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Metallacycle formation through the linking of an alkyne with phosphido and acetyl groups at an iron centre: X-ray structure of $[CpFe(CO)\{Ph_2PCH(CO_2Me)C(CO_2Me)=C(Me)O\}]$ ($Cp = \eta^5$-C_5H_5)

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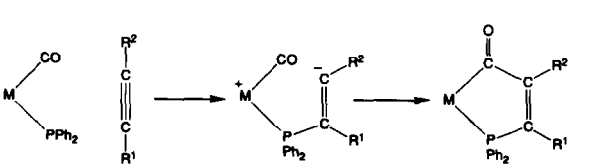
Abstract

The diphenylphosphine ligand of $[CpFe(CO)(PPh_2H)(COMe)]$ ($Cp = \eta^5$-C_5H_5) can be deprotonated with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) or n-butyllithium; subsequent alkylation with RI (R = Me, Et) gives the complexes $[CpFe(CO)(PPh_2R)(COMe)]$. Reaction of the anionic phosphido complex with the electrophilic alkyne methyl propiolate ($HC{\equiv}CCO_2Me$) followed by reprotonation with CH_3COOH gives the vinylphosphine complex $[CpFe(CO)(PPh_2CH{=}CHCO_2Me)(COMe)]$, whereas a similar reaction sequence with dimethyl acetylenedicarboxylate (DMAD, $MeO_2CC{\equiv}CCO_2Me$) produces two isomers of the complex $[CpFe(CO)\{Ph_2PCH(CO_2Me)C(CO_2Me){=}C(Me)O\}]$, in which linking of the alkyne with both the phosphido and acetyl ligands has occurred to form a six-membered metallacycle. The structure of one of the two isomers has been determined by X-ray diffraction and shows that the metallacyclic ring is bound to the iron atom through the phosphorus and the carbonyl oxygen of the acetyl group, and adopts a boat conformation in the solid state.

1. Introduction

Organometallic chemistry has largely been concerned with the coordination of organic fragments to metal centres and subsequent carbon–carbon bond formation to create more complex ligands. We are currently investigating the construction of novel coordinated species by the interaction of phosphido groups ($-PR_2$) with organic ligands at metal centres, resulting in phosphorus–carbon bond formation. For example, we have shown that the coupling of phosphido groups with alkynes in dinuclear molybdenum complexes can give phosphido-substituted vinyl [μ-$C(PPh_2){=}CH_2$ or μ-$CH{=}CHPPh_2$], vinylphosphine [μ-$Ph_2PC(Me){=}CH$-Me], or chelating *cis*-2,3-bis(diphenylphosphino)butane [$Ph_2PC(Me){=}C(Me)PPh_2$] ligands [1,2]. More recently we have described the cycloaddition reaction of the mononuclear phosphido complexes $[CpM(CO)_3PPh_2]$ ($Cp = \eta$-C_5H_5, M = Mo or W) with the electrophilic alkynes $R^1C{\equiv}CR^2$ (R^1 = H or CO_2Me, $R^2 = CO_2Me$) to give $[CpM(CO)_2\{Ph_2PCR^1{=}C(R^2)CO\}]$, in which the metallacycle is formed by linking of the phosphido group with the alkyne and a carbonyl ligand [3]. A similar metallacycle formation has been reported for the analogous iron complex $[CpFe(CO)_2PPh_2]$ [4]. Two plausible mechanisms have been proposed for this reaction, one a concerted cycloaddition process and the other a stepwise pathway in which the phosphido group attacks the alkyne to form a pseudo-carbanionic $PPh_2CR^1{=}CR^2$ group which then attacks the carbonyl ligand (Scheme 1). Some years ago, Treichel and Wong showed that such a carbanion formed from an anionic phosphido group could attack an adjacent secondary phosphine ligand to lead ultimately to a chelating $PPh_2CHR^1CHR^2PPh_2$ phosphine ligand after reprotonation [5]. We reasoned that the introduction of an-



Scheme 1. Proposed mechanism for the cyclisation of PPh_2 ligand, alkyne, and carbonyl group.

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other functional group that was susceptible to attack by the intermediate carbanion might allow cyclisation to occur in a novel way to provide new metallacycles. In this paper we describe the related coupling of an alkyne with a phosphido group and an acetyl ligand to yield a six-membered metallacyclic ring that is shown by crystallography to adopt the boat conformation in the solid state.

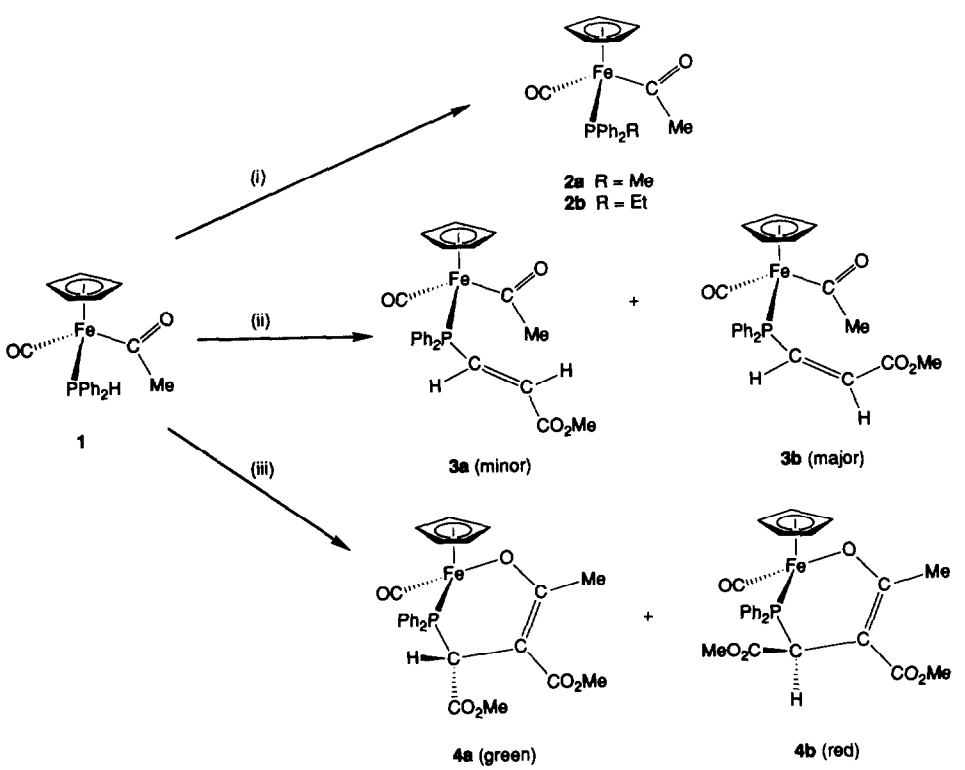
2. Results and discussion

2.1. Preparation, deprotonation and alkylation of [CpFe(CO)(PPh$_2$H)(COMe)] (1)

In recent years the properties and chemistry of the iron acyl species [CpFe(CO)(PPh$_3$)(COMe)] have been extensively studied in relation to its role as a chiral auxiliary, exemplified by the work of Davies [6]. We therefore decided to investigate the analogous diphenylphosphine complex [CpFe(CO)(PPh$_2$H)(COMe)] (**1**). This compound has been mentioned previously by Prock and Giering [7], and we have recently learnt that Cutler has also prepared it and studied some of its deprotonation reactions [8]. The synthesis of **1** was readily achieved by treating [CpFe(CO)$_2$Me] with PPh$_2$H in refluxing acetonitrile (as for the PPh$_3$ analogue [9]) and the complex was isolated as an air-stable yellow powder after column chromatography in 77% yield. The spectroscopic data (see Experimental section) were as expected, with a doublet observed in the ^{1}H NMR spectrum at δ 6.58 (J = 362 Hz) due to the P–H of the diphenylphosphine ligand.

As a test of the reactivity of complex **1**, we subjected it to a simple deprotonation-alkylation sequence, as previously carried out successfully on a number of PPh$_2$H complexes by Treichel and co-workers [10]. Addition of one equivalent of ^{n}BuLi to **1** in THF solution at −78°C caused an immediate colour change from yellow to deep red, indicating formation of the anionic phosphido complex [CpFe(CO)(PPh$_2$)(COMe)]$^-$. Alkylation of this species with MeI or EtI afforded excellent yields of the substituted phosphine complexes [CpFe(CO)(PPh$_2$R)(COMe)] (R = Me, **2a**; R = Et, **2b**) (see Scheme 2). These were purified by column chromatography and characterised by their spectroscopic data (see Experimental section) [7].

Deprotonation of the phosphine ligand can be effected equally readily at room temperature with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) or the ylid Ph$_3$P=CH$_2$, but use of 1 equiv of ^{n}BuLi at room temperature gave only a low yield (26%) of **2a**. Al-



Scheme 2. Reagents and conditions: (i) ^{n}BuLi, −78°C, then RI; (ii) ^{n}BuLi, −78°C, then HC≡CCO$_2$Me, then CH$_3$CO$_2$H; (iii) ^{n}BuLi, −78°C, then MeO$_2$CC≡CCO$_2$Me, then CH$_3$CO$_2$H.

though it is known that deprotonation of the acetyl group of [CpFe(CO)(PPh_3)(COMe)] occurs with butyllithium at −78°C to form the enolate [CpFe(CO)(PPh_3)($COCH_2$)]$^-$ [6,11], addition of 2 equiv of ^{n}BuLi to [CpFe(CO)(PPh_2H)(COMe)] at −78°C did not result in the production of an analogous enolate dianion; only the phosphido group was deprotonated, and **2a** (56%) was again isolated on alkylation with MeI. When 2 equiv of ^{n}BuLi were used at room temperature, a further change evidently did take place, because addition of MeI in this instance produced a bright purple solution; however no tractable products could be isolated from this by chromatography or crystallisation.

We have recently reported that deprotonation of the diphenylphosphine ligand of the related molybdenum complex [CpMo($CO)_2$(PPh_2H)(COMe)] with DBU occurs normally at −78°C, leading to [CpMo($CO)_2$-(PPh_2R)(COMe)] on alkylation with RI (R = Me, Et); if the deprotonation is carried out at room temperature, however, migration of the acyl group to the phosphido ligand occurs and alkylation produces the acylphosphine complexes [CpMo($CO)_2$(PPh_2COMe)-(R)] instead [12]. We consider it likely that this involves direct nucleophilic attack of the phosphido group on the acetyl carbon, and have demonstrated that it occurs largely intramolecularly, though there is a measurable intermolecular component [13]. In the case of the present iron complexes no such migration was observed, even when the deprotonated complex had been heated in refluxing THF for several hours. The phosphido group in the iron complex is appreciably more basic than that in the molybdenum complex, as shown by a competition experiment in which treatment of an equimolar mixture of [CpFe(CO)(PPh_2H)(COMe)] and [CpMo($CO)_2$(PPh_2H)(COMe)] with only one molar equivalent of DBU at −78°C followed by alkylation with MeI gave exclusively [CpMo($CO)_2$(PPh_2Me)(CO-Me)] while **1** remained unchanged. However the acetyl group in **1** is less susceptible to nucleophilic attack than that in the molybdenum complex; one manifestation of this is that compounds of the type [CpFe(CO)(PR_3)(COR)] can be deprotonated at the acyl group with ^{n}BuLi whereas compounds of the type [CpMo($CO)_2$(PR_3)(COR)] react by displacement of the acyl ligand, forming Li[CpMo($CO)_2$(PR_3)] and presumably BuCOR [14]. It is interesting to note that direct phosphido–acetyl linking does occur when the anion derived from **1** is treated with Me_3SiCl, forming [Cp-Fe(CO){PPh_2C($OSiMe_3$)Me}] [8]; however it is possible that this occurs by initial O-silylation to give the carbene [CpFe(CO)(PPh_2){=C($OSiMe_3$)Me}] followed by nucleophilic attack of the phosphido group on the carbene. There is precedent for this process in the molybdenum system; *e.g.* in the observation by Powell that deprotonation of the cationic cyclic carbene complex [CpMo($CO)_2$[=$COCH_2CH_2CH_2$}(PR_2H)][BPh_4] (R = Ph, Cy) forms the three-membered ring compound [CpMo($CO)_2$($PR_2COCH_2CH_2CH_2$)] [15].

2.2. Deprotonation of 1 and reaction with alkynes.

Sequential addition of ^{n}BuLi (1.1. equiv), methyl propiolate (1.1 equiv), and an excess of acetic acid to a THF solution of **1** at −78°C, followed by warming to room temperature, gave one major product, the substituted vinylphosphine acyl complex [CpFe(CO)(PPh_2-CH=$CHCO_2$Me)(COMe)] (**3**) (65% total yield), which exists as two isomers. These were partially separated by chromatography; thus the minor component **3a** was eluted first in 2.7% yield, but could only be obtained as a 2:1 mixture with **3b**; the latter was obtained as a spectroscopically pure compound in 62% yield. To **3b** we assign a structure in which the vinylphosphine ligand has the *Z* configuration, and to the minor isomer **3a** the corresponding *E* configuration of the ligand. Thus, the ^{1}H NMR spectrum of the major product **3b** shows a doublet of doublets at δ 6.46 with couplings of 14.0 Hz assigned as *J*(HH) and 29.3 Hz assigned as the large *trans* *J*(PH). Unfortunately in this isomer the other CH signal lies under the phenyl resonances and could not be successfully resolved. The minor component, however, displays two clear CH signals, at δ 7.87 with *J*(HH) 16.9 and *J*(PH) 18.0 Hz, and at δ 5.78 with *J*(PH) 14.0 Hz. This is most consistent with the *E*-isomer, in which the two H substituents are *trans* to each other but neither is *trans* to the phosphorus. Recent studies on the stereoselective radical addition of alkynes to coordinated phenyl- or diphenylphosphine ligands support these assignments [16]. The formation of the third possible isomer, with a *gem* $Ph_2PC(CO_2Me)$=CH_2 ligand, can be ruled out from the ^{13}C NMR spectrum (recorded with an attached proton test technique), showing that the attack of the phosphide anion on the alkyne is regioselective [3].

Addition of DMAD to deprotonated **1** at −78°C followed by reprotonation with an excess of CH_3COOH led to a mixture of compounds which were separated by column chromatography. The major products were two separable isomers of the metallacyclic complex [CpFe(CO){Ph_2PCH(CO_2Me)C(CO_2Me)=C(Me)O}]; the first isomer **4a** is yellow-green in colour and is converted into the second isomer, **4b**, which is red, on attempted crystallisation. It appears that if the reprotonation is carried out at low temperature then **4a** is the major product, but if the solution is allowed to warm to room temperature before addition of the acid the isomer **4b** is also formed in almost equal amount. The spectroscopic data for the two isomers are very similar, with the observation of ^{31}P coupling to the carbon

atoms of the alkyne and the acyl carbon in the ^{13}C NMR spectra clearly indicating the creation of a new ligand by P–C bond formation. The only appreciable differences between the ^1H NMR spectra of the isomers are in the position of the CH signal (δ 4.19 for **4a**, δ 4.84 for **4b**) and the small coupling between this proton and the methyl of the COMe moiety (confirmed by decoupling experiments) which is discernible in **4a** but not in **4b**. The possibility that this proton could be attached to a different carbon of the ligand in each isomer is, however, ruled out by the ^{13}C NMR spectrum. Since there are two chiral centres in the molecule (the iron atom and the $CHCO_2Me$ carbon) it seems possible that the two compounds differ either in the orientation of the CpFeCO fragment in relation to the metallacyclic ring, or in the configuration at the chiral carbon as shown in Scheme 2. Attempts to accelerate the conversion of pure **4a** in to **4b** by a deprotonation-reprotonation sequence were unsuccessful, but a similar type of isomerism was observed in the chelating $Ph_2PCHR^1CHR^2PPh_2$ ligands by Treichel [5]. Matt and co-workers have recently prepared a complex containing a related ligand, [(dmba)Pd{$PPh_2CH(CO_2Et)C(CO_2Me)$=$C(CO_2Me)$}] (dmba = C_6H_4-2-CH_2NMe_2), which displays spectroscopic properties similar to those of **4**, by reaction of DMAD with the cyclic phosphinoenolate [(dmba)Pd{$Ph_2PCHC(OEt)O$}]. Interestingly they also report that the analogous iron enolate complex [CpFe(CO){$Ph_2PCHC(OEt)O$}] fails to react with DMAD [17].

The exact structure of the metallacyclic ring was revealed by a single crystal X-ray study of the red isomer **4b**, and the result is shown in Fig. 1. The iron atom is in a roughly octahedral environment with three coordination positions occupied by the Cp ring and one by the terminal CO. The iron is also ligated by the phosphorus and oxygen atoms of the new phosphine-enolate ligand $Ph_2PCH(CO_2Me)C(CO_2Me)$=C(Me)O.

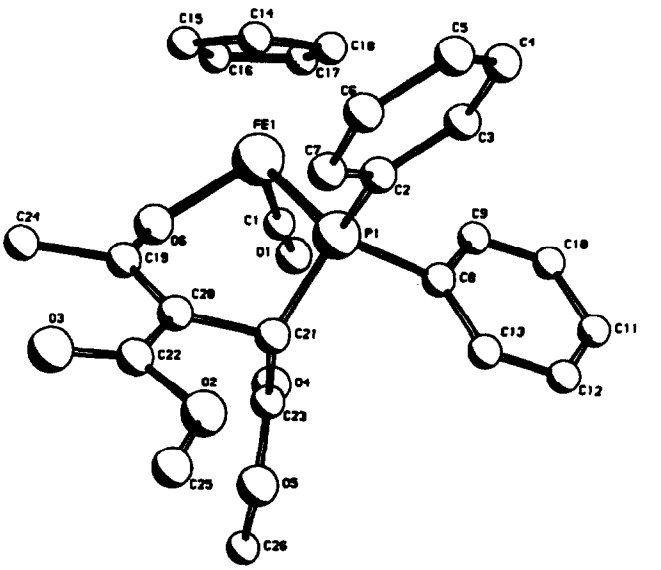
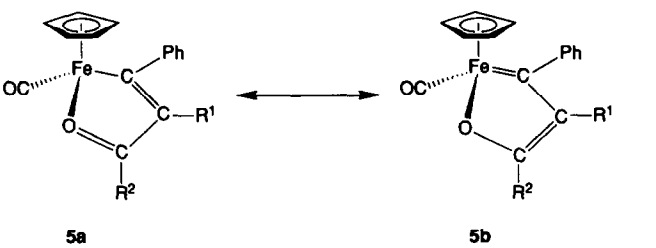
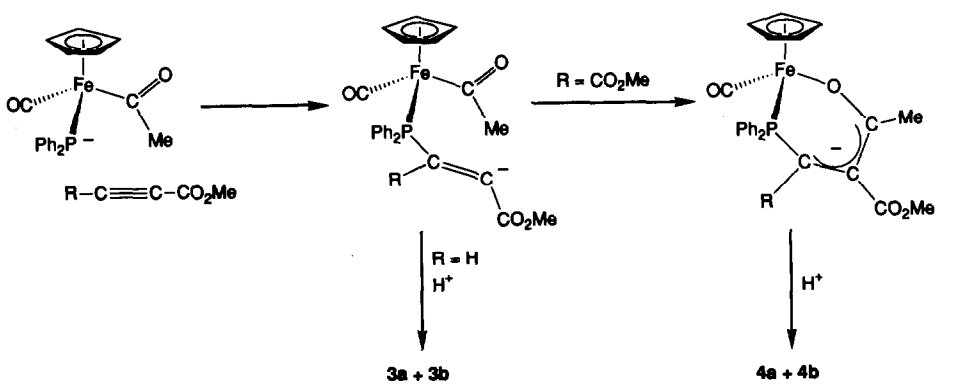


Fig. 1. Molecular structure of complex **4b** in the crystal, showing the crystallographic numbering scheme.

The carbon–carbon bond lengths in this ligand are typical of single [C(20)–C(21) 1.516(5) Å] and double [C(19)–C(20) 1.380(4) Å] bonds. The Fe(1)–O(6) distance of 1.964(3) Å is longer than that found in simple iron alkoxide or aryloxide complexes [18] but it is shorter than those in complexes where ketonic carbonyl groups are coordinated to iron [19]. Perhaps the most closely related compounds are the alkenylketone species [CpFe(CO){$C(Ph)$=$C(R^1)C(R^2)O$}] (**5**); one of





Scheme 3. Mechanism of formation of complexes **3** and **4**.

these (R^1 = Ph, R^2 = Me) was prepared by Alt by photochemical reaction of [$CpFe(CO)_2Me$] with diphenylacetylene [20], and more recently a further example (R^1 = H, R^2 = OMe) was prepared and structurally characterised by Akita [21]. In this compound the relatively short Fe–O distance of 2.009(2) Å is attributed to the contribution of the carbene-enolate resonance structure, a proposal backed up by the carbene-like shift of C(α) in the ^{13}C NMR spectrum.

A plausible mechanism for the reaction is shown in Scheme 3. Nucleophilic attack of the phosphide anion on the electrophilic alkyne produces the carbanionic intermediate, which in the case of methyl propiolate does not react further and is protonated to form the vinylphosphine products **3**. In the case of DMAD, attack on the acetyl carbon occurs with coordination of the carbonyl oxygen, and subsequent reprotonation at the carbon attached to phosphorus gives **4**. As observed previously [3–5], the degree of stabilisation of the intermediate carbanion by electron-withdrawing groups on the alkyne is an important factor in the success of such cyclisation reactions.

3. Experimental section

All reactions were carried out under argon by standard Schlenk techniques, but the products described are all relatively air stable and work-up can be carried out without special precautions. Solvents were dried by distillation from appropriate drying agents (sodium-benzophenone ketyl for THF, sodium for petroleum ether, supported P_2O_5 for MeCN). Petroleum ether refers to the fraction boiling between 60–80°C. Dichloromethane and other solvents were used as received. Chromatographic separations were carried out under a slight positive pressure of inert gas on silica columns (Merck Kieselgel 60, 230–400 mesh). IR spectra were recorded on a Perkin-Elmer 1600 FT-IR machine in CH_2Cl_2 solution in NaCl cells; NMR spectra were recorded on Bruker ACF 250 (^1H, ^{13}C, ^{31}P), AM250 (^1H, ^{13}C) and WP80SY (^{31}P) spectrometers in $CDCl_3$ solution. Chemical shifts are given on the δ scale relative to $SiMe_4$ = 0.0 ppm for ^1H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P, with coupling constants given in Hz. The ^{13}C and ^{31}P spectra were proton-decoupled; ^{13}C spectra were routinely recorded with an attached proton test technique [22]. Fast atom bombardment mass spectra were recorded on Kratos MS25 or MS80 instruments for samples in a *m*-nitrobenzyl alcohol matrix. Elemental analyses were carried out by the Microanalytical Service of the Department.

Diphenylphosphine, methyl propiolate, and n-butyllithium (1.6 M solution in hexanes) were purchased from Aldrich; the ^{n}BuLi was titrated with diphenylacetic acid before use [23]. The complex [$CpFe(CO)_2Me$] was prepared by the published method [24].

3.1. Synthesis of [CpFe(CO)(PPh_2H)(COMe)] (1)

A solution of [$CpFe(CO)_2Me$] (2.5 g, 13.02 mmol) and PPh_2H (2.50 ml, 14.38 mmol) in MeCN (175 ml) was heated to reflux for 17 h. After removal of the solvent, the residue was chromatographed. A faint yellow band of unchanged starting material was removed by elution with petroleum ether, after which the orange band of [CpFe(CO)(PPh_2H)(COMe)] was eluted with CH_2Cl_2. Yield 3.8 g, 77%.

1: M.p. 68°C. IR: ν(CO) 1922s, 1596m cm^{-1}. ^1H NMR: δ 7.62–7.30 (m, 10H, Ph); 6.58 (d, *J*(PH) 362.0 Hz, 1H, P–H); 4.50 (d, *J*(PH) 2.0 Hz, 5H, Cp); 2.36 (s, 3H, Me). $^{13}C\{^1H\}$ NMR: δ 2.75.5 (d, *J*(PC) 21 Hz, *C*OMe); 218.9 (d, *J*(PC) 31 Hz, CO); 134.9 (d, *J*(PC) 42 Hz, PC_{ipso}); 133.2 (d, *J*(PC) 47 Hz, PC_{ipso}); 84.3 (s, Cp); 51.7 (s, Me). $^{31}P\{^1H\}$ NMR δ 60.8. Anal. Found: C, 63.33; H, 4.95. $C_{20}H_{19}FeO_2P$ calc.: C, 63.48; H, 3.95%. MS: *m/z* 379 $(M + H)^+$.

3.2. Synthesis of [CpFe(CO)(PPh_2R)(COMe)] (2a, R = Me; 2b, R = Et) by deprotonation and alkylation of 1

A solution of **1** (200 mg, 0.528 mmol) in THF (30 ml) was cooled to −78°C and treated with ^{n}BuLi (0.370 ml of a 1.43 M solution), causing a colour change to dark red. After stirring for 15 min, MeI (0.040 ml, 6.42 mmol) was added and the solution was allowed to warm to room temperature . After removal of solvent, the residue was chromatographed to give a single orange band, eluted with CH_2Cl_2. The orange oil remaining after removal of the solvent was recrystallised from petroleum ether to give **2a** (150 mg, 72%) as an air-stable orange solid.

A similar reaction in which EtI (0.050 ml, 6.25 mmol) was used as the alkylating agent yielded an oil, which was triturated in petroleum ether to give **2b** (120 mg, 56%) as an orange powder.

2a: M.p. 108°C. IR: ν(CO) 1914s, 1591m cm^{-1}. ^1H NMR: δ 7.64–7.25 (m, 10H, Ph); 4.48 (d, *J*(PH) 1.5 Hz, 5H, Cp); 2.18 (s, 3H, COMe); 2.05 (d, *J*(PH) 9.5 Hz, PMe). $^{13}C\{^1H\}$ NMR: δ 276.9 (d, *J*(PC) 19 Hz, *C*OMe); 219.5 (d, *J*(PC) 31 Hz, CO); 138.0 (d, *J*(PC) 47 Hz, PC_{ipso}); 137.8 (d, *J*(PC) 41 Hz, PC_{ipso}); 132.1–127.8 (m, Ph); 84.4 (s, Cp); 51.6 (s, CO*Me*); 15.7 (d, *J*(PC) 30 Hz, PMe). $^{31}P\{^1H\}$ NMR: δ 61.1. Anal. Found: C, 64.64; H, 5.80. $C_{21}H_{21}FeO_2P$ calc. C, 64.31; H, 5.40%. MS: *m/z* 393 $(M + H)^+$.

2b: M.p. 110–112°C. IR: ν(CO) 1914s, 1594m cm^{-1}. ^1H NMR δ 7.56–7.36 (m, Ph); 4.39 (d, *J*(PH) 1.5 Hz, 5H, Cp); 2.45 (d, *J*(PH) 1.0 Hz, 3H, COMe); 2.40 (m, 2H, CH_2 of Et); 0.87 (dt, *J*(PH) 17.0 Hz, *J*(HH) 7.5

Hz, COMe); 219.9 (d, J(PC) 31 Hz, CO); 137.8 (d, J(PC) 38 Hz, PC_{ipso}); 135.2 (d, J(PC) 43 Hz, PC_{ipso}); 133.1–127.8 (m, Ph); 84.4 (s, Cp); 52.0 (s, CO*Me*); 22.7 (d, J(PC) 29 Hz, CH_2); 8.3 (s, Me of Et). $^{31}P\{^1H\}$ NMR δ 73.9. Anal. Found: C, 65.01; H, 5.78. $C_{22}H_{23}FeO_2P$ calc. C, 65.05; H, 5.71%. MS: m/z 406 (M^+).

3.3. Synthesis of (E)- and (Z)-[CpFe(CO)(PPh_2CH=$CHCO_2Me$)(COMe)] (3a, b)

A solution of **1** (1.00g, 2.64 mmol) in THF (30 ml) was cooled to −78°C and treated with ^{n}BuLi (2.0 ml of 1.43 M solution, 1.1 equiv); the orange-red solution was stirred for 10 min before the addition of methyl propiolate (0.24 ml, 2.70 mmol). After stirring of the mixture at the same temperature for a further 20 min, acetic acid (0.46 ml, 8.0 mmol) was added and the solution was allowed to warm to room temperature. The solvent was removed and the resulting red oil chromatographed. After removal of an unidentified green band (15 mg) with CH_2Cl_2 as eluant, a yellow orange zone was eluted with CH_2Cl_2–acetone (99:1) that consisted of a mixture of **3a** and **3b** in a ratio of approximately 2:1 as indicated by NMR integration (combined yield 50 mg, 4.1%). The major product **3b** was then eluted with CH_2Cl_2–acetone (19:1) as an orange band, which yielded an oil on removal of the solvent; trituration with diethyl ether produced an orange-red powder (756 mg, 62%). Further elution of the column with CH_2Cl_2-acetone (4:1) produced an unidentified orange-brown band (40 mg).

3a: IR: ν(CO) 1920s, 1720m, 1594m cm^{-1}. ^1H NMR: δ 7.87 (dd, J(PH) 18.0 Hz, J(HH) 16.9 Hz, 1H, CH); 7.53–7.26 (m, 10H, Ph); 5.78 (dd, J(HH) 16.9 Hz, J(PH) 14.0 Hz, 1H, CH); 4.47 (d, J(PH) 1.0 Hz, 5H, Cp); 3.78 (s, 3H, CO_2Me); 2.28 (s, 3H, COMe). $^{31}P\{^1H\}$ NMR δ 70.6.

3b: M.p. 96°C. IR: ν(CO) 1920s, 1720m, 1594m cm^{-1}. ^1H NMR: δ 7.53–7.26 (m, 10H, Ph); 6.46 (dd, J(PH) 29.3 Hz, J(HH) 14.0 Hz, 1H, CH); 4.55 (d, J(PH) 1.7 Hz, 5H, Cp); 3.07 (s, 3H, CO_2Me); 2.25 (s, 3H, COMe). $^{13}C\{^1H\}$ NMR: δ 277.5 (d, J(PC) 23 Hz, *C*OMe); 219.5 (d, J(PC) 30 Hz, CO); 165.0 (d, J(PC) 5 Hz, *C*O_2Me); 140.1 (d, J(PC) 30 Hz, CH); 129.7 (d, J(PC) 14 Hz, CH); 136.3 (d, J(PC) 45 Hz, PC_{ipso}); 135.4 (d, J(PC) 52 Hz, PC_{ipso}); 132.8–127.4 (m, Ph); 85.1 (s, Cp); 52.0 (d, J(PC) 6 Hz, CO*Me*); 51.1 (s, CO_2*Me*). $^{31}P\{^1H\}$ NMR δ 67.7. Anal. Found: C, 62.44; H, 5.01. $C_{24}H_{23}FeO_4P$ calc. C, 62,36; H, 5.02%. MS m/z 463 $(M+H)^+$.

3.4. Synthesis of [CpFe(CO){$PPh_2CH(CO_2Me)C(CO_2Me)$=$C(Me)O$}] (4a, b)

A solution of **1** (1.00g, 2.64 mmol) in THF (30 ml) was deprotonated as above with ^{n}BuLi (2.0 ml of 1.43M solution) at −78°C. After 10 min stirring a slight excess of DMAD (0.33 ml, 2.68 mmol) was added, causing the deep red solution to turn yellow brown. After a further 10 min, glacial acetic acid (0.45 ml, 7.86 mmol) was added and the solution allowed to warm to room temperature. After removal of solvent, column chromatography gave a weak red zone, eluted with CH_2Cl_2, which was discarded, followed by a green band which was eluted with CH_2Cl_2–acetone (19:1). Further elution of the chromatography column with a 9:1 mixture of the same solvents yielded a small amount of red **4b**. The green band obtained consisted of a mixture of **4a** and approximately 20% of an unidentified complex [^1H NMR: δ 5.13 (d, J(PH) 13.5 Hz, 1H); 4.43 (d, J(PH) 1.3 Hz, 5H, Cp); 3.58, 3.54 (both s, 3H, CO_2Me); 2.15 (s, 3H, Me); $^{31}P\{^1H\}$ NMR δ 26.4]. Rechromatography and rapid recrystallisation provided **4a** as an analytically pure compound (660 mg, 48%).

In a separate experiment, a THF solution of **1** (0.600 g, 1.59 mmol) was deprotonated as above (1.3 ml of ^{n}BuLi solution) and treated with DMAD (0.2 ml, 1.62 mmol). The solution was then warmed to room temperature before addition of acetic acid (0.45 ml, 7.86 mmol). Subsequent chromatographic work-up gave an unidentified green band (160 mg) eluted with petroleum ether–CH_2Cl_2 (1:4), followed by a green band of **4a** (200 mg, 24%) and a red band of **4b** (180 mg, 22%), both eluted as above.

4a: M.p. 118°C. IR: ν(CO) 1951s, 1730m, 1679w cm^{-1}. ^1H NMR: δ 7.75–7.36 (m, 10H, Ph); 4.48 (d, J(PH) 1.7 Hz, 5H, Cp); 4.19 (dq, J(PH) 12.0 Hz, J(HH) 1.0 Hz, 1H, C*H*CO_2Me); 3.50 (s, 3H, CO_2Me); 3.23 (s, 3H, CO_2Me); 2.17 (d, J(HH) 1.0 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR δ 217.8 (d, J(PC) 31.6 Hz, CO); 189.5 (d, J(PC) 4 Hz, COMe); 170.3 (d, J(PC) 6 Hz, *C*O_2Me); 169.8 (d, J(PC) 10 Hz, *C*O_2Me); 134.0 (d, J(PC) 38 Hz, PC_{ipso}); 133.3 (d, J(PC) 46 Hz, PC_{ipso}); 133.4–130.4 (m, Ph); 99.1 (d, J(PC) 2Hz, *C*CO_2Me); 83.0 (s, Cp); 51.3, 50.2 (both s, CO_2*Me*); 44.4 (d, J(PC) 17 Hz, *C*HCO_2Me); 25.9 (d, J(PC) 4 Hz, COMe). $^{31}P\{^1H\}$ NMR δ 78.3. Anal. Found: C, 59.73; H, 5.33; $C_{26}H_{25}FeO_6P$ calc. C, 60.00; H, 4.81%. MS: m/z 520 (M^+).

4b: M.p. 114°C; IR: 1967s, 1732m, 1669w cm^{-1}. ^1H NMR δ 7.62–7.37 (m, 10H, Ph); 4.84 (d, J(PH) 18.0 Hz, 1H, C*H*CO_2Me); 4.43 (d, J(PH) 1.2 Hz, 5H, Cp); 3.60 (s, 3H, CO_2Me); 3.22 (s, 3H, CO_2Me); 2.31 (s, 3H, Me). $^{13}C\{^1H\}$ NMR δ 218.5 (d, J(PC) 30 Hz, CO); 189.3 (d, J(PC) 7 Hz, COMe); 170.1 (d, J(PC) 7 Hz, *C*O_2Me); 169.3 (d, J(PC) 5 Hz, *C*O_2Me); 138.6 (d, J(PC) 60 Hz, PC_{ipso}); 132.6 (d, J(PC) 54 Hz, PC_{ipso}); 134.2–128.5 (m, Ph); 95.1 (s, *C*CO_2Me); 82.8 (s, Cp); 51.6, 50.5 (both s, CO_2*Me*); 39.1 (d, J(PC) 21 Hz, *C*HCO_2Me); 27.1 (d, J(PC) 3 Hz, Me). $^{31}P\{^1H\}$ NMR

δ 86.7. Anal. Found C, 59.52; H 4.69; $C_{26}H_{25}FeO_6P$ calc. C, 60.00, H 4.81%. MS m/z 520 (M^+).

3.5. Crystal structure determination

Crystal data for [CpFe(CO){$PPh_2CH(CO_2Me)C(CO_2Me)$=C(Me)O}] (**4b**); $C_{26}H_{25}FeO_6P$; M = 520.30; crystallises from dichloromethane/diethyl ether as red blocks; crystal dimensions 0.60 × 0.40 × 0.25 mm. Triclinic, a = 9.619(7), b = 9.927(5), c = 14.330(8) Å, α = 87.03(4), β = 83.61(5), γ = 62.35(4)°, U = 1204.5(12) Å^3; D_c = 1.435 g cm^{-3}, Z = 2. Space group $P\bar{1}$ (No. 2): graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), μ(Mo Kα) = 7.27 cm^{-1}, F(000) = 539.93.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the ω scan method. The 3443 independent reflections (of 4261 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz

TABLE 1. Bond lengths (Å) and angles (deg) for complex **4b**

(a) Bond lengths			
Fe(1)–P(1)	2.177(2)	Fe(1)–O(6)	1.964(3)
Fe(1)–C(1)	1.765(4)	Fe(1)–C(14)	2.084(3)
Fe(1)–C(15)	2.130(4)	Fe(1)–C(16)	2.108(4)
Fe(1)–C(17)	2.063(4)	Fe(1)–C(18)	2.059(3)
P(1)–C(2)	1.837(3)	P(1)–C(8)	1.826(3)
P(1)–C(21)	1.848(4)	O(1)–C(1)	1.147(5)
O(2)–C(22)	1.358(4)	O(2)–C(25)	1.430(7)
O(3)–C(23)	1.202(5)	O(4)–C(24)	1.190(5)
O(5)–C(23)	1.330(4)	O(5)–C(26)	1.446(4)
O(6)–C(19)	1.290(5)	C(2)–C(3)	1.389(4)
C(2)–C(7)	1.379(6)	C(3)–C(4)	1.381(4)
C(4)–C(5)	1.371(7)	C(5)–C(6)	1.358(6)
C(6)–C(7)	1.388(4)	C(8)–C(9)	1.383(6)
C(8)–C(13)	1.384(5)	C(9)–C(10)	1.374(6)
C(10)–C(11)	1.379(6)	C(11)–C(12)	1.367(7)
C(12)–C(13)	1.380(5)	C(14)–C(15)	1.405(4)
C(14)–C(18)	1.404(6)	C(15)–C(16)	1.385(7)
C(16)–C(17)	1.414(5)	C(17)–C(18)	1.402(5)
C(19)–C(20)	1.380(4)	C(19)–C(24)	1.510(6)
C(20)–C(21)	1.516(5)	C(20)–C(22)	1.455(6)
C(21)–C(23)	1.512(4)		
(b) Bond angles			
P(1)–Fe(1)–O(6)	90.2(1)	P(1)–Fe(1)–C(1)	95.8(1)
O(6)–Fe(1)–C(1)	94.4(1)	Fe(1)–P(1)–C(2)	116.5(1)
Fe(1)–P(1)–C(8)	118.1(1)	C(2)–P(1)–C(8)	100.8(1)
Fe(1)–P(1)–C(21)	110.9(1)	C(2)–P(1)–C(21)	103.6(2)
C(8)–P(1)–C(21)	105.3(1)	C(22)–O(2)–C(25)	116.5(3)
C(23)–O(5)–C(26)	116.1(3)	Fe(1)–O(6)–C(19)	132.3(2)
Fe(1)–C(1)–O(1)	173.4(4)	P(1)–C(2)–C(3)	118.8(3)
P(1)–C(2)–C(7)	123.2(2)	C(3)–C(2)–C(7)	117.8(3)
C(2)–C(3)–C(4)	121.0(4)	C(3)–C(4)–C(5)	120.3(3)
C(4)–C(5)–C(6)	119.4(3)	C(5)–C(6)–C(7)	120.9(4)
C(2)–C(7)–C(6)	120.6(3)	P(1)–C(8)–C(9)	119.0(2)
P(1)–C(8)–C(13)	122.2(3)	C(9)–C(8)–C(13)	118.5(3)
C(8)–C(9)–C(10)	120.7(4)	C(9)–C(10)–C(11)	120.1(5)
C(10)–C(11)–C(12)	119.7(4)	C(11)–C(12)–C(13)	120.3(3)
C(8)–C(13)–C(12)	120.6(4)	C(15)–C(14)–C(18)	107.8(4)
C(14)–C(15)–C(16)	109.0(4)	C(15)–C(16)–C(17)	107.3(3)
C(16)–C(17)–C(18)	108.5(4)	C(14)–C(18)–C(17)	107.4(3)
O(6)–C(19)–C(20)	124.6(3)	O(6)–C(19)–C(24)	111.8(3)
C(20)–C(19)–C(24)	123.5(4)	C(19)–C(20)–C(21)	119.7(3)
C(19)–C(20)–C(22)	121.7(3)	C(21)–C(20)–C(22)	118.5(3)
P(1)–C(21)–C(20)	112.9(2)	P(1)–C(21)–C(23)	110.7(3)
C(20)–C(21)–C(23)	109.4(2)	O(2)–C(22)–O(3)	120.4(4)
O(2)–C(22)–C(20)	111.5(3)	O(3)–C(22)–C(20)	128.1(3)
O(4)–C(24)–O(5)	122.8(3)	O(4)–C(23)–C(21)	127.1(3)
O(5)–C(23)–C(21)	110.1(3)		

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
Fe(1)	1950(1)	2907(1)	3810(1)	34(1)
P(1)	2656(1)	1656(1)	2493(1)	30(1)
O(1)	1328(3)	5869(3)	3023(2)	68(1)
O(2)	−219(3)	−15(3)	1500(2)	57(1)
O(3)	−1822(3)	276(3)	2801(2)	72(2)
O(4)	50(3)	4544(3)	1739(2)	63(1)
O(5)	−707(3)	3330(3)	821(2)	57(1)
O(6)	−203(2)	3173(2)	3798(2)	43(1)
C(1)	1523(4)	4694(4)	3295(2)	42(1)
C(2)	3897(3)	−410(3)	2563(2)	34(1)
C(3)	5522(3)	−979(3)	2524(2)	39(1)
C(4)	6499(4)	−2516(4)	2626(2)	48(2)
C(5)	5875(4)	−3511(4)	2763(3)	59(2)
C(6)	4288(4)	−2972(4)	2801(3)	68(2)
C(7)	3292(4)	−1428(4)	2712(3)	53(2)
C(8)	3798(3)	2154(3)	1564(2)	34(1)
C(9)	4687(4)	2826(4)	1804(3)	51(2)
C(10)	5678(5)	3084(5)	1137(3)	70(2)
C(11)	5776(4)	2699(4)	212(3)	63(2)
C(12)	4888(4)	2053(4)	−37(2)	53(2)
C(13)	3916(4)	1764(3)	634(2)	42(1)
C(14)	3091(4)	1043(4)	4674(2)	54(2)
C(15)	1855(4)	2189(4)	5231(2)	58(2)
C(16)	2073(4)	3476(4)	5185(2)	56(2)
C(17)	3492(4)	3119(4)	4611(2)	53(2)
C(18)	4122(4)	1616(4)	4296(2)	52(2)
C(19)	−742(3)	2321(4)	3498(2)	41(1)
C(20)	−239(3)	1569(3)	2648(2)	35(1)
C(21)	916(3)	1844(3)	1956(2)	33(1)
C(22)	−865(4)	587(4)	2366(2)	45(1)
C(23)	73(3)	3396(3)	1514(2)	37(1)
C(24)	−2041(4)	2282(5)	4177(3)	69(2)
C(25)	−719(5)	−1032(5)	1158(3)	80(3)
C(26)	−1714(4)	4769(4)	404(3)	64(2)

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

and polarisation effects, and for absorption by analysis of 9 azimuthal scans (minimum and maximum transmission coefficients 0.716 and 0.742). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final R 0.0449 (R_w 0.0405, 307 parameters, mean and maximum shift/e.s.d. 0.003 and 0.016 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron density synthesis showed peaks of −0.34 and +0.40 $eÅ^{-3}$. Complex scattering factors were taken from the program package SHELXTL [25] as implemented on the Data General DG30 computer, which was used for structure solution and refinement. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00015(F)^2]$ was used in the latter stages of the refinement. Table 2 lists the atomic positional parameters with estimated standard deviations.

Tables of anisotropic thermal parameters and hydrogen atom position parameters have been deported with the Cambridge Crystallographic Data Centre. Lists of observed and calculated structure factors are available from the authors.

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