

Recent advances in the field of multicarbene and multimetal carbene complexes of the Fischer-type

Daniela I. Bezuidenhout*, Simon Lotz, David C. Liles, Belinda van der Westhuizen

Chemistry Department, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa
E-mail: daniela.bezuidenhout@up.ac.za; Fax: (+27)12 420 4687; Tel: (+27)12 420 2626

Content

1.	Introduction.....	3
2.	Multicarbene metal complexes.....	5
2.1.	Mononuclear multicarbene complexes (I).....	6
2.1.1.	Mononuclear biscarbene complexes I(a)	6
2.1.2.	Mononuclear biscarbene chelates I(b)	10
2.1.3.	Carbene chelates.....	12
2.2.	Dinuclear biscarbene complexes (II).....	14
2.2.1.	Carbene ligand not involved in the bridging of metal fragments II(a)	14
2.2.2.	Complexes not bridged by carbene substituents <i>or</i> metal-metal bonds II(b)	14
2.3.	Carbene ligands linked via the carbon-chain substituent (III).....	17
2.3.1.	Biscarbene complexes from lithiated substrates (i).....	18
2.3.2.	Biscarbene complexes from organic substrates (ii).....	23
2.3.3.	Biscarbene complexes from monocarbene anions and monocarbene anion radicals (iii).....	24
2.3.4.	Fischer carbene complexes with α -alkynyl substituents (iv).....	30
2.3.5.	Metal carbyne complexes as intermediates or precursors to biscarbene complexes (v).....	36
2.4.	Carbene ligands linked via the heteroatom substituent (IV).....	38
2.5.	Doubly bridged biscarbene complexes and biscarbene complexes with two separate bridges (V).....	40
3.	Multimetal Fischer carbene complexes.....	40
3.1.	Metal fragments bonded directly to the carbene carbon atom.....	41

3.1.1.	Complexes containing carbene carbon metal substituent in the absence of a carbene heteroatom (VI)	41
3.1.2.	Complexes containing Fischer carbene carbon metal substituent (VII).....	45
3.2.	Complexes with a metal fragment bonded to the carbene substituent (VIII).....	46
3.2.1.	π -aryl monocarbene complexes VIII(a)	46
3.2.2.	Monocarbene complexes with metal fragment not π -bonded.....	55
3.2.3.	π -aryl biscarbene complexes VIII(b)	57
3.3.	Complexes with metal fragment bonded to the carbene heteroatom substituent (IX).....	63
3.3.1.	Metaloxycarbene complexes.....	63
3.3.2.	Metalthiocarbene complexes.....	70
3.3.3.	Metalaminocarbene complexes.....	70
3.3.4.	Metalphosphinocarbene complexes.....	74
3.4.	Carbene complexes with multimetal substituents (X).....	76
3.4.1.	Monocarbene multimetal complexes X(a)	76
3.4.2.	Biscarbene multimetal complexes X(b)	79
3.4.3.	Multimetal monocarbene cluster complexes.....	82
3.4.4.	Multimetal multicarbene cluster complexes.....	83
4.	Some structural aspects.....	84
4.1	Geometry around the carbene moiety.....	84
4.1.1	Orientation of (hetero)aryl ring substituents with respect to the carbene plane.....	84
4.1.2	Orientation of aromatic five-membered heterocycle substituents with respect to alkoxy substituents.....	85
4.2	Relative orientation of the heterocyclic rings in biscarbene rod complexes with multiple aromatic five-membered heterocyclic rings.....	86
5.	Concluding remarks.....	87

Abstract

This review article covers the development of Fischer carbene complexes since the year 2000, with specific focus on carbene complexes bearing metal-containing fragments as substituents, as well as multicarbene systems. The role of the metal-containing substituents on the character and reactivity of such complexes are discussed. In addition, larger systems containing more than one carbene ligand are also covered (rod-like biscarbenes, chelates, macrosystems, etc.) in terms of the synthesis, reactivity and structural aspects.

Keywords

Fischer carbene complexes, multicarbene complexes, multimetal complexes

Abbreviations

Ac, acetyl; Bu, butyl; COT, 1,3,5-cyclooctatriene; Cp, cyclopentadienyl; Cp^{*}, pentamethyl cyclopentadienyl; Cp', methyl cyclopentadienyl; DMF, dimethyl formamide; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, 1,2-bis(diphenylphosphino)methane; Et, ethyl; ESI-MS, electrospray ionization mass spectrometry; Fc, ferrocenyl; Fc', ferrocen-1,1'-diyl; HOMO, highest occupied molecular orbital; HB(pz)₃, hydrotris(pyrazol-1-yl)borate; MAO, methylaluminumoxane; Me, methyl; MOF, metal organic framework; NHC, *N*-heterocyclic carbene; Ph, phenyl; Pr, propyl; salen, bis(salicylidene)ethylenediaminato; TBS, *tert*-butyldimethylsilyl; terpy, 2,2',6,2''-terpyridine; THF, tetrahydrofuran; TMEDA, *N,N,N',N'*-tetramethylethylene diamine; tolan, diphenylacetylene; Tol, toluene; UV, ultraviolet; xyl, xylene;

1. Introduction

The activation of simple organic molecules by a transition metal constitutes an area of research of great importance. The applications of carbenes as active or auxiliary ligands in organic synthesis and catalysis are mostly focused on monocarbene systems. Most of these Fischer monocarbene complex applications center around the reactivity of the

metal-carbon double bond or the carbene-bonded heteroatom X (**A** in Fig. 1), or on modifications of vinyl- (**B**) or 1-alkynylcarbene ligands (**C**) for organic synthesis [1-10].

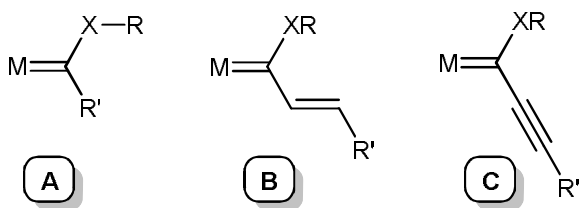


Fig. 1. Monocarbene systems utilized for applications in catalysis or synthesis.

In this review the focus is mainly on the synthesis, structures, properties and possible applications of bis- and multicarbene, and multimetal carbene complexes; and those areas of this carbene chemistry that have not been reviewed recently. A comprehensive review by Sierra in 2000 accounts for most of the results before 1999 [11]. The first section will deal especially with dinuclear biscarbene complexes and methods to prepare such compounds, whereas the following section covers the area of Fischer carbene complexes containing metal-fragments as carbene substituents. Some attention is given to spectral data in support of the carbene ligand character, while specific structural aspects are emphasized. Theoretical calculations in the past have focused mainly on the donor/acceptor nature of the carbene substituents of simple monocarbene complexes [12-17] or the steric and electronic effects of the heteroatom on the carbene ligand [18]. Reaction mechanisms of thermal and photochemical transformations have also been calculated by DFT methods [19-23], but reports on the modeling of multimetal carbene complexes are rare [17].

The enormous interest in nitrogen heterocyclic carbene (NHC) ligands, their complexes and applications resulted in this class of Fischer carbene complexes having branched off from mainstream Fischer carbene chemistry and obtaining an own identity.

Discrimination between NHC ligands and aminocarbene complexes referred to in this article will be based on steric properties and the criteria that bisaminocarbene ligands must be acyclic. Many subsequent review articles have appeared in literature on NHC chemistry and will not be included in this article. Suffice to say that the inherent stability of NHC complexes make them ideal candidates for the synthesis of multicarbene metal

complexes. Stable singlet carbenes [24] and the capture of free hydroxycarbenes [25] are areas of rapidly developing chemistry, but only metal complexes of these carbenes will be included here. Biscarbene cumulene complexes were not considered as they do not represent Fischer carbene complexes [26]. In addition bridging carbene or carbyne ligands were also not considered.

2. Multicarbene metal complexes

In this section the authors have divided the more recent examples of Fischer multicarbene complexes into different classes as shown in Fig. 2 for biscarbene complexes. Reference will be made to compounds that initiated the research and will be extended to compounds with more than two carbene ligands.

In complexes consisting of a single metal only, two or more Fischer carbene ligands may be coordinated as independent carbene ligands (**I(a)**) or form part of a chelate ring (**I(b)**). In complexes with more than one metal many possibilities exist for the placement of more than one carbene ligand. Two carbene ligands may be found as independent units on two separate metals joined by a metal-metal bond (**II(a)**) or alternatively by a bridging ligand between the metals (**II(b)**). Two or more metals may be linked via spacer units which are part of the carbene ligands and may be attached to either the alkyl/aryl substituent (**III**) or the heteroatom substituent (**IV**) or both (**V(a), (b)**). Biscarbene complexes with two bridges are found making use of a bridge with one terminal carbene and one other ligand (**V(c)**). The linker units can be π -conjugated allowing for metal-metal communication through the bridging biscarbene ligand or be separated by a nonconjugated spacer moiety which will serve to attach two monocarbene ligands.

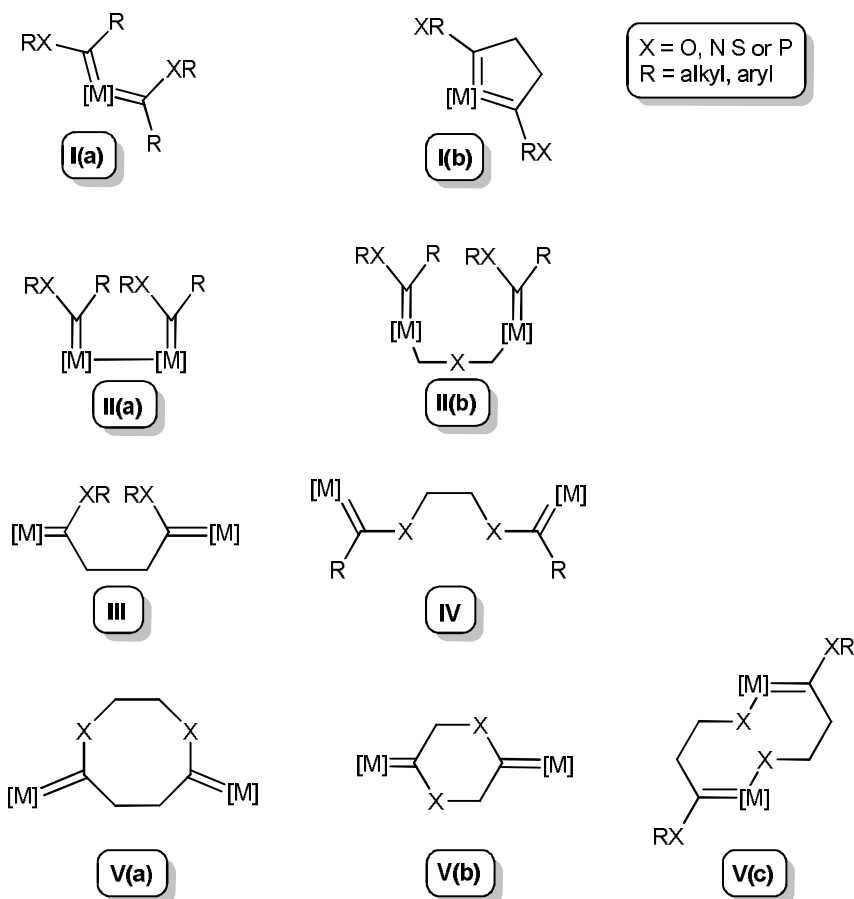


Fig. 2. Classes I - V of biscarbene complexes.

2.1. Mononuclear multicarbene complexes (I)

2.1.1. Mononuclear biscarbene complexes I(a)

Until recently stable mononuclear biscarbene complexes (Fig. 2, **I(a)**) of group 6 transition metals with alkoxyalkyl- or alkoxyarylcabene ligands were scarce and their potential in controlled template reactions remains to be explored. The handling of such carbene complexes is challenging mainly because of their instability or high reactivity in solution during synthesis or in conversion reactions [27]. Representative examples of mononuclear biscarbene complexes of groups 6 and 10 transition metals are shown in Fig. 3.

Single metal mono- and bisaminocarbene complexes (eg. NHC's) of manganese, iron, ruthenium, nickel and cobalt have been reported many years ago by Lappert and co-

workers following a different reaction route, involving the cleaving of the olefinic bond in 1,3-dialkylimidazol-2-ylidene [28]. The direct synthesis of group 6 metal carbonyl biscarbene complexes by employing the classical Fischer method of reacting metal carbonyls with organolithium reagents in a stepwise manner failed as the second organolithium reagent favored attack on the carbene carbon instead of a carbonyl ligand. Exceptions found were those shown in Fig. 3 whereby two equivalents LiPMe_2 afforded the acyclic *cis*-bis-dimethylphosphino(ethoxy)carbene complex **1** in low yields [29]. Starting with a mono-NHC carbene precursor, $[\text{M}(\text{CO})_5(\text{NHC})]$ ($\text{M} = \text{Cr}, \text{W}$) and reacting it with methyllithium gave, after subsequent alkylation, a biscarbene complex **2** containing both an alkoxy and a NHC-carbene ligand [30].

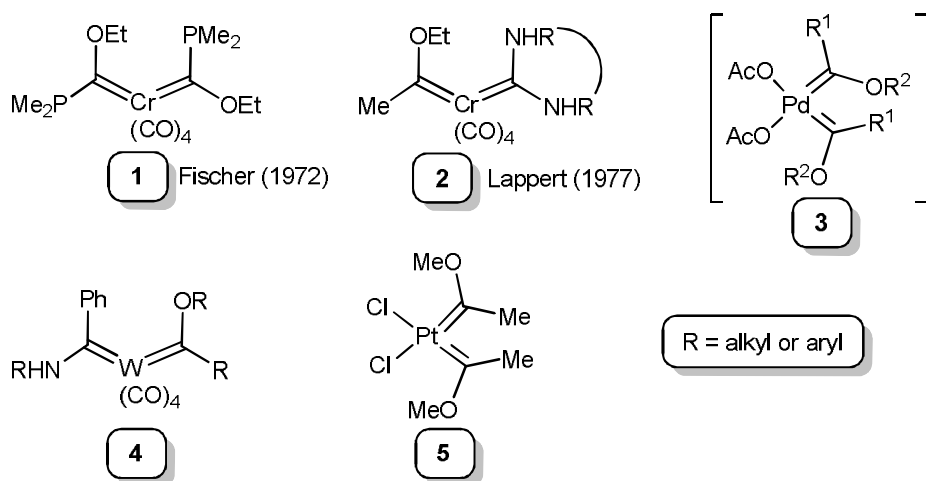


Fig. 3. Examples of mononuclear biscarbene complexes.

Sierra and co-workers studied carbene-carbene coupling reactions of mononuclear alkoxy-carbene complexes of chromium in the presence of palladium catalysts. These reactions proceeded via the transfer of the alkoxy-carbene ligand to the palladium resulting in the formation of a palladium monocarbene intermediate; and after a second transfer, in the biscarbene intermediate **3** [31-33]. The proposed catalytic cycle for the transmetalation of Fischer carbene complexes with Pd catalysts suggested by Sierra involves the participation of a palladium biscarbene intermediate in the key step before the carbene-carbene coupling reaction. Support thereof was found in the isolation of the bischelate biscarbene complex **6** (Fig. 4.) [34]. This bis(ethoxycarbene) intermediate of

palladium (**6**) could be stabilized by incorporating the carbene ligands into five-membered N,C-chelate rings [33,36].

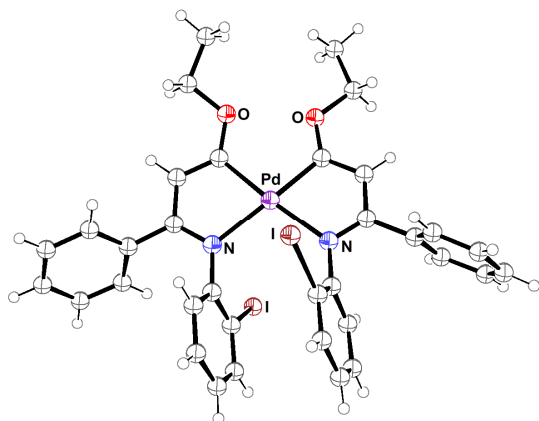
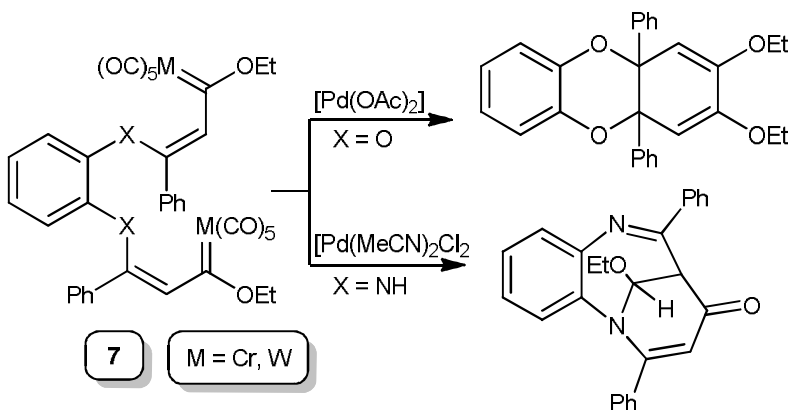


Fig. 4. Molecular structure of $[\text{Pd}\{\text{C}(\text{OEt})\text{CHCPhN}(o\text{-C}_6\text{H}_5\text{I})\}_2]$ (**6**) [34].

Sierra and co-workers used palladium catalysts for intramolecular carbene-carbene coupling reactions of biscarbene complexes of Cr and W (Scheme 1, **7**) to achieve a ring closure reaction with different outcomes for the final products depending on the precursors being of the *o*-dioxobenzene or *o*-diaminobenzene class of compounds [37]. In addition to the carbene-carbene coupling reaction, the oxygen derivative participated in an intramolecular cyclization process to afford three condensed six-membered rings. Intermolecular carbene-carbene coupling reactions in bimetallic biscarbene complexes have the potential of generating biscarbene complexes with extended spacer units between two metacarbene fragments (see section 2.3.1).



Scheme 1.

Barluenga reported the formation and intramolecular coupling of a hydroxy- and an alkoxy-carbene ligand of chromium and tungsten (Fig. 5, **8**) from the direct reaction of organolithium reagents on a carbonyl ligand of a monoalkoxycarbene precursor. When tungsten was used the alkoxy-alkoxy biscarbene complexes could be isolated and the molecular structure of a related biscarbene complex of tungsten was reported (Fig. 6, **4**) [38].

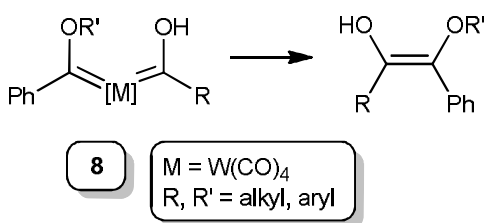


Fig. 5. Carbene-carbene coupling reaction from bisalkoxycarbene complexes of tungsten.

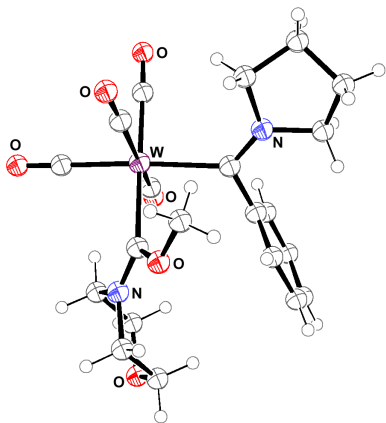
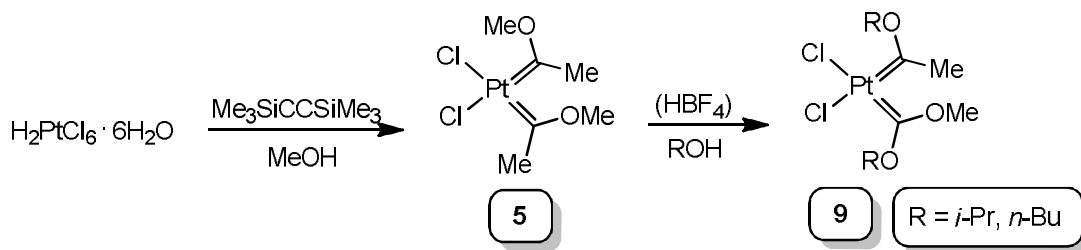


Fig. 6. Molecular structure of $[\text{W}\{\text{C}(\text{OEt})(\text{N}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2)\}\{\text{C}(\text{N}(\text{CH}_2)_3\text{CH}_2)\text{Ph}\}(\text{CO})_4]$ (**4**) [38].

Biscarbene complexes with acyclic bisaminocarbene ligands are stable and readily prepared from reacting platinum precursors containing isocyanide ligands with amines [39,40]. Stable biscarbene complexes (**5** and **9**) with *cis*- and *trans*-alkoxycarbene ligands were synthesized from hexachloroplatinic acid as shown in Scheme 2 [41]. Steinborn and

co-workers have extensively studied the chemistry of platina- β -diketones which can be described as hydroxycarbene complexes stabilized by strong hydrogen bonds to acyl ligands [42].



Scheme 2.

2.1.2. Mononuclear biscarbene chelates **I(b)**

Fischer carbene ligands incorporated into metallacyclic rings are stabilized by the chelate ring effect and are often encountered during carbene synthesis and reactions of carbene ligands involving heteroatoms (Fig. 2, **II(b)**). On the other hand, biscarbene chelates are rare mainly because of challenges associated with methods of synthesis resulting in the generation of two anions on adjacent carbons or heteroatoms in organic substrates. Some examples of symmetrically substituted biscarbene chelates (**10**) with identical carbene ligands were reported by Fischer and co-workers many years ago, but until recently very little progress was made in this area of Fischer carbene chemistry [43-46].

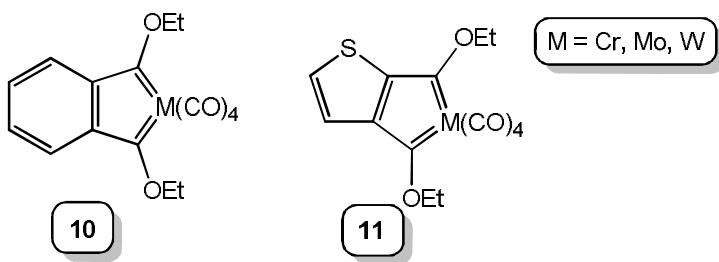


Fig. 7. Examples of biscarbene mononuclear chelates.

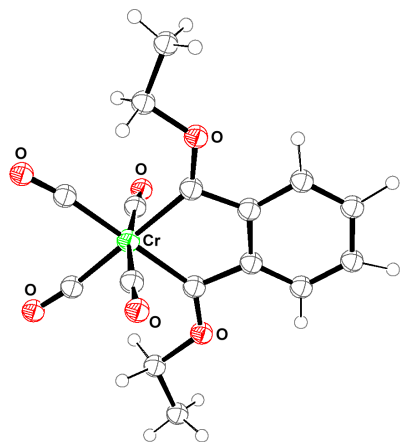
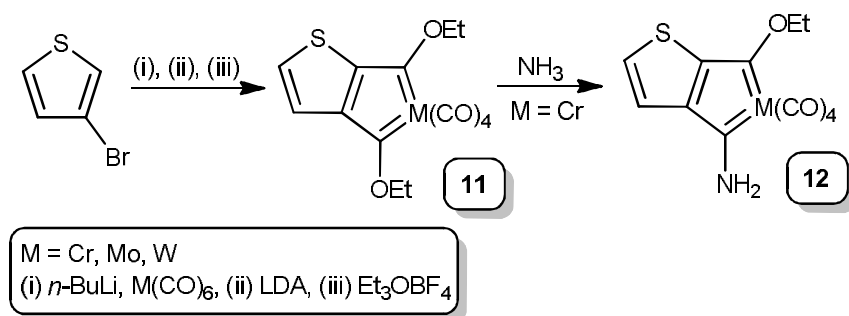


Fig. 8. Molecular structure of $[\text{Cr}\{o\text{-}(\text{C}(\text{OEt})\text{C}_6\text{H}_4\text{C}(\text{OEt}))\}(\text{CO})_4]$ (**10**) [45].

The activation of otherwise less active sites by halogen lithium exchange reactions was successfully exploited by Lotz and co-workers to synthesize **11**, 2,3-bis(ethoxycarbene)thiophene tetracarbonyl metal complexes of Cr, Mo, W (Scheme 3) [47].



Scheme 3.

Two significantly different chemical shifts for the two carbene carbons were observed for **11** in the ¹³C NMR spectra. Fig. 9 shows that the carbene carbon located on the opposite side of the sulphur of the thiophene ring is less shielded and therefore more electrophilic. Unlike the carbene ligands in the Fischer biscarbene chelates being electronically identical, they are very different in the analogous thiophene complexes. Both carbene ligands in the Fischer case are simultaneously aminolyzed whereas a single aminolysis was observed at the favored carbene site in the thiophene biscarbene chelate ring (Scheme 3).

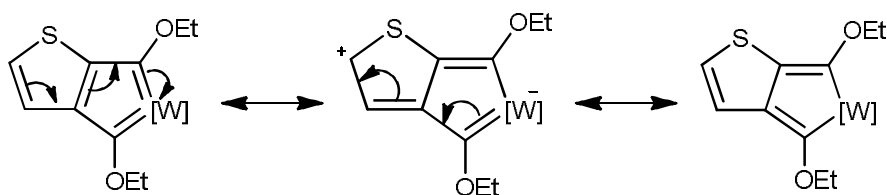
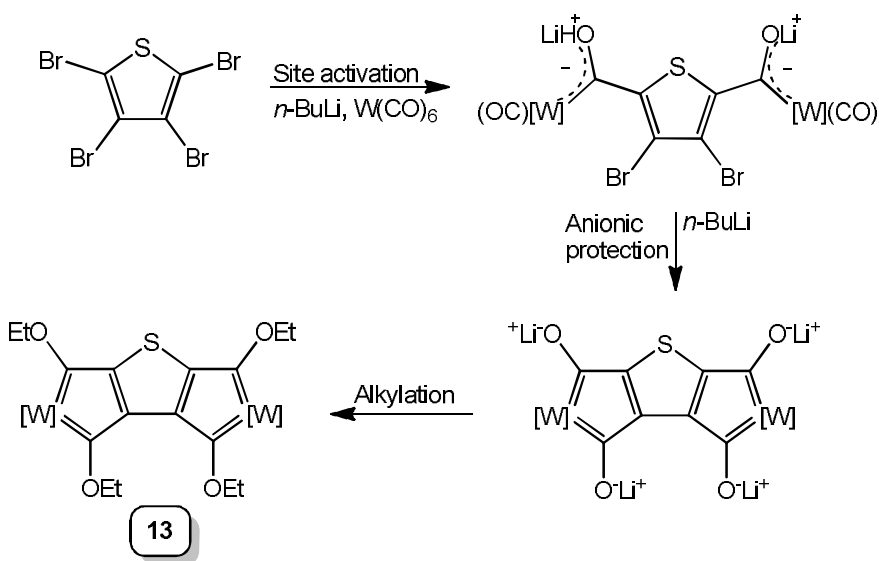


Fig. 9. Charge delocalization in bis-carbene chelates of thiophene.

2.1.3. Carbene chelates

Recently the first dimetallatetracarbene complexes of group 6 transition metals (**13**) were synthesized according to the classical Fischer method and structurally characterized (Fig. 10). The less active 3- and 4-positions of thiophene were activated by starting with tetrabromothiophene rather than thiophene, followed by the addition of *n*-butyllithium and the metal hexacarbonyl in two separate steps (Scheme 4). The dimetal diacylate stabilized the negative charge by delocalization and still rendered the two remaining bromo 3- and 4-positions active for a second bromo-lithium exchange reaction. The resulting dimetal tetraacylate was alkylated with Et_3OBF_4 to give the thiophene displaying four carbene ligands as two bis-carbene chelate rings (**13**). The stepwise incorporation of a metal carbonyl during the synthesis is important to distribute charge away from sites that need to be lithiated in the second step. The alkylation only at the end of the reaction serves to protect the acylate carbons against nucleophilic attack [47].



Scheme 4.

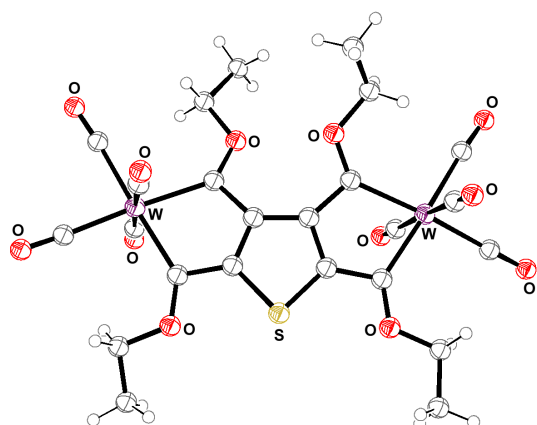


Fig. 10. Structure of 2,3,4,5-bis((bis-ethoxycarbene)tetracarbonyltungsten)thiophene (**13**) [47].

2.2. Dinuclear biscarbene complexes (**II**)

2.2.1. Carbene ligand not involved in the bridging of two metal fragments **II(a)**

Fig. 11 shows two older examples of biscarbene complexes incorporated into systems containing metal-metal bonds (small clusters). The reaction of dirhenium decacarbonyl with two equivalents organolithium reagent afforded a dirhenium biscarbene complex (**14**). As a result of steric strain the carbene ligands are found in different electronic environments with one ligand being in an axial and the other in an equatorial position [48]. The cyclic dioxycarbene ligands in the triangular tris-osmium carbonyl cluster (**15**) were obtained from reacting the osmium carbonyl precursor and ethylene oxide in the presence of bromide ions [49]. Recently, the synthesis and reactivity of carbene ligands in metal carbonyl clusters have not attracted much attention and needs to be revisited to study cooperative template effects. The extension of carbene cluster chemistry to metal surfaces holds promise for future studies. The engineering of designer surfaces of self-assembled monolayers functionalized with Fischer carbenes for immunosensing [50,51] represents a novel application.

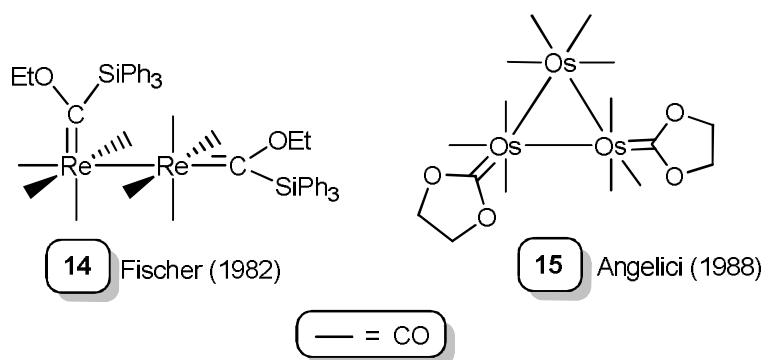


Fig. 11. Biscarbene ligands in cluster complexes.

2.2.2. Complexes not bridged by carbene substituents or metal-metal bonds **II(b)**

The bridging of mononuclear monocarbene complexes with oxygen or halogen spacers are often found when mononuclear species with such ligands are part of coordinatively unsaturated species. In solution the intermediates readily combine or dimerize to give dinuclear biscarbene complexes. Recent examples of biscarbene complexes obtained along this route are shown in Fig. 12. The acyclic diphosphino dianion $\text{Li}_2[\text{C}\{\text{P}(\text{Ph})_2\text{S}\}_2]$ reacted with zirconocene dichloride and zirconium tetrachloride to form two Zr-C-P-S metallacycles and in the process stabilizing the carbene carbons. In the case of $[\text{ZrCl}_4(\text{THF})_2]$ the zirconium carbene dimerized affording the chloro-bridged dizirconium biscarbene complex **(16)** [52].

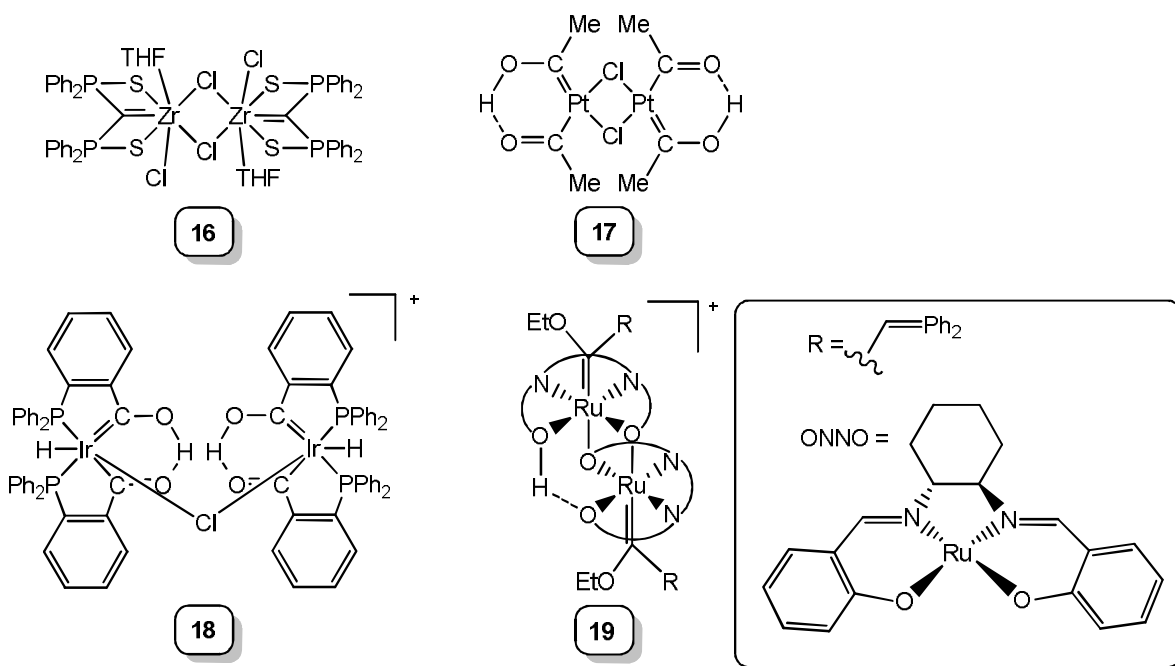


Fig. 12. Examples of biscarbene complexes bridged by ancillary ligands.

A class of compounds of interest is that of complexes with hydroxycarbene ligands. The hydroxycarbene ligand readily converts into an aldehyde with the loss of the metal and needs to be stabilized. Most isolated examples display hydroxyl substituents stabilized by hydrogen bonding. Pioneering work in this area with the middle transition metals (Mn, Re, Fe, etc.) was done in the laboratories of Lukehart and co-workers many years ago [53,54]. More recently, extensive ongoing studies (see Section 2.1.1) by Steinborn and co-workers focused on dimeric platinum- β -diketones, where the hydroxycarbene ligands are being stabilized by adjacent acyl ligands (Fig. 12, **17**) [55,56]. The diplatinum bishydroxycarbene dimer is a suitable precursor to a wide range of alkoxy carbene and diacetylplatinum(II) complexes [41,57].

To afford the cationic chloro-bridged bishydroxycarbene complex **18** shown in Fig. 12 [58], two equivalents of the chlorohydroirida- β -diketone, $[\text{Ir}(\text{H})\text{Cl}\{o\text{-P}(\text{Ph})_2\text{C}_6\text{H}_4\text{C}(\text{O})\}_2\text{H}]$, were reacted with one equivalent of AgBF_4 and Et_3OBF_4 to abstract a chloro ligand. The dinuclear ruthenium biscarbene complexes **19** have tetradentate-ONNO salen ligands in the equatorial planes of the metals, of which one oxygen atom of each salen is shared as a bridging ligand between the metals, while the

two other oxygens at the other ends of the salen ligand are bridged by a hydrogen. This biscarbene complex is an active catalyst for the cyclopropanation of alkenes and studies suggest electronic communication between the metal-metal centers [59].

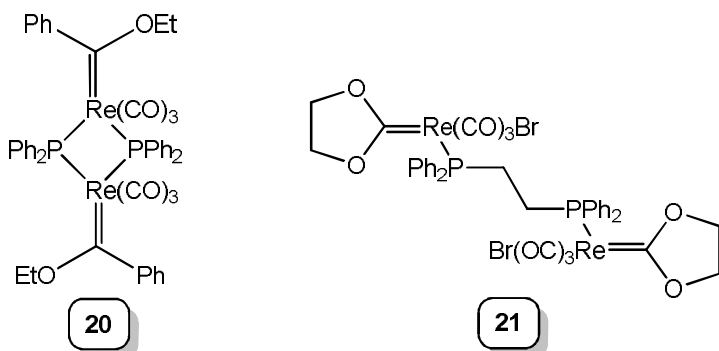


Fig. 13. Dinuclear biscarbene complexes of group 7.

Haupt and co-workers studied the reactivity of dinuclear complexes of group 7 transition metals with phosphido bridges. These dimers are without metal-metal bonds and reacted with organolithium agents to afford acylates with the acyl ligand in the axial site. A further reaction with a second organolithium reagent afforded diacyl dianions and after subsequent alkylation with Me_3OBF_4 afforded the biscarbene complexes **20**, Fig. 13 [60,61]. Attaching two mononuclear Fischer carbene complexes to one another by substituting two carbonyl ligands with a bidentate bridging ligand such as dppe or dppm is another route to dinuclear biscarbene complexes. A typical example is the reaction of $[\text{Re}\{\text{CO}(\text{CH}_2)_3\text{O}\}(\text{CO})_4\text{Br}]$ with dppe to give **21** (Fig. 14) [62].

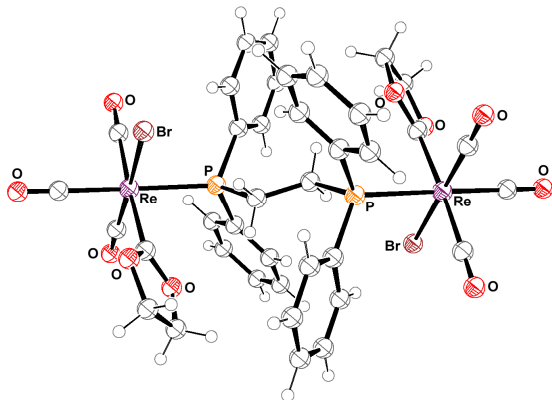


Fig. 14. The molecular structure of [μ -
 $\text{P}(\text{Ph})_2\text{CH}_2\text{CH}_2\text{P}(\text{Ph})_2$] $\{\text{Re}\{\text{CO}(\text{CH}_2)_3\text{O}\}(\text{CO})_3\text{Br}\}_2$ (**21**) [62].

2.3. Carbene ligands linked via the carbon chain substituent (**III**)

Fig. 15 shows some precursors that can be used to create a link between two carbene ligands whereby the R substituent becomes a spacer unit of a Fischer carbene complex of general formula [$\{\text{M}(\text{CO})_5\}\{\text{C}(\text{OR}')\text{RC}(\text{OR}')\}$] (Fig. 2, **III**). A general way to link two metal fragments with two Fischer carbene ligands would be to react two equivalents of a metal carbonyl precursor with a dilithiated substrate and thereafter alkylate the dimetal diacylate (Fig. 15, **(i)**). Alternatively the bridge can be established by starting with a monolithiated substrate and at a later stage create a second nucleophile to react with a second metal carbonyl precursor. Depending on the substrate, this could be done directly or in two or more steps. The coordination of organic substrates such as reactive bisalkynols, heteroarenes or activated alkynes, instead of using organolithium agents, provides an alternative route to biscarbene complexes with conjugated spacer units (**(ii)**). Also, widely employed is the modification of an existing carbene ligand (**(iii)**, **(iv)**) by exploiting the effect of an electrophilic carbene carbon by the deprotonation of reactive protons, the formation of a radical, redox reactions or making use of reactive unsaturated bonds in the carbene substituent to generate biscarbene complexes. Dinuclear biscarbene complexes have also been prepared along other unique routes including the use of carbyne precursors (**(v)**).

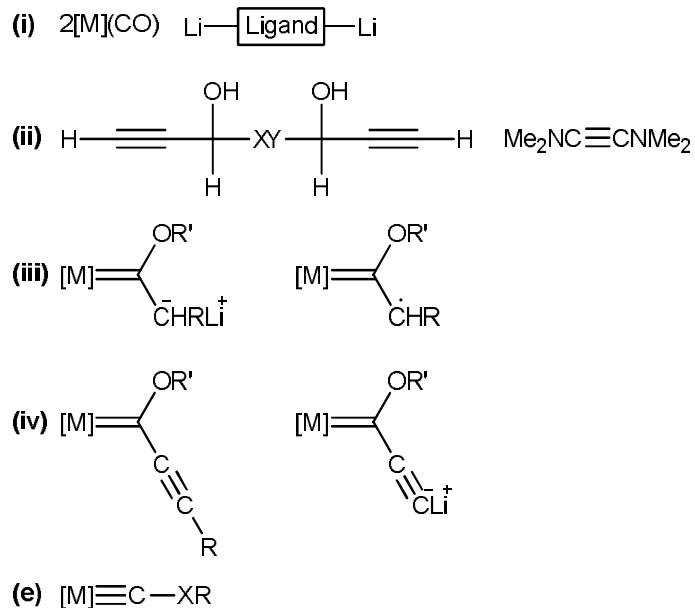
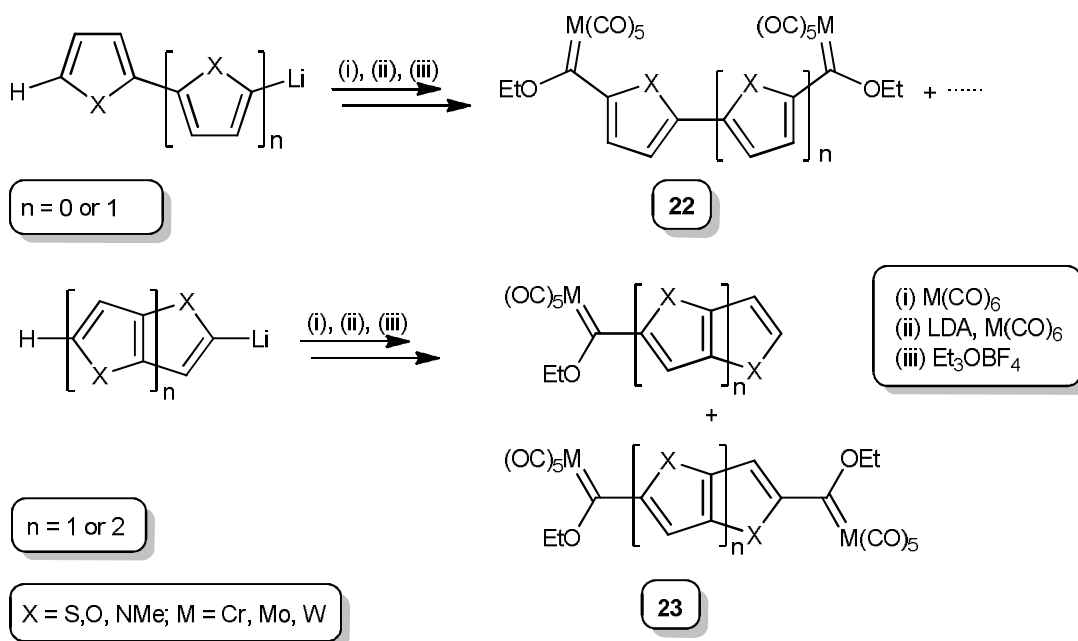


Fig.15. Examples of precursors used to synthesize dinuclear biscarbene complexes.

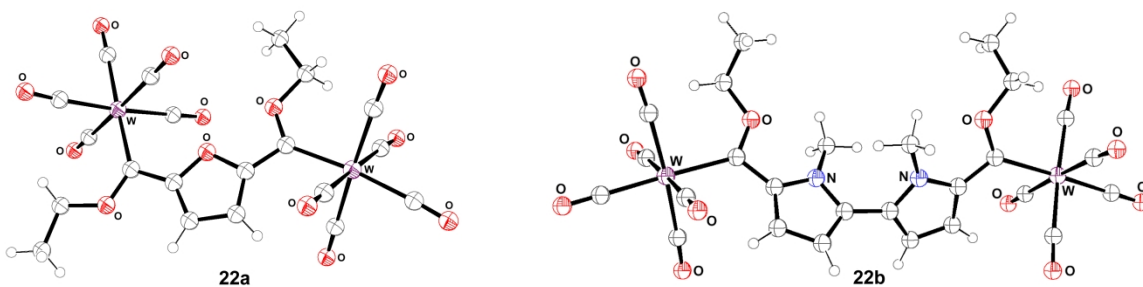
2.3.1. Biscarbene complexes from lithiated substrates (i)

The reaction of dilithiated substrates with two equivalents of a metal carbonyl and reaction with alkylating reagents has led to the formation of bimetallic biscarbene complexes [11]. The spacer unit may be a π -conjugated substrate in which case the terminal metal fragments will be in electronic contact with each other via the carbene moiety and through the spacer unit. Biscarbene complexes with heteroarene spacer units have been investigated [63-68]. Examples of biscarbene complexes with alternating unsaturated carbon-carbon bonds have been reported [69,70]. Metal carbene fragments can be electronically isolated as is the case with alkyl spacer units [71].



Scheme 5.

The dilithiation of heteroarenes is of interest and a variety of biscarbene complexes are possible by exploiting lithiation sites in such heteroarene derivatives. Dilithiation of thiophene, furan and *N*-methylpyrrole and their reaction with group 6 and 7 metal carbonyls afforded 2,5-biscarbene complexes (**22**) after alkylation. (Scheme 5) [64-66]. The 2,2'-heterobiaryls, bithiophene and *N,N'*-dimethylbipyrrole form biscarbene rod structures with π -conjugation and mostly planar orientations of the spacer ligands [67,68].



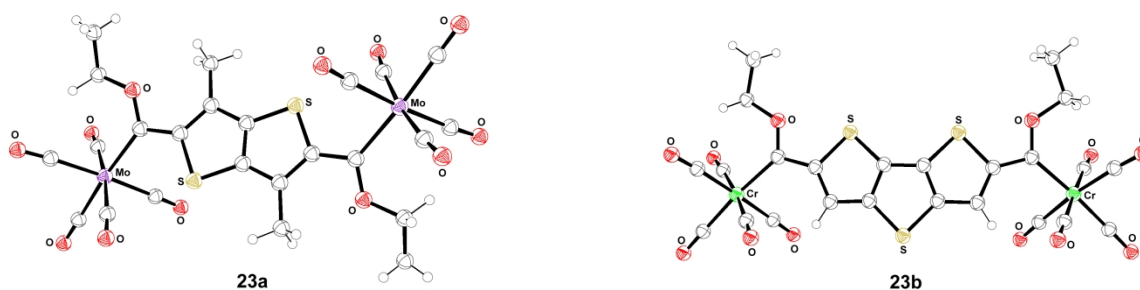
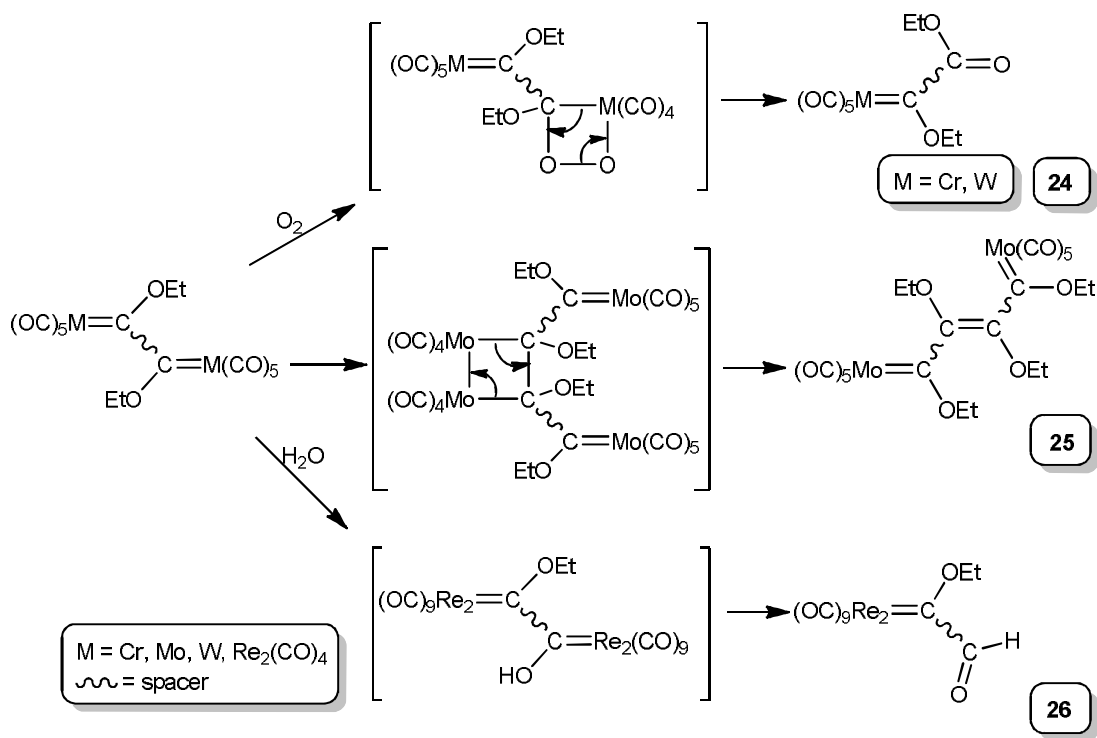


Fig. 16. Molecular structures of some biscarbene rods: **22a** [2,5- $\{(CO)_5W=C(OEt)\}_2$ furan] [65]; **22b** [5,5'- $\{(CO)_5W=C(OEt)\}_2$ (*N,N'*-dimethyl[2,2']bipyrrole)] [67], **23a** [2,5- $\{(CO)_5Mo=C(OEt)\}_2$ -3,6-dimethylthieno[3,2-*b*]thiophene] [72]; **23b** [2,5- $\{(CO)_5Cr=C(OEt)\}_2$ dithieno[3,2-*b*:2',3'-*d*]thiophene] [73].

The condensed heteroarenes, 3,6-dimethylthieno[3,2-*b*]thiophene, *N,N'*-dimethylpyrrolo[3,2-*b*]pyrrole and dithieno[3,2-*b*:2',3'-*d*]thiophene reacted similarly and gave terminal biscarbene complexes such as **23** [72,73,74,75]. Examples of molecular structures of biscarbene rods with heteroarene spacers are shown in Fig. 16. Most of the charge delocalization from the ring to the electrophilic carbene carbon came from the adjacent heteroarene. The thiophene β -proton was most affected by the electrophilic carbene carbon and was used as a probe to monitor ring involvement. Comparing mono- and biscarbene thiophene complexes, a significant difference in the chemical shifts of the β -proton was observed. This difference decreased when the number of bridging heteroarene units, hence the isolation of the carbene carbon, increased [73].

Group 7 transition metal carbonyl complexes reacted differently. The mononuclear precursors $[M(CO)_5X]$ ($M = Mn, Re$; $X = \text{halides}$) displayed two competitive activated sites (both the carbonyls and halide ligands) towards organolithium agents. The biscarbene complexes can be prepared directly from $Re_2(CO)_{10}$ and dilithiated thiophenes. The biscarbene complexes $[\{Re_2(CO)_9\}_2\{C(OEt)(C_4H_2S)_x C(OEt)\}]$ ($x=1,2$) have carbene ligands in the favored equatorial positions relative to the dirhenium nonacarbonyl fragments [76].



Scheme 6.

The biscarbene complexes with heteroarene spacers are more reactive compared to the analogous monocarbene complexes and group 6 metal biscarbene complexes are readily oxidized by trace amounts of oxygen to give monocarbene-ester complexes **24** (Scheme 6). On the other hand biscarbene complexes of dirhenium nonacarbonyl are more sensitive to moisture compared to oxygen and afforded monocarbene-aldehyde complexes **26** [76].

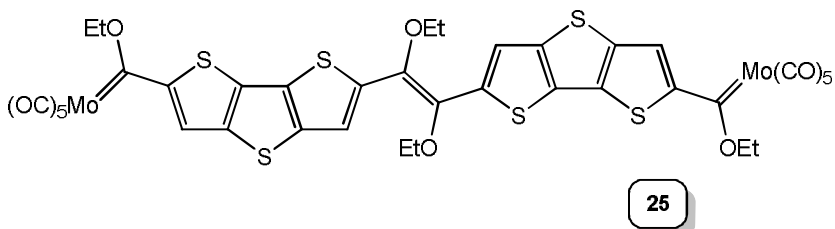


Fig. 17. Extended bis(thienothiophene) spacer found for **25** [75].

In addition to the expected biscarbene complex of molybdenum with a dithienothiophene spacer, a biscarbene with an extended spacer unit (**25**) formed in low yields (Fig. 17). The

product, resulting from a carbene-carbene coupling reaction, was unique to molybdenum and could not be found after refluxing the analogous biscarbene complexes of chromium and tungsten in hexane, or by adding Pd-catalysts to facilitate carbene-carbene coupling reactions.

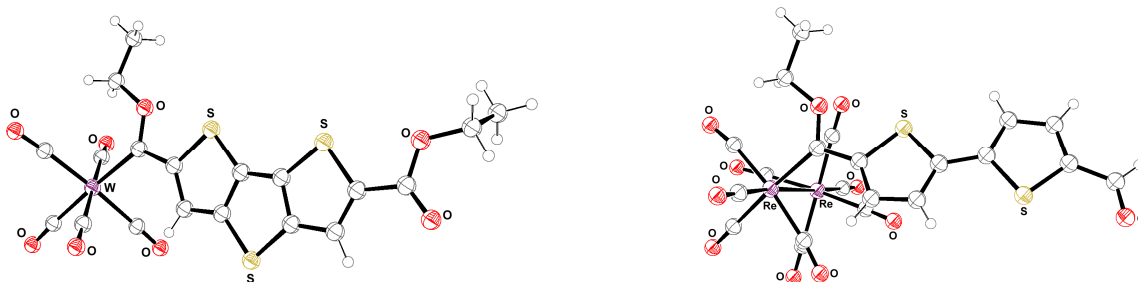


Fig. 18. Reaction products of biscarbene rods with trace amounts of oxygen or water, [2- $\{(CO)_5W=C(OEt)\}$ -5-(COOEt)dithieno[3,2-*b*:2',3'-*d*]thiophene] (**24**) [73] and [5- $\{(CO)_9Re_2=C(OEt)\}$ -5'-(CHO)[2,2']bithiophene)] (**26**) [76].

The second deprotonation of lithiated *N*-methylthieno[3,2-*b*]pyrrole, with the reactive 5-position blocked by a pyrrole unit or benzene ring, can occur for *N*-methylpyrrole either at the 3-position of thiophene or at the carbon in the α -position to the nitrogen atom (Fig. 19) [75]. Both the dimetal biscarbene rod **27** (30%) and monometal biscarbene chelate **28** (40%) were obtained in relative high yields.

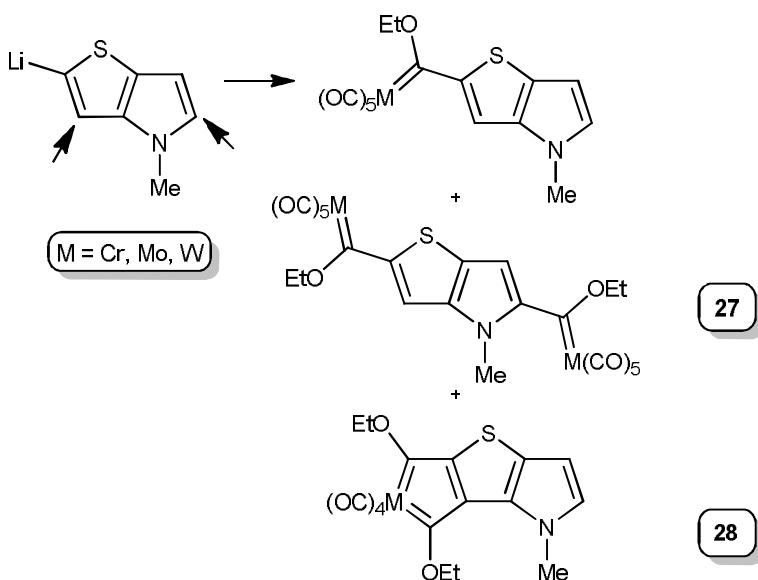


Fig. 19. *N*-methylthieno[3,2-*b*]pyrrole mono- and biscarbene complexes.

The stepwise addition of lithiating agent and metal carbonyl precursors allowed for the preparation of mixed-metal biscarbene complexes [65,68]. Synthesis as a result of differences in carbene reactivity at the ends of a spacer unit in biscarbene rods holds promise for creative applications. Regioselective benzannulation reactions were reported for the biscarbene $[\text{W}(\text{CO})_5\text{C}(\text{OEt})\text{-C}_4\text{H}_2\text{S-C}_4\text{H}_2\text{S-C}(\text{OEt})\text{Cr}(\text{CO})_5]$ (**22a**) favoring the chromium metal fragment, and for $[(\text{CO})_5\text{CrC}(\text{OEt})\text{-C}_4\text{H}_2\text{S-C}_4\text{H}_2\text{O-C}(\text{OEt})\text{Cr}(\text{CO})_5]$ (**22b**) favoring the thiophene ring [77].

2.3.2. Biscarbene complexes from organic substrates (ii)

Reactive terminal dialkynols in methanol with $[\text{W}(\text{CO})_5(\text{THF})]$ afforded mostly the monocarbene complex with a terminal alkynol but biscarbene complexes could also be isolated. Reactions of the monocarbene-alkynol complexes with amines and $[\text{M}(\text{CO})_5(\text{THF})]$ afforded symmetric and non-symmetric dinuclear alkenyl-bridged biscarbene complexes of chromium and tungsten (Fig. 20, **29a**) [63,77].

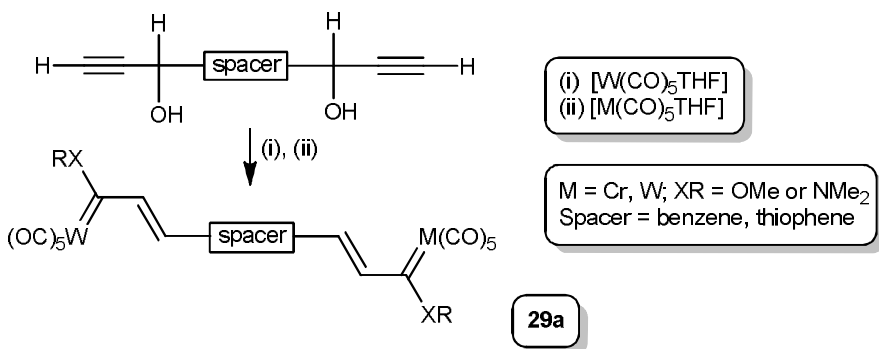


Fig. 20. Biscarbene complexes from dialkynols.

Two $\text{W}(\text{CO})_5$ fragments generated by the substitution of the carbene ligand in $[\text{W}(\text{CO})_5\{\text{C}(\text{H})\text{Ph}\}]$ reacted with the alkyne $\text{Me}_2\text{NCCNMe}_2$ and after rearrangement afforded the novel biscarbene complex $[\{(\text{CO})_5\text{W}=\text{C}(\text{NMe}_2)\}_2]$ **29b** (Fig. 21) [69].

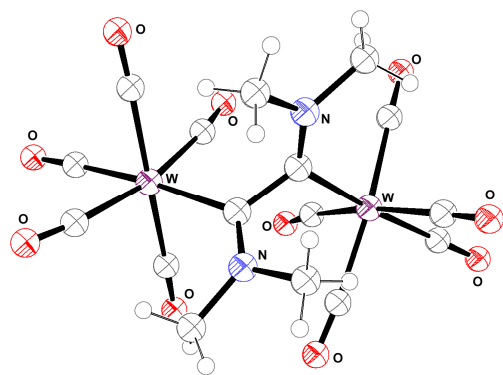


Fig. 21. The molecular structure of $[\{(CO)_5W=C(NMe_2)\}_2]$ (**29b**) [69].

The terpy ligand employed in Fig 22 generally acts as a tridentate ligand with an all *cis* configuration of the pyridine rings [78]. The η^4 -butadiene ligand rearranges to a κ^2C,C' -2-butenediyl during thermal treatment of the hydrotris(pyrazolyl)borate iridiumbutadiene precursor with 2,2':6'2''-terpyridine and afforded the mono- and the biscarbene complexes **30**. In the structure of the biscarbene complex the pyridine rings adopted a '*cis-trans*' configuration with the *cis* rings featuring a N-H \cdots N hydrogen bond interaction while the hydrogen of the *trans* ring participates in a hydrogen bond that now involves the π -electrons of the coordinated enediyl terminus.

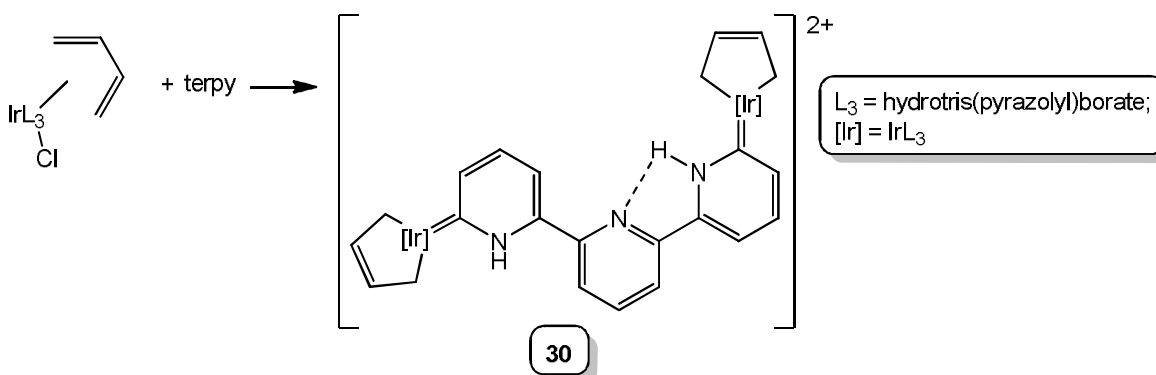
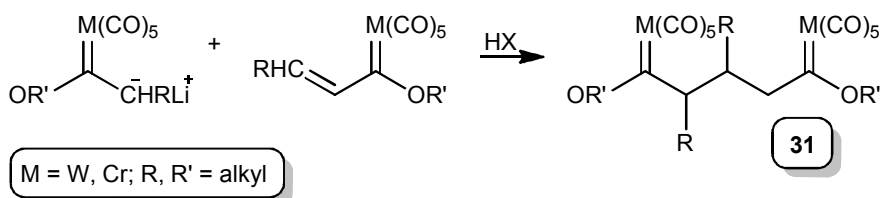


Fig. 22. Biscarbene complex from terpy substrate.

2.3.3. Biscarbene complexes from monocarbene anions and monocarbene radicals (iii).

As a consequence of the electrophilicity of the carbene carbon atom, the acidity of the α -CH groups is significantly enhanced and hence readily deprotonated. Fischer carbene anions were reacted with a large variety of metal carbonyl cations as electrophiles. One

equivalent of a carbon bidentate electrophile afforded dinuclear monocarbene complexes, whereas half an equivalent gave dinuclear biscarbene complexes **31** (Scheme 7) [11].



Scheme 7.

Generation of the carbene anions $[\text{MnCp}(\text{CO})_2\{\text{=C}(\text{OEt})\text{CH}_2\}]^-$ and their intermolecular oxidative coupling in the presence of CuI , CuI_2 and FeCl_3 salts, afforded the biscarbene complex $[\{\text{MnCp}(\text{CO})_2\{\text{=C}(\text{OEt})\text{CH}_2\}_2]$ **32** in high yields. Further deprotonation of the protons α and α' to the carbene carbons of the biscarbene complex was achieved with two equivalents $n\text{-BuLi}$ in ongoing work, and gave the corresponding dianionic dimanganese complex. The latter can again be oxidized with FeCl_3 to give $[\{\text{MnCp}'(\text{CO})_2\text{C}(\text{OEt})\text{CH}_2\}_2]$ (Fig. 23, **33**) or be alkylated with MeI to give $[\{\text{MnCp}'(\text{CO})_2\text{=C}(\text{OEt})\text{C}(\text{Me})\text{H}\}_2]$ (**34**). The former product is also accessible electrochemically with a two-electron oxidation [71].

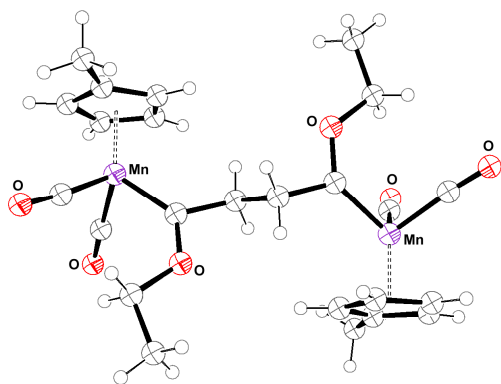
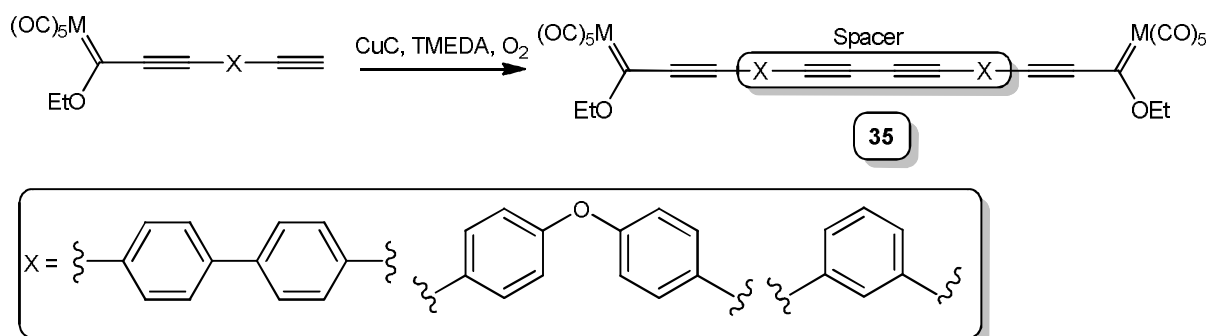
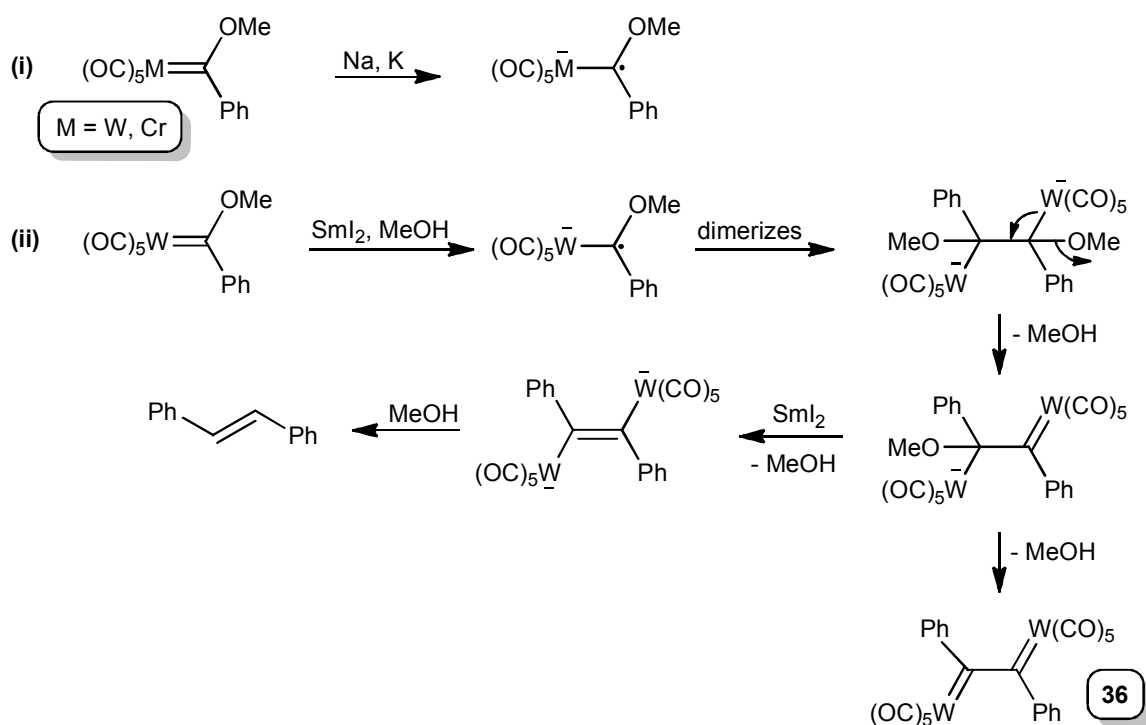


Fig. 23. Molecular structure of $[\{\text{MnCp}(\text{CO})_2\text{C}(\text{OEt})\text{CH}_2\}_2]$ (**33**) [71].



Scheme 8.

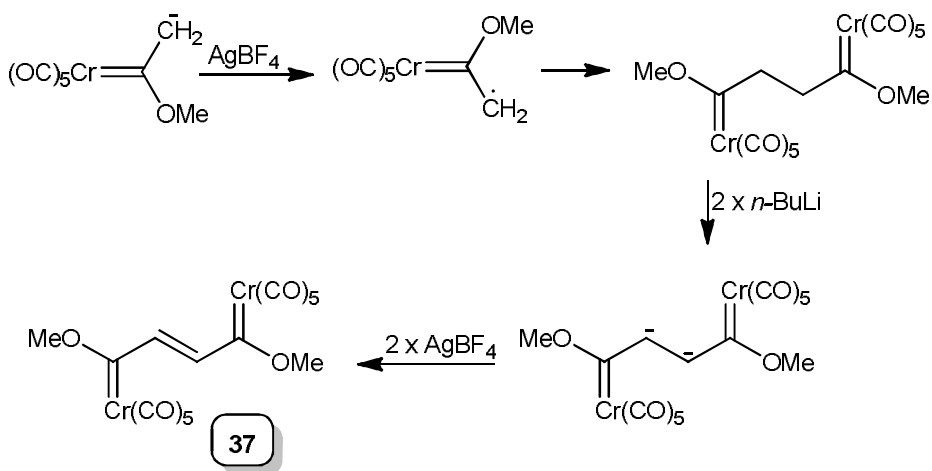
Biscarbene complexes with linear or bridged, elongated, conjugated π -spacers were synthesized, by oxidative coupling of alkyne groups of two monocarbene precursors using CuCl as catalyst. The biscarbene complexes are ideal building blocks to construct complexes with π -extended spacers **35** [70].



Scheme 9.

The one-electron reduction of the Fischer carbene complexes $[M(CO)_5\{C(OMe)Ph\}]$ ($M = W, Cr$) with Na/K indicated a carbon-centered radical making the carbene carbon nucleophilic (Scheme 9 (a)). The reactivity of the radical anions depended on the nature of the metal and the electrophile. Dimerization of two radicals of tungsten (Scheme 9 (b))

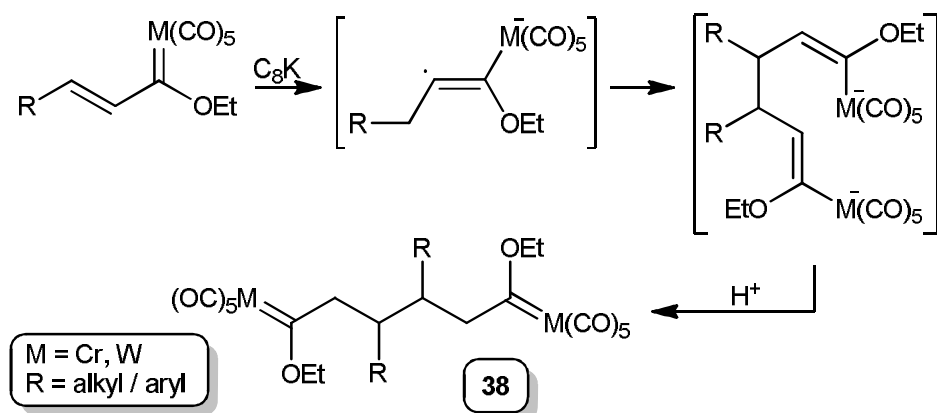
generated with SmI_2 in methanol in the absence of a radical acceptor afforded the dianion $[\{\text{W}(\text{CO})_5\}_2\text{C}(\text{OMe})(\text{Ph})\text{C}(\text{OMe})(\text{Ph})]^{2-}$. The loss of one methanol molecule yields a mono-anionic intermediate. Subsequent loss of a second methanol molecule gave the tungsten biscarbene **36**, or eliminated stilbene after further reduction [79].



Scheme 10.

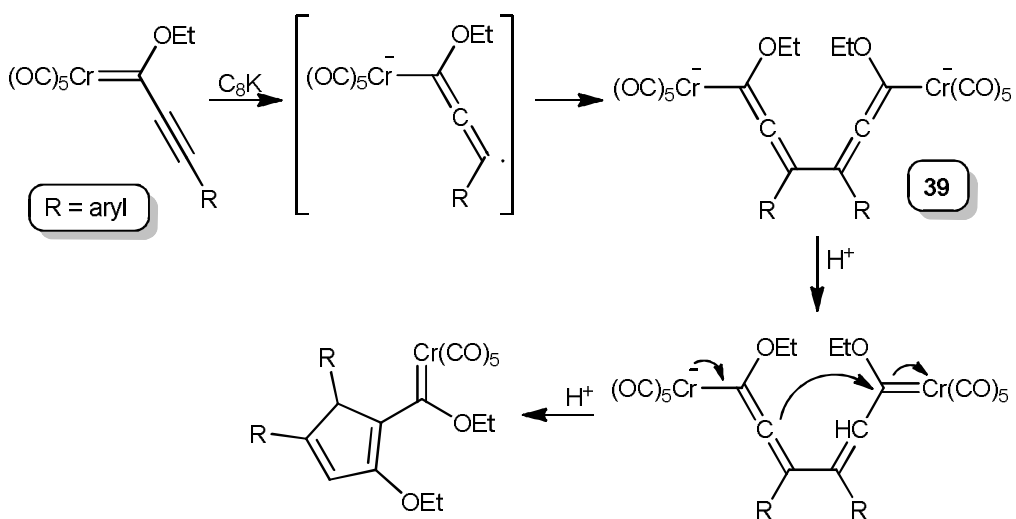
Anions derived from Fischer carbene complexes at the α -position are very reactive towards single electron transfer agents and readily transform into radicals with SmI_2 , C_8K , Na/K , AgBF_4 , etc. The radical anion dimerizes to give a biscarbene complex (Scheme 10) and subsequent deprotonation at the α - and α' -positions with butyllithium followed by an oxidation of the dianion with AgBF_4 generated the α, α' -unsaturated biscarbene complex $[\{\text{Cr}(\text{CO})_5\}_2\{\mu\text{-C}(\text{OMe})\text{CH}=\text{CHC}(\text{OMe})\}]$ **37** [80].

The formation of a radical anion on the β -carbon of the carbene substituent by an electron transfer reagent C_8K was found for α, β -unsaturated Fischer carbene complexes (Scheme 11). The carbene radicals dimerized affording biscarbene complexes **38** after quenching with sulphuric acid or magic methyl [80].



Scheme 11.

A single electron transfer reaction of 1-alkynylcarbene complex of chromium generated a radical anion which, after tail to tail dimerization, afforded the dianionic biscarbene intermediate **39** (Scheme 12). This biscarbene rearranges upon protonation and elimination of a chromium radical anion gave the chromium cyclopentadienecarbene complex [80].



Scheme 12.

Apart from studies dealing with the self-dimerization reactions of carbene radicals and the use of unconventional electron sources such as electron spray ionization (ESI) to induce electron transfer processes [81], this area of carbene chemistry is still under-explored [82].

Fig. 24 shows the open and closed forms of the dithienylethene bridge in the bimetallic bisiron compound [83]. The introduction of UV light to the open form of the dithienylethene arrangement transformed the molecule into the closed form of different geometrical and electronic structure. The same result is possible via a biscarbene intermediate. A two-electron oxidation of the redox-active organometallic iron precursor yielded a diiron diradical which under thermal conditions lead to closure of the switch with the formation of a biscarbene compound **40**. The biscarbene complex can be reduced to give the closed arrangement obtained from UV irradiation. Possible application is in the area of sophisticated devices such as multimodal switches and logic systems.

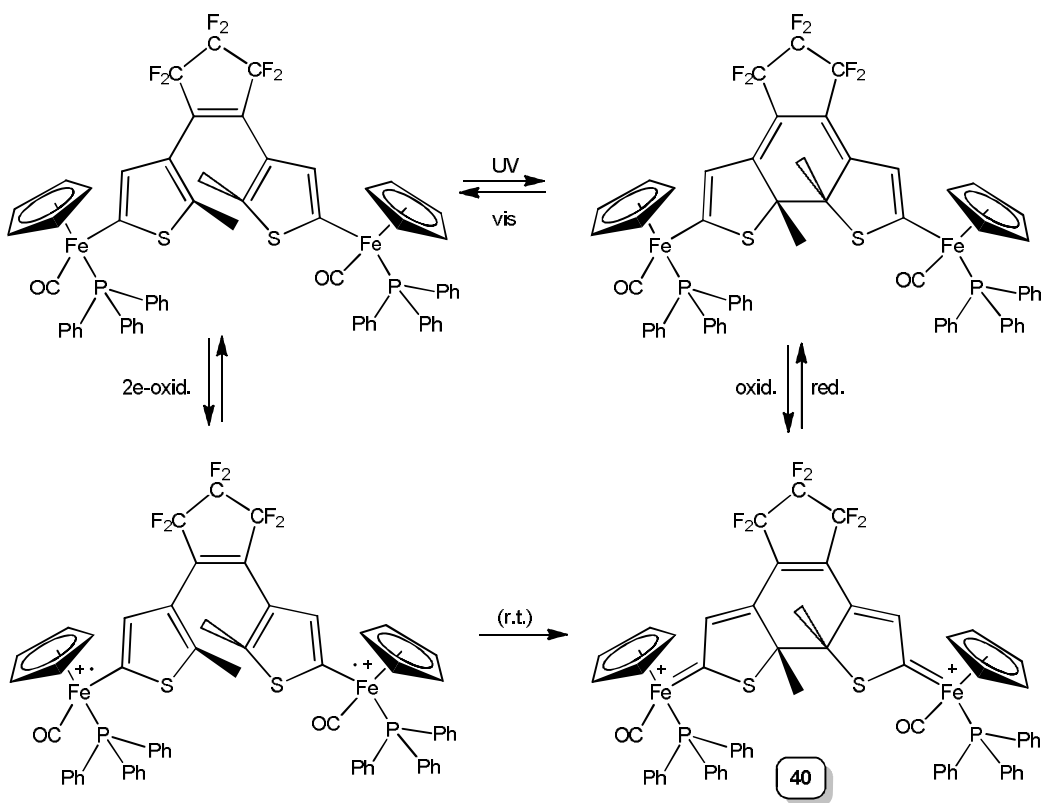


Fig. 24. Electro- and photochemical generation of a biscarbene complex **40** in switching mechanisms [83].

2.3.4. Fischer carbene complexes with α -alkynyl substituents (iv)

The reactivity of Fischer carbene complexes containing α,β -unsaturated carbon substituents with a variety of organic substrates have been thoroughly investigated and

extensively reviewed [1-11,84-87]. Well-known classes of monocarbene complexes used as precursors in organic synthesis via organometallic intermediates are those displaying carbene substituents with α -unsaturated carbon-carbon bonds. One of the first examples studied was the Dötz-reaction whereby 1-alkenylcarbene substituents of a group 6 transition metal carbonyl reacts with an alkyne in a [3 + 2] or [3 + 2 + 1] cycloaddition reaction [84]. This reaction has found wide application in organic synthesis.

Monocarbene precursors with 1-alkynyl carbene substituents are also widely used and react with a variety of substrates containing functional groups and unsaturated carbon-carbon chains [85]. Nucleophiles will generally attack either the β -carbon of the chain or the carbene carbon atom, while many possibilities exist for cycloaddition reactions at these reaction sites. Only recent examples affording multicarbene intermediates are considered here.

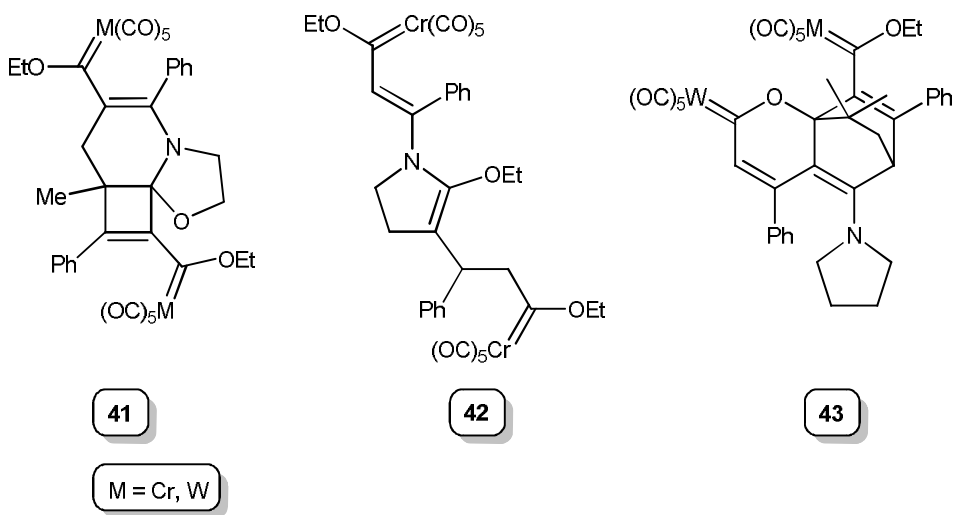
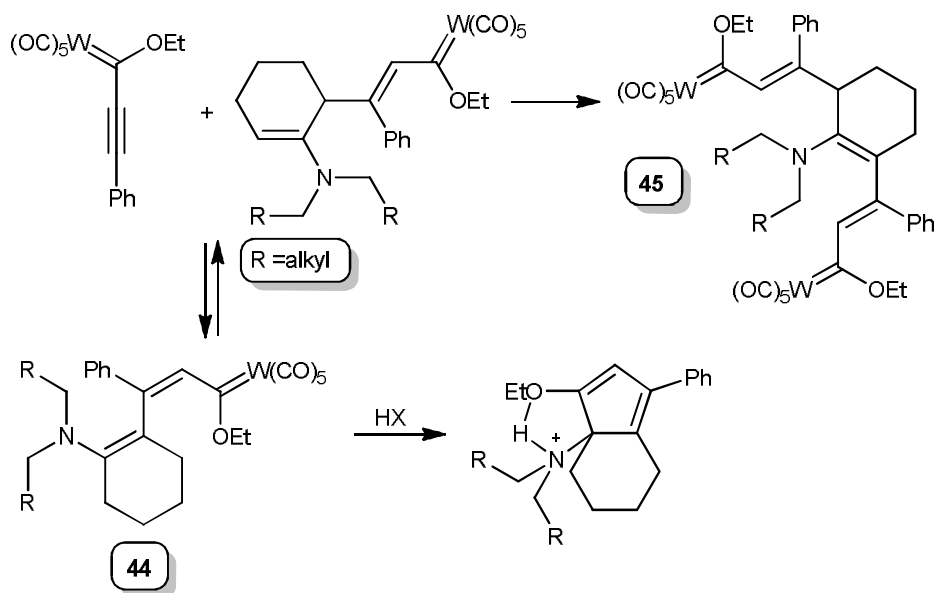


Fig. 25. Cycloaddition reaction products from 1-alkenylalkoxycarbene precursors.

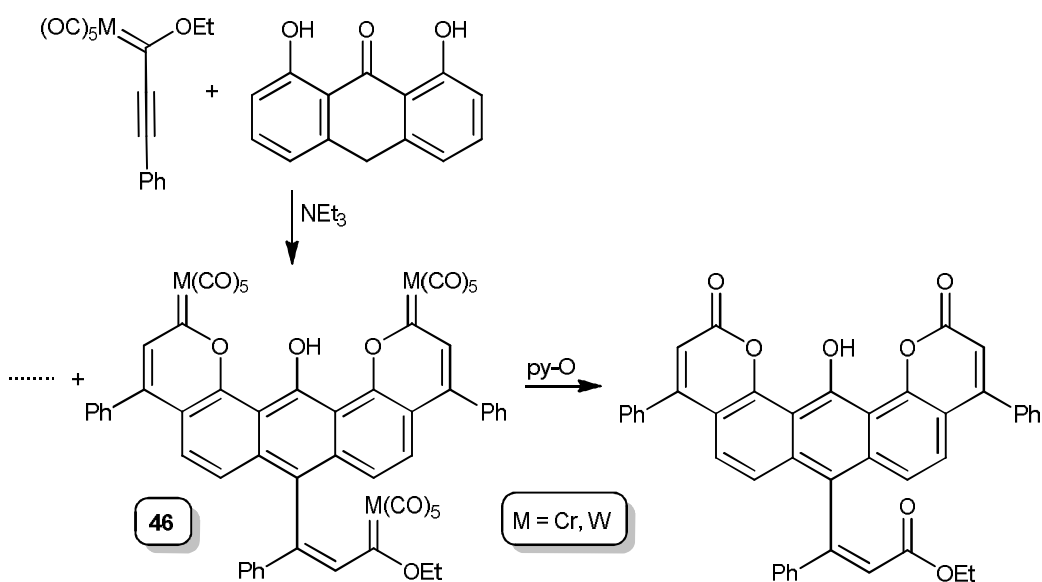
Consecutive [4 + 2] and [2 + 2] cycloaddition of 2-isopropenyl-2-oxazoline to 1-alkynyl Fischer carbene complexes $[M(CO)_5 \{=C(OEt)CCPh\}]$ afforded bis-carbene complexes (Fig. 25, **41**) with a bridging spacer containing novel four, five and six membered condensed rings [88]. Reactions of 1-alkynyl Fischer carbene complexes of chromium and tungsten with an azabicyclo[3.2.0]heptene core rearranges over silica gel to a modified bis-carbene complex (**42**) [89]. The dinuclear bis-carbene complexes (**43**) were

prepared by a [4 + 2]-cycloaddition reaction of pyrilium carbonylmetalate to 1-alkynylcarbene complexes by Aumann and co-workers [90].



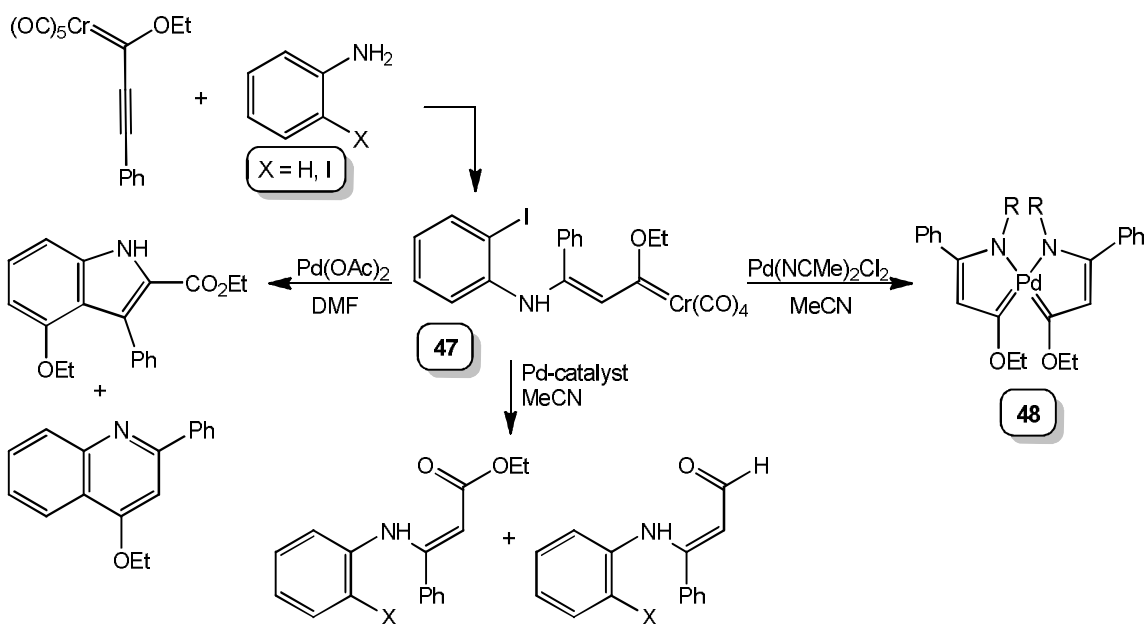
Scheme 13.

The products generated from 1-aminocyclohexenes and 1-alkynylcarbene complexes were found to be determined by the reaction conditions (Scheme 13). When the alkyne was slowly added to the amine a [2 + 2]-cycloaddition reaction occurred with a hydrogen transfer to open the four-membered ring and produce the monocarbene complex **(44)** as an intermediate. With **44** in excess this intermediate will eliminate cyclopentadienes after protonation. If the order was reversed and the alkyne was in excess during the reaction, the major product obtained was the ditungsten biscarbene complex **(45)** [91].



Scheme 14.

The reactivity of the anti-psoriasis drug dithranol with 1-alkynyl Fischer carbene complexes in the presence of base were studied under controlled conditions. The base induced C- and O-additions, electrophilic aromatic substitution and cyclization reactions occurred at up to five positions of dithranol. The multiple polyphenolic products included mono-, bis- and triscarbene complexes which could effectively be oxidized with pyridine-*N*-oxide to the corresponding esters. The solvent dependence of dithranol during conversions provides a new synthetic approach to functionalize the drug and could be valuable for medical purposes. The synthetic procedure presents a route to aromatic polyketides. Scheme 14 shows the formation of a triscarbene **46** and its oxidation to the tri-ester [92].

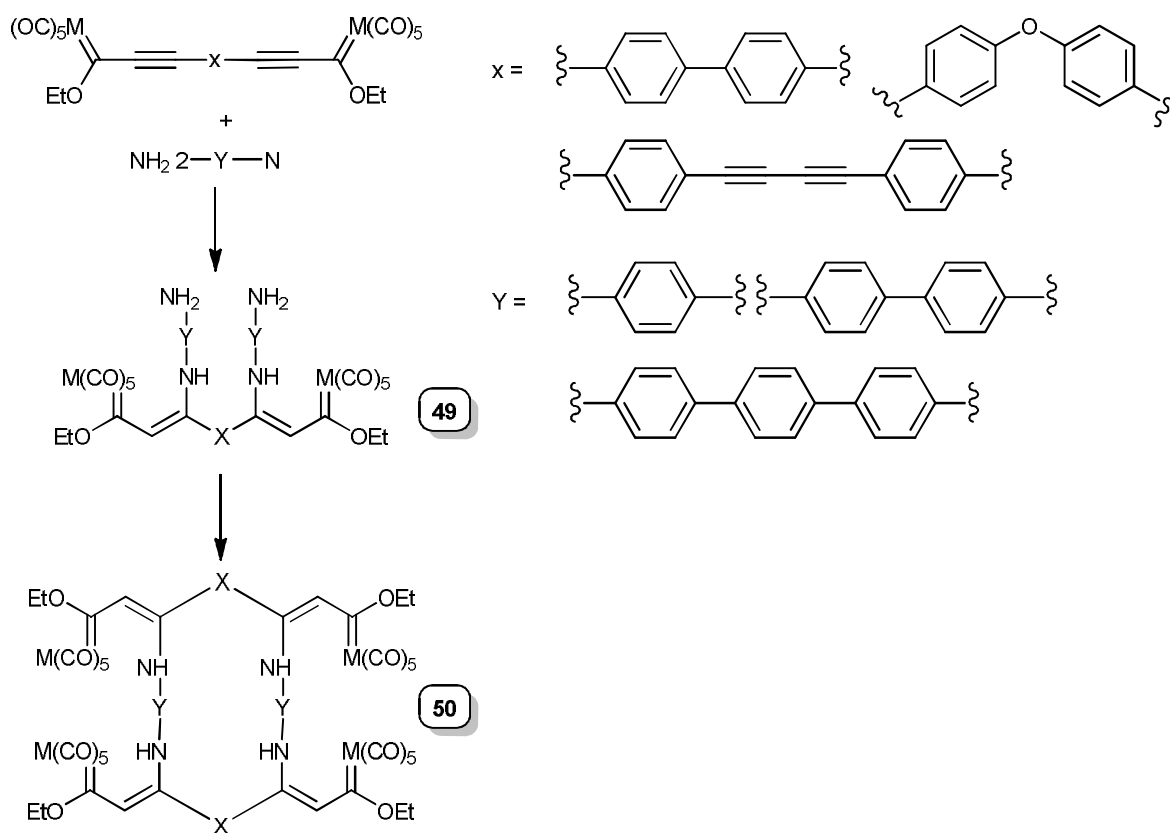


Scheme 15.

The nucleophilic addition reaction of aniline or *o*-iodoaniline with 1-alkynylcarbene complexes of group 6 transition metals (Scheme 15, **47**) afforded β -arylamino carbene complexes which were treated with various Pd-catalysts under different reaction conditions. The reaction route in DMF favors an initial oxidative addition reaction followed by intramolecular cyclization reactions; unlike for acetonitrile where the transmetalation route afforded aldehydes and esters as well as the stable pallada-biscarbene complex [34].

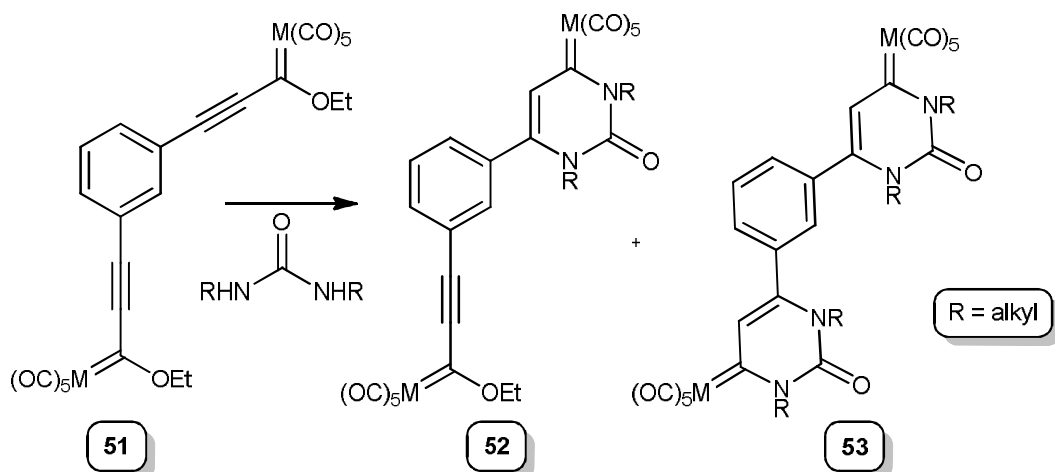
The nucleophilic attack of a terminal amine of the bisamine substrate, at the β -carbon of a 1-alkynylcarbene moiety at both sides of the bridging biscarbene ligand, afforded a modified biscarbene complex with two dangling amine groups (Scheme 16, **49**). A subsequent reaction with a second bis-1-alkynylcarbene precursor afforded a tetrametallic macrocyclic Fischer tetracarbene complex **50**. Variation of the number of 1,4-substituted benzene rings between the amine groups is a way of controlling the distance between the biscarbene strands. The method allows for attaching biscarbene strands of different transition metals by the connecting amine groups. Selection of the alkynylcarbene substituent, spacers and linkers allows for the construction of macromolecules with

multiple carbene ligands and represents an entry into the field of metal organic frameworks of different dimensions and arrangements [93,94].



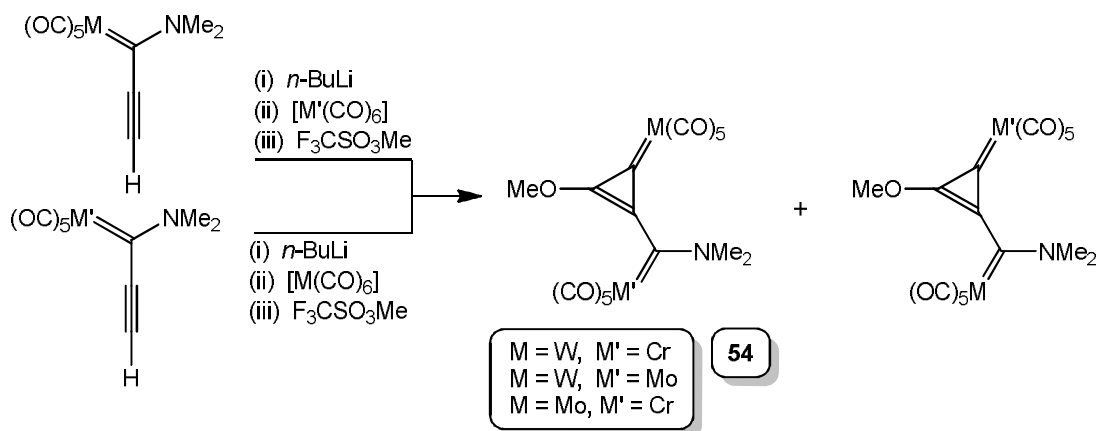
Scheme 16.

1-alkynyl alkoxy biscarbene complexes (Scheme 17, **51**) react with ureas in cycloaddition reactions to give mono- (**52**) and bisuracil (**53**) biscarbene complexes. The mono-uracil complex is asymmetric and display two carbene ligands with very different reactivities [95]. The electrophilic β -carbon can be exploited by the reaction of the alkynyl unit with a primary amine in a 1,4-Michael addition reaction to give an enamine.



Scheme 17.

In ongoing work, the lithiation of the β -carbon of dimethylamino(1-ethynyl)carbene of tungsten pentacarbonyl can be reacted with iodine and tris(*n*-butyl)stannylchloride to give iodoethynylcarbene and the stannylated ethynylcarbene complexes, respectively. These two ethynylcarbene complexes react in a carbon-carbon coupling reaction catalyzed by $[\text{Pd}(\text{CNMe})_2\text{Cl}_2]$ to give a biscarbene with a C_4 -, C_8 - and C_{12} -spacer linking the two carbene carbon atoms [11].



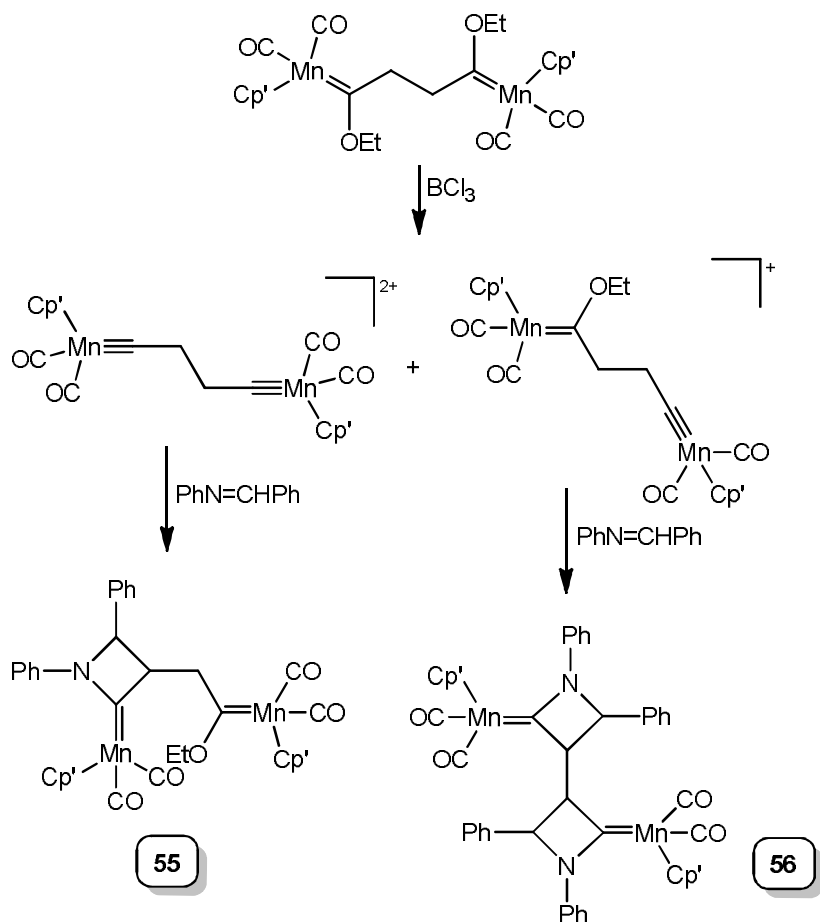
Scheme 18.

The reaction of the dimethylamino(1-ethynyl)carbene with butyllithium (Scheme 18) afforded the deprotonation at the β -carbon and after subsequent reaction with a group 6 transition metal followed by alkylation with magic methyl yielded the novel biscarbene

complexes **54**. The proposed mechanism includes attack on a carbonyl ligand, migration of the metal fragment to the adjacent carbon atom and alkylation at the terminal oxygen atom [96]. Repeating the reactions with two different metal carbonyls yielded two isomers of the aminocarbene-cyclopropenyldiene complex, where the two metal pentacarbonyl moieties had exchanged sites. Since the aminocarbene-cyclopropenyldiene biscarbene complexes do not interconvert, the authors proposed that isomerisation must occur during the course of the reaction sequence. A possible mechanism involving $M(CO)_5$ migration along the carbon chain, ring formation, ring enlargement and ring contraction was postulated.

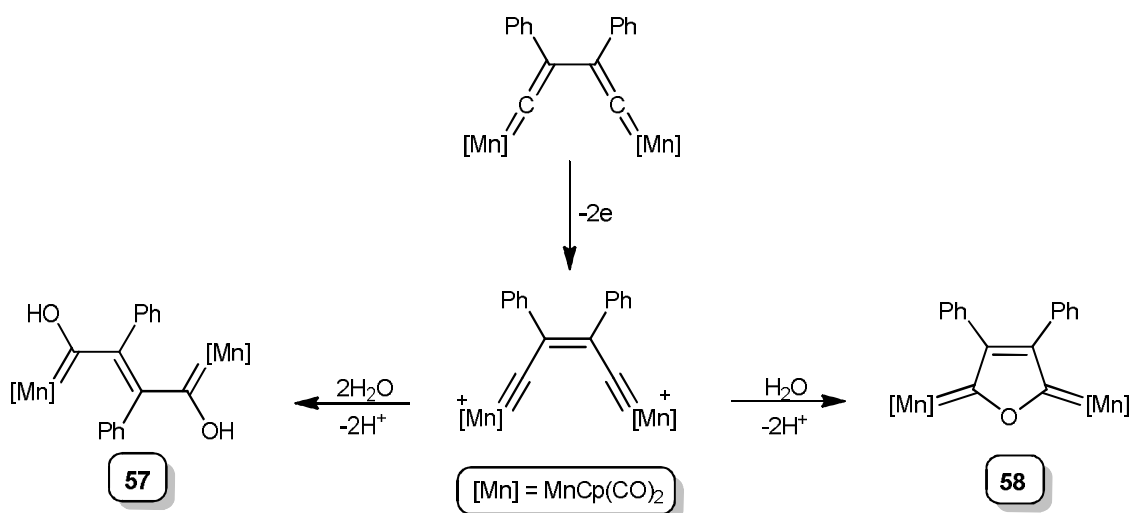
2.3.5. *Metal carbyne complexes as intermediates or precursors to biscarbene complexes (v)*

The bridging bis(carbene)dimanganese complex $[MnCp'(CO)_2\{C(OEt)CH_2CH_2C(OEt)\}MnCp'(CO)_2]$ (Scheme 19) can be converted by reaction with BCl_3 to carbene/carbyne and carbyne/carbyne mixtures. After reacting the mixture with $PhN=CHPh$, the mono- and bisazetidinyldiene dimanganese complexes **55** and **56** could be isolated [71].



Scheme 19.

The oxidative activation of the manganese bisvinylidene complexes $[\{\text{MnCp}(\text{CO})_2\{=\text{C}=\text{CPh}\}\}_2]$ towards the addition of a nucleophile was investigated (Scheme 20). Two electron oxidations lead to the formation of a dicationic biscarbyne complex which was isolated as a THF-solvate. In the reaction of the biscarbyne with water, the water adds to one of the carbyne carbon atoms which on the release of a proton afforded a hydroxycarbene intermediate **57**. Intramolecular cyclization as a result of the attack of the oxygen on the second carbyne gave, after the elimination of a second proton, the biscarbene complex **58** shown in Fig. 26 [97].



Scheme 20.

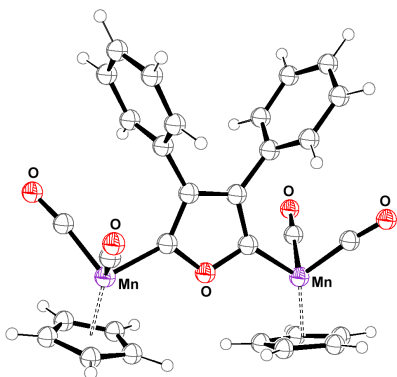
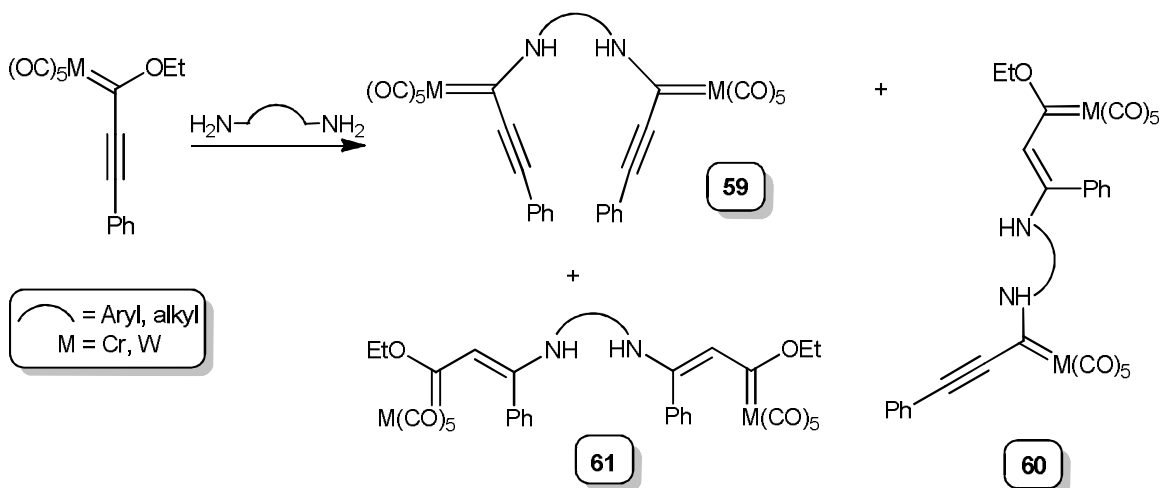


Fig. 26. Molecular structure of $[\{\text{Mn}(\eta^5\text{-Cp})(\text{CO})_2\}_2(\mu\text{-C}_4\text{Ph}_2\text{O})]$ (**58**) [97].

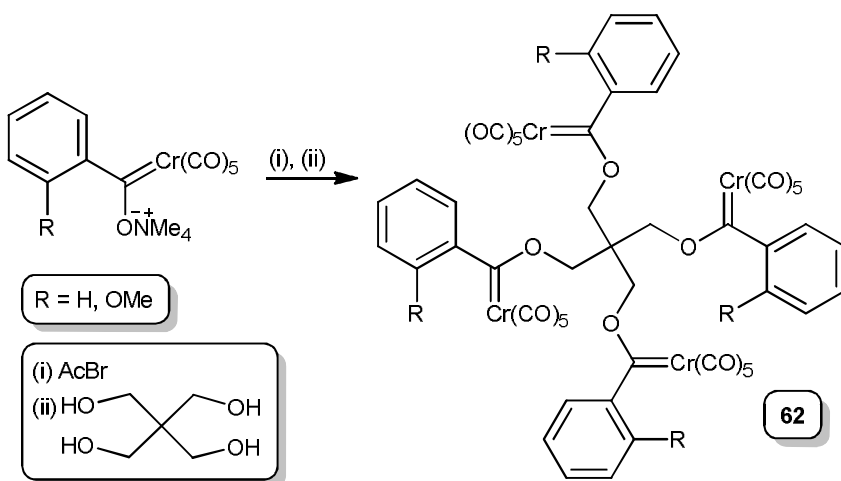
2.4. Carbene ligands linked via the heteroatom substituent (IV)

The role of the reaction conditions, electronic and steric effects of substituents on 1,2-primary and secondary diamines during aminolysis reactions of 1-alkynyl alkoxy-carbene complexes were investigated (Scheme 21). It was found that aminolysis (**59**) was in competition with nucleophilic addition reactions (**60** and **61**) at the alkyne β -carbon atom, but intramolecular cyclization reactions were not observed. The steric bulk of the ethylene played an important role and the bulky substituents favored monoaminolysis. Lower reaction temperatures favored aminolysis [98]. Electron-spray ionization mass spectra were recorded for anionic mono- and bisaminocarbene complexes and revealed an initial capture of an electron from the ESI-MS source [99].



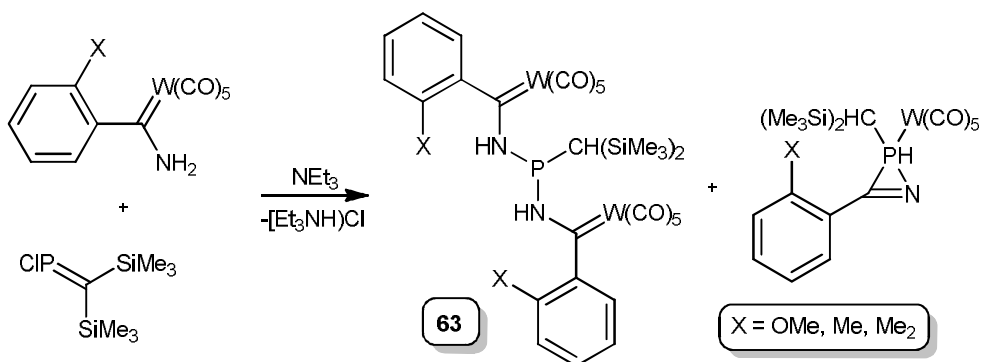
Scheme 21.

The synthesis of the tetrakis(alkoxy)carbene complexes (**62**, Scheme 22) requires firstly the exchange of the lithium counter ion with tetramethylammonium cation and secondly the conversion of the acylate to an acyloxycarbene intermediate [100]. Four equivalents of the acyloxycarbene reacted with pentaerythritol in an alcoholysis reaction to give the tetraalkoxycarbene complex. The molecular structure of the tetrakis(alkoxy)carbene complex displayed a distorted tetrahedron with a C_1 -center and because of the branched repetitive carbene fragments it can be viewed as a first generation dendrimer. The tetrakis(alkoxy)carbene complexes underwent a complete benzannulation reaction at all four carbene centers when reacted with 3-hexyne.



Scheme 22.

Substrates with more than one site to attach either by reaction such as aminolysis or other ways at the heteroatom of a Fischer carbene complex are versatile building blocks to construct multimetal and multicarbene macromolecules. Two aminocarbene complexes $[W(CO)_5\{=C(NH_2)C_5H_4R\}]$ were connected with a NPN-linker after reaction with the phosphines $P(=C(SiMe_3)_2)Cl$ (Scheme 23, **63**) [101].



Scheme 23.

2.5. Doubly bridged biscarbene complexes and biscarbene complexes with two separate bridges (V)

Such compounds are scarce but are found more commonly in Section 3 on multimetal biscarbene complexes.

3. Multimetal Fischer carbene complexes

The incorporation of different transition metal moieties in complexes has been widely investigated to study the role of different metal fragments on the reactivity of ligands and the chemistry of the complexes [102-104]. 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 carbon [65,96,98] or the carbene ligand is used as a connector to bridge the other transition metals [11,64,69,73,74]. In the ten years since Sierra's review article [11], very few applications of these multimetal complexes have been reported considering the interest in the cooperative mechanism of metals in catalytic transformations and the

ability of the electropositive metals to effect modulation of reactive centres otherwise not possible by traditional organic fragments; and there is still little known about the reactivity of this type of Fischer carbenes.

In this section, the synthesis and application of multimetallic carbene complexes will be discussed where a second metal (or more) is bonded either directly to the carbene carbon atom, or within close proximity as a metal-containing carbene carbon atom substituent. These multimetal carbene complexes have been grouped into classes **VI** – **X** in Fig. 27.

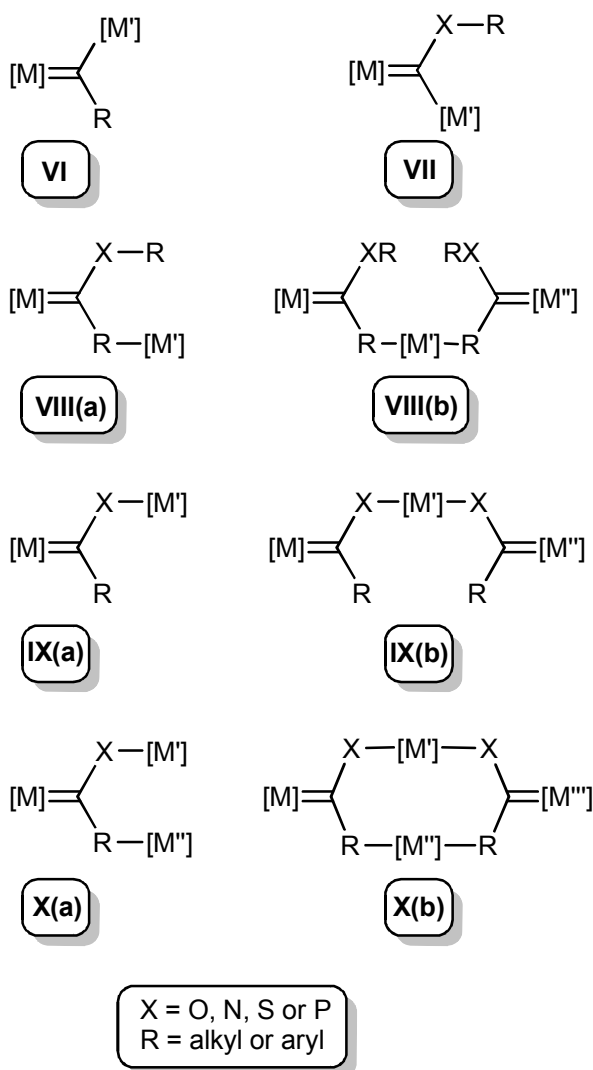
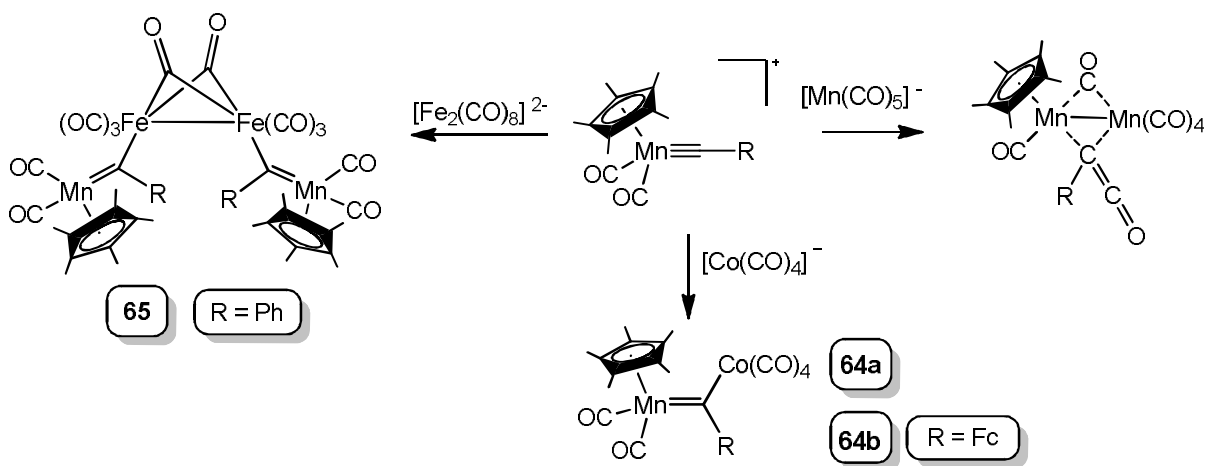


Fig. 27. Classes of multimetal carbene complexes.

3.1. Metal fragments bonded directly to the carbene carbon atom

3.1.1. Complexes containing a carbene carbon metal substituent in the absence of a carbene heteroatom (VI)

This class of multimetal carbene complexes, where a metal is directly bonded to the carbene carbon atom (Fig. 27, VI) was included even though it does not strictly adhere to the demarcation of heteroatom-stabilized Fischer carbenes. The classification of Fischer carbenes as singlet carbenes bonded to low-valent transition metals containing π -acid co-ligands, however, holds for these complexes. Very few examples of this class of carbene complexes exist. A number of complexes containing μ -CR ligands between two transition metals have been reported [107-118] but are structurally confirmed as having bridging *carbyne* ligands. The first examples of carbene complexes with a transition metal α -bonded to the carbene carbon were prepared by reaction of the corresponding cationic carbyne complexes with a carbonyl metalate (Scheme 24) [119].

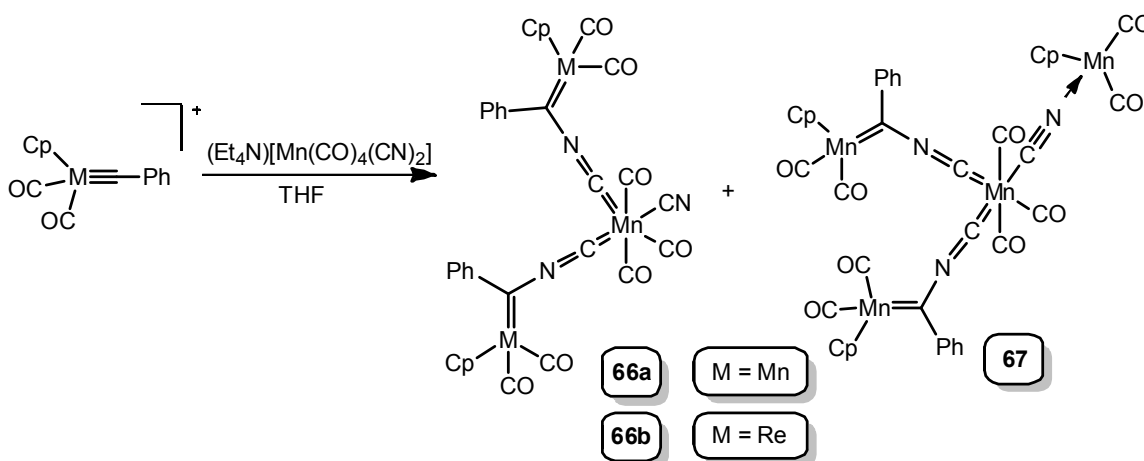


Scheme 24.

While reaction of $[\text{MnCp}^*(\text{CO})_2\text{CR}]^+$ with $\text{Na}[\text{Co}(\text{CO})_4]$ gave the desired carbene complexes **64**, the analogous reaction with $\text{K}[\text{Mn}(\text{CO})_5]$ gave only the more stable ketenyl complexes of which the molecular structure could be confirmed by X-ray crystallography [120]. By employing the dimeric carbonyl dianion $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$, the reaction yielded probably one of the first examples of a multimetal multicarbene complex **65**, where the transition metals are bonded directly to the carbene carbon atom.

Trinuclear biscarbene complexes of group 7 transition metals were synthesized from the reaction of cationic carbyne complexes with anionic cyanide complexes of manganese (Scheme 25). It was proposed that a nitrogen of the cyanide ligand attaches to the carbyne ligand through the nitrogen atom. Substitution of a carbonyl by a cyanide ligand from another molecule again generated an anionic, now tricyano, intermediate which reacts with a second carbyne complex to afford a trinuclear biscarbene complex (**66**) with CN linkers [121].

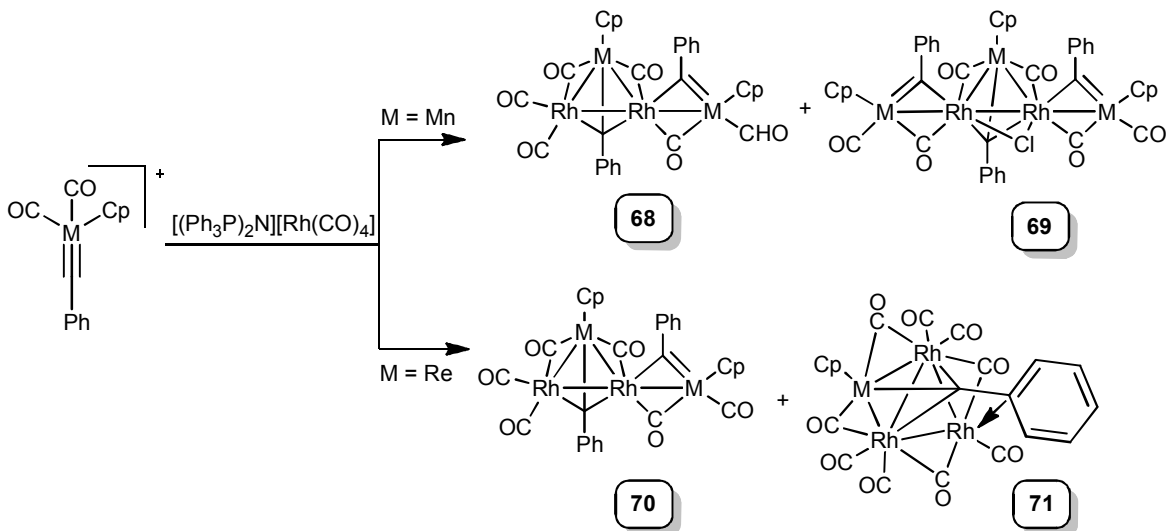
A difference in reactivity was observed in the expansion of this study to tri- and tetranuclear complexes. The reaction of $\text{Et}_4\text{N}[\text{Mn}(\text{CO})_4(\text{CN})_2]$ with the manganese carbyne complex gave both a trinuclear (**66a**) and a tetranuclear (**67**) biscarbene manganese complex, while reaction with the rhenium analogue yielded only the trinuclear rhenium biscarbene **66b**.



Scheme 25.

A more recent example of the reaction of cationic carbyne complexes of manganese and rhenium with $[\text{Rh}(\text{CO})_4]^-$ gave either the novel $\text{M}_2\text{-Rh}_2$ mixed-metal bridging carbyne complexes clusters **68-70**, or the Re-Rh_3 mixed-pentametal bridging carbyne complexes **71** (Scheme 26) instead of the expected carbenes [122]. It was found that different carbonyl metal anions greatly affect the reactivity of the cationic metal carbyne complexes and resulting products [119,123]. This class of compounds, and the reactions

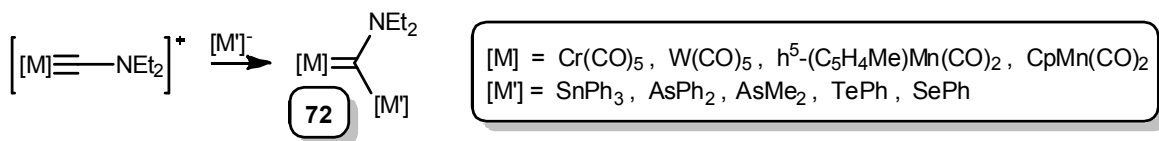
leading to the bridged carbene/carbyne ligand systems in clusters, is an area neglected in recent years.



Scheme 26.

3.1.2. Complexes containing a Fischer carbene carbon metal substituent (VII)

As far as we could ascertain, the only examples of class **VII** type multimetal carbene complexes (a heteroatom-substituted Fischer carbene complex with a metal-atom bonded to the carbene carbon, Fig. 27) that could be found, contain metalloid atoms rather than transition metals bonded to the carbene carbon (Scheme 27, **72**) [124,125]. The only other relevant complexes, resembling the type of complex where the second transition metal is directly bonded to the heteroatom-substituted carbene carbon atom, are once again older examples of bridging carbyne complexes, albeit carbyne carbon atoms substituted by heteroatoms such as oxygen, nitrogen and sulphur [126-128].



Scheme 27.

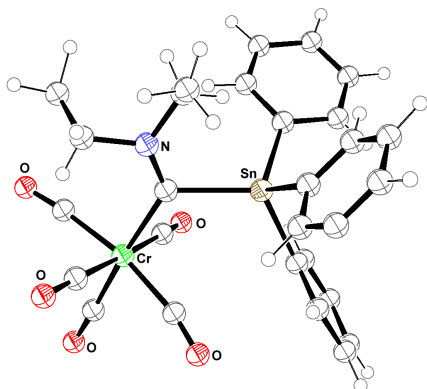


Fig. 28. Molecular structure of $[(\text{CO})_5\text{Cr}=\text{C}(\text{NEt}_2)(\text{SnPh}_3)]$ (**72**) [129].

3.2. Complexes with a metal fragment bonded to the carbene substituent (**VIII**)

This class of di- or trimetallic carbene complexes has the two metal centers joined through C-C bonds on the carbene carbon atom (monocarbene **VIII(a)** and biscarbene **VIII(b)**, Fig. 27). 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 [102]. 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 [130].

3.2.1. π -aryl monocarbene complexes **VIII(a)**

Applying the principle of σ , π -bridging ligands to Fischer carbene complexes of the type $[\text{M}(\text{CO})_5\{\text{C}(\text{OR}')\text{R}\}]$, π -bonded aryl or heteroaryl ligands have long been used to establish electronic contact of the R-substituent or the alkoxy R'-substituent with the carbene carbon atom. One of the first examples to be synthesized was the complex $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})(\eta^1:\eta^6\text{-PhCr}(\text{CO})_3)\}]$ (**73**) containing a π -conjugated phenyl ring [131] 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 6 transition metals were synthesized to study the electronic effects of the ferrocenyl substituent on the carbene ligand [132] as part of an investigation into the electron withdrawing nature of metal

carbonyl carbene groups. Fischer reaction of ferrocenyllithium with $[M(CO)_6]$ ($M = Cr, W$) and subsequent alkylation with either Me_3OBF_4 or Et_3OBF_4 gave the first heterodimetallic carbene complexes **74** $[M(CO)_5\{C(OR)Fc\}]$ ($M = Cr, W$ and $R = Me, Et$). Ferrocenes provide extraordinary stabilization of adjacent electron deficient centres, comparable to amino substituents for example [133], and the electron transfer behaviour of metal carbene complexes can be greatly influenced by the presence of additional metal centres [82]. 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 [134], illustrating some electronic communication between the above mentioned moieties and the donor-acceptor interaction of the couple.

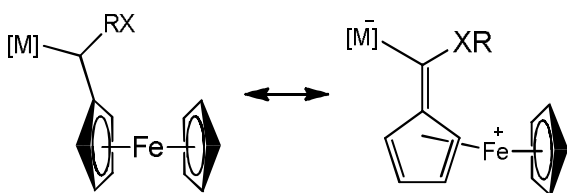
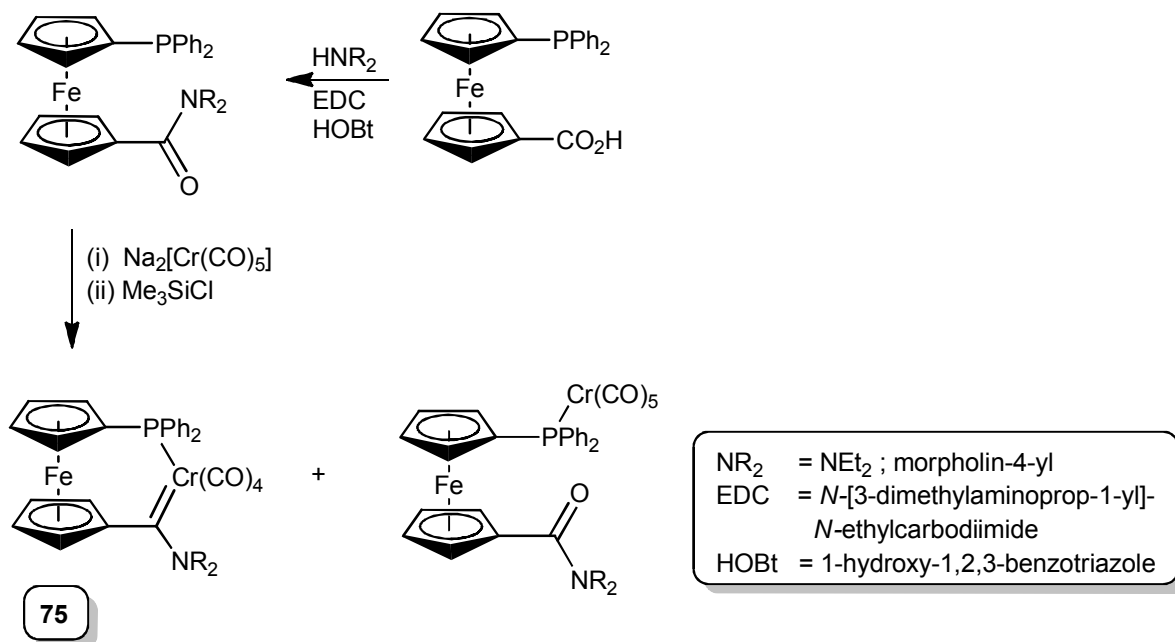


Fig. 29. Resonance interaction between the ferrocene Cp ring and the carbene carbon atom in $[M(CO)_n\{C(XR)Fc\}]$ complexes.

It seems that there is still not a clear answer to the extent of electronic communication between the M_{carbene} and the $M_{\pi\text{-aryl}}$. In the presence of two nonconjugated metal carbene moieties in homo- and heterobimetallic biscarbene complexes, these moieties behave as two independent monocarbene entities [81], but on the other hand, it has been cautioned that the electrochemical parameters of $[M(CO)_5\{C(X)Fc\}]$ complexes encompass both the redox M^0 and Fe^{2+} centers, as the HOMO is not simply localized at the former [135]. Another electrochemical study of ferrocenyl carbene complexes involved the reaction of ferrocene amides $(Ph_2P)Fc'C(O)NR_2$ (Scheme 28) with $[Cr(CO)_5]^{2-}$ in the presence of Me_3SiCl to give the respective P-chelated carbene complex $[Cr(CO)_4\{(Ph_2P)Fc'C(NR_2)-\mu_2-C,P\}]$ (**75**) (Fig. 30) and a ferrocenylamide-substituted phosphine complex [136]. An electrochemical analysis showed that the starting 1-diphenylphosphino-1'-amidoferrocene compound and the ferrocenylamide phosphine complex of chromium behave as a simple

ferrocene and two localized redox systems (ferrocene and chromium), respectively. The carbene **75** however, is an electronically delocalized system, where the redox change probably occurs in the whole molecule.



Scheme 28.

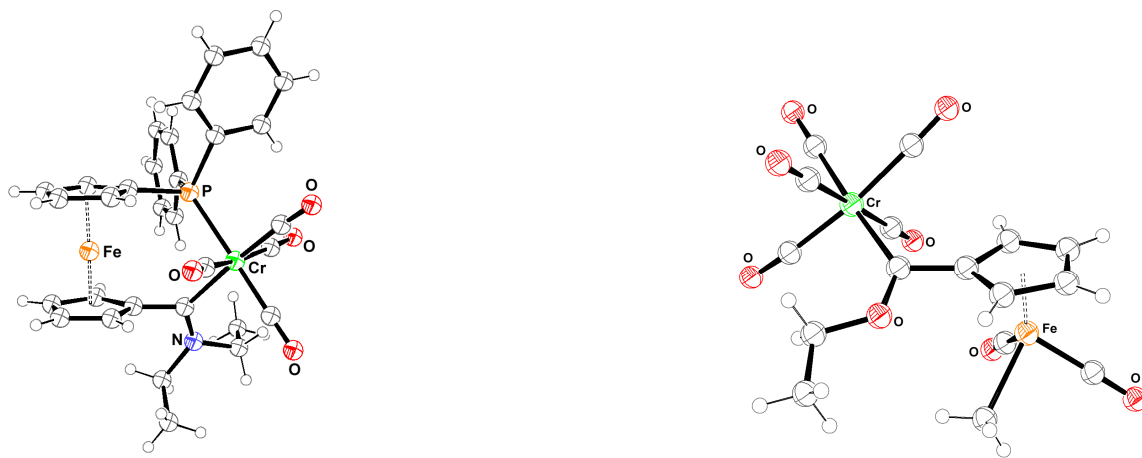


Fig. 30. Molecular structure of $[\text{Cr}(\text{CO})_4\{(\text{Ph}_2\text{P})\text{FcC}(\text{NR}_2)\text{-}\mu_2\text{-C,P}\}]$ (**75**) [137] and $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})(\text{CpFe}(\text{CO})_2\text{Me})\}]$ (**76**) [137].

Support for this finding was again seen in the cyclic voltammetric results obtained for a number of cyclopentadienylcarbene iron half sandwich complexes **76** [137,138]

(Fig. 31). In all cases, only one reduction and only one oxidation were observed (so that both metal atoms participate in one molecular orbital) although there are two redox active metal atoms in the molecule [139]. This was in direct contrast to the recent electrochemical results obtained where heterodimetallic carbene complexes with a π -aryl metal carbene substituent showed that the two metal moieties in each complex function as separate, localized redox centres [140]. This implies that a direct comparison of substituent effects on the pentacarbonyl metal can be made. See Table 1, in which a summary of the E° for the related chromium complexes are given.

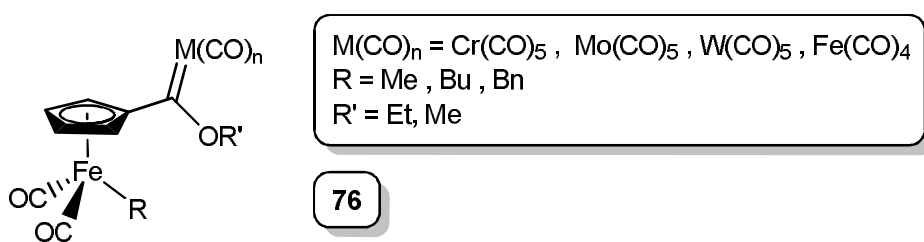
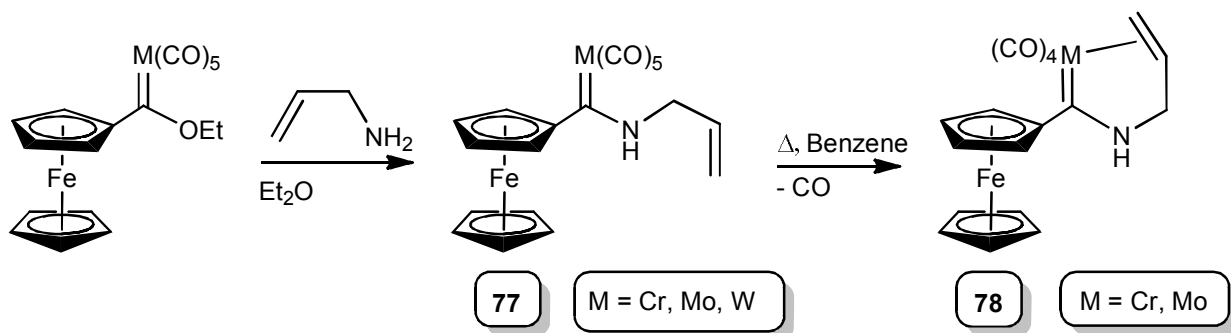


Fig. 31. Monocarbene complexes with redox-active CpFe-substituents.

In an attempt to improve early synthetic approaches to ferrocenyl carbene complexes López-Cortés *et al.* reported the synthesis of ferrocenylalkoxycarbene complexes of chromium, tungsten and molybdenum (Scheme 29) [141]. The aminolysis of these carbene complexes with unsaturated amines were described. The authors also reported the first X-ray structural characterization of such complexes **78** (Fig. 32).



Scheme 29.

Early hints of the increased stability and modified reactivity of ferrocenylcarbene complexes were reported by Dötz *et al.* [142]. Reaction of these ferrocenylcarbene complexes with tolan gave unexpected furanoid products in an alkyne, carbene and CO cyclization mode over the customary Dötz benzannulation that yields chromium-coordinated hydroquinones [143]. If an *o*-phenylene spacer was employed to remove the chemodirecting steric effect of Fc, heterobimetallic fused arenes from benzannulation reactions result [144]. As an extension of this work, the study of 1-ferrocenyl substituted chelated (η^2 -alkene) aminocarbene complexes were expanded to include different alkenyl-substituents, eg. hydroxyl-groups [145]. This was done to further investigate the potential handle on the overall complex reactivity of such η^2 -bonded exometallacyclic ligands.

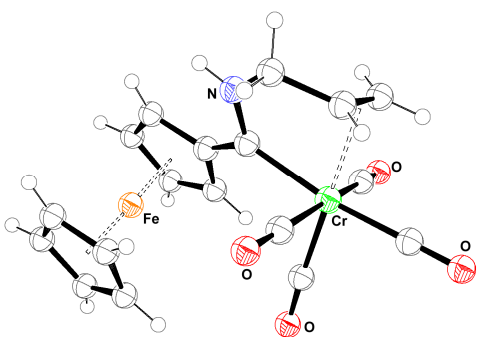


Fig. 32. Molecular structure of $[(\text{CO})_4\text{Cr}=\text{C}(\eta^2\text{-NHCH}_2\text{CHCH}_2)(\text{Fc})]$ (**78**) [141].

Table 1. Oxidation potentials for relevant π -aryl carbene complexes of chromium

Complex	E° (V)	Ref.
74 M = Cr, R = Et	0.31	[136]
74 M = Cr, R = Me	0.30	[136]
75 M = Cr, R = Et	-0.13 0.23	[136]
76 M = Cr, R = Me, R' = Et	0.64	[137]
76 M = Cr, R = Bn, R' = Et	0.63	[137]
78 M = Cr	-0.10 0.10 0.28 0.82	[145]
95 M = Cr	0.47	[139]
104 M = Cr	0.22	[159]

126 M = Cr	0.45		[159]
127 M = Cr	0.23	0.48	[159]
128 M = Cr	0.22	0.41	[159]
130 M = Cr	0.10	0.32	[159]

From the cyclic voltammetric results obtained, it was found in general that the ligation of the olefinic C=C bond diminished the donor effect of the Fc substituent. The carbene function is hereby maintained as relatively electrophilic. The whole complex is less prone to oxidation than the ferrocenylcarbene complexes with uncoordinated side-arm alkenes. A continuation of this study on the polymetallic π -bridged carbene complexes (of the type M- π -M'- π -M'') [134] (see Section 2.3.4) focused on the interaction between the carbene fragment and the central metal nucleus [81]. Here, ESI-MS was employed to study the electron transfer processes. A series of carbene complexes (Fig. 33) were synthesized that incorporated an extra metal centre. These included ferrocenyl carbenes **74**, **79** and **80**, for the donor ability of Fc in electron transfer reactions, conjugated biscarbenes **81** for interaction between the two M(CO)₅-moieties and **82** and **83** that incorporate the electron acceptor Co₂(CO)₆-moiety. Only when the Fc and the M(CO)₅-fragments were linked by a π -system (**79**, **80**) was electron transfer observed. For **81**, the biscarbenes behaved like the parent monocarbenes while the Co₂(CO)₆ acted as an electron sink, inhibiting any electron transfer to the Cr(CO)₅-fragment.

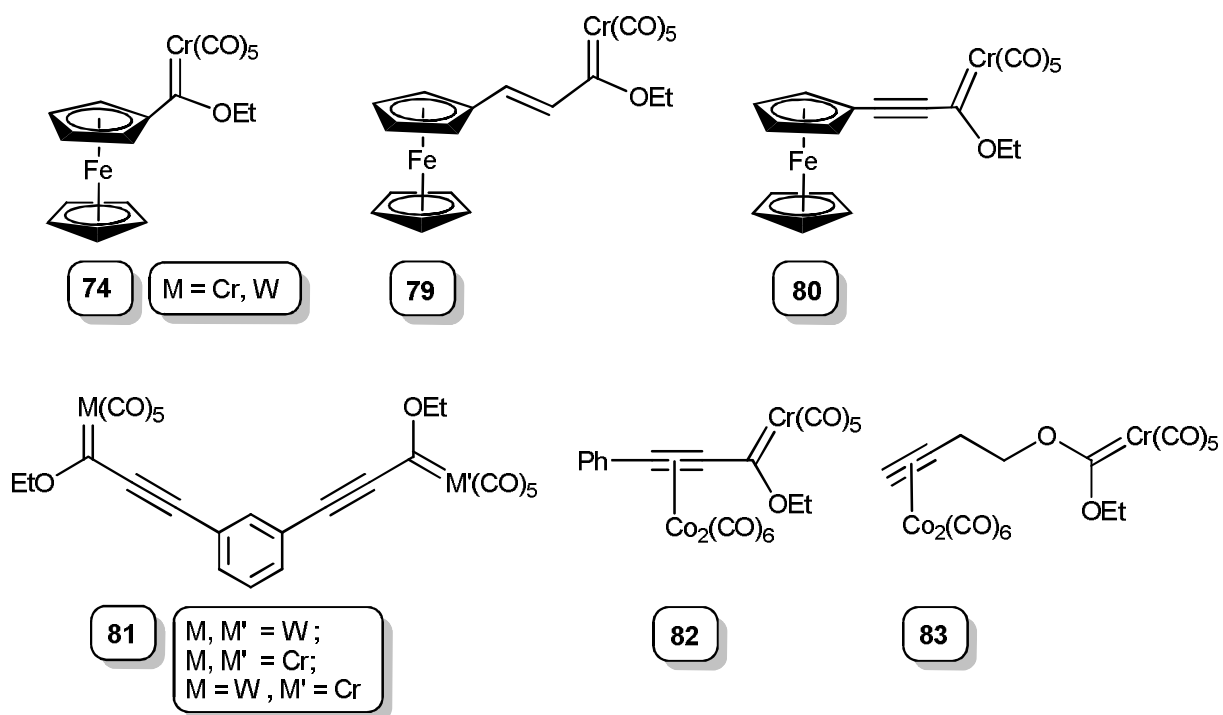
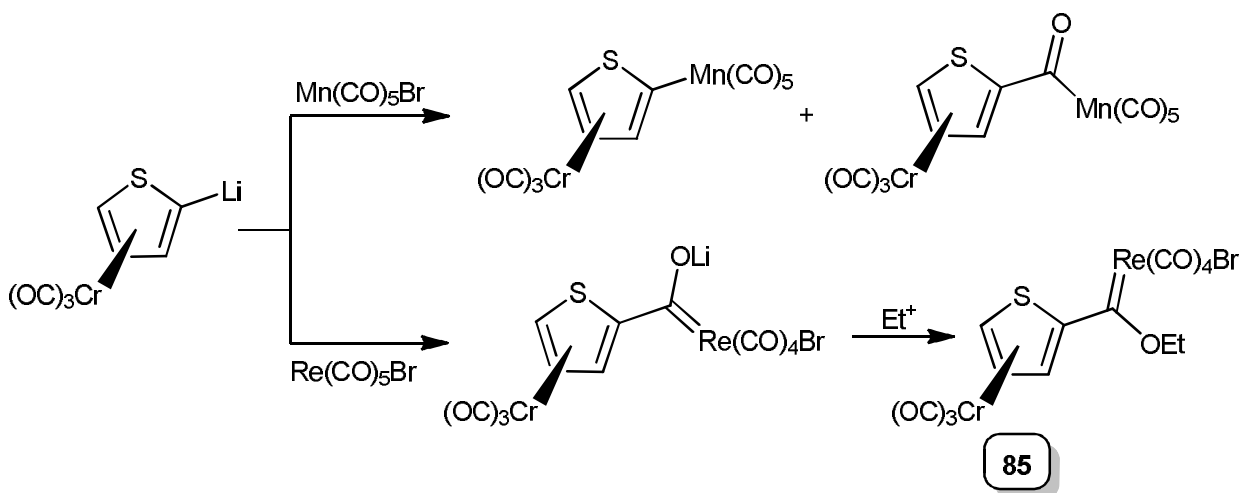


Fig. 33. Di- and trimetallic carbene complexes studied by ESI-MS.

Increasing interest in the pseudo-aromatic five membered rings containing a heteroatom led to the synthesis of **84** $[\text{M}(\text{CO})_5\{\text{C}(\text{OEt})(\eta^1:\eta^5\text{-}(\text{C}_4\text{H}_3\text{S})\text{Cr}(\text{CO})_3)\}]$ ($M = \text{Cr, W}$) in an effort to investigate the effect of π -coordination on the properties of such a carbene functionality [147].



Scheme 30.

Utilising group 7 metal carbonyls instead of group 6 metals illustrated the difference in reactivity of manganese compared to rhenium. The reaction of lithiated $[\text{Cr}(\text{CO})_3(\eta^5\text{-C}_4\text{H}_3\text{S})]$ with $[\text{Mn}(\text{CO})_5\text{Br}]$ involved attack either directly on the metal centre or on a carbonyl ligand with elimination of bromide, as shown in Scheme 30. This yielded the binuclear thienyl complexes $[\text{Mn}(\text{CO})_5(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{S})\text{Cr}(\text{CO})_3]$ and $[\text{Mn}(\text{CO})_5\{\text{C}(\text{O})\text{-}\eta^1:\eta^5\text{-C}_4\text{H}_3\text{S})\text{Cr}(\text{CO})_3\}]$ [148-150].

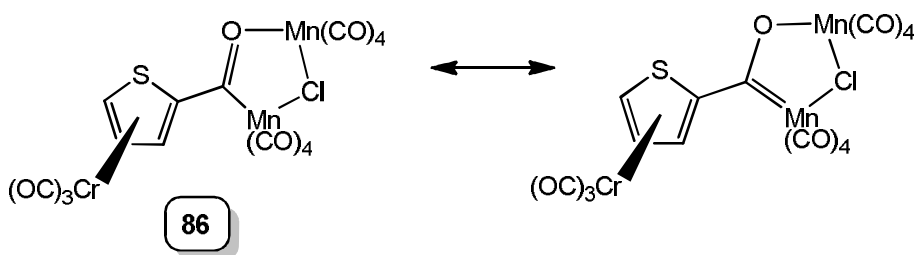


Fig. 34. Contributing structures of the trimetallic π -aryl carbene complex.

Reaction of the lithiated chromium thiophene precursor with three equivalents of $[\text{Mn}(\text{CO})_5\text{Cl}]$ gave the novel complex **86** (Fig. 34 and 35) [149]. The carbenic nature of the trimetallic moiety can be regarded as a resonance form of an *O*-metalated acylate, accompanied by a halogen elimination and subsequent carbonyl substitution at a second $[\text{Mn}(\text{CO})_5\text{Cl}]$.

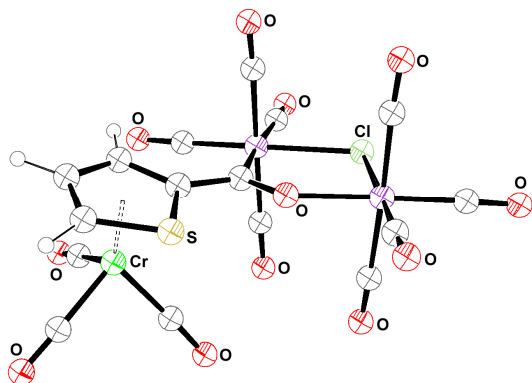
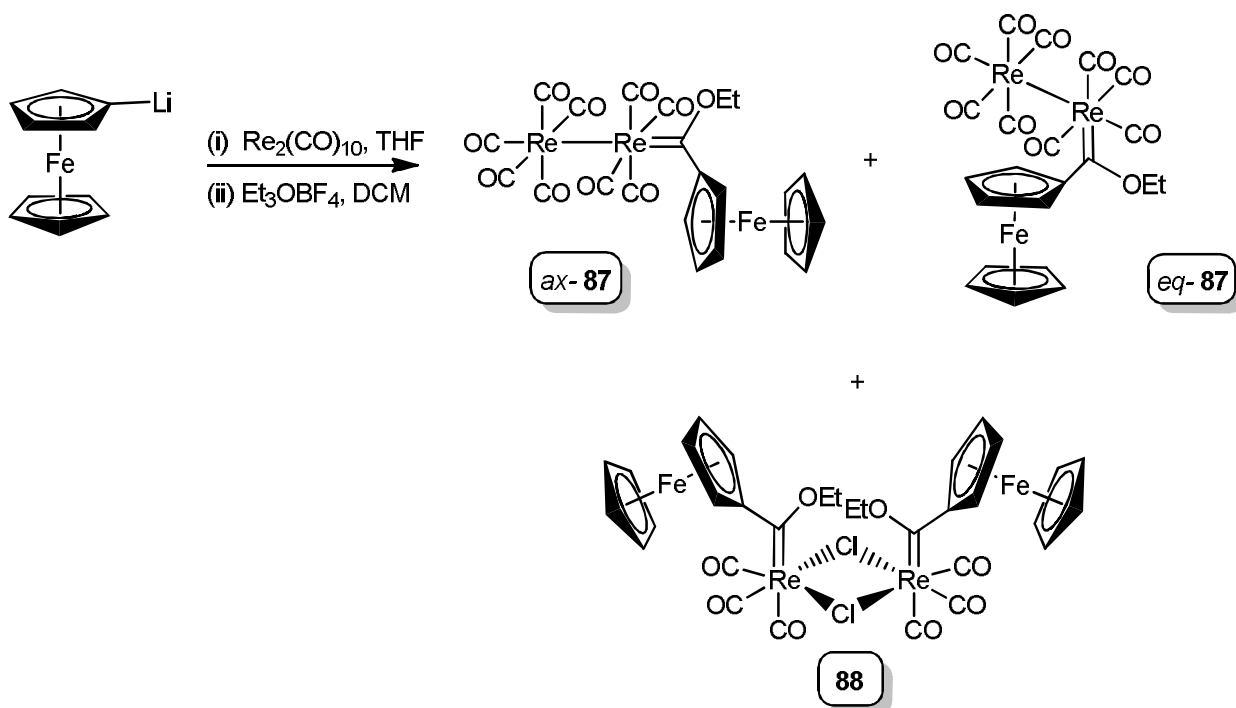


Fig. 35. Molecular structure of $[(\mu\text{-Cl})\{\mu\text{-}(\eta^1:\eta^1:\eta^5\text{-SCHCHCHCC}(\text{O})\text{Mn}(\text{CO})_4)\text{Cr}(\text{CO})_3\}\text{Mn}(\text{CO})_4]$ (**86**) [149].

In contrast, the corresponding reaction with $[\text{Re}(\text{CO})_5\text{Br}]$ (Scheme 30) involved attack on a carbonyl ligand without the elimination of bromide. Subsequent alkylation of the latter with Et_3OBF_4 yielded the carbene complex $[\text{Re}(\text{CO})_4\text{Br}\{\text{C}(\text{OEt})(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{S})\text{Cr}(\text{CO})_3\}]$ (**85**). The possibility of increasing the number of metal fragments in the multimetal complexes was investigated by employing the dinuclear group 7 binary metal carbonyl, $\text{Re}_2(\text{CO})_{10}$ as precursor in the reaction with FcLi [151]. Spectroscopic results indicated a mixture of the equatorial and the axial isomers of the formed monocarbene complexes (**87**) were present in solution, as the steric bulk of the ferrocenyl substituent could force the electronically less favored axial substitution. This is one of the rare examples for dirhenium nonacarbonyl complexes to deviate from equatorially coordinated ligands [152-154]. The presence of a coordinatively unsaturated monorhenium ferrocenyl intermediate in solution accounted for the formation of an unusual bridged dichloro biscarbene complex *fac*- $[(\mu\text{-Cl})_2\text{-}(\text{Re}(\text{CO})_3\{\text{C}(\text{OEt})\text{Fc}\})_2]$ (**88**) (Scheme 31).

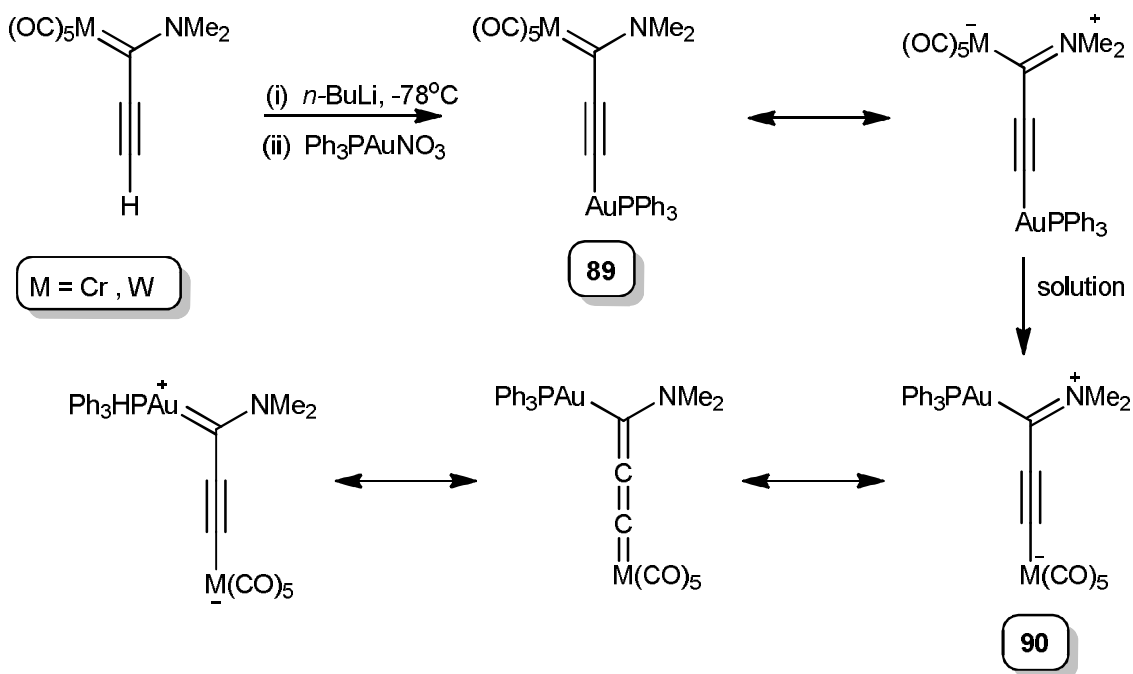


Scheme 31.

The formation of complex **88** displayed some similarities to the acyl-hydrido hydroxycarbene dirhenium complex (see section 3.4.2) [76]. In both cases a cleavage of the Re-Re bond of the precursor $\text{Re}_2(\text{CO})_{10}$ has occurred. The formation of **88** could be rationalized by the transfer of a chlorine atom from the solvent, and the concurrent breaking of the Re-Re bond. Loss of a carbonyl ligand occurs and two of the resultant coordinatively unsaturated *fac*- $[\text{Re}(\text{CO})_3\{\text{C}(\text{OEt})\text{Fc}\}\text{Cl}]$ molecules combine by means of bridging chloro ligands.

3.2.2. Monocarbene complexes with metal fragment not π -bonded

Bimetallic complexes containing unsaturated, conjugated carbon bridges with metal carbene termini are also well-known and newer examples of both the aforementioned types are mentioned in Sections 2.3.4 and 2.5. One of the few new examples published that involved unexpected metal-exchange, contains group 6 alkynyl aminocarbene complexes, which, after lithiation and reaction with $[\text{Ph}_3\text{PAuNO}_3]$ form β -substituted bimetallic carbene complexes $[(\text{CO})_5\text{M}=\text{C}(\text{NMe}_2)\text{C}\equiv\text{CAuPPh}_3]$ (Scheme 32, **89**) [155]. Surprisingly, when left in solution, it was found that compounds **89** converted into the linkage isomers **90**, in which two metal fragments present in each system had exchanged places. No evidence regarding the transition state could be extracted from theoretical calculations, nor could any experimental evidence for the existence of possible intermediates be found. However, this proved not to be the first example of metal-exchange, as discussed in Section 2.3.4.



Scheme 32.

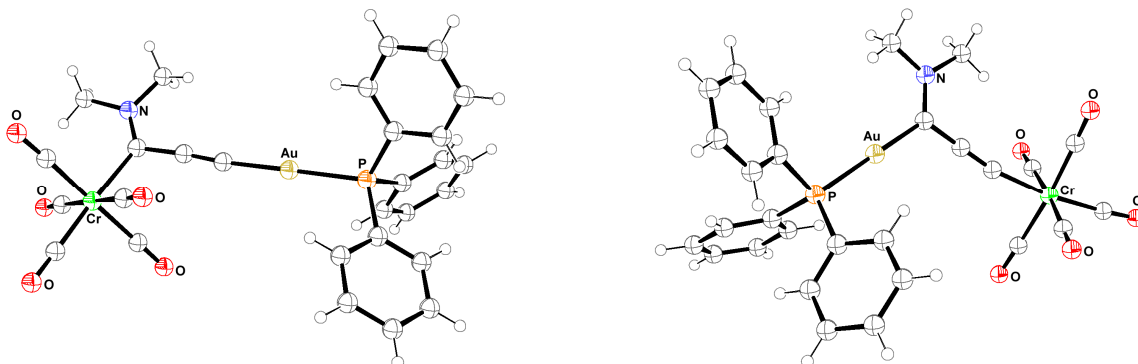
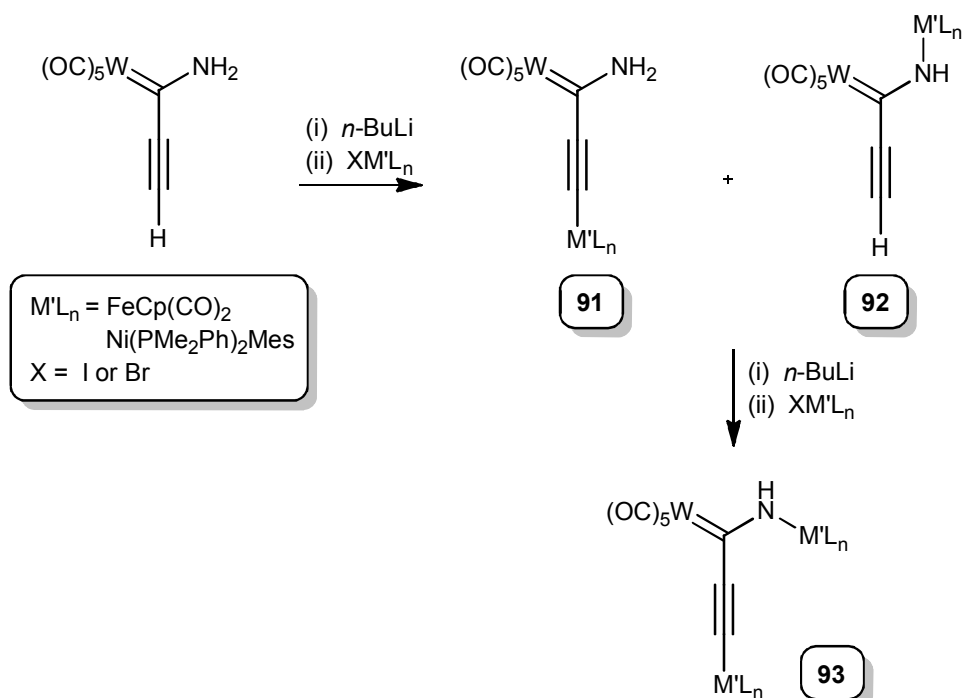


Fig. 36. Molecular structures of $[(CO)_5Cr=C(NMe_2)C\equiv CAuPPh_3]$ (**89**) and $[Ph_3PAu=C(NMe_2)C\equiv CCr(CO)_5]$ (**90**) [155].

When binuclear amino(ethynyl)carbene complexes were synthesized with $M'L_n$ -fragments in different positions (**91** ($\equiv C$ -bound) and **92** (N-bound) in Scheme 33), or trinuclear complexes with both $\equiv C$ - and N-bound $M'L_n$ -fragments (**93**), the $(CO)_5M=C(\text{carbene})$ interaction is more pronounced when the amino hydrogen is replaced instead of the ethynyl hydrogen [69,156,157]. Also, IR spectroscopy indicated

greater involvement of the $(\text{CO})_5\text{M}=\text{C}(\text{carbene})$ with the Ni-containing substituent compared to the $\text{Fe}(\text{CO})_2\text{Cp}$ -fragment.



Scheme 33.

3.2.3. π -aryl biscarbene complexes **VIII(b)**

Although there are examples of trimetallic biscarbene complexes with more than one Cp-moiety in the molecule (eg. **94**, Fig. 37) [11,158], the tethered biscarbene complexes (**95**) in Fig. 37 are two of the scarce examples with two cyclopentadienylcarbene moieties [139].

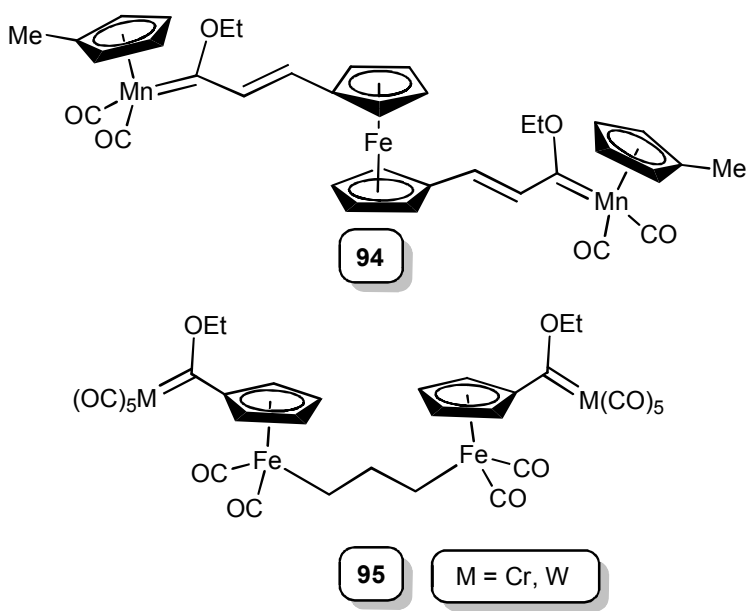
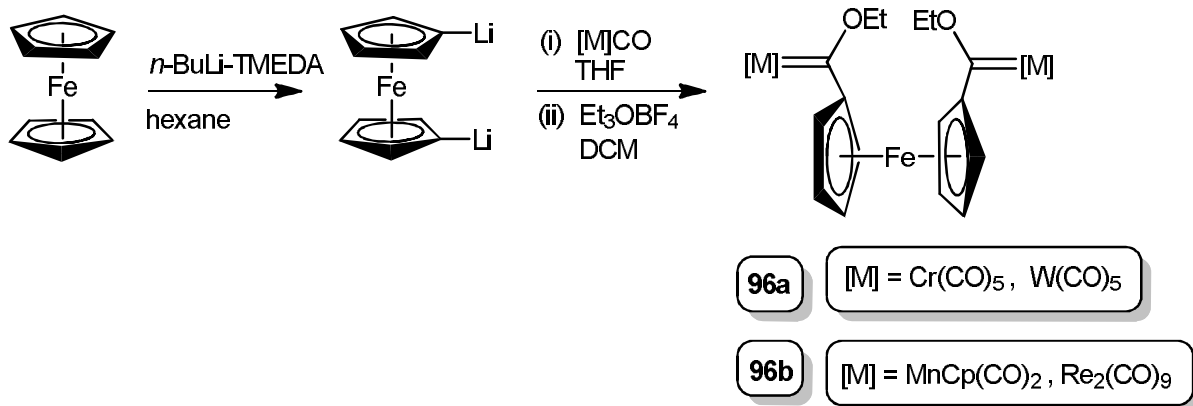


Fig. 37. Bis(cyclopentadienyl)carbene complexes.

Considering the ease of dilithiation of ferrocene, it is surprising that so few Fischer biscarbene complexes containing a bridging ferrocen-1,1'-diyl (Fc') spacer have been reported. To our knowledge, no crystal structure of any of these complexes have been reported before that of $[\{(CO)_5Cr\}_2\mu^2-\{=C(OEt)\}_2(Fc')]$ (Fig. 38) in 2008 [159]. The bisethoxy ferrocen-1,1'-diyl bridged biscarbene complexes of the group 6 metals were synthesized and structurally characterized (**96a**), and soon after similar complexes of group 7 transition metals (**96b**) were prepared (Scheme 34). These included both the bis(cyclopentadienyl manganese dicarbonyl carbene) as well as the pentanuclear bis(dirhenium nonacarbonyl carbene) complexes.



Scheme 34.

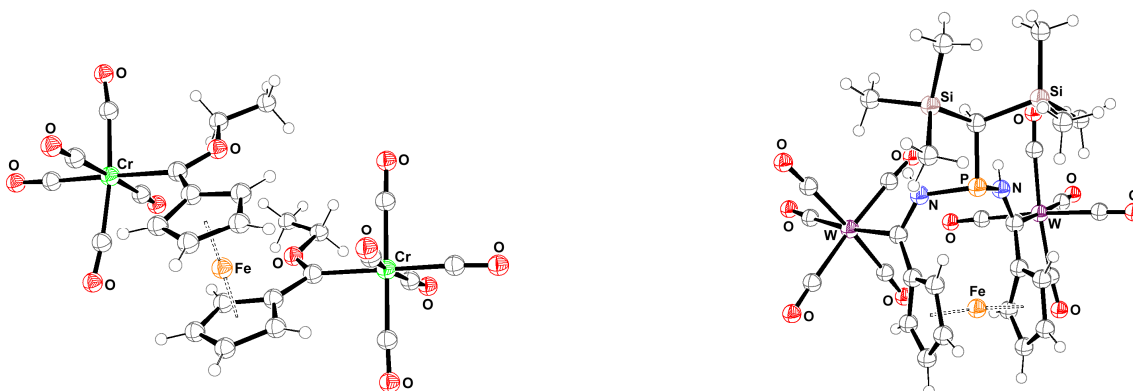


Fig. 38. Molecular structures of $[{(CO)_5Cr}_2\{\mu^2\text{-}\{=C(OEt)\}_2(Fc')\}]$ (**96a**) [159] and $[{(CO)_5W}_2\{\mu^2\text{-}C((NH)_2P(SiMe_3)_2)(Fc')C=}\}]$ (**99**) [160].

Shortly after, the corresponding ruthenocenyl biscarbene, $[\mu\text{-}Ru\{C_5H_4C(OEt)Cr(CO)_5\}_2]$ (Fig. 39, **97**) was prepared by Sierra *et al.* as another example of the class **VIII(b)** (Fig. 27) carbene complexes [161]. In 2010, the structure of the pentacarbonyl tungsten diamino ferrocen-1,1'-diyl biscarbene was published (Fig. 39, **98**) [162]. Following the report of an aminocarbene with a P-chelating 1'-(diphenylphosphino)ferrocenyl substituent **75** (Fig. 30, Section 3.2.1) [136], an unusual ferrocenophane biscarbene complex (Figs. 38 and 39, **99**) [160] was recorded.

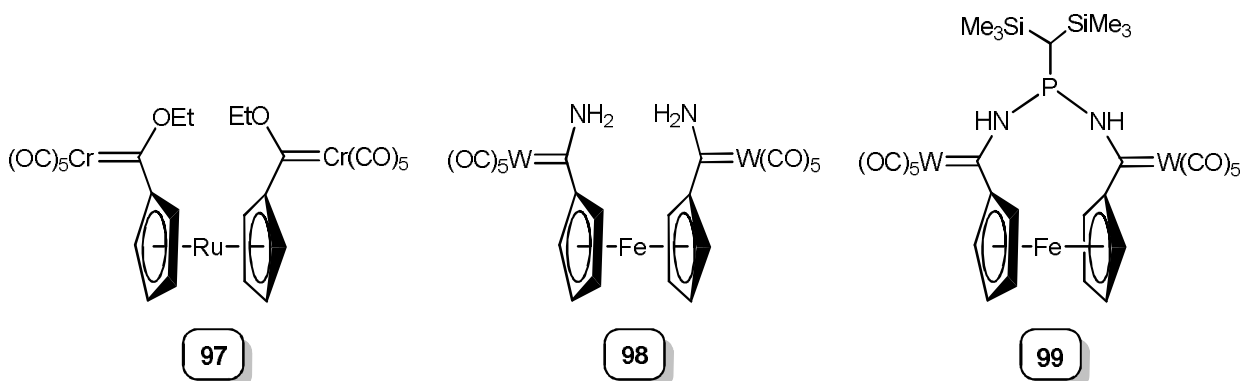
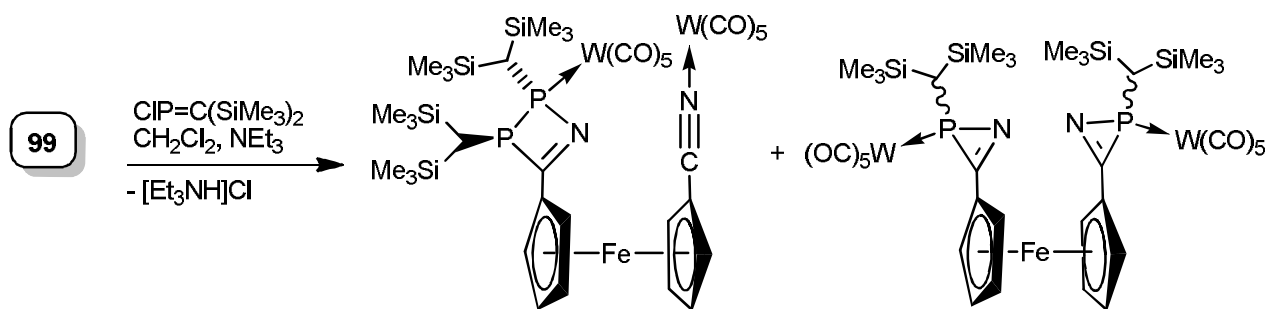


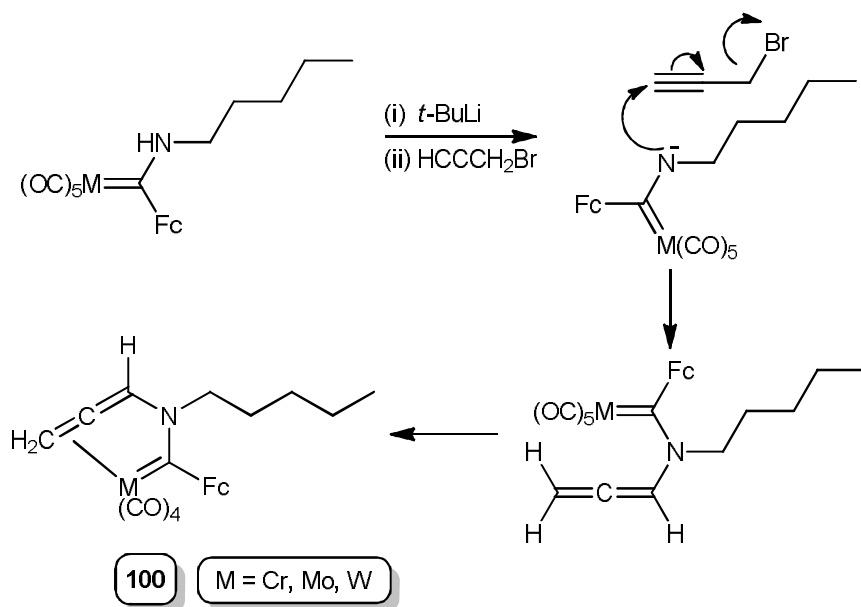
Fig. 39. Metallocenyl (bis)carbene complexes.

The reactivity of this diaminophosphane-bridged [5]ferrocenophane bis(carbene complex) **99** towards ring opening was tested by treating it with chloro(methylene)phosphane and triethylamine. Cleavage of the ferrocenophane bridge did in fact occur with formation of bis(2*H*-azaphosphirene) complexes and another ditungsten complex featuring a 2,3-dihydro-1,2,2-azadiphosphirene and a nitrile-W(CO)₅ unit (Scheme 35). Further reactions aimed at the construction of novel macrocyclic ligand architectures with redox-active functionalities were planned.



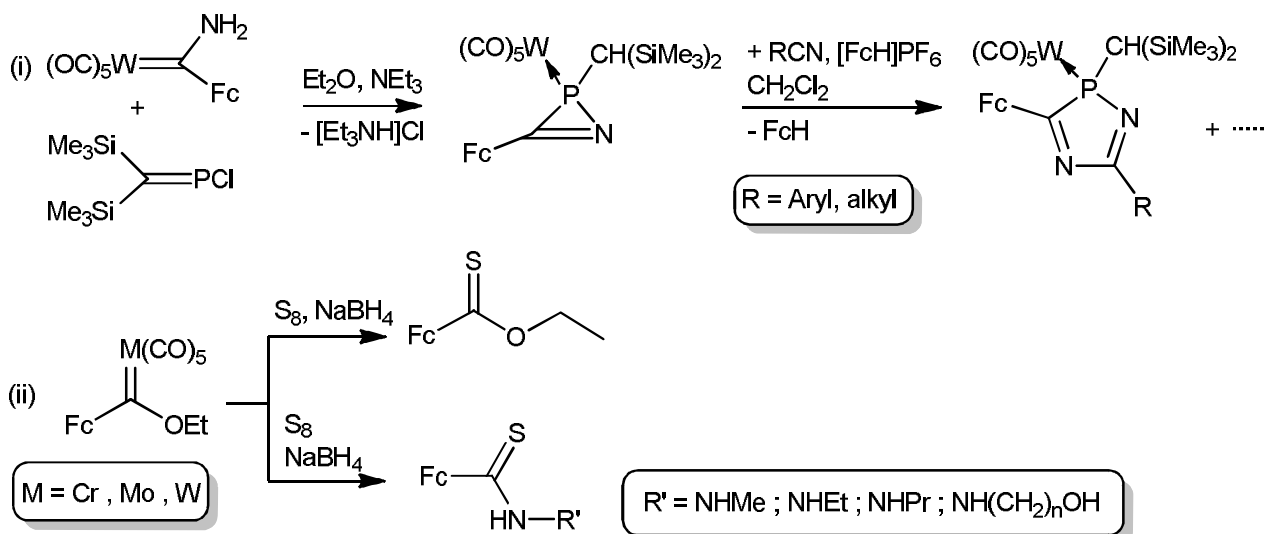
Scheme 35.

In another application that have arisen in the past few years for specifically ferrocenylcarbene complexes, the base-induced alkylation reaction of bromide at the N-atom of $[(\text{CO})_5\text{M}\{\text{C}(\text{NH}(\text{n-C}_5\text{H}_{11})\text{Fc})\}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) led to the unexpected Fischer carbene complexes **100** with bidentate *allene*-aminocarbene ligands (Scheme 36). These highly strained carbene complexes could show possible application as initiators for alkene and alkyne insertion reactions [163].



Scheme 36.

The significant influence of a ferrocenyl substituent was also evidenced by first reacting ferrocenylaminocarbene tungsten complex with [bis(trimethylsilyl)methylene]chlorophosphane and triethylamine to yield the azaphosphirene complex (Scheme 37, (a)) [164]. Subsequent reaction with aryl nitriles in the presence of ferrocenium hexafluorophosphate yielded, regioselectively, diazaphosphole complexes through single-electron transfer-induced ring expansion.

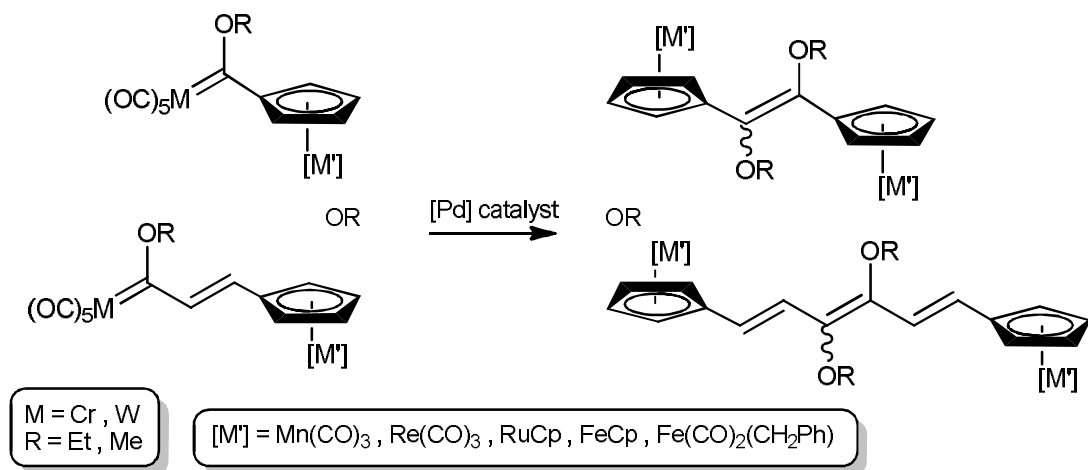


Scheme 37.

Oxidative demetalation of the $\text{M}(\text{CO})_5$ -moiety of ferrocenyl ethoxy- and aminocarbene complexes [165] could be achieved under mild conditions by reaction with elemental sulfur- NaBH_4 . *O*-ethyl ferrocenecarbothioate and novel ferrocenylthioamides were obtained in excellent yield, contrary to the general methods that involve several steps and overall low yields. The scope of the method above (Scheme 37, (b)) was evidenced by the tolerance to different functional groups on side chains of ferrocenyl aminocarbenes.

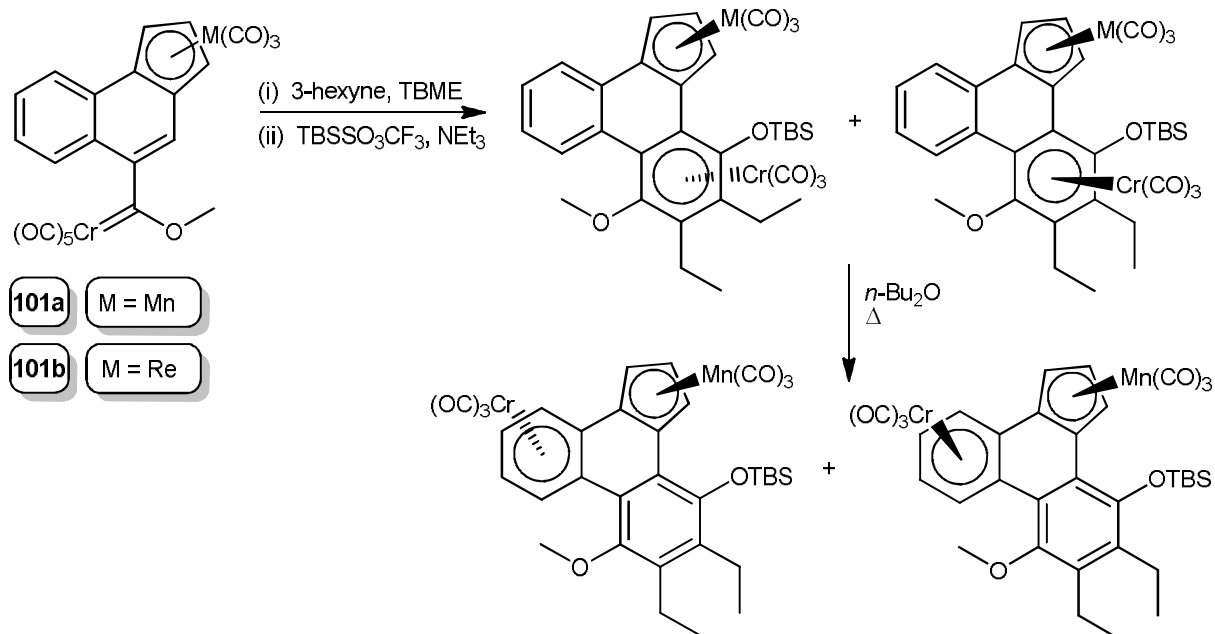
A final application details the preparation of a series of novel CpM-substituted bimetallic olefins and polyenes ($\text{M} = \text{Mn, Re, Fe}$) and metallocenyl ($\text{M} = \text{Fe, Ru}$) bimetallic olefins via the Pd-catalyzed carbene-carbene coupling reaction of group 6 bimetallic Fischer carbene complexes (Scheme 38) [166]. For these complexes, co-operative metal-metal interactions could result in a variation of the physical and chemical properties of one metal center due to the proximity of the other. This, in turn, could lead to the synthesis of molecular wires especially if proof could be found of electronic communication between the metal fragments. These reactions yielded no side products other than oxidation of the metal carbene complexes. The *E/Z* selectivity in these processes was shown to be modulated by the steric hindrance of the metallic moiety next to the carbene center, and again electrochemistry was used to demonstrate communication between ferrocene units.

Conversely, the diruthenocyl derivatives did not show any evidence of electronic communication between the ruthenocene units.



Scheme 38.

Application of other bimetallic π -aryl carbene complexes includes the synthesis of a novel type of polyene heterobimetallic Cr-M complex ($M = \text{Mn, Re}$). This was prepared from a cymanthrene-type Fischer carbene complex **101** [167,168] via chromium-templated benzannulation (Scheme 39) to give *syn*- and *anti*-diastereomers bearing $M(\text{CO})_3$ ($M = \text{Mn, Re}$) and $\text{Cr}(\text{CO})_3$ fragments coordinated to the cyclopentadienyl ring, and to the hydroquinoid ring of a dibenzo[*c,e*]indene skeleton, respectively. For the Mn-complexes, both diastereomers undergo a thermoinduced Cr-migration, while the manganese moiety remains coordinated to the Cp ring.

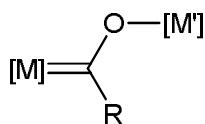


Scheme 39.

3.3. Complexes with metal fragment bonded to the carbene heteroatom substituent (IX)

3.3.1. Metaloxycarbene complexes

The incorporation of a second metal-containing fragment, joined to the oxygen atom bonded to the carbene carbon has first been explored by Fischer *et al.* [169], and is represented by class **IX** ($\text{M}=\text{C}(\text{R})\text{-O-M}'$) in Fig. 27. In this class both monocarbene (dimetallic class **IX(a)**) and biscarbene (di- or trinuclear class **IX(b)**) complexes will be discussed. The presence of this second electron deficient metal bound through the carbene oxygen substituent offers the opportunity to control the carbene reactivity by steric and electronic variation of the Lewis acidic component.



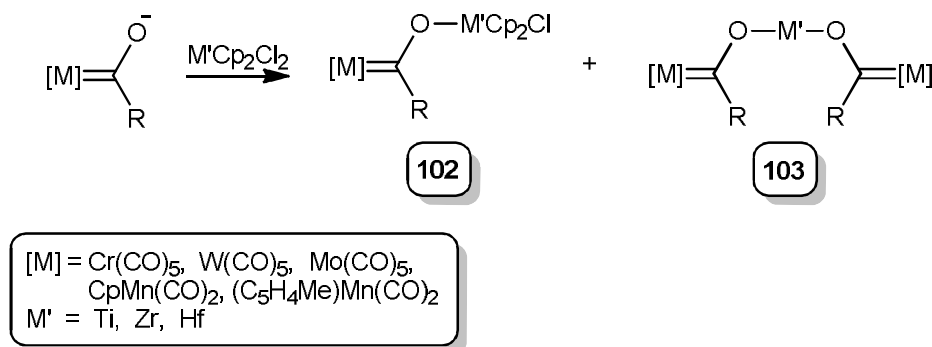
[M] = [V], [Nb], [Cr], [Mo], [W], [Mn],
[Re], [Fe], [Ru], [Co], [Rh], [Pt]

[M'] = [Sc], [Ti], [Zr], [Hf], [Th], [U],
[Si], [Sn], [B], [Al], [P]

Fig. 40. Metaloxycarbene complexes.

Numerous examples of these bimetallic carbene complexes exist, containing a wide variety of central metals and heteroatom bound metals (Fig. 40). The preparation and synthetic application of these bimetallic systems have been the subject of a number of review articles [11,125,170-174]. The heteroatom bound carbene substituents reported in the aforementioned articles include also metalloids ([B], [Ge] and [Sn]), nonmetals ([Si], [P] and [Se]) and actinides ([U] and [Th]).

The preparatory route employed by Fischer involved the *O*-metalation of an acyl chromate with titanocene dichloride to yield the complex $[\text{Cr}(\text{CO})_5\{\text{C}(\text{Me})\text{OTiCp}_2\text{Cl}\}]$ (**102**) as well as the trimetallic bismetaloxy carbene complex $[\{\mu\text{-O}_2\text{TiCp}_2\text{-O, O'}\}\{\text{C}(\text{Me})\text{Cr}(\text{CO})_5\}_2]$ (**103**) [169] (Scheme 40). A representative example, **104**, is shown in Fig. 41, to be discussed in section 3.4.1. Biscarbene complexes **103** are examples of multicarbene multimetal complexes of the class **IX(b)**, and are discussed in a later section 3.4.2.



Scheme 40.

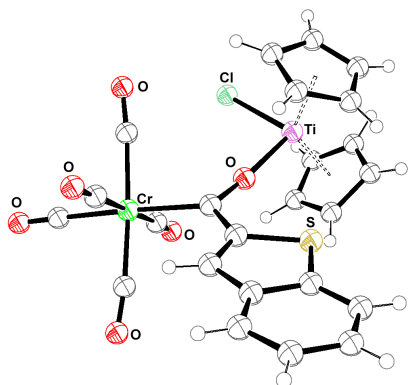


Fig. 41. Molecular structure of $[(\text{CO})_5\text{Cr}=\text{C}\{\text{O}(\text{TiCp}_2\text{Cl})\}(\text{benzothiophene})]$ (**104**) [159].

Acyl metalates also undergo nucleophilic attack with a variety of other metallocenes (zirconocene, hafnocene etc.) [140,159,175-178] to yield the corresponding metaloxycarbene complexes as illustrated in Scheme 40. However, this Fischer method is limited by the reactivity of the acyl metalate intermediate (**D** in Fig. 42 below). The intermediate **D** 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 Fischer-type metaloxycarbene complex **E**.

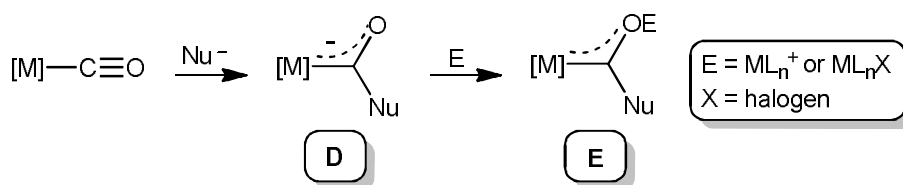


Fig. 42. Electrophilic attack on acylmetalate **D** to form Fischer carbene complex **E**.

In addition, 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 often leads to the formation of two chromium acylates being bridged by a titanocene fragment [179,180].

Nucleophilic addition of the second metal fragment directly to the metal carbonyl precursor is also possible and remains the most direct and highest yielding method of synthesis [125]. A host of metaloxycarbene complexes has also been prepared via non-nucleophilic addition to metal carbonyls, including metallacyclic metaloxycarbene complexes afforded by ring-closure reactions of η^2 -olefin complexes of titanocene, zirconocene or hafnocene, (η^4 -diene) metallocenes or alkylidene titanium complexes [125,171,181-185].

The metaloxycarbene moiety has, in general, been found to be rather unreactive [170], although it can be converted into a traditional $\text{M}=\text{C}(\text{R})\text{OR}'$ functional group. The metaloxycarbene complexes can therefore be regarded as 'protected' Fischer carbene

complexes. This low electrophilic reactivity of the metal carbene functionality underlines the pronounced metal acyl type character of these complexes (Fig. 43), and the significant ionic character of the Lewis acidic Ti/Zr/Hf-O bond. Structure data suggest a higher contribution of the acyl resonance structure in Fig. 43 to the bonding than in the alkoxycarbene complexes, with shorter M'-O bond lengths [140,151,159,170,186,187]. However, the corresponding M-C(carbene) bond distances are close to those of the alkoxycarbene derivatives, implying that significant carbenic character remains in these systems. The presence of the second metal unit, Cp₂ZrCl, can also lead to the activation of such carbene complexes as catalysts for the oligomerization of 1-pentene in the presence of MAO [188].

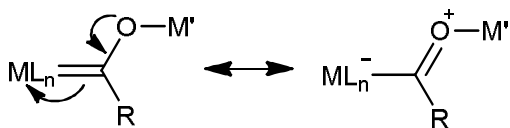
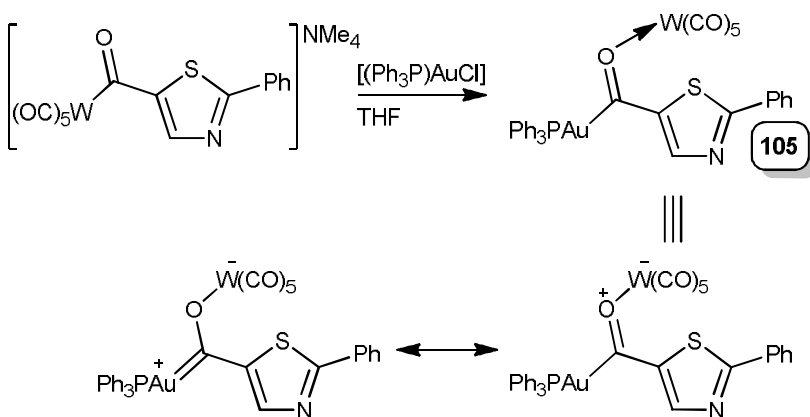


Fig. 43. Acyl character of metaloxycarbene complexes.

More support for the representation of the resonance contributing structures can be found in the recent synthesis of a gold acyl complex with significant carbenic character [189]. A tungsten thiazolylcarbene precursor was reacted with [(Ph₃P)AuCl] (Scheme 41). Unexpectedly, the liberated W(CO)₅-fragment remained bonded to the acyl oxygen yielding complex **105** (Fig. 44) can also be formulated as a zwitterionic tungstenoxycarbene complex of gold.



Scheme 41.

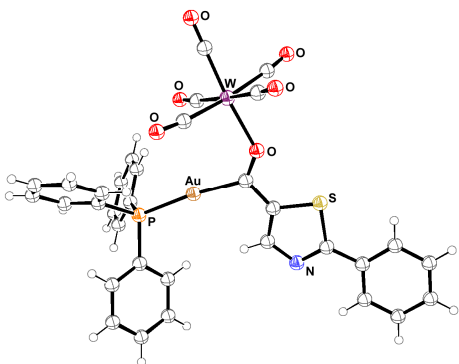
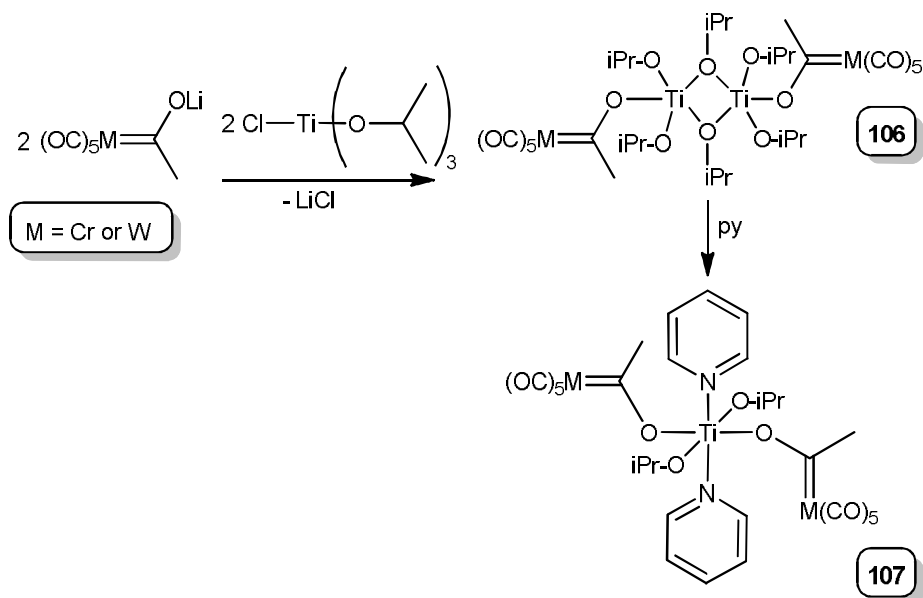


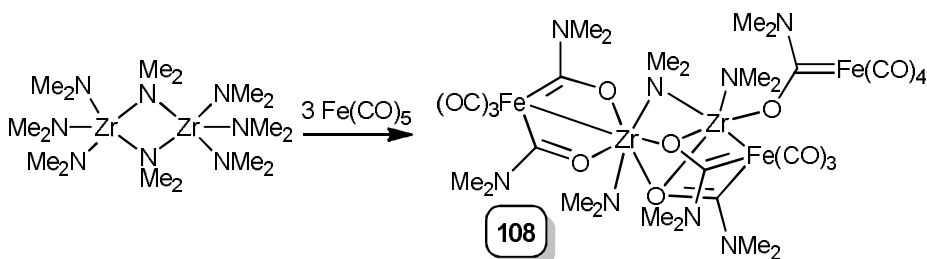
Fig. 44. Molecular structure of $[\text{Ph}_3\text{PAuC}\{\text{OW}(\text{CO})_5\}(\text{CSCPhNCH})]$ (**105**) [189].

Different variations of the Fischer approach to metallocene complexes have been followed, including the work of Sabat [125,170] describing the preparation of dimeric titanium compounds (**106**), and more recently, the unusual rearrangement of these dimeric titanium complexes, (Scheme 42), yielding a compound (**107**) where the titanium becomes coordinated by two oxycarbene units [190].



Scheme 42.

The first example of a multicarbene complex (**108**) containing two zirconium and three iron atoms was isolated from the reaction of $[\text{Zr}(\text{NMe}_2)_4]_2$ with $\text{Fe}(\text{CO})_5$ [191]. As shown in Scheme 43, insertion of the five CO groups into Zr-N bonds generated chelating biscarbene ligands at two iron atoms and one terminal carbene ligand at the third iron atom, retaining the dimeric nature of the starting $(\text{NMe}_2)_3\text{Zr}(\mu\text{-NMe}_2)_2\text{Zr}(\text{NMe}_2)_3$.



Scheme 43.

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), [192] which can be regarded as ‘complexes of complexes’ and can form tris-, bis- or mono-chelated polymetallic compounds, as illustrated in Fig. 45.

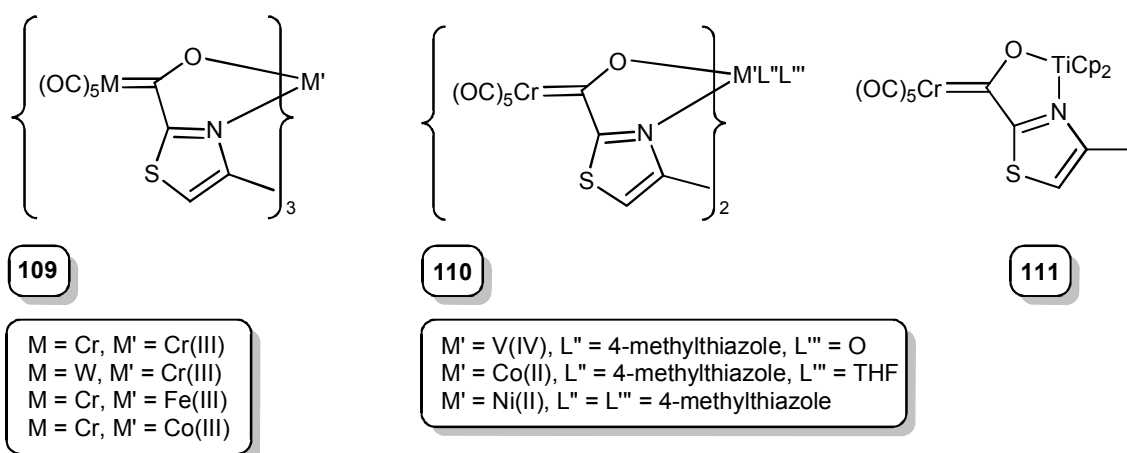


Fig. 45. Anionic Fischer-type carbene complexes as bidentate (N,O) ligands.

Many examples of metallacyclic mixed acyl carbene complexes have also been described as μ -oxycarbene complexes (see Section 2.2.2) [54,193,194] and have been prepared from different transition metals (Fig. 46).

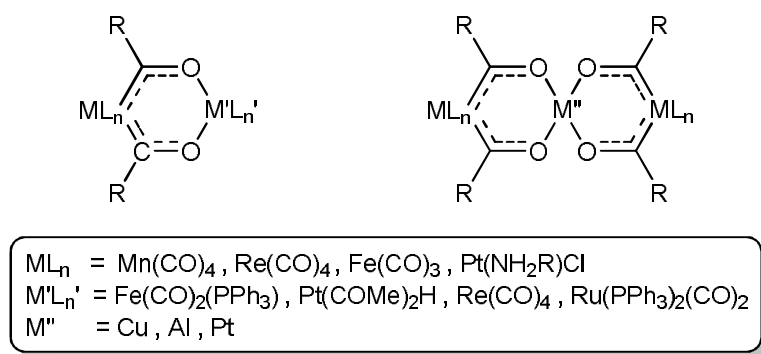


Fig. 46. Di- and trinuclear metallacyclic bis-acyl complexes.

The crystallographic data obtained for two of these metallacyclic bis-acyl analogues, **112** and **113** (Fig. 47), justify the classification of these complexes as carbenic [195]. Bond lengths confirmed the enhanced carbene character for the acyl carbon atoms of **112** as compared to the amine-substituted acyl carbon atoms of **113**. This compound can also be described by a resonance contributing form involving C=N multiple bonding and a concomitant increase of electron density within the metallabicyclic core.

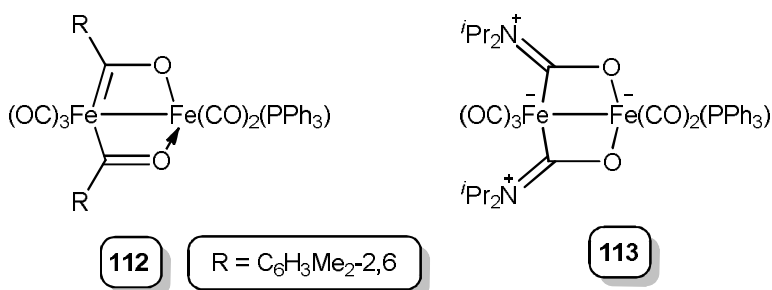
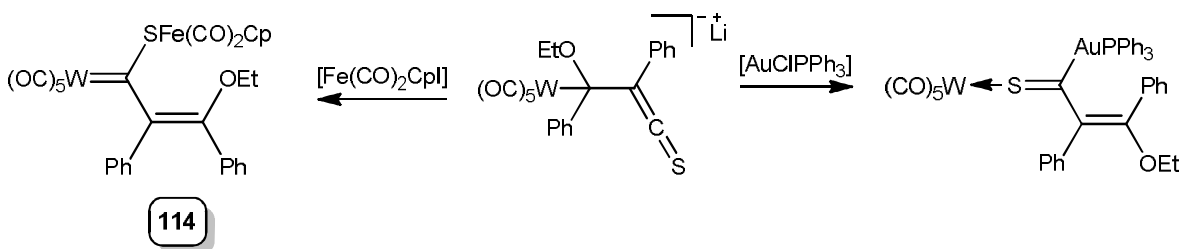


Fig. 47. Metallacyclic bis-acyl diiron complexes with aryl and amino acylsubstituents.

3.3.2. *Metalthiocarbene complexes*

Very few examples of thiocarbene complexes bearing a metal-fragment as a carbene substituent are known. One such example resulted from the reaction of an unusual thioketene adduct in Scheme 44 with $[Fe(CO)_2CpI]$ to give the metal-substituted α,β -unsaturated thiocarbene **114**. However, when the thioketene tungsten complex was reacted with the soft metal fragment $[AuPPh_3]^+$, the electrophile reacted at the α -thiocarbon to give an α,β -unsaturated thione complex [196]. In both cases the reaction

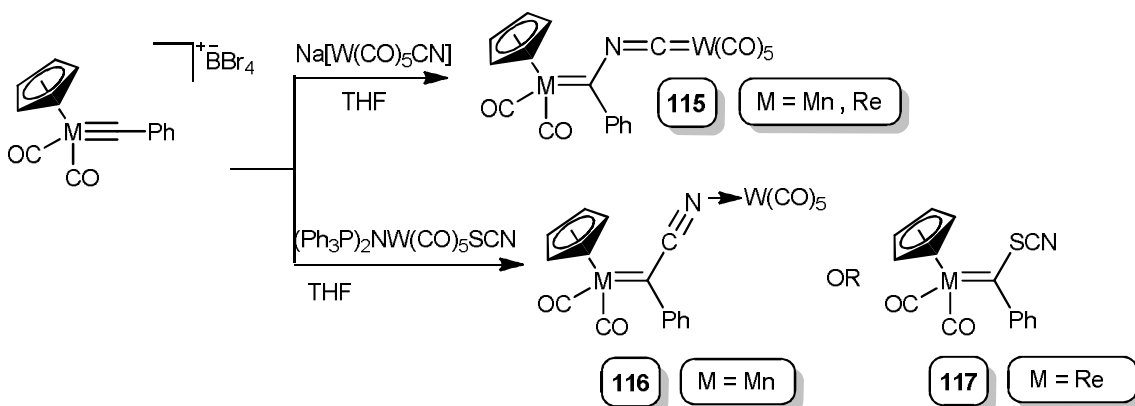
was chemo- and stereoselective. Besides this example, only thiocarbenes *bridging* two metals have been isolated as recently reported by Busetto and co-workers [197].



Scheme 44.

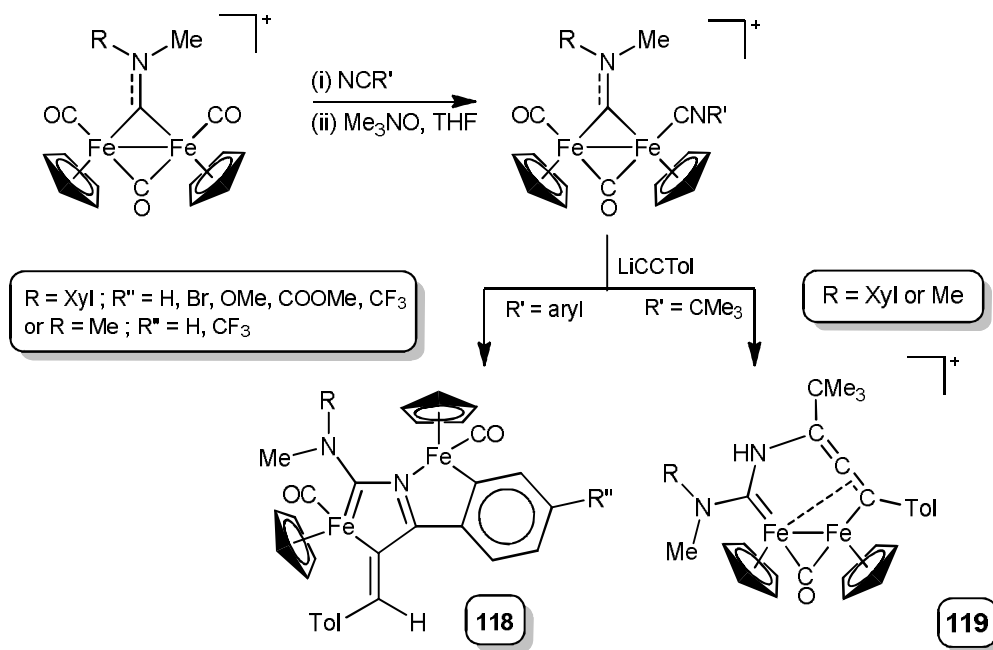
3.3.3. Metalaminocarbene complexes

The influence of the metal carbonyl fragment on the reactivity of complexes are shown in the reaction of cationic carbyne complexes of manganese and rhenium with metal carbonyl anions [121,198]. When a cyano-containing tungsten carbonyl anionic compound $\text{Na}[\text{W}(\text{CO})_5\text{CN}]$ (Scheme 45) was used as nucleophile, the product was a cyanotungsten carbene complex (115) for both Re and Mn. However, when the carbyne complexes were reacted with metal salts containing an SCN substituent, loss of the S atom yielded the novel isocyanotungsten carbene complex of manganese (116). The analogous reaction with the rhenium carbyne complexes gave no analogous product but rather the isothiocyanatocarbene rhenium complex 117.



Scheme 45.

The capability of diiron aminocarbene complexes to activate coordinated nitriles was demonstrated by the addition of acetylide. Nucleophilic attack at the coordinated nitrile is accompanied by coupling with the bridging aminocarbene ligand, resulting in C-N bond formation (Scheme 46).

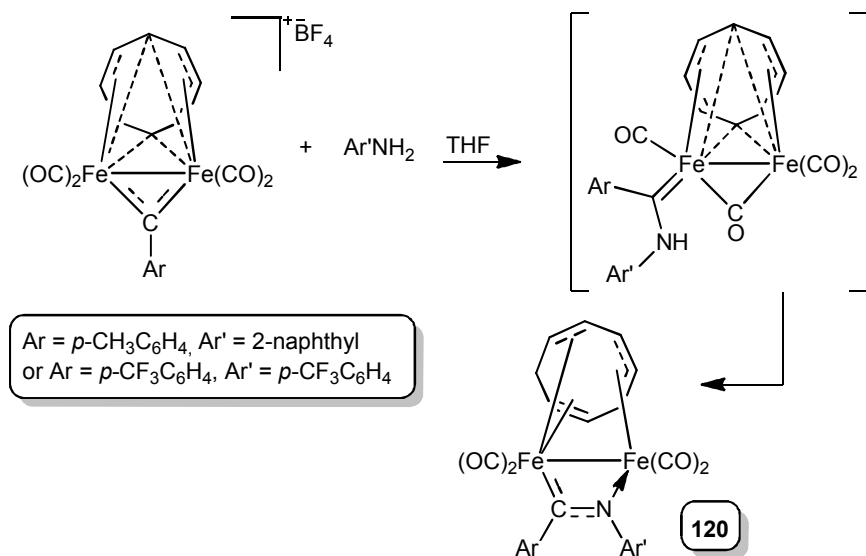


Scheme 46.

The resultant complexes **118** are composed of two five-membered metallacycles, of which the coordination sphere of one iron atom is completed by a diaminocarbene and a vinyl ligand. The other iron atom present in **118** shows some π -interaction with the metallated aromatic ring as shown by X-ray structural studies [128]. Further rearrangements take place depending on the nature of the nitrile ligand, and different products **119** (Scheme 46) are correspondingly formed. The role of the two adjacent metal centres in promoting intramolecular coupling of coordinated ligands and organic fragment build-up was emphasized. The metal atoms also provide stabilization to these species through a variety of coordination modes.

One of the very rare examples of a multimetal system with a chelating carbene ligand was again synthesized from a cationic diiron bridged complex [118]. The cationic carbene complex $[\text{Fe}_2(\mu\text{-CAr})(\eta^8\text{-C}_8\text{H}_8)(\text{CO})_4]\text{BF}_4$ ($\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$ or $p\text{-CF}_3\text{C}_6\text{H}_4$ in Scheme

47) yielded, after reaction with either (2-naphthyl)NH₂ or (*p*-CF₃C₆H₄)NH₂, the novel chelated iron-carbene complexes **120**. The authors postulated an iron carbene complex intermediate, which was transformed into the chelated products due to the lability of the complexes in solution at the relatively high reaction temperature. On the other hand, if the N nucleophile employed was disubstituted, the COT ring of the precursor was selectively attacked to give ring-addition products.



Scheme 47.

A recent diaminocarbene complex (*N*-heterocyclic carbene) that contains a metal bound to one of the carbene-N atoms is classified by the authors as a “Fischer carbene within an Arduengo carbene” **121** [199]. The C4 atom of an Arduengo carbene was replaced with a manganese atom belonging to a transition metal fragment, generating a carbene complex within the NHC skeleton. Upon coordination of a new metallic (Au) center, unprecedented heterometallic biscarbene derivatives were obtained. Several resonance structures for the bond description in the metallaheterocycle can be drawn (Fig. 48), describing the contributing formamidinyl form as well as the carbene forms. Structural evidence for these descriptors was obtained from X-ray crystallography. In accordance with the above interpretation, the biscarbene complex was alkylated at the carbamoyl oxygen, transforming the acyl complex into a cationic Fischer carbene complex **121** by treatment with methyl triflate.

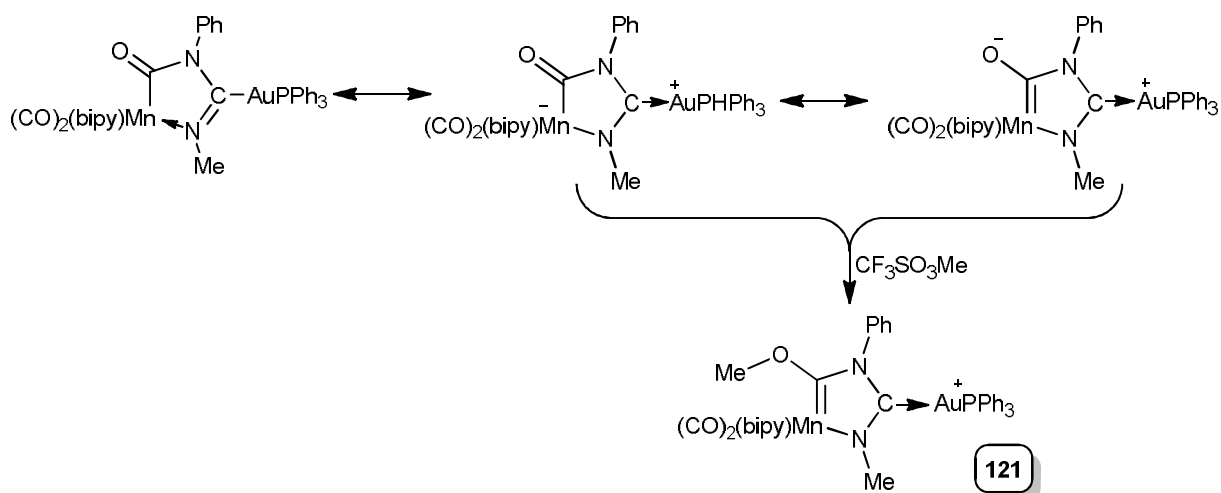
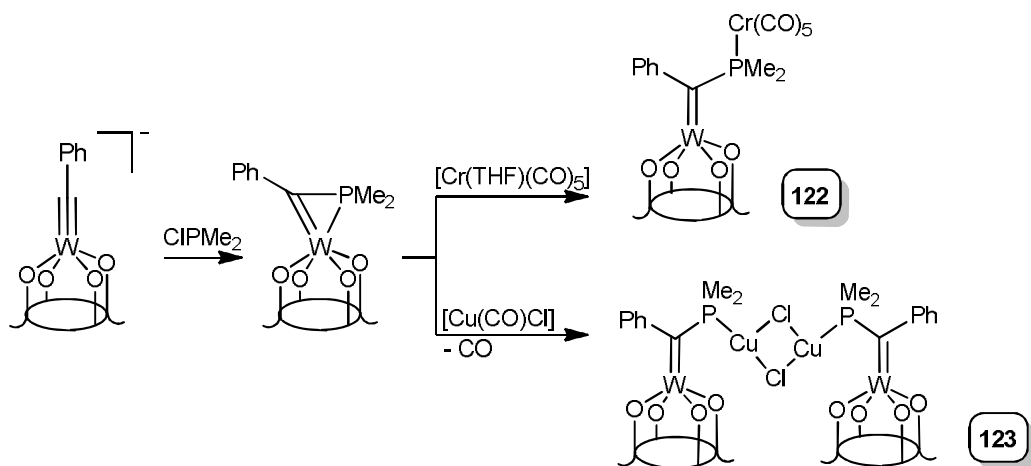


Fig. 48. Resonance structures of the diazamangana-heterocycle

3.3.4. Metalphosphinocarbene complexes

The majority of phosphinocarbene complexes with transition metal carbene substituents ($M=C(R)-P-M'$, class **IX**) were prepared more than ten years ago, with little recent development. In one notable case the presence of the P-atom at the alkylidene carbon was specifically employed to manipulate the properties of metal-alkylidene complexes in Fischer carbene chemistry to polarize the $M=C$ bond with the heteroatom. Anionic tungsten alkylidene derivatives, exemplified by $[W(\equiv CPh)cal]$ ($H_4cal = p-tBu-calix[4]arene$) were used as the starting material in the reaction with $ClPPh_2$ to give an η^2 -phosphanylalkylidene complex [200].



Scheme 48.

These complexes maintain the phosphorous atom as an available moiety for intermolecular binding to other metals. For example, reaction of the η^2 -phosphanylalkylidene tungsten complex with $[\text{Cr}(\text{THF})\text{CO}]_5$ and $[\text{Cu}(\text{CO})\text{Cl}]$ respectively, yielded the mono-phosphinocarbene **122** and the metal-bridged bis-phosphinocarbene **123** (Scheme 48). The possibility of assembling dimetallic units around an alkylidene functionality was illustrated, and indicated how structural parameters changed from the uncomplexed to the complexed form. In the precursor η^2 -phosphanylalkylidene tungsten complex, longer W=C and W-O bonds result, with a short P-C(alkylidene) bond compared to the significantly lengthened P-C bond in **123** (with consequent shortening of the W=C bond). The complexation of CuCl led to the cleavage of the metallaphosphacyclopentene ring, restoring the original W=C bond, and the dimer **123** displayed a phosphino-metal substituent bridge between the two tungsten carbene functionalities.

Both the mono- and biscarbene di-inserted derivatives **124** and **125** (Scheme 49) [201] were yielded after the insertion of isocyanide into a metal-phosphorus bond in bridging phosphide diplatinum complexes, and the addition of equimolar amounts of $\text{CF}_3\text{SO}_3\text{H}$ to the formed phosphaminoacyl complexes. Insertion of carbon into metal-heteroatom bonds with the exception of oxygen and nitrogen are rare; however such reactions are important in organometallic synthesis [201].

The complexes were prepared according to the classic Fischer method, where reaction of the precursor binary chromium or tungsten carbonyl with a lithiated (hetero)aryl π -metal fragment, yielded the corresponding metal acylate. Quenching the reaction with titanocene dichloride gave the multimetal carbene complexes **104**, **128** and **130**. The effect of both the heteroatom substituent as well as the (hetero)aryl substituent, and in addition, different combinations of the above could be qualitatively gauged using spectroscopic, structural, electrochemical and theoretical methods. A trend reflecting the effect of the combination of the two carbene substituents on the metal carbonyl centre was determined, and mirrored the extreme cases of greater donor ability of the ferrocenyl substituent and the ionic character of the titanoxyl substituent *vs* the electron withdrawing effect of the π -Cr(CO)₃ moiety and the ‘less’ donating ethoxy substituent. With the introduction of metal-containing fragments on both carbene substituents, modification of the electronic (Fig. 50) and steric nature of the carbene ligand could be effected by *both* the heteroatom and the (hetero)aryl substituent.

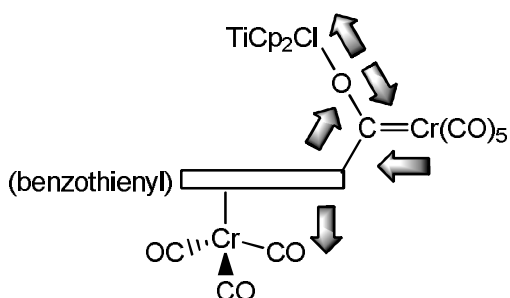
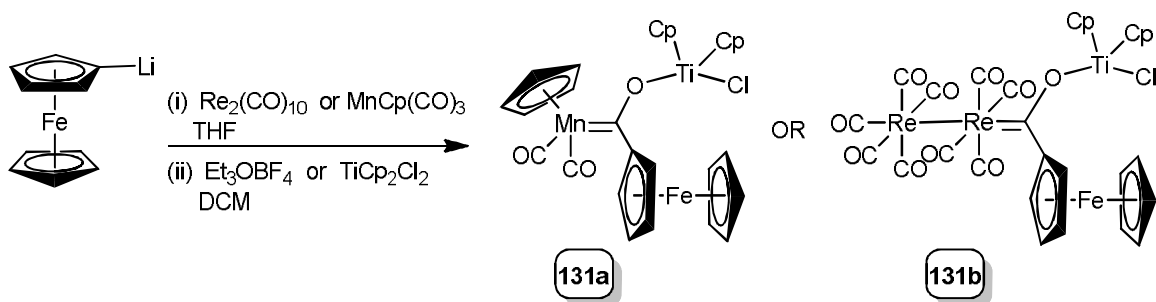


Fig. 50. The role of metal fragments on electron flow in the carbene complex **128**.

Whereas Fischer carbene synthesis is most successful with binary group 6 metal carbonyl precursors, this reaction is complicated for carbonyl precursors of groups 7 and 9 which require an X-type ligand for stability due to the uneven number of valence electrons. More reactive intermediates are therefore possible when group 7 metal complexes react with nucleophiles due to the presence of both L- and X-type (Re-Re bonds, halogens, H, carbon groups excluding Cp) ligands in the precursors, compared to group 6 metal carbonyl complexes. Binary dirhenium decacarbonyl and the mononuclear [MnCp(CO)₃]

precursor complexes were employed for the synthesis of multimetallic group 7 carbene complexes of the type $[ML_x\{C(OTiCp_2Cl)Fc\}]$ ($ML_x = MnCp(CO)_2$ (**131a**) or $Re_2(CO)_9$ (**131b**)) to prepare multimetal multicarbene complexes beyond group 6 [151]. The monocarbene target complex **131b** (Scheme 51), $ax-[Re_2(CO)_9\{C(OTiCp_2Cl)Fc\}]$ proved to be the least stable of the Fischer carbene multimetal complexes. The axial coordination site of the carbene ligand was based on the assignment of the carbonyl stretching modes. Steric constraints imparted by the bulky $TiCp_2Cl$ substituent are assumed to be responsible for this unique substitution pattern, as the electronically favorable substitution site remains the equatorial site [152].



Scheme 51.

3.4.2. Biscarbene multimetal complexes X(b)

In addition to monocarbene complexes, all of the reactions utilizing both ferrocene and titanocene dichloride as starting materials for the synthesis of ferrocenyl titanoxycarbene complexes also yielded the corresponding bimetallacyclic biscarbene complexes **132**, containing tetra- or hexanuclear biscarbenes (Fig. 51). This was ascribed to the ease of dilithiation of ferrocene and the enhanced activation of the remaining chloro ligand of the titanoxo substituent [179]. 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 substituent bound to the carbene carbon atom. This makes these complexes the only example of the Class **X(b)** metallacyclic multimetal multicarbene complexes having bridging ferrocen-1,1'-diyl and titandioxo substituents between the two carbene ligands. The novel biscarbene complex bridging the dirhenium nonacarbonyl moieties also displayed loss of the electronically favored equatorial positions resulting in the rare but

sterically less demanding axial coordination for one of the carbene ligands (Fig. 52, **132b**) [186], whilst the other is coordinated in the expected equatorial site.

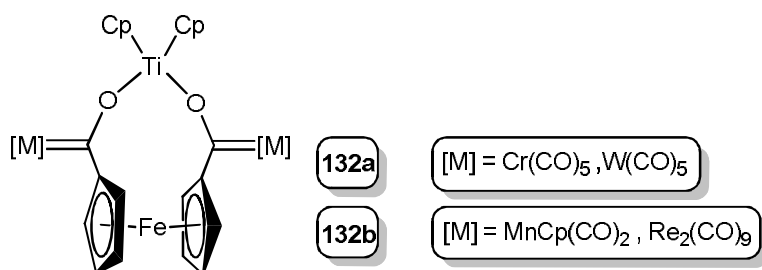


Fig. 51. Tetra- and hexanuclear bimetallic bicyclic biscarbene complexes.

The greater reactivity of the binary dirhenium acylate intermediates in solution, compared to that of the cyclopentadienyl manganese acylate, resulted in a complex reaction mixture with evidence for hydroxycarbene and hydrido-acyl intermediates. Although the stabilization of hydroxycarbene or hydrido-acyl intermediates of dirhenium carbonyls could not be achieved, their existence in solution was confirmed by the isolation of [Re₃(CO)₁₄H], [Re(CO)₅{C(O)Fc}], the unique hydroxycarbene-acyl complex [(μ-H)₂-(Re(CO)₄{C(O)Fc})₂] **133** and the aldehyde-functionalized *eq*-[Re₂(CO)₉{C(OTiCp₂Cl)(Fc'CHO)}] **134** (Scheme 52). Further confirmation was found in studies with thienyl-bridged biscarbene complexes of dirhenium nonacarbonyl and an analogous set of compounds [76].

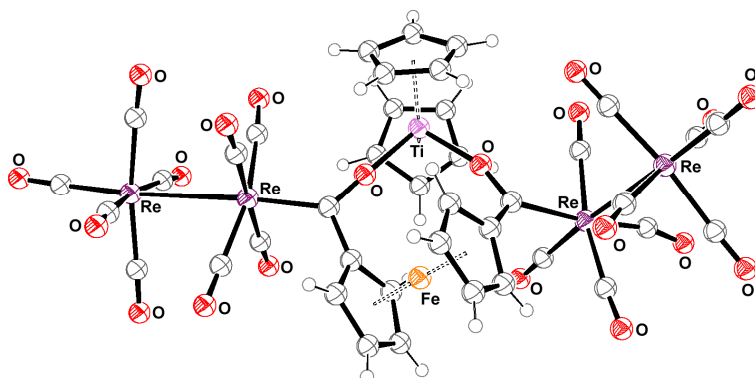
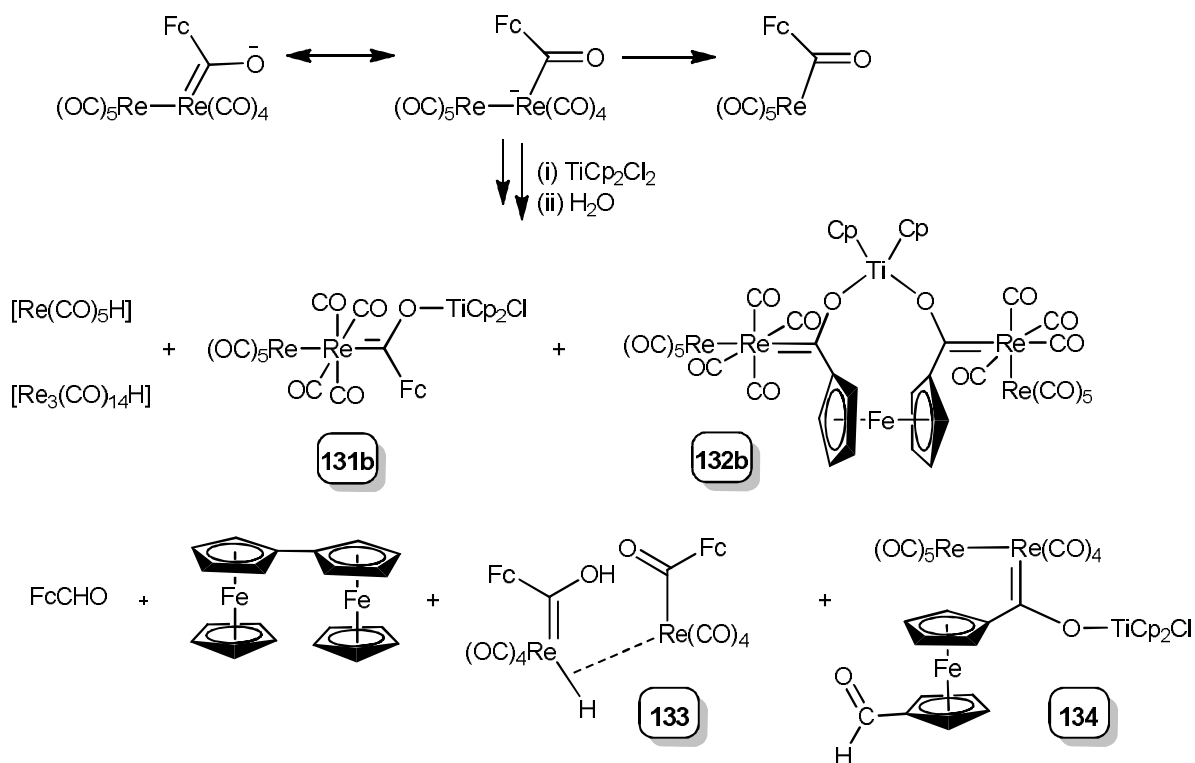


Fig. 52. Molecular structure of the bridging ferrocen-1,1'-diyl titandioxy biscarbene complexes [{(CO)₉Re₂ }₂ { μ²-(=C)₂(O₂TiCp₂)(Fc') }] (**132b**) [151].

The formation of secondary products isolated from the reaction mixture can mostly be ascribed to the transfer of a proton by either an ionic or a radical mechanism, with resultant bond cleavage into fragments which can be combined again to give the products. The isolation of the dimerization product biferrocene (Scheme 52) and FcCHO can be rationalized by the ionic nature of the titanoxo substituent, which would favor the rhenium acylate form of the intermediate because of enhanced backbonding from the anionic oxygen to the electrophilic carbene carbon. The ionic nature of titanoxycarbene complexes is supported by the ease of hydrolysis of this metal fragment and by structural studies, so that the titanoxycarbene complex can be viewed as an acyl synthon comparable to the situation observed by Barluenga and co-workers for $[\text{Mo}(\text{CO})_5\{\text{C}(\text{OBX}_2)\text{R}\}]$ [202].

Hydrolysis of ethoxy or the more susceptible titanoxo substituents afford hydroxycarbene complexes, and occurs during chromatography with polar solvents. Hydroxycarbene complexes can convert into aldehyde functionalities via the above equilibrium between the carbene and acyl-hydride intermediate [76]. As shown in Scheme 52, cleavage of the Re-Re bond of an intermediate species occurs to generate **133** and $[\text{Re}_2(\text{CO})_{10}]$. Complex **133** is unusual in that it exhibits a hydroxycarbene trapped in a dinuclear acyl-hydroxycarbene, and also displays a bridging rhenium hydride. The carbene heteroatom substituent therefore cannot contribute towards π -stabilization of the carbene, and much greater influence is felt on the ferrocenyl ring as evidenced by NMR studies. A final product was isolated, *eq*- $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OTiCp}_2\text{Cl})(\text{Fc}'\text{CHO})\}]$ (**134**), formed from a dilithiated ferrocene precursor, with reductive elimination of the $\text{Re}_2(\text{CO})_9$ -moiety only occurring on one side of the ferrocene, the other retaining its $[\text{Re}_2(\text{CO})_9\{\text{C}(\text{OTiCp}_2\text{Cl})]$ metal carbene fragment.



Scheme 52.

3.4.3. Multimetal monocarbene cluster complexes

Quite a few examples of clusters containing at least one carbene ligand exist (*viz.* Section 3.1.1 (**68-71** [122]), Section 3.3.1 (**103** [191]) and Section 3.3.3 [203]). These can be described by Cotton's definition of clusters of a compound where metals occupy the vertices of polyhedra and are linked via metal-metal bonds [204]. Less is known about cluster carbene complexes where one of the carbene substituents is bonded to another metal fragment, and these were seemingly found as unprecedented byproducts of metal carbonyl cluster reactions [205,206]. However, metal carbonyl cluster carbenes were also obtained from acyl complexes as the major products. The acyl cluster anion $[(\mu_3-Se)Fe_3(CO)_9(\mu_3, \eta^1, \eta^1, \eta^3-C(O)CHCCH_2)]^-$ could be alkylated with $MeOSO_3CF_3$, and both the *trans* and *cis* isomers of the Fischer-type cluster carbenes $(\mu_3-Se)Fe_3(CO)_9(\mu_3, \eta^1, \eta^1, \eta^3-C(OMe)CHCCH_2)$ **135** (Fig. 53) [207]. The metal cluster and pronounced chalcogen effects on the carbene formation were emphasized when comparing to the analogous tellurium-capped cluster carbene [208]. Only the *trans* Te-isomer could be

obtained, and theoretical calculations suggested that this phenomenon could be rationalized by the better metallic character of the tellurium atom vs the selenium.

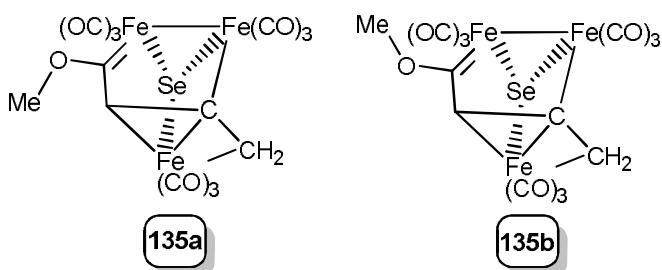


Fig. 53. *Cis*- (**135a**) and *trans*-isomers (**135b**) of triiron methoxycarbene clusters

3.4.4. Multimetal multicarbene cluster complexes

Only a very limited number of multimetal cluster systems with multicarbene ligands are known. Closely related to this definition are the bridging carbyne complexes mentioned in Section 3.1.1 [107,108,114,122], an interesting example (Fig. 54) being the tetranuclear metal complex **136** where the bridging alkylidyne carbon atoms are linked by a ferrocene moiety [209].

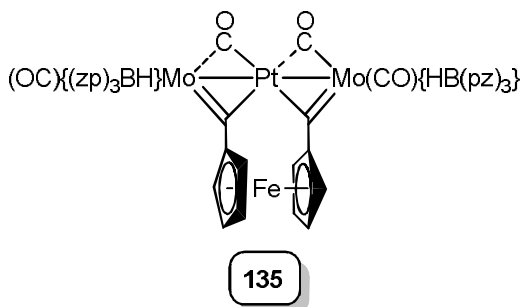
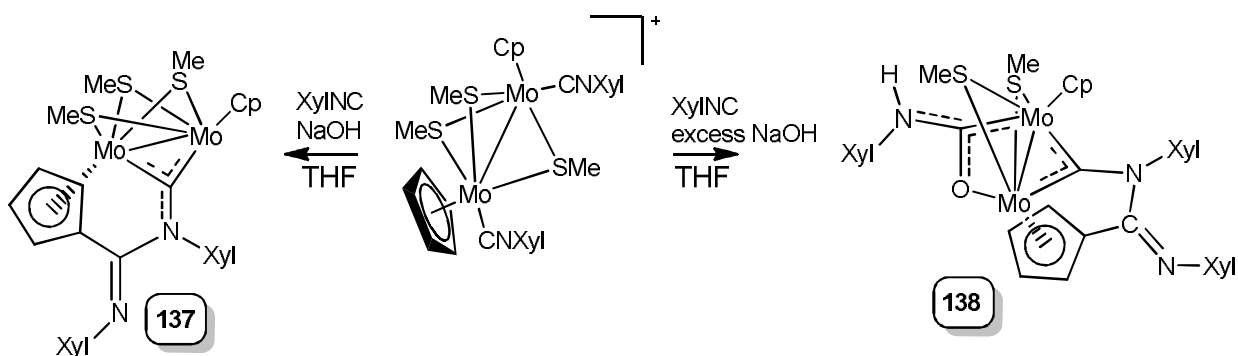


Fig. 54. Ferrocene-substituted bis(alkylidynemolybdenum) complex.

Recent developments demonstrate unprecedented synthesis of cluster compounds containing amino-oxycarbene ligands, with the carbene oxygen bound to another metal atom in the cluster [127]. The bis-isonitrile dimolybdenum complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{xy}|\text{NC})_2][\text{BF}_4]$, containing labile bridging groups, was shown to be a good starting point for the construction of bridging alkylidene (**137**) and amino-oxycarbene cluster complexes (**138**) via coupling reactions of the cyclopentadienyl and two isonitrile

ligands. A subsequent second isonitrile and hydroxide coupling gives the amino-oxycarbene (Scheme 53). Notably, when the xylene isonitrile ligands were replaced by *t*BuNC, different thermodynamic isomers were obtained.



Scheme 53.

4. Some structural aspects

The following descriptions apply to the solid state structures of the complexes and may not apply to the structures in solution.

4.1 Geometry around the carbene moiety

The bonding geometry around a carbene carbon atom is, in general, close to planar. The orientations of the substituents relative to the carbene plane are governed by, often conflicting, electronic and steric effects.

4.1.1 Orientation of (hetero)aryl ring substituents with respect to the carbene plane

Using the depiction of a generalized Fischer-type carbene as shown in Fig. 1, A (Section 1), when the substituent R' is a (hetero)aryl ring (i.e. 2-thienyl, 2-furyl, Cp, etc), this ring should, ideally, be coplanar with the carbene plane to maximize electron delocalization between the carbene and aryl moieties. The X-C_{carbene}-C_{ring}-Y (where Y is the ring hetero or ortho carbon atom) torsion angle may be used as an indication of the degree of coplanarity of the ring and the carbene plane. In the reported crystal structures of the classes of Fischer carbene complexes which fall within the ambit of this review and in which R' (Fig. 1, A, Section 1) is a hetero-aryl ring, the magnitudes of the torsion angle as defined above deviate from 0° or 180° by between 0.0° for [2,5-((CO)₅W=C(OEt))₂furan] [65]

(Fig. 16a, Section 2.3.1) and 30.7° and 50.1° for [2,5- $\{(\text{CO})_9\text{Re}_2=\text{C}(\text{OEt})\}_2$ thiophene] [75]. From some 26 observations (in some cases including more than one from a single structure) 9 were in the range 0.0° - 4.1°, 6 in the range 6.2° - 9.7°, 6 in the range 11.1° - 16.5°, 3 in the range 20.1° - 20.9° and 2 in the range 30.7° - 50.1°. The three deviations slightly greater than 20°, are all observed in structures with methyl substituents in the 3 position of fused thienothiophene ring systems [72,74] (Fig 16c, Section 2.3.1), [75]. The bulk of the methyl substituents may inhibit the thienyl rings adopting a more co-planar orientation with respect to the carbene plane. The two largest deviations, as indicated above, occur in a complex with two bulky $\text{Re}_2(\text{CO})_5$ groups. In many of these structures the hetero-aryl ring adopts an orientation close to co-planar with the carbene plane but the stabilization afforded by the π -electron delocalization is probably small and is easily overridden by intra-molecular steric requirements or inter-molecular lattice packing requirements. When R' is Fc, the extra bulk of this substituent can increase the importance of lattice packing effects leading to a wider range of deviations of the X-C_{carbene}-C_{ring}-Y torsion angle from 0°: 0.0° for $[(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{Fc}]$ [141] to 43.7° for $[(\text{CO})_4\text{W}=\text{C}\{\eta^2\text{-N}(\text{C}_3\text{H}_3)(\text{C}_5\text{H}_{11})\}\text{Fc}]$ [163]. The possibility of even more severe intra-molecular geometry requirements, as a bridging moiety, when R' is Fc' leads to a yet greater range of deviations: 0.0° for $[\{(\text{CO})_5\text{Cr}\}_2\mu^2\text{-}\{=\text{C}(\text{OEt})\}_2(\text{Fc}')]$ [159] (Fig. 38, Section 3.2.3) to 69.5° for $[\text{W}(\text{CO})_4\{(\text{Ph}_2\text{P})\text{Fc}'\text{C}(\text{NEt}_2)\text{-}\mu_2\text{-C,P}\}]$ [137] (Cr analogue is shown in Fig 30, Section 3.2.1).

4.1.2 Orientation of aromatic five-membered heterocycle substituents with respect to alkoxy substituents

The XR substituent on the carbene, in particular when it comprises a short-chain alkoxy group, generally lies approximately coplanar with the carbene plane and is orientated such that the lone pair on the oxygen is directed away from the adjacent carbonyl ligands: the "carbonyl wall" [18,210] and thus the alkyl group is orientated towards the carbonyls and normally nestles in a staggered position between two carbonyls (see, for example: [65-67,140]). This orientation may lead to an interaction between the alkoxy oxygen atom and the hetero atom (Y) of a hetero-aryl ring substituent. When Y is a sulfur atom (i.e. in a thiophene ring), in most cases the ring adopts an orientation with the sulfur close

to the alkoxy oxygen (i.e. in a *cis* arrangement about the C_{carbene}–C_{ring} bond [52,56] (Fig. 55), [140,159]. However, when Y is an oxygen atom (i.e. in a furan ring), normally the ring adopts an orientation with the furan oxygen in a *trans* arrangement with respect to the alkoxy oxygen about the C_{carbene}–C_{ring} bond. Few structures, relevant to the ambit of this review, containing a furan ring have been reported, but see, for example, [2- $\{(CO)_9Mn_2=C(OEt)\}$ furan] [152]. The favored orientations can be overridden by steric requirements. In three analogous biscarbene rod complexes: [2,5- $\{(CO)_5M=C(OEt)\}_2$ -3,6-dimethylthieno[3,2-*b*]thiophene], (M = Cr [74], Mo (Fig. 16c, Section 2.3.1) [72] or W [75]) the methyl substituents on the 3 and 6 positions of the fused ring system prevent these complexes from adopting the favored *cis* orientations for the sulfur atoms with respect to the ethoxy oxygen atoms since this would bring the M(CO)₅ moieties and the methyl groups into too close proximity. Thus *trans, trans* orientations are forced for these complexes. In two biscarbene rod structures with a single furan spacer [2,5- $\{(CO)_5M=C(OR)\}_2$ furan], (M = W, R = Et (Fig. 16a, Section 2.3.1) [65]; M = Cr, R = Me [66]), the complexes cannot adopt the preferred *trans, trans* orientation for the alkoxy oxygen atoms with respect to the furan oxygen atom since this would bring the two M(CO)₅ moieties into far too close proximity. Thus one of the carbene moieties has to adopt a *cis* orientation while the other can adopt the favored *trans* orientation and hence these complexes adopt *cis, trans* orientations. In contrast, the thiophene analogue [2,5- $\{(CO)_5Cr=C(OEt)\}_2$ thiophene] adopts the favored (for thiophene) *cis, cis* orientation [64]. Few relevant similar pyrrole (Y = N) structures have been published. In the structures of both [2,5- $\{(CO)_5W=C(OEt)\}_2$ -*N,N'*-dimethylpyrrolo[3,2-*b*]pyrrole] [74] and [5,5'- $\{(CO)_5W=C(OEt)\}_2$ (*N,N'*-dimethyl[2,2']bipyrrole)] (Fig. 16b, Section 2.3.1) [67] the pyrrole nitrogen atoms adopt *cis* orientations with respect to the ethoxy oxygen atoms. However in any case, by similar arguments as used for the complexes with 3,6-dimethylthieno[3,2-*b*]thiophene] spacers, as mentioned above, the methyl substituents on the nitrogen atoms force the *cis, cis* orientations.

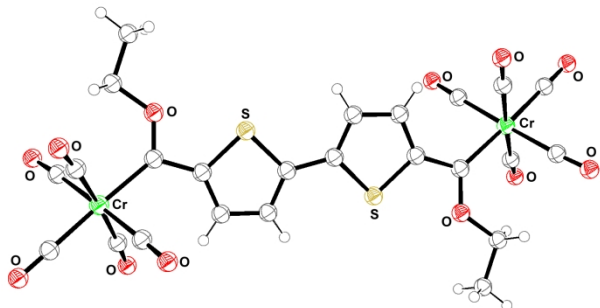


Fig. 55 Molecular structure of $[5,5'-\{(CO)_5Cr=C(OEt)\}_2[2,2']bithiophene]$ [68].

4.2 Relative orientation of the heterocyclic rings in biscarbene rod complexes with multiple aromatic five-membered heterocyclic rings

Only two structures of biscarbene rod complexes with multiple (non fused) heteroaromatic rings as spacers have been published. However, two more, as yet unpublished, structures are included in this discussion. In such complexes the rings are expected to be coplanar to maximize π -electron delocalization through the linked aromatic system. In the structures of the complex $[5,5'-\{(CO)_5Cr=C(OEt)\}_2[2,2']bithiophene]$ (Fig. 55) the molecule lie across centres of inversion and thus the pairs of rings in two two-ring structures and the centre pair of rings in the quaterthiophene structure are all exactly coplanar and the hetero atoms adopt *trans* orientations about the inter-ring bonds. In contrast, in the complex $[5,5'-\{(CO)_5W=C(OEt)\}_2(N,N'-dimethyl[2,2']bipyrrole)]$ (Fig. 16b, Section 2.3.1) [67] the two pyrrole rings tend towards adopting an orientation with the two nitrogen atoms *cis* to each other. However the proximity of the methyl substituents on the two nitrogen atoms prevents the rings being coplanar and the N—C—C—N torsion angle is 61.5° . Thus for thiophene-thiophene and furan-furan systems a *trans* orientation is favored, but for the pyrrole-pyrrole system a *cis* orientation is favored even at a loss of coplanarity of the rings.

5. Concluding remarks

During the last decade few examples of carbene unit assemblies have been reported and their chemistry and properties remain to be investigated [93,211]. One notable example is

the pioneer work by Macomber [212] reporting the first polymers containing multicarbene moieties as a forerunner to the evolution of the multimetal carbene field. The potential for macromolecular multicarbenes is increasing in the areas of synthesis, catalysis and materials. The application of Fischer monocarbene complexes in organic synthesis has grown remarkably over the last two decades. Associated with the metal-carbon double bond are novel template reactions and by adding carbene substituents with active sites, the Fischer carbene ligand is becoming a unique tool for the preparation of interesting new metal-containing as well as metal-free designer molecules [93,94,202]. Fischer carbene complexes have also not yet entered the nanochemistry arena. Metal clusters containing carbene ligands are mostly not designer molecules but the consequence of having reactive metal fragments and substrates present. The goal here would be to prepare macromolecules with regular metal-carbon double bonds by building up mononuclear fragments into larger molecules or clusters. Such molecules could form the interface between carbene ligands on surfaces or in frameworks, and on the other side, the well-studied mononuclear monocarbene chemistry.

Whereas much is known about varying metals or selecting carbene substituents in the chemistry of Fischer carbene chemistry, less is known of the chemistry of multimetal and multicarbene systems. Will the carbene ligands act independently, or is it possible to export co-operative effects for novel application in organic synthesis [167,168]?

In the field of non-linear optics, conjugated unsaturated systems with a transition metal moiety have been employed for their electron delocalization and so-called 'push-pull' characteristics [134,213,214], and the magnetic spin cross-over properties of such carbene-containing molecular wires examined [106,215]. The engineering of designer surfaces functionalized with carbenes [50,51,216-218], and the redox properties and intervalence charge transfer of such organometallic systems on electrode surfaces [219] are other rapidly expanding focus areas. A class of multimetal multicarbene complexes with great potential includes those with a large number of carbene ligands found in close proximity to each other in macromolecular assemblies or surfaces. Challenges that remain are the preparation of regular multicarbene polymers, dendrites and MOFs.

References

- [1] J.W. Herndon, *Coord. Chem. Rev.* 227 (2002) 1.
- [2] J.W. Herndon, *Coord. Chem. Rev.* 243 (2003) 3.
- [3] J.W. Herndon, *Coord. Chem. Rev.* 248 (2004) 3.
- [4] J.W. Herndon, *Coord. Chem. Rev.* 249 (2005) 999.
- [5] J.W. Herndon, *Coord. Chem. Rev.* 250 (2006) 1889.
- [6] J.W. Herndon, *Coord. Chem. Rev.* 251 (2007) 1158.
- [7] J.W. Herndon, *Coord. Chem. Rev.* 253 (2009) 86.
- [8] J.W. Herndon, *Coord. Chem. Rev.* 253 (2009) 1517.
- [9] J.W. Herndon, *Coord. Chem. Rev.* 254 (2010) 103.
- [10] J.W. Herndon, *Coord. Chem. Rev.* 255 (2011) 3.
- [11] M.A. Sierra, *Chem. Rev.* 100 (2000) 3591 and references therein.
- [12] J. Poater, M. Cases, X. Fradera, M. Duran, M. Sola, *Chem. Phys.* 294 (2003) 129.
- [13] A. Krapp, G. Frenking, *J. Am. Chem. Soc.* 130 (2008) 16646.
- [14] A. Krapp, K.K. Pandey, G. Frenking, *J. Am. Chem. Soc.* 129 (2007) 7596.
- [15] G. Frenking, M. Sola, S.F. Vyboishchikov, *J. Organomet. Chem.* 690 (2005) 6178.
- [16] M. Cases, G. Frenking, M. Duran, M. Sola, *Organometallics* 21 (2002) 4182.
- [17] M.L. Lage, I. Fernandez, M.J. Mancheno, M.A. Sierra, *Inorg. Chem.* 47 (2008) 5253.
- [18] D.M. Andrada, M.E.Z. Michoff, I. Fernandez, A.M. Granados, M.A. Sierra, *Organometallics* 26 (2007) 5854.
- [19] M.A. Sierra, I. Fernandez, F.P. Cossio, *Chem. Commun.* (2008) 4671.
- [20] I. Fernandez, M.A. Sierra, M.J. Mancheno, M. Gomez-Gallego, F.P. Cossio, *J. Am. Chem. Soc.* 130 (2008) 13892.

- [21] I. Fernandez, M.A. Sierra, M.J. Mancheno, M. Gomez-Gallego, F.P. Cossio, *Eur. J. Inorg. Chem.* (2008) 2454.
- [22] I. Fernandez, M.A. Sierra, M. Gomez-Gallego, M.J. Mancheno, F.P. Cossio, *Chem. Eur. J.* 11 (2005) 5988.
- [23] A. Arrieta, F.P. Cossio, I. Fernandez, M. Gomez-Gallego, B. Lecea, M.J. Mancheno, M.A. Sierra, *J. Am. Chem. Soc.* 122 (2000) 11509.
- [24] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39.
- [25] P.R. Schreiner, H.P. Reisenauer, F.C. Pickard IV, A.C. Simmonett, W.D. Allen, E. Matyus, A.G. Csaszar, *Nature* 453 (2008) 906.
- [26] M.I. Bruce, P.J. Low, *Adv. Organomet. Chem.* 50 (2004) 179.
- [27] W.A. Hermann, K. Ofele, D. von Preysing, E. Herdtweck, *J. Organomet. Chem.* 684 (2003) 235.
- [28] M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 2172.
- [29] E.O. Fischer, F.R. Kreissl, C.G. Kreiter, E.W. Meineke, *Chem. Ber.* 105 (1972) 2558.
- [30] P.B. Hitchcock, M.F. Lappert, P.L. Pye, *J. Chem. Soc., Dalton Trans.* (1977) 2160.
- [31] M.A. Sierra, J.C. del Amo, M.J. Mancheno, M. Gomez-Gallego, *J. Am. Chem. Soc.* 123 (2001) 851.
- [32] J.C. del Amo, M.J. Mancheno, M. Gomez-Gallego, M.A. Sierra, *Organometallics* 23 (2004) 5021.
- [33] M. Gomez-Gallego, M.J. Mancheno, M.A. Sierra, *Acc. Chem. Res.* 38 (2005) 44.
- [34] M.P. Lopez-Alberca, M.J. Mancheno, I. Fernandez, M. Gomez-Gallego, M.A. Sierra, R. Torres, *Org. Lett.* 9 (2007) 1757.
- [35] I. Fernandez, M.J. Mancheno, R. Vicente, L.A. Lopez, M.A. Sierra, *Chem. Eur. J.* 14 (2008) 11222.
- [36] M.P. Lopez-Alberca, M.J. Mancheno, I. Fernandez, M. Gomez-Gallego, M.A. Sierra, R. Torres, *Chem. Eur. J.* 15 (2009) 3595.
- [37] M.A. Sierra, J.C. del Amo, M.J. Mancheno, M. Gomez-Gallego, M.R. Torres, *Chem. Commun.* (2002) 1842.

- [38] J. Barluenga, A.A. Trabanco, I. Perez-Sanchez, R. De la Campa, J. Florez, S. Garcia-Granda, A. Aguirre, *Chem. Eur. J.* 14 (2008) 5401.
- [39] S.-W. Zhang, F. Motoori, S. Takahashi, *J. Organomet. Chem.* 574 (1999) 163.
- [40] S.-W. Zhang, T. Kaharu, N. Pirio, R. Ishii, M. Uno, S. Takahashi, *J. Organomet. Chem.* 489 (1995) C62.
- [41] M. Werner, T. Lis, U. Bruhn, R. Lindner, D. Steinborn, *Organometallics* 25 (2006) 5946.
- [42] D. Steinborn, S. Schwieger, *Chem. Eur. J.* 13 (2007) 9668.
- [43] E.O. Fischer, W. Roll, U. Schubert, K. Ackermann, *Angew. Chem. Int. Ed. Engl.* 20 (1981) 611.
- [44] E.O. Fischer, W. Roll, N.H.T. Huy, K. Ackermann, *Chem. Ber.* 115 (1982) 2951.
- [45] U. Schubert, K. Ackermann, N.H.T. Huy, W. Roll, *J. Organomet. Chem.* 232 (1982) 155.
- [46] N.H.T. Huy, C. Pascard, E.T.H. Dau, K.H. Dotz, *Organometallics* 7 (1988) 590.
- [47] N.A. van Jaarsveld, D.C. Liles, S. Lotz, *Dalton. Trans.* 39 (2010) 5777.
- [48] U. Schubert, K. Ackermann, P. Rustemeyer, *J. Organomet. Chem.* 231 (1982) 323.
- [49] S.J. Wang, L.L. Miller, R.A. Jacobson, R.J. Angelici, *Inorg. Chim. Acta* 145 (1988) 129.
- [50] P. Srivastava, A. Sarkar, S. Sawoo, A. Chakraborty, P. Dutta, O. Bouloussa, C. Methivier, C.-M. Pradier, S. Boujday, M. Salmain, *J. Organomet. Chem.* 696 (2011) 1102.
- [51] P. Dutta, S. Sawoo, N. Ray, O. Bouloussa, A. Sarkar, *Bioconjug. Chem.* 22 (2011) 1202.
- [52] T. Cantat, L. Ricard, N. Mezailles, P. le Floch, *Organometallics* 25 (2006) 6030.
- [53] C.M. Lukehart, *Acc. Chem. Res.* 14 (1981) 109.
- [54] C.M. Lukehart, *Adv. Organomet. Chem.* 25 (1986) 45.
- [55] D. Steinborn, M. Gerisch, K. Merzweiler, K. Schenzel, K. Pelz, H. Bogel, J. Magull, *Organometallics* 15 (1996) 2454.

- [56] D. Steinborn, M. Gerisch, T. Hoffmann, C. Bruhn, G. Israel, F.W. Muller, J. Organomet. Chem. 598 (2000) 286.
- [57] S. Schwieger, F.W. Heinemann, C. Wagner, R. Kluge, C. Damm, G. Israel, D. Steinborn, Organometallics 28 (2009) 2485.
- [58] F. Acha, M.A. Garralda, R. Hernandez, L. Ibarlucea, E. Pinilla, M.R. Torres, M. Zarandona, Eur. J. Inorg. Chem. (2006) 3893.
- [59] C.-Y. Wong, W.-L. Man, C. Wang, H.-L. Kwong, W.-Y. Wong, T.-C. Lau, Organometallics 27 (2008) 324.
- [60] H.-J. Haupt, D. Petters, U. Florke, J. Organomet. Chem. 558 (1998) 81.
- [61] U. Florke, D. Petters, Acta Cryst. E57 (2001) m237.
- [62] G.L. Miessler, S. Kim, R.A. Jacobson, R.J. Angelici, Inorg. Chem. 26 (1987) 1690.
- [63] K. Ulrich, V. Guerschais, K.H. Dotz, L. Toupet, H. le Bozec, Eur. J. Inorg. Chem. (2001) 725.
- [64] Y.M. Terblans, H.M. Roos, S. Lotz, J. Organomet. Chem. 566 (1998) 133.
- [65] C. Crause, H. Gorls, S. Lotz, Dalton. Trans. (2005) 1649.
- [66] D.C. Liles, S. Lotz, Acta Cryst. E62 (2006) m331.
- [67] S. Lotz, C. Crause, A.J. Olivier, D.C. Liles, H. Gorls, M. Landman, D.I. Bezuidenhout, Dalton. Trans. (2009) 697.
- [68] M. Landman, J. Ramontja, M. van Staden, D.I. Bezuidenhout, P.H. van Rooyen, D.C. Liles, S. Lotz, Inorg. Chim. Acta. 363 (2010) 705.
- [69] C. Hartbaum, E. Mauz, G. Roth, K. Weissenbach, H. Fischer, Organometallics 18 (1999) 2619.
- [70] M.P. Lopez-Alberca, M.J. Mancheno, I. Fernandez, M. Gomez-Gallego, M.A. Sierra, Org. Lett. 10 (2008) 365.
- [71] A. Rabier, N. Lugan, R. Mathieu, J. Organomet. Chem. 617-618 (2001) 681.
- [72] M. Landman, H. Gorls, S. Lotz, Z. Anorg. Allg. Chem. 628 (2002) 2037.
- [73] M. Landman, H. Gorls, S. Lotz, J. Organomet. Chem. 617-618 (2001) 280.

- [74] M. Landman, H. Gorls, S. Lotz, *Eur. J. Inorg. Chem.* (2001) 233.
- [75] S. Lotz, M. Landman, H. Gorls, C. Crause, H. Nienaber, A.J. Olivier, *Z. Naturforsch* 62b (2007) 419.
- [76] S. Lotz, M. Landman, A.J. Olivier, D.I. Bezuidenhout, D.C. Liles, E.R. Palmer, *Dalton. Trans.* 40 (2011) 9394.
- [77] K. Ulrich, E. Porhiel, V. Peron, V. Ferrand, H. le Bozec, *J. Organomet. Chem.* 601 (2000) 78.
- [78] M. Paneque, M.L. Poveda, F. Vattier, E. Alvarez, E. Carmona, *Chem. Commun.* (2009) 5561.
- [79] K. Fuchibe, N. Iwasawa, *Chem. Eur. J.* 9 (2003) 905.
- [80] M.A. Sierra, P.J. Ramirez-Lopez, M. Gomez-Gallego, T. Lejon, M.J. Mancheno, *Angew. Chem. Int. Ed. Engl.* 41 (2002) 3442.
- [81] R. Martinez-Alvarez, M. Gomez-Gallego, I. Fernandez, M.J. Mancheno, M.A. Sierra, *Organometallics* 23 (2004) 4647.
- [82] M.A. Sierra, M. Gomez-Gallego, R. Martinez-Alvarez, *Chem. Eur. J.* 13 (2007) 736.
- [83] K. Motoyama, T. Koike, M. Akita, *Chem. Commun.* (2008) 5812.
- [84] K.H. Dotz, J. Stendel (Jr), *Chem. Rev.* 109 (2009) 3227 and references therein.
- [85] R. Aumann, H. Nienaber, *Adv. Organomet. Chem.* 41 (1997) 163 and references therein.
- [86] A. de Meijere, H. Schirmer, M. Deutsch, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 3964 and references therein.
- [87] J. Barluenga, F. Rodriguez, F.J. Fananas, J. Florez, *Top. Organomet. Chem.* 13 (2004) 59 and references therein.
- [88] J. Chen, Z. Yu, Z. Zheng, K. Gu, S. Wu, F. Zeng, W. Tan, X. Wu, W. Xiao, *Organometallics* 24 (2005) 302.
- [89] Z. Zheng, Z. Yu, L. Wang, W. He, Z. Liu, X. Han, *J. Organomet. Chem.* 691 (2006) 5007.
- [90] R. Aumann, M. Kossmeier, K. Roths, R. Frohlich, *Tetrahedron* 56 (2000) 4935.

- [91] R. Aumann, M. Kossmeier, C. Muck-Lichtenfeld, F. Zippel, *Eur. J. Org. Chem.* (2000) 37.
- [92] N. Luo, Z. Yu, *J. Organomet. Chem.* 694 (2009) 3058.
- [93] I. Fernandez, M.J. Mancheno, M. Gomez-Gallego, M.A. Sierra, *Org. Lett.* 5 (2003) 1237.
- [94] M.P. Lopez-Alberca, M.J. Mancheno, I. Fernandez, M. Gomez-Gallego, M.A. Sierra, C. Hemmert, H. Gornitzka, *Eur. J. Inorg. Chem.* (2011) 842.
- [95] A. Llordes, M.A. Sierra, M.P. Lopez-Alberca, E. Molins, S. Ricart, *J. Organomet. Chem.* 690 (2005) 6096.
- [96] B. Fuss, M. Dede, B. Weibert, H. Fischer, *Organometallics* 21 (2002) 4425.
- [97] D.A. Valyaev, M.G. Peterleitner, L.I. Leont'eva, L.N. Novikova, O.V. Semeikin, V.N. Khrustalev, M.Y. Antipin, N.A. Ustynyuk, B.W. Skelton, A.H. White, *Organometallics* 22 (2003) 5491.
- [98] J.M. Moreto, S. Ricart, K.H. Dotz, E. Molins, *Organometallics* 20 (2001) 62.
- [99] M.L. Lage, M.J. Mancheno, R. Martinez-Alvarez, M. Gomez-Gallego, I. Fernandez, M.A. Sierra, *Organometallics* 28 (2009) 2762.
- [100] L. Quast, M. Nieger, K.H. Dotz, *Organometallics* 19 (2000) 2179.
- [101] C. Neumann, E. Ionescu, U. Schiemann, M. Schlenker, M. Bode, F. Ruthe, P.G. Jones, R. Streubel, *J. Organomet. Chem.* 643-644 (2002) 253.
- [102] S. Lotz, P.H. van Rooyen, R. Meyer, *Adv. Organomet. Chem.* 37 (1995) 219.
- [103] U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 969.
- [104] W. Beck, B. Niemer, M. Wieser, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 923.
- [105] H. Lang, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 547.
- [106] F. Paul, C. Lapinte, *Coord. Chem. Rev.* 178-180 (1998) 431.
- [107] T.V. Ashworth, M.J. Chetcuti, J.A.K. Howard, F.G.A. Stone, S.J. Wisbey, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1981) 763.
- [108] M.R. Awang, G.A. Carriedo, J.A.K. Howard, K.A. Mead, I. Moore, C.M. Nunn, F.G.A. Stone, *J. Chem. Soc., Chem. Commun.* (1983) 964.

- [109] G.A. Carriedo, V. Riera, G. Sanchez, X. Solans, M. Labrador, *J. Organomet. Chem.* 391 (1990) 431.
- [110] G.A. Carriedo, D. Hodgson, J.A.K. Howard, K. Marsden, F.G.A. Stone, M.J. Went, P. Woodward, *J. Chem. Soc., Chem Commun.* (1982) 1006.
- [111] S.J. Dossett, A.F. Hill, J.A.K. Howard, B.A. Nasir, T.P. Spaniol, P. Sherwood, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1989) 1871.
- [112] D.D. Ellis, J.M. Farmer, J.M. Malget, D.F. Mullica, F.G.A. Stone, *Organometallics* 17 (1998) 5540.
- [113] G.P. Elliott, J.A.K. Howard, C.M. Nunn, F.G.A. Stone, *J. Chem. Soc., Chem Commun.* 122 (1986) 431.
- [114] S.H.F. Becke, M.D. Bermudez, N.H.T. Huy, J.A.K. Howard, O. Johnson, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1987) 1229.
- [115] M. Terada, G. Higashihara, A. Inagaki, M. Akita, *Chem. Commun.* 38 (2003) 2984.
- [116] J. Wu, P.E. Fanwick, C.P. Kubiak, *J. Am. Chem. Soc.* 111 (1989) 7812.
- [117] S. Zhang, Q. Xu, J. Sun, J. Chen, *Organometallics* 22 (2003) 1816.
- [118] S. Zhang, Q. Xu, J. Sun, J. Chen, *Chem. Eur. J.* 9 (2003) 5111.
- [119] J.B. Chen, R.T. Wang, *Coord. Chem. Rev.* 231 (2002) 109.
- [120] E.O. Fischer, J.K.R. Wanner, G. Muller, J. Riede, *Chem. Ber.* 118 (1985) 3311.
- [121] Y. Tang, J. Sun, J. Chen, *Organometallics* 18 (1999) 4337.
- [122] L. Zhang, B. Zhu, N. Xiao, Q. Xu, N. Tsumori, J. Sun, Y. Yin, J. Chen, *Organometallics* 22 (2003) 4369.
- [123] Y. Tang, J. Sun, J. Chen, *Organometallics* 19 (2000) 72.
- [124] F.G.A. Stone (Ed.), *Advances in Organometallic Chemistry* 39, Academic Press Inc., California, 1996.
- [125] J. Barluenga, F.J. Fananas, *Tetrahedron* 56 (2000) 4597 and references therein.
- [126] M.E. Garcia, D. Garcia-Vivo, M.A. Ruiz, *Organometallics* 27 (2008) 543.

- [127] W.-S. Ojo, E. Paugam, F.Y. Petillon, P. Schollhammer, J. Talarmin, K.W. Muir, *Organometallics* 25 (2006) 4009.
- [128] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, E. Zoli, *J. Organomet. Chem.* 690 (2005) 1959.
- [129] E.O. Fischer, R.B.A. Pardy, U. Schubert, *J. Organomet. Chem.* 181 (1979) 37.
- [130] R.D. Topsom, *Acc. Chem. Res.* 16 (1983) 292.
- [131] E.O. Fischer, F.J. Gammel, D. Neugebauer, *Chem. Ber.* 113 (1980) 1010.
- [132] J.A. Connor, E.M. Jones, J.P. Lloyd, *J. Organomet. Chem.* 24 (1970) C20.
- [133] B. Bildstein, *J. Organomet. Chem.* 617-618 (2001) 28.
- [134] K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarkar, *Organometallics* 18 (1999) 3851.
- [135] A.J.L. Pombeiro, *J. Organomet. Chem.* 690 (2005) 6021.
- [136] L. Meca, D. Dvorak, J. Ludvik, I. Cisarova, P. Stepnicka, *Organometallics* 23 (2004) 2541.
- [137] U. Behrendt, R.-M. Pfeifer, R. Wartchow, H. Butenschon, *New J. Chem* 23 (1999) 891.
- [138] M. Schwarz, R. Wartchow, H. Butenschon, *J. Organomet. Chem.* 690 (2005) 6217.
- [139] M. Schwarz, M. Vollmann, R. Wartchow, H. Butenschon, *J. Organomet. Chem.* 690 (2005) 2263.
- [140] D.I. Bezuidenhout, W. Barnard, B. van der Westhuizen, E. van der Watt, D.C. Liles, *Dalton. Trans.* 40 (2011) 6711.
- [141] J.G. Lopez-Cortes, L.F.C. de la Cruz, M.C. Ortega-Alfaro, R.A. Toscano, C. Alvarez-Toledano, H. Rudler, *J. Organomet. Chem.* 690 (2005) 2229.
- [142] K.H. Dotz, R. Dietz, D. Neugebauer, *Chem. Ber.* 112 (1979) 1486.
- [143] M. Zora, E.U. Gungor, *Tetrahedron Lett.* 42 (2001) 4733.
- [144] J. Bennewits, M. Nieger, B. Lewall, K.H. Dotz, *J. Organomet. Chem.* 690 (2005) 5892.

- [145] R. Schobert, R. Kempe, T. Schmalz, A. Gmeiner, *J. Organomet. Chem.* 691 (2006) 859.
- [146] C. Hartbaum, G. Roth, H. Fischer, *Eur. J. Inorg. Chem.* (1998) 191.
- [147] Y.M. Terblans, S. Lotz, *J. Chem. Soc., Dalton Trans.* (1997) 2177.
- [148] T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 710.
- [149] T.A. Waldbach, R. van Eldik, P.H. van Rooyen, S. Lotz, *Organometallics* 16 (1997) 4056.
- [150] T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Organometallics* 12 (1993) 4250.
- [151] D.I. Bezuidenhout, S. Lotz, M. Landman, D.C. Liles, *Inorg. Chem.* 50 (2011) 1521.
- [152] D.I. Bezuidenhout, D.C. Liles, P.H. van Rooyen, S. Lotz, *J. Organomet. Chem.* 692 (2007) 774.
- [153] J.F. Janik, E.N. Duesler, R.T. Paine, *J. Organomet. Chem.* 323 (1987) 149.
- [154] E.O. Fischer, P. Rustemeyer, *J. Organomet. Chem.* 225 (1982) 265.
- [155] E. Stander, C. Esterhuysen, J.M. McKenzie, S. Cronje, H.G. Raubenheimer, *Dalton Trans.* (2007) 5684.
- [156] C. Hartbaum, H. Fischer, *J. Organomet. Chem.* 578 (1999) 186.
- [157] H. Fischer, C. Harbaum, C. Wespel, M. Dede, *Z. Anorg. Allg. Chem.* 630 (2004) 1863.
- [158] C. Mongin, Y. Ortin, N. Lugan, R. Mathieu, *Eur. J. Inorg. Chem.* (1999) 739.
- [159] D.I. Bezuidenhout, E. van der Watt, D.C. Liles, M. Landman, S. Lotz, *Organometallics* 27 (2008) 2447.
- [160] H. Helten, M. Beckmann, G. Schnakenburg, R. Streubel, *Eur. J. Inorg. Chem.* (2010) 2337.
- [161] M.L. Lage, I. Fernandez, M.J. Mancheno, M. Gomez-Gallego, M.A. Sierra, *Chem. Eur. J.* 15 (2009) 593.
- [162] P.G. Jones, C. Wismach, Private Communication, CCD Code QUWQEF, The Cambridge Structural Database (F.H. Allen, *Acta Cryst.* B58 (2002) 380)).

- [163] J.G. Lopez-Cortes, A. Samano-Galinda, M.C. Ortega-Alfaro, A. Toscano, H. Rudler, A. Parlier, C. Alvarez-Toledano, *J. Organomet. Chem.* 690 (2005) 3664.
- [164] R. Streubel, M. Beckmann, C. Neumann, S. Fankel, H. Helten, O. Feier-Iova, P.G. Jones, M. Nieger, *Eur. J. Inorg. Chem.* (2009) 2090.
- [165] C. Sandoval-Chavez, J.G. Lopez-Cortes, A.I. Gutierrez-Hernandez, M.C. Ortega-Alfaro, A. Toscano, C. Alvarez-Toledano, *J. Organomet. Chem.* 694 (2009) 3692.
- [166] M.L. Lage, D. Curiel, I. Fernandez, M.J. Mancheno, M. Gomez-Gallego, P. Molina, M.A. Sierra, *Organometallics* 30 (2011) 1794.
- [167] J.D. Offner, R. Frohlich, O. Kataeva, F. Rose-Munch, E. Rose, K.H. Dotz, *Organometallics* 28 (2009) 3004.
- [168] J.D. Offner, G. Schnakenburg, F. Rose-Munch, E. Rose, K.H. Dotz, *Inorg. Chem.* 50 (2011) 8153.
- [169] E.O. Fischer, S.J. Fontana, *J. Organomet. Chem.* 40 (1972) 163.
- [170] M. Sabat, M.F. Gross, M.G. Finn, *Organometallics* 11 (1992) 745.
- [171] G. Erker, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 397.
- [172] G. Erker, *Polyhedron* 7 (1988) 2451.
- [173] G. Erker, F. Sosna, U. Hoffmann, *J. Organomet. Chem.* 372 (1989) 41.
- [174] R. Beckhaus, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 686.
- [175] C. Esterhuysen, I.B.J. Nel, M.W. Esterhuysen, S. Cronje, *Acta Cryst. E* 64 (2008) m 1534.
- [176] C. Esterhuysen, A. Neveling, N. Luruli, G.J. Kruger, S. Cronje, *Acta Cryst. E* 64 (2008) m 1252.
- [177] C. Esterhuysen, I.B.J. Nel, S. Cronje, *Acta Cryst. E* 64 (2008) m 1150.
- [178] M. Bergamo, T. Beringheli, G. D'Alfonso, D. Maggioni, P. Mercandelli, A. Sironi, *Inorg. Chim. Acta.* 350 (2003) 475.
- [179] W. Petz, *J. Organomet. Chem.* 72 (1974) 369.
- [180] J. Pebler, W. Petz, *Z. Naturforsch* 29 (1974) 658.

- [181] P.T. Barger, B.D. Santarsiero, J. Armantrout, J.E. Bercaw, *J. Am. Chem. Soc.* 106 (1984) 5178.
- [182] G. Erker, G. Kehr, R. Frolich, *Adv. Organomet. Chem.* 51 (2004) 109.
- [183] M. Berlekamp, G. Erker, B. Schonecker, R. Krieg, A.L. Rheingold, *Chem. Ber.* 126 (1993) 2119.
- [184] C.P. Casey, S.H. Bertz, T.J. Burkhardt, *Tetrahedron Lett.* 14 (1973) 1421.
- [185] G. Erker, F. Sosna, R. Pfaff, R. Noe, C. Sarter, A. Kraft, C. Kruger, R. Zwettler, *J. Organomet. Chem.* 394 (1990) 99.
- [186] K. Mashima, K. Joydoi, A. Ohyoshi, H. Takaya, *J. Chem. Soc., Chem Commun.* (1986) 1145.
- [187] M. Berlekamp, G. Erker, J.L. Petersen, *J. Organomet. Chem.* 458 (1993) 97.
- [188] R. Briill, D. Kgosane, A. Neveling, H. Pasch, H.G. Raubenheimer, R. Sanderson, U.M. Wahner, *Macromol. Svmpl.* 165 (2001) 11.
- [189] C.E. Strasser, S. Cronje, H.G. Raubenheiber, *New J. Chem* 34 (2010) 458.
- [190] H.G. Raubenheimer, S. Cronje, C.E. Strasser, *J. Chem. Soc., Dalton Trans.* (2009) 8145.
- [191] W. Petz, F. Weller, E.V. Avtomonov, *J. Organomet. Chem.* 598 (2000) 403.
- [192] H.G. Raubenheimer, A. du Toit, M. du Toit, J. An, L. van Niekerk, S. Cronje, C. Esterhuysen, A.M. Crouch, *J. Chem. Soc., Dalton Trans.* (2004) 1173.
- [193] B.D. Rowsell, R. McDonald, M. Cowie, *Organometallics* 23 (2004) 3873.
- [194] W. Beck, *Inorganic Synthesis* 28, 1990.
- [195] S. Anderson, A.F. Hill, A.M.Z. Slawin, A.J.P. White, D.J. Williams, *Inorg. Chem.* 37 (1998) 594.
- [196] H.G. Raubenheimer, G.J. Kruger, C.F. Marais, J.T.Z. Hattingh, L. Linford, P.H. van Rooyen, *J. Organomet. Chem.* 355 (1988) 337.
- [197] L. Busetto, V. Zanotti, *Inorg. Chim. Acta.* 361 (2008) 3004.
- [198] Y. Tang, J. Sun, J. Chen, *Organometallics* 18 (1999) 2459.

- [199] J. Ruiz, L. Garcia, B.F. Perandones, M. Vivanco, *Angew. Chem. Int. Ed. Engl.* 50 (2011) 3010.
- [200] S. Dovesi, E. Solari, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 2388.
- [201] S. Cristofani, P. Leoni, M. Pasquali, F. Eisentraeger, A. Albinati, *Organometallics* 19 (2000) 4589.
- [202] J. Barluenga, F. Rodriguez, F.J. Fananas, *Chem. Eur. J.* 6 (2000) 1930.
- [203] C. Renouard, H. Stoeckli-Evans, G. Suss-Fink, *J. Organomet. Chem.* 492 (1995) 179.
- [204] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th Ed, Wiley-Interscience, 1999.
- [205] W.-S. Hong, C.-Y. Wu, C.-S. Lee, W.-S. Hwang, M.Y. Chiang, *J. Organomet. Chem.* 689 (2004) 277.
- [206] J.-M. Yang, B. Hu, C.-G. Xia, *J. Clust. Sci.* 19 (2008) 615.
- [207] M. Shieh, H.-S. Chen, Y.-W. Lai, *Organometallics* 23 (2004) 4018.
- [208] M. Shieh, H.-S. Chen, H.-H. Chi, C.-H. Chung, *Inorg. Chem.* 39 (2000) 5561.
- [209] S.J. Davies, A.H. Hill, M.U. Pilotti, F.G.A. Stone, *Polyhedron* 8 (1989) 2265.
- [210] I. Fernandez, F.P. Cossio, A. Arrieta, B. Lecea, M.J. Mancheno, M.A. Sierra, *Organometallics* 23 (2004) 1065.
- [211] J.C. Garrison, R.S. Simons, C.A. Tessier, W.J. Youngs, *J. Organomet. Chem.* 673 (2003) 1.
- [212] D.W. Macomber, M.-H. Hung, M. Liang, A.G. Verma, P. Madhukar, *Macromolecules* 21 (1988) 1189.
- [213] O. Briel, A. Fehn, W. Beck, *J. Organomet. Chem.* 578 (1999) 247.
- [214] J.P. Morrall, G.T. Dalton, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* 55 (2008) 61.
- [215] V. Guillaume, V. Mahias, A. Mari, C. Lapinte, *Organometallics* 19 (2000) 1422.
- [216] C. Floriani, R. Floriani-Moro, *Adv. Organomet. Chem.* 47 (2001) 167.

- [217] M. Lazar, R.J. Angelici, *Modern Surface Organometallic Chemistry*, 2009.
- [218] Y. Zhou, R.J. Angelici, L.K. Woo, *Cat. Lett.* 137 (2010) 8.
- [219] W. Chen, L.E. Brown, J.P. Konopelski, S. Chen, *Chem. Phys. Lett.* 471 (2009) 283.