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PAPER

Reactions of the phosphinidene-bridged complexes $[Fe_2(\eta^5-C_5H_5)_2(\mu-PR)-(\mu-CO)(CO)_2]$ (R = Cy, Ph) with electrophiles based on p-block elements[†]

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The title complexes reacted readily with the methylating agents MeI and CF_3SO_3Me , chalcogens (O_2, S_8) and borane adducts BH₃·L (L = THF, N^tBu₃, PPh₃) to initially give the corresponding neutral or cationic derivatives of the type $[Fe_2Cp_2 \{\mu - P(E)R\}(\mu - CO)(CO)_2]^n$ (Cp = $\eta^5 - C_5H_5$; $n = 0, E = O, S, BH_3$; n = +1, E = Me), which could be further functionalized through additional reactions. Thus, the oxophosphinidene complex $[Fe_2Cp_2{\mu-P(O)Cy}(\mu-CO)(CO)_2]$ could be protonated or alkylated with HBF₄·OEt₂ or CF_3SO_3Me , to give the complexes $[Fe_2Cp_2\{\mu-P(OR')Cy\}(\mu-CO)(CO)_2]^+$ (R' = H, Me) respectively, while the photochemical treatment of compounds $[Fe_2Cp_2\{\mu-P(BH_3)R\}(\mu-CO)(CO)_2]$ gave the dicarbonyl derivatives $[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)R\}(\mu-CO)(CO)]$, with a phosphinidene–borane ligand displaying coordination of a B–H bond to one of the iron atoms in a side-on fashion (Fe–H = 1.78(4) Å, Fe–B = 2.351(5) Å for the PCy compound). The title complexes also reacted readily with 3,5-di-tert-butyl-obenzoquinone or benzyl azide. The first reaction gave the phosphonite complex $[Fe_2Cp_2(\mu-CO)_2(CO) \{P(O_2C_6H_2^{\dagger}Bu_2)R\}$, while the second reaction yielded initially the corresponding 1 : 1 adducts $[Fe_2Cp_2{\mu-P(N_3CH_2Ph)R}(\mu-CO)(CO)_2]$, with a P:P-bound phosphatriazadiene ligand. The PCy compound underwent clean denitrogenation in toluene at 368 K to give the iminophosphinidene complex $[Fe_2Cp_2\{\mu-P(NCH_2Ph)Cy\}(\mu-CO)(CO)_2]$, which in turn could be protonated selectively with $[NH_4]PF_6$ at the P-bound nitrogen atom, to yield the aminophosphide derivative $[Fe_2Cp_2\{\mu-P(NHCH_2Ph)Cy\}(\mu-CO) (CO)_2$]PF₆ (Fe–Fe = 2.6362(8) Å). Denitrogenation could be also induced photochemically on the phosphatriazadiene complex, but this also caused fragmentation and recombination of different bonds to give the trinuclear compound [Fe₃Cp₃(μ_3 -PCy){ μ - κ^1 : κ^1 -C(O)(NHCH₂Ph)}(μ -CO)₂], having phosphinidene and C:O-bound aminoacyl ligands bridging the metal atoms.

Introduction

The study of the formation and reactivity of phosphinidene (PR) complexes has been a very active area of research within the organometallic chemistry during the last three decades.¹ The phosphinidene group is a very versatile ligand that can act either as a two-electron (**A** to **C** in Chart 1) or as a four-electron donor (**D** to **H** in Chart 1), and it can bind efficiently up to four metal atoms in many different ways (Chart 1). The phosphorus environment changes dramatically among these coordination modes, and this in turn gives rise to quite different chemical behaviours. Most of the previous research has been devoted to the terminal complexes (**A**, **B** and **D**). Since the M–P bonds in these species have a considerable multiplicity, these compounds are highly reactive, especially in the cases of bent coordination (**A** and **B**), where a lone pair at the phosphorus atom is also



present. This inherent reactivity, added to the conceptual analogy established between the chemistry of multiple M–P and M–C bonds, according to which the bent-phosphinidene complexes

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are usually compared to carbenes and can be analogously classified as either electrophilic or nucleophilic, ^{1*d*,*g*,*h*,²} have turned these compounds into very useful intermediates in the synthesis of new organophosphorus derivatives, ¹ and their reactivity is still the subject of extensive research.^{1,3}

In contrast, the chemistry of binuclear complexes having phosphinidene bridges has remained comparatively little explored until recently, even though the presence of multiple M-P bonds or lone pairs at phosphorus in their different coordination modes (C, E and F) should render them guite reactive.^{4,5} Recently, we developed efficient synthetic procedures to prepare new stable diiron compounds of the type $[Fe_2Cp_2(\mu-PR)(\mu-CO)(CO)_2]$ (R = Cy, Ph, 2,4,6-C₆H₂Me₃ or 2,4,6-C₆H₂^tBu₃), with a pyramidal phosphinidene bridge (type C) having a strongly nucleophilic character.⁶ Within the chemistry of binuclear phosphinidene compounds we noticed that, in particular, the number of iron derivatives previously described in the literature was very scarce, and that most of them were either thermally unstable (as the cyclopentadienyl complex $[Fe_2Cp_2(\mu-PPh)(CO)_4])^7$ or transient species generated in situ from suitable precursors, such as $[Fe_{2}{\mu-P(N^{i}Pr_{2})}_{2}(CO)_{6}]^{8}$ $[Fe_{2}(\mu-P'Bu)(CO)_{6}]^{9}$ $[Fe_{3}(\mu_{2}-PPh)-(\mu_{3}-PPh)(CO)_{9}]^{n-}$ $(n = 1, 2)^{10}$ or $[Fe_{2}(\mu-PR)_{2}(CO)_{6}]^{2-.11}$ All these circumstances impose significant restrictions upon the study of their chemical behaviour, which remains largely unexplored. Even if some recent examples of isolable diiron phosphinidene complexes can be mentioned, such as $[Fe_2 \{\mu-P-$ (OR)₂ $(CO)_6$ ¹² and $[Fe_2(\mu-PPh)_2(L_2)_2]^{13}$ (both of them having bulky protecting groups: $R = 4,2,6-C_6H_2Me'Bu_2$, $L_2 = HC (CMeNC_6H_3^{i}Pr_2)_2$), no reactivity appears to have been developed around them. In this context, the relative stability of our diiron complexes provided us with an excellent opportunity to study in detail the unexplored chemistry of strongly nucleophilic diiron phosphinidene complexes.14

Our preliminary studies on the chemistry of [Fe₂Cp₂(µ-PR)- $(\mu$ -CO)(CO)₂] complexes revealed that these neutral species react under mild conditions with different unsaturated organic molecules, such as 1-alkenes, 1-alkynes or diazoalkanes, to give novel organophosphorus ligands involving transformations that had not been observed in comparable reactions using complexes with bent-terminal (**A** and **B** in Chart 1) or trigonal-bridging (**E** and **F** in Chart 1) phosphinidene ligands. 6c,14d,e Our diiron complexes also proved to be suitable substrates for the rational synthesis of heterometallic derivatives and clusters,^{14c} and particularly intriguing was the remarkable ability of the supermesitvlphosphinidene complex $[Fe_2Cp_2\{u-P(2,4,6-C_6H_2^tBu_3)\}$ - $(\mu$ -CO)(CO)₂] to react with dihydrogen at room temperature, ^{14a} a chemical behaviour previously unreported for organophosphorus molecules, except under Frustrated Lewis Pairs conditions.¹⁵ In this paper we report a complete study on the reactions of the cyclohexylphosphinidene complex $[Fe_2Cp_2(\mu-PCy)(\mu-CO)-$ (CO)₂] (1a) toward different electrophilic reagents based on p-block elements, such as the methylating agents MeI and CF₃SO₃Me, several elemental chalcogens (O₂, S₈) and borane adducts (BH₃·L), as well as its reactions with several organic molecules containing multiple C-N or C-O bonds, such as azides and quinones. Some of these reactions were included in a preliminary report on this chemistry.^{6c} Besides this, the reactions with organic molecules having triple C=C bonds turned out to be of great complexity, and full details of them will be reported separately. Moreover, in order to examine the influence of the substituent at the phosphorus atom, we have also studied some reactions of the phenylphosphinidene complex [Fe₂Cp₂(μ -PPh)-(μ -CO)(CO)₂] (**1b**), a molecule less congested than **1a**. As will be shown below, these reactions not only confirm the high nucleophilicity of our diiron phosphinidene complexes, but they also allow the synthesis, either directly or after additional processes, of a variety of complexes having phosphine, phosphide or phosphinidene ligands functionalized in different ways.

Results and discussion

Methylation reactions of compounds 1

The phosphinidene complexes 1a,b react instantaneously with methyl iodide at room temperature or below to give, as the initial product, the corresponding methylphosphide complexes $[Fe_2Cp_2(\mu-PMeR)(\mu-CO)(CO)_2]I$, [R = Cy (2a), Ph (2b)], resulting from the nucleophilic attack of the phosphinidene ligand on the carbon atom of the added electrophile (Scheme 1). However, the phenyl compound 2b was only stable at temperatures below 273 K, otherwise rearranging rapidly to give the neutral iodo complex $[Fe_2Cp_2I(\mu-PMePh)(CO)_3]$ (3) almost completely. This new complex exists in solution as a mixture of two diastereoisomers (A and B) and results from subsequent nucleophilic attack of I⁻ on one of the iron atoms of the cation in 2b, this inducing the cleavage of the intermetallic bond and rearrangement of the bridging carbonyl ligand to a terminal position. Such a process, surely facilitated by the smaller size and lower donor properties of the PPh ligand (compared to the PCy one), is reversible since the removal of the solvent partially regenerates the cationic form 2b (see Scheme 1 and the Experimental section). To avoid the interference of the external ion we tested the reaction of 1b with CF₃SO₃Me; this led selectively to the triflate salt [Fe₂Cp₂(µ-PMePh)(µ-CO)(CO)₂]CF₃SO₃ (2b'), which expectedly does not undergo any further anion-cation reaction.



Synthesis and reactivity of chalcogenophosphinidene complexes

The phosphinidene complexes **1a,b** react rapidly at room temperature with different sources of oxygen atoms and with elemental sulphur to give the corresponding derivatives $[Fe_2Cp_2\{\mu-P(E)R\}-(\mu-CO)(CO)_2]$ [E = O; R = Cy (**4a**), Ph (**4b**). E = S; R = Cy (**5a**), Ph (**5b**)], containing oxo- or thiophosphinidene ligands bridging the dimetal centre exclusively through the P atom (Scheme 2). The synthesis of the P(O)R complexes **4** was not straightforward since the outcome of the reaction turned out to be strongly dependent on the phosphinidene substrate (**1a** or **1b**) and the oxygenating reagent used (air, *m*-chloroperbenzoic acid – MCPBA, olefin oxides, *etc.*). Air gave a clean reaction with the PCy complex **1a**, but led to an intractable mixture of products with the more reactive PPh complex **1b**. For the latter substrate, the highest yields of the oxophosphinidene product were obtained when using MCPBA as an oxygen source.

The chemistry of chalcogenophosphinidene species is of interest to both organic and inorganic chemists. Most of the studies carried out to date are related to uncoordinated phosphinidene oxides (R-P=O), unstable molecules which are thought to be generated in the thermal or photochemical decomposition of several precursors, such as phospholene, phosphirane or phosphanorbornadiene oxides, and others.¹⁶ These transient species undergo processes such as addition to dienes and diones or insertion into O-H and S-S bonds, and are therefore efficient reagents for the synthesis of new organophosphorus derivatives.^{16a,17} Although stabilization of R-P=O species can be achieved through coordination to metal centres, only a few oxophosphinidene complexes have been reported so far, and their reactivity has been little explored.^{18,19} In fact, only another diiron complex having a P(O)R ligand seems to have been previously reported $([Fe_2Cp_2\{\mu-P(O)OH\}(\mu-CO)(CO)_2])$ ²⁰ On the other hand, precedents for diiron complexes having thiophosphinidene ligands are very scarce too, actually restricted to the phenyl derivatives $[Fe_2Cp_2{\mu-P(S)Ph}(CO)_n]$ (n = 3, 4), both of which have no metal-metal bonds.²¹ Actually, the latter tricarbonyl complex is an isomer of 5b, but with a µ-P:P,S-bound thiophosphinidene ligand and no bridging carbonyls.

The presence of uncoordinated P=O and P=S groups in complexes 4 and 5 should facilitate further functionalization of these molecules through the reactions with suitable electrophiles. In particular, we have found that the P(O)R complex 4a reacts readily with HBF₄·OEt₂ to give the hydroxyphosphide complex [Fe₂Cp₂{ μ -P(OH)Cy}(μ -CO)(CO)₂]BF₄ (6), while the reaction with CF₃SO₃Me gives the analogous methoxyphosphide complex [Fe₂Cp₂{ μ -P(OMe)Cy}(μ -CO)(CO)₂]CF₃SO₃ (7) (Scheme 2). The formation of these two compounds involves the addition of the electrophile to the oxygen atom of the oxophosphinidene ligand and illustrates the residual nucleophilicity of the new chalcogenophosphinidene complexes that enables them for further functionalization of the P atom.

Synthesis and reactivity of borane adducts

Compounds **1a,b** react readily with several borane adducts $BH_3 \cdot L$ (L = THF, N'Bu₃, PPh₃) to give the corresponding acidbase adducts $[Fe_2Cp_2\{\mu-P(BH_3)R\}(\mu-CO)(CO)_2]$ (R = Cy (**8a**), Ph (**8b**), Scheme 3). These products follow from a process



Scheme 3

analogous to that occurring in the formation of the diplatinum complex $[Pt_2(dppe)_2 \{\mu - \kappa^1 : \kappa^1 - P(BH_3)Mes\}_2]$.¹⁸*c* As expected, the more labile THF adduct reacted rapidly with both **8a** and **8b** at room temperature, but the more robust adducts $BH_3 \cdot N'Bu_3$ and $BH_3 \cdot PPh_3$ reacted only with the more basic PCy complex **1a**, still this needing some thermal activation (343 K).

Surprisingly, complexes **8** exhibited considerable thermal stability, since they could be heated at 358 K in a toluene solution for 1 h without noticeable decomposition. Moreover, these complexes could be purified by column chromatography without hydrolysis of the BH₃ group. They underwent clean decarbonylation under photochemical activation, also without BH₃ degradation (Scheme 3), to give the dicarbonyl derivatives $[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)R\}(\mu-CO)(CO)]$ (**9a,b**). In these products the loss of a carbonyl ligand is counterbalanced by the

coordination of one of the B-H bonds of the RPBH₃ ligand, thus rendering an agostic Fe-H-B interaction. We note that related tricentric interactions are well known in the chemistry of iron complexes,²² and that phosphine-borane adducts PR₃·BH₃ are known to bind metal centres via their B-H bonds.²³ However, we have found no iron complexes described with a comparable phosphinidene-borane ligand. In fact, the coordination mode observed in 9 has a single precedent, the complex $[Mo_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)H\}(CO)_2(\eta^6-HMes^*)] \text{ recently pre-}$ pared in our laboratory.^{5g} Unlike their precursors, complexes 9a, **b** were easily hydrolyzed upon addition of water or just when attempting their chromatographic purification on hydrated alumina, to give the corresponding hydride-phosphide complexes $[Fe_2Cp_2(\mu-H)(\mu-PRH)(CO)_2]$, a reaction with no synthetic use, since the same products have been previously synthesized by us using more direct routes.^{14b}

Reactivity towards organic azides

Free phosphines (PR_3) react easily with organic azides to give initially phosphoranylidenetriazenes R₃PN₃R', a type of molecule usually of low thermal stability that lose nitrogen at room temperature or below to yield the corresponding iminophosphines R₃P=NR'.²⁴ This process, known as the Staudinger reaction,²⁵ has different uses in synthetic organic chemistry, for instance the formation of new C=N bonds via the aza-Wittig reaction.²⁶ On this basis, it might be anticipated that phosphinidene complexes might analogously react with organic azides to give coordinated phosphatriazadiene ligands (RPN₃R') initially, and perhaps iminophosphinidene (or phosphaimine) ligands (RP=NR'), if spontaneous denitrogenation would take place afterwards. Surprisingly, however, the reactions of PR complexes towards these molecules have been explored only recently, on complexes of the types **B** and **F**, these leading invariably to iminophosphinidene derivatives. 3c,4j It was thus of interest to examine the behaviour of the PR-bridged compounds 1 towards organic azides (Scheme 4).

Compound **1a** reacts under mild conditions with benzyl azide to give $[Fe_2Cp_2\{\mu-P(N_3CH_2Ph)Cy\}(\mu-CO)(CO)_2]$ (**10a**), which displays a P:P-bridged phosphatriazadiene ligand resulting from the biphilic P–N interaction of the phosphinidene ligand with the terminal nitrogen of the azide, without elimination of dinitrogen. A similar reaction takes place with the PPh complex **1b** to give the corresponding derivative $[Fe_2Cp_2\{\mu-P(N_3CH_2Ph)Ph\}(\mu-CO)-(CO)_2]$ (**10b**). However, the latter compound has a low thermal stability, and it decomposes above 263 K to give several unstable species that could be neither isolated nor properly characterized. We note that compounds **10** appear to be the first phosphatriazadiene complexes to be reported.

Thermal and photochemical activation experiments were performed on **10a** to examine potential denitrogenation processes or rearrangements involving the coordination of the N atoms to the dimetal centre (see our studies on the related phosphadiazadiene derivatives of **1a**).^{14*d*} First we found that heating toluene solutions of **10a** at 368 K gave rapidly the complex [Fe₂Cp₂{ μ -P-(NCH₂Ph)Cy}(μ -CO)(CO)₂] (**11**), with a P:P-bound iminophosphinidene ligand resulting from denitrogenation in the phosphatriazadiene precursor (Scheme 4). Although **11** was obtained



almost quantitatively, it turned out to be very air-sensitive, to give several species that could be neither isolated nor properly characterized. Fortunately, the presence of a lone electron pair at the N atom in **11** allows for further functionalization of the ligand, yielding more stable derivatives. In particular, we found that **11** reacts instantaneously with [NH₄]PF₆ to give the cationic complex [Fe₂Cp₂{ μ -P(NHCH₂Ph)Cy}(μ -CO)(CO)₂]PF₆ (**12**) in quantitative yield, with an aminophosphide ligand resulting from the attachment of a proton to the nitrogen atom of the iminophosphinidene group of the precursor.

Irradiation of toluene solutions of **10a** induced a slow but complex reaction eventually yielding the trinuclear complex $[Fe_3Cp_3(\mu_3-PCy)\{\mu-\kappa^1:\kappa^1-C(O)(NHCH_2Ph)\}(\mu-CO)_2]$ (**13**), as the only organometallic species present in the reaction mixture. This product displays a trimetal core bridged by a phosphinidene and a C,O-bound aminoacyl ligand, and its formation obviously requires several elemental steps, these including denitrogenation, P–N and Fe–Fe bond cleavage and H atom abstraction processes (perhaps from trace amounts of water in the medium), among others. IR and ³¹P{¹H} NMR monitoring of this reaction allowed the detection of complex **11** and a second intermediate species at shorter reaction times. This suggests that denitrogenation (to give **11**) most likely is the first event also in the photochemical reaction. As for the second species, it is likely a trinuclear compound already, since it displays a quite deshielded

 31 P NMR resonance at 430 ppm, possibly corresponding to a μ_3 -PCy ligand, but we could neither isolate nor properly characterize it.

Reactivity towards quinones

Compounds 1a,b react rapidly with 3,5-di-tert-butyl-o-benzoquinone to generate the corresponding derivatives [Fe₂Cp₂- $(\mu-CO)_2(CO) \{ P(O_2C_6H_2^{t}Bu_2)R \} [R = Cy (14a), Ph (14b)],$ with a phosphonite ligand formally derived from the oxidative addition of the quinone to the P atom of the PR ligand, a process analogous to that observed for the reactions of the free phosphines with this type of guinones.²⁷ Under similar conditions (room temperature or below) compounds 1a,b also react with p-benzoquinone. The IR spectra of the resulting solutions are analogous to those recorded for complexes 14, this suggesting that the newly formed species contain a similar local structure. However, these products had a low solubility in most common solvents and exhibited very broad resonances in the corresponding ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR spectra, so we could neither isolate nor properly characterize them. This situation could be related to the fact that, in the case of *p*-benzoquinone, the binding of both oxygen atoms of the quinone to the same phosphorus atom is not possible. As a result, the reaction likely involves the interaction of the quinone with two molecules of the complex, thus triggering an oligomerization process.

Spectroscopic data available in solution for compounds 14 indicate the presence of an equilibrium mixture of the

Table 1 Selected IR^a and ${}^{31}P{}^{1}H{}NMR^b$ data for new compounds

corresponding cis and trans isomers (Chart 2). Their IR spectra (Table 1) display two C–O stretches for the bridging CO ligands, with the pattern expected for a transoid relative positioning of these ligands,²⁸ and two C-O stretches for the terminal CO ligand, which agree with the presence in solution of the mentioned isomers. By comparing the frequency and relative intensity of the latter bands with analogous diiron complexes described in the literature, we conclude that the trans isomer is the major product, as usually observed in this sort of complexes.²⁹ As expected, complex 14a displays two ³¹P NMR resonances at ca. 280 ppm with different intensities. In contrast, the phenyl compound 14b displays just one broad resonance at ca. 240 ppm at this temperature, suggesting that the interconversion process between isomers is fast on the NMR timescale. Indeed this resonance eventually splits upon cooling, and two sharp resonances are observed at 233 K. It should be noted that the equilibrium process observed for these compounds has



Compound	<i>v</i> (CO)	$\delta_{ m P}\left(J_{ m PB} ight)$
[Fe ₂ Cp ₂ (μ-PMeCy)(μ-CO)(CO) ₂]I (2a)	2015 (vs), 1985 (w), 1829 (m)	271.2
$[Fe_2Cp_2(\mu-PMePh)(\mu-CO)(CO)_2]I(2b)$	2024 (vs), 1991 (w), 1831 (m)	250.6^{c}
$[Fe_2Cp_2(\mu-PMePh)(\mu-CO)(CO)_2]CF_3SO_3(2b')$	2025 (vs), 1992 (w), 1830 (m)	248.3
$[Fe_2Cp_2I(\mu-PMePh)(CO)_3]$ (3)	2024 (vs), 1995 (w, sh), 1976 (s), 1923 (m)	$37.5 (A)^{c}$
		$32.5 (B)^c$
$[Fe_2Cp_2{\mu-P(O)Cy}(\mu-CO)(CO)_2]$ (4a)	1985 (vs), 1951 (w), 1788 (m)	343.8 ^c
$[Fe_2Cp_2(\mu-P(O)Ph)(\mu-CO)(CO)_2]$ (4b)	1997 (vs), 1964 (w), 1795 (m)	319.6 ^c
$[Fe_2Cp_2\{\mu-P(S)Cy\}(\mu-CO)(CO)_2](5a)$	1989 (vs), 1957 (w), 1794 (m)	345.6^{c}
$[Fe_2Cp_2\{\mu-P(S)Ph\}(\mu-CO)(CO)_2]$ (5b)	2001 (vs), 1971 (w), 1799 (m)	313.4^{c}
$[Fe_2Cp_2\{\mu-P(OH)Cy\}(\mu-CO)(CO)_2]BF_4$ (6)	2015 (vs), 1985 (w), 1826 (m)	370.9 (cis, anti)
		352.6 (cis, syn)
$[Fe_2Cp_2{\mu-P(OMe)Cy}(\mu-CO)(CO)_2]CF_3SO_3(7)$	2016 (vs), 1988 (w), 1831 (m)	385.3 (cis, anti)
		387.9 (cis, syn)
		392.2 (trans)
$[Fe_2Cp_2{\mu-P(BH_3)Cy}(\mu-CO)(CO)_2]$ (8a)	1993 (vs), 1960 (w), 1797 (m)	367.9 (41)
$[Fe_2Cp_2{\mu-P(BH_3)Ph}(\mu-CO)(CO)_2]$ (8b)	2004 (vs), 1971 (w), 1802 (m)	343.0 (33)
$[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)Cy\}(\mu-CO)(CO)]$ (9a)	1972 (vs), 1801 (m) ^{d}	304.7 (62)
$[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)Ph\}(\mu-CO)(CO)]$ (9b)	1974 (vs), 1813 (m) ^{d}	250.3 (64)
$[Fe_2Cp_2{\mu-P(N_3CH_2Ph)Cy}(\mu-CO)(CO)_2]$ (10a)	1989 (vs), 1957 (w), 1793 (m)	319.1
$[Fe_2Cp_2{\mu-P(N_3CH_2Ph)Ph}(\mu-CO)(CO)_2]$ (10b)	2000 (vs), 1964 (w), 1798 (m)	302.8^{e}
$[Fe_2Cp_2{\mu-P(NCH_2Ph)Cy}(\mu-CO)(CO)_2]$ (11)	1977 (vs), 1943(w), 1773 (m)	274.6
$[Fe_2Cp_2{\mu-P(NHCH_2Ph)Cy}(\mu-CO)(CO)_2]PF_6$ (12)	2011 (vs), 1984 (w), 1824 (m)	315.1
$[Fe_3Cp_3(\mu_3-PCy)\{\mu-\kappa^1:\kappa^1-C(O)(NHCH_2Ph)\}(\mu-CO)_2]$ (13)	1776 (vs), 1727 (w)	624.8
$[Fe_2Cp_2(\mu-CO)_2(CO) \{P(O_2C_6H_2^{t}Bu_2)Cy\}]$ (14a)	1967 (w, sh), 1951 (m), 1782 (w), 1743 (vs)	277.5 (trans)
		280.0 (cis)
$[Fe_2Cp_2(\mu-CO)_2(CO)\{P(O_2C_6H_2{}^tBu_2)Ph\}] (14b)$	1972 (s), 1951 (s), 1794 (w), 1763 (vs) ^f	237.3 $(trans)^g$ 240.8 $(cis)^g$

^{*a*} Recorded in a dichloromethane solution, with C–O stretching bands (ν (CO)) in cm⁻¹. ^{*b*} Recorded in CD₂Cl₂ solutions at 290 K and 162.00 MHz unless otherwise stated; δ in ppm relative to external 85% aqueous H₃PO₄, and J_{PB} in Hz. ^{*c*} In CDCl₃ solution. ^{*d*} In toluene solution. ^{*e*} Recorded at 203 K. ^{*f*} In petroleum ether solution. ^{*g*} Recorded in toluene-d₈ solution at 233 K.

been studied in detail previously for analogous complexes $[Fe_2Cp_2(\mu-CO)_2(CO)L]$ (L = P(OPh)₃,³⁰ CO),³¹ and therefore needs not to be discussed in detail.

Structural characterization of neutral μ -P(E)R complexes (4, 5, 8, 10 and 11)

The structure of the P(O)R complex 4a was confirmed in a preliminary study (Fig. 1 and Table 2).^{6c} The molecule is built up from two CpFe(CO) fragments placed in a cisoid relative arrangement and bridged by a carbonyl and a P:P-bound oxophosphinidene ligand. The intermetallic distance of 2.601(2) Å is consistent with the single Fe-Fe bond to be proposed according to the EAN formalism, and it is very similar to that measured in $[Fe_2Cp_2\{\mu-P(O)OH\}(\mu-CO)(CO)_2]$ (2.615(4) Å),²⁰ while the bridging carbonyl ligand is slightly off the plane defined by the iron and phosphorus atoms. The cyclohexyl group in the bridging oxophosphinidene ligand points away from the cyclopentadienyl ligands, a conformation identical to those found in all phosphinidene precursors of type $1,^6$ and presumably more favoured on steric grounds. The Fe-P distances of 2.219 (2) and 2.216 (2) Å are comparable to those observed for the mentioned diiron complex (ca. 2.19 Å), and are marginally lower (by ca. 0.04 Å) than those observed for the phenylphosphinidene complex 1b.^{6c} The P–O bond length of 1.503(3) Å is also very similar to that measured in the mentioned oxophosphinidene complex, and it is consistent with the formulation of a double bond between these atoms. In any case, all the above data indicate that the incorporation of an oxygen atom does not disturb the geometry of the phosphinidene ligand to a significant extent, except for a slight shortening of the Fe–P lengths.

The spectroscopic data available for the neutral μ -P(E)R complexes (R = Cy, Ph; E = O, S, BH₃, N₃R', NR') are similar to each other (Table 1 and Experimental section) and indicate that



 Table 2
 Selected bond lengths (Å) and angles (°) for 4a^{6c}

Fe1-Fe2 Fe1-P1 Fe2-P1 Fe1-C1 Fe1-C3 Fe2-C2	2.601(2) 2.219(2) 2.216(2) 1.747(5) 1.914(5) 1.748(5)	C1-Fe1-Fe2 C2-Fe2-Fe1 C1-Fe1-C3 C2-Fe2-C3 C1-Fe1-P1 C2-Fe2-P1	99.2(1) 99.4(2) 89.3(2) 90.3(2) 92.0(1) 91.3(1)
Fe2–C2	1.748(5)	C2–Fe2–P1 Fe1 P1 O4	91.3(1)
P1-04	1.503(3)	Fe2–P1–O4	121.0(1)

all of them share the same basic structural features, in turn consistent with the solid-state structure just discussed for 4a. In particular, their IR spectra exhibit three C-O stretching bands indicative of the retention in solution of a bridging CO (ca. 1795 cm^{-1}) and almost parallel terminal CO ligands.²⁸ The pattern is similar to that displayed by the parent phosphinidene complexes 1,⁶ but the bands are generally shifted by some 10-20 cm⁻¹ to higher frequencies, in agreement with the expected decrease of electron density at the dimetal centre derived from the coordination of the phosphorus lone pair to the incoming electrophile. It should be noted, however, that this effect is not dominated by the electronegativity of the acceptor atom, since the experimental ordering of the average C-O stretches is $BH_3 > S > N_3R > O > NR > 1a,b$. It seems therefore that π bonding between P and the electrophile (absent in the borane adducts and expected to be prevalent for O and NR' groups) partially cancels the drift of charge away from the dimetal centre. Incidentally, the above data suggest that the π (P–N) interaction in the phosphatriazadiene complexes 10 is not as strong as the one in the iminophosphinidene complex 11, an effect that could be derived from a significant delocalization of the π interaction along the P–N–N–N chain in the former complex (represented by canonical forms of the type Fe₂RP⁺- $N=N-R'N^{-}).$

Our neutral P(E)R complexes display ³¹P NMR resonances in the range 275–370 ppm, some 200 ppm more shielded than those of the parent phosphinidene complexes 1. The borane adducts **8a** and **8b** gave the less shielded resonances, expectedly broadened due to scalar coupling to the ¹¹B nucleus, with the corresponding constants ($J_{PB} = 41$ and 33 Hz, respectively) being similar to those measured in other species containing P–BH₃ bonds.³² We finally note that the high symmetry of this group of compounds is clearly reflected in their ¹H and ¹³C NMR spectra (see the Experimental section), which denote in each case the presence of an effective symmetry plane relating both metal fragments of the molecule.

Structural characterization of cationic μ -P(E)R complexes (2, 6, 7 and 12)

The geometry of the cation in 12 (Fig. 2 and Table 3) can be related to that of the P(O)R complex 4a, and even more closely to those of the phosphadiazadiene complex [Fe2Cp2{µ-P- $(N_2CH_2)Cy{(\mu-CO)(CO)_2}$ and its aminophosphide derivative $[Fe_2Cp_2\{\mu-P(NHNCH_2)Cy\}(\mu-CO)(CO)_2]BF_4$.^{14d} The cation can be described as two cisoid FeCp fragments connected by a single metal-metal bond (2.6362(8) Å) and symmetrically bridging carbonyl and aminophosphide ligands. The coordination spheres around the metal atoms are completed by two terminal carbonyls, placed almost parallel to each other. The P-N distance of 1.657(4) Å is longer than the corresponding length in the neutral complex $[Fe_2Cp_2\{\mu-P(N_2CH_2)Cy\}(\mu-CO)(CO)_2]$ (1.612(2) Å), taken here as a reference for a double P=N bond, and is comparable to that measured in the mentioned aminophosphide complex (1.669(2) Å). These distances actually approach the single-bond lengths of ca. 1.67-1.72 Å measured in different aminophosphine iron complexes.³³ Thus we must conclude that, upon protonation at the N atom, the $\pi(N-P)$ bonding interaction



Fig. 2 ORTEP diagram (30% probability) of the cation in compound 12, with H atoms (except H1) omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for 12

Fe1–Fe2	2.6362(8)	Fe1-Fe2-C2	100.4(1)
Fe1-C1	1.768(4)	Fe2–Fe1–C1	96.8(1)
Fe1–C3	1.973(5)	P1–Fe1–C1	90.5(1)
Fe2–C2	1.776(5)	P1–Fe2–C2	91.9(1)
Fe2–C3	1.924(5)	P1-N1-C14	129.4(3)
Fe1–P1	2.187(1)	P1-N1-H1	113(3)
Fe2–P1	2.193(1)	H1-N1-C14	116(3)
P1-N1	1.657(4)	Fe1–P1–N1	123.4(1)
N1-H1	0.94(5)	Fe2–P1–N1	122.5(1)
N1-C14	1.470(6)		

in the parent iminophosphinidene ligand is substantially diminished, and therefore the resulting ligand can be properly described as an aminophosphide ligand. Yet, the degree of pyramidalization at the N atom is negligible (ΣX –N–Y *ca.* 358°; X, Y = C(14), P(1), H(1)), a circumstance still quite common for aminophosphine complexes, and the benzyl and cyclohexyl substituents are arranged in an *anti* conformation, more favoured on steric grounds.

The spectroscopic data available for the cationic μ -P(E)R complexes (R = Cy, Ph; E = Me, OH, OMe, NHR') are similar to each other (Table 1 and Experimental section), indicating that all of them share the same basic structural features, in turn consistent with the structure of **12** in the crystal. Their IR spectra display three C–O stretching bands indicative of the retention in solution of a bridging CO and two terminal CO ligands almost parallel to each other, also denoted by the presence of resonances at *ca*. 255 and 210 ppm (1 : 2 intensity) in the corresponding ¹³C {¹H} NMR spectra. The pattern of the C–O stretches is similar to that of their neutral precursors, but the bands are shifted by *ca*. 40 cm⁻¹ to higher frequencies, as expected from the cationic nature of these complexes. Moreover, the solid-state IR spectrum of the hydroxyphosphide complex **6** (Nujol mull) displays a broad band at *ca*. 3225 cm⁻¹ corresponding to the O–H stretch.

Compounds **2**, **6** and **7** display 31 P NMR resonances at chemical shifts (*ca.* 250 ppm for compounds **2**, *ca.* 380 ppm for compounds **6** and **7**) expected for complexes having respectively



Fig. 3 Projections of the possible isomers of compounds **6** and **7**, viewed along the axis joining the bridging PCyOR' and CO ligands.

alkylphosphide³⁴ and alkoxyphosphide^{29c,35} ligands bridging two metal atoms connected by a metal–metal bond. However, while the methylphosphide complexes **2a,b** exhibit a single resonance in the corresponding ³¹P{¹H} NMR spectra, compound **6** displays two resonances and compound **7** three resonances, with their relative intensities being solvent-dependent in each case (see the Experimental section). This implies the presence in solution of interconverting isomers in each case.

The major isomer (unique in the case of compounds 2) most likely is the one present for the parent compounds 1a,b and in their protonated derivatives $[Fe_2Cp_2(\mu-PHR)(\mu-CO)(CO)_2]BF_4$ (R = Cy, Mes, Mes*),⁶ that is, the one with the R group pointing away from the Cp ligands (isomer *cis, anti* in Fig. 3), expectedly more favoured on steric grounds. Out of the two other possible isomers (Fig. 3), we propose the *cis, syn* structure for the minor isomer of **6**, since it gives rise to single ¹³C and ¹H NMR Cp resonances. Finally, the two minor isomers of **7** can be also identified on the basis of the number of Cp resonances as the *cis, syn* and *trans* isomers respectively, although their relative amount is always very small under all conditions examined (see the Experimental section).

Compound **12** exhibits a single ³¹P NMR resonance at 315.1 ppm, a position very similar to that of the aminophosphide complex $[Fe_2Cp_2{\mu-P(NHNCH_2)Cy}(\mu-CO)(CO)_2]BF_4$ (313.7 ppm).^{14d} In the ¹H NMR spectrum, the Cp (5.20 ppm) and CH₂ (4.50 ppm) groups give rise to single resonances, consistent with the symmetry plane relating both FeCp(CO) fragments in a *cis* isomer, while the NH resonance is located at 4.40 ppm.

Structure of the iodide complex 3

Although compound **3** exists in solution as an equilibrium mixture of two diastereoisomers giving rise to separated NMR resonances, its IR spectrum gives no hint of it, since it displays three C–O stretches that might be assigned to a single complex having relatively uncoupled M(CO)₂ and M(CO) oscillators. In fact, the observed pattern is comparable to that reported for $[Fe_2Cp_2{\mu-\kappa^1:\kappa^2-P(S)Ph}(CO)_3]^{.21}$ From this we conclude that the two isomers of **3** must have very similar local environments at their metal centres, consistent with its identification as the two possible diastereoisomers in a complex having two stereogenic metal centres. It is also to be noted that the ³¹P resonances for

these isomers are located at *ca.* 35 ppm, that is, some 200 ppm more shielded than the resonance of the cationic isomer **2b**. This is consistent with the presence of phosphide ligands bridging metal atoms not connected by a metal–metal bond,³⁴ a consequence here of the coordination of the iodide ion.

Solid-state and solution structure of agostic phosphinideneborane complexes

The molecule of the PCy complex 9a in the crystal (Fig. 4 and Table 4) is built from two CpFe fragments placed in a cisoid relative arrangement and connected by a single metal-metal bond (ca. 2.63 Å) and two bridging ligands: carbonyl and phosphinidene-borane (CyPBH₃). The latter formally behaves as a fourelectron donor and is symmetrically bound to both metals through its phosphorus atom (P–Fe = 2.181(1) Å), while one of its B-H bonds binds the Fe2 atom, thus establishing an agostic M-H-B interaction that fills the vacancy left by the removal of a terminal CO ligand in the parent tricarbonyl 8a; besides, the Fe1 completes its coordination sphere with a terminal carbonyl ligand. To balance the lower donor ability of the B-H bond (compared to the terminal CO ligand), the bridging carbonyl expectedly binds the Fe2 atom much more tightly (Fe-C lengths 1.849(4) Å and 2.069(4) Å, respectively) and indeed it might be considered as semibridging. From a conformational point of view, we note that the cyclohexyl group in 9a is arranged syn with respect to the Cp ligands. This is unusual, since all derivatives of the phosphinidene complexes 1 usually retain the anti conformation present in the starting materials. This implies that a



Fig. 4 ORTEP diagram (30% probability) of compound **9a**, with H atoms (except those bound to B1) omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for 9a

Fe1–Fe2	2.6300(7)	P1–Fe1–Fe2	52.9(1)
Fe1–P1	2.181(1)	P1–Fe2–Fe1	52.9(1)
Fe2-P1	2.181(1)	C1–Fe1–Fe2	104.2(1)
Fe1-C1	1.765(5)	B1–Fe2–Fe1	85.7(1)
Fe1-C2	2.069(4)	C2–Fe1–Fe2	44.4(1)
Fe2–C2	1.849(4)	C2–Fe2–Fe1	51.5(1)
Fe2–B1	2.351(5)	O2–C2–Fe1	129.3(3)
Fe2-H1	1.78(4)	O2–C2–Fe2	146.5(3)
B1-P1	1.912(5)	H1–Fe2–P1	80(1)
B1-H01	1.27(4)	Fe2–P1–B1	69.8(1)
B1-H02	1.19(4)	P1-B1-H1	105(1)
B1-H03	1.13(4)	B1-H1-Fe2	100(2)

conformational change (from *anti* to *syn*) has occurred during the formation of compounds **9**, surely induced photochemically.

The Fe2–B1 bond length of 2.351(5) Å falls in the upper limit of the range usually found for agostic Fe-H-B interactions (2.05-2.38 Å),³⁶ it being similar to that measured in the carbaborane complex [FeCp(CO)₂(η^2 -B₉C₂H₁₂)] (2.377(1) Å),^{36a} and exceeds by ca. 0.4 Å the values measured for conventional twocentre/two-electron Fe-B interactions.37 As expected, the uncoordinated B1-H02 and B1-H03 bonds have lengths similar to those observed in simple phosphine-borane adducts such as (NH₂)₃P-BH₃ (1.1-1.2 Å),³⁸ while the coordinated B1-H01 bond is enlarged by some 0.1 Å, an effect comparable to that measured in the only other phosphinidene-borane complex structurally characterized so far (1.24(5) Å in [Mo₂Cp₂- $\{\mu - \kappa^1 : \kappa^1, \eta^2 - P(BH_3)H\}(CO)_2(\eta^6 - HMes^*)\}$, which displays an analogous M-H-B interaction.5g Finally, the B-P length of 1.912(5) Å can be viewed as a conventional figure for a single bond between these atoms. 32a,38

The spectroscopic data in solution for complexes 9a,b are consistent with the solid-state structure of 9a just discussed. In particular, the IR spectra display two C-O stretching bands at ca. 1973 cm⁻¹ and 1807 cm⁻¹, corresponding to the terminal and bridging carbonyls, respectively, which in turn give rise to quite differently deshielded 13 C resonances (at *ca.* 214 and 260 ppm, respectively), as expected. Their ${}^{31}P{}^{1}H{}$ and ${}^{11}B{}$ NMR spectra exhibit resonances at *ca.* 275 ppm and ca. -35 ppm, respectively, with chemical shifts somewhat lower than those of the corresponding precursors. As expected for fully asymmetric molecules, the ¹H NMR spectra of these complexes display independent resonances for the three protons of the BH₃ group, at ca. 0.5, -2 and -23 ppm. The most shielded resonance is thus unambiguously assigned to the H atom interacting with the iron atom. Although its very low chemical shift would be itself consistent with the presence of a hydride ligand bridging the iron atoms, 14b,29a,b the broadness of this resonance ($w_{1/2}$ ca. 100 Hz for 9a, transformed into a sharp multiplet in the ¹H{¹¹B} NMR spectrum) denotes an unresolved coupling to the ¹¹B nucleus of some 30–40 Hz, and hence the presence of direct H-B binding, if weakened, therefore consistent with an agostic B-H-Fe interaction. This coupling is to be compared with an H-B coupling of 149 Hz for the "normal" B-H protons in 9a, while the B-H couplings in the precursors 8a and 8b have intermediate values of ca. 100 Hz. Thus, as judged from these figures, we conclude that the agostic coordination of one of the B-H bonds in 9 causes a considerable weakening in that bond (in agreement with the increased B-H distance in the crystal), and a significant strengthening in the other two B-H bonds. Given the very low B-H coupling estimated for the agostic H atom, we are tempted to propose that such agostic interaction for compounds 9 in solution might be actually stronger than in the crystal. Should this be the case, we would anticipate a lower asymmetry for the bridging carbonyl in solution. Indeed, the spectroscopic parameters for this ligand in compounds 9 (v(C–O) ca. 1807 cm⁻¹ and $\delta_{\rm C}$ ca. 260 ppm) are indicative of the presence of a rather normal bridging (instead of semibridging) carbonyl in solution.

Compound **9b** displayed independent ¹H and ¹³C NMR resonances for all atoms in the phenyl ring, indicating the unexpected absence of free rotation of this ring around the P–C bond at

room temperature. A standard NOESY ¹H NMR experiment revealed that there is a positive NOE between one of the hydrogen atoms of the BH₃ group (δ 0.87 ppm) and one of the *ortho* protons of the ring (δ 8.28 ppm). Thus we propose for **9b** in solution the presence of dihydrogen bonding interactions between a BH₃ proton (negatively polarized) and one of the *ortho* protons of the phenyl ring (positively polarized). Dihydrogen bonds are inter- or intramolecular interactions typically occurring between positively charged hydrogen atoms of H–A bonds (A = O, N, C in alkenes, aromatic rings, ...) and negatively charged hydrogen atoms of H–X bonds (X = B, Al, Ga, ...).³⁹

Structural characterization of the acyl triiron complex 13

The molecule of **13** in the crystal (Fig. 5 and Table 5) is built up from three CpFe fragments bridged by a μ_3 -PCy ligand and defining a V-shaped metal core. The external FeCp groups are further bridged by an aminoacyl ligand and connected to the central metal atom by intermetallic bonds and a carbonyl bridge in each case. These three bridging ligands are placed opposite to the phosphinidene ligand, relative to the intermetallic plane, a feature also observed for other μ_3 -PR trinuclear complexes recently reported by us.^{14b,c} The Fe–Fe lengths of 2.6188(7) and 2.6000(8) Å in **13** are within the range of values previously measured for related 48- and 50-electron Fe₃(μ_3 -PR) clusters,^{40,41} while the Fe–P distances, similar to each other and

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Table 5 Selected bond lengths (Å) and angles (°) for 13

01

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Fe1-Fe3 Fe2-Fe3 Fe1-C1 Fe2-C2 Fe2-C3 Fe3-C1 Fe3-C1 Fe3-C2 Fe1-P1 Fe2-P1 Fe3-P1 Fe3-P1 Fe1-O3	$\begin{array}{c} 2.6188(7)\\ 2.6000(8)\\ 1.936(4)\\ 1.881(4)\\ 1.941(4)\\ 1.913(4)\\ 2.163(1)\\ 2.173(1)\\ 2.173(1)\\ 2.179(1)\\ 1.982(3) \end{array}$	Fe1-Fe3-Fe2 Fe1-P1-Fe2 Fe1-P1-Fe3 Fe2-P1-Fe3 Fe1-O3-C3 Fe2-C3-O3 Fe1-P1-C26 Fe2-P1-C26 Fe3-P1-C26 C3-N1-H1 C3-N1-C4	83.6(1) 106.7(1) 74.2(1) 73.4(1) 123.6(2) 124.4(3) 130.8(2) 121.1(1) 128.1(1) 116(3) 122.6(3)
Fe2–P1	2.173(1)	Fe3–P1–C26	128.1(1)
Fe3–P1	2.179(1)	C3–N1–H1	116(3)
Fe1-O3	1.982(3)	C3–N1–C4	122.6(3)
C3-O3	1.284(5)	C4–N1–H1	120(3)
C3-N1 N1-C4	1.359(5) 1.470(5)		



short (*ca.* 2.16–2.18 Å), indicate a strong coordination of the PCy group. In this ligand, the chemical environment around the P atom is not of the common tetrahedral type, but rather of a distorted trigonal-pyramidal type, with the P1, C26, Fe1 and Fe2 atoms placed almost in the same plane (ΣX –P–Y *ca.* 359°; X, Y = C26, Fe1, Fe2) and the third metal atom (Fe3) occupying the apical position. This environment, however, seems to be characteristic of 50-electron Fe₃(μ_3 -PR) and related clusters.^{1*n*,41}

The aminoacyl ligand in 13 spans a non-bonding Fe1...Fe2 distance of ca. 3.50 Å, with the coordinated O and C atoms defining an almost flat OCFe2 motif (torsion angle Fe1-O3-C3-Fe2 ca. 2°). In such a geometry, a generic metal-acyl interaction can be described as a resonance hybrid of acyl and oxycarbene canonical forms (A and B in Chart 3).⁴² In the case of an aminoacyl ligand, a third resonance form C involving the electron pair of the amino group still might be invoked. Indeed the facts that the H and C atoms of the amino group in 13 are placed in the OCFe₂ plane, and that the N-C3 length of 1.359(5) Å is ca. 0.11 Å shorter than the N-C4 one are consistent with such an interaction. Interestingly, although there are only a few aminoacyl-bridged diiron complexes previously characterized, all of them also display a conformation of the amino group coplanar with the OCFe₂ plane.⁴³ Incidentally, all these compounds are metal-metal bonded complexes of the type [Fe₂(μ - κ^{1} : κ^{1} -C(O)-NR₂)(µ-X)(CO)₄L₂], and display Fe-C, C-O, O-Fe and C-N distances of ca. 1.98, 1.27, 1.99 and 1.34 Å (±0.01 Å) respectively. The corresponding lengths in 13 are similar, except for the Fe2-C3 length of 1.941(4) Å, which is ca. 0.04 Å shorter, but still comparable to the single Fe-C lengths usually measured for bridging carbonyls. This suggests that, rather than due to a larger contribution of the oxycarbene form **B**, the stronger Fe–C interaction apparent in 13 might be just derived from a more favourable geometry: because of the large (nonbonding) intermetallic separation in 13, the Fe2-C3-O3 angle is 124.4(3)°, optimal for a strong σ bond involving an sp²-hybridized C atom. In contrast, the short intermetallic distances in the mentioned aminoacyl complexes force the corresponding Fe-C-O angles to be more acute (ca. 113°), this causing a less optimal Fe-C overlap, and therefore longer interatomic distances.

Spectroscopic data in solution for **13** are consistent with the structure in the crystal. Its IR spectrum exhibits two C–O stretches in the region of the bridging carbonyls, with relative intensities indicative of a cisoid arrangement,²⁸ while the band corresponding to the acyl ligand is located at much lower frequencies (1404 cm⁻¹), as expected. At the same time, the ¹³C NMR spectrum displays three quite deshielded resonances at 281.7, 279.2 and 233.4 ppm. The two most deshielded ones fall within the usual range of bridging CO ligands at diiron complexes (*ca.* 260–290 ppm), therefore the less deshielded resonance is assigned to the acyl group. The chemical shift of 233.4 ppm is comparable to those found in related complexes

having terminal acyl ligands,⁴⁴ and far from the values expected for a carbene ligand, thus suggesting little participation of the oxycarbene form **B**, in agreement with the crystal data. The ³¹P{¹H} NMR spectra of **13** exhibit a resonance at 624.8 ppm, a relatively high chemical shift, but not unusual for 48- and 50-electron clusters having iron atoms.^{14b,c} We finally note that the resonance of the HC¹ proton of the Cy group is unusually deshielded (δ 4.87 ppm). This could be a combined deshielding effect of the three anisotropic Cp rings of the molecule, relatively close to that H atom.

Concluding remarks

The phosphinidene complexes $[Fe_2Cp_2(\mu-PR)(\mu-CO)(CO)_2]$ (R = Cy, Ph) are strong nucleophiles able to react under mild conditions with different electrophilic reagents based on p-block elements, to give neutral or cationic derivatives of the type $[Fe_2Cp_2\{\mu-P(E)R\}(\mu-CO)(CO)_2]^n$ (n = 0, +1). After additional protonation, alkylation or photochemical processes, these complexes can lead to novel phosphide or phosphinidene derivatives otherwise difficult to prepare, such as the hydroxy- and alkoxyphosphide cations $[Fe_2Cp_2\{\mu-P(OR')Cy\}(\mu-CO)(CO)_2]^+$ or the agostic phosphinidene–borane complexes [Fe₂Cp₂{ μ - κ^{1} : κ^{1} , η^{2} -P- $(BH_3)R_{(\mu-CO)(CO)}$. Our phosphinidene complexes are also very reactive toward organic molecules containing multiple C-O or C-N bonds, such as quinones and azides, to give respectively phosphonite $[Fe_2Cp_2(\mu-CO)_2(CO) \{P(O_2C_6H_2^{t}Bu_2)R\}]$ and phosphatriazadiene $[Fe_2Cp_2\{\mu-P(N_3CH_2Ph)R\}(\mu-CO)(CO)_2]$ derivatives. The latter are the first examples containing a µ-P:Pcoordinated phosphatriazadiene ligand. Dinitrogen elimination can be forced upon the cyclohexyl product through either thermal or photochemical activation. In the first case, the corresponding iminophosphinidene complex $[Fe_2Cp_2\{\mu-P(NCH_2Ph)\}]$ $Cy{(\mu-CO)(CO)_2}$ is obtained, an air-sensitive product that could be transformed through protonation into a more stable aminophosphide derivative. In contrast, photochemical activation triggers additional bond-cleavage and formation processes (including H atom transfer) to eventually yield the trinuclear derivative [Fe₃Cp₃(μ_3 -PCy){ μ - κ^1 : κ^1 -C(O)(NHCH₂Ph)}(μ -CO)₂], having phosphinidene and C:O-bound aminoacyl bridging ligands. The smaller size and poorer donor properties of the PPh ligand, compared to the PCy ligand, make complex 1b less nucleophilic than 1a (as shown in the reactions with borane adducts), but more susceptible to further reactions in their derivatives (as shown in the reactions with MeI or O₂), which seem to be in general less stable than their cyclohexyl counterparts.

Experimental section

General procedures and starting materials

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.⁴⁵ Petroleum ether refers to that fraction distilling in the range 338–343 K. Compounds [Fe₂Cp₂(μ -PR)-(μ -CO)(CO)₂] (Cp = η^5 -C₅H₅; R = Cy(1a), Ph(1b)] were prepared as described previously.^{6a,c} All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K) unless otherwise stated. A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all the experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were performed using diatomaceous earth unless otherwise stated. IR C-O stretching frequencies were measured in solution or Nujol mulls, are referred to as v_{CO} (solvent) or v_{CO} (Nujol), respectively, and are given in wavenumber units (cm⁻¹). Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 400.13 (¹H), 162.00 $({}^{31}P{}^{1}H{})$, 128.38 $({}^{11}B{})$ or 100.62 MHz $({}^{13}C{}^{1}H{})$ at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (¹H, ¹³C), external 85% aqueous H₃PO₄ solution (³¹P) or external BF₃·OEt₂ (¹¹B). Coupling constants (*J*) are given in hertz (Hz).

Preparation of [Fe₂Cp₂(μ-PMeCy)(μ-CO)(CO)₂]I (2a). Methyl iodide (28 μL, 0.450 mmol) was added to a freshly prepared solution of complex **1a** (*ca.* 0.025 g, 0.057 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 10 min to give a red solution which was filtered. The solvent was then removed from the filtrate under vacuum, and the residue was washed with petroleum ether (2 × 5 mL) and dried under vacuum to give compound **2a** as a red microcrystalline solid (0.030 g, 91%). Anal. calcd for C₂₀H₂₄Fe₂IO₃P: C, 41.28; H, 4.16. Found: C, 41.12; H, 4.05. δ_H(200.13 MHz) 5.37 (s, 10H, Cp), 2.93 (d, J_{HP} = 12, 3H, Me), 2.06–0.88 (m, 11H, Cy).

Preparation of [Fe₂Cp₂I(µ-PMePh)(CO)₃] (3). Methyl iodide (8 µL, 0.129 mmol) was added to a freshly prepared solution of complex 1b (ca. 0.050 g, 0.115 mmol) in dichloromethane (5 mL) cooled at 273 K, and the mixture was stirred for 10 min at this temperature to give a red solution shown (by IR) to contain essentially pure complex $[Fe_2Cp_2(\mu-PMePh)(\mu-CO) (CO)_2$]I (2b). The solution was then filtered and the solvent was removed from the filtrate under vacuum. The residue was then washed with petroleum ether $(3 \times 5 \text{ mL})$ and dried under vacuum to give a brown solid shown (by IR in Nujol mull) to be a mixture of the isomers 2b and 3 (0.058 g, 88%). When this solid was dissolved in CH₂Cl₂ and stirred at room temperature for ca. 1 h, then a brown solution was obtained, shown by IR and NMR to be an equilibrium mixture of compounds 2b (very minor) and 3 (major), with the latter in turn appearing as two isomers A and B. The equilibrium ratio 2b : A : B was measured (by ${}^{31}P{}^{1}H{}$ NMR) to be *ca*. 1:55:60 in CDCl₃ solution at room temperature. Anal. calcd for C₂₀H₁₈Fe₂IO₃P: C, 41.71; H, 3.15. Found: C, 41.57; H, 3.10. Spectroscopic data for the mixture of **2b** and **3**: v_{CO} (Nujol): 2016 (s), 1966 (vs), 1917 (s), 1817 (w). Spectroscopic data for isomer A: $\delta_{\rm H}(300.13$ MHz, CDCl₃) 7.90–7.25 (m, 5H, Ph), 5.09 (d, $J_{\rm HP}$ = 1, 5H, Cp), 4.29 (s, 5H, Cp), 2.10 (d, J_{HP} = 7, 3H, Me). Spectroscopic data for

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isomer **B**: $\delta_{\rm H}(300.13 \text{ MHz, CDCl}_3)$ 7.90–7.25 (m, 5H, Ph), 5.00 (d, $J_{\rm HP} = 1$, 5H, Cp), 4.27 (s, 5H, Cp), 2.48 (d, $J_{\rm HP} = 7$, 3H, Me). The resonances due to isomer **2b** could not be identified in the ¹H NMR spectrum due to its low proportion and/or super-imposition with the resonances of the major isomers.

Preparation of [Fe₂Cp₂(μ-PMePh)(μ-CO)(CO)₂]CF₃SO₃ (2b'). Methyl triflate (8 μL, 0.071 mmol) was added to a freshly prepared solution of complex **1b** (*ca.* 0.025 g, 0.058 mmol) in dichloromethane (5 mL) cooled at 273 K, and the mixture was stirred for 10 min at this temperature to give a red solution which was filtered. The solvent was then removed from the filtrate under vacuum, and the residue was washed with petroleum ether (2 × 5 mL) to give compound **2b**' as a red microcrystalline solid (0.030 g, 88%). Anal. calcd for C₂₁H₁₈F₃Fe₂O₆PS: C, 40.99; H, 3.10. Found: C, 41.10; H, 3.22. δ_H(300.13 MHz) 7.78–7.50 (m, 5H, Ph), 5.43 (s, 10H, Cp), 2.96 (d, $J_{HP} = 12$, 3H, Me).

Preparation of [Fe₂Cp₂{μ-P(O)Cy}(μ-CO)(CO)₂] (4a). Air was admitted into a Schlenk tube containing a freshly prepared solution of complex **1a** (*ca.* 0.025 g, 0.057 mmol) in dichloromethane (5 mL), and the mixture was stirred at r.t. for 10 min to give a dark red solution. After removal of the solvent under vacuum, the residue was dissolved in a minimum amount of dichloromethane/petroleum ether (1/1) and chromatographed on alumina (activity IV) at 288 K. Elution with acetone gave a red fraction yielding, after removal of solvents, compound **4a** as a red microcrystalline solid (0.021 g, 81%). Anal. calcd for C₁₉H₂₁Fe₂O₄P: C, 50.04; H, 4.64. Found: C, 49.72; H, 4.30. *v*_{CO} (toluene): 1983 (vs), 1949 (w), 1791 (m). *δ*_H(200.13 MHz, CDCl₃) 4.87 (s, 10H, Cp), 2.30–1.25 (m, 11H, Cy).

Preparation of [Fe₂Cp₂{μ-P(O)Ph}(μ-CO)(CO)₂] (4b). Solid *m*-chloroperbenzoic acid (0.010 g, 0.058 mmol) was added to a freshly prepared solution of complex **1b** (*ca.* 0.025 g, 0.058 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min to give a red solution which was filtered. The solvent was then removed from the filtrate under vacuum, and the residue was washed with petroleum ether (3 × 5 mL) to give compound **4b** as a red micro-crystalline solid (0.020 g, 77%). Anal. calcd for C₁₉H₁₅Fe₂O₄P: C, 50.71; H, 3.36. Found: C, 50.59; H, 3.27. $\delta_{\rm H}$ (300.13 MHz, CDCl₃) 8.11–7.26 (m, 5H, Ph), 5.07 (s, 10H, Cp).

Preparation of [Fe₂Cp₂{μ-P(S)Cy}(μ-CO)(CO)₂] (5a). Solid sulphur (0.007 g, 0.218 mmol) was added to a freshly prepared solution of complex **1a** (*ca.* 0.025 g, 0.057 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min to give a red-brown solution. After removal of the solvent, the residue was dissolved in a minimum amount of dichloromethane/petroleum ether (1/1) and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a red fraction yielding, after removal of solvents, compound **5a** as a red-brown microcrystalline solid (0.025 g, 92%). Anal. calcd for C₁₉H₂₁Fe₂O₃PS: C, 48.34; H, 4.48. Found: C, 48.16; H, 4.13. δ_H(300.13 MHz, CDCl₃) 4.81 (s, 10H, Cp), 2.44–1.25 (m, 11H, Cy). δ_C(75.48 MHz, CDCl₃) 267.5 (s, μ-CO), 210.3 (d, *J*_{CP} = 14, FeCO), 91.8 (s, Cp), 62.7 [d, *J*_{CP} = 20, C¹(Cy)], 31.3 [d, *J*_{CP} = 4, C²(Cy)], 26.6 [d, *J*_{CP} = 13, C³(Cy)], 25.7 [s, C⁴(Cy)].

Preparation of [Fe₂Cp₂{μ-P(S)Ph}(μ-CO)(CO)₂] (5b). The procedure is completely analogous to that described for **5a**, but using complex **1b** instead (*ca.* 0.025 g, 0.058 mmol). In this way compound **5b** was obtained as a red-brown microcrystalline solid (0.022 g, 82%). Anal. calcd for C₁₉H₁₅Fe₂O₃PS: C, 48.97; H, 3.24. Found: C, 48.73; H, 3.11. $\delta_{\rm H}$ (200.13 MHz, CDCl₃) 7.75 (m, 2H, Ph), 7.35–7.30 (m, 3H, Ph), 4.97 (s, 10H, Cp).

Preparation of [Fe₂Cp₂{µ-P(OH)Cy}(µ-CO)(CO)₂]BF₄ (6). A slight excess of HBF₄·OEt₂ (18 µL of a 54% solution in Et₂O, 0.131 mmol) was added to a dichloromethane solution (5 mL) of compound 5a (0.050 g, 0.110 mmol), and the mixture was stirred at room temperature for 5 min to give a red solution. The solvent was then removed under vacuum, and the residue was washed with Et₂O (3 \times 5 mL) and then petroleum ether $(2 \times 5 \text{ mL})$ to give compound **6** as a red microcrystalline solid (0.057 g, 96%). This complex exists in solution as an equilibrium mixture of the corresponding cis, anti and cis, syn isomers, with their relative proportions being solvent-dependent $(5/2 \text{ in } CD_2Cl_2 \text{ and } 7/1 \text{ in acetone-d}_6)$. Anal. calcd for C₁₉H₂₂BF₄Fe₂O₄P: C, 41.96; H, 4.08. Found: C, 42.10; H, 4.20. Spectroscopic data for 6: v_{OH} (Nujol): 3224 (w, br); v_{CO} (Nujol): 2012 (vs), 1978 (s), 1835 (s). Spectroscopic data for cis, anti-6: δ_P (acetone-d₆) 367.0. δ_H 8.74 (s, br, 1H, OH), 5.22 (s, 10H, Cp), 2.46–1.20 (m, 11H, Cy). δ_H(acetone-d₆) 10.29 (s, br, 1H, OH), 5.48 (s, 10H, Cp), 2.47 (m, 2H, Cy), 2.30 (m, 2H, Cy), 1.95 (m, 2H, Cy), 1.74 (m, 1H, Cy), 1.57 (m, 1H, Cy), 1.49–1.22 (m, 3H, Cy). δ_C(acetone-d₆) 257.2 (s, μ-CO), 210.6 (d, $J_{CP} = 18$, FeCO), 90.6 (s, Cp), 58.2 [d, $J_{CP} = 33$, C¹(Cy)], 30.2 [d, $J_{CP} = 7$, $C^{2}(Cy)$], 27.4 [d, $J_{CP} = 14$, $C^{3}(Cy)$], 26.3 [s, $C^{4}(Cy)$]. Spectroscopic data for cis, syn-6: $\delta_{P}(acetone-d_{6})$ 348.7. $\delta_{\rm H}$ 5.15 (s, 10H, Cp), 2.46–1.20 (m, 11H, Cy). $\delta_{\rm H}$ (acetone-d₆) 8.99 (s, br, 1H, OH), 5.37 (s, 10H, Cp), 2.54–1.22 (m, 11H, Cy). $\delta_{\rm C}$ (acetone-d₆) 90.3 (s, Cp), 61.6 [d, $J_{\rm CP}$ = 25, C¹(Cy)]; other resonances of this minor isomer could not be identified in the corresponding spectra due to its low proportion and/or superimposition with the resonances of the major isomer.

Preparation of [Fe₂Cp₂{µ-P(OMe)Cy}(µ-CO)(CO)₂]CF₃SO₃ (7). Neat methyl triflate (40 µL, 0.354 mmol) was added to a dichloromethane solution (5 mL) of compound 5a (0.040 g, 0.088 mmol), and the mixture was stirred at room temperature for 2 h to give a red solution which was filtered. Solvent was then removed from the filtrate under vacuum and the residue was washed with Et₂O (3 \times 5 mL) and then petroleum ether $(2 \times 5 \text{ mL})$ to give compound 7 as a red microcrystalline solid (0.052 g, 95%). This complex exists in solution as an equilibrium mixture of the corresponding cis, anti, cis, syn and trans isomers, with their relative proportions being solvent-dependent (ca. 20:1:1 in CD₂Cl₂ and 40:2:1 in acetone-d₆). Anal. calcd for C₂₁H₂₄F₃Fe₂O₇PS: C, 40.67; H, 3.90. Found: C, 40.45; H, 3.75. Spectroscopic data for cis, anti-7: $\delta_{\rm H}$ 5.34 (s, 10H, Cp), 4.20 (d, $J_{\rm HP} = 11$, 3H, OMe), 2.38 [m, 2H, HC²(Cy)], 2.17 [m, 2H, HC²(Cy)], 1.98 [m, 2H, HC³(Cy)], 1.76 [m, 1H, HC⁴(Cy)], 1.53 [m, 1H, HC¹(Cy)], 1.38 [m, 1H, HC⁴(Cy)], 1.27 [m, 2H, HC³(Cy)]. $\delta_{\rm H}$ (acetone-d₆) 5.64 (s, 10H, Cp), 4.36 (d, $J_{\rm HP}$ = 11, 3H, OMe), 2.49 [m, 2H, HC²(Cy)], 2.25 [m, 2H, HC²(Cy)], 1.94 [m, 2H, HC³(Cy)], 1.74 [m, 1H, HC⁴(Cy)], 1.57 [m, 1H, HC¹(Cy)], 1.43 [m, 1H, HC⁴(Cy)], 1.28 [m, 2H, HC³(Cy)].

 $\delta_{\rm C}$ 254.2 (s, µ-CO), 208.1 (d, $J_{\rm CP}$ = 17, FeCO), 89.2 (s, Cp), 60.9 (d, $J_{CP} = 12$, OMe), 60.0 [d, $J_{CP} = 28$, C¹(Cy)], 31.5 [d, $J_{\rm CP} = 6, \, {\rm C}^2({\rm Cy})], \, 27.3 \, [{\rm d}, \, J_{\rm CP} = 13, \, {\rm C}^3({\rm Cy})], \, 25.9 \, [{\rm s}, \, {\rm C}^4({\rm Cy})].$ The assignment of the ¹H NMR resonances of the Cy ring was made on the basis of a standard ${}^{1}J({}^{13}C-{}^{1}H)$ correlation experiment (HSQC). Spectroscopic data for cis, syn-7: $\delta_{\rm H}$ 5.30 (s, 10H, Cp), 3.87 (d, $J_{\rm HP}$ = 11, 3H, OMe), 2.42–1.20 (m, 11H, Cy). $\delta_{\rm H}$ (acetone-d₆) 5.58 (s, 10H, Cp), 4.01 (d, $J_{\rm HP}$ = 11, 3H, OMe), 2.50–1.27 (m, 11H, Cy). $\delta_{\rm C}$ 89.1 (s, Cp). Spectroscopic data for *trans*-7: $\delta_{\rm H}$ 5.24 (d, $J_{\rm HP}$ = 1, 5H, Cp), 5.13 (s, 5H, Cp), 4.06 (d, $J_{\rm HP} = 12, 3$ H, OMe), 2.50–1.27 (m, 11H, Cy). $\delta_{\rm H}$ (acetone-d₆) 5.50, 5.40 (2s, 2 × 5H, Cp), 4.13 (d, $J_{\rm HP}$ = 12, 3H, OMe), 2.50–1.27 (m, 11H, Cy). $\delta_{\rm H}$ 90.8, 89.5 (2s, Cp). Other resonances of the minor isomers could not be identified in the corresponding spectra due to their low proportion and/or superimposition with the resonances of the major isomer.

Preparation of $[Fe_2Cp_2{\mu-P(BH_3)Cy}(\mu-CO)(CO)_2]$ (8a). *Method A*: a solution of BH₃·THF (102 µL of a 1 M solution in THF, 0.102 mmol) was added to a freshly prepared solution of complex **1a** (*ca.* 0.030 g, 0.068 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 30 min to give a red solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum amount of dichloromethane/petroleum ether (1/1) and chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a red fraction yielding, after removal of solvents, compound **8a** as a red microcrystalline solid (0.028 g, 94%).

Method B: solid $BH_3 \cdot NH_2'Bu$ (0.012 g, 0.138 mmol) was added to a freshly prepared solution of complex **1a** (*ca.* 0.030 g, 0.068 mmol) in toluene (5 mL), and the mixture was stirred at 348 K for 1 h to give a red solution. After workup as described above, compound **8a** was obtained as a red microcrystalline solid (0.027 g, 91%).

Method C: the procedure is completely analogous to that described in *method B*, but using BH₃·PPh₃ instead (0.038 g, 0138 mmol). In this way compound **8a** was obtained as a red microcrystalline solid (0.027 g, 91%). Anal. calcd for C₁₉H₂₄BFe₂O₃P: C, 50.28; H, 5.33. Found: C, 50.05; H, 5.14. $\delta_{\rm B}$ –25.7 (qd, $J_{\rm BH}$ = 96, $J_{\rm BP}$ = 41). $\delta_{\rm H}$ 4.93 (d, $J_{\rm HP}$ = 1, 10H, Cp), 2.29 (qt, $J_{\rm HH}$ = $J_{\rm HP}$ = 13, $J_{\rm HH}$ = 4, 2H, Cy), 1.79 (m, $J_{\rm HB}$ = 96, 3H, BH₃), 1.91–1.68 (m, 6H, Cy), 1.39 (qt, $J_{\rm HH}$ = $J_{\rm HP}$ = 13, $J_{\rm HH}$ = 4, 1H, Cy), 1.18 (m, 2H, Cy). ¹H{¹¹B} NMR: δ 1.79 (d, $J_{\rm HP}$ = 10, 3H, BH₃).

Preparation of [Fe₂Cp₂{μ-P(BH₃)Ph}(μ-CO)(CO)₂] (8b). The procedure is completely analogous to that described for compound **8a** (method A) but using compound **1b** (0.050 g, 0.115 mmol) and BH₃·THF (290 μL of a 1 M solution in THF, 0.290 mmol). A similar workup yielded compound **8b** as a red microcrystalline solid (0.049 g, 95%). Anal. calcd for C₁₉H₁₈BFe₂O₃P: C, 50.96; H, 4.05. Found: C, 50.78; H, 4.19. $\delta_{\rm B}$ –18.0 (qd, $J_{\rm BH}$ = 97, $J_{\rm BP}$ = 33). $\delta_{\rm H}$ 7.62 (m, 2H, Ph), 7.33–7.24 (m, 3H, Ph), 5.08 (d, $J_{\rm HP}$ = 1, 10H, Cp), 1.97 (m, $J_{\rm HB}$ = 97, 3H, BH₃). ¹H{¹¹B} NMR: δ 1.97 (d, $J_{\rm HP}$ = 9, 3H, BH₃).

Preparation of $[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)Cy\}(\mu-CO)(CO)]$ (9a). A toluene solution (4 mL) of complex 8a (0.040 g, 0.088 mmol) was irradiated with visible-UV light at 288 K in a quartz Schlenk tube for 30 min, while keeping a gentle N₂ purge, to give a green solution which was filtered using a canula. The solvent was then removed from the filtrate under vacuum, and the residue was washed with petroleum ether $(2 \times 4 \text{ mL})$ to give compound 9a as a green microcrystalline solid (0.034 g, 90%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. calcd for C₁₈H₂₄BFe₂O₂P: C, 50.77; H, 5.68. Found: C, 50.55; H, 5.49. $\delta_{\rm B}$ –36.8 (s, br). $\delta_{\rm H}$ 4.67, 4.59 (2s, 2 × 5H, Cp), 3.65 [m, 1H, HC¹(Cy)], 2.70 [m, 1H, HC²(Cy)], 2.33 [m, 1H, HC²(Cy)], 2.21–1.61 (m, 7H, Cy), 1.56 [m, 1H, C⁴(Cy)], 0.40, $-2.02 (2m, J_{HB} = 141, 2 \times 1H, BH_2), -22.69 (s, br, 1H, B-H-$ Fe). ¹H{¹¹B} NMR: δ 0.40 (dd, $J_{\text{HH}} = 8$, $J_{\text{HP}} = 7$, 1H, BH₂), -2.02 (d, $J_{\rm HH} = 21$, 1H, BH₂), -22.69 (ddd, $J_{\rm HH} = 21$, 8, $J_{\rm HP} =$ 3, 1H, B–H–Fe). $\delta_{\rm C}$ 262.2 (s, µ-CO), 214.0 (d, $J_{\rm CP}$ = 30, FeCO), 83.2, 83.0 (2s, Cp), 43.4 [d, $J_{CP} = 3$, C¹(Cy)], 36.0 [s, C²(Cy)], 33.7 [d, $J_{CP} = 3$, $C^{2}(Cy)$], 28.3 [d, $J_{CP} = 14$, $C^{3}(Cy)$], 27.7 [d, $J_{CP} = 10$, C³(Cy)], 26.6 [s, C⁴(Cy)]. The assignment of the ¹H NMR resonances of the Cy ring was made on the basis of a standard ${}^{1}J({}^{13}C-{}^{1}H)$ correlation experiment (HSQC).

Preparation of $[Fe_2Cp_2\{\mu-\kappa^1:\kappa^1,\eta^2-P(BH_3)Ph\}(\mu-CO)(CO)]$ (9b). The procedure is completely analogous to that described for compound 9a but using compound 8b as starting material (0.030 g, 0.067 mmol) in a Pyrex Schlenk tube, with an irradiation time of 25 min. After a similar workup, compound 9b was obtained as a green microcrystalline solid (0.027 g, 93%). Anal. calcd for C₁₈H₁₈BFe₂O₂P: C, 51.50; H, 4.32. Found: C, 51.17; H, 4.21. $\delta_{\rm B}$ –33.4 (s, br). $\delta_{\rm H}$ 8.28 (dd, $J_{\rm HH}$ = 12, $J_{\rm HP} = 2$, 1H, Ph), 8.24 (dd, $J_{\rm HH} = 12$, $J_{\rm HP} = 3$, 1H, Ph), 7.62-7.56 (m, 3H, Ph), 4.80, 4.42 (2s, 2 × 5H, Cp), 0.87, -1.61 $(2m, J_{HB} = 149, 2 \times 1H, BH_2), -22.48$ (s, br, 1H, B-H-Fe). ¹H {¹¹B} NMR: δ 0.87 (ddd, $J_{\text{HH}} = 8$, 5, $J_{\text{HP}} = 13$, 1H, BH₂), -1.61 (dd, $J_{\rm HH} = 21$, 5, 1H, BH₂), -22.48 (ddd, $J_{\rm HH} = 21$, 8, $J_{\rm HP} = 2$, 1H, B–H–Fe). $\delta_{\rm C}$ 257.6 (s, μ -CO), 213.6 (d, $J_{\rm CP} = 31$, FeCO), 143.1 [d, $J_{CP} = 2$, C¹(Ph)], 133.5 [d, $J_{CP} = 10$, C²(Ph)], 129.3 [s, $C^{3}(Ph)$], 129.1 [d, $J_{CP} = 10$, $C^{2}(Ph)$], 128.5 [s, $C^{3}(Ph)$], 127.7 [s, C⁴(Ph)], 84.5, 83.2 (2s, Cp).

Preparation of [Fe₂Cp₂{µ-P(N₃CH₂Ph)Cy}(µ-CO)(CO)₂] (10a). Neat benzyl azide (12 µL, 0.096 mmol) was added to a freshly prepared solution of complex 1a (ca. 0.040 g, 0.091 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min to give a dark green solution. The solvent was then removed from the mixture under vacuum and the residue was washed with petroleum ether $(2 \times 3 \text{ mL})$ to give compound 10a as a green microcrystalline solid (0.051 g, 98%). Anal. calcd for C₂₆H₂₈Fe₂N₃O₃P: C, 54.48; H, 4.92; N, 7.33. Found: C, 54.26; H, 4.77; N, 7.03. δ_H 7.35–7.25 (m, 4H, Ph), 7.17 (m, 1H, Ph), 4.99 (s, 10H, Cp), 4.82 (s, 2H, CH₂), 2.44, 2.28, 1.87 (3m, 3×2 H, Cy), 1.68 (m, 1H, Cy), 1.50–0.86 (m, 4H, Cy). $\delta_{\rm C}$ 267.3 (s, µ-CO), 211.2 (d, $J_{\rm CP}$ = 11, FeCO), 139.7 $[s, C^{1}(Ph)], 129.2 [s, C^{3}(Ph)], 128.7 [s, C^{2}(Ph)], 127.1$ [s, C⁴(Ph)], 88.1 (s, Cp), 67.0 (s, CH₂), 55.7 [d, $J_{CP} = 52$, $C^{1}(Cy)$], 31.9 [d, $J_{CP} = 6$, $C^{2}(Cy)$], 27.7 [d, $J_{CP} = 12$, $C^{3}(Cy)$], 26.3 [s, $C^4(Cy)$].

Preparation of $[Fe_2Cp_2{\mu-P(N_3CH_2Ph)Ph}(\mu-CO)(CO)_2]$ (10b). Neat benzyl azide (8 μ L, 0.064 mmol) was added to a freshly prepared solution of complex **1b** (*ca.* 0.025 g 0.058 mmol) in dichloromethane (4 mL) at 203 K, and the mixture was stirred at this temperature for 5 min to give a green solution. The solvent was then removed from the mixture under vacuum, keeping the temperature below 253 K, to give compound **10b** as a green microcrystalline solid. This species is thermally unstable and any manipulation in solution or in the solid state at temperatures above 263 K caused its progressive decomposition. $\delta_{\rm H}$ (203 K) 7.92–7.28 (m, 10H, Ph), 5.20 (s, 10H, Cp), 4.90 (s, 2H, CH₂).

Preparation of [Fe₂Cp₂{μ-P(NCH₂Ph)Cy}(μ-CO)(CO)₂] (11). A toluene solution (4 mL) of complex **10a** (0.030 g, 0.052 mmol) was stirred at 368 K for 10 min to give a dark green solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether (2 × 3 mL) and dried under vacuum conditions to give compound **11** as a dark green, very air-sensitive microcrystalline solid (0.026 g, 90%). Unfortunately, no satisfactory elemental analysis could be obtained for this product due to its rapid decomposition upon manipulation in the air. $\delta_{\rm H}$ 7.73 (m, 2H, Ph), 7.41–7.20 (m, 3H, Ph), 4.92 (d, $J_{\rm HP}$ = 25, 2H, CH₂), 4.42 (s, 10H, Cp), 2.85–1.29 (m, 11H, Cy).

Preparation of [Fe₂Cp₂{µ-P(NHCH₂Ph)Cy}(µ-CO)(CO)₂]PF₆ (12). Solid NH_4PF_6 (0.010 g, 0.061 mmol) was added to a freshly prepared solution of complex 11 (ca. 0.026 g, 0.048 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min to give a red solution which was filtered using a canula. After removal of the solvent from the filtrate under vacuum, the residue was washed with Et₂O (3 \times 4 mL) and then with petroleum ether (2 \times 4 mL) to give compound 12 as a red microcrystalline solid (0.031 g, 95%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of layers of toluene and petroleum ether into a dichloromethane solution of the complex at room temperature. Anal. calcd for C₂₆H₂₉F₆Fe₂NO₃P₂: C, 45.18; H, 4.23; N, 2.03. Found: C, 45.05; H, 3.98; N, 1.96. δ_H 7.35–7.25 (m, 4H, Ph), 7.39 (m, 1H, Ph), 5.20 (s, 10H, Cp), 4.50 (m, A_2BX , $J_{HH} = J_{HP} = 8$, 2H, CH₂), 4.40 (m, A_2BX , $J_{HH} = 8$, J_{HP} = 5, 1H, NH), 2.34, 2.10 [2m, $2 \times 2H$, HC²(Cy)], 1.95 [m, 2H, $HC^{3}(Cy)$], 1.75 [m, 1H, $HC^{4}(Cy)$], 1.54 [m, 1H, $HC^{1}(Cy)$], 1.41–1.21 (m, 3H, Cy). $\delta_{\rm C}$ 256.3 (s, µ-CO), 208.7 (d, $J_{\rm CP}$ = 16, FeCO), 138.7 [s, C¹(Ph)], 129.7 [s, C³(Ph)], 128.6 [s, C⁴(Ph)], 127.1 [s, $C^{2}(Ph)$], 89.1 (s, Cp), 56.4 [d, $J_{CP} = 34$, $C^{1}(Cy)$], 49.9 (d, $J_{CP} = 4$, CH₂), 32.2 [d, $J_{CP} = 6$, C²(Cy)], 27.5 [d, $J_{CP} = 13$, $C^{3}(Cy)$], 25.8 [s, $C^{4}(Cy)$]. The assignment of the ¹H NMR resonances of the Cy ring was made on the basis of a standard ${}^{1}J({}^{13}C-{}^{1}H)$ correlation experiment (HSQC).

Preparation of [Fe₃Cp₃(μ_3 -PCy){ μ - κ^1 : κ^1 -C(O)(NHCH₂Ph)} (μ -CO)₂] (13). A toluene solution (6 mL) of complex 10a (0.100 g, 0.174 mmol) was irradiated for 5 h with visible-UV light in a quartz Schlenk tube refrigerated with tap water while gently bubbling N₂ through the solution, to give a garnet-brown mixture. After removal of the solvent under vacuum, the residue was dissolved in a minimum amount of dichloromethane/ petroleum ether (1/2) and chromatographed on alumina (activity IV) at 263 K. Elution with the same solvent mixture gave a red fraction containing [Fe₂Cp₂(CO)₄]. Elution with dichloromethane/petroleum ether (2/1) gave a garnet-brown fraction yielding, after removal of solvents, compound 13 as a garnetbrown microcrystalline solid (0.047 g, 40%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at room temperature. Anal. calcd for C₃₁H₃₄Fe₃NO₃P: C, 55.81; H, 5.14; N, 2.10. Found: C, 55.68; H, 3.98; N, 1.99. $\delta_{\rm H}$ 7.25 (false t, $J_{\rm HH}$ = 7, 2H, m-Ph), 7.18 (t, $J_{\rm HH}$ = 7, 1H, p-Ph), 6.90 (d, $J_{\rm HH}$ = 7, 2H, o-Ph), 5.64 (dd, ABX, $J_{\rm HH} = 6, 5, 1$ H, NH), 4.87 [qt, $J_{\rm HH} = 12, 4, J_{\rm HP} = 12, 1$ H, $HC^{1}(Cy)$], 4.50, 4.31, 4.26 (3s, 3 × 5H, Cp), 3.61 (dd, ABX, $J_{\rm HH} = 15, 6, 1 \, \text{H}, \, \text{CH}_2$, 3.35 (dd, ABX, $J_{\rm HH} = 15, 5, 1 \, \text{H}, \, \text{CH}_2$), 3.40–3.31 [m, 2H, HC²(Cy)], 3.01, 2.75 [2 × tq, $J_{\rm HH}$ = 12, 4, $J_{\rm HP} = 4, 2 \times 1$ H, HC²(Cy)], 2.40–2.28 [m, 2H, HC³(Cy)], 2.16 [m, 1H, HC⁴(Cy)], 2.09–1.96 [m, 2H, HC³(Cy)], 1.85 [qt, $J_{\rm HH}$ = 13, 4, 1H, HC⁴(Cy)]. $\delta_{\rm C}$ 281.7, 279.2 (2s, μ -CO), 233.4 (d, $J_{\rm CP}$ = 17, NCO), 140.5 [s, $C^{1}(Ph)$], 128.5 [s, $C^{3}(Ph)$], 127.6 [s, C²(Ph)], 126.9 [s, C⁴(Ph)], 86.4, 84.3, 80.6 (3s, Cp), 56.3 [d, J_{CP} = 14, $C^{1}(Cy)$], 44.7 (s, CH_{2}), 36.0, 35.6 [2s, $C^{2}(Cy)$], 28.7 [d, $J_{\rm CP} = 11, \, {\rm C}^3({\rm Cy})], \, 28.6 \, [{\rm d}, \, J_{\rm CP} = 9, \, {\rm C}^3({\rm Cy})], \, 27.2 \, [{\rm s}, \, {\rm C}^4({\rm Cy})].$ The assignment of the ¹H NMR resonances of the Cy ring was made on the basis of a standard ${}^{1}J({}^{13}C-{}^{1}H)$ correlation experiment (HSQC).

Preparation of $[Fe_2Cp_2(\mu-CO)_2(CO){P(O_2C_6H_2^{t}Bu_2)Cy}]$ (14a). Solid 3,5-di-*tert*-butyl-o-benzoquinone (0.016 g, 0.072 mmol) was added to a freshly prepared solution of complex 1a (ca. 0.030 g, 0.068 mmol) in dichloromethane (5 mL), and the mixture was stirred at room temperature for 5 min to give a green-garnet solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum amount of dichloromethane/petroleum ether (1/6) and chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/4) gave a green-garnet fraction yielding, after removal of solvents, compound 14a as a green-garnet microcrystalline solid (0.042 g, 93%). This complex exists in solution as an equilibrium mixture of the corresponding trans and cis isomers, with the ratio trans/cis being *ca.* 14/1 in CD₂Cl₂ at room temperature (from the ${}^{31}P{}^{1}H{}$ NMR spectrum). Anal. calcd for C₃₃H₄₁Fe₂O₅P: C, 60.02; H, 6.26. Found: C, 59.83; H, 5.98. Spectroscopic data for 14a: $v_{\rm CO}$ (petroleum ether): 1953 (m), 1797 (w), 1761 (vs). Spectroscopic *data for trans*-14a: $\delta_{\rm H}$ 6.85, 6.80 (2d, $J_{\rm HH}$ = 2, 2 × 1H, C₆H₂), 4.75, 4.66 (2s, 2 × 5H, Cp), 1.97, 1.86 (2m, 2 × 1H, Cy), 1.72-1.68 (m, 3H, Cy), 1.60 (m, 1H, Cy), 1.36, 1.28 (2s, 2×9 H, ^tBu), 1.21–1.04 (m, 5H, Cy). $\delta_{\rm C}$ 278.1, 277.8 (2d, $J_{\rm CP}$ = 15, μ -CO), 214.1 (s, FeCO), 147.8 [d, $J_{CP} = 5$, $C^{1,2}(C_6H_2)$], 145.5 [s, $C^{5}(C_{6}H_{2})$], 143.5 [d, $J_{CP} = 5$, $C^{2,1}(C_{6}H_{2})$], 134.1 $[d, J_{CP} = 4, C^{3}(C_{6}H_{2})], 116.6 [s, C^{4}(C_{6}H_{2})], 107.4 [d, J_{CP} = 5,$ $C^{6}(C_{6}H_{2})]$, 87.9, 87.0 (2s, Cp), 52.1 [d, $J_{CP} = 13$, $C^{1}(Cy)]$, 35.1, 34.6 [2s, $C^{1}(Bu)]$, 31.7, 29.5 [2s, $C^{2}(Bu)]$, 26.6 [m, $C^{3}(Cy)]$, 26.3 [s, $C^2(Cy)$], 27.2 [s, $C^4(Cy)$]. The resonances due to the isomer cis-14a could not be identified in the corresponding ¹H and ¹³C{¹H} NMR spectra due to its low proportion and/or superimposition with the resonances of the major isomer.

Preparation of $[Fe_2Cp_2(\mu-CO)_2(CO){P(O_2C_6H_2'Bu_2)Ph}]$ (14b). The procedure is completely analogous to that described for 14a but using compound 1b (0.035 g, 0.081 mmol) as starting material and 0.018 g (0.082 mmol) of 3,5-di-*tert*-butyl-*o*-

Table 6 Crystal data for new compounds

Compound	9a	12	13 ·1.5C ₇ H ₈
Mol formula	C ₁₈ H ₂₄ BFe ₂ O ₂ P	C ₂₆ H ₂₉ Fe ₂ NO ₃ PF ₆ P	C ₈₃ H ₉₂ Fe ₆ N ₂ O ₆ P ₂
Mol wt	425.85	691.14	1610.63
Cryst syst	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	$P2_1$	C2/c
Radiation (λ, A)	0.71073	0.71073	0.71073
a (Å)	15.2331(11)	9.8882(2)	25.7535(5)
$b(\mathbf{A})$	11.0731(10)	11.9548(3)	15.5862(4)
$c(\dot{A})$	21.585(2)	12.1755(3)	19.4501(3)
α (°)	90	90	90
β (°)	90	100.9890(10)	111.9560(10)
γ (°)	90	90	90
$V(Å^3)$	3640.9(5)	1412.89(6)	7241.0(3)
Z	8	2	4
Calcd density $(g \text{ cm}^{-3})$	1.554	1.625	1.477
Absorpt. coeff. (mm^{-1})	1.688	1.209	1.271
Temperature (K)	100(2)	100(2)	100(2)
θ range (°)	1.89 to 25.35	1.7 to 25.24	2.26 to 25.24
Index ranges (h, k, l)	0, 18; 0, 13; -25, 0	-11, 11; -14, 14; 0, 14	-30, 28; 0, 18; 0, 23
No. of reflns collected	17 547	13 282	27 142
No. of indep reflns (R_{int})	3258 (0.0571)	4857 (0.0297)	6290 (0.0378)
Refins with $I > 2\sigma(I)$	2497	4637	5223
R indexes [data with $I > 2\sigma(I)$] ^a	$R_1 = 0.0385$	$R_1 = 0.0291$	$R_1 = 0.0447$
	$wR_2 = 0.0967^b$	$wR_2 = 0.0805^c$	$wR_2 = 0.135^d$
R indexes (all data) ^{a}	$R_1 = 0.0632$	$R_1 = 0.0369$	$R_1 = 0.0569$
	$wR_2 = 0.1212^b$	$wR_2 = 0.1129^c$	$wR_2 = 0.1563^d$
GOF	1.176	1.242	1.108
No. Of restraints/params	0/226	1/366	0/454
$\Delta \rho$ (max, min) (e ^A Å ⁻³)	0.691, -0.583	0.713, -0.923	1.996, -0.907
^{<i>a</i>} $R = \Sigma F_o - F_c / \Sigma F_o $. w $R = [\Sigma w(F_o ^2 - 0.0720, b = 0.0000.$ ^{<i>d</i>} $a = 0.0899, b = 28.2$	$- F_{\rm c} ^2)^2 / \Sigma {\rm w} F_{\rm o} ^2]^{1/2}. {\rm w} = 1/[\sigma^2 (F_{\rm o}^2)$ 2765.	$(aP)^{2} + bP$] where $P = (F_{o}^{2} + 2F_{c}^{2})/3$.	^o a = 0.0635, b = 0.4074. ^c a =

benzoquinone. After a similar workup, compound 14b was obtained as a green-purple microcrystalline solid (0.048 g, 91%). This complex also exists in solution as an equilibrium mixture of the corresponding trans and cis isomers, with the ratio trans/cis being *ca*. 4/1 in toluene-d₈ at 233 K (from the ¹H NMR spectrum). Anal. calcd for C₃₃H₃₅Fe₂O₅P: C, 60.58; H, 5.39. Found: C, 60.27; H, 5.43. Spectroscopic data for 14b: v_{CO} (CH₂Cl₂): 1958 (m), 1783 (w), 1749 (vs). v_{CO} (toluene): 1963 (m), 1789 (w), 1763 (vs). $\delta_{\rm P}$ (toluene-d₈) 239.4 (s, br). $\delta_{\rm H}$ (toluene-d₈) 7.74–7.66 (m, 2H, C₆H₂), 7.12–6.78 (m, 5H, Ph), 4.38 (s, br, 10H, Cp), 1.50, 1.06 (2s, 2 × 9H, ^tBu). Spectroscopic data for trans-14b: $\delta_{\rm H}$ (toluene-d₈, 233 K) 7.72–7.66 (m, 2H, C_6H_2), 7.12–6.74 (m, 5H, Ph), 4.26, 4.24 (2s, 2 × 5H, Cp), 1.54, 1.01 (2s, 2×9 H, ^tBu). Spectroscopic data for cis-14b: $\delta_{\rm H}$ (toluene-d₈, 233 K) 4.45, 4.39 (2s, 2 × 5H, Cp), 1.46, 1.03 $(2s, 2 \times 9H, {}^{t}Bu)$; other resonances of this isomer could not be identified due to its superimposition with those of the major isomer.

X-ray structure determination for compounds 9a, 12 and 13. The X-ray intensity data were collected at 100 K on a Nonius KappaCCD single crystal diffractometer, using graphitemonochromated MoK_{α} radiation. Images were collected at a fixed crystal-detector distance (40 mm for 9a, 39 mm for 12, 30 mm for 13) using the oscillation method, with 1° (9a) or 2° oscillations, and 60 s (9a) or 20 s exposure time per image respectively. Data collection strategies were calculated with the program Collect.⁴⁶ Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.⁴⁷ A semi-empirical absorption correction was applied using the program SORTAV.48 Using the program suite WinGX,49 the structures were solved by Patterson interpretation and phase expansion using SHELXL97, and refined with full-matrix least squares on F^2 using SHELXL97.⁵⁰ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at calculated positions except for the BH₃ (9a) and NH (12, 13) H atoms, which were located in the Fourier maps and refined; all of them were given an overall isotropic thermal parameter. For compound 13 a molecule of toluene was found to be present in the asymmetric unit and a second one (half a molecule per molecule of the complex) placed on a -x + 1, y, -z + 1/2 binary axis. Both of them contained its methyl group disordered, but the modelling of this disorder leads to an appropriate convergence just for the second of them (symmetry-imposed disorder over two positions). Further crystallographic data and structure refinement details are collected in Table 6. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [deposition numbers CCDC 890680 (9a), 890681 (12) and 890682 (13)].

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