

# Multimetal complexes of Fischer carbenes

by

**Daniela Ina Bezuidenhout**

Submitted in partial fulfilment of the requirements of  
the degree

**Philosophiae Doctor**

In the Faculty of Natural and Agricultural Sciences

University of Pretoria  
Pretoria

Supervisors:                      Professor Simon Lotz  
   Doctor Marilé Landman

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## Declaration

I declare that the thesis, which I hereby submit for the degree Philosophiae Doctor at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

The X-ray structure determinations reported in this thesis were performed by Mr DC Liles at the University of Pretoria.

Results obtained from this study have also been published in:

D.I. Bezuidenhout, E. van der Watt, D.C. Liles, M. Landman, S. Lotz,  
*Organometallics* **2008**, *27*, 2447-2456.

Signature:

Date:

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Daniela

# Table of Contents

Summary	viii
List of Abbreviations	x
List of Compounds	xv

## Chapter 1 Introduction

1.1	Background	1
1.1.1	Historical development of organometallic chemistry	1
1.1.2	Early development of carbene chemistry	3
1.1.3	Recent developments of polymetallic carbene complexes	6
1.2	Aim of the study	8

## Chapter 2 Group VI Transition Metal Carbene Cluster Complexes

2.1	Introduction	10
2.1.1	Background	10
2.1.2	Hetero-atom bonded carbene ligand substituent	12
2.1.3	Carbon-bonded carbene ligand substituent	15
2.1.3.1	Ferrocenyl carbene ligand substituent	16
2.1.3.2	$\pi$ -aryl carbene ligand substituent	18
2.1.4	Homo- and heteronuclear polymetallic biscarbene complexes	21
2.1.4.1	Conjugated bridging biscarbene complexes	22
2.1.4.2	Biscarbene complexes by connecting heteroatom substituents	25
2.2	Results and discussion	27
2.2.1	Focus of this study	27
2.3	Synthesis	29
2.3.1	Synthesis of ferrocenyl mono- and biscarbene Cr and Mo complexes	31
2.3.2	Synthesis of tungsten carbene complexes	33
2.3.3	Synthesis of mixed heteronuclear bridging biscarbene complex	35
2.3.4	Synthesis of $\pi$ -aryl-Cr(CO) <sub>3</sub> titanoxycarbene complexes of chromium	37

2.4	Spectroscopic characterization	39
2.4.1	<sup>1</sup> H NMR spectroscopy	40
2.4.2	<sup>13</sup> C NMR spectroscopy	47
2.4.3	IR spectroscopy	51
2.4.4	Mass spectrometry	54
2.4.5	Single crystal X-ray crystallography	59
	2.4.5.1 Molecular structures	59
	2.4.5.2 Crystal packing	70
2.5	Concluding remarks	75

### **Chapter 3                    Group VII Transition Metal Carbene Cluster Complexes**

3.1	Introduction	78
3.1.1	Background	78
3.1.2	Monomanganese carbene complexes	80
3.1.3	$\pi$ -arene substituted carbene complexes	82
3.1.4	Dirhenium carbene complexes	84
3.1.5	Axial or equatorial carbene ligands of nonacarbonyl dimetal complexes	85
3.1.6	Different reactivities of manganese and rhenium complexes	87
3.1.7	Hydrido-acyl and hydroxycarbene transition metal complexes	90
3.2	Results and discussion	95
3.2.1	Focus of this study	95
3.3	Synthesis	98
3.3.1	Synthesis of cyclopentadienyl manganese carbene complexes	98
3.3.2	Synthesis of dirhenium ethoxycarbene complexes	99
3.3.3	Synthesis of dirhenium cluster carbene cluster complexes	104
3.4	Spectroscopic investigation	113
3.4.1	<sup>1</sup> H NMR spectroscopy	114
3.4.2	<sup>13</sup> C NMR spectroscopy	122
3.4.3	IR spectroscopy	128
3.4.4	Mass spectrometry	131
3.4.5	Single crystal X-ray crystallography	137
	3.4.5.1 Molecular structures	137
	3.4.5.2 Crystal packing	147
3.5	Concluding remarks	150

<b>Chapter 4</b>	<b>Investigation of substituent effect on carbene ligands</b>	
4.1	Introduction	153
4.1.1	Background	153
4.1.2	Theoretical bonding model of carbene ligands	155
4.2	Molecular modelling	157
4.2.1	The theoretical method	157
4.2.2	Molecular modelling of transition metal complexes	158
4.2.3	Modelling of Fischer carbene complexes	159
4.2.4	Substituent effect	162
4.3	Electrochemical approach	166
4.3.1	Anodic electrochemical behaviour of Fischer carbene complexes	167
4.3.2	Cathodic behaviour of Fischer carbene complexes	170
4.4	Results and discussion	173
4.4.1	Focus of this study	173
4.5	Theoretical investigation of substituent effect	175
4.5.1	Computational details	175
4.5.2	Theoretical results	177
4.5.3	Vibrational spectroscopy results	181
4.5.4	Molecular orbital analysis	185
4.5.5	Correlation between UV/Vis spectroscopy and MO analysis	193
4.5.6	Natural bond orbital analysis	197
4.6	Electrochemical investigation of substituent effect	201
4.6.1	Cyclic voltammetric studies	202
4.7	Concluding remarks	207
4.7.1	Summary	207
4.7.2	Future work	209
<b>Chapter 5</b>	<b>Experimental</b>	
5.1	Standard operating procedure	210
5.2	Characterization techniques	210
5.2.1	Nuclear magnetic resonance spectroscopy	210
5.2.2	Infrared spectroscopy	211
5.2.3	Raman spectroscopy	211
5.2.4	Fast atom bombardment mass spectrometry	212

5.2.5	X-ray crystallography	212
5.2.6	UV/Visible spectroscopy	213
5.3	Electrochemistry	213
5.4	Preparation of compounds	214
5.4.1	Preparation of starting material compounds	214
5.4.1.1	Triethyl oxonium tetrafluoroborate	214
5.4.1.2	Chloromercury ferrocene	214
5.4.1.3	Bromoferrocene	215
5.4.1.4	Iodoferrocene	215
5.4.1.5	Trisammine tricarbonyl chromium	215
5.4.1.6	$\eta^5$ -thiophene chromium tricarbonyl	216
5.4.1.7	$\eta^6$ -benzene chromium tricarbonyl	216
5.4.2	Preparation of organometallic complexes	217
5.4.2.1	General carbene preparation with direct lithiation of ferrocene in the presence of TMEDA	217
5.4.2.2	General carbene complex preparation with aryl lithiation at low temperatures	219
5.4.2.3	Preparation of mixed heteronuclear carbene complex	219
5.5	Analytical data	221

## Appendices

Attached compact disk

Appendix 1	Crystallographic data of Complex <b>3</b>
Appendix 2	Crystallographic data of Complex <b>5</b>
Appendix 3	Crystallographic data of Complex <b>6</b>
Appendix 4	Crystallographic data of Complex <b>8</b>
Appendix 5	Crystallographic data of Complex <b>12</b>
Appendix 6	Crystallographic data of Complex <b>13</b>
Appendix 7	Crystallographic data of Complex <b>23</b>
Appendix 8	Crystallographic data of Complex <b>27</b>
Appendix 9	Crystallographic data of Complex <b>28</b>
Appendix 10	Crystallographic data of Complex <b>33</b>

# Summary

## Multimetal complexes of Fischer carbenes

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**Daniela Ina Bezuidenhout**

Supervisor: Prof S Lotz

Co-supervisor: Dr M Landman

Submitted in partial fulfilment of the requirements for the degree Philosophiae  
Doctor, Department of Chemistry, University of Pretoria

Fischer carbene complexes of the Group VI transition metals (Cr, Mo and W) containing at least two or three different transition metal substituents, all in electronic contact with the carbene carbon atom, were synthesized and studied both in solution and in the solid state. For the complexes of the type  $[M(CO)_5C(OR)R']$ , the substituents chosen included (hetero)aromatic (benzene or thiophene) rings  $\pi$ -bonded to a chromium tricarbonyl fragment or ferrocene as the  $R'$ -substituent, while the OR-substituent was systematically varied between an ethoxy or a titanoxo group, to yield the complexes **1** ( $M = Cr$ ,  $R = Et$ ,  $R' = Fc$ ), **2** ( $M = W$ ,  $R = Et$ ,  $R' = Fc$ ), **5** ( $M = Cr$ ,  $R = TiCp_2Cl$ ,  $R' = Fc$ ), **6** ( $M = W$ ,  $R = TiCp_2Cl$ ,  $R' = Fc$ ), **7** ( $M = Mo$ ,  $R = TiCp_2Cl$ ,  $R' = Fc$ ), **12** ( $M = Cr$ ,  $R = TiCp_2Cl$ ,  $R' = 2$ -thienyl) and **13** ( $M = Cr$ ,  $R = TiCp_2Cl$ ,  $R' = [Cr(CO)_3(\eta^6\text{-phenyl})]$ ).

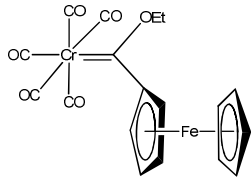
Direct lithiation of the ferrocene with *n*-BuLi/TMEDA at elevated temperatures, followed by the Fischer method of carbene preparation, also resulted, in most cases, in the formation of the novel biscarbene complexes with bridging ferrocene-1,1'-diyl carbene ligands  $[\mu\text{-Fe}\{C_5H_4C(OEt)M(CO)_5\}_2]$  (**3**:  $M = Cr$ , **4**:  $M = W$ ) or the unusual bimetallacyclic bridged biscarbene complexes  $[\{\mu\text{-TiCp}_2O_2\text{-O,O'}\}\{\mu\text{-Fe}(C_5H_4)_2\text{-C,C'}\}\{CM(CO)_5\}_2]$  (**8**:  $M = Cr$ , **9**:  $M = W$ , **10**:  $M = Mo$ ). It was attempted to prepare the mixed heteronuclear biscarbene complex **11**  $[W(CO)_5C\{\mu\text{-TiCp}_2O_2\text{-O,O'}\}\{\mu\text{-Fe}(C_5H_4)_2\text{-C,C'}\}CCr(CO)_5]$ , however the complex could not be fully characterized.



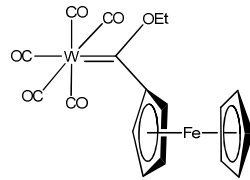
The investigation was expanded to include Group VII transition metals Mn and Re, and using the same methodology, the manganese complexes isolated included  $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OR})\text{Fc}\}]$  (**22**: R = Et, **24**: R =  $\text{TiCp}_2\text{Cl}$ ), **23**  $[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{MnCp}(\text{CO})_2\}_2]$  and **25**  $[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O'}\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C'}\}[\text{CMnCp}(\text{CO})_2\}_2]$ . The different reactivity of the binary dirhenium decacarbonyl precursor complex, compared to that of the Group VI complexes, resulted in the formation of a range of complexes. The target compounds  $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OR})\text{Fc}\}]$  (**26**: R = Et, **31**: R =  $\text{TiCp}_2\text{Cl}$ ), **27**  $[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{Re}_2(\text{CO})_9\}_2]$  and **33**  $[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O'}\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C'}\}[\text{CRe}_2(\text{CO})_9\}_2]$  were isolated displaying a variety of different geometric isomers. In addition, acyl (**30**) and aldehyde (**32**) decomposition products, as well as hydrido (**29**), and hydrido acyl hydroxycarbene (**34**) complexes and the unique dichloro-bridged biscarbene complex (**28**) were also characterized. Most of these complexes displayed Re-Re bond breaking, and two probable mechanisms, either radical or ionic, were proposed involving either hydrogen transfer or protonation followed by hydrolysis.

Finally, the structural features and their relevance to bonding in the carbene cluster compounds of the Group VI transition metals were investigated as they represent indicators of possible reactivity sites in multimetal carbene assemblies. The possibility of using DFT calculations to quantify the effect of metal-containing substituents on the carbene ligands was tested and correlated with experimental parameters by employing methods such as vibrational spectroscopy, molecular orbital analysis, and cyclic voltammetry. The best results were obtained from the cyclic voltammetric studies, where the localized metal centre's oxidation potential correlated to both the calculated HOMO energy, and the effect of both the heteroatom substituent and the (hetero)arene substituent, as well as different combinations of the above.

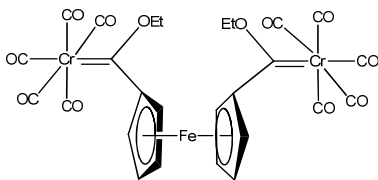
# List of Compounds



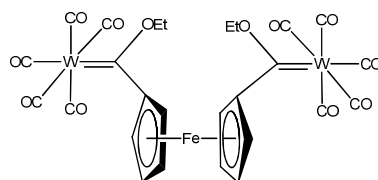
1  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})\text{Fc}\}]$



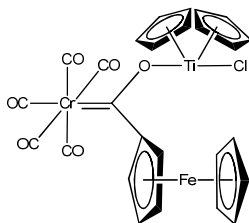
2  $[\text{W}(\text{CO})_5\{\text{C}(\text{OEt})\text{Fc}\}]$



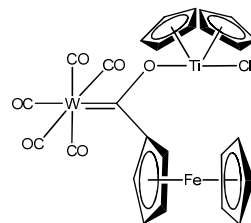
3  $[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{Cr}(\text{CO})_5\}_2]$



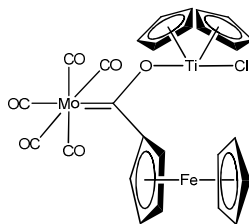
4  $[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{W}(\text{CO})_5\}_2]$



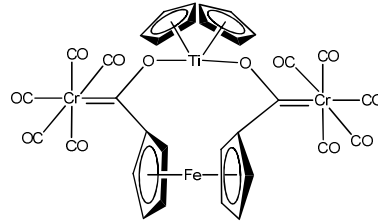
5  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OTiCp}_2\text{Cl})\text{Fc}\}]$



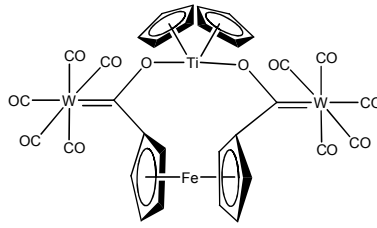
6  $[\text{W}(\text{CO})_5\{\text{C}(\text{OTiCp}_2\text{Cl})\text{Fc}\}]$



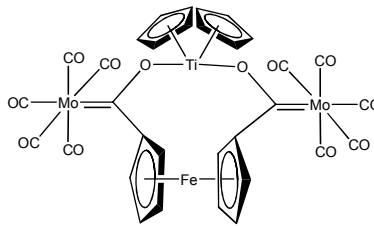
7  $[\text{Mo}(\text{CO})_5\{\text{C}(\text{OTiCp}_2\text{Cl})\text{Fc}\}]$



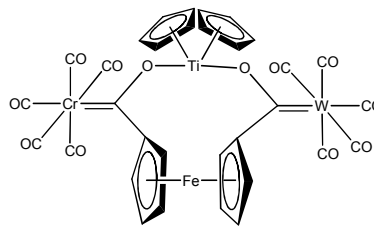
8  $[\mu\text{-TiCp}_2\text{O}_2\text{-O,O'}]\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C'}\}\{\text{CCr}(\text{CO})_5\}_2]$



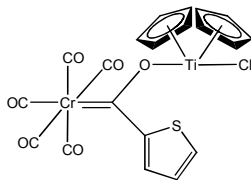
**9**  $[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O}'\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C}'\}\{\text{CW}(\text{CO})_5\}_2]$



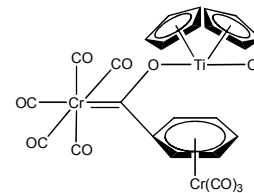
**10**  $[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O}'\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C}'\}\{\text{CMo}(\text{CO})_5\}_2]$



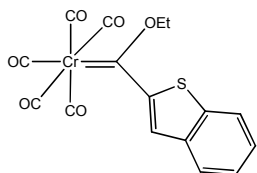
**11**  $[\text{W}(\text{CO})_5\text{C}\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O}'\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C}'\}\text{CCr}(\text{CO})_5]$



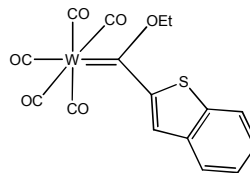
**12**  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OTiCp}_2\text{Cl})(\text{C}_4\text{H}_3\text{S})\}]$



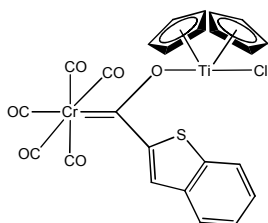
**13**  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OTiCp}_2\text{Cl})(\eta^1:\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}]$



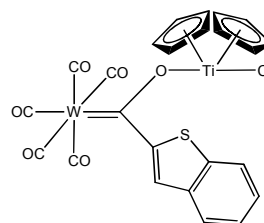
14  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})(\text{C}_8\text{H}_5\text{S})\}]$



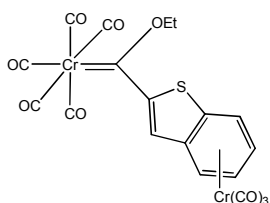
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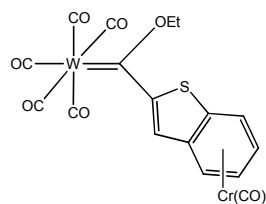
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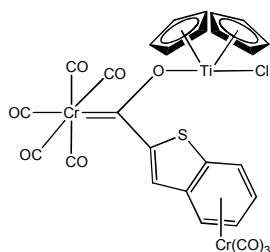
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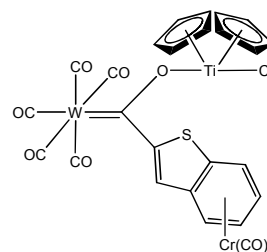
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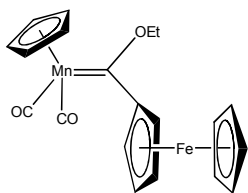
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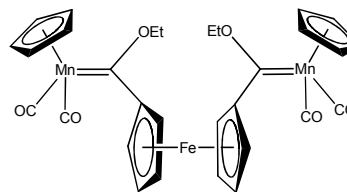
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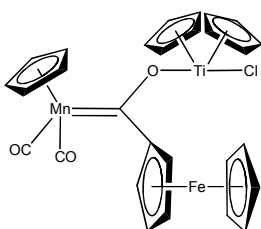
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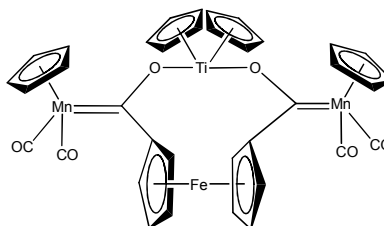
22  $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OEt})\text{Fc}\}]$



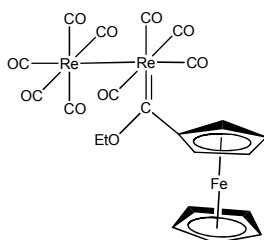
23  $[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{MnCp}(\text{CO})_2\}_2]$



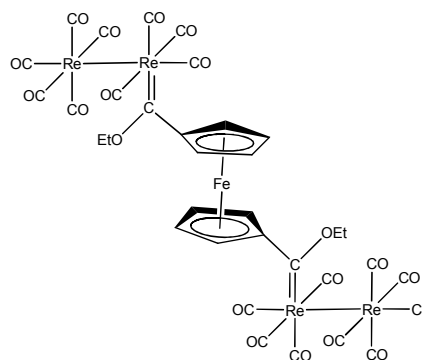
24  $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OTiCp}_2\text{Cl})\text{Fc}\}]$



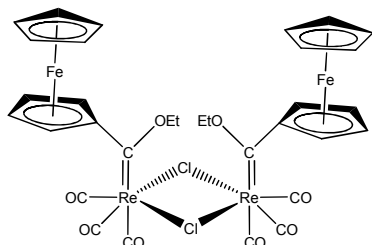
25  $[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O'}\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C'}\}[\text{CMnCp}(\text{CO})_2\}_2]$



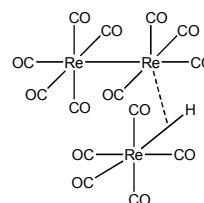
26  $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OEt})\text{Fc}\}]$



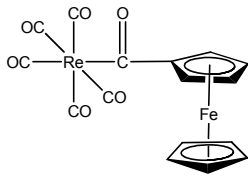
27  $eq,eq\text{-}[\mu\text{-Fe}\{\text{C}_5\text{H}_4\text{C}(\text{OEt})\text{Re}_2(\text{CO})_9\}_2]$



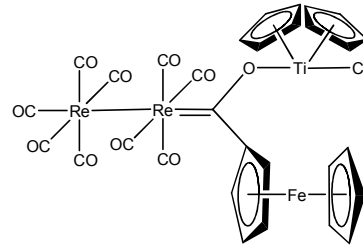
28  $fac\text{-}[(\mu\text{-Cl})_2\text{-}(\text{Re}(\text{CO})_3\{\text{C}(\text{OEt})\text{Fc}\})_2]$



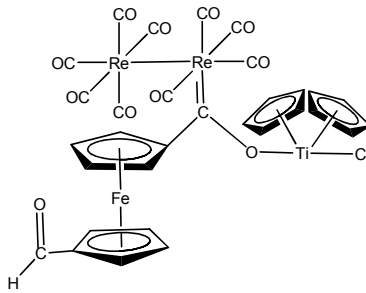
29  $[\text{Re}_3(\text{CO})_{14}\text{H}]$



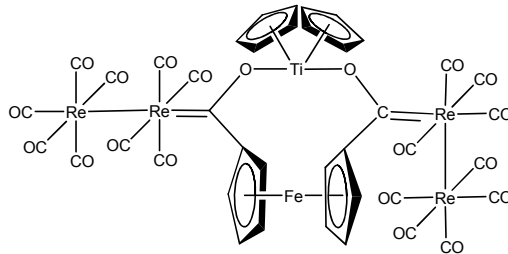
**30**  $[\text{Re}(\text{CO})_5\{\text{C}(\text{O})\text{Fc}\}]$



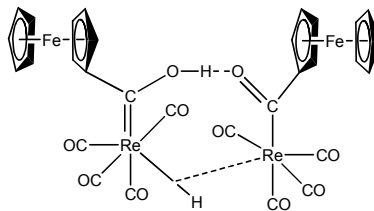
**31**  $ax\text{-}[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OTiCp}_2\text{Cl})\text{Fc}\}]$



**32**  $eq\text{-}[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OTiCp}_2\text{Cl})(\text{Fc}'\text{CHO})\}]$



**33**  $ax, eq\text{-}[\{\mu\text{-TiCp}_2\text{O}_2\text{-O,O'}\}\{\mu\text{-Fe}(\text{C}_5\text{H}_4)_2\text{-C,C'}\}\{\text{CRe}_2(\text{CO})_9\}_2]$



**34**  $[(\mu\text{-H})_2\text{-}(\text{Re}(\text{CO})_4\{\text{C}(\text{O})\text{Fc}\})_2]$

## List of Abbreviations

<i>ax</i>	:	axial
Bu	:	butyl
br	:	broad (IR, NMR)
BT	:	benzothieryl
Cp	:	$\eta^5\text{-C}_5\text{H}_5$
d	:	doublet
DCM	:	dichloromethane
DEE	:	diethyl ether
dd	:	doublet of doublets
ddd	:	doublet of doublets of doublets
DFT	:	density functional theory
Et	:	ethyl
<i>eq</i>	:	equatorial
eq	:	equivalent
Fc	:	ferrocenyl
Fc'	:	ferrocen-1,1'-diyl
$\eta^n$	:	hapticity of $\text{C}_n\text{H}_n$
HOMO	:	highest occupied molecular orbital
IR	:	infrared spectroscopy
<i>J</i>	:	coupling constant
LUMO	:	lowest unoccupied molecular orbital
m	:	medium (IR)
Me	:	methyl
MLCT	:	metal-to-ligand charge transfer
MO	:	molecular orbital
MS	:	mass spectrometry
NBO	:	natural bond orbital
NMR	:	nuclear magnetic resonance spectroscopy



n.o.	:	not observed
Ph	:	phenyl
R	:	alkyl group
RT	:	room temperature
s	:	singlet (NMR)
s	:	strong (IR)
T	:	thienyl
THF	:	tetrahydrofuran
TMEDA	:	<i>N, N, N', N'</i> -tetramethylethylenediamine
UV	:	ultraviolet
Vis	:	visible
vs	:	very strong (IR)
vw	:	very weak (IR)
w	:	weak (IR)
Å	:	angstrom
δ	:	chemical shift
λ	:	wavelength





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*I think the ways by which people gain knowledge  
are almost as wonderful as the nature of the things themselves*

Johannes Kepler  
German Astronomer (1571 – 1630)

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