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FERROCENYLPHOSPHINE DERIVATIVES
OF IRON AND RUTHENIUM CLUSTER CARBONYLS

By

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Abstract

The substitution reactions of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ with the ferrocenylphosphines PBuPhFc , PPh_2Fc , PPhFc_2 , PFc_3 and $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$ were carried by initiation with the diphenylketyl radical anion, or using photochemical or thermal conditions. The products $\text{Fe}(\text{CO})_4\text{L}$ ($\text{L}=\text{PBuPhFc}$, PPh_2Fc , PPhFc_2 and PFc_3); $\text{Fe}_3(\text{CO})_{11}\text{L}$ ($\text{L}=\text{PBuPhFc}$ and PPh_2Fc); $\text{Fe}_3(\text{CO})_{10}\text{L}_2$, ($\text{L}=\text{PBuPhFc}$), $\text{Ru}(\text{CO})_4(\text{PFc}_3)$, $\text{Ru}_3(\text{CO})_{11}\text{L}$ ($\text{L}=\text{PPh}_2\text{Fc}$, PPhFc_2 , PFc_3 and $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$); $\text{Ru}_3(\text{CO})_{10}\text{L}_2$ ($\text{L}=\text{PPh}_2\text{Fc}$, PPhFc_2 , PFc_3 and $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$), and $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L}=\text{PPh}_2\text{Fc}$ and PPhFc_2) were obtained in moderate to high yields with the exception of $\text{Ru}(\text{CO})_4(\text{PFc}_3)$ which was obtained in a very low yield and characterized by X-ray crystallographic analysis. The best method for the substitution reactions was found to be induction with the diphenylketyl radical anion.

Pyrolytic reactions of three of the trimetallic ruthenium derivatives produced high to moderate yields of compounds with interesting spectroscopic data. A structure (XXXI) is proposed for the product obtained from the pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$. It contains a ferrocene molecule bridging two metal atoms, a fluxional benzyne ring associated with all three metal atoms, and both doubly and triply bridging phosphido and phosphinidene ligands, respectively.

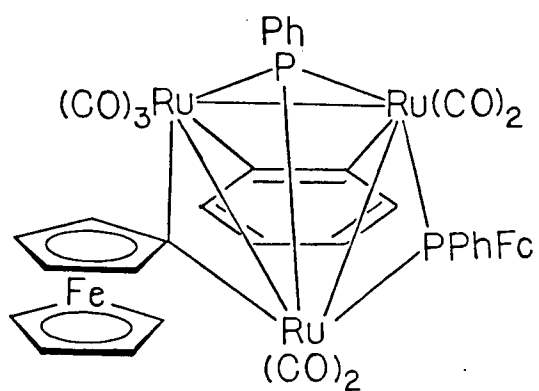


Table of Contents

Abstract	ii
Table of Contents	iv
List of Tables	vii
List of Figures	ix
List of Schemes	x
List of Structures	xi
List of Abbreviations	xiii
Acknowledgements	xv
Chapter One - Ferrocenylphosphines	
1.1 Introduction	1
1.2 Experimental	
1.2.1 General Methods	6
1.2.2 Chemicals and Supplies	7
1.2.3 Preparation of PBuPhFc	7
1.2.4 Preparation of PPh ₂ Fc	8
1.2.5 Preparation of PPhFc ₂	9
1.2.6 Preparation of PFc ₃	10
1.2.7 Preparation of Fe(C ₅ H ₄) ₂ PPh	11
1.3 Discussion	12
Chapter Two - Reactions of Ferrocenylphosphines with Metal Carbonyls	
2.1 Introduction	18
2.1.1 Metal Carbonyls of Iron and Ruthenium	18

2.1.2	Phosphine Derivatives of Iron	
	Carbonyls	21
2.1.3	Phosphine Derivatives of Ruthenium	
	Carbonyls	25
2.2	Experimental	34
2.2.1	General Methods	34
2.2.2	Chemicals and Supplies	35
2.2.3	Preparation of Phosphine Derivatives of Iron and Ruthenium Carbonyls	35
2.3	Discussion	57
2.3.1	Reactions of Phosphines with $\text{Fe}_3(\text{CO})_{12}$	57
2.3.2	Reactions of Phosphines with $\text{Ru}_3(\text{CO})_{12}$	61
2.3.3	General Comments on Reaction Types .	63
2.3.4	Characterization of Compounds	65
2.3.5	General Trends Encountered in Spectroscopic and Analytical Studies	69
2.3.6	Cone Angle Determination for PFc_3 ..	81
Chapter Three - The Pyrolysis of Ferrocenylphosphine Derivatives of Iron and Ruthenium Carbonyl Compounds		
3.1	Introduction	84
3.1.1	The Existence of Ferrocene	88
3.2	Experimental	92

3.2.1 General Methods	92
3.3 Discussion	98
3.3.1 Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	98
3.3.1.1 Discussion of the ^1H NMR	
Spectrum	101
3.3.2 Pyrolysis of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	105
3.3.3 Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	106
Chapter Four - Conclusions	108
Bibliography	113

List of Tables

Table I	Reactions of $\text{Fe}_3(\text{CO})_{12}$ with Ferrocenylphosphines: L	37
Table II	Reactions of $\text{Ru}_3(\text{CO})_{12}$ with Ferrocenylphosphines: L	39
Table III	Description of the $\text{Fe}_3(\text{CO})_{12}$ Derivatives	41
Table IV	Description of the $\text{Ru}_3(\text{CO})_{12}$ Derivatives	42
Table V	Isolation and Some Properties of the $\text{Fe}_3(\text{CO})_{12}$ Derivatives	43
Table VI	Isolation and Some Properties of the $\text{Ru}_3(\text{CO})_{12}$ Derivatives	45
Table VII	^1H NMR Chemical Shift Data for the $\text{Fe}_3(\text{CO})_{12}$ Derivatives (80 MHz)	47
Table VIII	^1H NMR Chemical Shift Data for the $\text{Ru}_3(\text{CO})_{12}$ Derivatives	49
Table IX	IR Data for the $\text{Fe}_3(\text{CO})_{12}$ Derivatives	51
Table X	IR Data for the $\text{Ru}_3(\text{CO})_{12}$ Derivatives	52
Table XI	Mass Spectroscopic Data for the $\text{Fe}_3(\text{CO})_{12}$ Derivatives	53
Table XII	Mass Spectroscopic Data for the $\text{Ru}_3(\text{CO})_{12}$ Derivatives	54

Table XIII	Elemental Analytical Data for the $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ Derivatives	56
Table XIV	Analysis of Mass Spectroscopic Data for $\text{Fe}(\text{CO})_4\text{L}$ Compounds	74
Table XV	Analysis of Mass Spectroscopic Data for $\text{Ru}_3(\text{CO})_{11}\text{L}$ Compounds	77
Table XVI	Isotope Combinations for the Molecule/Ion Fe_3	79
Table XVII	Isotope Combinations for the Molecule/Ion Fe_3C_{19}	80
Table XVIII	Selected Angles and Distances for the Molecule $\text{Ru}(\text{CO})_4(\text{PFc}_3)$ Used to Determine the Cone Angle for PFc_3	83
Table XIX	Pyrolytic Reactions of the $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ Derivatives	93
Table XX	NMR Chemical Shift Data for Some Products of the Pyrolytic Reactions .	95
Table XXI	IR Data for Some Products of the Pyrolytic Reactions	97
Table XXII	Mass Spectroscopic Data for the Product Obtained by the Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	97

List of Figures

Figure 1	Photochemical Reaction Vessel	64
Figure 2	Simplified View of the Structure of $\text{Ru}(\text{CO})_4(\text{PFC}_3)$	67
Figure 3	Structure of $\text{Ru}(\text{CO})_4(\text{PFC}_3)$	67
Figure 4	Structure of $\text{Ru}(\text{CO})_4(\text{PFC}_3)$ Showing Numbering	68
Figure 5	Isotope Pattern for Fe_3	79
Figure 6	Isotope Pattern for Fe_3C_{19}	80
Figure 7	Cone Angle Determination	82
Figure 8	^1H NMR Spectrum of (XXXI) - Ferrocenyl Region	103
Figure 9	^1H NMR Spectrum of (XXXI) - Phenyl Region	104

List of Schemes

Scheme 1	Formation of PFc_3 Under Friedel-Crafts Conditions	3
Scheme 2	Formation of Ferrocenylphosphines	13
Scheme 3	Formation of FcHgCl	15
Scheme 4	Formation of PFc_3 from FcHgCl and PCl_3 ...	16
Scheme 5	Formation of PFc_3 from FcHgCl , $n\text{-BuLi}$ and PCl_3	16
Scheme 6	Formation of PFc_3 from FcHgCl , N -bromosuccinimide, $n\text{-BuLi}$ and PCl_3	17
Scheme 7	Formation of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	26
Scheme 8	The Radical Anion Reaction	31
Scheme 9	Metal - Halogen Interconversion in the Reaction of FcCl with BuLi	89
Scheme 10	Metathesis in the Reaction of FcCl with BuLi	90
Scheme 11	Reaction of a Substituted Haloferrocene ..	91
Scheme 12	Reaction of $\text{Ru}_3(\text{CO})_{12}$ with PhLi	110
Scheme 13	Reaction of $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}$ and W) with (XXXVII)	111

List of Structures

(I)	Ferrocene	2
(II)	PPhFc ₂	4
(III)	PPh ₂ Fc	4
(IV)	Pt(Bu) ₂ (dppf)	5
(V)	Fe(C ₅ H ₄) ₂ PPh	5
(VI)	dppf	9
(VII)	PBuPhFc	12
(VIII)	Fe(CO) ₅	20
(IX)	Ru(CO) ₅	20
(X)	Fe ₂ (CO) ₉	20
(XI)	M ₂ (CO) ₉ (M=Ru or Os)	20
(XII)	Fe ₃ (CO) ₁₂	21
(XIII)	Ru ₃ (CO) ₁₂	21
(XIV)	Fe ₃ (CO) ₁₁ (PPh ₃)	25
(XV)	Ru(CO) ₃ (PMe ₃) ₂	28
(XVI)	Ru ₃ (CO) ₁₁ (PPh ₃)	30
(XVII)	Ru ₃ (CO) ₁₁ L	33
(XVIII)	Ru ₃ (CO) ₁₀ L ₂	33
(XIX)	Ru ₃ (CO) ₉ L ₃	33
(XX)	Ru ₃ (CO) ₈ L ₄	33
(XXI)	Ru ₃ (CO) ₁₀ ($\widehat{L}L$)	33
(XXII)	Ru ₃ (CO) ₈ ($\widehat{L}L$) ₂	33
(XXIII)	[Ru ₃ (CO) ₁₁] ₂ ($\mu\text{-}\widehat{L}L$)	33

(XXIV)	$\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$	86
(XXV)	$\text{Os}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)$	86
(XXVI)	$\text{HOs}_3(\text{CO})_9(\text{PPh}_3)(\text{PPhC}_6\text{H}_4)$	86
(XXVII)	$\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$	86
(XXVIII)	$\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$	87
(XXIX)	$\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_3)$	87
(XXX)	$\text{Ru}_3(\text{CO})_7(\text{PAr}_2)_2(\text{Ar}')$ ($\text{Ar}=\text{Ph}$, $\text{m-MeC}_6\text{H}_4$, and $\text{p-MeC}_6\text{H}_4$, $\text{Ar}'=\text{C}_6\text{H}_4$ and $\text{C}_6\text{H}_3\text{Me}$ respectively)	88
(XXXI)	$\text{Ru}_3(\text{CO})_7(\text{PPhFc})(\text{PPh})(\text{Fc})(\text{C}_6\text{H}_4)$	99
(XXXII)	$\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2(\text{PhC}_2\text{Ph})_2$	99
(XXXIII)	$\text{HRu}_3(\text{CO})_9(\text{PPhFc}_2)(\text{PC}_6\text{H}_4\text{Fc}_2)$	107
(XXXIV)	$\text{Ru}_3(\text{CO})_9\text{H}(\text{C}_6\text{H}_5\text{CC}_6\text{H}_4)$	110
(XXXV)	$\text{Ru}_3(\mu\text{-H})(\mu\text{-O=CMe})(\text{CO})_{10}$	111
(XXXVI)	$\text{Ru}_3(\mu\text{-H})(\mu\text{-Br})(\text{CO})_{10}$	111
(XXXVII)	$\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{Li})$	111
(XXXVIII)	$(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})\text{Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)$	112
(XXXIX)	$(\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{Fe}(\text{CO})\text{Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)$	112

List of Abbreviations

br	broad
Bu	normal butyl: $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$
Bz	benzyl: $\text{C}_6\text{H}_5\text{CH}_2$
C	Celsius
cm	centimetre
Cp	cyclopentadienyl
d	doublet
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	diphenylphosphinomethane
Et	ethyl: CH_3CH_2
FAB	fast atom bombardment
Fc	ferrocenyl: $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$
FT	Fourier transform
g	gram
h	hour
^1H	proton
IR	infrared
L	ligand
m	milli
m	multiplet
M	molar
m/e	mass over charge (units of mass spectra)
Me	methyl: CH_3
min	minutes

mL	millilitre
mol	mole
<u>n</u> -	normal
NMR	nuclear magnetic resonance
pet	petroleum
Ph	phenyl: C_6H_5
R	alkyl or aryl
s	singlet
s	strong
sh	shoulder
<u>t</u> -	tertiary
THF	tetrahydrofuran
TMED	N,N,N',N',-tetramethylethylenediamine
uv	ultraviolet
vs	very strong
vw	very weak
w	weak
X	halide: F, Cl, Br, I

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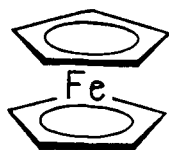
Chapter One - Ferrocenylphosphines

1.1 Introduction

The following ferrocenylphosphines were prepared in order to investigate their reactions with the iron and ruthenium carbonyls, $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$: *n*-butylferrocenylphenylphosphine (PBuPhFc), ferrocenyldiphenylphosphine (PPh_2Fc), diferrocenylphenylphosphine (PPhFc_2), triferrocenylphosphine (PFc_3), and the ferrocenophane 1,1'-ferrocenediylphenylphosphine ($\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$). General preparations of ferrocenylphosphines and some of their synthetic uses are described, since these phosphines have been studied less than others.

Ferrocene or dicyclopentadienyliron, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, (I), was discovered in 1951.¹ It proved to be the first example of a sandwich compound. This structure was first proposed² mainly on the basis of the infrared absorption spectrum which shows only one C-H stretching frequency. Later crystallographic evidence³ supports the sandwich structure and indicates an eclipsed array of the two rings. Further crystallographic evidence shows the presence of a molecular inversion centre and hence supports a staggered arrangement of the two cyclopentadienyl rings. After much investigation,⁴ the evidence leading to the staggered formation was attributed to disorder in the crystal. The most recent crystallographic study⁵ confirms that the two rings are eclipsed in the ferrocene molecule and sandwich the iron atom

between them.

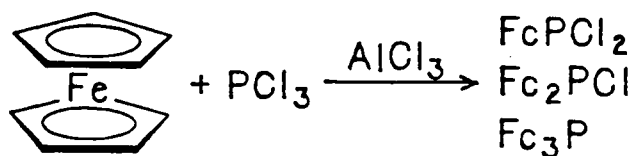


(I) Ferrocene

Tertiary phosphines are commonly used as ligands in organotransition metal compounds. Generally they are prepared by the reaction of halophosphines and organohalophosphines (PX_3 , RPX_2 and R_2PX) with Grignard ($R'MgCl$) or organolithium ($R'Li$) reagents. This affords the tertiary phosphines PR'_3 , RPR'_2 and R_2PR' , respectively. When all three substituents on the phosphorus atom are different, the phosphine is chiral and can be used to synthesize compounds useful for catalytic or stoichiometric asymmetric reactions. The planar chirality of 1,2-unsymmetrically substituted ferrocene molecules can also be utilized to synthesize optically active ferrocene derivatives. Chiral ferrocenylphosphines are readily prepared by way of stereoselective lithiation of (+)- or (-)- N,N-dimethyl-1-ferrocenylethylamine which is easily resolved with (R)-(+)-tartaric acid.^{6,7}

The first compound with phosphorus bonded to a ferrocene carbon atom, triferrocenylphosphine (PFe_3) was reported⁸ in 1962. At this time, aromatic hydrocarbons were known to react

with phosphorus trichloride in the presence of aluminum trichloride to give arylphosphonous dichlorides and diarylphosphinous chlorides. The formation of triferrocenylphosphine under Friedel-Crafts conditions (Scheme 1), was therefore unexpected, since a tertiary phosphine had not previously been prepared in that way, and especially because a three-fold excess of phosphorus trichloride was used. Trisubstitution occurs even with relatively short reflux periods which might be expected to favour monosubstitution.



Scheme 1 Formation of PFc_3 Under Friedel-Crafts Conditions

The first transition metal complex of triferrocenylphosphine that was prepared, is trans-bis(triferrocenylphosphine)chlorocarbonylrhodium(I) ($[\text{Rh}(\text{CO})\text{Cl}(\text{PFc}_3)_2]$) which is formed from rhodium dicarbonyl chloride dimer ($[\text{Rh}(\text{CO})_2\text{Cl}]_2$) by reaction with the phosphine.⁹

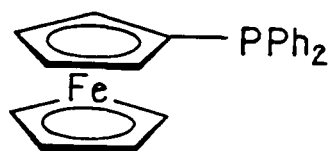
Infrared studies in a later investigation¹⁰ indicate that triferrocenylphosphine is a better σ -donor ligand than triphenylphosphine on comparison of the carbonyl stretching frequencies of the monosubstituted derivatives of $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$), $\text{Fe}(\text{CO})_5$, and $\text{Mn}_2(\text{CO})_{10}$. The triferrocenylphosphine derivatives exhibit bands at lower energies, indicating greater back-bonding from the metal into C-O

antibonding orbitals. Similar studies¹¹ show that the coordinating abilities of the phosphines PPh_2Fc , PPhFc_2 and PFc_3 , increase with an increase in the number of ferrocenyl groups present.

The unsymmetric tertiary phosphines diferrocenylphenylphosphine (PPhFc_2) (II), and ferrocenyldiphenylphosphine (PPh_2Fc) (III), are prepared¹² by the reaction of ferrocene with phenylphosphonous dichloride (PhPCl_2) and diphenylphosphinous chloride (Ph_2PCl) respectively. The reaction is carried out under Friedel-Crafts conditions and yields of 75% for PPhFc_2 , and 65% for PPh_2Fc are reported.



(II) PPhFc_2

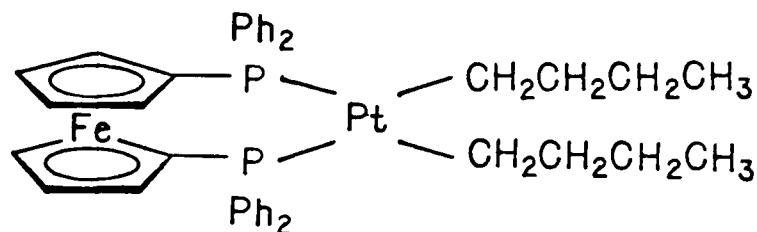


(III) PPh_2Fc

The 1,1'-phosphine substituted ferrocenes are readily prepared in high yields,¹³ since solutions of *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMED), readily dilithiate ferrocene, and dilithioferrocene readily reacts with organohalophosphines.

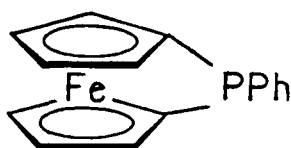
These bidentate ferrocenylphosphines have been more widely used as ligands than simple tertiary ferrocenylphosphines. An early example involves studies of the thermal stability of platinum complexes such as di-*n*-butyl[1,1'-bis(diphenylphosphino)ferrocene]platinum(II)¹⁴, (IV). The

bidentate chelating ligand was used to show that the dissociation of a phosphine ligand is the rate determining step in the decomposition of the platinum compound.



(IV) $\text{Pt}(\text{Bu})_2(\text{dppf})$

The reaction of a solution of 1,1'-dilithioferrocene/TMED with organodichlorophosphines gives ferrocenophanes, containing a bridging phosphorus unit,¹⁵⁻¹⁸ an example of which is 1,1'-ferrocenediylphenylphosphine ($\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$) (V).¹⁵⁻¹⁹ Two examples of metal carbonyl derivatives of this ligand are reported, $\text{Fe}(\text{CO})_4(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$ and $\text{W}(\text{CO})_5(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$, formed by the direct reactions of $\text{Fe}_2(\text{CO})_9$ and $(\text{THF})\text{W}(\text{CO})_5$ respectively, with the ferrocenophane. In both these compounds the ferrocenophane structure is retained. Ferrocenophanes have also been used as intermediates in the formation of oligomers and polymers.²⁰



(V) $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$

1.2 Experimental

1.2.1 General Methods

To avoid oxidation of phosphine compounds, reactions were carried out in a nitrogen atmosphere on a double manifold vacuum apparatus using standard Schlenk procedures.

Separation of products was carried out by column chromatography using 2.5 by 40 cm columns containing neutral Alumina, Brockman activity 1, 80-200 mesh. Columns were started in petroleum ether and elution was carried out by increasing solvent polarity through gradual addition of diethyl ether and then methylene chloride.

Proton NMR spectra were performed by the U.B.C. NMR service on Bruker WP-80, Varian XL-100, or Bruker HXS-270 spectrometers. Samples were prepared in deuterated chloroform. Chemical shifts were measured relative to residual solvent protons (CHCl_3 , $\delta = 7.24$).

Low resolution mass spectroscopic analyses were carried out by the U.B.C. service on a KRATOS MS 50 instrument. The m/e values given represent the most intense peak of a group made up from the different isotopic combinations. When the peak of greatest intensity could not be determined, the value in the centre of the group of peaks is quoted.

Elemental analyses were performed by Mr. Peter Borda of this department.

Melting points were measured using a Kofler microheating

stage, and are uncorrected.

1.2.2 Chemicals and Supplies

Reagent grade solvents were used for routine column chromatography as received. Petroleum ether refers to low boiling (35-60°C) or high boiling (60-80°C) fractions interchangeably, although low boiling petroleum ether was preferred since it is more easily removed. Solvents used for reactions and crystallizations were dried and distilled in a nitrogen atmosphere using standard procedures; hexanes and diethyl ether were distilled from calcium hydride. Spectroscopic grade solvent was used for the dissolution of samples for spectroscopic analysis. Thin layer chromatographic plates were MERCK silica gel 60 F254 on aluminum. Alumina was supplied by Fisher and ferrocene, dichlorophenylphosphine, chlorodiphenylphosphine, and *n*-butyllithium in hexanes were obtained from the Aldrich Chemical Company. All chemicals were used without further purification. Nitrogen was Linde U.S.P. Grade (Union Carbide Canada Ltd.).

1.2.3 Preparation of PBuPhFc

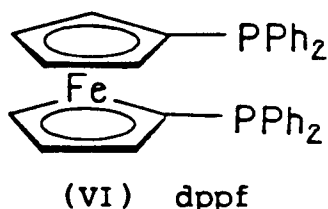
n-Butyllithium (126 mL, 1.6 M, 0.20 mol) was added to ferrocene (25 g, 0.13 mol) in diethyl ether (150 mL). The solution was stirred (20 h) at room temperature after which it was cooled in a dry ice-acetone bath and PhPCl_2 (15 g, 0.08 mol) added dropwise. The solution was allowed to warm to room

temperature with stirring and left for two hours after which water (50 mL) was added. The diethyl ether fraction was isolated, reduced in volume on a rotary evaporator, and applied to a chromatographic column. Unreacted ferrocene was eluted with a petroleum ether/diethyl ether (20:1) mixture. PBuPhFc was eluted with a petroleum ether/diethyl ether (9:1) mixture, evaporated to dryness under reduced pressure, recrystallized from hexanes as a yellow orange solid, and obtained in approximately 40% yield. ^1H NMR (δ): 7.50-7.45 (m, 2H), 7.31-7.28 (m, 3H), 4.35-4.32 (m, 2H), 4.30-4.27 (m, 2H), 4.14 (s, 5H), 1.99-1.91 (m, 2H), 1.50-1.38 (m, 4H), 0.94-0.88 (m, 3H). Mass spec. m/e: 350 (PBuPhFc $^+$), 293 (PPhFc $^+$), 216 (PFc $^+$), 186 (Fc $^+$), 121 (CpFe $^+$), 77 (Ph $^+$). Elemental analysis: calculated for C₂₀H₂₃FeP: C 68.58, H 6.63%, found C 68.41, H 6.60%. M. p.: 38-39°C.

1.2.4 Preparation of PPh₂Fc¹²

n-Butyllithium (32 mL, 1.6 M, 0.05 mol) was added to ferrocene (13 g, 0.07 mol) in diethyl ether (75 mL). The solution was stirred (60 h) at room temperature after which it was cooled in a dry ice-acetone bath and Ph₂PCl (9 g, 0.04 mol) added dropwise. The solution was allowed to warm to room temperature with stirring and left for two hours after which water (50 mL) was added. The diethyl ether fraction was isolated, reduced in volume on a rotary evaporator, and applied to a chromatographic column. Unreacted ferrocene was

eluted with a petroleum ether/diethyl ether (20:1) mixture. PPh_2Fc was eluted with a petroleum ether/diethyl ether (1:1) mixture, evaporated to dryness under reduced pressure, and the yellow orange solid recrystallized from hexanes. This phosphine was also a byproduct of the reaction designed to produce 1,1'-bis(diphenylphosphino)ferrocene (dppf) (VI),²¹ and additional samples were obtained from Dr. I.R. Butler from our laboratory. ^1H NMR (δ): 7.35-7.33 (m, 10 H), 4.35-4.30 (m, 2H), 4.13-4.10 (m, 2H), 4.08 (s, 5H). Mass spec. m/e: 370 (PPh_2Fc^+), 293 (PPhFc^+), 186 (Fc^+), 78 (Ph^+).



1.2.5 Preparation of PPhFc_2 ¹²

n-Butyllithium (63 mL, 1.6 M, 0.10 mol) was added to ferrocene (25 g, 0.13 mol) in diethyl ether (150 mL). The solution was stirred (60 h) at room temperature after which it was cooled in a dry ice-acetone bath and PhPCl_2 (7 g, 0.04 mol) added dropwise. The solution was allowed to warm to room temperature with stirring and left for two hours after which water (50 mL) was added. The diethyl ether fraction was isolated, its volume reduced on a rotary evaporator, and applied to a chromatographic column. Unreacted ferrocene was eluted with a petroleum ether/diethyl ether (20:1) mixture.

PBuPhFc, obtained as a byproduct, was eluted with a petroleum ether/diethyl ether (9:1) mixture. PPhFc₂ was eluted with a diethyl ether/chloroform (9:1) mixture, evaporated to dryness under reduced pressure, and recrystallized from a hexanes/diethyl ether (9:1) mixture as an orange yellow solid. Yields varied from 25 - 60%. ¹H NMR (δ): 7.65-7.27 (m, 5H), 4.30-4.25 (m, 4H), 4.23-4.13 (m, 2H), 4.10 (s, 10 H), 4.03-3.90 (m, 2H). Mass spec. m/e: 470 (PPhFc₂⁺), 401 (PFc₂⁺), 335 (PCpFeFc⁺), 304 (CpFeFc⁺), 216 (PFc⁺), 186 (Fc⁺), 121 (FeCp⁺), 78 (Ph⁺). Elemental analysis: calculated for C₂₆H₂₃Fe₂P: C 65.31, H 4.86%, found C 65.12, H 4.87%.

1.2.6 Preparation of PFc₃⁸

Literature methods were used to prepare this compound^{8,22-24} with some modifications. N,N-diethylphosphoramidous dichloride (8.7 g, 0.05 mol) in hexanes (100 mL) was added dropwise during 15 minutes to ferrocene (27.9 g, 0.15 mol) and AlCl₃ (6.7 g, 0.05 mol) in chloroform (250 mL). The solution was refluxed with stirring (20 h) under nitrogen, the volume reduced to 250 mL on a rotary evaporator, and hydrolysed with water (300 mL). The organic layer was isolated, evaporated to dryness under reduced pressure, and washed with hexanes (200 mL). The solid was then extracted with benzene (150 mL) using a Soxhlet extractor. The benzene solution was reduced in volume on a rotary evaporator and applied directly to a chromatographic column and the PFc₃

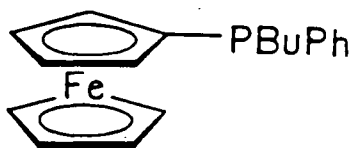
eluted with benzene. Evaporation to dryness under reduced pressure, and recrystallization from a chloroform/ethanol (1:1) mixture gave a 40% yield of a pale yellow solid. The identity was confirmed by IR spectroscopy²³, ¹H NMR (δ): 4.33 (s, 2H), 4.20 (s, 2H), 4.09 (s, 5H). Mass spec. m/e: 586 (PFc_3^+), 456 ($\text{PCp}_2\text{Fe}_2\text{Fc}^+$), 401 (PFc_2^+), 337 (PCpFeFc^+), 216 (PFc^+), 185 (Fc^+), 121 (CpFe^+).

1.2.7 Preparation of $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}^{15-18}$

n-Butyllithium (65 mL, 1.6 M, 0.10 mol) and TMED (6 g, 0.05 mol) were added to ferrocene (9.3 g, 0.05 mol) in diethyl ether (50 mL). The solution changed from orange yellow in colour to red and then to orange as it was stirred overnight. The solution was cooled in a dry ice-acetone bath and PhPCl_2 (8 g, 0.04 mol) added dropwise. The solution was allowed to warm to room temperature with stirring, and water (25 mL) was added. The organic layer was isolated, reduced in volume on a rotary evaporator and applied to a chromatographic column. The product was eluted with a petroleum ether/diethyl ether (5:1) mixture, evaporated to dryness under reduced pressure, and recrystallized from hexanes to give yields of approximately 30%. The identity of the product was confirmed by NMR spectroscopy¹⁵ and mass spectroscopic analysis.¹⁸

1.3 Discussion

The challenge in making these phosphines is to achieve the proper balance between the quantities of reagents and the reaction times. When lithiation by *n*-butyllithium is employed, it is necessary to use an excess of ferrocene when monolithiation is required, otherwise, considerable dilithiation occurs. However, the excess ferrocene is then difficult to remove. If lithiation is allowed to proceed for a shorter period of time, monolithiation is found to be preferred over dilithiation. This, however, results in the presence of an excess of *n*-butyllithium, which reacts with the organohalophosphine to give *n*-butyl substituted phosphines. The previously unreported phosphine, *n*-butylferrocenylphenylphosphine (PBuPhFc) (VII), was first isolated and characterized in the present investigation as a byproduct from the synthesis of PPhFc₂. This phosphine has three different substituents bonded to the phosphorus atom, so the possibility exists for the separation of optical isomers for use in the synthesis of catalytically active compounds for asymmetric reactions.



(VII) PBuPhFc

The formation of phosphine byproducts is another

difficulty, so usually, a smaller amount of organohalo-phosphine than required by the stoichiometry of the reaction (Scheme 2) was used to circumvent the byproducts. The smell is unpleasant, and the presence of the byproducts makes separation by column chromatography more difficult since they cause ferrocene and the phosphine products to elute more quickly and consequently separation is often incomplete. Repeated chromatography is often necessary when large amounts of phosphine byproducts are present, one column to remove most of the byproducts, and another column to separate ferrocene and the phosphine products. Kumada and coworkers⁷ used a sodium hydroxide solution to remove phosphine byproducts, but this method is not useful for this study. The addition of a small amount of petroleum ether to the crude reaction mixture, after removal of solvent by rotary evaporation, was found to be useful to remove enough of the phosphine byproducts to make column chromatography convenient. It also serves to remove some of the excess ferrocene.



Scheme 2 Formation of Ferrocenylphosphines

Phosphine oxide formation was initially a major cause of a decrease in yield of phosphine products, so air was excluded during their synthesis. The presence of phosphine oxides is revealed by infrared spectroscopy; the P-O stretching

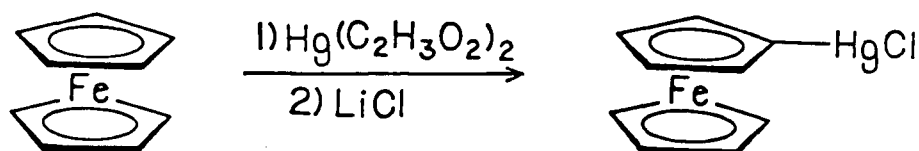
frequency is in the range $1200-1170\text{ cm}^{-1}$.²⁵ The presence of ferrocenylphosphine oxides is also revealed by thin layer chromatography as yellow or orange yellow bands that run behind the original phosphine. The formation of phosphine oxides is especially a problem during the synthesis of triferrocenylphosphine.

Triferrocenylphosphine is difficult to obtain in reasonable yields by the literature methods. In the first reported preparation of PFc_3 ,⁸ it was isolated as the oxide in a yield of 11%, using PCl_3 , and a reflux time of five hours (Scheme 1). The phosphine was actually characterized later²², when it was obtained in 47% yield, using N,N-diethylphosphoramidous dichloride in the preparation instead of PCl_3 , and with increased reflux times of 20 hours. The reason for the improved yield when $(\text{C}_2\text{H}_5)_2\text{NPCl}_2$ is used instead of PCl_3 seems to be that the intermediate species formed by the coordination of aluminum chloride to a nitrogen atom are more active than those formed by coordination to a phosphorus atom.²³ It was found that the reactivities of aluminum chloride catalyzed reactions with ferrocene are in the order $\text{PCl}_3 < (\text{R}_2\text{N})_2\text{PCl} < (\text{R}_2\text{N})_3\text{P}$.²³

In the present investigation, attempts to reproduce the preparation of PFc_3 gave much lower yields than those reported.²³ However, it was found that when chloroform is used as solvent instead of a hydrocarbon, the yields improve. Use of a Soxhlet extractor for the extraction with benzene, as

suggested in a more recent preparation,²⁴ facilitates isolation, however, the procedure is still unsatisfactory as it is very time consuming and messy.

Since the Friedel-Crafts method is less than satisfactory, an alternate route using lithioferrocenes is under investigation. The direct lithiation of ferrocene produces mono- and disubstituted ferrocenes, and such a solution of lithiated ferrocenes is expected to react with PCl_3 to give a low yield of the desired triferrocenylphosphine along with polymeric compounds. For this reason, a possible preparation of PFc_3 first involves the synthesis of a monosubstituted ferrocene such as chloromercuriferrocene,²⁶ which is formed in the reaction between mercuric acetate, ferrocene and lithium chloride (Scheme 3), and can be obtained without disubstituted impurities. This monosubstituted ferrocene compound could be used to prepare PFc_3 by appropriate selection of the routes outlined in Schemes 4-6.

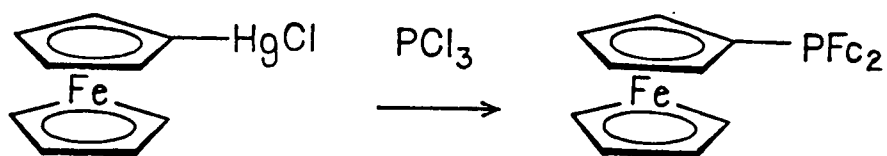


Scheme 3 Formation of FcHgCl

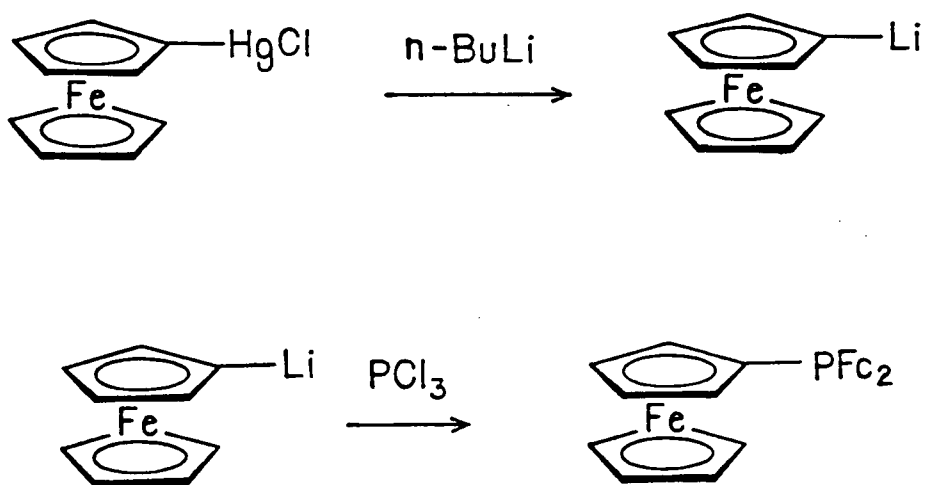
To circumvent possible problems with the Friedel-Crafts

method for the synthesis of PPh_2Fc and PPhFc_2 , lithiation procedures were developed. In these cases small amounts of dilithiated ferrocene do not pose as much of a problem and reactions proceed in moderate yields with easy work-up.

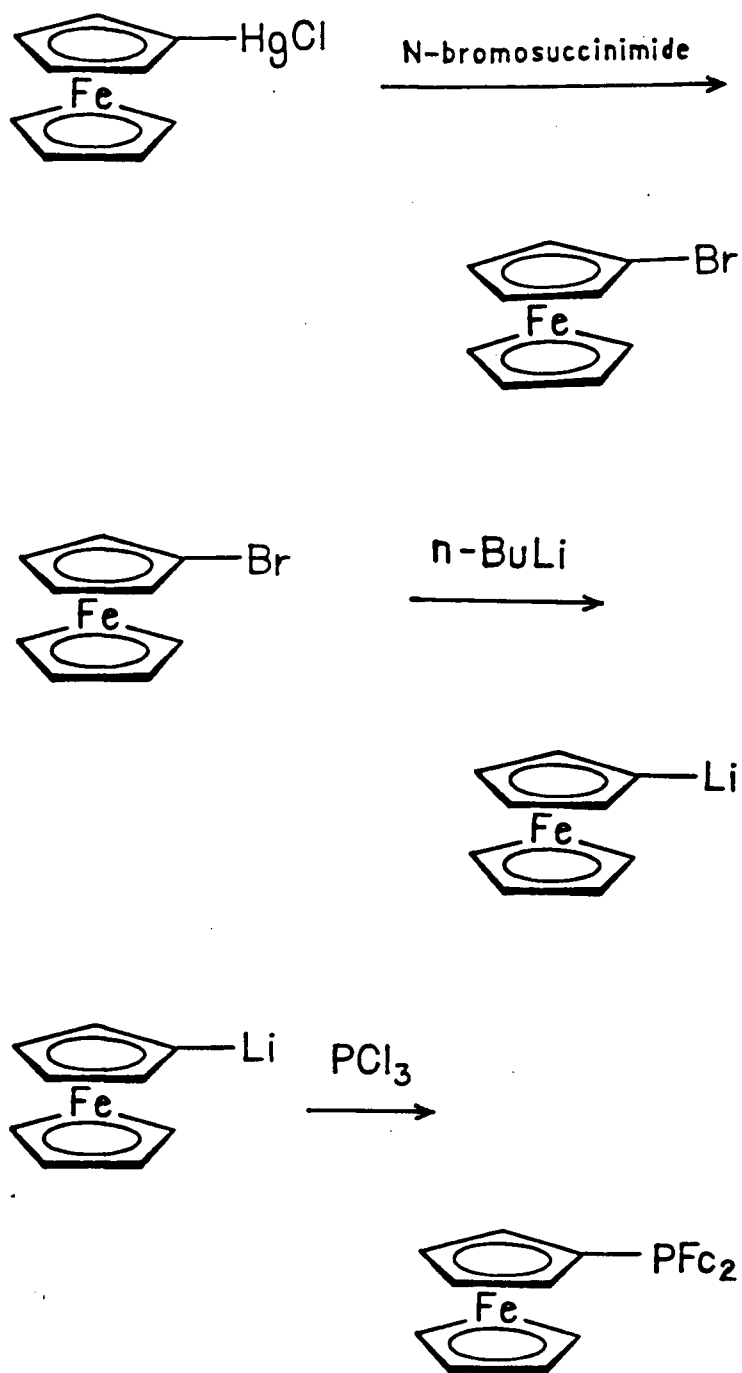
A recent publication²⁷ describes an improved version of the Friedel-Crafts procedure, which has been successfully repeated in these laboratories for the synthesis of PPh_2Fc .



Scheme 4 Formation of PFc_3 from FcHgCl and PCl_3



Scheme 5 Formation of PFc_3 from FcHgCl , $n\text{-BuLi}$ and PCl_3



Scheme 6 Formation of PFc_3 from FcHgCl , N-bromosuccinimide, $n\text{-BuLi}$ and PCl_3

Chapter Two - Reactions of Ferrocenylphosphines with Metal Carbonyls

2.1 Introduction

The reactions of the ferrocenylphosphines described in Chapter One, with the metal carbonyls $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$, were investigated. Phosphine substituted mono- and trinuclear products were isolated and characterized. As an introduction to this chapter, there is a description of the chemistry of the metal carbonyls, followed by a more extensive review of their reactions with tertiary phosphines.

2.1.1 Metal Carbonyls of Iron and Ruthenium

Metal carbonyl chemistry began in 1890 when Mond and coworkers²⁸ discovered tetracarbonylnickel ($\text{Ni}(\text{CO})_4$). This volatile compound was isolated from the reaction of carbon monoxide, at a pressure of one atmosphere, with nickel metal at 30°C. Extensive investigation found that the only other metal that can be converted to a carbonyl by this low pressure route is iron,^{29,30} which yields pentacarbonyliron ($\text{Fe}(\text{CO})_5$). Mond and Quinke³⁰ reported the formation of nonacarbonyldiiron ($\text{Fe}_2(\text{CO})_9$), by the action of light on pentacarbonyliron.

Metal carbonyl cluster chemistry, where cluster refers to a compound with a discrete unit containing three or more metal atoms in which metal-metal bonding is present, was initiated with the discovery³¹ of dodecacarbonyltriiron ($\text{Fe}_3(\text{CO})_{12}$), obtained by heating nonaqueous solutions of nonacarbonyl-

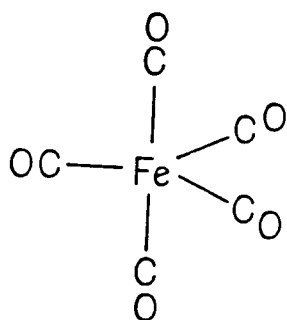
diiron. Dodecacarbonyltriiron is best prepared³² by the oxidation, with manganese dioxide, of alkaline solutions containing carbonylferrates.

The first ruthenium carbonyl was obtained, again by Mond and coworkers in 1910,³³ as an orange crystalline solid by the action of 400 atmospheres of carbon monoxide on metallic ruthenium at 300°C. The product was established as a ruthenium carbonyl, but it was not correctly characterized until it was formulated as $\text{Ru}_3(\text{CO})_{12}$ by Corey and Dahl³⁴ in 1961 on the basis of X-ray crystallography. The best current preparation of this compound was reported by Bruce and coworkers³⁵ and involves the carbonylation of a 1% methanol solution of hydrated ruthenium trichloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) at 50-60 atmospheres of carbon monoxide and 125°C. Almost quantitative conversion results when the mother liquors are recycled with fresh ruthenium trichloride. Pentacarbonylruthenium is obtained in poor yield from ruthenium powder and carbon monoxide under pressure and elevated temperature.³⁶ Nonacarbonyldiruthenium was not reported until 1977³⁷ and was only partially characterized by low temperature infrared studies.

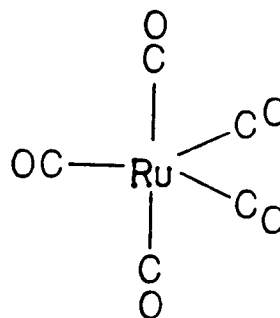
Pentacarbonyliron (VIII) and pentacarbonylruthenium (IX) are trigonal bipyramidal in structure as determined by X-ray crystallography³⁸ for iron, and as indicated by spectroscopic studies³⁹ for ruthenium. Three carbonyl ligands are equatorially bound and two are axially bound to the central

metal atom.

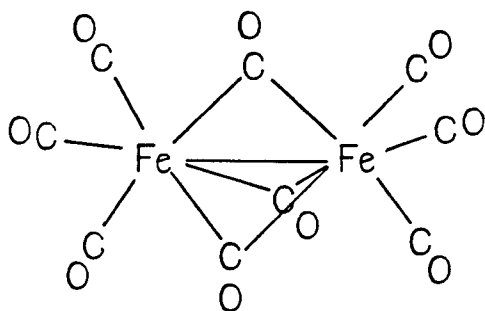
The X-ray crystal structure⁴⁰ of nonacarbonyldiiron (X) shows the presence of three carbonyl ligands which bridge the two iron atoms, and six terminally bound carbonyl ligands, three on each iron atom. The structure of nonacarbonyldiruthenium (XI) has not been determined, but it is thought³⁷ to be similar to that of nonacarbonyldiosmium (XI).³⁷



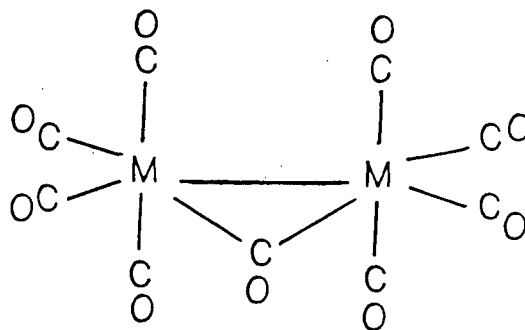
(VIII) $\text{Fe}(\text{CO})_5$



(IX) $\text{Ru}(\text{CO})_5$



(X) $\text{Fe}_2(\text{CO})_9$

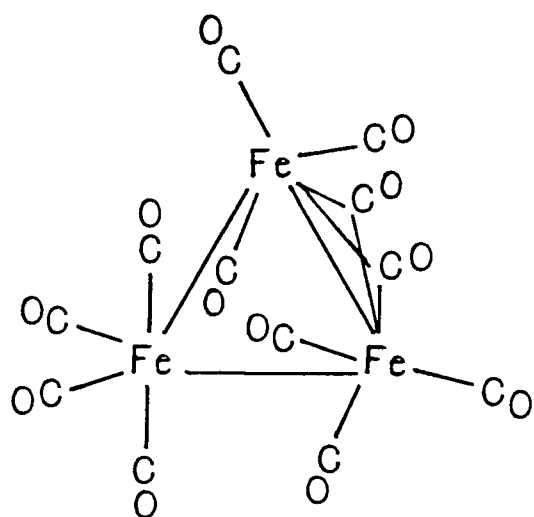


(XI) $\text{M}_2(\text{CO})_9$

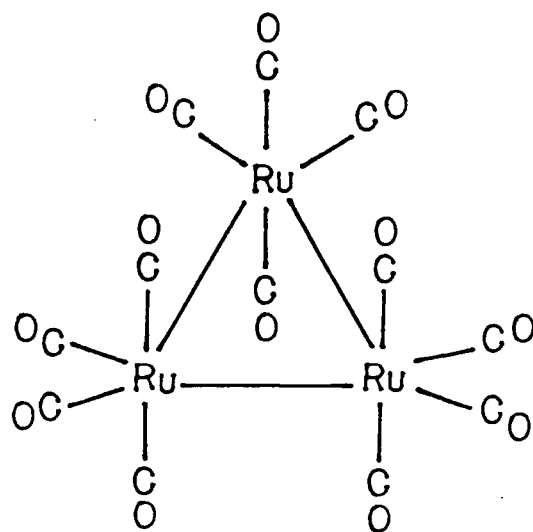
(M=Ru or Os)

Dodecacarbonyltriiron (XII) has a slightly distorted isosceles triangle of metal atoms while dodecacarbonyltri-ruthenium (XIII) has a slightly distorted equilateral triangle

of metal atoms. The iron derivative has one iron atom coordinated to two axial and two equatorial terminal carbonyl ligands, and the other two metal atoms each bond to three terminal and two bridging carbonyl ligands, (μ -CO).⁴¹ The two carbonyl groups bridge the same edge of the triangle which is shorter than the other two edges. In the ruthenium derivative, all the carbonyl ligands are terminally bound, four bonded to each metal atom, two in axial and two in equatorial positions.⁴²



(XII) $\text{Fe}_3(\text{CO})_{12}$



(XIII) $\text{Ru}_3(\text{CO})_{12}$

2.1.2 Phosphine Derivatives of Iron Carbonyls

In 1948 Reppe and Schwelendick⁴³ reported the synthesis of phosphine derivatives of an iron carbonyl. Direct reaction of $\text{Fe}(\text{CO})_5$ with triphenylphosphine (PPh_3) results in the substitution of carbonyl ligands by the phosphine to yield (triphenylphosphine)tetracarbonyliron $[\text{Fe}(\text{CO})_4(\text{PPh}_3)]$ and bis(triphenylphosphine)tricarbonyliron $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$.

Cotton and Parish⁴⁴ reinvestigated these products and concluded on the basis of infrared spectroscopy that these mono and bis derivatives are axially substituted trigonal bipyramidal compounds. The thermal reaction⁴⁵ of nonacarbonyldiiron with benzyldimethylphosphine (PMe_2Bz) also affords both the mono- and the disubstituted mononuclear species, $\text{Fe}(\text{CO})_4(\text{PMe}_2\text{Bz})$ and $\text{Fe}(\text{CO})_3(\text{PMe}_2\text{Bz})_2$. Later studies⁴⁶⁻⁴⁸ found that $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$ compounds can also be formed by the reaction of dodecacarbonyltriiron and the phosphine (L). This preparation is more convenient since the dodecacarbonyl derivative is a crystalline solid while pentacarbonyliron is a volatile, light sensitive, toxic liquid.

The X-ray crystal structures of (tri-t-butylphosphine)-tetracarbonyliron⁴⁹ and (triphenylphosphine)tetracarbonyliron⁵⁰, show that the trigonal bipyramidal compounds are axially substituted.

In 1960, Manuel and Stone⁵¹ reported the formation of the first trisubstituted iron carbonyl, tris(triphenylphosphine)dicarbonyliron. This tris(phosphine) was obtained from the reaction of triphenylphosphine with (butadiene)tricarbonyliron or with (cyclooctatriene)tricarbonyliron. It was thought to have been obtained as a mixture of isomers since the relative intensities of the two absorption bands seen in the carbonyl region of the infrared spectrum were found to change somewhat from experiment to experiment. The identity

of the tris(phosphine) complex was later disputed.⁵² The synthesis of tris(triethylphosphine)dicarbonyliron ($\text{Fe}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_5)_3]_3$) by the prolonged heating of triethylphosphine with (butadiene)dicarbonyliron, in a sealed tube at 150°C , was claimed as the first authentic trisubstituted iron carbonyl.

Sollott and coworkers reported that the thermal reaction of pentacarbonyliron with one of the ligands of interest in the present study, PFc_3 , yielded first the monosubstituted product and then the trisubstituted product⁵³ on prolonged reaction. No evidence for the presence of an intermediate disubstituted carbonyl was obtained. The transformation from the monosubstituted product directly to the trisubstituted product is thought to occur by a disproportionation process. The disubstituted carbonyl can be formed⁵³ from the reaction of the monosubstituted complex with triferrocenylphosphine. Another isomer of the tris(phosphine)dicarbonyliron, which is structurally unspecified, is obtained from the reaction of the ligand with (butadiene)tricarbonyliron.⁵³ The monosubstituted product was earlier suggested¹⁰ to have been axially substituted because of the similarity of the infrared spectrum to the spectra of the triphenylphosphine derivatives, which are known to be axially substituted.

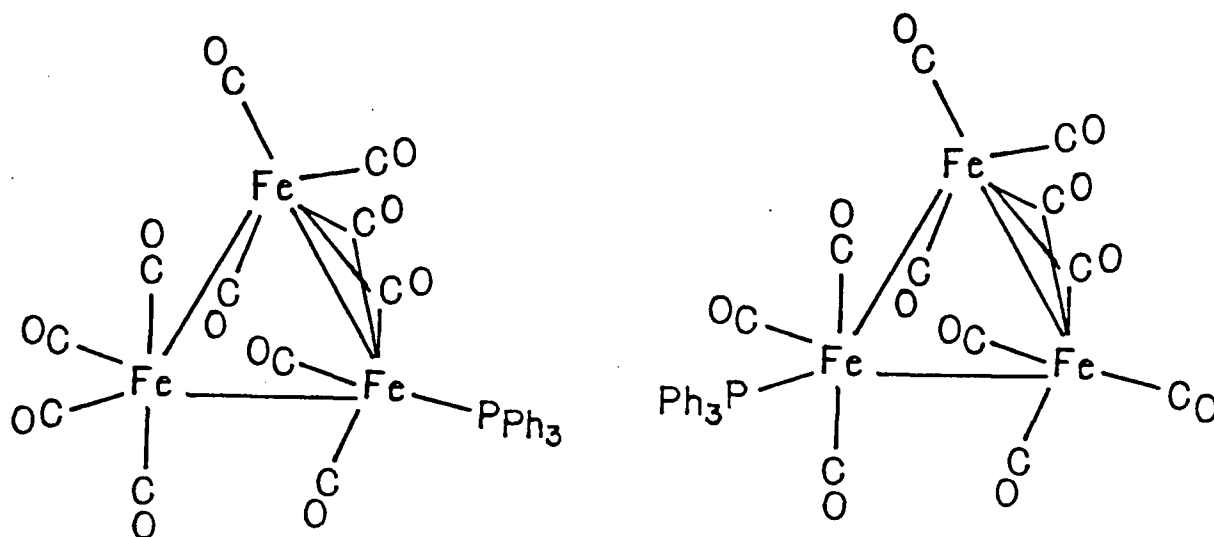
If sufficiently mild conditions are employed for a short period of time, trimetallic derivatives such as (triphenylphosphine)undecacarbonyltriiron $[\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)]$ (XIV) are obtained^{48,54} from the reaction of $\text{Fe}_3(\text{CO})_{12}$ with a tertiary

phosphine. The X-ray crystal structure of this example was determined^{55,56} and it consists of an isosceles triangle of iron atoms bridged on one side by two carbonyl groups. Phosphine substitution has occurred equatorially, and two isomeric forms exist. One isomer is substituted at the iron not bonded to any bridging carbonyl ligands, and the other, substituted at an iron bonded to bridging carbonyl ligands. As discussed below, the diphenylketyl radical anion was later used in the synthesis⁵⁷ of this compound with a much improved yield.

It is also possible to form trisubstituted trimetallic derivatives, as is shown with the synthesis⁵⁸ of di- μ -carbonylheptacarbonyltris(dimethylphenylphosphine)triiron ($\text{Fe}_3(\text{CO})_9(\text{PMe}_2\text{Ph})_3$), the structure of which^{58,59} shows equatorial phosphine substitution at each metal atom.

In 1978, a study by Grant and Manning⁴⁸ of the reaction of dodecacarbonyltriiron with each of six different phosphines was undertaken. It was found that cluster breakdown during the formation of trinuclear species to give the well known mono- and trans-disubstituted mononuclear species, is promoted by higher reaction temperatures, by more rapid addition of phosphines, and by the presence of phosphine oxides. It was reported that attempts to make tris(phosphine)trinuclear species were fruitless, with cluster breakdown always resulting. The previously known tris(phosphine)trinuclear compound, $\text{Fe}_3(\text{CO})_9(\text{PMe}_2\text{Ph})_3$, was originally synthesized⁵⁸

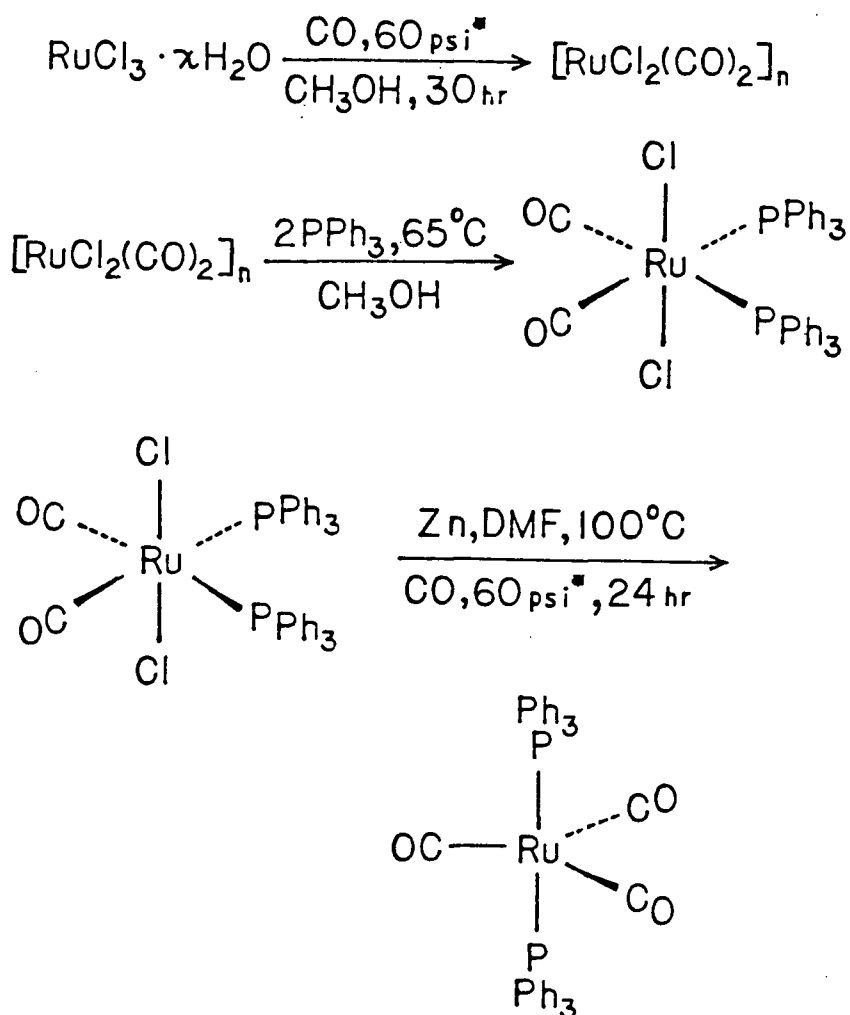
utilizing a one hour reflux of $\text{Fe}_3(\text{CO})_{12}$ and the phosphine in tetrahydrofuran solution, while the 1978 study used longer reflux times of three to six hours in benzene, conditions which must have been too forcing for the isolation of the trisubstituted trinuclear species.



(XIV) $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)$

2.1.3 Phosphine Derivatives of Ruthenium Carbonyls

The first example of a phosphine derivative of a ruthenium carbonyl, reported in 1965,⁶⁰ is trans-bis(triphenylphosphine)tricarbonylruthenium ($\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$). It is obtained when bis(triphenylphosphine)dicarbonyldichlororuthenium(II) ($\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$), (obtained by the carbonylation of hydrated ruthenium trichloride followed by reaction of the product with triphenylphosphine) is reduced by zinc in the presence of carbon monoxide (Scheme 7).



* 400 kPa

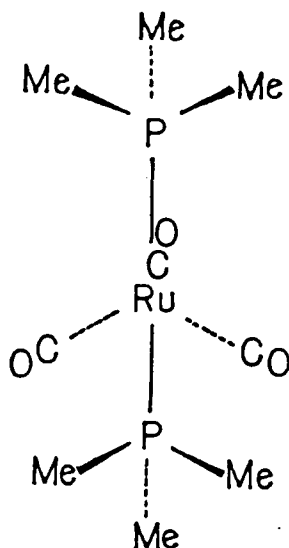
Scheme 7 Formation of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$

A few years later a monosubstituted ruthenium carbonyl,⁶¹ (triphenylphosphine)tetracarbonylruthenium $[\text{Ru}(\text{CO})_4(\text{PPh}_3)]$, was formed by the direct reaction of pentacarbonylruthenium with triphenylphosphine using ultraviolet irradiation. If induced thermally,⁶¹ the reaction produces the disubstituted mononuclear compound. The direct reaction of the trinuclear

ruthenium carbonyl, dodecacarbonyltriruthenium, with the following phosphines: triphenylphosphine, diphenylmethylphosphine, and tri-n-butylphosphine, induced photochemically with Pyrex filtered sunlight or fluorescent tubes, also affords the mono- and trans-disubstituted mononuclear compounds.^{62,63}

An X-ray crystallographic study⁶⁴ of $\text{Ru}(\text{CO})_3(\text{PMe}_3)_2$ (XV), shows the structure to be the expected diaxially substituted trigonal bipyramid. The phosphorus methyl and the ruthenium carbonyl groups minimize interligand repulsion by adopting a mutually staggered conformation. The diaxially substituted ruthenium compound is obtained by the reaction of $\text{Ru}_2(\mu\text{-CH}_2)_3(\text{PMe}_3)_6$ with carbon monoxide at five atmospheres pressure at 60°C. The fate of the $\text{-CH}_2\text{-}$ bridges is unknown; no methane was detected by mass spectroscopy in the residual gases.

A trinuclear phosphine substituted ruthenium carbonyl was reported⁶⁵ in 1966. Tris(triphenylphosphine)nonacarbonyltriruthenium ($\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$) is formed during the thermal reaction⁶⁵⁻⁶⁸ of triphenylphosphine with dodecacarbonyltriruthenium. In 1967 a trisubstituted, trinuclear complex was reported⁶⁶ for the tri-n-butylphosphine ligand. The thermal reaction of PMe_2Bz with dodecacarbonyltriruthenium also yields⁴⁵ the trisubstituted trinuclear species, $\text{Ru}_3(\text{CO})_9(\text{PMe}_2\text{Bz})_3$.



(XV) $\text{Ru}(\text{CO})_3(\text{PMe}_3)_2$

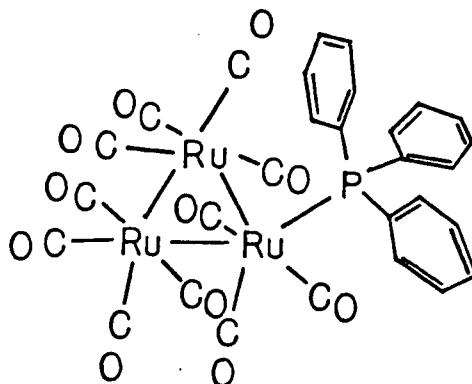
Despite the initial reports of mononuclear phosphine substituted ruthenium carbonyls formed from the reactions of dodecacarbonyltriruthenium with phosphines, most reactions of this type result in retention of the triangle of metal atoms.⁶⁹ The retention of the metal triangle for the ruthenium complexes contrasts the cluster breakdown with dodecacarbonyltriiron, as indicated above. This increased ease of cluster breakdown is presumably due to the decrease in the strength of metal-metal bonds on decreasing atomic mass in the transition metal triad.⁷⁰

Investigations of the thermal reactions of the trisubstituted trinuclear derivatives in a carbon monoxide atmosphere, indicate that monosubstituted mononuclear species were formed.⁶⁹ If excess phosphine is present, heating in a

carbon monoxide atmosphere yields disubstituted mononuclear complexes.^{66,71} When solid (triphenylphosphine)tetracarbonylruthenium is heated, it forms the trisubstituted trinuclear complex with evolution of carbon monoxide.⁶³

Before 1972, mono- or disubstituted trinuclear species had not been isolated. This was ascribed to their thermodynamic instability relative to the trisubstituted species.⁶⁹ Subsequently, it was found that reaction of low-valent platinum complexes containing tertiary phosphines with dodecacarbonyltriruthenium afford⁷² mono-, di-, and tri-phosphine substituted triruthenium carbonyl compounds, as a result of ligand transfer from the platinum complexes. Contiguously, it was discovered⁷³ that if chromatographic separation of the reaction products is employed, rather than crystallization as had previously been used, mono- and disubstituted trinuclear products can be isolated from the thermally induced reactions, although the trisubstituted complexes predominate.

The photochemical reaction of dodecacarbonyltriruthenium with triphenylphosphine was later found⁷⁴ to produce (triphenylphosphine)undecacarbonyltriruthenium (XVI) as well as the mono- and trans-disubstituted mononuclear species. Crystallographic analysis of (XVI) shows an equatorially substituted triangle of ruthenium atoms with all carbonyl groups terminally bound.



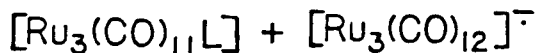
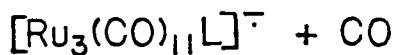
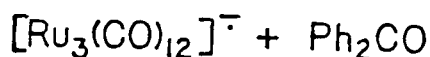
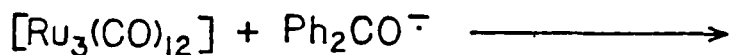
(XVI) $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$

In general, thermal or photochemical reaction conditions induce the formation of a mixture of substitution products. The column chromatography required to separate these mixtures is time consuming and the yields of the desired compounds are often low. For such reactions, reasonable yields of cluster compounds are limited to the trisubstituted products, for which excess phosphine can be used.

In 1982, Bruce and coworkers reported⁵⁷ that the radical anion generated from dodecacarbonyltriruthenium and sodium diphenylketyl (Ph_2CONa) reacts readily with phosphines. Thus, the addition of catalytic amounts of a diphenylketyl radical anion solution to the metal cluster, along with appropriate stoichiometric amounts of phosphines, affords the mono-, di-, tri-, or tetrasubstituted cluster compounds. The reactions are complete within five minutes at room temperature. This method also works for dodecacarbonyltriiron.

The reactive species is thought to be a dodecacarbonyltriruthenium radical anion ($[\text{Ru}_3(\text{CO})_{12}]^{\cdot-}$), where the extra

electron is in an antibonding orbital, leading to a weakened ruthenium-ruthenium metal bond. This bond cleaves, leaving a seventeen electron ruthenium centre, which can undergo attack by the phosphine with elimination of CO. Reformation of the metal-metal bond yields a substituted radical anion $[\text{Ru}_3(\text{CO})_{11}\text{L}]^{\cdot-}$, which transfers an electron to an unsubstituted ruthenium cluster to continue the catalytic cycle (Scheme 8).



Scheme 8 The Radical Anion Reaction

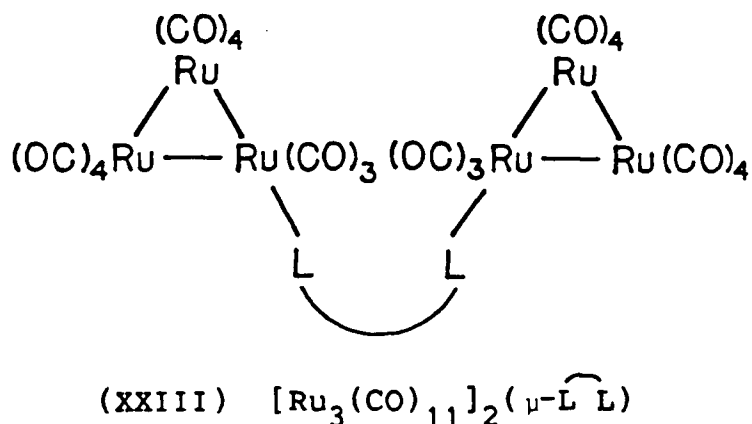
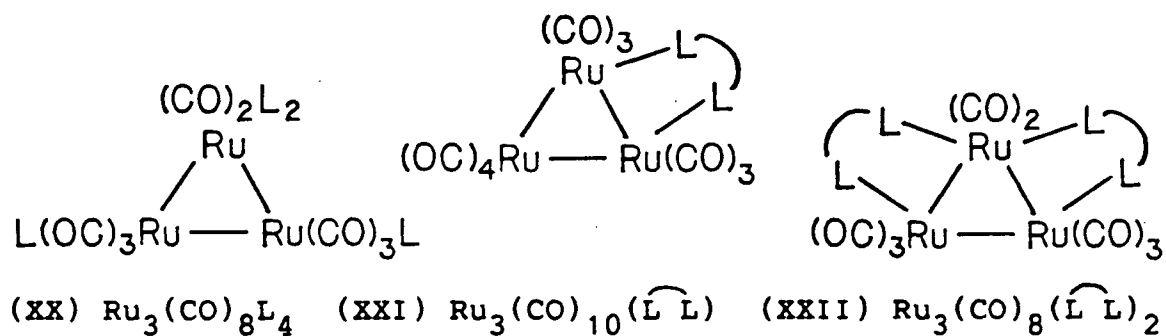
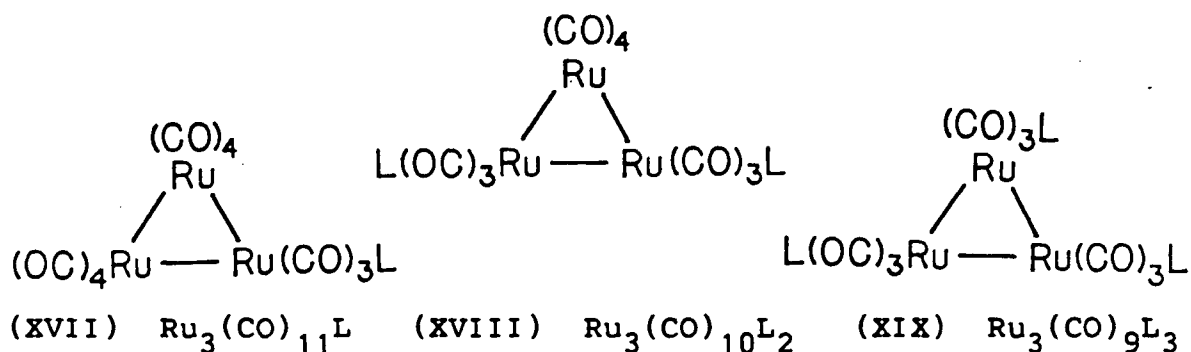
There are three requirements for this reaction to occur:
 (1) the cluster carbonyl has to be reduced without fragmentation, and the resulting anion has to have a long

enough lifetime to allow for substitution; (2) to facilitate the transfer of an electron from the substituted to the unsubstituted radical anion, the substituting ligand must be a better Lewis base than the carbonyl ligand; (3) the ligand must not be reduced by the diphenylketyl radical anion. When these conditions are met, this method allows for short reaction times, mild conditions and high product yields, and has led to the isolation of many complexes which were previously difficult to obtain.^{57,75,76}

The utility of this technique was illustrated in a subsequent paper by Bruce and coworkers,⁷⁵ which describes the synthesis of over sixty substituted ruthenium carbonyl cluster compounds. Eighteen of these compounds are phosphine substituted trinuclear ruthenium carbonyl complexes. These compounds include $\text{Ru}_3(\text{CO})_{11}\text{L}$ (XVII), $\text{Ru}_3(\text{CO})_{10}\text{L}_2$ (XVIII), $\text{Ru}_3(\text{CO})_9\text{L}_3$ (XIX), and $\text{Ru}_3(\text{CO})_8\text{L}_4$ (XX), where L is a tertiary phosphine ligand. Di(tertiary phosphines) afford complexes substituted as in (XXI) and (XXII), where the diphosphines are bonded in a biligate bimetallic mode across a ruthenium-ruthenium metal bond, and another compound which contains two undecacarbonyltriruthenium units joined by a bridging bidentate phosphine ligand (XXIII).

More recently, Bruce and coworkers⁷⁶ synthesized a ruthenium complex containing a ferrocenylphosphine ligand, [bis(diphenylphosphino)ferrocene]decacarbonyltriruthenium [$\text{Ru}_3(\text{CO})_{10}(\text{dppf})$]. The X-ray crystal structure has been

determined,⁷⁶ and it shows the ferrocenylphosphine bonded in a biligate bimetallic mode across a ruthenium-ruthenium metal bond as in (XXI). This compound is the first characterized ruthenium carbonyl cluster containing a ferrocenylphosphine ligand.



2.2 Experimental

The experimental methods, chemicals and supplies were the same as described in Chapter One unless otherwise mentioned.

2.2.1 General Methods

Separation of products was also carried out using Florisil F-100, 60-100 mesh. When tetrahydrofuran was used as reaction solvent it was removed and replaced by cyclohexane before addition to the column. Solutions were evaporated to dryness under reduced pressure and products were recrystallized from hexanes, hexanes/diethyl ether, or from methylene chloride layered with cyclohexane.

Proton NMR spectra were also run on a Bruker WH-400 spectrometer.

Infrared spectra were run using a Perkin-Elmer 598 infrared spectrophotometer using the polystyrene band at 1601 cm^{-1} for calibration. Fourier transform infrared spectra were run with assistance from Mr. Chris Chan of the U.B.C. High Resolution Molecular Spectroscopy Group using a BOMEM spectrometer. Liquid cells were used with KBr windows at a 0.2 mm separation and samples were dissolved in cyclohexane or dichloromethane.

Fast atom bombardment mass spectra were run on a AEI MS 9 spectrometer by the U. B. C. service. Some fast atom bombardment mass spectral analyses were carried out in the laboratories of Professor J. M. Miller of Brock University in

St. Catharines, Ontario.

2.2.2 Chemicals and Supplies

Tetrahydrofuran was left over calcium hydride overnight after which it was distilled from sodium wire and benzophenone. Florisil was supplied by Fisher. $\text{Fe}_3(\text{CO})_{12}$ was obtained from Mr. Ben Clifford in this department. $\text{Ru}_3(\text{CO})_{12}$ was obtained from Dr. Roland K. Pomeroy from S.F.U. and from Professor Michael I. Bruce from The University of Adelaide in Australia.

2.2.3 Preparation of Phosphine Derivatives of Iron and Ruthenium Carbonyls

Diphenylketyl radical anion initiated reactions were carried out at room temperature in tetrahydrofuran solutions to which 1 mL of sodium diphenylketyl solution (approximately 0.025 mM)⁷⁵ was added dropwise with stirring. Work-up was initiated ten minutes after mixing.

Photochemical reactions were carried out in degassed hexanes solutions cooled by dry ice-acetone slurries. A 100 W Hanovia lamp (903A-1) was used at a distance of ten cm from a Pyrex Schlenk type apparatus, fitted with an internal well to contain the dry ice-acetone slurry. Three or four irradiation periods of twenty minutes were used, between which the slurry was renewed. Longer periods of irradiation resulted in loss of cooling agent.

The thermal reactions were carried out in either hexanes or tetrahydrofuran solutions which were heated just below reflux for ten to thirty minutes.

The reactions were monitored by thin layer chromatography.

The reactions carried out, a description of the compounds synthesized and characterized, the isolation technique for the products, their melting points, NMR and IR data, mass spectroscopic peaks, and analytical data are listed in Tables I-XIII.

Table I Reactions of $\text{Fe}_3(\text{CO})_{12}$ with Ferrocenylphosphines: L

$\text{Fe}_3(\text{CO})_{12}$ Amount	L Amount	Reaction Cndns Solvent	Products	Yield*
$\text{Fe}_3(\text{CO})_{12}$ 100 mg 0.20 mmol	PBuPhFc 70 mg 0.20 mmol	uv irradiation 45 min 10 mL hexanes	$\text{Fe}_3(\text{CO})_{11}\text{L}$ $\text{Fe}_3(\text{CO})_{10}\text{L}_2$	moderate moderate
$\text{Fe}_3(\text{CO})_{12}$ 100 mg 0.20 mmol	PPh ₂ Fc 73.4 mg 0.20 mmol	1 mL ketyl** 10 mL THF heat 30 min 10 mL THF uv irradiation 60 min 10 mL hexanes	$\text{Fe}_3(\text{CO})_{11}\text{L}$ $\text{Fe}(\text{CO})_4\text{L}$ $\text{Fe}_3(\text{CO})_{11}\text{L}$ $\text{Fe}(\text{CO})_4\text{L}$ $\text{Fe}_3(\text{CO})_{11}\text{L}$	high low moderate low moderate
$\text{Fe}_3(\text{CO})_{12}$ 100 mg 0.20 mmol	PPhFc ₂ 80 mg 0.20 mmol	1 mL ketyl 10 mL THF	$\text{Fe}(\text{CO})_4\text{L}$	low
200 mg 0.40 mmol	190 mg 0.40 mmol	heat 20 min 10 mL THF	$\text{Fe}(\text{CO})_4\text{L}$	high

$\text{Fe}_3(\text{CO})_{12}$	PFc_3	heat	10 min	$\text{Fe}(\text{CO})_4\text{L}$	high
100 mg	90 mg	10 mL THF			
0.20 mmol	0.20 mmol				

* yields are estimated by visual inspection of t.l.c. plates

** diphenylketyl radical anion solution

Table II Reactions of $\text{Ru}_3(\text{CO})_{12}$ with Ferrocenylphosphines: L

$\text{Ru}_3(\text{CO})_{12}$ Amount	L Amount	Reaction Cndns Solvent	Products	Yield*
$\text{Ru}_3(\text{CO})_{12}$ 100 mg 0.16 mmol	PPh_2Fc 57.9 mg 0.16 mmol	2 ml ketyl**	$\text{Ru}_3(\text{CO})_{11}\text{L}$	high
		10 mL THF		
		heat 10 min	$\text{Ru}_3(\text{CO})_{11}\text{L}$	low
		10 mL THF	$\text{Ru}_3(\text{CO})_{10}\text{L}_2$	low
			$\text{Ru}_3(\text{CO})_9\text{L}_3$	high
		uv irradiation	$\text{Ru}_3(\text{CO})_{10}\text{L}_2$	low
		35 min	$\text{Ru}_3(\text{CO})_9\text{L}_3$	high
		20 mL hexanes		
$\text{Ru}_3(\text{CO})_{12}$ 100 mg 0.16 mmol	PPhFc_2 74.8 mg 0.16 mmol	1 ml ketyl	$\text{Ru}_3(\text{CO})_{11}\text{L}$	high
		10 mL THF	$\text{Ru}_3(\text{CO})_{10}\text{L}_2$	low
		heat 10 min	$\text{Ru}_3(\text{CO})_{11}\text{L}$	low
		10 mL THF	$\text{Ru}_3(\text{CO})_{10}$	low
			$\text{Ru}_3(\text{CO})_9\text{L}_3$	low

$\text{Ru}_3(\text{CO})_{12}$	PFc_3	0.5 mL ketyl	$\text{Ru}_3(\text{CO})_{11}\text{L}$	high
100 mg	91.6 mg	5 mL THF		
0.16 mmol	0.16 mmol			

heat 10 min	$\text{Ru}_3(\text{CO})_{11}\text{L}$	low
10 mL THF	$\text{Ru}_3(\text{CO})_{10}\text{L}_2$	moderate

$\text{Ru}_3(\text{CO})_{12}$	$\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$	1 mL ketyl	$\text{Ru}_3(\text{CO})_{11}\text{L}$	high
100 mg	46.7 mg	15 mL THF		
0.16 mmol	0.16 mmol			

100 mg	93.5 mg	2 mL ketyl	$\text{Ru}_3(\text{CO})_{10}\text{L}_2$	high
0.16 mmol	0.32 mmol	15 mL THF		

* yields are estimated by visual inspection of t.l.c. plates

** diphenylketyl radical anion solution

Table III Description of the $\text{Fe}_3(\text{CO})_{12}$ Derivatives

Structural Formula	Physical Description	Molecular Formula
$\text{Fe}(\text{CO})_4(\text{PBuPhFc})$	yellow solid	$\text{C}_{24}\text{H}_{23}\text{Fe}_2\text{O}_4\text{P}$
$\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	dark green solid	$\text{C}_{31}\text{H}_{23}\text{Fe}_4\text{O}_{11}\text{P}$
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	olive green solid	$\text{C}_{50}\text{H}_{46}\text{Fe}_5\text{O}_{10}\text{P}_2$
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	orange solid	$\text{C}_{26}\text{H}_{19}\text{Fe}_2\text{O}_4\text{P}$
$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	dark green solid	$\text{C}_{33}\text{H}_{19}\text{Fe}_3\text{O}_{11}\text{P}$
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	orange red solid	$\text{C}_{30}\text{H}_{23}\text{Fe}_3\text{O}_4\text{P}$
$\text{Fe}(\text{CO})_4(\text{PFc}_3)$	orange solid	$\text{C}_{34}\text{H}_{27}\text{Fe}_4\text{O}_4\text{P}$

Table IV Description of the $\text{Ru}_3(\text{CO})_{12}$ Derivatives

Structural Formula	Physical Description	Molecular Formula
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	orange solid	$\text{C}_{33}\text{H}_{19}\text{FeO}_{11}\text{PRu}_3$
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	dark purple solid	$\text{C}_{54}\text{H}_{38}\text{Fe}_2\text{O}_{10}\text{P}_2\text{Ru}_3$
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Fc})_3$	dark purple solid	$\text{C}_{75}\text{H}_{57}\text{Fe}_3\text{O}_9\text{P}_3\text{Ru}_3$
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$	orange solid	$\text{C}_{37}\text{H}_{23}\text{Fe}_2\text{O}_{11}\text{PRu}_3$
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	dark red solid	$\text{C}_{62}\text{H}_{46}\text{Fe}_4\text{O}_{10}\text{P}_2\text{Ru}_3$
$\text{Ru}_3(\text{CO})_9(\text{PPhFc}_2)_3$	dark purple solid	$\text{C}_{87}\text{H}_{69}\text{Fe}_6\text{O}_9\text{P}_3\text{Ru}_3$
$\text{Ru}(\text{CO})_4(\text{PFc}_3)$	orange solid	$\text{C}_{34}\text{H}_{27}\text{Fe}_3\text{O}_4\text{PRu}$
$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	orange solid	$\text{C}_{41}\text{H}_{27}\text{Fe}_9\text{O}_{11}\text{P}_3\text{Ru}_3$
$\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$	dark red solid	$\text{C}_{70}\text{H}_{54}\text{Fe}_6\text{O}_{10}\text{P}_2\text{Ru}_3$
$\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$	orange solid	$\text{C}_{27}\text{H}_{13}\text{FeO}_{11}\text{PRu}_3$
$\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$	red orange solid	$\text{C}_{42}\text{H}_{26}\text{Fe}_2\text{O}_{10}\text{P}_2\text{Ru}_3$

Table V Isolation and Some Properties of the $\text{Fe}_3(\text{CO})_{12}$ Derivatives

Compound	Isolation Technique or Chromatographic Medium	Mol. Wt. (g/mole)	Melting Pt.* (°C)
$\text{Fe}(\text{CO})_4(\text{PBuPhFc})$	crystallization following decomposition from solution of $\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	518.13	73-75 M
$\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	Alumina pet ether/ Et_2O (1:1)	825.90	---
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	Alumina Et_2O	1148.14	59-62
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	Florisil pet ether	538.14	169-173

$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	Florisil $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (4:1)	790.03	95-100
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	Florisil pet ether/ Et_2O (4:1)	646.07	165 M
$\text{Fe}(\text{CO})_4(\text{PFc}_3)$	Alumina pet ether	753.97	225-230

* M=melted, other compounds decomposed

Table VI Isolation and Some Properties of the $\text{Ru}_3(\text{CO})_{12}$ Derivatives

Compound	Isolation or Chromatographic Medium	Mol. Wt. (g/mole)	Melting Pt.* (°C)
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	Alumina $\text{Et}_2\text{O}/\text{CHCl}_3$ (1:1)	981.55	110 turned deep red 112-115
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	Alumina $\text{Et}_2\text{O}/\text{CHCl}_3$ (1:1)	1323.76	103-107
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Fc})_3$	Alumina $\text{Et}_2\text{O}/\text{CHCl}_3$ (2:1)	1665.97	---
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$	Alumina pet ether/ Et_2O (1:2)	1089.47	147-150
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	Alumina $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (18:1)	1539.62	117-119

$\text{Ru}_3(\text{CO})_9(\text{PPhFc}_2)_3$	Alumina CH_2Cl_2	1989.77	---
$\text{Ru}(\text{CO})_4(\text{PFc}_3)$	crystallization following decomposition from solution of $\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	799.22	---
$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	Florisil Et_2O	1594.42	115-116
$\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$	Florisil CH_2Cl_2	1755.47	---
$\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$	crystallization	903.43	---
$\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$	crystallization	1167.52	---

*all compounds decomposed

Table VII ^1H NMR Chemical Shift Data (δ) for $\text{Fe}_3(\text{CO})_{12}$ Derivatives (80 MHz)

Compound	Phenyl Region	Ferrocenyl Region	Butyl Region
$\text{Fe}(\text{CO})_4(\text{PBuPhFc})$	7.93-7.65 m 2H 7.55-7.40 m 3H	4.50-4.33 m 3H 4.33-4.22 m 1H 4.00 s 5H	1.70-0.70 br m 9H
$\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	7.95-7.63 br m 3H 7.63-7.38 br m 3H	4.55-4.18 br m 4H 4.13 s 5H	2.13-2.20 br m 2H 1.70-1.25 br m 4H 1.10-0.80 br m 3H
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	7.88-7.15 br m 5H	4.60-3.95 br m 9H	2.40-0.70 br m 9H
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	7.70-7.33 m 10H	4.56-4.45 m 4H 3.78 s 5H	

$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ 7.75-7.35 4.55-4.40

m 10 H m 2H

4.18-4.08

m 2H

3.93 s 5H

$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$ 8.23-7.95 4.60-4.52

m 2H m 2H

7.52-7.38 4.48-4.40

m 3H m 6H

3.98 s 10H

Table VIII ^1H NMR Chemical Shift Data (δ) for $\text{Ru}_3(\text{CO})_{12}$
Derivatives

Compound NMR Frequency	Phenyl Region	Ferrocenyl Region
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ 400 MHz	8.03-7.48 m 2H 7.43-7.40 m 3H	4.52-4.49 m 2H 4.21-4.18 m 2H 3.97 s 5H
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ 80 MHz	7.75-7.35 m 10H	4.45 m 2H 4.20 m 2H 3.93 s 5H
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$ 80 MHz	7.90-7.60 m 2H 7.43-7.27 m 3H	4.55-4.42 m 4H 4.40-4.31 m 2H 4.20 s 5H 4.15-4.05 m 2H
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ 400 MHz	7.81-7.67 m 2H 7.36-7.29 m 3H	4.49 m 2H 4.45 m 2H 4.40 m 2H 4.19 s 10H 4.13 m 2H

$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	4.50-4.47 m 4H
100 MHz	4.14 s 5H

$\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$	4.42-4.31 m 4H
100 MHz	4.13 s 5H

$\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$	7.88-7.68 m 2H	5.00-4.87 m 2H
80 MHz	7.63-7.42 m 3H	4.68-4.56 m 2H
		4.56-4.45 m 2H
		4.38-4.23 m 2H

$\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$	7.87-7.65 m 2H	5.00-4.85 m 2H
80 MHz	7.52-7.26 m 3H	4.62-4.50 m 2H
		4.50-4.39 m 2H
		4.33-4.20 m 2H

Table IX IR Data for the $\text{Fe}_3(\text{CO})_{12}$ Derivatives

Compound	Spec*	Solvent	Absorption (cm^{-1})
$\text{Fe}(\text{CO})_4(\text{PBuPhFc})$	FT	C_6H_{12}	2050s 1975s 1943vs 1936vs
$\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	N	C_6H_{12}	2083w 2030m 2010m 2007m
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	FT	C_6H_{12}	2053s 2029w 2007vs 1980s 1959sh 1945sh 1930w 1816m 1794m
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	FT	C_6H_{12}	2050s 1977m 1947s 1936s
$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	N	C_6H_{12}	2085m 2033s 2012s 2002sh
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	N	C_6H_{12}	2040s 1970s 1937vs 1932vs
$\text{Fe}(\text{CO})_4(\text{PFc}_3)$	N	CH_2Cl_2	2055s 1968m 1932vs

*IR spectrometer used: FT=BOMEM spectrometer, N=Perkin-Elmer 598 spectrometer

Table X IR Data for the $\text{Ru}_3(\text{CO})_{12}$ Derivatives

Compound	Spec*	Solvent	Absorption (cm^{-1})			
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	FT	C_6H_{12}	2099sh	2095m	2060sh	2046s
			2028sh	2015s	2003sh	
			1997sh	1986m	1970w	1964w
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	FT	C_6H_{12}	2075w	2063w	2045vw	2019m
			1998s	1990sh	1976m	1960m
			1921w			
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$	FT	C_6H_{12}	2096w	2045s	2028m	2015s
			1995w	1984w	1966vw	1958vw
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	FT	CH_2Cl_2	2075w	2044w	2029s	2005sh
			1998s	1974vw	1957vw	1948vw
$\text{Ru}(\text{CO})_4(\text{PFc}_3)$	FT	CH_2Cl_2	2056s	1978w	1938s	
$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	N	CH_2Cl_2	2100m	2045s	2016s	1970sh
			1955sh			
$\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$ N		C_6H_{12}	2100w	2050s	2030m	2020s
			2000sh	1995sh	1988w	1964w
			1956sh			
$\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$ N		C_6H_{12}	2025s	2010sh	1998sh	1990s
			1975sh	1967sh	1953sh	
			1945sh	1932sh	1925sh	

* IR spectrometer used: FT=BOMEM spectrometer, N=Perkin-Elmer 598 spectrometer

Table XI Mass Spectroscopic Data* for the $\text{Fe}_3(\text{CO})_{12}$ Derivatives

Compound	Peak (m/e value)
Probe Temperature ($^{\circ}\text{C}$)	
$\text{Fe}(\text{CO})_4(\text{PBuPhFc})$	56, 78, 121, 186, 216, 226, 241, 272,
110	293, 350, 406, 434, 462, 490, 518
$\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$	56, 78, 121, 186, 226, 272, 293, 350,
250	406, 756, 784, 840
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	56, 78, 121, 186, 272, 293, 350, 406,
150	434, 462, 490, 518, 756
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	56, 121, 213, 262, 293, 317, 346, 370,
120	426, 454, 482, 510, 538
$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	56, 84, 121, 171, 226, 293, 370, 426,
140	454, 482, 510, 538
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	59, 74, 121, 186, 239, 304, 346, 370,
100	401, 478, 534, 562, 590, 618, 646
$\text{Fe}(\text{CO})_4(\text{PFc}_3)$	304, 321, 335, 370, 388, 401, 456,
180	502, 568, 586, 642, 670, 726, 754

*mass spectrometer used: N=KRATOS MS 50 spectrometer

Table XII Mass Spectroscopic Data for the $\text{Ru}_3(\text{CO})_{12}$ Derivatives

Compound	Type*	Peak (m/e value)
Probe Temperature ($^{\circ}\text{C}$)		
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ 100	N	52, 63, 78, 93, 105, 121, 186, 297 303, 347, 362, 389, 419, 444, 473, 501, 520, 527, 583, 596, 611, 640, 679, 698, 730
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ ---	FAB	572, 600, 628, 656, 673, 684, 701, 712, 729, 740, 757, 785, 813, 841, 869, 897, 925, 953, 981
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ 280	N	52, 56, 63, 78, 121, 154, 186, 262, 293, 321, 337, 370, 402, 428, 446, 487, 496, 572, 602, 630, 655, 713, 770
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ ---	FABM	107, 135, 177, 205, 234, 275, 304, 339, 370, 437, 466, 501, 569, 629, 654, 686, 714, 815, 889
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Fc})_3$ 150	N	52, 78, 121, 154, 186, 262, 321, 370
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$ 100	N	56, 78, 121, 186, 207, 221, 262, 281, 401, 429, 478, 503, 577, 607, 635, 663, 680

$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$ ---	FAB	607, 635, 680, 708, 736, 764, 781, 809, 820, 837, 848, 865, 876, 893, 921, 949, 977, 1005, 1033, 1061, 1089
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ 100	N	58, 78, 121, 186, 239, 262, 304, 370, 478, 554, 602, 607, 635, 648, 671, 710, 746, 768
$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$ 210	N	57, 121, 149, 167, 189, 279, 305, 318, 370, 398, 415, 444, 472, 500, 529, 586, 612, 640
$\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$ 100	N	370, 401, 455, 586
$\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$ 100	N	358, 370, 389, 415, 441, 464, 494, 522, 538, 551, 568, 578, 595, 623 651, 681, 709, 734, 765, 793, 819, 847
$\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$ 280	N	78, 186

*mass spectrometer used: N=KRATOS MS 50 spectrometer,
FAB=AEI MS 9 spectrometer FABM=measured in the laboratories of
Professor J. M. Miller

Table XIII Elemental Analytical Data for the $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ Derivatives

Complex	Percent C		Percent H		Percent O	
	Calc.	Found	Calc.	Found	Calc.	Found
$\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$	52.30	51.88	4.05	4.00	13.94	14.09
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	58.02	57.79	3.57	3.63	11.89	12.20
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	55.77	55.79	3.60	3.70	9.91	9.92
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	40.38	40.78	1.96	2.15	17.93	17.97
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	48.99	49.24	2.90	3.00	12.07	12.25
$\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$	40.79	41.11	2.13	2.20	16.15	16.0
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	48.36	45.75	3.02	3.21	10.39	10.34
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ • 1.5 CH_2Cl_2	45.75	45.75	2.97	3.21	9.60	10.34
$\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$	41.13	41.45	2.27	2.47	14.70	---

2.3 Discussion

The reactions between the ferrocenylphosphines described in the first chapter and the metal carbonyls $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ were investigated. The reactions were carried out using the diphenylketyl radical anion, or using thermal or photochemical procedures. The details of the reaction conditions, products, and yields estimated by visual inspection of thin layer chromatographic plates are given in Tables I and II. Eighteen phosphine substituted carbonyls were obtained and are detailed in Tables III and IV.

With the exception of $\text{Ru}_3(\text{CO})_{10}(\text{dppf})$,⁷⁶ these compounds include the first examples of cluster compounds containing ferrocenylphosphine ligands.

2.3.1 Reactions of Phosphines with $\text{Fe}_3(\text{CO})_{12}$

The 1:1 radical anion reaction with the phosphine PPh_2Fc affords the expected product, $\text{Fe}_3(\text{CO})_{11}\text{L}$ in high yield. Under the same conditions, the reaction with the more bulky ligand PPhFc_2 does not give the expected product. Instead, small amounts of $\text{Fe}(\text{CO})_4\text{L}$ are obtained. It seems likely that the more bulky ligand causes the $\text{Fe}_3(\text{CO})_{11}\text{L}$ compound to be unstable. The low yield of the $\text{Fe}(\text{CO})_4\text{L}$ compound could result from breakdown of the initially formed $[\text{Fe}_3(\text{CO})_{11}\text{L}]^{\cdot-}$, the breakdown occurring before the extra electron can be passed along to an $\text{Fe}_3(\text{CO})_{12}$ molecule to complete the radical anion chain reaction.

Another $\text{Fe}_3(\text{CO})_{12}$ derivative that has been synthesized using the diphenylketyl radical anion is $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_3)$.⁵⁷

The thermal reactions were all carried out with 1:1 molar ratios of phosphine to metal carbonyl. Cluster breakdown is evident as $\text{Fe}(\text{CO})_4\text{L}$ compounds are formed for the ligands PPh_2Fc , PPhFc_2 and PFc_3 . Only one trinuclear compound, $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, was isolated, probably because of the steric bulk of ligands containing more than one ferrocenyl substituent.

In the initial studies^{45,46} of the thermal reaction of $\text{Fe}_3(\text{CO})_{12}$ with the phosphine PPh_3 , only the mononuclear products $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$ were obtained. This is presumably because the reaction mixtures were refluxed until the green colour of the parent iron carbonyl disappeared, to ensure complete reaction. Since the trinuclear products are green, decomposition of trinuclear products is also inevitable under such conditions. Later studies^{47,54} show the formation of both mono- and trinuclear species under less forcing conditions. Consequently, care was taken in the present investigation not to use conditions that are too forcing.

Photochemical reactions were carried out with the two least bulky phosphines PBuPhFc and PPh_2Fc . With the former less bulky phosphine, both mono- and disubstituted trinuclear compounds are obtained. The more bulky PPh_2Fc phosphine yields $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}_3(\text{CO})_{11}\text{L}$.

The $\text{Fe}(\text{CO})_4\text{L}$ compounds synthesized are all yellow or

yellow orange in colour, whereas $\text{Fe}_3(\text{CO})_{11}\text{L}$ and $\text{Fe}_3(\text{CO})_{10}\text{L}_2$ are all dark green. In reactions where both mono- and trinuclear compounds are formed, the mononuclear compounds are found to elute more slowly than the trinuclear compounds on thin layer chromatography. Increasing substitution in compounds of the same nuclearity causes decreasing rates of elution on thin layer chromatography.

The present study shows no evidence for the formation of trinuclear compounds containing ferrocenylphosphines with more than one ferrocene substituent. The phosphine PPh_2Fc affords $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, and two dark green compounds are obtained from the substitution reaction involving the phosphine PBuPhFc , $\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$ and $\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$. The former was isolated as the only analytically pure powder obtained for a phosphine substituted carbonyl in this study.

The trinuclear species that have been isolated previously contain the phosphine ligands PEt_3 ,⁴⁷ PMe_2Ph ,^{47,58} PEt_2Ph ,⁴⁷ PMePh_2 ,⁴⁷ PEtPh_2 ,⁴⁷ PPh_2CMe_3 ⁴⁷ and PPh_3 .⁵⁴ These phosphines are all less bulky than the ligands used in this study that would not form trinuclear species. It seems likely, therefore, that steric bulk is responsible for the lack of formation of these species in the present studies.

The cone angle of PFc_3 is estimated in this study to be 178° (see 2.3.6 Cone Angle Determination for PFc_3) which is only slightly less bulky than $\text{P}(\text{CMe}_3)_3$, for which the cone angle is 182° .⁷⁷ Other representative cone angles for

tertiary phosphines are 118° for PMe_3 , 132° for PEt_3 , 136° for PMePh_2 and 145° for PPh_3 .⁷⁷ From these values it can be inferred that PPh_2Fc , which forms a trinuclear iron compound, is slightly less bulky than PPh_2CMe_3 previously found in the trinuclear iron compounds $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{CMe}_3)$ and $\text{Fe}_3(\text{CO})_{10}(\text{PPh}_2\text{CMe}_3)_2$.⁴⁴

No $\text{Fe}(\text{CO})_3\text{L}_2$ species were isolated during the course of this study, possibly because a 1:1 molar ratio of carbonyl to ligand was used, and this is not expected to favour the formation of such species. Also, it seems that these species are not easily isolated by column chromatography.

The three trinuclear iron carbonyls obtained in the present investigation, $\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$, $\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$ and $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, all decompose to the monosubstituted mononuclear iron carbonyls, $\text{Fe}(\text{CO})_4\text{L}$ ($\text{L}=\text{PBuPhFc}$ and PPh_2Fc). Even in Schlenk tubes under nitrogen at -20°C , yellow crystals of $\text{Fe}(\text{CO})_4\text{L}$ form from dark green solutions of the trinuclear compounds. Thin layer chromatography results for these solutions initially do not indicate the presence of any other coloured species. The presence of $\text{Fe}(\text{CO})_4\text{L}$ compounds is indicated on examination by thin layer chromatography, after a period of time varying from thirty minutes to overnight.

In all the spectroscopic studies of the trinuclear iron compounds in solution, this decomposition to mononuclear monosubstituted compounds is evident. When a long time is necessary for the collection of spectroscopic data, this

decomposition is a difficulty, causing complication of the spectroscopic information.

2.3.2 Reactions of Phosphines with $\text{Ru}_3(\text{CO})_{12}$

Radical anion reactions of each of the four phosphines with $\text{Ru}_3(\text{CO})_{12}$ using a 1:1 molar ratio of reactants, and one reaction with a 1:2 molar ratio of metal carbonyl to ligand all give the anticipated products in good yields $\text{Ru}_3(\text{CO})_{11}\text{L}$ ($\text{L}=\text{PPh}_2\text{Fc}$, PPhFc_2 , PFc_3 and $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$) and $\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$. In one case, with the phosphine PPhFc_2 , a small amount of $\text{Ru}_3(\text{CO})_{10}\text{L}_2$ was unexpectedly produced. It is possible that this disubstituted product was formed in a thermal or photochemical reaction occurring concurrently.

Previous studies^{57,75,78} have used the diphenylketyl radical anion to produce a variety of phosphine substituted ruthenium carbonyl compounds in good yields.

Mono-, di-, and trinuclear trisubstituted compounds are obtained from the thermal reactions. With the least bulky ligand used, PPh_2Fc , the trisubstituted species predominates. The more bulky ligand, PPhFc_2 , yields equal amounts of di- and trisubstituted species, and smaller amounts of monosubstituted derivatives. The most bulky ligand used, PFc_3 , does not yield any trisubstituted species, although the disubstituted compound is still formed in greater yields than the monosubstituted cluster.

Trisubstitution is known to predominate in the thermal reactions.^{48,65-68} It is nonetheless not unusual that the reactions in this study produced less highly substituted carbonyls, since equimolar ratios of phosphine to carbonyl were used. It is surprising that in some cases the formation of trisubstituted species is not at all favoured. This is most likely due to the high bulk of ferrocene containing phosphine ligands.

Photochemical reactions were carried out for $\text{Ru}_3(\text{CO})_{12}$ with PPh_2Fc , and yield both the di- and the trisubstituted carbonyls.

Earlier studies of photochemical reactions of phosphines with $\text{Ru}_3(\text{CO})_{12}$ report the production of only mononuclear derivatives, $\text{Ru}(\text{CO})_4\text{L}$ and $\text{Ru}(\text{CO})_3\text{L}_2$ ($\text{L}=\text{PPh}_3$,^{62,63} PMePh_2 ⁶³ and PBu_3 ⁶³) when an excess of ligand is used. In a later photochemical study,⁷⁴ which used 1:3 molar ratios of carbonyl to phosphine, $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ was isolated from the reaction mixture as well as the $\text{Ru}(\text{CO})_4\text{L}$ and $\text{Ru}(\text{CO})_3\text{L}_2$ mononuclear products.

The $\text{Ru}_3(\text{CO})_{11}\text{L}$ compounds synthesized are all orange or orange red in colour. As substitution increases, the colour deepens to shades of red and purple and the compounds are slower to elute on thin layer chromatography, as is the case for the iron carbonyl derivatives.

One mononuclear compound, $\text{Ru}(\text{CO})_4(\text{PFC}_3)$, was isolated and its structure determined. This compound is obtained only in

a very low yield, by crystallization from a solution containing $\text{Ru}_3(\text{CO})_{11}(\text{PFC}_3)$, the latter produced by the radical anion reaction. The formation of this mononuclear species is probably due to cluster breakdown caused by the great steric bulk of the PFC_3 ligand.

2.3.3 General Comments on Reaction Methods.

The radical anion reaction is the most useful for preparing specific compounds. Yields are good and column chromatography is not required although it was usually employed to simplify crystallization and characterization because it removed most benzophenone and byproducts formed in the reactions. This method is the least wasteful of reactants.

When excess phosphine is available, the thermal reaction is fairly convenient for the production of trisubstituted compounds, since the reactions still take place in a relatively short period of time.

The photochemical process was found to be the least useful, but this may be mainly because of problems encountered in the development of a small scale system (Figure 1). All the other photochemical equipment on hand necessitates the use of much larger volumes of solvent and scarce reagents than desired.

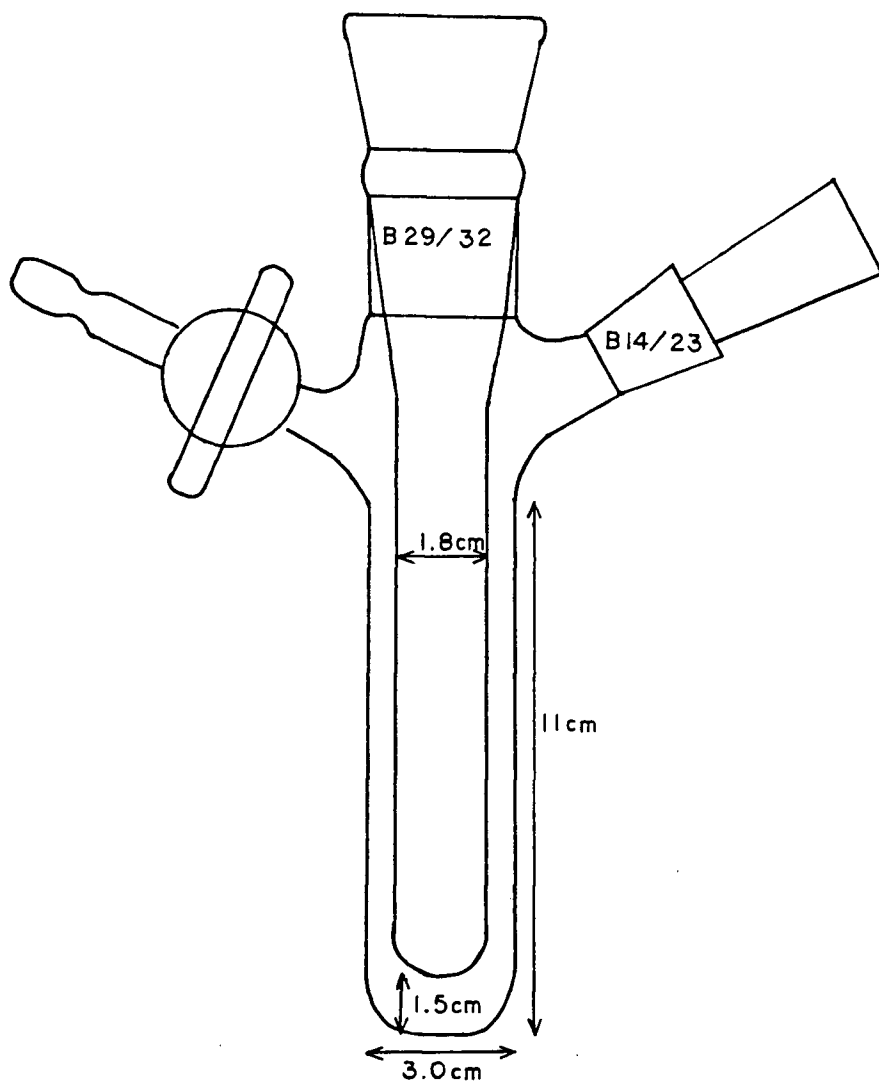


Figure 1 Photochemical Reaction Vessel

The reaction vessel shown in Figure 1 has the following features: (1) a central cooling well filled with a dry ice-acetone slurry to eliminate thermal reactions, (2) a small solution volume allowing efficient cooling, (3) an outlet to allow for degassing by freeze-pump-thaw cycles, and (4) an outlet for sampling of solutions for monitoring purposes.

Two main problems were encountered with this apparatus. Frost forms on the outside of the reaction vessel which reduces the efficiency of irradiation and the cooling mixture is exhausted within thirty minutes so it has to be regenerated.

Possible improvements in an apparatus to study photochemical reactions, especially for reactions of this type which are induced thermally at low temperatures, would be the utilization of fibre optics. Since light can be transmitted through glass or quartz fibres by internal reflections, but heat would not be transmitted in the same way, irradiation of cold reaction mixtures by light transmitted by fibres would be useful to establish the distinction between thermal and photochemical reactions.

2.3.4 Characterization of Compounds

The compounds $\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$, $\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$, and $\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$ and $\text{Ru}_3(\text{CO})_{11}\text{L}$ ($\text{L}=\text{PPh}_2\text{Fc}$, PPhFc_2 and PFc_3) and $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ were characterized using NMR and IR spectroscopy, mass spectroscopic and elemental analysis, and melting points were measured.

The compounds $\text{Fe}(\text{CO})_4(\text{PBuPhFc})$, $\text{Fe}_3(\text{CO})_{11}(\text{PBuPhFc})$, $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, $\text{Ru}_3(\text{CO})_{11}\text{L}$ and $\text{Ru}_3(\text{CO})_{10}\text{L}_2$ ($\text{L}=\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$) are characterized by all the above methods except elemental analysis because samples could not be readily obtained that give good analytical results. The data indicate that the

ferrocenophane bridge has remained intact in the compounds containing the phosphine $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$. Melting points were measured for $\text{Fe}(\text{CO})_4(\text{P}^i\text{BuPhFc})$ and $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$.

The known compound $\text{Fe}(\text{CO})_4(\text{PFc}_3)$, was made from $\text{Fe}_3(\text{CO})_{12}$ rather than $\text{Fe}(\text{CO})_5$ as outlined in the original preparation.¹⁰ The melting point and infrared spectrum compare with the literature values⁵³ and the mass spectrum confirms the formulation.

$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ is characterized by NMR and IR spectroscopy and mass spectroscopic analysis. The elemental analytical data suggests the presence of 1.5 moles of CH_2Cl_2 per mole of product. This is confirmed by the ^1H NMR spectrum. The crystals submitted for analysis were well formed, and thin layer chromatography showed them to be free from coloured impurities.

The compounds of probable formula $\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$, and $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L}=\text{PPh}_2\text{Fc}$ and PPhFc_2) were synthesized; the limited data obtained, NMR and mass spectra for $\text{Ru}_3(\text{CO})_{10}(\text{PFc}_3)_2$, a mass spectrum for $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Fc})_3$, and thin layer chromatography results for all the compounds support the probable formulations.

A few unique crystals formed in a solution of what was initially $\text{Ru}_3(\text{CO})_{11}(\text{PFc}_3)$, and they were found to be $\text{Ru}(\text{CO})_4(\text{PFc}_3)$ by X-ray crystallographic analysis. The structure (Figures 2-4) is an axially substituted trigonal bipyramid. Crystals of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ and

$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ have also been submitted for X-ray crystal structure determination.

It is probable that successive substitution takes place at different ruthenium atoms in the multisubstituted clusters as is known from the X-ray crystallographic results for other compounds of the same type such as $\text{Fe}_3(\text{CO})_9(\text{PMe}_2\text{Ph})_3$ ⁵⁶ and $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$ ⁷⁸.

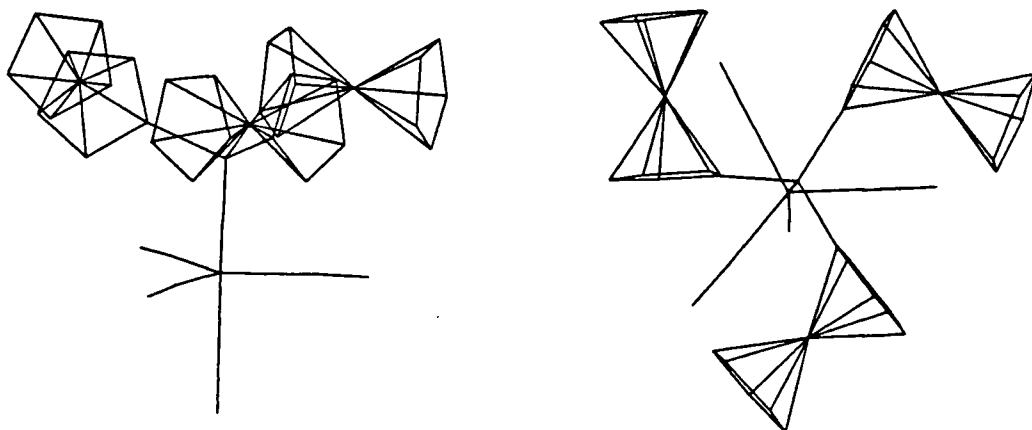


Figure 2 Simplified View of the Structure of $\text{Ru}(\text{CO})_4(\text{PFc}_3)$

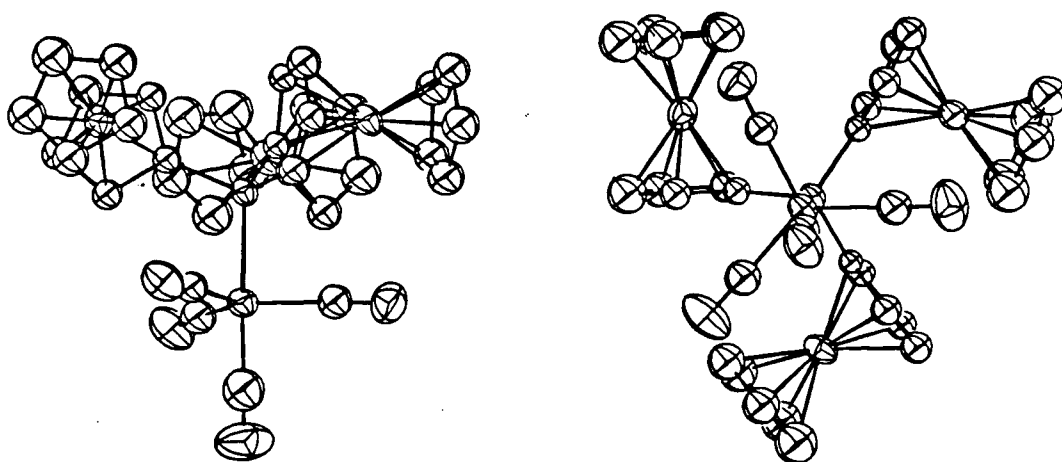


Figure 3 Structure of $\text{Ru}(\text{CO})_4(\text{PFc}_3)$

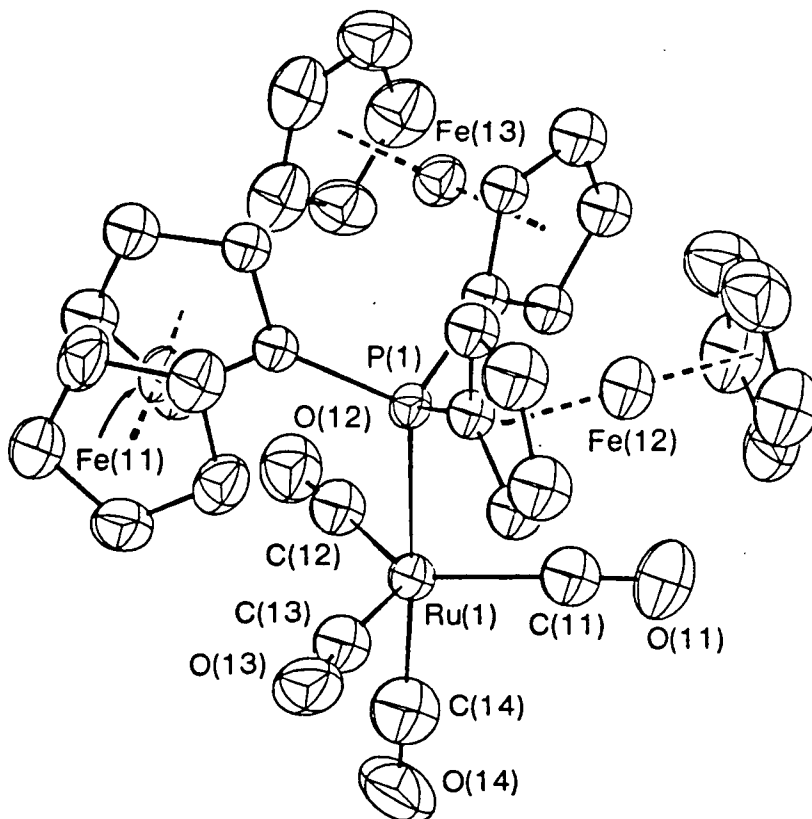


Figure 4 Structure of $\text{Ru(CO)}_4(\text{PFc}_3)$ Showing Numbering
Ellipsoids Enclose 50% Probabilities

Melting points of the compounds synthesized can be found in Tables V and VI. Most of the compounds decomposed before melting. The only compounds that melted cleanly were the two mononuclear iron derivatives, $\text{Fe(CO)}_4(\text{PBuPhFc})$ and $\text{Fe(CO)}_4(\text{PPhFc}_2)$. The compounds containing the phosphine ligand containing the butyl group melted or decomposed at lower temperatures than the other compounds.

Elemental analysis clearly distinguishes between the

likely compositions for the products of the reactions of the metal carbonyls with the phosphines used. Analytically pure samples were difficult to obtain because of problems encountered in the crystallization of these compounds.

For all spectroscopic studies, obtaining the compound in a pure form is a major difficulty. This makes crystallization the most important technique in this study. The most easy to crystallize have the lowest degree of substitution and the lowest number of ferrocenyl substituents on the phosphorus atom of the substituting ligand.

2.3.5 General Trends Encountered in Spectroscopic and Analytical Studies

NMR data are listed in Tables VII and VIII. In all the compounds prepared, protons from the unsubstituted cyclopentadienyl ring resonate as a sharp singlet between 3.78 ppm and 4.20 ppm. Protons from the substituted ring resonate between 3.95 and 5.00 ppm and appear as one multiplet, two multiplets of 3:1 or 1:1 or as four separate multiplets. Phenyl resonances appear as one broad multiplet or as two broad multiplets of ratio 3:2. The smaller, more deshielded multiplet corresponds to the two protons ortho to the site of substitution, while the larger is assigned to the three protons para and meta to the site of substitution. Phenyl protons resonate between 8.23 and 7.15 ppm. The butyl protons appear between 2.40 and 0.70 ppm as multiplets in a 2:4:3

ratio from low to high field.

Some general trends can be observed. With increased substitution on the metal cluster, the ligand protons become less shielded. This is presumably because the donation of the ligand decreases with decreasing numbers of π -acceptor carbonyl ligands.

As the σ -donating abilities of the ligands increase from Ph_2FcP to Fc_3P , the ligand protons should become less shielded. Generally that seems to be the case, but the different splitting patterns make comparison difficult and there also must be some electronic and steric effects that the ligand substituents have on each other. Since the number of ferrocene groups is different for each ligand, these comparisons of NMR frequencies are dubious.

In all of the compounds but two, the protons from the substituted cyclopentadienyl ring of the ferrocene are deshielded compared to the protons on the unsubstituted cyclopentadienyl ring. The exceptions are $\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$ and $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$, where two of the protons of the substituted cyclopentadienyl ring are more shielded than the protons of the unsubstituted ring. It is interesting to note that the monosubstituted mononuclear iron derivative of the same ligand does not show this phenomenon. Metal centres of the cluster other than the one coordinated to the ligand could have a shielding effect and be responsible for the shift of frequencies.

The NMR spectra of the trinuclear iron complexes have broadened signals, probably due to the formation of small quantities of paramagnetic iron compounds.

Infrared spectroscopy is a very useful technique for the characterization of these compounds due to the presence of carbonyl ligands which show characteristic sharp intense absorption bands. Infrared absorption frequencies of the compounds synthesized in this study are given in Tables IX and X.

The mononuclear carbonyl compounds $[M(CO)_4L]$ ($M=Fe$, $L=PBuPhFc$, PPh_2Fc , $PPhFc_2$ and PFc_3 ; $M=Ru$, $L=PFc_3$) most likely have axially monosubstituted trigonal bipyramidal structures. If the ligand L is considered to be a point, the compounds have C_{3v} symmetry and three infrared active bands are expected in the carbonyl region $2a_1$ and e . The lowest frequency band is assigned to the e mode⁵² and the higher of the two a_1 modes is mainly due to the equatorial symmetric stretches.⁸⁰ Less symmetric ligands can decrease the symmetry of the complex to C_s so that it exhibits four infrared active bands in the carbonyl region, one for each carbonyl ligand present. The extra band can be regarded as arising from a splitting of the e mode in a C_{3v} spectrum.⁸¹

The solution infrared spectra of the mononuclear compounds, $M(CO)_4(PFc_3)$ ($M=Fe$ and Ru), containing the most symmetric ligand used in this study, show three carbonyl stretching vibrational frequencies. Other $M(CO)_4L$ ($M=Fe$, $L=PMe_3$)⁸² and

PPh_3 ⁴⁴; $\text{M}=\text{Ru}$, $\text{L}=\text{PBu}_3$ ⁶³, PPh_3 ⁶¹, and PMePh_2 ⁶³) compounds give three infrared stretching modes. The remaining $\text{M}(\text{CO})_4\text{L}$ ($\text{M}=\text{Fe}$, $\text{L}=\text{PBuPhFc}$, PPh_2Fc and PPhFc_2) compounds synthesized in this study show four infrared active bands in the carbonyl region as do the reported compounds $\text{M}(\text{CO})_4\text{L}$ ($\text{M}=\text{Fe}$, $\text{L}=\text{PMe}_2\text{Bz}$ ⁴⁸ and $\text{P}(\text{CMe}_3)_3$ ⁸³).

The symmetry of $\text{M}_3(\text{CO})_{(12-n)}\text{L}_n$ ($\text{M}=\text{Fe}$ or Ru , $\text{L}=\text{PR}_3$) compounds is generally quite low so that many bands are seen in the infrared spectra. For the simplest analysis of these spectra, each metal centre unit can be considered as a separate entity with the appropriate symmetry at that centre. Electronic and steric effects are relayed from one metal centre of the cluster to another, to further complicate the spectra. Nevertheless, patterns can be recognized⁷⁵ that are indicative of mono-, di- and trisubstituted trinuclear compounds.

An increase in substitution is accompanied by a decrease in the frequency of carbonyl bands. There is also an increase in the band width. Phosphine ligands are better σ -donors than carbonyl ligands, so with increasing substitution more electron density is shifted to the π^* -antibonding orbitals of the remaining carbonyl ligands. The metal-carbon bond is strengthened which induces lengthening of the CO bonds.⁸⁵ This enhancement of π -back-bonding causes lowering of the frequency of the infrared stretching vibrations. This trend has been shown for a number of compounds^{47,75} and is

maintained by the compounds synthesized in this study.

As the number of ferrocene constituents in the substituting ligand is increased, the frequencies of the absorption bands of the carbonyl ligands decrease. This is in agreement with the studies of Kotz and Nivert,¹¹ and those of Pittman and Evans,¹⁰ as discussed in the introduction to this chapter. The effect appears to be enhanced with the more highly substituted compounds, where there are fewer carbonyl ligands. For the same reason, the effect is less extreme for the clusters than for the mononuclear compounds. The σ -donating ability of PBuPhFc appears to be about the same as for PPh₂Fc, by comparison of infrared frequencies.

When making comparisons of infrared stretching frequencies from solution studies, it is important to consider which solvents have been used. As the acceptor ability of the solvent increases, the carbonyl stretching frequencies decrease.^{84,85} Consequently, a compound dissolved in cyclohexane will show higher carbonyl frequencies than the same compound dissolved in methylene chloride.

A problem encountered in the present investigation, with the higher molecular weight compounds, is their low solubility. The best solvents are those such as cyclohexane which interact negligibly with the compound of interest, and do not have any major bands in the region of interest. Such solvents allow for sharp, well resolved bands. Unfortunately many of the new carbonyl clusters are insufficiently soluble

in cyclohexane to achieve a high enough concentration for analysis, even with the availability of more sensitive F.T. instruments. Dichloromethane often has to be used to achieve optimum concentration for analysis, and spectra are often broad, poorly resolved, and weak.

Electron impact mass spectroscopic analysis proved to be very useful for the identification of mononuclear compounds. All of these compounds show parent peaks and other peaks indicating sequential loss of the four carbonyl ligands, followed by loss of the central metal atom (Table XIV). Smaller peaks are associated with fragmentation of the ligand.

Table XIV Analysis of Mass Spectroscopic Data for $\text{Fe}(\text{CO})_4\text{L}$ Compounds

L	Fragment Observed (m/e value)					
	$\text{Fe}(\text{CO})_4\text{L}^+$	$\text{Fe}(\text{CO})_3\text{L}^+$	$\text{Fe}(\text{CO})_2\text{L}^+$	$\text{Fe}(\text{CO})\text{L}^+$	FeL^+	L^+
PBuPhFc	518	490	462	434	406	350
PPh ₂ Fc	538	510	482	454	426	370
PPhFc ₂	646	618	590	562	534	478
PFc ₃	754	726		670	642	586

The iron clusters $\text{Fe}_3(\text{CO})_{10}(\text{PBuPhFc})_2$ and $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ show cluster breakdown and exhibit $\text{Fe}(\text{CO})_4\text{L}^+$

fragments and fragments originating from its breakdown as do the mononuclear derivatives of the same ligands. In addition, they show evidence for loss of methylene groups.

With compounds of higher nuclearity, the electron impact mass spectra are less useful. The cluster compounds seem to be less stable resulting in more fragmentation of the ligand from the cluster which tends to swamp the detector so that only the ligand peak and its fragmentation peaks can be observed to any great extent. Some success was achieved by increasing the probe temperature. Thus, the spectrum of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ initially afforded a fragment corresponding to the ligand as the peak of highest m/e when the probe was heated to 150°C . When it was heated to 280°C , a peak corresponding to $\text{Ru}_2(\text{CO})_7(\text{PPh}_2\text{Fc})_2^+$ was observed. It would be worth trying these conditions with other samples.

Electron impact ionization was useful for the compound $\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$ for which the largest fragment corresponds to the parent peak minus two carbonyl ligands. Smaller fragments correspond to sequential loss of carbonyl ligands, breakdown of the metal cluster, and fragmentation of the ligand (Table XV).

Generally, the compounds with higher molecular weight seem less likely to show parent peaks. The compound $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ gives fragments corresponding to L^+ (370), $\text{Ru}_2\text{PPhFc}^+$ (496), $\text{Ru}(\text{CO})\text{L}^+$ (501), Ru_2L^+ (572), $\text{Ru}_2(\text{CO})\text{L}^+$ (602), $\text{Ru}_2(\text{CO})_2\text{L}^+$ (630), $\text{Ru}_2(\text{CO})_3\text{L}^+$ (655), $\text{Ru}_2(\text{CO})_5\text{L}^+$ (713)

and $\text{Ru}_3(\text{CO})_{10}\text{PPh}_2^+$ (770). The compound $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ shows fragments corresponding to L^+ (478), $\text{Ru}_2\text{PFC}_2^+$ (603), $\text{Ru}(\text{CO})\text{L}^+$ (607), $\text{Ru}(\text{CO})_2\text{L}^+$ (635), $\text{Ru}_2(\text{CO})_2(\text{PPhCpFeFc})^+$ (671), $\text{Ru}_2(\text{CO})\text{L}^+$ (710) and $\text{Ru}_3(\text{CO})(\text{PPhCpFeFc})^+$ (746). It seems that with electron impact ionization, fragmentation of the phosphine ligand can occur before loss of the carbonyl ligands.

Peaks corresponding to larger fragments than the ligands are not observed for the compounds $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Fc})_3$, $\text{Ru}_3(\text{CO})_{11}(\text{PFC}_3)$ and $\text{Ru}_3(\text{CO})_{10}(\text{PFC}_3)_2$, and for the compound $\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$ peaks observed were of lower m/e values than expected for the ligand.

Fast atom bombardment (FAB) mass spectra of the compounds $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, $\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ and $\text{Ru}_3(\text{CO})_{10}(\text{PFC}_3)_2$ were obtained. Initially the spectra were run in glycerol, thioglycerol, nitrophenyloctyl ether and sulpholane without success. Diamylphenol was tried for $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ and peaks were obtained for the formulation $\text{Ru}_2(\text{CO})_4(\text{PPh}_2\text{Fc})^+$. The isotopic array and relative intensities of the peaks obtained also fit this formulation.

The compound $\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, was dissolved in methanol and chloroform and then glycerol was added, but the fragment of greatest m/e observed was only due to the ligand ion. The next sample, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$, gave a larger fragment which corresponds to $\text{Ru}_2(\text{CO})(\text{PPh}_2\text{Fc})^+$, when methanol, benzene and

polyethylene glycol were used. Finally diallyl phthalate was used for the samples $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$ and $\text{Ru}_3(\text{CO})_{11}(\text{PPhFc}_2)$, both of which gave parent peaks and peaks corresponding to the loss of carbonyl ligands and fragmentation of the cluster of metal atoms and fragmentation of the ligand (Table XV).

Table XV Analysis of Mass Spectroscopic Data for $\text{Ru}_3(\text{CO})_{11}\text{L}$ Compounds

Compound $\text{Ru}_3(\text{CO})_{11}\text{L}$			
L	$\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$	PPh_2Fc	PPhFc_2
Fragment ⁺		m/e Value	
$\text{Ru}_3(\text{CO})_{11}\text{L}$		981	1089
$\text{Ru}_3(\text{CO})_{10}\text{L}$		953	1061
$\text{Ru}_3(\text{CO})_9\text{L}$	847	925	1033
$\text{Ru}_3(\text{CO})_8\text{L}$	819	897	1005
$\text{Ru}_3(\text{CO})_7\text{L}$	793	869	977
$\text{Ru}_3(\text{CO})_6\text{L}$	765	841	949
$\text{Ru}_3(\text{CO})_5\text{L}$	734	813	921
$\text{Ru}_3(\text{CO})_4\text{L}$	709	785	893
$\text{Ru}_3(\text{CO})_3\text{L}$	679	757	865
$\text{Ru}_3(\text{CO})_2\text{L}$	651	729	837
$\text{Ru}_3(\text{CO})\text{L}$	623	701	809
Ru_3L	595	673	781
$\text{Ru}_2(\text{CO})_7\text{L}$			876

$\text{Ru}_2(\text{CO})_6\text{L}$		740	848
$\text{Ru}_2(\text{CO})_5\text{L}$		712	820
$\text{Ru}_2(\text{CO})_4\text{L}$		684	
$\text{Ru}_2(\text{CO})_3\text{L}$	578	656	764
$\text{Ru}_2(\text{CO})_2\text{L}$	550	628	736
$\text{Ru}_2(\text{CO})\text{L}$	522	600	708
Ru_2L	494	572	680
$\text{Ru}(\text{CO})_2\text{L}$			635
$\text{Ru}(\text{CO})\text{L}$			607

Thus, FAB mass spectra in diallyl phthalate show the presence of parent ions for clusters when electron impact mass spectroscopy fails.

The isotopic pattern for the peaks of a mass spectrum of a fragment (M^+) of a particular formula, can be calculated using the computer program ISOC. Two examples are given in Tables XVI and XVII and Figures 5 and 6. These theoretical patterns can be compared with the patterns obtained to confirm peak assignment.

Table XVI Isotope Combinations for the Molecule/Ion Fe_3^+

Nominal Mass	Peak Mass	Relative Abundance
164	163.814133	1.207717
166	165.809449	19.024851
167	166.809906	0.908900
168	167.804769	100.000000
169	168.805223	7.160471
170	169.803454	1.249733

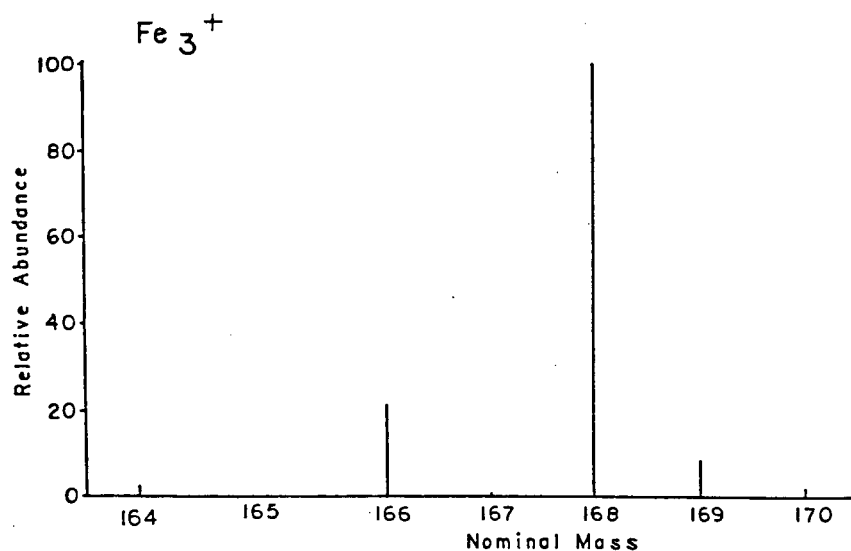


Figure 5 Isotope Pattern for Fe_3^+

Table XVII Isotope Combinations for the Molecule/Ion $\text{Fe}_3\text{C}_{19}^+$

Nominal Mass	Peak Mass	Relative Abundance
392	391.814138	1.201015
393	392.817192	0.284738
394	393.809467	18.942644
395	394.812274	4.938732
396	395.804831	100.000000
397	396.807408	28.361591
398	397.808546	4.904083
399	398.809621	0.607159

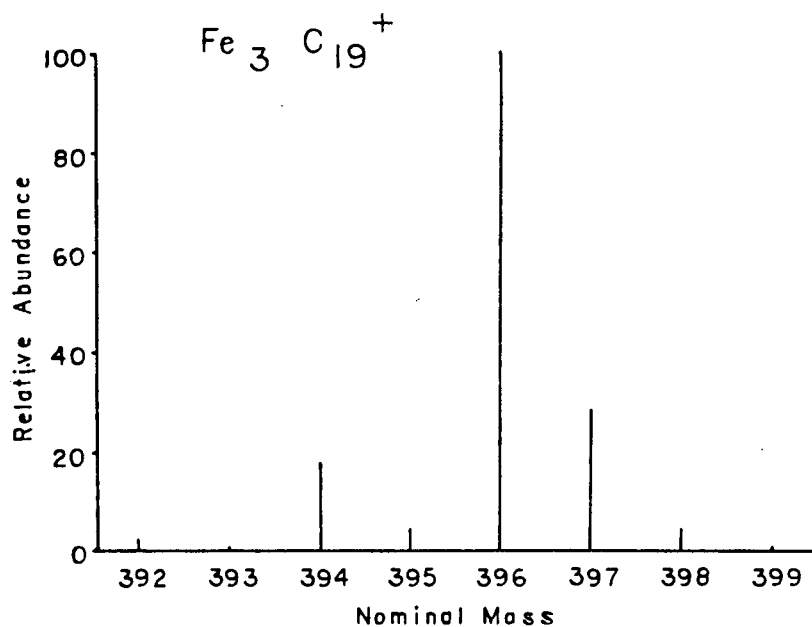


Figure 6 Isotope Pattern for $\text{Fe}_3\text{C}_{19}^+$

2.3.6 Cone Angle Determination for PFc_3

The useful concept of cone angle has been introduced and defined by Tolman,⁷⁴ and is generally accepted as a measure of bulk of a ligand. The ferrocenylphosphines are expected to be bulky, and it is desirable to have some semiquantitative expression of this degree of bulk. Since the structure of $\text{Ru}(\text{CO})_4(\text{PFc}_3)$ is known,⁸⁶ the data⁸⁷ listed in Table XVIII have been used in scale drawings to determine the cone angle as shown in Figure 7, of PFc_3 , to be 178° .

The cone angle is defined as the apex angle of a cylindrical cone, centered 2.28 \AA from the centre of the phosphorus atom in the direction of the metal, to the edge of the van der Waals radii of the outermost atoms in the ligand. A van der Waals radius of 1.2 \AA for the hydrogen atom⁸⁸ was used. For unsymmetrical ligands, two thirds of the sum of the half angles ($\theta/2$) is equal to the cone angle.

The values from Table XVIII that determine the cone angle are those for the hydrogen atoms 219, 224 and 234.

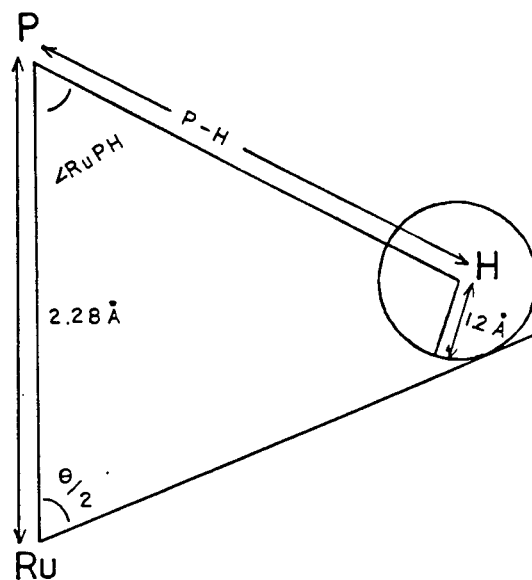


Figure 7 Cone Angle Determination

Table XVIII Selected Angles and Distances for the Molecule
 $\text{Ru}(\text{CO})_4(\text{PFC}_3)^*$

H Atom	Angle Ru-P-H ($^\circ$)	Distance P-H (Å)
114	72.1	3.125
119	78.8	4.712
124	72.8	3.125
129	83.5	4.910
134	72.0	3.136
139	81.0	4.857
214	72.0	3.106
219	74.9	4.710
224	72.6	3.112
229	81.4	4.775
234	72.8	3.119
239	84.1	5.043

* The first column number refers to the two molecules in the unit cell; the second column number is dictated by the choice of three ferrocene molecules; the third number is a four for the hydrogen atom attached to the carbon atom of the substituted cyclopentadienyl ring that is closest to the ruthenium atom, and a nine is for the corresponding carbon atom of the unsubstituted cyclopentadienyl ring.

Chapter Three - The Pyrolysis of Ferrocenylphosphine Derivatives of Iron and Ruthenium Carbonyl Compounds

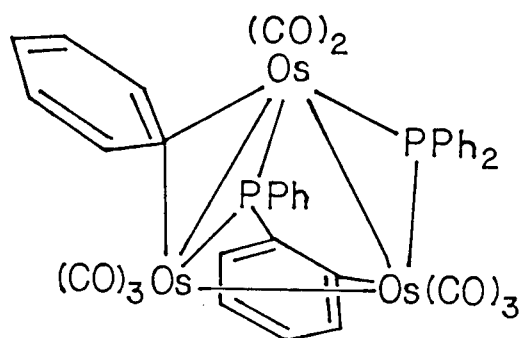
3.1 Introduction

One purpose of the present investigation is to establish if the compounds described in Chapter Two would produce novel complexes by pyrolytic reactions. It is particularly interesting to determine if the formation of a benzyne fragment would be more favourable than the formation of a ferrocene fragment. The preparation of a compound containing a ferrocene fragment would be a significant achievement. As an introduction, a survey of the thermal decomposition reactions of this type is given.

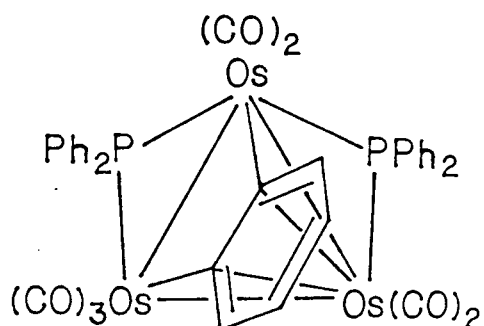
Muetterties has suggested⁸⁹⁻⁹¹ that metal carbonyl cluster compounds are attractive models of metal surfaces involved in chemisorption and heterogeneous catalysis. In heterogeneous catalysis, the catalytic reactions occur between chemisorbed reactants on the surface of the catalyst. A ligated metal cluster can be considered to be a model of the surface of a metal where there is chemisorption. The cluster ligands are analogous to a chemisorbed species on the metal surface. Thus, migration of atoms or small molecules over or within polymetal aggregates which contain metal-metal bonds is of considerable interest with regard to the possible relationship of such migrations to those occurring during the chemisorption of substrates on a metal surface.

The chemistry of $\text{Os}_3(\text{CO})_{12}$ ⁹²⁻⁹⁴ affords early examples of molecules derived from metal clusters which seem to emulate metal surfaces. The thermal reaction⁹² of PPh_3 and $\text{Os}_3(\text{CO})_{12}$ in the molar ratio 2:1, in xylene, gives principally the expected substitution products $\text{Os}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n=1-3$) as well as low yields of six other derivatives, most of which are characterized^{92,93} by X-ray crystallographic analysis. These are $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$ (XXIV), $\text{Os}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)$ (XXV), $\text{HOs}_3(\text{CO})_9(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$ (XXVI), where the hydride, although not located in the crystal structure, is thought to bridge the two osmium atoms that share the bridging phenylphosphine, $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$ (XXVII), where the unlocated hydride is thought to be terminally bound, and $\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$ (XXVIII), where the unlocated hydride is thought to bridge the two osmium atoms with osmium-phosphorus bonds. Crystals suitable for X-ray crystallographic analysis were not obtained for the compound $\text{Os}_3(\text{CO})_8(\text{PPh}_3)(\text{PPh}_2)$, which is thought to have formed from loss of an ortho-hydrogen atom from one of the phenyl groups. An additional compound obtained from the thermal decomposition reaction⁹³ of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ was $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_3)$ (XXIX), where the unlocated hydride is thought to be terminally bound. This compound (XXIX) is also characterised by X-ray crystallography. The decomposition of the osmium cluster to give these products is

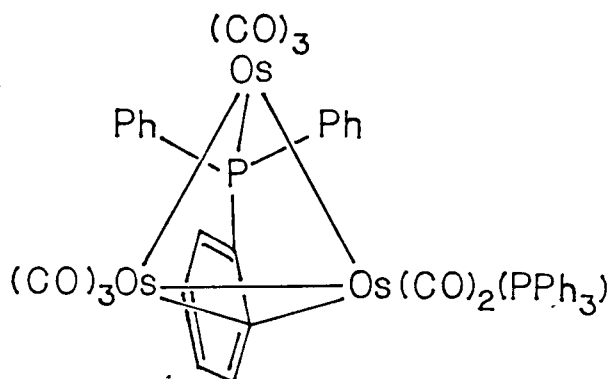
suggested to proceed via the hydrides (XXVI) and (XXVIII) since their yields decrease as the reaction time is increased.



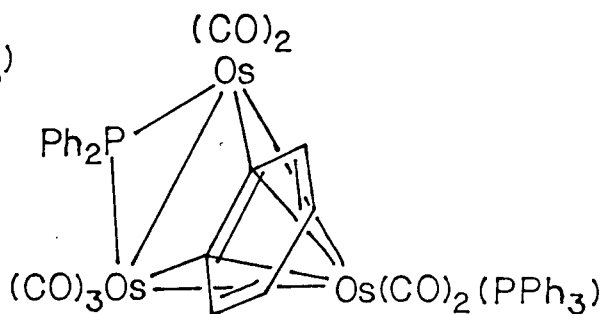
(XXIV) $\text{Os}_3(\text{CO})_8(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$



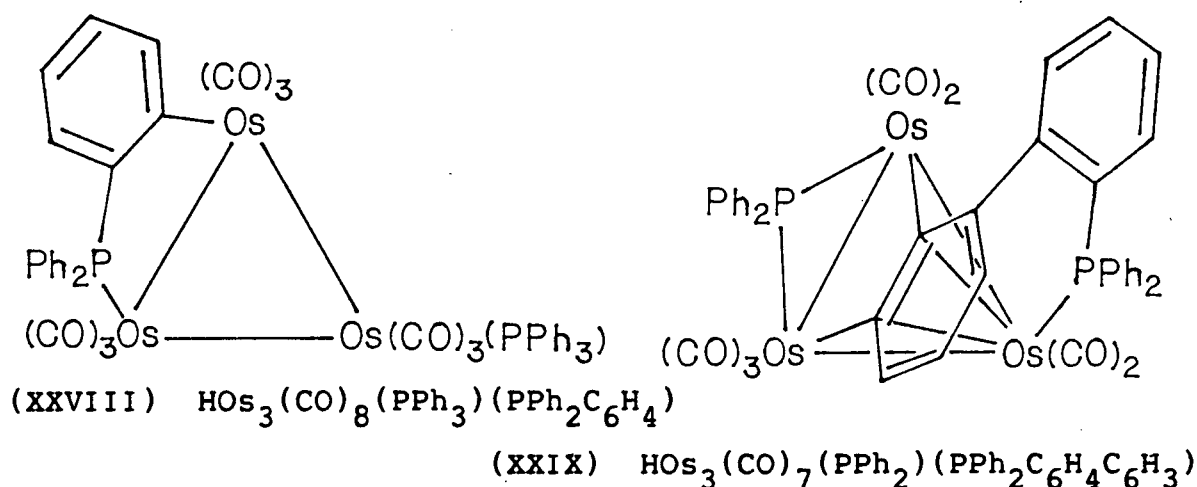
(XXV) $\text{Os}_3(\text{CO})_7(\text{PPh}_2)_2(\text{C}_6\text{H}_4)$



(XXVI) $\text{HOs}_3(\text{CO})_9(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)$



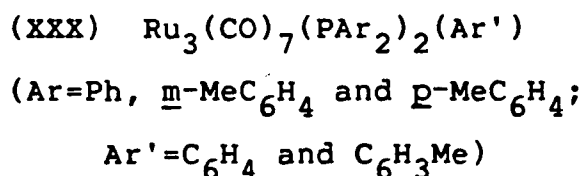
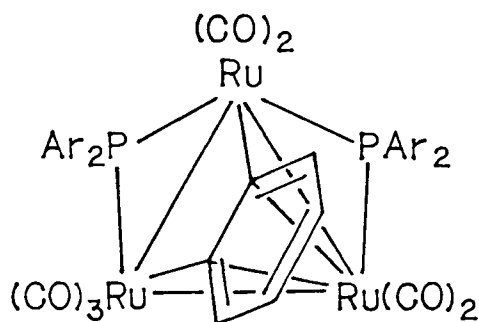
(XXVII) $\text{HOs}_3(\text{CO})_7(\text{PPh}_2)(\text{PPh}_3)(\text{C}_6\text{H}_4)$



The compounds so generated contain a remarkable set of new ligands attached to the cluster in a variety of ways. On some of the phenyl rings in (XXIV) and (XXVIII) the C-H bonds have been involved in oxidative addition reactions which result in phenyl carbon atoms bridging Os-Os bonds via σ -bonds. In (XXVI), a five membered chelate ring is formed on one edge of the metal cluster. Some PPh_3 molecules have lost phenyl rings to give bridging PPh_2 phosphido groups as in (XXV). In (XXV) and (XXVII), the three osmium atoms are bridged by a benzyne fragment. The formation of the phosphine ligand in (XXIX) can be thought to be due to an intracuster assisted coupling reaction between the benzyne fragment and a phenyl ring of a terminal phosphine ligand. This breaking of C-H and formation of C-C bonds, which occurs during the formation of these compounds, is formally analogous to reactions that occur at metal surfaces.

Compounds of this type have also been proposed⁷³ for some

derivatives of ruthenium clusters, $\text{Ru}_3(\text{CO})_7(\text{PAr}_2)_2(\text{Ar}')$ ($\text{Ar}=\text{Ph}$, $\text{m-MeC}_6\text{H}_4$ and $\text{p-MeC}_6\text{H}_4$; $\text{Ar}'=\text{C}_6\text{H}_4$ and $\text{C}_6\text{H}_3\text{Me}$ respectively) (XXX). These compounds are obtained by heating solutions containing $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L}=\text{PPh}_3$, $\text{P}(\text{m-MeC}_6\text{H}_4)_3$ and $\text{P}(\text{p-MeC}_6\text{H}_4)_3$). The proposed structures (XXX) are based on elemental analyses, mass spectra, IR spectra and ^1H NMR spectra. There was no evidence for any ruthenium hydride species, unlike the osmium system.

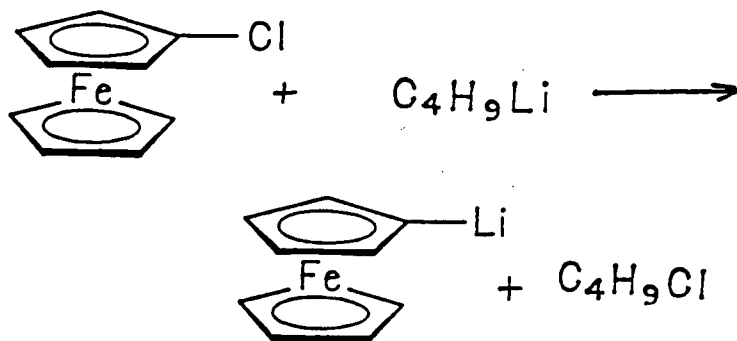


3.1.1 The Existence of Ferrocene

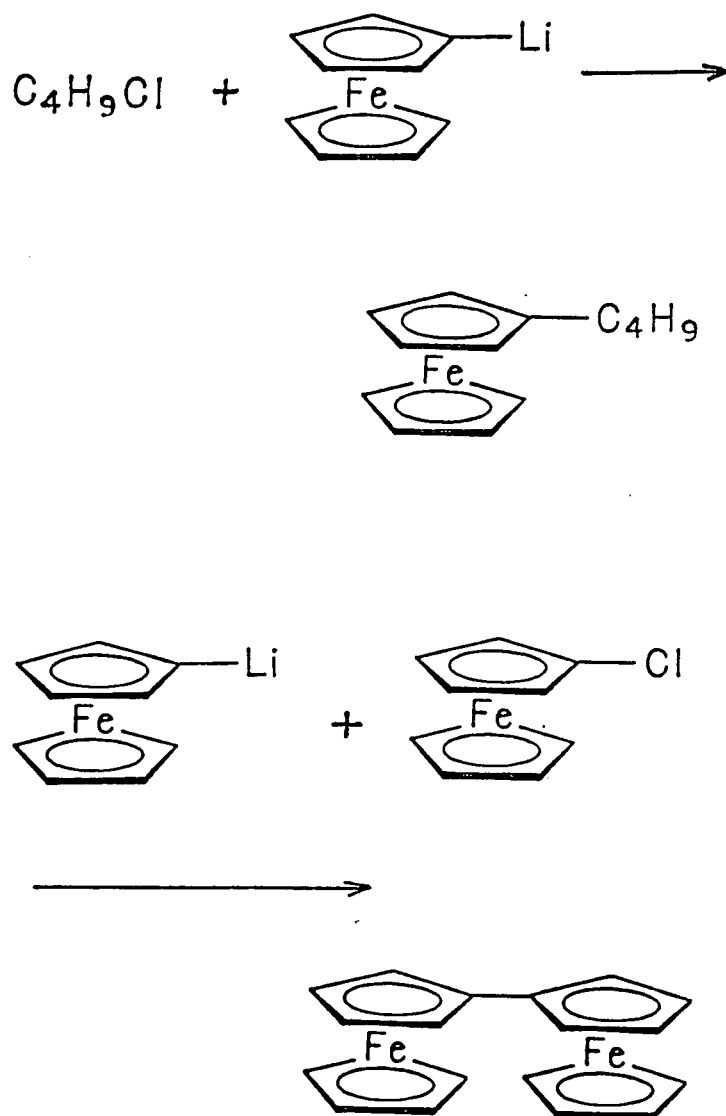
Many aromatic halogen compounds are known to react with strong base to afford products that are rationalised by invoking a benzyne intermediate. Such reactions would be expected to proceed less readily for haloferrocenes, because

of the electron-rich nature of the metallocene nucleus and the difficulty of forming a formal triple bond in a five-membered ring. Nevertheless, the existence of ferrocene as an intermediate was proposed⁹⁵ for the reaction of chloroferrocene with butyllithium which gives butylferrocene and biferrocenyl. These reactions could also occur by metal-halogen interconversion (Scheme 9) followed by metathesis (Scheme 10). Stronger evidence for a ferrocene intermediate was later reported,⁹⁶ as shown in Scheme 11, for the reaction of a substituted haloferrocene. It is difficult to envisage any other mechanism which would yield the two products in approximately equimolar quantities.

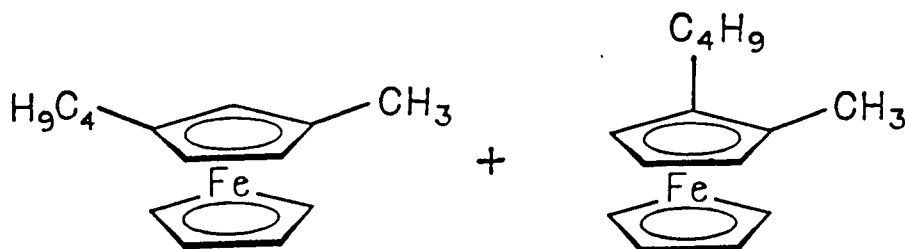
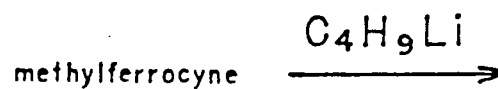
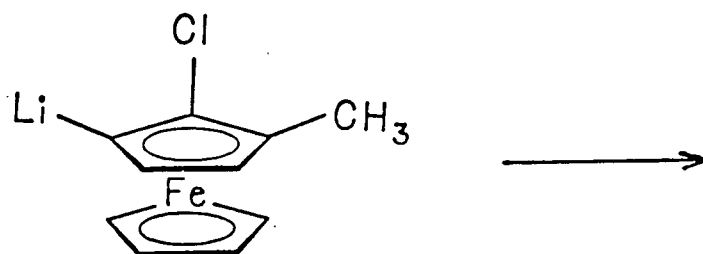
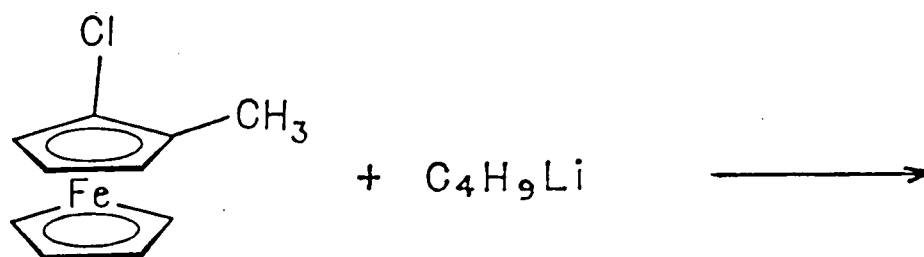
Thus, it may be possible to isolate a ferrocene fragment if it is associated with a metal cluster.



Scheme 9 Metal-Halogen Interconversion in the Reaction of $FcCl$ with $BuLi$



Scheme 10 Metathesis in the Reaction of FcCl with BuLi



Scheme 11 Reaction of a Substituted Haloferrocene

3.2 Experimental

The methods and supplies used are as already described unless otherwise mentioned.

3.2.1 General Methods

Extra care was taken in the pyrolysis experiments described below since the products are expected to be more air sensitive than their parent compounds. Solvents not previously mentioned were of spectral grade, and all solvents were degassed by freeze-pump-thaw cycles.

Proton NMR spectra were also run on a Varian XL-300 spectrometer. Phosphorus data are given relative to trimethylphosphite.

The details of the thermal reactions carried out are listed in Table XIX. Small amounts (20 - 100 mg) of the ferrocenylphosphine substituted metal carbonyl were dissolved in 10 - 20 mL of the appropriate solvent and refluxed in a nitrogen atmosphere. Spectroscopic data are tabulated in Tables XX to XXII. IR spectra were FT and electron impact ionization was used for mass spectroscopic analysis as described above.

Table XIX Pyrolytic Reactions of the $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ Derivatives.

Compound	Solvent	Time (min)	Product Description and Isolation
$\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$	hexanes	30	no reaction
	C_6H_{12}	15	no isolable products
$\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$	hexanes	60	no isolable products
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	C_8H_{10}	20	no isolable products
	C_6H_{12}	60	red orange solid moderate yield, chromatographic separation on Alumina pet ether/ Et_2O (1:1) less polar than reactant
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	hexanes	60	no reaction
	hexanes/ C_6H_{12} (1:1)	60	no reaction

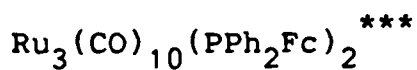
C_6H_{12}	30	purple red solid
		high yield,
		chromatographic separation
		on Alumina
		Et_2O
		less polar than reactant
$Ru_3(CO)_{10}(PPhFc_2)_2$	hexanes 60	dark orange solid
		high yield,
		chromatographic separation
		on Alumina
		Et_2O/CH_2Cl_2 (5:1)
		more polar than reactant

Table XX NMR Chemical Shift Data (δ) for Some Products of the Pyrolytic Reactions

Compound Pyrolysed					
Phenyl Region			Ferrocenyl Region		

$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})^*$					
7.58-7.30	br m	15H	5.53	m	2H
			5.35	m	1H
			5.15	m	1H
			4.85	s	5H
			4.80	m	1H
			4.70	m	1H
			4.02	s	5H
			3.15	m	1H
			3.03	m	1H
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2^{**}$					
8.00-7.95	m	2H	4.55	br s	1H
7.82-7.76	br m	2H	4.44-4.41	m	2H
7.74-7.71	br m	1H	4.29	s	5H
7.55-7.45	br m	7H	4.09	br s	1H
7.30-7.32	br m	1H	4.01	br s	1H

6.98-7.00	br m	1H	4.00	s	5H
6.61-6.57	br m	1H	3.78	br s	1H
6.51-6.47	br m	1H	3.69	br s	1H
6.40-6.36	br m	1H	2.88	br s	1H



131.04 d, J(PP) 200 Hz, 67.82 d, J(PP) 200 Hz

* 80 MHz Spectrometer ^1H NMR

** 400 MHz Spectrometer ^1H NMR

*** 270 MHz Spectrometer ^{31}P { ^1H } NMR (109.3 MHz for ^{31}P)

Table XXI IR Data for Some Products of Pyrolytic Reactions

Compound Pyrolysed	Absorption (cm^{-1})
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$	2078 w, 2043 m, 2037 s, 2020 m, 2018 m, 1989 w, 1822 w
$\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$	2054 s, 2013 m, 2003 s, 1996 m, 1961 sh, 1956 m, 1951 w, 1943 sh
$\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$	2070 m, 2048 m, 2009 s, 1999 m, 1980 w, 1949 w

Table XXII Mass Spectroscopic Data for the Product Obtained by Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$

Peak (m/e)
1163, 1106, 1079, 1050, 1023, 994, 967, 888, 821, 810, 783, 766, 746, 734, 703, 655, 600, 577, 503, 489, 478, 446, 429, 415, 401, 386, 370, 355, 262, 186, 149, 121, 77, 56

3.3 Discussion

The thermal decomposition reactions of the iron derivatives $\text{Fe}(\text{CO})_4(\text{PPh}_2\text{Fc})$ and $\text{Fe}(\text{CO})_4(\text{PPhFc}_2)$ were investigated. In both cases decomposition to a brown solid occurs, from which no isolable products can be obtained.

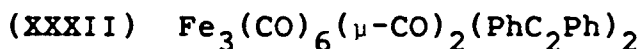
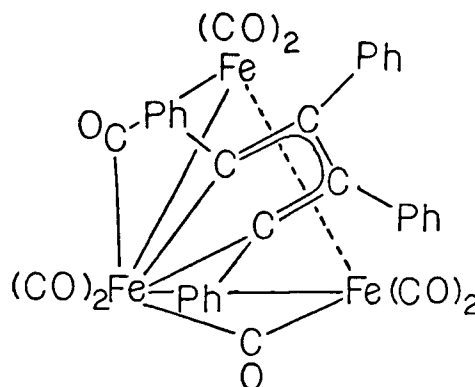
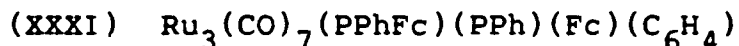
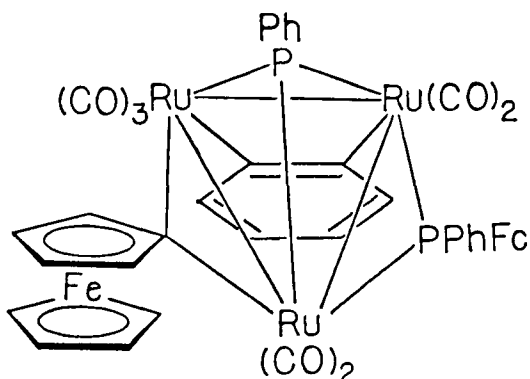
Thermal decomposition reactions of the three ruthenium carbonyl cluster compounds $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ and $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$ give promising results. Initially, pyrolysis in high boiling solvents was tried but no isolable products were obtained. Pyrolysis in lower boiling solvents was more successful. There is evidence for the formation of other products if pyrolysis is allowed to take place for longer periods than those given, but the production of the first formed product was optimised. The products are darker in colour than the parent compounds.

3.3.1 Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$

The decomposition of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{Fc})_2$ gives a high yield of a product for which NMR, IR and mass spectroscopic data were obtained. A structure (XXXI) is proposed for this compound which seems consistent with all the data. The structure contains three ruthenium atoms and seven carbonyl ligands, a benzyne fragment that acts as a two electron donor to two metal atoms and is fluxional between all three metal atoms, and a ferrocene group which bridges two metal atoms. In addition it contains a triply bridging phosphinidene and a

doubly bridging phosphido group.

The number of ruthenium atoms proposed is consistent with the colour of the complex and with the mass spectroscopic data. The number of carbonyl ligands is supported by infrared data and mass spectroscopic data. The IR spectrum is similar to that obtained⁹⁷ for the terminal carbonyl region of $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2(\text{PhC}_2\text{Ph})_2$, (XXXII), a cluster containing carbonyl ligands that are in environments of similar symmetry to the carbonyl ligands in (XXXI).



The presence of two phosphorus atoms is supported by mass spectroscopic and NMR data. The proton decoupled phosphorus NMR spectrum shows two doublets coupled by 200 Hz. The difference in chemical shifts of the two phosphorus atoms is 63 ppm. The difference in chemical shifts of the two phosphorus atoms in $\text{Ir}_3(\text{CO})_6(\text{Ph})(\text{PPh})(\text{dppm})$ ⁹⁸ is 152 ppm, so the two phosphorus atoms in $\text{Ru}_3(\text{CO})_7(\text{PPhFc})(\text{PPh})(\text{Fc})(\text{C}_6\text{H}_4)$

should be in chemical environments that are more similar than those in $\text{Ir}_3(\text{CO})_6(\text{Ph})(\text{PPh})(\text{dppm})$. It is proposed that one of the phosphorus atoms is involved in a triply bridging interaction between the three metal atoms as a phosphinidene, and that the other phosphorus atom doubly bridges two metal atoms as a phosphido ligand.

Doubly bridging phosphido ligands are well known. Examples have been given in (XXIV),^{92,94} (XXVII),^{93,94} (XXIX),^{93,94} (XXV),^{92,94} and (XXX).⁷³ Triply bridging phosphinidenes are less well known, but examples have been reported for iridium,⁹⁸ iron,⁹⁹ ruthenium,^{100-102,104} and osmium¹⁰³ clusters. The osmium example, $\text{Os}_3(\text{CO})_9(\text{PEt})(\text{C}_6\text{H}_4)$ contains both a triply bridging phosphorus ligand and a fluxional benzyne group as proposed for (XXXI). A ruthenium example, $\text{H}_2\text{Ru}_3(\text{CO})_9(\text{PPh})$ ¹⁰⁵ exhibits a proton decoupled ^{31}P chemical shift of 137.4 ppm relative to trimethylphosphite for the triply bridging phosphinidene group, which compares favourably with that obtained for (XXXI), 131.04 ppm.

The peak of the mass spectrum representing the largest m/e value, 1163, could be associated with an ion of formula $\text{Ru}_3(\text{CO})_7(\text{PPhFc})(\text{PPh})(\text{Fc})(\text{C}_6\text{H}_4)^+$. Other peaks at appropriate intervals represent the loss of two carbonyl ligands followed by sequential loss of the remaining five. After loss of carbonyl ligands, further peaks can be rationalized by loss of the benzyne, and ferrocene fragments.

3.3.1.1 Discussion of the ^1H NMR Spectrum

Chemical shift values were obtained from a 400 MHz spectrum (Table XX) and decoupling experiments were run using a 300 MHz spectrometer. The ferrocenyl region of the 300 MHz NMR spectrum is shown in Figure 8. The two singlets C and F arise from the two unsubstituted cyclopentadienyl rings. The singlet F is in the usual region for ferrocenylphosphines and C is at lower field than usual. The other peaks A, D, E, G, H and J all integrate as one proton while B integrates as two protons. The total number of protons is therefore ten for the two unsubstituted cyclopentadienyl rings and eight for the two substituted cyclopentadienyl rings. Two types of ferrocenyl groups are observed in equimolar quantities, as well as an impurity labelled I which seems to represent another cluster compound with unusual ferrocenyl proton chemical shifts. The chemical shift of J is very high for a ferrocenyl proton and the other protons from the substituted cyclopentadienyl rings are in the usual range for ferrocenylphosphines. The appearance of the protons as separate peaks is not unusual for high field NMR spectra of ferrocenylphosphines.

Homonuclear decoupling experiments were used to determine which resonances are associated with protons from each substituted cyclopentadienyl ring. Irradiation at A showed that it coupled to B and G since those peaks narrowed. The peak B was shown to be coupled to A, D, E, G, H and J. Irradiation at G and H showed coupling to B, and irradiation

at J showed coupling to B, D and E. Hence the protons of one of the substituted cyclopentadienyl rings have chemical shifts represented by A, B, G and H, while the other is represented by B, D, E and J. This confirms that each ferrocenyl group is monosubstituted.

The ring protons represented by A,B,G and H have chemical shifts in the usual region of the NMR spectrum for metal substituted ferrocenylphosphines, and probably belong to the same ferrocenyl group as the cyclopentadienyl ring assigned to F, and could arise from either a terminal or a bridging ferrocenylphosphine.

The unusual chemical shift value for J which is associated with B, D and E and probably C for which there is also an unusual chemical shift, could be due to the interaction shown in (XXXI), where the ferrocene molecule is bridging two of the ruthenium atoms. This sort of ligation is known for phenyl rings as shown in (XXIV).^{92,94} Terminal σ -bonding of a phenyl group in a cluster to an iridium atom is also known.⁹⁸ Precedence for ferrocene bridging two metals in this manner does not exist apart from the known structures of lithioferrocenes.¹⁰⁴

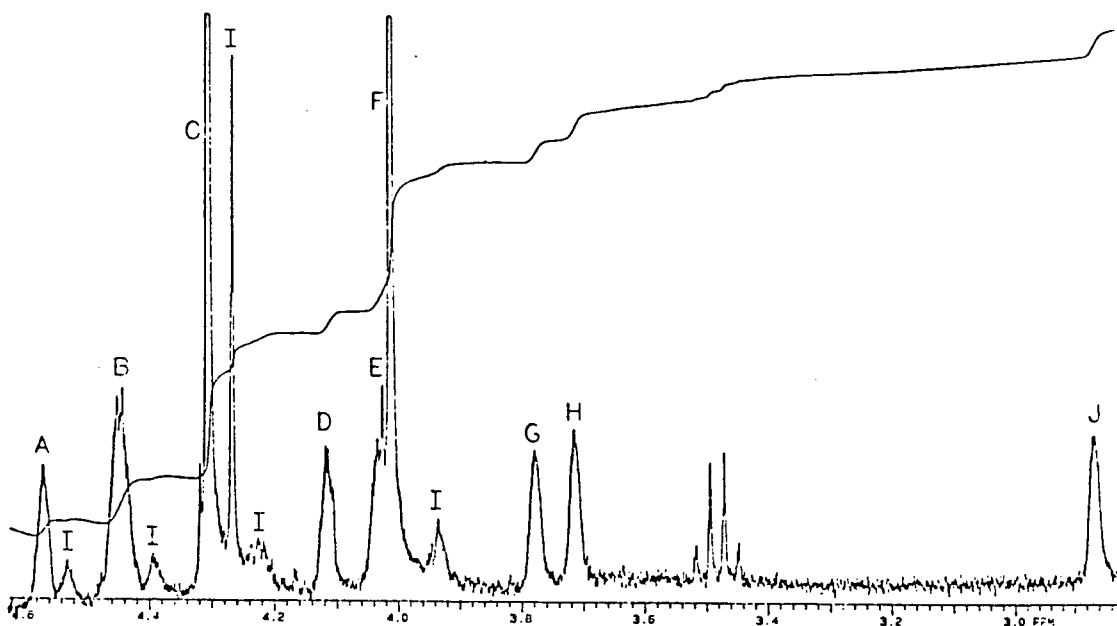


Figure 8 ^1H NMR Spectrum of (XXXI) - Ferrocenyl Region

The 300 MHz ^1H NMR spectrum of the phenyl region of the product is shown in Figure 9. The peaks K, L, M and N are in the usual region for phenylphosphines. Usually monosubstituted phenyl rings appear in a 3:2 ratio, the ortho and para protons in the region occupied by N and the meta protons in the region occupied by K, L and M.

Homonuclear decoupling experiments were found to be particularly informative. Irradiation at K decoupled N; irradiation at L and M decoupled O; irradiation at N decoupled K, L and O, but not M causing K and L to form doublets with fine structure; irradiation at O showed the presence of coupling at L and N. This means that the protons of one

phenyl group show chemical shifts at K and N with protons in the ratio 2:3 and the protons of the other phenyl group show chemical shifts at L, N and O with protons in the ratio 2:2:1. The peak M as well as some of N, is probably caused by the impurity mentioned above.

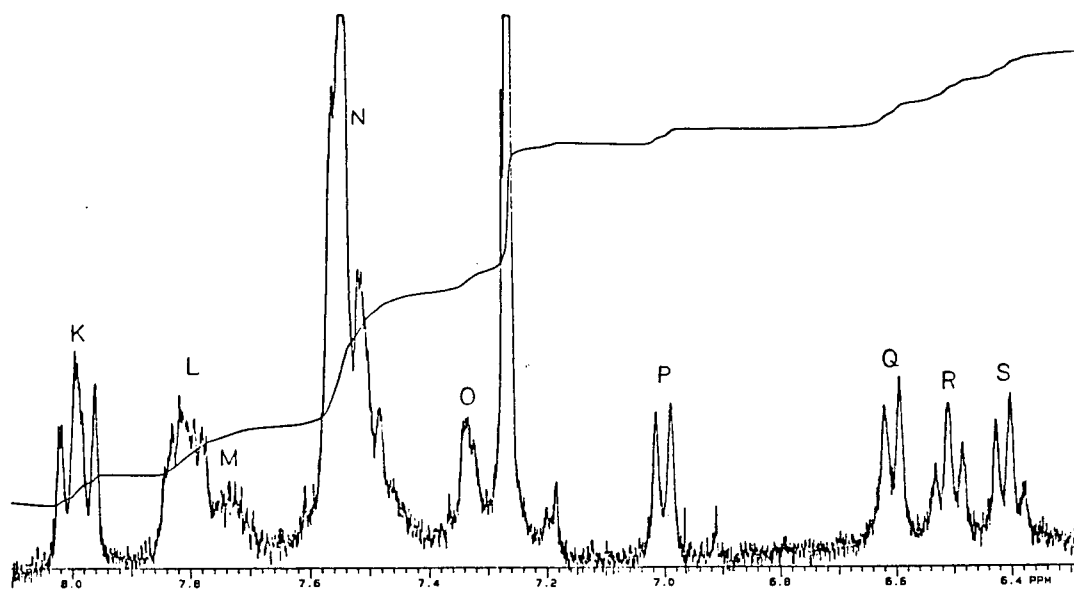


Figure 9 ^1H NMR Spectrum of (XXXI) - Phenyl Region

The peaks P, Q, R and S exhibit unusual splitting patterns for phenyl phosphines.

Homonuclear decoupling experiments involving P, Q, R and S give unusual results. Irradiation at P causes Q to disappear, while effects at R and S are difficult to determine due to the poor quality of the spectrum in that region. Irradiation at Q also causes P to disappear and effects at R and S are again difficult to ascertain because of the proximity of the chemical shifts to the irradiated area. Irradiation between P and Q causes them both to decrease in intensity, while irradiation at R causes S to disappear and P and Q to become singlets. Results from decoupling at S are difficult to analyse due to the "glitch" in that area.

The total collapse of one peak due to irradiation at another peak is most likely caused by fluxional processes. Fluxional behaviour can transfer the spin saturation effects of decoupling.^{105,106} Irradiation of hydride resonances has been used to indicate exchange of bridging and terminal hydrides¹⁰⁷ when similar collapse of resonances is encountered.

Since the integration of these peaks shows them to be due to four protons, a C_6H_4 benzyne fragment as in (XXVII)^{93,94}, (XXV)^{92,94} and (XXX)⁷³ is proposed. An NMR study¹⁰⁸ of osmium clusters containing benzyne fragments formed from $Os_3(CO)_{11}(EMe_2Ph)$ and $Os_3(CO)_{10}(EMe_2Ph)_2$ (E=P or As), show

these fragments to have fluxional behaviour. Their spectra show ABXY patterns upon cooling to 183 K. The benzyne fragment suggested for (XXXI) shows a similar pattern at room temperature so the fluxional process must be occurring somewhat more slowly, which seems reasonable in light of the increased steric hindrance of the two ferrocene fragments in the cluster. The fluxional properties of benzyne fragments of similar metal clusters have also been investigated.¹⁰⁹⁻¹¹¹

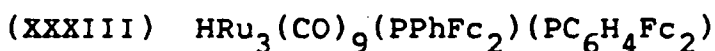
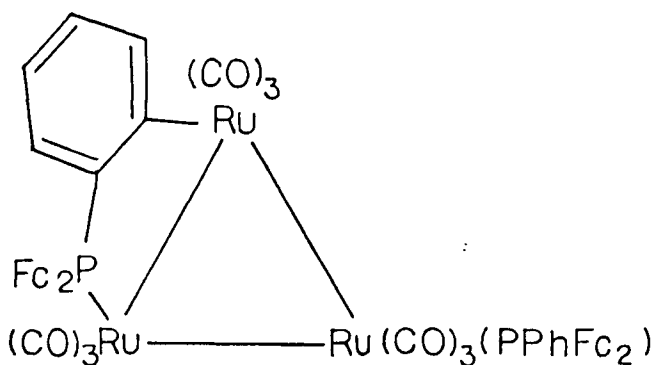
3.3.2 Pyrolysis of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$

Interesting features are observed for the product obtained from the pyrolysis of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{Fc})$. The proton NMR spectrum in the ferrocenyl region shows the presence of two types of ferrocenyl groups, including a proton with an unusually high chemical shift value. Also present is a singlet of unusually low chemical shift value that represents an unsubstituted cyclopentadienyl ring as is observed for (XXXI). Integration of the spectrum shows evidence for the loss of one phenyl group for each two ferrocenyl groups present. The infrared spectrum is similar to that of the edge double bridged cluster $\text{Ru}_3(\mu\text{-H})(\mu\text{-Br})(\text{CO})_{10}$,¹¹² which suggests a complex with a bridging carbonyl ligand and another ligand perhaps also bridging one edge of the cluster.

3.3.3 Pyrolysis of $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$

The product obtained from heating $\text{Ru}_3(\text{CO})_{10}(\text{PPhFc}_2)_2$

gives an infrared spectrum that is very similar to the spectrum reported for complex $\text{HOS}_3(\text{CO})_9(\text{PPh}_3(\text{PPh}_2\text{C}_6\text{H}_4))$ (XXVI), so it is possible that this compound has the related structure (XXXIII).



To date, the products obtained by pyrolysis of ferrocenylphosphine containing metal clusters have not been obtained in large enough amounts to allow for full characterization and elucidation of structures. Initial results indicate that both the ferrocenyl groups and the phenyl groups of the phosphine ligands are reactive, although only a benzyne fragment seems to be formed. There is strong evidence that the ferrocene groups have reacted to form unusual fragments.

The initial results are interesting and further investigation into the nature of these compounds should be rewarding.

Chapter Four - Conclusions

The reactions of the ferrocenylphosphines PBuPhFc, PPh₂Fc, PPhFc₂, PFc₃ and Fe(C₅H₄)₂PPh with the metal carbonyls Fe₃(CO)₁₂ and Ru₃(CO)₁₂ have been investigated. Ferrocenylphosphines react readily with both metal carbonyls. With iron carbonyl, mononuclear products predominate, and with ruthenium carbonyl, trinuclear complexes are the principal products as follows: Fe(CO)₄L (L=PBuPhFc, PPh₂Fc, PPhFc₂ and PFc₃); Fe₃(CO)₁₁L (L=PPh₂Fc and PBuPhFc), Fe₃(CO)₁₀(PBuPhFc)₂, Ru(CO)₄(PFc₃), Ru₃(CO)₁₁L (L=PPh₂Fc, PPhFc₂, PFc₃ and Fe(C₅H₄)₂PPh); Ru₃(CO)₁₀L₂ (L=PPh₂Fc, PPhFc₂, PFc₃ and Fe(C₅H₄)₂PPh), Ru₃(CO)₉(PPh₂Fc)₃ and Ru₃(CO)₉(PPhFc₂)₃. These compounds were characterized using NMR and IR spectroscopy, mass spectroscopy, elemental analysis, and in one instance an X-ray crystal structure determination. The method of choice for the synthesis of these compounds is to initiate the reactions at room temperature with a solution of the diphenylketyl radical anion. This method gives high yields and easy isolation of products.

The pyrolytic chemistry of the ferrocenylphosphine clusters seems to be of considerable interest. The reactions studied in this investigation afford high yields of primarily one product. The partial characterization of one such product gives an indication of the variety of new compounds that could be expected to be produced in this manner. Unfortunately,

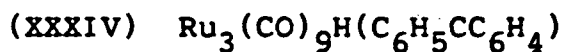
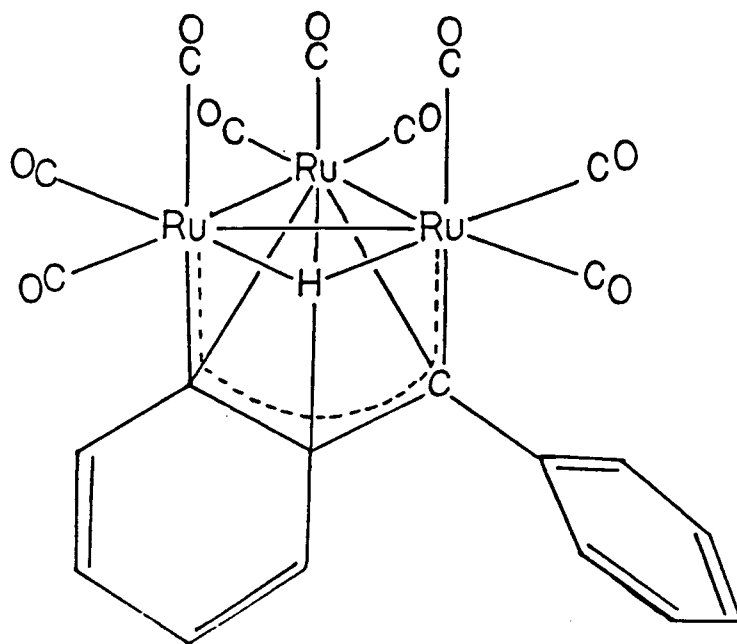
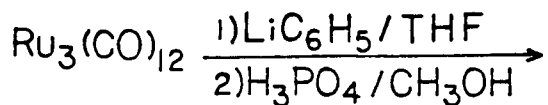
because of their complexity, most characterizations of unusual metal clusters rely on X-ray crystallographic analysis so that further progress in this study will be considerably dependent on the growth of suitable crystals.

Nevertheless, further study of the products of the pyrolytic reactions of ferrocenylphosphines should be useful, especially if these studies include detailed spectroscopic studies of compounds of known structures. With the establishment of a broader knowledge of the spectroscopic properties of these compounds, structures will be more readily assigned without recourse to X-ray crystallography. Single crystals will hopefully be obtained of the compound (XXXI). More certain spectroscopic assignments should then be possible.

Other related studies that could give interesting results would involve the reactions of lithio-compounds with metal cluster carbonyls. The reactions of aryl- or alkyl lithium compounds with mononuclear metal carbonyl complexes are well known¹¹³ and lead to metal carbene complexes. Reactions of lithio-compounds with metal cluster carbonyls are much less studied. Fischer¹¹⁴ has reported the reaction of $\text{Ru}_3(\text{CO})_{12}$ with phenyllithium (Scheme 12) from which a very low yield was obtained of $\text{Ru}_3(\text{CO})_9\text{H}(\text{C}_6\text{H}_5\text{CC}_6\text{H}_4)$ (XXXIV). The structure was established by X-ray crystallographic analysis.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with MeLi and LiBr¹¹⁵ gives

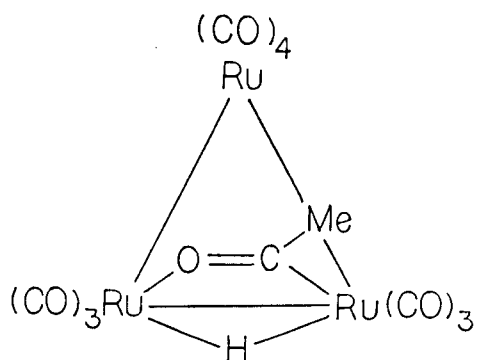
moderate yields of the edge double bridged clusters $\text{Ru}_3(\mu\text{-H})(\mu\text{-O=CMe})(\text{CO})_{10}$ (XXXV) and $\text{Ru}_3(\mu\text{-H})(\mu\text{-Br})(\text{CO})_{10}$ (XXXVI).



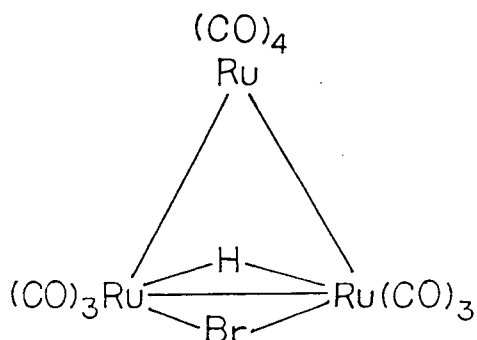
Scheme 12 Reaction of $\text{Ru}_3(\text{CO})_{12}$ with PhLi

It was shown^{18,116,117} that the ferrocenophane, $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$ (V), if cleaved with phenyllithium, yields a monolithiated ferrocenylphosphine $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{Li})$ (the intermediate (XXXVII) in Scheme 13). This species reacts with chromium and tungsten hexacarbonyls to form zwitterions and carbene based ferrocenophanes¹¹⁸ (Scheme 13).

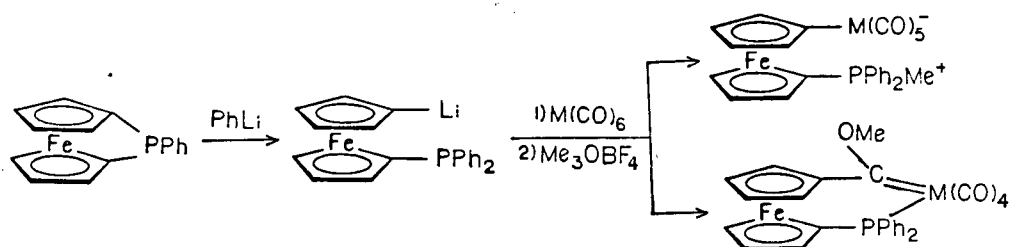
The reaction of (XXXVII) with a metal cluster carbonyl, such as $\text{Ru}_3(\text{CO})_{12}$, could form compounds of this type, perhaps with a ferrocene fragment bridging two metals of the cluster. It would also be interesting to try to cleave the $\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh}$ ligand already associated with a metal cluster. The compounds $\text{Ru}_3(\text{CO})_{11}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})$ and $\text{Ru}_3(\text{CO})_{10}(\text{Fe}(\text{C}_5\text{H}_4)_2\text{PPh})_2$, which were prepared in this study would be ideal. Subsequent reactions of the lithio intermediates could form carbenes or compounds containing an acyl group as in (XXXV).



(XXXV) $\text{Ru}_3(\mu\text{-H})(\mu\text{-O=CMe})(\text{CO})_{10}$



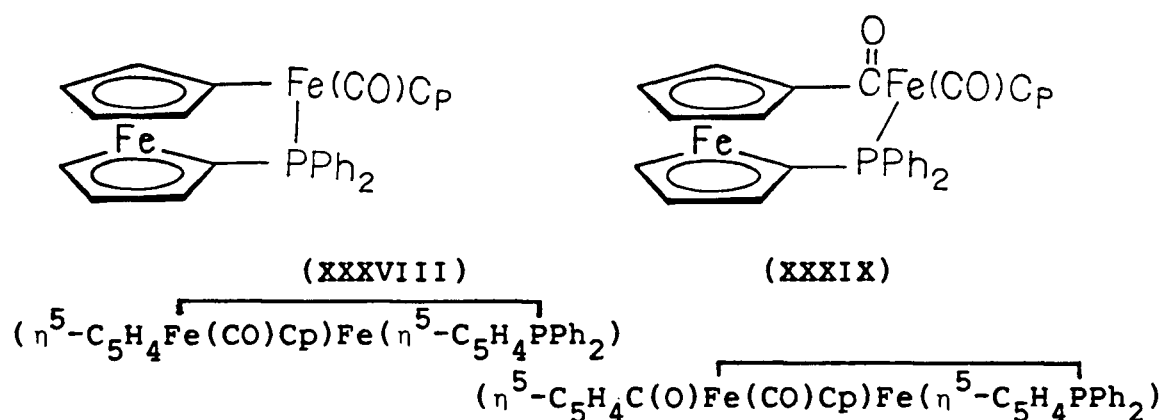
(XXXVI) $\text{Ru}_3(\mu\text{-H})(\mu\text{-Br})(\text{CO})_{10}$



(XXXVII) $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{Li})$

Scheme 13 Reaction of $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}$ and W) with (XXXVII)

The reactions of metal cluster carbonyls containing halogens with lithiated compounds may also be a fruitful area. A solution of (XXXVII) has been reacted with $\text{Fe}(\text{CO})_2\text{CpI}$.¹¹⁹ Two of the products obtained were (XXXVIII) and (XXXIX). Edge double bridged halide containing ruthenium clusters are available¹¹⁵ (XXXVI) and could be used in reactions of this type which could produce σ -bonded ferrocenylphosphine or acyl containing clusters.



Since these clusters are being studied as models for catalytic reactions occurring at metal surfaces, it is important to identify the organic products produced during the formation of these complex clusters. There has been little study in this area so far,¹²⁰ probably because of the large number of possible products. The ferrocenylphosphine derivatives in this study give moderately high yields of primarily one product, so they would be useful systems for the study of the organic products formed concurrently.

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