

What are the consequences of the different electronic properties of carbonyl and nitrosyl ligands? It has been found that nucleophiles attack η^3 -allyl complexes such as the $(\eta^{5}-C_{5}H_{5})MO(CO)(NO)(1,3-dimethylallyl)^{+}$ cation stereospecifically [20]. The structures of the olefinic derivatives formed by the addition of the nucleophile to the allyl ligand reveal that attack occurs trans to NO when the organic ligand is in the endo confirmation and cis to NO in the exo isomer. It is believed that the nucleophile approaches the allyl ligand at the point determined by the lowest electron density. This control position of of regiochemistry is exerted by an electronic effect arising from the different effective electronegativities of the carbonyl and nitrosyl ligands. The CO and NO ligands tend to polarize the electronic distribution at the metal centre and at the coordinated allyl ligand.

The above evidence shows that nitrosyl ligands exert an exploitable influence on the organic ligands in a metal's coordination sphere. It is the intention of this work to investigate other such phenomena. Previous work from this laboratory has delineated some of the chemistry of the $(\eta^5-C_5H_5)M(NO)_2$ (M=Cr,Mo or W) functional groups [21-29]. This will now be extended to a study of alkene, alkyne and alkyl derivatives of these groups. By way of comparison, the cyclopentadienyl metal dicarbonyl fragment, $(\eta^5-C_5H_5)M(CO)_2$,

is a common constituent of a large class of organometallic complexes, $(\eta^5-C_5H_5)M(CO)_2X$. The molecules have widespread utility in transition-metal-aided organic synthesis, especially the iron variant [30]. It is now possible to compare and contrast the chemistry of compounds such as 1, where L=CO or NO.



CHAPTER TWO

THE CHARACTERIZATION OF $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$

The preparation of several salts of the bimetallic cation $[(\eta^5-C_5H_5)_2W_2(NO)_4H]^+$ has been reported [28]. The physical and chemical properties of these compounds indicated that the cation could be viewed as a Lewis acid-base adduct. In this view, the formally 18-e unit, $(\eta^{5}-C_{5}H_{5})W(NO)_{2}H$, provides a pair of electrons from a filled metal- or ligand-centred orbital to a vacant metal-centred orbital of the formally $16-e^-$ unit, $(\eta^5-C_5H_5)W(NO)_2^+$. Further support for the donor-acceptor character of this interaction was provided by the fact that $(\eta^5 - C_5 H_5) W(NO)_2 H$ also forms adducts with other Lewis acids. On the basis of these studies, it was concluded that $(\eta^5 - C_5 H_5) W(NO)_2 H$ functions as a fairly weak and soft Lewis base. However, little could be said at that time about the acid component of the bimetallic cation.

To further investigate the characteristic chemistry of $(\eta^5-C_5H_5)W(NO)_2^+$ an independent (i.e. Free of $(\eta^5-C_5H_5)W(NO)_2H)$ synthesis was required. Based on chemical precedents and availability, three possible syntheses could

be proposed:

i)
$$(\eta^5 - C_5 H_5) W(NO)_2 Cl + A \longrightarrow (\eta^5 - C_5 H_5) W(NO)_2^+ + ClA^-$$

A = chloride ion acceptor

ii) $(\eta^{5}-C_{5}H_{5})W(NO)_{2}CH_{3} + H^{+} \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}^{+} + CH_{4}$ iii) $(\eta^{5}-C_{5}H_{5})W(NO)_{2}(CO)^{+} \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}^{+} + CO.$

For reasons of convenience, route (i) is the most attractive. This reaction was attempted with Ag⁺ being the chloride acceptor.

Experimental Section

All chemicals used were of reagent grade or comparable purity and were either purchased from commercial suppliers or prepared according to published procedures. Purity was routinely ascertained by elemental analyses and/or melting point determinations. However, the purity of commercially obtained liquid organic substrates was usually verified by a combination of ¹H NMR and IR spectroscopies. All melting points are uncorrected and were taken in capillaries (under prepurified nitrogen for air-sensitive compounds) using a Gallenkamp Melting Point Apparatus. All manipulations involving organometallic reagents were performed on the bench using conventional techniques for the manipulation of air-sensitive compounds or Atmospheres in а Vacuum

Corporation Dri-Lab model HE-43-2 dry box filled with prepurified nitrogen and equipped with a HE-493 Dri-Train purification system. Solvents were dried according to standard procedures [31], distilled and thoroughly deaerated prior to use.

Infrared spectra were recorded on a Perkin Elmer 598 spectrometer calibrated with the 1601 cm⁻¹ absorption band of a polystyrene film or on a Nicolet 5DX FT instrument internally calibrated by the He/Ne laser. Proton magnetic resonance spectra were recorded on a Bruker WP-80 instrument with reference either to internal tetramethylsilane or to the residual protons of the solvent used. All ¹H chemical shifts are reported in parts per million downfield from Me₄Si. Carbon-13 NMR spectra were recorded on a Varian Associates CFT-20 spectrometer with reference to the solvent used, but the ¹³C chemical shifts are reported in ppm downfield from Me₄Si. Low-resolution mass spectra were obtained at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method by the departmental service laboratory. Elemental analyses were performed by Mr. P. Borda. Gas chromatographic analyses were carried out on a Perkin Elmer Sigma 4B instument employing a 8 ft x 0.125 in column packed with 3% OV-17 on Supelcoport.

Generation of a CH_2Cl_2 Solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$

Solid AgBF₄ was added to a green solution of

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}Cl$ [32] (0.69 g, 2,0 mmol) in $CH_{2}Cl_{2}$ (25) mL) which displayed characteristic nitrosyl absorptions at 1733 and 1650 cm⁻¹ in its IR spectrum. The reaction mixture was stirred at room temperature for 20 min, after which time it consisted of a flocculent white precipitate and a darker supernatant solution. The final mixture was filtered green through a medium-porosity frit to obtain a clear, green solution whose IR spectrum exhibited $\nu(NO)$'s at 1754 and 1674 cm⁻¹. This solution of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ slowly deposited an intractable red-brown solid when stirred at ambient temperature in a atmosphere of prepurified nitrogen, the decomposition being clearly evident after 30 min. The rate of decomposition was markedly enhanced by removal of the solvent in vacuo, an operation which afforded only the red-brown solid. Consequently, the CH₂Cl₂ solutions of $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ generated according to this procedure were used immediately for the subsequent transformations described below.

Preparation of $[(\eta^5 - C_5H_5)W(NO)_2L]BF_4$ (L = PPh₃, P(OPh)₃ or $\eta^2 - C_8H_{1,4}$)

The CH_2Cl_2 solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ was added to a colourless solution of PPh₃ (0,53 g, 2.0 mmol) in dichloromethane (10 mL). The resulting green solution was stirred briefly and was then permitted to stand for about 10 min, whereupon lustrous green platelets began to

crystallize. The crystallization was completed by the addition of Et_2O (50 mL). The solid was collected by filtration, washed with ether (3 x 10 mL), and dried in vacuo (5 x 10^{-1} mm) at room temperature for 0.5 h to obtain 0.94 g (69% yield) of analytically pure $[(\eta^5-C_5H_5)W(NO)_2(PPh_3)]BF_4 \cdot 0.5CH_2Cl_2$.

Anal. Calcd for $C_{23.5}H_{21}N_2BClF_4O_2W$: C, 40.29; H, 3.02; N, 4.00. Found: C, 40.29; H,3.06; N,4.04. $IR(CH_2Cl_2)$: $\nu(NO)$ 1770 (s), 1694 (vs) cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 7.69 (m, 15H, C_6H_5), 6.54 (d,5H, C_5H_5 , ³J=1.2 Hz), 5.63 (s, 1H, CH_2Cl_2). Mp (in air) 170° dec.

A similar sequence of operations involving P(OPh)₃ in place of PPh₃ afforded $[(\eta^5-C_5H_5)W(NO)_2{P(OPh)_3}]BF_4$ as a lime-green solid in 82% yield.

Anal. Calcd for $C_{23}H_{20}N_{2}BF_{4}O_{5}PW$: C, 39.13; H,2.86; N, 3.97. Found: C, 39.26; H, 2.90; N, 3.89. $IR(CH_{2}Cl_{2})$: $\nu(NO)$ 1786 (s), 1711 (vs) cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 7.53 (m, 15H, $C_{6}H_{5}$), 6.40 (d, 5H, $C_{5}H_{5}$, ³J 1.0 Hz). Mp (in air) 135° dec.

When a CH_2Cl_2 (5 mL) solution of cyclooctene (2.00 mL, 1.69 g, 15.4 mmol) was employed in place of the CH_2Cl_2 solution of PPh₃ in the above procedure, a blue-green solution resulted. The addition of Et_2O (60 mL) to this solution induced the crystallization of 0.37 g (37% yield) of bright green $[(\eta^5-C_5H_5)W(NO)_2(\eta^2-C_8H_{14})]BF_4$ which was isolated in the manner decribed above.

Anal. Calcd for C₁₃H₁₉N₂BF₄O₂W: C, 30.86; H, 3.78; N,

13

5.54. Found: C,30.46; H, 3.64; N, 5.48. $IR(CH_2Cl_2)$: $\nu(NO)$ 1785 (s), 1704 (vs) cm⁻¹. IR(Nujol mull): $\nu(NO)$ 1776 (s), 1674 (vs) cm⁻¹; $\nu(BF)$ 1050 (s,br) cm⁻¹. Mp 104° dec.

Reaction of $[(\eta^5-C_5H_5)W(NO)_2(\eta^2-C_8H_{14})]BF_4$ with P(OPh)₃

То dark а green suspension of $[(\eta^5 - C_5 H_5)W(NO)_2(\eta^2 - C_8 H_{14})]BF_4$ (0.29 g, 0.58 mmol) in CH₂Cl₂ (40 mL) was added neat P(OPh)₃ (1.00 mL, 1.18 g, 3.82 mmol). The reaction mixture was stirred for 1 h, whereupon the solid slowly dissolved and the colour of the solution changed to light green. Hexanes (40 mL) were then added, and the resulting suspension was filtered through a column of Celite (3 x 5 cm). The filtrate was slowly concentrated . under reduced pressure to induce the precipitation of lime-green $[(\eta^{5}-C_{5}H_{5})W(NO)_{2}{P(OPh)_{3}}]BF_{\mu}$ (0.28 g, 67% yield) which was identified by its characteristic physical properties (vide supra).

Reaction of $(\eta^5-C_5H_5)W(NO)_2BF_4$ with Ph_2CCH_2

The CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to a colourless CH_2Cl_2 (10 mL) solution of 1,1-diphenylethene (4.00 mL, 4.12 g, 22.8 mmol). Initially, the reaction mixture became bright blue-green in colour, but while it was stirred at room temperature for 18 h, the colour lightened and a red-brown precipitate formed. The final mixture was filtered through a 3 x 5 cm column of Florisil supported on a medium-porosity frit. Removal of solvent from the colourless filtrate under reduced pressure left a viscous syrup. Crystallization of this material from light $(30-60^{\circ})$ petroleum ether afforded a white solid (26% yield based on Ph₂CCH₂) which was identified as 1,1,3,-triphenyl-3-indan by its characteristic spectral properties [33].

¹H NMR (CDCl₃): δ 7.4-7.0 (m, 19H, C₆H₅), 3.45 (AB q, 2H, J=12 Hz, CH₂), 1.80 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 150.4, 149.2, 148.7, 147.3, 129.1-124.3, 61.22, 60.85, 51.07, 28.79. Low-resolution mass spectrum (probe temperature 90°): m/z 360 (P⁺), 345 ([P-Me]⁺), 283([P-Ph]⁺).

Reaction of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ with $H_2CC(CH_3)CH(CH_3)_2$

The CH_2Cl_2 solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ was treated with 10.0 mL (6.80 q, 80.8 mmol) of neat 2,3-dimethyl-1-butene. Initially, the reaction mixture acquired a blue-green colour which gradually faded over the course of 18 h as a red-brown solid deposited. The final mixture was filtered through a short (3 x 3 cm) column of Florisil to obtain a colourless filtrate. Fractional distillation of the filtrate afforded three fractions: (1) CH_2Cl_2 as the major component of the mixture (40-41°), (2) a second, volatile fraction (ca. 2 mL, bp 48 °), and (3) a small amount of an involatile tar which was not investigated further. ¹H NMR [(CDCl₃): δ 5.27 (s, 1H, CH₂Cl₂), 1.64 (s, 22H, $(CH_3)_2C=C(CH_3)_2$ and gas chromatographic analysis of

the second fraction indicated that it was ca. 4:1 mixture of 2,3-dimethyl-2-butene and dichloromethane.

Polymerization of Phenylethyne

 CH_2Cl_2 solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ was added to The a colourless solution of phenylethyne (1.31 mL, 1.02 g, 10.0 mmol) in 5 mL of CH₂Cl₂. The mixture immediately became green-brown in colour. It was stirred at room temperature for 30 min before being filtered through a 3 x 4 cm column alumina (Woelm neutral, activity grade 1) supported on a of medium-porosity frit. The red-brown filtrate was concentrated to ca. 5 mL and then diluted with 50 mL of methanol. This precipitated an auburn-coloured solid which collected by filtration to yield 0.87 g (85%) of was poly(phenylethyne). It was identified as the trans-cisoidal polymer by its solubility in benzene and by a single, broad and unresolved resonance (ca. δ 7.2) in the ¹H NMR [34].

Condensation of Phenylethyne and 2,3-Dimethyl-2-butene

One half of the $(\eta^5-C_5H_5)W(NO)_2BF_4$ solution was filtered into a precooled (-10°) solution of phenylethyne (1.10 mL, 1.02 g, 10.0 mmol), 2,3-dimethyl-2-butene (1.19 mL, 0.842 g, 10.0 mmol) and CH_2Cl_2 (5 mL). The resulting green solution was stirred for 2 min at -10° before being quickly filtered through a short $(2 \times 4 \text{ cm})$ column of alumina supported on a medium-porosity frit. Volatile

components were removed from the filtrate under reduced pressure at room temperature to leave 1-phenyl-3,3,4,4,-tetramethylcyclobutene (1.36 g, 73% yield) as an oil.

¹H NMR (CDCl₃): ca. 7.3 (m, 5H, C_6H_5), 6.28 (s, 1H, vinyl H), 1.30 (s, 6H, CH₃). Low-resolution mass spectrum (probe temperature 110°): m/z, 186 (P⁺), 171 ([P-Me]⁺), 156 ([P-2Me]⁺), 143([P-2Me-CH]⁺), 128([P-3Me-CH]⁺), 91(C₇H₇⁺).

Attempted Cycloaddition of Phenylethyne and 2,3-Dimethyl-2-butene in Acetonitrile

A CH_2Cl_2 (10 mL) solution containing approximately 1 mmol of $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ was added to a mixture of phenylethyne (1.10 mL, 10.0 mmol), 2,3-dimethyl-2-butene (1.19 mL, 10.0 mmol), acetonitrile (0.53 mL, 0.42 g, 10.1 mmol) and CH₂Cl₂ (5 mL). The green solution was stirred at room temperature for 15 h. At the end of that time, a solution infrared spectrum revealed $[(\eta^5-C_5H_5)W(NO)_2(CH_3CN)]BF_4$ [25] to be the only nitrosylcontaining ($\nu(NO)$: 1770 and 1690 cm⁻¹) species present. The reaction mixture was filtered through alumina and volatiles were removed from the filtrate under reduced pressure. The involatile residue proved to be only unreacted PhCCH.

Further Reaction of Phenylethyne and 2,3-Dimethyl-2-butene A solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ (ca. 1 mmol) in 10 mL

of CH_2Cl_2 was added to a CH_2Cl_2 (5 mL) solution of phenylethyne (0.55 mL, 5.0 mmol) and 2,3-dimethyl-2-butene (6.18 mL, 50.0 mmol). The mixture was stirred at room temperature for 30 min before being filtered through a column (3 x 4 cm) of alumina. Volatile components were removed from the filtrate in vacuo to leave a yellow oil. ¹H NMR spectroscopy revealed the characteristic resonances of 1-phenyl-3,3,4,4-tetramethylcyclobutene in addition to some other unassignable phenyl and methyl resonances. A low-resolution mass spectrum displayed the fragmentation pattern of the cyclobutene as well as peaks at m/z values of 270 and 255.

Attempted Condensation of Phenylethyne and Cyclohexene

A CH_2Cl_2 (10 mL) solution approximately 0.1 M in $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to a mixture of phenylethyne (0.55 mL, 5.0 mmol) and cyclohexene (5.1 mL, 4.1 g, 50 mmol) diluted with 5 mL of dichloromethane. The mixture was stirred at room temperature for 30 min before being filtered through a short column of alumina. Removal of volatile components from the filtrate left a viscous oil.

¹H NMR (CDCl₃): ca. 7.3 (br m, 5H,), ca. 1.7 (br m, 10H). Low-resolution mass spectrum (probe temperature 100°): m/z 368, 286, 105, 91, 78.

Reaction of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with Ph₃CBr

The CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to a colourless CH_2Cl_2 (10 mL) solution of Ph_3CBr (0.64 g, 2.0 mmol) whereupon the reaction mixture immediately became olive-green in colour. Solvent was removed in vacuo, the resulting residue was extracted with diethyl ether (3 x 40 mL), and the combined extracts were filtered through a Florisil column (3 x 3 cm) to obtain a bright green filtrate. Hexanes (100 mL) were added to the filtrate, and the resulting solution was slowly concentrated under reduced pressure to induce the crystallization of 0.30 g (33% yield) of bright green ($\eta^5-C_5H_5$)W(NO)_2Br [35] which was collected by filtration.

Anal. Calcd for $C_5H_5N_2BrO_2W$: C, 15.44; H, 1.30; N,7.20. Found: C, 15.44; H, 1.38; N, 7.12. $IR(CH_2Cl_2)$: $\nu(NO)$ 1737 (s), 1656 (vs) cm^{-1} . ¹H NMR (CDCl₃): δ 6.17 (s). Low-resolution mass spectrum (probe temperature 80°): m/z388,390 (P⁺), 358,360 ([P-NO]⁺).

Reaction of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with [PPN]Br

The CH_2Cl_2 solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ was added to a colourless solution of [PPN]Br (1.25 g, 2.0 mmol) in CH_2Cl_2 (5 mL). The resulting green solution was stirred briefly at room temperature before being treated with Et_2O (75 mL). This operation resulted in the precipitation of most of the [PPN]BF₄ by-product as a white solid which was

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removed by filtration. Solvent was removed from the filtrate solid was redissolved in a in vacuo, and the remaining minimum amount of CH_2Cl_2 (5 mL). This solution was transferred by syringe onto the top of a Florisil column (3 x 4 cm) made up in CH_2Cl_2 . Elution of the column with CH_2Cl_2 resulted in the development of a single, green band which The eluate was concentrated under reduced was collected. pressure to 20 mL before being diluted with hexanes (40 mL). Further concentration of this solution led to the crystallization of $(\eta^5 - C_5 H_5) W(NO)_2 Br (0.51 q, 58\% yield)$ as a bright green solid (vide supra).

Reaction of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with [PPN]BH₄

The CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to a colourless solution of [PPN]BH₄ (1.16 g, 2.00 mmol) [36] in CH_2Cl_2 (5 mL) at -78°. The resulting green solution was permitted to warm to room temperature while being stirred. Volatile components were removed from the final reaction mixture in vacuo to leave a solid residue which was extracted with Et_2O (3 x 20 mL). The extracts were taken to dryness under reduced pressure to obtain 0.35 g (56% yield) of a green solid which was identified as $(\eta^5-C_5H_5)W(NO)_2H$ by comparison with an authentic sample [25].

IR (CH_2Cl_2) : $\nu(NO)$ 1718 (s), 1632 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 6.00 (s, 5H, C₅H₅), 2.07 (s, 1H, WH).

Reaction of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with Na[BPh₄]

The CH_2Cl_2 solution of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ was added to a suspension of $Na[BPh_4]$ (0.69 g, 2.0 mmol) in CH_2Cl_2 (35 mL). The resulting mixture was stirred at room temperature for 1 h, during which time it developed a red-brown colouration. The final mixture was filtered through a short (3 x 6 cm) column of alumina supported on a medium-porosity frit. The bright green filtrate was taken to dryness in vacuo to obtain 0.38 g (48% yield) of a bright green solid which was readily identified as $(\eta^5 - C_5H_5)W(NO)_2Ph$ by its characteristic spectroscopic properties [22].

IR (CH_2Cl_2) : $\nu(NO)$ 1720 (s), 1634 (vs) cm⁻¹. ¹H NMR (C₆D₆): δ 7.42 (m, 5H, C₆H₅), 5.06 (s, 5H, C₅H₅). Low-resolution mass spectrum (probe temperature 80°): m/z 386 (P⁺), 356 ([P-NO]⁺), 326 ([P-2NO]⁺).

Reaction of $(\eta^5-C_5H_5)W(NO)_2BF_4$ with $(C_2H_5)_3A1$

The CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to 1 mL of a 25% by weight, colourless solution of $(C_2H_5)_3Al$ in toluene maintained at -78°. Immediately, the mixture became red-brown in colour. It was stirred at -78° for 5 min before being allowed to warm to room temperature. The final mixture was then filtered through a column (3 x 6 cm) of alumina supported on a medium-porosity frit to obtain a bright green filtrate. Removal of solvent from this filtrate under reduced pressure produced a viscous green oil. Sublimation of this residue (40°, 5 x 10^{-3} mm) onto a water-cooled probe afforded 0.11 g (16% yield) of $(\eta^5-C_5H_5)W(NO)_2C_2H_5$ as an analytically pure, crystalline, green solid.

Anal. Calcd for $C_7H_{10}N_2O_2W$: C, 24.87; H, 2.98; N, 8.29. Found: C,25.05; H, 2.97; N, 8.31. IR (CH_2Cl_2) : $\nu(NO)$ 1707 (s), 1619 (vs) cm⁻¹. ¹H NMR (C_6D_6) : δ 4.98 (s, 5H, C_5H_5), 1.96 (m, 5H, C_2H_5). Low-resolution mass spectrum (probe temperature 55°): m/z 338 (P⁺), 308 ([P-NO]⁺), 278 ([P-2NO]⁺).

Preparation of (PhCH₂)₄Sn

solution of benzyl chloride (1.73 mL, 2.53 q, 20.0 Α mmol) in THF was added to a mixture of magnesium turnings (1.00 q, 41.1 mmol) and THF (100 mL). The mixture was stirred for 2 h without being allowed to warm above room temperature. At the end of this time, it was treated with a THF (15 mL) solution of $(PhCH_2)_3SnCl$ (4.27 g, 10.0 mmol) [37], and the resulting mixture was stirred at reflux for 18 h before being hydrolyzed with cold, deionized water (50 mL). The organic phase was separated and dried over anhydrous CaCl₂ before the solvent was removed from it in vacuo. The remaining colourless syrup was crystallized from light $(30-60^{\circ})$ petroleum ether at -78° to obtain pure $(PhCH_2)_4Sn$ (2.33 g, 48% yield) as a white solid.

Anal. Calcd for $C_{28}H_{28}Sn$: C, 69.60; H, 5.84. Found: C,69.75; H, 5.91. ¹H NMR (CDCl₃): δ 7.24-7.05 (m, 20H,

C₆H₅), 2.21 (s, 8H, CH₂). Mp 42°.

Reaction of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with $(PhCH_2)_4 Sn_5$

The CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ was added to a colourless solution of $(PhCH_2)_4Sn (0.96 \text{ g}, 2.0 \text{ mmol})$ in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 90 min during which time a brown precipitate formed and the colour of the supernatant solution became olive-green. The final mixture was filtered through a 3 x 4 cm column of Florisil to obtain an olive-green filtrate. The addition of hexanes (50 mL) to the filtrate and slow concentration under reduced pressure induced the crystallization of 0.14 g (18% yield) of $(\eta^5-C_5H_5)W(NO)_2CH_2Ph$ as a green solid which was collected by filtration.

Anal. Calcd for $C_{12}H_{12}N_2O_2W$: C, 36.02; H, 3.02; N, 7.00. Found: C, 36.68; H, 3.11; N, 6.75. $IR(CH_2Cl_2)$: $\nu(NO)$ 1714 (s), 1626 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 7.30-7.07 (m, 5H, C_6H_5), 5.81 (s, 5H, C_5H_5), 3.17 (s, 2H, CH₂). Low-resolution mass spectrum (probe temperature 75°): m/z 400 (P⁺), 370 ([P-NO]⁺), 340 ([P-2NO]⁺), 91 ($C_7H_7^+$).

Preparation of $(\eta^5 - C_5 H_5) W(NO)_2 OSO_2 C_6 H_4 CH_3$

Solid $(\eta^5-C_5H_5)W(NO)_2Cl$ (0.69 g, 2.0 mmol) was added to a slurry of silver p-toluenesulfonate (0.56 g, 2.0 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 3 h during which time its physical appearance did not change. The final mixture was filtered through a short (3 x 4 cm) column of Celite supported on a medium-porosity frit. Concentration of the filtrate in vacuo resulted in the formation of a green solid which was collected by filtration, washed with hexanes (3 x 10 mL), and dried (5 x 10^{-3} mm). The powdery solid was readily identified as $(\eta^{5}-C_{5}H_{5})W(NO)_{2}OSO_{2}C_{6}H_{4}CH_{3}$ (0.67 g, 70% yield) by comparison of its IR, ¹H NMR, and mass spectra with those displayed by an authentic sample prepared previously [25].

IR (CH_2Cl_2) : $\nu(NO)$ 1737 (s), 1650 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 7.41 (m, 4H, C₆H₄), 6.15 (s, 5H, C₅H₅), 2.70 (s, CH₃). Low-resolution mass spectrum (probe temperature 165 °): m/z 480 (P⁺).

Preparation of $(\eta^5 - C_5 Me_5) W(NO)_2 Cl$

rapidly stirred, orange solution То а of $(\eta^{5}-C_{5}Me_{5})W(CO)_{2}NO$ (4.68 g, 11.6 mmol) [38] in $CH_{2}Cl_{2}$ at -78° was added dropwise a CH₂Cl₂ solution of ClNO (containing 2.0 g of ClNO in 30 mL of CH_2Cl_2 [39]). Gas evolution occurred, and the reaction mixture darkened in colour. The progress of the reaction was monitored by IR spectroscopy, and the ClNO was added until the carbonyl absorptions due to the organometallic reactant had disappeared. The final reaction mixture was then permitted to warm to room temperature before being concentrated in vacuo to approximately 10 mL. This solution was transferred

via syringe onto the top of a 3 x 5 cm column of Florisil made up in CH_2Cl_2 . Elution of the column with CH_2Cl_2 produced a green band which was collected. Addition of hexanes (100 mL) to the eluate, followed by slow concentration under reduced pressure, afforded 2.48 g (52% yield) of the green crystalline product which was collected by filtration.

Anal. Calcd for $C_{10}H_{25}N_2ClO_2W$: C, 28.97; H, 3.64; N, 6.76. Found: C, 28.97; H, 3.70; N,6.68. $IR(CH_2Cl_2)$: $\nu(NO)$ 1705 (s), 1625 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 2.03 (s). Low-resolution mass spectrum (probe temperature 95°): m/z 414 (P⁺). Mp 188°.

Preparation of $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}H$

Α green toluene (25 mL) solution containing $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}Cl$ (0.73 g, 1.76 mmol) at -78° was treated with a colourless toluene dropwise solution of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (0.6 mL of a 70% toluene solution diluted to 10 mL). No change in the appearance of the reaction mixture was immediately apparent. After all of the aluminum reagent had been added, the mixture was stirred for 30 min to ensure complete reaction. At the end of that time, and without being warmed to room temperature, the final reaction mixture was quickly filtered through a column of Florisil (3 x 5 cm) supported on a medium-porosity frit. The filtrate was taken to dryness in vacuo, and the resulting

residue was crystallized from hexanes to obtain $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}H$ as well-formed, green crystals (0.42 g, 63% yield).

Anal. Calcd for $C_{10}H_{16}N_2O_2W$: C, 31.60; H, 4.24; N, 7.39. Found: C, 31.36; H, 4.27; N, 7.24. IR(hexanes): ν (WH) 1894 (w) cm⁻¹; ν (NO) 1704 (s), 1626 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 3.17 (s, 1H, W-H), 2.17 (s, 15H, C₅(CH₃)₅). Low-resolution mass spectrum (probe temperature 35°): m/z 380 (P⁺). Mp 77° (dec).

Preparation of $[(\eta^5 - C_5 Me_5)W(NO)_2(PPh_3)]BF_4$

<u>Method A.</u> Solid AgBF₄ (0.20 g, 1.0 mmol) was added to a stirred green solution of $(\eta^5-C_5Me_5)W(NO)_2Cl$ (0.42 g, 1.0 mmol) in CH₂Cl₂ (20 mL). A flocculent white precipitate formed while the reaction mixture was stirred for 30 min. The final mixture was filtered into a a CH₂Cl₂ (5 mL) solution of PPh₃ (0.27 g, 1.0 mmol) to obtain a green solution. Hexanes (25 mL) were added, and the solution was slowly concentrated under reduced pressure to induce the crystallization of $[(\eta^5-C_5Me_5)W(NO)_2(PPh_3)]BF_4$ as a green solid (0.46 g, 63% yield).

<u>Method B.</u> To a stirred green solution of $(\eta^5-C_5Me_5)W(NO)_2H$ (0.38 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added solid Ph_3CBF_4 (0.33 g, 1.0 mmol). The resulting solution was stirred for ca. 15 min, whereupon PPh₃ (0.27 g, 1.0 mmol) was added. The subsequent addition of hexanes (15
mL) and slow concentration of the final solution in vacuo led to the precipitation of 0.61 g (84% yield) of the product complex.

Anal. Calcd for $C_{28}H_{30}N_{2}BF_{4}O_{2}PW$: C, 46.18; H, 4.15; N, 3.85. Found: C, 45.73; H, 4.21; H, 3.77. $IR(CH_{2}Cl_{2})$: $\nu(NO)$ 1744 (s), 1673 (vs) cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 2.05 (d, 15H, $C_{5}(CH_{3})_{5}$, ⁴J=0.5 Hz), 7.72 (m, 15H, $C_{6}H_{5}$). Mp (in air) 144° dec.

Preparation of $(\eta^5 - C_5 Me_5) W(NO)_2 C_2 H_5$

solution of $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4}$ was generated from Α AgBF₄ (0.20 g, 1.0 mmol) and $(\eta^5 - C_5 Me_5)W(NO)_2Cl$ (0.41 g, 1.0 mmol) in CH₂Cl₂ (10 ML) (vide supra). This solution was added to a colourless solution of $(C_2H_5)_3Al$ (0.11 g, 1.0 mmol) in toluene (2 mL) at -78° . This operation resulted in formation a dark red solution which, upon warming to the temperature, gradually acquired room а green-brown colouration. The final mixture was filtered through an alumina column (3 x 6 cm), and the green filtrate was taken to dryness in vacuo. Sublimation of the oily residue (75°, 5 х 10^{-3} mm) onto a water-cooled probe afforded the product complex as a green solid (0.02 g, 5% yield).

Anal. Calcd for $C_{12}H_{20}N_2O_2W$: C, 35.31; H, 4.94; N, 6.86. Found: C, 35.31; H, 5.02; N, 6.68. IR(hexanes): ν (NO) 1685 (s), 1606 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 1.95 (s, 15H, $C_5(CH_3)_5$), 1.97 (q, 2H, CH₂, J=7.3 Hz), 1.27 (t, 3H, CH₃).

Low-resolution mass spectrum (probe temperature 55°): m/z408 (P⁺).

Preparation of $[(\eta^5 - C_5 H_5)W(NO)(\eta^3 - C_3 H_5)(NCCH_3)]BF_4$

An orange solution of $(\eta^5 - C_5 H_5) W(NO) (\eta^3 - C_3 H_5) I$ (2.0 q, 4.5 mmol) [40] in acetonitrile (100 mL) was treated with 0.89 g (4.5 mmol) of AgBF₄. The reaction mixture was stirred for 1 h, during which time the colour was bleached from the. supernatant liquid and an off-white precipitate formed. The precipitated solid was removed by filtration of the mixture through Celite (3 x 3 cm), and the filtrate was taken to in vacuo. Recrystallization of the remaining solid dryness from CH₂Cl₂-Et₂O provided 0.75 (87% yield) q of $[(\eta^5 - C_5H_5)W(NO)(\eta^3 - C_3H_5)(NCCH_3)]BF_{\mu}$ as a pale yellow powder.

Anal. Calcd for $C_{10}H_{13}N_2BF_4OW$: C, 26.82; H,2.93; N, 6.25. Found: C,26.64; H, 2.86; N, 6.06. IR(Nujol mull): ν (CN) 2301, 2326 cm⁻¹; ν (NO) 1640 cm⁻¹. ¹H NMR of major isomer(CD₃CN): δ 6.17 (s, 5H, C₅H₅), 6.17 (m, 1H, H₂₁), 4.18 (d, 1H, H₃₁, J₃₁₋₂₃ 12.9 Hz), 3.97 (d of d, 1H, H₃₂, J₃₂₋₂₁ 7.3 Hz), 2.73-2.52 (m, 2H, H₁₁, H₁₂), 1.96 (s, free acetonitrile) [41] Mp 157° dec.

Preparation of $(\eta^5 - C_5H_5)W(NO)(\eta^3 - C_3H_5)Cl$

To a pale yellow acetonitrile (50 mL) solution of $[(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)(NCCH_3)]BF_4$ (generated from 3.98 mmol of $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)I$ in the manner described

above) was added an excess of solid KCl (1.00 g, 13.4 mmol). The resulting suspension was stirred at room temperature for 15 h, the colour of the solution gradually intensifying. Volatiles were then removed from the final reaction mixture in vacuo, and the remaining residue was extracted into 3 x 10 mL of CH_2Cl_2 . The combined extracts were filtered through a 3 x 4 cm column of Celite supported on a medium-porosity frit. Hexanes (30 mL) were added to the filtrate, and the solution was slowly concentrated under reduced pressure. These manipulations resulted in the crystallization of $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)Cl (1.17 g, 83\% yield)$ as a pale orange solid.

Anal. Calcd for $C_8H_{10}NClOW$: C, 27.03; H, 2.84; N, 3.94. Found: C, 26.91; H, 2.83; N, 3.90. $IR(CH_2Cl_2:) \nu(NO)$ 1630 cm^{-1} . ¹H NMR (CDCl_3): δ ca. 6.29 (m, 1H, H₂₁), 5.99 (s, 5H, C_5H_5), 4.67 (d, 1H, H₃₁, $J_{31_21}=14.2$ Hz), 3.84 (d of d, 1H, H_{32} , $J_{32_221}=6.9$ Hz, $J_{32_212}=3.8$ Hz), 2.45 (d of d of d, 1H, H_{12} , $J_{1221}=6.4$ Hz, $J_{12_211}=2.9$ Hz), 2.12 (d of d, 1H, H₁₁, $J_{11_21}=9.0$ Hz). Low-resolution mass spectrum (probe temperature 110°): m/z 355 (P⁺), 325 (P-NO⁺). Mp 149° dec.

Preparation of $(\eta^5 - C_5H_5)W(NO)(\eta^3 - C_3H_5)Br$

This compound was prepared by a route analogous to that descrbed for chloro complex in the preceeding section.

Anal. Calcd for $C_8H_{10}NBrOW$: C, 24.03; H, 2.52; N,3.41. Found: C, 23.88; H,2.46; N, 3.41. $IR(CH_2Cl_2)$: $\nu(NO)$ 1634

cm⁻¹. Low-resolution mass spectrum (probe temperature 105°): m/z 401 (P⁺), 371 ([P-NO]⁺).

Results and Discussion

I) Preparation of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$. When a dichloromethane solution of $(\eta^5 - C_5 H_5) W(NO)_2 Cl$ is treated with an equimolar amount of AgBF₄, a precipitate of AgCl rapidly forms. The chloride-abstraction reaction which occurs, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}Cl + AgBF_{4} \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + AgCl$ (1)

is complete in 20 min at room temperature as monitored by solution IR spectroscopy. The nitrosyl-stretching 1733 and 1650 cm⁻¹ characteristic of the absorptions at organometallic reagent diminish in intensity and are replaced by new bands at 1754 and 1674 cm⁻¹ which can be assigned as the $\nu(NO)$'s of $(\eta^5 - C_5H_5)W(NO)_2BF_4$. [When reaction 1 is effected in CD_2Cl_2 , its progress can easily be monitored by 'H NMR spectroscopy, the cyclopentadienyl proton resonance of $(\eta^5 - C_5 H_5) W(NO)_2 Cl$ at δ 6.16 being replaced cleanly by a new singlet at slightly lower field (δ 6.27).] relatively facile manner in which this The transformation proceeds is noteworthy. The related reactions between $(\eta^5 - C_5 H_5) Fe(CO)_2 X$ (X = Br or I) and Ag(I) salts are slower and proceed in a stepwise fashion [42,43], e.q.,

$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}I + 0.5 AgBF_{4}$

(2)

$$0.5 [{(\eta^5 - C_5 H_5) Fe(CO)_2}_2 I]BF_4 + 0.5 AgI$$

0.5 AgBF₄ $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}BF_{4} + 0.5 AgI,$

the second step not occurring until the first is completed. The isoelectronic chromium nitrosyl analogue of the intermediate halide-bridged, bimetallic cation has also recently been synthesized in a similar manner [44], i.e.,

$$(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Cl + [(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}(SO_{2})]AsF_{6} \longrightarrow SO_{2} + [{(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}}_{2}Cl]AsF_{6}.$$
 (3)

However, spectroscopic monitoring of the progress of reaction 1 provides no evidence for even the transient formation of $[{(\eta^5-C_5H_5)W(NO)_2}_2C1]BF_4$ during this conversion.

Removal by filtration of the AgCl byproduct formed in reaction 1 produces a bright green, CH_2Cl_2 solution of the desired organometallic product which fumes profusely when

exposed to the atmosphere. Regrettably, this solution is also thermally unstable, depositing only insoluble decomposition products when maintained under an atmosphere of prepurified nitrogen at room temperature. Consequently, $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ cannot be isolated in the solid state to determine its exact identity. Nevertheless, given what is currently known about such related complexes as $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}FPF_{5}$ [45], $(\eta^{5}-C_{5}H_{5})W(CO)_{3}Y$ (Y = FBF₃ or FPF₅) [46], and $(\eta^5 - C_5 H_5)$ Fe(CO)₂FBF₃ [43], it is likely that the complex possesses the BF_{μ}^{-} anion weakly ligated in a monodentate fashion. Alternatively, $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ may discrete ion exist in CH₂Cl₂ as pairs with the coordinatively unsaturated organometallic cation possibly incorporating a molecule of solvent into the metal's coordination sphere. In any event, the characteristic chemistry of the compound in CH_2Cl_2 is dominated by its electrophilic nature, and during its reactions with various nucleophiles it behaves as though it were the formally 16-electron $[(\eta^{5}-C_{5}H_{5})W(NO)_{2}]^{+}$.

II) The characteristic chemistry of $(\eta^5 - C_5H_5)W(NO)_2BF_4$. (a) Reaction with strong Lewis bases. Not surprisingly, $(\eta^5 - C_5H_5)W(NO)_2BF_4$ readily forms adducts with good donor ligands as in Equation 4 where L = triphenylphosphine or triphenylphosphite).

$$(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + L \longrightarrow [(\eta^{5}-C_{5}H_{5})W(NO)_{2}L]BF_{4}$$
 (4)

The resulting salts are isolable in good yields. The organometallic cations obtained from reaction 4 have been previously prepared as their PF₆ salts by substitution of the carbonyl ligand in $[(\eta^5-C_5H_5)W(NO)_2(CO)]PF_6$ [35]. The physical properties of the BF₄ salts are generally indistinguishable from those of their PF6 analogues. Thus, $\left[\left(\eta^{5}-C_{5}H_{5}\right)W(NO)_{2}(PPh_{3})\right]BF_{4}$ spectra of IR and $[(\eta^5 - C_5 H_5)W(NO)_2 \{P(OPh)_3\}]BF_4$ in $CH_2 Cl_2$ display strong nitrosyl-stretching absorptions at 1770, 1694 and 1786, 1711 cm⁻¹, respectively, which are some 40-60 cm⁻¹ higher in energy than those exhibited by $(\eta^5 - C_5 H_5) W(NO)_2 Cl$ in the same solvent. Significantly, they are also some 20-30 cm⁻¹ higher in energy than the $\nu(NO)$'s of $(\eta^5 - C_5H_5)W(NO)_2BF_4$. This fact is not consistent with the latter undergoing dissociation in CH_2Cl_2 to form discrete or even solvated, $[(\eta^5-C_5H_5)W(NO)_2]^+$ cations. Such an inference is based, of course, solely on the anticipated amount of electron density available on the metal centre for back-donation to the NO ligands in the various complexes and takes no account of any geometrical differences between them. The ¹H NMR spectra of the BF " ¯ complexes in d₆-acetone display the expected features.

(b) Reactions with olefins and acetylenes. The introduction of an excess of cyclooctene into a CH_2Cl_2

33 ..

solution of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ results in the establishment of an equilibrium, i.e.,

$$(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + C_{8}H_{14} \leq [(\eta^{5}-C_{5}H_{5})W(NO)_{2}(\eta^{2}-C_{8}H_{14})]BF_{4}, (5)$$

which can be disturbed by the addition of Et₂O to induce the precipitation of the new alkenedinitrosyl product in 37% yield. The product is a bright green, crystalline solid which is thermally stable, but unlike the phosphine and derivatives discussed above must be handled phosphite exclusively in an atmosphere completely free of moisture and oxygen. It is insoluble in nonpolar organic solvents such as but sparingly hexanes benzene, soluble in or spectral properties dichloromethane. The of $[(\eta^5 - C_5H_5)W(NO)_2(\eta^2 - C_8H_{14})]BF_4$ are consistent with the organometallic cation having the "piano-stool" molecular structure



Thus an IR spectrum of the complex as a Nujol mull exhibits two strong absorptions at 1776 and 1674 cm⁻¹ attributable to the terminal nitrosyl ligands. Furthermore, there is a broad, strong band at 1050 cm⁻¹ characteristic of a tetrahedral BF₄ anion.

¹H NMR spectrum of $[(\eta^5 - C_5H_5)W(NO)_2(\eta^2 - C_8H_{14})]BF_4$ The in CD_2Cl_2 (Figure 1) confirms the equilibrium nature of reaction 5. The two cyclopentadienyl proton resonances at δ 6.39 and 6.27 of relative intensity 2:1 can be assigned to $[(\eta^{5}-C_{5}H_{5})W(NO)_{2}(\eta^{2}-C_{8}H_{1})]BF_{\mu}$ and $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{\mu}$, respectively. The multiplet at δ 5.65 is due to the vinyl protons of free cyclooctene and has an integrated area 2/5 that of the signal at δ 6.27. By analogy, the broad, unresolved multiplet at δ 5.93 which is 2/5 as intense as the resonance at δ 6.39 can be assigned as the vinyl protons of coordinated $C_{8}H_{14}$. [The remaining signals between δ 2.61 and 1.41 are attributable to the ring methylene protons of both free and complexed cyclooctene.] The shift of the vinyl proton signals to lower field on complexation of C_8H_{14} to $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ is exactly opposite to what is customarily observed when olefins coordinate to transition metals [47] (cf. $(\eta^5 - C_5 H_5) Cr(CO)(NO)(\eta^2 - C_8 H_{14})$ [48]). Within the confines of the generally accepted Dewar-Chatt-Duncanson model for olefin-metal bonding [49], it is tempting to indicating deshielding as diminished interpret this π -back-bonding from W to the $\eta^2 - C_8 H_{1.4}$ ligand.

Figure 1. The 80-MHz ¹H NMR spectrum of $[(\eta^5-C_5H_5)W(NO)_2(\eta^2-C_8H_{14})]BF_4$ in CD_2Cl_2* .



This view that the $C_8H_{14}-W$ σ -bonding is the principal contributor to the metal-olefin bonding is supported by the fact that the linkage is relatively weak, being readily cleaved by Lewis bases capable of better σ -donation than cyclooctene. Thus, when a small mount of d₆-acetone is added to the CD₂Cl₂ solution of the complex, the only ¹H NMR signals which persist are those due to free C₈H₁₄ and a singlet at δ 6.47 probably due to the C₅H₅ protons of [(η^5 -C₅H₅)W(NO)₂{(CD₃)₂CO}]BF₄. In a similar manner, the conversion

$$[(\eta^{5}-C_{5}H_{5})W(NO)_{2}(\eta^{2}-C_{8}H_{14})]BF_{4} + P(OPh)_{3} \longrightarrow [(\eta^{5}-C_{5}H_{5})W(NO)_{2}\{P(OPh)_{3}\}]BF_{4} + C_{8}H_{14} (6)$$

affords the familiar phosphite complex in good yield.

In view of the various factors which influence the stability of transition-metal-alkene complexes [50], it was originally anticipated that it would be possible to stable $[(\eta^5-C_5H_5)W(NO)_2(\eta^2-olefin)]BF_{\mu}$ synthesize more by simply replacing C_8H_{14} in reaction 5 with complexes ethene, propene, cis-2-butene olefins such as etc. Unfortunately, such has not proven to be the case. Even though the CH_2Cl_2 solutions of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ do develop blue-green colouration when treated with olefinic а substrates, the decomposition of the organometallic reactant is not significantly diminished. Consequently, attention was

turned to ascertaining the eventual fate of the organic substrates.

Some olefins, such as allylbenzene, simply do not react with $(\eta^5-C_5H_5)W(NO)_2BF_4$ and can be recovered unchanged from the final reaction mixture. Others, however, do undergo interesting transformations. For example, 1,1-diphenylethene undergoes a clean (but not efficient) "dimerization", i.e.,



The initiation step of this conversion probably involves formation of a tungsten-alkene complex which then localizes the positive charge on an alkene carbon thereby rendering it susceptible to nucleophilic attack by another molecule of olefin, i.e.,



2,3-Dimethyl-1-butene, on the other hand, undergoes a rapid double-bond isomerization, i.e.,



a fact that again provides evidence for the ability of $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ to generate incipient carbocations. In this connection, it can be noted that the electrophilicity of the related $[W(NO)_{2}(CH_{3}CN)_{4}]^{2+}$ (from which $(\eta^{5}-C_{5}H_{5})W(NO)_{2}$ may be considered, at least in a formal sense, to be derived) has recently been exploited by Sen and Thomas [33] during catalysis of similar polymerization, oligomerization and rearrangement reactions of various olefins.

It thus appears that in order to form an adduct with $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ via reaction 5, olefin an must simultaneously satisfy two criteria, namely (1) it must be capable of functioning as a reasonably strong σ -electron donor (considering both steric and electronic effects), and it must not readily undergo electrophile-induced (2)transformations. The only olefin that has met these criteria cyclooctene. Interestingly, the recently to date is described $[(\eta^5 - C_5H_5)Co(NO)(\eta^2 - C_8H_{14})]PF_6$ is also the only olefin-containing complex in its class of compounds[51].

In light of the $(\eta^5-C_5H_5)W(NO)_2BF_4$ -induced reactions of

alkenes and the fact that alkynes usually react more readily with transition metal complexes than do alkenes [52], the ready reaction of $(\eta^5-C_5H_5)W(NO)_2BF_4$ with acetylenes is to be expected. Indeed, introduction of $(\eta^5-C_5H_5)W(NO)_2BF_4$ into a CH_2Cl_2 solution of phenylacetylene results in rapid polymerization, i.e.,

The solubility of the polymer in benzene, combined with its ¹H NMR spectrum suggest that the polymer is the trans-cisoidal stereoisomer, i.e., [34]



Not surprisingly, this polymer is of the same geometry as that obtained from other cationic initiators such as TiCl₄ [34]. However, this polymerization contrasts with the reactivity of PhCCH in the presence of other organometallic electrophiles. When phenylethyne is reacted with

 $[(\eta^5-C_5H_5)Mo(CO)_2(PPh_3)]BF_4$ a stable complex is isolated [53], i.e.,

 $[(\eta^{5}-C_{5}H_{5})MO(CO)_{2}(PPh_{3})]BF_{4} + PhCCH - CO + [(\eta^{5}-C_{5}H_{5})MO(CO)(PPh_{3})(PhCCH)]BF_{4}. (11)$

When the substrate is reacted with $[(\eta^5-C_5H_5)Fe(CO)_2(C_4H_8)]BF_4$, 2-phenylnaphthalene is inefficiently produced [54], i.e.,



As with the reaction of 1,1-diphenylethene, the polymerization of PhCCH probably proceeds via a complex where the positive charge is localized on the ligand yielding a metallovinyl cation, i.e.



If such a species is formed it should be possible to trap it with other nucleophiles such as alkenes. This is indeed the case as $(\eta^5-C_5H_5)W(NO)_2BF_4$ catalyzes a rapid cycloaddition reaction between phenylethyne and 2,3-dimethyl-2-butene to yield 3,3,4,4-tetramethyl-1-phenylcyclobutene , i.e.,



This product (Figure 2) could easily be obtained via an intermediate metallovinyl cation, e.g.,



Thus, a reaction which is forbidden on orbital symmetry grounds [55] is allowed to proceed via an ionic intermediate

Figure 2. The 80-MHz ¹H NMR spectrum of 3,3,4,4-tetramethyl-1-phenylcyclobutene in CDCl₃.



56,57].

There are several examples in the literature of reactions related to equation 12. Snider has thoroughly investigated the aluminum halide catalyzed reactions between alkenes and alkynoic esters [58]. For example, the reactions between methyl propynoate and 1.2-disubstituted ethenes give stereospecific cycloaddition, e.g.,



However, 1,1-disubstituted, trisubstituted and tetrasubstituted ethenes give exclusively ene adducts, e.g.,



The $(\eta^5-C_5H_5)Fe(CO)_2$ cation also catalyzes the formation of cyclobutenes and dienes from alkenes and propynoic esters [59]. However, the reaction is strongly dependent on the structure of the olefinic reactant; 1,1-disubstituted and tetrasubstituted alkenes yield only lactones.



A vinyl cation is presumably formed in the reaction of 1-bromo-1-(4-methoxyphenyl)propene with 2-butene in the presence of AgBF₄ [60], i.e.,



Finally, $C_2H_5AlCl_2$ catalyzes the [2+2] cycloaddition of alkenes with 1-alkynes [61], e.g.,



It was found that dialkylsubstituted alkynes give polymeric products or trimerize to hexaalkylbenzenes. Trimerization to 1,3,5,-trialkylbenzenes also occurs as a side reaction with 1-alkynes. In addition, further reaction leads to bicyclo[2.2.0]hexenes.

Similar behaviour to this latter reaction is observed

in the $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ system. If the reaction mixture is allowed to warm to room temperature and stirred for 30 min, products other than 1-phenyl-3,3,4,4,-tetramethylcyclobutene are obtained. Several new methyl resonances are observed in ¹H NMR spectrum. In the the mass spectrum, peaks are observed at m/z values indicative of addition of another phenylethyne unit to the initial product. Conversely, all activity of the $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ catalyst system is quenched by the addition of acetonitrile. This presumably coordinates to the metal and prevents the coordination of phenylethyne. Indeed, an infrared spectrum of the reaction mixture reveals that the only nitrosyl-containing species is $[(\eta^{5}-C_{5}H_{5})W(NO)_{2}(CH_{3}CN)]BF_{\mu}.$

Attempts to generalize the $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ -catalyzed cycloaddition reactions to other substrates have not been rewarding. When phenylethyne is replaced by phenylpropyne, trimethyl(phenylethynyl)silane, methyl proynoate, dimethyl acetylenedicarboxylate, or 1-hexyne, no [2+2] cycloadducts are formed. Unfortunately, reaction 12 may be unique to phenylethyne. This could be rationalized by the stability of the intermediate carbocation. Restrictions on the alkene substrate appear to be less severe. The fact that the reaction proceeds readily with a tetrasubstituted reactant indicates that steric constraints are not overly demanding. fact, the methyl groups probably aid the reaction by In promoting the nucleophilicity of the alkene. Cyclohexene

also reacts with phenylethyne in the presence of $(\eta^5-C_5H_5)W(NO)_2BF_4$. However, the reaction proceeds less readily. Under the same conditions as equation 12, no reaction occurs. However, when the mixture is warmed to room temperature for a period of time, all of the phenylethyne is consumed. A lack of vinyl proton resonances in the ¹H NMR spectrum suggests that the isolated product is not the expected bicyclo[4.2.0]octene, i.e.,



In addition, the mass spectrum shows that the parent mass is double that which is expected. These observations suggest that reaction 19 does take place but is followed by an addition reaction that couples two of the product molecules.



(d) Reactions with anionic nucleophiles. If reaction 1 is attempted with the silver salt of a coordinating anion such as p-toluenesulfonate, the anion becomes firmly bound to the tungsten centre, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}Cl + AgOSO_{2}C_{6}H_{4}CH_{3} \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}OSO_{2}C_{6}H_{4}CH_{3} + AqCl(s).$ (21)

(This organometallic product has been obtained previously by treatment of $(\eta^5 - C_5 H_5) W(NO)_2 H$ with a stoichiometric amount of anhydrous p-toluenesulfonic acid [25].) This binding of anion the by the metal centre suggests that $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ would be prone to nucleophilic attack by various anions. However, in order to exploit this reactivity successfully, it is mandatory that the desired reactions proceed promptly in CH_2Cl_2 so that the integrity of the nitrosyl-containing electrophile maintained. is This practical limitation thus excludes the use of anionic reagents which either react with CH₂Cl₂ or have insufficient solubility to permit rapid reaction with $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$. Fortunately, [PPN]⁺ salts are not hampered by either restriction.

As an unremarkable example of this type of chemistry, $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ reacts cleanly with [PPN]Br to yield the well-known $(\eta^{5}-C_{5}H_{5})W(NO)_{2}Br$ complex, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + [PPN]Br \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}Br + [PPN]BF_{4}.$ (22)

More significantly, treatment of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ with

[PPN]BH4 produces the corresponding metal hydride, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + [PPN]BH_{4} \longrightarrow [PPN]BF_{4} + "BH_{3}" + (\eta^{5}-C_{5}H_{5})W(NO)_{2}H, (23)$

The isolated yield of $(\eta^5 - C_5 H_5)W(NO)_2H$ from this reaction (56%) compares favourably with that previously reported from the reaction of Na[AlH₂(OCH₂CH₂OCH₃)₂] with $(\eta^5 - C_5 H_5)W(NO)_2Cl$ (i.e. 61%) and is considerably better than the yields obtained from the reactions of NaBH₄ (in THF) with $(\eta^5 - C_5 H_5)W(NO)_2Cl$ or $[(\eta^5 - C_5 H_5)W(NO)_2(CO)]PF_6$ (13% and 23% respectively) [25]. In fact, reaction 23 represents the cleanest and most convenient method for the synthesis of the hydridonitrosyl complex.

The affinity of $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$ for halide ion demonstrated by reaction 22 is also evident during its reaction with bromotriphenylmethane, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + Ph_{3}CBr \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}Br + [Ph_{3}C]BF_{4}.$ (24)

Hence, as far as Br^- is concerned, $(\eta^5 - C_5H_5)W(NO)_2^+$ is a more potent electrophile than Ph_3C^+ . In contrast, when H^- is the nucleophile involved, the reverse of reaction 24 occurs [28]. This pronounced affinity of $(\eta^5 - C_5H_5)W(NO)_2BF_4$ for halide ions may account for the fact that $[{(\eta^5-C_5H_5)W(NO)_2}_2Cl]BF_4$ is not detectable as an intermediate during the progress of reaction 1.

Of greater interest than these new synthetic routes leading to the $(\eta^5-C_5H_5)W(NO)_2X$ (X = H or Br) compounds was the possibility that $(\eta^5-C_5H_5)W(NO)_2BF_4$ might be utilized for the preparation of new alkyl or aryl derivatives of the type $(\eta^5-C_5H_5)W(NO)_2R$ (R = alkyl or aryl). Previous studies directed at the synthesis of these complexes [22] have established the following features:

(1) metathesis reactions between $(\eta^5-C_5H_5)W(NO)_2Cl$ and various RLi and RMgX reagents fail to yield even spectroscopically detectable quantities of $(\eta^5-C_5H_5)W(NO)_2R$. Evidently this is because the organolithium and Grignard reagents are too potent to selectively displace Cl⁻ and attack other functional groups as well [62].

(2) When the gentler and more selective R_3Al compounds are employed as the alkylating or arylating agents in place of RLi or RMgX, the transformations

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}Cl + R_{3}Al \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}R + ClAlR_{2} (25)$

are successful when $R = CH_3$ or Ph. However, unlike for the congeneric Cr and Mo complexes, reaction

25 is not generally applicable for the synthesis of a variety of $(\eta^5-C_5H_5)W(NO)_2R$ complexes. This fact is probably a reflection of the greater strength of the metal-chlorine bond in the tungsten reactant [26,63].

Fortunately, $(\eta^5 - C_5 H_5)W(NO)_2 BF_4$ is indeed sufficiently electrophilic to cleave a variety of main-group-metal to carbon bonds and so produce the desired alkyl and aryl derivatives.

In a manner analogous to reaction 25, the addition of an equimolar amount of $Na[BPh_4]$ to a CH_2Cl_2 solution of $(\eta^5-C_5H_5)W(NO)_2BF_4$ results in a clean transfer of a phenyl group from B to W, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + Na[BPh_{4}] \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}Ph + NaBF_{4} + BPh_{3}, (26)$

relatively rare mode of reactivity for an organoboron а complex [64]. The 48% isolated yield of $(\eta^5 - C_5 H_5) W(NO)_2 Ph$ from this conversion is comparable to that obtained from the reaction of $(\eta^5 - C_5 H_5) W(NO)_2 Cl$ and Ph₃Al [22]. Reaction 26 probably involves initial anion exchange followed by electrophilic aromatic substitution of BPh₃ by $(\eta^{5}-C_{5}H_{5})W(NO)_{2}$ as depicted in Scheme I. Certainly, the success of this transformation refects the mediating effect of BPh₃ since, as noted above, $(\eta^5 - C_5 H_5) W(NO)_2 Ph$ cannot be





where W = (η^5 -C₅H₅)W(NO)₂

prepared using nucleophilic carbanion sources such as PhLi. Furthermore, the fact that reaction 26 does occur also demonstates that $[BPh_4]^-$ may not always function as an innocent counterion during the attempted isolation of electrophilic organometallic cations.

The phenyl derivative of $(\eta^5-C_5H_5)W(NO)_2$ can also be prepared in moderate yield by employing Ph₄Sn, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + Ph_{4}Sn \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}Ph$ (27) + Ph_{3}SnBF_{4}.

This transformation is very similar to reaction 26 and indicates that this method of forming $(\eta^5-C_5H_5)W(NO)_2R$ complexes is general, limited only by the ready availability of the main-group-metal reagent. Consistent with this view is the fact that the analogous use of $(PhCH_2)_4Sn$ [65] affords the new benzyl derivative, i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + (PhCH_{2})_{4}Sn \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}CH_{2}Ph + (PhCH_{2})_{3}SnBF_{4}, (28)$

although the yield of this stable olive-green solid (18%) is lower than that of the phenyl complex obtained from reaction 27.

As discussed earlier, $(C_2H_5)_3Al$ does not react with $(\eta^5-C_5H_5)W(NO)_2Cl$. However, it reacts readily with

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ at -78° , i.e.,

 $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4} + (C_{2}H_{5})_{3}Al \longrightarrow (\eta^{5}-C_{5}H_{5})W(NO)_{2}C_{2}H_{5} + \{(C_{2}H_{5})_{2}AlBF_{4}\}, (29)$

the new tungsten-ethyl complex being isolable in 16% yield from the final reaction mixture. [The fate of the aluminum has not been ascertained.] This conversion is remarkable because both of the reactants are Lewis acids. The new $(\eta^{5}-C_{5}H_{5})W(NO)_{2}R$ (R = $C_{2}H_{5}$ or $CH_{2}Ph$) complexes exhibit physical properties that are similar to those of the methyl analogue. These green solids are very soluble in organic solvents (including hexanes), and they may be exposed to air for short periods of time without undergoing noticeable decomposition. Without doubt, the failure to prepare these complexes by other preparative routes cannot be attributed to their inherent instability but rather must be ascribed to the unsuitability of the previous synthetic methodology. The IR spectra of all the $(\eta^5 - C_5 H_5) W(NO)_2 X$ complexes in $CH_2 Cl_2$ display two strong absorptions assignable to terminal nitrosyl ligands. The frequencies of these absorptions decrease in the order X = Cl > Ph H > CH_2Ph > C_2H_5 which reflects the diminishing ability of these ligands to withdraw electron density from the central metal.

III) The related chemistry of $(\eta^5 - C_5 Me_5)W(NO)_2 BF_4$. It is

possible to extend this chemistry to encompass some of the pentamethylcyclopentadienyl analogues of the complexes discussed in the previous sections. The new precursor complexes required for this portion of the study can be prepared by straightforward extensions of standard procedures [32, 25], i.e.,

 $(\eta^{5}-C_{5}Me_{5})W(CO)_{2}NO + CINO \longrightarrow (\eta^{5}-C_{5}Me_{5})W(NO)_{2}Cl + 2 CO (30)$ and

 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}Cl + Na[AlH_{2}(OCH_{2}CH_{2}OCH_{3})_{2}]$ $\rightarrow (\eta^{5}-C_{5}Me_{5})W(NO)_{2}H (31),$

and their physical properties resemble those of the C_5H_5 analogues. Interestingly, CH_2Cl_2 solutions of $(\eta^5-C_5Me_5)W(NO)_2BF_4$ can be generated from either of these two compounds, i.e.,

 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}Cl + AgBF_{4} \longrightarrow (\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4} + AgCl (32)$

 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}H + Ph_{3}CBF_{4} \longrightarrow (\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4} + PhC_{3}H.$ (33)

Reaction 32 is, of course, the direct analogue of reaction 1, but reaction 33 has no precedent in the C_5H_5 system.

[Indeed, treatment of $(\eta^5 - C_5 H_5) W(NO)_2 H$ with Ph₃CBF₄ in CH₂Cl₂ results in the precipitation of $[(\eta^5-C_5H_5)_2W_2(NO)_4H]BF_4$ which is immune to further reaction with Ph₃CBF₄ in this solvent [28].) The IR spectrum of $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4}$ in CH₂Cl₂ displays nitrosyl absorptions at 1730 and 1645 cm⁻¹ which are some 20-30 cm⁻¹ lower in energy than those exhibited by its cyclopentadienyl analogue. This feature simply reflects the fact that the C_5Me_5 ligand is a better electron donor than the C_5H_5 ligand. Consequently, it can be reasonably anticipated that $(\eta^5 - C_5 Me_5) W(NO)_2 BF_4$ may well be somewhat weaker а electrophile than $(\eta^5 - C_5 H_5) W(NO)_2 BF_4$. Nevertheless, it readily forms adducts with PPh₃, i.e.,

$$(\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4} + PPh_{3} \longrightarrow [(\eta^{5}-C_{5}Me_{5})W(NO)_{2}(PPh_{3})]BF_{4}, (34)$$

the product being obtainable in 63% yield. On the other hand, the 5% yield of the new ethyl complex, $(\eta^5-C_5Me_5)W(NO)_2C_2H_5$ from the conversion

 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}BF_{4} + (C_{2}H_{5})_{3}Al \longrightarrow (\eta^{5}-C_{5}Me_{5})W(NO)_{2}C_{2}H_{5} + \{(C_{2}H_{5})_{2}AlBF_{4}\}$ (35)

is even less appealing than that of its C_5H_5 analogue from reaction 29.

IV) The chemistry of some related allyl complexes. The compouds $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)X$ (X = halide) are formally derived from $(\eta^5-C_5H_5)W(NO)_2X$ by replacement of a linear nitrosyl ligand by a trihapto allyl ligand. Halide ion abstraction by Ag(I) salts is also a useful synthetic route to new derivatives in this class of compounds. Thus, the previously prepared $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)I$ [40] reacts with AgBF₄ in acetonitrile solution, i.e.,

$$(\eta^{5}-C_{5}H_{5})W(NO)(\eta^{3}-C_{3}H_{5})I + AgBF_{4} - AgI + [(\eta^{5}-C_{5}H_{5})W(NO)(\eta^{3}-C_{3}H_{5})(CH_{3}CN)]BF_{4}.$$
 (36)

The molybdenum congener of this stable, yellow salt has been obtained via an analogous reaction [66]. The acetonitrile ligand in this new tungsten complex can be easily replaced by halide ions, i.e.,

$$[(\eta^{5}-C_{5}H_{5})W(NO)(\eta^{3}-C_{3}H_{5})(CH_{3}CN)]BF_{4} + KX - > KBF_{4} + (\eta^{5}-C_{5}H_{5})W(NO)(\eta^{3}-C_{3}H_{5})X (37) X = Cl or Br$$

The 'H NMR spectra of these three new complexes indicate that their allyl ligands display the same σ, π^- distortion crystallographically verified for $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)I[40]$. For example, the ¹H NMR specrum of $(\eta^5-C_5H_5)W(NO)(\eta^3-C_3H_5)Cl$ clearly shows the

Figure 3. The 80 MHz ¹H NMR spectrum of

 $(\eta^{5}-C_{5}H_{5})W(NO)(\eta^{3}-C_{3}H_{5})Cl$ in CDCl₃*.


CHAPTER THREE

THE EFFECT OF NITROSYL LIGANDS ON METAL-CARBON. σ BONDS

The work described in the previous chapter attempted to answer some questions regarding the reactivity of alkenes and alkynes bonded to the $(\eta^5-C_5H_5)W(NO)_2^+$ functional group. This chapter summarizes the attempts to study the reactivity of alkyl ligands in congeneric systems, i.e., can the $(\eta^5-C_5H_5)M(NO)_2$ (M = Cr, Mo or W) functional groups influence the reactivity of metal-alkyl bonds?

One of the most common reactions of metal-carbon σ -bonds is cleavage by electrophiles. Cleavage reactions of metal-alkyl bonds generally fall into two classes [52], insertion-like,

M-R + E ----> M-E-R and eliminative,

M-R + E ----> RE + M.

With regard to the second process, it is intriguing that the transmetallation reaction

 $(\eta^{5}-C_{5}H_{5})M(LO)_{2}CH_{3} + HgCl_{2} - CH_{3}HgCl$

+ $(\eta^5 - C_5 H_5) M(LO)_2 Cl$ (38)

proceeds much more readily when M = Cr and L = N than when M = Fe and L = C [67]. This has been rationalized by formal charge arguments. Since the nitrosyl complex contains Cr(0) and the carbonyl complex contains Fe(II), the nitrosyl complex should be more susceptible to electrophilic attack. Mindful of the caveat in Chapter One, further investigation of this phenomenom seemed warranted. Therefore, a study has been made of the reactions of some alkylnitrosyl complexes with such typical electrophiles as mercuric chloride, triand diphenylcarbenium ions as well as aluminum trichloride.

Experimental Section

Reaction of $(\eta^5 - C_5 H_5) Mo(CO)_3 C_2 H_5$ with HgCl₂

To a yellow solution of $(\eta^5-C_5H_5)Mo(CO)_3C_2H_5$ [68] (0.35 g, 1.3 mmol) in THF (25 mL) was added solid HgCl₂ (0.35 g,1.3 mmol). The mixture was stirred at room temperature for 4.5 h during which time a tan-coloured solid precipitated from the orange supernatant solution. At the end of that time, the reaction mixture was taken to dryness in vacuo. The residue was extracted into a small (ca. 5 mL) amount of CH_2Cl_2 , and the resulting extract was transferred to the top of a 3 x 6 cm column of Florisil. Elution with CH_2Cl_2 developed a bright-orange fraction that was collected. Addition of hexanes to the eluate, followed by slow reduced-pressure concentration led to the crystallization of $(\eta^5-C_5H_5)Mo(CO)_3Cl$ [68]. The orange solid was collected by

filtration in 28% yield (0.10 g).

Anal. Calcd for $C_8H_5O_3ClMo$: C, 34.25; H, 1.80; O, 17.11. Found: C, 34.00; H, 1.72; O, 17.16. $IR(CH_2Cl_2)$: $\nu(CO)$ 2050, 1971 cm⁻¹. ¹H NMR (CDCl₃): δ 5.65 (s). Low-resolution mass specrum (probe no heating): m/z 282 (P⁺), 254 ([P-CO]⁺), 226 ([P-2CO]⁺), 198 ([P-3CO]⁺), 163 ([P-3CO-Cl]⁺).

Reaction of $(\eta^5 - C_5 H_5) MO(NO)_2 CH_3$ with HgCl₂

A green solution of $(\eta^5 - C_5 H_5) Mo(NO)_2 CH_3$ [22] (0.47 q, 2.0 mmol) in THF (25 mL) was treated with solid HgCl₂ (0.57 g, 2.2 mmol). The reaction mixture was stirred at room temperature for 2.5 h before the solvent was removed in vacuo. The green residue was dissolved in 4 mL benzene and the resulting solution was syringed onto the top of a 2 x 15 cm column of Florisil. Elution with benzene slowly developed green band which was collected. Removal of the a wide solvent under reduced pressure, followed by recrystallization from dichloromethane/hexanes left a light-green solid which was identified as a mixture of $(\eta^{5}-C_{5}H_{5})MO(NO)_{2}Cl^{2}$ [32] and CH₃HgCl.

IR(CH₂Cl₂): ν (NO) 1759 (s), 1666 (vs) cm⁻¹. ¹H NMR: δ 6.09 (s, C₅H₅), 1.13 (s, CH₃).

Reaction of $(\eta^5 - C_5 H_5) Cr(NO)_2 CH_3$ with Ph₃CPF₆

Solid Ph_3CPF_6 (0.78 g, 2.0 mmol) was added to a

stirred, green solution of $(\eta^5-C_5H_5)Cr(NO)_2CH_3$ [22] (0.34 g, 2.0 mmol). The colour of the solution immediately changed to golden-brown. An infrared spectrum of the solution displayed nitrosyl-stretching absorptions at ca. 1740 and ca. 1840 cm⁻¹. The mixture was filtered through a short (3 x 3 cm) column of alumina to leave a colourless filtrate. Removal of solvent in vacuo left 0.16 g (31% yield) of Ph₃CCH₃.

¹H NMR (CDCl₃): δ 7.3-7.1 (m, 15H, C₆H₅), 2.19 (s, 3H, CH₃). Low-resolution mass spectrum (probe no heating): m/z 258 (P⁺), 243 [(P-CH₃)⁺].

Reaction of $(\eta^5 - C_5 H_5) Mo(NO)_2 CH_3$ with PhC₃PF₆

A bright green solution of $(\eta^5 - C_5 H_5) MO(NO)_2 CH_3$ [22] (0.12 g, 0.50 mmol) in CH_2Cl_2 (7 mL) was treated with an equimolar amount of Ph_3CPF_6 (0.20 g). The reaction mixture was stirred at room temperature for ca. 1 h and its colour changed to olive-green. At the end of that time, an IR spectrum of the solution revealed complete consumption of the starting material and the presence of a new species with ν (NO)'s at ca. 1770 and ca. 1680 cm⁻¹. Addition of PPh₃ (0.13 g, 0.50 mmol) caused the colour of the solution to change back to bright green. The somewhat cloudy reaction mixture was filtered through a medium-porosity frit and diethyl ether (30 mL) was added to the filtrate to precipitate a green solid which was collected by filtration washed with ether. The solid was identified as the and

dichloromethane solvate of $[(\eta^5-C_5H_5)Mo(NO)_2(PPh_3)]PF_6$ [35] (0.21 g, 66% yield). [IR (CH₂Cl₂): $\nu(NO)$ 1792 (s), 1710 (vs) cm⁻¹. ¹H NMR (d⁶-acetone): δ 7.7-7.5 (m, 15H, C₆H₅), 6.40 (d, 5H, C₅H₅, J=1.2 Hz), 5.62 (s, 0.6H, CH₂Cl₂)] The slightly-green-coloured filtrate was taken to dryness. The residue was extracted into light petroleum ether to yield a colourless solution which, when evaporated to dryness, gave a white solid which was identified as Ph₃CCH₃ (0.09 g, 67% yield) by its characteristic physical properties (vide supra).

Reaction of $(\eta^5 - C_5 H_5) Cr(NO)_2 CH_3$ with Ph₂CHCl

To a slurry of anhydrous $ZnCl_2$ (0.136 g, 1.00 mmol) in CH_2Cl_2 (25 mL) was added $(\eta^5 - C_5H_5)Cr(NO)_2CH_3$ (0.19 g, 1.0 mmol) and neat Ph_2CHCl (0.18 mL, 0.21 g, 1.1 mmol). The mixture was stirred at room temperature for 2 h during which time the colour of the supernatant solution changed from green to golden-brown. At the end of that time, the suspension was filtered through a 2 x 4 cm column of Florisil supported on а medium-porosity frit. The golden-brown filtrate was concentrated in vacuo to ca. 10 mL, 30 mL of hexanes were added and the concentration was continued until $(\eta^5 - C_5 H_5) Cr(NO)_2 Cl$ (0.14 g, 66% yield) precipitated. After the organometallic product was collected by filtration, removal of the solvent from the filtrate left Ph₂CHCH₃ as an involatile liquid.

¹H NMR (CDCl₃): δ 7.23 (s, 10H, C₆H₅), 4.14 (q, 1H, J=7.3 Hz, CH), 1.62 (d, 2H, CH₃).

Reaction of $(\eta^5 - C_5 H_5) MO(NO)_2 C_2 H_5$ with Ph₃CPF₆

A green solution of $(\eta^{5}-C_{5}H_{5})MO(NO)_{2}C_{2}H_{5}$ [22] (0.47 g, 1.9 mmol) in 25 mL of CH_2Cl_2 was treated with 0.72 q (1.9 mmol) of Ph₃CPF₆. After being stirred for 5 min at room temperature, an IR spectrum of the olive-green solution showed complete consumption of the starting material and the presence nitrosyl-containing species of new а with nitrosyl-stetching absorptions at ca. 1680 and ca. 1770 cm⁻¹. Triphenylphosphine (0.49 g, 1.9 mmol) was added to the reaction mixture. Subsequent addition of hexanes (25 mL) caused the precipitation of a light-green solid which was · collected filtration identified by and as $[(\eta^5-C_5H_5)MO(NO)_2PPh_3]PF_6$ (0.84 g, 75% yield). The filtrate taken to dryness under reduced pressure to leave 0.37 g was (80% yield) of Ph_3CH .

¹H NMR (CDCl₃): 7.4-7.1 (m,15H, C₆H₅), 5.59 (s,1H, CH).

Reaction of $(\eta^5 - C_5 H_5) Cr(NO)_2 CH_3$ with AlCl₃

A dichloromethane (30 mL) solution of $(\eta^5-C_5H_5)Cr(NO)_2CH_3$ (0.37 g, 2.0 mmol) was treated with solid AlCl₃ (0.27 g, 2.0 mmol). The reaction mixture was stirred at room temperature for 2 h during which time its

colour changed from yellow-green to dark green and a light-green solid precipitated. The solid was removed by filtration and the filtrate was concentrated in vacuo to ca. 5 mL before being syringed onto the top of a 3 x 7 cm column of Florisil. Elution with CH_2Cl_2 developed a golden-brown band which was collected and concentrated under reduced pressure to approximately 25 mL. Addition of hexanes (25 mL), followed by slow concentration afforded golden platelets of $(\eta^5-C_5H_5)Cr(NO)_2Cl$ [32] (0.25 g, 60% yield).

IR (CH_2Cl_2) : $\nu(NO)$ 1816 (s), 1711 (vs) cm⁻¹. ¹H NMR (CDCl₃): 5.69 (s).

Results and Discussion

Although mercuric halide cleavage of the iron-carbon bond alkyl derivatives in the of dicarbonyl(η^{5} -cyclopentadienyl)iron has been well studied [67,69], the same is not true for electrophilic cleavage reactions of analogous nitrosyl complexes of chromium, molybdenum and tungsten. While $(\eta^5 - C_5 H_5) MO(CO)_3 CH_3$ is unreactive [70], $(\eta^5 - C_5 H_5) Mo(CO)_3 C_2 H_5$ reportedly yields only an "orange rather insoluble material" upon treatment with HqCl₂ [71]. It has now been found that, although а is formed during precipitate the reaction. $(\eta^{5}-C_{5}H_{5})MO(CO)_{3}Cl$ can easily be isolated from the reaction of $(\eta^5 - C_5 H_5) Mo(CO)_3 C_2 H_5$ with HgCl₂ in tetrahydrofuran, i.e.,

HgCl₂

 $(\eta^{5}-C_{5}H_{5})MO(CO)_{3}C_{2}H_{5} \longrightarrow (\eta^{5}-C_{5}H_{5})MO(CO)_{3}Cl.$

(39)

The relatively low yield from the reaction, as well as the lack of reactivity of the methyl analogue, suggests that the $(\eta^5-C_5H_5)Mo(CO)_3R$ complexes are less nucleophilic than the related dicarbonyl derivatives of iron. This appears to be an electronic, rather than a steric, effect since the substituted complexes $(\eta^5-C_5H_5)Mo(CO)_2(L)CH_3$ (L = PPh₃ or $P(C_4H_9)_3$) react cleanly with HgX₂ (X = Cl, Br, I or SCN) [70]. Presumably, the presence of the better donor ligands

than CO enhances reactivity towards electrophiles.

In light of the above, it is somewhat surprising that $(\eta^5 - C_5 H_5) MO(NO)_2 R$ (R = CH₃ or C₂H₅) react readily with HgCl₂. When a THF solution of $(\eta^5 - C_5H_5)MO(NO)_2CH_3$ is treated with the mercuric salt, the nitrosyl-stretching absorptions infrared spectrum of the reaction solution at 1728 in the and 1640 cm⁻¹ diminish in intensity over the course of 2.5 h and are replaced by a new set of absorptions at 1758 and cm⁻¹, 1665 the latter being characteristic of $(\eta^{5}-C_{5}H_{5})MO(NO)_{2}Cl$. This is confirmed by ¹H NMR spectroscopy which shows that $(\eta^5 - C_5 H_5) MO(NO)_2 Cl$ and $CH_3 HqCl$ are the only organometallic species present at the end of the reaction, i.e.,

$$(\eta^{5}-C_{5}H_{5})MO(NO)_{2}CH_{3} + HgCl_{2} ----> CH_{3}HgCl + (\eta^{5}-C_{5}H_{5})MO(NO)_{2}Cl . (40)$$

A possible explanation for the enhancement of metel-carbon bond reactivity in changing from $(\eta^5-C_5H_5)MO(CO)_3R$ to $(\eta^5-C_5H_5)MO(NO)_2R$ is that the nitrosyl complexes are more readily oxidized. The accepted mechanism for mercuric halide cleavage in the iron system requires attack of the electrophile at, and oxidation of, the metal centre [67,69]. [This is probably a result of the fact that alkyl complexes of the d'-d' transition metals have Highest Occupied Molecular Orbitals (HOMO's) that are metal-based

rather than metal-carbon σ -bond based. For example, for $(\eta^5-C_5H_5)MO(CO)_3CH_3$ [72], the energy separation between the HOMO and the metal-carbon σ -bonding orbital is approximately kJ/mol.] However, 124 the relative reactivities of $(\eta^5-C_5H_5)MO(CO)_3CH_3$ and $(\eta^5-C_5H_5)MO(NO)_2CH_3$ do not correlate with oxidation potential. Recorded under identical conditions [73], the cyclic voltammograms of both complexes display a single irreversible oxidation wave. The peak for the carbonyl complex occurs at +1.10 V (vs SCE) at а scan rate of 0.12 V sec⁻¹, whereas the peak for the nitrosyl complex is found at +1.67 V at 0.19 V sec⁻¹. The fact that the complex which is harder to oxidize reacts more readily with electrophiles suggests that the reaction does not via oxidation of proceed the metal. This leaves the possibility that the metal-carbon bond might be the site of electrophilic attack.

The reaction of transition metal methyl complexes with triphenylcarbenium salts is a useful synthetic strategy for the preparation of cationic methylene complexes. This has been successfully applied to synthesize methylene complexes from $(\eta^5 - C_5 H_5) W(CO)_2 (PPh_3) CH_3$ [74] and $(\eta^5-C_5H_5)Re(NO)(PPh_3)CH_3$ [75]. Furthermore, it has been suggested that the MR/Ph_3C^+ *a*-hydride abstraction reactions occur via initial electron transfer [76,77]. Since oxidation does not appear to be the dominant reaction mode in the chemistry of $(\eta^5 - C_5 H_5) MO(NO)_2 R$ with electrophiles, it seems

reasonable to anticipate that reactions of these substrates with Ph_3C^+ might resemble reactions of main group alkylmetals, such as $(CH_3)_4Sn$, with Ph_3C^+ , i.e., alkyl abstraction and formation of Ph_3CR [78]. This is indeed the case, $(\eta^5-C_5H_5)Mo(NO)_2CH_3$ reacting guickly with Ph_3CPF_6 to form Ph_3CCH_3 , i.e.,

$$(\eta^{5}-C_{5}H_{5})MO(NO)_{2}CH_{3} + Ph_{3}CPF_{6} \longrightarrow Ph_{3}CCH_{3} + (\eta^{5}-C_{5}H_{5})MO(NO)_{2}PF_{6}.$$
 (41)

The organometallic product is unisolable. However, spectral data ($\nu(NO)$: 1680 and 1770 cm⁻¹), trapping with PPh₃ (i.e.,

$$(\eta^{5}-C_{5}H_{5})MO(NO)_{2}PF_{6} + PPh_{3} \longrightarrow [(\eta^{5}-C_{5}H_{5})MO(NO)_{2}PPh_{3}]PF_{6}, (43)$$

as well as comparison with tungsten (Chapter Two) and chromium (Chapter Four) complexes suggest the formulation $(\eta^5-C_5H_5)MO(NO)_2PF_6$. In a reaction analogous to reaction 41, $(\eta^5-C_5H_5)Cr(NO)_2CH_3$ can be transformed to the known [45] $(\eta^5-C_5H_5)Cr(NO)_2PF_6$. The diphenylmethyl cation also cleaves the metal-methyl bond of $(\eta^5-C_5H_5)M(NO)_2CH_3$ (M= Cr or Mo) as both of these complexes react with chlorodiphenylmethane under zinc chloride catalysis, i.e.,

 $(\eta^5 - C_5 H_5) M(NO)_2 CH_3 + Ph_2 CHCl \longrightarrow Ph_2 CHCH_3 +$

$$(\eta^{5}-C_{5}H_{5})M(NO)_{2}C1$$
 . (43)

M = Cr or Mo

The reaction of $(\eta^5 - C_5 H_5) Mo(NO)_2 C_2 H_5$ with triarylcarbenium salts does not lead to metal-carbon bond cleavage. Instead, hydide abstraction occurs. The organometallic product can be efficiently trapped by coordination of PPh₃ to the metal centre, i.e.,

 $(\eta^{5}-C_{5}H_{5})MO(NO)_{2}C_{2}H_{5} + Ph_{3}CPF_{6} \longrightarrow Ph_{3}CH + C_{2}H_{4} + (\eta^{5}-C_{5}H_{5})MO(NO)_{2}PF_{6}.$ (44)

$$(\eta^{5}-C_{5}H_{5})MO(NO)_{2}PF_{6} + PPh_{3} \xrightarrow{\prime} [(\eta^{5}-C_{5}H_{5})MO(NO)_{2}PPh_{3}]PF_{6}$$

(45)

There is no evidence for formation of a phosphonium salt by coordination of the phosphine to an ethene ligand. This is not surprising in light of the previously discussed chemistry of $(\eta^{5}-C_{5}H_{5})W(NO)_{2}BF_{4}$ and alkenes.

It is known that Lewis acids such as AlBr₃ promote the insertion of CO into the metal-carbon bonds of alkylcarbonyl complexes [79], i.e.,



However, this strategy is not useful for inducing the insertion of NO into metal-carbon bonds, i.e.,

$LnM(NO)R \longrightarrow LnM-N(O)-R.$

Treatment of $(\eta^5 - C_5 H_5) M(NO)_2 CH_3$ (M= Cr, Mo or W) with aluminum trihalides invariably leads to demetallation, e.g.,

AlCl₃

$$(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}CH_{3} \longrightarrow (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Cl.$$

(47)

This is another demonstration of the ability of the nitrosyl ligands in these systems to enhance the nucleophilicity of metal-carbon σ -bonds making them more accessible to a range of electrophiles.

CHAPTER FOUR

PROTONATION VS. OXIDATIVE CLEAVAGE OF $[(\eta^5 - C_5H_5)Cr(NO)_2]_2$

The previous two chapters describe how the reactivity of alkyl, alkene and alkyne ligands are influenced by bonding to the $(\eta^5-C_5H_5)M(NO)_2$ (M= Cr, Mo or W) functional group. An extension of these studies might include an investigation of the reactivity of metal-metal bonds in the same environment. As mentioned in previous chapters, salts containing the bimetallic cations $[(\eta^5-C_5H_5)_2M_2(NO)_4H]^+$ (M= Mo or W) can be synthesized in good yields by treatment of the monomeric hydrides, $(\eta^{5} - C_{5}H_{5})M(NO)_{2}H$ (M Мо or W), with = hydride-abstracting carbocations in non-donor solvents [28], e.g.,

 $2(\eta^{5}-C_{5}H_{5})W(NO)_{2}H + Ph_{3}CBF_{4} \longrightarrow [(\eta^{5}-C_{5}H_{5})_{2}W_{2}(NO)_{4}H]BF_{4} + Ph_{3}CH. (48)$

Unlike related carbonyl complexes, the bimetallic cations are not deprotonated by a variety of bases to afford the as yet unknown $[(\eta^5-C_5H_5)M(NO)_2]_2$ (M = Mo or W) dimers. Instead, they are cleaved to the monomeric products

 $(\eta^{5}-C_{5}H_{5})M(NO)_{2}H$ and $[(\eta^{5}-C_{5}H_{5})M(NO)_{2}(B)]^{+}$ (B = base) by these reagents. In light of these observations, two questions to mind. (1) Can came the analogous $[(\eta^5 - C_5 H_5)_2 Cr_2 (NO)_4 H]^+$ cation be prepared by protonation of well-known dimer, $[(\eta^5-C_5H_5)Cr(NO)_2]_2$? (2) Is the the protonation of the chromium dimer a reversible process? Initial experiments in this regard indicated that both questions could be answered in the negative [28]. This chapter describes a more detailed investigation into the reaction of $[(\eta^5 - C_5 H_5)Cr(NO)_2]_2$ with HBF₄ which allows the above questions to be answered more fully. By way of comparison, the protonation of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ is also discussed. The combined results allow a qualitative assessment of the propensities of the two dimeric complexes to undergo either protonation or oxidative cleavage under these experimental conditions.

Experimental Section

Reaction of $[(\eta^5 - C_5H_5)Fe(CO)_2]_2$ with HBF₄.O(CH₃)₂

To a stirred, dark red-violet solution of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ (1.0 g, 2.8 mmol) in CH_2Cl_2 (30 mL) was added 13.6 M HBF₄.O(CH₃)₂ (0.48 mL, 6.5 mmol) whereupon the solution lightened in colour. The reaction mixture was stirred at ambient temperature for 30 min, and the final red solution was filtered through a short (2 x 3 cm) column of Celite. The volume of the filtrate was reduced to ca. 15 mL

in vacuo, and diethyl ether (40 mL) was then added. This resulted in the precipitation of 0.54 g (43% yield) of $[(\eta^5-C_5H_5)_2Fe_2(CO)_4H]BF_4$ as a red-violet, crystalline solid which was collected by filtration.

Anal. Calcd for $C_{14}H_{11}Fe_2O_4BF_4$: C, 38.07; H, 2.51. Found: C, 37.77; H, 2.52. $IR(CH_2Cl_2)$: $\nu(CO)$ 2068 (s), 2045 (s) cm^{-1} . ¹H NMR (CD_2Cl_2) : δ 5.32 (s, 10H, C_5H_5), -26.61 (s, 1H, Fe₂H).

Reaction of $[(\eta^5 - C_5 H_5)Cr(NO)_2]_2$ with HBF₄.O(CH₃)₂

A stirred, red-violet solution of $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ [22] (0.21 g, 0.60 mmol) in CH_2Cl_2 (25 mL) was treated with 13.6 M HBF₄.(OCH₃)₂ (0.09 mL, 1.2 mmol), whereupon the colour of the solution immediately changed to green-brown and a small amount of dark solid precipitated. An IR spectrum of the supernatant solution exhibited two strong, sharp absorptions at 1838 and 1728 cm⁻¹. The reaction mixture was then filtered through a column of Celite (2 x 3 cm), and the volume of the filtrate was reduced to ca. 10 mL. The nature of the organometallic products isolated from this dark green filtrate depended on the work-up procedures employed in the manner decribed below.

<u>Procedure A.</u> The dark green filtrate was taken to dryness in vacuo, and the resulting residue was extracted with H_2O (3 x 10 mL). A solution of NaBPh₄ (0.60 g, 1.7 mmol) in H_2O (15 mL) was slowly added to the extracts to

induce the formation of a finely-divided yellow precipitate. The solid was collected by filtration, washed with H_2O (3 x 10 mL), and dried in vacuo (5 x 10⁻³ mm Hg). Recrystallization of this solid from CH_2Cl_2 -hexanes produced 0.16 g (31% yield) of $(\eta^5-C_5H_5)Cr(NO)_2(OHBPh_3)$ as a fine green-brown powder.

Anal. Calcd for $C_{23}H_{21}CrN_2O_3B$: C, 63.33; H, 4.85; N, 6.42. Found: C, 63.23; H, 4.77; N, 6.37. IR(Nujol mull): $\nu(NO)$ 1813 (s), 1714 (vs) cm⁻¹. IR(CH₂Cl₂): $\nu(NO)$ 1823 (s), 1712 (vs) cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 7.51-7.04 (m, 15H, C₆H₅), 5.60 (s, 5H, C₅H₅), 3.13 (s, 1H, OH). Mp (in air) 104° dec.

Procedure B. The dark green filtrate was treated with solid [PPN]Br (0.76 q, 1.2 mmol), and the resulting mixture was stirred for 15 min. Volatile components were then under reduced pressure, and the removed residue was extracted with $(C_2H_5)_2O$ (3 x 15 mL). The combined, golden extracts were filtered through a short (2 x 3 cm) column of Florisil supported on a medium-porosity frit. The volume of filtrate was doubled by addition of hexanes. Slow the concentration of the resulting solution in vacuo induced the crystallization of 0.19 yield) q (63% of qolden $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Br$ which was identified by comparison of its spectroscopic properties with those of an authentic sample [86].

 $IR(CH_2Cl_2): \nu(NO) 1819 (s), 1713 (vs) cm^{-1}.$ ¹H NMR

 $(CDCl_3): \delta 5.75 (s, C_5H_5).$ Low-resolution mass spectrum (probe temperature 80°): m/z 256 (P⁺), 226 ([P-NO]⁺), 196 ([P-2NO]⁺), 131 ([P-2NO-C_5H_5]⁺), 117 ([P-2NO-Br]⁺).

Results and Discussion

I) $[(\eta^5-C_5H_5)Fe(CO)_2]_2$. In accordance with the published observations of other investigators concerning the behaviour of the iron dimer in strongly protic media [80,81,82] treatment of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ with $HBF_4.O(CH_3)_2$ in CH_2Cl_2 results in the clean formation of $[(\eta^5-C_5H_5)_2Fe_2(CO)_4H]BF_4$ which can be isolated in good yields, i.e.,

$$[(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}]_{2} + HBF_{4}.O(CH_{3})_{2} \longrightarrow [(\eta^{5}-C_{5}H_{5})_{2}Fe_{2}(CO)_{4}H]BF_{4} + O(CH_{3})_{2} (49)$$

The spectroscopic properties of this red-violet, air-sensitive complex $[IR(CH_2Cl_2): \nu(CO) 2068, 2045, 2008$ cm^{-1} . ¹H NMR $(CD_2Cl_2): \delta$ 5.32 (s, 10H, C₅H₅; -26.61 (s, 1H, Fe₂H)] are consistent with the bimetallic cation possessing, on average, the molecular structure



Its 'H NMR spectrum does not exclude the possibility that

the closed 3-centre-2-electron Fe-H-Fe linkage may well be bent in the instantaneous structures [83]. However, its IR spectrum does suggest that in solution the complex exists as a mixture of rotamers [82].

Reaction (49) is reversible, the $[(\eta^5-C_5H_5)_2Fe_2(CO)_4H]^+$ cation being converted to the parent neutral dimer by a variety of Lewis bases such as aqueous acetone [80] or $(C_2H_5)_3N$. This fact explains a previous report that solutions of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ are virtually unchanged by the addition of aqueous HBF₄. Furthermore, in light of reaction (49), it is clear why oxidations of the iron dimer in aqueous acetone to $[(\eta^5-C_5H_5)Fe(CO)_2L]^+$ (L = H₂O or η^2 -alkene) species require another oxidant in addition to . HBF₄ in order to be effected successfully [84,85].

II) $[(\eta^5 - C_5 H_5)Cr(NO)_2]_2$. The addition of HBF₄.O(CH₃)₂ to a red-violet CH_2Cl_2 solution of $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ results in an immediate reaction, as evidenced by the solution becoming green-brown. Monitoring of the progress of the conversion by IR spectroscopy reveals that the strong nitrosyl-stretching absorptions due to the reactant at 1667 1512 cm⁻¹ gradually diminish in intensity. and Concomitantly, new absorptions attributable to terminal nitrosyl ligands appear and grow at 1838 and 1728 cm^{-1} . After an equimolar amount of acid has been added, the reaction mixture appears to contain approximately equal

amounts of the reactant and the new nitrosyl- containing species. Addition of a further equivalent of acid consumes completely the remaining $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ and doubles the concentration of the new species.

Similar observations are made when the course of the reaction (in CD_3NO_2) is monitored by ¹H NMR spectroscopy. Again, complete consumption of the nitrosyl dimer requires two equivalents of acid, and the final reaction mixture contains predominantly one organometallic product. The spectrum of this mixture displays a singlet resonance in the region characteristic of $\eta^5-C_5H_5$ protons. However, the this resonance (δ 6.03) considerably position of is downfield from that characteristic of $[(\eta^5 - C_5H_5)Cr(NO)_2]_2$ (δ 4.89). This indicates that there is less electron density on the cyclopentadienyl ligand in the former species.

The observed stoichiometry of the reactants and the spectroscopic properties of the organometallic product are consistent with the occurrence of a simple oxidative cleavage reaction, i.e.,

 $\left[\left(\eta^{5}-C_{5}H_{5}\right)Cr(NO)_{2}\right]_{2} + 2 HBF_{4} \longrightarrow 2 \left(\eta^{5}-C_{5}H_{5}\right)Cr(NO)_{2}BF_{4} + H_{2} (50)$

Unfortunately, it has been impossible to isolate the $(\eta^5-C_5H_5)Cr(NO)_2BF_4$ product as such. This is not surprising given the observations described in previous chapters and

the recent report of $(\eta^5-C_5H_5)Cr(NO)_2PF_6$ which may be generated by the protonation of $(\eta^5-C_5H_5)Cr(NO)_2CH_3$ in CH₃NO₂ [45]. Completely analogously, it can be verified spectroscopically that treatment of the methyl precursor with HBF₄.O(CH₃)₂ in CH₂Cl₂ or CD₃NO₂ affords solutions of $(\eta^5-C_5H_5)Cr(NO)_2BF_4$.

The formulation of the organometallic product in reaction 50 is also supported by chemical evidence (summarized in Scheme II) which indicates that the BF₄ group is weakly ligated. For instance, solvent removal from CH_2Cl_2 or CH_3NO_2 solutions of $(\eta^5-C_5H_5)Cr(NO)_2BF_4$ produces a viscous, green oil. Dissolution of this oil in CH_3CN results in the clean formation of the previously prepared $[(\eta^5-C_5H_5)Cr(NO)_2(CH_3CN)]BF_4$, [88] i.e.,

$$(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}BF_{4} + CH_{3}CN \longrightarrow [(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}(CH_{3}CN)]BF_{4}.$$
 (51)

Furthermore, the addition of solid [PPN]Br to CH_2Cl_2 solutions of $(\eta^5-C_5H_5)Cr(NO)_2BF_4$ initiates the metathesis reaction

 $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}BF_{4} + [PPN]Br \longrightarrow (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Br + [PPN]BF_{4} (52)$



from which the well-known [87] $(\eta^5 - C_5 H_5) Cr(NO)_2 Br$ complex may be conveniently isolated in 63% yield.

Attempts to isolate $(\eta^5 - C_5 H_5)Cr(NO)_2BF_4$ from reaction 50 have afforded other new nitrosyl complexes of chromium [29]. Thus, addition of $(C_2H_5)_2O$ to the final reaction mixture does not result in the precipitation of $(\eta^5 - C_5H_5)Cr(NO)_2BF_4$ or even $[(\eta^5 - C_5H_5)Cr(NO)_2\{O(C_2H_5)_2\}]BF_4$ but rather results in the deposition in low yields of $[\{(\eta^5 - C_5H_5)Cr(NO)_2\}_2OH]BF_4$ as a dark green, microcrystalline solid [29].

Attempts to isolate the organometallic product of reaction 50 as its BPh_4^- salt by metathesis in aqueous solutions result instead in the formation of $(\eta^5-C_5H_5)Cr(NO)_2(OHBPh_3)$, i.e.,

 $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}BF_{4} + H_{2}O + BPh_{4}^{-} \longrightarrow PhH + BF_{4}^{-} + (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}(OHBPh_{3}), (53)_{2}$

the final organometallic complex being isolable in moderate yields. Conversion 53 probably proceeds via deprotonation of a coordinated aquo ligand in $[(\eta^5-C_5H_5)Cr(NO)_2(OH_2)]^+$ by BPh₄⁻ as one of its steps. It certainly does not involve heterolytic cleavage of preformed $[{(\eta^5-C_5H_5)Cr(NO)_2}_2OH]^+$ by BPh₄⁻, i.e.,

$$[\{(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}\}_{2}OH]^{+} + BPh_{4}^{-} - (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Ph + (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}(OHBPh_{3}), (54)$$

since it has been established independently [29] that these two reactants engage only in simple metathesis under these experimental conditions, i.e.,

$$[\{(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}\}_{2}OH]BF_{4} + NaBPh_{4} ----> NaBF_{4} + [\{(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}\}_{2}OH]BPh_{4}. (55)$$

The new complex, $(\eta^5-C_5H_5)Cr(NO)_2(OHBPh_3)$, resembles other $(\eta^5-C_5H_5)Cr(NO)_2X$ species which have been shown to have monomeric, three-legged piano-stool molecular structures [26]. It is a green-brown, air-stable solid whose IR spectra both in solution and the solid state display two strong absorptions at ca. 1818 and ca. 1713 cm⁻¹ due to terminal nitrosyl ligands. Furthermore, its ¹H NMR spectrum (in d⁶-acetone) consists of signals attributable to C₆H₅ (δ 7.51-7.04), C₅H₅ (δ 5.60), and OH (δ 3.13) protons, as expected for



which involves a relatively hard-hard Lewis acid-base interaction. However, this linkage is not particularly strong as evidenced by the fact that the 70 eV mass specrum of the complex displays only signals due to ions resulting from the fragmentation of the individual acid and base entities, the parent ion not being detectable.

These results verify that the two questions posed at the beginning of this chapter concerning the protonation of $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ can indeed be answered in the negative. In addition, this work indicates that the unidentified solid isolated previously [28] from CH_2Cl_2 solutions of $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ which had been treated with HBF₄ and HPF₆ does not correspond to any of the organometallic nitrosyl complexes of chromium described in this chapter. Possibly, the former species requires an excess of the acid to be present.

III) Protonation Versus Oxidative Cleavage. It is clear from the preceding results that the treatment of the $[(\eta^5-C_5H_5)M(LO)_2]_2$ (M = Cr or Fe; L = N or C) dimers with HBF₄.O(CH₃)₂ in CH₂Cl₂ results in different types of products. A possible explanation for these varied experimental observations is that entirely different reaction pathways are being followed during the conversions. For instance, one pathway might involve initial proton transfer (protonation), i.e.,

$$[(\eta^{5}-C_{5}H_{5})M(LO)_{2}]_{2} + H^{+} - [(\eta^{5}-C_{5}H_{5})M(LO)_{2}]_{2}H^{+}$$
(56)

whereas another might have electron transfer (oxidative cleavage) as the first step, i.e.,

$$\left[\left(\eta^{5}-C_{5}H_{5}\right)M(LO)_{2}\right]_{2} + 2H^{+} \xrightarrow{} 2 \left[\left(\eta^{5}-C_{5}H_{5}\right)M(LO)_{2}\right]^{+} + H_{2}.$$
(57)

In other words, it is possible that the different chemical behaviour of the organometallic dimers towards H⁺ may simply be а manifestation of their intrinsically different tendencies to undergo oxidation. This view seems to be supported at first glance by previously documented chemistry $[(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}]_{2}$ and $[(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}]_{2}$ of which indicates that the Cr-Cr bond in the chromium dimer is more readily cleaved by electrophiles. Thus, while the reaction

 $[(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}]_{2} + PbCl_{2} - 2 (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Cl + Pb (58)$

proceeds cleanly in refluxing tetrahydrofuran, the iron dimer apparently does not react with PbCl₂ [23]. In similar fashion, the chromium complex dehalogenates vicinal or benzylic organic halides whereas the iron compound does not [24]. Furthermore, $[(\eta^5-C_5H_5)Cr(NO)_2]_2$ is oxidized rapidly (10 min) by two equivalents of Ph₃CBF₄, i.e.,

$$[(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}]_{2} + 2 Ph_{3}CBF_{4} \longrightarrow 2 (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}BF_{4} + 2 \{Ph_{3}C\}, (59)$$

whereas when $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ in CH_2Cl_2 is treated with approximately three equivalents of Ph_3CBF_4 , the complex is only slowly consumed over the course of 45 h [89].

To gain some qualitative information about the redox properties of the reactant dimers, some electrochemical data been acquired [90]. Thus at a platinum bead electrode have with $(n-C_{\mu}H_{\eta})_{\mu}NPF_{\eta}$ supporting as the electrolyte, $[(\eta^5 - C_5 H_5)Fe(CO)_2]_2$ in CH_2Cl_2 exhibits a cyclic voltammogram having a high degree of reversibility with E(1/2) = +0.68 V(vs SCE) and a peak separation of 100 mV at a scan rate of sec⁻¹. 0.067 contrast, V In the isoelectronic $[(\eta^5 - C_5 H_5) Cr(NO)_2]_2$ is oxidized irreversibly under the same experimental conditions, E(pa) being +0.85 V at a scan rate of 0.077 V sec⁻¹. Although a direct comparison of E(1/2)values cannot be made, it is clear that the chromium complex undergoes oxidation at a more positive potential. In the context of the reactions being considered here, this indicates that if H⁺ is a sufficiently strong oxidant to oxidize $[(\eta^5 - C_5 H_5)Cr(NO)_2]_2$ in CH_2Cl_2 according to equation 57, then it should certainly be sufficiently potent to effect the same oxidative cleavage of $[(\eta^5 - C_5H_5)Fe(CO)_2]_2$.

The fact that the iron dimer is simply protonated instead (equation 56) suggests that viewing the reactions of the $[(\eta^5-C_5H_5)M(LO)_2]_2$ dimers with HBF₄.O(CH₃)₂ in CH₂Cl₂ as involving simple electron transfer is too simplistic.

On the basis of currently available data, another more unified rationale is possible. The first step consists of adduct formation to produce the cationic $[(\eta^5-C_5H_5)M(LO)_2]_2H^+$ species as summarized in equation 56. This adduct may prove to be sufficiently stable to be isolable (as in the case of M = Fe). Alternatively, the adduct may undergo unsymmetrical dissociation. For instance, in the case of M = Cr, such dissociation, i.e.,

 $[(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}]_{2}H^{+} \longrightarrow (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}^{+} + (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}H, (60)$

would afford the ultimate $(\eta^5 - C_5 H_5) Cr(NO)_2^+$ product and the neutral hydrido complex, $(\eta^5 - C_5 H_5) Cr(NO)_2 H$. However, this latter complex is thermally unstable [25] and can revert to the original dimeric reactant thus allowing sequential recycling of conversions 55 and 60. Alternatively, $(\eta^5 - C_5 H_5) Cr(NO)_2 H$ could simply be protonated in the manner previously observed for $(\eta^5 - C_5 H_5) W(NO)_2 H$ [28], i.e.,

 $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}H + H^{+} \longrightarrow (\eta^{5}-C_{5}H_{5})Cr(NO)_{2}^{+} + H_{2}.$ (61)

CHAPTER FIVE

EPILOGUE

The research described in Chapter Two has shown that the thermally unstable $(\eta^5 - C_5 H_5) W(NO)_2 BF_{\mu}$ is а versatile organometallic electrophile that can be employed for the synthesis of a variety of $(\eta^5 - C_5 H_5) W(NO)_2$ -containing compounds under appropriate experimental conditions. Furthermore, the characteristic reactivity of this complex with unsaturated organic substrates has established that its component $(\eta^5 - C_5 H_5) W(NO)_2^+$ entity is a Lewis acid with reactivity similar to AlCl₃. This reactivity is significantly different from that observed for similar transition metal complexes. The work described in Chapter Three has shown that stable $(\eta^5 - C_5 H_5) M(NO)_2 R$ (M = Mo or Cr) complexes are organometallic nucleophiles that react with both inorganic and organic electrophiles. Again, this reactivity seems closer to that displayed by complexes of the main group metals. The results in Chapter Four have shown significant differences in the reactivity of $[(\eta^{5}-C_{5}H_{5})M(LO)_{2}]_{2}$ (M = Cr or Fe, L = N or O) with electrophiles.

There must be some fundamental reasons which explain the chemical differences between organometallic nitrosyl complexes and their carbonyl analogues. Α complete discussion on the electronic structures of these complexes is far beyond the scope of this work. However, some of the compounds utilized in the previous chapters have been analyzed by Ultra-Violet Photoelectron Spectroscopy (UPS) [91]. In fact, some of the conclusions reached in that study are directly related to the experimental results described here. In particular, an attempt has been made to delineate the effect on the molecular electronic energies of replacing dicarbonyliron fragment by a dinitrosylchromium one. With а certain amount of trepidation, these results а are summarized below.

The $Fe(CO)_2$ to $Cr(NO)_2$ perturbation on metal σ levels can be evaluated by a comparison of the UPS data for $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}CH_{3}$ and $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}CH_{3}$ (Table II) as taken from reference 91. The valence analysis for these complexes shows that the ionizations or $(\eta^5 - C_5 H_5) Cr(NO)_2 CH_3$ "compressed" be compared appear to to those of $(\eta^5-C_5H_5)Fe(CO)_2CH_3$. This stabilization of metal $d\pi$ levels is accompanied by a pronounced destabilization in the metal-CH₃ bond ionizations. For example, the metal-carbon σ -bond in the iron compound is 140 kJ/mole below the HOMO, whereas for the chromium compound the difference is reduced

to 94 kJ/mole. Thus, in changing from a Fe(CO)₂ group to а $Cr(NO)_2$ group, the metal $d\pi$ density is stabilized by localization onto the nitrosyl ligands while the M-CH₃ σ density is destabilized by the loss of charge and remains largely in the vicinity of the metal. This description accounts for the higher reactivity of the $(\eta^5 - C_5 H_5) M(NO)_2 R$ (M = Mo or Cr) complexes over carbonyl analogues towards electrophilic attack at the metal-carbon bond. It can also accomodate the reactivity of $(\eta^5 - C_5 H_5) W(NO)_2 H$, which has а metal-hydrogen bond that is very susceptible to electrophilic attack [25].

The HeI/HeII UPS analyses for $(\eta^5 - C_5 H_5) Fe(CO)_2 Cl$ and $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Cl$ provide data that is useful for establishing the effects on the metal π levels when the $M(CO)_2$ group is replaced by a $M'(NO)_2$ group. A significant difference between the two compounds is that there is a marked stabilization of the highest occupied 'd' level in the nitrosyl complex. For the chromium complex this level is 81 kJ/mole below the average position of the Cr-Cl π^* levels. For the carbonyl complex, the analogous separation is reduced to 76 kJ/mole. Furthermore, this 'd' level separation is probably even greater in the tungsten congener of $(\eta^5 - C_5 H_5) Cr(NO)_2 Cl.$ A comparison of the UP spectra of the two nitrosyl complexes has been published [63]. There are some differences in resolution and assignment between the studies. using two However, the

Table	II.	He(I)	and	He(II)	Valenc	e Band	Analys	is (eV)			
Result	s for	(η ⁵ -C ₅]	H ₅)Fe	(CO) ₂ CH ₃	and (η	⁵ - C ₅ H ₅)	$Cr(NO)_{2}Cl$	H ₃			
								•			
				He(I)	He(I	I) H	le(I)-He(II)			
Peak		I.E.		Area	Area	Ĺ	78				
$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}CH_{3}$											
A		7.71		0.23	0.33	4	13				
В		7.97									
С		8.51		0.12	0.14	. 1	17				
D		9.17		0.25	0.19	-2	-24				
$(\eta^5 - C_5 H_5) Cr(NO)_2 CH_3$											
A		7.93		0.28	0.37		32				
В		8.18									
С		8.65		0.15	0.21	4	40				
D		8.91		0.18.12		- :	33	· .			

Assignment:	Bands A,	в,	and	С	are	metal	'd'	levels
	Band D i	s me	etal-	۰CF	Η3 σ	level		

assignments discussed above, the separation between the highest occupied 'd' level and the W-Cl π^* levels is approximately 85 kJ/mole. The consequence of this 'd' level stabilization on metal-alkene complexes can be seen by reviewing the Dewar-Chatt-Duncanson model for metal-alkene bonding. The scheme, as loosely depicted below consists of two components:



(a) overlap of the π -electron density of the olefin with a σ -type acceptor orbital on the metal; and (b) a "back-bond" resulting from flow of electron density from filled metal π -orbitals into antibonding orbitals on the carbon atoms. The effect of strongly stabilized metal $d\pi$ density is to make less metal $d\pi$ density available for interaction with remaining ligands. Thus, a stable alkene complex in the $(\eta^5-C_5H_5)W(NO)_2$ system requires that the σ -donor interaction supply the majority of the bond strength. This seems to agree with the empirical conclusion reached in Chapter Two.

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(89) See reference 85. It is tempting to formulate the organometallic product formed in this reaction as $(\eta^5-C_5H_5)Fe(CO)_2BF_4$. However, the IR data reported for this species $(\nu(CO) \ 2050, \ 2010 \ \text{cm}^{-1})$ do not agree with those displayed by authentic $(\eta^5-C_5H_5)Fe(CO)_2BF_4$ ($\nu(CO) \ 2078, \ 2032 \ \text{cm}^{-1})$ recently isolated by Mattson and Graham [43].

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APPENDIX

Selected Infrared Spectra of Compounds Described in this Thesis





3 **σ** $-C_{5}H_{5}W(NO)_{2}(\eta^{2}-C_{8}H_{14})]BF_{4}$ as Nujol mull











Phenylethyne as neat liquid



3,3,4,4-Tetramethyl-1-phenylcyclobutene as neat liquid



 η^{5} -C₅H₅)W(NO)₂Br as CH₂Cl₂ solution















 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}Cl$ as $CH_{2}Cl_{2}$ solution



 $(\eta^{5}-C_{5}Me_{5})W(NO)_{2}PPh_{3}]BF_{4}$ a s CH₂Cl₂ solution







 $\eta^{5} - C_{5}Me_{5}W(NO)_{2}C_{2}H_{5}$ as hexanes solution



 (η^5) $-C_{5}H_{5}W(NO)(\eta^{3}-C_{3}H_{5})(NCCH_{3})]BF_{4}$ a s Nujol mull











 $(\eta^{5}-C_{5}H_{5})MO(NO)_{2}Cl \text{ as } CH_{2}Cl_{2} \text{ solution}$



 $[(\eta^{5}-C_{5}H_{5})MO(NO)_{2}PPh_{3}]PF_{6}$ as $CH_{2}Cl_{2}$ solution



 $(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}Cl \text{ as } CH_{2}Cl_{2} \text{ solution}$





 $[(\eta^{5}-C_{5}H_{5})Cr(NO)_{2}]_{2}$ as $CH_{2}Cl_{2}$ solution



