Unusual reactions of a cationic carbyne complex of manganese with carbonyliron dianions to form a novel dimetal carbene-bridged complex $[MnFe\{\mu\text{-}C(COEt)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$

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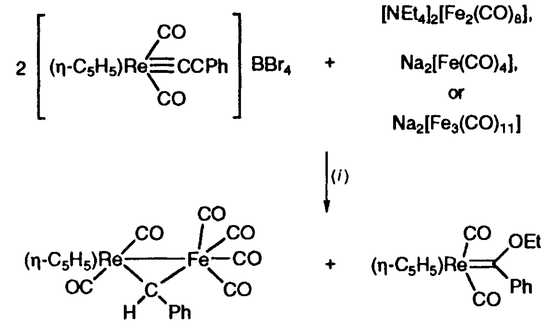
The reaction of $[Mn(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ **1** with $[NEt_4]_2[Fe_2(CO)_8]$ in tetrahydrofuran at low temperature gave a novel heteronuclear dimetal carbene-bridged complex $[MnFe\{\mu\text{-}C(COEt)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$ **3**, and a dimetal dicarbene complex $[\{(OC)_2(\eta\text{-}C_5H_5)Mn(=CPh)\}_2Fe_2(CO)_8]$ **4**, as well as $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ **2**. The same products, **2** and **3**, were obtained from the reaction of **1** with $Na_2[Fe(CO)_4]$. The structure of **3** has been established by X-ray crystallography.

In previous papers[1-4] we reported that several carbene complexes containing a special substituent bonded to the carbene carbon atom were synthesized by the reactions of cationic carbyne complexes of transition metals with nucleophiles. However, only a few carbene complexes with a transition or a main group metal bonded to the carbene carbon atom are known.[1,5,6] Recently, we have shown the reactions of a cationic carbyne complex of rhenium $[Re(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$, with nucleophiles containing a carbonyliron dianion to form an unexpected dimetal carbene-bridged complex $[(OC)_2(\eta\text{-}C_5H_5)Re(\mu\text{-}CHPh)Fe(CO)_4]$[7] (Scheme 1), instead of the expected dimetal dicarbene complex. To examine the effect of the central metal on the reactivity of the cationic carbyne complex and on the reaction products, we have now studied the reactions of the complex $[Mn(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ **1** with carbonyliron dianions, which afforded a novel heteronuclear dimetal carbene-bridged complex and a tetranuclear dicarbene complex, and the structures of the products.



Scheme 1 (*i*) Tetrahydrofuran (thf), −90 to −60 °C

Experimental

All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. All solvents employed were dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N_2. Tetrahydrofuran and diethyl ether were distilled from sodium–benzophenone, light petroleum (b.p. 30–60 °C) from CaH_2, and CH_2Cl_2 from P_2O_5. The neutral alumina used for chromatography was deoxygenated at room temperature in a high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water and stored under N_2. The complex $[Mn(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ **1** was prepared as previously described,[8] as were $[NEt_4]_2[Fe_2(CO)_8]$[9] and $Na_2[Fe(CO)_4]$.[10]

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer, ^1H NMR spectra at ambient temperature in $(CD_3)_2CO$ solution with $SiMe_4$ as the internal reference using a Varian-200 spectrometer and electron ionization (EI) mass spectra on a Finnigan 4021 GC/MS/DS spectrometer. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

Reactions of complex 1

To $[NEt_4]_2[Fe_2(CO)_8]$ (0.44 g, 0.74 mmol) dissolved in thf (50 cm^3) at −90 °C was added portionwise complex **1** (0.86 g, 1.44 mmol) with vigorous stirring. Immediately the red solution turned brick-red. The mixture was stirred initially at −90 to −80 °C for 1 h and then allowed to warm to −50 °C during 3 h. The resulting brick-red solution was evaporated at −40 °C under high vacuum to dryness, and the black-red residue obtained was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15 cm) at −25 °C with light petroleum–CH_2Cl_2 (20 : 1) as the eluent. The yellow band which eluted first was collected, and then the brown-red band was eluted with light petroleum–CH_2Cl_2 (10 : 1). A third purple-red band was eluted with light petroleum–CH_2Cl_2–Et_2O (10 : 1 : 1). The solvents were removed from the above three eluates *in vacuo*, and the residues recrystallized from light petroleum–CH_2Cl_2 solution at −80 °C. From the first fraction was obtained 0.035 g (23%, based on **1**) of yellow crystals of the known compound $[Mn(\eta\text{-}C_5H_5)(CO)_3]$[11] identified by comparison of its melting point (77–78 °C, lit. 76.8–77.1 °C) and IR [ν(CO) 2005vs 1935vs(br) cm^{-1} (CH_2Cl_2)] and ^1H NMR [CD_3COCD_3: δ 5.00 (s, C_5H_5)] spectra with those of an authentic sample. The second fraction gave 0.13 g (39%, based on **1**) of brick-red crystals of $[MnFe\{\mu\text{-}C(COEt)Ph\}(\eta\text{-}C_5H_5)(CO)_5]$ **3**, m.p. 114–116 °C (decomp.) IR (ν_{CO}): (in hexane) 2010s, 1998vs, 1972vs and 1930s; (in KBr) 2008s, 1999m, 1982 (sh), 1960vs, 1910vs and 1595w cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.50 (m, 3 H, C_6H_5), 7.35 (m, 2 H, C_6H_5), 4.76 (s, 5 H, C_5H_5), 2.56 (q, 2 H, $COCH_2CH_3$) and 0.88 (t, 3 H, $COCH_2CH_3$). Mass spectrum: m/z 462 (M^+), 434 (M^+ − CO), 406 (M^+ − 2CO), 378 (M^+ − 3CO), 350 (M^+ − 4CO) and 322 (M^+ − 5CO) (Found: C, 52.05; H, 3.25. Calc. for $C_{20}H_{15}FeMnO_6$: C, 52.00; H, 3.25%). The third fraction gave

0.12 g (19%, based on **1**) of $[\{(OC)_2(\eta\text{-}C_5H_5)Mn(=CPh)\}_2Fe_2(CO)_8]$ **4** as purple-red crystals, m.p. 81–83 °C (decomp.). IR (ν_{CO}) (hexane): 2003vs (br), 1988vs (br), 1980m, 1970s, 1902s and 1865m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 7.58 (m, 4 H, C_6H_5), 7.24 (m, 6 H, C_6H_5) and 4.97 (s, 10 H, C_5H_5). Mass spectrum: *m/z* 866 (M^+), 601 $\{[(OC)_2(C_5H_5)Mn(CPh)Fe_2(CO)_8]^+\}$, 545 $\{[(C_5H_5)Mn(CPh)Fe_2(CO)_8]^+\}$, 517 $\{[(C_5H_5)Mn(CPh)Fe_2(CO)_7]^+\}$, 336 $\{[Fe_2(CO)_8]^+\}$, 308 $\{[Fe_2(CO)_7]^+\}$, 280 $\{[Fe_2(CO)_6]^+\}$, 265 $\{[(OC)_2(C_5H_5)Mn(CPh)]^+\}$ and 209 $\{[(C_5H_5)Mn(CPh)]^+\}$ (Found: C, 49.80; H, 2.55. Calc. for $C_{36}H_{20}Fe_2Mn_2O_{12}$: C, 49.90; H, 2.35%).

To a solution of $Na_2[Fe(CO)_4]$ (0.23 g, 1.09 mmol) in thf (50 cm^3) at −90 °C was added portionwise complex **1** (1.30 g, 2.17 mmol) with strong stirring. The orange-yellow solution immediately turned dark red. The mixture was stirred at −90 to −80 °C for 1 h and then at −60 °C for 3 h. After removal of the solvent under vacuum at −40 °C, the dark red residue was chromatographed on Al_2O_3 (neutral) at −25 °C with light petroleum–CH_2Cl_2 (15:1) as the eluent. The yellow band which eluted first was collected, and the second brick-red band was eluted with light petroleum–CH_2Cl_2–Et_2O (10:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from light petroleum–CH_2Cl_2 solution at −80 °C. The first fraction gave 0.057 g (26%, based on **1**) of yellow crystals of **2**, the second 0.22 g (44%, based on **1**) of **3** as brick-red crystals. Products **2** and **3** were identified by comparison of their melting points and IR, ^{1}H NMR and mass spectra with those of the same compounds characterized above.

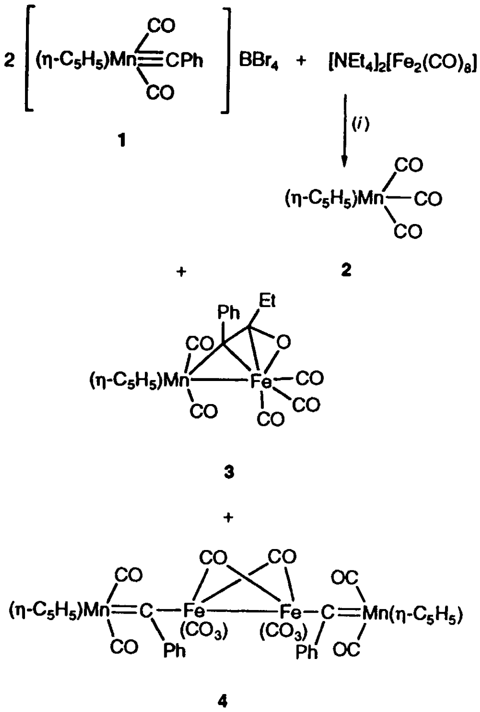
Crystallography

Crystals of complex **3** suitable for X-ray diffraction were obtained by recrystallization from light petroleum–CH_2Cl_2 at −80 °C. A suitable brick-red single crystal with dimensions 0.10 × 0.30 × 0.30 mm was sealed in a glass capillary under N_2 and aligned on an Enraf-Nonius CAD4 diffractometer. The unit-cell parameters were determined on the basis of 25 reflections with $9.4 < \theta < 13.7°$. Intensity measurements employed graphite-monochromated Mo-Kα radiation (λ 0.7107 Å) and ω–2θ scan mode in the range $0 < 2\theta < 50°$ at room temperature. During data collection the intensities of three standard reflections monitored at every 3600s of X-ray exposure time decreased linearly by 4.8% and the data set was corrected for this decay. After taking into account Lorentz and polarization effects, an empirical absorption correction with minimum 67.31% and maximum 99.63% transmission was applied, based on seven ψ scans.

The structure solution by direct methods (MULTAN 82)[12] revealed the metal atoms and subsequent Fourier-difference methods yielded the positions of all remaining non-hydrogen atoms and most hydrogen atoms. All non-hydrogen atoms were refined anisotropically by unit-weight full-matrix least squares, while the hydrogen atoms located from the Fourier-difference map were allowed to ride on the related carbon atoms with fixed isotropic thermal parameters in the refinement and those placed at calculated positions were not refined. The refinement converged at $R = 0.046$ and $R' = 0.050$ for 2813 observed reflections with $I > 3\sigma(I)$. A final Fourier-difference map exhibited no significant peaks greater than 0.21 e Å^{-3}. The scattering factors were taken from ref. 13. All computations were performed on a micro VAX-II computer with SDP PLUS[14] and ORTEP[15] programs.

Details of the crystallographic data are given in Table 2, positional parameters of non-hydrogen atoms in Table 3 and bond lengths and selected angles in Table 1.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.



Scheme 2 (*i*) Tetrahydrofuran (thf), −90 to −50 °C

Results and Discussion

Two molar equivalents of $[Mn(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ **1** were treated with one of $[NEt_4]_2[Fe_2(CO)_8]$ in thf at low temperature (−90 to −50 °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 crystalline **2**,[11] brick-red crystals of **3** and purple-red crystals of **4** (Scheme 2) in 23, 39 and 19% isolated yields, respectively. Complex **1** also reacted with $Na_2[Fe(CO)_4]$ under the same conditions to afford **2** and **3** in 26 and 44% yield, respectively, but no **4** 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.

On the basis of elemental analyses, spectroscopic evidence, and X-ray crystallography, compound **3** is formulated as a novel heteronuclear dimetal carbene-bridged complex with a COEt group bonded to the bridging carbene carbon atom and Fe respectively through carbon and oxygen atoms of the acyl (C=O) moiety. Compound **4** is formulated as a tetranuclear dicarbene complex with a $Fe_2(CO)_8$ core in which each Fe atom is bonded to one carbene carbon.

Complexes **3** and **4** are readily soluble in polar organic solvents but sparingly soluble in non-polar solvents. Complex **3** is air-sensitive in solution but relatively stable as the solid, while **4** is extremely sensitive to air and temperature in both solution and crystalline states. The composition of **3** was established by elemental analysis, IR, ^{1}H and mass spectroscopy, all of which are consistent with the structure shown. The IR spectrum in hexane showed CO stretching vibration bands at 2010s, 1998vs, 1972vs and 1930s cm^{-1}, but in KBr showed a weak absorption band at 1595 cm^{-1}, in addition to the five CO absorption bands (see Experimental section). The band at 1595w cm^{-1} is characteristic of an acyl ligand. Its intensity was obviously weakened due to the co-ordination of the oxygen atom of the acyl group to the Fe atom, as in the carboranylcarbonyl complex $[ReFe(\mu\text{-}CPh)(\eta\text{-}C_5H_5)(\mu\text{-}CO)(CO)_3(COC_2HB_{10}H_{10})]$.[16] The weaker co-ordination of the oxygen atom in **3**, as compared with the carboranylcarbonyl complex, is indicated by the lower wavenumber for the latter (1575w cm^{-1}).

Table 1 Bond lengths (Å) and angles (°)* of [MnFe{μ-C(COEt)Ph}(η-C_5H_5)$(CO)_5$] **3**

Fe–Mn	2.6929(8)	Mn–C(22)	1.787(4)	O(21)–C(21)	1.145(6)	C(63)–C(64)	1.372(7)
Fe–O(101)	2.004(3)	Mn–C(251)	2.148(6)	O(22)–C(22)	1.129(6)	C(64)–C(65)	1.386(6)
Fe–C	2.020(4)	Mn–C(252)	2.167(7)	O(101)–C(10)	1.303(5)	C(65)–C(66)	1.366(6)
Fe–C(10)	2.134(5)	Mn–C(253)	2.15(1)	C–C(10)	1.438(6)	C(101)–C(102)	1.45(5)
Fe–C(11)	1.771(5)	Mn–C(254)	2.13(1)	C–C(61)	1.482(5)	C(251)–C(252)	1.41(2)
Fe–C(12)	1.805(5)	Mn–C(255)	2.113(5)	C(10)–C(101)	1.496(7)	C(251)–C(255)	1.413(8)
Fe–C(13)	1.796(4)	O(11)–C(11)	1.129(5)	C(61)–C(62)	1.406(6)	C(252)–C(253)	1.42(1)
Fe–C(21)	2.700(4)	O(12)–C(12)	1.135(6)	C(61)–C(66)	1.383(6)	C(253)–C(254)	1.369(8)
Mn–C	2.021(4)	O(13)–C(13)	1.135(6)	C(62)–C(63)	1.375(7)	C(254)–C(255)	1.39(2)
Mn–C(21)	1.781(6)						
Mn–Fe–O(101)	82.77(9)	C(11)–Fe–C(13)	90.6(2)	Fe–C(12)–O(12)	176.5(5)	O(101)–C(10)–C	115.0(4)
Mn–Fe–C	48.2(2)	Mn–C–C(10)	121.1(3)	Fe–C(13)–O(13)	176.1(4)	O(101)–C(10)–C(101)	120.5(4)
Mn–Fe–C(10)	76.6(1)	Mn–C–C(61)	20.3(3)	C(10)–C–C(61)	115.0(3)	C–C(10)–C(101)	124.4(4)
Mn–Fe–C(11)	86.1(2)	C(12)–Fe–C(13)	94.2(2)	C–C(61)–C(62)	122.5(4)	C–C(61)–C(66)	121.0(3)
Mn–Fe–C(12)	108.5(2)	Fe–Mn–C	48.2(1)	C–C(61)–C(66)	121.0(3)	C(62)–C(61)–C(66)	116.6(4)
Mn–Fe–C(13)	157.2(2)	Fe–Mn–C(21)	70.9(1)	C(10)–C(61)–C(66)	114.5(3)	C(61)–C(62)–C(63)	120.7(4)
O(101)–Fe–C	70.1(1)	C–Mn–C(21)	109.9(2)	C(62)–C(61)–C(66)	116.6(4)	C(62)–C(63)–C(64)	121.4(5)
O(101)–Fe–C(10)	36.5(1)	C–Mn–C(22)	82.5(2)	C(61)–C(62)–C(63)	120.7(4)	C(63)–C(64)–C(65)	118.7(4)
O(101)–Fe–C(11)	165.2(2)	Fe–Mn–C(22)	106.6(1)	C–C(10)–C(101)	124.4(4)	C(64)–C(65)–C(66)	119.9(4)
O(101)–Fe–C(12)	96.8(2)	Fe–C(10)–O(101)	66.3(2)	Fe–C(11)–O(11)	177.5(5)	C(61)–C(66)–C(65)	122.8(4)
O(101)–Fe–C(13)	96.0(2)	Fe–C(10)–C	65.7(2)	C(62)–C(63)–C(64)	121.4(5)	C(253)–C(254)–C(255)	109.9(7)
C–Fe–C(10)	40.4(2)	Fe–C(10)–C(101)	135.4(4)	C(63)–C(64)–C(65)	118.7(4)	C(251)–C(255)–C(254)	107.6(9)
C–Fe–C(11)	95.0(2)	O(101)–C(10)–C	115.0(4)	Mn–C(21)–O(21)	169.9(4)	C(10)–C(101)–C(102)	117(2)
C–Fe–C(12)	53.21(2)	O(101)–C(10)–C(101)	120.5(4)	Mn–C(22)–O(22)	178.8(4)	C(252)–C(251)–C(255)	108(1)
C–Fe–C(13)	110.0(2)	Fe–O(101)–C(10)	77.2(2)	C(64)–C(65)–C(66)	119.9(4)	C(251)–C(252)–C(253)	107.3(6)
C(10)–Fe–C(11)	130.7(3)	Fe–C–Mn	83.6(1)	C(61)–C(66)–C(65)	122.8(4)	C(252)–C(253)–C(254)	107.6(9)
C(10)–Fe–C(12)	133.2(2)	Fe–C–C(10)	74.0(2)	C(10)–C(101)–C(102)	117(2)	C(253)–C(254)–C(255)	109.9(7)
C(10)–Fe–C(13)	88.8(2)	Fe–C–C(61)	132.4(3)	C(10)–C–C(61)	115.0(3)	C(251)–C(255)–C(254)	107.6(9)
C(11)–Fe–C(12)	96.1(2)	O(11)–C(11)–C(13)	132.4(4)				

* Numbers in parentheses are estimated standard deviations in the least significant digits.

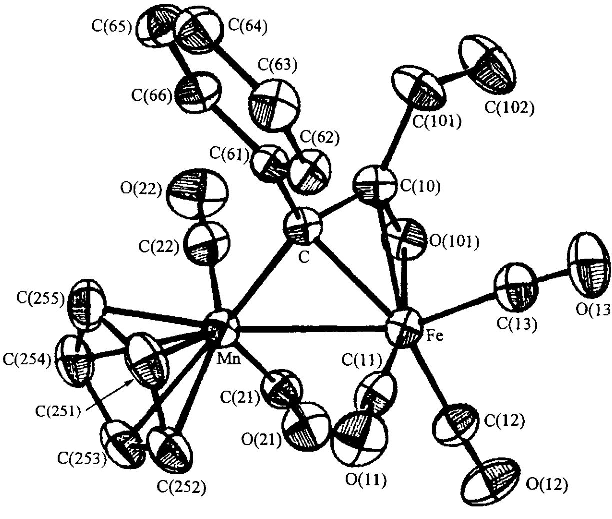


Fig. 1 Molecular structure and labelling for [MnFe{μ-C(COEt)Ph}-(η-C_5H_5)$(CO)_5$] **3**

In the ^1H NMR spectrum of **3** a triplet (δ 0.88) and a quartet (δ 2.56) were observed characteristic of an ethyl group, in addition to the expected proton signals attributed to the phenyl and cyclopentadienyl groups.

The structure of complex **3** (Fig. 1) determined by X-ray diffraction studies resembled that of [ReFe(μ-CHPh)(η-C_5H_5)$(CO)_6$],[7] except that the substituent on the bridging carbene carbon is an acyl group (COEt) in **3** but a hydrogen atom in [ReFe(μ-CHPh)(η-C_5H_5)$(CO)_6$]. The Mn–Fe bond is bridged by C(COEt)Ph, giving a dimetallacyclopropane ring, and the COEt group is bridged to the μ-C–Fe bond through atom C(10). The oxygen atom of the COEt group co-ordinates to the Fe atom and provides one electron, thus giving the Fe an 18-electron configuration. The Fe–O(101) bond length of 2.004(3) Å is very close to that found in the analogous complex [ReFe(μ-CPh)(η-C_5H_5)(μ-CO)$(CO)_3$$(COC_2HB_{10}H_{10})$] [1.98(3) Å].[16] The longer bond length of C(10)–O(101) [1.303(5) Å] as compared with that in [Fe($COC_6H_4CF_3$-*p*)(η-C_5H_5)-$(CO)_2$] [1.217(6) Å][17] suggests that the C=O bond of the acyl group is obviously stretched, as a result of the co-ordination of the oxygen with the Fe atom, similar to that in [ReFe(μ-CPh)-(η-C_5H_5)(μ-CO)$(CO)_3$$(COC_2HB_{10}H_{10})$] [1.31(5) Å].[16] The Mn–Fe distance of 2.6929(8) Å in **3** is somewhat shorter than that found in the analogous carbene-bridged complex [ReFe(μ-CHPh)(η-C_5H_5)$(CO)_6$] [2.7581(8) Å][7] but is obviously longer than that in the analogous carbyne-bridged complex [(OC)-(η-C_5H_5)Fe(μ-COEt)(μ-CO)Mn(η-C_5H_4Me)(CO)] [2.572(1) Å].[18] In contrast to [ReFe(μ-CHPh)(η-C_5H_5)$(CO)_6$] [μ-C–Re 2.120(5), μ-C–Fe 2.097(5) Å], the alkylidene carbon in **3** is symmetrically bridged to the Mn–Fe bond [μ-C–Mn 2.021(4), μ-C–Fe 2.020(4) Å], in a similar manner to that found in the alkoxycarbyne complex [(OC)(η-C_5H_5)Fe(μ-COEt)(μ-CO)-Mn(η-C_5H_4Me)(CO)] [μ-C–Mn 1.839(4), μ-C–Fe 1.843(4)][18] The μ-C atom lies essentially in the plane of the benzene ring (±0.003 Å). The benzene ring plane is at an angle of 123.74(2)° to the plane comprised of Mn, Fe and C, which is much larger than the corresponding angle [84.4(3)°] in [Re-Fe(μ-CHPh)(η-C_5H_5)$(CO)_6$]. This could be caused by the steric repulsion between the COEt group and the μ-C atom.

As anticipated from the IR spectrum, of six CO groups, two are attached to the Mn atom and the other four to the Fe. Among the four CO groups bonded to the Fe atom, one is a formacyl bonded to the μ-C and the ethyl with an Fe–C(10) bond length of 2.134(5) Å. The average Fe–C(CO) bond length is 1.79 Å which is somewhat shorter than that found (1.83 Å) in [ReFe(μ-CHPh)(η-C_5H_5)$(CO)_6$] but the same as that in [ReFe(μ-CPh)(η-C_5H_5)(μ-CO)$(CO)_3$$(COC_2HB_{10}H_{10})$] (1.79 Å).[16] 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 bridging carbene carbon.

The structure of complex **4** shown in Scheme 2 is supported by an X-ray diffraction study[19] which gave an *R* value of 0.16 due to serious decay. However, the elemental analyses and IR, ^1H NMR and mass spectra are all consistent with this geometry.

Table 2 Crystal data and experimental details for complex **3**

Empirical formula	$C_{20}H_{15}FeMnO_6$
M	462.12
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	8.901(9)
b/Å	13.041(9)
c/Å	16.315(5)
β/°	95.62(2)
U/Å^3	1884.9
Z	4
D_c/g cm^{-3}	1.628
μ(Mo-Kα)/cm^{-1}	14.45
F(000)	936
No. unique data, total	3358
with $I > 3\sigma(I)$	2813
No. parameters refined, N_p	293
Correction factors, maximum, minimum	0.9963, 0.6731
R[a]	0.046
R'[b]	0.050
Quality-of-fit indicator[c]	1.56
Largest shift/e.s.d., final cycle	0.40
Largest difference peak/e Å^{-3}	0.21

[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] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$.

Table 3 Positional parameters and their estimated standard deviations for complex **3**

Atom	x	y	z
Fe	0.751 53(8)	0.174 63(6)	0.264 08(4)
Mn	0.710 38(8)	0.020 55(6)	0.154 30(4)
O(11)	1.072 8(4)	0.137 9(4)	0.264 0(3)
O(12)	0.747 4(5)	0.372 3(3)	0.177 3(3)
O(13)	0.815 2(5)	0.271 3(4)	0.425 9(3)
O(21)	0.583 9(5)	0.201 3(3)	0.067 9(3)
O(22)	0.395 3(5)	−0.041 9(4)	0.150 4(3)
O(101)	0.527 7(4)	0.161 1(3)	0.266 0(2)
C	0.696 1(5)	0.025 6(4)	0.277 1(3)
C(10)	0.579 7(6)	0.083 9(4)	0.310 9(3)
C(11)	0.947 2(6)	0.151 4(4)	0.262 3(4)
C(12)	0.748 4(6)	0.294 5(5)	0.208 5(4)
C(13)	0.785 4(6)	0.234 0(4)	0.363 5(4)
C(21)	0.637 5(6)	0.136 0(4)	0.107 6(3)
C(22)	0.517 3(6)	−0.017 6(5)	0.152 7(3)
C(61)	0.763 6(5)	−0.057 2(4)	0.330 9(3)
C(62)	0.895 0(6)	−0.042 5(4)	0.384 8(3)
C(63)	0.954 4(6)	−0.121 3(4)	0.433 6(3)
C(64)	0.887 9(6)	−0.216 3(4)	0.431 6(3)
C(65)	0.758 0(6)	−0.232 0(4)	0.379 1(3)
C(66)	0.700 0(6)	−0.154 0(4)	0.329 8(3)
C(101)	0.527 2(7)	0.065 5(5)	0.394 0(4)
C(102)	0.408 3(8)	0.132 0(7)	0.416 9(4)
C(251)	0.920 7(6)	−0.061 5(5)	0.167 4(4)
C(252)	0.930 0(6)	0.015 0(5)	0.107 8(4)
C(253)	0.814 8(7)	−0.005 4(5)	0.042 8(3)
C(254)	0.741 1(7)	−0.092 5(5)	0.063 1(3)
C(255)	0.800 5(8)	−0.127 4(5)	0.139 3(4)

The IR spectrum in the ν(CO) region showed an absorption band at 1865 attributable to the bridging CO ligands, in addition to five terminal CO bands, indicative of the $(OC)_6Fe_2(\mu\text{-}CO)_2$ and $(C_5H_5)Mn(CO)_2$ moieties. The ^1H NMR spectrum showed the expected proton signals due to the phenyl and cyclopentadienyl groups. The mass spectrum provided further structural information (see Experimental section) showing the molecular ion peak and the fragments $[(OC)_2(C_5H_5)Mn(CPh)Fe_2(CO)_8]^+$, $[(OC)_2(C_5H_5)Mn(CPh)]^+$ and $[Fe_2(CO)_8]^+$ produced by splitting of the molecule together with the principal fragments produced by loss of CO ligands and from further cleavage of these.

The reaction pathway to complexes **2** and **3** is as yet unclear. However, the formation of **2** might proceed *via* an initial decomposition of **1** owing to its ability to lose the carbyne ligand (CPh) and then *via* the abstraction of one molecule of CO. The formation of **3** is unexpected, but it could involve initial formation of the '$Fe(CO)_4{}^{2-}$' species derived from $[NEt_4]_2[Fe_2(CO)_8]$, which could then attack at the carbyne carbon atom of **1**, as confirmed by the reaction of **1** with $Na_2[Fe(CO)_4]$ to give **3**, to generate an anionic carbene intermediate $[(OC)_2(\eta\text{-}C_5H_5)Mn(CPh)Fe(CO)_4]^-$ as in the reaction[7] of $[Re(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]BBr_4$ 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 in $[Fe(COC_6H_4CF_3\text{-}p)(\eta\text{-}C_5H_5)(CO)_2]$.[17] This would yield a 16e intermediate $[(OC)_2(\eta\text{-}C_5H_5)Mn(CPh)Fe(CO)_3(COEt)]$ which then undergoes intramolecular cyclization involving bonding of the acyl carbon atom to the bridging carbene carbon and the oxygen atom to the Fe, giving the latter an 18-electron configuration and affording complex **3**. It is not known 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 $Na_2[Fe(CO)_4]$ reacts with **1** also to give the same product **3**. We tentatively speculate that the source could be $BBr_2(OEt)$ which exists in the starting material **1**[8] since the preparation of **1** by the reaction of $[Mn\{C(OEt)Ph\}(\eta\text{-}C_5H_5)(CO)_2]$ with BBr_3 was accompanied by the formation of $BBr_2(OEt)$.

The formation of complex **4** in Scheme 2 is not surprising since the analogous reactions of $[Re(CPh)(\eta\text{-}C_5H_5)(CO)_2]BCl_4$ and $[Cr(CNEt_2)(CO)_5]BF_4$ with $LiPbPh_3$ gave carbene complexes $[Re\{C(PbPh_3)Ph\}(C_5H_5)(CO)_2]$[1] and $[Cr\{C(PbPh_3)NEt_2\}(CO)_5]$,[6a] respectively, where the $PbPh_3$ group is directly bonded to the carbene-carbon atom through Pb.

A number of dimetal carbene-bridged complexes were synthesized by Stone and co-workers[20–22] by the reactions of carbene complexes with low-valent metal species or by reactions[23,24] of neutral carbyne complexes with metal hydrides. Recently, we found that olefin-ligated metal carbonyl compounds, such as pentacarbonyl(cyclooctatetraene)diiron and tetracarbonylbis(η-cyclopentadienyl)diiron, reacted with aryllithium reagents followed by alkylation with $[Et_3O]BF_4$ in a one-pot reaction to afford a series of olefin-co-ordinated carbene-bridged complexes in high yields, which is a simple, convenient and high-yield synthesis of dimetal carbene-bridged complexes.[25,26] We also found an unusual reaction of a cationic rhenium carbyne complex with the carbonyliron dianion which yielded a heterodinuclear carbene-bridged complex[7] (Scheme 1). Complex **3**, as a heteronuclear dimetal complex with a bridging carbene ligand, was synthesized by the reaction of a cationic manganese carbyne complex with carbonyliron dianion under analogous conditions. To our knowledge, there are no examples of heterodinuclear manganese carbene-bridged complexes although a heterodinuclear manganese–iron carbyne-bridged complex has recently been reported by Hersh and co-workers.[18] The present reaction further demonstrates a new and convenient route for the preparation of heteronuclear dimetal carbene-bridged complexes.

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