Pergamon

0277-5387(95)00145-X

Polyhedron Vol. 14, No. 19, pp. 2723–2743, 1995
Elsevier Science Ltd
Printed in Great Britain
0277–5387/95 $9.50+0.00

REACTIONS OF $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ WITH ALKYNES: STEPWISE SYNTHESIS OF TROPONE AT A DINUCLEAR METAL CENTRE*

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Abstract—The di-iron complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ [**1**; dppm = bis(diphenylphosphino)methane] reacts with alkynes $R^1C{\equiv}CR^2$ under UV irradiation to produce dimetallacyclopentenone complexes $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}CR^1CR^2C(O)\}(\mu\text{-dppm})]$ (**2a–e**; $R^1 = R^2 =$ H, Me or Ph; $R^1 =$ H, $R^2 =$ Me or Ph). The complexes exist in two isomeric forms in which the diphosphine ligand is either *cis* or *trans* with respect to the organic ligand. In the *cis* isomers of complexes **2** the R^1 site is occupied by hydrogen, while in the *trans* isomers the R^1 site is occupied by Me or Ph, suggesting that steric factors control the geometry. The molecular structure of *cis*-$[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}CHCHC(O)\}(\mu\text{-dppm})]$ (**2a**) has been elucidated by X-ray diffraction. The complex exists in the solid state as a mixture of enantiomers, shown by variable temperature NMR spectroscopy to interconvert in solution via ethyne migration from one CO ligand to another. Further reaction of **2a** with ethyne affords $[Fe_2(CO)_4\{\mu\text{-}\sigma,\sigma':\eta^2,\eta^{2'}\text{-}CHCHC(O)CHCH\}(\mu\text{-dppm})]$ (**3**) and $[Fe_2(CO)_4\{\mu\text{-}\eta^3:\eta^{3'}\text{-}C_6H_6C(O)\}(\mu\text{-dppm})]$ (**4**) stepwise, containing two and three molecules of ethyne, respectively. X-ray diffraction studies show that **3** is a pentadienone "fly-over bridge" complex and that **4** is a complex of tropone, stabilized by a weak intramolecular C—H···O hydrogen bond. Addition of diphenylacetylene to *trans*-$[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}CPhCPhC(O)\}(\mu\text{-dppm})]$ (**2e**) affords the "ferrole" complex *trans*-$[Fe_2(CO)_5\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4\}(\mu\text{-dppm})]$ (**5**), also crystallographically characterized. The different pathways for alkyne linking with **2a** and **2e** are traced to steric factors, arising from the different orientations of the diphosphine and organic ligands in the two species.

Over 30 years have passed since Weiss and Hübel[1] reported the isolation of the cycloheptatrienone (tropone) complex $[Fe(CO)_3\{\eta^4\text{-}C_6H_6C(O)\}]$ from the reaction of ethyne with $[Fe_2(CO)_9]$. During that time the reactions of alkynes with metal carbonyls have been shown to be a source of many carbonyl-containing cyclic organic species, including cyclopentadienones, quinones and lactones, in some cases otherwise inaccessible.[2, 3] The pathways for these important syntheses are generally obscure. Thus, for example, no intermediate species were detected in the reaction of ethyne with $[Fe_2(CO)_9]$ leading to the mononuclear tropone complex. In the belief that di-iron species are involved, we sought to stabilize the di-iron unit in $[Fe_2(CO)_9]$, notorious

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*In appreciation of Prof. E. W. Abel's contribution to the practice and profession of chemistry.

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for its propensity to undergo metal–metal bond cleavage, in an effort to isolate such intermediates.

The use of a bridging diphosphine ligand to stabilize a dinuclear metal centre is now well documented.[4, 5] We have adopted this strategy in synthesizing a number of derivatives of the form $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)]$, substitution resulting in both enhanced solubility and stability.[6] We report here the reactions of one of these complexes, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ [**1**; dppm = bis(diphenylphosphino)methane], with alkynes, which has allowed the isolation of a di-iron tropone complex and the intermediates in its construction. Aspects of this work have been communicated previously.[7]

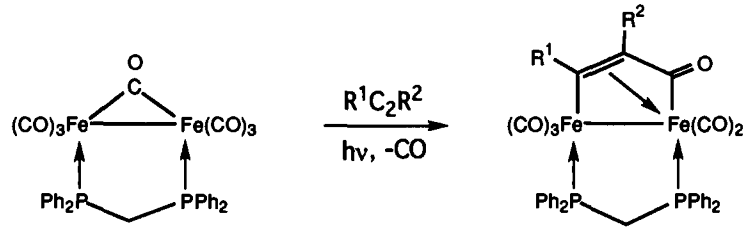
RESULTS AND DISCUSSION

Synthesis and characterization of dimetallacyclopentenone complexes

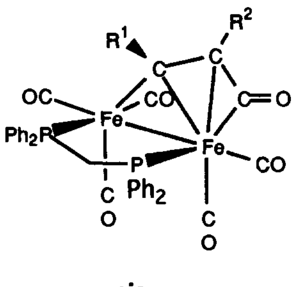
UV irradiation of toluene solutions of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) in the presence of a range of alkynes $R^1C{\equiv}CR^2$ ($R^1 = R^2 =$ H, Me, or Ph; $R^1 =$ H, $R^2 =$ Me or Ph) for 0.3–30 h results in the formation of the red crystalline diferracyclopentenone complexes $[Fe_2(CO)_5\{\mu\text{-}\sigma{:}\eta^3\text{-}CR^1CR^2C(O)\}(\mu\text{-dppm})]$ (**2a**–**e**) in yields varying between 12 and 53%.

Characterization of the complexes **2** was straightforward (Table 1) in the light of our previous studies on the reactions of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with alkynes, which gave analogous diferracyclopentenone species.[8] Those complexes with a proton in the R^1 site, **2a**–**c**, are readily identified by the characteristic low field signal (δ 8–9) of this proton in the ^1H NMR spectrum, arising from the considerable μ-alkylidene character of the $C(R^1)$ carbon atom (see later). With the unsymmetrical alkynes propyne and phenylacetylene, two isomers of the product **2** are clearly possible, depending on which carbon of the alkyne links with CO. In the event, single isomers **2b** and **2c** are produced as a result of the alkyne linking preferentially to CO via the substituted carbon, i.e. the alkynic proton occupies the R^1 site. A similar situation arose in the related cyclopentadienyl-stabilized diferracyclopentenone systems[8] and, since observed for both electron-withdrawing (Ph) and electron-releasing (Me) substituents, it is attributed to a steric effect. Certainly, in **2** the R^2 site is the least crowded, being further from the centre of the molecule, and therefore the favoured position for a non-hydrogen group.

From IR and NMR spectra it is apparent that the complexes **2** fall into two structurally different

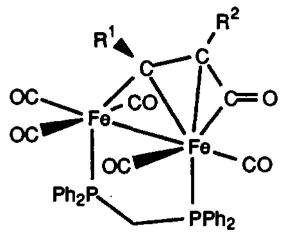


1 **2**



cis

2a, $R^1 = R^2 =$ H
2b, $R^1 =$ H, $R^2 =$ Me
2c, $R^1 =$ H, $R^2 =$ Ph



trans

2d, $R^1 = R^2 =$ Me
2e, $R^1 = R^2 =$ Ph

Table 1. Spectroscopic data for new complexes

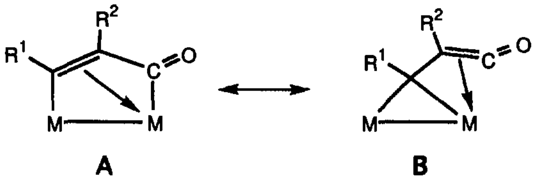
Complex	$\nu(CO)$ $(cm^{-1})^a$	^{31}P NMR^b	^1H NMR^b	^{13}C NMR^b
2a $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2H_2\}(\mu\text{-dppm})]$	2043m, 1975s, 1960sh, 1923w, 1747w, 1725w	67.92 (d, J = 117), 52.03 (d, J = 117)^c	8.63 [ddd, J = 19, 7, 4, 1H, H(2)], 7.60–6.98 (m, 20H, Ph), 4.01 (q, J = 12, 1H, C$\underline{H}$H), 3.63 [dd, J = 7, 2, 1H, H(1)], 2.82 (dt, J = 12, 10, 1H, CH$\underline{H}$)^c	240.2 (d, J = 24, CO), 219.8 (s, CO), 215.0 (d, J = 20, CO), 210.6 (s, C=O), 168.4 [d, J = 22, C(2)], 138.0–128.0 (m, Ph), 44.8 [d, J = 11, C(1)], 44.4 (dd, J = 22, 13, CH_2)^c
2b $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}C(O)CMeCH\}(\mu\text{-dppm})]$	2039s, 1969s, 1956sh, 1923w, 1726m	69.12 (d, J = 120), 55.21 (d, J = 120)	8.24 (dd, J = 18, 4, 1H, CH), 7.88–7.12 (m, 20H, Ph), 4.04 (q, J = 10, 1H, C$\underline{H}$H), 2.93 (dt, J = 14, 10, 1H, CH$\underline{H}$), 1.71 (s, 3H, Me)	210.8 (s, C=O), 164.8 (d, J = 23, CH), 134.6–127.8 (m, Ph), 41.0 (t, J = 12, CH_2), 40.1 (s, $\underline{C}$Me), 20.3 (s, Me)
2c $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}C(O)CPhCH\}(\mu\text{-dppm})]$	2041s, 1975s, 1960sh 1923w, 1743w, 1709w	67.92 (d, J = 112), 52.30 (d, J = 112)^d	9.11 (dd, J = 19, 4, 1H, CH), 7.98–7.10 (m, 25H, Ph), 4.60 (q, J = 11, 1H, C$\underline{H}$H), 3.28 (dt, J = 14, 9, 1H, CH$\underline{H}$)	233.7 (br, CO), 211.3 (s, C=O), 161.4 (d, J = 18, CH), 134.3–127.4 (m, Ph), 41.8 (t, J = 11, CH_2), 40.9 (s, CPh)
2d $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Me_2\}(\mu\text{-dppm})]$	2012m, 1981s, 1948m, 1919m, 1701m	51.76 (d, J = 56), 29.44 (d, J = 56)^e	7.40–7.21 (br, 20H, Ph), 3.44 (m, 2H, CH_2), 2.75 [t, J = 2, 3H, Me(2)], 2.14 [s, 3H, Me(1)]	
2e $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Ph_2\}(\mu\text{-dppm})]$	2022m, 1987s, 1950m, 1931m, 1707m	51.19 (d, J = 54), 28.23 (d, J = 54)^e	7.65–7.08 (m, 30H, Ph), 3.69 (q, J = 12, 2H, CH_2)	220–212 (unres, CO), 189.6 (d, J = 14, C=O), 169.9 [s, C(2), 137.7–125.0 (m, Ph), 29.7 (t, J = 18, CH_2), 20.9 [s, C(2)]
3 $[Fe_2(CO)_4\{\mu\text{-}\sigma:\eta^4\text{-}C_2H_2C(O)C_2H_2\}(\mu\text{-dppm})]$	2010m, 1985s, 1950s, 1657m	50.85 (s)^c	8.17 [q, J = 7, 1H, H(1)], 7.56–7.26 (m, 20H, Ph), 4.57 (t, J = 9, 2H, CH_2), 3.86 [d, J = 7, 2H, H(2)]^c	216.4 (br, CO), 212.2 (br, CO), 204.4 (s, C=O), 177.8 [t, J = 7, C(1)], 131.5–128.7 (m, Ph), 80.0 [t, J = 3, C(2)], 51.9 (t, J = 26, CH_2)^c
4 $[Fe_2(CO)_4(\eta^6\text{-}C_7H_6O)(\mu\text{-dppm})]$	1994m, 1962s, 1935w, 1907sh, 1551w	59.06 (s)^c	7.57–7.09 (m, 20H, Ph), 5.07 (q, J = 13, 1H, C$\underline{H}$H), 4.36 [br, 2H, H(2)], 3.93 [br, 2H, H(1)], 3.60 (q, J = 13, 1H, CH$\underline{H}$), 3.09 [d, J = 7, 2H, H(3)]^c	217.4 (t, J = 5, CO), 212.1 (t, J = 8, CO), 191.3 (s, C=O), 134.5–119.5 (m, Ph), 71.7 [s, C(2)], 66.3 [s, C(1)], 61.2 [s, C(3)], 30.5 (t, J = 20, CH_2)^c
5 $[Fe_2(CO)_4\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)(\mu\text{-dppm})]$	1992m, 1966s, 1934m, 1907m	44.5 (d, J = 72), 26.3 (d, J = 72)	7.9–6.5 (m, 40H, Ph), 4.30 (m, 2H, CH_2)^c	220.8 (d, J = 4.1, CO), 217.7 (d, J = 19.5, CO), 215.9 (J = 16.2, CO), 214.5 (d, J = 12.5, CO), 191.6 (d, J = 28.5, CO), 162.8 (dd, J = 12.0, 7.3 $\underline{C}$Ph), 148.1 (d, J = 6.2, $\underline{C}$Ph), 143.9 (dd, J = 39.0, 16.3, $\underline{C}$Ph), 138–120 (m, Ph), 39.8 (dd, J = 30.0, 11.5, CH_2)^c

^{a} In CH_2Cl_2. ^{b} In CD_2Cl_2 unless otherwise stated. J values in Hz. ^{c} In $CDCl_3$.

groups, **2a–c** and **2d**, **e**. Thus, the patterns of the carbonyl stretching bands in the IR spectrum for the two groups are different, betraying different molecular symmetries, while the ^{31}P NMR data for **2a–c** show the two phosphorus nuclei near 68 and 54 ppm, with a coupling constant of 112–120 Hz, while for **2d**, **e** the corresponding nuclei are seen near 51 and 29 ppm with a coupling constant of 55 Hz. Moreover, although all the complexes **2** undergo the same fluxional process (see below), the energy barrier is very different for the groups **2a–c** and **2d**, **e**. These differences are attributed, in the light of an X-ray diffraction study carried out on **2a**, to the existence of two isomeric forms for the complexes **2**, in which the diphosphine ligand is either *cis* (**2a–c**) or *trans* (**2d**, **e**) with respect to the organic ligand.

Molecular structure of cis-$[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}CHCHC(O)\}(\mu\text{-dppm})]$ (**2a**)

The structure of **2a** as a 1,2-dichloroethane solvate was determined by an X-ray diffraction study, the results of which are given in Table 2. The centrosymmetric crystal structure of $\mathbf{2a}\cdot0.5C_2H_4Cl_2$ contains a racemic mixture of enantiomers **2a′** and **2a″** and two independent molecules which show only slight variations in interatomic distances and bond angles. The structures of each are shown in Fig. 1. The organic ligand is similar to that found in another structurally characterized complex of this type, $[Ru_2(CO)(\mu\text{-CO})\{\mu\text{-}\sigma:\eta^3\text{-CPhCPhC(O)}\}(\eta\text{-}C_5H_5)_2]$.[8] The bonding in such systems has previously been discussed as lying between the extremes of a dimetallacyclopentenone representation (**A**) and a substituted μ-alkylidene representation (**B**).



For **2a′** the relatively short olefinic distance C(17)—C(18) of 1.396(5) Å, when compared to the corresponding distance of 1.423(6) Å found in $[Ru_2(CO)(\mu\text{-CO})\{\mu\text{-}\sigma:\eta^3\text{-CPhCPhC(O)}\}(\eta\text{-}C_5H_5)_2]$, is indicative of more **A** character in the former, as is the larger difference in the metal to C(R^1) carbon distances, i.e. 0.104 Å compared to 0.074 Å.

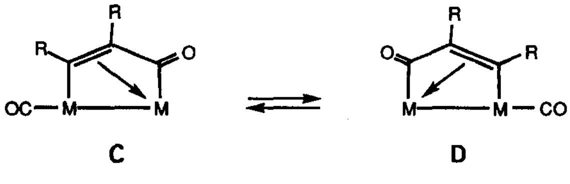
The diphosphine ligand in **2a′** lies *cis* to the μ-carbon C(18), with a dihedral angle of 93.4° between the planes Fe(11)Fe(12)C(18) and Fe(11)Fe(12)P(11)P(12), leading us to conclude that this is the structural arrangement adopted also by **2b** and **2c**, for the reasons outlined earlier. Further, we conclude that **2d** and **2e** have the alternative, isomeric structure in which the diphosphine lies *trans* to C(1), spanning the sites occupied by the carbonyls C(12)O(12) and C(13)O(13) in **2a**. The reason for **2a–c** adopting the *cis* configuration and **2d**, **e** the *trans* can be traced to the steric interactions of the substituent on C(18) which, as shown by inspection of Fig. 1, is held close to two of the phenyl rings of the dppm ligand in the *cis* form. In each of **2a–c** there is a sterically undemanding hydrogen on the μ-carbon and the complexes adopt the *cis* configuration, presumably the thermodynamically more stable form in the absence of steric effects. This is likely to be a consequence of the *fac* geometry of the $Fe(CO)_3$ moiety in **2a–c** and the *mer* arrangement required in **2d** and **2e**, the latter stereochemistry leading to unfavourable competition for π-back-donation between mutually *trans* CO ligands. However, when the μ-carbon carries methyl or phenyl, as in **2d** and **2e**, respectively, the steric demands of these groups apparently destabilize the *cis* form and lead to the adoption of the *trans* structure, in which interaction between the diphosphine phenyl groups and methyl or phenyl on C(1) will be minimal.

During the course of these studies, the complex **2c** was independently synthesized and characterized by X-ray crystallography.[9] The structural features of **2c** are very similar to those of **2a** and confirm the *cis* configuration and the linking of CO with the C(Ph) carbon of the alkyne.

A number of other dimetallacyclopentenone complexes are now known, the majority being formed, as in this instance, via the linking of an alkyne and carbon monoxide at a dinuclear metal centre.[8–13] Indeed, the synthesis of the diruthenium analogue of **2a**, $[Ru_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-CHCHC(O)}\}(\mu\text{-dppm})]$, was achieved by the use of this method.[14]

Fluxionality of the complexes **2**

The complexes **2a**, **2d** and **2e** of symmetrical alkynes are fluxional, undergoing the process depicted below, which was first observed for the dimetallacyclopentenone analogues $[M_2(CO)(\mu\text{-CO})\{\mu\text{-}\sigma:\eta^3\text{-CRCRC(O)}\}(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru).[8]



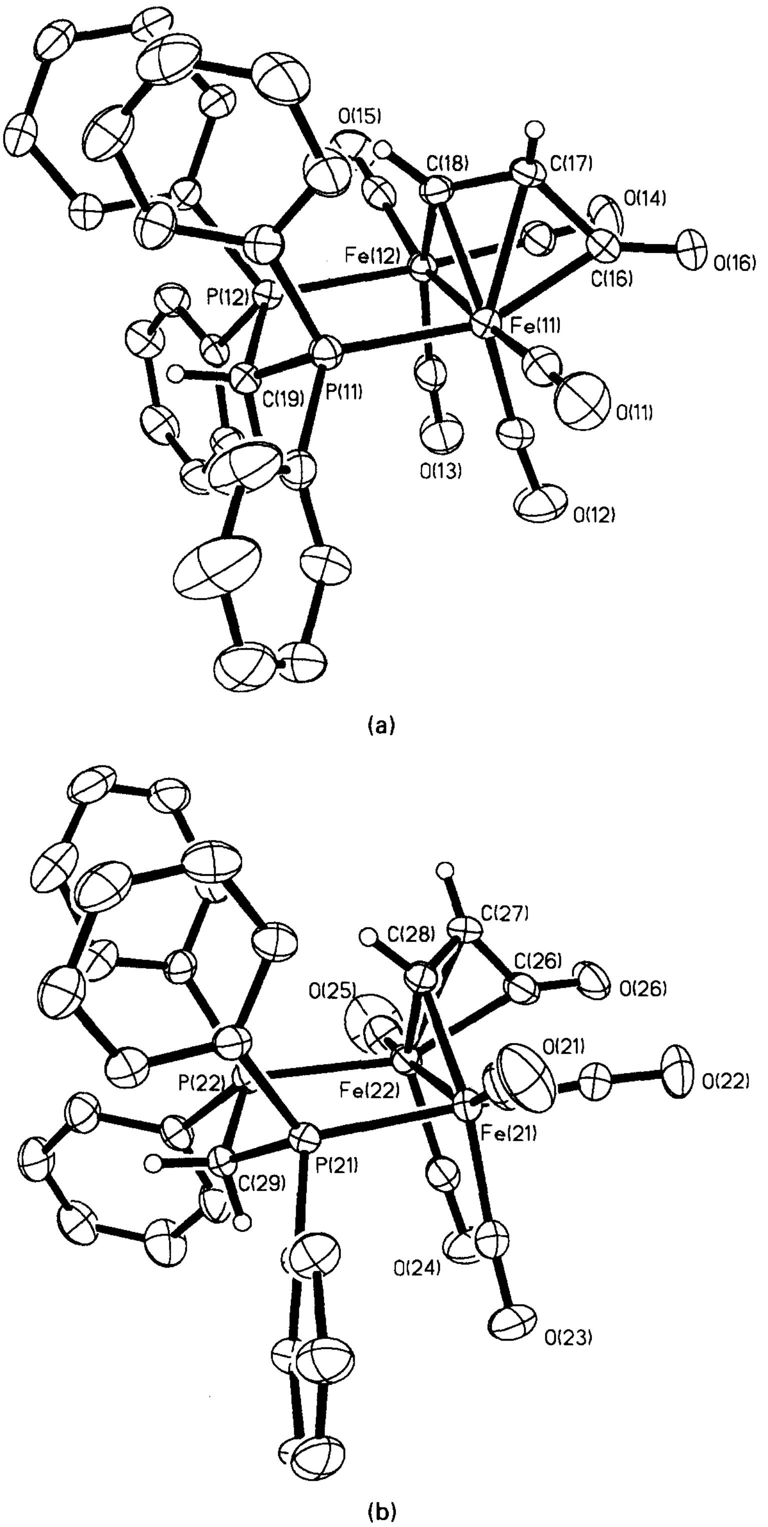


Fig. 1. Molecular structures of the two independent, enantiomeric molecules **2a**′ and **2a**″ (the structure shown for **2a**″ is inverted relative to the coordinates listed). All phenyl group hydrogen atoms have been omitted for clarity.

The species **C** and **D** are enantiomers and their interconversion occurs via reversible linking of the alkyne with two carbon monoxides, which are alternately a terminal CO ligand and a ketonic group of the metallacycle. This rapid carbon–carbon bond making and breaking on the NMR time scale results in the generation of time-averaged mirror symmetry, seen in the coalescence of the alkynic R group signals and those due to the phosphorus nuclei of the dppm ligand. The energy barrier for the process is, however, much lower for the *trans* complexes **2d** and **2e** than for the *cis* complex **2a**. Thus, for **2d** and **2e** the ^{31}P NMR spectrum of the static molecules, i.e. two sharp AB pattern doublets, is seen only at −10°C, while that for **2a** is seen at 30°C. On warming, the signals for **2d** and **2e** broaden, coalesce at about 35°C and sharpen to give singlets at 80°C. For **2a**, broadening and coalescence of the ^{31}P NMR signals occurs on warming to 90°C, but at this temperature new signals appear and by 100°C complete conversion to a new species occurs (see below).

From the coalescence temperatures and limiting low temperature ^{31}P NMR spectra, the free energies of activation of the fluxional process have been calculated, giving values of $\geqslant 70$ kJ mol^{-1} for *cis*-**2a** and 55 (± 2) kJ mol^{-1} for *trans*-**2d** and *trans*-**2e**. As discussed above, the *trans* complexes **2d** and **2e** appear to adopt that structure for steric reasons, and this factor may be responsible for the lower barriers to the fluxional process. Although **2a** has only hydrogen substituents on the alkyne, the μ-carbon has to move substantially while close to the phenyl rings in axial sites on the five-membered Fe_2P_2C ring (which adopts an envelope conformation in both independent molecules present in the crystal structure). Alternatively, it is possible that in **2a**, where the electron-donating phosphorus atoms are directly *trans* to the CO groups, π-back donation from iron to the latter strengthens their coordination and consequently raises the energy barrier of the fluxional process.

The X-ray determination of the structures of both the components of the fluxional process for complex **2a**, i.e. the two enantiomers, gives an unusual insight into the nature of the molecular rearrangement. By reference to Fig. 1 the process can be seen to comprise the cleavage of the C(16)–C(17) bond of **2a′** to generate the terminal carbonyl C(22)O(22) of **2a″** while, simultaneously, C(18) links with the C(14) carbon to regenerate the diferracycle, with C(17) now occupying the bridging site [C(28) in **2a″**]. In effect, the molecule of ethyne "slides" back and forward between the C(16)O(16) and C(14)O(14) carbonyls. Were the C(18) carbon of **2a′** to remain fixed with the C(17) carbon oscillating between carbonyl groups, this process would also average the phosphorus NMR signals, but not the ethynic proton signals, which clearly broaden at high temperature, consistent with the "slide" mechanism described above.

As referred to earlier, above 90°C the complex **2a** transforms into a new species, as do the *cis* analogues **2b** and **2c**. The full description of this complicated isomerization, involving irreversible cleavage of the alkyne–carbonyl bond and the linking of the dppm and alkyne fragments, is beyond the scope of this report; it has been communicated previously.[15] Interestingly, the complexes **2d** and **2e** are thermally stable, presumably because their *trans* geometry precludes linking of the dppm ligand with the alkyne.

Prolonged reaction of [$Fe_2(CO)_6(\mu$-CO)(μ-dppm)] (**1**) *with ethyne*: *stepwise synthesis of tropone*

The optimum reaction time for the production of complex **2a** from [$Fe_2(CO)_6(\mu$-CO)(μ-dppm)] (**1**) and ethyne under UV irradiation is 1 h, when a yield of 53% is obtained. At this stage a second product is also present, the pentadienone complex [$Fe_2(CO)_4\{\mu$-$\sigma:\eta^4$-CHCHC(O)CHCH$\}$(μ-dppm)] (**3**), isolated in 5% yield as orange crystals. After irradiation under ethyne for a further 2 h, the yield of **2a** falls to 15% while that of **3** increases to 28%, and a third product, identified as the brown crystalline tropone complex [$Fe_2(CO)_4\{\mu$-$\eta^3:\eta^{3\prime}$-$C_6H_6C(O)\}$(μ-dppm)] (**4**), appears in 17% yield. Irradiation for a further 1.5 h (4 h in all) affords the latter in an optimum yield of 25%, with **2a** in 13% and **3** in 9% yield.

The complexes **3** and **4** were characterized spectroscopically (Table 1) and by single-crystal X-ray diffraction studies as products from the linking of two and three molecules of ethyne respectively with CO, as described below.

Molecular structure of [$Fe_2(CO)_4\{\mu$-$\sigma:\eta^4$-CHCH-C(O)CHCH$\}$(μ-dppm)](**3**)

The results of an X-ray diffraction study on the "fly-over" pentadienone complex **3** are summarized in Fig. 2 and Table 3. Crystals of **3** contain two crystallographically independent molecules in the asymmetric unit, which differ quite markedly in the disposition and twist of the phenyl groups, a result of a "flip" of the five-membered ring formed by the di-iron unit and diphosphine. It seems likely that the two forms will be near identical in energy, the differences arising from perturbations of the crystal packing forces. The central organo-di-iron-diphosphine cores of the molecules are virtually identical

Table 2. Selected bond lengths (Å) and angles (°) for **2a**·$0.5C_2H_4Cl_2$

Fe(11)—Fe(12)	2.725(1)	Fe(11)—P(11)	2.266(1)	Fe(11)—C(11)	1.764(4)
Fe(11)—C(12)	1.752(4)	Fe(11)—C(16)	1.928(3)	Fe(11)—C(18)	2.084(3)
Fe(11)—C(17)	2.111(3)	Fe(12)—P(12)	2.275(1)	Fe(12)—C(13)	1.817(4)
Fe(12)—C(14)	1.794(4)	Fe(12)—C(15)	1.777(4)	Fe(12)—C(18)	1.980(3)
Fe(21)—Fe(22)	2.709(1)	Fe(21)—P(21)	2.270(1)	Fe(21)—C(21)	1.775(4)
Fe(21)—C(22)	1.795(4)	Fe(21)—C(23)	1.812(4)	Fe(21)—C(28)	1.977(4)
Fe(22)—P(22)	2.277(1)	Fe(22)—C(24)	1.753(4)	Fe(22)—C(25)	1.754(4)
Fe(22)—C(26)	1.922(3)	Fe(22)—C(28)	2.085(3)	Fe(22)—C(27)	2.108(3)
P(11)—C(19)	1.832(4)	P(11)—C(110)	1.827(4)	P(11)—C(120)	1.833(4)
P(12)—C(19)	1.824(3)	P(12)—C(130)	1.831(3)	P(12)—C(140)	1.830(3)
P(21)—C(29)	1.825(3)	P(21)—C(210)	1.833(3)	P(21)—C(220)	1.826(4)
P(22)—C(29)	1.839(4)	P(22)—C(230)	1.834(3)	P(22)—C(240)	1.832(3)
O(11)—C(11)	1.147(6)	O(12)—C(12)	1.148(5)	O(13)—C(13)	1.134(5)
O(14)—C(14)	1.134(5)	O(15)—C(15)	1.143(5)	O(16)—C(16)	1.200(4)
O(21)—C(21)	1.139(5)	O(22)—C(22)	1.136(5)	O(23)—C(23)	1.139(5)
O(24)—C(24)	1.150(5)	O(25)—C(25)	1.145(6)	O(26)—C(26)	1.207(4)
C(16)—C(17)	1.447(5)	C(18)—C(17)	1.396(5)	C(26)—C(27)	1.443(5)
C(28)—C(27)	1.393(5)				

Fe(12)—Fe(11)—P(11)	94.1(1)	Fe(12)—Fe(11)—C(11)	175.6(1)
P(11)—Fe(11)—C(11)	90.1(1)	Fe(12)—Fe(11)—C(12)	84.6(1)
P(11)—Fe(11)—C(12)	103.5(1)	C(11)—Fe(11)—C(12)	93.2(2)
Fe(12)—Fe(11)—C(16)	85.7(1)	P(11)—Fe(11)—C(16)	155.9(1)
C(11)—Fe(11)—C(16)	91.1(2)	C(12)—Fe(11)—C(16)	100.5(2)
Fe(12)—Fe(11)—C(18)	46.3(1)	P(11)—Fe(11)—C(18)	89.2(1)
C(11)—Fe(11)—C(18)	135.2(2)	C(12)—Fe(11)—C(18)	130.3(2)
C(16)—Fe(11)—C(18)	73.2(1)	Fe(12)—Fe(11)—C(17)	75.8(1)
P(11)—Fe(11)—C(17)	114.9(1)	C(11)—Fe(11)—C(17)	103.6(2)
C(12)—Fe(11)—C(17)	137.6(2)	C(16)—Fe(11)—C(17)	41.7(1)
C(18)—Fe(11)—C(17)	38.9(1)	Fe(11)—Fe(12)—P(12)	93.5(1)
Fe(11)—Fe(12)—C(13)	102.1(1)	P(12)—Fe(12)—C(13)	91.1(1)
Fe(11)—Fe(12)—C(14)	91.8(1)	P(12)—Fe(12)—C(14)	174.4(1)
C(13)—Fe(12)—C(14)	89.6(2)	Fe(11)—Fe(12)—C(15)	156.9(1)
P(12)—Fe(12)—C(15)	84.8(1)	C(13)—Fe(12)—C(15)	101.0(2)
C(14)—Fe(12)—C(15)	89.6(2)	Fe(11)—Fe(12)—C(18)	49.5(1)
P(12)—Fe(12)—C(18)	90.8(1)	C(13)—Fe(12)—C(18)	151.6(2)
C(14)—Fe(12)—C(18)	91.2(2)	C(15)—Fe(12)—C(18)	107.4(2)
Fe(22)—Fe(21)—P(21)	94.5(1)	Fe(22)—Fe(21)—C(21)	157.7(1)
P(21)—Fe(21)—C(21)	85.0(1)	Fe(22)—Fe(21)—C(22)	89.6(1)
P(21)—Fe(21)—C(22)	175.9(1)	C(21)—Fe(21)—C(22)	91.0(2)
Fe(22)—Fe(21)—C(23)	102.8(1)	P(21)—Fe(21)—C(23)	90.5(1)
C(21)—Fe(21)—C(23)	99.6(2)	C(22)—Fe(21)—C(23)	89.1(2)
Fe(22)—Fe(21)—C(28)	49.9(1)	P(21)—Fe(21)—C(28)	90.3(1)
C(21)—Fe(21)—C(28)	107.8(2)	C(22)—Fe(21)—C(28)	92.1(2)
C(23)—Fe(21)—C(28)	152.6(2)	Fe(21)—Fe(22)—P(22)	93.7(1)
Fe(21)—Fe(22)—C(24)	83.1(1)	P(22)—Fe(22)—C(24)	103.0(1)
Fe(21)—Fe(22)—C(25)	173.3(1)	P(22)—Fe(22)—C(25)	92.6(1)
C(24)—Fe(22)—C(25)	93.2(2)	Fe(21)—Fe(22)—C(26)	87.4(1)
P(22)—Fe(22)—C(26)	153.7(1)	C(24)—Fe(22)—C(26)	103.2(2)
C(25)—Fe(22)—C(26)	88.0(2)	Fe(21)—Fe(22)—C(28)	46.5(1)
P(22)—Fe(22)—C(28)	88.3(1)	C(24)—Fe(22)—C(28)	129.3(2)
C(25)—Fe(22)—C(28)	136.1(2)	C(26)—Fe(22)—C(28)	73.5(1)
Fe(21)—Fe(22)—C(27)	76.4(1)	P(22)—Fe(22)—C(27)	113.2(1)
C(24)—Fe(22)—C(27)	139.1(2)	C(25)—Fe(22)—C(27)	103.2(2)
C(26)—Fe(22)—C(27)	41.6(1)	C(28)—Fe(22)—C(27)	38.8(1)
Fe(11)—C(11)—O(11)	176.8(4)	Fe(11)—C(12)—O(12)	174.2(4)
Fe(12)—C(13)—O(13)	174.4(3)	Fe(12)—C(14)—O(14)	172.7(4)

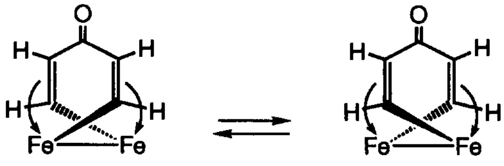
Table 2—*continued*

Fe(12)—C(15)—O(15)	178.1(3)	Fe(11)—C(16)—O(16)	144.6(3)
Fe(11)—C(16)—C(17)	75.9(2)	O(16)—C(16)—C(17)	138.3(3)
Fe(11)—C(18)—Fe(12)	84.2(1)	Fe(11)—C(18)—C(17)	71.6(2)
Fe(12)—C(18)—C(17)	125.2(3)	Fe(11)—C(17)—C(16)	62.4(2)
Fe(11)—C(17)—C(18)	69.5(2)	C(16)—C(17)—C(18)	114.7(3)
P(11)—C(19)—P(12)	111.8(2)	Fe(21)—C(21)—O(21)	176.5(4)
Fe(21)—C(22)—O(22)	173.7(4)	Fe(21)—C(23)—O(23)	176.5(3)
Fe(22)—C(24)—O(24)	175.1(4)	Fe(22)—C(25)—O(25)	177.0(4)
Fe(22)—C(26)—O(26)	145.2(3)	Fe(22)—C(26)—C(27)	76.1(2)
O(26)—C(26)—C(27)	137.5(3)	Fe(21)—C(28)—Fe(22)	83.6(1)
Fe(21)—C(28)—C(27)	126.1(3)	Fe(22)—C(28)—C(27)	71.5(2)
Fe(22)—C(27)—C(26)	62.2(2)	Fe(22)—C(27)—C(28)	69.7(2)
C(26)—C(27)—C(28)	115.6(3)	P(21)—C(29)—P(22)	111.9(2)

and thus only one will be considered in the following discussion. The iron–iron bond, which at 2.545(1) Å is significantly shorter than that in **2a** but within the expected range, is spanned by both the diphosphine moiety and a pentadienone ligand. The latter is coordinated such that the β-carbons of the two π-bound carbon–carbon double bonds are *trans* to the diphosphine while, in contrast, the carbon–iron σ bonds to the alternate metals are located *cis* to the diphosphine. Thus, overall, the pentadienone ligand lies essentially *trans* to the diphosphine moiety, a situation which is in contrast to that found in **2a**. The two CHCHCO units of the pentadienone moiety can be compared to the organic ligand found in **2a**, but in **3** the ketonic carbonyl is no longer bound to the metal; instead, it is held in a central position away from the iron–iron vector as a consequence of the linking of the two alkynes. The carbon–carbon bond lengths in the pentadienone unit indicate a change from partial π-allyl character in **2a** to π-alkene coordination in **3**. Thus, the two coordinated carbon–carbon double bonds are short [C(16)—C(17) 1.393(7), C(19)—C(110) 1.389(7) Å] in comparison with those involving the ketonic carbonyl [C(17)—C(18) 1.471(8), C(18)—C(19) 1.481(8) Å]. The α-carbons C(16) and C(110) bridge the di-iron vector asymmetrically, each having one short [Fe(11)—C(16) 1.960(4), Fe(12)—C(110) 1.954(5) Å] and one long [Fe(11)—C(110) 2.018(5), Fe(12)—C(16) 2.044(5) Å] interaction, while the β-carbons C(19) and C(17) are each bound to only a single metal centre via a slightly longer iron–carbon interaction [Fe(11)—C(19) 2.160(5), Fe(12)—C(17) 2.162(5) Å].

Complexes of this type have previously been obtained from reactions of $[Fe_2(CO)_9]$ with disubstituted alkynes, often being the major reaction product,[3, 16] and several have previously been characterized crystallographically,[17–22] most relevant to this study being the diphosphine complex $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^4\text{-CEtCEtC(O)CEtCEt}\}(\eta^1\text{-dppm})]$,[22] in which the diphosphine is bound in monodentate fashion to a single iron atom. The gross structural features of this complex and **3** are very similar; most notably, and quite remarkably, the iron–iron distances vary by less than 0.001 Å, indicating that it is the pentadienone ligand which demands the short iron–iron contact and not the diphosphine.

Despite the asymmetry of complex **3** in the solid state, the ^{31}P NMR spectrum shows a single resonance. Moreover, at room temperature the ^{1}H NMR spectrum shows a quartet at δ 8.17 ($J = 7$ Hz) and a doublet at δ 3.86 ($J = 7$ Hz) for the α-CH and β-CH protons, respectively, the couplings of these protons to one another and to the two equivalent phosphorus nuclei appearing identical. These observations are consistent with the existence in solution of a low energy fluxional process which generates time-averaged mirror symmetry. In confirmation, the proton signals broaden on cooling, but even at −90 °C no resolution is achieved. It is suggested that the σ–π exchange process shown is occurring, as has been proposed for related pentadienone complexes.[16]



Molecular structure of $[Fe_2(CO)_4\{\mu\text{-}\eta^3:\eta^{3\prime}\text{-}C_6H_6C(O)\}(\mu\text{-dppm})]$ (**4**)

The results of an X-ray diffraction study on the tropone complex $[Fe_2(CO)_4\{\mu\text{-}\eta^3:\eta^{3\prime}\text{-}C_6H_6C(O)\}$

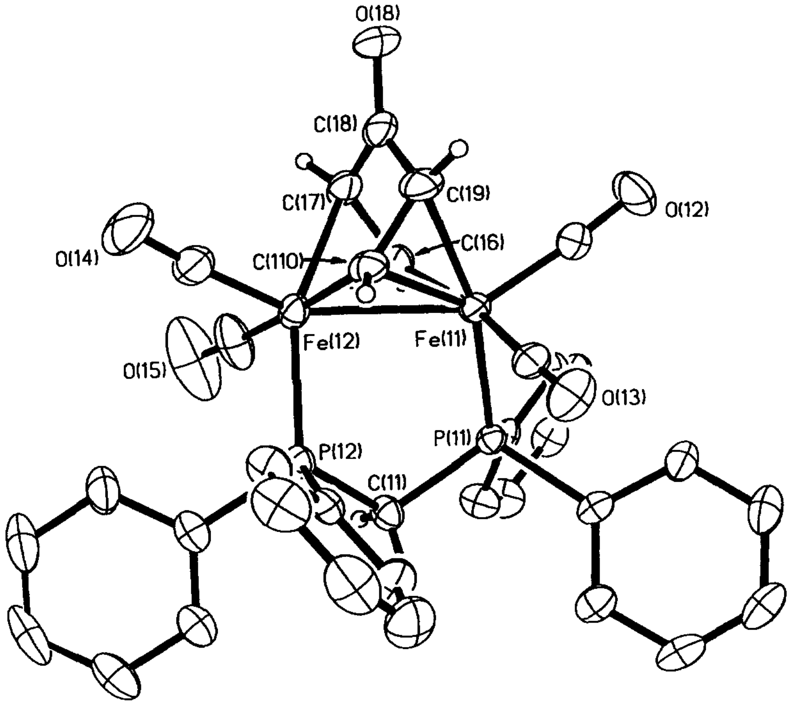


Fig. 2. Molecular structure of **3** showing labelling scheme for the first of the two independent molecules present in the crystal structure. All phenyl group hydrogen atoms have been omitted for clarity.

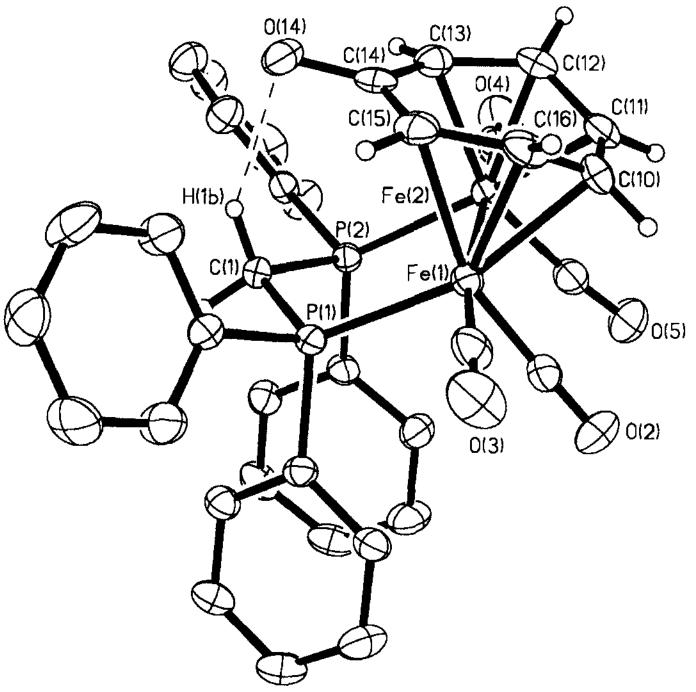


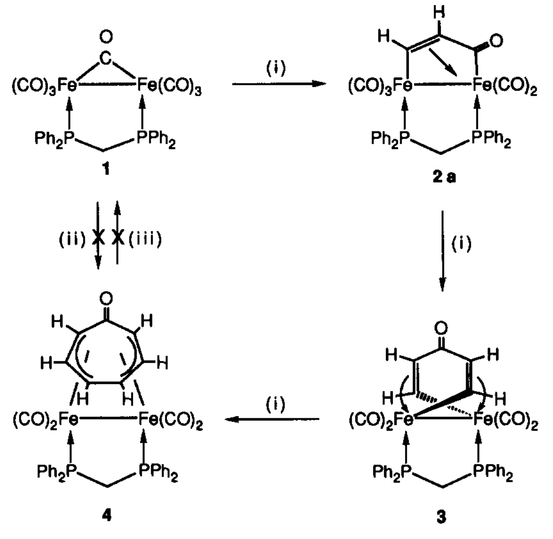
Fig. 3. Molecular structure of **4** showing labelling scheme. All phenyl group hydrogen atoms have been omitted for clarity.

(μ-dppm)] (**4**) are summarized in Fig. 3 and Table 4. The di-iron unit is symmetrically bridged by diphosphine and tropone ligands, the latter interacting with each iron in an η^3 manner as a di-η-allyl ligand. As a consequence, the tropone ring is considerably distorted from the planarity observed in the free molecule.[23] The iron–iron bond is unusually long at 2.950(1) Å, almost certainly a result of the demands of the $\eta^3, \eta^{3'}$-tropone binding. The bridging diphosphine ligand also adopts an unusual geometry, with the $Fe_2P_2CH_2$ ring folded in an envelope conformation which allows the close approach of the methylene hydrogen H(1b) to the tropone oxygen in a weak C—H···O interaction [H(1b)···O(14) 2.32 Å]. This interaction appears to be retained in solution, in view of the relatively low stretching frequency of the ketonic carbonyl in the IR spectrum, namely 1551 cm^{-1} (cf. 1583 cm^{-1} in free tropone and 1637 cm^{-1} in $[Fe(CO)_3\{\eta^4\text{-}C_6H_6C(O)\}]$).[24]

In accord with the mirror symmetry of the solid state structure, the ^{31}P NMR spectrum of **4** in solution shows a single resonance (Table 1), while the ^1H NMR spectrum has three signals for the tropone protons, a doublet at δ 3.09 ($J = 7$ Hz) and two multiplets at δ 4.36 and 3.93, assigned to the protons α, β and γ with respect to the ketonic moiety. The ^{13}C NMR spectrum displays singlets at δ 71.7, 66.3 and 61.2 for the three pairs of equivalent ring carbons, while the ketonic carbonyl appears at δ 191.3. At still lower field, triplets at δ 212.1 ($J = 8$ Hz) and 217.4 ($J = 5$ Hz) are attributable to the two different types of terminal carbonyl ligand, namely those lying *trans* or *cis* to the metal–metal bond.

Mechanism of formation of tropone

The probability of a stepwise **1** → **2a** → **3** → **4** sequence of formation for tropone (Scheme 1) was confirmed by subjecting **2a** and **3** separately to UV irradiation while purging with ethyne for 3–4 h, when **3** and **4** were produced in 9 and 18% yields, respectively.



Scheme 1. Reagents: (i) HC_2H, UV; (ii) tropone, UV; (iii) Me_3NO or CO.

UV irradiation promotes each of the steps shown in Scheme 1 and in its absence reaction of **1** with ethyne results in only a slow 10% conversion to **2a** after 16 h. It is likely that photochemical activation induces CO loss from **1** and **2a** and olefinic bond decoordination in **3**, creating the vacant sites needed for successive coordination of ethyne, and that this is followed at each step by rapid thermal carbon–carbon bond formation, which our previous studies have shown to occur readily at dinuclear metal centres.[25]

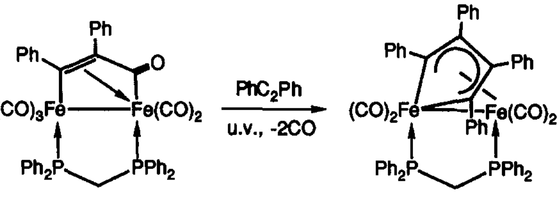
The reaction of $[Fe_2(CO)_9]$ with ethyne yields the mononuclear tropone complex $[Fe(CO)_3\{\eta^4\text{-}C_6H_6C(O)\}]$ as the only tractable product.[1] On the evidence of the studies described here, it is now possible to conclude that this reaction follows a similar sequence to that in Scheme 1, with stepwise ethyne linking occurring at a di-iron centre to give an unstable tropone complex $[Fe_2(CO)_6\{\mu\text{-}\eta^3:\eta^{3'}\text{-}C_6H_6C(O)\}]$, analogous to **4**, which fragments to give $[Fe(CO)_3\{\eta^4\text{-}C_6H_6C(O)\}]$ via release of $Fe(CO)_3$. The isolation of products $[Fe_2(CO)_6\{\mu\text{-}\sigma,\sigma':\eta^2,\eta^{2'}\text{-}CRCRC(O)CRCR\}]$, analogous to **3**, from the reactions of $[Fe_2(CO)_9]$ with bulky alkynes provides further support.[2]

Attempts to obtain **4** directly from **1** and tropone under UV irradiation were unsuccessful, because of the rapid polymerization of tropone under these conditions, as were efforts to remove tropone from complexation by treating **4** with CO or Me_3NO.

Experiments designed to produce substituted tropone complexes through prolonged reactions of **1** and **2a** with alkynes other than ethyne, and of **2d** and **2e** with ethyne, gave low yields of very air-sensitive species. Only the reaction of diphenylacetylene with **2e** gave an identifiable product, described below.

Synthesis and molecular structure of $[Fe_2(CO)_4(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)(\mu\text{-dppm})]$ (5)

As described earlier, the photochemical reaction of diphenylacetylene with **1** gives $[Fe_2(CO)_5\{\mu\text{-}\sigma:\eta^3\text{-}CPhCPhC(O)\}(\mu\text{-dppm})]$ (**2e**) in 21% yield after 30 h. After a reaction time of 60 h the yield of **2e** increases to 27% but the major product (36%) is the orange crystalline complex $[Fe_2(CO)_4(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)(\mu\text{-dppm})]$ (**5**). The intermediacy of **2e** in the formation of **5** was clearly established by reaction of the former with diphenylacetylene under UV irradiation for 48 h, when **5** was obtained in 21% yield.



2e **5**

Analytical data and mass and ^1H NMR spectra (Table 1) for **5** clearly indicated the presence of two molecules of alkyne, but the absence of a ketonic carbonyl in the IR spectrum ruled out the formation of a "fly-over" complex analogous to **3**. The ^{31}P NMR spectrum showed two signals and the ^{13}C NMR spectrum four for the C(Ph) carbons, indicating asymmetry and suggesting a metallacyclopentadienyl or "ferrole" structure.[26] This was confirmed by an X-ray diffraction study, the results of which are summarized in Fig. 4 and Table 5.

The molecular structure of complex **5** is based on two iron dicarbonyl fragments with an iron–iron distance bridged symmetrically by the diphosphine ligand which is consistent with the presence of a single metal–metal bond [Fe(1)—Fe(2) 2.601(2) Å]. The iron–iron bond is also bridged by a C_4Ph_4 ligand which is σ,σ'-bound to one iron, forming a ferracyclopentadiene ring, and $\eta^2,\eta^{2'}$-bound to the other. The two terminal carbons of this ligand therefore bridge the di-iron unit [Fe(1)—C(5) 1.929(5), Fe(2)—C(5) 2.203(5), Fe(1)—C(8) 1.988(6), Fe(2)—C(8) 2.110(5) Å], while the internal carbons are bonded to only one iron [Fe(2)—C(6) 2.131(5), Fe(2)—C(7) 2.140(5) Å]. The asymmetry of these distances reflects the variation in *trans* influence of the phosphine and carbonyl ligands *trans* to C(5) and C(8), respectively. The carbon–carbon bond lengths in the ferracyclopentadiene ring are effectively equal [1.412(8)–1.434(8) Å]. Interestingly, the organic and diphosphine ligands lie mutually *trans*, a feature which may provide an insight into the mechanism of formation of the complex.

A large number of such "ferrole" complexes has been prepared previously and many have been characterized crystallographically. Two structural types have been identified, the so-called "sawhorse" and "non-sawhorse" configurations. The former contains an approximately linear OC—Fe—Fe—CO backbone with eclipsed iron substituents, while in the latter the substituents are staggered, allowing a carbonyl on the π-bound metal centre [Fe(2)] to become semi-bridging. As seen in Fig. 4, the structure of **5** is best considered as being intermediate between these two extremes. Thus, while C(1) and C(4) are approximately eclipsed, as to a lesser extent are P(1) and P(2), the remaining carbonyls C(2) and C(3) adopt a more staggered arrangement. However, in **5** the closest approach of any carbonyl to a second metal centre [Fe(2)—C(1) 3.745 Å] is clearly outside the range of a bonding interaction.

Two complexes closely related to **5**, namely $[Fe_2(CO)_6(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)]$[26] and $[Fe_2(CO)_5(PPh_3)(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)]$,[27] have also been crystallographically characterized and show the "non-sawhorse" configuration. A comparison of the three structures reveals a number of interesting effects of phosphine substitution. Thus, while substitution of one carbonyl by PPh_3 has little effect on the iron–iron bond length [increase from 2.505(1) to 2.515(2) Å], substitution of two by dppm results in a substantial lengthening [to 2.601(2) Å], which may be due in part to the steric demands of the diphosphine ligand, but seems likely to be accounted for by the absence of a semi-bridging carbonyl in **5**. Indeed, the two crystallographically characterized "sawhorse" type complexes (i.e. without a semi-bridging carbonyl) have slightly elongated metal–metal bond lengths (*ca* 2.54 Å). A further point to note is that in the monosubstituted complex $[Fe_2(CO)_5(PPh_3)(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Ph_4)]$ the phosphine is located approximately *trans* to the metal–metal bond [P—Fe—Fe 141.1(1)°], while in **5** the dppm of necessity lies *cis*. This suggests that the preferred initial site of substitution in $[Fe_2(CO)_6(\mu\text{-}\sigma:\eta^4\text{-}C_4Ph_4)]$ is *trans* to the metal–metal bond and that **5** would not be accessible via the reaction of this complex with dppm.

Complexes **2a** and **2e** react very differently with a second molecule of alkyne. Formally, the former undergoes insertion into the Fe—C(O)CHCH bond, while the latter appears to undergo insertion into the Fe—CPhCPhC(O) bond followed by CO ejection. The difference may be traced to geometric factors, in that **2a** has the organic and dppm ligands *cis* to one another while in **2e** they are *trans*. Thus, in **2a** a second alkyne attack at the μ-carbon of the pentenone moiety is blocked by the bulk of the *cis* diphosphine ligand, thus directing the insertion to the M—C bond involving the ketonic carbonyl. In contrast, in the *trans* complex **2e** the ketonic carbonyl lies more nearly *cis* to the diphosphine, while the alkylidene carbon lies *trans* to it. Thus, it is the latter site which is more sterically accessible, directing attack of the bulky diphenylacetylene to this position and leading to formation of the "ferrole" after carbonyl loss. Hence it appears that the orientation of the diphosphine may, at least in part, be responsible for the differing reactivities of these dimetallacyclopentenone complexes.

Table 3. Selected bond lengths (Å) and angles (°) for **3**

Fe(11)—Fe(12)	2.545(1)	Fe(11)—P(11)	2.219(1)	Fe(11)—C(12)	1.772(6)
Fe(11)—C(13)	1.800(5)	Fe(11)—C(16)	1.960(5)	Fe(11)—C(19)	2.160(5)
Fe(11)—C(110)	2.018(5)	Fe(12)—P(12)	2.210(1)	Fe(12)—C(14)	1.760(6)
Fe(12)—C(15)	1.785(7)	Fe(12)—C(16)	2.044(5)	Fe(12)—C(17)	2.162(5)
Fe(12)—C(110)	1.954(5)	Fe(21)—Fe(22)	2.544(1)	Fe(21)—P(21)	2.201(1)
Fe(21)—C(22)	1.760(5)	Fe(21)—C(26)	1.949(5)	Fe(21)—C(27)	2.161(5)
Fe(21)—C(210)	2.041(5)	Fe(22)—P(22)	2.222(1)	Fe(22)—C(24)	1.802(5)
Fe(22)—C(25)	1.772(5)	Fe(22)—C(26)	2.033(5)	Fe(22)—C(29)	2.159(5)
Fe(22)—C(210)	1.957(5)	P(11)—C(11)	1.847(4)	P(11)—C(120)	1.836(4)
P(11)—C(130)	1.832(4)	P(12)—C(11)	1.841(4)	P(12)—C(140)	1.815(4)
P(12)—C(150)	1.837(5)	P(21)—C(21)	1.832(4)	P(21)—C(220)	1.831(4)
P(21)—C(230)	1.826(5)	P(22)—C(21)	1.853(4)	P(22)—C(240)	1.840(4)
P(22)—C(250)	1.825(4)	O(12)—C(12)	1.144(6)	O(13)—C(13)	1.134(5)
O(14)—C(14)	1.146(6)	O(15)—C(15)	1.125(7)	O(18)—C(18)	1.219(6)
O(22)—C(22)	1.148(6)	O(23)—C(23)	1.144(6)	O(24)—C(24)	1.130(5)
O(25)—C(25)	1.138(5)	O(28)—C(28)	1.224(5)	C(16)—C(17)	1.393(7)
C(17)—C(18)	1.471(8)	C(18)—C(19)	1.481(8)	C(19)—C(110)	1.389(7)
C(26)—C(29)	1.393(7)	C(27)—C(28)	1.452(8)	C(28)—C(29)	1.461(8)
C(210)—C(27)	1.404(8)				

P(11)—Fe(11)—Fe(12)	93.5(1)	C(12)—Fe(11)—Fe(12)	140.6(2)
C(12)—Fe(11)—P(11)	105.0(2)	C(13)—Fe(11)—Fe(12)	118.4(2)
C(13)—Fe(11)—P(11)	88.9(2)	C(13)—Fe(11)—C(12)	96.8(2)
C(16)—Fe(11)—Fe(12)	52.0(1)	C(16)—Fe(11)—P(11)	90.7(2)
C(16)—Fe(11)—C(12)	92.6(2)	C(16)—Fe(11)—C(13)	170.4(2)
C(19)—Fe(11)—Fe(12)	73.2(2)	C(19)—Fe(11)—P(11)	166.3(2)
C(19)—Fe(11)—C(12)	87.8(2)	C(19)—Fe(11)—C(13)	94.5(2)
C(19)—Fe(11)—C(16)	83.7(2)	C(110)—Fe(11)—Fe(12)	49.1(1)
C(110)—Fe(11)—P(11)	129.1(2)	C(110)—Fe(11)—C(12)	125.9(2)
C(110)—Fe(11)—C(13)	83.9(2)	C(110)—Fe(11)—C(16)	88.9(2)
C(110)—Fe(11)—C(19)	38.7(2)	P(12)—Fe(12)—Fe(11)	86.8(1)
C(14)—Fe(12)—Fe(11)	134.6(2)	C(14)—Fe(12)—P(12)	105.8(2)
C(15)—Fe(12)—Fe(11)	127.3(2)	C(15)—Fe(12)—P(12)	88.7(2)
C(15)—Fe(12)—C(14)	96.9(3)	C(16)—Fe(12)—Fe(11)	49.1(1)
C(16)—Fe(12)—P(12)	117.2(1)	C(16)—Fe(12)—C(14)	136.8(2)
C(16)—Fe(12)—C(15)	88.4(2)	C(17)—Fe(12)—Fe(11)	73.4(1)
C(17)—Fe(12)—P(12)	155.7(1)	C(17)—Fe(12)—C(14)	98.2(2)
C(17)—Fe(12)—C(15)	92.2(3)	C(17)—Fe(12)—C(16)	38.6(2)
C(110)—Fe(12)—Fe(11)	51.3(1)	C(110)—Fe(12)—P(12)	94.8(1)
C(110)—Fe(12)—C(14)	83.9(3)	C(110)—Fe(12)—C(15)	176.0(2)
C(110)—Fe(12)—C(16)	88.3(2)	C(110)—Fe(12)—C(17)	83.8(2)
P(21)—Fe(21)—Fe(22)	87.3(1)	C(22)—Fe(21)—Fe(22)	136.7(2)
C(22)—Fe(21)—P(21)	104.3(2)	C(26)—Fe(21)—Fe(22)	51.8(1)
C(26)—Fe(21)—P(21)	93.0(1)	C(26)—Fe(21)—C(22)	85.6(2)
C(27)—Fe(21)—Fe(22)	73.3(1)	C(27)—Fe(21)—P(21)	158.1(2)
C(27)—Fe(21)—C(22)	96.9(2)	C(27)—Fe(21)—C(26)	82.9(2)
P(22)—Fe(22)—Fe(21)	92.4(1)	C(24)—Fe(22)—Fe(21)	121.5(2)
C(24)—Fe(22)—P(22)	89.1(1)	C(25)—Fe(22)—Fe(21)	137.9(2)
C(25)—Fe(22)—P(22)	105.0(2)	C(25)—Fe(22)—C(24)	97.2(2)
C(26)—Fe(22)—Fe(21)	48.8(1)	C(26)—Fe(22)—P(22)	126.9(1)
C(26)—Fe(22)—C(24)	85.7(2)	C(26)—Fe(22)—C(25)	128.1(2)
C(29)—Fe(22)—Fe(21)	73.2(1)	C(29)—Fe(22)—P(22)	164.6(1)
C(29)—Fe(22)—C(24)	93.8(2)	C(29)—Fe(22)—C(25)	89.6(2)
C(29)—Fe(22)—C(26)	38.7(2)	P(12)—C(11)—P(11)	110.0(2)
O(12)—C(12)—Fe(11)	175.2(5)	O(13)—C(13)—Fe(11)	178.6(5)
O(14)—C(14)—Fe(12)	175.7(6)	O(15)—C(15)—Fe(12)	175.1(7)
Fe(12)—C(16)—Fe(11)	78.9(2)	C(17)—C(16)—Fe(11)	114.0(4)

Table 3—*continued*

C(17)—C(16)—Fe(12)	75.3(3)	C(16)—C(17)—Fe(12)	66.1(3)
C(18)—C(17)—Fe(12)	104.2(4)	C(18)—C(17)—C(16)	114.3(5)
C(17)—C(18)—O(18)	124.2(6)	C(19)—C(18)—O(18)	123.3(7)
C(19)—C(18)—C(17)	112.4(5)	C(18)—C(19)—Fe(11)	104.6(4)
C(110)—C(19)—Fe(11)	65.1(3)	C(110)—C(19)—C(18)	114.2(5)
Fe(12)—C(110)—Fe(11)	79.7(2)	C(19)—C(110)—Fe(11)	76.2(3)
C(19)—C(110)—Fe(12)	114.1(4)	P(22)—C(21)—P(21)	109.9(2)
O(22)—C(22)—Fe(21)	175.6(5)	O(24)—C(24)—Fe(22)	177.0(4)
O(25)—C(25)—Fe(22)	174.9(5)	Fe(22)—C(26)—Fe(21)	79.4(2)
C(29)—C(26)—Fe(21)	114.2(4)	C(29)—C(26)—Fe(22)	75.5(3)
C(28)—C(27)—Fe(21)	105.3(4)	C(29)—C(28)—C(27)	112.5(4)
C(26)—C(29)—Fe(22)	65.8(3)	C(28)—C(29)—Fe(22)	104.7(4)
C(28)—C(29)—C(26)	114.2(5)		

In complex **3** the organic and diphosphine moieties are *trans* to one another, but further insertion of ethyne across the two metal bound carbons affords the tropone complex **4**, in which they adopt a relative *cis* configuration. This change in geometry upon formation of **4** may be a consequence of the hydrogen bonding between the ring oxygen and one of the methylene protons of the diphosphine backbone, which would not be possible with a *trans* configuration.

EXPERIMENTAL

All reactions were carried out with Schlenk techniques under dry dinitrogen using pre-dried solvents. Separation of products was achieved by chromatography on alumina. Photolysis reactions were carried out in silica glass tubes, using a 500 W mercury vapour lamp as the source of UV radiation. Ethyne (BOC) was purified by passing the gas successively through water, concentrated sulphuric acid, solid potassium hydroxide and solid calcium chloride. Phenylacetylene, diphenylacetylene, propyne and 2-butyne were used as supplied (Aldrich). The complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) was prepared as described previously.[6]

Reaction of **1** *with ethyne*

Irradiation of a toluene solution (150 cm^3) of **1** (200 mg, 0.29 mmol) while purging gently with ethyne resulted in a colour change from red to brown. Chromatography led to the isolation of three products, the yields of which were dependent upon the time of irradiation. Eluting with dichloromethane–hexane (7:3) gave an orange band identified as **2a**. Found: C, 54.4; H, 3.4. Requires: C, 54.9; H, 3.4%. Further elution with dichloromethane–hexane (9:1) gave an orange band which afforded orange crystalline **3**. Found: C, 59.0; H, 3.7. Requires: C, 59.3; H, 3.8%. A brown band eluted with dichloromethane afforded brown crystalline **4**. Found: C, 60.0; H, 4.0. Requires: C, 60.5; 3.9%. Crystals of **2a**, **3** and **4** suitable for X-ray crystallography were grown from 1,2-dichloroethane at −20 °C. Optimized yields of products were: **2a**, 53% after 0.5 h; **3**, 28% after 2.5 h; **4**, 25% after 4 h.

Reaction of **2a** *with ethyne*

A toluene solution (150 cm^3) of **2a** (81 mg, 0.12 mmol) was irradiated for 4 h while purging with ethyne. Chromatography resulted in the isolation of **3** (8 mg, 9%) and **4** (17 mg, 20%).

Reaction of **3** *with ethyne*

A toluene solution (150 cm^3) of **3** (143 mg, 0.21 mmol) was irradiated for 3 h while purging with ethyne. Chromatography recovered 25 mg of **3** and gave 26 mg (18%) of **4**.

Reaction of **1** *with propyne*

Propyne (450 mg, 11.25 mmol) was condensed into a toluene solution (150 cm^3) of **1** (780 mg, 1.13 mmol) and the mixture subjected to UV irradiation for 20 h. Chromatography, eluting with dichloromethane–hexane (2:3), gave a red band which afforded 484 mg of starting material. Further elution with dichloromethane gave an orange band which afforded 95 mg (12%) of **2b**. Found: C, 53.3;

Table 4. Selected bond lengths (Å) and angles (°) for **4**$\cdot C_2H_4Cl_2$

Fe(1)—Fe(2)	2.950(1)	Fe(1)—P(1)	2.242(2)	Fe(1)—C(2)	1.779(7)
Fe(1)—C(3)	1.760(7)	Fe(1)—C(10)	2.174(6)	Fe(1)—C(15)	2.134(6)
Fe(1)—C(16)	2.033(6)	Fe(2)—P(2)	2.235(2)	Fe(2)—C(4)	1.772(7)
Fe(2)—C(5)	1.773(7)	Fe(2)—C(11)	2.177(6)	Fe(2)—C(12)	2.025(6)
Fe(2)—C(13)	2.133(6)	P(1)—C(1)	1.817(6)	P(1)—C(20)	1.831(5)
P(1)—C(30)	1.835(6)	P(2)—C(1)	1.830(6)	P(2)—C(40)	1.828(6)
P(2)—C(50)	1.836(6)	O(2)—C(2)	1.143(8)	O(3)—C(3)	1.142(9)
O(4)—C(4)	1.145(9)	O(5)—C(5)	1.143(8)	O(14)—C(14)	1.261(8)
C(10)—C(11)	1.452(10)	C(10)—C(16)	1.385(10)	C(11)—C(12)	1.394(10)
C(12)—C(13)	1.420(9)	C(13)—C(14)	1.436(9)	C(14)—C(15)	1.472(9)
C(15)—C(16)	1.420(9)				

Fe(2)—Fe(1)—P(1)	93.8(1)	Fe(2)—Fe(1)—C(2)	81.0(2)
P(1)—Fe(1)—C(2)	101.4(2)	Fe(2)—Fe(1)—C(3)	171.6(2)
P(1)—Fe(1)—C(3)	91.3(2)	C(2)—Fe(1)—C(3)	91.5(3)
Fe(2)—Fe(1)—C(10)	69.3(2)	P(1)—Fe(1)—C(10)	158.3(2)
C(2)—Fe(1)—C(10)	89.5(3)	C(3)—Fe(1)—C(10)	107.2(3)
Fe(2)—Fe(1)—C(15)	85.8(2)	P(1)—Fe(1)—C(15)	96.0(2)
C(2)—Fe(1)—C(15)	158.7(3)	C(3)—Fe(1)—C(15)	100.2(3)
C(10)—Fe(1)—C(15)	70.2(2)	Fe(2)—Fe(1)—C(16)	92.3(2)
P(1)—Fe(1)—C(16)	134.6(2)	C(2)—Fe(1)—C(16)	124.0(3)
C(3)—Fe(1)—C(16)	88.8(3)	C(10)—Fe(1)—C(16)	38.3(3)
C(15)—Fe(1)—C(16)	39.7(3)	Fe(1)—Fe(2)—P(2)	87.1(1)
Fe(1)—Fe(2)—C(4)	178.6(2)	P(2)—Fe(2)—C(4)	91.7(2)
Fe(1)—Fe(2)—C(5)	94.5(2)	P(2)—Fe(2)—C(5)	104.9(2)
C(4)—Fe(2)—C(5)	86.5(3)	Fe(1)—Fe(2)—C(11)	70.5(2)
P(2)—Fe(2)—C(11)	155.2(2)	C(4)—Fe(2)—C(11)	110.5(3)
C(5)—Fe(2)—C(11)	87.7(3)	Fe(1)—Fe(2)—C(12)	92.3(2)
P(2)—Fe(2)—C(12)	137.0(2)	C(4)—Fe(2)—C(12)	88.0(3)
C(5)—Fe(2)—C(12)	118.0(3)	C(11)—Fe(2)—C(12)	38.5(3)
Fe(1)—Fe(2)—C(13)	84.0(2)	P(2)—Fe(2)—C(13)	97.6(2)
C(4)—Fe(2)—C(13)	95.4(3)	C(5)—Fe(2)—C(13)	157.4(3)
C(11)—Fe(2)—C(13)	70.5(2)	C(12)—Fe(2)—C(13)	39.8(3)
P(1)—C(1)—P(2)	110.1(3)	Fe(1)—C(2)—O(2)	173.2(6)
Fe(1)—C(3)—O(3)	177.7(6)	Fe(2)—C(4)—O(4)	176.7(6)
Fe(2)—C(5)—O(5)	171.3(6)	Fe(1)—C(10)—C(11)	111.5(4)
Fe(1)—C(10)—C(16)	65.4(3)	C(11)—C(10)—C(16)	127.2(6)
Fe(2)—C(11)—C(10)	108.8(4)	Fe(2)—C(11)—C(12)	64.8(4)
C(10)—C(11)—C(12)	126.2(6)	Fe(2)—C(12)—C(11)	76.6(4)
Fe(2)—C(12)—C(13)	74.2(4)	C(11)—C(12)—C(13)	124.1(6)
Fe(2)—C(13)—C(12)	66.0(4)	Fe(2)—C(13)—C(14)	110.7(4)
C(12)—C(13)—C(14)	128.7(6)	O(14)—C(14)—C(13)	118.3(6)
O(14)—C(14)—C(15)	117.2(6)	C(13)—C(14)—C(15)	124.4(6)
Fe(1)—C(15)—C(14)	107.7(4)	Fe(1)—C(15)—C(16)	66.3(4)
C(14)—C(15)—C(16)	127.9(6)	Fe(1)—C(16)—C(10)	76.4(4)
Fe(1)—C(16)—C(15)	73.9(4)	C(10)—C(16)—C(15)	124.1(6)

H, 3.5. Requires: C, 53.3; H, 3.6%. The product was recrystallized from dichloromethane–hexane.

Reaction of 1 *with phenylacetylene*

A toluene solution (150 cm^3) of **1** (400 mg, 0.60 mmol) and phenylacetylene (257 mg, 2.52 mmol) was irradiated for 4 h while purging with nitrogen. The colour changed from red to brown. Chromatography, eluting with dichloromethane–hexane (4 : 1), gave an orange band which provided 190 mg (39%) of **2c**. Found: C, 56.4; H, 3.5. Requires: C, 56.5; H, 3.5%. The product was recrystallized from dichloromethane–hexane.

Reaction of 1 *with* 2-*butyne*

A toluene solution (80 cm^3) of **1** (1.0 g, 1.45 mmol) and 2-butyne (420 mg, 7.78 mmol) was

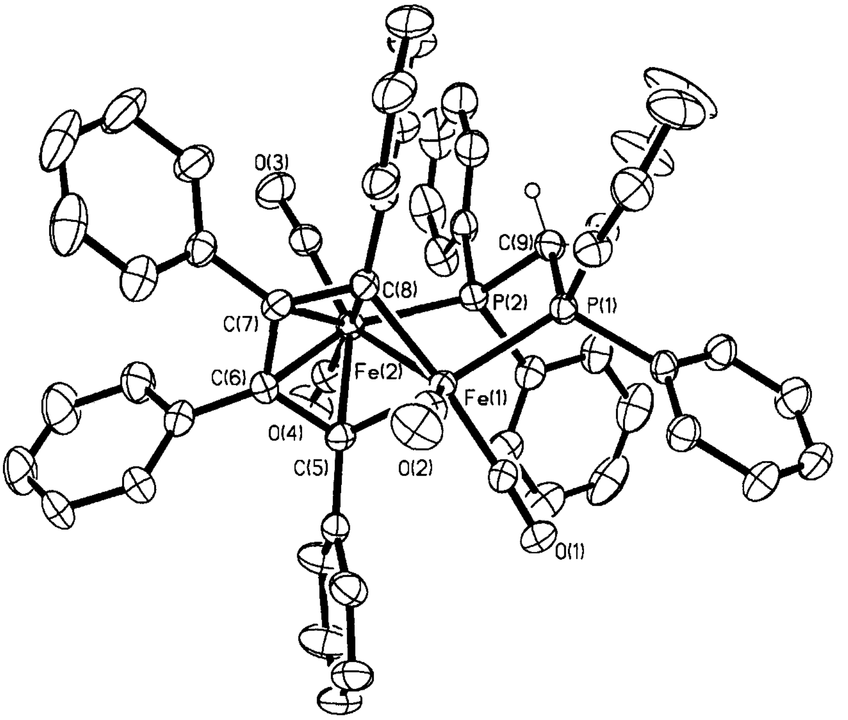


Fig. 4. Molecular structure of **5** showing labelling scheme. All phenyl group hydrogen atoms have been omitted for clarity.

irradiated for 17 h. Chromatography, eluting with dichloromethane, afforded 224 mg (22%) of red crystalline **2d**. Found: C, 58.5; H, 3.9. Requires: C, 58.5; H, 4.12%.

Reaction of **1** *with diphenylacetylene*

A toluene solution (150 cm^3) of **1** (600 mg, 0.86 mmol) and diphenylacetylene (770 mg, 4.32 mmol) was irradiated for 72 h while purging with nitrogen. Chromatography, eluting with dichloromethane–hexane (2 : 3), gave an orange band which afforded 300 mg (36%) of orange crystalline **5**. A red band eluted with dichloromethane–hexane (4 : 1) provided 200 mg (27%) of a dark red powder identified as **2e**. Found: C, 62.2; H, 3.7. Requires: C, 61.8; H, 3.9%.

Reaction of **2e** *with diphenylacetylene*

A toluene solution (100 cm^3) of **2e** (200 mg, 0.23 mmol) and diphenylacetylene (200 mg, 1.12 mmol) was irradiated for 48 h while purging with nitrogen. Chromatography as above afforded 50 mg (21%) of **5**. Found: C, 68.0; H, 4.2; P, 6.1. Requires, with $0.5CH_2Cl_2$ of crystallisation: C, 67.9; H, 4.1; P, 6.5%.

Structure determinations for **2a**$\cdot 0.5\ C_2H_4Cl_2$, **3**, **4**$\cdot C_2H_4Cl_2$ *and* **5**

Many of the details of the structure analyses carried out on **2a**$\cdot 0.5\ C_2H_4Cl_2$, **3**, **4**$\cdot C_2H_4Cl_2$ and **5** are listed in Table 6. X-ray diffraction measurements were made at room temperature using Siemens four-circle R3m/V diffractometers on single crystals mounted in thin-walled glass capillaries. Cell dimensions for each analysis were determined from the setting angle values of 20–30 centred reflections. For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarization and long-term intensity fluctuations on the basis of the intensities of check reflections repeatedly measured during data collection. Corrections for X-ray absorption effects were applied for **2a**$\cdot 0.5\ C_2H_4Cl_2$, **4**$\cdot C_2H_4Cl_2$ and **5** on the basis of azimuthal scan data, and for **3** on the basis on the indexed crystal faces. The structures were solved by heavy atom (Patterson and difference Fourier) methods and refined by least-squares against *F*. The dichloroethane solvent molecules showed disorder in each case. In each of **2a**$\cdot 0.5\ C_2H_4Cl_2$ and **3** there are two crystallographically distinct molecules of the complexes. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined

Table 5. Selected bond lengths (Å) and angles (°) for **5**

Fe(1)—Fe(2)	2.601(2)	Fe(1)—P(1)	2.248(2)	Fe(1)—C(1)	1.787(6)
Fe(1)—C(2)	1.745(6)	Fe(1)—C(5)	1.929(5)	Fe(1)—C(8)	1.988(6)
Fe(2)—P(2)	2.230(2)	Fe(2)—C(3)	1.774(7)	Fe(2)—C(4)	1.754(6)
Fe(2)—C(5)	2.203(5)	Fe(2)—C(6)	2.131(5)	Fe(2)—C(7)	2.140(5)
Fe(2)—C(8)	2.110(5)	P(1)—C(9)	1.845(6)	P(1)—C(10)	1.840(6)
P(1)—C(20)	1.833(6)	P(2)—C(9)	1.835(6)	P(2)—C(30)	1.834(6)
P(2)—C(40)	1.844(6)	O(1)—C(1)	1.147(8)	O(2)—C(2)	1.145(7)
O(3)—C(3)	1.141(9)	O(4)—C(4)	1.161(7)	C(5)—C(6)	1.434(8)
C(5)—C(50)	1.503(8)	C(6)—C(7)	1.427(8)	C(6)—C(60)	1.491(8)
C(7)—C(8)	1.412(8)	C(7)—C(70)	1.506(8)	C(8)—C(80)	1.503(8)

Fe(2)—Fe(1)—P(1)	105.3(1)	Fe(2)—Fe(1)—C(1)	116.0(2)
P(1)—Fe(1)—C(1)	89.2(2)	Fe(2)—Fe(1)—C(2)	135.7(2)
P(1)—Fe(1)—C(2)	103.2(2)	C(1)—Fe(1)—C(2)	97.4(3)
Fe(2)—Fe(1)—C(5)	55.8(2)	P(1)—Fe(1)—C(5)	158.7(2)
C(1)—Fe(1)—C(5)	90.9(2)	C(2)—Fe(1)—C(5)	98.0(2)
Fe(2)—Fe(1)—C(8)	52.7(2)	P(1)—Fe(1)—C(8)	94.9(2)
C(1)—Fe(1)—C(8)	168.7(2)	C(2)—Fe(1)—C(8)	91.9(3)
C(5)—Fe(1)—C(8)	81.4(2)	Fe(1)—Fe(2)—P(2)	79.4(1)
Fe(1)—Fe(2)—C(3)	147.3(2)	P(2)—Fe(2)—C(3)	94.1(2)
Fe(1)—Fe(2)—C(4)	124.7(2)	P(2)—Fe(2)—C(4)	92.5(2)
C(3)—Fe(2)—C(4)	87.3(3)	Fe(1)—Fe(2)—C(5)	46.4(1)
P(2)—Fe(2)—C(5)	115.7(1)	C(3)—Fe(2)—C(5)	150.1(2)
C(4)—Fe(2)—C(5)	93.5(2)	Fe(1)—Fe(2)—C(6)	74.2(2)
P(2)—Fe(2)—C(6)	152.8(2)	C(3)—Fe(2)—C(6)	111.6(2)
C(4)—Fe(2)—C(6)	97.2(2)	C(5)—Fe(2)—C(6)	38.6(2)
Fe(1)—Fe(2)—C(7)	73.6(2)	P(2)—Fe(2)—C(7)	136.8(2)
C(3)—Fe(2)—C(7)	91.0(2)	C(4)—Fe(2)—C(7)	130.7(2)
C(5)—Fe(2)—C(7)	66.0(2)	C(6)—Fe(2)—C(7)	39.0(2)
Fe(1)—Fe(2)—C(8)	48.5(2)	P(2)—Fe(2)—C(8)	98.4(1)
C(3)—Fe(2)—C(8)	102.0(2)	C(4)—Fe(2)—C(8)	165.1(2)
C(5)—Fe(2)—C(8)	72.6(2)	C(6)—Fe(2)—C(8)	68.6(2)
C(7)—Fe(2)—C(8)	38.8(2)	Fe(1)—C(1)—O(1)	176.3(5)
Fe(1)—C(2)—O(2)	177.4(5)	Fe(2)—C(3)—O(3)	175.5(6)
Fe(2)—C(4)—O(4)	176.2(6)	Fe(1)—C(5)—Fe(2)	77.7(2)
Fe(1)—C(5)—C(6)	117.0(4)	Fe(2)—C(5)—C(6)	68.0(3)
Fe(1)—C(5)—C(50)	122.1(4)	Fe(2)—C(5)—C(50)	135.2(4)
C(6)—C(5)—C(50)	119.5(5)	Fe(2)—C(6)—C(5)	73.4(3)
Fe(2)—C(6)—C(7)	70.8(3)	C(5)—C(6)—C(7)	111.7(5)
Fe(2)—C(6)—C(60)	126.9(4)	C(5)—C(6)—C(60)	125.0(5)
C(7)—C(6)—C(60)	123.2(5)	Fe(2)—C(7)—C(6)	70.1(3)
Fe(2)—C(7)—C(8)	69.4(3)	C(6)—C(7)—C(8)	114.7(5)
Fe(2)—C(7)—C(70)	136.6(4)	C(6)—C(7)—C(70)	120.6(5)
C(8)—C(7)—C(70)	124.2(5)	Fe(1)—C(8)—Fe(2)	78.7(2)
Fe(1)—C(8)—C(7)	113.8(4)	Fe(2)—C(8)—C(7)	71.8(3)
Fe(1)—C(8)—C(80)	127.2(4)	Fe(2)—C(8)—C(80)	131.0(4)
C(7)—C(8)—C(80)	116.8(5)	P(1)—C(9)—P(2)	107.3(3)

Table 6. Details of structure analyses

	2a · $0.5C_2H_4Cl_2$	**3**	**4** · $C_2H_4Cl_2$	**5**
Crystal data[a]				
Formula	$C_{34}H_{26}ClO_6P_2Fe_2$	$C_{34}H_{26}O_5P_2Fe_2$	$C_{38}H_{32}O_5Cl_2P_2Fe_2$	$Fe_2C_{57}H_{42}O_4P_2$
M	739.7	688.2	813.2	964.6
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group (No.)	$P1$ (No. 2)	$P1$ (No. 2)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
a (Å)	10.697(3)	9.494(2)	11.589(2)	13.206(3)
b (Å)	16.606(3)	16.673(4)	15.822(3)	13.980(6)
c (Å)	18.625(4)	20.142(5)	19.428(6)	25.910(6)
α (°)	85.97(2)	94.70(2)	90	90
β (°)	86.71(2)	98.61(2)	90	100.25(2)
γ (°)	84.99(2)	95.13(2)	90	90
U ($Å^3$)	3283.3(12)	3125.3(14)	3562.2(14)	4707(2)
Z	4	4	4	4
D_c (g cm^{-3})	1.49	1.46	1.51	1.36
$F(000)$	1592	1408	1664	1992
μ(Mo-K_α) (cm^{-1})	11.9	10.3	11.0	7.3
Data collection and reduction				
Crystal dimensions (mm)	$0.6 \times 0.4 \times 0.3$	$1.0 \times 0.3 \times 0.05$	$0.5 \times 0.32 \times 0.2$	$0.46 \times 0.24 \times 0.2$
2θ range (°)	3–50	3–50	3–50	5–50
Scan method	Wyckoff ω	θ–2θ	θ–2θ	Wyckoff ω
Total data	12687	12628	3779	9342
Unique data	11560	11062	3526	8738
"Observed" data (NO)	8911	6068	2972	4763
Observation criterion $[F_0^2 > n\sigma(F_0^2)]$	2	2.5	2	3
Refinement				
Disordered atoms	solvent	none	solvent	none
Least squares variables (NV)	862	800	460	586
R[b]	0.041	0.043	0.040	0.047
R_w[b]	0.042	0.041	0.042	0.054
g	0.0007	0.0005	0.0008	0.0044
Largest difference map peak (e $Å^{-3}$)	+0.45	+0.37	+0.40	+0.27

[a] Data common to all: $T = 295$ K; wavelength 0.71073 Å.

[b] $R = \Sigma|\Delta|/\Sigma|F_0|$; $R_w = [\Sigma w^{1/2}|\Delta|/\Sigma w F_0]$; $\Delta = F_0 - F_c$; $w = [\sigma_c^2(F_0) + gF_0^2]^{-1}$, $\sigma_c^2(F_0)$ = variance in F_0 due to counting statistics.

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2a**·$0.5C_2H_4Cl_2$

Atom	*x*	*y*	*z*	U_{eq}[a]
Fe(11)	7262(1)	7628(1)	6719(1)	34(1)
Fe(12)	9158(1)	7580(1)	7642(1)	34(1)
Fe(21)	1403(1)	7428(1)	1753(1)	37(1)
Fe(22)	3656(1)	7349(1)	2360(1)	36(1)
P(11)	6126(1)	8672(1)	7235(1)	35(1)
P(12)	8280(1)	8669(1)	8221(1)	32(1)
P(21)	732(1)	6338(1)	2422(1)	32(1)
P(22)	3219(1)	6281(1)	3140(1)	34(1)
O(11)	5399(3)	7632(2)	5640(2)	83(1)
O(12)	8954(3)	8386(2)	5661(2)	80(1)
O(13)	11021(3)	8528(2)	6813(2)	78(1)
O(14)	10530(3)	6146(2)	7068(2)	70(1)
O(15)	10479(3)	7174(2)	8965(2)	65(1)
O(16)	8218(3)	6034(2)	6160(1)	57(1)
O(21)	−1262(3)	7852(2)	1562(2)	90(2)
O(22)	2000(4)	8842(2)	809(2)	81(1)
O(23)	1947(4)	6474(2)	478(2)	82(1)
O(24)	4620(3)	6603(2)	1056(2)	80(1)
O(25)	6189(3)	7377(3)	2828(3)	109(2)
O(26)	4271(3)	8988(2)	1738(2)	62(1)
C(11)	6114(4)	7616(2)	6078(2)	50(1)
C(12)	8305(4)	8109(2)	6106(2)	49(1)
C(13)	10272(4)	8199(2)	7140(2)	49(1)
C(14)	9937(3)	6696(2)	7262(2)	46(1)
C(15)	9946(3)	7324(2)	8452(2)	45(1)
C(16)	7810(3)	6508(2)	6590(2)	41(1)
C(18)	7544(3)	7073(2)	7742(2)	35(1)
C(17)	7191(3)	6494(2)	7301(2)	38(1)
C(19)	7140(3)	9292(2)	7685(2)	36(1)
C(111)	4572(3)	8836(3)	8502(2)	52(1)
C(112)	3743(4)	8550(3)	9043(3)	73(2)
C(113)	3239(5)	7843(4)	8987(3)	85(2)
C(114)	3526(4)	7397(3)	8394(3)	84(2)
C(115)	4381(4)	7661(3)	7859(3)	65(2)
C(110)	4919(3)	8383(2)	7916(2)	43(1)
C(121)	5991(4)	9881(2)	6130(2)	60(2)
C(122)	5436(6)	10522(3)	5708(3)	76(2)
C(123)	4202(7)	10746(4)	5818(3)	117(3)
C(124)	3500(7)	10319(5)	6330(4)	157(4)
C(125)	4044(5)	9688(4)	6751(3)	107(3)
C(120)	5314(3)	9473(2)	6664(2)	44(1)
C(131)	10010(3)	9303(2)	9058(2)	47(1)
C(132)	10981(4)	9770(3)	9161(2)	56(1)
C(133)	11424(4)	10279(3)	8611(3)	58(2)
C(134)	10879(4)	10343(2)	7958(2)	55(1)
C(135)	9893(3)	9891(2)	7849(2)	46(1)
C(130)	9456(3)	9358(2)	8399(2)	35(1)
C(141)	6940(3)	9173(2)	9458(2)	43(1)
C(142)	6324(3)	9063(3)	10134(2)	51(1)
C(143)	6265(4)	8294(3)	10457(2)	60(2)
C(144)	6802(4)	7638(3)	10121(2)	59(2)
C(145)	7425(3)	7737(2)	9445(2)	46(1)
C(140)	7485(3)	8501(2)	9109(2)	37(1)
C(21)	−218(4)	7709(2)	1646(2)	56(1)
C(22)	1823(4)	8301(2)	1198(2)	52(1)
C(23)	1738(4)	6820(2)	983(2)	55(1)
C(24)	4190(4)	6884(2)	1570(2)	50(1)
C(25)	5177(4)	7362(3)	2662(2)	59(2)
C(26)	3699(3)	8484(2)	2083(2)	44(1)
C(28)	1880(3)	7895(2)	2635(2)	36(1)
C(27)	2758(3)	8462(2)	2670(2)	39(1)
C(29)	2036(3)	5689(2)	2794(2)	33(1)
C(211)	−876(4)	5806(2)	3548(2)	53(1)
C(212)	−1719(4)	5880(3)	4134(2)	68(2)
C(213)	−2084(4)	6640(3)	4370(3)	72(2)
C(214)	−1659(4)	7317(3)	4010(3)	65(2)
C(215)	−831(3)	7242(2)	3407(2)	46(1)
C(210)	−418(3)	6480(2)	3180(2)	37(1)
C(221)	624(4)	5111(2)	1469(2)	47(1)
C(222)	22(5)	4697(2)	984(2)	60(2)
C(223)	−1244(5)	4865(3)	900(2)	68(2)
C(224)	−1918(5)	5434(3)	1294(3)	67(2)
C(225)	−1331(3)	5850(2)	1776(2)	51(1)
C(220)	−55(3)	5693(2)	1868(2)	37(1)
C(231)	4503(4)	4997(2)	3968(2)	57(1)
C(232)	5396(4)	4347(3)	4057(3)	66(2)
C(233)	6244(4)	4159(3)	3502(3)	67(2)
C(234)	6217(4)	4607(3)	2866(3)	74(2)
C(235)	5321(4)	5264(3)	2772(2)	62(2)
C(230)	4455(3)	5465(2)	3315(2)	40(1)
C(241)	1696(4)	6123(3)	4432(2)	52(1)
C(242)	1188(4)	6400(3)	5083(2)	67(2)
C(243)	1595(5)	7079(3)	5345(2)	71(2)
C(244)	2517(5)	7471(3)	4977(2)	69(2)
C(245)	3024(4)	7215(2)	4322(2)	53(1)
C(240)	2602(3)	6538(2)	4040(2)	40(1)
Cl(1)	535(2)	9341(1)	4068(1)	103(1)
Cl(2A)[b]	4341(7)	4477(5)	1014(3)	131(3)
Cl(2B)[b]	3815(5)	4382(5)	767(4)	119(3)
C(50)[b]	−390(14)	9967(7)	4681(5)	63(4)
C(51)[b]	606(12)	9773(7)	4961(9)	68(4)
C(52)[b]	5238(20)	4694(10)	304(8)	78(5)
C(53)[b]	4430(20)	4875(18)	96(13)	105(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Occupancy 0.5.

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq}[a]
Fe(11)	568(1)	5852(1)	2849(1)	35(1)
Fe(12)	−1432(1)	4953(1)	2081(1)	41(1)
Fe(21)	4478(1)	9314(1)	7082(1)	36(1)
Fe(22)	6695(1)	9946(1)	7887(1)	33(1)
P(11)	−933(1)	6606(1)	3293(1)	32(1)
P(12)	−2429(1)	6073(1)	1873(1)	35(1)
P(21)	5698(1)	8288(1)	6865(1)	29(1)
P(22)	7066(1)	8778(1)	8310(1)	30(1)
O(12)	2929(4)	5715(3)	3925(2)	80(2)
O(13)	1857(4)	7297(2)	2339(2)	67(2)
O(14)	−1573(7)	4009(3)	792(2)	125(3)
O(15)	−4149(6)	4247(4)	2383(3)	155(3)
O(18)	1932(5)	3660(2)	2446(2)	97(2)
O(22)	3029(5)	9654(3)	5775(2)	90(2)
O(23)	7662(5)	11855(3)	2522(2)	94(2)
O(24)	9567(4)	10039(2)	7511(2)	65(2)
O(25)	7320(4)	11195(2)	9015(2)	72(2)
O(28)	4197(5)	11714(2)	7425(3)	95(2)
C(11)	−2587(5)	6625(3)	2684(2)	41(2)
C(12)	1983(6)	5794(3)	3520(3)	49(2)
C(13)	1342(5)	6741(3)	2534(3)	44(2)
C(14)	−1571(7)	4386(3)	1294(3)	71(3)
C(15)	−3087(7)	4538(4)	2294(3)	78(3)
C(16)	−499(6)	4864(3)	3052(3)	44(2)
C(17)	−222(7)	4163(3)	2690(3)	57(2)
C(18)	1182(7)	4215(3)	2462(3)	64(2)
C(19)	1582(6)	5019(3)	2242(3)	56(2)
C(110)	447(6)	5360(3)	1891(3)	45(2)
C(120)	−1595(5)	6343(3)	4067(2)	35(2)
C(121)	−2912(6)	6536(3)	4209(3)	53(2)
C(122)	−3281(6)	6419(3)	4840(3)	63(2)
C(123)	−2359(7)	6124(3)	5326(3)	56(2)
C(124)	−1055(6)	5933(3)	5186(3)	51(2)
C(125)	−684(5)	6031(3)	4561(2)	40(2)
C(130)	−213(5)	7655(3)	3575(2)	36(2)
C(131)	1190(6)	7796(3)	3905(3)	52(2)
C(132)	1764(6)	8569(3)	4166(3)	64(2)
C(133)	960(8)	9200(3)	4091(3)	64(3)
C(134)	−406(8)	9077(3)	3766(3)	64(3)
C(135)	−1006(6)	8307(3)	3508(3)	52(2)
C(140)	−1625(5)	6803(3)	1383(2)	37(2)
C(141)	−1285(6)	6509(3)	763(3)	53(2)
C(142)	−749(6)	7037(4)	341(3)	70(3)
C(143)	−583(6)	7844(4)	529(4)	76(3)
C(144)	−909(7)	8143(4)	1129(3)	75(3)
C(145)	−1430(6)	7623(3)	1554(3)	56(2)
C(150)	−4288(5)	5962(3)	1436(2)	44(2)
C(151)	−5160(6)	6577(3)	1485(3)	56(2)
C(152)	−6533(6)	6494(4)	1125(3)	71(3)
C(153)	−7055(7)	5803(5)	722(3)	85(3)
C(154)	−6209(7)	5198(5)	668(3)	85(3)
C(155)	−4835(6)	5266(4)	1021(3)	65(2)
C(21)	6430(5)	7915(2)	7663(2)	36(2)
C(22)	3573(6)	9491(3)	6287(3)	54(2)
C(23)	6834(6)	11394(3)	2676(3)	55(2)
C(24)	8450(6)	9984(3)	7645(2)	41(2)
C(25)	7123(5)	10687(3)	8588(3)	46(2)
C(26)	5982(5)	10108(3)	6909(3)	41(2)
C(27)	3846(6)	10343(3)	7648(3)	57(2)
C(28)	4630(6)	11045(3)	7443(3)	59(2)
C(29)	6006(6)	10868(3)	7256(3)	51(2)
C(210)	4704(5)	9860(3)	8042(3)	40(2)
C(220)	4671(5)	7378(3)	6402(2)	36(2)
C(221)	5125(5)	6619(3)	6462(2)	45(2)
C(222)	4369(7)	5947(3)	6079(3)	57(2)
C(223)	3159(7)	6032(4)	5645(3)	70(3)
C(224)	2696(7)	6772(4)	5575(3)	83(3)
C(225)	3445(6)	7444(3)	5961(3)	61(2)
C(230)	7153(5)	8392(2)	6369(2)	35(2)
C(231)	6804(6)	8608(3)	5719(3)	51(2)
C(232)	9141(7)	8434(4)	5498(4)	73(3)
C(233)	7800(7)	8624(3)	5290(3)	62(2)
C(234)	9502(6)	8229(4)	6140(4)	83(3)
C(235)	8515(5)	8209(3)	6576(3)	57(2)
C(240)	6240(4)	8495(3)	9039(2)	35(2)
C(241)	6151(5)	9097(3)	9544(2)	48(2)
C(242)	5710(6)	8903(4)	10138(3)	59(2)
C(243)	5349(6)	8120(4)	10240(3)	68(3)
C(244)	5427(7)	7521(4)	9749(3)	70(3)
C(245)	5863(6)	7700(3)	9149(3)	60(2)
C(250)	8932(5)	8676(3)	8640(2)	34(2)
C(251)	9577(5)	7976(3)	8563(3)	50(2)
C(252)	10996(6)	7953(4)	8843(3)	69(3)
C(253)	11768(6)	8610(5)	9200(3)	71(3)
C(254)	11157(6)	9301(4)	9286(3)	71(3)
C(255)	9750(5)	9341(3)	9013(3)	52(2)

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[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4**$\cdot C_2H_4Cl_2$

Atom	x	y	z	$U_{eq}{}^{a}$
Fe(1)	1149(1)	3469(1)	3133(1)	35(1)
Fe(2)	769(1)	1633(1)	3279(1)	35(1)
P(1)	2835(1)	3444(1)	3699(1)	30(1)
P(2)	2506(1)	1572(1)	3776(1)	31(1)
O(2)	1809(5)	3005(4)	1734(2)	73(2)
O(3)	1496(5)	5227(3)	2763(3)	78(2)
O(4)	430(5)	−185(3)	3419(3)	74(2)
O(5)	1083(5)	1194(4)	1838(2)	78(2)
O(14)	616(4)	2840(3)	5011(2)	50(2)
C(1)	2963(6)	2517(3)	4246(3)	31(2)
C(2)	1580(6)	3142(4)	2296(3)	48(2)
C(3)	1341(6)	4540(4)	2917(4)	49(2)
C(4)	560(6)	532(5)	3384(3)	51(2)
C(5)	1027(6)	1410(4)	2398(3)	48(2)
C(10)	−624(5)	3141(4)	2882(4)	48(2)
C(11)	−832(5)	2241(4)	2964(3)	46(2)
C(12)	−885(5)	1802(4)	3585(3)	48(2)
C(13)	−193(6)	1990(4)	4169(3)	43(2)
C(14)	177(5)	2800(4)	4419(3)	42(2)
C(15)	90(6)	3593(4)	4026(3)	46(2)
C(16)	−508(5)	3737(4)	3400(4)	47(2)
C(21)	4165(6)	3829(4)	2531(3)	44(2)
C(22)	5162(7)	3893(5)	2159(4)	59(3)
C(23)	6199(6)	3600(5)	2432(4)	57(3)
C(24)	6205(5)	3258(4)	3089(4)	51(2)
C(25)	5201(5)	3201(4)	3458(3)	41(2)
C(20)	4164(5)	3476(3)	3189(3)	33(2)
C(31)	2505(7)	4372(4)	4921(3)	52(2)
C(32)	2725(9)	5020(5)	5379(4)	68(3)
C(33)	3562(8)	5600(5)	5247(4)	67(3)
C(34)	4186(8)	5564(5)	4631(5)	74(3)
C(35)	3967(7)	4909(4)	4177(4)	57(2)
C(30)	3123(5)	4302(4)	4310(3)	35(2)
C(41)	3793(6)	1477(5)	2551(3)	46(2)
C(42)	4809(6)	1392(5)	2174(4)	61(3)
C(43)	5801(6)	1158(5)	2491(4)	60(3)
C(44)	5820(6)	1022(4)	3202(4)	55(2)
C(45)	4826(5)	1115(4)	3576(3)	43(2)
C(40)	3790(5)	1341(3)	3262(3)	36(2)
C(51)	2247(7)	902(4)	5118(3)	49(2)
C(52)	2219(7)	261(5)	5596(4)	60(3)
C(53)	2525(7)	−540(5)	5412(4)	64(3)
C(54)	2836(8)	−714(5)	4729(5)	72(3)
C(55)	2871(7)	−73(4)	4256(4)	54(2)
C(50)	2579(5)	751(4)	4442(3)	36(2)
Cl(1)	2853(5)	2779(3)	8849(2)	156(2)
Cl(2)	4105(6)	2805(3)	10488(2)	197(3)
C(60A)[b]	3811(22)	3470(18)	9201(12)	109(10)
C(60B)[b]	4046(21)	2299(12)	9027(12)	99(9)
C(61A)[b]	4430(37)	3287(30)	9654(27)	160(22)
C(61B)[b]	4802(40)	2774(21)	9670(27)	160(21)

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[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Occupancy 0.5.

Table 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**.

Atom	x	y	z	$U_{eq}{}^{a}$
Fe(1)	2778(1)	7337(1)	973(1)	34(1)
Fe(2)	2203(1)	8048(1)	1803(1)	36(1)
P(1)	3452(1)	5898(1)	1221(1)	37(1)
P(2)	3471(1)	7081(1)	2172(1)	39(1)
O(1)	4773(3)	7975(3)	753(2)	64(2)
O(2)	1803(4)	7065(3)	−107(2)	73(2)
O(3)	1022(4)	7853(4)	2645(2)	75(2)
O(4)	3092(4)	9711(3)	2393(2)	76(2)
C(1)	4009(4)	7714(4)	854(2)	44(2)
C(2)	2202(5)	7154(4)	320(2)	45(2)
C(3)	1476(5)	7892(4)	2310(2)	50(2)
C(4)	2767(5)	9045(4)	2151(2)	46(2)
C(5)	2361(4)	8649(4)	1035(2)	37(2)
C(6)	1355(4)	8808(4)	1154(2)	38(2)
C(7)	842(4)	7930(4)	1219(2)	41(2)
C(8)	1459(4)	7104(4)	1221(2)	38(2)
C(9)	3498(5)	5845(4)	1937(2)	43(2)
C(10)	2859(5)	4756(4)	977(2)	45(2)
C(11)	2876(8)	3970(5)	1287(3)	98(4)
C(12)	2504(10)	3108(5)	1079(3)	128(6)
C(13)	2078(7)	3036(5)	558(3)	86(4)
C(14)	2031(5)	3810(5)	246(3)	61(2)
C(15)	2403(4)	4687(4)	455(2)	48(2)
C(20)	4764(4)	5666(4)	1112(2)	41(2)
C(21)	4941(5)	5816(4)	603(2)	50(2)
C(22)	5907(5)	5633(5)	477(3)	60(2)
C(23)	6692(5)	5306(5)	859(3)	62(3)
C(24)	6528(5)	5168(5)	1362(3)	67(3)
C(25)	5575(5)	5345(5)	1488(2)	56(2)
C(30)	4809(4)	7486(4)	2238(2)	49(2)
C(31)	5592(5)	6958(5)	2541(3)	61(2)
C(32)	6599(6)	7274(8)	2602(3)	86(4)
C(33)	6816(6)	8122(8)	2378(4)	96(4)
C(34)	6041(6)	8653(6)	2076(3)	77(3)
C(35)	5041(5)	8315(5)	2006(3)	59(2)
C(40)	3402(5)	6907(5)	2870(2)	50(2)
C(41)	3781(6)	7631(5)	3223(2)	66(3)
C(42)	3656(8)	7571(7)	3744(3)	89(4)
C(43)	3173(8)	6786(8)	3912(3)	99(4)
C(44)	2830(6)	6083(7)	3573(3)	84(3)
C(45)	2910(5)	6143(5)	3048(3)	64(3)
C(50)	2943(4)	9470(4)	854(2)	42(2)
C(51)	3419(6)	10188(5)	1166(3)	72(3)
C(52)	4016(7)	10878(5)	971(3)	88(4)
C(53)	4113(6)	10885(6)	454(3)	79(3)
C(54)	3635(6)	10185(5)	135(3)	72(3)
C(55)	3042(5)	9502(4)	329(3)	57(2)
C(60)	856(4)	9763(4)	1166(2)	46(2)
C(61)	656(5)	10319(5)	716(3)	64(3)
C(62)	131(6)	11170(5)	718(4)	86(4)
C(63)	−176(7)	11496(6)	1162(4)	95(4)
C(64)	32(7)	10964(6)	1613(4)	98(4)
C(65)	531(6)	10095(5)	1611(3)	70(3)
C(70)	−302(4)	7911(4)	1209(2)	46(2)

Table 10—*continued.*

C(71)	−939(5)	8280(5)	784(3)	65(3)
C(72)	−1987(7)	8196(7)	723(4)	94(4)
C(73)	−2435(7)	7740(8)	1075(5)	108(5)
C(74)	−1838(6)	7334(7)	1496(4)	94(4)
C(75)	−756(5)	7410(5)	1579(3)	69(3)
C(80)	942(4)	6157(4)	1266(2)	43(2)
C(81)	925(5)	5691(5)	1745(3)	60(2)
C(82)	380(6)	4852(6)	1760(4)	84(3)
C(83)	−151(6)	4446(5)	1307(4)	90(4)
C(84)	−126(5)	4892(5)	843(3)	73(3)
C(85)	406(4)	5732(4)	813(3)	54(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

without positional constraints. All phenyl and methylene group hydrogen atoms were constrained to ideal geometries (with C—H = 0.96 Å), while other hydrogens were refined without positional constraints. All hydrogen atoms were assigned isotropic displacement parameters. Final difference syntheses showed no chemically significant features, the largest being close to the metal or solvent atoms. The absolute structure of **4** $\cdot C_2H_4Cl_2$ was assigned on the basis of refinement[28] [$\eta = 1.19(5)$]. Refinements converged smoothly to residuals given in Table 6. Tables 7–10 report the positional parameters for these structure determinations. Full tables of interatomic distances and bond angles, displacement parameters, hydrogen atomic parameters and observed and calculated structure amplitudes are given as supplementary material. All calculations were made with programs of the SHELXTL-PLUS[29] package as implemented on a Siemens R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 30.

Acknowledgements—We are grateful to the SERC for the award of Research Studentships (G. H., D. A. V. M., M. L. T.) and for support.

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