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Reactions of σ - π alkenyl complexes [Fe₂(CO)₆(µ-alkenyl)(µ-PPh₂)] with bis(diphenylphosphino)methane (dppm); carbonyl substitution, migratory carbonyl insertion, phosphorus–carbon bond formation and cleavage, proton shift and alkenyl isomerisation reactions

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Abstract

Products of the thermal reactions of μ -alkenyl complexes [Fe₂(CO)₆(μ -R¹C=CHR²)(μ -PPh₂)] (1) (a, R¹ = R² = H; b, R¹ = EtO, $R^2 = H$; c, $R^1 = H$, $R^2 = Ph$; d, $R^1 = Ph$, $R^2 = H$; e, $R^1 = R^2 = Ph$; f, $R^1 = CMe = CH_2$, $R^2 = H$), with bis(diphenylphosphino)methane (dppm) are substituent dependent. Complexes 1a-c afford simple substitution products trans-[Fe₂(CO)₄(μ alkenyl)(μ -PPh₂)(μ -dppm)] (2a-c); while with 1d,e, α , β -unsaturated acyl complexes *trans*-[Fe₂(CO)₄{ μ -O=C-C(Ph)= $CH(R^2)$ (µ-PPh₂)(µ-dppm)] (3d,e) are the major products formed via a migratory-insertion reaction. A minor product of the reaction with 1d is $[Fe_2(CO)_5{\mu-Ph_2PC(Ph)=CH_2}(\mu-dppm)]$ (4), the result of phosphorus-carbon bond formation. Reaction of 1f also leads to phosphorus-carbon bond formation together with a 1.4-proton shift giving the μ -alkylidene complex [Fe₂(CO)₄{ μ - $HC-C(Me)=C(Me)PPh_{2}(\mu-dppm)$ (5). Dppm addition to 1c has been followed in detail, allowing a complete reaction scheme to be developed. Initial carbonyl substitution affords the η^1 -dppm complex [Fe₂(CO)₅(η^1 -dppm)(μ -HC=CHPh)(μ -PPh₂)] (6). This subsequently isomerises to trans-[Fe₂(CO)₄(μ -O=C-CH=CHPh)(μ -PPh₂)(μ -dppm)] (3c) which then readily loses CO to give the μ -alkenyl 2c. Loss of CO from isomeric 3d occurs only upon prolonged thermolysis and also affords 2c, a result of α , β -alkenyl isomerisation. Further, heating 4 also yields 2c after CO loss, phosphorus-carbon bond cleavage, and alkenyl isomerisation. While the β -substituted phenylethenyl complex 2c is stable to prolonged reflux in toluene, heating isomeric cis-[Fe₂(CO)₄(μ -PhC=CH₂)(μ -PPh₂)(μ -dppm)] (7) results in formation of the 5-electron μ -acyl complex [Fe₂(CO)₃{ μ -O=C-C(Ph)=CH₂}(μ dppm)(µ-PPh₂)]) (8); also prepared upon heating 4. Crystal structures have been carried out on 3e and 5. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of small metal-bound hydrocarbyl ligands continues to be an area of intense research activity. The alkenyl moiety is one such species, being formally a metalated alkene, and over the past 30 years a large number of alkenyl complexes have been prepared and studied. More recent interest in this class of compound stems from their proposed role as key intermediates in the Fischer–Tropsch process [1]. Consequently, the reactivity of the ligand, which had previously received little attention, has become an active area of research and Maitlis and co-workers [2], Ros and Mathieu [3], and Knox [4] have shown that

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coupling of alkenyl and C_1 fragments can occur readily at the binuclear metal centre.

At the binuclear metal centre, the preferred ligand binding is that in which it bridges the two metal centres acting as both a σ - and π -donor ligand. In 1975, Shapley et al. [5] first reported that such ligands can display stereochemical non-rigidity via 'windshield wiper' fluxionality. Here, while the α -carbon remains bound to both metal centres, the β -carbon oscillates between them and since it generally occurs with retention of stereochemistry [6], the proposed transition state is one in which the two carbons are symmetrically bound to both metal centres.

We became interested in this fluxional process as a result of preparing isomeric µ-alkenyl complexes, $[Fe_2(CO)_4(\mu-alkenyl)(\mu-PR_2)(\mu-dppm)]$, which displayed quite different free energies of activation for the process [7-9]. In an effort to investigate this further, we sought access to a wider range of such complexes, to date prepared via the room temperature (r.t.) hydrodimetalation of alkynes to cis-[Fe₂(CO)₄(μ -H)(μ -CO)(μ -PPh₂)-(u-dppm)] [7,9]. While this works well for primary alkynes and the activated alkyne dimethylacetylene dicarboxylate [10], less reactive disubstituted alkynes require elevated temperatures at which benzene elimination vielding $[Fe_2(CO)_5(\mu-PhPCH_2PPh_2)(\mu-$ PPh₂)] is rapid and dominant [11]. In contrast, r.t. hydrodimetalation of $[Fe_2(CO)_7(\mu-H)(\mu-PPh_2)]$ occurs with both mono- and di-substituted alkynes [12]. We thus sought to prepare further dppm-bridged alkenyl complexes via the carbonyl substitution of hexacarbonyl complexes $[Fe_2(CO)_6(\mu-R^1C=CHR^2)(\mu-PPh_2)]$ (1). While in a number of cases simple carbonyl substitution did occur to give the dppm-bridged alkenyl complexes, in many reactions the alkenyl group was non-innocent and took part in the reaction; migratory carbonyl insertion, alkenyl isomerisation, phosphorus-carbon bond formation and 1,4-proton shift reactions all being observed. Herein, we report full details of this work.

2. Results and discussion

2.1. Carbonyl substitution reactions

Heating a toluene solution of $[Fe_2(CO)_6(\mu-HC=CH_2)(\mu-PPh_2)]$ (1a) and dppm for 10 min resulted in the formation of *trans*- $[Fe_2(CO)_4(\mu-HC=CH_2)(\mu-PPh_2)(\mu-dppm)]$ (2a) in 75% yield, while the β -phenylalkenyl complex $[Fe_2(CO)_6(\mu-HC=CHPh)(\mu-PPh_2)]$ (1c) reacts in a similar fashion to afford *trans*- $[Fe_2(CO)_4(\mu-HC=CHPh)(\mu-PPh_2)(\mu-dppm)]$ (2c) in 60% yield after 1 h. Both have been previously prepared [7] via hydrodimetalation of respective alkynes by *cis*- $[Fe_2(CO)_4(\mu-H)(\mu-CO)(\mu-PPh_2)(\mu-dppm)]$. Reaction of $[Fe_2(CO)_6(\mu-EtOC=CH_2)(\mu-PPh_2)]$ (1b) and dppm was somewhat slower, occurring over 3 h in refluxing toluene to afford *trans*-[Fe₂(CO)₄(μ -EtOC=CH₂)(μ -PPh₂)(μ -dppm)] (**2b**) in 90% yield. The *trans* structure was readily ascertained from the phosphorus–phosphorus coupling constants to the phosphido-bridge (77.4 and 77.1 Hz), and is unusual as to date all such α -substituted complexes have adopted a *cis* conformation [7,9,10]. Isolation of the *trans* isomer here may reflect the site selectivity of the substitution process or result from the initial formation of the *cis* isomer which rearranges to the more stable *trans* form under the reaction conditions.



Characterisation of 2b was straightforward, being based on a comparison of spectroscopic data with that of 1b. Noteworthy is the extremely low-field resonance for the α -carbon at 219.60 (d, J 25.9 Hz) ppm, while in the ¹H NMR spectrum the alkenvl protons are observed at δ 2.51 (dt, J 17.4, 6.4) and 2.29 (ddd, J 13.7, 10.6, 6.4 Hz). The static nature of the alkenyl ligand at r.t. on the NMR timescale is clearly shown by the inequivalence of the two ends of the diphosphine, represented by signals at 76.2 (dd, J 121.8, 77.4) and 72.3 (dd, J 121.8, 77.1 Hz) ppm in the ³¹P NMR spectrum and the appearance of four separate carbonyl resonances in the ¹³C NMR spectrum. Consequently, a variable temperature ³¹P NMR study was carried out in d⁸-toluene; raising the temperature to 87°C resulted in the coalescence of the two diphosphine signals allowing a free energy of activation to be calculated at 67.1 ± 2 kJ mol $^{-1}$. This is essentially the same as that found for unsubstituted **2a** (67.5 \pm 2) [13], and methyl substituted trans-[Fe₂(CO)₄(μ -MeC=CH₂)(μ -PCy₂)(μ -dppm)] (≥ 68 ± 2 kJ mol⁻¹) [8], suggesting that substitution at the α -position has little effect on the rate of alkenyl fluxionality. In contrast, we have previously shown that substitution at the β -carbon leads to a considerable reduction in the free energy of activation for this process [7,9].

2.2. Bridging acyl complexes via migratory carbonyl insertion

The thermal reaction of $[Fe_2(CO)_6(\mu-PhC=CH_2)(\mu-PPh_2)]$ (1d) and dppm appears to follow a quite different course to that found for isomeric 1c. Heating a toluene solution of 1d and dppm to 100°C resulted in a considerable and immediate darkening of the solution and formation of the α,β -unsaturated bridging acyl

complex *trans* - [Fe₂(CO)₄{ μ - O = C - C(Ph) = CH₂}(μ -PP-h₂)(μ -dppm)] (**3d**) in 81% yield as the major reactionproduct. In an analogous manner, reaction of [Fe₂(CO)₆(μ -PhC=CHPh)(μ -PPh₂)] (**1e**) gave *trans*-[Fe₂(CO)₄{ μ -O=C - C(Ph)=CHPh}(μ -PPh₂)(μ -dppm)] (**3e**) in 72% yield as the only isolable product. Characterisation as bridging acyl complexes was based on spectroscopic and analytical data. Significantly, both showed a low field resonance in the ¹³C NMR spectrum attributed to the acyl carbon, appearing at 300.1 (t, *J* 20.5) and 297.9 (t, *J* 30.5 Hz) ppm for **3d** and **3e**, respectively, while the *trans* arrangement of phosphorus-containing ligands was again clear from ³¹P NMR spectroscopy.



In order to unambiguously establish the migratory carbonyl insertion reaction, an X-ray crystallographic study was carried out on **3e** the results of which are summarised in Table 1 and Fig. 1. The diiron vector $[Fe(1)-Fe(2) \ 2.6637(10) \ \text{Å}]$ is bridged symmetrically by the phosphido $[Fe(1)-P(3) \ 2.2250(12), \ Fe(2)-P(3) \ 2.2263(13) \ \text{Å}]$ and diphosphine $[Fe(1)-P(1) \ 2.2830(13), \ Fe(2)-P(2) \ 2.2653(13) \ \text{Å}]$ ligands which adopt a relative *trans* arrangement. The bridging acyl ligand lies *cis* to both, being bound through oxygen to one metal $[Fe(1)-O(5) \ 2.005(3) \ \text{Å}]$ and carbon to the sec-

Table 1 Selected bond lengths (Å) and bond angles (°) for 3e

Bond lengths (Å)			
Fe(1)-Fe(2)	2.6637(10)	Fe(1)-C(1)	1.794(4)
Fe(1) - C(2)	1.761(4)	Fe(2)–C(3)	1.789(4)
Fe(2)-C(4)	1.819(4)	Fe(2)–C(5)	1.992(4)
Fe(1)–O(5)	2.005(3)	Fe(1) - P(1)	2.2830(13)
Fe(2)-P(2)	2.2653(13)	Fe(1) - P(3)	2.2250(12)
Fe(2) - P(3)	2.2263(13)	O(5)–C(5)	1.291(4)
C(5)–C(6)	1.516(5)	C(6)–C(7)	1.351(5)
Bond angles (°)			
Fe(1)-Fe(2)-C(3)	155.1(2)	Fe(1)-Fe(2)-C(4)	101.80(14)
Fe(1) - Fe(2) - C(5)	68.64(11)	Fe(2)-Fe(1)-C(1)	159.7(2)
Fe(2) - Fe(1) - C(2)	95.34(13)	Fe(2)-Fe(1)-O(5)	71.08(7)
Fe(1)-Fe(2)-C(5)	68.64(11)	C(1)-Fe(1)-C(2)	93.9(2)
C(3)-Fe(2)-C(4)	90.3(2)	P(1)-Fe(1)-P(3)	151.71(4)
P(2)-Fe(2)-P(3)	144.54(5)	Fe(1)-P(3)-Fe(2)	73.51(4)
Fe(2)–C(5)–O(5)	113.1(3)	C(5)-C(6)-C(7)	120.5(4)
O(5)–C(5)–C(6)	112.7(3)		



Fig. 1. Molecular structure of 3e.

ond [Fe(2)-C(5) 1.992(4) Å]. The carbon-oxygen bond length of 1.291(4) Å is typical of values found for related acyl complexes [9,14-16] as is the planar nature of the $Fe_2-C(5)-O(5)$ arrangement (the biggest deviation from this plane being 0.03 Å). The carbon-carbon bonds within the acyl ligand [C(5)-C(6) 1.516(5), C(6)-C(7) 1.351(5) Å] are consistent with a localised single and double bond formulation, while the two phenyl groups have maintained their *cis* arrangement.

Migratory carbonyl insertion into a metal-alkenyl moiety has previously been noted [17], while a number of related diiron α,β -unsaturated acyl complexes have also been reported [9,14,15]. We have crystallographically characterised the dicyclohexylphosphido analogue of 3d, being isolated as a minor product of the reaction of *trans*-[Fe₂(CO)₄(μ -H)(μ -CO)(μ -PCy₂)(μ dppm)] and PhC=CH [9], while Seyferth and co-workers have prepared related thiolate- [14] and phosphido-bridged [15] diiron hexacarbonyl complexes. For example, the hexacarbonyl analogue of **3c**, namely $[Fe_2(CO)_6(\mu-O=C-CH=CHPh)(\mu-PPh_2), re$ sults from addition of the acid chloride to $Na[Fe_2(CO)_6(\mu-PPh_2)]$ [15]. A noteworthy feature of the thiolate-bridged hexacarbonyl complexes is the generally ready loss of CO and formation of the alkenyl complex upon dissolution in THF [14]. Both 3d and 3e are indefinitely stable under these conditions, however, at higher temperatures CO is lost from 3d as discussed below.

2.3. Phosphorus-carbon bond formation and cleavage

A minor product from the reaction of 1d and dppm was characterised as the vinylphosphine complex $[Fe_2(CO)_5{\mu-Ph_2PC(Ph)=CH_2}(\mu-dppm)]$ (4) (12% yield). The IR spectrum is characteristic of a diiron pentacarbonyl fragment, a formulation confirmed by mass spectrometry. The formation of a new carbonphosphorus bond was clearly shown by the absence of a low-field phosphido-bridge resonance in the ³¹P NMR spectrum, which consists of doublets of doublets at 77.7 (J 113.6, 21.4), 75.7 (J 113.6, 98.2) and 58.2 (J 98.2, 21.4 Hz) ppm. Formation of 4 from 1d is a result of carbonyl loss, diphosphine coordination and coupling of the alkenyl and phosphido moieties. Mays and co-workers [18] have described the synthesis of vinylphosphine dimolybdenum complexes via an analogous phosphorus-carbon bond forming process. Further, we have previously prepared the related complex $[Fe_2(CO)_5(\mu-Ph_2PCH=$ ethenylphosphine CH₂)(µ-dppm)] [13] via irradiation of diphenylvinylphosphine and $[Fe_2(CO)_6(\mu-CO)(\mu-dppm)]$, and spectroscopic data for this and 4 are similar.



The reaction between $[Fe_2(CO)_6 \{\mu-C(CMe=CH_2)=$ CH_2 (µ-PPh₂)] (1f) and dppm followed a quite different course to those described above. Overnight reflux was required and resulted in a colour change from vellow to orange with the isolation of the complex $[Fe_2(CO)_4 \{\mu-HC-C(Me)=C$ µ-alkylidene $(Me)PPh_{2}(\mu-dppm)$] (5) in 51% yield. The appearance of four carbonyl bands in the IR spectrum initially appeared to suggest that it was a simple diphosphine derivative of 1f, however, the absence of a low-field phosphido-bridge resonance in the ³¹P NMR spectrum was again indicative of phosphorus-carbon bond formation. Likewise, the appearance of two methyl resonances in the ¹H NMR spectrum suggested that a significant rearrangement of the alkenyl ligand had occurred. In order to elucidate the precise nature of 5 an X-ray crystallographic study was carried out, the results of which are summarised in Table 2 and Fig. 2.

The molecule consists of two iron atoms [Fe(1)-Fe(2) 2.6325(4) Å] bridged by the dppm ligand with each carrying two carbonyls. The diiron centre is also bridged somewhat asymmetrically by what can be considered as a substituted alkylidene ligand [Fe(1)-C(6)]

Table 2 Selected bond lengths (Å) and bond angles (°) for 5

Bond lengths (Å)			
Fe(1)–Fe(2)	2.6325(4)	Fe(1)-C(1)	1.7770(22)
Fe(1) - C(2)	1.7519(21)	Fe(2) - C(3)	1.7393(22)
Fe(2)-C(4)	1.7554(24)	Fe(1)-C(6)	1.9827(21)
Fe(2)-C(6)	2.0488(18)	Fe(2)–C(7)	2.0826(21)
Fe(2)-C(8)	2.1252(22)	Fe(1) - P(1)	2.2358(6)
Fe(1) - P(3)	2.2139(6)	Fe(2) - P(2)	2.1794(6)
P(3)-C(8)	1.7809(22)	C(6)–C(7)	1.411(3)
C(7)–C(8)	1.439(3)	C(7)–C(9)	1.509(3)
C(8)–C(10)	1.513(3)		
Bond angles (°)			
Fe(1)-Fe(2)-C(3)	164.30(8)	Fe(1)-Fe(2)-C(4)	76.03(7)
Fe(1)-Fe(2)-C(6)	48.15(6)	Fe(1)-Fe(2)-C(7)	77.40(6)
Fe(1)-Fe(2)-C(8)	80.02(6)	Fe(2)-Fe(1)-C(1)	111.73(6)
Fe(2)-Fe(1)-C(2)	153.07(8)	Fe(2)-Fe(1)-C(6)	50.33(5)
Fe(1)–Fe(2)–P(2)	99.094(18)	Fe(2)-Fe(1)-P(1)	93.060(13)
Fe(2)–Fe(1)–P(3)	72.437(18)	C(1)-Fe(1)-C(2)	93.91(10)
C(3)-Fe(2)-C(4)	96.66(11)	P(1)-Fe(1)-P(3)	165.491(24)
P(3)-Fe(1)-C(6)	81.62(6)	Fe(2)-C(6)-C(7)	71.32(11)
Fe(2)-C(7)-C(6)	68.74(11)	Fe(2)-C(7)-C(8)	71.61(12)
Fe(2)-C(7)-C(9)	127.95(15)	C(6)–C(7)–C(8)	114.31(19)
C(6)–C(7)–C(9)	123.09(20)	C(8)–C(7)–C(9)	122.59(19)
C(7)–C(8)–C(10)	121.26(20)		

1.9827(21), Fe(2)–C(6) 2.0488(18) Å]. This carbon carries an unsaturated substituent, the carbon–carbon double bond of which [C(7)–C(8) 1.439(3) Å] is π -bonded to Fe(2) [Fe(2)–C(7) 2.0826(21), Fe(2)–C(8) 2.1252(22) Å]. The other end of the olefinic group is bound to what was the phosphido-bridge [P(3)–C(8) 1.7809(22) Å] and is now linked to only a single metal centre [Fe(1)–P(3) 2.2358(6) Å]. This phosphorus atom lies approximately *trans* to one end of the



Fig. 2. Molecular structure of 5.



Scheme 1.

diphosphine $[P(1)-Fe(1)-P(3) 165.491(24)^{\circ}]$, accounting for the coupling constant of 163.8 Hz between them.

The overall transformation of 1f to 5 involves: (i) substitution of two carbonyls for dppm, (ii) phosphorus-carbon bond formation between the phosphidobridge and the α -carbon of the alkenyl ligand, (iii) a 1,4-proton shift from the olefinic carbon to the β -carbon of the alkenyl ligand, and (iv) coordination of the deprotonated olefinic carbon. The precise order of these steps is not known, however, the close proximity of the phosphido-bridge to the α -carbon of the alkenyl ligand may facilitate the carbon-phosphorus bond formation process. A possible route is shown (Scheme 1). If metal coordination of the diphosphine promotes attack of the phosphido-bridge at the α -carbon of the alkenyl group then this will facilitate a 1,4-proton transfer to the β -carbon. One might expect this process to be facile since 1f can be viewed as a metalated 1,4-diene. Finally, coordination of the carbene carbon and the olefinic bond give rise to 5 as shown.

2.4. Mechanistic insights: a closer look at the reaction of **1c** and dppm

As noted earlier, thermolysis of **1c** and dppm for 1 h afforded the μ -alkenyl complex **2c** in 60% yield. When this reaction was followed spectroscopically, two intermediates were characterised enabling a clear reaction scheme to be established. In the presence of a slight excess of dppm, warming **1c** to reflux resulted in the rapid formation of a bright orange solution from which the η^1 -dppm complex [Fe₂(CO)₅(η^1 -dppm)(μ -HC=CHPh)(μ -PPh₂)] (6) was isolated in 45% yield after chromatography. Characterisation was straight-forward, the uncoordinated phosphorus cen-

tre appearing at δ – 19.0 (J 60.8 Hz) ppm in the ³¹P NMR spectrum. Further heating of a toluene solution of 6 gave a vellow solution after 40 min, which after chromatography afforded an inseparable mixture of μ -acyl trans-[Fe₂(CO)₄(μ -O=C-CH=CHPh)(μ -PPh₂)(μ trans-[Fe2(CO)4(µ-(magb (**3c**) and µ-alkenyl $HC=CHPh)(\mu-PPh_2)(\mu-dppm)$] (2c) in an approximate 2:3 ratio. Complex 3c could not be isolated free of 2c but unambiguous characterisation was based on a comparison of spectroscopic data with isomeric 3d. Pertinently, the two acyl protons appear as AB doublets at δ 6.22 and 6.00 in the ¹H NMR spectrum with a coupling constant of 15.9 Hz indicating their trans disposition. Further heating of this mixture for 90 min resulted in quantitative conversion to the µalkenyl complex 2c.



2.5. Thermal stability of α,β -unsaturated acyl complexes and alkenyl isomerisation

As previously alluded to, many of the thiolatebridged α , β -unsaturated acyl complexes reported by Seyferth undergo ready CO loss to afford the corresponding alkenyl complexes [14], a process shown to follow first-order kinetics [19]. Exceptions to this ready CO loss are complexes with alkyl groups on the α -carbon, which lose CO only very slowly upon prolonged thermolysis, under which conditions dithiolate-bridged $[Fe_2(CO)_6(\mu-SEt)_2]$ is a major product [14]. This enhanced stability of the acyl-bridge has been attributed to electronic factors, as electron-donating groups are known to stabilise acyl binding. A further point of note is that when $Na[Fe_2(CO)_6(\mu -$ PPh₂)] reacts with $H_2C=CH-C(O)Cl$, the alkenyl complex 1a was the sole product, suggesting that here CO loss from the acyl may be facile [15].

In an attempt, then, to assess the stability of μ -acyl complexes **3d** and **3e**, prolonged toluene thermolysis of both was carried out. Complex **3e** was found to be indefinitely stable under these conditions, however,

further isomerisation of the α - to β -phenyl ethenyl ligand was observed upon heating the vinylphosphine complex **4** in toluene for 1 h which afforded **2c** (52%). Closely related to the latter is our earlier observation that the ethenylphosphine complex [Fe₂(CO)₅(μ -Ph₂PCH=CH₂)(μ -dppm)] converts cleanly into **2a** after CO loss and phosphorus–carbon bond cleavage [13]. A second complex isolated from the thermal degradation of **4** was the dppm cleavage product [Fe₂(CO)₆(μ -CH₂PPh₂)(μ -PPh₂)] (22%) [20], which presumably forms upon loss of the vinylphosphine and CO scavenging.



In a recent communication we reported that the α -phenylethenyl ligand can isomerise to its β -isomer at the diiron centre. For example, **1d** transforms into **1c** over 1 h in refluxing toluene [21], and we proposed that this may occur via a hydrido-alkyne complex, the latter acting as a 2-electron ligand lying parallel to the metal-metal vector. We were never able to detect such a species spectroscopically nor did we see any evidence of reversible CO insertion into the alkenyl ligand. Clearly, further experiments are required in order to fully elucidate the nature of this novel α - β alkenyl isomerisation reaction.

2.6. Thermal instability of cis-[Fe₂(CO)₄(μ -PhC=CH₂)-(μ -PPh₂)(μ -dppm)] (7): synthesis of a π -bound 5-electron donor α , β -unsaturated acyl complex

In earlier work we showed that hydrodimetalation of phenylethyne by $[Fe_2(CO)_4(\mu-H)(\mu-CO)(\mu-PPh_2)(\mu-dppm)]$ afforded isomeric *trans*- $[Fe_2(CO)_4(\mu-HC=CHPh)(\mu-PPh_2)(\mu-dppm)]$ (**2c**) and *cis*- $[Fe_2(CO)_4(\mu-PhC=CH_2)(\mu-PPh_2)(\mu-dppm)]$ (7) in an approximate 1:10 ratio [7]. The *cis*-disposition of phosphorus-containing ligands in 7 is noteworthy and is believed to be a consequence of the relatively bulky α -phenyl group.

In the preceding section, two examples were given in which the α -phenyl ethenyl ligand was transformed into its β -isomer. In light of this, and the absence of isolation of **7** from the reaction of **1c** with dppm, we decided to test the thermal stability of **7**, specifically to see if it would convert to a *trans* α -substituted complex or isomeric **2c**.



Heating a toluene solution of 7 for 30 min resulted in the isolation of three products after chromatography. The β -substituted isomer **2c** was formed in 22% yield, together with the carbon-phosphorus bond formation product $[Fe_2(CO)_5 \{\mu - Ph_2PC(Ph) = CH_2\}(\mu - dppm)]$ (4) (7%). Since we have already noted that under thermolysis 4 transforms into 2c, alkenyl isomerisation here presumably proceeds via 4. A third product was identified as the novel 5-electron donor α,β -unsaturated acyl $[Fe_2(CO)_3{\mu-O=C-C(Ph)=CH_2}(\mu-dppm)(\mu-dppm)]$ complex PPh₂)] (8) isolated as an orange crystalline solid in 14% yield. Characterisation was made on the basis of analytical and spectroscopic data, and a comparison of the latter with the related bis(diphenylphosphino)ethane (dppe) complex $[Fe_2(CO)_3 \{\mu - O = C - C(Ph) = CH_2\}(\eta^2 - CH_2)$ dppe)(µ-PPh₂)] which we have recently prepared and crystallographically characterised [22]. In the IR spectrum, two intense absorptions at 1968 and 1917 cm⁻¹ are characteristic of an Fe₂(CO)₃ fragment, a formulation supported by the carbonyl region of the ¹³C NMR spectrum. In the ¹H NMR spectrum, the two alkenyl protons appear at δ 3.43 (d, J 7.9) and 2.05 (t, J 9.3 Hz), both showing couplings to phosphorus but not to each other, and in the ¹³C NMR spectrum the acyl carbon appears at 303.1 (t, J 19.6 Hz) ppm, being shifted some 3 ppm down-field of the same resonance in the isomeric 3-electron acyl complex 3d. Complexation of the carbon-carbon double bond results in a significant shift of these carbon atoms from 155.4 and 78.6 in **3d** to 161.3 and 114.3 for the α - and β -carbons, respectively.

Isomerisation of 7 to 8 results from migratory CO insertion into the alkenyl fragment and subsequent metal coordination of the olefinic double bond such that the steric and electronic saturation of the diiron centre is preserved, while it should also be noted that there is a *cis-trans* rearrangement of phosphorus-containing ligands. Trace amounts of 8 were also isolated from the direct reaction of $[Fe_2(CO)_6(\mu-PhC=CH_2)(\mu-PPh_2)]$ (1d) and dppm and thus, it appears that here a



Scheme 2.

small amount of 7 is generated but cannot be isolated due to later thermal rearrangements to 4 and 8. The 5-electron acyl complex 8 is also formally related to 3d via CO loss and olefin coordination, yet it is not formed upon thermolysis of the latter, suggesting that here, thermal carbonyl extrusion from the acyl bridge is more facile than metal-carbonyl loss. In contrast, the related 5-electron acyl dppe complex $[Fe_2(CO)_3 \{\mu - O = C - C - CO)_3\}$ $C(Ph)=CH_2\{(\eta^2-dppe)(\mu-PPh_2)\}$ is generated slowly (>4 h) upon thermolysis of the analogous 3-electron $[Fe_2(CO)_4 \{\mu - O = C - C(Ph) = CH_2\}(\eta^2 - C(Ph)) = CH_2 \}$ acyl complex dppe)(µ-PPh₂)] [22]. However, since it formed from the thermal reaction of dppe with 1d at 90°C for 10 min, this must be a minor pathway to it.

3. Conclusions

We have shown in this paper that the potentially simple substitution reaction of two carbonyls by dppm in μ -alkenyl complexes [Fe₂(CO)₆(μ -alkenyl)(μ -PPh₂)] (1), leads to a number of different products and reaction pathways as summarised (Scheme 2). In all cases it seems that initial carbonyl substitution occurs to yield an η^1 -dppm complex, a reaction which is site-selective, probably occurring at the σ -bound iron centre and *trans* to the phosphido-bridge as this pattern of substitution has been noted with monodentate phosphines [21,23]. This then isomerises to afford the μ -acyl complex as a result of an intramolecular phosphine assisted migratory carbonyl insertion reaction, with all such complexes adopting a relative trans disposition of phosphorus-containing ligands. The rate of carbonyl extrusion from 3 is strongly dependent upon the alkenyl substituents, allowing their isolation in a number of instances. For 1a,b, the rate determining step is presumably the initial carbonyl substitution with subsequent steps being rapid, thus precluding the observation of any intermediates. We cannot rule out the possibility that here the second CO substitution reaction occurs much more rapidly than carbonyl insertion, and thus that **1a** and **1b** are formed directly from an η^1 -dppm complex. With 1c, the rates of the three separate steps are similar, the use of a slight excess of diphosphine serving to accelerate the initial carbonyl substitution reaction and thus allowing the isolation of 6. With 1d,e, carbonyl loss from the μ -acyl complexes **3d**,e is slow and these are the major products.

The reaction of 1d and dppm also affords some minor yield products, namely 2c (6%), 4 (12%) and 8 (trace), the relative amounts of which depend upon reaction time and scale. The expected dppm-bridged complex *cis*-[Fe₂(CO)₄(μ -PhC=CH₂)(μ -PPh₂)(μ -dppm)] (7) is not isolated, but separate experiments reveal that at toluene reflux this converts rapidly to a mixture of 2c (22%), 4 (7%) and 8 (14%), while heating 4 itself affords 2c (52%) and 8 (26%). These experiments suggest that the putative η^1 -dppm adduct [Fe₂(CO)₅(μ -PhC=CH₂)(μ -PPh₂)(η^1 -dppm)] initially formed upon addition of dppm to 1d preferentially isomerises to give μ -acyl 3d,

but a small amount loses CO to yield dppm-bridged 7, which is unstable under the reaction conditions and rearranges to afford a mixture of **2c**, **4** and **8**. We cannot, however, rule out the possibility that the η^1 dppm complex also isomerises to **4** directly, a result of carbon-phosphorus bond formation which competes with the migratory insertion reaction and results in the coupling of the alkenyl and phosphido-bridges. Certainly with **1f**, carbon-phosphorus bond formation is more facile than the migratory insertion reaction and the subsequent 1,4-proton shift produces a new organophosphorus ligand which does not undergo carbon-phosphorus bond cleavage, thus accounting for the isolation of **5**.

These experiments have shown that seemingly simple carbonyl substitution reactions at the μ -alkenyl supported diiron centre are more complex than initially might have been envisaged, this being primarily due to the high reactivity of the alkenyl ligand itself. Thus, it participates in a number of reactions including coupling to a carbonyl ligand to give a μ -acyl ligand, coupling to the phosphido-bridge (which may occur with internal proton transfer) to give alkenyl phosphines and α - β isomerisation.

4. Experimental

4.1. General procedures

General experimental methods have been described previously. Alkenyl complexes 1a-f [12] and 8 [7], were prepared by literature methods. All reactions were carried out in dry toluene under a nitrogen atmosphere but work-up was carried out in air unless otherwise stated.

4.2. $[Fe_2(CO)_6(\mu - HC = CH_2)(\mu - PPh_2)]$ (1a)

Heating a toluene solution (25 cm³) of **1a** (120 mg, 0.24 mmol) and dppm (109 mg, 0.28 mmol) resulted in a colour change from yellow to orange over 10 min. After removal of the solvent, chromatography eluting with ether:light-petroleum (1:9) gave a yellow band which afforded *trans*-[Fe₂(CO)₄(μ -HC=CH₂)(μ -PPh₂)(μ -dppm)] (**2a**) (150 mg, 75%).

4.3. $[Fe_2(CO)_6(\mu - EtOC = CH_2)(\mu - PPh_2)]$ (1b)

Heating a toluene solution (20 cm³) of **1b** (55 mg, 0.103 mmol) and dppm (45 mg, 0.117 mmol) for 3 h resulted in a colour change from yellow to orange. After removal of the solvent, chromatography eluting with ether:light-petroleum (2:3) afforded *trans*-[Fe₂(CO)₄(μ -EtOC=CH₂)(μ -PPh₂)(μ -dppm)] (**2b**) (80 mg, 90%).

2b: IR (CH₂Cl₂): 1978s, 1947vs, 1914s, 1900sh cm⁻¹; ¹H NMR (CDCl₃): δ 8.72–7.0 (m, Ph, 30H), 4.03 (dt, J 18.5, 15.2, 1H, PCH₂P), 3.22 (dt, J 14.6, 11.6, 1H, PCH₂P), 2.93 (t, J 11.9, 1H, C=CH₂), 2.51 (dt, J 17.4, 6.4, 1H, OCH₂), 2.29 (ddd, J 13.7, 10.6, 6.4, 1H, OCH₂), 2.02 (t, J 8.9, 1H, C=CH₂), 0.12 (t, J 6.4, 3H, CH₃); ¹³C NMR (CDCl₃): 221.8 (s, CO), 219.9 (d, J 9.5, CO), 219.6 (d, J 25.9, C_α), 216.5 (t, J 21.7, CO), 213.6 (t, J 20.7, CO), 142-126 (m, Ph), 67.8 (s, OCH₂), 59.4 (d, J 9.8, C_B), 34.5 (t, J 26.8, PCH₂P), 13.5 (s, CH₃) ppm; ³¹P NMR (CDCl₃): 193.5 (t, J 77.3, μ-PPh₂), 76.2 (dd, J 121.8, 77.4, dppm), 72.3 (dd, J 121.8, 77.1, dppm) ppm; mass spectrum (FAB⁺): m/z 864 (M^+), 837 (M-CO), 808 (M-2CO), 780 (M-3CO), 753 (M - 4CO); Anal. Calc. for Fe₂C₄₅H₃₉O₅P₃·0.25CH₂Cl₂: C, 61.33; H, 4.46. Found: C, 61.01; H, 4.41%.

4.4. $[Fe_2(CO)_6(\mu - HC = CHPh)(\mu - PPh_2)]$ (1c)

Heating a toluene solution (25 cm³) of **1c** (50 mg, 0.088 mmol) and dppm (37 mg, 0.097 mmol) for 1 h resulted in a slight darkening of the solution. After removal of the solvent, chromatography eluting with ether:light-petroleum (1:4) gave a yellow band which afforded trans-[Fe₂(CO)₄(μ -HC=CHPh)(μ -PPh₂)(μ -dppm)] (**2c**) (47 mg, 60%).

Heating a toluene solution (25 cm³) of **1c** (70 mg, 0.12 mmol) and dppm (60 mg, 0.16 mmol) for 10 min resulted in a colour change from yellow to orange. After removal of the solvent, chromatography afforded: a yellow band eluting with light-petroleum which gave unreacted **1c** (8 mg); an orange band eluting with ether:light-petroleum which gave [Fe₂(CO)₅(η^{1} -dppm)(μ -HC=CHPh)(μ -PPh₂)] (6) (45 mg, 45%); a yellow band eluting with ether:light-petroleum (1:4) which gave 50 mg of an inseparable mixture of **2c** and *trans*-[Fe₂(CO)₄(μ -O=C-CH=CHPh)(μ -PPh₂)(μ -dppm)] (**3c**) in a 1:2 ratio (by ¹H NMR spectroscopy).

Heating a toluene solution (25 cm^3) of **6** (40 mg, 0.043 mmol) for 40 min resulted in the formation of a yellow solution. Proton NMR spectroscopy revealed this to be a mixture of **2c** and **3c** (3:2) with the complete absence of **6**.

Heating a toluene solution (25 cm^3) of a 1:2 mixture of **2c** and **3c** (85 mg) for 90 min resulted in the isolation of pure **2c** (80 mg, ca. 100%) after column chromatography.

6: IR (CH₂Cl₂): 2031s, 1978vs, 1950s, 1916m cm⁻¹; ¹H NMR (CDCl₃): δ 8.22 (ddd, J 27.3, 13.0, 6.4, 1H, H_α), 7.85–6.95 (m, Ph, 33H), 6.54 (d, J 7.3, 2H, Ph), 3.98 (dd, J 13.0, 5.3, 1H, H_β), 3.43 (m, 2H, CH₂); ¹³C NMR (CDCl₃): 218.8 (t, J 12.0, CO), 213.8 (br, 3CO), 213.2 (t, J 19.3, CO), 153.8 (t, J 26.1, C_α), 141.5–124.5 (m, Ph), 89.8 (d, J 17.1, C_β), 32.1 (dd, J 34.5, 21.7, CH₂) ppm; ³¹P NMR (CDCl₃): 178.6 (d, J 93.4, μ-PPh₂), 64.3 (dd, J 93.4, 60.8, Fe–PPh₂), -19.0 (d, J 60.8, PPh₂) ppm; mass spectrum (FAB⁺): m/z 925 (M^+), 896 (M – CO), 868 (M – 2CO), 813 (M – 4CO), 784 (M – 5CO); *Anal*. Calc. for Fe₂C₅₀H₃₉O₅P₃: C, 64.94; H, 4.22. Found: C, 65.45; H, 4.49%.

3c: IR (CH₂Cl₂): 1982s, 1949vs, 1917s, 1900 sh (KBr) 1479w, 1433m, 1415w cm⁻¹; ¹H NMR (CDCl₃): δ 8.00 – 6.85 (m, Ph), 6.47 (t, *J* 7.7, 1H, Ph), 6.27 (d, *J* 7.4, 1H, Ph), 6.22 (d, *J* 15.9, 1H, C=CH), 6.00 (d, *J* 15.9, 1H, C=CH), 3.59 (dt, *J* 13.2, 10.1, 1H, CH₂), 2.79 (dt, *J* 14.4, 10.4, 1H, CH₂); ¹³C NMR (CDCl₃): 297.6 (t, *J* 18.6, C=O), 233.1 (d, *J* 31.9, CO), 219.7 (t, *J* 22.5, CO), 218.1 (t, *J* 16.4, CO), 216.9 (s, CO), 213.1 (s, CO), 144.1 (s, C_{α}), 143–122 (m, Ph), 68.1 (s, C_{β}), 37.3 (dd, *J* 25.4, 13.5, CH₂) ppm; ³¹P NMR (CDCl₃): 218.8 (dd, *J* 111.0, 54.5, µ-PPh₂), 59.6 (dd, *J* 63.6, 54.5, dppm), 49.7 (dd, *J* 111.0, 63.6, dppm) ppm.

4.5. $[Fe_2(CO)_6(\mu - PhC = CH_2)(\mu - PPh_2)]$ (1d)

Heating a toluene solution (60 cm³) of 1d (160 mg, 0.31 mmol) and dppm (150 mg, 0.39 mmol) for 10 min resulted in a considerable darkening of the solution. After removal of the solvent, chromatography gave: an orange band eluting with ether:light-petroleum (1:5) which afforded trans- $[Fe_2(CO)_4 \{\mu - O = C - C(Ph) = CH_2\}$ - $(\mu$ -PPh₂)(μ -dppm)] (3d) (130 mg, 81%); a yellow band eluting with ether:light petroleum (1:4) which gave 2c (10 mg, 6%); a red band eluting with ether: lightpetroleum (1:1) which afforded $[Fe_2(CO)_5]\mu-Ph_2PC (Ph)=CH_2$ (µ-dppm)] (4) (20 mg, 12%). This was airsensitive in chlorinated solvents and was handled accordingly. When the experiment was carried out on a larger scale a small amount of 8 was isolated which proved difficult to separate from **3d** by chromatography (see later).

3d: IR (CH₂Cl₂): 1981s, 1949vs, 1917s, 1902sh (KBr) 1479w, 1433m, 1404m cm⁻¹; ¹H NMR (CDCl₃): δ 8.2–6.85 (m, 33H, Ph), 5.88 (d, *J* 7.1, 2H, Ph), 5.42 (s, 1H, C=CH₂), 5.30 (s, 1H, C=CH₂), 3.55 (m, 1H, CH₂), 2.50 (ddd, *J* 10.3, 8.3, 1.9, 1H, CH₂); ¹³C NMR (CDCl₃): 300.1 (t, *J* 20.5, C=O), 219.7 (t, *J* 22.0, CO), 218.2 (t, *J* 17.1, CO), 217.8 (s, CO), 212.7 (s, CO), 155.4 (s, C_α), 142–124 (m, Ph), 78.6 (s, C_β), 37.8 (dd, *J* 23.8, 13.1, CH₂) ppm; ³¹P NMR (CDCl₃): 218.7 (dd, *J* 109.1, 56.4, μ-PPh₂), 58.9 (t, *J* 60, dppm), 48.1 (dd, *J* 109.1, 62.6, dppm) ppm; mass spectrum (FAB⁺): m/z 896 (*M* – CO), 868 (*M* – 2CO), 841 (*M* – 3CO), 812 (*M* – 4CO), 784 (*M* – 5CO); *Anal.* Calc. for Fe₂C₅₀H₃₉O₅P₃: C, 64.94; H, 4.22. Found: C, 64.77; H, 3.97%.

4: IR (CH₂Cl₂): 2012m, 1981vs, 1954s, 1925s, 1521w cm⁻¹; ¹H NMR (CDCl₃): δ 7.9–7.0 (m, 36H, Ph + C=CH₂), 5.16 (d, *J* 27.0, 1H, C=CH₂), 5.16 (q, *J* 12.1, 1H, CH₂), 3.10 (q, *J* 12.4, 1H, CH₂); ¹³C NMR (CDCl₃): 237.0 (br, CO), 217.3 (s, CO), 212.7 (d, *J* 25.6, CO), 212.3 (t, *J* 13.7, CO), 209.0 (t, *J* 14.9, CO), 142–125 (m, Ph), 66.9 (d, *J* 25.9, C_α), 53.9 (d, *J* 6.4,

C_β), 27.7 (t, *J* 16.4, CH₂) ppm; ³¹P NMR (CDCl₃): 77.7 (dd, *J* 113.6, 21.4), 75.7 (dd, *J* 113.6, 98.2), 58.2 (dd, *J* 98.2, 21.4) ppm; mass spectrum (FAB⁺): m/z 925 (*M*), 868 (*M* – 2CO), 812 (*M* – 4CO), 784 (*M* – 5CO); *Anal.* Calc. for Fe₂C₅₀H₃₉O₅P₃: C, 64.93; H, 4.22; P, 10.06. Found: C, 64.58; H, 3.94; P, 10.29%.

4.6. $[Fe_2(CO)_6(\mu - PhC = CHPh)(\mu - PPh_2)]$ (1e)

Heating a toluene solution (45 cm³) of **1e** (230 mg, 0.36 mmol) and dppm (165 mg, 0.43 mmol) for 5 min resulted in a considerable darkening of the solution. After removal of the solvent, chromatography recovered 30 mg of **1e** while eluting with ether:light-petroleum (1:4) gave an orange band which afforded *trans* - [Fe₂(CO)₄{ μ -O=C - C(Ph)=CHPh}(μ -PPh₂)(μ -dppm)] (**3e**) (200 mg, 65%). Large red crystals suitable for X-ray crystallography were grown upon slow diffusion of methanol into a saturated dichloromethane solution.

3e: IR (CH₂Cl₂): 1981s, 1950vs, 1911s, 1985sh (KBr) 1481w, 1433m, 1405m cm⁻¹; ¹H NMR (CDCl₃): δ 8.1–6.8 (m, Ph, 38H, Ph), 6.26 (d, *J* 7.6, 2H, Ph), 5.72 (br, 1H, H_β), 3.61 (q, *J* 12.9, 1H, CH₂), 2.62 (dt, *J* 13.6, 10.0, 1H, CH₂); ¹³C NMR (CDCl₃): 297.9 (t, *J* 30.5, C=O), 219.8 (t, *J* 21.1, CO), 218.3 (t, *J* 18.3, CO), 218.0 (s, CO), 212.9 (s, CO), 146.3 (s, C_α), 146–126 (m, Ph), 77.2 (d, *J* 12.0, C_β), 37.6 (dd, *J* 25.1, 12.2, CH₂) ppm; ³¹P NMR (CDCl₃): 217.8 (dd, *J* 111.0, 56.9, µ-PPh₂), 58.8 (t, *J* 59.3, dppm), 48.2 (dd, *J* 111.0, 61.2, dppm) ppm; mass spectrum (FAB⁺): *m/z* 1002 (*M*), 972 (*M* – CO), 944 (*M* – 2CO), 860 (*M* – 5CO); *Anal.* Calc. for Fe₂C₅₆H₄₃O₅P₃: C, 67.20; H, 4.30. Found: C, 66.47; H, 4.09%.

4.7. $[Fe_2(CO)_6 \{ \mu - C(CMe = CH_2) = CH_2 \} (\mu - PPh_2)]$ (1f)

Thermolysis of a toluene solution (20 cm³) of 1f (55 mg, 0.103 mmol) and dppm (45 mg, 0.113 mmol) for 24 h resulted in the formation of a bright orange solution. After removal of the solvent, chromatography afforded: an orange band eluting with dichloromethane: light-petroleum (1:3) which gave 15 mg of an unidentified product. IR (CH₂Cl₂): 1993s, 1957vs, 1924vs, 1901sh cm⁻¹; ³¹P NMR (CDCl₃): 158.6 (d, br, J 59), 54.0 (br), -27.7 (d, J 59) ppm; eluting with dichloromethane:light-petroleum (1:2) gave an orange which afforded $[Fe_2(CO)_4]\mu$ -HC-C(Me)=C band (Me)PPh₂ $(\mu$ -dppm)] (5) (45 mg, 51%). Orange crystals suitable for X-ray crystallography were grown upon slow diffusion of methanol into a saturated dichloromethane solution.

5: IR (CH₂Cl₂): 1975s, 1929vs, 1908s, 1882m cm⁻¹; ¹H NMR (CDCl₃): δ 8.2–6.9 (m, 21H, Ph + μ -CH), 3.67 (q, *J* 13.8, 1H, CH₂), 2.42 (dt, *J* 14.3, 10.3, 1H, CH₂), 1.71 (s, 3H, CH₃), 1.57 (s, 3H, CH₃) ppm; ¹³C NMR (CDCl₃): 227.8 (t, *J* 8.0, CO), 217.2 (t, *J* 18.9, CO), 216.4 (t, 12.9, CO), 216.3 (d, *J* 13.6, CO), 150.8 (t, *J* 17.7, μ -C), 140–127 (m, Ph), 112.8 (dd, *J* 36.6, 6.7, CMe), 46.8 (dd, *J* 33.6, 9.2, CMe), 43.1 (t, *J* 12.2, CH₂), 22.2 (d, *J* 4.3, Me), 16.3 (s, Me) ppm; ³¹P NMR (CDCl₃): 81.2 (d, *J* 94.7, dppm), 78.7 (d, *J* 163.8, Ph₂), 72.2 (dd, *J* 163.8, 94.7, dppm) ppm; mass spectrum (FAB⁺): m/z 860 (*M*), 804 (*M* – 2CO), 748 (*M* – 4CO); *Anal.* Calc. for Fe₂C₄₆H₃₉O₄P₃ · 0.5CH₂Cl₂: C, 61.82; H, 4.43. Found: C, 61.93; H, 4.30%.

4.8. Thermolysis of $cis-[Fe_2(CO)_4(\mu-PhC=CH_2)-(\mu-PPh_2)(\mu-dppm)]$ (7)

A toluene solution (35 cm^3) of 7 (410 mg, 0.46 mmol) was heated at reflux for 30 min resulting in a considerable darkening of the solution. After removal of the solvent, chromatography afforded: an orange band eluting with ether:light-petroleum (1:5) which gave [Fe₂(CO)₃{ μ -O=C-C(Ph)=CH₂}(μ -PPh₂)(μ -dppm)] (8) (60 mg, 14%); a yellow band eluting with ether:light-petroleum (1:4) gave **2c** (90 mg, 22%); an orange band eluting with ether:light-petroleum (3:2) gave **4** (30 mg, 7%).

8: IR (CH₂Cl₂): 1968s, 1917s cm⁻¹; ¹H NMR (CDCl₃): δ 8.1–6.4 (m, Ph, 35H), 3.59 (q, *J* 11.5, 1H, CH₂), 3.43 (d, *J* 7.9, 1H, C=CH₂), 2.67 (dt, *J* 12.3, 9.4, 1H, CH₂), 2.05 (t, *J* 9.3, 1H, CH₂); ¹³C NMR (CDCl₃): 303.1 (t, *J* 19.6, C=O), 220.1 (dd, *J* 23.6, 13.2, CO), 218.3 (t, *J* 22.0, CO), 214.1 (s, CO), 161.3 (s, C_α), 114.3 (s, C_β), 37.7 (dd, *J* 24.7, 9.7, CH₂) ppm; ³¹P NMR (CDCl₃): 218.9 (dd, *J* 98.6, 42.4, µ-PPh₂), 61.1 (dd, *J* 62.1, 42.4, dppm), 43.1 (dd, *J* 98.6, 62.1, dppm) ppm; mass spectrum (FAB⁺): m/z 896 (*M*), 868 (*M* – CO), 840 (*M* – 2CO), 812 (*M* – 3CO), 784 (*M* – 4CO); *Anal.* Calc. for Fe₂C₄₉H₃₉O₄P₃ · 0.25CH₂Cl₂: C, 64.43; H, 4.31. Found: C, 64.37; H, 4.70%.

4.9. Thermolysis of $[Fe_2(CO)_5{\mu-Ph_2PC(Ph)=CH_2}-(\mu-dppm)]$ (4)

A toluene solution (30 cm³) of **4** (20 mg, 0.022 mmol) was refluxed for 1 h. After removal of the solvent, chromatography afforded: a yellow band eluting with ether:light-petroleum (1:9) which gave $[Fe_2(CO)_6(\mu-PPh_2CH_2)(\mu-PPh_2)]$ (3 mg, 22%); an orange band eluting with ether:light-petroleum (1:4) which gave **8** (5 mg, 26%); a yellow band eluting with ether:light-petroleum (1:3) which gave **2c** (10 mg, 52%).

4.10. Crystallographic structure determinations

Crystals of 3e and 5 were grown from slow diffusion of methanol into dichloromethane solutions. Crystals were mounted on a glass fibre. For 3e; all geometric

Table 3	
Crystallographic	data

	3e	$5 \cdot 0.45$ CHCl ₃
Empirical formula	Fe ₂ C ₅₅ H ₄₃ O ₅ P ₃	Fe ₂ C _{46.45} H _{39.45} O ₄ P ₃ Cl _{1.35}
Colour	red	orange
Space group	$P2_1/n$	$P\overline{1}$
Unit cell dimensions		
a (Å)	12.839(3)	10.2324(10)
b (Å)	19.583(4)	11.96720(11)
c (Å)	19.980(4)	19.54540(20)
α (°)	90	102.768(5)
β (°)	90.08(3)	95.870(5)
γ (°)	90	110.711(5)
V (Å ³)	5024	2140
Ζ	4	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.286	1.392
μ (Mo K α) (cm ⁻¹)	7.17	8.90
No. data measured	8809	8708
No. unique data used for sln	8807	6934
No. parameters	595	653
R (all data)	0.053(0.079)	0.033(0.047)
$R_{\rm w}$ (all data)	0.128(0.152)	0.032(0.033)
Largest peak (e Å ⁻³)	0.802	0.430
Largest hole (e $Å^{-3}$)	-0.494	-0.400

and intensity data were taken using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo K α radiation ($\lambda = 0.71073$ Å) at 19 ± 1°C. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The $\omega - 2\theta$ technique was used to measure reflections in the range $5^{\circ} \le 2\theta \le 50^{\circ}$. 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 unique data with $I \ge 2.0\sigma(I)$ were used to solve and refine the structure. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. All hydrogens except H(7) were placed in idealised positions (C-H, 0.96 Å) which was found in a difference map. All were assigned a common isotropic thermal parameter (U = 0.08 Å²). Structure solution was made using the SHELXTL PLUS programme package [24] on a PC. Crystallographic data for 3e and 5 are presented in Table 3. Positional parameters are listed in Table 4.

For $5 \cdot 0.45$ CHCl₃; all geometric and intensity data were taken using a Siemens SMART CCD diffractometer equipped with Mo K α radiation ($\lambda = 0.71073$ Å) at $19 \pm 1^{\circ}$ C. The lattice vectors were identified by centring 6502 reflections with $I > 5\sigma(I)$. The ω technique was

Table 4	
Positional parameters ($\times 10^4$) and	$U_{\rm eq}$ (Å ² ×10 ³) for 3e

Table 5 Positional parameters and B_{iso} for 5

	x	у	Ζ	$U_{ m eq}$	_		x	у	Ζ	B _{iso}
Fe(1)	515(1)	2769(1)	6127(1)	35(1)	F	e1	0.12639(3)	0.84113(3)	0.225853(16)	2.021(13)
Fe(2)	2199(1)	2304(1)	6759(1)	36(1)	F	e2	0.28769(3)	1.07668(3)	0.287904(16)	2.303(13)
P(1)	1102(1)	2683(1)	5052(1)	37(1)	P	1	0.03851(5)	0.88187(5)	0.12901(3)	2.130(24)
P(2)	2961(1)	2019(1)	5776(1)	38(1)	P	2	0.20468(5)	1.15995(5)	0.21457(3)	2.360(25)
P(3)	761(1)	2721(1)	7228(1)	39(1)	P	3	0.24228(6)	0.85246(5)	0.33085(3)	2.57(3)
O(1)	-1420(3)	3529(2)	5848(2)	8/(1)	0	1	0.27689(16)	0.70627(15)	0.14560(9)	4.22(9)
O(2)	-623(3)	14/3(2)	0130(2)	04(1) 01(1)	0	2	-0.11725(18)	0.61123(16)	0.20598(11)	5.66(11)
O(3)	1586(3)	883(2)	7115(2)	77(1)	0	3	0.52175(21)	1.30300(18)	0.37210(11)	7.13(12)
O(5)	1568(2)	3523(1)	6188(1)	39(1)	0	4	0.46791(17)	1.00631(16)	0.19534(10)	4.90(10)
C(1)	-634(3)	3264(2)	5962(2)	48(1)	С	1	0.22118(20)	0.76268(19)	0.17741(11)	2.67(10)
C(2)	-160(3)	1987(2)	6142(2)	43(1)	C	2	-0.02310(22)	0.70461(20)	0.21518(12)	3.20(12)
C(3)	3152(4)	2285(2)	7413(2)	53(1)	С	3	0.42442(24)	1.21477(22)	0.33849(13)	3.94(12)
C(4)	1814(3)	1434(2)	6960(2)	49(1)	C	5	0.11569(21)	1.04542(19)	0.12710(11)	2.67(10)
C(5)	2390(3)	3268(2)	6465(2)	39(1)	C	4	0.39052(22)	1.02520(20)	0.23188(13)	3.23(12)
C(6)	3296(3)	3763(2)	6479(2)	41(1)	C	6	0.07916(20)	0.97239(18)	0.28632(11)	2.40(10)
C(7)	4216(3)	3579(2)	6754(2)	48(1)	Č	7	0.14990(22)	1.03306(19)	0.35814(11)	2.80(10)
C(8)	2549(3)	2573(2)	5061(2)	42(1)	Č	8	0.27269(22)	1.00708(19)	0.37910(11)	2.95(11)
C(10)	544(3)	2006(2)	4519(2)	45(1)	Č	9	0.1027(3)	1.11952(23)	0.40864(13)	4.19(13)
C(11)	1115(4)	1600(3)	40/8(2)	62(1)	C	10	0.3628(3)	1.06663(24)	0.45381(13)	4.52(14)
C(12)	601(5)	1121(3) 1061(2)	$\frac{36}{2(3)}$	/9(2)	Č	11	0.06601(21)	0.79761(20)	0.04484(11)	2.70(10)
C(13)	-403(0) 1045(5)	1001(3) 1467(2)	3093(3)	83(2) 77(2)	Ċ	12	0.1819(3)	0.84592(24)	0.01411(14)	4.53(14)
C(14) C(15)	-1043(3) 542(4)	1407(3) 1030(3)	4123(3) 4534(2)	58(1)	Č	13	0.2025(3)	0.7747(3)	-0.04722(17)	6 23(19)
C(20)	-908(3)	3448(2)	4509(2)	$\frac{38(1)}{41(1)}$	Č	14	0.1086(3)	0.6554(3)	-0.07802(15)	5.62(17)
C(20) C(21)	573(3)	3391(2)	3843(2)	53(1)	Č	15	-0.0038(3)	0.60485(24)	-0.04754(14)	4 95(14)
C(22)	417(4)	3980(3)	3457(2)	67(1)	Č	16	-0.02561(25)	0.67515(22)	0.01323(13)	3.78(12)
C(23)	599(4)	4622(3)	3719(3)	65(1)	Č	21	-0.15324(19)	0.84665(18)	0.10729(11)	2,39(9)
C(24)	929(4)	4685(2)	4377(3)	68(1)	C	22	-0.24001(21)	0.82153(20)	0.15669(12)	2.92(11)
C(25)	1082(4)	4102(2)	4771(2)	58(1)	C	23	-0.38333(23)	0.80112(24)	0 13986(14)	3 97(13)
C(30)	2764(3)	1153(2)	5409(2)	44(1)	C	24	-0.44042(23)	0.8045(3)	0.07417(14)	4.38(14)
C(31)	3541(4)	840(3)	5011(3)	68(1)	C	25	-0.35630(24)	0.8278(3)	0.02424(14)	4.36(14)
C(32)	3346(5)	206(3)	4709(3)	89(2)	C	26	-0.21275(22)	0.85001(23)	0.04117(12)	3 55(12)
C(33)	2402(5)	-115(3)	4785(3)	83(2)	C	31	0.07735(21)	1.22806(19)	0.24187(12)	2.77(10)
C(34)	1626(4)	185(2)	5174(3)	66(1) 52(1)	Č	32	0.12813(25)	1.34219(22)	0.29343(14)	3.91(12)
C(35)	1812(4)	814(2)	5488(2)	52(1)	C	33	0.0369(3)	1.39499(24)	0.31940(15)	4.93(15)
C(40) C(41)	4404(3)	2077(2) 1735(2)	5760(2)	40(1)	C	34	-0.1091(3)	1.3332(3)	0.29479(17)	5.44(17)
C(41) C(42)	6049(4)	1733(2) 1717(3)	6269(3)	$\frac{38(1)}{77(2)}$	C	35	-0.1608(3)	1.2205(3)	0.24526(17)	5.26(17)
C(42) C(43)	6597(4)	2049(3)	5771(4)	88(2)	C	36	-0.06912(23)	1.16803(22)	0.21761(14)	3.86(13)
C(44)	6072(4)	2403(3)	5273(4)	87(2)	Ċ	41	0.33098(21)	1.28410(19)	0.18533(12)	2.87(10)
C(45)	4975(4)	2411(3)	5261(3)	67(1)	Č	42	0.28611(24)	1.35696(23)	0.15028(14)	4.01(13)
C(50)	-81(3)	2209(2)	7786(2)	45(1)	Ċ	43	0.3811(3)	1.44583(24)	0.12540(16)	4.86(16)
C(51)	339(4)	1823(2)	8315(2)	56(1)	Č	44	0.5229(3)	1.46347(24)	0.13516(16)	5.06(15)
C(52)	-309(5)	1458(3)	8751(2)	69(1)	Ċ	45	0.56898(25)	1.39235(24)	0.16944(16)	4.91(15)
C(53)	-1383(5)	1486(3)	8670(3)	74(2)	С	96	0.47463(23)	1.30294(22)	0.19451(15)	3.97(13)
C(54)	-1813(4)	1854(3)	8154(3)	72(2)	С	51	0.41012(23)	0.83038(24)	0.33284(12)	3.73(13)
C(55)	-1163(4)	2216(3)	7708(3)	63(1)	C	52	0.5415(3)	0.9284(3)	0.34900(15)	5.46(17)
C(60)	1/4(3)	3539(2)	7697(2)	45(1)	C	53	0.6648(3)	0.9025(4)	0.34689(18)	8.5(3)
C(61)	1667(5)	$\frac{381}{(3)}$	/964(3)	81(2)	C	54	0.6578(4)	0.7845(5)	0.32922(20)	10.2(4)
C(62)	752(6)	4447(4)	8381(4)	109(2) 99(2)	C	55	0.5282(4)	0.6874(4)	0.31200(19)	8.5(3)
C(64)	-112(7)	4567(4)	8062(4)	120(3)	С	56	0.4039(3)	0.7091(3)	0.31367(16)	5.50(19)
C(65)	-105(5)	3942(3)	7726(3)	99(2)	С	61	0.15573(23)	0.76019(20)	0.38952(12)	3.02(11)
C(70)	3143(3)	4435(2)	6120(2)	48(1)	С	62	0.0102(3)	0.7242(3)	0.38500(14)	4.30(14)
C(71)	2461(4)	4940(2)	6349(3)	69(1)	С	63	-0.0563(3)	0.6703(3)	0.43479(16)	5.50(17)
C(72)	2338(5)	5548(3)	5974(4)	99(2)	С	64	0.0214(3)	0.6536(3)	0.48973(16)	5.59(18)
C(73)	2876(6)	5649(4)	5388(4)	107(3)	С	65	0.1657(3)	0.6888(3)	0.49552(15)	5.32(17)
C(74)	3544(5)	5148(4)	5156(3)	96(2)	С	66	0.2329(3)	0.74168(23)	0.44552(14)	4.26(14)
C(75)	3683(4)	4547(3)	5517(3)	68(1)	Н	42	0.1858(22)	1.3434(20)	0.1432(12)	4.8(6)
C(80)	5139(3)	4031(3)	6878(2)	54(1)	Н	43	0.3414(24)	1.4906(22)	0.1007(13)	6.0(6)
C(81)	5030(4)	4708(2)	7099(3)	61(1)	Н	44	0.5882(23)	1.5245(21)	0.1164(13)	5.4(6)
C(82)	5893(5)	5111(3)	7282(3)	77(2)	Н	45	0.6674(24)	1.4048(22)	0.1796(13)	5.6(6)
C(83)	0830(3) 7017(4)	4831(4)	1202(3) 6074(4)	100(2) 114(2)	Н	46	0.5099(21)	1.2577(20)	0.2183(12)	4.5(5)
C(85)	6146(4)	$\frac{1}{203(3)}$	6825(3)	94(2)						(Continued)
C(03)	0140(4)	5774(4)	0025(5))T(2)						(Communed)

	x	У	Ζ	B _{iso}
H32	0.2274(22)	1.3840(20)	0.3117(12)	4.6(5)
H33	0.0731(23)	1.4714(21)	0.3548(13)	5.5(6)
H34	-0.1736(25)	1.3678(23)	0.3134(14)	6.4(7)
H35	-0.259(3)	1.1776(23)	0.2275(14)	6.9(7)
H36	-0.1057(22)	1.0915(20)	0.1827(12)	4.6(5)
H22	-0.1995(20)	0.8186(18)	0.2028(11)	3.3(5)
H23	-0.4398(22)	0.7848(20)	0.17 54(12)	4.8(6)
H24	-0.5370(23)	0.7920(21)	0.0636(13)	5.4(6)
H25	-0.3936(23)	0.8264(21)	-0.0214(13)	5.5(6)
H26	-0.1557(21)	0.8669(20)	0.0062(12)	4.4(5)
H52	0.5478(24)	1.0094(21)	0.3626(13)	5.7(6)
H53	0.751(3)	0.975(3)	0.3594(17)	9.1(9)
H54	0.735(4)	0.764(3)	0.3262(20)	12.2(11)
H55	0.516(3)	0.605(3)	0.3005(18)	10.5(10)
H56	0.312(3)	0.642(3)	0.3007(15)	8.0(8)
H62	-0.0432(23)	0.7335(21)	0.3472(13)	5.1(6)
H63	-0.159(3)	0.6445(24)	0.4271(15)	7.2(7)
H64	-0.026(3)	0.6154(24)	0.5256(14)	6.8(7)
H65	0.224(3)	0.6779(23)	0.5329(14)	6.8(7)
H66	0.3320(23)	0.7660(21)	0.4488(13)	5.3(6)
H12	0.2490(23)	0.9290(21)	0.0363(13)	5.4(6)
H13	0.284(3)	0.812(3)	-0.0649(15)	8.3(8)
H14	0.1213(25)	0.6093(23)	-0.1191(14)	6.6(7)
H15	-0.0741(23)	0.5209(21)	-0.0682(13)	5.8(6)
H16	-0.1020(22)	0.6387(20)	0.0323(12)	4.9(6)
H5A	0.0470(20)	1.0650(18)	0.1003(11)	3.6(5)
H5B	0.1875(20)	1.0515(18)	0.1007(11)	3.5(5)
H9A	0.1781(24)	1.1880(22)	0.4391(13)	6.2(6)
H9B	0.0357(23)	1.1474(21)	0.3847(13)	5.4(6)
H9C	0.0578(24)	1.0800(22)	0.4424(13)	5.9(6)
H10A	0.3863(24)	1.1563(22)	0.4704(13)	5.9(6)
H10B	0.3171(24)	1.0297(22)	0.4873(13)	6.3(6)
H10C	0.4504(24)	1.0571(22)	0.4577(13)	6.1(6)
H6	-0.0028(19)	0.9950(17)	0.2693(10)	2.9(4)

used to measure reflections in the range $3^{\circ} \le 2\theta \le$ 52.5°. No significant loss in intensity occurred during data collection. The data were corrected for Lorentz and polarisation effects and empirically for absorption. The unique data with $I \ge 2.5\sigma(I)$ were used to solve and refine the structure. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically except the chlorine which was refined isotropically as were the hydrogens. Structure solution was carried out on the NRCVAX system [25]. Positional parameters are listed in Table 5.

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