

1 Introduction

1.1 Background

1.1.1 Historical development of organometallic chemistry

The first recorded organometallic compound, “Cadet’s fuming liquid”, was prepared as early as 1760 in a Parisian military pharmacy.¹ In an effort to make cobalt-based inks, cobalt minerals containing arsenic was used, and *in situ* formation of $[\text{Me}_2\text{As}]_2\text{O}$ resulted. However, as arsenic is classified as a metalloid or ‘semi-metal’, the title of the first organometallic compound may well belong to the first olefin complex, the complex $\text{Na}[\text{PtCl}_3\text{C}_2\text{H}_4]$ known as Zeise’s salt,² prepared by the Danish pharmacist Zeise by boiling a solution of chloroplatinic acid in ethanol, and then adding KCl .³

The term ‘organometallic’ was only introduced by Frankland in 1849, following his preparation of important alkylmercury compounds such as Me_2Hg .⁴ After this, a wealth of main-group organometallic compounds were isolated and characterized in the late nineteenth century,⁵ and industrial applications for

¹ Cadet de Gassicourt, L.C. *Mem. Math. Phys.* **1760**, 3, 623.

² Zeise, W.C. *Pogg. Ann. Phys. Chem.* **1827**, 9, 632.

³ (a) Zeise, W.C. *Pogg. Ann. Phys. Chem.* **1831**, 21, 497, (b) Zeise, W.C. *Pogg. Ann. Phys. Chem.* **1831**, 21, 542.

⁴ (a) Frankland, E. *Phil. Trans. Roy. Soc.* **1852**, 142, 417, (b) Frankland, E. *Ann. Chem. Pharm.* **1855**, 95, 28.

⁵ (a) Krause, E.; von Grosse, A. *Die Chemie der metall-organischen Verbindungen*, Verlag Gebrüder Bornträger, Berlin, **1937**, (b) Thayer, J.S. *Adv. Organomet. Chem.* **1975**, 13, 1.

these complexes grew exponentially. However, little was known about the true nature and structure of these complexes. For example, the first binary metal carbonyl $\text{Ni}(\text{CO})_4$ was discovered by Mond during the commercial process for refining nickel.⁶ Iron pentacarbonyl was reported almost simultaneously,⁷ but the product was initially misformulated as $\text{Fe}(\text{CO})_4$, and the nature of the compound was not elucidated.

Organometallic chemistry came to be recognized in its full right with the discovery of the first sandwich complex, ferrocene.⁸ In 1951 and 1952, Pauson reported in the journals *Nature*⁹ and *Journal of the Chemical Society*¹⁰ the serendipitous preparation of “a new type of organo-iron compound”. Pauson proposed a linear structural arrangement where two planar cyclopentadienyl rings linked to the iron metal as shown for resonance structure I in Figure 1.1. He attributed the remarkable stability of $\text{FeC}_{10}\text{H}_{10}$ to the prevalence of resonance structure II, where the cyclopentadienyl groups attain aromatic character with the acquisition of a negative charge.

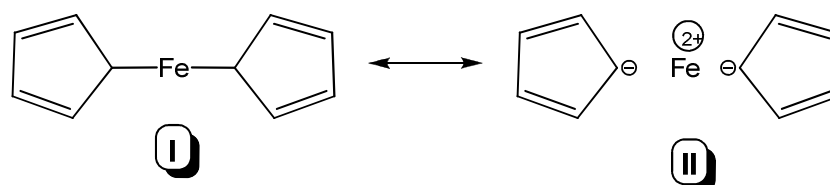


Figure 1.1 The resonance forms proposed by Pauson for ferrocene

Investigation of the structure of ferrocene by Fischer in Munich, and Wilkinson and Woodward at Harvard, lead to the proposal of a double-cone arrangement (III in Figure 1.2) by Fischer,¹¹ and an antiprismatic structure (IV)

⁶ Mond, L.; Langer, C.; Quincke, F. *J. Chem. Soc.* **1890**, 57, 749.

⁷ (a) Berthelot, M. *Compt. Rend Acad. Sci.* **1891**, 112, 1343, (b) Mond, L.; Quincke, F. *J. Chem. Soc.* **1891**, 59, 604.

⁸ Werner, H. *Landmarks in Organo-Transition Metal Chemistry: A Personal View*, Springer Science + Business Media, New York, **2009**.

⁹ Kealy, T.J.; Pauson, P.L. *Nature* **1951**, 168, 1039.

¹⁰ Miller, S.A.; Tebboth, J.A.; Tremaine, J.F. *J. Chem. Soc.* **1952**, 632.

¹¹ Fischer, E.O.; Pfab, W. *Z. Naturforsch., Part B* **1952**, 7, 377.

by Woodward and Wilkinson.¹² Three different, independent studies confirmed the structural proposals offered by Fischer, Woodward and Wilkinson.¹³ Wilkinson coined the term ‘sandwich complexes’¹⁴ and in 1973, Fischer and Wilkinson won the Nobel Prize for Chemistry for their structural elucidation of this landmark organometallic complex. Eminent scientists such as Ron Nyholm proclaimed that they had witnessed “a renaissance of inorganic chemistry”.¹⁵

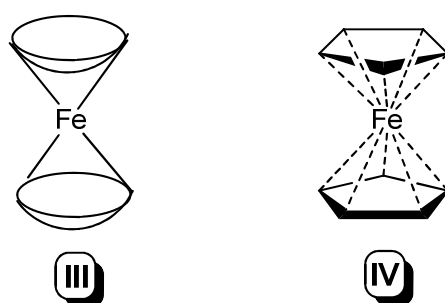


Figure 1.2 The structural proposals for ferrocene offered by Fischer (III) and Wilkinson (IV)

1.1.2 Early development of carbene chemistry

Approximately ten years later, King synthesized a manganese complex from the reaction of a pentacarbonyl manganate complex with 1,3-dibromopropane.¹⁶ He correctly gave the molecular formula as $[\text{Mn}_2(\text{CO})_{10}(\text{CH}_2)_3]$, but wrongly assigned the structure as illustrated in Figure 1.3.

¹² Wilkinson, G.; Rosenblum, M.; Whiting, M.C.; Woodward, R.B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

¹³ (a) Fischer, E.O.; Pfab, W. *Z. Naturforsch., Part B* **1952**, *7*, 377, (b) Eiland, P.F.; Pepinsky, R. *J. Am. Chem. Soc.* **1952**, *74*, 4971, (c) Dunitz, J.D.; Orgel, L.E. *Nature* **1953**, *171*, 121.

¹⁴ Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 3458.

¹⁵ Nyholm, R.S. *The Renaissance of Inorganic Chemistry*, Inaugural Lecture delivered at University College London, 1 March **1956**, published for the College by H.K. Lewis & Co. Ltd., London.

¹⁶ King, R.B. *J. Am. Chem. Soc.* **1963**, *85*, 1922.

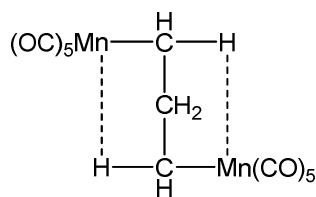


Figure 1.3 The proposed structure of King's compound

Only seven years later in 1970, did the group of Casey correctly assign the structure of King's compound as a dimanganese nonacarbonyl complex containing a cyclic carbene ligand with an oxygen atom bonded to the carbene carbon (Figure 1.4).¹⁷ Although this was actually the first example of a Fischer carbene complex, it was never recognized as such.

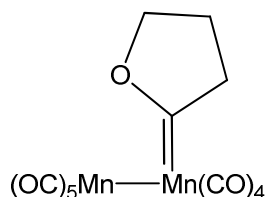


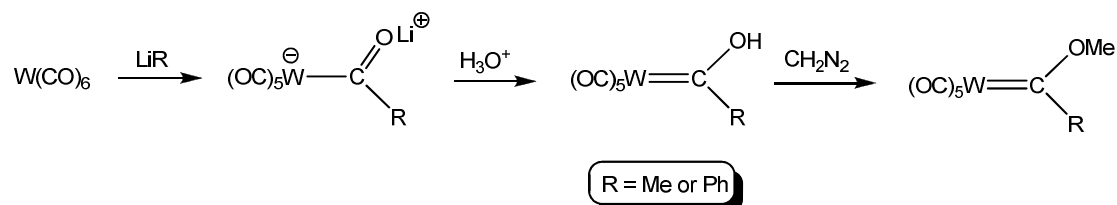
Figure 1.4 Casey's assignment of the structure of the King compound

In the meantime, E.O. Fischer continued with his pioneering work in Munich. With his graduate student Maasböl, they reacted tungsten hexacarbonyl with methyl and phenyl lithium, and after protonation of the *in situ* formed tungsten acylates, treated the corresponding hydroxycarbenes with diazomethane to afford the desired methoxy methyl- and methoxy phenyl carbene complexes,¹⁸ demonstrated in Scheme 1.1; the first isolated and fully characterized

¹⁷ (a) Casey, C.P. *J. Chem. Soc., Chem. Commun.* **1970**, 1220, (b) Casey, C.P.; Cyr, C.R.; Anderson, R.L.; Marten, D.F.; *J. Am. Chem. Soc.* **1975**, *97*, 3053, (c) Casey, C.P.; Anderson, R.L. *J. Am. Chem. Soc.* **1971**, *93*, 3554, (d) Casey, C.P.; Cyr, C.R. *J. Organomet. Chem.* **1973**, *37*, C69.

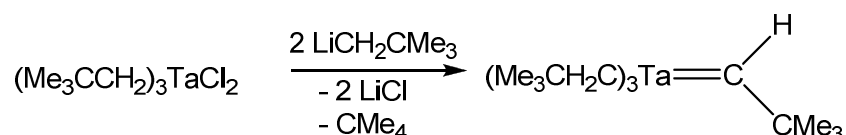
¹⁸ Fischer, E.O.; Maasböl, A. *Angew. Chem. Int. Ed.* **1964**, *3*, 580.

complexes of this new class of metal complexes containing organic ligands coordinated by a metal-carbon double bond.



Scheme 1.1

Another important development for the chemistry of carbene complexes was achieved by R.R. Schrock, in his communication about the preparation of a stable tantalum carbene complex (Scheme 1.2) in 1974.¹⁹ In contrast to Fischer's carbene complexes containing a heteroatom-substituted carbene ligand with an electrophilic nature, the carbene carbon of his complexes proved to be nucleophilic.



Scheme 1.2

In the years thereafter, applications for the metal-carbon double bond complexes exploded. Fischer carbene complexes have received a great deal of attention for their application as organic building blocks²⁰ and stabilization by bonding to a metal allowed for isolation and selective reactivity.²¹ Metal carbene complexes were found to be frequent intermediates in metal

¹⁹ Schrock, R.R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.

²⁰ Dötz, K.H.; Stendel, Jr., *J. Chem. Rev.* **2009**, *109*, 3227.

²¹ Dötz, K.H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

mediated reactions²² and were applied in the construction of multicomponent and multistep methodologies.²³ Important applications also include olefin metathesis, Fischer-Tropsch intermediates²⁴ and cycloaddition reactions.²⁵

The work on olefin metathesis done by Schrock in the preparation of molybdenum and tungsten complexes of the general composition $[M(CHR)(NAr)(OR')_2]$ and derivatives thereof,²⁶ Grubbs's first generation ruthenium compounds $[Ru(CHR)(PCy_3)_2X_2]$ and later with sterically protected *N*-heterocyclic carbenes $[Ru(CHR)(NHC)(PCy_3)X_2]$, and their metathesis reactions with olefins,²⁷ as well as the mechanism proposed by Chauvin,²⁸ culminated in the Nobel Prize for Chemistry in 2005 being awarded to the aforementioned three scientists.

1.1.3 Recent developments of polymetallic carbene complexes

The activation of simple organic molecules by more than one transition metal constitutes an area of research that has grown in importance.²³ The applications of carbenes as active or auxiliary ligands in organic synthesis and catalysis, however, are mostly focused on monocarbene systems. No assemblies of carbene units (carbene supramolecular chemistry) have been reported and only a few carbene complexes are known to be part of small metal organic frameworks (MOF).²⁹ In addition, no carbene complexes have

²² (a) Barluenga, J. *Pure Appl. Chem.*, **1996**, *68*, 543 (b) de Meijere, A. *Pure Appl. Chem.*, **1996**, *68*, 61 (c) Harvey, D.F.; Sigano, D.M. *Chem. Rev.*, **1996**, *96*, 271 (d) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.*, **1997**, *41*, 163 (e) J. Barluenga, J. *Pure Appl. Chem.*, **1999**, *71*, 1385 (f) K.H. Dötz, K.H.; Tomuschat, P. *Chem. Soc. Rev.*, **1999**, *28*, 187 (g) Davies, M.W.; Johnson, C.N.; Harrity, J.P.A. *J. Org. Chem.*, **2001**, *66*, 3525 (h) Gómez-Gallego, M.; Mancheño, M.J.; Sierra, M.A. *Acc. Chem. Rev.*, **2005**, *38*, 44.

²³ Dötz, K.H.; Fischer, H.; Hofmann, P.; Kreissl, F.R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*, Verlag Chemie: Weinheim, Germany, **1983**.

²⁴ Toomey, L.M.; Atwood, J.D. *Organometallics* **1997**, *16*, 490.

²⁵ Dötz, K.H. *Metal carbenes in organic synthesis*, **2004**, Springer-Verlag, Germany.

²⁶ Schrock, R.R. *Acc. Chem. Res.* **1986**, *19*, 342, (b) Schrock, R.R. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 3748 (Nobel lecture).

²⁷ (a) Nguyen, S.T.; Johnson, L.K.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc.* **1992**, *114*, 3974, (b) Grubbs, R.H. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 3760 (Nobel lecture).

²⁸ Hérrison, J.-L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

²⁹ (a) Garrison, J.C.; Simons, R.S.; Tessier, C.A.; Youngs, W.J. *J. Organomet. Chem.* **2003**, *673*, 1, (b) Fernández, I.; Mancheño, M.J.; Gómez-Gallego, M.; Sierra, M.A. *Org. Lett.* **2003**, *5*, 1237.

featured in materials of note, no dendrimers with carbene functionalities have been prepared and no carbene complexes showing liquid crystalline properties have been reported. In fact very few studies on multimetal carbene complexes or cluster carbene complexes have been recorded.³⁰ In the field of non-linear optics, conjugated unsaturated systems with a transition metal moiety have been employed for their electron delocalisation and so-called 'push-pull' characteristics.³¹

However, the incorporation of different transition metal fragments in complexes has been widely investigated to study the role of different metal fragments on the reactivity of ligands and the chemistry of the complexes³². When applied in the area of Fischer carbene complexes of the type $[M(CO)_5\{C(OR')R\}]$, the carbene properties have either been modified by introducing metal-containing substituents to further activate the carbene carbon³³ or the carbene ligand is used as a connector to bridge the other transition metals.³⁴ The introduction of a metal fragment to the carbene oxygen offers the possibility to modulate the carbene reactivity by the electronic and steric properties of this second metal fragment.³⁵

³⁰ Sierra, M.A. *Chem. Rev.* **2000**, *100*, 3591.

³¹ Seed, A. *Chem. Soc. Rev.* **2007**, *36*, 2046.

³² (a) Lotz, S.; van Rooyen, P.H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219. (b) Bunz, U.H.F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (c) Beck, W.; Niemer, M.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (d) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. (e) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178-180*, 431.

³³ (a) Fuss, B.; Dede, M.; Weibert, B.; Fischer, H. *Organometallics* **2002**, *21*, 4425, (b) Crause, C.; Görls, H.; Lotz, S. *Dalton Trans.* **2005**, 1649, (c) Moretó, J.M.; Ricart, S.; Dötz, K.H.; Molins, E. *Organometallics* **2001**, *20*, 62.

³⁴ (a) Bartik, T.; Weng, W.; Ramsden, J.A.; Szafert, S.; Fallon, S.B.; Arif, A.M.; Gladysz, J.A. *J. Am. Chem. Soc.* **1998**, *120*, 11071, (b) Weng, W.; Ramsden, J.A.; Arif, A.M.; Gladysz, J.A. *J. Am. Chem. Soc.* **1993**, *115*, 3824, (c) Weng, W.; Arif, A.M.; Gladysz, J.A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 891. (d) Fischer, E.O.; Röhl, W.; Huy, N.H.T.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 2951, (e) Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber./Recueil* **1997**, *130*, 479. (f) Hartbaum, C.; Mauz, E.; Roth, G.; Weissenbach, K.; Fischer, H. *Organometallics* **1999**, *18*, 2619, (g) Terblans, Y.M.; Roos, H.M.; Lotz, S. *J. Organomet. Chem.* **1998**, *566*, 133, (h) Landman, M.; Görls, H.; Lotz, S. *Eur. J. Inorg. Chem.* **2001**, 233, (i) Landman, M.; Görls, H.; Lotz, S. *J. Organomet. Chem.* **2001**, *617-618*, 280.

³⁵ Barluenga, J.; Fañanás, F.J. *Tetrahedron* **2000**, *56*, 4597 and references therein.

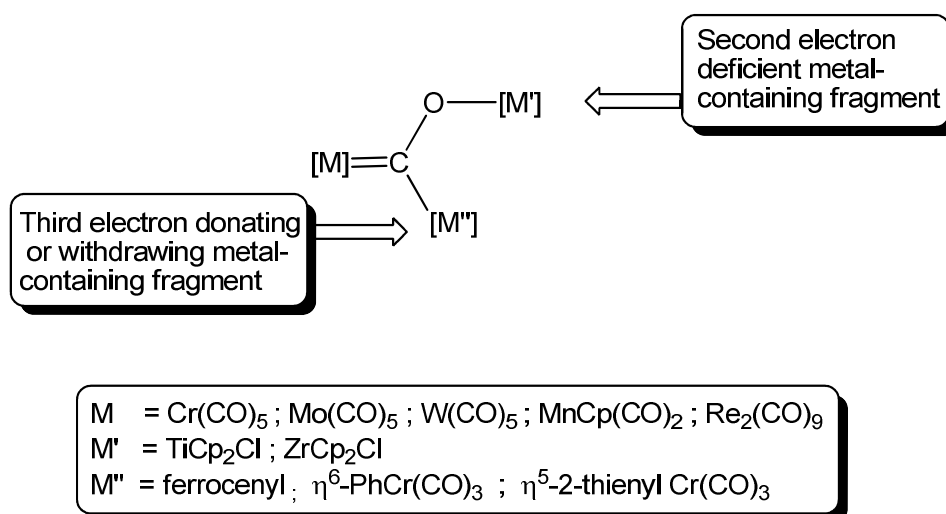
1.2 Aim of the study

As far as could be ascertained, no carbene complex has been reported with three different transition metal substituents that are all in electronic contact with the carbene carbon atom; a class of compounds we call carbene transition metal cluster compounds. Unlike the clusters defined by Cotton *et al.*,³⁶ these complexes do not contain metal-metal bonds, but rather refer to metals clustered around the carbene carbon atom.

The objective was not only to synthesize trimetallic carbene complexes of the type $[M(CO)_n\{C(OR)R'\}]$, 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 (Scheme 1.3). The substituents chosen included aromatic (benzene) and heteroaromatic (thiophene) rings π -coordinated to a $Cr(CO)_3$ -fragment, or ferrocenyl as the R' substituent, while the OR substituent would be varied systematically between an organic ethoxy group and an organometallic titanoxo group. Initially, Group VI transition metals (Cr, Mo, W) with carbonyl ligands were chosen as being representative of a class of Fischer carbene complexes that exhibit high stability.

To expand the study towards the investigation of Group VII transition metals (Mn, Re) and their character and reactivity towards the metal-substituted carbene ligands, the binary dirhenium decacarbonyl and the mononuclear $MnCp(CO)_3$ were included as precursor complexes.

³⁶ Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Ed, Wiley-Interscience, **1999**.



Scheme 1.3

The structural features and their relevance to bonding in the carbene cluster compounds of the Group VI and VII transition metals were to be investigated as they represent indicators of possible reactivity sites in multimetal carbene assemblies. Finally, the possibility of using molecular modelling calculations to quantify the effect of metal-containing substituents on the carbene ligands was proposed, as well as the correlation of the theoretical results with experimental parameters were planned to test the viability of DFT calculations as a tool for substituent effect trend prediction in carbene cluster complexes.