Stereoselective Alkyne Insertion into a Bridging Hydride at a Diiron Centre: *cis–trans* Isomerisation and Metallacycle Formation†

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Addition of the activated alkyne dimethyl acetylenedicarboxylate (dmad) to [$Fe_2(CO)_4(\mu$-H)(μ-CO)(μ-PPh_2)(μ-dppm)] **1** (dppm = $Ph_2PCH_2PPh_2$) afforded the σ–η vinyl complex *cis*-[$Fe_2(CO)_4${μ-C(CO_2Me)=CH(CO_2Me)}(μ-PPh_2)(μ-dppm)] **2**. Crystallography showed that the insertion is stereoselectively *cis*, with the phosphorus-containing ligands also adopting a *cis* configuration. Ultraviolet irradiation of **2** resulted in slow conversion into a second isomer, *trans*-[$Fe_2(CO)_4${μ-C(CO_2Me)=CH(CO_2Me)}(μ-PPh_2)(μ-dppm)] **3**, which still retains the *cis* arrangement of phosphines as shown by ^{31}P NMR spectroscopy. This transformation is reversible, **3** slowly converting back into **2** at room temperature, a process which is accelerated upon heating. At temperatures of ⩾80 °C, **2** (and **3**) was converted irreversibly into a third isomer [$Fe_2(CO)_4${C(CO_2Me)=CHC(OMe)=O}(μ-PPh_2)(μ-dppm)] **4**, containing a metallacyclic ring by virtue of metal co-ordination of an ester carbonyl. X-Ray crystallography revealed a *trans* vinyl orientation and a *trans* disposition of the phosphorus-containing groups.

We have recently been investigating the reactivity of hydride ligands when bridging the diiron centre, and have shown that primary alkynes readily insert to form σ–η vinyl complexes with high regioselectivity.[1,2] For example, propyne inserts into [$Fe_2(CO)_4(\mu$-H)(μ-CO)(μ-PPh_2)(μ-dppm)] **1** (dppm = $Ph_2PCH_2PPh_2$) to give the 1-methylvinyl complex [$Fe_2(CO)_4$(μ-MeC=CH_2)(μ-PPh_2)(μ-dppm)].[2] In contrast, under similar conditions **1** is inert to insertion by normal disubstituted alkynes.[3] We were interested in the latter process since it would allow us to assess the stereoselectivity of the insertion process, namely towards the formation of *cis* or *trans* vinyl complexes, and provide mechanistic details of the insertion process. This has been studied in some detail,[4,5] at mononuclear centres *cis* addition being generally observed, which is rationalised by initial co-ordination of the alkyne to the metal centre followed by *cis* addition of the hydride *via* a planar four-centre transition state.[6] Recently, however, in a number of instances *trans* addition products have been isolated,[7–9] which can be accounted for by postulating rapid isomerisation of the initially formed *cis* addition product,[7] or a free-radical pathway.[8,9] At the binuclear metal centre the stereochemistry of the insertion process has been studied to a lesser extent, although in a number of instances *cis* addition has been noted.[10] Herein we describe the insertion of the activated alkyne dimethyl acetylenedicarboxylate (dmad) into [$Fe_2(CO)_4(\mu$-H)(μ-CO)(μ-PPh_2)(μ-dppm)] **1**, which initially affords the *cis* addition product. Upon photolysis or thermolysis however *cis–trans* isomerisation is observed, the former being reversible but the latter irreversible by virtue of the co-ordination of one of the ester carbonyls to an iron centre (Scheme 1).

Results

Formation of cis-[$Fe_2(CO)_4${μ-C(CO_2Me)=CH(CO_2Me)}(μ-PPh_2)(μ-dppm)] **2**.—Addition of a slight excess of dmad to a toluene solution of [$Fe_2(CO)_4(\mu$-H)(μ-CO)(μ-PPh_2)(μ-dppm)] **1** at 50 °C results in slow dissolution of the latter and the formation of a bright orange solution from which *cis*-[$Fe_2(CO)_4${μ-C(CO_2Me)=CH(CO_2Me)}(μ-PPh_2)(μ-dppm)] **2** is isolated in 60% yield after chromatography. Insertion of the alkyne into the bridging hydride and loss of a carbonyl is easily shown by the disappearance of the relevant signals in the ^1H NMR and IR spectra respectively. In the ^{31}P NMR spectrum the appearance of well resolved doublets of doublets at δ 162.4 (*J* 51.7, 29.9) assigned to the phosphido-bridge and 57.4 (*J* 83.9, 29.9) and 42.2 (*J* 83.9, 52.1 Hz) due to inequivalent ends of the diphosphine reveals that σ–η vinyl fluxionality is slow at this temperature while the magnitude of the coupling constants strongly suggests a *cis* disposition of the phosphido and diphosphine moieties. A doublet of doublets at δ 2.49 (*J* 7.0, 1.8 Hz) in the ^1H NMR spectrum is assigned to the vinyl proton, the high-field chemical shift indicating that it is bound to the β-carbon, while singlets at δ 3.90 and 3.48 are attributed to inequivalent methyl groups. In the ^{13}C NMR spectrum four well resolved signals at δ 218.2 (dd, *J* 13.3, 3.0), 217.2 (dd, *J* 31.4, 24.0), 216.6 (dd, *J* 22.2, 5.5) and 214.7 (t, *J* 28.0) are observed for the metal-bound carbonyls, while C_α appears at δ 171.1 (dd, *J* 24.0, 14.7) and C_β at δ 57.7 (d, *J* 14.9 Hz). On the basis of these data however it was not possible unambiguously to assign the stereochemistry of the insertion process and thus an X-ray crystallographic study was carried out, the results of which are summarised in Table 1, while Fig. 1 shows the molecular geometry and numbering scheme.

The major features of the molecule are as expected in light of the spectroscopic data. The phosphorus-containing ligands bridge the iron–iron bond [Fe(1)–Fe(2) 2.653(1) Å] symmetrically [Fe(1)–P(3) 2.271(1), Fe(2)–P(3) 2.256(1), Fe(1)–P(1) 2.262(1), Fe(2)–P(2) 2.254(1) Å] and lie *cis* to one another as found in the starting hydride complex **1**. The vinyl ligand bridges the diiron centre in the familiar σ–η mode and lies *trans* to the diphosphine and *cis* to the phosphido-bridge. Most significantly, the structure clearly reveals a *cis* disposition of the ester substituents, both of which are orientated away from the sterically demanding phosphido-bridge.

Formation of trans-[$Fe_2(CO)_4${μ-C(CO_2Me)=CH(CO_2Me)}-(μ-PPh_2)(μ-dppm)] **3** *and* cis–trans *Isomerisation*.—The UV photolysis of a toluene solution of complex **2** results in slow conversion (over 12 h) to a new complex identified on the basis of spectroscopic data as an isomer, *trans*-[$Fe_2(CO)_4${μ-C-

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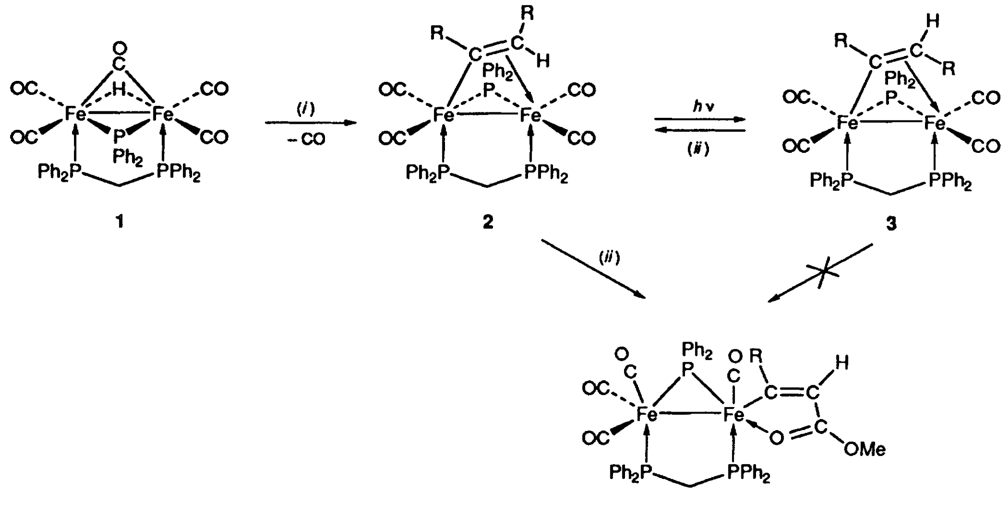
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 R = CO_2Me. (*i*) dmad; (*ii*) heat

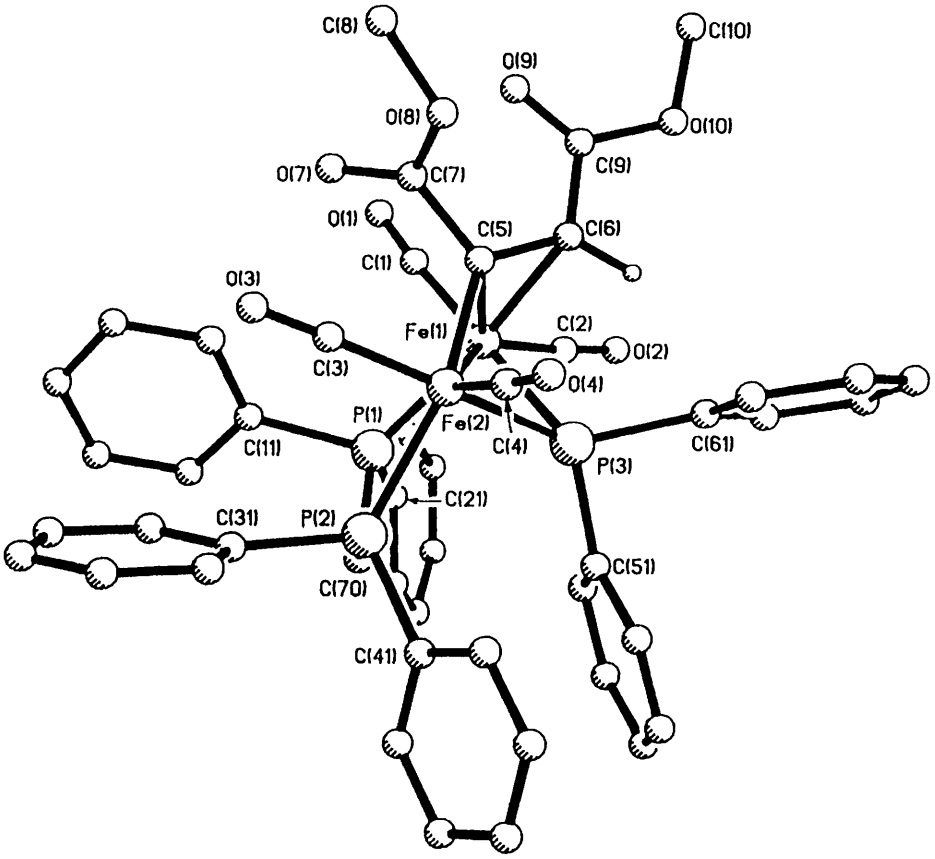


Fig. 1 Molecular structure of complex **2** with the labelling scheme

(CO_2Me)=$CH(CO_2Me)\}(\mu$-$PPh_2)(\mu$-dppm)] **3**. The process is conveniently followed by IR spectroscopy, new absorptions growing in at 1988s, 1947s and 1901s cm^{-1}. In the ^{31}P NMR spectrum three doublets of doublets are observed at δ 164.2 (*J* 37.1, 21.1), 51.2 (*J* 70.4, 37.1) and 45.3 (*J* 70.4, 21.1 Hz), the magnitude of the coupling constants revealing that the *cis* disposition of phosphorus-containing ligands is maintained in **3**, and that as in **2** σ–η vinyl fluxionality is slow at room temperature. In the ^1H NMR spectrum the unique vinyl proton is now observed as a slightly broadened signal at δ 2.05, while inequivalent methyl groups appear as singlets at δ 4.03 and 3.64. It has not proved possible to obtain an analytically pure sample of **3** since in the absence of UV irradiation it readily converts back into **2** as monitored by ^{31}P NMR spectroscopy. Hence at room temperature in [$^2H_8$]toluene *trans–cis* isomerism occurs over a period of 72 h, **3** cleanly converting back into **2**, while at higher temperatures the process occurs over an even shorter time-scale. Attempts at crystallising **3** simply resulted in the cocrystallisation of *cis* and *trans* isomers, while chromatography led to the isolation of **2** and a third isomer $[Fe_2(CO)_4$-$\{C(CO_2Me)$=$CHC(OMe)$=$O\}(\mu$-$PPh_2)(\mu$-dppm)] **4** (see below). The interconversion of **2** and **3** occurred in high yield and both could be cycled a number of times. Prolonged irradiation however led to the formation of small amounts of the previously characterised bis(phosphido) complex $[Fe_2(CO)_4(\mu$-$PPh_2)_2(\mu$-dppm)] **5**[11] together with other unidentified species. While the

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Fe(1)–Fe(2)	2.653(1)	Fe(1)–P(1)	2.262(1)
Fe(1)–P(3)	2.271(1)	Fe(1)–C(1)	1.786(5)
Fe(1)–C(2)	1.770(5)	Fe(1)–C(5)	2.082(4)
Fe(1)–C(6)	2.153(4)	Fe(2)–P(2)	2.254(1)
Fe(2)–P(3)	2.256(1)	Fe(2)–C(3)	1.786(5)
Fe(2)–C(4)	1.755(5)	Fe(2)–C(5)	1.954(4)
C(5)–C(6)	1.437(6)	C(5)–C(7)	1.497(6)
C(6)–C(9)	1.469(6)	C(7)–O(7)	1.260(6)
C(7)–O(8)	1.304(6)	C(8)–O(8)	1.441(11)
C(9)–O(9)	1.214(6)	C(9)–O(10)	1.337(6)
C(10)–O(10)	1.448(6)		
Fe(1)–Fe(2)–P(2)	103.1(1)	Fe(1)–Fe(2)–P(3)	54.4(1)
Fe(1)–Fe(2)–C(3)	115.2(2)	Fe(1)–Fe(2)–C(4)	140.0(2)
Fe(1)–Fe(2)–C(5)	51.0(1)	Fe(2)–Fe(1)–P(1)	85.7(1)
Fe(2)–Fe(1)–P(3)	53.9(1)	Fe(2)–Fe(1)–C(1)	121.7(2)
Fe(2)–Fe(1)–C(2)	144.8(1)	Fe(2)–Fe(1)–C(5)	46.9(1)
Fe(2)–Fe(1)–C(6)	77.9(1)	Fe(1)–P(3)–Fe(2)	71.8(1)
P(1)–Fe(1)–P(3)	93.7(1)	P(2)–Fe(2)–P(3)	90.6(1)
P(1)–Fe(1)–C(5)	122.8(1)	P(2)–Fe(2)–C(5)	149.3(1)
P(3)–Fe(1)–C(5)	82.5(1)	P(3)–Fe(2)–C(5)	85.8(1)
P(1)–Fe(1)–C(6)	162.3(1)	P(3)–Fe(1)–C(6)	82.2(1)
Fe(1)–C(5)–Fe(2)	82.1(1)	Fe(1)–C(6)–C(5)	67.5(2)
C(7)–C(5)–C(6)	115.0(4)	Fe(1)–C(5)–C(6)	72.9(2)
Fe(1)–C(5)–C(7)	127.3(3)	Fe(2)–C(5)–C(6)	127.2(3)
Fe(2)–C(5)–C(7)	117.2(3)	C(5)–C(6)–C(9)	120.6(3)

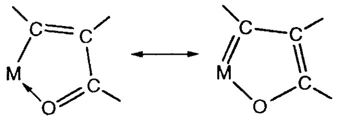
nature of this secondary reaction has not been fully discerned, we envisage that **5** might be formed from the addition of photogenerated $PHPh_2$ with **2** and/or **3**. Indeed, in a separate experiment, photolysis of a toluene solution of **2** with $PHPh_2$ was shown to afford **5**.

Irreversible Formation of Metallacyclic $[Fe_2(CO)_4\{C(CO_2Me){=}CHC(OMe){=}O\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **4**.—As previously stated, the well resolved nature of the ^{31}P NMR spectra of both complexes **2** and **3** at room temperature indicate that the well established 'windshield-wiper' fluxionality[12] often observed in σ–η vinyl complexes is slow on the NMR time-scale. Warming a $[^2H_8]$toluene solution of **2** to 70 °C results in no appreciable broadening in the ^{31}P NMR spectrum, however at this temperature signals due to a new complex appear, and at 100 °C all signals due to **2** disappear to be quantitatively replaced by those of the former. Column chromatography of the NMR sample or the residue following thermolysis of **2** in toluene affords a third isomer of the alkyne insertion, namely $[Fe_2(CO)_4\{C(CO_2Me){=}CHC(OMe){=}O\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **4** in 86% yield. That a major structural change has occurred is readily apparent from the IR spectrum, the metal–carbonyl absorptions at 2019m, 1957s, 1940(sh) and 1900m cm^{-1} varying considerably from those of **2** and **3** which contain two iron dicarbonyl units. In the ^{31}P NMR spectrum the phosphido-bridge resonance appears as a doublet of doublets at δ 199.1 (*J* 93.7, 33.7 Hz), the magnitude of the coupling constants indicating that the diphosphine lies *trans* to it. In the ^1H NMR spectrum again two methyl singlets are observed at δ 3.79 and 2.55, while the vinyl proton appears as a doublet at δ 6.52 (*J* 1.6 Hz), and in the ^{13}C NMR spectrum singlets at δ 242.5 and 117.4 are assigned to the α- and β-carbons of the vinyl ligand respectively. In order fully to elucidate the nature of the transformation an X-ray crystallographic study was carried out on **4**, the results of which are summarised in Table 2, while Fig. 2 shows the molecular structure.

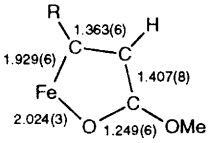
As expected the molecule consists of a diiron vector [Fe(1)–Fe(2) 2.796(1) Å] symmetrically spanned by phosphido [Fe(1)–P(3) 2.191(1), Fe(2)–P(3) 2.232(2) Å] and diphosphine [Fe(1)–P(1) 2.261(2), Fe(2)–P(2) 2.235(2) Å] moieties which adopt a *trans* disposition with respect to one another [P(1)–Fe(1)–P(3) 146.1(1), P(2)–Fe(2)–P(3) 142.5(1)°]. One of the iron atoms, Fe(2), carries three carbonyl ligands while the second, Fe(1) carries one. The co-ordination geometry at this iron atom is made up by the vinyl ligand which is co-ordinated through the α-carbon [Fe(1)–C(5) 1.929(6) Å] and one of the carbonyl oxygens of an ester substituent [Fe(1)–O(9) 2.024(3) Å]. The carbon–carbon double bond [C(5)–C(6) 1.363(6) Å] is no longer co-ordinated to the metal centres and unlike **2** the ester moieties adopt a *trans* configuration. The bonding within the metallacycle can be considered to lie between two mesomeric formulations (shown above) as previously discussed by a number of authors.[13–15] In **4** it is apparent from both structural and spectroscopic data that there is a significant contribution from the carbene formulation (**B**). The iron–carbon bond is short for a simple σ interaction, being more like an iron–carbene, for example the iron–carbon bond length in $[Fe(CO)_4(=CNMeCH_2CH_2NMe)]$ is 2.007 Å,[16] while the difference between formal double (C_α–C_β) [C(5)–C(6) 1.363(6) Å] and single (C_β–C_γ) [C(6)–C(9) 1.407(8) Å] carbon–carbon bonds based on formulation **A** is less than 0.05 Å. Spectroscopic data support this formulation, most notably the low-field chemical shift of the α-carbon at δ 242.5 which is characteristic of carbene complexes.[17]

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

Fe(1)–Fe(2)	2.796(1)	Fe(1)–P(1)	2.261(2)
Fe(1)–P(3)	2.191(1)	Fe(1)–C(1)	1.733(5)
Fe(1)–C(5)	1.929(6)	Fe(1)–O(9)	2.024(3)
Fe(2)–P(2)	2.235(2)	Fe(2)–P(3)	2.232(2)
Fe(2)–C(2)	1.807(5)	Fe(2)–C(3)	1.777(6)
Fe(2)–C(4)	1.792(5)	C(5)–C(6)	1.363(6)
C(6)–C(9)	1.407(8)	C(9)–O(9)	1.249(6)
C(5)–C(7)	1.479(8)	C(7)–O(7)	1.189(9)
C(7)–O(8)	1.330(7)	C(8)–O(8)	1.432(7)
C(9)–O(10)	1.344(5)	C(10)–O(10)	1.436(7)
Fe(1)–Fe(2)–P(2)	92.5(1)	Fe(1)–Fe(2)–P(3)	50.1(1)
Fe(1)–Fe(2)–C(2)	89.2(2)	Fe(1)–Fe(2)–C(3)	157.5(2)
Fe(1)–Fe(2)–C(4)	83.9(2)	Fe(2)–Fe(1)–P(1)	95.5(1)
Fe(2)–Fe(1)–P(3)	51.4(1)	Fe(2)–Fe(1)–C(1)	93.9(2)
Fe(2)–Fe(1)–C(5)	159.9(1)	Fe(2)–Fe(1)–O(9)	91.6(1)
P(1)–Fe(1)–P(3)	146.1(1)	P(2)–Fe(2)–P(3)	142.5(1)
Fe(1)–P(3)–Fe(2)	78.4(1)	Fe(1)–C(5)–C(6)	114.9(4)
C(5)–C(6)–C(9)	112.7(5)	C(6)–C(9)–O(9)	119.5(4)
C(5)–Fe(1)–O(9)	80.4(2)		



A **B**



Discussion

Crystallographic analysis of *cis*-$[Fe_2(CO)_4\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **2** reveals that the insertion of the activated alkyne dmad into $[Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **1** occurs with complete stereoselectivity. It also shows that the *cis* configuration of the phosphorus-containing ligands, previously deduced for **1** from spectroscopic data, is retained during the reaction. In a previous publication[1] we reported that insertion of primary alkynes into **1**, while occurring with high regioselectivity to give α-substituted vinyl complexes, gave both *cis* and *trans* isomers (with respect to the phosphine arrangements), the ratio of which was highly dependent upon the steric bulk of the α-substituent (R), such that when R = H only the *trans* isomer was observed, but when R = Ph a 10 : 1 ratio of *cis* to *trans* isomers resulted. Thus the selective formation of **2** which contains the relatively bulky

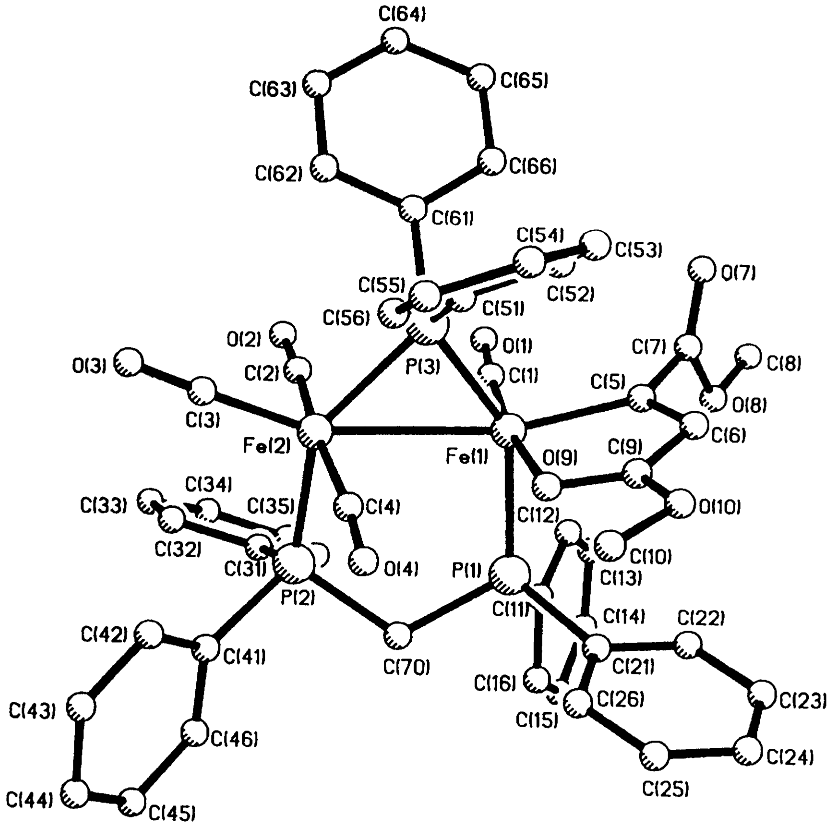


Fig. 2 Molecular structure of complex **4** with the labeling scheme

CO_2Me substituent at the α position is anticipated, however, it should be noted that the role of the β-carbon substituent has not yet been addressed in such detail.

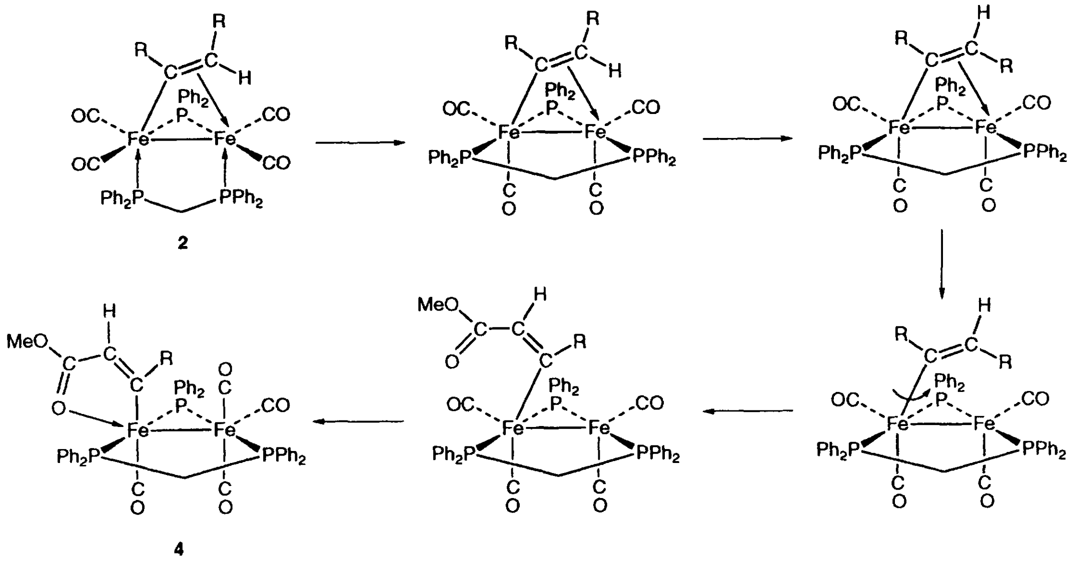
Upon photolysis of complex **2** in toluene a slow conversion into a second isomer *trans*-$[Fe_2(CO)_4\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **3** occurs. Similar UV-mediated *cis–trans* isomerisation of vinyl ligands has previously been reported at iridium centres[18] and is probably a result of a π–π* transition followed by rapid rotation about the carbon–carbon bond. The *trans* isomer **3** is kinetically quite stable and only converts back into the thermodynamically stable *cis* isomer over 3 d at room temperature. During the *cis–trans* isomerisation process, the phosphines retain their *cis* configuration, suggesting that the *cis–trans* phosphine rearrangement process may have a relatively high activation barrier. We did initially consider that the isomerisation process may be due to *endo–exo* exchange of the σ–η vinyl ligand, however inspection of the crystal structure of **2** (in which the vinyl is *endo*) cleary shows that a shift to the *exo* position would result in considerable steric interactions between one of the phenyl rings of the phosphido-bridge and the substituent on the α-carbon. Indeed four crystal structures of complexes of this type[1,3] all show *endo* vinyl co-ordination.

We have previously noted that the energy barriers to σ–η vinyl fluxionality in complexes of this type are high for those with a *cis* arrangement of phosphines, but lower for those with *trans* phosphines. For example the approximate free energies of activation for the 'windshield-wiper' fluxionality in isomers of $[Fe_2(CO)_4(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ are 45 ± 1 (*trans*) and 63 ± 1 (*cis*) kJ mol^{-1}.[1] In order to determine the free energy of activation for this process in **2**, a $[^2H_8]$toluene solution was slowly warmed whilst monitoring by ^{31}P NMR spectroscopy. At temperatures up to 70 °C no broadening of signals was apparent indicating that σ–η vinyl fluxionality is slow on the NMR time-scale under these conditions. At greater than 70 °C, however, further sharp signals due to the new complex $[Fe_2(CO)_4\{C(CO_2Me){=}CHC(OMe){=}O\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **4** began to grow in, while at 100 °C complete and quantitative conversion of **2** into **4** occurred within the time-scale of the experiment. A number of monomeric metallacyclic complexes of this type have previously been described,[9,13–15,18,19] however **4** appears to be the first such binuclear species.

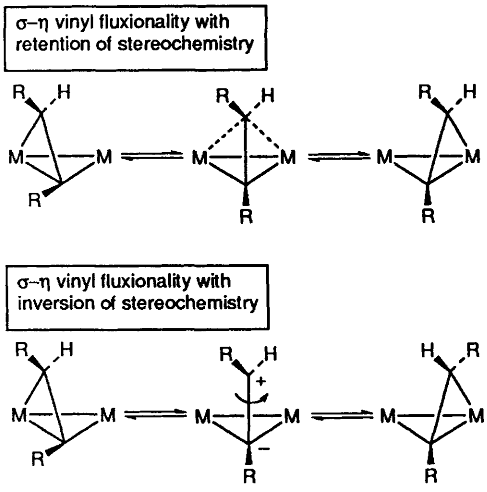
The transformation of complex **2** into **4** occurs as a result of a number of changes: (*i*) a *cis–trans* rearrangement of the phosphorus-containing ligands, (*ii*) *cis–trans* isomerisation of the vinyl moiety, (*iii*) a carbonyl shift from one metal to the other, and (*iv*) metal co-ordination of the oxygen of an ester carbonyl and displacement of the η^2-alkene co-ordination. A plausible reaction route is shown in Scheme 2, based on an initial *cis–trans* rearrangement of the phosphine moieties.

From previous work,[1] the vinyl ligand in the *trans*-phosphine complex formed is expected to be highly fluxional. The 'windshield-wiper' fluxionality however generally occurs with retention of stereochemistry,[12,20] although in two instances *cis–trans* isomerisation has been noted to occur during the process.[21,22] In order to invoke inversion of stereochemistry, it is necessary to postulate that the vinyl fluxionality occurs *via* a transition state in which rotation about the C_α–C_β bond is possible (Scheme 3). Such a transition state could be zwitterionic in nature, with localisation of positive charge on the β-carbon. Indeed, the two reported examples of σ–η vinyl fluxionality which occur with inversion of stereochemistry support this postulation. In one case the complex itself, namely $[Mo_2(CO)_4(\mu\text{-}HC{=}CH_2)(\eta^5\text{-}C_5H_5)_2]^+$,[22] is cationic, while in $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}HC{=}CH_2)]$ the stereochemical inversion only occurs in the presence of pyridine which is proposed to stabilise the development of positive charge on the β-carbon.[23] Such a transition-state differs from that in which retention of stereochemistry is noted, since here the β-carbon is bound to both metal atoms.

In order to proceed to complex **4**, formation of a σ-vinyl complex must be postulated. While this could occur for both *cis*



Scheme 2 R = CO_2Me



Scheme 3

and *trans* vinyl isomers, it is only the latter that is in the correct orientation to enable the irreversible co-ordination of the ester carbonyl to an iron centre, and this could be followed by carbonyl migration. In support of this last step, Vessey and Mawby[9] have recently shown that this reaction proceeds rapidly at mononuclear ruthenium centres.

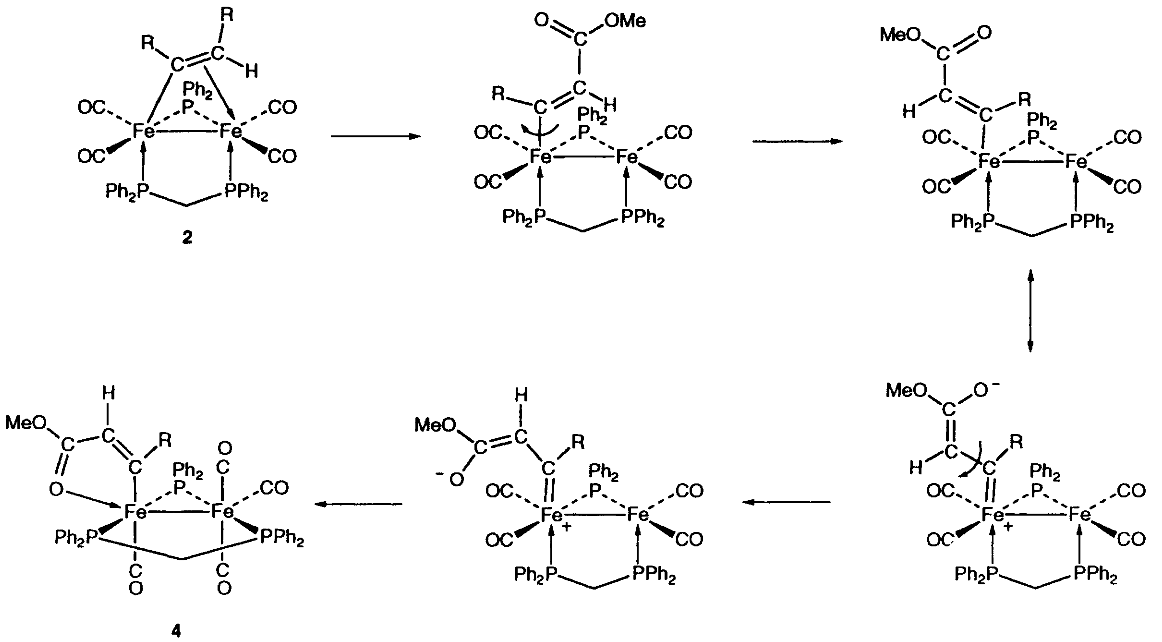
A second reaction route was also considered based on an initial rearrangement of the vinyl ligand from a bridging to a terminal binding mode (Scheme 4). Such a scheme then requires rotation about both metal–carbon and C_α–C_β bonds. The latter may seem unlikely since it involves rotation about a double bond, however, it can readily occur in the zwitterionic formulation shown. The final step would again be the carbonyl migration, however this could occur concomitantly with the *cis–trans* rearrangement of the phosphorus-containing ligands. Since complex **3** already contains a *trans* vinyl ligand we considered that it may rearrange directly to **4** and not *via* the intermediacy of **2**. Heating a [$^2H_8$]toluene solution of **3** led to a gradual increase in the concentration of **2**. At 70 °C, and before the onset of formation of **4**, conversion of **3** into **2** was complete, and thus it can be concluded that the latter pathway does not occur under these conditions. Interestingly, however, chromatography of a mixture of **2** and **3** at room temperature did lead to the formation of **4**, and since **2** alone does not it can be concluded that **3** converts into **4** on an alumina chromatography column. While the role of the alumina support in this conversion is not known, we have previously noted that the conversion of $[Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **1**, which contains a *cis* arrangement of phosphine moieties, into $[Fe_2(CO)_4(\mu\text{-}OH)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ in which the phosphines are *trans* occurs under similar conditions.[11] This may indicate that the energy barrier to the *cis–trans* rearrangement of phosphines is lowered significantly on an alumina support, however it cannot be discounted that the role of the alumina may be one of stabilising any zwitterionic intermediate(s). Indeed, further support for this route (Scheme 4) comes from the observation that **3** does not convert directly into **4**. In an attempt to trap out a σ-vinyl intermediate, **2** was heated in the presence of an excess of PPh_3, however the only product isolated was **4** in a yield comparable to that in the absence of the phosphine.

Experimental

General Comments.—Techniques and instrumentation were as previously described in another paper in this series[1] and $[Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **1** was prepared as previously reported.

Syntheses.—*cis*-$[Fe_2(CO)_4\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **2**. A toluene solution (20 cm^3) of complex **1** (0.30 g, 0.36 mmol) and dmad (0.20 cm^3, 1.63 mmol) was stirred at room temperature for 24 h resulting in dissolution of **1** and formation of a bright orange solution. Removal of the solvent under reduced pressure gave an orange solid which was chromatographed on alumina. Elution with light petroleum (b.p. 40–60 °C)–dichloromethane (3:7) gave an orange band which afforded **2** (0.20 g, 60%). Crystals suitable for X-ray diffraction were grown upon slow diffusion of methanol into a dichloromethane solution (Found: C, 59.70; H, 4.30; P, 10.05. Calc. for $C_{47}H_{39}Fe_2O_8P_3$: C, 60.30; H, 4.20; P, 9.90%). NMR ($CDCl_3$): ^1H, δ 8.2–6.1 (m, 30 H, Ph), 3.90 (s, 3 H, CO_2Me), 3.77 (q, *J* 10.9, 1 H, CH_2), 3.48 (s, 3 H, CO_2Me), 3.43 (q, *J* 14.0, 1 H, CH_2) and 2.49 (dd, *J* 7.0, 1.8, 1 H, CH); ^{13}C, δ 218.2 (dd, *J* 13.3, 3.0, CO), 217.2 (dd, *J* 31.4, 24.0, CO), 216.6 (dd, *J* 22.2, 5.5, CO), 214.7 (t, *J* 28.0, CO), 179.6 (d, *J* 5.1, CO_2Me), 171.6 (dd, *J* 6.9, 3.7, CO_2Me), 171.1 (dd, *J* 24.0, 14.7, C_α), 140.4–126.4 (m, Ph), 57.7 (d, 14.9, C_β), 52.0 (s, CO_2Me), 51.2 (s, CO_2Me) and 43.0 (dd, *J* 26.3, 17.6, CH_2); ^{31}P, δ 162.4 (dd, *J* 51.7, 29.9, μ-PPh_2), 57.4 (dd, *J* 83.9, 29.9, ½dppm) and 42.2 (dd, *J* 83.9, 52.1 Hz, ½dppm). IR (CH_2Cl_2): 2005s, 1982vs, 1953s and 1926s cm^{-1}.

trans-$[Fe_2(CO)_4\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **3**. A toluene solution (150 cm^3) of complex **2** (0.15 g,



Scheme 4 R = CO_2Me

Table 3 Crystallographic data for *cis*-$[Fe_2(CO)_4\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **2** and $[Fe_2(CO)_4\{C(CO_2Me){=}CHC(OMe){=}O\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **4***

	2	**4**
Formula	$C_{47}H_{39}Fe_2O_8P_3$	$C_{47}H_{39}Fe_2O_8P_3$
Space group	$P2_1/a$	$P2_1/c$
a/Å	17.4738(56)	19.2953(28)
b/Å	12.7840(28)	11.5876(38)
c/Å	20.3881(53)	20.3391(42)
β/°	101.100(23)	106.550(14)
U/Å^3	4469.19	4359.14
D_c/g cm^{-3}	1.39	1.43
μ(Mo-Kα)/cm^{-1}	8.04	8.24
Orientation reflections and range/°	24, $15 \leqslant 2\theta \leqslant 29$	27, $27 \leqslant 2\theta \leqslant 14$
Data measured	8589	8442
Unique data	8471	8207
No. unique with $I \geqslant 3.0\sigma(I)$	5767	5274
No. parameters	550	541
R	0.048	0.0499
R'	0.053	0.0541
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.001\,315F^2$	$\sigma^2(F) + 0.002\,018F^2$
Largest shift/e.s.d. in final cycle	0.008	0.002
Largest peak/e Å^{-3}	1.03	0.63

* Details in common: M 936; monoclinic; $Z = 4$; $F(000)$ 1928; 19 °C.

0.16 mmol) was irradiated for 12 h. Removal of the solvent under reduced pressure afforded an orange solid which was washed with light petroleum (b.p. 40–60 °C) and dried. The resulting solid contained up to 95% of **3** as shown by ^{31}P NMR spectroscopy. NMR ($C_6D_5CD_3$): ^1H, δ 8.2–6.2 (m, Ph), 4.03 (s, CO_2Me), 3.80 (m, CH_2), 3.64 (s, CO_2Me), 3.50 (m, CH_2) and 2.05 (br, CH); ^{31}P, δ 164.2 (dd, J 37.1, 21.1, μ-PPh_2), 51.2 (dd, 70.4, 37.1, $\frac{1}{2}$dppm) and 45.3 (dd, J 70.4, 21.1, $\frac{1}{2}$dppm). IR (CH_2Cl_2): 1988s, 1947s and 1901s cm^{-1}. Monitoring by ^{31}P NMR spectroscopy resulted in the steady growth of **2**, complete conversion occurring over 3 d at room temperature, while at 70 °C conversion occurred within 5 min. After longer irradiation periods small amounts of $[Fe_2(CO)_4(\mu\text{-}PPh_2)_2(\mu\text{-dppm})]$ **5** appeared together with some unidentified peaks between δ 50 and 0. Chromatography of a sample that had been irradiated for 3 d gave three products, namely **5** (20), **2** (20) and **4** (40%).

$[Fe_2(CO)_4\{C(CO_2Me){=}CHC(OMe){=}O\}(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ **4**. A toluene solution (50 cm^3) of complex **2** (0.20 g, 0.21 mmol) was refluxed for 2 h resulting in a colour change fróm orange to red. Removal of the solvent under reduced pressure gave a red solid which was chromatographed on alumina. Elution with light petroleum (b.p. 40–60 °C)–dichloroemethane (7:3) gave a red band which afforded **4** (0.18 g, 86%). Crystals suitable for X-ray diffraction were grown upon slow diffusion of methanol into a dichloromethane solution (Found: C, 58.75; H, 4.40; P, 9.00. Calc. for $C_{47}H_{39}Fe_2O_8P_3{\cdot}0.5CH_2Cl_2$: C, 58.25; H, 4.10; P, 9.50%). NMR ($C_6D_5CD_3$): ^1H, δ 8.4–6.6 (m, 30 H, Ph), 6.52 (d, J 1.6, 1 H, CH), 4.17 (m, 2 H, CH_2), 3.79 (s, 3 H, CO_2Me) and 2.55 (s, 3 H, CO_2Me); ^{13}C, δ 242.5 (s, C_α), 221.3 (t, J 20.8, CO), 217.0 (dd, J 30.3, 22.5, CO), 215.5 (dd, J 26.2, 20.6, CO), 215.0 (s, CO), 179.4 (s, $\mathit{C}O_2Me$), 176.1 (s, $\mathit{C}O_2Me$), 142.0–127.0 (m, Ph), 117.4 (s, C_β), 52.9 (s, $CO_2\mathit{Me}$), 51.1 (s, $CO_2\mathit{Me}$) and 49.6 (dd, J 28.7, 16.5, CH_2); ^{31}P ($CDCl_3$), δ 199.1 (dd, J 93.7,

Table 4 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	2422(1)	784(1)	7929(1)	C(22)	4450(3)	2994(4)	8725(3)
Fe(2)	2836(1)	−228(1)	6917(1)	C(23)	4727(5)	3504(4)	9325(3)
P(1)	3274(1)	2031(1)	7742(1)	C(24)	4204(7)	3857(5)	9694(3)
P(2)	3953(1)	574(1)	6806(1)	C(25)	3421(6)	3676(4)	9484(3)
P(3)	3316(1)	−522(1)	8009(1)	C(26)	3143(4)	3160(4)	8880(3)
O(1)	1200(2)	2382(3)	7797(2)	C(31)	3984(2)	1206(3)	6001(2)
O(2)	2494(3)	777(3)	9367(2)	C(32)	3812(4)	2256(4)	5876(3)
O(3)	2185(2)	495(4)	5558(2)	C(33)	3798(5)	2667(5)	5244(3)
O(4)	2836(3)	−2341(3)	6392(2)	C(34)	3955(3)	2070(4)	4735(3)
O(7)	996(2)	1072(3)	6462(2)	C(35)	4108(3)	1026(4)	4850(2)
O(8)	728(2)	−649(3)	6355(2)	C(36)	4121(3)	599(4)	5475(2)
O(9)	338(2)	235(3)	7642(2)	C(41)	4861(2)	−181(3)	6926(2)
O(10)	681(2)	−1070(3)	8370(2)	C(42)	5577(3)	311(4)	7123(2)
C(1)	1672(3)	1753(3)	7799(2)	C(43)	6250(3)	−262(5)	7204(3)
C(2)	2490(3)	801(3)	8807(2)	C(44)	6226(3)	−1325(5)	7084(3)
C(3)	2422(3)	262(4)	6106(2)	C(45)	5521(3)	−1816(4)	6882(3)
C(4)	2866(3)	−1505(4)	6606(2)	C(46)	4838(3)	−1244(3)	6804(2)
C(5)	1816(2)	−164(3)	7174(2)	C(51)	4322(2)	−360(3)	8480(2)
C(6)	1621(2)	−512(3)	7791(2)	C(52)	4888(3)	−1107(3)	8400(2)
C(7)	1135(3)	138(4)	6643(2)	C(53)	5637(3)	−1037(5)	8770(3)
C(8)	35(6)	−429(11)	5865(6)	C(54)	5835(3)	−244(5)	9232(3)
C(8A)	386(9)	1330(12)	5967(8)	C(55)	5274(3)	489(5)	9326(3)
C(9)	826(3)	−381(3)	7916(2)	C(56)	4518(3)	426(4)	8954(2)
C(10)	−113(3)	−1078(4)	8480(3)	C(61)	3134(2)	−1734(3)	8448(2)
C(11)	2933(3)	3087(3)	7146(2)	C(62)	3167(3)	−1701(4)	9133(3)
C(12)	2296(3)	2942(4)	6623(2)	C(63)	3081(4)	−2592(4)	9488(3)
C(13)	2113(3)	3708(4)	6133(3)	C(64)	2960(3)	−3549(4)	9162(3)
C(14)	2563(4)	4592(4)	6155(3)	C(65)	2944(3)	−3600(4)	8491(3)
C(15)	3183(3)	4750(4)	6672(3)	C(66)	3035(3)	−2697(3)	8125(2)
C(16)	3367(3)	4010(3)	7164(2)	C(70)	4162(2)	1617(3)	7439(2)
C(21)	3671(3)	2796(3)	8500(2)				

Table 5 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	2 235(1)	787(1)	8 845(1)	C(22)	2 745(3)	4 190(5)	9 101(3)
Fe(2)	2 889(1)	−947(1)	8 273(1)	C(23)	3 110(4)	4 948(5)	9 602(3)
P(1)	2 563(1)	2 254(1)	8 264(1)	C(24)	3 839(3)	4 854(5)	9 876(3)
P(2)	3 090(1)	251(1)	7 485(1)	C(25)	4 210(3)	4 005(5)	9 654(3)
P(3)	2 380(1)	−1 039(1)	9 129(1)	C(26)	3 844(3)	3 239(5)	9 143(3)
O(1)	799(2)	396(4)	7 948(3)	C(31)	2 417(3)	212(4)	6 648(2)
O(2)	1 483(2)	−1 549(4)	7 309(2)	C(32)	2 401(3)	−754(5)	6 235(3)
O(3)	3 450(3)	−3 251(4)	8 132(3)	C(33)	1 849(4)	−846(6)	5 615(3)
O(4)	4 259(2)	−44(4)	9 154(2)	C(34)	1 342(3)	−4(6)	5 404(3)
O(7)	695(3)	1 230(5)	9 643(4)	C(35)	1 363(3)	941(5)	5 802(3)
O(8)	835(2)	2 783(3)	9 062(2)	C(36)	1 889(3)	1 065(5)	6 425(3)
O(9)	3 159(2)	1 066(3)	9 604(2)	C(41)	3 940(3)	80(4)	7 252(2)
O(10)	3 599(2)	1 796(3)	10 669(2)	C(42)	4 432(3)	−771(5)	7 544(3)
C(1)	1 383(3)	545(4)	8 287(3)	C(43)	5 087(3)	−867(5)	7 388(3)
C(2)	2 016(3)	−1 292(5)	7 690(3)	C(44)	5 259(3)	−86(5)	6 947(3)
C(3)	3 234(3)	−2 340(5)	8 181(3)	C(45)	4 761(3)	750(6)	6 640(3)
C(4)	3 710(3)	−384(4)	8 836(3)	C(46)	4 114(3)	835(5)	6 795(3)
C(5)	1 845(3)	1 589(4)	9 491(3)	C(51)	2 952(3)	−1 391(4)	10 002(3)
C(6)	2 344(3)	1 923(5)	10 081(3)	C(52)	2 752(3)	−985(5)	10 564(3)
C(7)	1 072(3)	1 824(5)	9 414(3)	C(53)	3 197(4)	−1 168(5)	11 223(3)
C(8)	78(3)	3 019(7)	8 910(5)	C(54)	3 833(3)	−1 745(5)	11 332(3)
C(9)	3 051(3)	1 585(4)	10 104(3)	C(55)	4 031(3)	−2 177(5)	10 782(3)
C(10)	4 287(3)	1 312(6)	10 677(3)	C(56)	3 590(3)	−1 997(4)	10 113(3)
C(11)	1 911(3)	3 214(4)	7 673(2)	C(61)	1 607(2)	−2 010(4)	9 030(2)
C(12)	1 188(3)	3 134(5)	7 600(3)	C(62)	1 561(3)	−3 074(5)	8 697(3)
C(13)	694(3)	3 885(5)	7 167(3)	C(63)	960(3)	−3 764(5)	8 610(3)
C(14)	936(4)	4 697(7)	6 809(3)	C(64)	402(3)	−3 417(5)	8 861(3)
C(15)	1 658(4)	4 810(7)	6 890(5)	C(65)	440(3)	−2 389(5)	9 203(3)
C(16)	2 154(4)	4 083(6)	7 324(4)	C(66)	1 038(3)	−1 682(5)	9 288(3)
C(21)	3 103(3)	3 328(4)	8 859(3)	C(70)	3 174(2)	1 786(4)	7 752(2)

33.7, μ-PPh_2), 64.6 (dd, *J* 81.0, 33.7, $\frac{1}{2}$dppm) and 57.2 (dd, *J* 93.7, 81.0 Hz, $\frac{1}{2}$dppm). IR (CH_2Cl_2): 2019m, 1957s, 1940sh and 1900m cm^{-1}. Thermolysis of **2** (0.10 g, 0.11 mmol) and PPh_3 (0.14 g, 3.81 mmol) for 2 h in toluene (25 cm^3) resulted in the isolation of **4** (0.09 g, 90%).

Crystal-structure Determinations.—A red single crystal of complex **2**, approximate size 0.76 × 0.70 × 0.42 mm, was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation

(λ = 0.710 73 Å). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 24 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 8589 reflections (8471 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and empirically for absorption. The 5767 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/a$.

The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically. The hydrogen atom H(1) of the vinyl group was located in the Fourier-difference map while other hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 Å^2). The final cycle of least-squares refinement included 550 parameters for 5762 variables and did not shift any parameter by more than 0.008 times its standard deviation. The final R values were 0.048 and 0.053. The final Fourier-difference map contained a peak of 1.03 e Å^{-3} close to C(8). A disorder at the latter was modelled by allowing for 60% occupany of C(8) and 40% for an alternative site, C(8a). Structure solution used the SHELXTL PLUS program package[23] on a microVax II computer.

Crystallographic analysis of complex **4** was carried out in an analogous manner on a brown single crystal of approximate size 0.50 × 0.50 × 0.25 mm. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in idealised positions. All important crystallographic parameters are summarised in Table 3 and atomic coordinates in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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