

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

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The reaction of a cationic carbyne complex of manganese $[\text{Mn}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **1** with the salt $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ **3** in thf at low temperature gave $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ **4** and a novel dimetal carbene-bridged complex $[\text{MnFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$ **5**. The cationic rhenium carbyne complex $[\text{Re}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **2** similarly reacted with **3** to give $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ **6** and $[\text{ReFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_6]$ **7**. Complex **5** reacted with carbon monoxide gas leading to cleavage of the $\mu\text{-C-Mn}$ and Mn-Fe bonds to afford **4** and a novel benzene-co-ordinated acyltricarbynyliron complex $[\text{Fe}(\text{PhCHCO})(\text{CO})_3]$ **8**. The reaction of **7** with PPh_3 yielded $[\text{ReFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_5(\text{PPh}_3)]$ **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 $[\text{M}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ ($\text{M} = \text{Re}$ or Mn) with $[\text{Fe}(\text{CO})_4]^{2-}$ 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 $[\text{HFe}(\text{CO})_4]^-$ **3** as a nucleophile for the reaction with the cationic carbyne complexes $[\text{M}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ ($\text{M} = \text{Mn}$ **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 $[\text{Mn}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **1**⁹ and $[\text{Re}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **2**¹⁰ were prepared as previously described, as was $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ **3**.¹¹

The IR spectra were recorded on a Shimadzu-IR-440 spectrophotometer, ¹H NMR spectra at ambient temperature (20 °C) in $(\text{CD}_3)_2\text{CO}$ 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 $[\text{Mn}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **1** with $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ **3** to give $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ **4** and $[\text{MnFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_5]$ **5**

The compound $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ **3** (0.64 g, 2.63 mmol) was dissolved in thf (80 cm³) 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): $\tilde{\nu}(\text{CO})$ 2002s, 2000s, 1995s, 1952vs (br) and 1918s cm^{–1}. ¹H NMR (CD_3COCD_3): δ 10.26 (s, 1 H, $\mu\text{-CH}$), 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 ($M^+ - 3\text{CO}$) (Found: C, 49.60; H, 2.55. Calc. for $\text{C}_{17}\text{H}_{11}\text{FeMnO}_5$: C, 50.03; H, 2.73%).

Reaction of $[\text{Re}(\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]\text{BBr}_4$ **2** with $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ **3** to give $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ **6** and $[\text{ReFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_6]$ **7**

Compound **2** (0.47 g, 0.65 mmol) was treated, in a manner similar to that described above, with $[\text{NMe}_4][\text{HFe}(\text{CO})_4]$ (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 (CH₂Cl₂) $\tilde{\nu}$ 2016s, 1996vs, 1950s (br) and 1891vs (br) cm⁻¹. ¹H NMR (CD₃COCD₃) δ 9.02 (s, 1 H, μ -CH), 7.42 (m, 2 H, C₆H₅), 7.21 (m, 2 H, C₆H₅), 7.00 (m, 1 H, C₆H₅) and 5.70 (s, 5 H, C₅H₅). Mass spectrum *m/z* 566 (*M*⁺, based on ¹⁸⁷Re, ⁵⁶Fe) (Found: C, 38.56; H, 2.15. Calc. for C₁₈H₁₁FeO₆Re: C, 38.24; H, 1.96%).

Reaction of complex **5** with CO to give **4** and [Fe(PhCHCO)(CO)₃]**8**

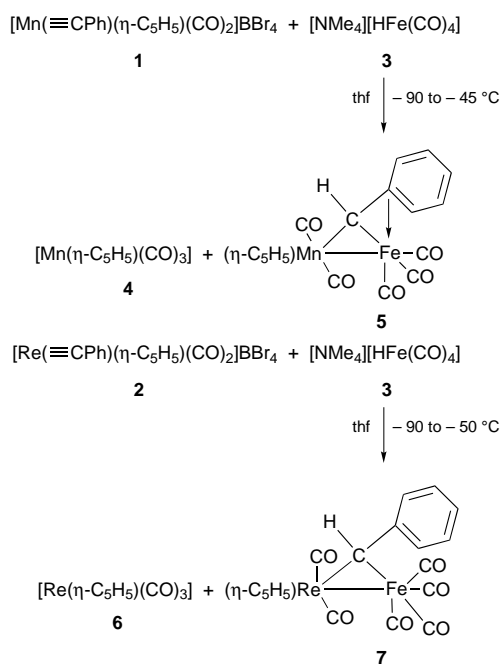
Carbon monoxide gas was bubbled through a solution of complex **5** (0.037 g, 0.09 mmol) in thf (40 cm³) at -40 to -10 °C for 6 h, during which time the purple-red solution gradually turned brown-red. After removal of the solvent *in vacuo*, the residue was chromatographed on Al₂O₃ with light petroleum as the eluent. The orange band which eluted first was collected, and then the brown-red band was eluted with light petroleum-CH₂Cl₂-Et₂O (20:1:1). The solvents were removed from the above two eluates under vacuum, and the residues recrystallized from light petroleum or light petroleum-CH₂Cl₂ 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 (CD₃COCD₃) δ 7.30–7.17 (m, 5 H, C₆H₅) 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 C₁₁H₆FeO₄: C, 51.21; H, 2.34%).

Reaction of complex **7** with PPh₃ to give [ReFe{ μ -C(H)Ph}(η -C₅H₅)(CO)₅(PPh₃)]**9**

To complex **7** (0.050 g, 0.09 mmol) dissolved in thf (30 cm³) at -55 °C was added PPh₃ (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-CH₂Cl₂ (10:1) as the eluent. After leaving the orange-red band which contains unchanged **7**, the orange band was eluted with light petroleum-CH₂Cl₂-Et₂O (5:1:1) and collected. The solvent was removed under vacuum, and the residue recrystallized from light petroleum-CH₂Cl₂ 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 (CH₂Cl₂) $\tilde{\nu}$ (CO) 2040w, 2033s, 1959vs and 1878vs cm⁻¹; ¹H NMR (CD₃COCD₃) δ 8.50 (s, 1 H, μ -CH), 7.47–7.34 (m, 15 H, C₆H₅), 6.98–6.84 (m, 5 H, C₆H₅) and 5.47 (s, 5 H, C₅H₅); mass spectrum *m/z* 543 (*M*⁺ - H - PPh₃), 515 (*M*⁺ - H - PPh₃ - CO), 431 (*M*⁺ - H - PPh₃ - 4CO) and 403 (*M*⁺ - H - PPh₃ - 5CO) (Found: C, 44.60; H, 2.90. Calc. for C₃₅H₂₆FePReO₅·2CH₂Cl₂: 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-CH₂Cl₂ 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-K α radiation (λ 0.710 69 Å) and the ω -2 θ scan mode within the ranges $5 \leq 2\theta \leq 40^\circ$ for **5**, $5 \leq 2\theta \leq 50^\circ$ for **8**, and $5 \leq 2\theta \leq 45^\circ$ 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 DIFABS¹⁴ 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



Scheme 1

was applied which resulted in transmission factors ranging from 0.96 to 1.00.

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 -C₅H₅)(CO)₂]BBr₄ **1** was treated with an equimolecular amount of [NMe₄][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-CH₂Cl₂ 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 -C₅H₅)(CO)₃]¹² and **5** is a novel heteronuclear dimetal carbene-bridged complex with the composition [MnFe{ μ -C(H)Ph}(η -C₅H₅)] the structure of which has been confirmed by X-ray crystallography.

The complex [Re(≡CPh)(η -C₅H₅)(CO)₂]BBr₄ **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 -C₅H₅)(CO)₃]¹³ and the latter, a dimetal carbene-bridged

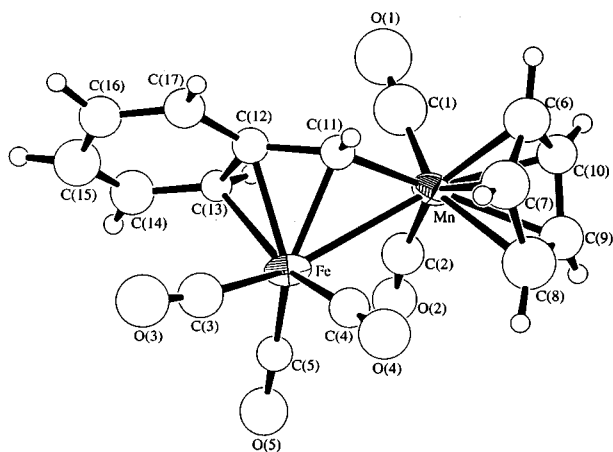
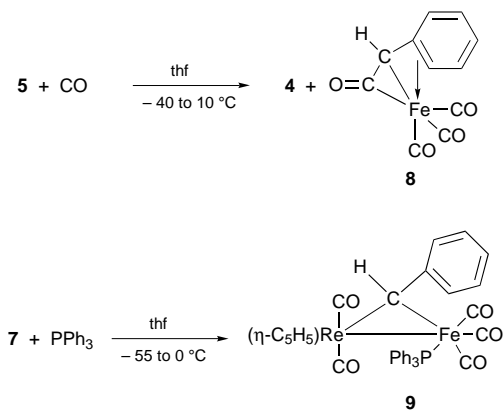


Fig. 1 Molecular structure and atom labelling for $[\text{MnFe}\{\mu\text{-C(H)Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3] \mathbf{5}$

complex, is identical with that produced by the reaction of **2** with $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$, $\text{Na}_2[\text{Fe}(\text{CO})_4]$ or $\text{Na}_2[\text{Fe}_3(\text{CO})_{11}]$.

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 $\mu\text{-C-Mn}$ 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 $[\text{Fe}(\text{Ph}_2\text{CHCO})(\text{CO})_3]$ 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 $[\text{ReFe}\{\mu\text{-C(H)Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_5(\text{PPh}_3)] \mathbf{9}$, 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 $[\text{PtW}\{\mu\text{-}\eta^1:\eta^3\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PEt}_3)_2][\text{BF}_4]$ ¹⁶ or complex **7** with PPh_3 , but decomposition products such as $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ 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 $5 \leq 2\theta \leq 40^\circ$ 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,

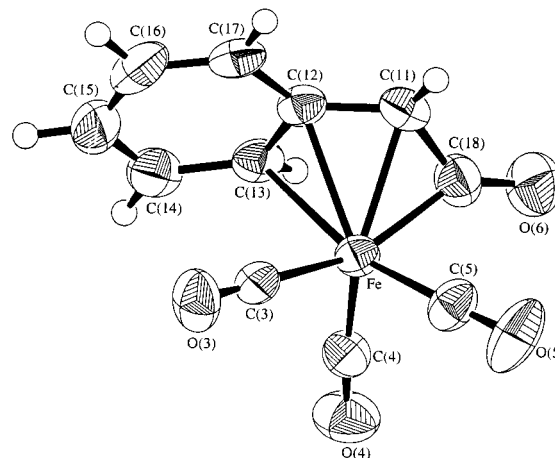


Fig. 2 Molecular structure and atom labelling for $[\text{Fe}(\text{PhCHCO})(\text{CO})_3] \mathbf{8}$

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 $[\text{CoW}\{\mu\text{-}\eta^1:\eta^3\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(\text{CO})_3][\text{BF}_4]$ 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 $[\text{MnFe}\{\mu\text{-C}(\text{COEt})\text{Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ [$2.6929(8)$ Å]⁸ and $[\text{ReFe}\{\mu\text{-C(H)Ph}\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_6]$ [$2.7581(8)$ Å].⁷

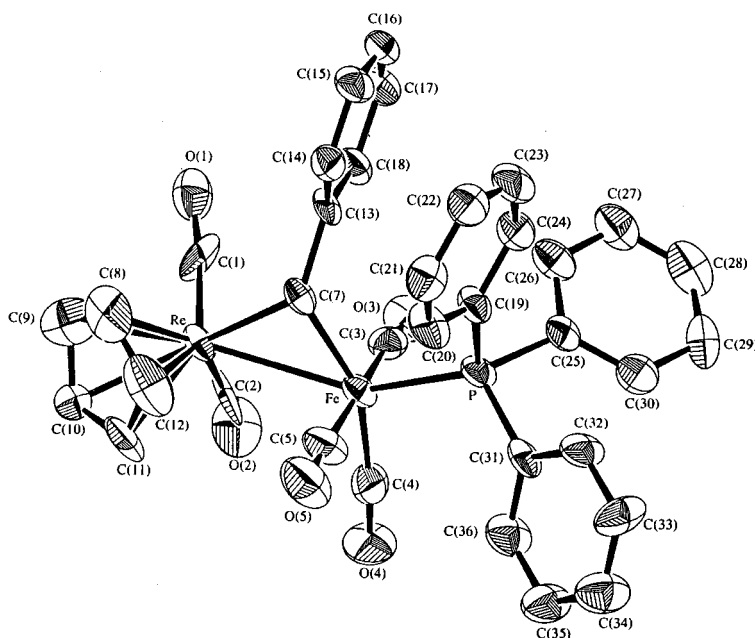
The molecular structure of complex **8** (Fig. 2) shows that the benzene ring is still bonded to the Fe atom, and a formyl (C=O) group is bonded to the original alkylidene carbon [C(11)] and the Fe atom through the C(18) atom and provides one electron for the Fe atom to satisfy an 18-electron configuration. 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 $\mu\text{-C(H)-C}_6\text{H}_4\text{Me}$ in $[\text{PtW}\{\mu\text{-}\eta^1:\eta^3\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PMe}_3)_2][\text{BF}_4]$.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 coordination 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 [$\mu\text{-C-Re}$ $2.17(1)$, $\mu\text{-C-Fe}$ $2.03(1)$ Å] with an angle Re–C(7)–Fe of $82.7(5)^\circ$ similar to that in **7** [$\mu\text{-C-Re}$ $2.120(5)$, $\mu\text{-C-Fe}$ $2.097(5)$ Å; Re–C(7)–Fe $81.7(2)^\circ$]. The $\mu\text{-C-Re}$ distance in **9** is comparable with that of **7** and the complex $[\text{Re}_2(\mu\text{-H})_2(\mu\text{-CHBu})(\eta\text{-C}_6\text{H}_6)_2]$ [$2.13(3)$ Å],¹⁸ and the $\mu\text{-C-Fe}$ 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 $[\text{PFe}(\text{NO})_2(\text{CO})(\text{PPh}_3)]$,¹⁹ $2.244(1)$ Å in $[\text{Fe}(\text{CO})_4(\text{PPh}_3)_2]$ ²⁰]. The P–Fe–C(7) and P–Fe–Re bond angles are $96.7(4)$ and $147.3(1)^\circ$, 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 ₆ FeO ₄	C ₃₇ H ₂₉ Cl ₄ FeO ₅ PRe
<i>M</i>	406.06	258.01	969.48
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ 2 ₁ (no. 19)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	7.326(7)	10.977(5)	11.744(3)
<i>b</i> /Å	17.650(8)	14.384(3)	16.132(3)
<i>c</i> /Å	6.809(4)	6.646(4)	10.803(3)
<i>a</i> ^o	94.73(7)		100.32(2)
<i>β</i> ^o	113.93(6)		110.50(2)
<i>γ</i> ^o	87.35(7)		91.14(2)
<i>U</i> /Å ³	801(1)	1049.4(8)	1878.4(9)
<i>Z</i>	2	4	2
<i>D</i> _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 ^o	12 (6.6–18.6)	16 (18.5–21.7)	23 (13.6–21.5)
No. unique data, total	1649	1106	3788
with <i>I</i> > 3.00σ(<i>I</i>)	704 [<i>I</i> > 2.00σ(<i>I</i>)]	864	2860
No. parameters refined	107	145	442
<i>R</i> ^a	0.090	0.031	0.049
<i>R</i> ^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 $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. ^c $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$, where *N*_o, *N*_p = numbers of observations and parameters.

**Fig. 3** Molecular structure and atom labelling for [ReFe{μ-C(H)Ph}(η-C₅H₅)(CO)₅(PPh₃)] **9**

The possible reaction pathway to complex **5** (Scheme 1) could involve initial formation of a carbene intermediate [(OC)₂(η-C₅H₅)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-η¹:η³-CH(C₆H₄Me-4)}(η-C₅H₅)(CO)₂(L_n)][BF₄] [ML_n = Cr(η-C₅H₅)(CO)(NO), Co(CO)(η-C₅Me₅), or Pt(PR₃)₂] and [PtW{μ-η¹:η³-CH(C₆H₄Me-4)}(η-C₅H₅)(CO)₂(PEt₃)₂][BF₄], 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-CC₆H₄Me-4)(η-C₅H₅)₂(CO)₃(NO)], [CoW(μ-CC₆H₄Me-4)(η-C₅H₅)(η-C₅Me₅-

(CO)₃], and [PtW(μ-CC₆H₄Me-4)(η-C₅H₅)(CO)₂(PR₃)₂] (PR₃ = PMe₃, PMe₂Ph, or PMePh₂) with HBF₄·Et₂O, or by the reaction²² of the neutral carbyne complex [W(≡CC₆H₄Me-4)(η-C₅H₅)(CO)₂] with the cationic metal hydride *trans*-[Pt(H)(PEt₃)₂(Me₂CO)][BF₄].

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 η³-co-ordinated carbene ligand to give an (vinylketene)iron complex with an η⁴-co-ordinated acyl ligand has been observed in the reaction of tricarbonyl-(η³-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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