Cluster Chemistry. 72.[1] An Octanuclear Heterometallic Dicarbido Cluster with an Unusual Geometry: X-ray Structure of $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$

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Introduction

The range of cluster carbides is extensive,[4] but there are relatively few dicarbido species. Examples include $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{24}]^{2-}$,[5] $[Co_{13}(C)_2(CO)_{24}]^{4-}$,[6] and $[Rh_{15}(C)_2(CO)_{23}]^{-}$.[7] The $Ru_{10}(C)_2$ species was obtained by heating $[Ru_6C(CO)_{16}]^{2-}$in tetraglyme; recently, its reversible reaction with C_2Ph_2 was shown to give the related cluster $[Ru_{10}(\mu_6\text{-}C)_2(\mu\text{-}C_2Ph_2)(CO)_{22}]^{2-}$, in which two apical Ru atoms of the two edge-fused Ru_6C octahedra are now bonded and bridged by the alkyne.[8] We now describe the isolation and crystallographic characterization of $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$, containing a square-pyramidal $Fe_2Ru_3(\mu_5\text{-}C)$ cluster fused to an octahedral $Fe_3Ru_3(\mu_6\text{-}C)$ cluster via a shared Fe_2Ru face. It was formed by formal cleavage of P—C(sp) and C≡C bonds in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ in a reaction of the latter with $Fe_2(CO)_9$.

Experimental Section

Toluene was dried over sodium and distilled from sodium/benzophenone under nitrogen before use. $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**)[9] and $Fe_2(CO)_9$[10] were prepared by the cited procedures. Preparative thin-layer chromatography (TLC) was performed on 20 × 20 cm glass plates using a 0.5 mm thick adsorbent (silica gel 60, GF_{254}, Merck). Microanalyses were performed by the Canadian Microanalytical Service, Delta, British Columbia V4G 1G7, Canada. NMR spectra were recorded on a Bruker ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer 1720X FT spectrometer (NaCl optics, calibrated using polystyrene absorption at 1601.4 cm^{-1}). FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressure typically 10^{-6} mbar; the FAB voltage was 7 kV and current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 mol dm^{-3} solutions in dichloromethane; a drop was added to a drop of matrix, and the mixture was applied to the FAB probe tip.

Synthesis of $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$ (6). A mixture of **1** (220 mg, 0.17 mmol) and $Fe_2(CO)_9$ (300 mg, 0.82 mmol) in toluene (15 mL) was heated in a Carius tube (40 h, 100 °C). TLC (SiO_2; petroleum ether/acetone, 4/1) separated **2** (R_f 0.6; 20 mg, 9%), orange **5** (R_f 0.4; 80 mg, 35%), and brown **6** (R_f 0.3; 92 mg, 35%) (crystals from CH_2Cl_2/MeOH), mp > 300 °C dec. Anal. Calcd for $C_{43}H_{20}Fe_3O_{17}P_2Ru_5\cdot CHCl_3$: C, 33.46; H, 1.31. Found: C, 34.17; H, 1.30. ν(CO) (C_6H_{12}): 2066 (w), 2028 (vs), 2009 (m), 1993 (w), 1982 (vw), 1971 (vw), 1949 (vw) cm^{-1}. ^{13}C NMR: δ ($CDCl_3$) 127.9–129.2, 130.2–133.1 (2 × m, Ph), 138.15 (d), 140.75 (d), 142.17 (t, ipso C), 193.08 (m), 198.18 (s), 199.17 (d), 201.77 (s), 203.16 (s), 208.98 (s), 214.90 (s), 215.27 (d, CO). FAB MS: m/z 1543 ($[M]^+$), 1487–1151 ($[M - nCO]^+$, n = 2–14). Two other minor products, purple **3** (R_f 0.20; 9 mg, 4%) and green **4** (R_f 0.15; 2 mg, 1%), were also isolated. Details of the characterization of **3–5** have been given elsewhere.[11]

Table I. Crystallographic Data for $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}\cdot CHCl_3$ (**6**)

$C_{43}H_{20}Fe_3O_{17}P_2Ru_5\cdot CHCl_3$	monoclinic, $P2_1/c$ (No. 14)
$M_r = 1662.9$	$T \approx 295$ K
$a = 14.341\ (3)$ Å	$\lambda = 0.7107_3$ Å
$b = 18.357\ (5)$ Å	$\rho_c = 2.11$ g cm^{-3}
$c = 23.679\ (10)$ Å	μ(Mo Kα) = 23.1 cm^{-1}
$\beta = 123.10\ (2)°$	$R^a = 0.056$
$V = 5222$ Å^3	$R_w{}^b = 0.057$
$Z = 4$	

^{a} $R = \sum\Delta|F|/\sum|F_o|$. ^{b} $R_w = (\sum\Delta w|F|^2/\sum w|F_o|^2)^{0.5}$.

Table II. Selected Bond Distances (Å) in $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}\cdot CHCl_3$ (**6**)

Ru(1)–Ru(2)	2.830(2)	Ru(1)–P(1)	2.282(4)
Ru(1)–Ru(5)	2.943(2)	Ru(2)–P(1)	2.290(4)
Ru(1)–Fe(6)	2.814(3)	Ru(3)–P(2)	2.287(5)
Ru(1)–Fe(8)	2.913(2)	Ru(4)–P(2)	2.294(6)
Ru(2)–Ru(5)	2.946(2)	Ru(1)–C(A)	2.04 (1)
Ru(2)–Fe(6)	2.815(3)	Ru(2)–C(A)	2.06 (1)
Ru(2)–Fe(7)	2.859(2)	Ru(3)–C(B)	2.04 (2)
Ru(3)–Ru(4)	2.733(2)	Ru(4)–C(B)	2.01 (1)
Ru(3)–Ru(5)	2.824(2)	Ru(5)–C(A)	2.05 (2)
Ru(3)–Fe(7)	2.829(3)	Ru(5)–C(B)	2.15 (1)
Ru(4)–Ru(5)	2.905(2)	Fe(6)–C(A)	1.89 (2)
Ru(4)–Fe(8)	2.857(3)	Fe(7)–C(A)	1.94 (1)
Ru(5)–Fe(7)	2.710(3)	Fe(7)–C(B)	1.89 (1)
Ru(5)–Fe(8)	2.664(3)	Fe(8)–C(A)	1.91 (1)
Fe(6)–Fe(7)	2.737(4)	Fe(8)–C(B)	1.92 (2)
Fe(6)–Fe(8)	2.752(3)	C(A)···C(B)	2.46 (2)
Fe(7)–Fe(8)	2.648(3)		

X-ray Crystallography. Structure Determination. A unique diffractometer data set was measured within the limit $2\theta_{max} = 50°$, yielding 7538 independent reflections, 4434 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement in the standard $P2_1/c$ setting after Gaussian absorption correction and solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Statistical weights (derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$) were used; neutral-atom complex scattering factors were employed.[12] Computation used the XTAL 3.0 program system[13] implemented by S. R. Hall. Pertinent results are given in Figure 1 and Tables I–III.

Abnormal Features. Thermal motion of the chloroform solvent molecule is very high, but disorder was not resolvable and the site occupancy did not differ significantly from unity, at which value it was constrained, with difference residues of ca. 1 e $Å^{-3}$ in its vicinity. Extinction effects were not significant.

Results

The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; Scheme I)[9] and $Fe_2(CO)_9$ (toluene; 40 h, 100 °C) gave three pentanuclear complexes, namely an isomer of **1**, $Ru_5(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)(CO)_{13}$ (**2**),[1] and $MRu_4(\mu_5\text{-}C)(\mu\text{-}dppm)(CO)_{13}$ [M = Fe (**3**), Ru (**4**)],[11] together with the hexanuclear cluster $FeRu_5C(\mu\text{-}PPh_2)_2(CO)_{14}$ (**5**)[11] and the novel octanuclear iron–ruthenium cluster $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$ (**6**). The

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Table III. Non-Hydrogen Fractional Atomic Coordinates for $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}\cdot CHCl_3$ (**6**)

atom	*x*	*y*	*z*
Ru(1)	0.8085(1)	0.17160(7)	0.76611(6)
Ru(2)	0.8603(1)	0.03717(7)	0.83557(6)
Ru(3)	0.4821(1)	−0.03435(7)	0.70527(6)
Ru(4)	0.4177(1)	0.08804(7)	0.62695(6)
Ru(5)	0.6271(1)	0.08665(7)	0.75759(6)
Fe(6)	0.8499(2)	0.0472 (1)	0.7136 (1)
Fe(7)	0.6868(2)	−0.0299 (1)	0.7139 (1)
Fe(8)	0.6331(2)	0.0950 (1)	0.64733(9)
C(11)	0.760 (1)	0.2610 (9)	0.7814 (7)
O(11)	0.732 (1)	0.3152 (6)	0.7897 (6)
C(12)	0.893 (1)	0.2166 (9)	0.7409 (7)
O(12)	0.953 (1)	0.2445 (7)	0.7274 (6)
C(21)	0.861 (1)	0.013 (1)	0.9123 (8)
O(21)	0.868 (1)	0.0003 (7)	0.9613 (6)
C(22)	0.980 (1)	−0.0270 (8)	0.8622 (9)
O(22)	1.053 (1)	−0.0652 (7)	0.8790 (7)
C(31)	0.500 (1)	−0.0870 (9)	0.7792 (8)
O(31)	0.514 (1)	−0.1173 (7)	0.8250 (6)
C(32)	0.418 (1)	−0.1163 (8)	0.6512 (8)
O(32)	0.379 (1)	−0.1652 (6)	0.6169 (6)
C(41)	0.360 (1)	0.1841 (8)	0.6145 (8)
O(41)	0.316 (1)	0.2399 (6)	0.6050 (6)
C(42)	0.325 (1)	0.0690 (8)	0.5363 (7)
O(42)	0.272 (1)	0.0575 (7)	0.4784 (5)
C(51)	0.623 (1)	0.0559 (9)	0.8316 (8)
O(51)	0.6277(9)	0.0406 (8)	0.8798 (6)
C(52)	0.558 (1)	0.1731 (9)	0.7576 (8)
O(52)	0.5191(9)	0.2259 (6)	0.7612 (6)
C(61)	0.995 (1)	0.0610 (9)	0.7594 (9)
O(61)	1.0895(9)	0.0658 (8)	0.7867 (7)
C(62)	0.856 (1)	−0.046 (1)	0.6985 (8)
O(62)	0.884 (1)	−0.1026 (6)	0.6891 (7)
C(63)	0.831 (2)	0.084 (1)	0.6401 (9)
O(63)	0.828 (1)	0.1076 (8)	0.5934 (6)
C(71)	0.648 (1)	−0.0990 (9)	0.6535 (8)
O(71)	0.621 (1)	−0.1438 (7)	0.6129 (6)
C(72)	0.724 (1)	−0.093 (1)	0.7795 (9)
O(72)	0.740 (1)	−0.1396 (6)	0.8180 (6)
C(81)	0.597 (2)	0.0745 (9)	0.5650 (9)
O(81)	0.570 (1)	0.0656 (8)	0.5092 (5)
C(82)	0.597 (1)	0.1894 (9)	0.6302 (9)
O(82)	0.567 (1)	0.2479 (6)	0.6137 (7)
C(0A)	0.747 (1)	0.0683 (8)	0.7376 (6)
C(0B)	0.554 (1)	0.0248 (8)	0.6659 (6)
P(1)	0.9427(3)	0.1483 (2)	0.8763 (2)
C(111)	1.087 (1)	0.1658 (8)	0.9075 (7)
C(112)	1.118 (1)	0.2361 (9)	0.9022 (8)
C(113)	1.230 (1)	0.254 (1)	0.9307 (9)
C(114)	1.307 (1)	0.203 (1)	0.9639 (9)
C(115)	1.282 (1)	0.134 (1)	0.9698 (9)
C(116)	1.171 (1)	0.1149 (9)	0.9419 (8)
C(121)	0.932 (1)	0.1860 (8)	0.9434 (8)
C(122)	1.028 (1)	0.1927 (9)	1.0089 (8)
C(123)	1.016 (1)	0.2145 (9)	1.0595 (8)
C(124)	0.916 (2)	0.230 (1)	1.0508 (8)
C(125)	0.821 (1)	0.224 (1)	0.9861 (9)
C(126)	0.831 (1)	0.201 (1)	0.9339 (8)
P(2)	0.3213(3)	0.0300 (2)	0.6655 (2)
C(211)	0.189 (1)	−0.0189 (8)	0.6123 (7)
C(212)	0.164 (1)	−0.0519 (8)	0.5533 (8)
C(213)	0.068 (1)	−0.0927 (9)	0.5175 (8)
C(214)	0.001 (1)	−0.1023 (9)	0.5404 (9)
C(215)	0.022 (1)	−0.069 (1)	0.599 (1)
C(216)	0.119 (1)	−0.0274 (9)	0.6348 (8)
C(221)	0.297 (1)	0.0864 (8)	0.7193 (7)
C(222)	0.359 (1)	0.080 (1)	0.7878 (8)
C(223)	0.342 (2)	0.128 (1)	0.825 (1)
C(224)	0.265 (2)	0.183 (1)	0.797 (1)
C(225)	0.203 (2)	0.188 (1)	0.729 (1)
C(226)	0.220 (2)	0.140 (1)	0.6891 (9)
Cl(1)	0.765 (1)	0.1122 (8)	1.1639 (7)
Cl(2)	0.572 (1)	0.047 (1)	1.0796 (8)
Cl(3)	0.666 (1)	0.120 (1)	1.0332 (7)
C	0.685 (3)	0.064 (2)	1.097 (2)

molecular structure of **6** was determined at 295 K by a single-crystal X-ray study, and a plot of the molecule is shown in Figure 1; significant bond distances are given in the caption. Non-hydrogen atomic coordinates are listed in Table III.

The central Fe_3Ru_5 core consists of an Fe_3Ru_3 octahedron fused to an Fe_2Ru_3 square pyramid by the shared Fe(7)Fe(8)Ru(5) face. The two carbide atoms, C(A) and C(B), are found in the center of the octahedral and the base of the square pyramidal clusters, respectively, C(B) being 1.15 (2) Å below the Fe_2Ru_2 plane. Opposite Ru(1)Ru(2) and Ru(3)Ru(4) edges are bridged by P(1) and P(2), respectively, of the two PPh_2 groups. All metal atoms carry two terminal CO ligands; in addition, Fe(6) carries a CO ligand which incipiently bridges the Fe(6)–Fe(7) vector [Fe(6)–C(62)–O(62) = 162 (2)°]. Unlike the case of $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_3(CO)_{14}$,[14] there are no bridging CO groups.

The "outer" Fe–Ru separations (average 2.85 Å) are similar to the mean of the corresponding Fe–Fe [average 2.75 Å; cf. 2.64 Å in $Fe_5(\mu_5\text{-}C)(CO)_{15}$[15]] and Ru–Ru distances [average 2.91 Å; cf. 2.89 Å in $Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)(CO)_{13}(\eta\text{-}PhMe)$[16]] in related complexes; the phosphido-bridged Ru–Ru distances (average 2.78 Å) are similar to that [2.771 (1) Å] found in $Ru_5(\mu\text{-}H)_3(\mu_5\text{-}C)(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$.[17] Of note are the shorter "inner" Fe–Fe (2.65 Å) and Fe–Ru distances (2.66, 2.71 Å) in the shared face. Short M–M bonds have also been found in electron-precise $Ru_8(CO)_{17}(\eta^6\text{-}tol)(\mu_4\text{-}S)_2$[18] and electron-rich $[Ru_8(\mu\text{-}H)(\mu_6\text{-}H)(CO)_{21}]^{2-}$.[19] No explanation for this feature is immediately obvious. The Ru–C(carbide) distances [average 2.04 Å, except Ru(5)–C(B), 2.15 Å] are normal; the Fe–C(carbide) distances (average 1.91 Å) are considerably longer than those found in $Fe_5(\mu_5\text{-}C)(CO)_{15}$ (average 1.75 Å) but fall within the range found in $[Fe_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$.[20]

The spectroscopic properties of **6** include an all-terminal IR $\nu(CO)$ spectrum and well-resolved ^{13}C resonances for the phenyl and CO carbons, but no resonances were found which could be assigned to the interstitial carbido carbons, either in the anticipated regions[21] or further downfield to δ 600. The FAB mass spectrum contained a molecular ion at *m/z* 1543, together with ions formed by loss of between 2 and 14 of the CO groups.

Discussion

The title complex has an unusual metal core containing face-sharing Fe_2Ru_3C and Fe_3Ru_3C carbide clusters. The metal connectivity (6) of Ru(5) is one of the highest that has been observed in metal clusters of this size, this atom being within bonding distance of all other metal atoms except Fe(6). It is also attached to both carbido atoms and to two CO ligands, giving it a coordination number of 10. This part of the cluster resembles the packing of the central metal atom in a close-packed array. The two M_4C planes containing the carbide atoms have a dihedral angle of 64.59 (9)°. The electron count of this cluster ($17CO + 2PPh_2 + 2C + 8M = 112$) agrees with that expected from Mingos' method[22] of calculating electron counts for polyhedra containing shared faces ($86 + 74 - 48 = 112$). However, the cluster as a whole has two electrons more than the total required if each metal atom were to achieve an 18 e configuration.

In the formation of **6**, formal cleavage of the P—C(sp) and C≡C bonds in **1** has occurred in the C_2PPh_2 ligand; one Ru–Ru bond has also been cleaved, with a Fe_3 unit inserting into the

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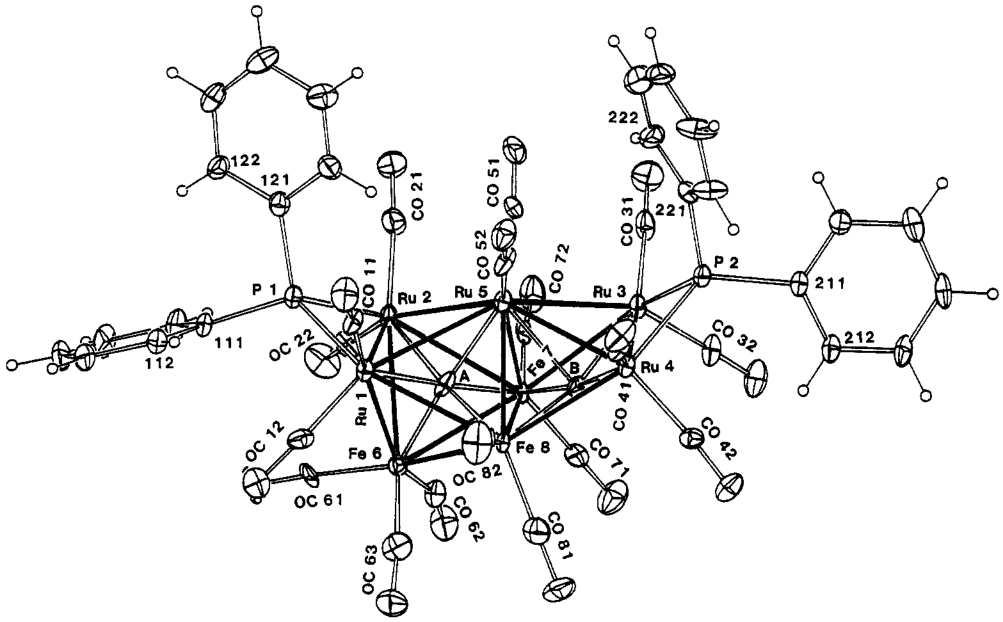
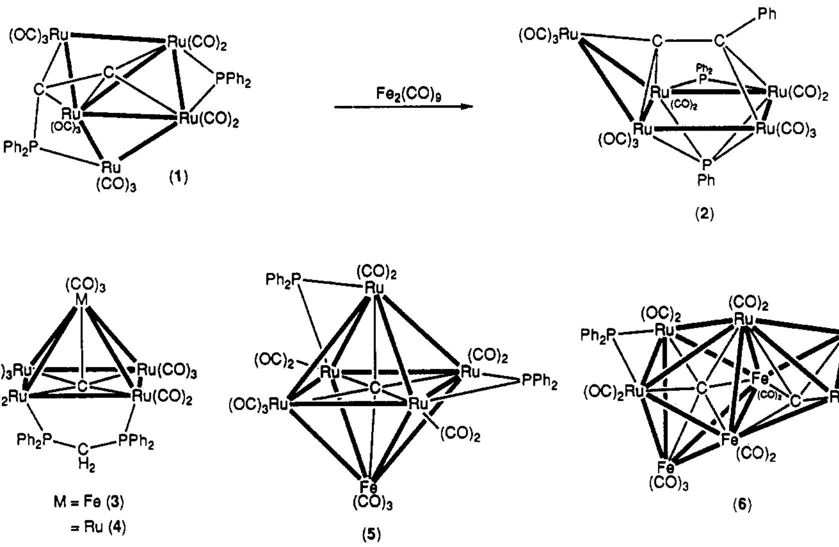


Figure 1. Plot of a molecule of $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}\cdot CHCl_3$ (**6**) (20% thermal ellipsoids for non-hydrogen atoms).

Scheme I



C≡C bond. One possible route to the formation of **6** is via condensation of smaller heterometallic carbide units such as complexes **3**–**5**. In the case of **3** and **4**, which are obtained in only small yield, it may be that the intermediates leading to their formation are also responsible for the formation of **6**. The overall reaction by which **6** is formed from $C_2(PPh_2)_2$, $Ru_3(CO)_{12}$, and $Fe_2(CO)_9$ in three steps has resulted in conversion of the phosphinoalkyne into two C atoms and two PPh_2 groups:

$$Ph_2PC{\equiv}CPPh_2 \xrightarrow{Ru_3(CO)_{12}} \underset{(\text{in } 1)}{Ph_2PCC + PPh_2} \xrightarrow{Fe_2(CO)_9} \underset{(\text{in } 6)}{2PPh_2 + 2C}$$

We have previously described cleavage reactions of the C≡C bond in **1** leading to the formation of (C + Me) (by hydrogenation)[16] or (C + CH) (in reactions with cyclopentadienes)[23] and of the P—C(sp) bond to give C_2 (reaction with CO);[16] this is the first occasion on which we have observed formation of two carbido carbons, further illustrating the rich variety of chemistry exhibited by **1**.[24]

The source of the H atoms in the dppm ligands on **3** and **4** is unknown. However, they may come from trace amounts of water in the $Fe_2(CO)_9$ used; the use of extensively dried $Fe_2(CO)_9$ resulted in lower yields of **3** and **4**. Conversely, when 1 equiv of water was added, the amount of **4** increased although that of **3** remained about the same. Under the above reaction conditions, hexanuclear **5** did not react with $Fe_2(CO)_9$. Monitoring the original reaction by TLC showed that $Fe_3(CO)_{12}$ was the only other product formed in the early stages of the reaction that was not present in the final workup. The reactions of **1** with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ produced results similar to those obtained with $Fe_2(CO)_9$; the reaction with $Fe(CO)_5$ was somewhat slower, and no $Fe_3(CO)_{12}$ was formed during this reaction. Complex **6** remains unchanged on heating in refluxing toluene overnight.

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Supplementary Material Available: Tables of crystal and refinement data, hydrogen positional and isotropic displacement parameters, atomic anisotropic displacement parameters, bond distances, and bond angles for **6** (Tables S1–S5) (10 pages); a listing of observed and calculated structure factor amplitudes for **6** (Table S6) (20 pages). Ordering information is given on any current masthead page.

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