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Unusual reactions of cationic carbyne complexes of manganese and rhenium with [NMe_4][$HFe(CO)_4$] to form heteronuclear dimetal carbene-bridged complexes

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The reaction of a cationic carbyne complex of manganese [Mn(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **1** with the salt [NMe_4][$HFe(CO)_4$] **3** in thf at low temperature gave [Mn(η-C_5H_5)$(CO)_3$] **4** and a novel dimetal carbene-bridged complex [MnFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_5$] **5**. The cationic rhenium carbyne complex [Re(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **2** similarly reacted with **3** to give [Re(η-C_5H_5)$(CO)_3$] **6** and [ReFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_6$] **7**. Complex **5** reacted with carbon monoxide gas leading to cleavage of the μ-C–Mn and Mn–Fe bonds to afford **4** and a novel benzene-co-ordinated acyltricarbonyliron complex [Fe(PhCHCO)$(CO)_3$] **8**. The reaction of **7** with PPh_3 yielded [ReFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_5$(PPh_3)] **9**. The structures of complexes **5**, **8** and **9** have been established by X-ray diffraction studies.

Our interest in the synthesis, structure, and chemistry of di- and tri-metal carbene- and carbyne-bridged complexes stems from the possible involvement of these species in some reactions catalysed by organometallic compounds.[1,2] The chemistry of the carbene- and carbyne-bridged complexes has been extensively studied by Stone and co-workers and a number of dimetal carbene-bridged complexes has been synthesized by the reactions of carbene complexes with low-valent metal species[3,4] or of neutral carbyne complexes with metal hydrides.[5,6] Recently, we reported the reaction of a cationic carbyne complex [M(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 (M = Re or Mn) with $[Fe(CO)_4]^{2-}$ to yield unexpected dimetal carbene-bridged complexes.[7,8] This represents a new route to such complexes. We are now interested in examining the application range of this new synthetic method for dimetal carbene-bridged complexes and the effect of different nucleophiles containing the carbonyliron anion on the reactivities of cationic carbyne complexes and on the reaction products. Thus, we chose the monoanion $[HFe(CO)_4]^-$ **3** as a nucleophile for the reaction with the cationic carbyne complexes [M(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 (M = Mn **1** or Re **2**) which afforded new heteronuclear dimetal carbene-bridged complexes. Herein we describe this unusual reaction and the structures of the resulting products.

Experimental

All reactions were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under a nitrogen atmosphere. Tetrahydrofuran (thf) and diethyl ether (Et_2O) were distilled from sodium–benzophenone, while light petroleum (b.p. 30–60 °C) was distilled from CaH_2 and CH_2Cl_2 from P_2O_5. The neutral alumina (Al_2O_3) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. The compounds [Mn(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **1**[9] and [Re(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **2**[10] were prepared as previously described, as was [NMe_4][$HFe(CO)_4$] **3**.[11]

The IR spectra were recorded on a Shimadzu-IR-440 spectrophotometer, ^1H NMR spectra at ambient temperature (20 °C) in $(CD_3)_2CO$ solution with $SiMe_4$ as internal reference using a Bruker AM-300 spectrometer and electron ionization (EI) mass spectra on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Reaction of [Mn(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 1 with [NMe_4][$HFe(CO)_4$] 3 to give [Mn(η-C_5H_5)$(CO)_3$] 4 and [MnFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_5$] 5

The compound [NMe_4][$HFe(CO)_4$] **3** (0.64 g, 2.63 mmol) was dissolved in thf (80 cm^3) and cooled to −90 °C. To this solution was added portionwise **1** (1.57 g, 2.63 mmol) with vigorous stirring. The reaction mixture was stirred at −90 to −45 °C for 4 h, during which time the orange solution gradually turned dark purple-red. The resulting solution was evaporated to dryness under high vacuum at −45 to −40 °C. The dark purple-red residue was chromatographed on an alumina column (neutral, 200–300 mesh; 1.6 × 15 cm) at −25 °C with light petroleum as the eluent. The orange band which eluted first was collected, and then the purple-red band was eluted with light petroleum–CH_2Cl_2 (20 : 1). The solvents were removed from the above two eluates under vacuum, and the residues recrystallized from light petroleum or light petroleum–CH_2Cl_2 solution at −80 °C. From the first fraction, 0.15 g (25%, based on **1**) of yellow crystals of **4**[12] was obtained, a known compound identified by comparison of its melting point, IR and ^1H NMR spectra with those of the actual sample. From the second fraction, 0.68 g (63%, based on **1**) of **5** as purple-red crystals was obtained, m.p. 142–144 °C (decomp.) IR (*n*-hexane): ṽ(CO) 2002s, 2000s, 1995s, 1952vs (br) and 1918s cm^{-1}. ^1H NMR (CD_3COCD_3): δ 10.26 (s, 1 H, μ-CH), 7.34–7.13 (m, 5 H, C_6H_5) and 5.11 (s, 5 H, C_5H_5). Mass spectrum *m*/*z* 406 (M^+) and 322 ($M^+ - 3CO$) (Found: C, 49.60; H, 2.55. Calc. for $C_{17}H_{11}FeMnO_5$: C, 50.03; H, 2.73%).

Reaction of [Re(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 2 with [NMe_4][$HFe(CO)_4$] 3 to give [Re(η-C_5H_5)$(CO)_3$] 6 and [ReFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_6$] 7

Compound **2** (0.47 g, 0.65 mmol) was treated, in a manner similar to that described above, with [NMe_4][$HFe(CO)_4$] (0.16 g, 0.66 mmol). The reaction mixture was stirred at −90 to −50 °C for 3.5 h, during which time the orange-yellow solution gradually turned purple-red. Further treatment of the resulting mixture as described above afforded 0.015 g (6%, based on **2**) of yellow crystals of **6**[13] and 0.26 g (71%, based on **2**) of brick-red crystals of **7**.[7] Complex **6** was identified by comparison of its melting point, IR and ^1H NMR spectra with those of the actual sample. Complex **7**: m.p. 84–85 °C (decomp.) IR (CH_2Cl_2) $\tilde{\nu}$ 2016s, 1996vs, 1950s (br) and 1891vs (br) cm^{-1}. ^1H NMR (CD_3COCD_3) δ 9.02 (s, 1 H, μ-CH), 7.42 (m, 2 H, C_6H_5), 7.21 (m, 2 H, C_6H_5), 7.00 (m, 1 H, C_6H_5) and 5.70 (s, 5 H, C_5H_5). Mass spectrum *m*/*z* 566 (M^+, based on ^{187}Re, ^{56}Fe) (Found: C, 38.56; H, 2.15. Calc. for $C_{18}H_{11}FeO_6Re$: C, 38.24; H, 1.96%).

Reaction of complex 5 with CO to give 4 and [Fe(PhCHCO)-(CO)$_3$] 8

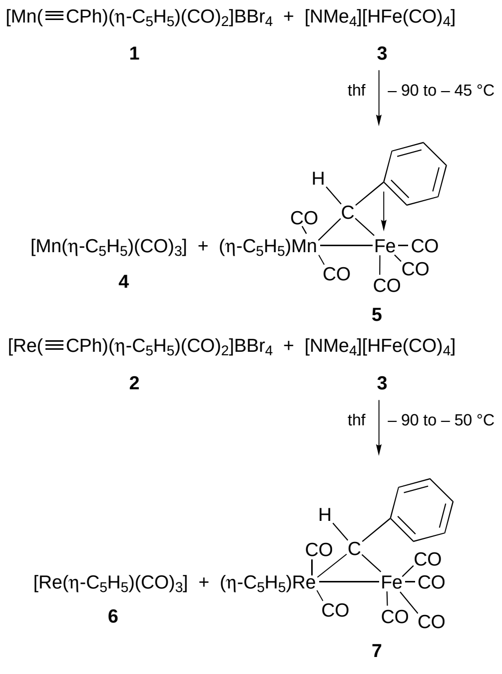
Carbon monoxide gas was bubbled through a solution of complex **5** (0.037 g, 0.09 mmol) in thf (40 cm^3) at −40 to −10 °C for 6 h, during which time the purple-red solution gradually turned brown-red. After removal of the solvent *in vacuo*, the residue was chromatographed on Al_2O_3 with light petroleum as the eluent. The orange band which eluted first was collected, and then the brown-red band was eluted with light petroleum–CH_2Cl_2–Et_2O (20 : 1 : 1). The solvents were removed from the above two eluates under vacuum, and the residues recrystallized from light petroleum or light petroleum–CH_2Cl_2 solution at −80 °C. From the first fraction, 0.006 g (31%, based on **5**) of yellow crystals of **4** was obtained. From the second, 0.011 g (46%, based on **5**) of brown-red crystals of **8** was obtained: m.p. 66–68 °C (decomp.); IR (*n*-hexane) $\tilde{\nu}$(CO) 2063s, 2004vs, 1994vs and 1788s cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.30–7.17 (m, 5 H, C_6H_5) and 6.13 (s, 1 H, CH); mass spectrum *m*/*z* 258 (M^+) and 202 (M^+ − 2CO) (Found: C, 50.85; H, 2.50. Calc. for $C_{11}H_6FeO_4$: C, 51.21; H, 2.34%).

Reaction of complex 7 with PPh$_3$ to give [ReFe{μ-C(H)Ph}-(η-C$_5$H$_5$)(CO)$_5$(PPh$_3$)] 9

To complex **7** (0.050 g, 0.09 mmol) dissolved in thf (30 cm^3) at −55 °C was added PPh_3 (0.026 g, 0.10 mmol). The mixture was stirred at −55 to 0 °C for 7 h, during which time the brown-red solution turned gradually orange-red. After evaporation of the solvent *in vacuo*, the residue was chromatographed on alumina with light petroleum followed by light petroleum–CH_2Cl_2 (10 : 1) as the eluent. After leaving the orange-red band which contains unchanged **7**, the orange band was eluted with light petroleum–CH_2Cl_2–Et_2O (5 : 1 : 1) and collected. The solvent was removed under vacuum, and the residue recrystallized from light petroleum–CH_2Cl_2 solution at −80 °C to give 0.045 g (52%, based on **7**) of orange-yellow crystals of **9**: m.p. 85–86 °C (decomp.); IR (CH_2Cl_2) $\tilde{\nu}$(CO) 2040w, 2033s, 1959vs and 1878vs cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.50 (s, 1 H, μ-CH), 7.47–7.34 (m, 15 H, C_6H_5), 6.98–6.84 (m, 5 H, C_6H_5) and 5.47 (s, 5 H, C_5H_5); mass spectrum *m*/*z* 543 (M^+ − H − PPh_3), 515 (M^+ − H − PPh_3 − CO), 431 (M^+ − H − PPh_3 − 4CO) and 403 (M^+ − H − PPh_3 − 5CO) (Found: C, 44.60; H, 2.90. Calc. for $C_{35}H_{26}FePReO_5\cdot 2CH_2Cl_2$: C, 45.10; H, 3.15%).

Crystallography

Single crystals of complexes **5**, **8** and **9** suitable for X-ray diffraction study were obtained by recrystallization from light petroleum–CH_2Cl_2 solutions at −80 °C. They were sealed in capillaries under a nitrogen atmosphere. X-Ray diffraction data were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo-Kα radiation (λ 0.710 69 Å) and the ω–2θ scan mode within the ranges $5 \leqslant 2\theta \leqslant 40°$ for **5**, $5 \leqslant 2\theta \leqslant 50°$ for **8**, and $5 \leqslant 2\theta \leqslant 45°$ for **9**, respectively. Intensity data for 1649, 1106 and 3788 independent reflections, of which 704, 864 and 2860 had $I > 2.00\sigma(I)$ (for **5**) and $I > 3.00\sigma(I)$ (for **8** and **9**), were corrected for Lorentz-polarization effects. An empirical absorption correction using the program DIFABS[14] was applied which resulted in transmission factors ranging from 0.66 to 0.97 and 0.84 to 1.17 for **5** and **9**, respectively. For **8**, an empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.96 to 1.00.



Scheme 1

The structures of complexes **5** and **9** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically for **9**, but only the Fe and Mn were anisotropic for **5**. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 704 and 2860 observed reflections and 107 and 442 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.090$ and $R' = 0.092$ for **5** and 0.049 and 0.057 for **9**, respectively. For **8** the structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined; the final cycle of full-matrix least-squares refinement was based on 864 observed reflections and 145 variables and converged with $R = 0.031$ and $R' = 0.035$. All the calculations were performed using the TEXSAN software package.[15]

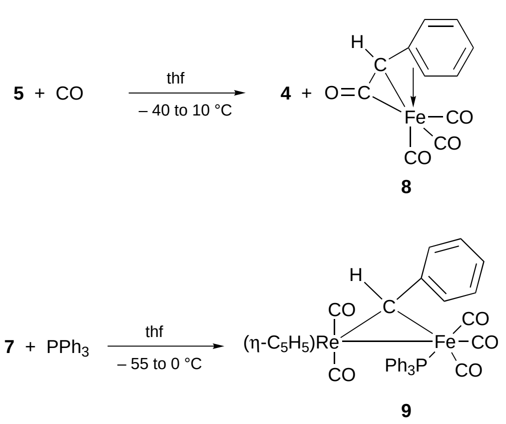
Details of the crystallographic data and the procedures used for data collection and reduction are given in Table 1, selected bond lengths and angles in Tables 2 and 3, respectively.

CCDC reference number 186/861.

Results and Discussion

The complex [Mn(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **1** was treated with an equimolecular amount of [NMe_4][$HFe(CO)_4$] **3** in thf at −90 to −45 °C for 4 h. After removal of the solvent under high vacuum, the residue was chromatographed on an alumina column at low temperature and the crude products were recrystallized from light petroleum–CH_2Cl_2 at −80 °C to give yellow crystals of **4** and purple-red crystals of **5** (Scheme 1) in 25 and 63% isolated yields, respectively. Complex **4** is a known compound [Mn(η-C_5H_5)$(CO)_3$][12] and **5** is a novel heteronuclear dimetal carbene-bridged complex with the composition [MnFe{μ-C(H)Ph}(η-C_5H_5)] the structure of which has been confirmed by X-ray crystallography.

The complex [Re(≡CPh)(η-C_5H_5)$(CO)_2$]BBr_4 **2** reacted similarly under the same conditions to afford yellow crystals of **6** and the brick-red crystals of **7** in 6 and 71% yields, respectively. Complexes **6** and **7** are known compounds, the former is [Re(η-C_5H_5)$(CO)_3$][13] and the latter, a dimetal carbene-bridged



Scheme 2

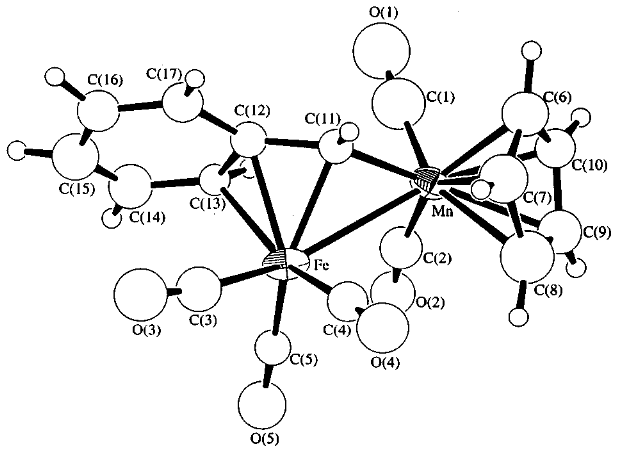


Fig. 1 Molecular structure and atom labelling for $[MnFe\{\mu\text{-}C(H)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$ **5**

complex, is identical with that produced by the reaction[7] of **2** with $[NEt_4]_2[Fe_2(CO)_8]$, $Na_2[Fe(CO)_4]$ or $Na_2[Fe_3(CO)_{11}]$.

Interestingly, the reaction of complex **5** 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 **5** to afford **4** and brown-red crystals of **8** (Scheme 2) in 31 and 46% yields, respectively. Compound **8** is formulated as a novel benzene-co-ordinated acyltricarbonyliron complex with the composition $[Fe(Ph_2CHCO)(CO)_3]$ the structure of which has been established by X-ray diffraction analysis. However, complex **7** did not react with carbon monoxide gas under the same conditions. When a stoichiometric amount of CO gas was used for the reaction with **5** no product **8** was isolated, indicating that an excess of CO is necessary. It is equally interesting that complex **7** when treated with PPh_3 in thf at −55 to 0 °C gave $[ReFe\{\mu\text{-}C(H)Ph\}(\eta\text{-}C_5H_5)(CO)_5(PPh_3)]$ **9**, in which a CO ligand on iron has been displaced by PPh_3, in 52% yield. Unexpectedly, the reaction of **5** with PPh_3 under the same conditions gave no analogous PPh_3-substituted complex, as in the reaction of $[PtW\{\mu\text{-}\eta^1:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(\eta\text{-}C_5H_5)(CO)_2(PEt_3)_2][BF_4]$[16] or complex **7** with PPh_3, but decomposition products such as $[Fe(CO)_3(PPh_3)_2]$.[17]

Complexes **5**, **8** and **9** are readily soluble in polar organic solvents but slightly soluble in non-polar solvents, and sensitive to air and temperature in solution but relatively stable as solids. Their structures were confirmed by elemental analyses, spectroscopic data (Experimental section) and X-ray diffraction analyses.

The molecular structure of complex **5** is shown in Fig. 1. Owing to serious intensity decay of the crystal during the data collection at room temperature (20 °C), only reflections within the range $5 \leqslant 2\theta \leqslant 40°$ were collected, so that only 668 reflections with $I > 3.00\sigma(I)$ were observable, which led to a poor refinement and larger errors for the bond parameters. However, the result undoubtedly confirms the overall structure of **5**. The molecular structure **5** shows a bridge system in which two carbon atoms[C(12) and C(13)] of the phenyl 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 attributed to the proton attached to the 'olefinic' bond was observed. We tentatively explain it 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 (20 °C) as that observed in the analogous complex $[CoW\{\mu\text{-}\eta^1:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(CO)_3][BF_4]$ which showed dynamic behaviour for the tolyl group at 25 °C, ceasing at −70 °C.[16] The Mn–Fe distance of 2.770(7) Å in **5** is somewhat longer than that found in analogous carbene-bridged complexes $[MnFe\{\mu\text{-}C(COEt)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$ [2.6929(8) Å][8] and $[ReFe\{\mu\text{-}C(H)Ph\}(\eta\text{-}C_5H_5)(CO)_6]$ [2.7581(8) Å].[7]

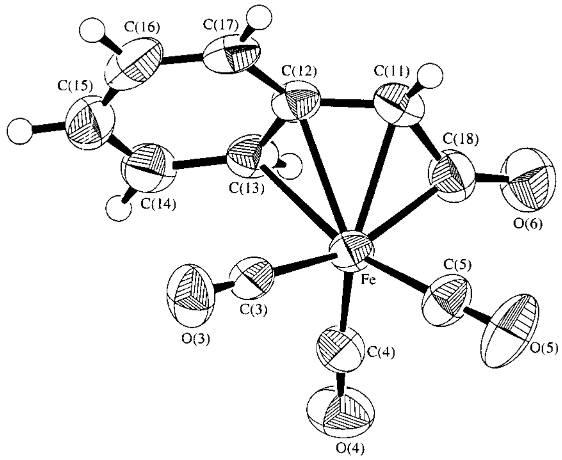


Fig. 2 Molecular structure and atom labelling for $[Fe(PhCHCO)(CO)_3]$ **8**

The molecular structure of complex **8** (Fig. 2) 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 the 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 $\mu\text{-}C(H)C_6H_4Me$ in $[PtW\{\mu\text{-}\eta^1:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(\eta\text{-}C_5H_5)(CO)_2(PMe_3)_2]BF_4$.[16] However, the ^1H NMR data for **8** at 20 °C show dynamic behaviour for the phenyl group and reveal that in solution it rotates about the C(11)–C(12) bond on the NMR timescale as in **5**.

The molecular structure of complex **9** (Fig. 3) resembles that of **7**, except that the substituents on the Fe atom are three CO and one PPh_3 groups in **9** but four CO groups in **7**. The co-ordination geometry around the Re atom is that of a pseudo-trigonal bipyramid if the (η^5)-bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex, and the Fe atom is in an approximately octahedral environment. The Re–Fe bond length of 2.777(2) Å in **9** is slightly longer than that of **7** [2.7581(8) Å].[7] 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)° similar to that in **7** [μ-C–Re 2.120(5), μ-C–Fe 2.097(5) Å; Re–C(7)–Fe 81.7(2)°]. The μ-C–Re distance in **9** is comparable with that of **7** and the complex $[Re_2(\mu\text{-}H)_2(\mu\text{-}CHBu^t)(\eta\text{-}C_6H_6)_2]$ [2.13(3) Å],[18] and the μ-C–Fe distance is close to that found in **5**. 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 $[PFe(NO)_2(CO)(PPh_3)]$,[19] 2.244(1) Å in $[Fe(CO)_4(PPh_3)]$[20]}. The P–Fe–C(7) and P–Fe–Re bond angles are 96.7(4) and 147.3(1)°, respectively.

Table 1 Crystal data and experimental details for complexes **5**, **8** and **9**

	5	**8**	**9**
Formula	$C_{17}H_{11}FeMnO_5$	$C_{11}H_6FeO_4$	$C_{37}H_{29}Cl_4FeO_5PRe$
M	406.06	258.01	969.48
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a/Å	7.326(7)	10.977(5)	11.744(3)
b/Å	17.650(8)	14.384(3)	16.132(3)
c/Å	6.809(4)	6.646(4)	10.803(3)
α/°	94.73(7)		100.32(2)
β/°	113.93(6)		110.50(2)
γ/°	87.35(7)		91.14(2)
U/Å^3	801(1)	1049.4(8)	1878.4(9)
Z	2	4	2
D_c/g cm^{-3}	1.681	1.633	1.712
μ(Mo-Kα)/cm^{-1}	17.13	14.28	39.74
Orientation reflections: 2θ range/°	12 (6.6–18.6)	16 (18.5–21.7)	23 (13.6–21.5)
No. unique data, total	1649	1106	3788
with $I > 3.00\sigma(I)$	704 [$I > 2.00\sigma(I)$]	864	2860
No. parameters refined	107	145	442
R^a	0.090	0.031	0.049
R'^b	0.092	0.035	0.057
Goodness of fit^c	2.04	1.26	1.81
Largest shift/e.s.d. in final cycle	0.07	0.00	0.19
Maximum, minimum electron density/e Å^{-3}	0.79, −0.62	0.31, −0.23	1.28, −1.63

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(|F_o|)$. [c] $[\Sigma w(|F_o| - F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, where N_o, N_p = numbers of observations and parameters.

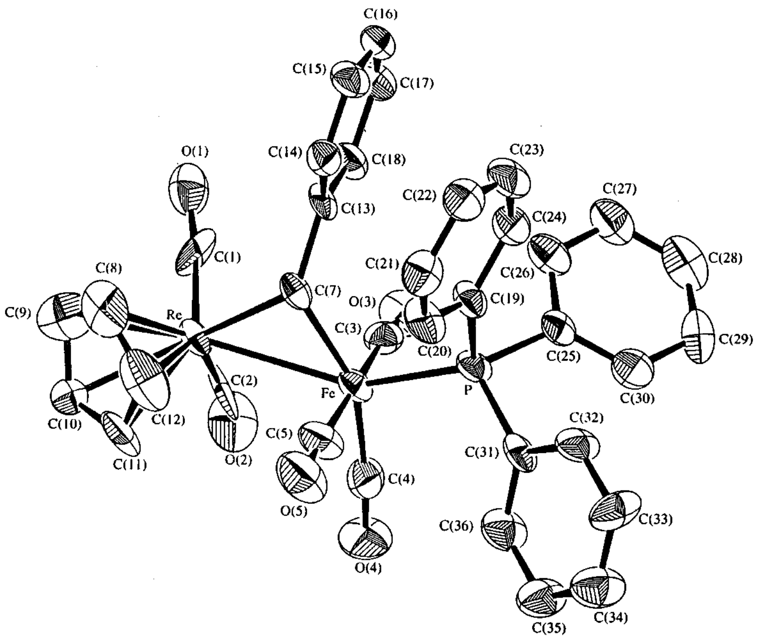


Fig. 3 Molecular structure and atom labelling for [ReFe{μ-C(H)Ph}(η-C_5H_5)$(CO)_5$$(PPh_3)$] **9**

The possible reaction pathway to complex **5** (Scheme 1) could involve initial formation of a carbene intermediate [$(OC)_2$-(η-C_5H_5)Mn=C(Ph)FeH$(CO)_4$], where the FeH$(CO)_4$ moiety is directly bonded to the carbene carbon through Fe, by attack of the $[HFe(CO)_4]^-$ anion on the cationic carbyne carbon of **1**. The carbene intermediate would then undergo a hydrogen migration from Fe to the carbene carbon and bonding of the Fe to Mn accompanied by loss of one CO ligand from the Fe$(CO)_4$ moiety and co-ordination of the benzene ring to the Fe atom. Analogous heteronuclear dimetal carbene-bridged complexes, [MW{μ-η^1:η^3-CH(C_6H_4Me-4)}(η-C_5H_5)$(CO)_2$$(L_n)$][$BF_4$] [$ML_n$ = Cr(η-C_5H_5)(CO)(NO), Co(CO)(η-C_5Me_5), or Pt$(PR_3)_2$] and [PtW{μ-η^1:η^3-CH(C_6H_4Me-4)}(η-C_5H_5)$(CO)_2$$(PEt_3)_2$]-[$BF_4$], with the co-ordination of the benzene ring to the metal, have been reported by Stone and co-workers[16,21] by protonation of dimetal carbyne-bridged complexes [CrW(μ-CC_6H_4Me-4)(η-C_5H_5)$_2$$(CO)_3$(NO)], [CoW(μ-C$C_6H_4$Me-4)(η-$C_5H_5$)(η-$C_5Me_5$)-$(CO)_3$], and [PtW(μ-C$C_6H_4$Me-4)(η-$C_5H_5$)$(CO)_2$$(PR_3)_2$] ($PR_3$ = PMe_3, PMe_2Ph, or $PMePh_2$) with HBF_4·Et_2O, or by the reaction[22] of the neutral carbyne complex [W(≡CC_6H_4Me-4)-(η-C_5H_5)$(CO)_2$] with the cationic metal hydride *trans*-[Pt(H)-$(PEt_3)_2$$(Me_2CO)$][$BF_4$].

The reaction pathway to complex **8** (Scheme 2) might proceed by an initial attack of CO on the μ-C–Mn or/and Mn–Fe bond of **5** which could then suffer heterolytic cleavage of these bonds with addition of one CO molecule to the Mn and the insertion of another CO molecule into the μ-C–Fe bond to form complexes **4** and **8**, respectively. The formation of **8** is not surprising since the analogous insertion of CO into the Fe–C (carbene) bond of an η^3-co-ordinated carbene ligand to give an (vinylketene)iron complex with an η^4-co-ordinated acyl ligand has been observed in the reaction of tricarbonyl-(η^3-vinylcarbene)iron with carbon monoxide.[23]

The heteronuclear dimetal carbene-bridged complexes **5** and

Table 2 Selected bond lengths (Å) for complexes **5**, **8** and **9**

	5	**8**		**5**	**8**
Fe–Mn	2.770(7)		Fe–C(3)	1.73(4)	1.869(6)
Fe–C(4)	1.75(4)	1.784(6)	Fe–C(5)	1.73(4)	1.772(6)
Fe–C(11)	2.05(3)	2.088(5)	Fe–C(12)	2.09(3)	2.177(5)
Fe–C(13)	2.24(3)	2.274(5)	Mn–C(1)	1.71(4)	
Fe–C(18)		1.914(6)	Mn–C(6)	2.15(4)	
Mn–C(2)	1.66(4)		Mn–C(8)	2.18(4)	
Mn–C(7)	2.16(4)		Mn–C(10)	2.05(3)	
Mn–C(9)	2.19(3)		O(1)–C(1)	1.15(4)	
Mn–C(11)	1.92(3)		O(3)–C(3)	1.14(4)	1.127(6)
O(2)–C(2)	1.26(4)		O(5)–C(5)	1.18(3)	1.136(7)
O(4)–C(4)	1.17(3)	1.148(6)	O(6)–C(18)		1.196(6)
C(12)–C(13)	1.44(4)	1.428(7)	C(11)–C(12)	1.47(4)	1.396(8)
C(13)–C(14)	1.39(4)	1.412(8)	C(12)–C(17)	1.44(4)	1.445(7)
C(15)–C(16)	1.36(4)	1.425(10)	C(14)–C(15)	1.31(4)	1.360(9)
C(16)–C(17)	1.40(4)	1.335(10)	C(11)–C(18)		1.441(8)

Complex **9**

Re–Fe	2.777(2)	Fe–C(5)	1.78(2)	Re–C(1)	1.72(2)	Fe–C(7)	2.03(1)
Re–C(2)	1.91(2)	P–C(19)	1.85(1)	Re–C(7)	2.17(1)	P–C(25)	1.84(2)
Re–C(8)	2.30(2)	P–C(31)	1.81(2)	Re–C(9)	2.23(2)	O(1)–C(1)	1.25(2)
Re–C(10)	2.31(2)	O(2)–C(2)	1.15(2)	Re–C(11)	2.32(2)	O(3)–C(3)	1.15(2)
Re–C(12)	2.33(2)	O(4)–C(4)	1.13(2)	Fe–P	2.258(4)	O(5)–C(5)	1.13(2)
Fe–C(3)	1.78(2)	C(7)–C(13)	1.54(2)	Fe–C(4)	1.81(2)		

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3 Selected bond angles (°) for complexes **5**, **8** and **9**

	5	**8**		**5**	**8**
Mn–Fe–C(3)	160(1)		Mn–Fe–C(4)	84(1)	
Mn–Fe–C(5)	107(1)		Mn–Fe–C(11)	43.9(8)	
Mn–Fe–C(12)	76.7(9)		Mn–Fe–C(13)	88.4(8)	
C(11)–Fe–C(12)	41(1)	38.2(2)	C(11)–Fe–C(13)	73(1)	67.6(2)
C(12)–Fe–C(13)	38(1)	37.4(2)	Fe–Mn–C(1)	105(1)	
Fe–Mn–C(2)	71(1)		C(1)–Mn–C(11)	80(1)	
Fe–Mn–C(11)	47.7(9)		C(2)–Mn–C(11)	110(1)	
Mn–C(2)–O(2)	168(3)		Mn–C(1)–O(1)	175(3)	
Fe–C(4)–O(4)	174(3)	175.0(5)	Fe–C(3)–O(3)	170(3)	178.9(5)
Fe–C(11)–C(12)	70(1)	74.4(3)	Fe–C(5)–O(5)	178(3)	178.5(6)
Fe–C(12)–C(11)	67(1)	67.5(3)	Fe–C(11)–Mn	88(1)	
Fe–C(12)–C(17)	124(2)	124.0(4)	Mn–C(11)–C(12)	128(2)	
C(11)–C(12)–C(17)	125(2)	122.6(5)	Fe–C(12)–C(13)	76(1)	75.0(3)
Fe–C(13)–C(12)	64(1)	67.6(3)	C(11)–C(12)–C(13)	124(2)	118.8(5)
Fe–C(11)–C(18)		62.6(3)	C(5)–Fe–C(18)		87.5(3)
Fe–C(18)–O(6)		144.9(5)	Fe–C(13)–C(14)	126(2)	121.8(4)
O(6)–C(18)–C(11)		138.3(5)	C(12)–Fe–C(18)		72.0(2)
C(13)–Fe–C(18)		81.2(2)	C(4)–Fe–C(18)		99.8(3)
C(3)–Fe–C(18)		157.4(3)	C(11)–Fe–C(18)		41.9(2)
C(12)–C(11)–C(18)		116.6(5)	Fe–C(18)–C(11)		75.5(3)

Complex **9**

Fe–Re–C(1)	108.8(6)	Fe–Re–C(2)	76.1(5)	C(25)–P–C(31)	102.1(7)	Re–C(1)–O(1)	175(1)
Fe–Re–C(7)	46.6(4)	C(1)–Re–C(7)	91.7(6)	Re–C(2)–O(2)	175(4)	Fe–C(3)–O(3)	174(1)
C(1)–Re–C(2)	83.3(8)	C(2)–Re–C(7)	117.1(6)	Fe–C(4)–O(4)	174(1)	Fe–C(5)–O(5)	176(1)
Re–Fe–P	147.3(1)	C(3)–Fe–C(4)	86.9(7)	Re–C(7)–C(13)	122.3(9)	Re–C(7)–Fe	82.7(5)
Re–Fe–C(4)	106.3(5)	C(3)–Fe–C(7)	96.7(6)	C(4)–Fe–C(7)	156.6(6)	Fe–C(7)–C(13)	125.4(9)
Re–Fe–C(7)	50.7(3)	C(4)–Fe–C(5)	88.1(8)	Fe–P–C(19)	115.5(5)	Re–Fe–C(3)	90.6(5)
P–Fe–C(7)	96.7(4)	Fe–P–C(25)	116.3(5)	Fe–P–C(31)	116.4(5)	Re–Fe–C(5)	87.1(6)
C(3)–Fe–C(5)	173.7(7)	C(19)–P–C(25)	104.0(6)	C(19)–P–C(31)	100.3(7)		

7 were synthesized by a new route. Thus, the cationic carbyne complexes of manganese and rhenium not only react with the carbonyliron dianion but also with the carbonyliron monoanion to produce dimetal carbene-bridged complexes. Moreover, the present method is a more simple and convenient route to the preparation of such complexes.

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