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Reactions of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$, with $PhC{\equiv}CH$ and the phospha-alkyne, $^tBuC{\equiv}P$. Crystal and molecular structures of the four diiron complexes $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, $[Fe_2(CO)_5(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}CHC(CO)Ph]$, $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}{}^tBuCP)]$, and $[Fe_2(CO)_5(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}PC(CO){}^tBu)]$ *

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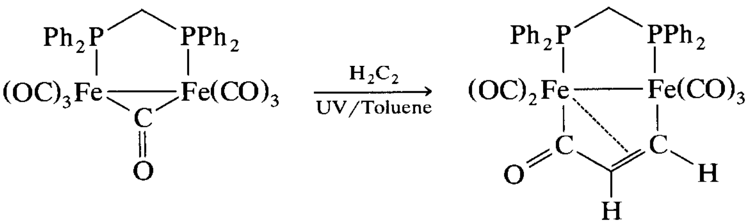
Abstract

The alkyne and phospha-alkyne complexes $[Fe_2(CO)_5(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}CHC(CO)Ph)]$, $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}{}^tBuCP)]$, and $[Fe_2(CO)_5(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}PC(CO){}^tBu]$ have been synthesized. Their structures are discussed together with that of $[Fe_2CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$.

1. Introduction

Knox *et al.* [1] have studied the reactivity of organic species at dinuclear metal centres in order to provide a greater understanding of the reactivity of organic compounds at metal surfaces. As a part of this investigation, the reaction of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]$ (M = Fe, Ru) with alkynes under UV irradiation afforded the complexes $[M_2(CO)(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2$ $(R'C = C(CO)R'')]$, (R' and R'' = H, Me, Ph) as the major products.

More recently, the mixed metal dimer $[FeRu(CO)_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ was found [2] to undergo similar reactions with alkynes and the resulting complexes to undergo a number of further interesting reactions [3,4]. The reaction of acetylene with $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ under UV irradiation led initially to $[Fe_2(CO)_5(\mu\text{-}dppm)(\mu\text{-}\eta^2\text{-}HCCH(CO))]$ (Scheme 1), and subsequently to a series of insertion products, finally giving a coordinated tropone complex [5,6]. Un-



Scheme 1.

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expected reactions, such as P–C bond cleavage within the dppm ligand to afford μ-PR_2 units, have also been reported [7].

In previous papers [8–10], we established the similarity in reactivity between alkynes and phospha-alkynes, RC≡P, mainly in mononuclear metal complexes, and it therefore was of interest to study the reactions of the phosphaalkynes with diiron systems.

2. Results and discussion

2.1. Reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ with $^tBuC{\equiv}P$

UV irradiation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**), with $^tBuC{\equiv}P$ in toluene for 9 h [8] gives a red-purple crystalline complex (45% yield), formulated as $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}PC(CO)^tBu)]$ (**2**), (Scheme 2).

The IR spectrum of **2** shows both terminal carbonyl stretching bands at 2040m, 1985sh, 1974s, and 1934m cm^{-1}, and bridging carbonyl absorption bands at 1753w and 1720w cm^{-1}, which are similar to those observed for the alkyne complexes [5,6].

The $^{31}P\{^1H\}$ NMR spectrum of **2** at 32.4 MHz is deceptively simple, only exhibiting two singlets. The high field peak is readily attributable to the phosphorus nuclei of the dppm backbone, by analogy with data published [5] for $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}R'CC(CO)\text{-}R'']$, which all give signals with similar chemical shifts, and the low field resonance can therefore be assigned to the coordinated $^tBuC{\equiv}P$. Since the dppm resonance for complex **2** could result from either a small chemical shift difference or arise from a fluxional process in solution, as observed [6] for the related alkyne complex at elevated temperatures, the 145.8 MHz $^{31}P\{^1H\}$ NMR spectrum of **2** was recorded and the dppm resonance observed as an AB quartet ($\delta(P)_A = 52.2$ and $\delta(P)_B = 50.3$ ppm, $^2J(PP) = 91$ Hz). Further small couplings to the phospha-alkyne (*ca.* 10 Hz and *ca.* 5 Hz) allow the two dppm phosphorus nuclei to be distinguished. The structure proposed for **2** was subsequently confirmed by a single X-ray crystal study (Fig. 1). As expected, the P–C bond length in the coordinated phospha-alkyne in **2** is elongated, 1.741(9) Å, compared with that, 1.544 Å, for the free ligand, and is longer than that in simple mononuclear η^2-phospha-alkyne complexes, such as $[Pt(PPh_3)_2(\eta^2\text{-}^tBuC{\equiv}P)]$ [11] and even than that in free phospha-alkenes, (1.67 Å [12,13]. The P–C bond length in **2** is comparable with that in the pseudotetrahedral complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^2\text{-}^tBuC{\equiv}P)]$ [14,15], 1.719(3) Å.

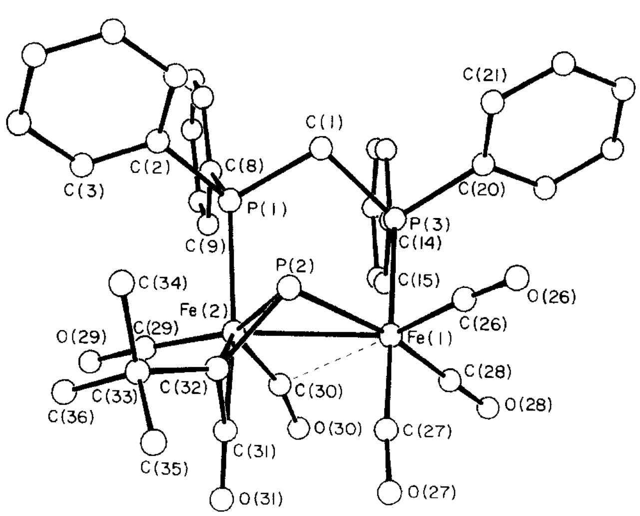
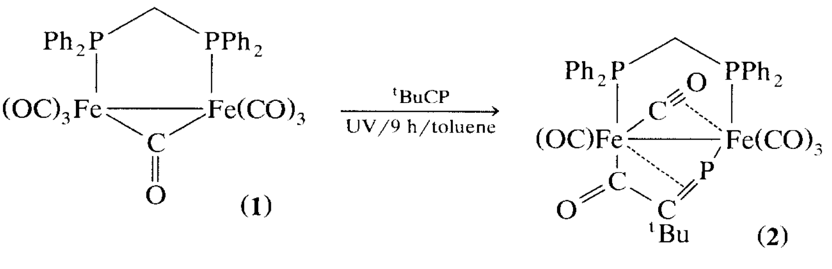
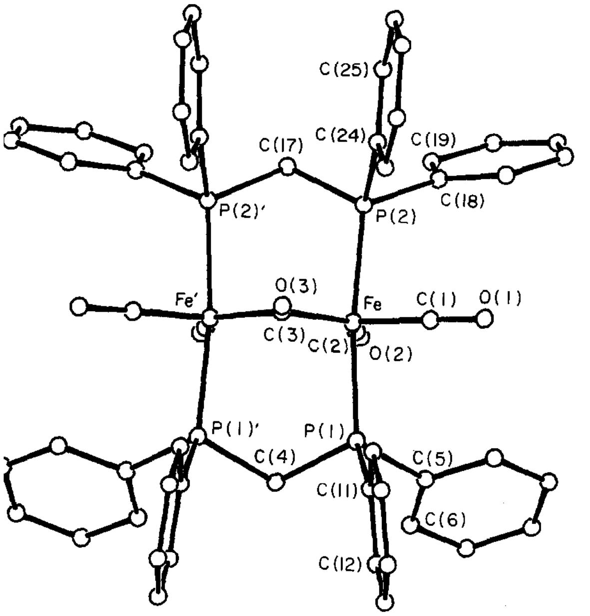


Fig. 1. Molecular structure of $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}PC(CO)^tBu)]$ (**2**). Selected bond lengths (Å) and bond angles (°) Fe(1)–Fe(2) 2.780(2); Fe(1)–P(2) 2.343(2); Fe(1)–P(3) 2.284(2); Fe(1)–C(27) 1.786(9); Fe(2)–P(1) 2.274(2); Fe(2)–P(2) 2.295(3); Fe(2)–C(30) 1.752(9); P(2)–C(32) 1.741(9); Fe(2)–C(31) 1.965(8); Fe(1)···C(30) 2.808(9); Fe(2)–C(32) 2.149(8); Fe(2)–Fe(1)–P(2) 52.37(6); Fe(2)–Fe(1)–P(31) 85.72(6).

When the diiron dppm backbone in the phospha-alkyne complex **2** is compared with that in the diiron complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ **1** [10] and the related *bis*-dppm complex $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$ (**3**), whose molecular structure we determined by a single crystal X-ray study during this work, several important differences are observed (Fig. 2). The length of the Fe–Fe bond in **3** is not significantly different from that of the mono-dppm complex **1**, (2.711(1) Å) in **3** *cf.* 2.709(2) Å, in **1**, but the Fe–Fe bond in the phospha-alkyne complex **2**, (2.780(2) Å), is significantly longer, probably owing to the steric requirements of



Scheme 2.



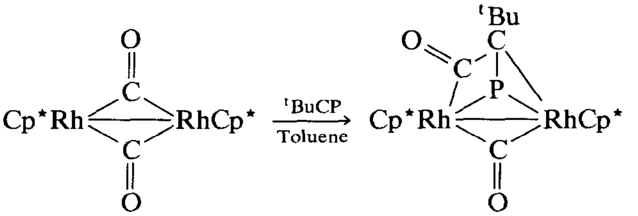
ig. 2. Molecular structure of [$Fe_2(CO)_4(\mu$-$CO)(\mu$-dppm$)_2$] (**3**). Se- cted bond lengths (Å) and bond angles (°) Fe–P(1) 2.212(2); Fe–P(2) .212(2); Fe–C(1) 1.727(6); Fe–C(2) 1.789(6); Fe–C(3) 1.959(6); 'e···Fe' 2.711(1); C(2)–Fe–C(3) 138.8(3); P(1)–Fe–P(2) 170.35(7); (1)–Fe–C(1) 88.9(2).

he ^{t}BuC≡P ligand. The Fe–P distances to the dppm ackbone are different in all three complexes, increasng in the order: **3**, 2.212(2) Å; **1**, 2.254(3) Å; and **2**, .279(2) Å (average). The major difference between omplex **2** and the alkyne complex is the distance from he two iron centres to the η^2-ligand. In the phoshaalkyne complex, the bond between Fe(2) and P(2) is horter, 2.295(3) Å, than the bond Fe(1)–P(2), 2.343(2) , whereas in the alkyne complex the opposite is the ase. This difference presumably reflects the stronger nteraction of the metal centre with the phospha-alyne π-system than with the alkyne π-system.

Previously [16,17] in related work on metal comlexes of phospha-allenes, $R^1P=C=CR^2{}_2$, (R^1 = ,4,6-$^tBu_3C_6H_2$, R^2 = Ph), we observed a preferential igation of metal-ligand fragments [ML_2], (M = Pd, Pt, = PPh_3), to the P=C bond rather than to the C=C nit. This increased interaction of a transition-metal entre with the P=C π-system compared with that with he C=C π-system has also been demonstrated recently y PE studies and theoretical calculations on related ^{4}-1,3-diphosphacyclobutadiene metal systems, [M(η^4-$_2C_2{}^tBu_2$)L_n], M = Co, L_n = C_5H_5; M = Fe, L_n = $CO)_3$], and η^4-cyclobutadiene complexes.

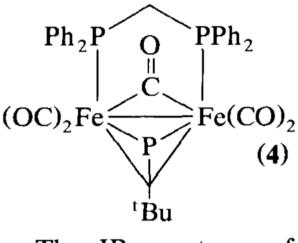
Another interesting feature of the molecular strucure of **2** is the presence of a semi-bridging carbonyl. emi-bridging carbonyls are well known, and Cotton 18] attributed the phenomenon in the structurally related complex [$Fe_2(CO)_7$(bipy)] (bipy = bipyridine) to differences in electron density at the two iron centres. By analogy, the Fe(1) atom in the phospha-alkyne complex **2** is expected to have a higher electron density than the Fe(2) centre.

Confirmation of the existence of a bridging PC(CO)^{t}Bu unit in **2** is of interest with regard to our previous results on a similar type of complex from the reaction of ^{t}BuC≡P with [$Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$], which affords either [$Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-CO)(COP-^{t}Bu)] or [$Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-CO(PC^{t}Bu$)_2$)CO], depending on the conditions [19]. The structure proposed for the former, which was originally based solely on NMR and IR data, is similar to that now firmly established for **2**.



The likely mechanism for the phospha-alkyne insertion reaction leading to **2** presumably involves an initial formation of an η^2-alkyne complex, as was proposed in a study by Bursten *et al.* [20] of the insertion reaction of alkynes into [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_2(\mu$-$CO)_2$] using laser flash photolysis. Because of the asymmetry of the phospha-alkyne, the insertion step can involve two possible orientations to give complexes containing new C–C or P–C bonds, but only the former is observed experimentally.

The reaction between [$Fe_2(CO)_6(\mu$-$CO)(\mu$-dppm)] and ^{t}BuC≡P was also carried out under prolonged UV irradiation (12–30 h) in toluene, and resulted in an oily mixture containing several further products. A small number of brown crystals suitable for a single crystal X-ray study was obtained by using a toluene/petroleum ether solvent mixture, and the new compound proved to be the μ-η^2-phospha-alkyne complex [$Fe_2(CO)_4(\mu^2$-$CO)(\mu$-η^2-^{t}BuCP)], (**4**).



(**4**)

The IR spectrum of **4** shows terminal carbonyl stretches at 1984s cm^{-1} and 1958s cm^{-1}, and a bridging mode at 1734 cm^{-1}, while in its ^{31}P{^{1}H} NMR spectrum the resonance at +74.2 ppm can be assigned to the two dppm ligands and the resonance at −88.8

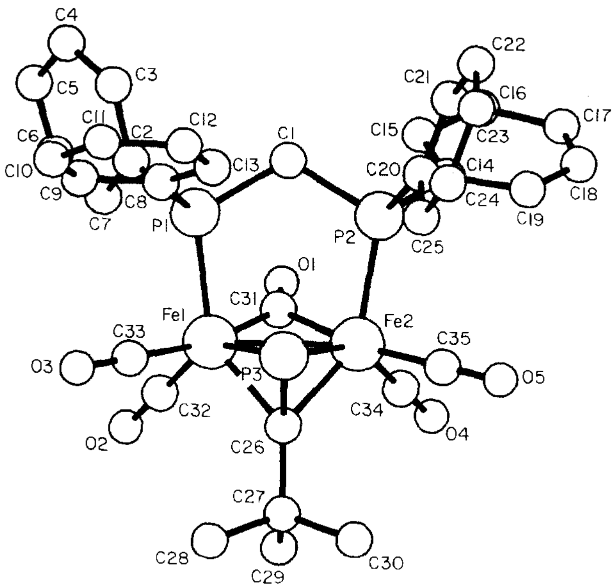
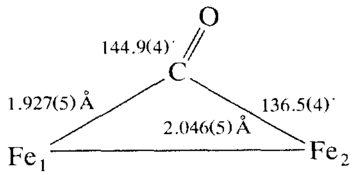


Fig. 3. Molecular structure of $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}^tBuCP)(\mu\text{-dppm})]$ (4). Selected bond lengths (Å) and bond angles (°) Fe(1)–Fe(2) 2.519(1); Fe(1)–P(1) 2.258(2); Fe(1)–P(3) 2.294(1); Fe(2)–P(2) 2.247(2); Fe(1)–C(26) 2.032(5); Fe(2)–P(3) 2.298(2); P(3)–C(26) 1.702(6); Fe(2)–Fe(1)–P(1) 97.74(5); Fe(2)–Fe(1)–P(3) 56.79(4).

ppm to the coordinated phospha-alkyne. As expected, the latter high field resonance is very different from that observed in 2. The single crystal X-ray study confirmed that 4 is a symmetrical complex (Fig. 3) containing a bridging carbonyl like that in $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (1) and $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$ (3), and a symmetrically bridging η^2-ligated ^{t}BuC≡P.

The length of the coordinated phospha-alkyne P–C bond in 4 (1.702(6) Å) is similar to that in $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^2\text{-}P{\equiv}C^tBu)]$, and the geometry might therefore be considered as being pseudotetrahedral with an additional bridging carbonyl ligand. However, an interesting alternative viewpoint arises if the structure of 4 is compared with that of the well known dinuclear complex $[Fe_2(CO)_9]$. If the dppm ligand in 4 is considered to be equivalent to two terminal carbonyls in $[Fe_2(CO)_9]$ and the μ-η^2-phospha-alkyne in 4 replaces two of the three bridging carbonyls, there is a close similarity of the Fe–Fe bond lengths in 4 (2.519(1) Å) and $[Fe_2(CO)_9$ (2.523(1) Å) both of which are much shorter than those found in the dppm-iron complexes 1, 2.709(2) Å, and 3, 2.711(1) Å.

Unlike 1 and 3, the bridging carbonyl in 4 is asymmetrical with respect to the molecular plane of symmetry. Likewise, although the Fe(1)–C bond (1.927(5) Å) is shorter than the Fe(2)–C bond (2.046(5) Å), the Fe(1)–P and Fe(2)–P bond lengths and Fe(1)–P (alkyne) and Fe(2)–P (alkyne) distances in the rest of the molecule show no distortion.



Scheme 3. The twisted bridging carbonyl in complex 4.

2.2. Reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ with PhC≡CH

In order to obtain an alkyne complex that is closer in terms of steric bulk to the phosphaalkyne complexes, PhC≡CH was irradiated with 1 in toluene for 12 h to afford an orange powder (35%), which is formulated as $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-HCC(CO)Ph})]$, (5). The IR spectrum of 5 exhibits terminal carbonyl bands at 2037s, 1973s, 1961sh, and 1911m cm^{-1}, and bridging carbonyl bands at 1732w and 1698w cm^{-1}, which are similar to those observed for $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-HCC(CO)H})]$. The $^{31}P\{^1H\}$ NMR spectrum of 5 shows the expected characteristic AB quartet $\delta(P_A) = 68.1$ and $\delta(P_B) = 52.3$ ppm, $^2J(PP) = 115$ Hz), which suggests a similar molecular structure to that of the acetylene complex ($\delta(P) = +74.2$ ppm and $\delta(P) = -88.8$ ppm). The molecular structure of 5, which was determined by

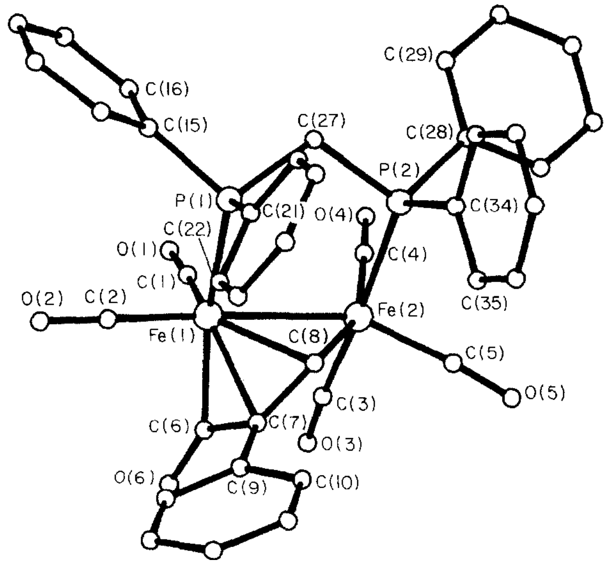


Fig. 4. Molecular structure of $[Fe_2(CO)_5(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-CHC(CO)Ph})]$ (5). Selected bond lengths (Å) and bond angles (°) Fe(1)–Fe(2) 2.690(1); Fe(1)–P(1) 2.259(2); Fe(2)–P(2) 2.285(2); Fe(1)–C(8) 2.073(6); Fe(1)–C(7) 2.137(6); Fe(1)–C(6) 1.917(6); Fe(2)–C(8) 1.979(6); C(7)–C(8) 1.376(9); Fe(2)–Fe(1)–P(1) 92.98(5); Fe(2)–Fe(1)–C(1) 81.9(2).

a single crystal X-ray diffraction study is shown in Fig. 4.

3. Experimental section

All manipulations were carried out under dry argon or dinitrogen, or *in vacuo*. All reactions were handled by standard vacuum and/or Schlenk tube techniques. All solvents were dried by standard methods and were freshly distilled before use unless otherwise stated. For air-sensitive compounds, the solvents were degassed by repeated freeze-thaw methods. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP80SY (32.4 MHz), WM360 (145.8 MHz), or AC250SY (101.3 MHz) spectrometer, operating in FT mode. Infra-red spectra were recorded on a Perkin-Elmer 1710 FT spectrometer. Elemental analyses for carbon and hydrogen were carried out by Miss M. Patel and Miss K. Plowman of this School. [$Fe_2(CO)_6(\mu$-CO)(dppm)] [8], [$Fe_2(CO)_4(\mu$-CO)(dppm)$_2$] [8], and $^tBuC{\equiv}P$ [21–23] were prepared by published procedures.

3.1. Reaction of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)] with $^tBuC{\equiv}P$

To a solution of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)], (0.69 g, 1 mmol), in toluene (40 ml) was added $^tBuC{\equiv}P$ (0.1 g, 1 mmol). The mixture was stirred under UV irradiation for 9 h. The solution was reduced in volume by half *in vacuo* and then cooled to −20°C for 12 h to give red-purple crystals of 1-dicarbonyl-2-tricarbonyl-μ-(*bis*(diphenylphosphino)-methane-*P*,*P*)-μ-[1-phospha-2-tert-butyl-3-oxo-prop-en-1,3-diyl-$C^2(Fe^1)$-, $C^3(Fe^1)$, $P(Fe^1, Fe^2)$]diiron(Fe–Fe). [$Fe_2(CO)_5(\mu$-dppm$)(\mu$-η^2-$P{=}C(CO)^tBu)$], (0.36 g, 45%). (Found: C, 56.1; H, 4.2; $C_{36}H_{31}Fe_2O_6P_3$. Requires: C, 56.6; H, 4.1%). $^{31}P\{^1H\}$ NMR (toluene): $\delta(P_A) = +52.2$ ppm, $\delta(P_B) = +50.3$ ppm, $\delta(P_C) = +319.4$ ppm; $^2J(P_AP_B) = 91$ Hz, $J(P_AP_C)$ *ca.* 5 Hz, $J(P_BP_C)$ *ca.* 10 Hz. ^1H NMR (d_8-toluene): $\delta = 1.3$ ppm (s, ^tBu), $\delta = 3.0$ ppm (m, CH_2), and $\delta = 7.1$–7.9 ppm (m, Ph). IR ν(CO) (nujol): 2040m, 1985sh, 1974s, 1934m, 1753w, and 1720w cm^{-1}.

3.2. Extended reaction of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)] with $^tBuC{\equiv}P$

To a solution of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)], (0.69 g, 1 mmol), in toluene (25 ml) was added an excess of $^tBuC{\equiv}P$, (0.44 g, 4.4 mmol). The mixture was stirred under UV irradiation for 30 h and volatiles then removed *in vacuo*. The resulting brown oil was dissolved in toluene/60-80 petroleum ether (2:1), and eluted through a silica column. The resulting brown solution was reduced in volume to 2 ml and then kept at −20°C for 7 days to afford a few crystals of 1,2-dicarbonyl-μ-carbonyl-μ-(*bis*(diphenylphosphino)methane-*P*,*P*)-μ-η-(2,2-dimethylpropylidynephosphine)diiron(Fe–Fe). $^{31}P\{^1H\}$ (toluene): $\delta(P_A) = +74.2$ ppm and $\delta(P_B) = -88.8$ ppm. IR ν(CO) (60-80 petroleum ether): 1984s, 1958s, and 1734 cm^{-1}.

3.3. Reaction of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)] with $PhC{\equiv}CH$

A solution of [$Fe_2(CO)_6(\mu$-CO$)(\mu$-dppm)], (0.8 g, 1.42 mmol), and $PhC{\equiv}CH$, (0.2 ml, 2 mmol), in toluene (60 ml) was stirred under UV irradiation for 19 h. An orange precipitate was collected, washed with cyclohexane (10 ml), and dried *in vacuo* to yield 1-dicarbonyl-2-tricarbonyl-μ-(*bis*(diphenylphosphino)methane-*P*,*P*)-μ-[2-phenyl-3-oxo-prop-en-1,3-diyl-$C^1(Fe^1, Fe^2)$, $C^2(Fe^1)$, $C^3(Fe^1)$]diiron(Fe–Fe). [$Fe_2(CO)_5(\mu$-dppm$)(\mu$-η^2-$HC{=}C(CO)Ph)$], (0.35 g, 35%). (Found: C, 60.35; H, 3.8; $C_{39}H_{28}Fe_2O_6P_2$. Requires: C, 61.13; H, 3.68%). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): $\delta(P_A) = +68.1$ ppm, $\delta(P_B) + 52.3$ ppm, $^2J(P_AP_B) = 115$ Hz. ^1H NMR ($CDCl_3$): $\delta = 2.9$ ppm (m, CH_2), $\delta = 6.7$ ppm (m, HC=C). IR ν(CO) (nujol): 2037s, 1973s, 1961sh, 1911m, 1732w, and 1698w cm^{-1}.

4. Crystallographic studies

4.1. Compound 2. Crystal data-$C_{36}H_{31}Fe_2O_6P_3 \cdot CH_2Cl_2$

M = 849.2, monoclinic, space group $P2_1/c$, $a = 18.176(4)$, $b = 11.696(2)$, $c = 18.312(5)$ Å, $\beta = 100.29(2)°$, $U = 3830.4$ Å^3, $Z = 4$, $D_c = 1.47$ g cm^{-3}. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 10.6$ cm^{-1}. Data were collected using a crystal *ca.* $0.4 \times 0.4 \times 0.2$ mm on an Enraf-Nonius CAD4 diffractometer and a total of 6716 unique reflections was measured and 4531 reflections with $I > \sigma(I)$ were used in the refinement. The Fe and P atoms were located using MULTAN and the remaining non-hydrogen atoms located on difference maps. Refinement was by full matrix least squares with anisotropic temperature factors. The structure is of lower quality then the others owing to partial occupancy of the dichloromethane solvate atoms which refined to 0.7 presumably because of loss of solvate during mounting of the crystal. The crystal data were calculated for the idealized formula. The final residuals were $R = 0.078$, $R' = 0.109$. The atom coordinates are listed in Table 1.

4.2. Compound 4. Crystal data-$C_{42}H_{39}Fe_2O_5P_3$

M = 828.4, triclinic, space group $P\bar{1}$, $a = 12.002(4)$, $b = 12.827(6)$, $c = 13.535(4)$ Å, $\alpha = 82.72(3)$, $\beta = 73.80(3)$, $\gamma = 88.70(3)°$, $U = 1984.7$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 8.9$ cm^{-1}. Data were collected using a crystal *ca.* $0.3 \times 0.2 \times 0.08$ mm on an Enraf-Nonius CAD4 diffractometer. A total of 4856 unique reflections was measured and 3449 reflections with $|F^2| > 3\sigma(F)^2$ were used in the refinement. The positions of most non-hydrogen atoms were located using the heavy atoms routines of SHELX-86. Refinement was by full matrix least squares using the programmes from the Enraf-Nonius SDP-PLUS package. The refinement converged to give $R = 0.047$, $R' = 0.059$. The atom coordinates are listed in Table 2.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound **2**

	x	y	z
Fe(1)	6465.5(7)	1531.4(9)	648.6(6)
Fe(2)	7566.8(7)	3206.6(9)	900.3(6)
P(1)	7695.3(12)	3182.2(16)	2158.4(10)
P(2)	6326.0(12)	3454.0(17)	957.1(11)
P(3)	6870.0(11)	1022.9(16)	1857.8(11)
O(26)	4906(4)	1045(7)	756(5)
O(27)	5942(5)	2106(7)	−916(3)
O(28)	6849(5)	−737(6)	125(4)
O(29)	8954(4)	4479(8)	936(5)
O(30)	8257(4)	1357(5)	193(3)
O(31)	7299(4)	3631(6)	−717(3)
C(1)	7008(4)	2239(6)	2492(4)
C(2)	7533(4)	4578(6)	2574(4)
C(3)	7990(6)	5448(7)	2440(5)
C(4)	7877(7)	6559(7)	2715(6)
C(5)	7314(7)	6761(8)	3112(6)
C(6)	6871(6)	5887(7)	3238(5)
C(7)	6958(5)	4796(7)	2955(5)
C(8)	8582(4)	2722(7)	2735(4)
C(9)	9135(5)	2251(7)	2410(5)
C(10)	9769(5)	1852(8)	2855(5)
C(11)	9868(6)	1927(8)	3625(6)
C(12)	9319(6)	395(9)	3920(6)
C(13)	8679(5)	2797(7)	3487(5)
C(14)	7724(4)	183(6)	2145(4)
C(15)	8174(5)	−198(7)	1667(4)
C(16)	8851(5)	−777(8)	1933(6)
C(17)	9073(5)	−904(7)	2735(5)
C(18)	8634(5)	−524(8)	3191(5)
C(19)	7960(5)	24(6)	2929(4)
C(20)	6191(4)	126(6)	2214(4)
C(21)	5659(5)	584(7)	2581(5)
C(22)	5128(5)	−99(8)	2812(5)
C(23)	5114(5)	−1240(8)	2657(5)
C(24)	5636(5)	−1710(7)	2303(6)
C(25)	6167(5)	−1044(7)	2054(5)
C(26)	5524(5)	1260(8)	732(5)
C(27)	6170(6)	1923(8)	−301(5)
C(28)	6729(6)	138(8)	338(5)
C(29)	8390(6)	4009(8)	940(5)
C(30)	7956(5)	2007(8)	541(5)
C(31)	7170(5)	3700(7)	−120(4)
C(32)	6695(5)	4282(6)	319(4)
C(33)	6621(5)	5618(7)	232(5)
C(34)	6323(9)	6135(9)	877(6)
C(35)	6092(9)	5807(11)	−506(7)
C(36)	7372(8)	6152(10)	218(9)
C(37)	986(7)	4271(13)	5570(7)
Cl(1)	1265(3)	3163(4)	5151(2)
Cl(2)	207(2)	4024(5)	5994(2)

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for compound **4**

	x	y	z	U_{eq} [a]
Fe(1)	205.3(6)	2680.6(6)	8186.2(5)	38.0(2)
Fe(2)	2083.6(6)	2499.9(6)	6811.3(5)	36.7(2)
P(1)	−967.1(11)	1877.6(11)	7460.1(10)	36(1)
P(2)	1402.9(11)	1628.1(11)	5756.8(10)	36(1)
P(3)	883.9(12)	3916.8(12)	6771.3(11)	41(1)
O(1)	1137(3)	516(3)	8213(3)	56(3)
O(2)	134(4)	2086(5)	10360(3)	93(4)
O(3)	−1621(4)	4213(4)	8832(3)	69(3)
O(4)	3958(4)	1447(4)	7515(4)	86(4)
O(5)	3914(4)	3489(4)	5077(3)	76(4)
C(1)	−124(4)	1186(4)	6370(4)	41(4)
C(2)	−1949(4)	824(4)	8227(4)	43(4)
C(3)	−2788(6)	428(6)	7844(5)	72(5)
C(4)	−3530(6)	−384(7)	8426(6)	92(6)
C(5)	−3444(6)	−775(6)	9377(6)	80(6)
C(6)	−2606(6)	−420(6)	9749(5)	81(6)
C(7)	−1865(5)	388(5)	9184(5)	58(5)
C(8)	−1930(4)	2738(4)	6906(4)	40(4)
C(9)	−3015(5)	2970(5)	7543(5)	61(5)
C(10)	−3737(5)	3660(6)	7170(6)	76(6)
C(11)	−3403(5)	4137(5)	6158(6)	71(5)
C(12)	−2342(5)	3922(5)	5532(5)	63(5)
C(13)	−1594(5)	3242(5)	5910(4)	47(4)
C(14)	2178(4)	428(4)	5421(4)	44(4)
C(15)	1811(5)	−574(5)	5858(5)	62(5)
C(16)	2496(7)	−1433(5)	5569(6)	82(6)
C(17)	3561(6)	−1315(6)	4838(5)	80(5)
C(18)	3925(6)	−314(6)	4411(6)	79(6)
C(19)	3260(5)	539(5)	4692(5)	68(5)
C(20)	1345(4)	2262(4)	4472(4)	37(4)
C(21)	1171(5)	1646(5)	3757(4)	62(5)
C(22)	1057(6)	2101(6)	2801(5)	73(5)
C(24)	1120(6)	3176(6)	2569(5)	65(5)
C(24)	1311(5)	3794(5)	3256(5)	62(5)
C(25)	1429(5)	3330(5)	4213(4)	48(4)
C(26)	1605(4)	3668(5)	7693(4)	44(4)
C(27)	2226(5)	4332(5)	8224(4)	57(4)
C(28)	1375(7)	5147(6)	8737(6)	104(6)
C(29)	2738(6)	3697(7)	9022(5)	96(6)
C(30)	3210(6)	4937(6)	7389(6)	79(6)
C(31)	1093(4)	1422(4)	7940(4)	43(4)
C(32)	173(5)	2300(5)	9501(4)	56(4)
C(33)	−899(5)	3626(5)	8574(4)	51(4)
C(34)	3208(5)	1852(5)	7260(5)	55(4)
C(35)	3165(5)	3137(5)	5757(4)	50(4)
C(36)	6135(8)	2233(7)	1674(7)	108(8)
C(37)	6133(8)	2661(9)	699(6)	118(8)
C(38)	5281(11)	3386(11)	555(8)	154(12)
C(39)	4396(9)	3669(9)	1339(8)	131(10)
C(40)	4422(8)	3218(8)	2324(7)	123(8)
C(41)	5250(7)	2516(7)	2493(6)	98(7)
C(42)	7020(10)	1496(10)	1836(10)	160(12)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.3. Compound 5. Crystal data-$C_{39}H_{28}Fe_2O_6P_2$, CH_2Cl_2 M = 851.2, orthorhombic, space group $P2_12_12$ (No 18), $a = 21.707(3)$, $b = 16.409(4)$, $c = 10.483(1)$ Å, $U = 3734.0$ Å^3, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $F(000) = 1568$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 9.0$ cm^{-1}. Data were collected using a crystal *ca.* 0.2 × 0.15 × 0.10 mm on an Enraf-Nonius CAD4 diffractometer. A total of 3705 unique reflections was measured and 2251 reflections with $|F^2| > 3\sigma(F)^2$ were used in the refinement. The structure was solved using the direct methods routines of SHELX-86. Non-hydrogen atoms were refined anisotropically by full matrix least squares. The refinement converged at $R =$

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) for compound **5**

	x	y	z	U_{eq} [a]
Fe(1)	6597.4(4)	2417(0(5)	2447.9(9)	33.1(2)
Fe(2)	7728.3(4)	1873.2(5)	1835.5(9)	33.4(2)
P(1)	6952.8(7)	3654.7(10)	3037.9(16)	33(1)
P(2)	8232.9(7)	3038.8(10)	2409.6(17)	32(1)
O(1)	6474(2)	2615(4)	−282(4)	74(4)
O(2)	5328(2)	2904(3)	2892(6)	81(4)
O(3)	7145(3)	468(3)	626(5)	65(3)
O(4)	8012(3)	2315(4)	−836(5)	81(4)
O(5)	8714(2)	805(3)	2688(7)	87(4)
O(6)	6007(2)	773(3)	2382(5)	57(3)
C(1)	6548(3)	2545(4)	790(6)	44(4)
C(2)	5837(3)	2712(4)	2744(7)	49(4)
C(3)	7331(3)	1012(4)	1156(6)	42(4)
C(4)	7914(3)	2164(4)	198(7)	49(4)
C(5)	8346(3)	1249(4)	2348(8)	53(4)
C(6)	6361(3)	1303(4)	2700(6)	39(3)
C(7)	6750(3)	1463(4)	3800(6)	34(3)
C(8)	7289(3)	1857(4)	3490(5)	35(3)
C(9)	6516(3)	1330(4)	5138(6)	42(4)
C(10)	6940(3)	1241(4)	6133(7)	50(4)
C(11)	6738(3)	1111(4)	7365(7)	58(4)
C(12)	6119(4)	1054(5)	7614(8)	70(5)
C(13)	5689(4)	1128(5)	6635(8)	70(5)
C(14)	5901(3)	1260(5)	5407(8)	55(5)
C(15)	6487(3)	4514(4)	2524(7)	39(3)
C(16)	6432(3)	4698(5)	1242(7)	60(5)
C(17)	6052(4)	5320(5)	813(8)	81(6)
C(18)	5715(4)	5754(5)	1670(10)	78(5)
C(19)	5755(4)	5591(6)	2955(9)	94(6)
C(20)	6148(4)	4981(5)	3371(8)	68(5)
C(21)	7058(3)	3815(4)	4745(6)	41(4)
C(22)	6689(4)	3371(4)	5565(7)	55(4)
C(23)	6772(5)	3452(5)	6904(7)	83(6)
C(24)	7214(5)	3971(5)	7371(8)	81(5)
C(25)	7577(4)	4412(5)	6563(8)	72(5)
C(26)	7492(4)	4347(5)	5252(7)	54(4)
C(27)	7702(3)	3904(4)	2331(6)	38(3)
C(28)	8866(3)	3300(4)	1335(6)	37(4)
C(29)	8862(3)	3987(4)	551(7)	50(4)
C(30)	9360(4)	4144(5)	−248(7)	63(5)
C(31)	9851(3)	3626(5)	−275(7)	61(5)
C(32)	9857(3)	2941(5)	484(8)	65(5)
C(33)	9365(3)	2779(5)	1293(7)	55(4)
C(34)	8616(3)	3167(4)	3960(6)	39(3)
C(35)	8630(3)	2554(5)	4881(7)	52(4)
C(36)	8900(4)	2705(6)	6046(8)	77(5)
C(37)	9165(4)	3441(6)	6291(8)	84(6)
C(38)	9169(4)	4048(5)	5378(9)	73(5)
C(39)	8890(4)	3903(5)	4216(7)	58(5)
Cl(1)	281(3)	751(4)	1593(5)	108(4)
Cl(3)	−65(2)	8543(4)	4029(5)	103(4)
Cl(2)	104(3)	295(3)	3629(6)	132(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound **3**

	x	y	z
Fe	1642.0(3)	8690.1(4)	953.4(6)
P(1)	2411(1)	9380(1)	1057(1)
P(2)	816(1)	8115(1)	1041(1)
O(1)	1983(2)	8001(3)	2699(3)
O(2)	986(2)	10034(2)	1071(4)
O(3)	2222(2)	7492(3)	0
C(1)	1843(3)	8271(3)	1986(5)
C(2)	1241(3)	9511(3)	1011(5)
C(3)	1950(3)	8033(4)	0
C(4)	2505(3)	9913(4)	0
C(5)	2359(3)	10070(3)	1984(4)
C(6)	2370(3)	10786(3)	1833(5)
C(7)	2298(4)	11278(4)	2555(6)
C(8)	2211(4)	11052(4)	3433(6)
C(9)	2187(5)	10328(5)	3621(6)
C(10)	2267(5)	9839(4)	2880(6)
C(11)	3116(2)	8999(3)	1263(4)
C(12)	3583(3)	9453(4)	1383(6)
C(13)	4117(3)	9164(4)	1516(7)
C(14)	4193(3)	8430(4)	1532(6)
C(15)	3743(3)	7973(4)	1414(6)
C(16)	3208(3)	8256(4)	1277(5)
C(17)	387(3)	8270(4)	0
C(18)	359(3)	8402(3)	2013(4)
C(19)	−90(3)	8864(4)	1936(5)
C(20)	−411(4)	9066(5)	2703(6)
C(21)	−289(4)	8817(6)	3555(6)
C(22)	161(5)	8334(7)	3662(6)
C(23)	485(4)	8117(6)	2884(6)
C(24)	778(3)	7132(3)	1189(5)
C(25)	250(3)	6807(4)	1223(6)
C(26)	213(4)	6066(4)	1354(7)
C(27)	701(4)	5667(4)	1462(7)
C(28)	1214(3)	5987(3)	1434(6)
C(29)	1255(3)	6725(3)	1302(5)
C(30)	3447(4)	1884(5)	0
C(31)	3691(3)	1668(4)	839(5)
C(32)	4172(3)	1265(5)	832(6)
C(33)	4411(5)	1072(7)	0
C(34)	2923(5)	2353(7)	0
C(35)	1478(7)	3236(10)	0
C(36)	1429(4)	2963(9)	836(8)
C(37)	1303(4)	2270(9)	817(10)
C(38)	1252(6)	1872(7)	0
C(39)	1579(10)	4055(10)	0

0.033, $R' = 0.038$. Atom coordinates are listed in Table 3.

4.4. *Compound 3. Crystal data*-$C_{55}H_{44}Fe_2O_5P_4 \cdot 2C_7H_8$

M = 1204.8, orthorhombic, space group *Pnnm* (No 58), $a = 23.409(5)$, $b = 18.524(3)$, $c = 14.219(9)$ Å, $U = 6165.6$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}. Monochromated Mo Kα radiation, $\lambda = 0.71069$, $\mu = 6.2$ cm^{-1}. Data were collected using a crystal *ca*. 0.4 × 0.3 × 0.2 mm on an Enraf-Nonius CAD4 diffractometer. A total of 5990 unique reflections was measured and 2499 reflections with $|F^2| > 3\sigma(F)^2$ were used in the refinement. The structure was solved using the direct methods routines of SHELX-86. The final residuals were $R = 0.048$, $R' = 0.058$. The molecule has crystallographic mirror symmetry. Atom coordinates are listed in Table 4.

Supplementary data, including full lists of bond lengths and angles, for all four structures have been deposited with the Cambridge Crystallographic Data Centre.

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References

1 A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, *J. Chem. Soc., Dalton Trans.*, (1982) 1297.

2 B.P. Gracey, S.A.R. Knox, K.A. MacPherson, A.G. Orpen and S.R. Stobart, *J. Chem. Soc., Dalton Trans.*, (1985) 1935.

3 A.F. Dyke, S.A.R. Knox, M.J. Morris and P.J. Naish, *J. Chem. Soc., Dalton Trans.*, (1983) 1417.

4 R.E. Colborn, D.L. Davies, A.F. Dyke, A. Endesfelder, S.A.R. Knox, A.G. Orpen and D. Plaas, *J. Chem. Soc., Dalton Trans.*, (1983) 2661.

5 G. Hogarth, F. Kayser, S.A.R. Knox, D.A.V. Morton, A.G. Orpen and M.L. Turner, *J. Chem. Soc., Chem. Commun.*, (1988) 358.

6 G. Hogarth, S.A.R. Knox, B.R. Lloyd, K.A. MacPherson, D.A.V. Morton and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1988) 360.

7 N.M. Doherty, G. Hogarth, S.A.R. Knox, K.A. MacPherson, F. Melchior and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1986) 540.

8 G. de Leeuw, J.S. Field, R.J. Haines, B. McCulloch, E. Meintjies, C. Monberg, G.M. Olivier, P. Ramdial, C.N. Sampson, B. Sigwarth, N.D. Steen and K.G. Moodley, *J. Organomet. Chem.*, *275* (1984) 99.

9 P.B. Hitchcock, T.J. Madden and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1989) 1660.

10 F.A. Cotton and J.M. Troup, *J. Am. Chem. Soc.*, *96* (1974) 4422.

11 J.C.T.R. Burkett-St. Laurent, P.B. Hitchcock, H.W. Kroto and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1981) 1141.

12 H.W. Kroto, J.F. Nixon and K. Ohno, *J. Mol. Spectrosc.*, *90* (1981) 367.

13 R.D. Brown, P.D. Godfrey, and D. McNaughton, *Aust. J. Chem.*, *34* (1981) 465.

14 G. Becker, W.A. Herrmann, W. Kalcher, G.W. Kreichbaum, C. Pahl, C.J. Wagner and M.L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, *22* (1983) 413, Suppl. 501.

15 M.F. Meidine, C.J. Meir, S. Morton and J.F. Nixon, *J. Organomet. Chem.*, *297* (1985) 255.

16 C. Akpan, DPhil thesis, University of Sussex, 1986.

17 C. Akpan, P.B. Hitchcock, M. Yoshifuji and J.F. Nixon, in preparation.

18 F.A. Cotton, *Prog. Inorg. Chem.*, *21* (1976) 1.

19 P.B. Hitchcock, M.J. Maah and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1987) 928.

20 B.E. Bursten, S.D. McKee and M.S. Platz, *J. Am. Chem. Soc.*, *111* (1989) 3428.

21 G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch, 36B* (1981) 16.

22 G. Becker, H. Schmidt, G. Uhl and W. Uhl, *Inorg. Synth.*, *27* (1990) 243.

23 W. Rosch, U. Vogelbacker, T. Allspach and M. Regitz, *J. Organomet. Chem.*, *306* (1986) 39.