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Remarkable reactions of cationic carbyne complexes of manganese, rhenium, and diiron with carbonylmetal anions

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Contents

Abstract

The cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (**1**) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (**2**), are the entry points for the synthesis of a variety of di- or tri-metal bridging carbene and bridging carbyne complexes resulting from nucleophilic attack on the carbyne carbon. Both cationic complexes, **1** and **2**, undergo a wide range of reactions with carbonylmetal mono- and di-anions, mixed-dimetal carbonyl anions, and reactive salts. Analogous studies of diiron cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ ($Ar = C_6H_5$, $p\text{-}MeC_6H_4$) and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ ($Ar = C_6H_5$, $p\text{-}MeC_6H_4$, $p\text{-}CF_3C_6H_4$) are also reviewed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cationic carbyne complexes; Carbonylmetal anions; Bridging carbene complexes; Bridging carbyne complexes

1. Introduction

The metal–metal bonded cluster complexes are well-known to have important roles in many catalytic reactions. Since many dinuclear and polynuclear metal bridging carbene and carbyne complexes are themselves metal clusters or are the precursors of metal cluster

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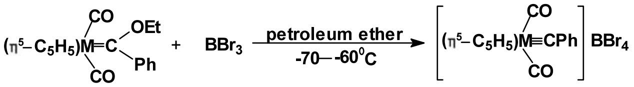
complexes, the chemistry of transition metal bridging carbene and carbyne complexes is an area of current interest. In recent years, we are interested in developing the methodologies of the synthesis of transition-metal bridging carbene and bridging carbyne complexes. A considerable number of metal bridging carbene and carbyne complexes have been synthesized by Stone and co-workers by reactions [1,2] of carbene or carbyne complexes with low-valent metal compound or by reactions [3] of neutral or anionic carbyne complexes with metal hydrides or metal cationic compounds. In our laboratory, one of the methods for the synthesis of bridging carbene and bridging carbyne complexes has used the reactions of the highly electrophilic cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2M{\equiv}CPh]BBr_4$ (M = Mn, Re), with anionic carbonylmetal compounds at low temperature. Although cationic carbyne complexes of transition-metals are widely used as starting materials in the synthesis of transition-metal carbene complexes and their reactions with nucleophiles have been extensively examined [4] and there is also a number of reaction starting from the cationic carbyne complexes of manganese and rhenium [4], only very little is known about the reactivity of cationic carbyne complexes toward metal-containing nucleophiles. Up to now, only the reactions of the cationic carbyne complexes with carbonylmetal anions $[M(CO)_5]^-$ (M = Mn, Re) and $[Fe(CO)_3NO]^-$, which led to formation of the metal–metal and μ-C–metal bonds, have been reported [5]. We found another method for the preparation of such complexes: the reactions of olefin-ligated dimetal carbonyl compounds such as pentacarbonyl(cyclooctatetraene)diiron, bis(η^5-cyclopentadienyl)diiron, and di-μ-carbonyl-*cis*-μ-(1-5-η:1′-5′-η-dicyclopentadienyldimethylsilane)bis(carbonyliron) with aryllithium reagent nucleophiles, followed by alkylation with alkylating reagent Et_3OBF_4 to give the corresponding olefin-coordinated dimetal bridging alkoxycarbene complexes in high yields [6–8]. However, this method can be only used for the synthesis of the bridging alkoxycarbene complexes. To examine the scope of this new synthetic method for dimetal bridging carbene and bridging carbyne complexes, the diiron bridging alkoxycarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (Ar = C_6H_5, *p*-MeC_6H_4) and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (Ar = C_6H_5, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$) were converted into the respective diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ by treating them with Lewis acid such as BBr_3. These diiron cationic carbyne complexes react with nucleophilic carbonylmetal anions to produce a series of new dimetal bridging carbene or bridging carbyne complexes. Since the cationic carbyne complexes and their reaction products were sensitive to air, moisture, and temperature in both solution and solid states, all procedures must be performed under a dry, oxygen-free N_2 atmosphere at low temperature using standard Schlenk techniques. In this review, we describe these remarkable reactivity of cationic carbyne complexes of manganese, rhenium, and diiron toward carbonylmetal anions.

2. Syntheses of cationic carbyne complexes of manganese, rhenium, and diiron

2.1. *Syntheses of* $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (**1**) *and* $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (**2**)

The cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (**1**) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (**2**), were prepared in high yield from the alkoxycarbene complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(OEt)Ph]$ (M = Mn, Re) [9,10], and an excess of BBr_3 in pentane or petroleum ether (30–60 °C) at −70 to −60 °C as shown in Eq. (1) [9–11].



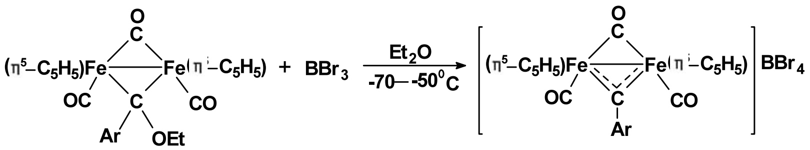
1, M = Mn
2, M = Re

(1)

The $[BF_4]^-$, $[BCl_4]^-$, and $[SbCl_6]^-$ salts of dicarbonyl(cyclopentadienyl)phenyl–carbyne manganese and rhenium were similarly prepared from the alkoxycarbene complexes of manganese or rhenium and BF_3 or BCl_3 and $SbCl_5$ [4,12]. The cationic carbyne complexes of manganese and rhenium, **1** and **2**, were extremely labile, very sensitive to air, moisture and temperature. The manganese cationic carbyne complex **1** decomposed explosively on exposure to air. They can be only stored at low temperature (below −70 °C) for a short period.

2.2. *Syntheses of* $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ *and* $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$

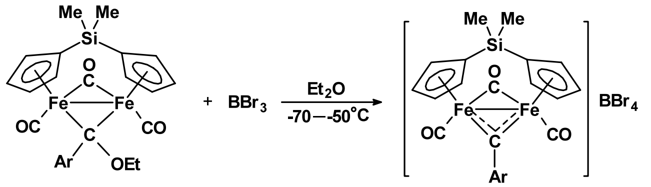
The bis(η^5-cyclopentadienyl)diiron bridging alkoxycarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (Ar = C_6H_5, *p*-MeC_6H_4) [6] in diethyl ether were treated, similar to that for preparation of the cationic carbyne complexes of **1** and **2**, with an excess of BBr_3 at −70 °C to give cationic carbyne complexes of diiron, $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**3**, Ar = C_6H_5; **4**, Ar = *p*-MeC_6H_4), as brown–red solids in 75–76% yields Eq. (2) [13].



3, Ar = Ph
4, Ar = p-MeC_6H_4

(2)

In a similar way, the analogous diiron cationic carbyne complexes, $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ (**5**, Ar = C_6H_5; **6**, Ar = p-MeC_6H_4; **7**, Ar = p-$CF_3C_6H_4$), were prepared in high yields (84–87%) from the reactions of dimethylsilane-bridged bis(η^5-cyclopentadienyl)diiron bridging alkoxycarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (Ar = C_6H_5, p-MeC_6H_4, p-$CF_3C_6H_4$) [8] with an excess of BBr_3 in ether at −70 to −50 °C as shown in Eq. (3) [14].



5, Ar = Ph
6, Ar = p-MeC_6H_4
7, Ar = p-$CF_3C_6H_4$

(3)

The other dimetal cationic bridging carbyne complexes have been obtained by reactions of dimetal bridging alkoxycarbene complexes, e.g. $[MPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}(CO)_2(PR_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mn, $PR_3 = PMe_3$; M = Re, $PR_3 = PMe_2Ph$), with Me_3OBF_4 or Et_3OBF_4 in CH_2Cl_2, which produced heteronuclear dimetal cationic bridging carbyne complexes $[MPt\{\mu\text{-}CC_6H_4Me\text{-}p\}(CO)_2(PR_3)_2(\eta^5\text{-}C_5H_5)]BF_4$ [15,16].

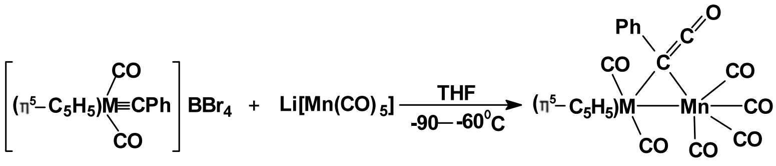
The cationic bridging carbyne complexes **3**–**7** are only sparingly soluble in polar organic solvents, such as THF and CH_2Cl_2. They are very sensitive to air, moisture, and temperature and can be only stored at low temperatures (below −65 °C) for a short period.

3. Reactions of $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (1) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (2) with metal carbonyl monoanions

The pronounced electrophilic character of the carbyne carbon in the cationic carbyne complexes makes possible an important synthetic route to neutral carbene or carbyne complexes, which are inaccessible through the usual synthetic approach. We were interested to try the reactions of cationic carbyne complexes **1** and **2** with nucleophiles containing carbonylmetal anions to determine whether or not they could be applied to synthesize di- or polymetal bridging carbene and bridging carbyne complexes. The reactions of cationic carbyne complexes **1** and **2** with carbonylmetal monoanions were firstly studied.

Thus, the freshly prepared (in situ) cationic carbyne complex $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (**1**) was allowed to react with equimolar amounts of freshly prepared (in situ) $Li[Mn(CO)_5]$ in THF at low temperatures (−90 to −60 °C) for 4–5 h. A deep red crystalline complex $[Mn_2\{\mu\text{-}C(CO)Ph\}(CO)_6(\eta^5\text{-}C_5H_5)]$ (**8**) [17] was obtained in 84% yield, Eq. (4). The cationic carbyne complex $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (**2**) reacts similarly with $[Mn(CO)_5]^-$ under the same conditions to afford $[ReMn\{\mu\text{-}C(CO)Ph\}(CO)_6(\eta^5\text{-}C_5H_5)]$ (**9**) [17] (Eq. (4)) in 86% yield. Complex **9** has also been obtained by Fischer and co-workers from the reaction [5] of $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BCl_4$ with $Na[Re(CO)_5]$ and its structure was characterized by X-ray diffraction study [5].

The analogous reactions of complexes **1** and **2** with $[Co(CO)_4]^-$ under similar conditions produced dark green crystals of $[MnCo\{\mu\text{-}C(CO)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$

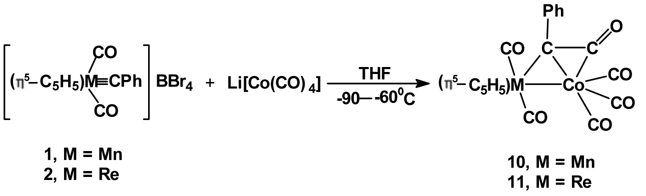


1, M = Mn
2, M = Re

8, M = Mn
9, M = Re

(4)

(**10**) and black crystals of [ReCo{μ-C(CO)Ph}$(CO)_5$(η^5-C_5H_5)] (**11**) (Eq. (5)) [17] in 82 and 81% yields, respectively.



1, M = Mn
2, M = Re

10, M = Mn
11, M = Re

(5)

Complexes **8**–**11** are formulated as possessing a ketenyl ligand bonded to a carbene carbon, which are postulated to form via CO transfer in the carbene intermediate [η^5-$C_5H_5(CO)_2M{=}C(Ph)M'(CO)_n$] (M = Mn, Re; M′ = Mn, Co; $n = 4$, 5) or via transfer of a CO ligand from $M'(CO)_n$ moiety to a metal–carbyne center [18]. The analogous bridging ketenyl complexes [Mn_2{μ-C(CO)C_6H_4Me-*p*}$(CO)_6$(η^5-C_5H_5)] [18] and [Mn_2{μ-C(CO)R}(Me)$(CO)_6$(η^5-C_5H_5)] (R = Ph, CpFeCp) [19] have been synthesized by the reactions of cationic carbyne complex [η^5-$C_5H_5(CO)_2M{\equiv}CC_6H_4$Me-*p*]$BF_4$ (M = Mn, Re) or [Me(η^5-C_5H_5)$(CO)_2$Mn≡CR]BCl_4 (R=Ph, CpFeCp) with [$(Ph_3P)_2N$][$Mn(CO)_5$] or K[$Mn(CO)_5$]. Interestingly, the reaction of [Me(η^5-C_5H_5)$(CO)_2$Mn≡CR]BCl_4 (R = Ph, CpFeCp) with $[Co(CO)_4]^-$, reported by Fischer et al. [19], produced the neutral carbene complexes [Me(η^5-C_5H_5)$(CO)_2$Mn=C(R)$Co(CO)_4$] instead of the bridging ketene complexes.

The structure of **8** (Fig. 1) is similar to that of analogous complexes **9** [5] and [Mn_2{μ-C(CO)C_6H_4Me-*p*}$(CO)_6$(η^5-C_5H_5)] [18]. The Mn–Mn bond (2.726(3) Å), similar in length to that found (2.735(1) Å) in [Mn_2{μ-C(CO)C_6H_4Me-*p*}$(CO)_6$(η^5-C_5H_5)] [18], is symmetrically bridged by the α-carbon atom of a phenylketenyl group (Mn(1)–C(8) 2.13(1), Mn(2)–C(8) 2.12(1) Å) and semibridged by a CO group (Mn–C(2) 1.80(1), Mn(2)–C(2) 2.48(1) Å, Mn(1)–C(2)–O(2) 161(1), Mn(2)–C(2)–O(2) 122.0(9)°). The C(7)···Mn(2) distance of 2.76 Å is much longer than the similar bond (C(7)–Co 1.983(8) Å) in **11** (below), which indicates the different ways in which the ketenyl ligand is bridged to the metal–metal bonds, as seen in the structures shown in Eqs. (4) and (5). An unique structural feature is the presence of the C(7)O(7) group bonded to C(8) with C(7)–O(7) 1.16(2) Å and C(8)–C(7) 1.37(2) Å and an angle C(8)–C(7)–O(7) of 177(1)°. The former distance might correspond either to a C≡O or a C=O bond and the latter suggests C=C character, so that the μ-C(Ph)CO group is regarded as an one-electron ketene bridge PhC=C=O [18].

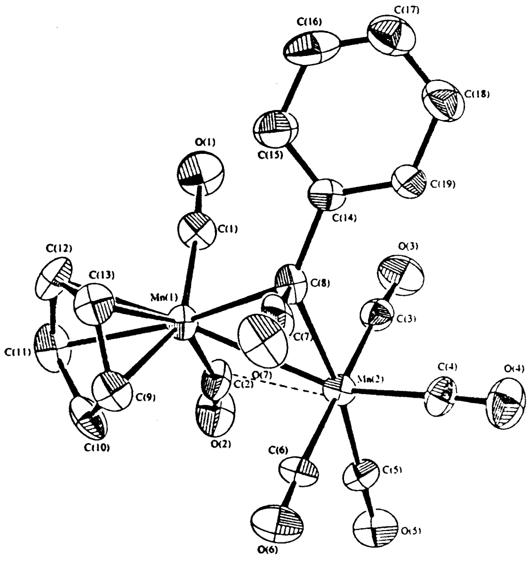


Fig. 1. Molecular structure of **8**.

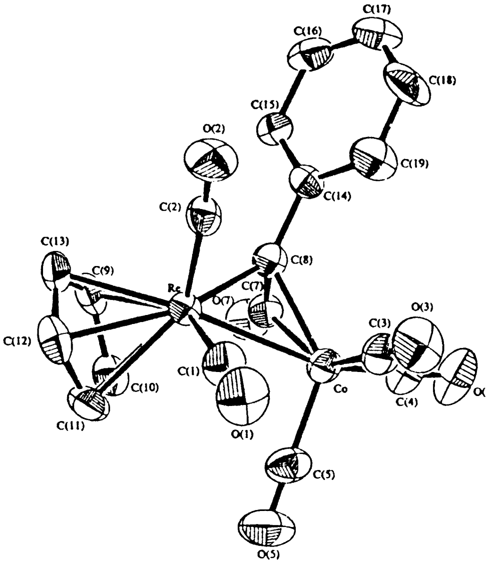


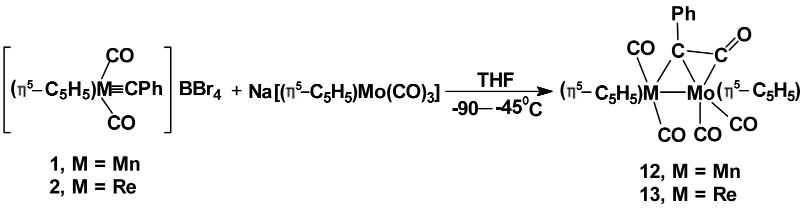
Fig. 2. Molecular structure of **11**.

The structure of **11** (Fig. 2) resembles that of **8**, except that the C=O moiety of the phenylketenyl group is linked to the Co atom through carbon (C(7)) atom in **11**.

As contrasted to that of **8**, the Re–Co bond of **11** is asymmetrically bridged by the C(CO)Ph group (Re–C(8) 2.135(9), Co–C(8) 2.021(7) Å), and the ketenyl C=C=O ligand is bridged to the Co atom through its two carbon atoms with an angle C(8)–C(7)–O(7) of 151.0(9)°. The Co–C(7) distance of 1.983(8) Å is much shorter than the corresponding bond in **8**, indicating a stronger bond between the C(7) and Co atom. The μ-C(8)–Re bond length of 2.135(9) Å is somewhat shorter than that found (2.24(3) Å) in **9** [5], while the μ-C(8)–Co distance of 2.02(7) Å is significantly shorter than the corresponding bond distance in **8**. Thus, complex **11** (and **10**) may be a dimetal bridging carbene complex but it is better regarded a ketenyl complex.

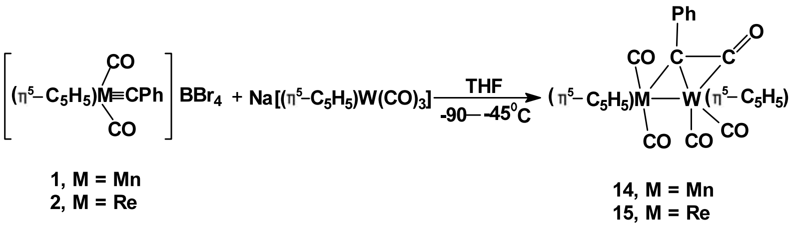
In order to examine the effect of carbonylmetal anions containing different ligands on the reactivity of the cationic carbyne complexes and reaction products, the metalcarbonyl monoanion compounds of Group VIB, such as Na[η^5-$C_5H_5M(CO)_3$] (M = Mo, W), and Group VIII, such as Na[$Co(CO)_3PPh_3$], Na[η^5-$C_5H_5Fe(CO)_2$], (NMe_4)[$HFe(CO)_4$], and [$(Ph_3P)_2N$][$Fe(CO)_3NO$] were chosen as nucleophiles for the reactions with cationic carbyne complexes **1** and **2**.

Complexes **1** and **2** react with carbonylmolybdenum anion containing a bulky subsitituent of the cyclopentadienyl group, Na[η^5-$C_5H_5Mo(CO)_3$], similar to that in reaction of **1** with Li[$Mn(CO)_5$], to give ketenyl-bridged Mn–Mo and Re–Mo complexes [MnMo{μ-C(CO)Ph}$(CO)_4(\eta^5$-$C_5H_5)_2$] (**12**) and [ReMo{μ-C(CO)Ph}$(CO)_4(\eta^5$-$C_5H_5)_2$] (**13**) (Eq. (6)) in 93 and 90% yield, respectively [20].



(6)

Like the molybdenum anion, the carbonyltungsten anion [η^5-$C_5H_5W(CO)_3$]$^-$ reacts with complexes **1** and **2** under the same conditions to afford ketenyl-bridged Mn–W and Re–W complexes [MnW{μ-C(CO)Ph}$(CO)_4(\eta^5$-$C_5H_5)_2$] (**14**) and [ReW{μ-C(CO)Ph}$(CO)_4(\eta^5$-$C_5H_5)_2$] (**15**) (Eq. (7)) [20] in 92 and 90% yield, respectively.

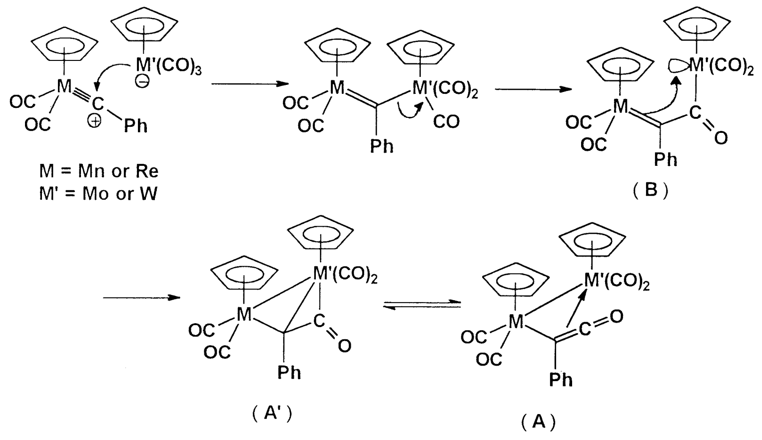


(7)

The structures of the products **12**–**15** shown in Eqs. (6) and (7) are based on elemental analyses, spectroscopic evidence, and X-ray diffraction study of **14**. The structure of **14** (Fig. 3) resembles that of **11**. The Mn–W bond (2.905(2) Å) is asymmetrically bridged by the α-carbon atom of a phenylketenyl group (Mn–C(8) 2.05(1), W–C(8) 2.15(1) Å). An unique feature of the structure, the presence of the C(7)O(7) group bonded to C(8) with a C(7)–O(7) distance of 1.21(2) Å and a C(8)–C(7) distance of 1.38(2) Å, is very similar to that in analogous complexes **8** and **11**. Thus, compounds **12**–**15** might also be described as η^1,η^2-ketenyl complexes (**A** or **A′**) (Scheme 1). The W–C(7) distance (2.25(2) Å) is much longer than the corresponding Co–C(7) distance (1.983(8) Å) in **11** since the atom radius of W is larger than that of Co.

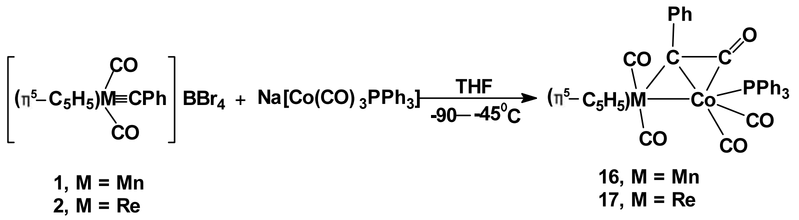
The possible reaction pathway to complexes **12**–**15** could involve initial formation of a carbene intermediate [η^5-$C_5H_5(CO)_2M{=}C(Ph)M'(CO)_3(\eta^5$-$C_5H_5)$] (M = Mn or Re, M′ = Mo or W), where the $M'(CO)_3(\eta^5$-$C_5H_5)$ moiety is directly bonded to the carbene carbon through the M′ atom, by attack of [$M'(CO)_3(\eta^5$-$C_5H_5)$]$^-$ anion on the carbyne carbon of **1** or **2**. After initial M–C bond formation, the migration of the M′=C bond of the carbene to a coordinated CO gives a coordinately unsaturated ketene complex (**B**). Then addition of the $M{=}C_{carbene}$ bond to the vacant site at M′ completes the reaction to produce the η^1,η^2-ketene complex (**A** or **A′**) (Scheme 1).

Interestingly, the bulky PPh_3-substituted carbonylcobalt anionic compound Na[$Co(CO)_3PPh_3$] can also react with **1** and **2** to give PPh_3-coordinated ketenyl bridged complexes [MnCo{μ-C(CO)Ph}$(CO)_4(PPh_3)(\eta^5$-$C_5H_5)$] (**16**) and [ReCo{μ-C(CO)Ph}$(CO)_4(PPh_3)(\eta^5$-$C_5H_5)$]



Scheme 1.

(**17**) (Eq. (8)) [20] in 89 and 81% yield, respectively. The formation pathway for complexes **16** and **17** could be analogous to that of cyclopentadienyl-substituted complexes **12**–**15**.

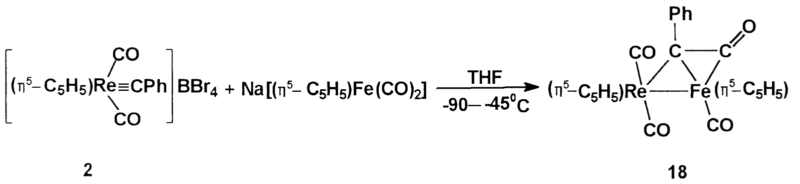


(8)

The crystal structure of complex **17** shown in Fig. 4 resembles that of **11**, except that the substituents on the Co atom are two CO and one PPh_3 group in **17** but three CO ligands in the latter. The Re–Co bond asymmetrically bridged by the α-carbon atom of the ketenyl group of C(CO)Ph has a length of 2.717(2) Å), which is nearly the same as that in **11** (2.716(2) Å). The C(7)–O(7) and C(8)–C(7) bond lengths are 1.20(1) and 1.40(1) Å, respectively, which are the same within experimental error as those in **14**. Thus the C(CO)Ph group in **17** is also regarded as a ketenyl ligand.

Unlike Mo, W, and Co anionic compounds, the iron compound $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ reacted only with complex **2** to form a ketenyl-bridged Re–Fe complex $[ReFe\{\mu\text{-}C(CO)Ph\}(CO)_3(PPh_3)(\eta^5\text{-}C_5H_5)_2]$ (**18**) (Eq. (9)) [20] in a somewhat lower yield (75%); its structure is supported by its elemental analysis and IR, ^1H-NMR, and mass spectra and by comparison of the ^1H-NMR spectrum with those of complexes **12**–**15**.

The hydridocarbonyliron anion, $(NMe_4)[HFe(CO)_4]$, can react similarly with cationic carbyne complexes **1** and **2**. However, the products were the novel heteronuclear dimetal bridging carbene complexes rather than ketenyl complexes. Thus, when complexes **1** and **2** were allowed to react with equimolar amount of $(NMe_4)[HFe(CO)_4]$ in THF at low temperature (−90 to −45 °C)



(9)

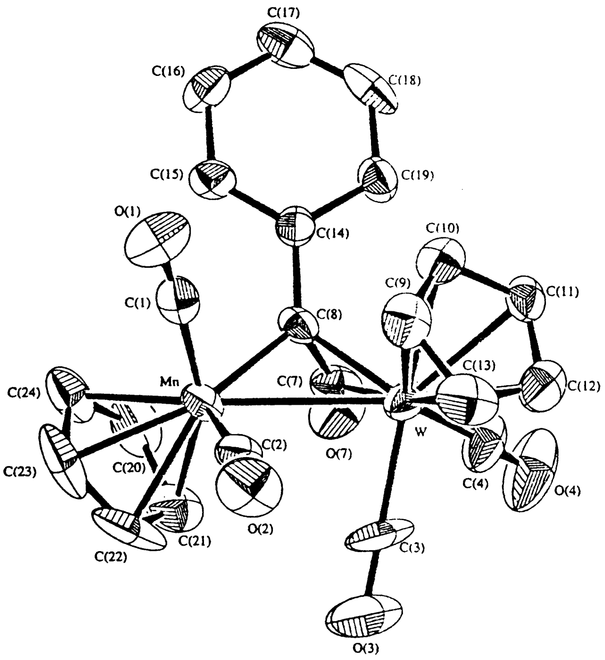


Fig. 3. Molecular structure of **14**.

for 4–5 h, the bridging carbene complexes [MnFe{μ-C(H)Ph}(CO)$_5$(η^5-C$_5$H$_5$)] (**19**) [21] (Eq. (10)) and [ReFe{μ-C(H)Ph}(CO)$_6$(η^5-C$_5$H$_5$)] (**20**) [21] (Eq. (11)) were obtained in 63 and 71% yields, respectively. For both reactions the by-products were the known compounds [η^5-C$_5$H$_5$Mn(CO)$_3$] (25%) and [η^5-C$_5$H$_5$Re(CO)$_3$] (6%), respectively. The structure of **19** shown in Eq. (10) has been confirmed by its X-ray crystallography. Complex **20** can also obtained by the reaction of **2** with dianionic compound (NEt$_4$)$_2$[Fe$_2$(CO)$_8$] or Na$_2$[Fe(CO)$_4$] and Na$_2$[Fe$_3$(CO)$_{11}$] and was characterized by X-ray diffraction (see below). In the reaction Eq. (11), its identity was established by its IR, ^{1}H-NMR, and mass spectra and elemental analysis.

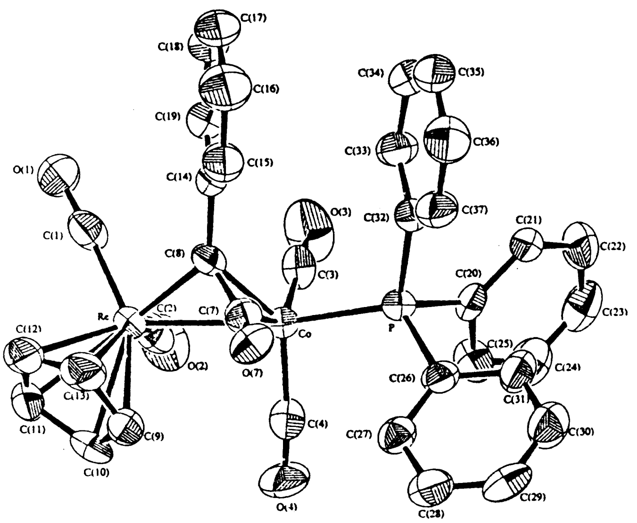
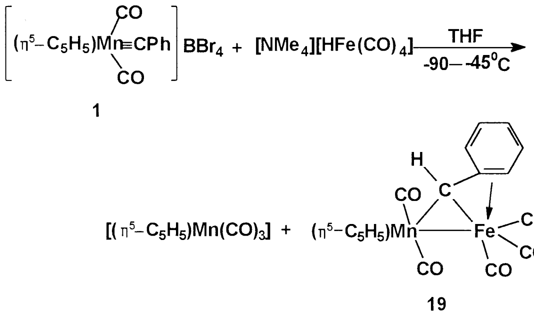
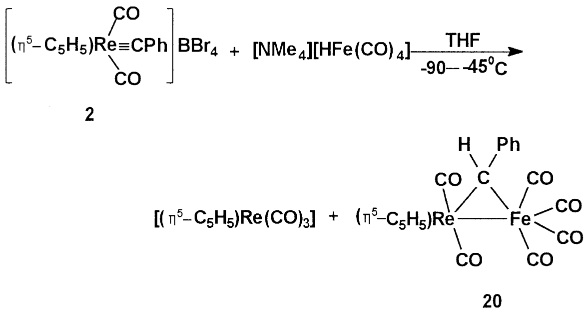


Fig. 4. Molecular structure of **17**.



(10)



(11)

Unexpectedly, the reaction (Eq. (12)) of complex **19** with carbon monoxide gas in THF at −40 to −10 °C led to heterolytic cleavage of the Mn–Fe bond and breaking of the μ-C–Mn bond of **19** to afford [η^5-C$_5$H$_5$Mn(CO)$_3$] and a novel benzene-coordinated acyltricarbonyliron complex [Fe(PhCHCO)(CO)$_3$] (**21**) [21] in 31 and 46% yield, respectively. The structure of **21** has been established by X-ray diffraction analysis.

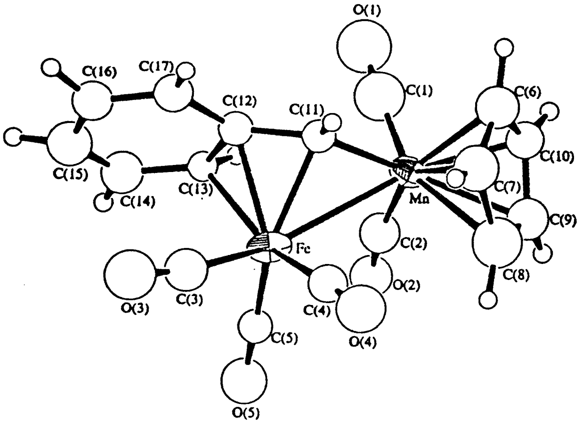
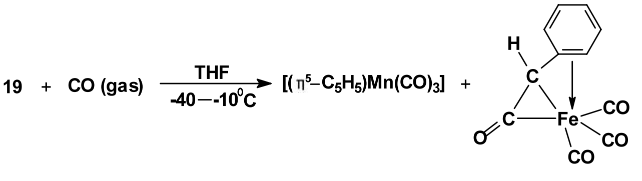


Fig. 5. Molecular structure of **19**.

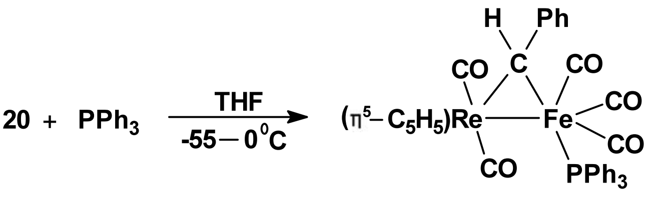


21

(12)

When a stoichiometric amount of CO gas was used for the reaction with **19**, no product **21** was isolated, indicating that an excess of CO is necessary for the reaction. Complex **20** did not react with carbon monoxide under the same conditions.

It is equally interesting that complex **20** when treated with PPh_3 in THF at −55 to 0 °C gave $[ReFe\{\mu\text{-}C(H)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)(PPh_3)]$ (**22**), in which a CO ligand on Fe has been displaced by PPh_3, in 52% yield (Eq. (13)) [21]. Unexpectedly, the reaction of **19** with PPh_3 under the same conditions gave no analogous PPh_3-substituted compound, as in the reaction of $[PtW\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_2(\eta^5\text{-}C_5H_5)(PEt_3)_2]BF_4$ [22] or complex **20** with PPh_3, but decomposition products such as $[Fe(CO)_3(PPh_3)_2]$ [23].



22

(13)

Of particular interest are the structures of the products. The structure of **19** (Fig. 5) contains a bridge system in which two carbon atoms (C(12) and C(13)) of the benzene ring are bonded to the Fe atom to construct a ferracyclopropane ring. However, there is no ^1H-NMR evidence for this because no high-field shift due to the proton attached to the 'olefinic' bond was observed. This might be explained by the C(12) and C(13) atoms being involved in η^2 instead of η^1,η^1 bonding to the Fe atom; thus, in solution the phenyl group rotates about the C(11)–C(12) bond on the NMR timescale at room temperature (r.t.) (20 °C) as that observed in analogous complex $[WCo\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]BF_4$ which showed dynamic behavior for the tolyl group at 25 °C, ceasing at −70 °C [22]. The Mn–Fe distance of 2.770(7) Å in **19** is somewhat longer than that found in analogous bridging carbene complex $[MnFe\{\mu\text{-}C(COEt)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**35**) (2.6929(8) Å) (see blow) but is obviously longer than that in the analogous bridging carbyne complex $[MnFe\{\mu\text{-}C(COEt)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (2.572(1) Å) [24].

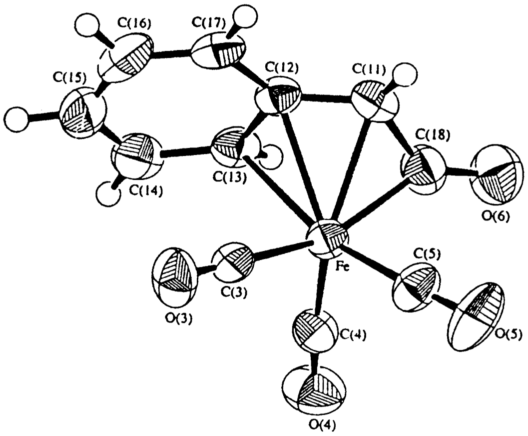


Fig. 6. Molecular structure of **21**.

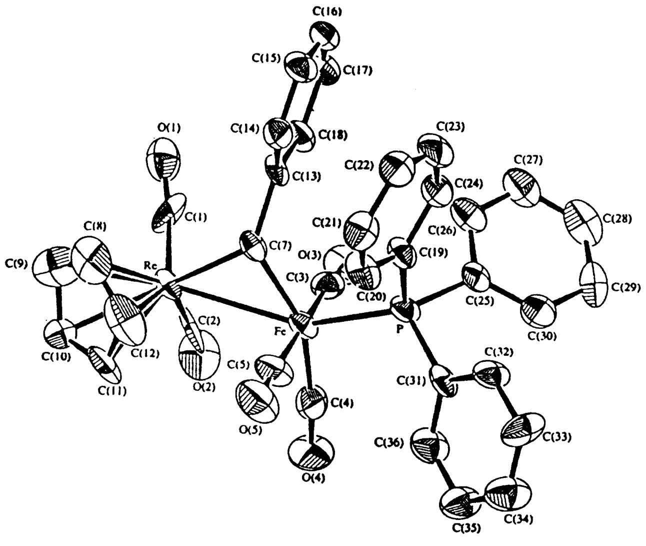


Fig. 7. Molecular structure of **22**.

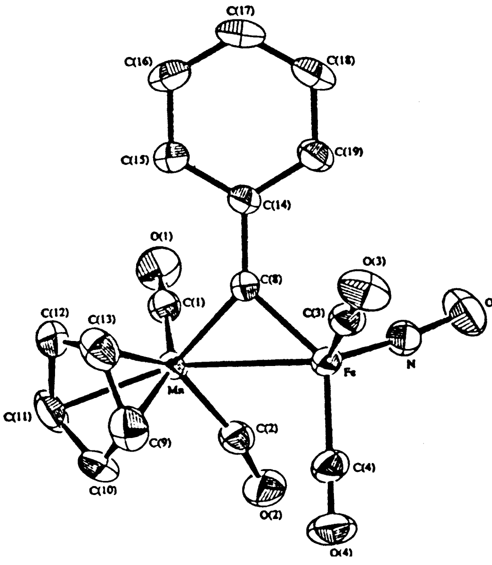
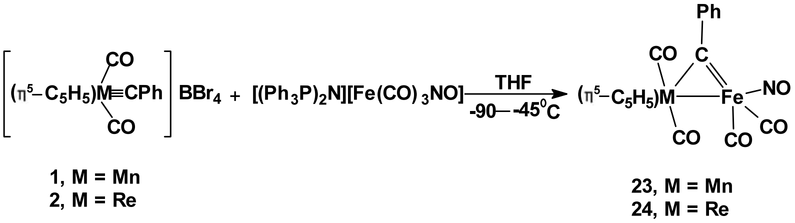


Fig. 8. Molecular structure of **23**.

The molecular structure of **21** (Fig. 6) shows that the benzene ring is still bonded to the Fe atom, and a formyl (C=O) group is bonded to the original alkylidene carbon (C(11)) and the Fe atom through the C(18) atom and provides one electron for the Fe atom to satisfy an 18-electron configuration. The molecular structure reveals a bridge system in which two carbon atoms (C(12) and C(13)) of aryl ring form an η^2 attachment to the iron, so that the C(H)Ph group as a whole adopts an η^3-bonding mode to the metal as that of μ-$C(H)C_6H_4Me$ in complex $[WPt\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_2(\eta^5\text{-}C_5H_5)(PMe_3)_2]BF_4$ [22]. However, the ^1H-NMR data for **21** at 20 °C show dynamic behavior for the phenyl group and reveal that in solution it rotates about the C(11)–C(12) bond on the NMR timescale as in **19**.

The product **22** has the structure shown in Fig. 7 as determined by an X-ray diffraction study. The coordination geometry around the Re atom is that of a pseudotrigonal bipyramid if the (η^5)-bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex, and the Fe atom is in an ca. octahedral environment. The bond length of Re–Fe (2.777(2) Å) is the same within experimental error as that of Mn–Fe in **19**. The alkylidene carbon asymmetrically bridges the Re–Fe bond (μ-C–Re 2.17(1), μ-C–Fe 2.03(1) Å) with an angle Re–C(7)–Fe of 82.7(5)°. The μ-C–Re distance in **22** is comparable with that in complex $[Re_2(\mu\text{-}H)_2(\mu\text{-}CHBu^t)(\eta^6\text{-}C_6H_6)_2]$ (2.13(3) Å) [25], and the μ-C–Fe distance is close to that in **19**. The P–Fe bond length of 2.258(4) Å is nearly the same as the normal P–Fe bond distance (2.260(3) Å in $[Fe(NO)_2(CO)(PPh_3)]$ [26].



(14)

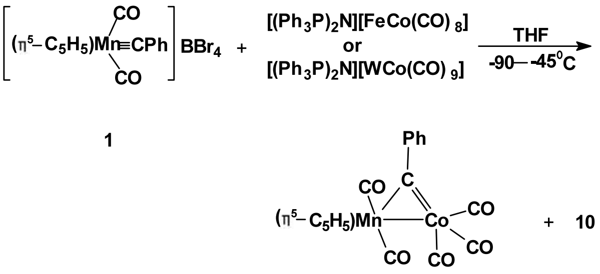
The possible reaction pathway to complexes **19** and **20** (Eqs. (10) and (11)) could be through a carbene intermediate $[(\eta^5\text{-}C_5H_5)(CO)_2M{=}C(Ph)FeH(CO)_4]$ (M = Mn, or Re) formed by attack of the $[HFe(CO)_4]^-$ anion on the cationic carbyne carbon of **1** or **2**. The carbene intermediate would then undergo a hydrogen migration from the Fe atom to the carbene carbon and bonding of the Fe atom to Mn or Re, accompanied by loss of one CO ligand from the $Fe(CO)_4$ moiety and coordination of the benzene ring to the Fe atom for **19**. Analogous heteronuclear dimetal bridging carbene complexes, $[MW\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_2(\eta^5\text{-}C_5H_5)(L_n)]BF_4$ (ML_n=$Cr(CO)(NO)(\eta^5\text{-}C_5H_5)$, $Co(CO)(\eta^5\text{-}C_5Me_5)$, or $Pt(PR_3)$) and $[PtW\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_2(\eta^5\text{-}C_5H_5)(PEt_3)_2]BF_4$, with the coordination of the benzene ring to the metal, have been reported by Stone and co-workers [22,27]. However, the heteronuclear dimetal bridging carbene complexes **19** and **20** were synthesized by a new route. While the formation of **21** (Eq. (12)) might proceed by an initial attack of CO on the μ-C–Mn or/and Mn–Fe bond of **19** which could then suffer heterolytic cleavage of these bonds with addition of one CO molecule to the Mn atom and the insertion of another CO molecule into the μ-C–Fe bond to form $[\eta^5\text{-}C_5H_5Mn(CO)_3]$ and complex **21**, respectively. The analogous insertion of CO into the Fe–$C_{carbene}$ bond of an η^3-coordinated carbene ligand to give a (vinylketene)iron complex with an η^4-coordinated acyl ligand has been observed in the reaction of tricarbonyl(η^3-vinylcarbene)iron with carbon monoxide [28].

Unexpectedly, the reactions of compound $[(Ph_3P)_2N][Fe(CO)_3NO]$, containing a three-electron NO ligand, with complexes **1** and **2** under similar conditions gave no expected bridging carbene or ketene complexes but heteronuclear dimetal bridging carbyne complexes $[MnFe(\mu\text{-}CPh)(CO)_4(NO)(\eta^5\text{-}C_5H_5)]$ (**23**) and $[ReFe(\mu\text{-}CPh)(CO)_4(NO)(\eta^5\text{-}C_5H_5)]$ (**24**) (Eq. (14)) [20] in 93 and 86% yield, respectively.

An X-ray study of **23** confirmed its structure (Fig. 8). In **23** the Mn–Fe bond is bridged by a CPh group, giving a dimetallacyclopropene ring with the dimensions: Mn–Fe 2.6494(3), C(8)–Mn 1.865(3), and C(8)–Fe 1.853(3) Å. The Mn–Fe separation is significantly longer than that in analogous bridging carbyne complex $[MnFe\{\mu\text{-}C(COEt)\}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (2.572(1) Å) [24] but is somewhat shorter than in the bridging carbene complex **19** (2.770(7) Å). The C(8)–Mn linkage is slightly longer than the corresponding distance (1.839(4) Å) in $[MnFe\{\mu\text{-}C(COEt)\}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ [24] but significantly shorter than the corresponding distance (1.92(3) Å) in **19**. The C(8)–Fe distance in **23** (1.853(3) Å) is as expected for a C=Fe bond, which is comparable with the corresponding distance in $[MnFe\{\mu\text{-}C(CO\text{-}Et)\}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ (1.843(4) Å) [24] and is obviously shorter than the corresponding distance in **19** (2.05(3) Å).

The formation of complexes **23** and **24** (Eq. (14)) could proceed via $[Fe(CO)_2NO]^-$, which attacked on the carbyne carbon of cationic **1** or **2** with bonding of the Fe atom to the Mn or Re atom to construct a dimetallacyclopropene ring. The synthon of $[Fe(CO)_2NO]^-$ could come from either an $[Fe(CO)_3NO]^-$ anion that lost a CO ligand in the presence of **1** or **2** or a carbene intermediate $[\eta^5\text{-}C_5H_5M{=}C(Ph)Fe(CO)_3NO]$ (M = Mn or Re) formed by attack of the $[Fe(CO)_3NO]^-$ anion on the carbyne carbon of **1** or **2**. The carbene intermediate then underwent cleavage of a CO group to generate the $[Fe(CO)_2NO]^-$ species.

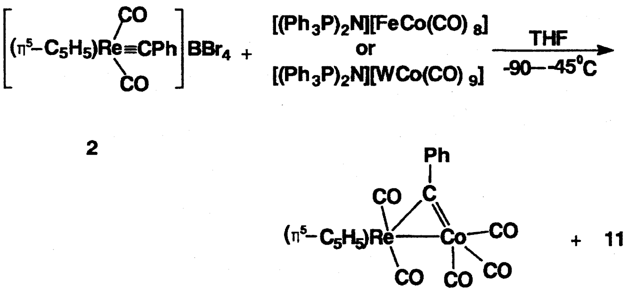
Of special interest are the reactions of mixed-dimetal carbonyl anionic compounds $[(Ph_3P)_2N][FeCo(CO)_8]$ and $[(Ph_3P)_2N][WCo(CO)_9]$. The reaction of $[(Ph_3P)_2N][FeCo(CO)_8]$ with an equimolar amount of **1** in THF at −90 to −45 °C for 4–5 h gave a heteronuclear dimetal bridging carbyne complex $[MnCo(\mu\text{-}CPh)(CO)_5(\eta^5\text{-}C_5H_5)]$ (**25**) and a ketene complex **10** (Eq. (15)) [29] in 81 and 11% isolated yield, respectively.



25

(15)

Analogous reaction (Eq. (16)) [29] of complex **2** with $[(Ph_3P)_2N][FeCo(CO)_8]$ under the same conditions afforded the dimetal bridging carbyne complex $[ReCo(\mu\text{-}CPh)(CO)_5(\eta^5\text{-}C_5H_5)]$ (**26**) as the major product (80% yield). The other product **11** was obtained in 13% isolated yield, which is a ketene complex.



26

(16)

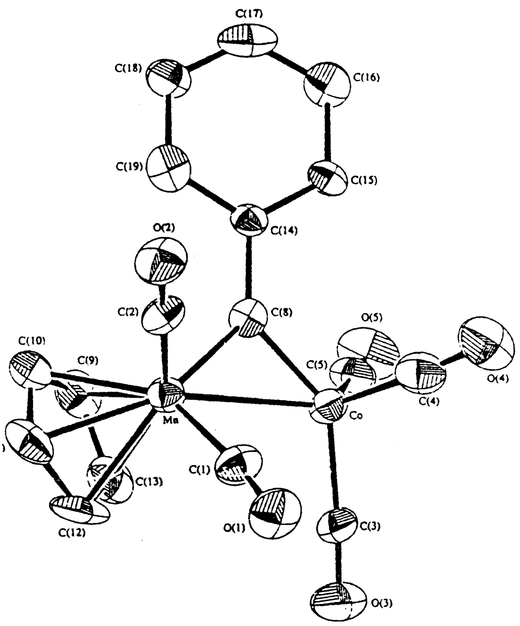


Fig. 9. Molecular structure of **25**.

Complex **1** also reacted with $[(Ph_3P)_2N][WCo(CO)_9]$ under the same conditions to yield products **25** and **10** (Eq. (15)) [29] in similar yields. Complex **2** reacted similarly with $[(Ph_3P)_2N][WCo(CO)_9]$ (Eq. (16)) [29]. However, the main product was complex **11** (57%) instead of complex **26** (37%).

The structures of complexes **25** and **26** shown in Figs. 9 and 10, established by X-ray diffraction, have many common features. The structural features of the dime-

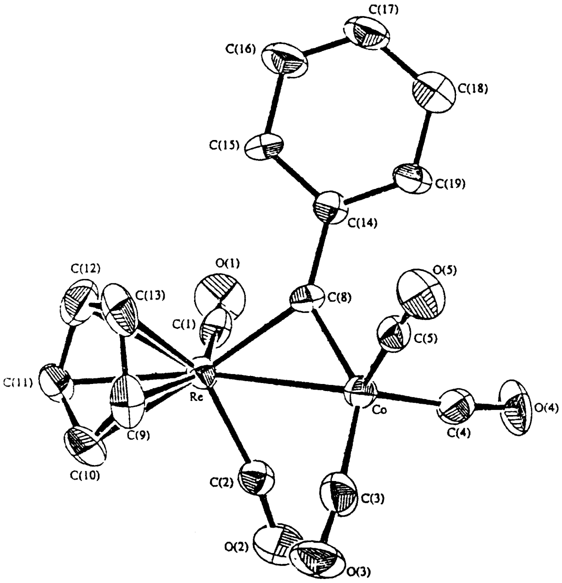


Fig. 10. Molecular structure of **26**.

tallacyclopropene part of **25** (Fig. 9) are very similar to those in analogous bridging carbyne complex **23**, except the μ-C–Co bond distance (1.77(1) Å) is obviously shorter than the corresponding bond in **23** (μ-C–Fe 1.853(3) Å). Since the radii of Co and Fe are nearly the same, it is interesting to compare the Mn–Co bond distance (2.608(3) Å) in **25** with the longer Mn–Fe separation (2.6494(3) Å) in **23**. The C(8)–Mn linkage (1.85(1) Å) in **25** is slightly shorter than that found (1.865(3) Å) in **23**. The μ-C(8)–Co distance is as expected for a C=Co bond, which is obviously shorter than the corresponding distance in [MnFe{μ-C(COEt)(μ-CO)(CO)$_2$(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Me)] (μ-C–Fe 1.843(4) Å) [24]. In **26** the dimensions of the dimetallacyclopropene ring are Re–Co 2.710(2), C(8)–Re 2.01(1), and C(8)–Co 1.82(1) Å. Since the radii of Re and W are ca. the same, it can compare the metal–metal bond distance in **26** with the slightly longer W–Co separation (2.758(1) Å) in analogous carbyne complex [WCo(μ-CC$_6$H$_4$Me-*p*)(CO)$_3$(η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)] [30]. The C(8)–Re bond length in **26** is significantly longer than the corresponding distance in analogous carbyne complex [ReFe(μ-CPh)(μ-CO)(CO)$_3$(η^5-C$_5$H$_5$)(COC$_2$B$_{10}$H$_{10}$)] ((1.86(4) Å) [31]. The C(8)–Co distance (1.82(1) Å) in **26** is also as expected for a C=Co bond based on the comparable μ-C=Co separation (1.77(1) Å) found in **25**.

The possible reaction pathway to complexes **25** and **26** could proceed via Co(CO)$_3^-$, which attacked on the carbyne carbon of cationic carbyne complex **1** or **2** with bonding of the Co atom to the Mn or Re atom to construct a dimetallacyclopropene ring, since the analogous reaction [17] of the [Co(CO)$_4$]$^-$ anion with **1** or **2** under the same conditions gave no bridging carbyne complex **25** or **26** but ketene complex **10** or **11**. The Co(CO)$_3^-$ intermediate could come from either expulsion of Fe(CO)$_5$ or W(CO)$_6$ directly from the FeCo(CO)$_8^-$ or WCo(CO)$_9^-$ anion in the presence of **1** or **2** or a carbene intermediate [η^5-C$_5$H$_5$(CO)$_2$M=C(Ph)M′Co(CO)$_n$] (M = Mn or Re, M′ = Fe or W, $n = 8$ or 9) formed by attack of the [M′Co(CO)$_n$]$^-$ anion on the carbyne carbon of **1** or **2**. The carbene intermediate then underwent expulsion of Fe(CO)$_5$ or W(CO)$_6$ to generate the Co(CO)$_3^-$ species. We have indeed isolated Fe(CO)$_5$ and W(CO)$_6$ in the course of the column chromatography. The formation of **10** and **11** (Eqs. (15) and (16)) could proceed via an intermediate complex **25** or **26**. To explore this possibility, complex **25** was allowed to react with CO gas, which gave complex **10** in 70% yield as shown in Eq. (17) [29].

$$\mathbf{25} + \mathrm{CO} \xrightarrow[-50--40\ ^{\circ}\mathrm{C}]{\mathrm{THF}} \mathbf{10} \qquad (17)$$

This result shows that complex **25** can indeed convert to complex **10** and suggests that **10** is derived from **25** by addition of one CO molecule presumably generated by cleavage of the dimetal carbonyl anions or other species.

Although a number of dimetal bridging carbyne complexes have been prepared by Stone et al. as mentioned in the Introduction, complexes **23**–**26**, as heteronuclear dimetal bridging carbyne complexes, were first synthesized by reactions of the cationic carbyne complexes with the carbonylmetal anionic compounds. Undoubtedly, this is a convenient and useful method for the synthesis of such dimetal bridging carbyne complexes.

It is quite interesting that the bridging carbyne complex **25** reacted with an excess of Fe$_2$(CO)$_9$ in THF at −40 to 0 °C to give a purple-red compound [MnFeCo(μ$_3$-CPh)(μ-CO)(CO)$_7$(η^5-C$_5$H$_5$)] (**27**) (Eq. (18)) [29] in 72% yield. Surprisingly, the ketenyl complex

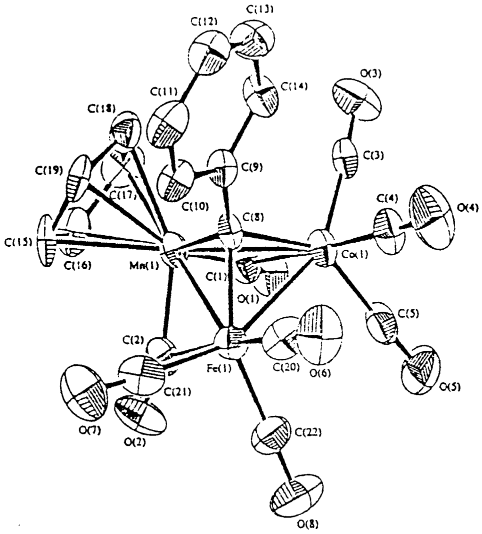


Fig. 11. Molecular structure of **27**, showing only one of the two independent molecules for clarity.

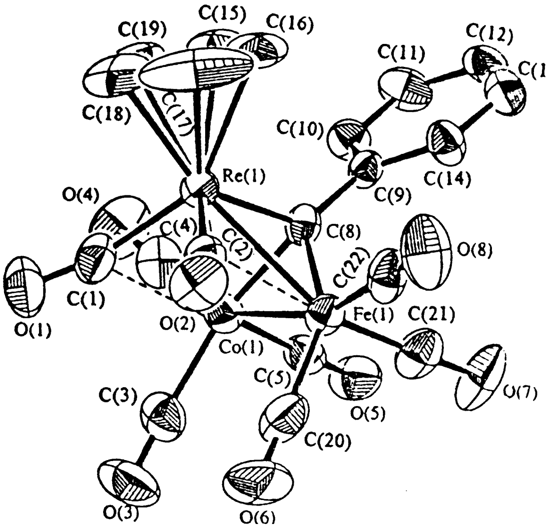
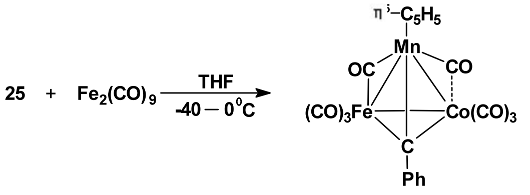


Fig. 12. Molecular structure of **28**, showing only one of the two independent molecules for clarity.

10 can also react with $Fe_2(CO)_9$ under similar conditions to yield the same product **27** (Eq. (19)) [29] in nearly the same yield.

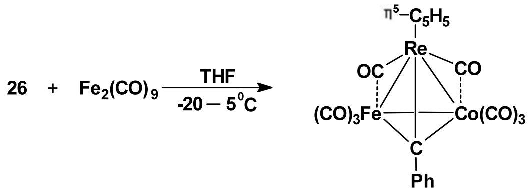


27

(18)

$$\mathbf{10} + Fe_2(CO)_9 \xrightarrow[-20\text{–}5°]{THF} \mathbf{27} \qquad (19)$$

Complexes **26** and **11** react similarly with $Fe_2(CO)_9$ to give the same blackish-red crystalline compound **28**, $[ReFeCo(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_5H_5)]$, in 74–75% yields (Eqs. (20) and (21)) [29].



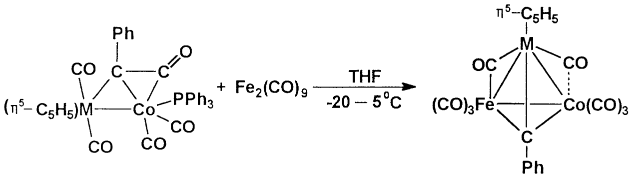
28

(20)

$$\mathbf{11} + Fe_2(CO)_9 \xrightarrow[-20\text{–}5°C]{THF} \mathbf{28} \qquad (21)$$

Surprisingly, PPh_3-substituted ketenyl complexes **16** and **17** can also react with $Fe_2(CO)_9$ under similar conditions, leading to loss of the PPh_3 ligand to produce a purple–red complex **27** and a blackish-red complex **28** (Eq. (22)) [20] in > 70% yields, respectively. The formation of complexes **27** and **28** in reaction (22) could proceed either via a dimetal bridging carbene intermediate $[MCo\{\mu\text{-}C(CO)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (M = Mn or Re) or via an unstable trimetal bridging carbyne intermediate $[MnFeCo(\mu_3\text{-}CPh)(CO)_7(PPh_3)(\eta^5\text{-}C_5H_5)]$ (M = Mn or Re). The former, which is formed by displacement of a PPh_3 ligand of **16** or **17** by a CO ligand derived from $Fe_2(CO)_9$, reacted with $Fe_2(CO)_9$ to give **27** or **28**. The latter, which is formed directly by the reaction of **16** or **17** with $Fe_2(CO)_9$ as in the reaction of **25** or **26** with $Fe_2(CO)_9$, occurred from PPh_3 ligand displacement by a CO ligand arising from the great steric hindrance of the PPh_3 group to afford the stable product **27** or **28**.

Complexes **27** and **28** are formulated as the heteronuclear trimetal bridging carbyne complexes. Their structures were established by X-ray studies to be that shown in Eq. (22). The molecular structure of **27** is shown in Fig. 11. Complex **27** crystallizes with two independent molecules in the asymmetric unit. However, its ^{1}H-NMR spectrum showed that the two molecules are separated in solution, giving a single normal molecule. In **27** the triangular MnFeCo arrangement with a capping μ_3-CPh ligand is confirmed. The three metal atoms construct an approximate isosceles triangle (Mn(1)–Fe(1) = 2.570(2), Mn(1)–Co(1) = 2.575(3), and Fe(1)–Co(1) = 2.549(3) Å). The μ-C(8)–Mn(1), μ-C(8)–Fe(1), and μ-C(8)–Co(1) distances are 1.94(1), 1.91(1), and 1.94(1) Å, respectively. Compound **27** appears to be the first example of a species with Mn–Co, Mn–Fe, and Fe–Co bonds studied by X-ray crystallography, and hence, comparison of these metal–metal bond distances with others involving these elements is not possible.



16, M = Mn
17, M = Re

27, M = Mn
28, M = Re

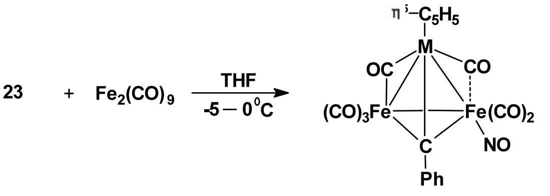
(22)

In **27**, the Fe and Co atoms each carry three terminal CO groups and the Mn atom carries one bridging CO group to Fe, with a second CO on Mn being semibridging to Co (Mn(1)–C(2)–O(2) = 155(1)°, Fe(1)–C(2) = 2.26(1) Å; Mn(1)–C(1)–O(1) = 160(1)°, Co(1)–C(1) = 2.32(1) Å), thus giving each metal atom 18 valence electrons.

The molecular structure of **28** shown in Fig. 12 has many common features with that of **27**. As that of **27**, there are two independent molecules in the asymmetric unit of **28**. The two molecules in the cell are the same. The molecule of **28** possesses a trimetalatetrahedrane ReFeCo core with the dimensions: Re(1)–Fe(1) 2.707(2), Re(1)–Co(1) 2.707(1), and Fe(1)–Co(1) 2.542(2) Å. The Re–Co bond length is closely related to that of the analogous complex $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}p)(CO)_{10}]$ (average Re–Co 2.70 Å) [32]. The μ-C–Re, μ-C–Fe, and μ-C–Co distances are 2.052(8), 1.936(8), and 1.922(7) Å, respectively, of which, the μ-C–Co bond distance is comparable to that in $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}p)(CO)_{10}]$ (average 1.89 Å) [32], while the μ-C–Re bond length is slightly shorter than that in $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}p)(CO)_{10}]$ (average 2.189 Å) [32].

In **28** the Co and Fe atoms each carry three terminal CO groups and the Re atom carries two CO groups being semibridging to the Co and Fe atoms, respectively. Complex **28** is a 48 cluster valence electron (CVE) compound, where the Re and Fe atoms formally have 19 and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyl. The analogous 48-valence-electron structure was found in complex $[MW_2(\mu_3\text{-}C_2R_2)(CO)_7(\eta^5\text{-}C_5H_5)_2]$ (M = Ru, Os) [33].

The NO-substituted bridging carbyne complex **23** can also react with $Fe_2(CO)_9$ under similar conditions to give heteronuclear trimetal bridging carbyne complex **29**, [$MnFe_2(\mu_3\text{-}CPh)(CO)_7(NO)(\eta^5\text{-}C_5H_5)$], in 76% isolated yield (Eq. (23)) [20].



29

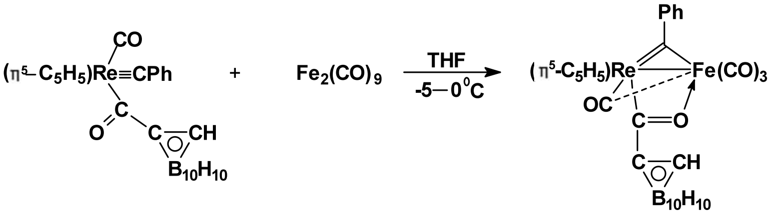
(23)

The structure of **29** shown in Eq. (15) was established by an X-ray diffraction study [34], which gave an *R* value of 0.15 from substantial decomposition. However, the elemental analysis and IR, ^{1}H-NMR, and mass spectra are consistent with this geometry. Its IR spectrum in the ν(CO) region showed an absorption band at 1840 cm^{-1} attributed to a bridging or semi-bridging CO ligand, in addition to six terminal CO absorption bands at 2065, 2033, 2012, 1985, 1963, and 1925 cm^{-1}, indicative of a $(CO)_6Fe_2Mn((\mu\text{-}CO)$ moiety. The ^{1}H-NMR spectrum showed the expected proton signals due to the phenyl and cyclopentadienyl group and the mass spectrum showed the molecular ion peak and feature fragments generated by loss of CO ligands.

Not all such ketene complexes can react with $Fe_2(CO)_9$ to produce trimetal bridging carbyne complexes since analogous ketene complexes **12**–**15** and **18** do not react similarly under the same conditions. This suggests that the Co or Fe moiety is important; it probably promotes this reaction by forming a stable trimetal μ_3-CMFeCo core.

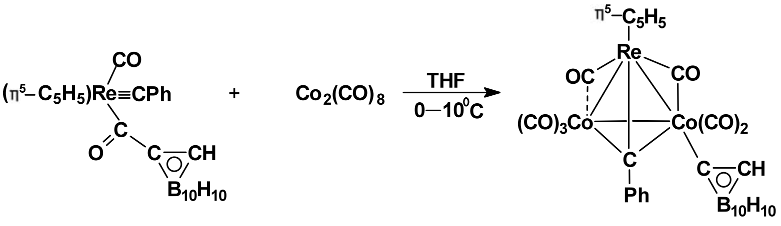
A series of trimetal bridging carbyne complexes have been synthesized by Stone et al. by reactions [2d,2f,35] of alkylidyne complexes with low-valent metal species. However, complexes **27**–**29**, as heteronuclear trimetal bridging carbyne complexes, were obtained by the reactions of dimetal bridging carbyne complexes or ketene complexes with $Fe_2(CO)_9$. Only two analogous reactions are known: one is the reaction of the carbyne complex [$M{\equiv}CC_6H_4Me\text{-}p(CO)_2(\eta^5\text{-}C_5H_5)$] (M = Mo or W) with an excess of $Fe_2(CO)_9$ to afford a trimetal bridging carbyne complex [$MFe_2(\mu_3\text{-}CC_6H_4Me\text{-}p)(CO)_9(\eta^5\text{-}C_5H_5)$] (M = Mo or W) [2f]. In this reaction, the initially formed bridging carbyne intermediate [$MFe(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_6(\eta^5\text{-}C_5H_5)$] reacted further with $Fe_2(CO)_9$ to give the trimetal species. The other interesting reaction is that the carbyne complex [$\eta^5\text{-}C_5H_5(CO)(COC_2HB_{10}H_{10})Re{\equiv}CPh$] [36], prepared by the reaction of **1** with 1-lithio-*o*-carborane, in which a bulky icosahedral o-carboranyl moiety is bound to a CO ligand to form a carboranylcarbonyl group, with $Fe_2(CO)_9$ and $Co_2(CO)_8$ to give the novel heteronuclear dimetal bridging carbyne complex [$ReFe(\mu\text{-}CPh)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_5H_5)(COC_2HB_{10}H_{10})$] (**30**) (Eq. (24)) and heteronuclear trimetal bridging carbyne complex [$ReCo_2(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_5(\eta^5\text{-}C_5H_5)(COC_2HB_{10}H_{10})$] (**31**) (Eq. (25)) in 76 and 73% yields, respectively [31]. The structures of both complexes have been established by X-ray crystallography [31].

The reaction of the dimetal bridging ketene complex with low-valent metal species giving a trimetal bridging



30

(24)



31

(25)

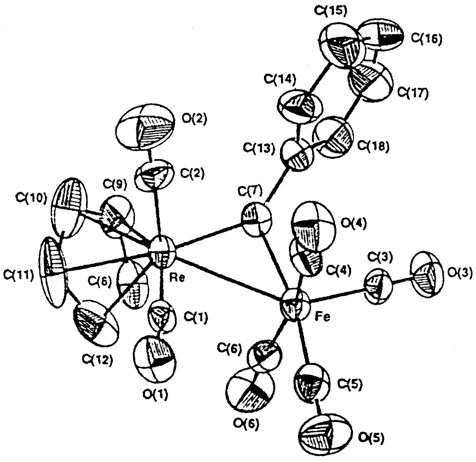


Fig. 13. Molecular structure of **20**.

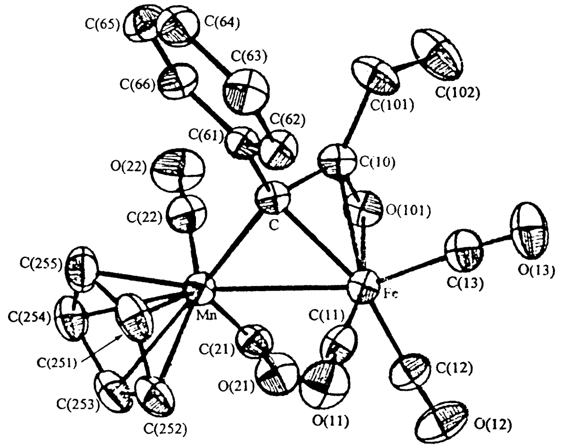
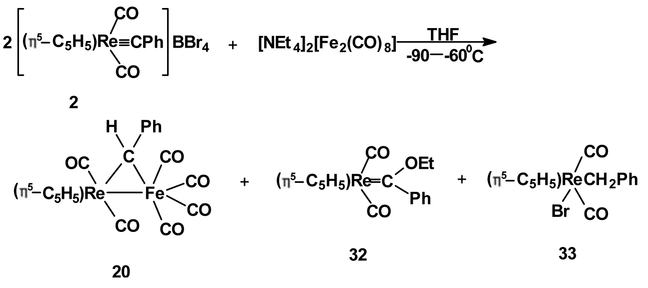


Fig. 14. Molecular structure of **35**.

carbyne complex is quite unusual. This may represent a new route to trimetal bridging carbyne complexes.

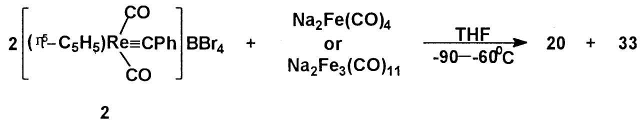
4. Reactions of $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (1) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (2) with metal carbonyl dianions

As discussed in Section 3, cationic carbyne complexes **1** and **2** react with the carbonylmetal monoanions to form dimetal bridging carbene or bridging carbyne complexes and related complexes. In this section we explore the reactions of **1** and **2** with carbonylmetal dianions in order to determine whether or not they follow the same patterns of reactivity as the carbonylmetal monoanions. Thus, two molar equivalents of the cationic carbyne complex of rhenium, **2**, reacted with one of iron dianionic compound $(NEt_4)_2[Fe_2(CO)_8]$ in THF at low temperature (−90 to −60 °C) for 3–4 h to give three isolated products (Eq. (26)) [37]: the brick-red crystalline $[ReFe(\mu\text{-}CPh)(CO)_6(\eta^5\text{-}C_5H_5)]$ (**20**), orange-yellow crystalline $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(OEt)Ph]$ (**32**), and red crystalline $[\eta^5\text{-}C_5H_5(CO)_2BrReCH_2Ph]$ (**33**).



(26)

Complex **2** also reacted with $Na_2[Fe(CO)_4]$ and $Na_2[Fe_3(CO)_{11}]$ under the same conditions to afford products **20** and **32** in similar yields, but no product **33** was produced (Eq. (27)) [37].



(27)

Complex **20**, formed in 41% yield in Eq. (26), is a heteronuclear dimetal bridging carbene complex which can also be obtained from the reaction of **2** with $[FeH(CO)_4]^-$ (Eq. (11)). Its IR spectrum (in hexane) showed ν(CO) bands at 2075, 1998 1982, 1962, and 1915 cm^{-1}. The ^{1}H-NMR spectrum of **20** shows a resonance at δ 9.03 in the region expected for a μ-CHR ligand which may be comparable with that (8.09 ppm) in analogous bridging carbene complex $[(Ph_3P)_2N][WRe\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_9]$ [38]. The molecular structure of **20** (Fig. 13) showed that the Re–Fe bond is asymmetrically bridged by the C(H)Ph group (μ-C–Re 2.120(5), μ-C–Fe 2.097(5) Å). The coordination geometry of the Re atom is that of a pseudotrigonal bipyramid and the Re atom is nearly coplanar with C(2), Fe, and C(cen) (C(cen) denotes centroid of the cyclopentadienyl) which define the 'equatorial' plane of the trigonal bipyramid. The Re–Fe distance of 2.7581(8) Å in **20** is much shorter than that in $[(Ph_3P)_2N][WRe\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_9]$ (3.033(1) Å) [38]. The μ-C–Re distance of **20** is comparable with that in analogous complex $[Re_2(\mu\text{-}H)_2(\mu\text{-}CHBu^t)(\eta^6\text{-}C_6H_6)_2]$ (2.13(3) Å) [25]. The μ-C–Fe distance is comparable with that in complexes **19** (2.05(3) Å) and $[WFe\{\mu\text{-}C(C_6H_4Me\text{-}p)(CO)O\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (2.054(4) Å) [39].

The product **32**, isolated in 36% yield from reaction (26), whose structure has been established by X-ray crystallography [37], is a precursor of **2** and can be readily prepared by the reaction of $[\eta^5\text{-}C_5H_5Re(CO)_3]$ with PhLi followed by alkylation with Et_3OBF_4, analogous to the preparation of $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(OEt)C_6H_4CF_3\text{-}p]$ [9].

The third product **33**, isolated in 25% yield from reaction 26, is a benzyl rhenium bromide and was characterized by X-ray study [37]; its crystal structure shows that the CH_2Ph group is σ-bonded to the Re atom.

The mechanism for the formation of complex **20** (Eqs. (26) and (27)) is likely to involve initial formation of the '$[Fe(CO)_4]^{2-}$'species arising from $(NEt_4)_2[Fe_2(CO)_8]$ or $Na_2[Fe(CO)_4]$ and $Na_2[Fe_3(CO)_{11}]$, which then attacked at the carbyne carbon of **2** to generate an anionic carbene intermediate $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(Ph)Fe(CO)_4]^-$. This was confirmed by the reaction of **2** with $Na_2[Fe(CO)_4]$, giving product **20**. There are analogous precedents for this type of intermediate in the literature [3b,40]. The protonation of the anionic carbene intermediate affords the bridging carbene complex **20**. The source of the H atom could be THF or water which is a trace contaminant in solvent THF or from glassware [37].

The formation of complex **32** might proceed by following pathway: loss of the '$[Fe(CO)_4]$' species from **20** and subsequent abstraction of the OEt species from the reaction mixture leading to the isolation of ethoxycarbene complex **32**. It is not clear how the OEt group is formed during the reaction. Speculatively, it is derived from the solvent THF. Evidence in favor of this is that when the brick-red crystals of **20** were recrystallized from THF–petroleum ether solution at −10 to −80 °C for 96 h, orange–yellow crystals of **32** were obtained in 47% yield. It is also noted that when the NMR sample tube of **20** was allowed to stand at 0–10 °C, the color of the solution of **20** in THF-d_8 turned from brick-red to orange–red after standing for 24 h. The ^1H-NMR spectrum of the resulting solution showed proton signals at δ 7.25 (m, 3H), 6.95 (m, 2H), and 5.27 (s, 5H) which is assigned to the phenyl and cyclopentadienyl protons of $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(OC_2D_5)Ph]$, respectively, together with the original proton signals of **20**. This suggests that a partial transformation of **20** into deuterated ethoxycarbene complex might have occurred.

A reasonable mode for formation of complex **33** is via the release of '$Fe(CO)_4$' species from **20** to generate a carbene intermediate complex $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(H)Ph]$ (**34**), a known compound [41], which could then abstract a hydrogen from solvent THF and a bromide ion from the BBr_4^- species during the reaction, resulting in the formation of **33** in lower yield. Formation of the analogous compound was observed in the reaction of **34** with Et_2AlH leading to $[\eta^5\text{-}C_5H_5(CO)_2HReCH_2Ph]$ [41]. Direct evidence for the formation of the intermediate carbene complex **32** through initial loss of the $Fe(CO)_4$ moiety from **20** is based on the following fact: when brick-red **20** was recrystallized from toluene–petroleum ether (1:10) at −10 to −80 °C for 96 h, deep red crystals of **34** were obtained in 70% yield (Eq. (28)) [37].

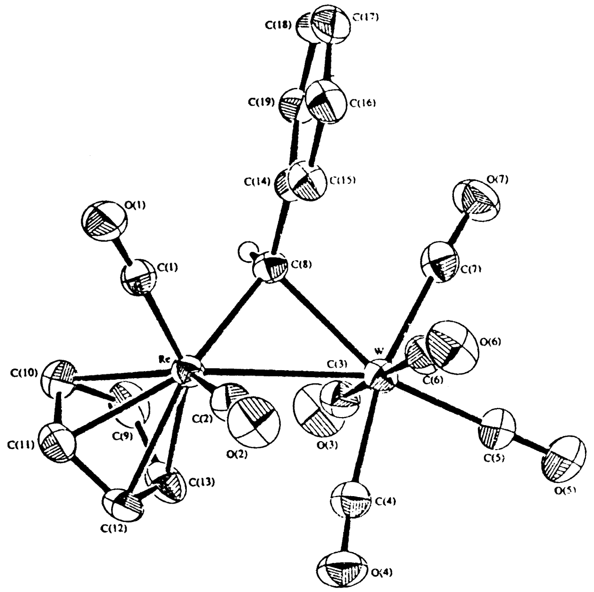
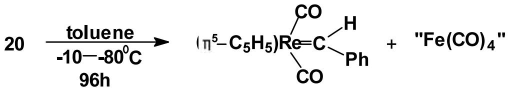


Fig. 15. Molecular structure of **38**.

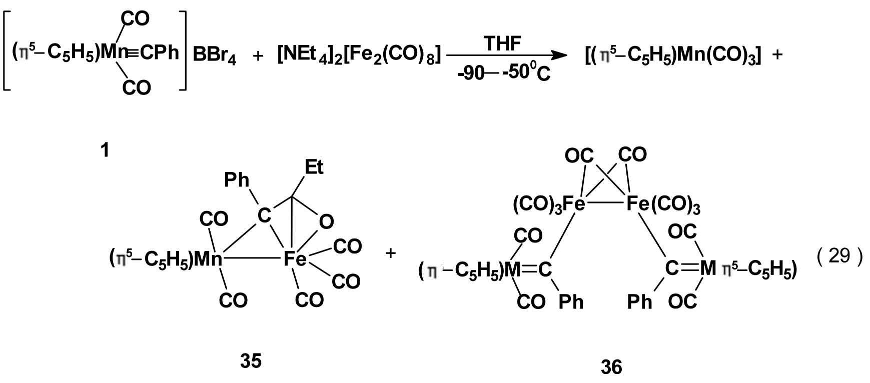


$$\mathbf{20}\ \xrightarrow[\text{-10—-80}^{\circ}\text{C},\ 96\text{h}]{\text{toluene}}\ (\eta^5\text{-}C_5H_5)Re(CO)_2{=}C(H)Ph\ +\ \text{"}Fe(CO)_4\text{"} \qquad (28)$$

34

Complex **1** can also react with $(NEt_4)_2[Fe_2(CO)_8]$ under the similar conditions to give a novel heteronuclear dimetal bridging carbene complex $[MnFe\{\mu\text{-}C(COEt)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**35**), a dimetal dicarbene complex $[\{\eta^5\text{-}C_5H_5(CO)_2Mn{=}CPh\}_2Fe_2(CO)_8]$ (**36**), and $[\eta^5\text{-}C_5H_5Mn(CO)_3]$ (Eq. (29)) [42] in 39, 19 and 23% isolated yields, respectively. The same products, **35** and $[\eta^5\text{-}C_5H_5Mn(CO)_3]$, were also obtained from the reaction of **1** with $Na_2[Fe(CO)_4]$ in 44 and 26% yield, respectively, but no product **36** was isolated. When $Na_2[Fe_3(CO)_{11}]$ was used for the reaction with **1** under the same conditions, no analogous products were obtained [42].

The structures of the air- and temperature-sensitive complexes **35** and **36** have been confirmed by X-ray diffraction studies. The molecular structure of **35** (Fig. 14) resembles that of complexes **19** and **20**. An unusual structural feature is the presence of the (COEt)Ph group bonded to μ-$C_{carbene}$ carbon through C(10) and to the Fe atom through C(10) and O(101) with μ-C–C(10) 1.438(6), C(10)–Fe 2.134(5) and O(101)–Fe 2.004(3) Å and an angle C–C(10)–Fe of 65.7(2)°. The Fe–O(101) bond length is very close to that found in the analogous complex $[ReFe(\mu\text{-}CPh)(\mu\text{-}CO)(CO)_3(COC_2HB_{10}H_{10})]$ (**30**) (1.98(3) Å) [31]. The longer bond length of C(10)–O(101) (1.303(5) Å) as compared with that in $[Fe(COC_6H_4CF_3\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)]$ (1.217(6) Å) [43] suggests that the C=O bond of the acyl group is obviously stretched, as a result of the coordination of



1

35

36

(29)

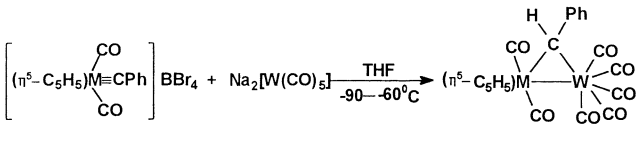
the oxygen with the Fe atom, similar to that in **30** (1.31(5) Å) [31]. The Mn–Fe distance of 2.6929(8) Å in **35** is somewhat shorter than that in **20** (2.7581(8) Å). In contrast to complexes **19** and **20**, the alkylidene carbon in **35** is symmetrically bridged to the Mn–Fe bond (μ-C–Mn 2.021 (4), μ-C–Fe 2.020(4) Å). It is worth noting that the bond angle Fe–C(10)–C(101) is 135.4(4)°, greatly deviating from 120°, probably due to the bonding of the acyl carbon atom (C(10)) to the μ-carbene carbon.

The structure of **36** shown in Eq. (31) is supported by an X-ray diffraction study [44] which gave an *R* value of 0.16 owing to substantial decomposition. However, the elemental analyses and IR, ^{1}H-NMR, and mass spectra are all consistent with this geometry. The IR spectrum in the ν(CO) region showed an absorption band at 1865 cm^{-1} attributable to the bridging CO ligands, in addition to five terminal CO bands, indicative of the $(CO)_6Fe_2(\mu\text{-}CO)_2$ and $(C_5H_5)Mn(CO)_3$ moieties. The ^{1}H-NMR spectrum of **36** showed the expected proton signals due to the phenyl and cyclopentadienyl groups. The mass spectrum provides further structural information showing the parent ion and fragments producing by loss of CO ligands.

The formation of **35** is unexpected, presumably it could proceed via a generation of '$[Fe(CO)_4]^{2-}$' species derived from $(NEt_4)_2[Fe_2(CO)_8]$, which might then attack at the carbyne carbon of **1**, as confirmed by the reaction of **1** with $Na_2[Fe(CO)_4]$ to give **35**, to generate an anionic carbene intermediate $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)Fe(CO)_4]^-$ as in the reaction of **2** with $(NEt_4)_2[Fe_2(CO)_8]$. An ethyl group may then become attached to a CO ligand of the Fe(CO)$_4$ moiety of the anionic carbene intermediate forming an acyl ligand, as occurs that in $[Fe(COC_6H_4CF_3\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)]$ [43], to yield a 16e intermediate $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)Fe(CO)_3(COEt)]$, which then undergoes intramolecular cyclization involving bonding of the acyl carbon atom to the bridging carbene carbon and the oxygen atom to the Fe atom, giving the latter an 18-electron configuration and affording complex **35**. It is not clear how the Et group is formed during the reaction. It could arise from NEt_4^+ which under the circumstances is an alkylating agent. However, this is not the case since $Na_2[Fe(CO)_4]$ reacted with **1** also to give the same product **35**. So the source could be $BBr_2(OEt)$ which exists in the starting material **1** since the preparation of **1** by the reaction of $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(OEt)Ph]$ with BBr_3 was accompanied by the formation of $BBr_2(OEt)$.

The formation of complex **36** could proceed by simultaneous attack of $[Fe(CO)_4]^{2-}$ on the carbyne carbon of the two molecules of **1**. The formation of the dicarbene complex **36** is not surprising since the analogous reactions of $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ and $[(CO)_5Cr{\equiv}CNEt_2]BF_4$ with $LiPbPh_3$ gave the carbene complexes $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(Ph)PbPh_3]$ [45] and $[(CO)_5Cr{=}C(NEt_2)PbPh_3]$ [46], respectively, where the $PbPh_3$ group is directly bonded to the carbene carbon through Pb atom.

The carbonyltungsten dianionic compound $Na_2[W(CO)_5]$ also reacts with complexes **1** and **2** under similar conditions to afford bridging carbene complexes $[WMn\{\mu\text{-}C(H)Ph\}(CO)_7(\eta^5\text{-}C_5H_5)]$ (**37**) and $[WRe\{\mu\text{-}C(H)Ph\}(CO)_7(\eta^5\text{-}C_5H_5)]$ (**38**), (Eq. (30)), isolated in 78 and 76% yields, respectively [17], similar to those reactions of the dianions $(NEt_4)_2[Fe_2(CO)_8]$ or $Na_2[Fe(CO)_4]$ and $Na_2[Fe_3(CO)_{11}]$ with complex **2** (Eqs. (26) and (27)).



1, M = Mn
2, M = Re

37, M = Mn
38, M = Re

(30)

The features in the ^{1}H-NMR spectra of complexes **37** and **38** also support a μ-CHR (R = Ph) group in both complexes, which had a resonance at δ 16.35 and 11.07, respectively. Surprisingly, this chemical shift has moved downfield dramatically by comparison with that of analogous bridging carbene complexes **20** (δ 9.03) and $[(Ph_3P)_2N][WRe\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_9]$ (δ 8.09) [38].

The molecular structure of **38** (Fig. 15) established by X-ray crystallography resembles that of analogous complexes **20** and $[(Ph_3P)_2N][WRe\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_9]$ [38]. The Re–W (3.0233(5) Å), μ-C–Re (2.126(7) Å), and μ-C–W (2.355(7) Å) distances in **38** could be compared with those in $[(Ph_3P)_2N][WRe\{\mu\text{-}C(H)C_6H_4Me\text{-}p\}(CO)_9]$ (Re–W 3.033(1), μ-C–Re (2.155(8), μ-C–W 2.404(6) Å) [38].

The mechanism for reaction Eq. (30) was proposed to follow that for the analogous reaction of complex **2** with $Na_2[Fe(CO)_4]$ or $(NEt_4)_2[Fe_2(CO)_8]$, involving initial formation of an anionic carbene intermediate $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(Ph)W(CO)_5]^-$ (M = Mn or Re), where the $W(CO)_5^{2-}$ moiety is bonded to the carbene carbon through the W atom. The protonation of the anionic carbene intermediate then afforded the bridging carbene complexes **37** or **38**. The origin of the hydrogen atom could be either THF or water as in the reaction of **2** with $Na_2[Fe(CO)_4]$ and $(NEt_4)_2[Fe_2(CO)_8]$.

Evidently, the cationic carbyne complexes **1** and **2** not only reacted with the carbonylmetal monoanions but also with the carbonylmetal dianions to give the dimetal bridging carbene complexes. This offers a convenient and useful method for the preparation of such complexes.

5. Reactions of $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (1) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (2) with the reactive salts $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}ER)(CO)_6]$ (E = S, Se)

During the course of our investigation of the reactions of carbonylmetal anions, we have noted the chemistry of the reactive salts $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SR)Fe_2(CO)_6]$, developed by Seyferth and co-workers in the late 1980s, and the applications of the $[(\mu\text{-}CO)(\mu\text{-}SeR)Fe_2(CO)_6]^-$ anions, the selenium analogous of reactive $[(\mu\text{-}CO)(\mu\text{-}SR)Fe_2(CO)_6]^-$ anions, in organometallic chemistry. In their reactions, the Fe–Fe bond and RS–Fe or RSe–Fe bond are retained and the bridging CO is usually replaced by another bridging ligand. Although these reactive salts have been extensively investigated, their reactions with cationic transition-metal carbyne complexes were unknown. Therefore, we studied the reaction of cationic carbyne complexes **1** an **2** with the reactive $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ and $[(\mu\text{-}CO)(\mu\text{-}SeR)Fe_2(CO)_6]^-$ anions, which produced a series of novel heteronuclear dimetal bridging carbene complexes.

Complex **1** treated with equimolecular amounts of freshly prepared $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SBu^n)Fe_2(CO)_6]$ in THF at −90 to −70 °C for 5 h to give the known compounds $[\eta^5\text{-}C_5H_5Mn(CO)_3]$ and $[Fe(CO)_3(^nBuS)]_2$ (**39**) [47], the dark green complex $[MnFe\{\mu\text{-}C(SBu^n)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**40**), and the reddish-

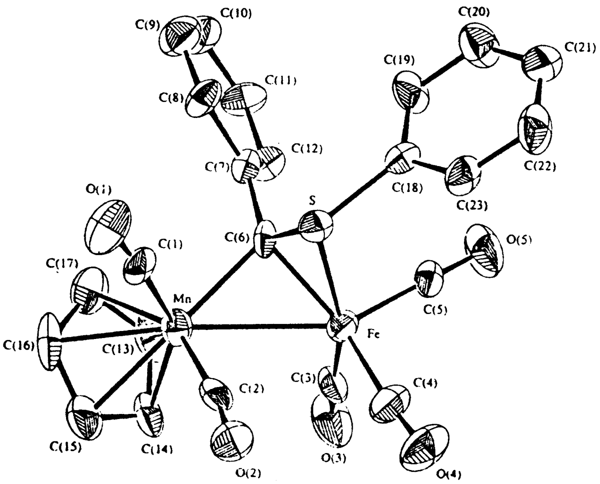


Fig. 17. Molecular structure of **44**.

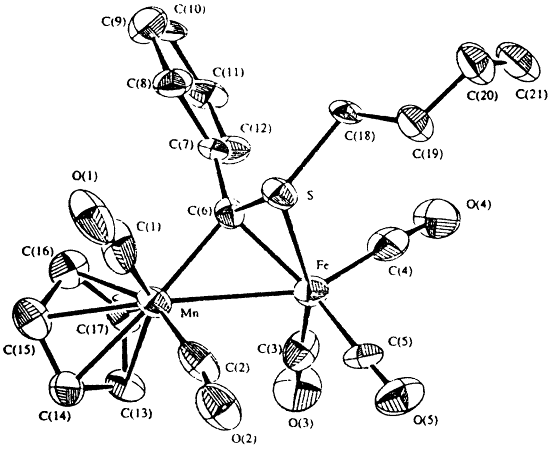


Fig. 16. Molecular structure of **40**.

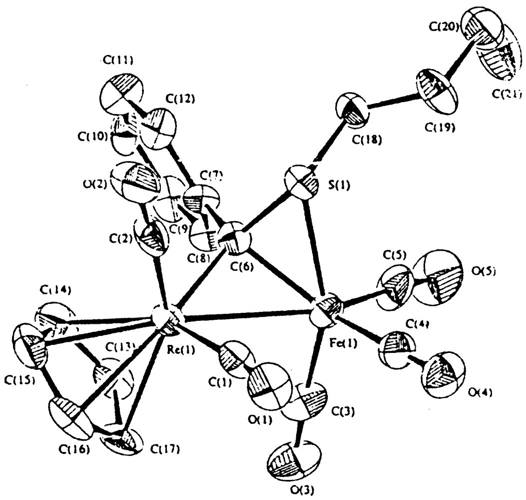
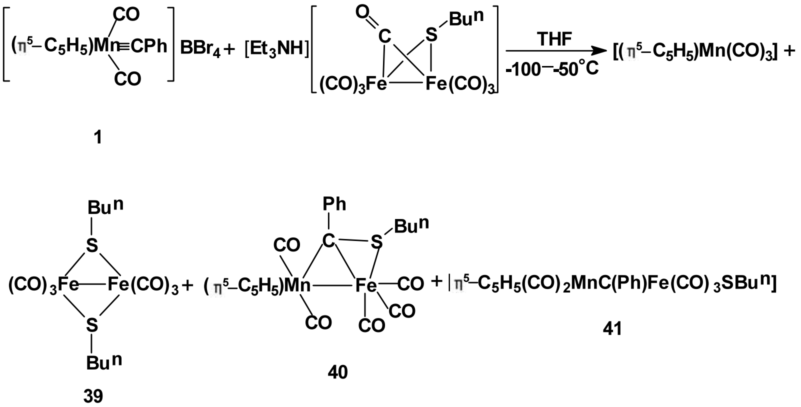


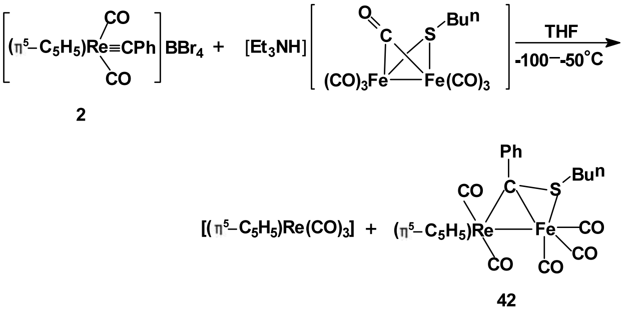
Fig. 18. Molecular structure of **42**.

brown crystalline complex [η^5-$C_5H_5(CO)_2MnC(Ph)Fe(CO)_3(SBu^n)$] (**41**) (Eq. (31)) [48] in 3, 4, 85, and 6% yields, respectively.



(31)

Complex **2** reacted similarly with [Et_3NH][(μ-CO)(μ-SBu^n)$Fe_2(CO)_6$] under the same conditions to give [η^5-$C_5H_5Re(CO)_3$] and orange–yellow crystalline complex [ReFe{μ-C(SBu^n)Ph}$(CO)_5$(η^5-C_5H_5)] (**42**) (Eq. (32)) [48] in 6 and 40% yields, respectively.



(32)

Complexes **40** and **42** are formulated as dimetal bridging carbene complexes, which have been confirmed by their single-crystal X-ray diffraction studies. The other product **41** in Eq. (31) could not be obtained as crystals of sufficient quality for X-ray diffraction characterization, and the spectroscopic studies did not result in an unambiguous proof of structure. In solution, complex **41** was transformed into complex **40**, as observed by ^{1}H-NMR spectroscopy [48]. Further evidence for this transformation came from the recrystallization of complex **41**. In order to obtain X-ray crystals suitable for an X-ray study, recrystallization of **41** was attempted from petroleum ether–CH_2Cl_2 solution at −80 °C for 72–96 h. However, only dark green crystals of **40** were obtained in 95% yield. The parent ion (M^+) and the principal fragment ions in the mass spectrum and C, H elemental analysis of **41** indicate the same composition as that of **40**. The ν(CO) absorptions of **41** are similar to those of **40**. The phenyl signals (δ 7.70–7.00) and the cyclopentadienyl (Cp) signal (δ 4.58) in its ^{1}H-NMR spectrum are different from those of **40** (δ 7.65–7.29 for phenyl and δ 4.61 for Cp). At present, there is not sufficient evidence to assign a structure to **41**.

In order to examine the effect of different substituents on the RS group on the reactivity of the reactive salts and on the reaction products, [Et_3NH][(μ-CO)(μ-SPh)–$Fe_2(CO)_6$], where the substituent on RS is a phenyl group, and the *p*-tolyl analog were used in the reaction with complex **1** under the same conditions. The known thiolato-bridged iron carbonyl compound [$Fe(CO)_3$-(SPh)]$_2$ (**43**), Mn–Fe bridging carbene complex [MnFe{μ-C(SPh)Ph}$(CO)_5$(η^5-C_5H_5)] (**44**), and phenylthiocarbene–manganese complex [η^5-$C_5H_5(CO)_2Mn$=C(SPh)Ph] (**46**) (Eq. 33)) [48] were formed in 5, 84,

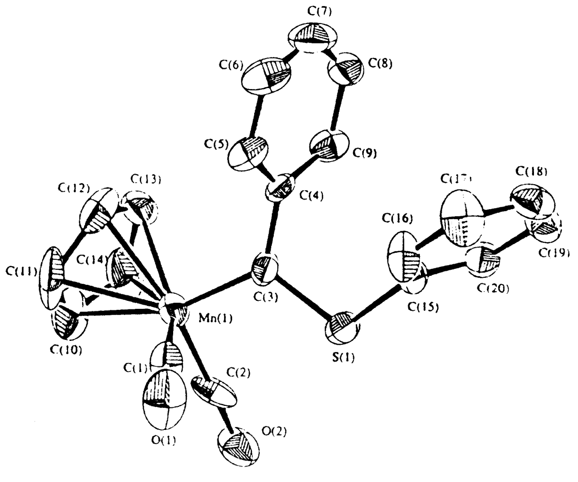
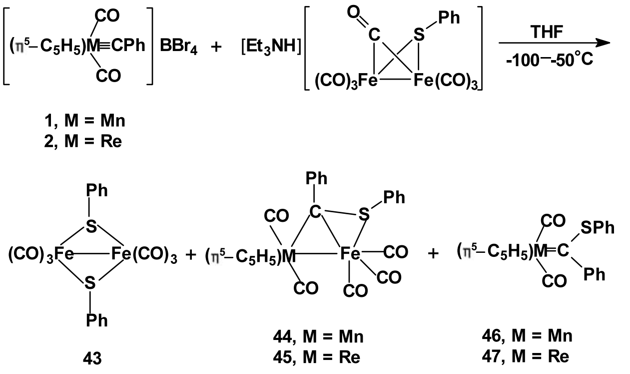


Fig. 19. Molecular structure of **46**.

and 9% yields, respectively, in the case of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$.

The analogous reaction [48] of complex **2** with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ gave **10**, Re–Fe bridging carbene complex $[ReFe\{\mu\text{-}C(SPh)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**45**), and rhenium phenylthiocarbene complex $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(SPh)Ph]$ (**47**) (Eq. (33)) in 6, 32, and 16% yields, respectively. The structures of products **44**, **45**, and **47** have been confirmed by X-ray diffraction analyses [48].



(33)

Analogous products $[Fe(CO)_3(p\text{-}MeC_6H_4S)]_2$ (**48**) and $[MnFe\{\mu\text{-}C(SC_6H_4Me\text{-}p)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**49**) were obtained in the reaction [48] of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SC_6H_4Me\text{-}p)Fe_2(CO)_6]$ with complex **1**.

Complex **40** (Fig. 16) was established by X-ray diffraction to have a novel structure in which the S atom bridges the μ-carbene carbon (C(3)) and the Fe atoms and provides two electrons to give Fe to the favored 18-electron configuration. The Mn–Fe distance of 2.705(4) Å is slightly longer than that in the analogous bridging carbene complex **35** (2.6929(8) Å) but is obviously longer than that in analogous bridging carbyne complex **23** (2.6494(3) Å). The μ-C–Fe distance of 1.94(1) Å in **40** is shorter than that in **35** (2.020(4) Å) but is longer than that in **23** (1.853(3) Å). The S–Fe distance of 2.265(5) Å is the same as the normal distance of S–Fe bond (2.270 Å) in $[Et_3NH][(\mu\text{-}SO_2)\{\mu\text{-}(Me_3)CS\}Fe_2(CO)_6]$ [49]. The C(6)–S bond length of 1.76(1) Å is nearly the same as the C(3)–S(1) distance (1.74(1) Å) in carbene complex **46**.

The structure of complex **44** (Fig. 17) resembles that of **40**, except the substituent on the S atom is a phenyl group instead of a butyl group. The Mn–Fe bond length (2.704(2) Å) is the same within experimental error as that in **40**. The C(6)–Mn distance of 2.057(9) Å is slightly longer than that in **40**, but the C(6)–Fe distance of 1.897(9) Å and S–Fe distance of 2.279(3) Å are both slightly longer than those in **40**.

The structure of complex **42** (Fig. 18) is very similar to that of **40** and **44**. The Re–Fe distance of 2.784(2) Å in **42** is very close to that in analogous complex **20** (2.7581(8) Å) but is slightly longer than that found in **30** (2.682(6) Å) [31]. The μ-C–Re(1) distance of 2.128(10) Å is nearly the same as that in **20** (2.120(5) Å), while the μ-C–Fe(1) distance of 1.951(1) Å is shorter than that in **20**.

The molecular structure of complex **46** shown in Fig. 19 has many common features of the analogous alkoxycarbene complexes **32** and $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(OEt)Ph]$ [10]. The μ-C–Mn distance of 1.84(1) Å in **46** is close to that in $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(OEt)Ph]$ (1.865(14) Å) [10]. The X-ray structure [48] of complex **47** is essentially the same as that of **46**. The Re–$C_{carbene}$ distance of 1.966(9) Å in **47** is slightly shorter than that in **32** (1.990(5) Å). The bond length of S–C(3) (1.749(9) Å) in **47** is close to that of S(1)–C(6) (1.785(9) Å) in **42**.

Complexes **46** and **47** might arise by loss of an $Fe(CO)_3$ moiety from the $Fe(CO)_3(SPh)^-$ anion invol-

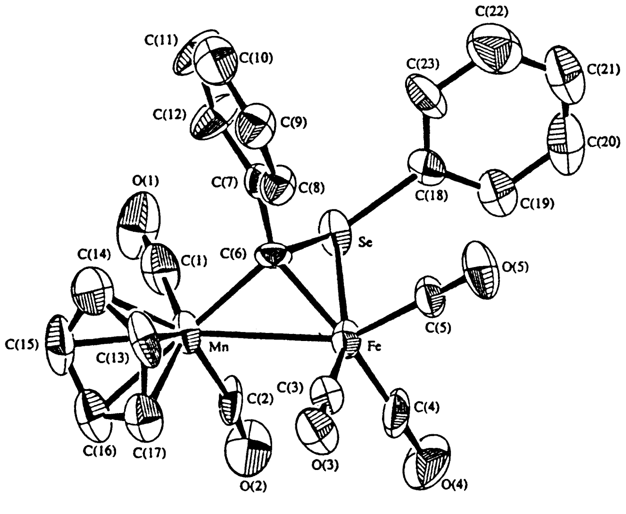


Fig. 20. Molecular structure of **50**.

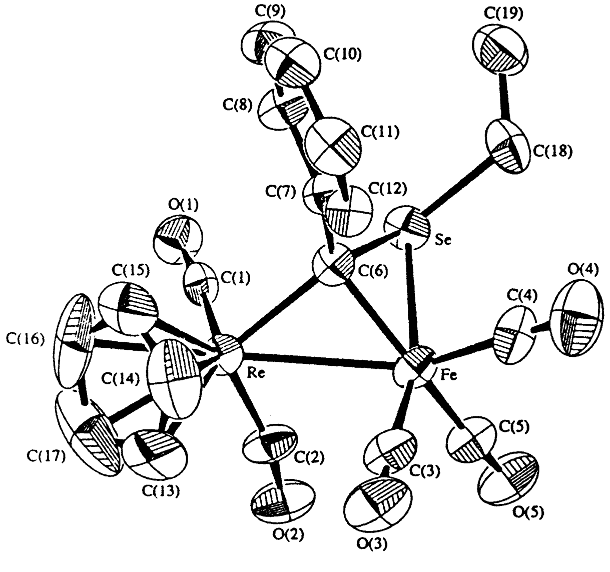


Fig. 21. Molecular structure of **57**.

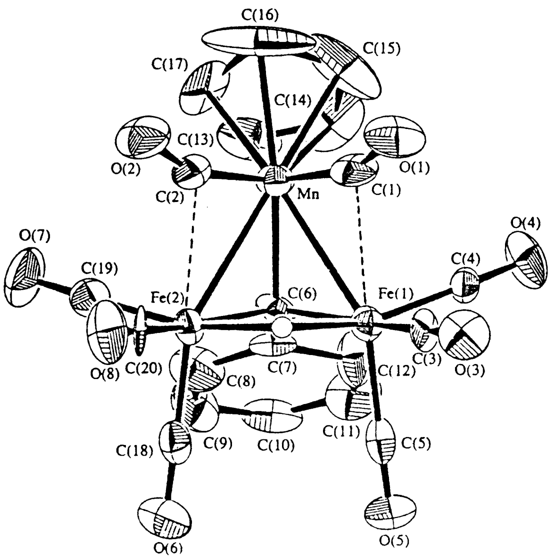
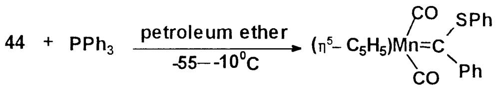


Fig. 22. Molecular structure of **59**.

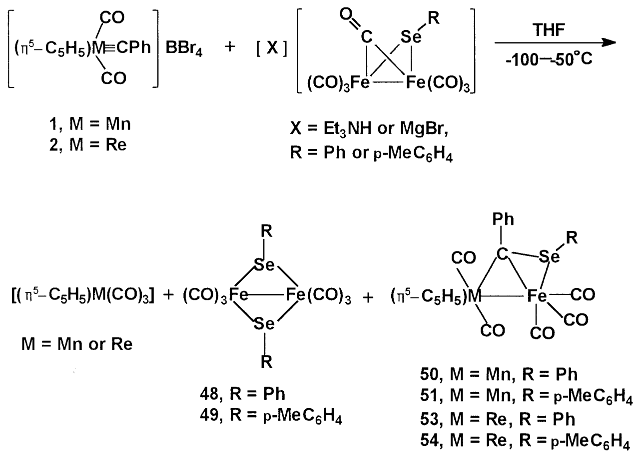
ving the breaking of an Fe–S bond of [(μ-CO)(μ-SPh)$Fe_2(CO)_6$]$^-$ anion or by cleavage of the carbene intermediate [η^5-$C_5H_5(CO)_2Mn{=}C(Ph)Fe(CO)_3(SPh)$] (M = Mn or Re) to generate a PhS^- species, which then becomes bonded to the carbene carbon to afford **46** or **47**. Both possibilities result from the stabilization of the negative charge on the S atom by the phenyl group. Up to now, no such Fe–S bond cleavage in reactions of the reactive [Et_3NH][(μ-CO)(μ-SR)$Fe_2(CO)_6$] salts has been reported. In order to explore this possibility, complex **44** was allowed to react with PPh_3 in petroleum ether at −55 to −10 °C to gave orange–red crystals of **46** in 39% yield (Eq. (34)) [48]. This result shows that the S–Fe bond of **44** can indeed be broken, since **44** was converted to **46** by loss of the $Fe(CO)_3$ moiety. However, complex **40** did not react with PPh_3 under the same conditions.



46

(34)

Like the reactive [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ anions, the [(μ-CO)(μ-SeR)$Fe_2(CO)_6$]$^-$ anions also reacts with the cationic carbyne complexes **1** and **2**. When complex **1** was treated, in separate experiments, with an equimolar quantity of freshly prepared (in situ) [Et_3NH][(μ-CO)(μ-SePh)$Fe_2(CO)_6$] and [Et_3NH][(μ-CO)(μ-SeC_6H_4Me-*p*)$Fe_2(CO)_6$] in THF at low temperature (−100 to −50 °C) for 4–5 h, the yellow compound [η^5-$C_5H_5Mn(CO)_3$], red selenolato-bridged iron carbonyl compounds [Fe(μ-SePh)$(CO)_3$]$_2$ (**48**) [50] and [Fe(μ-SeC_6H_4Me-*p*)$(CO)_3$]$_2$ (**49**) [51], and blackish-green Mn–Fe dimetal bridging carbene complexes [MnFe{μ-C(SePh)Ph}$(CO)_5$(η^5-C_5H_5)] (**50**) (from [Et_3NH][(μ-CO)(μ-SePh)$Fe_2(CO)_6$]$^-$) and [MnFe{μ-C(SeC_6H_4Me-*p*)Ph}$(CO)_5$(η^5-C_5H_5)] (**51**) (from [Et_3NH][(μ-CO)(μ-SeC_6H_4Me-*p*)$Fe_2(CO)_6$]) (Eq. (35)) [52] were obtained in 5–6, 24–25, and 63–66% yields, respectively, among which [η^5-$C_5H_5Mn(CO)_3$] and **48** [50] are known compounds.



(35)

Complex **2** reacts similarly with the anionic compounds [Et_3NH][(μ-CO)(μ-SePh)$Fe_2(CO)_6$] and [Et_3NH][(μ-CO)(μ-SeC_6H_4Me-*p*)$Fe_2(CO)_6$] under the same conditions to afford the Re–Fe dimetal bridging carbene complexes [ReFe{μ-C(SePh)Ph}$(CO)_5$(η^5-C_5H_5)] (**52**) and [ReFe{μ-C(SeC_6H_4Me-*p*)Ph}$(CO)_5$-(η^5-C_5H_5)] (**53**) in 70 and 72% yields, respectively, in addition to [η^5-$C_5H_5Re(CO)_3$] and **48** or **49** (Eq. (35)) [52].

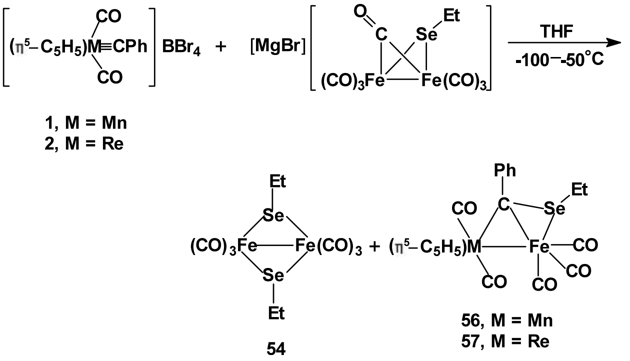
The products **50**–**53** are proposed to have the structure shown in Eq. (35) based on elemental analysis and spectroscopic data, among which the structures of **50** and **52** have been further confirmed by X-ray diffraction analyses. The molecular structure of complex **50** (Fig. 20) confirmed that the SeR ligand bridges the carbene carbon (C(6)) and the Fe atom through the Se atom and provides two electrons for Fe to satisfy a 18-valence-electron structure. The Mn–Fe distance of 2.697(3) Å is ca. the same as that found in analogous bridging carbene complexes **40** (2.705(4)), **44** (2.704(2)), and **35** (2.6929(8) Å), but obviously longer than that in bridging carbyne complex in [MnFe{μ-C(COEt)}(μ-CO)$(CO)_2$(η^5-C_5H_5)(η^5-C_5H_4Me)] (2.572(1) Å) [24]. The μ-C–Mn distance of 2.00(2) Å is slightly shorter than that in **44** (2.057(9) Å). The μ-C–Fe distance of 1.86(2) Å is not only shorter than that in **35** (2.020(4) Å) but also shorter than that in **40** (1.94(1)) and **44** (1.897(9) Å) and is comparable to that in bridging carbyne complex **23** (1.853(3) Å). This might be caused by bridging of the SeR group leading to the ring shrinkage. The Se–Fe bond length of 2.398(3) Å is somewhat longer than that in [Fe_2(μ-Se)$_2(CO)_6$] (average 2.363 Å) [53]. The C(6)–Se distance (1.99(2) Å) and Se–Fe distance in **50** are both obviously longer than the

C(6)–S distance (1.799(9) Å) and S–Fe distance (2.279(3) Å), respectively, in **44**.

The structure of complex **52** is very similar to that of **50**. Both structures have many common features. The Re–Fe distance (2.7731(9) Å) is very close to that in analogous complexes **42** (2.784(2)) and **20** (2.7581(8) Å). The μ-C–Re distance of 2.118(6) Å is the same within experimental error as that in **42** (2.128(10) Å) and **20** (2.120(5) Å), while the μ-C–Fe distance of 1.918(6) Å is somewhat shorter than that in **42** (1.951(1)) and **20** (2.097(5) Å). The Se–Fe (2.397(1)) and Se–C(6) (1.965(6) Å) bond lengths in **52** are close to those of **50**.

In order to firmly establish the steric configuration of **48** and **49**, a single-crystal X-ray diffraction study was carried out on **49**, which confirmed that the two *p*-MeC_6H_4 groups lie in trans position [52]. Complex **49** appears to be the first example of a species with Fe–Fe and Fe–Se(R) bonds studied by X-ray crystallography.

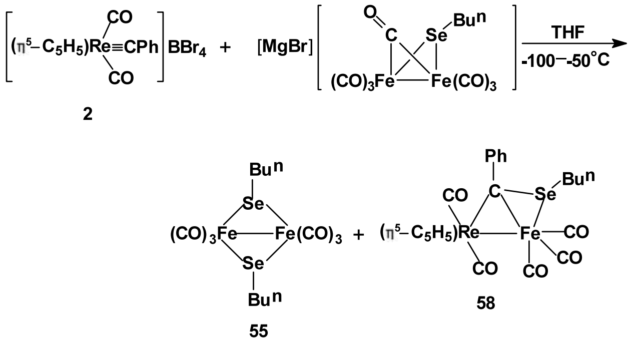
To explore the effect of different substituents on the Se atom on the reactivity of the reactive anions and reaction products, $[MgBr][(\mu\text{-}CO)(\mu\text{-}SEt)Fe_2(CO)_6]$, where the substituent on Se is an ethyl group, and the *n*-butyl analogue were used in reactions with complexes **1** and **2** under the same conditions. The bis(μ-SeEt)–hexacarbonyldiiron complex $[Fe_2(\mu\text{-}SeEt)_2(CO)_6]$ (**54**) and bridging carbene complexes $[MnFe\{\mu\text{-}C(SeEt)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**56**) and $[ReFe\{\mu\text{-}C(SeEt)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**57**) were formed in 18–19 and 72–73% yields, respectively, in the case of $[MgBr][(\mu\text{-}CO)(\mu\text{-}SEt)Fe_2(CO)_6]$ (Eq. (36)) [52].



(36)

Analogous products $[Fe_2(\mu\text{-}SeBu^n)_2(CO)_6]$ (**55**) and $[ReFe\{\mu\text{-}C(SeBu^n)Ph\}(CO)_5(\eta^5\text{-}C_5H_5)]$ (**58**) in 16 and 60% yield, respectively, were obtained in the reaction of $[MgBr][(\mu\text{-}CO)(\mu\text{-}SeBu^n)Fe_2(CO)_6]$ with **2** (Eq. (37)) [52].

The structures of complexes **56**–**58** shown in Eqs. (36) and (37) have been further confirmed by X-ray crystallography of **57**. The molecular structure of **57** (Fig. 21) is very similar to that of **52**, except that the substituent on the Se atom is an ethyl group instead of a phenyl group. The Re–Fe distance of 2.782(1) Å is nearly the same as that in **52**. The μ-C–Re (2.130(9)) and μ-C–Fe (1.927(9) Å) distances are both slightly longer than those in **52**, while the Se–C(6) (1.963(8)) and Se–Fe (2.395(2) Å) are both the same within experimental error as those in **52**.



(37)

The reaction pathways to complexes **50**–**53** and **56**–**58** are not clear. Presumably, their formation occurred via an $[Fe(CO)_3(SeR)]^-$ anion derived from dissociation of the $[(\mu\text{-}CO)(\mu\text{-}SeR)Fe_2(CO)_6]^-$ anion, a process involving the breaking of Fe–Fe and Fe–Se bonds. The anion might then attack the carbyne carbon of **1** or **2** with bonding of the Fe atom to the Mn or Re atom and the Se atom to the carbyne carbon to construct a RSe-bridged dimetallacyclopropane ring. Two $[Fe(CO)_3(SeR)]$ fragments could combine a selenolato-bridged iron carbonyl compound $[Fe_2(\mu\text{-}SeR)_2(CO)_6]$ by their dimerization. To the best of our knowledge, no such Fe–Se and Fe–Fe bond cleavage in the reactions of the $[(\mu\text{-}CO)(\mu\text{-}SeR)Fe_2(CO)_6]^-$ anions has been reported up to now. However, unlike $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$, the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SePh)Fe_2(CO)_6]$ salt did not undergo cleavage to generate a $PhSe^-$ species, and formation of a phenylseleno–carbene complex, an analogue of the phenylthiocarbene complex **46**

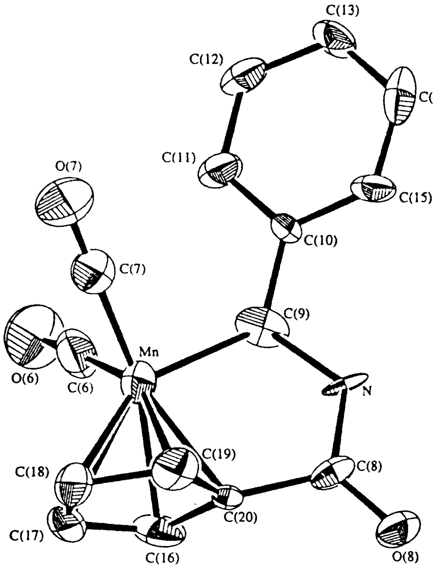


Fig. 23. Molecular structure of **60**.

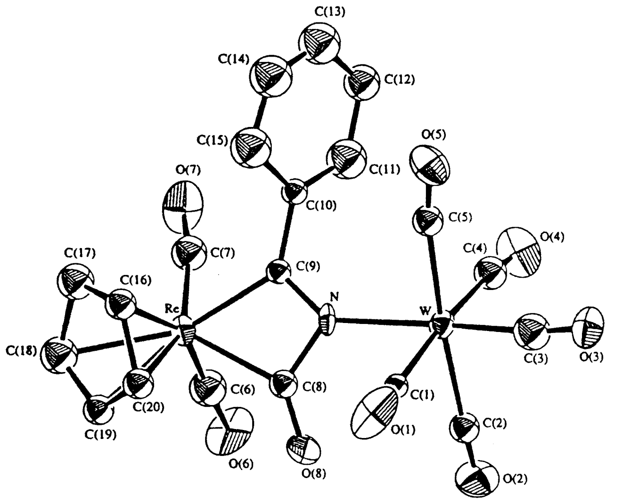
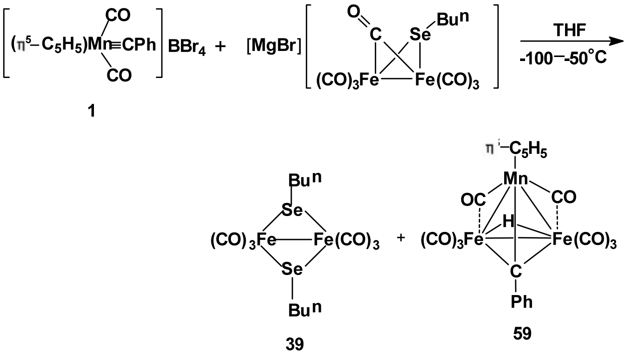


Fig. 24. Molecular structure of **61**.

or **47**, was not observed in the reaction of [Et$_3$NH][(μ-CO)(μ-SePh)Fe$_2$(CO)$_6$] with **1** or **2**.

Surprisingly, the reaction of **1** with [MgBr][(μ-CO)(μ-SeBu^n)Fe$_2$(CO)$_6$] under the same conditions gave no analogous dimetal bridging carbene complex but rather an unexpected trimetal bridging carbyne complex, [MnFe(μ-H)(μ-CO)$_2$(μ$_3$-CPh)(CO)$_6$(η^5-C$_5$H$_5$)] (**59**), in reasonable yield, in addition to product **39** (Eq. (38)) [52].



(38)

Complex **59** is a μ-H-bridged heteronuclear trimetal bridging carbyne complex whose structure has been confirmed by its ^{1}H-NMR spectrum and X-ray diffraction study. The existence of the bridging H atom in **59** was initially revealed by its ^{1}H-NMR spectrum, which showed a high-field resonance at δ −23.84, characteristic for an Fe–H–Fe species.

The structure of complex **59** (Fig. 22) contains a triangular MnFeFe arrangement with a capping μ$_3$-CPh ligand. The three metal atoms construct an approximate isosceles triangle (Mn–Fe(1) = 2.606(3) Å, Mn–Fe(2) = 2.612(3) Å, and Fe(1)–Fe(2) = 2.640(5) Å). An analogous bridging carbyne complex with a trimetalatetrahedrane CMnFe$_2$ core has been synthesized by reaction [54] of [Mn$_3$(μ-H)$_3$(CO)$_{12}$] with *trans*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η^5-C$_5$H$_5$)$_2$]. The Mn–Fe bond lengths (average 2.609 Å) in **59** are slightly longer than that in analogous complex **27** (2.570(2) Å). The Fe–Fe bond length is somewhat longer than that of similar complex [WFe$_2$(μ$_3$-CC$_6$H$_4$Me-*p*)(μ-CO)(CO)$_8$(η^5-C$_5$H$_5$)] (2.538(2) Å) [2f]. The μ-C(6)–Mn, μ-C(6)–Fe(1), and μ-C(6)–Fe(2) distances are 2.00(1), 1.94(1), and 1.95(1) Å, respectively, of which the μ-C–Mn and μ-C–Fe (average 1.945 Å) bond lengths are closely related to that in **27**. In **59**, the Fe(1) and Fe(2) atoms are bridged by a hydrogen atom, the average Fe–H distance being 1.77 Å. Similar to **28**, compound **59** is a 48 CVE complex, where the Mn and Fe atoms formally have 19 and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyl and bridging hydrogen. The semibridging CO ligands reveal themselves in the IR spectrum with the two bands at 1879 and 1870 cm^{-1}, respectively.

Complex **59** may be produced by loss of a μ-CO and a μ-SeBu^n moiety from the [(μ-CO)(μ-SeBu^n)Fe$_2$(CO)$_6$]$^-$ anion involving the breaking of Fe–C(μ-CO) and Fe–Se bonds or by cleavage of the formed carbene intermediate [η^5-C$_5$H$_5$(CO)$_2$Mn=C(Ph){(μ-CO)(μ-SeBu^n)Fe$_2$(CO)$_6$] to generate a [Fe$_2$(CO)$_6$H]$^-$ species, which then becomes bonded to the carbyne or carbene carbon through the two Fe atoms with bonding of Mn to the two Fe atoms to form complex **59**. The origin of the H$^-$ on this reaction could be either the THF solvent or water. The latter is a trace contaminant in the solvent THF or from glassware. To our knowledge, no such Fe–C and Fe–Se bond cleavage, namely, the bridging CO and SeR groups were simultaneously replaced by another bridging ligand in reaction of reactive [X][(μ-CO)(μ-SeR)Fe$_2$(CO)$_6$] salts, has been reported. Complex **59**, as a trimetal bridging carbyne complex, was synthesized by the reaction of a cationic carbyne complex with a carbonylmetal anion for the first time.

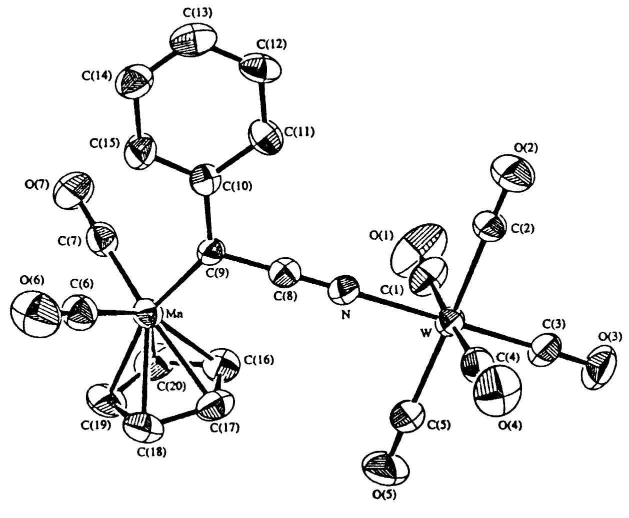


Fig. 25. Molecular structure of **62**.

Such a reaction of a cationic carbyne complex with the reactive salt producing a trimetal bridging carbyne complex is quite remarkable.

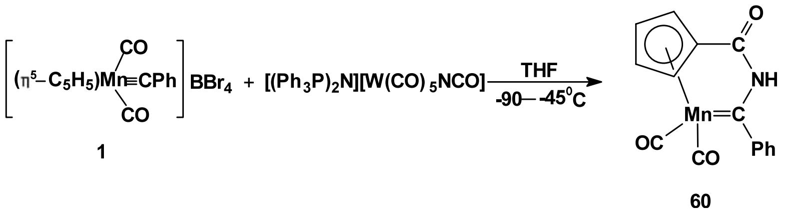
In conclusion, the cationic carbyne complexes of manganese and rhenium, **1** and **2**, show a variety of unusual reactions with the reactive salts to afford novel dimetal bridging carbene complexes or trimetal bridging carbyne complexes. This demonstrates a useful route to the heteroatom-bridged dimetal bridging carbene and trimetal bridging carbyne complexes.

6. Reactions of [η^5-$C_5H_5(CO)_2Mn{\equiv}CPh$]$BBr_4$ (1) and [η^5-$C_5H_5(CO)_2Re{\equiv}CPh$]$BBr_4$ (2) with carbonylmetal anions containing NCO, SCN, and CN group

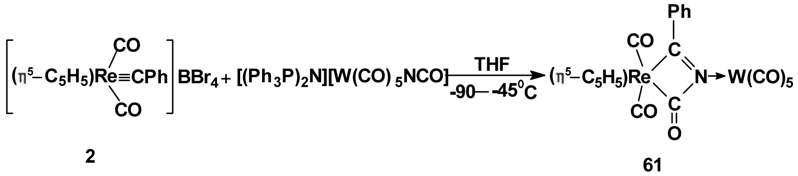
Since the carbyne carbon in complexes **1** and **2** is a highly electrophilic center toward nucleophiles, as shown by their reactions with H-, NO- and PPh_3-substituted carbonylmetal anions, the complexes **1** and **2** also form adducts with a variety of carbonylmetal anions containing negative substituents such as NCO, SCN, and CN groups. When complex **1** was allowed toreact with an equimolar quantity of [$(Ph_3P)_2N$][$W(CO)_5NCO$] in THF at low temperatures (−90 to −45 °C) for 4–5 h, a novel chelated carbene complex [η^5-$C_5H_4(CO)_2Mn{=}C(NHC{=}O)Ph$] (**60**) (Eq. (39)) [55] was obtained in 74% isolated yield. Complex **2** reacts similarly with [$(Ph_3P)_2N$][$W(CO)_5NCO$] (Eq. (40)) under the same conditions. However, the product is not an analogous chelated carbene complex. Instead, the product is an azametallacyclic complex [η^5-$C_5H_4(CO)ReC(Ph)(C{=}O)NW(CO)_5$] (**61**) (80% yield) [55].

The structures for complexes **60** and **61** established by their X-ray diffraction studies are shown in Figs. 23 and 24, respectively. In **60** (Fig. 23), the Mn–C(9) bond length of 1.89(2) Å signifies some double-bond character, and is essentially the same as that in analogous carbene complex [$C_5H_5(\eta^5$-$C_6H_6)(CO)_2Mn{=}C(OEt)Ph$] (1.89(1) Å) [56]. The C(9)–N bond length of 1.40(2) Å is somewhat shorter than a normal C–N distance arising from the ring tension. The other unusual feature is the C(8)–N bond length (1.33(2) Å) of the HNC=O group, which is the same within experimental error as a normal C=N distance. The shorter C(8)–N distance in **60** signifies some double-bond character between the C(8) and N atoms. In **61** (Fig. 24) the Re–C(8) (2.16(3)) and Re–C(9) (2.09(3) Å) bond lengths are both slightly longer than the Re–$C_{carbene}$ distance in carbene complex **32** (1.990(5) Å) [37], which could be caused by the ring shrinkage. The C(8)–N bond length of 1.43(4) Å is much longer than that in **60**, while the C(9)–N distance of 1.30(3) Å is markedly shorter than that of **60**. The shorter C(9)–N distance signifies a high double-bond character. The W–N distance of 2.27(2) Å is somewhat longer than the corresponding W–N distance in [$W{-}N\{Bu^tCMe_2(Me)(NBu^t)\}\{N(Bu^t)CMe{=}CMe_2\}$] (1.907–1.940 Å) [57], and is obviously longer than the W=N distance in [$W{-}N\{Bu^tCMe_2(Me)(NBu^t)\}$-$\{N(Bu^t)CMe{=}CMe_2\}$] (1.757(12) Å) [57], which indicates that the W–N bond in **61** is a weaker coordinating bond.

While the mechanism of the reaction Eq. (39) is not known, it is possible that it proceeds via the attack of the $^-$NCO anion, arising from breakage of the $^-$W(CO)NCO anion, on the carbyne carbon of **1** with bonding of the N atom to the carbene carbon C(9) and the carbon atom C(8) to the cyclopentadienyl ring C(20) to form a chelated manganese carbene complex accompanied by migration of a H atom from the cyclopentadienyl ring to the N atom. Analogous results have



(39)



(40)

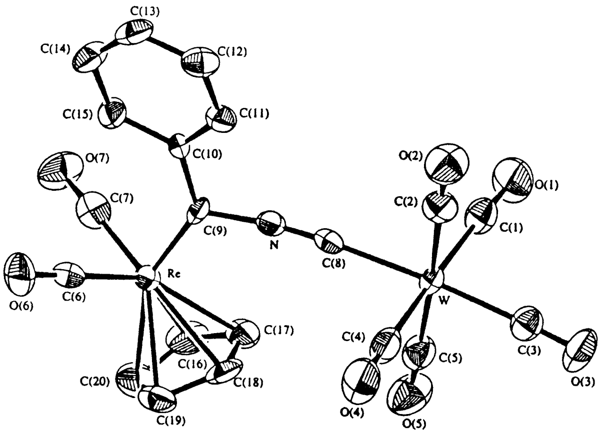


Fig. 26. Molecular structure of **65**.

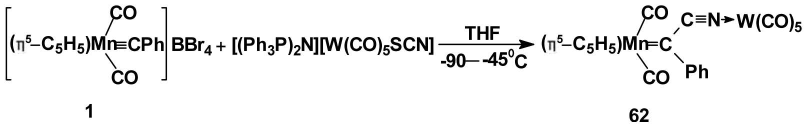
been observed in the reactions of cationic **1** with imines Ph(H)C=NR (R = Me, –N = C(H)Ph), which give the chelated metallacyclic carbene complexes [η^5-$C_5H_5(CO)_2Mn{=}C(Ph)N(R)C(H)Ph$] [58,59].

The generation of **61** may involve initial formation of the carbene intermediate [η^5-$C_5H_5(CO)_2Re{=}C(Ph)W(CO)_5NCO$], where the $W(CO)_5NCO$ moiety is directly bonded to carbene carbon through the W atom. Then the N–C bond of the NCO group is opened to respectively bond to the carbene carbon and Re atom through the N and C(8) atoms with dissociation of the W–$C_{carbene}$ bond, resulting in formation of an azametallacyclobutene ring. A similar intermediate has been observed in the reaction [60] of [$(CO)_5W{=}C(R)Ph$] (R = Ph, OMe) with carbodiimides.

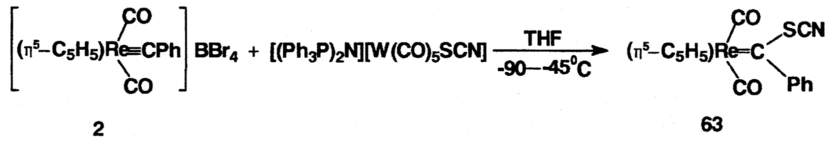
Surprisingly, [$(Ph_3P)_2N$][$W(CO)_5NCS$] reacted with complex **1** under similar conditions with loss of the sulfur atom to give a phenyl(pentacarbonylisocyano–tungsten)carbene–manganese complex [η^5-C_5H_5-$(CO)_2Mn{=}C(Ph)CNW(CO)_5$] (**62**) in 70% yield (Eq. (41)) [55], whose structure has been established by X-ray diffraction. However, the reaction between complex **2** and [$(Ph_3P)_2N$][$W(CO)_5SCN$] under the same conditions gave no analogous product but rather the (isothiocyanato)phenyl–carbene–rhenium complex **63** in 64% yield (Eq. (42)) [55]. The latter reaction showed that the SCN group was dissociated from the [$W(CO)_5SCN$]$^-$ moiety and bonded to the carbyne carbon of **2** to form the carbene complex **63**. This was confirmed by the reaction of **2** with KSCN under the same conditions, which yielded the same product **63** in 92% yield (Eq. (43)) [55]. Complex **63** is a known compound and was obtained by Fischer and co-workers from the reaction of cationic **2** with LiSCN in lower yield (35%) [61].

An X-ray study of **62** establishes (Fig. 25) the structure shown in Eq. (41). The Mn–C(9) bond length of 1.897(8) Å is the same as that in **60**. The C(9)–C(8) distance is 1.44(1) Å, which is between normal C–C and C=C distances and indicates certain double-bond character in the C(9)–C(8) bond. The C(8)–N bond length of 1.15(1) Å is a normal C≡N distance, which is nearly the same as that in [[$(Ph_3P)_2N$][$Fe(CO)_4CN$] (1.147(7) Å) [62]. The W–N distance (2.161(8) Å) in **62** is somewhat shorter than that in **61**. The C(9), C(8), N, and W atoms are coplanar, and the angles C(9)–C(8)–N and C(8)–N–W are 176.9(9) and 171.9(7)°, respectively, which signifies that the C(9)–C(8)–N–W fragment is nearly linear; thus, the C(9)–C(8)–N–W chain is a conjugate system.

It is not clear how the sulfur atom is lost and how the $^-CNW(CO)_5$ species becomes bonded to the carbene carbon in reaction (42). We suppose that the formation of **62** might be via a '$(CO)_5WN\equiv C^-$' species derived from loss of the S atom of the $W(CO)_5SCN$ moiety, which then attacks at the carbyne carbon of **1**. A possible alternate formation pathway is not excluded that could proceed via a ^-CN anion generated by either loss of the S atom from the SCN group or loss of the $W(CO)_5$ moiety from the $^-CNW(CO)_5$ species. The ^-CN anion attacks at the carbyne carbon to produce the carbene intermediate [η^5-$C_5H_5(CO)_2Mn=$



$$\underset{\mathbf{1}}{\left[(\eta^5\text{-}C_5H_5)\overset{CO}{\underset{CO}{Mn}}\equiv CPh\right]}BBr_4 + [(Ph_3P)_2N][W(CO)_5SCN] \xrightarrow[-90\text{--}45^\circ C]{THF} \underset{\mathbf{62}}{(\eta^5\text{-}C_5H_5)\overset{CO}{\underset{CO}{Mn}}{=}C\begin{matrix}C\equiv N\rightarrow W(CO)_5\\ Ph\end{matrix}} \tag{41}$$



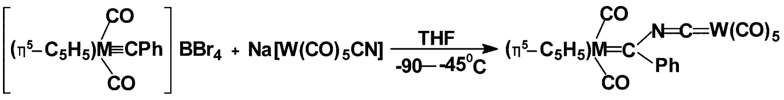
$$\underset{\mathbf{2}}{\left[(\eta^5\text{-}C_5H_5)\overset{CO}{\underset{CO}{Re}}\equiv CPh\right]}BBr_4 + [(Ph_3P)_2N][W(CO)_5SCN] \xrightarrow[-90\text{--}45^\circ C]{THF} \underset{\mathbf{63}}{(\eta^5\text{-}C_5H_5)\overset{CO}{\underset{CO}{Re}}{=}C\begin{matrix}SCN\\ Ph\end{matrix}} \tag{42}$$

$$\mathbf{2} + KSCN \xrightarrow[-90\text{--}45^\circ C]{THF} \mathbf{63} \tag{43}$$

C(Ph)CN]; the N atom of its CN group then coordinated to the W atom of the $W(CO)_5$ moiety and provides two electrons for the W atom to satisfy an 18-electron structure.

As contrasted with the reactions of $[(Ph_3P)_2N][W(CO)_5SCN]$, the reaction of $Na[W(CO)_5CN]$, where the negative CN group is directly bonded to the W atom, with complexes **1** and **2** under the same conditions gave the novel phenyl(penta-carbonylcyanotungsten)-carbene–manganese and –rhenium complexes $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)NCW(CO)_5]$ (**64**) and $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(Ph)NCW(CO)_5]$ (**65**) (Eq. (44)) [55] in 89 and 92% yields, respectively.

The formation of complexes **64** and **65** could proceed via the attack of the $(CO)_5W{=}C{=}N^-$ anion, a representation of the same electronic structure of the $^-W(CO)_5CN$ anion, on the carbyne carbon of cationic **1** or **2**.



$$\left[(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}CPh\right]BBr_4 + Na[W(CO)_5CN] \xrightarrow[-90-\,-45^{\circ}C]{THF} (\eta^5\text{-}C_5H_5)(CO)_2M{=}C(Ph)N{\equiv}C{=}W(CO)_5 \qquad (44)$$

1, M = Mn
2, M = Re

64, M = Mn
65, M = Re

The composition of **64** supported by elemental analyses and mass spectrum, which shows peaks for the parent ion and fragments resulting from loss of the CO ligands, is the same as that of complex **62**. The IR and ^{1}H-NMR spectra of **64** are similar to those of **65** but are very different from those of **62**. The IR spectrum of **62** showed four $\nu(CO)$ absorption bands at 2072, 2055, 1956, and 1917 cm^{-1}, but complexes **64** and **65** showed only three bands at ca. 2054, 2030, and 1951 cm^{-1}. The ^{1}H-NMR spectra of **62** showed two sets of proton signals attributed to the phenyl group at δ 7.73 and 7.44 and a singlet signal due to cyclopentadienyl protons at δ 5.12, whereas complexes **64** and **65** showed two sets of the phenyl proton signals at ca. 7.95–7.99 and 7.56–7.59 ppm and the cyclopentadienyl proton signal at ca. 5.44–6.09 ppm. These data indicate that the structures of complexes **64** and **65** would be different from that of **62**. This has been further confirmed by the X-ray single-crystal determination of **65**.

The structure of **65** (Fig. 26) is different from that of **62**, although their steric configurations are almost the same. The substituent on the carbene carbon is a pentadienylcyanotungsten group in **65** but a pentadienylisocyanotungsten group in the latter. The Re–C(9) bond length of 1.96(1) Å signifies considerable double-bond character and is nearly the same as that in **32**. The two C–N bond lengths in **65** are very different. C(8)–N has a bond length of 1.16(1) Å, which exhibits high triple-bond character and is essentially the same as that in **62**. The other, C(9)–N, has a bond distance of 1.40(1) Å, which is between the normal C–N and C=N distances. The shorter W–C(8) distance (2.13(1) Å) indicates a high double-bond character of the W–C(8) bond. The C(9), N, C(8), and W atoms are coplanar with a C(9)–N–C(8) angle of 176.8(10)° and a N–C(8)–W angle of 175.6(9)°, which shows that the C(9)–N–C(8)–W fragment is almost linear and the C(9), N, C(8), and W atoms could form a conjugate chain, as that in **62**.

Like $Na[W(CO)_5CN]$, $Na[Fe(CO)_4CN]$ can also react with **1** and **2** under the same conditions to give analogous phenyl(tetracarbonylcyanoiron)carbene–manganese and –rhenium complexes $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph]NCFe(CO)_4]$ (**66**) and $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(Ph)NCFe(CO)_4]$ (**67**) (Eq. (45)) [63] in 65 and 68% yields, respectively, whose structures have been established by their X-ray diffraction analyses.

The formation of products **66** and **67** was presumed to be via an attack of the $(CO)_4Fe{=}C{=}N^-$ anion (a

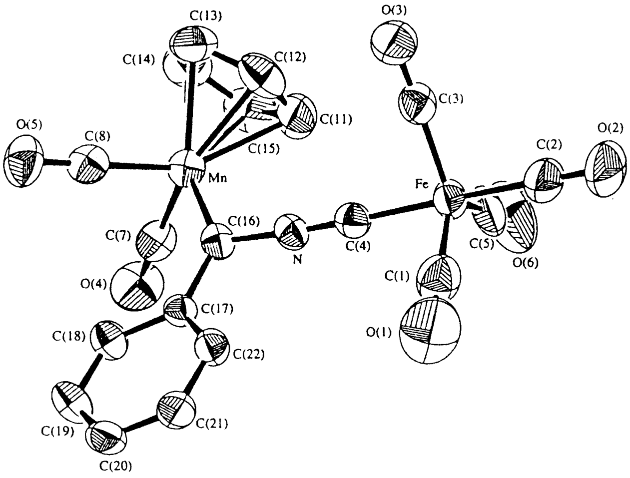
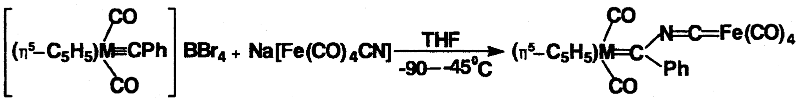


Fig. 27. Molecular structure of **66**.



1, M = Mn
2, M = Re

66, M = Mn
67, M = Re

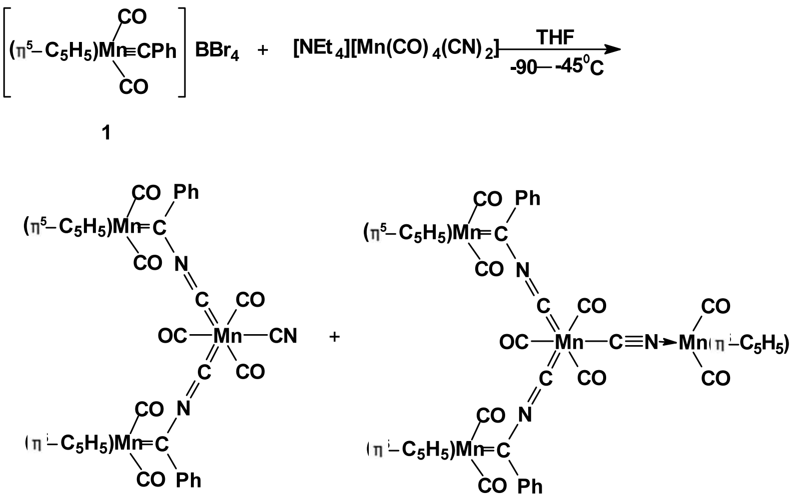
(45)

representation of the same electronic structure of the $^{-}Fe(CO)_4CN$ anion) on the carbyne carbon of **1** or **2**, similar to that of **64** and **65**.

Although the composition and structure of both complexes **66** and **67** are very similar, their IR and ^{1}H-NMR spectra are very different. The IR spectrum of **67** showed five ν(CO) stretching vibration bands at 2078, 2042, 2023, 1970, and 1924 cm^{-1}, but complex **66** showed only four bands at 2070, 2054, 2041, and 1970 cm^{-1}, which indicates that the different central metal exerts an obvious effect on the vibration frequency ν(CO). The ^{1}H-NMR spectrum of **66** shows three sets of the proton signals attributed to the phenyl at 7.88, 7.53, and 7.35 ppm and a singlet signal due to the cyclopentadienyl proton at 5.42 ppm, while **67** shows the phenyl signals at 7.36, 7.18, and 7.01 ppm, shifting to upfield and the cyclopentadienyl signal at 5.63 ppm, shifting to downfield. These suggest that the different central metal also exerts a significant effect on the chemical shifts of the phenyl and cyclopentadienyl protons. It is also worth noting that both ^{1}H-NMR spectra are very different from those of analogous complexes **64** and **65** (two sets of the phenyl proton signals at 7.95–7.99 and 7.56–7.59 ppm and a cyclopentadienyl signal at 5.44–6.09 ppm), which shows that the carbonylmetal substituent on the carbene carbon has a certain effect on the chemical shifts of the phenyl and cyclopentadienyl protons as well.

The structures of **66** (Fig. 27) and **67** (Fig. 28) are nearly identical. The bond lengths of Mn–C(16) (1.868(4) Å) in **66** and Re–C(16) (1.99(1) Å) in **67** signify a high double bond character. The two C–N bond distances in both complexes **66** and **67** are very different. C(4)–N has a bond length of 1.165(5) Å for **66** and of 1.17(2) Å for **67**, which exhibit high triple-bond character and are nearly the same as that found in **65**. The other, C(16)–N, has a bond length of 1.410(5) Å for **66** and of 1.42(2) Å for **67**, which are between the normal C–N and C=N distances. The shorter Fe–C(4) distance of 1.859(5) Å for **66** and of 1.85(1) Å for **67** indicates its high double-bond character, which is comparable with the Fe–C$_{carbene}$ bond in the carbene–iron complex $[\eta^4\text{-}C_{10}H_{16}(CO)_2Fe{=}C(OEt)C_6H_4Me\text{-}o]$ (1.915(15) Å) [64]. In **66** the C(16), N, C(4), and Fe atoms are coplanar with a C(16)–N–C(4) angle of 176.1(4)° and a N–C(4)–Fe angle of 178.9(4)°, indicating that the C(16)–N–C(4)–Fe fragment is almost linear and that the C(16), N, C(4), and Fe atoms form a conjugate chain, similar to that in **65**. In **67**, the C(16)–N–C(4)–Fe chain is also a nearly linear conjugate system as that in **66**.

It is quite interesting that the reaction of a carbonylmetal anionic compound containing two CN groups,



1

68

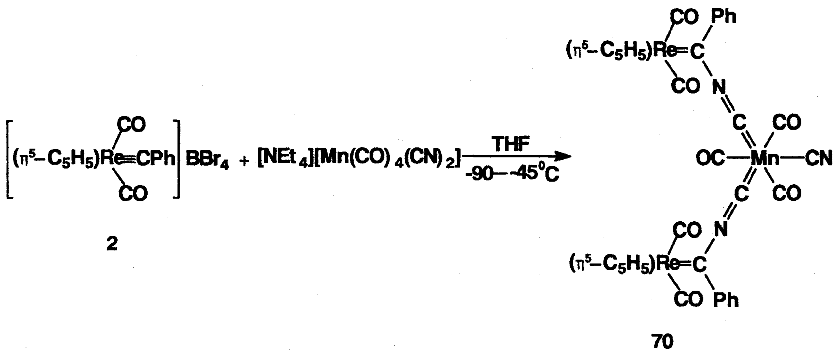
69

(46)

$(Et_4N)[Mn(CO)_4(CN)_2]$, with **1** under the same conditions gave a novel trinuclear dicarbene–manganese complex $[\{\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)NC\}_2Mn(CO)_3CN]$ (**68**) and a tetranuclear dicarbene–manganese complex $[\{\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)NC\}_2Mn(CO)_3CNMn(CO)_2(\eta^5\text{-}C_5H_5)]$ (**69**) (Eq. (46)) [63] in 30 and 52% yield, respectively.

Likewise, complex **2** can react with $(Et_4N)[Mn(CO)_4(CN)_2]$. The only isolated product (69% yield) from this reaction is the trinuclear dicarbene–rhenium complex $[\{\eta^5\text{-}C_5H_5(CO)_2Re{=}C(Ph)NC\}_2Mn(CO)_3CN]$ (**70**) (Eq. (47)) [63].

The formation of complexes **68** and **70** could proceed via an attack of the $(CO)_4(CN)Mn{=}C{=}N^-$ anion, a representation of the same electronic structure of the $^-Mn(CO)_4(CN)_2$ anion, on the carbyne carbon of cationic complex **1** or **2** to form a unstable carbene intermediate $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(Ph)NCMn(CO)_4CN]$ ($M = Mn$ or Re), similar to that of **66** and **77**. This unstable intermediate was then converted into an intermediate $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(Ph)NCMn(CO)_3(CN)_2]^-$ ($M = Mn$ or Re) anion by losing a CO ligand from the $Mn(CO)_4CN$ moiety and abstracting a CN group from another molecule of $(Et_4N)[Mn(CO)_4(CN)_2]$. Subsequently, the $[\eta^5\text{-}C_5H_5(CO)_2\text{–}M{=}C(Ph)NC(CO)_3(CN)Mn{=}C{=}N^-]$ anion, a representation of the same electronic structure of $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(Ph)NCMn(CO)_3(CN)_2]^-$, attacked



(47)

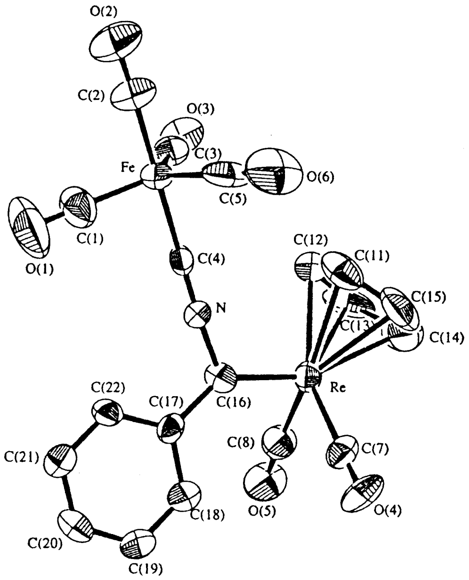


Fig. 28. Molecular structure of **67**.

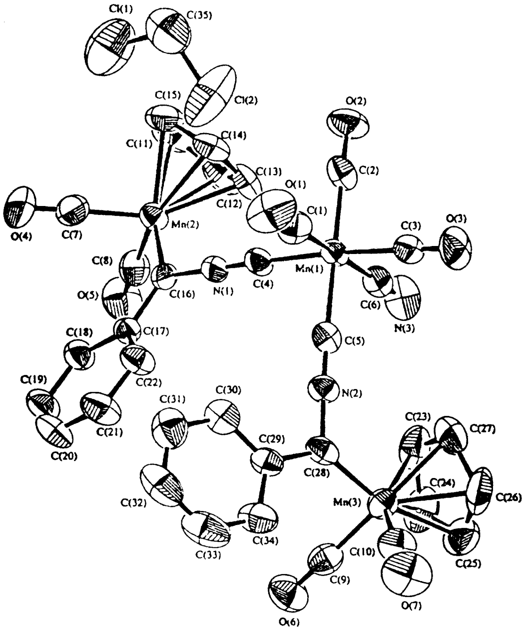


Fig. 29. Molecular structure of **68**.

the carbyne carbon of another molecule of **1** or **2** to yield eventually the product **68** or **70**, while the formation of **69** might involve initial formation of a dicarbene intermediate complex [$\{\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)NC\}_2Mn(CO)_3CN$] (**68**). Then the N atom of its CN group coordinates to the Mn atom of the '(η^5-C_5H_5)$Mn(CO)_2$' moiety presumably generated by loss of the carbyne ligand from **1** and provides two electrons for the Mn atom to give Mn an 18-electron structure.

The structures proposed in Eqs. (46) and (47) for complexes **68**–**70** were based on their elemental analyses and spectroscopic data. Surprisingly, complex **70** contains one molecule of $Br(CH_2)_4OH$, which cannot be separated from **70**. It is not known how the $Br(CH_2)_4OH$ molecule is formed. We suppose that it might form by a ring-opening reaction of the solvent THF (C_4H_8O) companied by abstraction of a hydrogen from THF and a bromide ion from the BBr_4^- species during a reaction such as that in the reaction of **2** with $(Et_4N)[Fe_2(CO)_8]$ giving [η^5-$C_5H_5(CO)_2BrReCH_2Ph$] (**33**) (Eq. (26)). The source of the H atom could be either the solvent THF itself or water, which is a trace contaminant in solvent THF or from glassware [63]. The existence of the $Br(CH_2)_4OH$ molecule in **70** was initially revealed by its ^{1}H-NMR and mass spectra. The ^{1}H-NMR spectrum of **70** showed two sets of the signal due to the methylene protons at 3.60–3.50 and 1.90 ppm and a signal attributed to the hydroxy (OH) proton at 2.25 ppm, while the mass spectrum of **70** showed a peak at *m*/*e* 152 assigned to the molecular ion of $Br(CH_2)_4OH$.

X-ray diffraction studies of **68** and **69** (Figs. 29 and 30) show that the principal structural fragment [$\{\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(Ph)NC\}_2Mn(CO)_3CN$] of **69** is nearly the same as **68**, as illustrated by the following parameters. The M–$C_{carbene}$ bond distances Mn(2)–C(16) and Mn(3)–C(28), respectively, are 1.866(6) and 1.872(7) Å for **68** and 1.871(10) and 1.865(9) Å for **69**. Both distances in **68** and **69** signify a high double-bond character and are the same within experimental error as that found (1.868(4) Å) in **66**. The C(4)–N(1) and C(5)–N(2) distances are 1.162(7), 1.164(7) Å and 1.16(1), 1.15(1) Å for **68** and **69**, respectively, very close to that of the corresponding bond in **66**, while the C(16)–N(1) and C(28)–N(2) distances are 1.418(8) and 1.390(8) Å for **68** and 1.42(1) and 1.44(1) Å for **69**. The distances of the Mn(1) atom to the C(4) and C(5) atoms, 1.925(7) and 1.927(7) Å for **68** and 1.933(10) and 1.93(1) Å for **69**, indicating some double-bond character of the Mn(1)–C(4) and Mn(1)–C(5) bonds in both complexes, are somewhat shorter than the Mn(1)–C(6) distance of 2.002(9) Å for **68** and 1.979(10) Å for **69**. As in complexes **66** and **67**, the C(16)–N(1)–C(4)–Mn(1) and C(28)–N(2)–C(5)–Mn(1) fragments in **68** and **69** are almost linear conjugate chains. The angles between the two conjugate chains are 88.0(3) and 85.4(4)° for **68** and **69**, respectively. In **69**, the C(6)–N(3) bond length of 1.154(10) Å, slightly longer than that (1.129(9) Å) in **68**, is a normal C≡N distance and is nearly the same as that in similar complex **62** (1.151(1) Å). Complex **69** appears to be the first example of a species with a CN–Mn bond studied by X-ray crystallography and, hence, comparison of the Mn–N(CN) bond distance with others is not possible. However, the Mn(4)–N(3) distance of 1.970(8) Å in **69** is markedly shorter than the Mn–N distances in $[C_6H_4CH_2N(Me)_2Mn(CO)_4]$ (2.139(3) Å) [65] and $[Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)]$ (2.086–2.110 Å) [66], suggesting that the Mn(4)–N(3) bond in **69** is a more strongly coordinating bond. Thus, the molecule of **69** is a stable conjugate system.

The X-ray structure study of complex **70** (Fig. 31) confirmed the presence of one molecule of $Br(CH_2)_4OH$ in **70**. Its configuration resembles that of **68**. In **70**, the Re–$C_{carbene}$ bond lengths are 2.00(2) and 1.99(2) Å for Re(2)–C(16) and Re(3)–C(28), respectively, which are essentially the same as that (1.99(1) Å) in **67**. The C(16)–N(1) distance (1.41(2) Å) is longer than that of C(28)–N(2) (1.37(2) Å), while the C(4)–N(1) distance of 1.16(2) Å is nearly the same as that of C(2)–N(2) (1.15(2) Å) but is slightly longer than that of C(6)–N(3) (1.13(2) Å). The distances of Mn(1) to the C(4) and C(5) atoms are shorter than that of Mn(1) to C(6) (2.01(2) Å). The bond angle data indicate that C(16)–N(1)–C(4)–Mn(1) and C(28)–N(2)–C(5)–Mn(1) chains in **70** are nearly linear conjugate chain with an angle of 89.6(7)° between them.

Apparently, the reactions of carbonylmetal anions containing NCO, SCN, and CN group with cationic carbyne complexes **1** and **2** give novel cyano-containing mono-, or tri- and tetrametal mono- or dicarbene complexes or azametallacyclic compounds, instead of

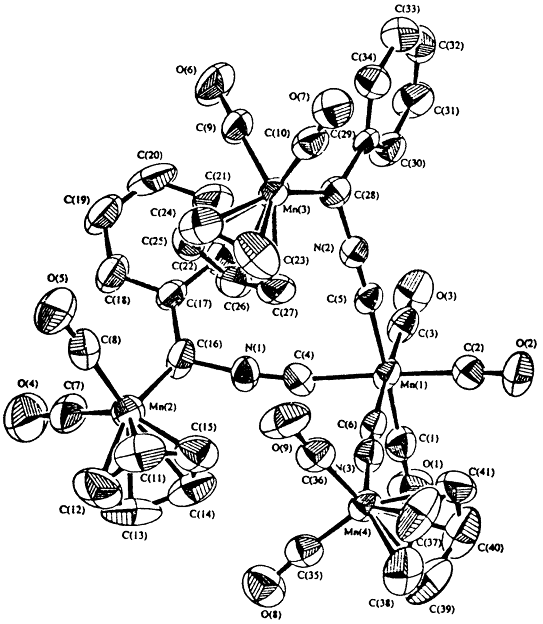
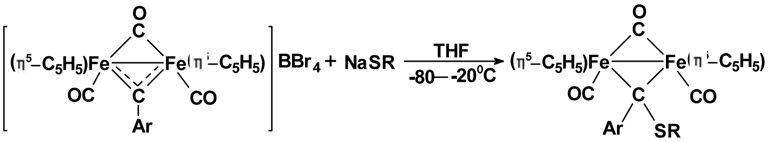


Fig. 30. Molecular structure of **69**.

the expected dimetal bridging carbene complex having a negative substituent on the bridging carbene carbon, and these compounds are related to metal cyanide complexes. The metal cyanide complexes have been examined extensively and can be used for synthesis of heterocycles [67]. However, not all carbonylmetal anions containing negative substituents can react with cationic carbyne complexes since carbonylmetal anions containing halogen such as $[W(CO)_5Br]^-$, $[Cr(CO)_5I]^-$, and $[Co_4(CO)_{11}I]^-$ do not react with complexes **1** and **2** under the same conditions, indicating that the negative substituent on the carbonylmetal anion is important. The reaction results show that the different carbonylmetal anions exert great influence on the reactivity of the cationic carbyne complexes and resulting products.



3, Ar = Ph
4, Ar = p-MeC$_6$H$_4$

71, Ar = Ph, R = Me
72, Ar = Ph, R = Et
73, Ar = Ph, R = Ph
74, Ar = Ph, R = p-MeC$_6$H$_4$
75, Ar = Ph, R = p-NO$_2$C$_6$H$_4$
76, Ar = p-MeC$_6$H$_4$, R = Ph
77, Ar = p-MeC$_6$H$_4$, R = p-MeC$_6$H$_4$

(48)

7. Reactions of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ with nucleophiles containing S, O, and N atoms

In principle, the highly electrophilic cationic carbyne complexes of diiron, $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$, should be highly reactive toward nucleophiles as those of cationic carbyne complexes **1** and **2**, which is actually the case.

The fresh prepared (in situ) complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CPh)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**3**) was treated with an equimolar quantity of nucleophiles, NaSR (R = Me, Et, Ph, *p*-MeC$_6$H$_4$, *p*-NO$_2$C$_6$H$_4$), in THF at low temperatures (−80 to −20 °C) for 4–5 h to yield the diiron bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**71**, R = Me; **72**, R = Et, **73**, R = Ph, **74**, R = *p*-MeC$_6$H$_4$; **75**, R = *p*-NO$_2$C$_6$H$_4$) in 51–74% yields (Eq. (48)) [13]. The analogous reactions of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**4**) with NaSR (R = Ph, *p*-MeC$_6$H$_4$) under the same conditions give the corresponding bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)C_6H_4Me\text{-}p\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**76**, R = Ph; **77**, R = *p*-MeC$_6$H$_4$) (Eq. (48)) [13] in 72–75% yields.

The IR spectra of complexes **71**–**77** showed two CO absorption bands at 1898–1994 cm^{-1} and one at 1756–1786 cm^{-1} in the bridging *v*(CO) region, evidence for an $Fe_2(\mu\text{-}CO)(CO)_2$ moiety in these complexes. In the ^{1}H-NMR spectra of **71**–**77**, the signal due to the cyclopentadienyl protons at about 5.10–5.40 ppm was only a single resonance. However, in a complex with a μ-carbene with different substituents, the cis form displays one C$_5$H$_5$ resonance and the trans form two, as shown

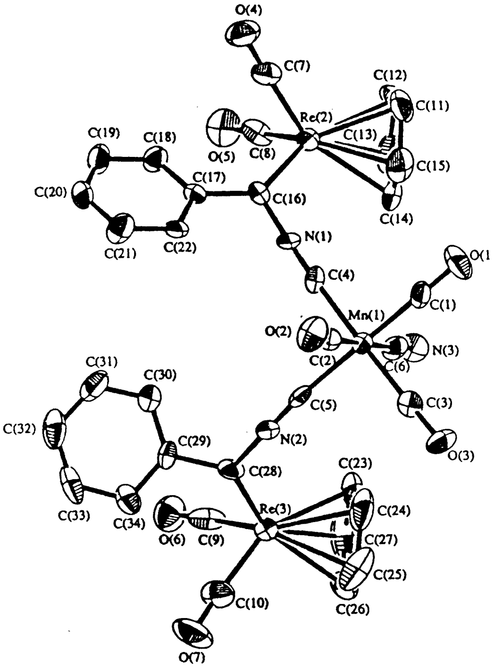


Fig. 31. Molecular structure of **70**. Br(CH$_2$)$_4$OH has been omitted for clarity.

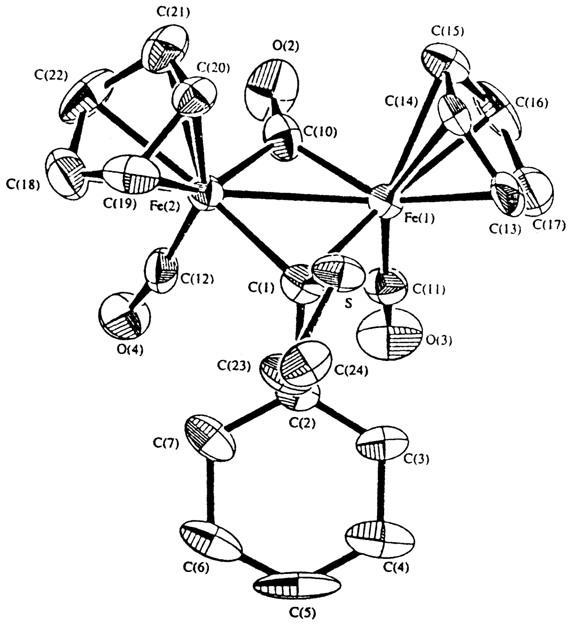


Fig. 32. Molecular structure of **72**.

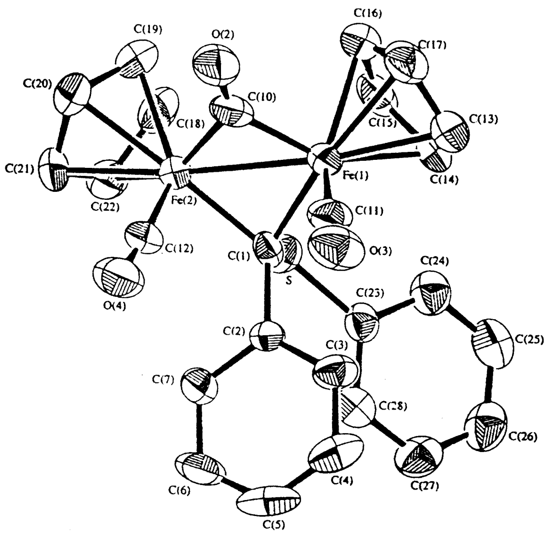
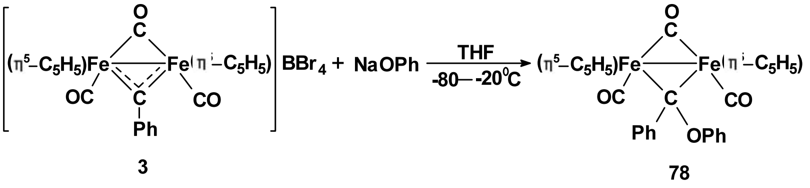


Fig. 33. Molecular structure of **73**.

in complex $[Ru_2(\mu\text{-CO})\{\mu\text{-C(H)COOEt}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ [68]. Hence, complexes **71**–**77** are the cis products, which has been confirmed by the X-ray diffraction analyses of complexes **72** and **73**.

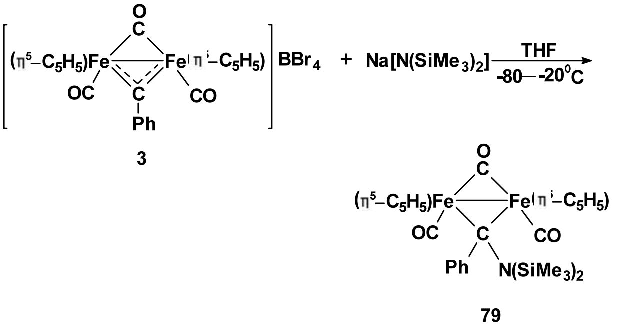
The structures of both complexes **72** (Fig. 32) and **73** (Fig. 33) are similar to those of the precursor compounds $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)Ar}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (Ar = Ph, *p*-MeC_6H_4) [6]. The difference between these structures is the replacement of an OEt group with SR. The mercapto and aryl groups are attached to the μ-C(1), and the two cyclopentadienyl rings are in cis, almost totally eclipsed configuration, as anticipated from the IR and ^{1}H-NMR spectra. The least-squares plane calculations show that the carbon atoms in the Cp ring are coplanar and the two CO groups coordinated on the same Fe atom are not coplanar arising from bridging. The distances of the Fe–Fe bond bridged by μ-carbene ligand in **72** and **73** are 2.527(2) and 2.523(2) Å, respectively, which are slightly longer than that in $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (2.512(1) Å) [6]. The μ-carbene carbon almost symmetrically bridges the Fe–Fe bond with C(1)–Fe(1) 2.03(1) Å and C(1)–Fe(2) 2.00(1) Å for **72** and C(1)–Fe(1) 2.026(8) Å and C(1)–Fe(2) 2.032(8) Å for **73**. The μ-C–Fe distances in **72** and **73** are much longer than the μ-CO bond (C(10)–Fe(1) 1.91(1), C(10)–Fe(2) 1.91(1) Å for **72**; C(10)–Fe(1) 1.89(1), C(10)–Fe(2) 1.902(9) Å for **73**). The C(1)–S bond lengths (1.83(1) Å for **72** and 1.829(8) Å for **73**) indicate that they are essentially single bonds by comparison with standard $C(sp^2)$–S (1.76 Å) single bond and $C(sp^3)$–S (1.81 Å) single bond distances [69]. In **72** and **73**, the benzene ring lies in the trans position of the cyclopentadienyl rings to avoid steric repulsion between the six-membered aryl ring and the cyclopentadienyl rings.

Like NaSR, the nucleophiles NaOPh and $Na[N(SiMe_3)_2]$ also react with complex **3** under the same conditions to produce bridging carbene complex $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OPh)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**78**) (Eq. (49)) and $[Fe_2(\mu\text{-CO})\{\mu\text{-C(N(SiMe_3)_2)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**79**) (Eq. (50)) [13] in 38 and 32% yield, respectively.



(49)

The IR spectra, the solution ^{1}H-NMR spectra, and mass spectra are consistent with the proposed structures



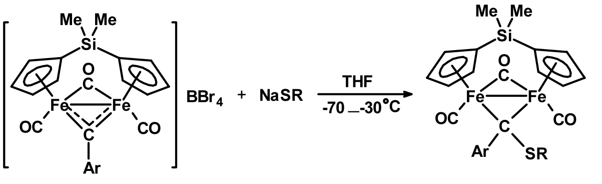
3

79

(50)

shown in Eqs. (49) and (50), respectively. In the IR spectra of **78** and **79**, the CO absorption bands in the ν(CO) region are similar to those in complexes **71**–**77**. In the ^{1}H-NMR spectra of **78** and **79**, except for the proton signals attributed to the OEt and $N(SiMe_3)_2$ group, the chemical shift, multiplicity, and integral intensity of the proton signals due to the aryl and cyclopentadienyl groups are also similar to those of complexes **71**–**77**. This implies that the structural framework of complexes **78** and **79** is similar to those of **71**–**77**.

The cationic carbyne complexes of dimethylsilane-bridged bis((η^5-cyclopentadienyl)diiron, $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ (**5**, Ar = Ph; **6**, Ar = p-MeC_6H_4; **7**, Ar = p-$CF_3C_6H_4$), also react with NaSR under similar conditions to afford diiron bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ (**80**, Ar = Ph, R = Me; **81**, Ar = Ph, R = Ph; **82**, Ar = Ph, R = p-MeC_6H_4; **83**, Ar = p-MeC_6H_4, R = Me; **84**, Ar = p-MeC_6H_4, R = Ph; **85**, Ar = p-MeC_6H_4, R = p-MeC_6H_4; **86**, Ar = p-$CF_3C_6H_4$, R = Me; **87**, Ar = p-$CF_3C_6H_4$, R = Ph; **88**, Ar = p-$CF_3C_6H_4$, R = p-MeC_6H_4) (Eq. (51)) [14] in 64–78% yields.



5, Ar = Ph
6, Ar = p-MeC6H4
7, Ar = p-CF3C6H4

	Me	Ph	p-MeC6H4
Ph	80	81	82
p-MeC6H4	83	84	85
p-CF3C6H4	86	87	88

(51)

The IR spectra of complexes **80**–**88** showed two CO absorption bands at 1984–1949 cm^{-1} and one at 1779–1771 cm^{-1} in the bridging ν(CO) region, indicating an $Fe_2(\mu\text{-}CO)(CO)_2$ moiety in these complexes. In the ^{1}H-NMR spectra of **80**–**88**, the signals from the dicyclopentadienyl protons showed four resonances at about 6.30–5.05 ppm, similar to those of precursor complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2\text{-}SiMe_2\}]$ (Ar = Ph, p-MeC_6H_4, p-$CF_3C_6H_4$) [8].

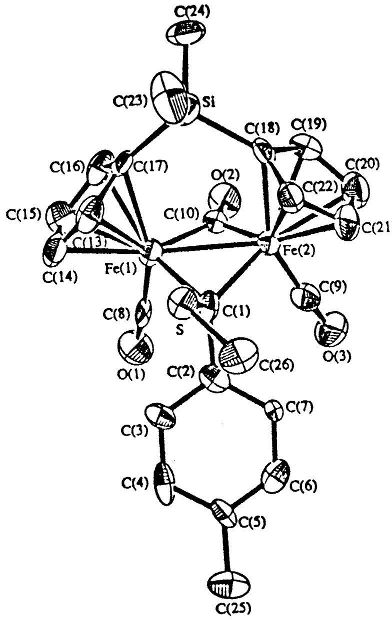


Fig. 34. Molecular structure of **80**.

The structures of complexes **80** (Fig. 34), **84** (Fig. 35), and **87**, established by X-ray diffraction [14], resemble closely that of the precursor alkoxycarbene compound $[Fe_2\{\mu\text{-}CO)(\mu\text{-}C(OEt)Ph\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]$ [8], except the SR group on the μ-carbene carbon is replaced by a OEt group in the latter. The structural features of the $[Fe_2\{\mu\text{-}C(SR)Ar\}]$ portion of the three complexes are very similar to those in complexes **72** and **73**, except the C–S bond distances are slightly shorter than the corresponding distances in **72** and **73**. The distances of

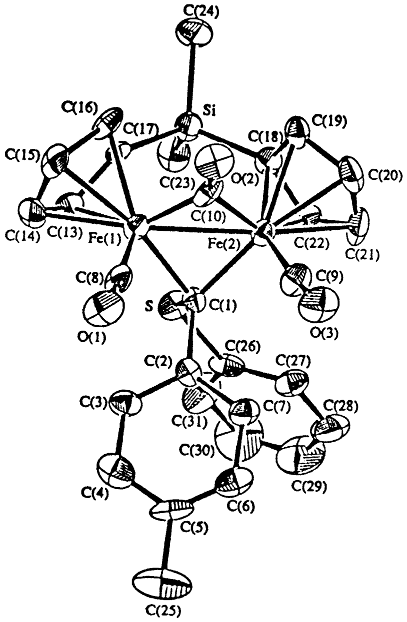


Fig. 35. Molecular structure of **84**.

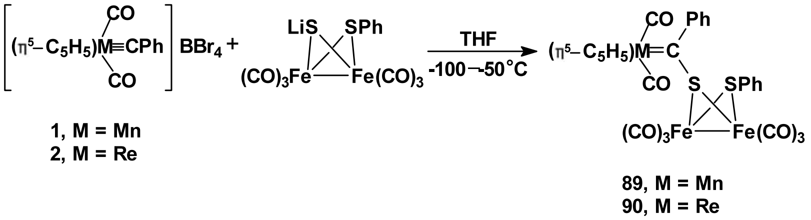
the Fe–Fe bond bridged by the μ-carbene ligand in **80**, **84**, and **87** are 2.515(3), 2.510(2), and 2.516(3) Å, respectively, which are the same as that in [Fe_2(μ-CO){μ-C(OEt)Ph}$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}] (2.513(1) Å) [8].

8. Reactions of [Fe_2(μ-CO)(μ-CAr)$(CO)_2$(η^5-$C_5H_5)_2$]BBr_4 and [Fe_2(μ-CO)(μ-CAr)$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}]BBr_4 with the [(μ-S)(μ-SPh)$Fe_2(CO)_6$]$^-$ anion

In view of the catalytic activity and use in organic synthesis of the iron-cluster complexes, we were very interested in this type of complexes. We have previously shown that cationic carbyne complex **1** reacted with (μ-thiolato)(μ-phenylthio)hexacarbonyldiiron, [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$] [70], prepared by reductive cleavage of S–S bond of [(μ-S)$_2Fe_2(CO)_6$] with PhLi, in THF at low temperature (−100 to −75 °C) to produce a novel iron–sulfur cluster carbene–manganese complex [η^5-$C_5H_5(CO)_2$Mn=C(Ph)(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**89**) (Eq. (52)) in 32% yield, whose structure has been established by X-ray crystallography [71].

Complex **2** reacts similarly with [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$] under the same conditions to give the iron–sulfur cluster carbene–rhenium complex [η^5-$C_5H_5(CO)_2$–Re=C(Ph)(μ-S)$_2Fe_2(CO)_6$] (**90**) (Eq. (52)) in the same yield [72]. Its structure was established by X-ray diffraction study [72].

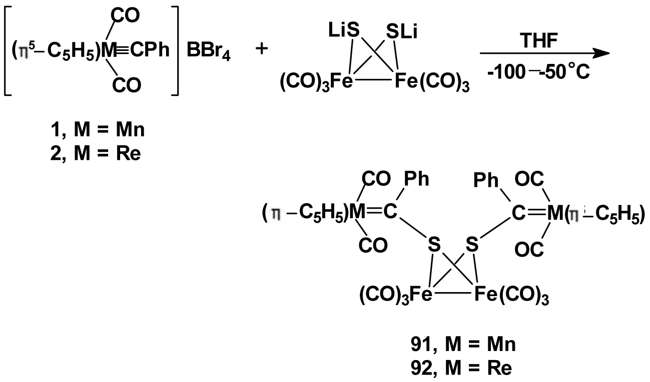
Complexes **1** and **2** also react with [(μ-SLi)$_2Fe_2(CO)_6$], prepared by the reaction [73] of [(μ-S)$_2Fe_2(CO)_6$] with $LiBEt_3H$, under the same conditions to yield iron–sulfur cluster dicarbene complexes [{η^5-$C_5H_5(CO)_2$Mn=C(Ph)}$_2$(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**91**) and [{η^5-$C_5H_5(CO)_2$Re=C(Ph)}$_2$(μ-S)$_2Fe_2(CO)_6$] (**92**) (Eq. (53)) [71] in 23 and 26% yield, respectively.



1, M = Mn
2, M = Re

89, M = Mn
90, M = Re

(52)

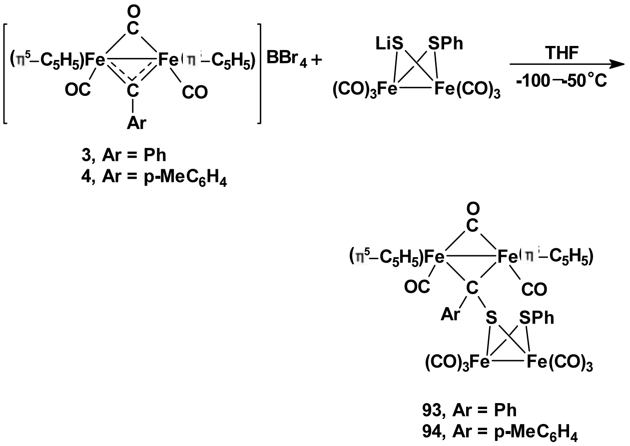


1, M = Mn
2, M = Re

91, M = Mn
92, M = Re

(53)

Like complexes **1** and **2**, the cationic carbyne complex **3** and **4** can also react with [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$] under similar conditions to give the diiron iron–sulfur cluster bridging carbene complexes [Fe_2(μ-CO)(μ-CPh)$(CO)_2$(η^5-$C_5H_5)_2$(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**93**) and [Fe_2(μ-CO)(μ-CC_6H_4Me-*p*)$(CO)_2$(η^5-$C_5H_5)_2$(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**94**) (Eq. (54)) [14] in higher yields (68 and 72%), respectively.

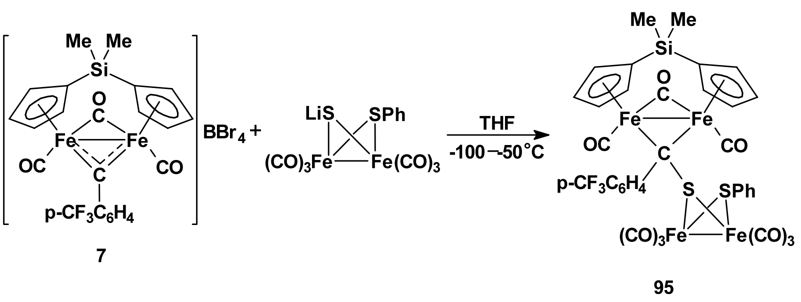


3, Ar = Ph
4, Ar = p-MeC₆H₄

93, Ar = Ph
94, Ar = p-MeC₆H₄

(54)

Analogous iron–sulfur cluster bridging carbene complex [Fe_2(μ-CO)(μ-$CC_6H_4CF_3$-*p*)$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**95**) was obtained in 68% yield by the reaction of cationic bridging carbyne complex **7** with [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$] (Eq. (55)) [14].



(55)

The diiron cationic carbyne complexes **5** and **6**, in which the aryl-substituents at the μ-carbyne carbon are a phenyl and a *p*-tolyl group respectively, do not give analogous iron–sulfur cluster bridging carbene complexes upon reaction with [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$] under the same conditions. Only decomposition to an uncharacterized mixture occurs, which can not be separated by column chromatography or by recrystallization. The lack of reactivity of complexes **5** and **6** suggests that the different cyclopentadienyl ligands and aryl-substituents at bridging carbyne carbon exert a great influence on the reactivity of the diiron cationic bridging carbyne complexes. In the case of **7**, the electron-withdrawing *p*-$CF_3C_6H_4$ group increased the electrophilic reactivity of the bridging carbyne carbon owing to its strong electron-withdrawing action, which promotes the nucleophilic attack of the [(μ-S)(μ-SPh)$Fe_2(CO)_6$]$^-$ anion on the μ-carbyne carbon of **7**, resulting in the formation of iron–sulfur cluster bridging carbene complex **95**.

The formulas shown in Eqs. (54) and (55) for complexes **93**–**95** were based on the elemental analysis and IR, ^{1}H-NMR, and mass spectroscopy, as well as X-ray crystallography. The IR spectra of **93**–**95** in the ν(CO) region showed a absorption band at ca. 1810 cm^{-1} attributed to the bridging CO ligand, in addition to four terminal CO bands at 2062–1974 cm^{-1}, which signifies an Fe_2(μ-CO)$(CO)_2$ and $Fe_2(CO)_6$ moieties in these complexes.

The structure (Fig. 36) of **95**, which has been established by X-ray diffraction analysis, showed that it is a derivative of (μ-S)$_2Fe_2(CO)_6$ in which the bridging carbene carbon is bonded by a (μ-S)(μ-SPh)$Fe_2(CO)_6$ moiety. The average Fe-μ-C distance of 2.047 Å is slightly longer than that (2.020–2.022 Å) in mercaptocarbene complexes **80** and **84**. The μ-C–S(1) bond length of 1.847(12) Å in **95** is significantly longer than that in analogous iron–sulfur cluster carbene complex **90** (1.70(2) Å) [72] and slightly longer than that in **80** and **84** (1.80(1)–1.81(1) Å). Except for [Fe_2(μ-CO)(μ-$CC_6H_4CF_3$-*p*)$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}] unit, the structure of (μ-S)(μ-SPh)$Fe_2(CO)_6$ portion of **95** is nearly the same as that in analogous complexes **90** and [(PhS)$Fe_2(CO)_6$S–S$(CO)_6Fe_2$(SPh)] [74], as illustrated by the following parameters (the value for **95** is following by the same parameters for **90** and [(PhS)$Fe_2(CO)_6$S–S$(CO)_6Fe_2$(SPh)]): Fe–Fe (2.531(3), 2.523(4), 2.523(av) Å), average Fe–S (2.269, 2.260, 2.261 Å, average Fe–S–Fe (67.83, 67.45, 68.25°). The distance of the S atom to the phenyl (S(2)–C(26) 1.780(11) Å) in **95** is somewhat shorter than that in **90** (S(2)–C(13) 1.82(2) Å) [72]. In fact, the structural features of [Fe_2(μ-CO)(μ-$CC_6H_4CF_3$-*p*)$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}] unit of **95** are very similar to those of the same unit in complexes **80**, **84**, and [Fe_2(μ-CO){μ-C(OEt)Ph}$(CO)_2${(η^5-$C_5H_4)_2SiMe_2$}].

By contrast to [(μ-SLi)(μ-SPh)$Fe_2(CO)_6$], the [(μ-SLi)$_2Fe_2(CO)_6$] reacted with complexes **3** and **4** under the same conditions to give not the expected dinuclear diiron iron–sulfur cluster bridging carbene complexes but rather the bridging arylcarbene complexes [Fe_2(μ-CO){μ-C(H)Ph}$(CO)_2$(η^5-$C_5H_5)_2$] (**96**) and [Fe_2(μ-

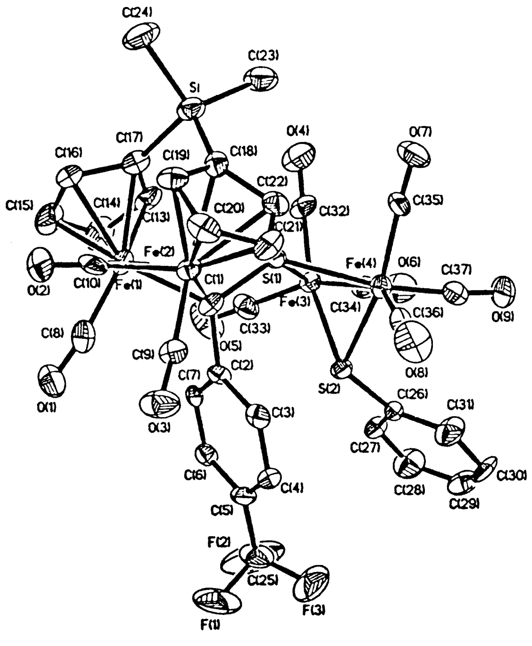
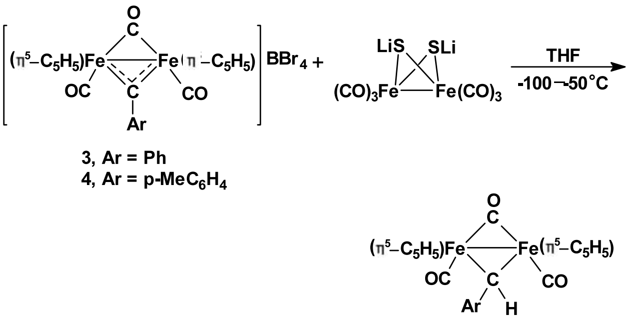


Fig. 36. Molecular structure of **95**.

CO){μ-C(H)C_6H_4Me-*p*}$(CO)_2(\eta^5\text{-}C_5H_5)_2$] (**97**) (Eq. (56)) [75] in lower yields (27 and 30%), respectively.



3, Ar = Ph
4, Ar = p-MeC_6H_4

96, Ar = Ph
97, Ar = p-MeC_6H_4

(56)

Products **96** and **97** are known compounds from the reactions [13] of complexes **3** and **4** with reactive [Et_3NH][(μ-CO)(μ-SR)$Fe_2(CO)_6$] (R = Ph, *p*-MeC_6H_4) salts or $Na_2[M(CO)_n]$ (M = W, *n* = 5; M = Fe, *n* = 4), respectively, and have been characterized by X-ray crystallography (Section 9).

Analogous bridging arylcarbene complex [Fe_2(μ-CO){μ-C(H)$C_6H_4CF_3$-*p*}$(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}$(μ-S)(μ-SPh)$Fe_2(CO)_6$] (**98**) in 46% yield was also obtained from the reaction of **7** with [(μ-SLi)$_2Fe_2(CO)_6$] (Eq. (57)), whose structure was characterized by its single-crystal X-ray diffraction analysis [75].

9. Reactions of [Fe_2(μ-CO)(μ-CAr)$(CO)_2(\eta^5\text{-}C_5H_5)_2$]$BBr_4$ with the reactive salts [Et_3NH][Fe_2(μ-CO)(μ-SR)$(CO)_6$]

The ability of complexes **3** and **4** to form complexes [Fe_2(μ-CO){μ-C(L)Ar}$(CO)_2(\eta^5\text{-}C_5H_5)_2$] (L = SR, OPh, $N(SiMe_3)_2$, (μ-S)(μ-SPh)$Fe_2(CO)_6$) suggests that it could also react with [Et_3NH][Fe_2(μ-CO)(μ-SR)$(CO)_6$] to yield either tri- or tetrametal bridging carbene and carbyne complexes or adducts which might then undergo Fe–S and Fe–Fe bond cleavage of the [Fe_2(μ-CO)(μ-SR)$(CO)_6$]$^-$ anion to give new types of complexes. Indeed, complexes **3** and **4** react with [Et_3NH][(μ-CO)(μ-SBu^n)$Fe_2(CO)_6$] in THF at −80 to −40 °C for 5–6 h to give the diiron bridging mercaptocarbene complex [Fe_2(μ-CO){μ-C(SH)Ph}$(CO)_2(\eta^5\text{-}C_5H_5)_2$] (**99**) (Eq. (58)) and bridging butylthiocarbene complex [Fe_2(μ-CO){μ-C(SBu^n)C_6H_4Me-*p*}$(CO)_2(\eta^5\text{-}C_5H_5)_2$] (**100**) (Eq. (58)) [13] in 56 and 66% isolated yield, respectively.

The structure of complex **99** shown in Eq. (58) was established by X-ray diffraction [13], which yield an *R* value of only 0.19 due to substantial decomposition. However, the elemental analysis and IR, ^{1}H-NMR, and mass spectra are consistent with this geometry. The IR spectrum in the *ν*(CO) region of **99** showed an absorption band at 1772 cm^{-1} from a bridging or semibridging carbonyl ligand, in addition to the two terminal CO absorption bands at 1972 and 1932 cm^{-1}, indicative of an Fe_2(μ-CO)$(CO)_2$ moiety. The features in the ^{1}H-NMR spectrum of **99** also support a SH group showing a signal at 5.68 ppm, which could be assigned to the proton of the mercapto group (SH). The SH occurred downfield shift might arise from the bonding of the SH group to the highly positive μ-carbene carbon. The mass spectrum of **99** provided further structural information, showing the parent ion and fragment ions generated by loss of CO and SH ligands. The formation of **99** is surprising since no analogous desulfurization has been observed in reactions of the reactive salts.

The structure of **100** by X-ray determined (Fig. 37) is nearly identical with that of **72** and **73**, as illustrated by the following parameters: the Fe–Fe distance (2.530(3) Å), the Fe-μ-$C_{carbene}$ bond distances, Fe(1)–C(1) (1.997(7) Å) and Fe(2)–C(1) (1.991(7) Å), and the C(1)–S bond length (1.82(1) Å) are essentially the same within experimental error as those in **72** and **73**.

It is not known how the SH group is formed and how it becomes bonded to the μ-carbene carbon during the reaction. Presumably, the formation of **99** occurred via an [$Fe(CO)_4(SH)$]$^-$ anion derived from cleavage of the reactive salt, a process involving the breaking of Fe–S and R–S bonds. The anion might then attack the μ-carbyne carbon of **3** to produce an unstable bridging carbene intermediate [Fe_2(μ-CO){μ-CFe$(CO)_4$(SH)-Ph}$(CO)_2(\eta^5\text{-}C_5H_5)_2$], in which the $Fe(CO)_4$(SH) moiety is directly bonded to the μ-carbene carbon through the Fe atom. The carbene intermediate would then undergo a SH group migration from Fe to the μ-carbene carbon accompanied by loss of an $Fe(CO)_4$ moiety to afford

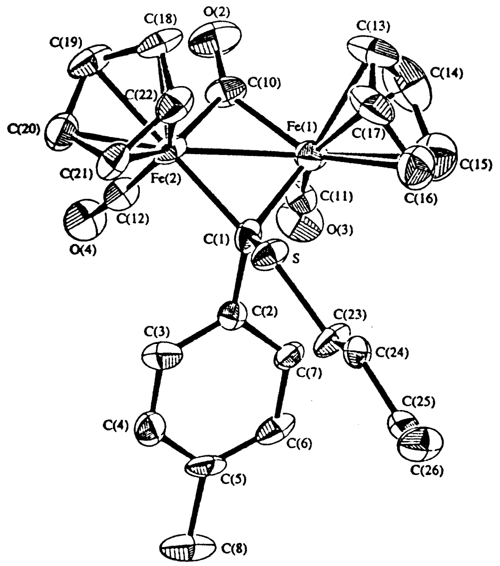


Fig. 37. Molecular structure of **100**.

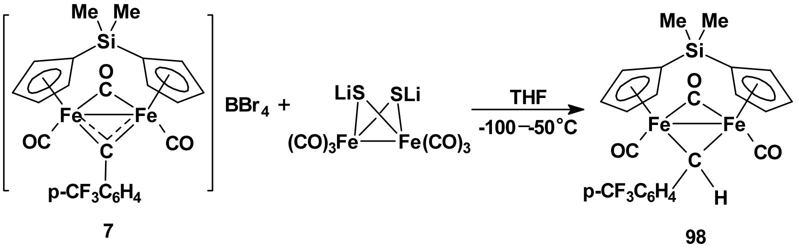
product **99**. A possible alternative formation pathway might involve loss of the $Fe(CO)_4$ moiety from the $[Fe(CO)_4(SH)]^-$ anion to generate an HS^- species, which then attacks the μ-carbyne carbon of **3** to yield product **99**. The origin of the H atom in the SH group could be solvent THF (see below). Such breaking of Fe–S and R–S bonds in the reactions of the reactive $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SR)Fe_2(CO)_6]$ salts was observed for the first time.

Although it is not known how complex **100** forms in the reaction (58), one can imagine that the Fe–S bond cleavage of the reactive salt to generate a Bu^nS^- species, which then becomes bonded to the μ-carbene carbon would lead to product **100**. Such a process appears to have occurred in the reactions of cationic carbyne complexes **1** and **2** with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ to produce phenylcarbene complexes **46** and **47** (Eq. (33))

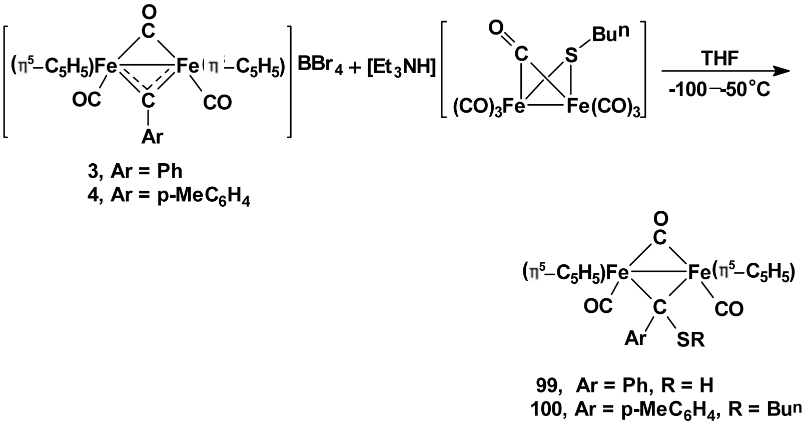
To examine the effect of different SR substituents on reactivity of the reactive salts and reaction products, $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ was used for reaction with **3** under the same conditions. Unlike $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SBu^n)Fe_2(CO)_6]$, the reactive salt $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ did not undergo cleavage to generate a HS^- or PhS^- species, and the formation of bridging mercaptocarbene complex **99** or bridging phenylthiocarbene complex **73** was not observed. Instead, a known thiolato-bridged iron carbonyl compound **43** and a bridging phenylcarbene complex **96** (Eq. (59)) [13] were isolated in 11 and 68% yield, respectively. The analogous reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SPh)Fe_2(CO)_6]$ with **4** gave **43** and bridging *p*-tolylcarbene complex **97** (Eq. (59)) [13] in 8 and 56% isolated yield, respectively.

Analogous thiolato-bridged iron carbonyl compound **44** and bridging phenyl–carbene complex **96** were also obtained in 10 and 51% yield, respectively, from the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SC_6H_4Me\text{-}p)Fe_2(CO)_6]$ with **3** (Eq.(59)) [13].

Complexes **96** and **97**, which were also obtained from the respective reaction of **3** and **4** with $[(\mu\text{-}SLi)_2Fe_2(CO)_6]$ (Eq.(56)), were formulated as arylcarbene complexes based on their microanalystical and spectroscopic data, as well as the X-ray crystallography of **96**. Their ^{1}H-NMR spectra had a resonance at δ 12.38 and 12.40, respectively, characteristic for a μ-CHR group.



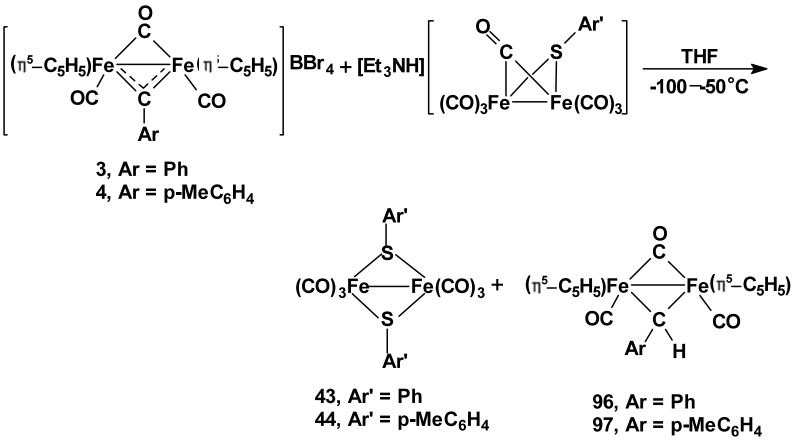
(57)



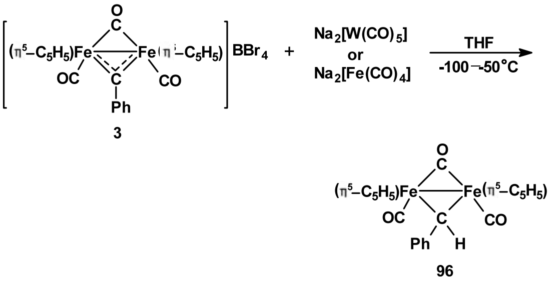
(58)

The X-ray structure (Fig. 38) of **96** is very similar to that of **72**, **73** and **100** except that the SR group in **72**, **73**, and **100** is replaced by a H atom in **96**. Many structural features of **96** are the same as those in **72** (or **73** and **100**). An apparent difference in the structures of **72** (or **73** and **100**) and **96** is the shorter C(1)–C(2) bond in **96** (1.463(9) Å), which in intermediate between C–C single and C=C double bond distances, as compared with **72** (1.54(1)) (or **73** (1.50(1)) and **100** (1.52(2) Å)).

By what pathway complexes **96** and **97** form in reaction (59) that is not known. It seems that no initial PhS^- or p-$MeC_6H_4S^-$ species formed since no bridging mercaptocarbene complex was obtained in the reaction. The reaction of $Na_2[W(CO)_5]$ or $Na_2[Fe(CO)_4]$ with **3** (Eq. (60)) under the same conditions also yielded **96** in high yield (82–85%) [13].



(59)



(60)

These reactions possibly could involve the formation of $[MH(CO)_n]^-$ ($M = W$, $n = 5$ or $M = Fe$, $n = 4$) anion via protonation of $[M(CO)_n]^{2-}$. Hydride transfer from the $[MH(CO)_n]^-$ anion to the μ-carbyne carbon of **3** could produce the bridging arylcarbene complex **96**. Indeed, the attack of $[MH(CO)_5]^-$ ($M = Cr$ or W) species on unsaturated $M{\equiv}C_{carbyne}$ bond has been documented [3a].

Since $Na_2[W(CO)_5]$ and $Na_2[Fe(CO)_4]$ cannot provide a hydride for the formation of **96**, the only other source of the H^- in this reaction is the THF solvent. It is not excluded that the source of the H^- could be water, which is a trace contaminant in THF or from glassware. It is certain that complexes **96** and **97** were not formed directly from reaction of cationic **3** or **4** with THF solvent in reaction (60) because no product **96** or **97** was isolated in the absence of the reactive salt, suggesting that the carbonylmetal anions $[(\mu\text{-}CO)(\mu\text{-}SAr')Fe_2(CO)_6]^-$ or $[W(CO)_5]^{2-}$ and $[Fe(CO)_4]^{2-}$ are necessary; they probably promote the reaction by forming a metal hydride species.

Unlike the reaction of complexes **3** and **4** with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SBu^n)Fe_2(CO)_6]$ to give bridging mercaptocarbene or bridging butylthiocarbene complex, the reactions of cationic carbyne complexes **5**–**7** with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SBu^n)Fe_2(CO)_6]$ gave only arylcarbene complexes in high yields [75]. The further investigation of such reactions is underway.

10. Reactions of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ and with $Na[M(CO)_nCN]$ (M = Cr, Mo, W, Fe; $n = 4, 5$)

As mentioned in Section 6, cationic carbyne complexes **1** and **2** reacted with CN-substituted carbonylmetal anionic compounds $Na[W(CO)_5CN]$ and $Na[Fe(CO)_4CN]$ to give cyanometal carbene complexes. This suggests that the highly electrophilic diiron bridging carbyne complexes should be highly reactive

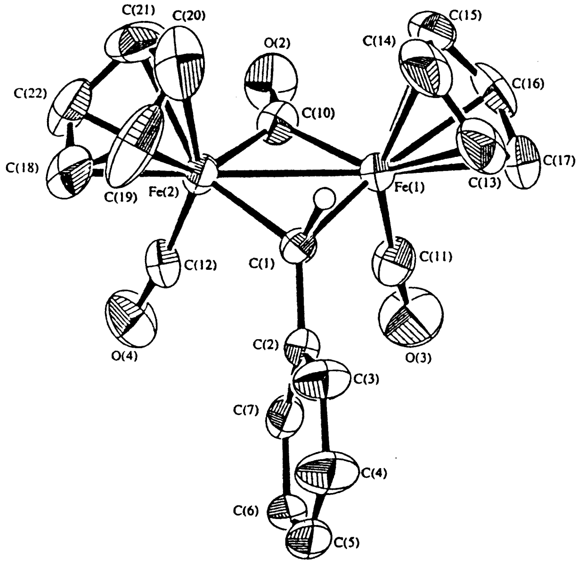
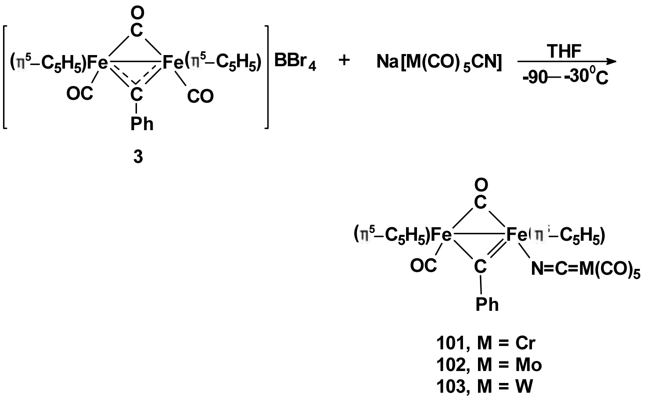


Fig. 38. Molecular structure of **96**.

toward such CN-substituted carbonyl-metal anions, which is indeed the case. When cationic carbyne complex **3** reacts with about 10–15% molar excess of the anionic carbonylmetal compounds Na[M(CO)$_5$CN] (M = Cr, Mo, W) in THF at low temperatures (−90 to −30 °C) for 4–5 h, the novel bridging carbyne complexes [Fe$_2$(μ-CO)(μ-CPh)(CO)$_2$(η^5-C$_5$H$_5$)$_2$NCM(CO)$_5$] (**101**, M = Cr; **102**, M = Mo, **103**, M = W) (Eq.(61)) [76] were obtained in 64–80% yields.



(61)

Products **101**–**103** are formulated as diiron bridging carbyne complexes with an M(CO)$_5$CN (M = Cr, Mo, W) moiety bonded to an Fe atom through the N atom of the CN group, which has been confirmed by X-ray diffraction studies of complexes **102** and **103**.

The IR spectra of **101**–**103** in ν(CO) region showed an absorption band at ca. 1771–1795 cm^{-1} attributed to the bridging CO ligand, in addition to four terminal CO bands at 2056–1926 cm^{-1}, signifying an Fe$_2$(μ-CO)$_2$(CO)$_6$ and a M(CO)$_5$ (M = Cr, Mo, W) moiety in these complexes. It is interesting to note that the ^{1}H-NMR spectra of **101**–**103** showed a multiplet resonance due to the cyclopentadienyl protons at about 5.90–4.90 ppm, instead of the normal singlet. This might arise from destruction of the C_{5v} symmetry of the Cp ring when there are different substituents on the Cp ring or that the cyclopentadienyl-coordinated metal are bonded to different ligands, which could lead to partial localization of electrons on the Cp ring [77]. In complexes **101**–**103**, the C_{5v} symmetry of the Cp ring was destroyed by bonding of the M(CO)$_5$CN ligand to the Fe(1) atom, which increased π-localization of electrons on the two Cp rings coordinated respectively to the Fe(1) and Fe(2) atoms. This would change the chemical environment of the cyclopentadienyl protons, resulting in the splitting of the singlet signal into a multiplet of cyclopentadienyl protons.

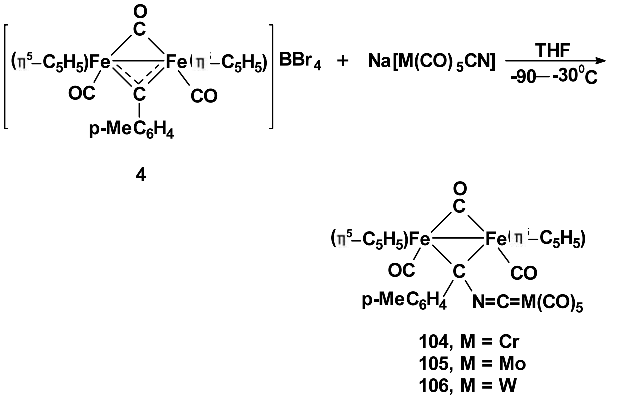
The molecular structures of **102** and **103** established by X-ray diffraction analyses are shown in Fig. 39 and Fig. 40, respectively. Both structures are nearly identical. The distances of the Fe–Fe bond bridged by the μ-CPh ligand in **102** and **103** are 2.501(2) and 2.495(3) Å, respectively, which are slightly shorter than those in bridging carbene complexes **72** (2.527(2)) and **73** (2.523(2) Å) but significantly shorter than that in diiron bridging carbyne complex [Fe$_2${μ-C(OEt)}{μ-η^4:η^3-C$_7$H$_7$C(OEt)(C$_6$H$_4$CF$_3$-*p*)}(CO)$_4$] (2.6706(7) Å) [78]. The μ-carbyne carbon asymmetrically bridges the Fe–Fe bond with C(1)–Fe(1) = 1.755(10) and C(1)–Fe(2) = 1.854(9) Å in **102**, which is more marked than that in **103** (C(1)–Fe(1) = 1.81(8) and C(1)–Fe(2) = 1.84(2) Å). The Fe(1)-μ-C(1) distances in both **102** and **103** not only are much shorter than the corresponding bond in **72** (2.03(2) and 2.00(1) Å) but also obviously shorter than the Fe=C$_{\text{carbene}}$ bond in iron carbene complex [Fe{C(OEt)C$_6$H$_4$Me-*o*}(C$_{10}$H$_{16}$)(CO)$_2$] (1.915(15) Å) [64]. These data strongly suggest that the Fe(1)-μ-C(1) linkage in **102** and **103** is a double bond, thus giving the Fe(1) atom 18 valence electrons.

The M(CO)$_5$CN (M = Mo, W) moiety attached to the Fe(1) atom in **102** and **103** has a Fe(1)–N bond length of 1.941(9) Å for **102** and 1.95(1) Å for **103**, which are ca. the same as that in [Fe$_2$(CO)$_6$(N=CHCH$_3$)$_2$] (1.942(7) Å) [79], in which the closing of the Fe$_2$N$_2$ core with the shorter Fe–N bond distance results in partial double-bond character in Fe–N bond. The shorter Fe(1)–N bond distance suggests a some double-bond character of the Fe(1)–N bond in both complexes. C(23)–N has a bond length of 1.15(1) Å for **102** and 1.11(2) Å for **103**, which indicates a high triple-bond character and is essentially the same as that in **65** (1.16(1) Å). The shorter M–C(23) distance (Mo–C(23) = 2.18(1) Å for **102**, W–C(23) = 2.20(2) Å for **103**) indicates a high double-bond character on the M–C(23) bond in both complexes. The Fe(1), N, C(23), and Mo or W atoms are coplanar with an Fe(1)–N–C(23) angle of 175.3(9)° and an N–C(23)–Mo angle of 177.5(9)° for **102** and an

Fe(1)–N–C(23) angle of 167(1)° and an N–C(23)–W angle of 169(1)° for **103**, which shows that the Fe(1)–N–C(23)–M fragment is ca. linear; thus, Fe(1), N, C(23), and Mo or W atoms form a conjugate chain. Moreover, C(1)–C(2) bond length (1.46(1) Å for **102** and 1.44(2) Å for **103**) are intermediate between C–C single and C=C double bond distances, indicating some π-bond character between the μ-C(1) atom and C(2) atom of the benzene ring in complexes **102** and **103**.

The formation of complexes **101**–**103** could involve a cationic bridging carbyne intermediate $[Fe_2(\mu\text{-}CO)(\mu\text{-}CPh)(CO)(\eta^5\text{-}C_5H_5)_2]^+$ formed by loss of a CO ligand from an Fe atom (e.g. Fe(1)) accompanied by formation of a $M(CO)_6$ (M = Cr or Mo, W) in the presence of the metalcarbonyl anion. Then the $(CO)_5M{=}C{=}N^-$ (M = Cr or Mo, W) anion (a representation of the same electronic structure of the $^-M(CO)_5CN$ anion) attacks the unsaturated Fe(1) center of the carbyne intermediate to yield products **101**–**103**. We indeed have isolated small amounts of compound $M(CO)_6$ in the course of the column chromatography. Such reactions of cationic **3** with $[M(CO)_5CN]^-$ anions giving bridging carbyne complexes are quite unusual.

Unexpectedly, complex **4** reacts with $Na[M(CO)_5CN]$ under the same conditions to give not the analogous bridging carbyne complexes but instead the novel diiron bridging *p*-tolyl(pentacarbonylcyanometal)carbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4Me\text{-}p)NCM(CO)_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**104**, M = Cr; **105**, M = Mo; **106**, M = W) (Eq. (62)) [76] in 57–76% isolated yields.



(62)

The C, H elemental analysis and the principal fragment ions in mass spectra of complexes **104**–**106** indicate the same composition as that of **101**–**103**, but the IR and ^{1}H-NMR spectra of **104**–**106** are different from those of **101**–**103**. The IR spectra of **104**–**106** in the ν(CO) region showed four to six CO absorption bands at 2057–1772 cm^{-1}, similar to **101**–**103**, whereas the characteristic ν(CN) stretching vibration occurs at 2059–2051 cm^{-1} for **101**–**103** but at 2127–2125 cm^{-1} for **104**–**106**, shifting to high vibration frequency by about 70 cm^{-1}. This may be due to the coordination of the $M(CO)_5CN$ (M = Cr, Mo, W) moiety to the Fe(1) atom through a CN group leading to a weakening of the C–N bond to a greater extent in **101**–**103**, as compared with that of **104**–**106**, in which the $M(CO)_5CN$ moiety is bonded to the μ-carbene carbon through the CN group. The ^{1}H-NMR spectra of **101**–**103** showed five to seven sets of proton signals attributed to the cyclopentadienyl protons at 5.90–4.90 ppm, while complexes **104**–**106** showed only a singlet cyclopentadienyl proton signal at ca. 5.81 ppm since the $M(CO)_5CN$ moiety is linked to the Fe atom in **101**–**103** but to the μ-carbene carbon in

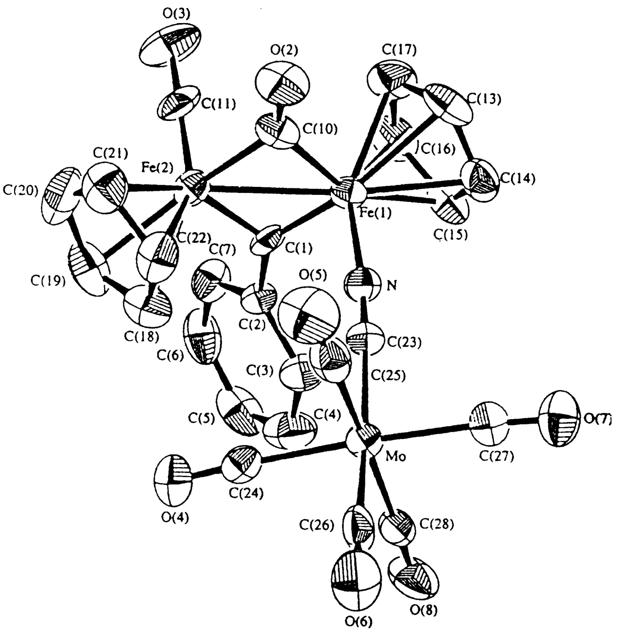


Fig. 39. Molecular structure of **102**.

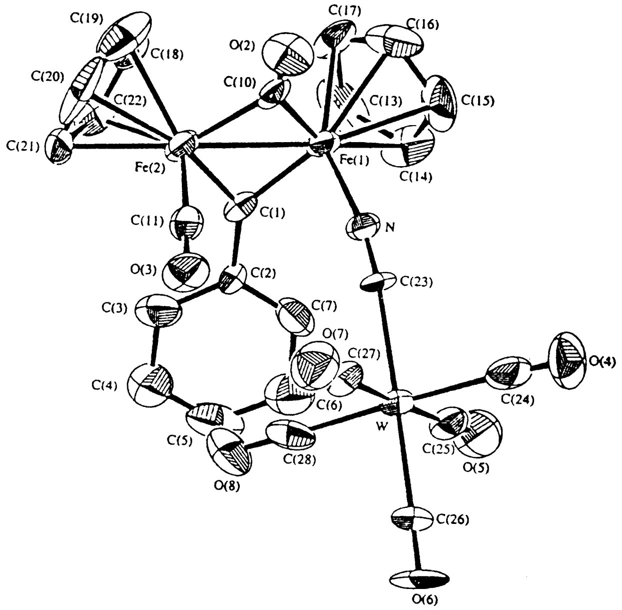


Fig. 40. Molecular structure of **103**.

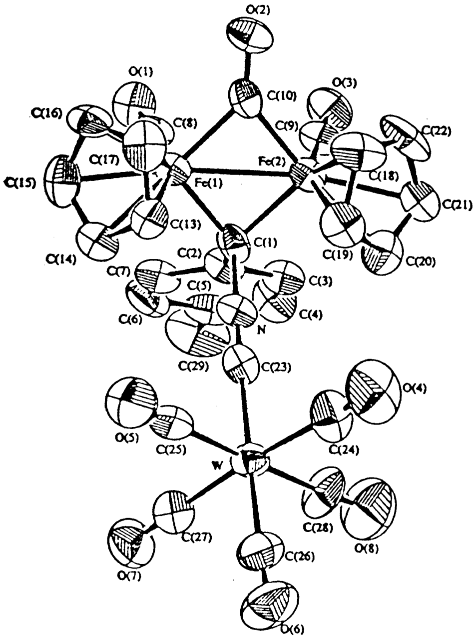


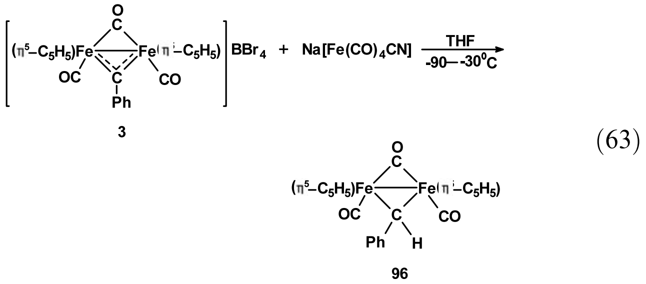
Fig. 41. Molecular structure of **106**.

the latter. In complexes **104**–**106**, the C_{5v} symmetry of the Cp ring has not been destroyed. This suggests that the structures of **104**–**106** are quite different from those of **101**–**103**, a fact that is further confirmed by an X-ray diffraction study of **106**.

The structure (Fig. 41) of the principal portion of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]$ in **106** is very similar to that in **102** and **103**. An apparent difference in structures of **102** (or **103**) and **106** is the longer Fe-μ-C(1) bonds (Fe(1)–C(1) = 1.98(2), Fe(2)–C(1) = 1.99(2) Å) and the longer C(1)–C(2) bond (1.53(2) Å) in **106**, as compared with **102** and **103**. The structural features of the $(CO)_5W{=}C{=}N$ portion of **106** are very similar to those in **65**. The C(1), N, C(23), and W atoms are coplanar and form a conjugate chain.

The reaction pathway to complexes **104**–**106** could proceed via attack of the $(CO)_5M{=}C{=}N^-$ (M = Cr, Mo, W) anion on the μ-carbyne carbon of **4**. In the reaction of **4** (Eq. (62)), no analogous cationic carbyne intermediate $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]^+$ would be formed as in the case of **3** owing to the electron-pushing action of the *p*-tolyl group, which could provide partial charge for the μ-carbyne carbon to stabilize cationic **4**. Thus, the $(CO)_5M{=}C{=}N^-$ anion directly attacks the μ-carbyne carbon of **4** to produce products **104**–**106**.

In contrast to the reactions of CN-substituted Cr, Mo, and W anionic compounds, the reaction of $Na[Fe(CO)_4CN]$ with **3** under the same conditions gave a 54% yield of bridging phenylcarbene complex **96** (Eq. (63)) [76], instead of the expected bridging carbyne complex. This suggests that the metal atom in the CN-substituted carbonylmetal anionic compound is important; the Cr, Mo, and W atoms probably promote the reaction by forming a stable $(CO)_5M{=}C{=}NFe$ (M = Cr, Mo, W) core. The formation of product **96** in the reaction (63) is unexpected, and we do not know the chemistry involved.



(63)

Further investigation of reactivity of diiron cationic carbyne complexes **3**–**4** and **5**–**7** with metalcarbonyl anions will be published [75].

11. Concluding comments

The cationic carbyne complexes of manganese, rhenium, and diiron exhibit a remarkable range of reactivity. Fortunately, the products of these reactions often formed crystals at low temperature that could be characterized by X-ray diffraction studies. The cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CPh]BBr_4$ (**1**) and $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CPh]BBr_4$ (**2**), undergo nucleophilic attack by variety of carbonylmetal mono- and dianions, and mixed-dimetal carbonyl anions, as well as other reactive anions to produce a series of novel di- or trimetal bridging carbene and/or bridging carbyne complexes. This offers a new, convenient and useful method for synthesis of such complexes. The cationic carbyne complexes, **1** and **2**, also react with metalcarbonyl anions containing negative substituents such as NO, NCO, SCN, and CN groups. Of particular interest are the reactions with CN-substituted metalcarbonyl anions that yield novel carbonylcyanometal mono- or dicarbene complexes, which are related to metal cyanide complexes.

The cationic bridging carbyne complexes of diiron, $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}]BBr_4$ also readily undergo nucleophilic attack by a variety of non-metal- and metal-containing nucleophiles to afford a wide range of diiron bridging carbene and bridging carbyne complexes. Undoubtedly, this represents a new and useful approach to the preparation and structural modification of dimetal bridging carbene and bridging carbyne complexes.

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