2

Group VI Transition Metal Carbene Cluster Complexes

2.1 Introduction

2.1.1 Background

Bi- and polymetallic transition metal complexes not containing direct metal-metal bonds, but rather different metal-containing fragments linked by bridging ligands, can be broadly divided into three classes based on the mode of coordination of the ligand. These classes are (i) σ, σ (ii) σ, π or (iii) π, π bonding of a ligand to the different metal centres. Activation of these ligands is achieved in both the σ (through inductive effects) and the π (through π-resonance effects) modes of the bridging ligand.[1] Utilizing π-conjugated bridging ligands brings the metal centres in direct electronic contact through π-resonance effects.[2]

This type of communication was illustrated in our laboratories where an unprecedented irreversible metal exchange process (Scheme 2.1) in the complex [Mn(η^1:η^5-C_4H_3S)$(CO)_5$Cr$(CO)_3$] lead to the exchange of coordination sites of the manganese and chromium metals .[3]

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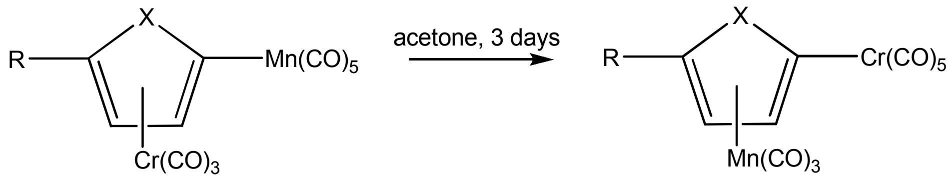
[1] Topsom, R.D. *Acc. Chem. Res.* **1983**, *16*, 292.

[2] Collman, J.P.; Hegedus, L.S.; Norton, J.R.; Finke, R.G. *Principles and Applications of Organotransition Metal Chemistry,* University Science Books, Mill Valley, Ca. **1987**

[3] (a) Waldbach, T.A.; van Rooyen, P.H.; Lotz, S. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 710. (b) Waldbach, T.A.; van Rooyen, P.H.; Lotz, S. *Organometallics,* **1993**, *12*, 4250.



R = H, Me or $Mn(CO)_5$; X = S or Se

Scheme 2.1

Applying the principle of σ, π-bridging ligands to Fischer carbene complexes of the type $[M(CO)_5\{C(OR')R\}]$, π-bonded aryl or heteroaryl ligands have been used to establish electronic contact of the R-substituent or the alkoxy R'-substituent with the carbene carbon atom.[4] The first example to be synthesized was the complex $[Cr(CO)_5\{C(OEt)(\eta^1{:}\eta^6\text{-}PhCr(CO)_3)\}]$ containing a π-conjugated phenyl ring[4(a)] and the series was expanded to include either tungsten or molybdenum as the pentacarbonyl metal centre.

Even before this, ferrocenyl carbene complexes of the Group VI transition metals were synthesized to study the electronic effects of the ferrocenyl substituent on the carbene ligand.[5] Thiolate, selenolate, tellurolate and $[Co(CO)_4]^-$ were used to modify cationic ferrocenyl carbyne complexes of manganese, constituting another example of neutral bimetallic monocarbene complexes.[6]

Increasing interest in the pseudo-aromatic five membered rings containing a heteroatom lead to the synthesis of $[M(CO)_5\{C(OEt)(\eta^5\text{-}2\text{-}thienylCr(CO)_3\}]$ complexes (M = Cr, W) in an effort to investigate the effect of π-coordination on the properties of such a carbene functionality.[7] Scheme 2.2 illustrates the expected bimetallic Fischer carbene complexes that were afforded, as well as the modified carbene complexes obtained from the incorporation of a cleaved

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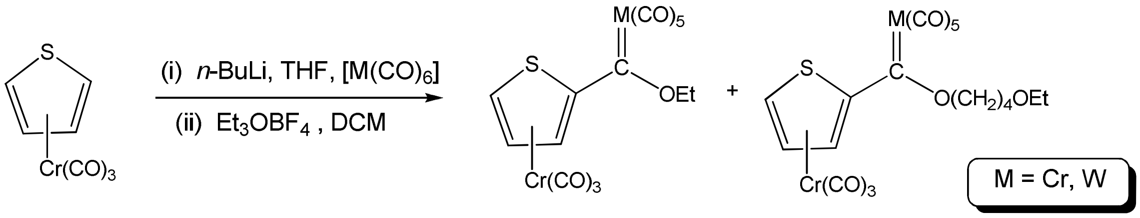
[4] (a) Fischer, E.O.; Gammel, F.J.; Neugebauer, D. *Chem. Ber.* **1980**, *113,* 1010. (b) Behrendt, U.; Pfeifer, R-M.; Wartchow, R.; Butenschön, H. *New. J. Chem.* **1999**, *23*, 891.

[5] Connor, J.A.; Jones, E.M.; Lloyd, J.P. *J. Organomet. Chem.* **1970***,* *24*, C20.

[6] Fischer, E.O. ; Wanner, J.K.R. *Chem. Ber.* **1985**, *118*, 2489.

[7] Terblans, Y.M.; Lotz, S. *J. Chem. Soc., Dalton Trans.* **1997**, 2177.

tetrahydrofuran (THF) molecule into the ethoxy substituent of the carbene ligand.



Scheme 2.2

2.1.2 Heteroatom-bonded carbene ligand substituent

The incorporation of a second metal-containing fragment, joined to the heteroatom bonded to the carbene carbon has first been explored by Fischer *et al.*[8] This involved the *O*-alkylation of an acyl chromate with titanocene dichloride to yield the corresponding metaloxycarbene complex $[Cr(CO)_5\{C(Me)OTiCp_2Cl\}]$ as well as the trimetallic bismetaloxycarbene complex $[\{\mu\text{-}O_2TiCp_2\text{-}O,O'\}\{C(Me)Cr(CO)_5\}_2]$. However, the above Fischer method is limited by the reactivity of the acyl metalate intermediate (**A** in Figure 2.1 below). The intermediate **A** requires stabilization; but if too stable, *O*-alkylation is resisted in the following step and metal alkylation can result in an acyl complex rather than the desired Fisher-type metaloxycarbene complex **B**.

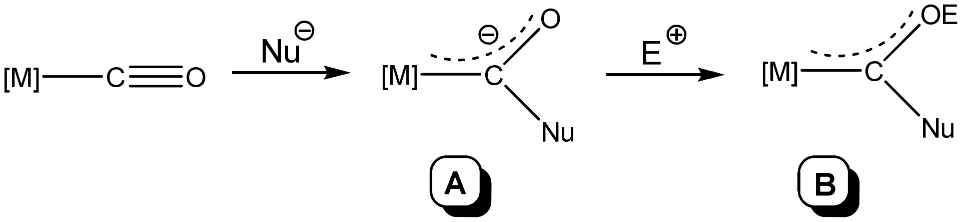


Figure 2.1 Electrophilic attack on acylmetalate **A** to form Fischer carbene complex **B**

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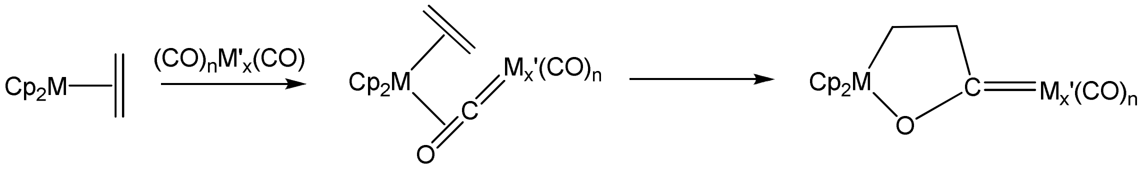
[8] Fischer, E.O.; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 159.

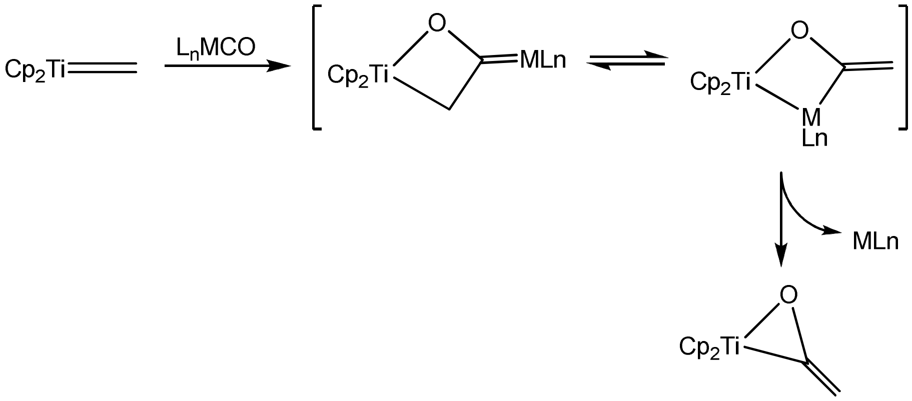
A variety of examples of metaloxycarbene complexes has been reported,[9] including metallacyclic metaloxycarbene complexes afforded by ring-closure reactions (Scheme 2.3) of η^2-olefin complexes of titanocene, zirconocene or hafnocene or (η^4-diene) metallocenes.[10]



M = Ti, Zr, Hf
$M'_x(CO)_n$ = $Cr(CO)_5$, $W(CO)_5$, $Mo(CO)_5$, $Mn_2(CO)_9$, $Re_2(CO)_9$

Scheme 2.3

Alkylidene titanium complexes may also be used as starting materials to prepare titanoxycarbene complexes by reaction with metal carbonyls. β,β-dimethyltitanocene metallacyclobutane, for example, reacts with metal carbonyls to yield a titanocene adduct through the intermediates formation (Scheme 2.4) of a cyclic titanoxycarbene complex.[11]



Scheme 2.4

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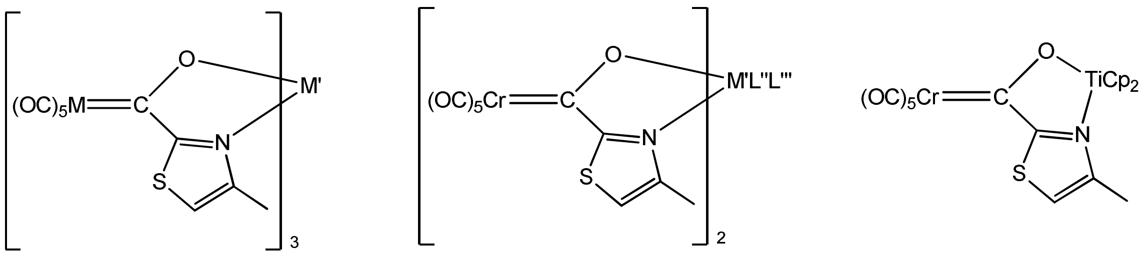
[9] (a) Barluenga, J.; Fañanás, F.J. *Tetrahedron,* **2000**, *56*, 4597, (b) Sabat, M.; Gross, M.F.; Finn, M.G. *Organometallics* **1992**, *11*, 745.

[10] Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

[11] Anslyn, E.V.; Santarsiero, B.D.; Grubbs, R.H. *Organometallics* **1988**, *7*, 2137.

Examples of metaloxycarbene complexes not containing metallocenes as carbene ligand substituents but other transition metal fragments, e.g. the rheniooxycarbene complexes of Beck,[12] are prepared by addition of the 16-electron system $Re(CO)_5^+$ (as $[Re(CO)_5BF_4]$) to acetyl pentacarbonyl chromate to form $[Cr(CO)_5\{C(ORe(CO)_5)Me\}]$.

The presence of a second metal unit, Cp_2ZrCl, leads to the activation of such carbene complexes as catalysts for the oligomerisation of 1-pentene in the presence of MAO.[13] More recently, Raubenheimer and co-workers reported an anionic Fischer-type carbene complex utilized as a bidentate ligand for complexation of a second metal, *i.e.* Cr(III), Fe(III), V(IV),[14] which can be regarded as 'complexes of complexes' and can form tris-, bis- or mono-chelated polymetallic compounds, as illustrated in Figure 2.2.



M = Cr, M' = Cr(III)
M = W, M' = Cr(III)
M = Cr, M' = Fe(III)
M = Cr, M' = Co(III)

M' = V(IV), L'' = 4-methylthiazole, L''' = O
M' = Co(II), L'' = 4-methylthiazole, L''' = THF
M' = Ni(II), L'' = L''' = 4-methylthiazole

Figure 2.2 Anionic Fischer-type carbene complexes as bidentate (N,O) ligands

Bimetallic titanoxycarbene complexes have been widely studied as a way to use the electron deficient Lewis acid properties of the titanium to increase the electrophilicity of the carbene carbon atom. This was demonstrated by

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[12] Fritz, P.M.; Steimann, M.; Beck, W. *Chem. Ber.* **1987**, *120*, 253.

[13] Brüll, R.; Kgosane, D.; Neveling, A.; Pasch, H.; Raubenheimer, H.G.; Sanderson, R.; Wahner, U.M. *Macromol. Symp.* **2001**, *165*, 11.

[14] Raubenheimer, H.G.; du Toit, A.; du Toit, M.; An, J. ; van Niekerk, L. ; Cronje, S.; Esterhuysen, C.; Crouch, A.M. *J. Chem. Soc., Dalton Trans.* **2004**, 1173.

successfully reacting the titanoxycarbene complex of [MnCp(CO)$_2${C(OTiCp$_2$Cl)R}] in benzannulation reactions whereas the corresponding alkoxycarbene complexes failed to react.[15] The most direct and highest yielding method of synthesis remains the Fischer route of reacting metal carbonyls with Ti(NMe$_2$)$_4$.[16] In the context of this work the resulting acyl chromate was reacted with titanocene dichloride to afford [M(CO)$_5${C(OTiCp$_2$Cl)(heteroaryl)}] in high yields.[8, 11]

2.1.3 Carbon-bonded carbene ligand substituent

In a study performed prior to this investigation in our laboratories, mono- and dimetal substituted carbene complexes (listed as complexes **14** – **21** in Scheme 2.5) were derived from a lithiated benzothienyl substituent (2-BT) or a benzo[*b*]thienyl ring π-coordinated to Cr(CO)$_3$, (Cr(CO)$_3$(η^6-2-BT)), followed by alkylation of the acyl metalate by triethyloxonium tetrafluoroborate or metalation with titanocene dichloride.[17]

The [Cr(CO)$_3$(η^6-2-BT)]-substituent has the π-bonded chromium tricarbonyl fragment coordinated to the ring furthest away from the carbene carbon atom, leaving an unoccupied space directly beneath the thiophene bonded to the carbene carbon atom. This prompted the investigation into the possibility of replacing the benzo[*b*]thiophene fragment by a more compact, redox-active ferrocenyl substituent in order to increase the electronic communication between the π-bonded transition metal and the carbene carbon atom, as well as heteroaryl rings with the π-Cr(CO)$_3$-moiety in closer proximity to the carbene carbon atom, using the Group VI transition metals Cr, Mo and W (Figure 2.10).

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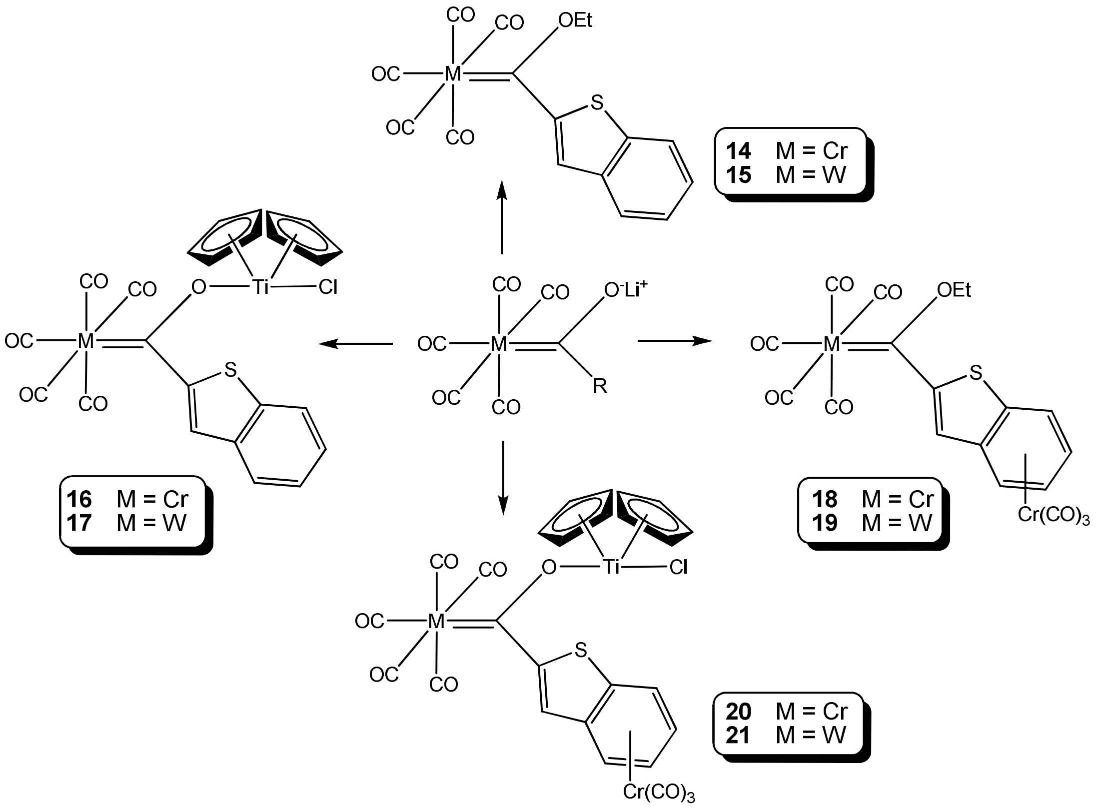
[15] Balzer, B.L.; Cazanoue, M.; Sabat, M.; Finn, M.G. *Organometallics* **1992**, *11*, 1759.

[16] (a) Petz, W. *J. Organomet. Chem*. **1974**, *72,* 369. (b) Pebler, J.; Petz, W. *Z. Naturforsch. B* **1974**, *29*, 658.

[17] Bezuidenhout, D.I.; van der Watt, E.; Liles, D.C.; Landman, M.; Lotz, S. *Organometallics* **2008**, *27*, 2447.



Scheme 2.5

2.1.3.1 Ferrocenyl carbene ligand substituent

Ferrocene was chosen as carbene substituent due to its wide application and the rapidly expanding field of ferrocenyl-containing ligands, where they can be used in catalytic transformations of organic compounds, especially when in contact with a second transition metal.[18] The first examples of ferrocenyl Fischer carbene complexes were synthesized by Connor *et al.*[5] as part of an investigation into the electron withdrawing nature of metal carbonyl carbene groups and comprehensively reviewed as dimetallic heteroatom stabilized Fischer carbenes.[19]

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[18] (a) Colacot, T.J. *Chem. Rev.* **2003**, *103*, 3101. (b) Dai, L.; Tu, T.; You, S.; Deng, W.; Hou, X. *Acc. Chem. Res.* **2003**, *36*, 659.

[19] Sierra, M.A. *Chem. Rev.* **2000**, *100*, 3591.

Ferrocenes display extraordinary stabilization of adjacent electron deficient centres, comparable to amino substituents for example.[20] The electron transfer behaviour of metal carbene complexes can also be greatly influenced by the presence of additional metal centres.[21] If polyene units are introduced between the metal carbonyl carbene moiety and the ferrocenyl (Fc) substituent, both the oxidation potential and the reduction potential of these complexes decrease with increasing length of polyene,[22] illustrating the electronic communication between the above mentioned moieties and the donor-acceptor interaction of the couple.

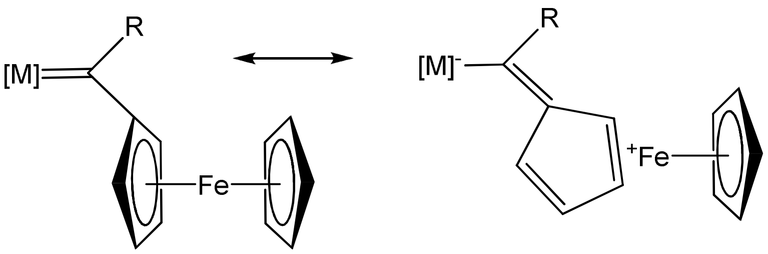

Figure 2.3 Resonance interaction between the ferrocene Cp ring and the carbene carbon atom

The electron release from the Fc group to the empty carbene carbon p_z orbital takes place via a delocalized π-system rather than through inductive effects (Figure 2.3)[23] which correlates with the findings that the normal donor strength of ferrocene is increased by interaction with strongly electrophilic centres.

The steric bulk of ferrocenyl substituents directly attached to chromium carbene complexes blocks the chromium templated benzannulation upon reaction with alkynes in favour of formation of the furan ring[24], however the reactivity patterns of other carbene complexes are followed to produce organic compounds such as cyclobutenones, ketoesters, etc.[25]

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[20] Bildstein, B. *J. Organomet. Chem.* **2001***, 617 – 618*, 28.
[21] Sierra, M.A.; Gómez-Gallego, M.; Martínez-Álvarez, R. *Chem. Eur. J.* **2007**, *13*, 736.
[22] Jayaprakash, K.N.; Pay, P.C.; Matsuoka, I.; Bhadbhake, M.M.; Puranik, V.G.; Das, P.K.; Nishihura, H.; Sarkar, A. *Organometallics,* **1999**, *18*, 3851.
[23] Connor, J.A.; Lloyd, J.P. *J. Chem. Soc. Dalton Trans.* **1972**, 1470.
[24] Bennewits, J.; Nieger, M.; Lewall, B.; Dötz, K.H. *J. Organomet. Chem.* **2005**, *690*, 5892.
[25] Zora, M.; Güngör, E.U. *Tetrahedron Lett.* **2001**, *42*, 4733.

In the presence of two nonconjugated metal carbene moieties in homo- and heterobimetallic biscarbene complexes, these moieties behave as two independent monocarbene entities,[26] but ferrocene functions as an internal electron carrier introducing the push-pull nature of these Fc-substitued carbene complexes.

2.1.3.2 π-aryl carbene ligand substituent

Besides ferrocene, both thiophene and benzene with a chromium tricarbonyl fragment π-bonded to it were chosen as carbene substituents. The effect of π-coordination of metal fragments to different types of ring systems has been extensively studied, especially for arenes containing no heteroatoms like cyclopentadienyl and benzene. In particular, arene chromium tricarbonyls have attracted attention (Figure 2.4) as the activating substituent.

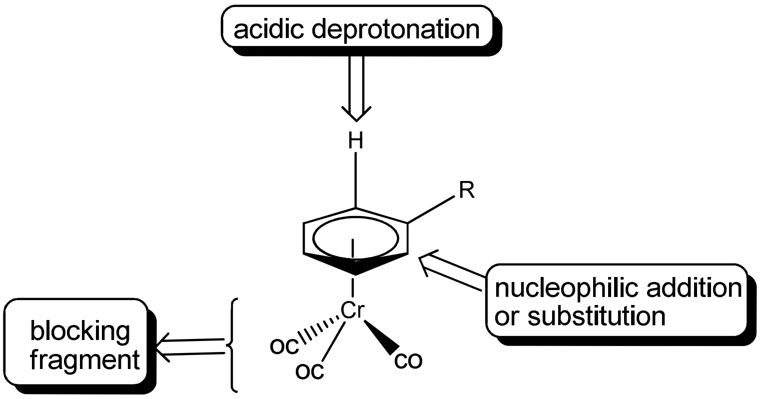

Figure 2.4 $Cr(CO)_3$ – ring activation

$Cr(CO)_3$ is symmetrically bonded to the arene ring carbons[27] and no directing effect of the $Cr(CO)_3$-substituent is observed apart from the steric crowding on one face of the arene ring therefore the substituents attached by σ-bonds to the arene ligand will have the primary influence on site selectivity.[28] X-ray analysis

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[26] Martínez-Álvarez, R.; Gómez-Gallego, M.; Fernández, I.; Mancheño, M.J.; Sierra, M.A. *Organometallics,* **2004**, *23*, 4647.

[27] (a) Fischer, E.O.; Öfele, K. *Chem. Ber.* **1957***, 90*, 2543. (b) Natta, G.; Ercoli, R.; Calderazzo, F. *Chim. Ind.* **1958**, *40*, 287.

[28] Jackson, W.R.; Jennings, W.B.; Rennison, S.C.; Spratt, R. *J. Chem. Soc. B. Phys. Org. Chem.* **1969***,* 1214.

has, however, indicated that for an unsubstituted benzene ring in [$Cr(CO)_3(\eta^6$-$C_6H_6)$], the staggered conformation of the CO ligands with regards to the ring carbons is found, rather than the eclipsed conformation[29], illustrated in Figure 2.5. In a substituted benzene complex with electron donating substituents, *ortho* and *para*-ring protons would have relatively high π-electron density, hence protons attached to these would be shielded as in the free ligand. However, π-electron density distribution will tend to orientate the tricarbonyl chromium group into an eclipsed conformation (Figure 2.5) where the three ring carbons as well as substituent R are eclipsed, in contrast to the other possible eclipsed conformation (where three ring carbons are again eclipsed, but the substituent R resides on a noneclipsed ring carbon atom), preferred for electron withdrawing substituents.[29]

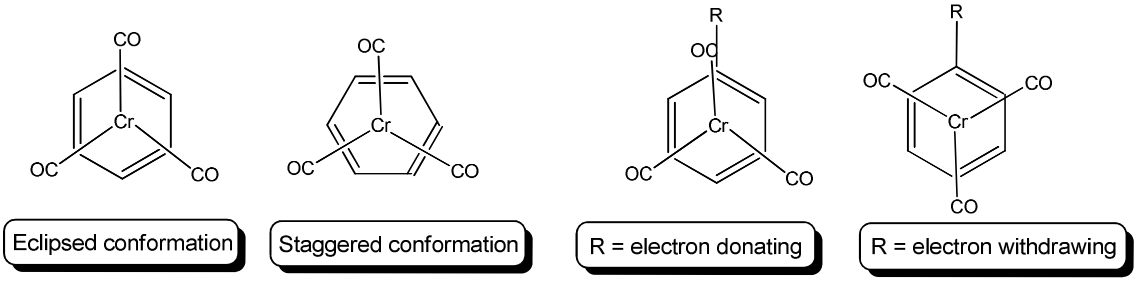

Figure 2.5 Substituent directing effect on π-arene chromium tricarbonyl complexes

The π-bond of the metal to the ring carbons is known to lessen the electron delocalization of the ring, causing a decrease in the "ring current" and localizing the π-bonds.[30] Evidence indicates that the $Cr(CO)_3$ unit exerts an electron withdrawing inductive effect[31] whereby the chromium tricarbonyl fragment can be

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[29] Muetterties, E.L. ; Bleeke, J.R. ; Wucherer, E.J. ; Albright, T.A. *Chem. Rev.* **1982**, *82*, 499.

[30] Mangini, A.; Taddei, F. *Inorg. Chim. Acta* **1968**, *2*, 8.

[31] (a) Holmes, J.D.; Jones, D.A.K.; Pettit, R. *J. Organomet. Chem.* **1965**, *4*, 324, (b) Trahanovsky, W.S. ; Wells, D.K. *J. Am. Chem. Soc.* **1969**, *91*, 5870, (c) Bly, R.S. ; Strickland, R.C. *J. Am. Chem. Soc.* **1970**, *92*, 7459, (d) Wells, D.K. ; Trahanovsky, W.S. *J. Am. Chem. Soc.* **1970**, *92*, 7461.

described as an "electron sink" disrupting the prevalent aromaticity of the benzene ring.

The σ-coordination of the abovementioned type of π-arene chromium tricarbonyls therefore causes polarization and activation of chemical bonds. The first examples of such a σ,π-bimetallic monocarbene complex to be synthesized were the Group VI transition metal complexes of Cr, Mo and W,[4(a)] which were subsequently converted to carbyne complexes after reaction with strong Lewis acids. From the initial metalation of the ring with butyllithium, it was demonstrated that the resultant negative charge is not diffused over the entire complex as believed. Instead it is very much localized on the metalated carbon and is still strong enough to act as a nucleophile and to attack a carbonyl of a metal carbonyl complex.

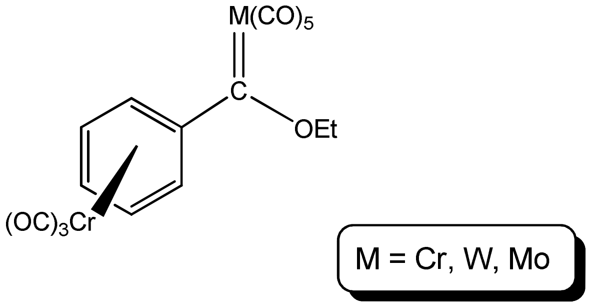

Figure 2.6 σ,π-bimetallic monocarbene complexes synthesized by Fischer *et al.*[4(a)]

The discovery of stable π-arene complexes evolved naturally into the study of related π-complexes of thiophene (TH): an electron excessive[32] aromatic ring containing sulphur as the heteroatom.[33] Compared to benzene, thiophene is more nucleophilic as indicated by the ionization potential of 8.9 eV for thiophene, in contrast to 9.3 eV for benzene,[33(a)] which would make the $Cr(\eta^5\text{-}T)(CO)_3$-fragment a weaker electron withdrawing group than $Cr(\eta^6\text{-}Ph)(CO)_3$. Coordination of thiophenes can occur either through the S-atom or through η^1,

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[32] Albert, A. *Heterocyclic Chemistry*, Athlone Press, London, **1968**.

[33] (a) Rauchfuss, T.B. *Prog. Inorg. Chem.* **1991**, *39*, 259, (b) Angelici, R.J. *Coord. Chem. Rev.* **1990**, *105*, 61.

η^2, η^4 or η^5-binding. The first [Cr(η^5-TH)(CO)$_3$] structure was reported in 1965,[34] but the utilization of these π-heteroaryl tricarbonyl chromium complexes as carbene ligand substituents was only reported in 1997.[7]

In the case of η^5-coordination, the five *p* orbitals orthogonal to the ring give rise to five nondegenerate π-states, of which three of the π-molecular orbitals are occupied. This means that benzene would represent a better model for binding of the η^5-thiophene than for example the cyclopentadienyl anion. However, it also presents an explanation for the weaker π-coordination of the Cr(CO)$_3$-fragment to the thiophene ring than to the benzene ring, which results in the evident lability of the tricarbonyl chromium fragment as reported by Terblans *et al.* during the synthesis of the first thienyl and benzothienyl σ,π-bimetallic carbene complexes illustrated in Scheme 2.2.[7]

2.1.4 Homo- and heteronuclear polymetallic biscarbene complexes

In the field of non-linear optics, the advantages of using organometallic compounds have been described as a combination of the effect of the delocalized π-electron backbone of conjugated organic polymer systems and the incorporation of transition metals.[35] Such organometallic systems have great possibilities for redox changes and can possess metal→ligand or ligand→metal charge transfer bands in the visible spectrum.

The application employs electron transfer between two redox active termini, as illustrated by the example of biferrocenes (Figure 2.7), linked by heteroaromatic spacers in which the effect of both the length and the substitution of the oligothiophene group have been investigated.[36] Many examples exist of bimetallic complexes in which the two metal centres are connected by an acetylene bridge, $L_nM\text{-}C\equiv C\text{-}ML_n$ or an ethylene bridge, $L_nM\text{-}C(X)\text{=}C(X)\text{-}ML_n$.[37]

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[34] Bailey, M.F.; Dahl, L.F. *Inorg. Chem.* **1965**, *4*, 1306.
[35] Long, N.J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.
[36] Justin Thomas, K.R.; Lin, J.T.; Wen, Y.S. *Organometallics* **2000**, *19*, 1008.
[37] (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *37*, 547, (b) Beck, W.; Niemar, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 4176.

However, examples of bimetallic biscarbene complexes in which the bridging ligand is a conjugated system, $L_nM{=}CX(CR{=}CR)_nCX{=}ML_n$ are less well known. Homonuclear bimetallic carbene complexes with conjugated even-numbered carbon atoms ranging from C_4 to C_{14} and heteronuclear bimetallic carbene complexes with C_3 bridges have been reported by using reactive carbene precursors in coupling reactions.[38]

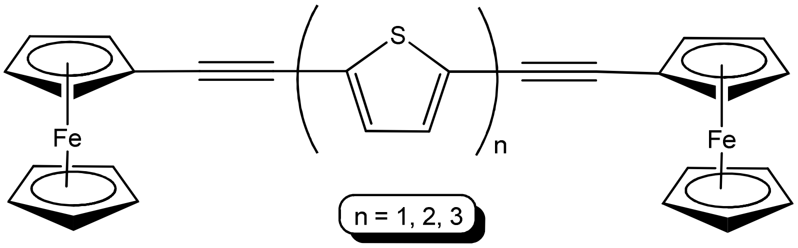

Figure 2.7 Molecular wires incorporating redox active ferrocenyl termini

2.1.4.1 Conjugated bridging biscarbene complexes

The use of aromatic rings as spacers between biscarbene units was first achieved by Fischer's group in the synthesis of dimetallic homonuclear biscarbene complexes of the Group VI transition metals with one-dimensional conjugated phenylene[39] or benzene derivatives.[40]

The reaction of *p*-phenylenedilithium with Group VI metal hexacarbonyls yielded the corresponding μ-(*p*-phenylene)bisethoxycarbene bis(pentacarbonyl metal) complexes (Scheme 2.6) while the analogous reaction of *o*-phenylenedilithium with the metal hexacarbonyls gave the mononuclear 1,4-chelated biscarbene complexes $[M(CO)_4\{C(OEt)\text{-}o\text{-}C_6H_4\text{-}C(OEt)\}]$. Subsequent reaction of the

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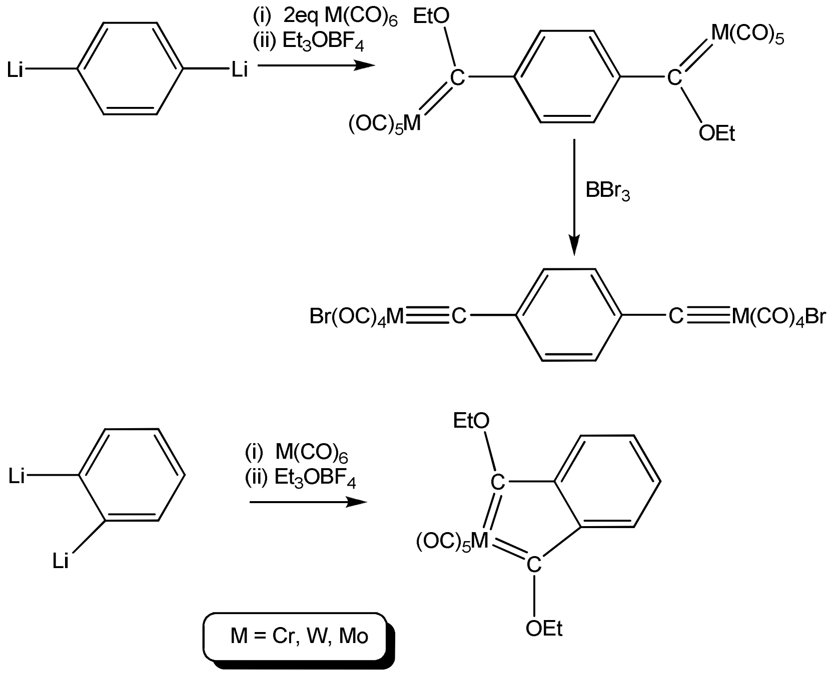
[38] (a) Weng, W.; Ramsden, J.A.; Arif, A.M.; Gladysz, J.A. *J. Am. Chem. Soc.* **1993**, *115*, 889, (b) Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber. /Recueil* **1997**, *130,* 479, (c) Harbaum, C.; Fischer, H. *J. Organomet. Chem.* **1999**, *578*, 186, (d) Hartbaum, C.; Mauz, E.; Roth, G.; Weissenbach, K.; Fischer, H. *Organometallics* **1999**, *18*, 2619.

[39] Fischer, E.O.; Röll, W.; Huy, N.H.T.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 2951.

[40] Huy, N.H.T.; Lefloch, P.; Robert, F.; Jeannin, Y. *J.Organomet. Chem.* **1987**, *327*, 211.

bimetallic bridged biscarbene complexes with borontrihalides BX_3 afforded the corresponding *trans*-halocarbyne complexes, $[X(CO)_4M{\equiv}C$-*p*-C_6H_4-$C{\equiv}M(CO)_4X]$.[39]



Scheme 2.6

In contrast, similar bimetallic biscarbene complexes with conjugated heteroarene moieties instead of carbon units have received less attention, but have been an important topic of research in our laboratories. Maiorana and co-workers prepared the first mixed-metal biscarbene complex of bithiophene[41] to study the interaction of the π electrons of the conjugated system and the d electrons of the transition metal atom resulting from the large overlap between the electronic systems through the carbonic link.[42] A series of homo- and heteronuclear mixed biscarbene complexes containing a variety of heteroaromatic spacers have been synthesized in our laboratory[43] and some examples are listed in Figure 2.8.

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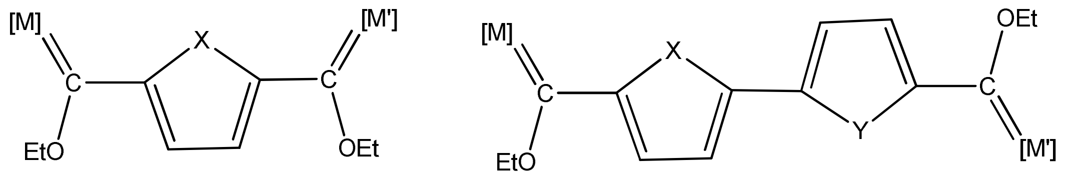
[41] Maiorana, S.; Papagni, A.; Licandro, E.; Persoons, A.; Clay, K.; Houbrechts, S.; Porzio, W. *Gazz. Chim. Ital.* **1995**, *125*, 377.

[42] Lancellotti, L.; Tubino, R.; Luzzati, S.; Licandro, E.; Maiorana, S.; Papagni, A. *Synth. Met.* **1998**, *93*, 27.

[43] (a) Terblans, Y.M.; Roos, H.M.; Lotz, S. *J. Organomet. Chem.* **1998**, *566,* 133, (b) Landman, M.; Görls, H.; Lotz, S. *J. Organomet. Chem.* **2001**, *617-618*, 280, (c) Landman, M.; Görls, H.



[M] = $Cr(CO)_5$; $Mo(CO)_5$; $W(CO)_5$: $MnCpMe(CO)_2$
[M'] = $Cr(CO)_5$; $Mo(CO)_5$; $W(CO)_5$: $MnCpMe(CO)_2$
X = S; O; NMe
Y = S; O; NMe

Figure 2.8 Various combinations of [M], [M'], X and Y was utilized to prepare a series of homo- and heteronuclear mixed biscarbene complexes.[43]

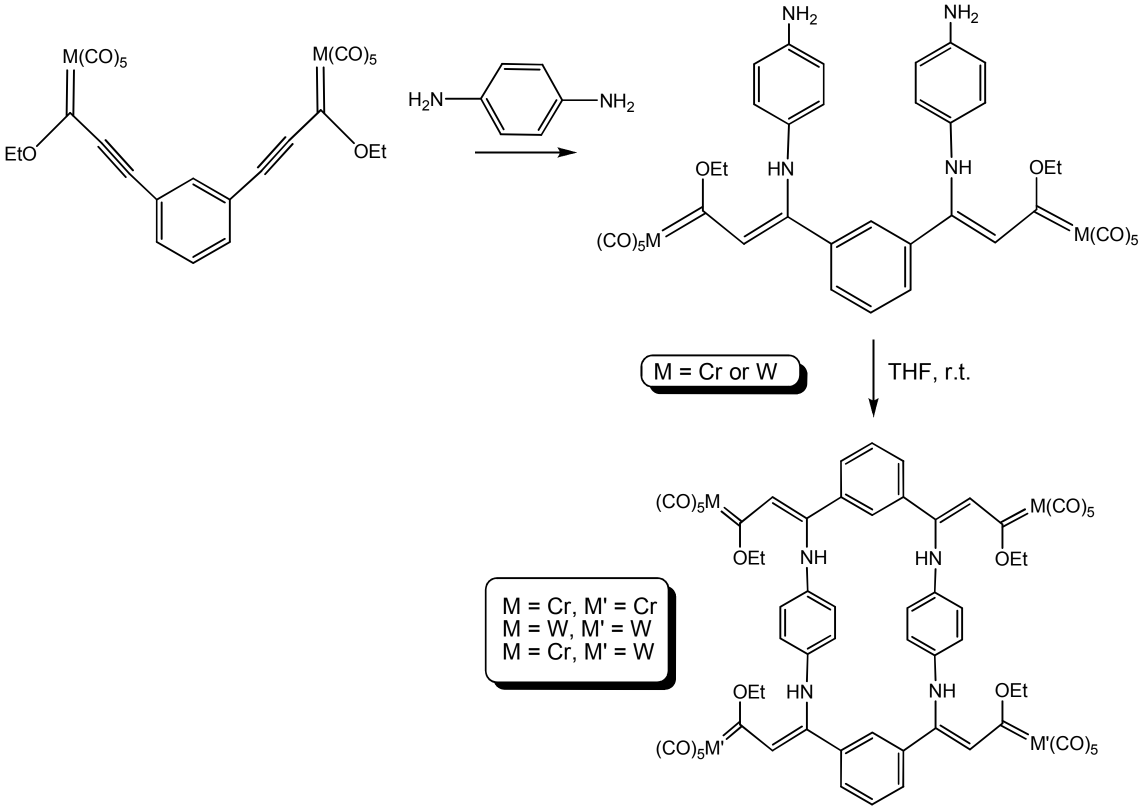
The role of the heteroatom in the bridging heteroarene was investigated, and known monocarbene reaction pathways for carbene modification and carbon-carbon coupling reactions was tested.[43(d)] Biscarbene complexes displayed enhanced reactivity at the carbene carbon compared to the monocarbene complexes in benzannulation reactions.[43(f)]

As far as could be ascertained, no biscarbene complexes containing a bridging ferrocen-1,1'-diyl (Fc') spacer have been reported; however the corresponding ruthenocenyl biscarbene, $[\mu\text{-Ru}\{C_5H_4C(OEt)Cr(CO)_5\}_2]$ has been prepared by Sierra *et al.*[44] Recently, the Sierra group has also extended the idea of conjugated biscarbene complexes by preparing homo- and heteronuclear tetrametallic macrocycles (Scheme 2.7) *via* a self-assembly route, in order to explore the electrochemical properties of the four metal centres in the cyclophanic structures.[45]

Lotz, S. *Z. Anorg. Allg. Chem.* **2002**, *628,* 2037, (d) Crause, C.; Görls, H.; Lotz, S. *J. Chem. Soc., Dalton Trans.* **2005**, 1649, (e) Lotz, S.; Crause, C.; Olivier, A.J.; Liles, D.C.; Görls, H.; Landman, M.; Bezuidenhout, D.I. *J. Chem. Soc., Dalton Trans.* **2009**, 697, (f) Landman, M.; Ramontja, J.; van Staden, M.; Bezuidenhout, D.I.; van Rooyen, P.H.; Liles, D.C.; Lotz, S. *Inorg. Chim. Acta* **2010**, *363*, 705.

[44] Lage, M.L.; Fernández, I.; Mancheño, M.J.; Gómez-Gallego, M.; Sierra, M.A. *Chem. Eur. J.* **2009**, *15*, 593.

[45] Fernández, I.; Mancheño, M.J.; Gómez-Gallego, M.; Sierra, M.A. *Org. Lett.* **2003**, *5*, 1237.



Scheme 2.7

2.1.4.2 Biscarbene complexes by connecting carbene heteroatom substituents

The principle of connecting carbene alkoxy substituents to form biscarbene complexes involves the alkylation of the oxygen where nucleophilic attack by the oxygen on a coordinated carbocationic carbon atom yields the desired product. An example[46] illustrating this is shown in Figure 2.9, where a solution of a methoxy(diethylamino)carbene complex was added to the tetramethylammonium salt of the $[(CO)_5MC(O)R]^-$ anion at low temperature. In this case, M = Cr or W and R = p-$C_6H_4CH_3$ or CH_3 and the bimetallic biscarbene complex $[Cr(CO)_5\{C(NEt_2)OC(R)\}Cr(CO)_5]$ as well as the mixed bimetallic complex $[Cr(CO)_5\{C(NEt_2)OC(R)\}W(CO)_5]$ were obtained.

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[46] Fischer, E.O.; Kleine, W. *J.Organomet. Chem.* **1981**, *208*, C27.

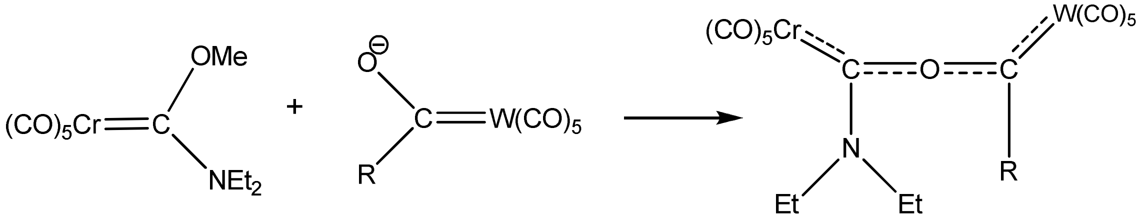
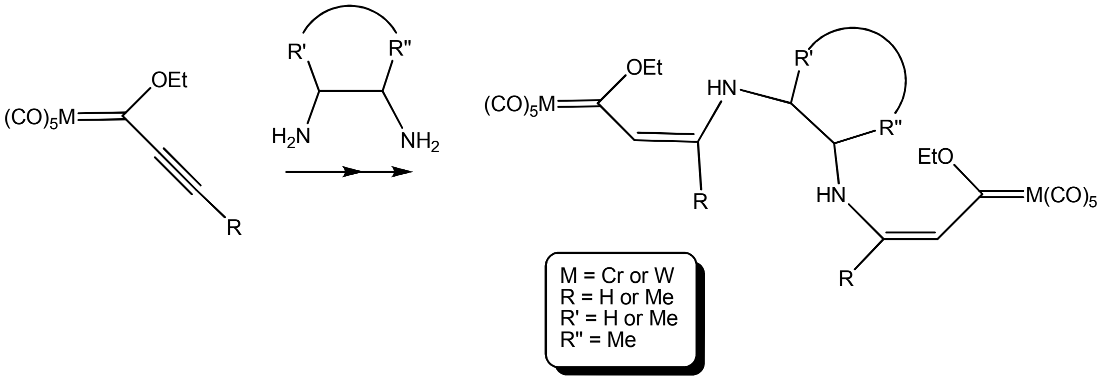


Figure 2.9 Metal acylates as nucleophiles

Another possibility to link two carbene metal moieties is to substitute the alkoxy carbene substituents in aminolysis reactions, using diamines to form amino bridged biscarbenes,[8] or to link the carbene substituents, such as alkynyl substituents, through the reaction of alkynyl alkoxycarbenes with 1,2-primary and secondary diamines as shown in Scheme 2.8.[47]



M = Cr or W
R = H or Me
R' = H or Me
R" = Me

Scheme 2.8

A number of different routes exist to prepare titanoxy biscarbene complexes. The simplest method is the Fischer route in which the reaction of acyl metalate complexes, generated by the Fischer method[48] with titanocene dichloride furnishes an equimolar mixture of titanoxycarbene and biscarbene complexes.[8] Different variations of this approach have been followed, including the work of Sabat[9(b)] describing the preparation of dimeric titanium compounds, and more recently, the unusual rearrangement of these dimeric titanium complexes,

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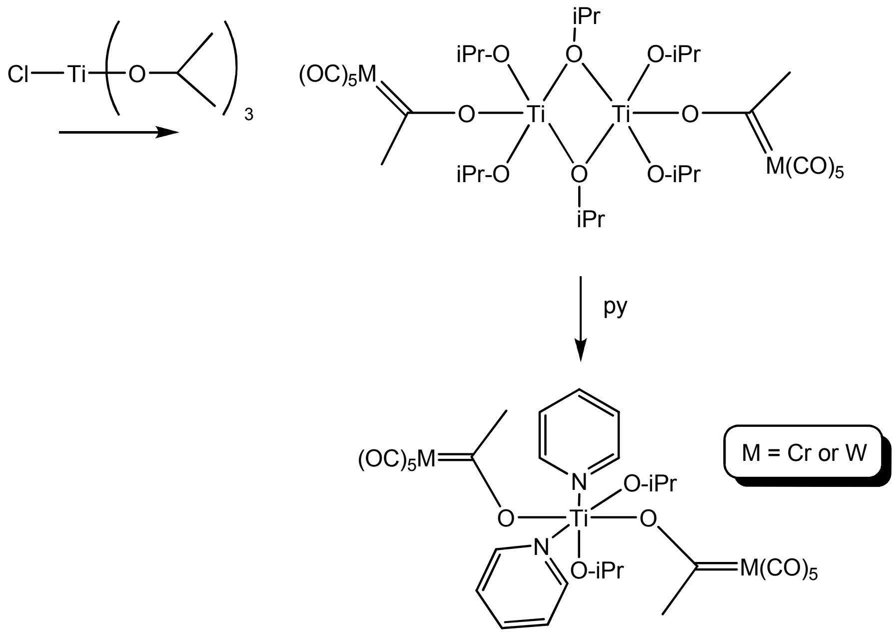
[47] Moretó, J.M.; Ricart, S.; Dötz, K.H.; Molins, E. *Organometallics,* **2001**, *20*, 62.
[48] Fischer, E.O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(Scheme 2.9), yielding a compound where the titanium becomes coordinated by two oxycarbene units.[49]



Scheme 2.9

The abovementioned method was also the approach followed in our study. However, to the best of our knowledge, no biscarbene complexes exist that are bridged both through the carbene heteroatom substituent, as well as through the α-C susbtituent bonded to the carbene carbon atom.

2.2 Results and discussion

2.2.1 Focus of this study

Expanding on the concept of σ,π-bimetallic Fischer carbene complexes, the objective was not only to synthesize trimetallic carbene complexes, but also to systematically study the electronic and steric effects of the different metal-containing substituents by introducing these fragments in a stepwise manner on both the R- and the R'-substituent. A list of the complexes synthesized is given

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[49] Raubenheimer, H.G.; Cronje, S.; Strasser, C.E. *J. Chem. Soc., Dalton Trans.* **2009**, 8145.

in Figure 2.10. The structural features and their relevance to bonding in the carbene cluster compounds of the Group VI transition metals are discussed and represent indicators of possible reactivity sites in multimetal carbene assemblies.

In an effort to investigate the effect of different metal moieties end-capping the bridging biscarbene clusters it was attempted to synthesize the mixed heteronuclear bridging biscarbene complex **11** containing both $Cr(CO)_5$- and $W(CO)_5$-fragments on the termini.

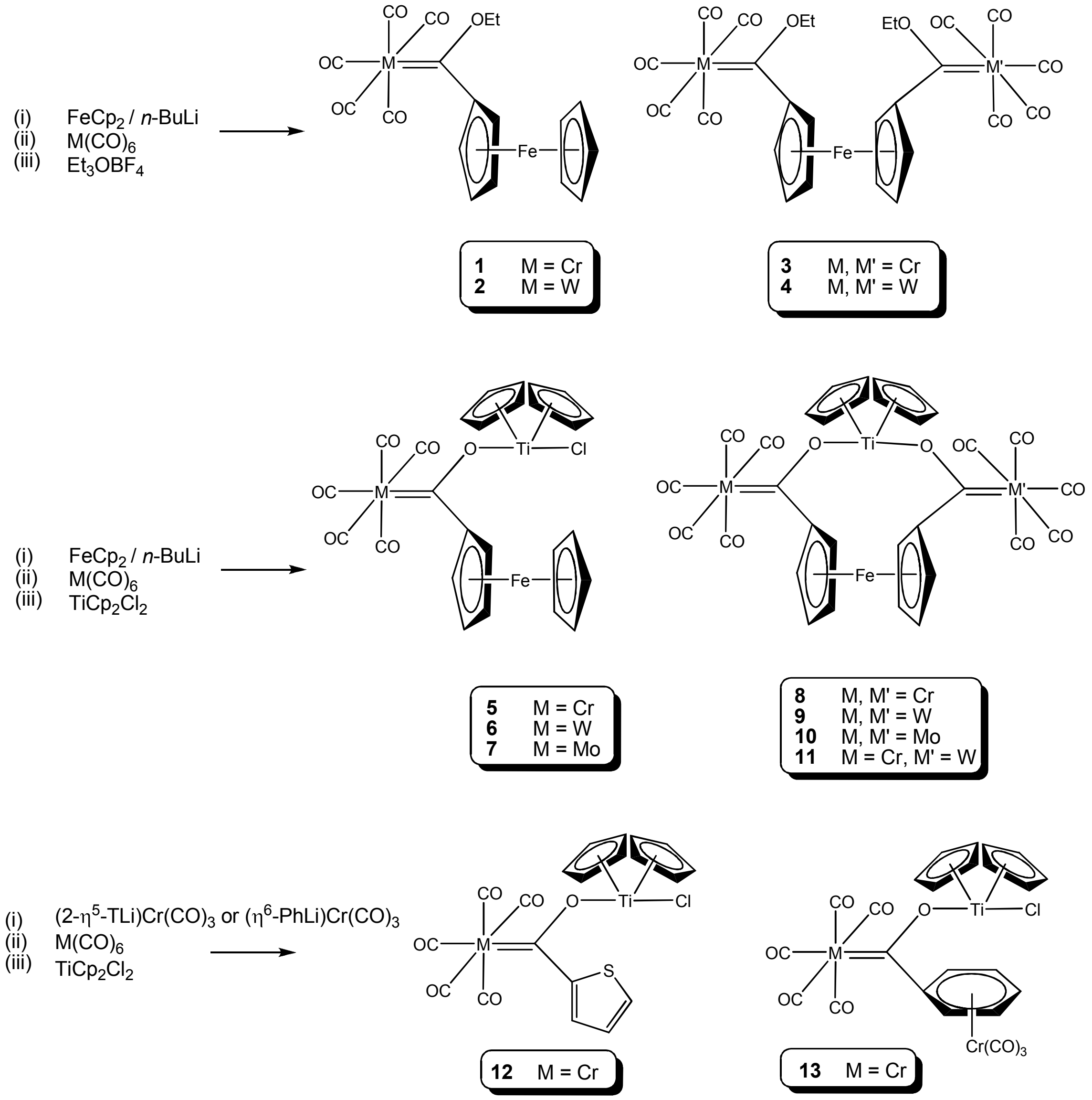


Figure 2.10 Group VI carbene complexes synthesized

2.3 Synthesis

In general, Fischer carbene complexes can be prepared following a variety of strategies.[50] These strategies include the formation of new carbene complexes from non-carbene complex precursors as well as by modification of pre-existing carbene complexes.

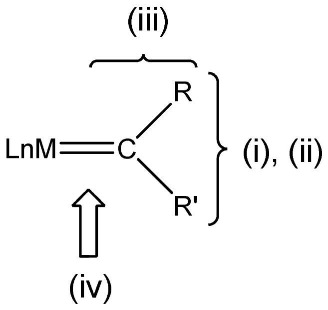
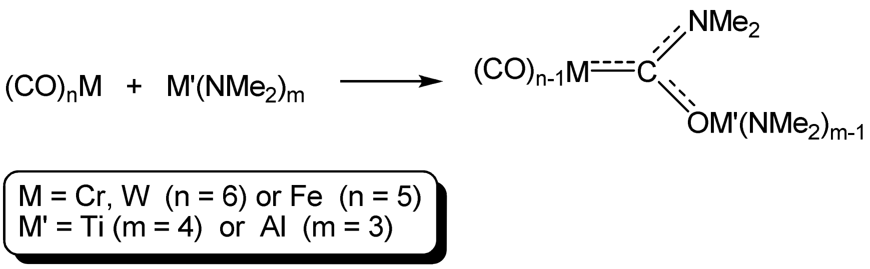


Figure 2.11 Synthetic strategies for the preparation of transition metal Fischer carbene complexes.

Specifically for Fischer carbene complexes, synthetic routes include (i) transformation of a non-carbene ligand into a carbene ligand, where the carbene carbon is already attached to the metal in the complex precursor, (ii) transfer of a pre-existing carbene ligand from one metal centre to another metal, (iii) modification of the carbene ligand and (iv) the insertion of an unsaturated organic molecule into the metal-carbene bond. The reaction sites (i) – (iv) listed above are indicated in Figure 2.11.



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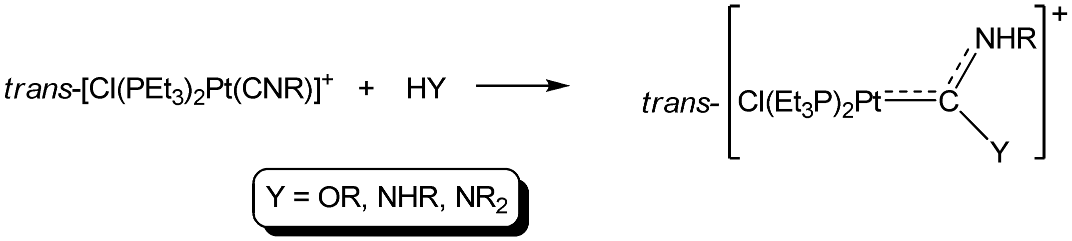
[50] Dötz, K.H.; Fischer, H.; Hofmann, P.; Kreissl, F.R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes,* VCH Verlag Chemie, Weinheim, **1983**, and references therein.

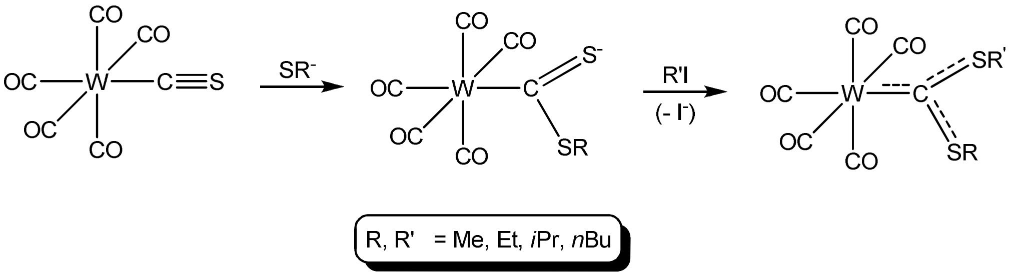
Scheme 2.10

Transformation of non-carbene ligand precursors into carbene ligands can be achieved, for example, in one step by employing metal amides[16(a), 51] to convert carbonyl ligands as shown in Scheme 2.10



Scheme 2.11

Treatment of isonitrile complexes with nucleophilic alcohols and amines (Scheme 2.11), followed by alkylation, also yield Fischer carbenes according to the Hegedus-Semmelhack method[52] but the most useful and direct route remains the direct, two-step procedure of Fischer and Maasböl.[48]



Scheme 2.12

Nucleophilic attack of the carbanion in a lithium organometallic reagent on the carbon atom of a carbonyl ligand forms an acyl metalate (Scheme 2.12) which can be alkylated with a variety of alkylating agents.[53]

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[51] (a) Petz, W.; Schmid, G. *Angew. Chem.* **1972**, *84*, 997, (b) Petz, W.; Jonas, A. *J. Organomet. Chem.* **1973** *55,* C42.

[52] (a) Semmelhack, M.F.; Lee, G.R. *Organometallics,* **1987**, *6*, 1839, (b) Imwinkelried, R.; Hegedus, L.S. *Organometallics,* **1988**, *7*, 702.

[53] (a) Casey, C.P.; Cyr, C.R.; Boggs, R.A. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 249, (b) Fischer, E.O.; Gibbins, S.G.; Kellerer, W. *J. Organomet. Chem.* **1981***, 218*, C51, (c) Fischer,

2.3.1 Synthesis of ferrocenyl mono- and biscarbene Cr and Mo complexes

Monolithiation of ferrocene is best achieved by reaction of ferrocenyl bromide with *n*-BuLi in diethyl ether at -78℃.[54] Lithiation of ferrocene in this case was carried out in hexane with 1 eq. TMEDA at a temperature of 45˚C, yielding both mono- and dilithiated ferrocene. This *n*-BuLi-TMEDA chelate method[55] has the advantage of being applicable at temperatures up to 70℃, since the reagent is stable at higher temperatures. In THF, however, the solution of *n*-BuLi and TMEDA is not stable since the ethereal solvent is readily attacked at room temperature by the chelation complex, leading to the formation of lithium ethenolate and ethane.

After reacting the lithiated ferrocene with the hexacarbonyls $Cr(CO)_6$ or $Mo(CO)_6$ and quenching the metalate with titanocene dichloride, both the trimetallic carbene complexes $[Cr(CO)_5\{C(OTiCp_2Cl)Fc\}]$ (**5**) and $[Mo(CO)_5\{C(OTiCp_2Cl)Fc\}]$ (**7**) and the biscarbene complexes containing both bridging bisoxytitanocene and bridging ferrocen-1,1'-diyl substituents, $[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}\{CCr(CO)_5\}_2]$ (**8**) $[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}\{CMo(CO)_5\}_2]$ (**10**) were obtained. The general synthetic route is outlined in Scheme 2.13.

The novel complexes **8** and **10** are remarkable in that they display a bimetallacycic ring bridging two carbene carbons. In order for comparison with the bisoxytitanocene bridged biscarbene complex, the dilithiation of ferrocene was repeated, and metalation (with either $Cr(CO)_6$ or $W(CO)_6$) followed by alkylation with the Meerwein salt[56] Et_3OBF_4 afforded complex **3**, $[\mu\text{-}Fe\{C_5H_4C(OEt)Cr(CO)_5\}_2]$ and **4** $[\mu\text{-}Fe\{C_5H_4C(OEt)W(CO)_5\}_2]$ (illustrated on p. 28) in high yield. Although the monomers $[M(CO)_5\{C(OEt)Fc\}]$ (**1** (M = Cr) and **2**

E.O.; Selmayr, T.; Kreissl, F.R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574, (d) Berke, H.; Härter, P.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317.

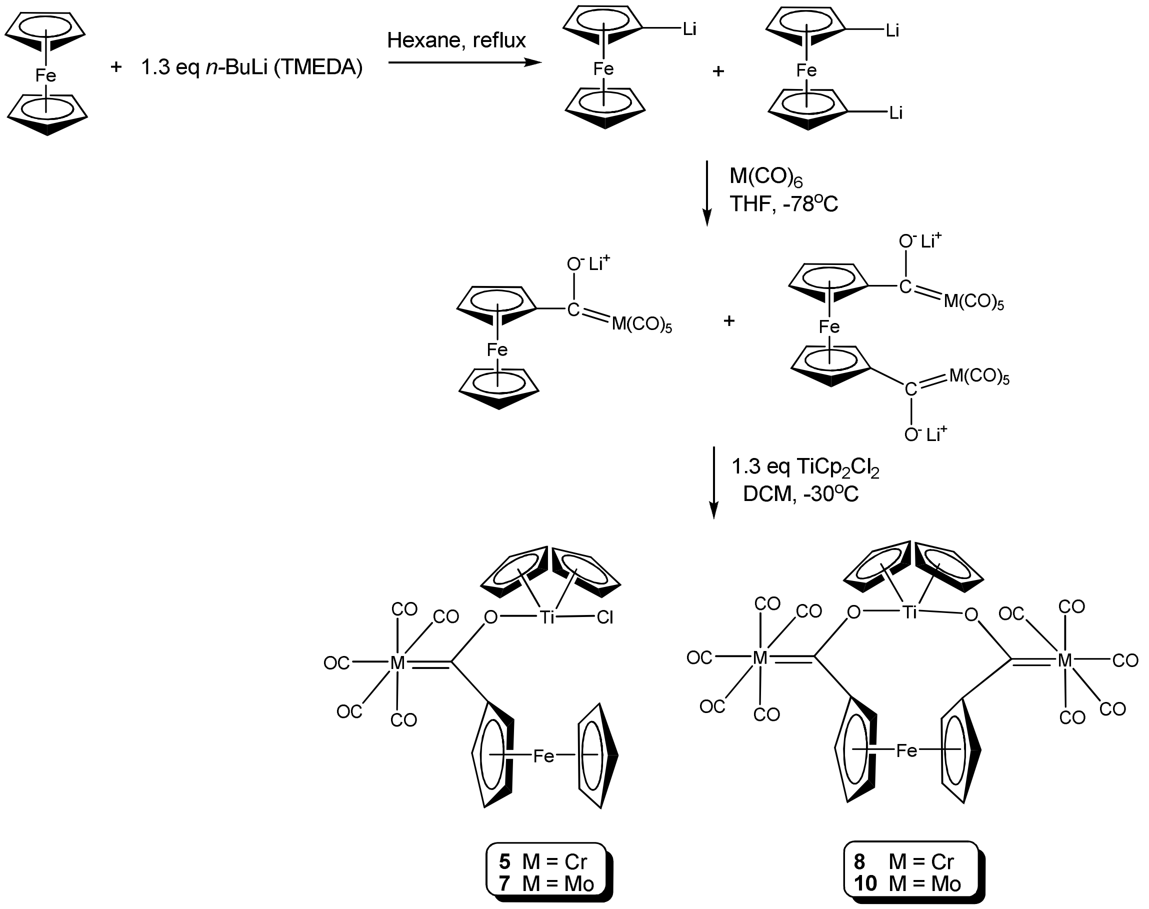
[54] Fish, R.W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253.

[55] Butler, I.R.; Cullen, W.R.; Ni, J.; Rettig, S.J. *Organometallics* **1985**, *4*, 2196.

[56] Meerwein, H. *Org. Synth.* **1966**, *46*, 113.

(M = W)) are known[57], the bisethoxy Fc'-bridged biscarbene (**3** and **4**) have not been synthesized before.

Unexpectedly, the chromium complexes proved more stable than the previously synthesized trimetallic carbene complexes **20** and **21** (Scheme 2.5), where a [Cr(2-η^6-BT)$(CO)_3$]-group is bonded to the carbene carbon atom. This could be ascribed to the absence of a displaceable $Cr(CO)_3$ fragment from BT (benzothienyl) in the cluster carbene complexes, the greater electron-donating character of the ferrocenyl substituent as compared to the [Cr(2-η^6-BT)$(CO)_3$]-substituent, and the prediction that a ferrocenyl group would not greatly increase the steric crowding around the carbene carbon atom.



Scheme 2.13

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[57] López-Cortés, J.G.; de la Cruz, L.F.C.; Ortega-Alfaro, M.C.; Toscano, R.A.; Alvarez-Toledano, C.; Rudler, H. *J. Organomet. Chem.* **2005**, *690*, 2229.

When comparing the monocarbene complex **5** and the biscarbene complex **8**, the absence of an activated chloro ligand on the titanium atom of **8** accounts for its greater stability. It is known that the reaction of a metal acylate with titanocene dichloride by displacement of one of the chloro ligands results in the activation of the remaining chloro ligand and can lead to the formation of two chromium carbene acylates being bridged by a titanocene fragment.[16(a)]

It should also be noted that in each of the reactions described above, unreacted *n*-butyllithium reacted with the different metal carbonyls and afforded the corresponding butylcarbene complexes $[(CO)_5M\{C(OR)(Bu)\}]$ (M = Cr, Mo, W; R = Et, $TiCp_2Cl$).[58]

2.3.2 Synthesis of tungsten carbene complexes

In the case of tungsten as central metal moiety, the above synthetic method yielded only the bridged biscarbene complex $[\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}\{CW(CO)_5\}_2]$ (**9**) but no monocarbene could be isolated. Initially, this was ascribed to the lability of the titanium chloro ligand,[16(a)] but later proved to be the result of the low yield of the monolithiated ferrocene compared to the dilithiated ferrocene.

In an attempt to overcome this limitation, the reaction was repeated as described in Section 2.3.1 above, but after addition of the titanocene dichloride, the reaction mixture was allowed to warm to room temperature and one mole equivalent of thiophenol was added to replace the remaining chloro ligand on the titanoxy substituent (Scheme 2.14). However, none of the desired monocarbene complex $[W(CO)_5\{C(OTiCp_2SPh)Fc\}]$ was obtained. Instead, column chromatography yielded only the bright purple complex $TiCp_2(SPh)_2$[59] and the tungsten metalate remained immobile on the silica gel column.

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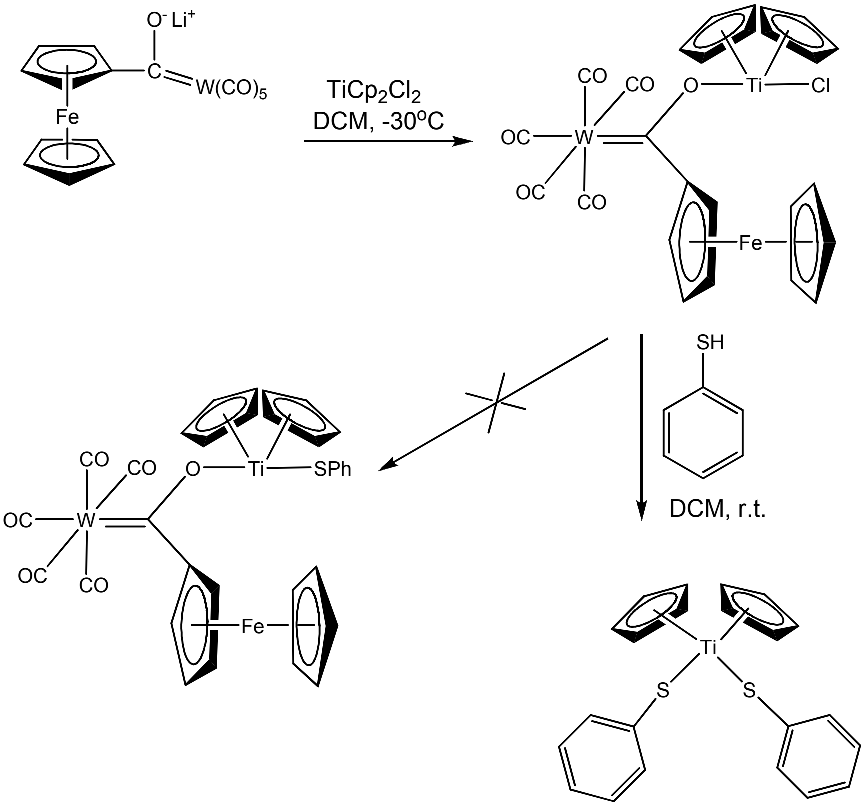
[58] Hedberg, F.L.; Rosenberg, H. *Tetrahedron Lett.* **1969**, 4011.

[59] (a)Köpf, H.; Schmidt, M. *Zeitschrift für Anorganische und Allgemeine Chemie* **1965**, *340*, 139, (b) Giddings, S.A. *Inorg. Chem.* **1967**, *6*, 819, (c) Muller, E.G.; Watkins, S.F.; Dahl, L.F. *J. Organomet. Chem.* **1976**, *111*, 73.

This lead us to prepare only monolithiated ferrocene instead of the mono- and dilithiated mixture. Ferrocenyl bromide was prepared according to literature procedure.[58] Mercury acetate was added to a ferrocene solution in benzene, followed by addition of 1 mole eq LiCl to yield chloromercury ferrocene. Subsequent reaction with N-bromo succinimide gave the ferrocenyl bromide (FcBr) reagent. FcBr was lithiated using 1 mole eq of *n*-BuLi in THF, followed by addition of $W(CO)_6$ dissolved in THF. The desired monocarbene complex **6** $[W(CO)_5\{C(OTiCp_2Cl)Fc\}]$ was isolated after reaction quenching with $TiCp_2Cl_2$ in dichloromethane and purification on a silica gel column.



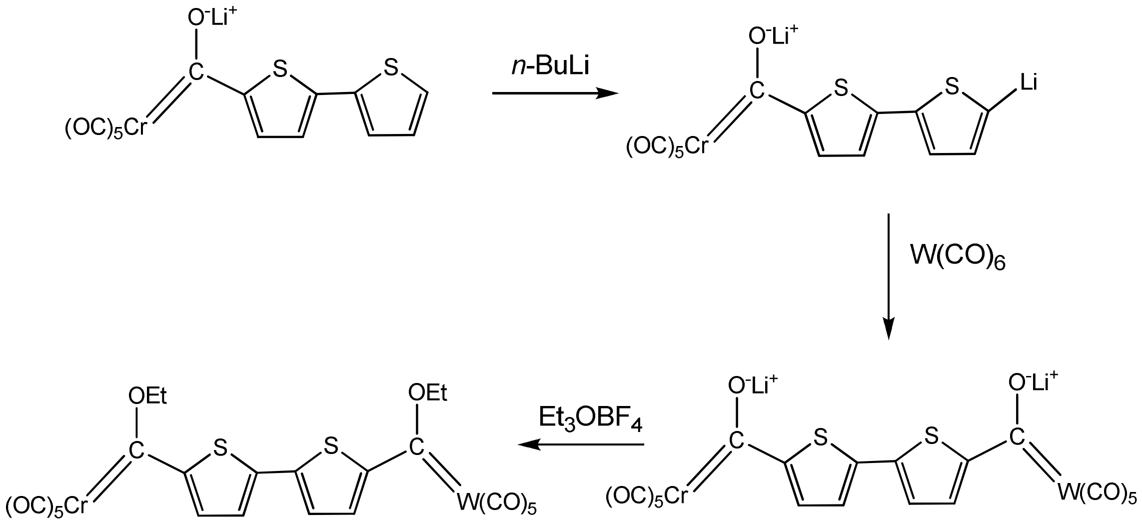
Scheme 2.14

O-metalation with $ZrCp_2Cl_2$ instead of $TiCp_2Cl_2$ was attempted but proved unsuccessful. This was ascribed to the instability of the resultant O-Zr bond in view of the greater activity of the zirconium metal compared to titanium.[9(a)]

2.3.3 Synthesis of mixed heteronuclear bridging biscarbene complexes

The investigation of mixed heteronuclear biscarbene complexes was included in the aims of this study in order to probe the possibility of enhancing the polarization across the conjugated bridge by introducing asymmetry.

The method employed by Maiorana[41] in the preparation of a heteronuclear bridging bithiophenyl biscarbene complex involved the synthesis of an anionic acyl complex of chromium, followed by metalation with *n*-BuLi and reactions with $W(CO)_6$ and Et^+ (Scheme 2.15) to yield a mixture of both the mono- and biscarbene complexes.



Scheme 2.15

Adaptation of the Aoki method[60] increases the yield of the heteronuclear biscarbene complexes significantly. Aoki and co-workers treated $M(CO)_6$ with a suitable lithium reagent, followed by the sequential addition of lithium diisopropyl amide (LDA), an electrophile, water and finally alkylated with an oxonium salt in a one pot reaction. This anionic protection strategy was modified in our laboratories by using a second mole equivalent of a different metal hexacarbonyl to obtain mixed metal biscarbene complexes bridged by furyl spacers.[43(d)]

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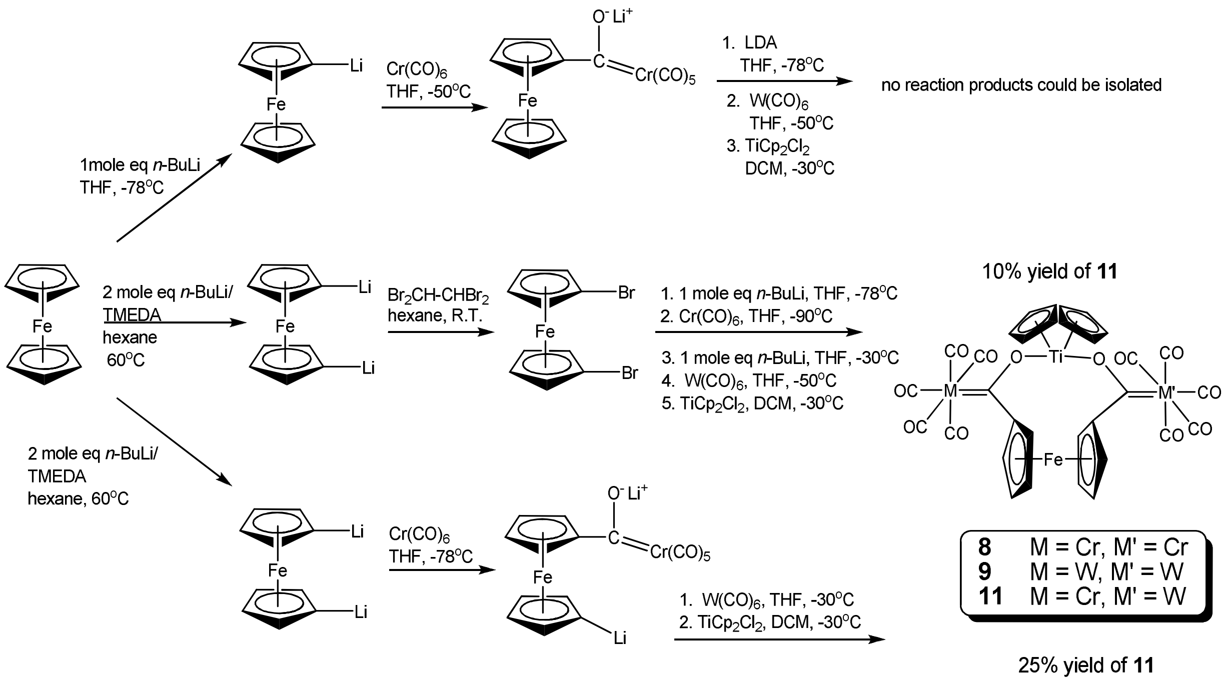
[60] Aoki, A.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985.

The method entailing sequential lithiation with first *n*-BuLi and then LDA, described above, was followed in an attempt to synthesize the heteronuclear biscarbene complex **11** $[W(CO)_5C\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}CCr(CO)_5]$, but no product could be isolated.

In the next attempt, it was decided to employ 1,1'-dibromoferrocene as starting material for lithiation. Ferrocene was dilithiated with *n*-BuLi/TMEDA and reacted with 1,2-tetrabromoethane, which, after recrystallization, afforded 1,1'-dibromoferrocene.[61] Monolithiation was achieved by metal-halogen exchange of one of the bromo ligands with 1 mole eq of *n*-BuLi followed by metalation with $Cr(CO)_6$ at -90°C. After allowing the reaction to warm to -30°C, a second mole eq of *n*-BuLi was added. The second mole eq of metal hexacarbonyl, $W(CO)_6$, was then added. Finally $TiCp_2Cl_2$ was reacted with the resulting bis(acyl metalate). A mixture of the homonuclear dimetallic biscarbene complexes **8** and **9**, as well as heteronuclear **11** was obtained, albeit in very low yield (< 10%).



Scheme 2.16

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[61] Kovar, R.F.; Rausch, M.D.; Rosenberg, H. *Organometallics in Chemical Synthesis* **1970**, *1*, 173.

In a final attempt to increase the yield as well as the selectivity of the preparation of the mixed metal complex, direct dilithiation of ferrocene was carried out as before. At -78℃ the first mole equivalent of $Cr(CO)_6$ was added, and the sequential addition of $W(CO)_6$ at -30℃, and quenching with titanocene dichloride gave the best result. $[W(CO)_5C\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}CCr(CO)_5]$, complex **11**, was isolated on a silica gel column, and crystallized from a dichloromethane/hexane (1:3) solution. The single crystals obtained were analysed by X-ray diffraction.

However, the X-ray structure obtained (R factor 6.21%) showed co-crystallization of the homonuclear biscarbene complex **8** and the desired heteronuclear complex **11**, with Cr-atoms occupying 84.5(2)% of the central metal atom sites, and W occupying 15.5(2)%. The only plausible explanation of the above finding would constitute greater reactivity of the $[Cr(CO)_5\{C(OLi)Fc'Li\}]$ intermediate than of dilithiated ferrocene $Fc'Li_2$ towards $Cr(CO)_6$. The homonuclear chromium biscarbene would therefore form preferentially. Only after all of the $Cr(CO)_6$ has been consumed, the remaining $[Cr(CO)_5\{C(OLi)Fc'Li\}]$ intermediate would react with the subsequently added $W(CO)_6$ to produce heteronuclear biscarbene **11**, and the remaining dilithiated ferrocene reacts with tungsten hexacarbonyl to yield homonuclear **9**.

The synthetic strategies describing the attempted synthesis of complex **11** are given in Scheme 2.16.

2.3.4 Synthesis of π-aryl-$Cr(CO)_3$ titanoxycarbene complexes of chromium

The first example of a π-aryl chromium tricarbonyl substituted carbene complex and, incidentally, the first example of a σ,π-carbene complex was synthesized by Fischer[4(a)] *via* lithiation of $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ with phenyl lithium. The starting material, π-benzene chromium tricarbonyl, was also originally prepared by the Fischer group in the reaction of chromium hexacarbonyl with the bis(π-arene) chromium complex $[Cr(\eta^6\text{-}C_6H_6)_2]$.[27(a)]

In this study, however, the π-benzene chromium tricarbonyl reagent was synthesized according to an improved direct reaction procedure, by heating the benzene and chromium hexacarbonyl together in dibutyl ether.[62]

Following lithiation of $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ with *n*-BuLi and sequential metalation with $Cr(CO)_6$ and $TiCp_2Cl_2$, the dark brown-purple **13** $[Cr(CO)_5\{C(OTiCp_2Cl)(\eta^1{:}\eta^6\text{-}PhCr(CO)_3)\}]$, was formed exclusively in high yield.

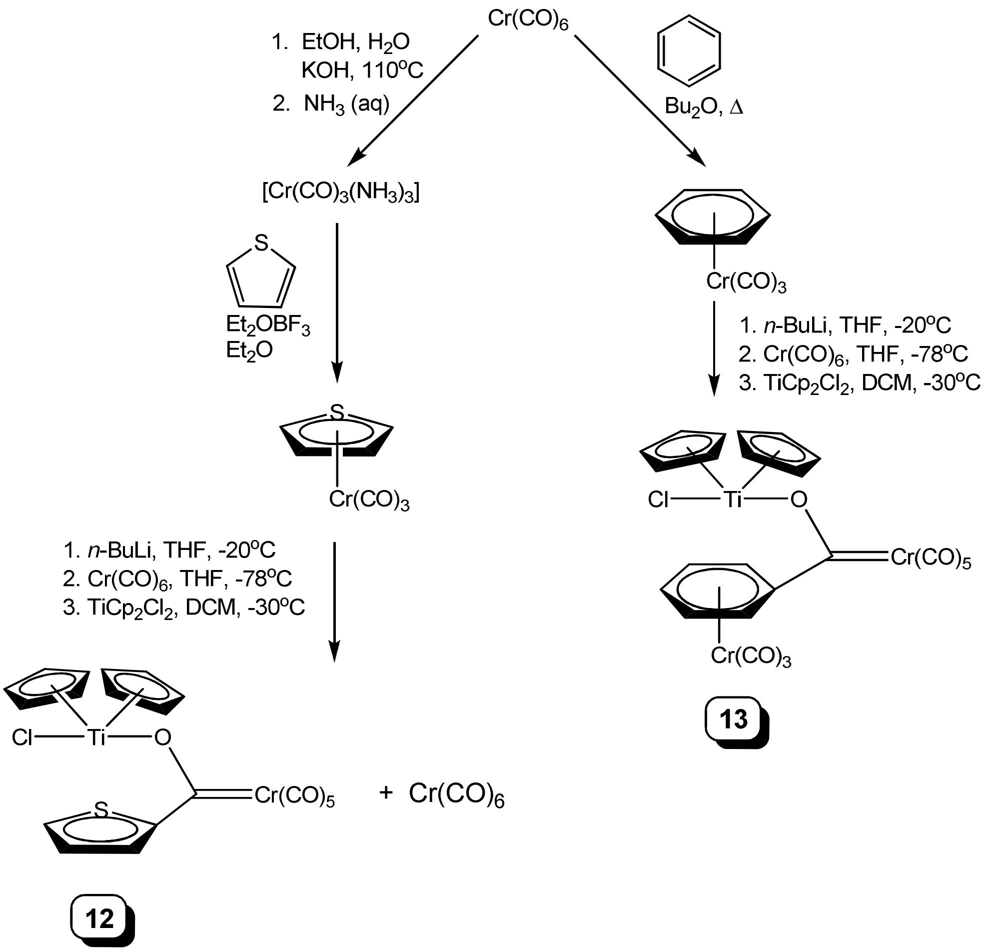

Figure 2.12 Synthesis of $[Cr\{\pi\text{-(hetero)aryl}\}(CO)_3]$ chromium titanoxycarbene complexes.

As with the $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ complex, the precursor $[Cr(CO)_3(\eta^5\text{-}SC_4H_4)]$ was prepared for the first time in a low yield by Fischer and Öfele in the thermal

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[62] Fischer, E.O.; Goodwin, H.A.; Kreiter, C.G.; Simmons, H.D.; Sonogashira, K.; Wild, S.B. *J. Organomet. Chem.* **1968**, *14*, 359.

reaction of chromium hexacarbonyl and thiophene.[63] An increased yield was achieved by converting the $Cr(CO)_6$ to $[Cr(CO)_3(NH_3)_3]$[64] whereafter treatment with excess thiophene and 3 mole equivalents of the Lewis acid BF_3 in diethyl ether yielded $[Cr(CO)_3(\eta^5\text{-}C_4H_4S)]$.[65]

The readily achieved lithiation of $[Cr(CO)_3(\eta^5\text{-}C_4H_4S)]$ at low temperatures has been reported[66] and subsequent carbene formation and alkylation with the introduction of the third metal-containing fragment occurred as before.

During evaporation of the solvent before column chromatography, the dark red solution of desired reaction product turned orange, and thin layer chromatography indicated a large amount of $Cr(CO)_6$ present. After separation, a lighter orange complex **12** $[Cr(CO)_5\{C(OTiCp_2Cl)(C_4H_3S)\}]$, was the only other product obtained besides the $Cr(CO)_6$ and unreacted titanocene dichloride. It is known that complexes with a benzene (here, incidentally, it is a phenyl group) instead of a π-coordinated thiophene substituent are less labile, and exhibit greater stability against $Cr(CO)_3$ displacement in polar solvents. However the high yield of previously reported ethoxy analogues[7] in contrast to the high reactivity of this titanoxy equivalent would seem to indicate increased lability of the $Cr(CO)_3$-fragment as a result of overall increased lability when two transition metal fragments are bonded to the carbene carbon atom.

2.4 Spectroscopic characterization

The carbene complexes were characterized using ^1H and ^{13}C NMR spectroscopy. Chemical shift assignments were substantiated by two-dimensional HSQC-NMR experiments. Other spectroscopic characterization methods include infrared spectroscopy, mass spectrometry and single crystal X-ray diffraction where possible.

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[63] Fischer, E.O.; Öfele, K. *Chem. Ber.* **1958**, *91*, 2385.
[64] Rausch, M.D.; Moser, G.A.; Zaiko, E.J.; Lipman, A.L. *J. Organomet. Chem.* **1970**, *23*, 185.
[65] Novi, M.; Guanti, G.; Dell'Erba, C. *J. Heterocycl. Chem.* **1975**, *12*, 1055.
[66] Nefedova, M.N.; Setkina, V.N.; Kursanov, D.N. *J. Organomet. Chem.* **1983**, *244*, C21.

2.4.1 ^{1}H NMR spectroscopy

The coordination of a metal fragment to an organic ligand markedly affects the electronic environment of the ligand protons and is reflected in the resonance frequencies of the ligand nuclei. The chemical shifts (^{1}H and ^{13}C) of the uncoordinated precursor molecules employed in this chapter are given below.

The carbene moiety, coordinated to an electropositive metal, causes draining of electron density[5] from the double bonds of the arene rings to the electrophilic carbene moiety, resulting in a downfield shift of the ring proton resonances compared to the chemical shifts of the uncoordinated arenes.

The resonance signals for the protons of the cyclopentadienyl rings on titanium uniformly occur at lower field than for ferrocene. Complex **12** contains the heteroaromatic thiophene ring bonded to the carbene carbon, while the phenyl ring of **13** has a $Cr(CO)_3$-fragment π-bonded to it. This π-coordination disrupts the aromaticity of the benzene ring and is reflected in the upfield shift of the benzene protons from 7.15 ppm in a benzene ring compared to the 4.27 ppm resonance seen for the precursor $[Cr(\eta^6-C_6H_6)(CO)_3]$.

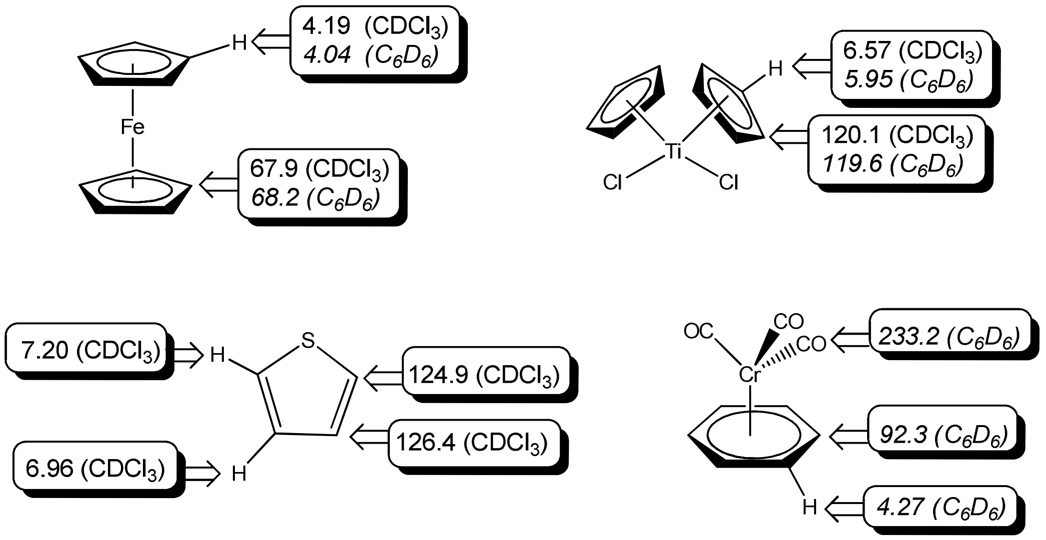
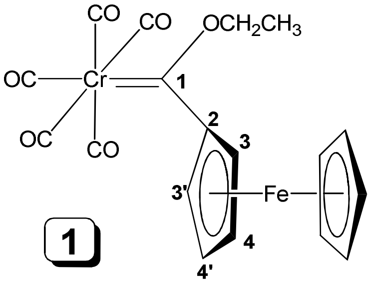
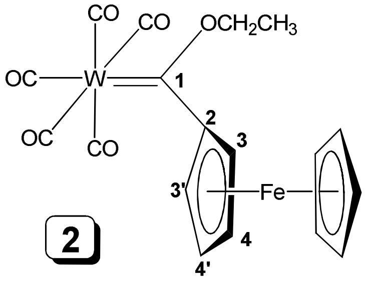


Figure 2.13 ^{1}H and ^{13}C chemical shifts (in units ppm) of precursor molecules

The NMR spectra of the chromium complexes **3**, **5**, **8** and **12**; and the tungsten complex **9**, were recorded in deuterated chloroform as solvent. Spectra of high resolution could only be obtained in d_6-benzene for the remainder and the assignments are listed in Tables 2.1 – 2.5. Slow decomposition of products with time was observed in the spectra, and broadening of the signals in the case of complex **5** was observed. The spectrum of **1** could not be determined due to decomposition, and for complexes **1** and **2** (Table 2.1) the literature values are given in brackets. In all cases, the atom numbering system employed is indicated in the relevant table.

Table 2.1 ^{1}H NMR data of ferrocenyl ethoxy monocarbene complexes

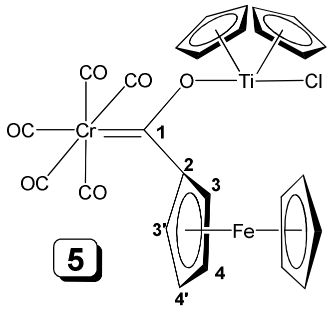
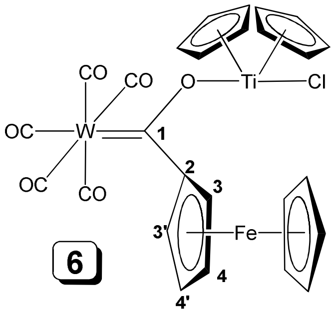
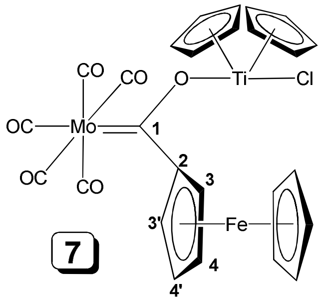
Proton Assignment	Chemical shifts (δ) and coupling constants (J)		
			
	δ *(*[57])*	δ** *(*[57])*	J (Hz)**
H3, H3'	*(5.00, 4H, br, m)*	4.78, 2H, dd *(4.98, 2H, br, s)*	2.2, 1.8
H4, H4'	*(4.77, 2H, br, s)*	4.27, 2H, dd *(4.85, 4H, br, m)*	2.3, 1.7
Fe-Cp	*(4.22, 5H, s)*	3.92, 5H, s *(4.25, 5H, s)*	-
CH_2	*(5.00, 4H, br, m)*	4.49, 2H, q *(4.85, 4H, br, m)*	7.0
CH_3	*(1.60, 3H)*	0.96, 3H, t *(1.58, 3H, m)*	7.0

* Recorded in $CDCl_3$
** Recorded in C_6D_6

Different deuterated solvents were employed during NMR analysis, due to poor solubility in benzene-d_6 preventing the recording of all NMR spectra in this solvent, while the use of chlorinated solvent $CDCl_3$ caused decomposition of some of the carbene complexes. The use of different deuterated solvents during NMR analysis complicates direct comparison of the different proton resonances, as the ^1H NMR spectra of complexes recorded in $CDCl_3$ are shifted more downfield as compared to the spectra recorded in C_6D_6.

Analogous complexes containing the same ligands and substituents, with only the central metal being varied from Cr to Mo to W, afforded chemical resonances shifted more downfield for the Cr-complexes, while the W-complexes display spectra that appear to have more upfield shifts, owing to the better shielding of the protons by the larger metal nucleus.

Table 2.2 ^1H NMR data of ferrocenyl titanoxy monocarbene complexes

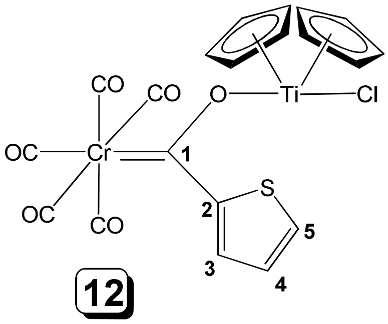
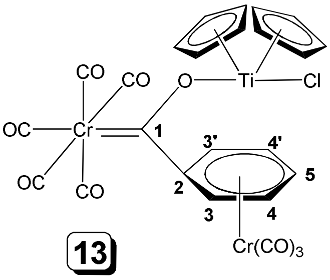
Proton Assignment	Chemical shifts (δ) and coupling constants (J)					
	 **5**		 **6**		 **7**	
	δ*	J (Hz)	δ*	J (Hz)	δ**	J (Hz)
Ti-Cp_2	6.52, 10H, s	-	6.46,10H, s	-	5.91, 10H, s	-
H3, H3'	4.70, 2H, br,m	-	5.04, 2H, br	-	4.89, 2H, d	2.9
H4, H4'	4.57, 2H, br,m	-	4.68, 2H, br	-	4.51, 2H, d	3.0
Fe-Cp	4.33, 5H, s	-	4.29, 5H, s	-	4.26, 5H, s	-

* Recorded in $CDCl_3$
** Recorded in C_6D_6

Relative to the Cp resonance of 4.19 ppm ($CDCl_3$) or 4.04 ppm (C_6D_6) for ferrocene, the α-proton of the attached FeCp-ring of all the ferrocenyl carbene complexes display a similar downfield shift compared to other substituted ferrocenes with an electron withdrawing group, such as $FeCp(C_5H_4(C(O)OMe))$

(δ: 4.80 H3, H3'; 4.39 H4, H4'; 4.20 Cp).[67] Since the α-proton (H3, H3') occupies the position closest to the site of the carbene carbon atom, the chemical shift of this proton is influenced most easily and is a sensitive probe for electronic ring substituent involvement with the electrophilic carbene carbon atom. Figure 2.14 demonstrates this phenomenon by considering the π-resonance effect in these compounds, as explained by Connor and Lloyd[23] (Figure 2.3). This is consistent with the finding that the donor strength of the ferrocenyl group is considerably increased by interaction with strong electrophilic centres.[68]

Table 2. 3 ^1H NMR data of π-aryl titanoxycarbene complexes

Proton Assignment	Chemical shifts (δ) and coupling constants (J)			
	 **12**		 **13**	
	δ*	J (Hz)	δ**	J (Hz)
Ti-Cp_2	6.50, 10H, s	-	6.33, 10H, s	-
H3, H3'	8.16, 1H, br	-	4.52, 2H, dd	6.3, 3.2
H4, H4'	7.28, 1H, br	-	4.39, 2H, dd	6.3, 6.3
H5	7.72, 1H, d	4.67	4.31, 1H, br	-

* Recorded in $CDCl_3$
** Recorded in C_6D_6

The thienyl ethoxycarbene complex of Cr was first prepared by Connor and Jones[69] and the ^1H NMR spectrum of $[Cr(CO)_5\{C(OEt)(C_4H_3S)\}]$ reported. The large downfield shift of the methylene protons of the ethoxy group were seen as being consistent with the electron withdrawing property of $(CO)_5Cr{=}C(2\text{-thienyl})$-

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[67] Pickett, T.E., Richards, C.J.; *Tetrahedron Lett.* **1999**, *40*, 5251.
[68] Nesmeyanov, A.N.; Perevalova, E.G.; Gubin, S.P.; Gradberg, K.I.; Koslavsky, A.G. *Tetrahedron Lett.* **1966**, *28*, 237.
[69] Connor, J.A.; Jones, E.M. *J. Chem. Soc. A* **1971**, 1974.

group, and the assignment of H3, H4 and H5 were made according to Gronowitz:[70] H3 8.23, H4 7.20 and H5 7.68 ppm in $CDCl_3$. Likewise to the downfield shift of H3 of ferrocene, H3 of thienyl carbene complexes display a downfield shift due to π-resonance effects.

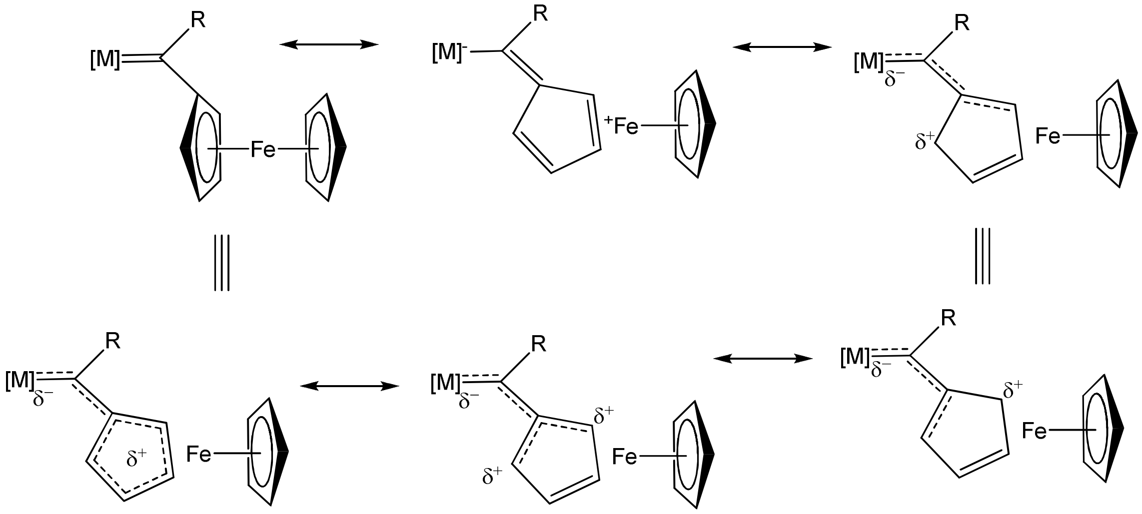

Figure 2.14 π-Resonance effects in ferrocenyl carbene complexes

Compared to the literature values obtained for $[Cr(CO)_5\{C(OEt)(C_4H_3S)\}]$, the upfield shift of H3 of complex **12** would seem to support the expectation that the titanoxy substituent leads to increased electron density on the oxygen atom. Greater interaction with the carbene carbon atom and less involvement of the thienyl substituent would result, and can be ascribed to the ionic character of the Ti-O bond. A higher contribution of the acyl resonance structure[9] illustrated in Figure 2.15 is therefore proposed. This phenomenon was also observed for the ferrocenyl complexes: compare for example $[Cr(CO)_5\{C(OEt)Fc\}]$ **1** (δ: H3,H3' 5.00; H4, H4' 4.77)[57] and $[Cr(CO)_5\{C(OTiCp_2Cl)Fc\}]$ **5** (δ: H3, H3' 4.70; H4, H4' 4.57).

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[70] Gronowitz, S. *Adv. Heterocycl. Chem.* **1963**, *1*, 1.

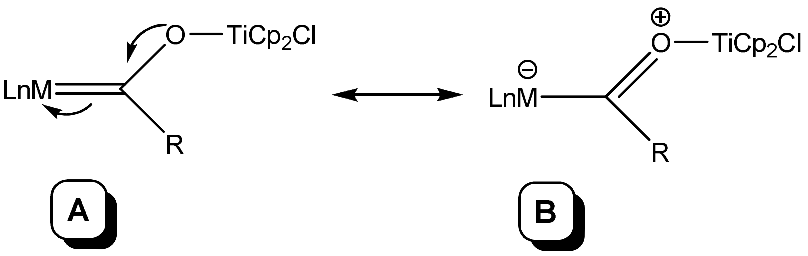
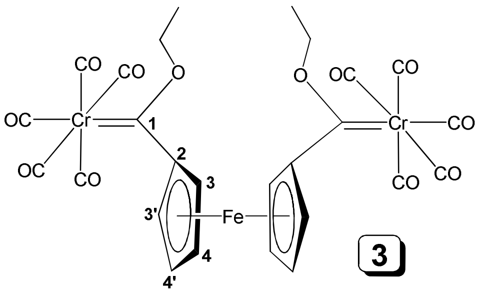
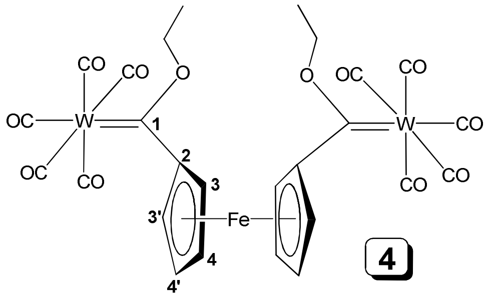


Figure 2.15 Acyl character of titanoxycarbene complexes

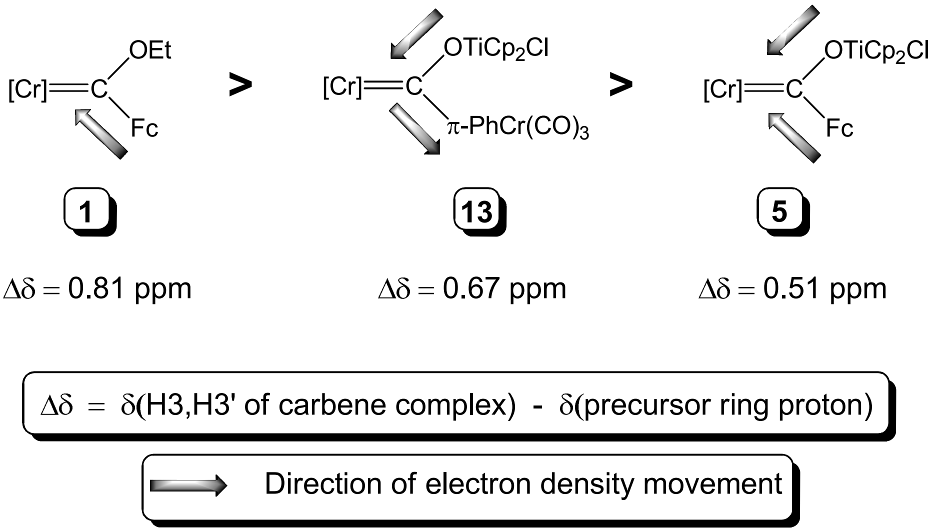
The same upfield shift of the π-aryl substituent is seen in the case of complex **13**. H3, H3'-values of 4.52 ppm (recorded in C_6D_6) when $-TiCp_2Cl$ is bonded to the oxygen atom, compared to a value of 5.72 ppm (recorded in acetone-d_6) with an ethoxy substituent.[4(a)]

Table 2. 4 ^1H NMR data of ferrocenyl ethoxy biscarbene complexes

Proton Assignment	Chemical shifts (δ) and coupling constants (J)			
	 **3**		 **4**	
	δ*	J (Hz)	δ**	J (Hz)
H3, H3'	5.00, 4H, dd	2.3, 1.9	4.94, 4H, dd	2.0, 1.8
H4, H4'	4.73, 4H, dd	2.3, 1.9	4.39, 4H, dd	2.0, 1.8
CH_2	5.07, 4H, q	7.1	4.55 4H, q	7.0
CH_3	1.63, 6H, t	7.1	1.06, 6H, t	7.0

* Recorded in $CDCl_3$
** Recrded in C_6D_6

When the downfield shifts of H3, H3' of the carbene complexes are compared to those of the precursor compounds, the formula $\Delta\delta = \delta_{complex} - \delta_{precursor}$ can be used to estimate the extent to which titanoxy fragments stabilize the carbene carbon atoms. The greater the downfield shift, the greater the electronic stabilization of the ring towards the carbene carbon atom, which in turn implies less stabilization of the heteroatom bonded substituent. Using the above formula for Δδ, the effect of the substituent –OEt and electron withdrawing π-(C_6H_6)Cr($CO)_3$ *vs* electron donating Fc and –OTiCp$_2$Cl can be roughly estimated as shown in Scheme 2.17.



1 $\Delta\delta = 0.81$ ppm

13 $\Delta\delta = 0.67$ ppm

5 $\Delta\delta = 0.51$ ppm

$\Delta\delta$ = δ(H3,H3' of carbene complex) - δ(precursor ring proton)

Direction of electron density movement

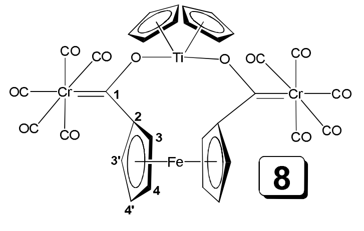
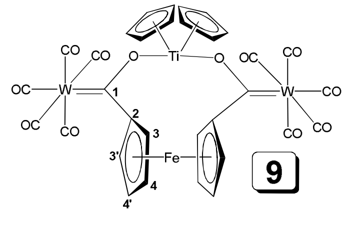
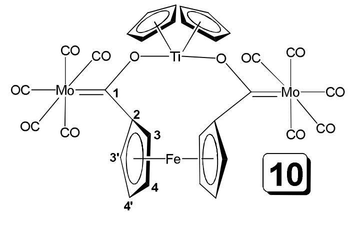
Scheme 2. 17

Ethoxy-substituted **1** shows the greatest contribution from the ferrocene towards stabilizing C1, while the titanoxy substituent of **5** results in the chemical shift resonance of H3, H3' being least affected. Complex **13** contains both an electron withdrawing carbene substituent (Cr(η^1:η^6-Ph)($CO)_3$) and an electron donating substituent (OTiCp$_2$Cl). The titanoxy fragment in **13** compensates for the electron-draining effect of the Cr($CO)_3$ moiety, and an intermediate Δδ value is obtained.

In the case of ethoxy biscarbene **3** and titanoxy biscarbene **8**, another direct comparison of the chemical environment of the ferrocenyl protons can be made as evidence for the increased π delocalization in the Cr-C$_{carbene}$-O-Ti unit. The

Fc chemical shifts of **3** are 5.00 and 4.73 ppm for H3 and H4 respectively, while **8** display resonances at 4.70 and 4.43 ppm. The relative contribution of the acyl resonance form **B** in Figure 2.16 is greater for a titanoxycarbene structure than for an alkoxycarbene complex, because a titanium(IV) cyclopentadienyl fragment can accommodate a positive charge more easily than an alkyl group.

Table 2. 5 ^{1}H NMR data of ferrocenyl titanoxy biscarbene complexes

Proton Assignment	Chemical shifts (δ) and coupling constants (J)					
	 **8**		 **9**		 **10**	
	δ*	J (Hz)	δ*	J (Hz)	δ**	J (Hz)
Ti-Cp$_2$	6.70, 10H, s	-	6.67, 10H, s	-	5.89, 10H, s	-
H3, H3'	4.70, 4H, dd	2.0, 1.9	4.74, 4H, dd	2.2, 1.9	4.52, 4H, dd	1.5, 1.4
H4, H4'	4.43, 4H, dd	2.0, 1.9	4.58, 4H, dd	2.3, 1.9	4.06, 4H, dd	1.5, 1.4

* Recorded in $CDCl_3$
** Recorded in C_6D_6

2.4.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **1** – **13** are summarized in Tables 2.6 – 2.9, using the same atom numbering scheme as found in Tables 2.1 – 2.5. Due to long acquisition times, decomposition of complexes **7** and **12** occurred and no ^{13}C NMR spectra of these compounds could be recorded.

Fischer carbene carbon atoms are defined as being electron-deficient *sp*^{2}-hybridized carbons stabilized by dative π-bonding from the alkoxy/metaloxy substituent and from the central metal, combined with inductive release from the aromatic substituent of the carbene carbon. Spectroscopic data supports this model as metal carbene carbon shifts can be found very downfield in a broad range of 200[71] to 400 ppm.[53(c)] The carbene carbon resonances depend both on the carbene substituents and on the metal, and are more sensitive to changes in the electronic environment than carbonyl ligands.

Table 2.6 ^{13}C NMR data of ferrocenyl ethoxy monocarbene complexes

Carbon Assignment	Chemical shifts (δ)	
	1	**2**
	δ(*[57])	δ** (*[57])
C1	*(329.7)*	303.1 *(304.3)*
CO	*(223.0* (trans), *217.3* (cis)*)*	198.3 (*trans*), 190.8 (*cis*) *(202.5* (trans), *198.0* (cis)*)*
C2	*(93.6)*	n.o. *(95.2)*
C3, C3’	*(74.5)*	74.0 *(75.0)*
C4, C4’	*(72.3)*	71.4 *(73.3)*
Fe-Cp	*(70.6)*	68.0 *(70.8)*
CH_2	*(75.5)*	77.6 *(78.1)*
CH_3	*(15.5)*	15.3 *(15.4)*

* Recorded in $CDCl_3$
** Recorded in C_6D_6

Chemical shifts for terminal metal carbonyls lie in the range of 150 to 240 ppm[72] with shielding of the carbonyl nucleus increasing with increasing atomic number of the metal (compare analogous complexes **8** – **10** : $Cr(CO)_5$ 224.3, 218.0 ppm; $Mo(CO)_5$ 219.9, 213.1 ppm and $W(CO)_5$ 199.7, 191.1 ppm). On the other hand, carbonyl groups are fairly insensitive to changes of substituents on the other ligands present.

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[71] Anderson, B.A.; Wulff, W.D.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602.
[72] Mann, B.E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

Table 2.7 ^{13}C NMR data of ferrocenyl titanoxy monocarbene complexes

Carbon Assignment	Chemical shifts (δ) and coupling constants (J)		
	5	**6**	**13**
	δ*	δ*	δ**
C1	n.o.	300.8	n.o.
$M(CO)_5$	223.1 (*trans*), 217.9 (*cis*)	200.4 (*trans*), 191.4 (*cis*)	223.0 (*trans*), 218.3 (*cis*)
$Cr(CO)_3$	-	-	233.2, 232.0
$Ti\text{-}Cp_2$	118.4, 117.5	119.0, 118.5	119.1
C2	n.o.	n.o.	n.o.
C3, C3’	75.7	74.3	95.7
C4, C4’	72.3	70 .2	89.7
C5	-	-	90.7

* Recorded in $CDCl_3$
** Recorded in C_6D_6

Only for complexes **2** – **4**, **6** and **8** were carbene carbon atom resonances observed. The carbene carbon resonances are shifted more downfield in biscarbene complexes but this tendency is not carried over to C2 in the ring system. For the ethoxy monocarbene tungsten complex **2** the carbene carbon resonates at 303.1 ppm. The titanoxy monocarbene tungsten complex **6** displays a carbene carbon chemical shift at 300.3 ppm, *ca.* 3 ppm upfield when the alkoxy substituent is replaced by a titanoxy substituent.

As with the proton NMR spectra and the comparison of H3 chemical shifts, this would seem to support the statement that the metaloxy fragment better stabilize the electrophilic carbene carbon atom. In broad terms, the titanoxy fragment can therefore be seen as more electron donating than the ethoxy substituent.

Table 2. 8 ^{13}C NMR data of ferrocenyl ethoxy biscarbene complexes

Carbon Assignment	Chemical shifts (δ)	
	3	**4**
	δ*	δ**
C1	306.2	303.7
CO	223.6 (*trans*), 217.1 *(cis)*	203.9, 202.7(*trans)*, 198.7 *(cis)*
C2	99.2	n.o.
C3, C3'	76.2	76.5
C4, C4'	72.7	74.2
CH_2	77.4	78.0
CH_3	15.5	14.8

* Recorded in $CDCl_3$
** Recorded in C_6D_6

Table 2. 10 ^{13}C NMR data of ferrocenyl titanoxy biscarbene complexes

Carbon Assignment	Chemical shifts (δ)		
	8	**9**	**10**
	δ*	δ**	δ**
C1	351.9	n.o.	n.o.
CO	224.3 (*trans*), 218.0 (*cis*)	199.7 (*trans)*, 191.1 (*cis*)	219.9 (*trans*), 213.1 (*cis*)
Ti-Cp_2	118.4	118.7	118.4
C2	n.o.	n.o.	n.o.
C3, C3'	76.6	72.8	70.7
C4, C4'	72.3	70.8	69.5

* Recorded in $CDCl_3$
** Recorded in C_6D_6

The titanium Cp-rings in the monocarbene complexes **12** and **13** rotate freely in solution, as is evident from a single peak for the Cp-protons and also for the carbon atoms in the NMR spectra, while the ^{13}C NMR spectrum of the ferrocenyl monocarbene complexes **5** – **7** display two signals. This observation is ascribed to restricted rotation of the C(carbene)-C(Fc) bond caused by the proximity of the bulky metal substituents. For the biscarbene complexes **8** – **10**, the symmetry of the structures precludes electronic inequivalency and only one titanium Cp-resonance is seen.

2.4.3 IR spectroscopy

The stretching vibrational frequency of terminal carbonyl ligands lies between 1820 and 2120 cm^{-1}.[73] In contrast to M-C stretching frequencies, the C-O stretching frequencies can be seen as being independent from other vibrations in the molecule. Qualitative correlation between C-O bond order can therefore be drawn from analysis of ν(CO) frequencies, as well as information about the bonding properties of ligands substituting metal carbonyl complexes. A weaker π-acceptor ligand, such as a carbene ligand, would result in more metal electron density available for backdonation towards π-acidic carbonyl ligands, resulting in absorption bands at lower wave numbers for the $[M(CO)_n(carbene)]$ complexes than for the corresponding binary $[M(CO)_{n+1}]$.

Octahedral complexes of the general formula $M(CO)_5L$ display pseudo-C_{4v} symmetry. This implies four stretching vibration modes, illustrated in Figure 2.16. The IR-active bands include the A_1^2 and the two degenerate E bands. Coupling of the A_1^1 band with the A_1^2 band can cause the A_1^1 band to also become IR active. The E band is usually the broad strongest peak, sometimes overlapping with A_1^1. For complexes where L is a good π-acceptor ligand, A_1^1 is found at higher wavenumbers than the E band, with the A_1^2 band always at the highest frequency. The B_1 mode is Raman active and IR inactive, but when L is a very bulky substituent, the equatorial plane is distorted and the stretching vibration

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[73] Braterman, P.S. *Metal Carbonyl Spectra,* Academic Press Inc., London, **1975**, 68.

induces a change in the dipole. For sterically hindered carbene ligands, the B_1 mode can become IR active and result in a fourth band in the IR spectra.[74]

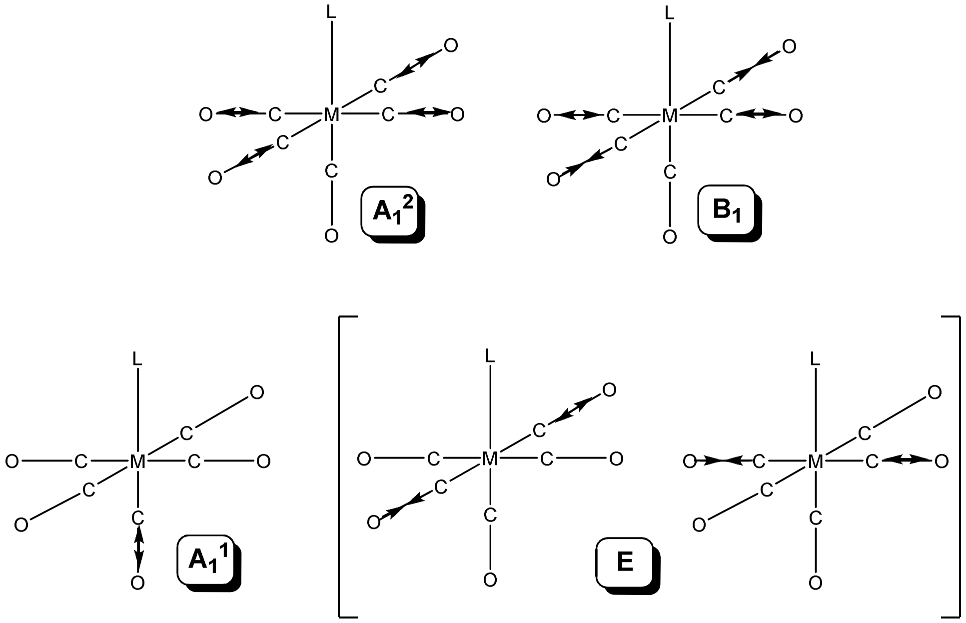

Figure 2.16 Normal modes of stretching vibrations for $M(CO)_5L$ systems

The infrared data of all the complexes **1** – **13** are summarized in Table 2.10, and representative spectra of analogous Cr, W and Mo complexes are given in Figure 2.17. The spectra were recorded in dichloromethane, due to the insolubility of the complexes in hexane. In the case of **13**, resolution of the bands could only be obtained for a spectrum recorded in the solid state in a CsI matrix.

Complex **13** contains both a $Cr(CO)_5$ and a $Cr(CO)_3$ moiety. In the case of [M(π-arene)$(CO)_3$] systems, the IR-active bands are one A_1 and two, degenerate E bands. The E mode is generally broader than A_1, presumably due to partial lifting of the degeneracy by asymmetric ligands.

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[74] Adams, D.M. *Metal-Ligand and Related Vibrations,* Edward Arnold Publishers Ltd., London, **1967**, 98.

Table 2.10 Infrared data of Group VI cluster carbene complexes

Complex	$M(CO)_5$ assignment, [ν(CO), cm^{-1}]		
	A_1^2	B_1 overlapping A_1^1	E
1	2054 s	1979 m	1933 vs
2	2065 w	1975 w	1927 vs
3	2054 s	1979 sh, 1938 vs sh overlap E	1938 vs sh overlap A_1^1
4	2061 s	1927 vs overlap E	1927 vs overlap A_1^1
5	2046 w	1972 vw	1926 vs
6	2052 m	1958 m	1916 vs
7	2056 w	1984 s	1934 vs
8	2044 m	1971 sh	1929 vs
9	2055 w	1975 vs	1923 m
10	2055 m	1977 s	1934 vs
11	2050 m (W) 2028 m (Cr)	1983 w, 1936 vs overlap E (W) 1968 w, 1915 vs overlap E (Cr)	1936 vs (W) overlap A_1^1, 1915 vs (Cr) overlap A_1^2
12	2050 m	1977 w, 1933 vs overlap E	1933 vs overlap A_1^1
13* $Cr(CO)_5$	2050 s	1972 s	1929 vs
13* $Cr(CO)_3$	1990 vs (A_1)	1887 vs (E)	

* Recorded as a CsI pellet

The A_1^1 mode in the C_{4v} local symmetry represents the mode with the greatest contribution to the stretching of the C-O bond *trans* to L, and should therefore be most affected by changes in the electronic environment caused by the carbene ligand.

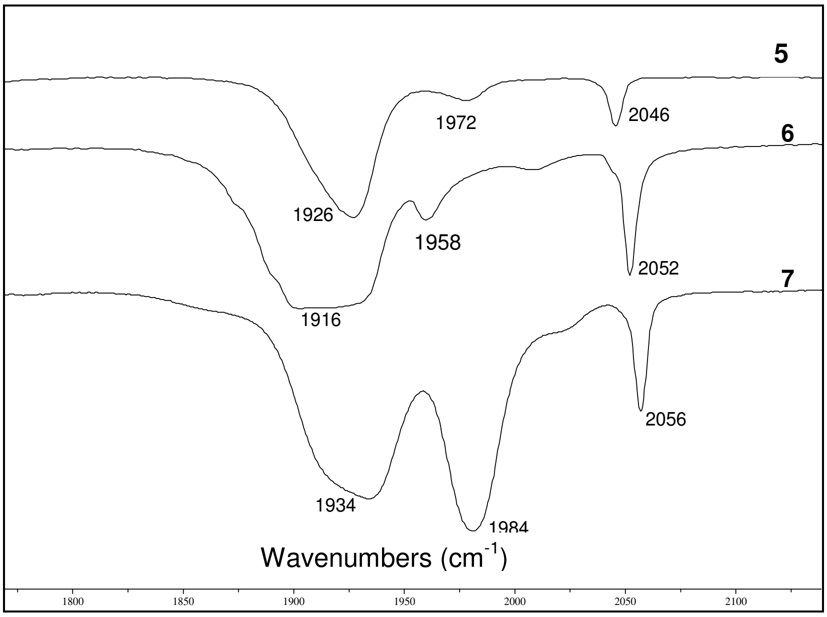


Figure 2.17 Stacked IR spectra of the carbonyl region of complexes **5**, **6** and **7**

Stabilization by carbene substituents *via* electron donation, should be reflected by ν(CO) bands of A_1^1 at higher wavenumbers. If the ethoxy (OEt), the thienyl substituent (T) and the Cr(π-Ph)$(CO)_3$ substituents are broadly classified as more electron withdrawing relative to the other two carbene substituents, while the titanoxy ($OTiCp_2$) and ferrocenyl (Fc) fragments are seen as electron donating, then it should be possible to observe this trend reflected in the ν(CO) values. However, due do the broadened peaks, and overlapping bands, no clear trend could be established. The A_1^2 mode defines the symmetric stretch of the CO ligands in the equatorial plane, and can therefore not be used as a direct measure of the π-acceptor ability of the carbene ligand

2.4.4 Mass spectrometry

The mass spectra of complexes **3**, **5** – **7**, **12** and **13** were recorded using fast atom bombardment (FAB) techniques. In the case of complexes **1** and **2**, no molecular ion peak (M^+) was observed. The biscarbene complexes (**4**, **8** – **11**) were not appreciably soluble in the 3-nitrobenzyl alcohol matrix employed, and the high molar masses of these compounds also contributed to the difficulty in observing an M^+ peak.

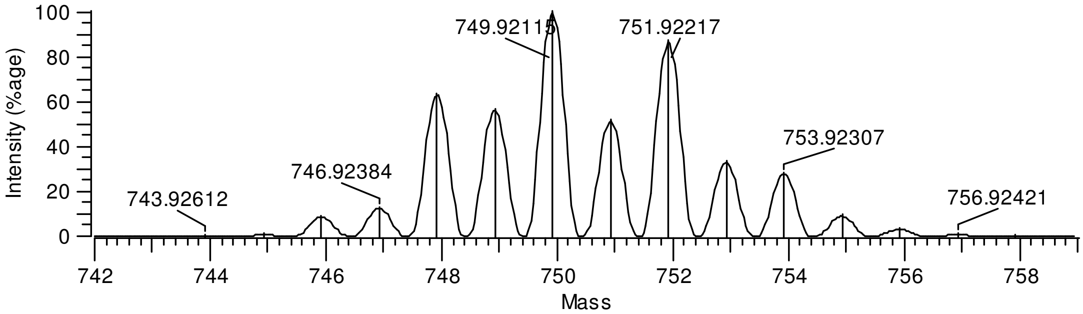


Figure 2.18 M^+ peak observed for complex **6**, with molar mass 750.45 g.mol^{-1}

The presence of an M^+ peak (illustrated in Figure 2.18) provides strong evidence of correct structure assignments, and the identified fragment ions are summarized in Table 2.11. The assignments are based on the isotopes ^{52}Cr, ^{96}Mo and ^{184}W.

Table 2.11 Mass spectral data of Group VI cluster carbene complexes

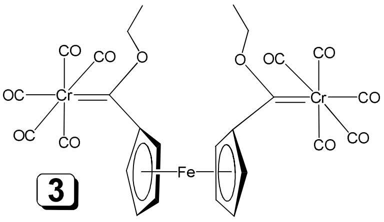
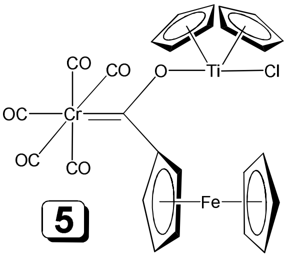
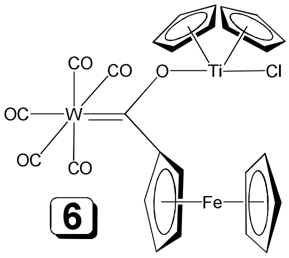
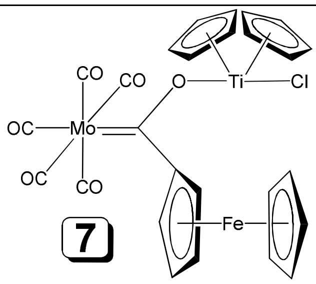
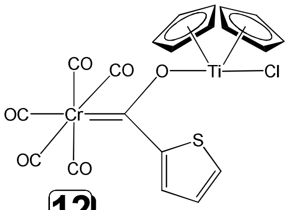
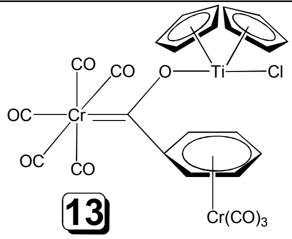
Complex	m/z	Intensity (%)	Fragment Ion
 3	682	0.4	$[M]^+$
	542	0.6	$[M - 5CO]^+$
	434	3.4	$[M - Cr(CO)_5 - 2CO]^+$
	430	2.7	$[M - 9CO]^+$
	402	1.2	$[M - 10CO]^+$
	378	4.4	$[M - \{Cr(CO)_5C(OEt)\}]^+$
 5	619	1.5	$[M]^+$
	505	2.6	$[M - 4CO]^+$
	478	1.6	$[M - 5CO]^+$
	377	0.8	$[M - TiCp_2Cl - CO]^+$
	230	3.5	$[OTiCp_2Cl]^+$

Table 2.11 *contd.* Mass spectral data of Group VI cluster carbene complexes

Complex	m/z	Intensity (%)	Fragment Ion
 **6**	750	10	$[M]^+$
	721	0.3	$[M - CO]^+$
	694	0.7	$[M - 2CO]^+$
	635	0.6	$[M - 3CO]^+$
	601	0.8	$[M - 3CO - Cp]^+$
	537	2.4	$[M - TiCp_2Cl]^+$
	511	1.4	$[M - TiCp_2Cl - CO]^+$
	509	1.6	$[M - Fc - 2CO]^+$
	480	1.1	$[M - TiCp_2Cl - 2CO]^+$
 **7**	663	1.5	$[M]^+$
	605	1.7	$[M - 2CO]^+$
	578	1.3	$[M - 3CO]^+$
	551	1.4	$[M - 4CO]^+$
	523	1.9	$[M - 5CO]^+$
 **12**	516	1.9	$[M]^+$
	460	2.0	$[M - 2CO]^+$
	433	1.8	$[M - 3CO]^+$
	404	5.5	$[M - 4CO]^+$
	376	5.4	$[M - 5CO]^+$
	370	2.0	$[M - 4CO - Cl]^+$
	304	9.0	$[M - TiCp_2Cl]^+$
 **13**	647	0.6	$[M]^+$
	511	0.8	$[M - Cr(CO)_3]^+$
	506	2.5	$[M - 5CO]^+$
	479	3.0	$[M - 6CO]^+$

All of the mass spectra demonstrate the stepwise fragmentation of the complexes with the loss of carbonyl ligands (see Figure 2.19). The higher intensities of the $[M - 4CO]^+$ and $[M - 5CO]^+$ ions compared to $[M - 2CO]^+$ and $[M - 3CO]^+$, as well as the low occurrence of $[M - CO]^+$ indicate rapid loss of the carbonyl ligands.

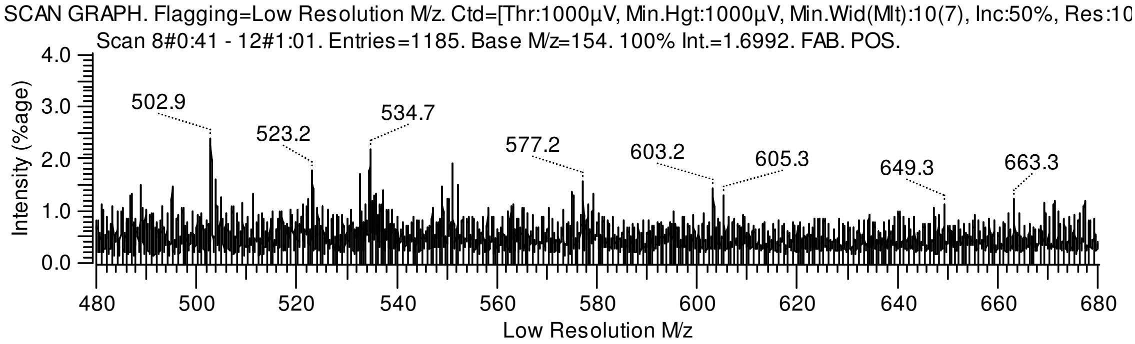


Figure 2.19 Stepwise loss of CO ligands in the mass spectrum of complex **7**

However, this is not the only possible fragmentation route. For the titanoxy monocarbene complexes, initial loss of the titanocene chloride fragment, followed by the loss of one or more carbonyl ligands constitutes another possible fragmentation pattern. Loss of the Fc-unit and the chloro ligand is also observed for complexes **6** and **12**, respectively. Complex **13** displayed the expected decomplexation of the $Cr(CO)_3$- moiety.

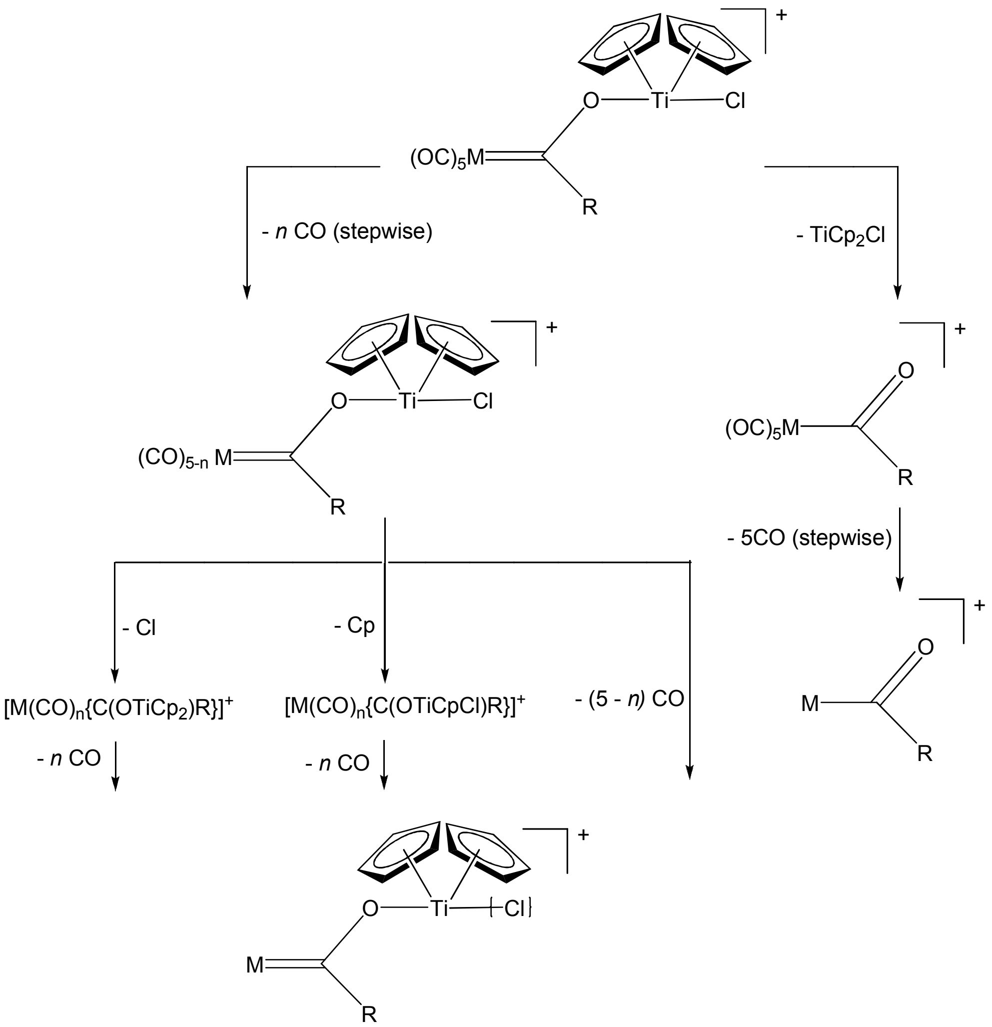


Figure 2.20 Different MS fragmentation routes observed for titanoxycarbene complexes

The mass spectral data of **3** showed fragmentation patterns containing at least one possible route unlike that of other biscarbene complexes.[75] Although the successive loss of all ten CO ligands were observed, the loss of a $Cr(CO)_5$-unit and subsequent loss of the entire carbene moiety $Cr(CO)_5\{C(OEt)\}$ were also seen. In previous studies, sequential loss of some carbonyls, then an ethyl fragment before the breakaway of the rest of the carbonyls yielded a *m/z* ion peak of the two transition metals directly bonded to the heteroaryl carbene

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[75] (a) Crause, C. *Synthesis and application of carbene complexes with heteroaromatic substituents,* PhD Thesis, University of Pretoria, Pretoria, **2004**, 33, (b) Terblans, Y.M. *Thiophene Bimetallic Carbene Complexes,* PhD Thesis, University of Pretoria, Pretoria, **1996**, 45.

substituent. However, no loss of a pentacarbonyl metal moiety was observed before.

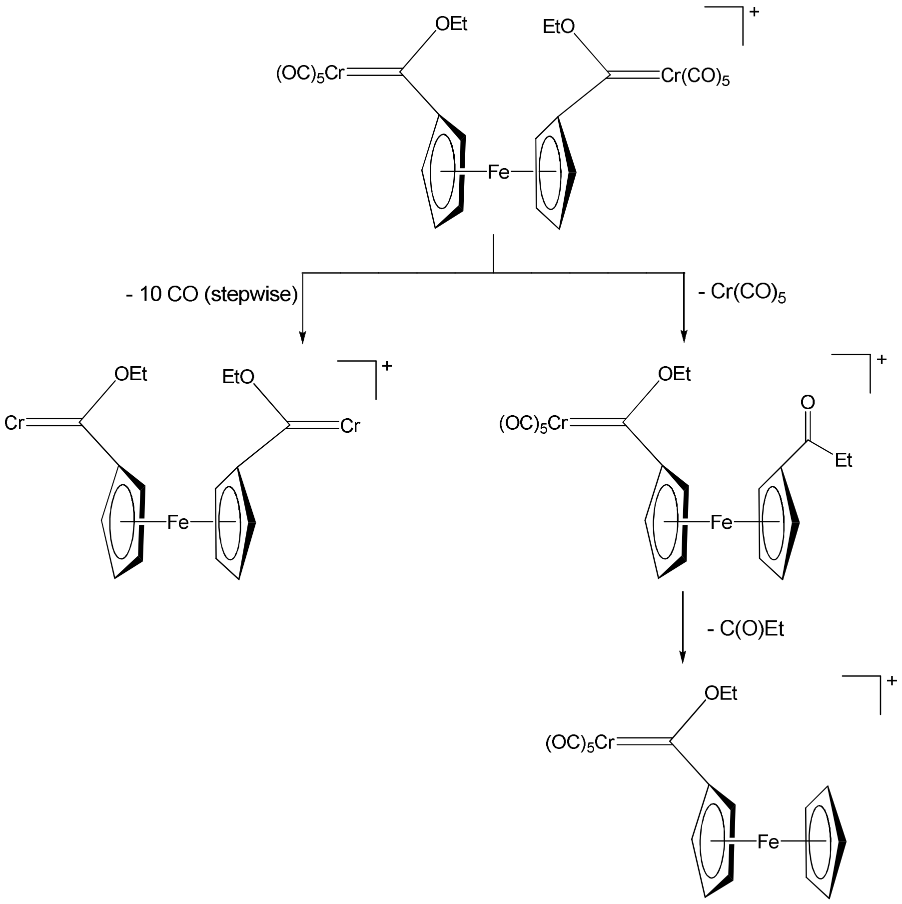

Figure 2.21 MS fragmentation routes observed for complex **3**

2.4.5 Single crystal X-ray crystallography

2.4.5.1 Molecular structures

Final confirmations of the structures of the complexes **3**, **5**, **6**, **8**, **12** and **13** were obtained from single crystal diffraction studies. The complexes crystallized from different ratios of dichloromethane/hexane solutions by layering of the solvents, yielding crystals suitable for diffraction studies. ORTEP[76] + POV-Ray[77] drawings of the molecular structures of the above listed complexes, showing the atom numbering scheme employed, are presented in Figures 2.22 – 2.27. Crystallographic data and refinement parameters are listed in the Appendices, while experimental details are given in the experimental section. Selected bond lengths, bond angles and torsion angles are given in Table 2.12 (**5**, **6**, **12** and **13**) and Table 2.13 (**3** and **8**).

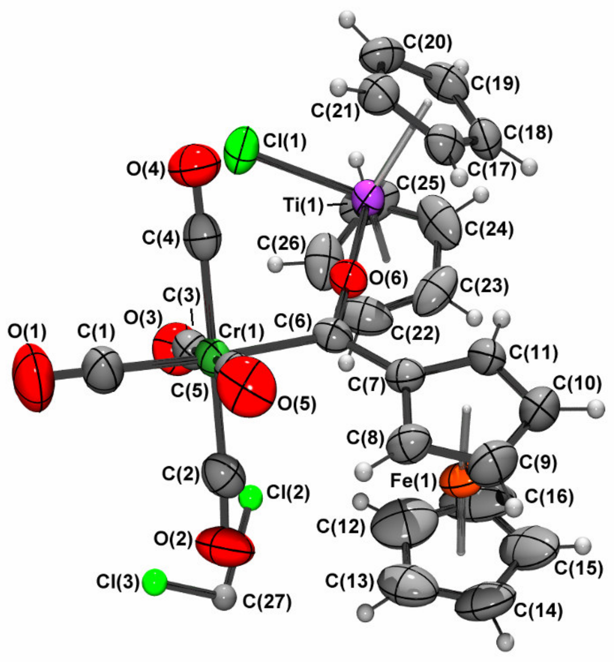

Figure 2.22 ORTEP + POV-Ray drawing of the molecular structure of **5**. Atomic displacement ellipsoids are shown at the 50% probability level.

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[76] Farrugia, L.J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

[77] The POV-Ray Team, POV-Ray 2004. URL: http://www. povray.org/download/.

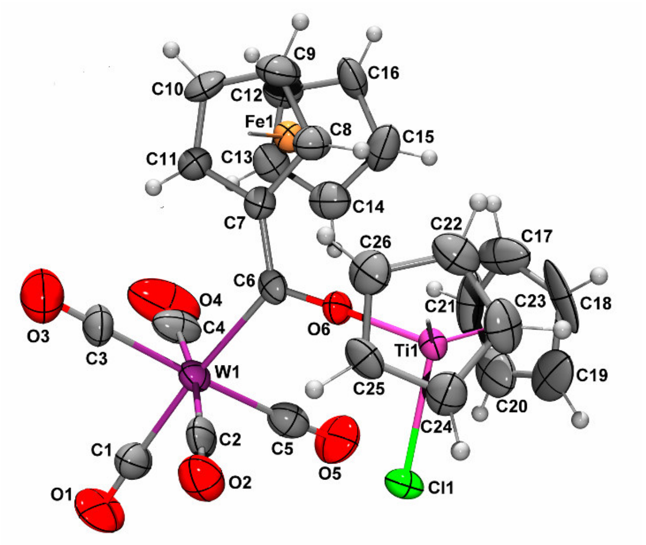

Figure 2.23 ORTEP + POV-Ray drawing of the molecular structure of **6**. Atomic displacement ellipsoids are shown at the 50% probability level.

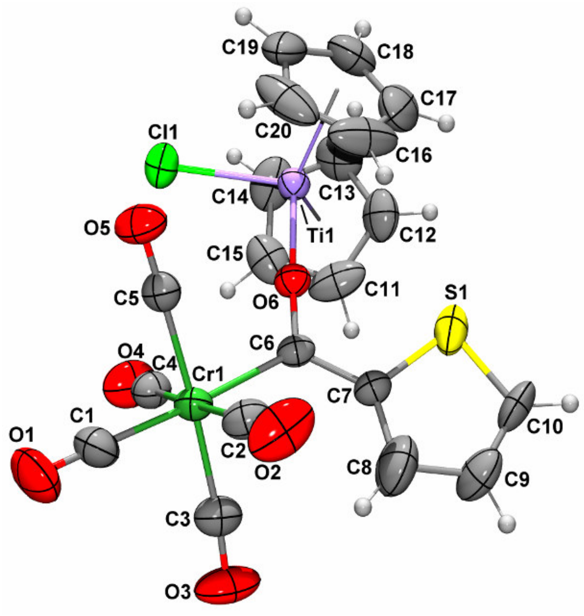

Figure 2.24 ORTEP + POV-Ray drawing of the molecular structure of **12**. Atomic displacement ellipsoids are shown at the 50% probability level.

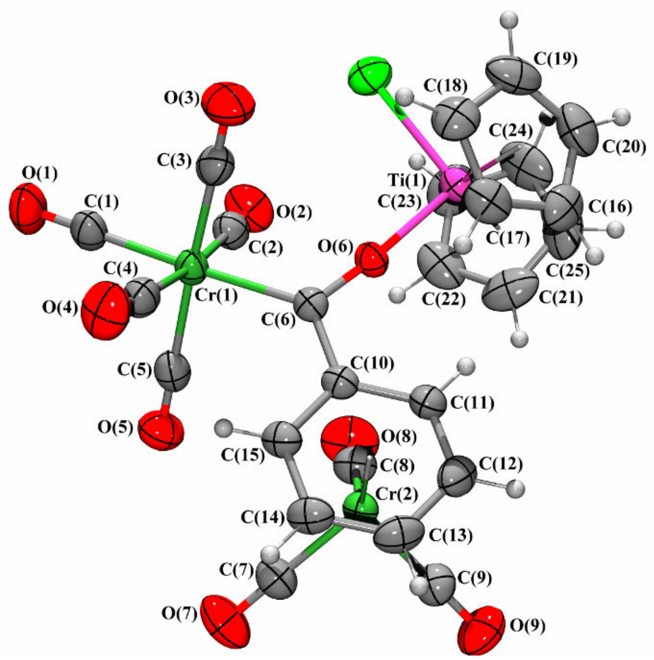

Figure 2.25 ORTEP + POV-Ray drawing of the molecular structure of **13**. Atomic displacement ellipsoids are shown at the 50% probability level.

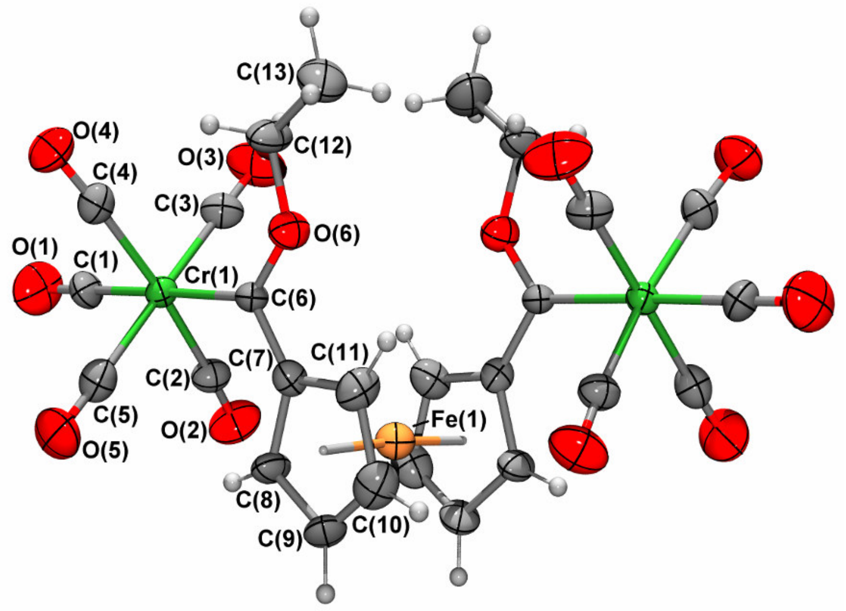

Figure 2.26 ORTEP + POV-Ray drawing of the molecular structure of **3**. Atomic displacement ellipsoids are shown at the 50% probability level.

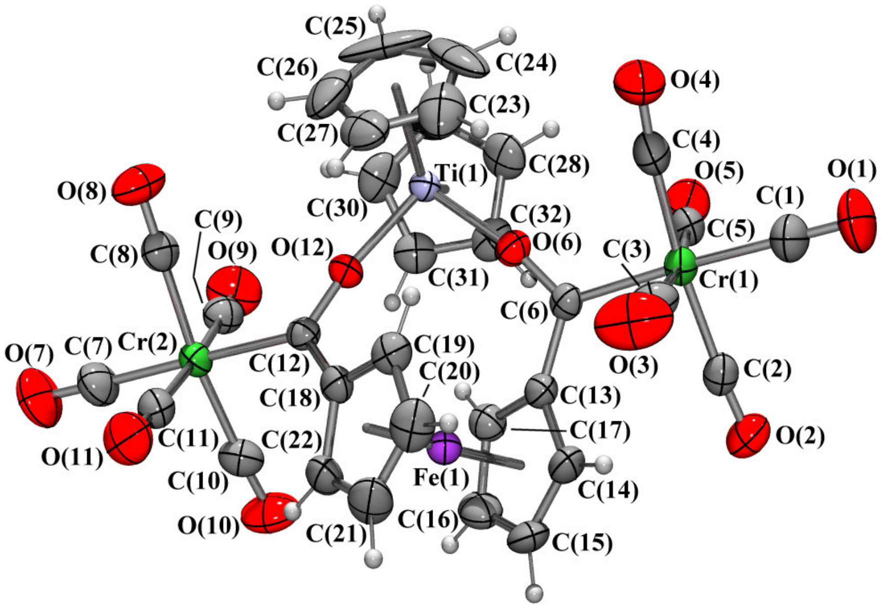

Figure 2.27 ORTEP + POV-Ray drawing of the molecular structure of **8**. Atomic displacement ellipsoids are shown at the 50% probability level.

In general, in the molecular structures of the thienyl monocarbene complexes, the sulfur atom of the thienyl ring is *cis* to the oxygen atom of the ethoxy/titanoxy substituent, indicating either restricted rotation around the C(6)-C(7) bond or a preferred packing order in the solid state.[43(e),78] Some disorder of the 2-thienyl substituent of **12** was observed: it exhibits an isomeric form with the sulfur atom in the thienyl ring *trans* to the ethoxy substituent (50.8(3)%) in addition to the *cis* isomer (49.2(3)%). The second component is rotated approximately 180° about the C(6)-C(7) bond with respect to the other component. The disorder is such that C(8A) nearly coincide with S(1) of the major component (C(7A), C(9A), C(10A) and S(1A) also nearly coincide with C(7), C(10), C(9) and C(8) respectively).

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[78] Liles, D.C.; Lotz, S. *Acta Cryst.* **2006**, *E26*, M331.

Table 2.12 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **5**, **6**, **12** and **13**

Bond lengths	**5** (M = Cr)	**6** (M = W)	**12** (M = Cr)	**13** (M = Cr)
M(1)-C(6)	2.090(4)	2.253(9)	2.081(2)	2.067(3)
C(6)-O(6)	1.286(5)	1.273(11)	1.283(2)	1.287(4)
C(6)-C(7) / C(6)-C(7A)**/ C(6)-C(10) ‡	1.472(6)	1.465(15)	1.442(5) 1.472(5)	1.513(5)
O(6)-Ti(1)	1.905(3)	1.901(6)	1.9192(15)	1.933(2)
M(1)-C(1)	1.863(5)	2.008(13)	1.866(3)	1.879(4)
M(1)-C(2,3,4,5)*	1.893(6)	2.022(12)	1.894(2)	1.901(4)
Bond angles	**5** (M = Cr)	**6** (M = W)	**12** (M = Cr)	**13** (M = Cr)
C(1)-Cr(1)-C(6)	175.9(2)	174.2(4)	175.86(10)	175.44(14)
O(6)-C(6)-C(7) / O(6)-C(6)-C(7A)** / O(6)-C(6)-C(10) ‡	112.9(3)	114.5(8)	116.1(2) 110.3(2)**	111.5(3)
O(6)-C(6)-M(1)	119.7(3)	118.5(7)	119.92(15)	119.9(2)
C(7)-C(6)-M(1), C(7A)-C(6)-M(1)** / C(10)-C(6)-M(1) ‡	127.3(3)	127.0(7)	123.95(19) 129.6(2)**	128.5(2)
C(6)-O(6)-Ti(1)	178.5(3)	175.4(7)	174.81(16)	173.6(2)
C(6)-C(7)-C(8) / C(6)-C(7A)-C(8A)**/ C(6)-C(10)-C(15) ‡	126.2(4)	127.2(9)	129.6(2) 129.9(3)**	121.5(3)
C(6)-C(7)-C(11) / C(6)-C(7)-S(1)† / C(6)-C(7A)-S(1A)**/ C(6)-C(10)-C(11) ‡	127.4(4)	127.1(9)	129.6(3) 118.2(3)**	121.0(3)
Torsion angles	**5** (M = Cr)	**6** (M = W)	**12** (M = Cr)	**13** (M = Cr)
C(3)-M(1)-C(6)-O(6)	44.1(3)	-45.0(7)	54.76(16)	38.2(3)
O(6)-C(6)-C(7)-C(11) / O(6)-C(6)-C(7)-S(1)† / O(6)-C(6)-C(7A)-S(1A)**/ O(6)-C(6)-C(10)-C(11) ‡	-1.0(6)	179.1(9)	-5.5(8) -172.3(4)**	173.2(3)
Cr(1)-C(6)-C(7)-C(8) / Cr(1)-C(6)-C(7A)-C(8A)** / Cr(1)-C(6)-C(10)-C(15) ‡	2.7(6)	-177.5(8)	2.2(10) -170.5(5)**	-6.0(4)

* Averaged value

** Second component of **12**, with the 2-thienyl substituent rotated about C(6)-C(7) bond

† Equivalent atoms of **12** compared to **5** and **6**

‡ Equivalent atoms of **13** compared to **5** and **6**

Table 2.13 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **3** and **8**

Bond lengths*	**3**	**8**	
Cr(1)-C(6), Cr(2)-C(36)	2.083(3)	2.063(2)	2.077(2)
C(6)-O(6), C(36)-O(36)	1.305(4)	1.276(2)	1.274(2)
C(6)-C(7), C(36)-C(12)	1.464(4)	1.480(3)	1.483(3)
O(6)-C(18)	1.447	-	-
O(6)-Ti(1), O(36)-Ti(1)		1.9507(14)	1.9514(15)
Cr(1)-C(1), Cr(2)-C(31)	1.865(3)	1.882(3)	1.873(3)
Cr(1)-C(2,3,4,5)**	1.903(3)	1.892(3)	
Bond angles*	**3**	**8**	
C(1)-Cr(1)-C(6), C(31)-Cr(2)-C(36)	178.71(11)	177.32(10)	175.84(11)
O(6)-C(6)-C(7), O(36)-C(36)-C(12)	105.2(3)	113.81(18)	113.66(18)
O(6)-C(6)-Cr(1), O(36)-C(36)-Cr(2)	130.2(2)	122.91(15)	123.29(15)
C(7)-C(6)-Cr(1), C(12)-C(36)-Cr(2)	124.6(2)	123.12(14)	122.93(15)
C(6)-O(6)-C(18)	123.1(3)	-	-
C(6)-O(6)-Ti(1), C(36)-O(36)-Ti(1)	-	169.76(15)	170.10(14)
C(6)-C(7)-C(8), C(36)-C(12)-C(13)	127.6(3)	127.0(2)	126.4(2)
C(6)-C(7)-C(11), C(36)-C(12)-C(16)	126.0(3)	127.2(2)	127.7(2)
Torsion angles*	**3**	**8**	
C(3)-Cr(1)-C(6)-O(6) C(33)-Cr(2)-C(36)-O(36)	49.6(5)	24.79(19)	30.81(18)
Cr(1)-C(6)-O(6)-C(12)	2.1(9)	-	-
O(6)-C(6)-C(7)-C(11) O(36)-C(36)-C(12)-C(13)	0.6(7)	29.5(3)	25.9(3)
Cr(1)-C(6)-C(7)-C(8) Cr(2)-C(36)-C(12)-C(16)	0.7(7)	34.3(3)	31.0(3)

* The 2nd designated bond length, bond angle or torsion angle refers to geometry involving the 2nd Cr-carbene moiety in **8**. These values are tabulated in the 2nd column under **8**

** Averaged value, (Cr(1)-C(2,3,4,5) + Cr(2)-C(32,33,34,35) for **8**

In the structures of complexes **3**, **5** and **6**, the ferrocenyl cyclopentadienyl ring is approximately coplanar with the carbene moiety (Cr(1), C(6), O(6), C(7)). The torsion angles of the plane of the carbene and that of the 5-membered ring, Cr(1)-C(6)-C(7)-C(8) and O(6)-C(6)-C(7)-C(11) are all in the range 0.6(7)° to 2.7(6)° for the four complexes. However, the resonance stabilization afforded by the carbene moiety being approximately coplanar with the adjacent ring is presumably weak and may easily be overridden by the exigencies of either packing forces - as observed in complex **12** where the O-C(carbene)-C(ring)-S torsion angle 5.5(8)°, or the steric requirements of the molecule - as observed in **8** where the corresponding angles are 32.17(10)° and 28.78(9)°.

The Ti(1)-O(6/36) bonds in **5**, **6**, **8**, **12** and **13** are significantly longer (1.901(6) – 1.9514(15) Å) than those of typical terminal titanium(IV) alkoxides (1.855(2) Å in $TiCp_2(OEt)Cl$]).[79] This is indicative of O(6) → C(6) π-donation occurring at the expense of O(6) → Ti(1) π-donation and is further supported by the short C(6)-O(6) and C(36)-O(36) bond distances (1.274(2) – 1.286(5) Å) that are significantly shorter than the range of 1.305(4) – 1.324(3) Å observed for **3**, **14**, **15**, **18** and **19** (see Scheme 2.5),[17] $[Cr(CO)_5\{C(OEt)Fc\}]$[57] and $[Cr(CO)_5\{C(OMe)(C_5H_4)Fe(C_5H_4Br)\}]$.[80] Erker has also noted that an acyl resonance structure is an important contributor to the bonding of zirconoxycarbene complexes.[10]

Observing the near linear C(6/36)-O(6/36)-Ti(1) bond angles, in the range 169.76(15)° – 178.5(3)°, for all complexes except **3**, the acyl character of the carbene-oxygen bond and the very long titanium-oxygen bond, one can conclude that a significant ionic character is present in the titanium-oxygen bonds, with the electropositive Lewis acid $TiCp_2X$-fragment on the one side of the carbene oxygen atom and an electrophilic carbene carbon on the other side. This manifests in a short C(carbene)-O distance and a long Ti-O distance, the net result of strong competition between these two fragments for electron density.

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[79] Huffman, J.C.; Moloy, K.G.; Marsella, J.A.; Caulton, K.G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

[80] Hursthouse, M.B.; Hibbs, D.E.; Butler, I.R. Private Communication **2003**, Cambridge Structural Database (Allen, F.H. *Acta Crystallogr.* **2002**, *B58*, 380), CCDC 262965.

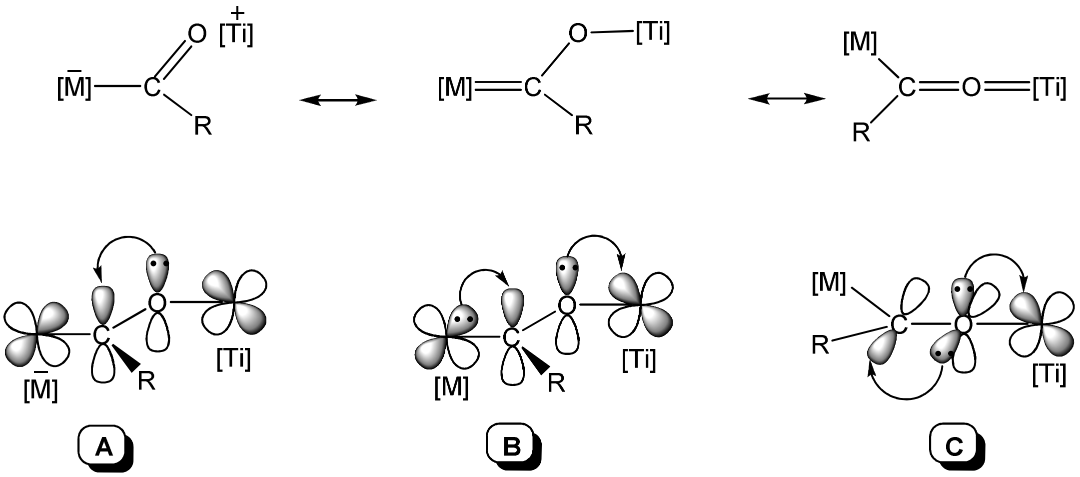


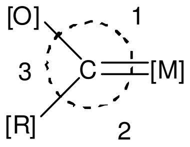
Figure 2.28 Orbital overlap for titanoxycarbene stabilization.

These experimental bond lengths support the electronic conclusions drawn from the NMR spectroscopy, and the spectroscopic observation (Figure 2.15) can therefore be extended to that shown in Figure 2.28. The resonance form **A** in the Figure below represents the most relevant structure, accounting most efficiently for the observed structural and electronic aspects.

The C(carbene)-C(Fc) distances are similar for all the complexes and fall in the range 1.464(4) – 1.483(3) Å. For **12**, C(carbene)-C(2-thienyl) bond distance is shorter (1.442(5) Å), demonstrating the heteroarene ring involvement in carbene carbon stabilization. The other extreme is **13**, where the long C(carbene)-C(PhCr(CO)$_3$) bond length of 1.513(5) Å indicates less ring participation in carbene stabilization, possibly due to the presence of the π-Cr(CO)$_3$ group, pulling electron density towards itself.

The tripod described by the carbonyl ligands of the Cr(CO)$_3$-fragment in **13** adopted an eclipsed conformation with respect to the aromatic ring which correlates with an electron-donating group bonded thereto (Figure 2.5).[28] This is in direct contrast with the view that [M(CO)$_5$(carbene)]-moiety is electron withdrawing.[5] However, closer inspection of the structure reveals that steric considerations determine the Cr(CO)$_3$ conformation: the only way to accommodate the tricarbonyl group in such close proximity to the pentacarbonyl group, is to place one of the tricarbonyl CO ligands interlocked in between two pentacarbonyl equatorial CO ligands and forcing the loss of the staggered conformation.

Table 2.14 Selected bond lengths (Å) and angles (°) around the carbene carbon



R = ferrocenyl, 2-thienyl or π-PhCr(CO)$_3$

Angle	**5**	**6**	**12**	**13**	**3**	**8**
1	119.7(3)	118.5(7)	119.92(15)	119.9(2)	130.2(2)	122.9(2) 123.3(2)
2	127.3(3)	127.0(7)	123.95(19) /129.6(2)*	128.5(2)	124.6(2)	123.1(1) 122.9(2)
3	112.9(3)	114.5(8)	116.1(2)/ 110.3(2)*	111.5(3)	105.2(3)	113.8(2) 113.7(2)
Bond	**5**	**6**	**12**	**13**	**3**	**8**
M-C$_{carb}$	2.090(4)	2.253(9)	2.081(2)	2.067(3)	2.083(3)	2.063(2) 2.077(2)
C$_{carb}$-O	1.286(5)	1.273(11)	1.283(2)	1.287(4)	1.305(4)	1.276(2) 1.274(2)
C$_{carb}$-C(R)	1.472(6)	1.465(15)	1.442(5)/ 1.472(5)*	1.513(5)	1.464(4)	1.480(3) 1.483(3)

* Second component of **12**, with the 2-thienyl substituent rotated about C(6)-C(7) bond

Table 2.14 summarizes the bond distances and bond angles surrounding the carbene carbon atom. The Cr-C(carbene) distances fall in the range 2.063(2) – 2.090(4) Å, which is typical for carbene complexes of Cr(CO)$_5$, while the same is true for the W-C(carbene) bond length of 2.253(9) Å and reported variations in the literature.[50]

The bond angles around the carbene carbon atom, defined as angles 1 - 3 in Table 2.14, depend on the steric requirements of the groups bonded to that carbon atom. Angle 2 (Cr-C-C) remains more or less constant for all seven complexes as the steric requirements of the cyclopentadienyl, thienyl and phenyl moieties, with respect to the carbonyl ligands *cis* to the carbene, are similar. The complexes have a ring C-H *ortho* to the carbene lying staggered with respect to two adjacent carbonyl ligands and in close contact with them leading to somewhat strained sp^2 angles in the range 122.9(2)° – 127.3(3)° for angle 2, compared to the Cr-C-C bond angle of *ca* 121° for the sterically undemanding substituted complex $[Cr(CO)_5\{C(OEt)Me\}]$.[81]

In contrast, the moiety bonded to the carbene via the oxygen atom results in marked differences in the geometry around the carbene carbon atom. In the complexes with a titanoxy substituent, the nearly linear geometry at oxygen together with the comparatively long Ti-O bonds allow the $OTiCp_2X$ moieties to be accommodated in the complexes with little or no steric strain allowing angle 1 (Cr-C-O) to adopt unstrained sp^2 values of *ca* 120° (these angles are *ca* 3° larger in **8** to accommodate both the -O-Ti-O- and the ferrocen-1,1'-diyl bridges between the two carbene ligands). Whereas in complex **3**, the ethoxy group adopts an orientation such that the methylene carbon is in a similar position relative to the second pair of carbonyl ligands *cis* to the carbene as the *ortho* carbon in the thienyl, cyclopentadienyl or phenyl ring is to the first pair of carbonyls. This observation agrees well with that of Sierra that alkoxycarbenes occur in the *anti* conformation, where the oxygen lone pairs are found *trans* to the M=C bond, even in the case of the titanoxycarbene complexes.[82] The presence of two hydrogen atoms bonded to the methylene carbon, together with shorter C-O bond distances compared with the C-C(ring) bond distances, induces even greater strain than induced by the ring C-H leading to values of *ca*

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[81] Kruger, C.; Goddard, R.; Claus, K.H. *Z. Naturforsch., B. Chem. Sci.* **1983**, *38*, 1431.
[82] Andrada, D.M.; Zoloff Michoff, M.E.; Fernàndez, I.; Granados, A.M.; Sierra, M.A. *Organometallics,* **2007**, *26*, 5854.

130° for angle 1, similar to the Cr-C-O bond of 132.01° of the sterically unhindered [Cr(CO)$_5${C(OEt)Me}].[81]

2.4.5.2 Crystal packing

The Mercury software[83] available from the Cambridge Crystallographic Database Centre (CCDC)[84] was used to visualize the crystal structures in order to analyze the crystal packing. [Cr(CO)$_5${C(OTiCp$_2$Cl)Fc}] (**5**) crystallized with one solvent dichloromethane molecule per complex molecule. The complex molecules display π-stacking (Figure 2.29), where the ferrocenyl Cp-rings are stacked (with a slight glide) one above the other, separated by 3.584 Å.

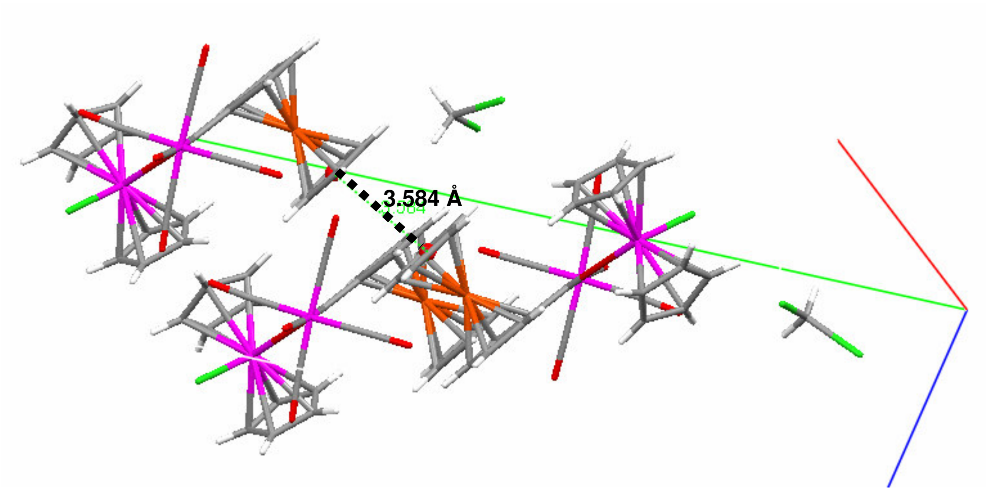

Figure 2.29 π-stacking of complex **5**

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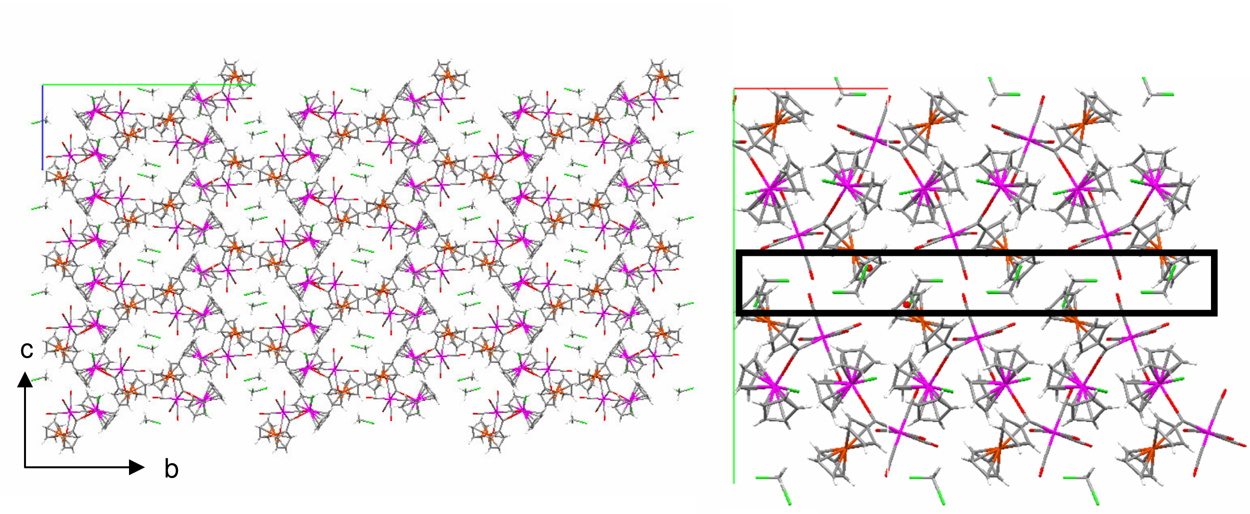
[83] (a) Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures, Macrae, C.F.; Bruno, I.J.; Chisholm, J.A.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A. *J. Appl. Cryst.* **2008**, *41*, 466, [DOI: 10.1107/S0021889807067908], (b) Mercury: visualization and analysis of crystal structures, Macrae, C.F.;Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453, [DOI: 10.1107/S002188980600731X]

[84] The Cambridge Structural Database: a quarter of a million crystal structures and rising Allen, F.H. *Acta Cryst.* **2002**, *B58*, [DOI: 10.1107/S0108768102003890].

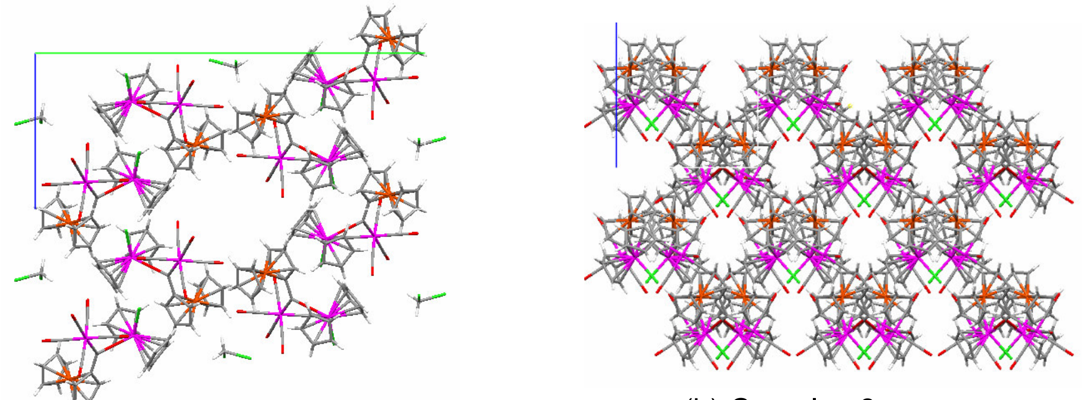


(a) (b)

Figure 2.30 (a) Filling of channels with solvent molecules, and (b) layering of solvent molecules in crystal structure of **5**

The cell volumes of the different structures also indicate that although tungsten has a considerably larger atomic radius, the solvent inclusion increases unit cell size. For **5**, the unit cell has a volume of 2838.47 Å^3, while **6** has a unit cell volume of 2539.21 Å^3. This can be seen when looking at the crystal packing of **5** from which the solvent molecules have been deleted from the pocket, compared to the much smaller empty space/pocket of **6** in Figure 2.31.

For complexes **12** and **8**, the crystal packing seems to be the result of close-packing only, as no H-bonding, π-stacking or solvent inclusion is observed. However, the close-packing is structured and displays alternate layers of titanium fragments with chromium pentacarbonyl thienyl carbene fragment for **12**, arranged in a glided stack (Figure 2.32).



(a) Complex **5**

(b) Complex **6**

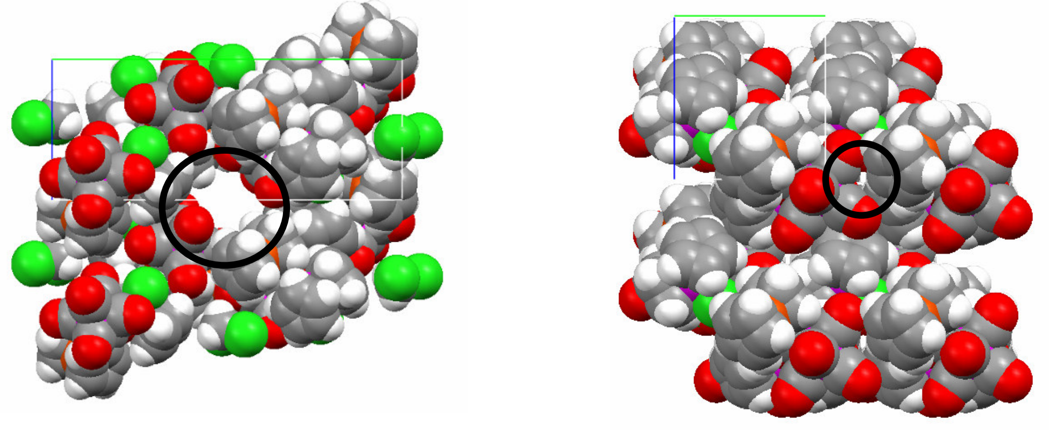


Figure 2.31 View along the a-axis to indicate presence of pocket / channel of (a) **5** (from which solvent molecules have been deleted), and (b) **6**

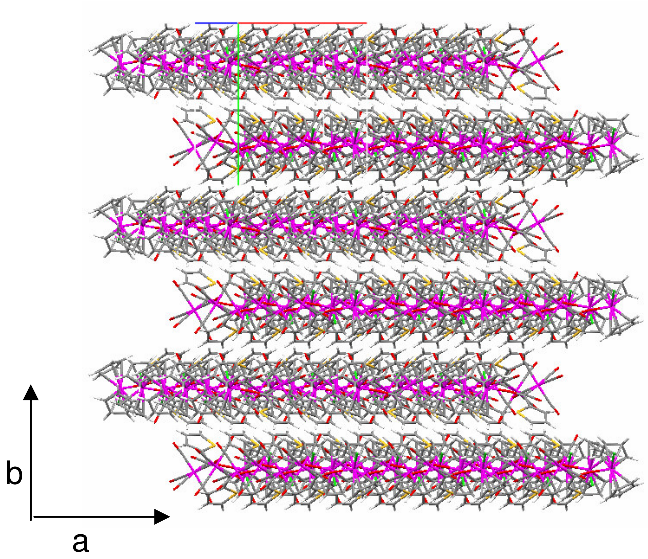


Figure 2.32 Alternate layers as viewed along the c-axis of **12**

Close contact (2.646 Å) of the titanocene Cp-protons and the chromium tricarbonyl CO-ligands of adjacent molecules are observed for **13**. This results in a zig-zag pattern (Figure 2.33) where layers are separated by the carbonyl ligands of adjacent layers.

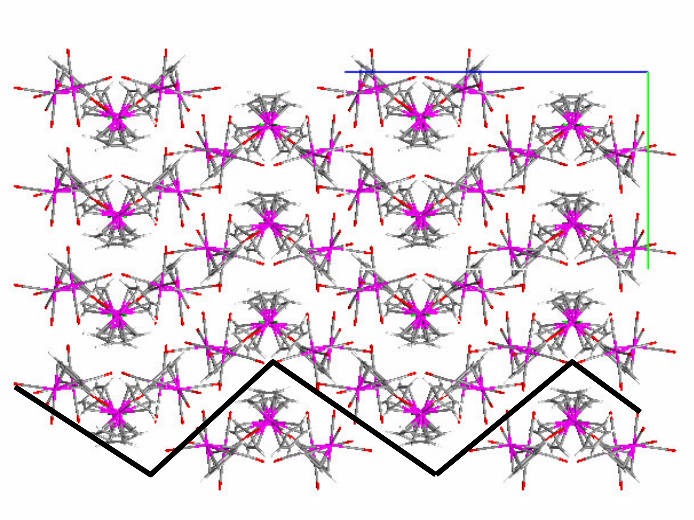
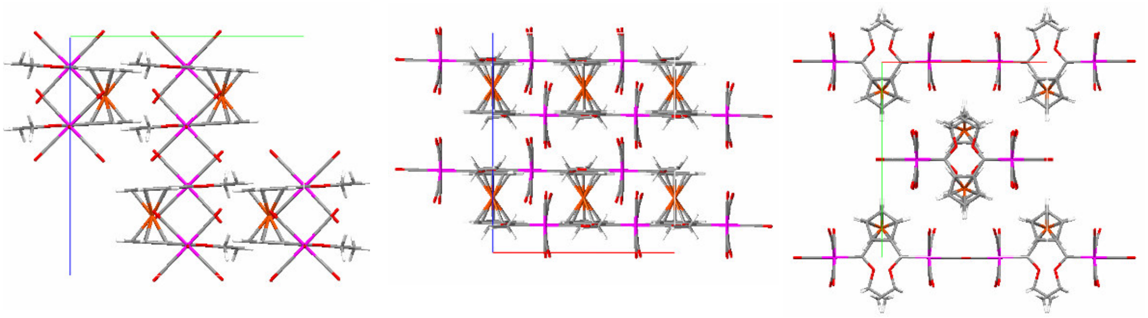


Figure 2.33 Zig-zag pattern of crystal packing of **13**

Finally, the crystallographically symmetrical ethoxy ferrocenyl biscarbene complex **3** crystallizes in such a fashion that adjacent biscarbene molecules stack one above the other so that the two ethoxy groups of one complex will eclipse the ferrocene Cp-rings of the molecule below it. This results in alternate metal (inorganic)-organic layers. This columnar packing shows a slight glide: every second row or layer is displaced by half a unit cell length along the a axis. Weak H-bonds between the methylene protons of the ethoxy groups and neighbouring molecules' carbonyl ligands are observed.



(a) (b) (c)

Figure 2.34 Ordered packing of **3**, viewed along all three axes

Intramolecular packing disorder, with interchange of the –Fc and the two –OEt sites are observed in (c) of Figure 2.34, since the size and shape of the crystal space occupied by the Fc and the two OEt moieties are very similar. Intermolecular packing disorder with the complex displayed a quarter of the cell length along the c-axis (vertical direction in (a)) so that the two $Cr(CO)_5$-moieties of the new molecule occupy the upper $Cr(CO)_5$-site of one molecule as shown, and the lower $Cr(CO)_5$-site of the molecule directly above.

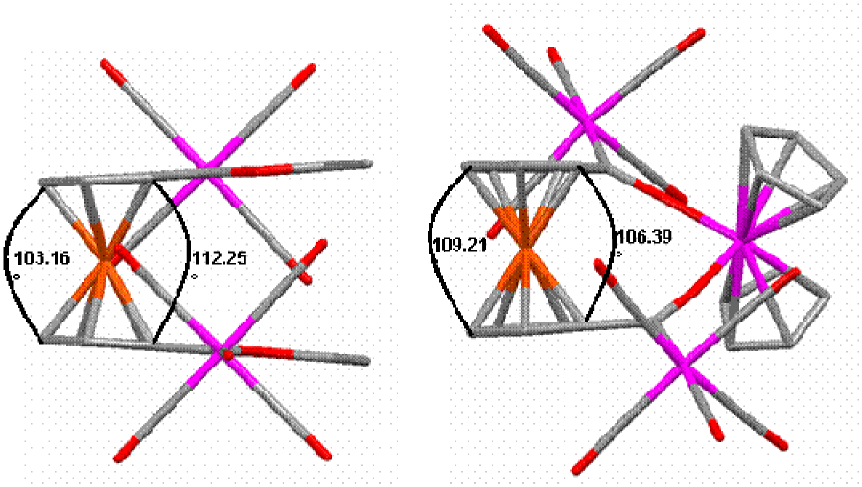


Figure 2.35 Sandwich-tilt angles of ferrocenyl substituents of **3** and **8**

A tilt-deformation of the sandwich-type ferrocenyl substituent is seen. The inner Cp-Fe-Cp angle is 112.25°, greater than the outer angle of 103.16° in **3**. This is not unexpected, as the two Cp-rings are bonded *via* the Fe but there is no bonding interaction to overcome the steric repulsion between the two OEt moieties. For **8**, the titanoxy analogue of **3**, the bridging Ti pulls the O-atom closer together.

2.5 Concluding remarks

The syntheses of di- and trimetallic cluster carbene complexes of Group VI transition metals (Cr, Mo and W) yielded monocarbene complexes containing either an ethoxy or a titanoxy substituent as the heteroatomic carbene ligand substituent, and ferrocenyl, 2-thienyl or η^6-PhCr(CO)$_3$ groups as ring substituents on the carbene carbon atom (Complexes **1** – **13**).

A direct, one-pot synthesis of both mono- and dilithiated ferrocene resulted in the formation of both titanoxy or ethoxy ferrocenyl mono- and biscarbene complexes for the chromium complexes **1**, **3**, **5** and **8**) and molybdenum complexes (complexes **7** and **10**), as well as the ethoxy tungsten carbene complexes **2** and **4**. However, no monocarbene tungsten complex could be isolated from the reaction conditions followed for the Cr- and Mo analogues; instead, the ferrocenyl biscarbene tungsten complex **9** was obtained excusively. Various lithiation procedures were tested to obtain only monolithiated ferrocene before the titanoxy ferrocenyl monocarbene tungsten complex **6** could be successfully prepared.

Lithiation of the arenes η^5-thiophene chromium tricarbonyl and η^6-benzene chromium tricarbonyl, followed by reaction with Cr(CO)$_6$ and reaction quenching with titanocene dichloride yielded the complexes **12** and **13**, respectively. Complex **12** displayed a carbene ligand with a thienyl substituent, after decomplexation of the Cr(CO)$_3$-fragment, as the thiophene rings are less stable towards chromium decomplexation in polar solvents than the analogous benzene derivatives.

Attempts to synthesize the mixed heteronuclear biscarbene complex **11** [$W(CO)_5C\{\mu\text{-}TiCp_2O_2\text{-}O,O'\}\{\mu\text{-}Fe(C_5H_4)_2\text{-}C,C'\}CCr(CO)_5$] were only partially successful. Monolithiation of ferrocene and metalation by $Cr(CO)_6$, followed by anionic protection of the acylate and second lithiation, and metalation by $W(CO)_6$ gave very low yields of the mixed biscarbene complex. Another attempt, whereby ferrocenes were dilithiated directly, followed by sequential metalation with the two different starting material hexacarbonyl metal complexes, gave the best results. However, the presence of mixtures of the corresponding chromium and tungsten homonuclear biscarbenes persisted, and single crystal X-ray diffraction confirmed the co-crystallization of both these homonuclear carbene complexes with the heteronuclear biscarbene complex.

The complexes synthesized were characterized by various spectroscopic techniques. The downfield shifts of the (hetero)aryl substituent chemical resonances demonstrated the electron withdrawing character of the $M(CO)_5$-fragments. NMR spectroscopy also lead to the conclusion that the titanoxy substituent resulted in increased electron density on the O-atom, due to greater interaction with the C(carbene) atom and less involvement of the ring substituents. This implies that the titanoxycarbenes show a greater relative contribution of the acyl resonance form of the carbene complexes compared to that of the ethoxycarbene complexes.

IR spectroscopy revealed that the systematic arrangement of the A_1^2 symmetric *cis*-CO stretching frequency demonstrated the stronger donating ability of the $-TiCp_2Cl$ *vs* the –OEt group. The monocarbene complexes displayed higher νCO frequencies, correlating to greater π-acceptor ability of the monocarbene ligands compared to the corresponding bridging biscarbene ligands.

The mass spectral data confirmed the expected stepwise fragmentation of the carbonyl ligands of the complexes; however, a different fragmentation route was identified where the loss of the $-TiCp_2Cl$ once again proved the ionic nature of the Ti-O bond. Ethoxy ferrocenyl biscarbene **3** displayed a unique fragmentation pattern, where loss of the $Cr(CO)_5$-unit and subsequent loss of the entire carbene $Cr(CO)_5\{C(OEt)\}$-moiety were observed.

Structural confirmation came from the crystal structures obtained by X-ray diffraction studies of complexes **3**, **5**, **6**, **8**, **12** and **13**. In all cases considered, the long Ti-O bond and short C(carbene)-O bond correlated with the acyl-like character of the titanoxycarbene ligands, and supported the conclusions drawn form the spectroscopic studies of an ionic structure.

For complex **13**, the electron withdrawing property of the π-$Cr(CO)_3$ moiety caused the lengthening of the C(carbene)-C(Ph) bond, as less ring participation in carbene stabilization is found in the presence of the 'electron sink' π-$Cr(CO)_3$ group. Steric considerations were seen to force interlocking of one of the tricarbonyl CO ligands in between two pentacarbonyl *eq*-CO ligands. This resulted in loss of the staggered conformation of the tricarbonyl ligands, which is the expected conformation when electron withdrawing groups such as the $Cr(CO)_5$(carbene)-fragment is bonded to the η^6-phenyl $Cr(CO)_3$.

Finally, the crystal packing of the molecules of complex **5** $[Cr(CO)_5\{C(OTiCp_2Cl)Fc\}]$ displayed π-stacking features between adjacent ferrocenyl groups. Solvent inclusion in **5** increased the unit cell size compared to the analogous tungsten complex **6**, which contains the larger W-atom. However, **6** also exhibited the presence of small, unfilled 'pockets' corresponding to the larger, dichloromethane-filled pockets observed for **5**.