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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:

Acknowledgements

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Mr Dave Liles, who performed the data collections and structure determinations of my single crystal X-ray diffraction results. Your inputs were very valuable, and are much appreciated.

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My parents, Danie and Ina Bezuidenhout, and sister Annalie, who have always believed in me, and provided all the inspiration needed to complete this degree.

Sean, for your love, support and encouragement. I could not have done it without you.

Daniela

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Attached compact disk

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

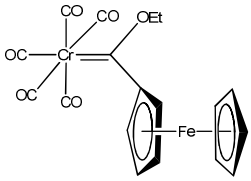
Fischer carbene complexes of the Group VI transition metals (Cr, Mo and W) containing at least two or three different transition metal substituents, all in electronic contact with the carbene carbon atom, were synthesized and studied both in solution and in the solid state. For the complexes of the type $[M(CO)_5\{C(OR)R'\}]$, the substituents chosen included (hetero)aromatic (benzene or thiophene) rings π-bonded to a chromium tricarbonyl fragment or ferrocene as the R'-substituent, while the OR-substituent was systematically varied between an ethoxy or a titanoxy 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 ferrocen-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.

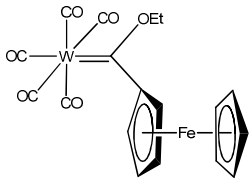
The investigation was expanded to include Group VII transition metals Mn and Re, and using the same methodology, the manganese complexes isolated included [$MnCp(CO)_2${C(OR)Fc}] (**22**: R = Et, **24**: R = $TiCp_2Cl$), **23** [μ-$Fe\{C_5H_4C(OEt)MnCp(CO)_2\}_2$] and **25** [{μ-$TiCp_2O_2$-O,O'}{μ-$Fe(C_5H_4)_2$-C,C'}$[CMnCp(CO)_2\}_2]$. 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 [$Re_2(CO)_9${C(OR)Fc}] (**26**: R = Et, **31**: R = $TiCp_2Cl$), **27** [μ-$Fe\{C_5H_4C(OEt)Re_2(CO)_9\}_2$] and **33** [{μ-$TiCp_2O_2$-O,O'}{μ-$Fe(C_5H_4)_2$-C,C'}$[CRe_2(CO)_9\}_2]$ 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.

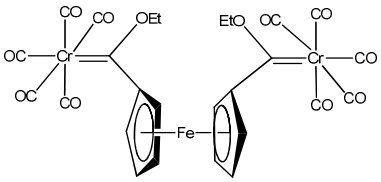
List of Compounds



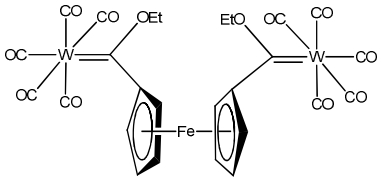
1 $[Cr(CO)_5\{C(OEt)Fc\}]$



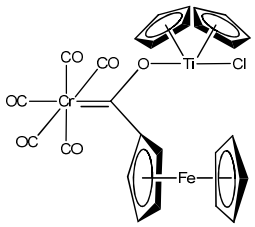
2 $[W(CO)_5\{C(OEt)Fc\}]$



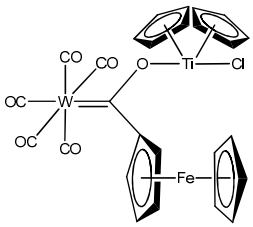
3 $[\mu\text{-}Fe\{C_5H_4C(OEt)Cr(CO)_5\}_2]$



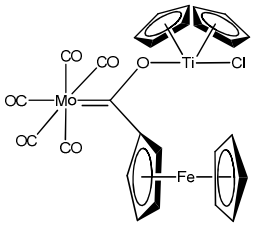
4 $[\mu\text{-}Fe\{C_5H_4C(OEt)W(CO)_5\}_2]$



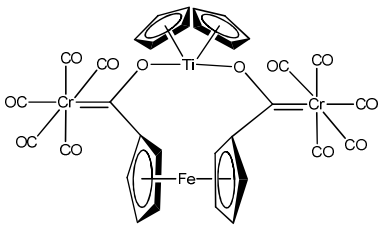
5 $[Cr(CO)_5\{C(OTiCp_2Cl)Fc\}]$



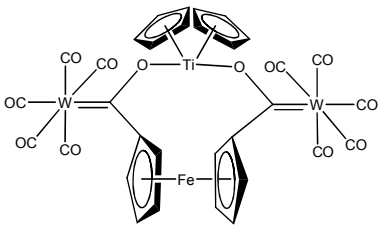
6 $[W(CO)_5\{C(OTiCp_2Cl)Fc\}]$



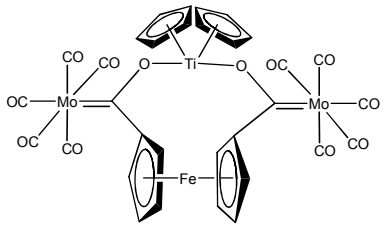
7 $[Mo(CO)_5\{C(OTiCp_2Cl)Fc\}]$



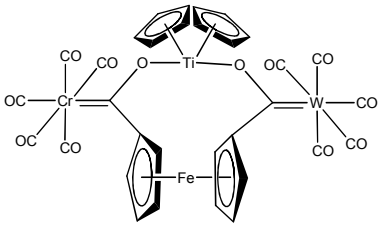
8 $[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}\{CCr(CO)_5\}_2]$



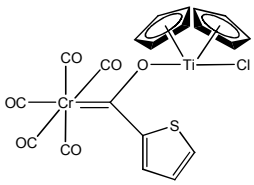
9 [{μ-TiCp$_2$O$_2$-O,O'}{μ-Fe(C$_5$H$_4$)$_2$-C,C'}{CW(CO)$_5$}$_2$]



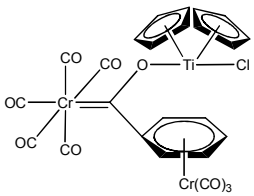
10 [{μ-TiCp$_2$O$_2$-O,O'}{μ-Fe(C$_5$H$_4$)$_2$-C,C'}{CMo(CO)$_5$}$_2$]



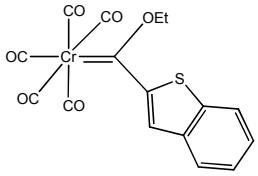
11 [W(CO)$_5$C{μ-TiCp$_2$O$_2$-O,O'}{μ-Fe(C$_5$H$_4$)$_2$-C,C'}CCr(CO)$_5$]



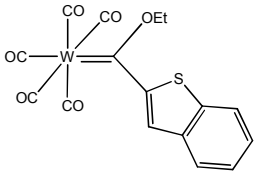
12 [Cr(CO)$_5$C(OTiCp$_2$Cl)(C$_4$H$_3$S)]



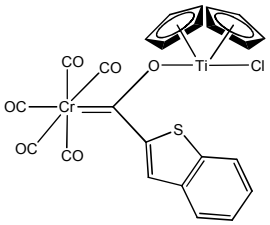
13 [Cr(CO)$_5$C(OTiCp$_2$Cl)(η^1:η^6-C$_6$H$_5$)Cr(CO)$_3$]



14 $[Cr(CO)_5\{C(OEt)(C_8H_5S)]$



15 $[W(CO)_5\{C(OEt)(C_8H_5S)]$



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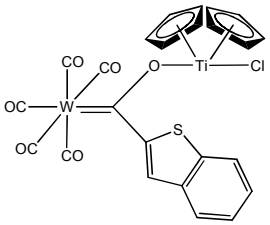

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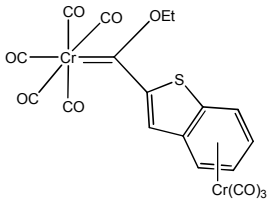
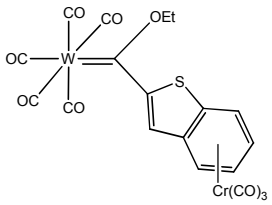


18 $[Cr(CO)_5\{C(OEt)(\eta^1{:}\eta^6\text{-}C_8H_5S)Cr(CO)_3]$



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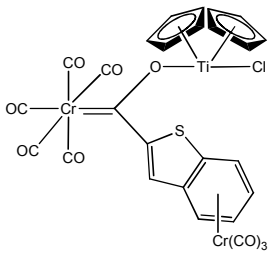
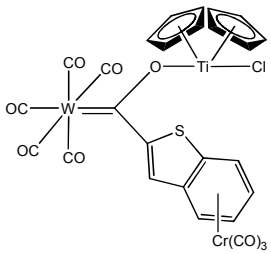
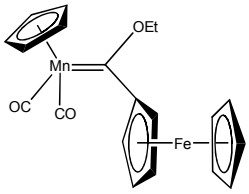


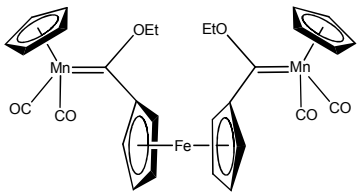
20 $[Cr(CO)_5\{C(OTiCp_2Cl)(\eta^1{:}\eta^6\text{-}C_8H_5S)Cr(CO)_3]$



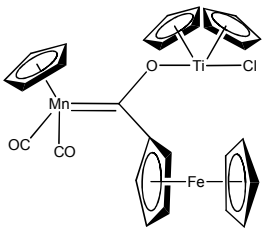
21 $[W(CO)_5\{C(OTiCp_2Cl)(\eta^1{:}\eta^6\text{-}C_8H_5S)Cr(CO)_3]$



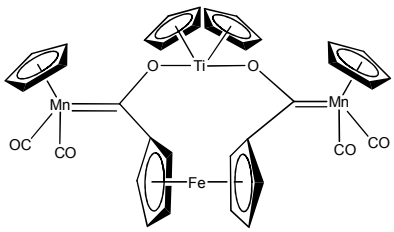
22 $[MnCp(CO)_2\{C(OEt)Fc]$



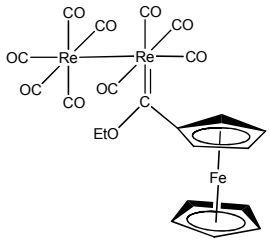
23 $[\mu\text{-}Fe\{C_5H_4C(OEt)MnCp(CO)_2\}_2]$



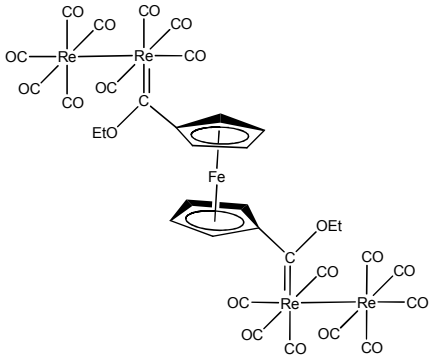
24 $[MnCp(CO)_2\{C(OTiCp_2Cl)Fc]$



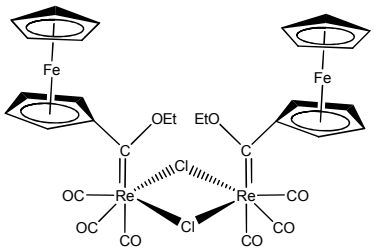
25 $[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}[CMnCp(CO)_2\}_2]$



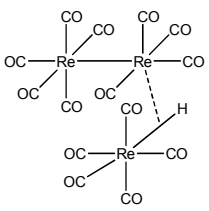
26 $[Re_2(CO)_9\{C(OEt)Fc\}]$



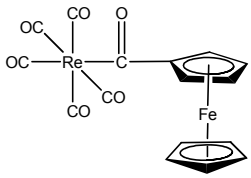
27 *eq,eq*-$[\mu\text{-}Fe\{C_5H_4C(OEt)Re_2(CO)_9\}_2]$



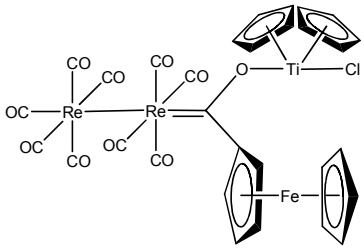
28 *fac*-$[(\mu\text{-}Cl)_2\text{-}(Re(CO)_3\{C(OEt)Fc\})_2]$



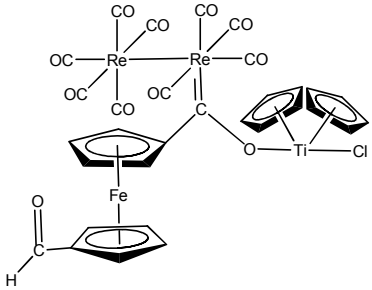
29 $[Re_3(CO)_{14}H]$



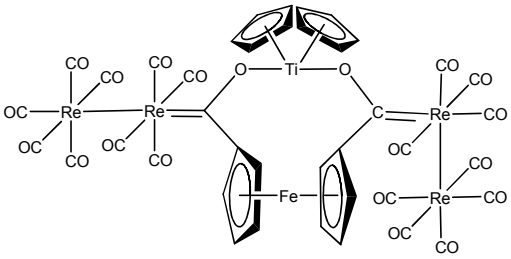
30 $[Re(CO)_5\{C(O)Fc\}]$



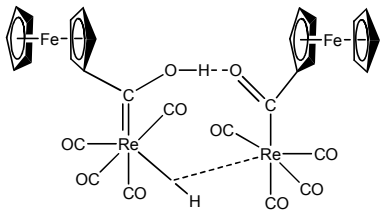
31 *ax*-$[Re_2(CO)_9\{C(OTiCp_2Cl)Fc\}]$



32 *eq*-$[Re_2(CO)_9\{C(OTiCp_2Cl)(Fc'CHO)\}]$



33 *ax, eq*-$[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}\{CRe_2(CO)_9\}_2]$



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

List of Abbreviations

ax	:	axial
Bu	:	butyl
br	:	broad (IR, NMR)
BT	:	benzothienyl
Cp	:	η^5-C_5H_5
d	:	doublet
DCM	:	dichloromethane
DEE	:	diethyl ether
dd	:	doublet of doublets
ddd	:	doublet of doublets of doublets
DFT	:	density functional theory
Et	:	ethyl
eq	:	equatorial
eq	:	equivalent
Fc	:	ferrocenyl
Fc'	:	ferrocen-1,1'-diyl
η^n	:	hapticity of C_nH_n
HOMO	:	highest occupied molecular orbital
IR	:	infrared spectroscopy
J	:	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	:	*N, N, N'. N'*-tetramethylethylenediamine
UV	:	ultraviolet
Vis	:	visible
vs	:	very strong (IR)
vw	:	very weak (IR)
w	:	weak (IR)
Å	:	angstrom
δ	:	chemical shift
λ	:	wavelength

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)