Synthesis and Structures of Phosphinidene and Phosphido Complexes of Iron and Cobalt*

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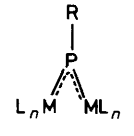
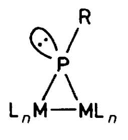
Treatment of $Na[Co_2(CO)_2(\eta\text{-}C_5H_5)_2]$ with R^1PCl_2 ($R^1 = 2,4,6\text{-}Bu^t_3C_6H_2$) results in a dicobalt phosphinidene complex, $[Co_2(CO)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PR^1)]$, of the 'open' type containing a trigonal-planar phosphorus, no metal–metal bond, and some degree of Co–P multiple bonding as established by an *X*-ray diffraction study. The attempted synthesis of di-iron phosphinidene complexes *via* the reaction of $[NEt_4]_2[Fe_2(CO)_8]$ with dichlorophosphines $RPCl_2$ failed to produce an isolable species containing the desired phosphinidene fragment. For R = $(Me_3Si)_2CH$ a large number of products were formed, two of which were isolated and identified within the same crystal structure by *X*-ray crystallography. Both complexes were found to contain a di-iron centre bridged by a phosphido ligand: $[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$ and $[Fe_2(CO)_7(\mu\text{-}H)\{\mu\text{-}P(OH)[CH(SiMe_3)_2]\}]$. In contrast, for R = R^1, a mixture of mono- and di-nuclear iron species were observed by ^{31}P n.m.r. spectroscopy, these being $[Fe_2(CO)_6(\mu\text{-}PHR^1)_2]$, $[Fe(CO)_4\{PH[CH_2C(Me)_2C_6H_2Bu^t_2]\}]$, $[Fe(CO)_4(PH_2R^1)]$, and also the diphosphine R^1PHPHR^1. In addition to the synthetic and structural studies, extended Hückel molecular orbital calculations have been carried out on model phosphinidene complexes in an attempt to understand their electronic and structural features.

Organotransition metal complexes containing diphosphene (RP=PR)[1] and phosphinidene (RP)[2] species as ligands are currently attracting significant attention. A large part of this interest concerns the diverse ways in which ligation can occur both in terms of the bonding mode and number of electrons donated to the metal(s). Thus for diphosphenes, electron donation can occur through the phosphorus lone pair(s) or P=P π-bond, or a combination of these modes,[1,3] while phosphinidene ligands can act as either μ-, μ_3, or μ_4-bridging groups.[2] Of particular interest with regard to the present work is the μ-bridging mode for phosphinidenes in dinuclear complexes. Four types of complex are possible depending on the geometry at phosphorus and the formal electron count at the metal centre. Thus complexes of types (**A**) and (**C**) contain a trigonal-planar phosphorus atom while in the (**B**) and (**D**) complexes the phosphorus is pyramidal. This in turn influences the formal M–M bond order which is zero and one for complexes of types (**A**) and (**B**) respectively which feature 16-electron metal fragments [*e.g.* $Cr(CO)_5$, $Mn(CO)_2(\eta\text{-}C_5H_5)$]. For the type (**C**) and (**D**) complexes, which involve 15-electron fragments [*e.g.* $Mo(CO)_2(\eta\text{-}C_5H_5)$, $Co(CO)_3$], the M–M bond orders are one and two respectively. The vast majority of phosphinidene complexes are of type (**A**) which have been extensively studied by Huttner.[2a,b] More recently Cowley and co-workers[4] have reported several complexes of type (**C**). At the present time complexes of types (**B**) and (**D**) are unknown although an analogue of type (**B**) has been reported containing antimony instead of phosphorus, namely $[Fe_2(CO)_8\{\mu\text{-}SbCH(SiMe_3)_2\}]$ (**I**).[5] The fact that almost all 'open' type (**A**) complexes contain either a Group 6A metal (Cr, Mo, or W) or a Group 7A metal (Mn) while the only 'closed' type (**B**) complex contains iron prompted a search for further examples of type (**B**) complexes containing Group 8A metals. The results of this study are reported herein.



(**A**)



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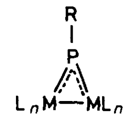
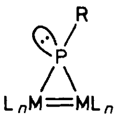


(**C**)



(**D**)

Results and Discussion

Synthetic and Spectroscopic Studies.—As mentioned in the Introduction, all known type (**A**) phosphinidene structures contain either a Group 6A or 7A transition metal fragment[2a,b] whereas the only known type (**B**) structure is found, albeit with antimony rather than phosphorus, for iron.[5] In order to examine whether a 'closed' type (**B**) structure was favoured when Group 8A metal fragments were present, the reaction between R^1PCl_2 ($R^1 = 2,4,6\text{-}Bu^t_3C_6H_2$) and $Na[Co_2(CO)_2(\eta\text{-}C_5H_5)_2]$ was examined.[6] Reaction in tetrahydrofuran (thf) at −78 °C produced a deep blue solution from which, after chromatographic work-up, two products were isolated. The first orange compound was shown by ^{31}P n.m.r. spectroscopy to be

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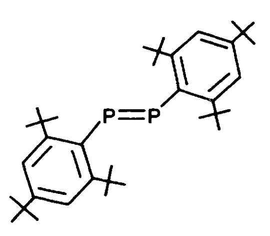
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.



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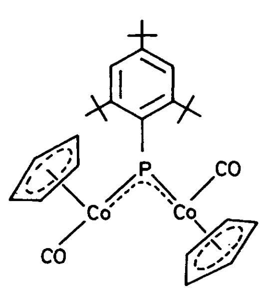

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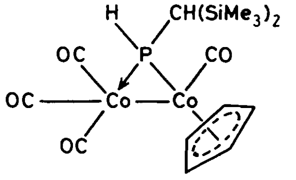

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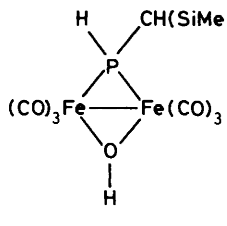

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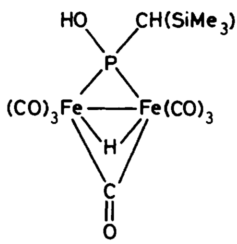


(6)

the known diphosphene, $R^1P=PR^1$ (**2**).[1,7] The second blue complex, (**3**), showed a deshielded ^{31}P n.m.r. signal at δ +612 p.p.m. characteristic of an 'open' type (**A**) phosphinidene complex.[2a,b,8] This formulation was confirmed by *X*-ray crystallography which revealed that (**3**) contains a μ-PR^1 ligand bonded to two $Co(CO)(\eta\text{-}C_5H_5)$ fragments. The structure is described in detail in the next section; however, the important points are a trigonal-planar geometry at phosphorus and the absence of a Co–Co bond which establish (**3**) as an 'open' type (**A**) complex. This result thus implies that the presence of a Group 8A metal alone is not sufficient for the formation of a 'closed' type (**B**) structure.

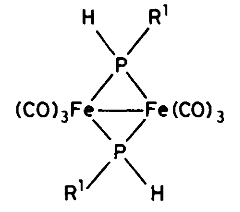
Attention was next focussed on the nature of the R group and its possible influence on the type of structure adopted. The work of Huttner[2a,b] has shown that for 'open' type (**A**) phosphinidene complexes containing Group 6A and 7A metals, a large variety of R groups can be employed for phosphorus (and also arsenic and antimony analogues). These include alkyl, aryl, halide, alkoxy, thiolate, and even univalent metal fragments. It would therefore seem that the role of the R group is of limited importance. However in (**1**) and (**3**) the R groups are very bulky, *i.e.* $(Me_3Si)_2CH$ and 2,4,6-$Bu^t{}_3C_6H_2$ respectively, and in such cases this degree of steric bulk may be much more influential. Thus it was conceivable that, while an 'open' type (**A**) structure would be adopted for 2,4,6-$Bu^t{}_3C_6H_2$, the different steric properties of $(Me_3Si)_2CH$ might favour a 'closed' structure. Indeed, molecular mechanics calculations based on the structures of (**1**) and (**3**) supported this view. These will be discussed in detail in a later section.

The reaction of $Na[Co_2(CO)_2(\eta\text{-}C_5H_5)_2]$ with $(Me_3Si)_2CHPCl_2$ affords the phosphido species (**4**), rather than a phosphinidene complex, and so a direct comparison is therefore not possible in the cobalt system. Details of this reaction have been reported elsewhere.[9] Accordingly, the reactions of $(Me_3Si)_2CHPCl_2$ and R^1PCl_2 with $[NEt_4]_2[Fe_2(CO)_8]$ were investigated to examine this hypothesis. If phosphinidene complexes were formed, it was expected that the former reaction might give rise to a 'closed' complex analogous to (**1**) whilst the latter might produce an 'open' complex similar to (**3**).

The reaction of $(Me_3Si)_2CHPCl_2$ with $[NEt_4]_2[Fe_2(CO)_8]$ in thf at room temperature produced a yellow-orange solution after a few hours. Filtration, followed by removal of the solvent, gave a crude orange oil which was redissolved in hexane and purified by column chromatography. This produced a single hexane-soluble yellow-orange fraction, although a ^{31}P n.m.r. spectrum of this reaction mixture revealed that a large number of compounds were present. Repeated attempts at purification were unsuccessful; however, cooling of a methylcyclohexane solution to −20 °C produced a small crop of orange crystals which were investigated by *X*-ray crystallography. The *X*-ray study revealed that the orange crystals are composed of two compounds, (**5**) and (**6**), details of which are presented in the next section. Neither compound contains a phosphinidene ligand but both compounds feature a phosphido fragment bridging an Fe–Fe bond. In complex (**5**) a $Fe_2(CO)_6$ unit is bridged by a $(Me_3Si)_2CHPH$ phosphido and a hydroxide group whereas in (**6**) a similar dimetal unit is triply bridged by $(Me_3Si)_2CHP(OH)$, hydride, and CO. They are thus both formally derived from a di-iron phosphinidene complex (possibly present as a reactive intermediate) and adventitious water.

Knowledge of the structures of (**5**) and (**6**) permits a limited interpretation of the ^{31}P and ^1H n.m.r. spectra obtained from this reaction. Thus in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, two major signals occur at δ +192.3 and +146.4. In the ^1H-coupled ^{31}P n.m.r. spectrum the former signal remains as a singlet whilst the latter becomes a doublet with a J_{PH} coupling of 379 Hz indicative of the presence of a P–H fragment. These signals are therefore assigned to (**6**) and (**5**) respectively. The ^1H n.m.r. spectrum exhibits a large number of signals in the region associated with $SiMe_3$ groups. However, a doublet is observed at δ +8.28 (J_{PH} = 380 Hz) consistent with the P–H group in (**5**) while at δ −9.64 a broad doublet (J_{PH} = 60 Hz) is detected due to the bridging hydride in (**6**). In addition, a broad singlet occurs at δ +3.5 and is most likely due to one of the O–H groups in either (**5**) or (**6**). The nature of the other products formed in this reaction, other than $(Me_3Si)_2CHPH_2$, identified by a triplet in the ^{31}P n.m.r. spectrum (δ −41.9, $^1J_{PH}$ = 355, $^2J_{PH}$ = 14 Hz), remains uncertain.

The corresponding reaction of R^1PCl_2 (R^1 = 2,4,6-$Bu^t{}_3C_6H_2$) with $[NEt_4]_2[Fe_2(CO)_8]$ also failed to produce a phosphinidene complex and again gave rise to a large number of products. Treatment of a suspension of $[NEt_4]_2[Fe_2(CO)_8]$ in thf with one equivalent of R^1PCl_2 at room temperature for 10 h afforded a dark red solution. After removal of the solvent, a green solution was obtained on extraction with hexane and a red solution was obtained with CH_2Cl_2. Purification of the former by column chromatography afforded several fractions from which compounds (**7**)—(**10**) were identified by ^{31}P n.m.r. spectroscopy. The nature of (**8**) and (**10**) was established by comparison with previous work[10,11] and that of (**7**) and (**9**) was confirmed by *X*-ray crystallography, details of which will be reported elsewhere. In addition to the above four products, the presence of further unidentified phosphorus-containing compounds was evident from ^{31}P n.m.r. spectroscopy. In contrast to the plethora of products present in the hexane extract, the CH_2Cl_2 extract contained a single major product,



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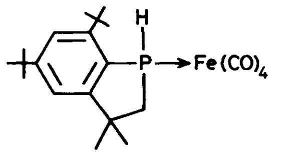

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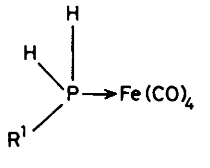

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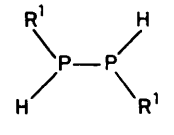

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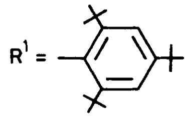
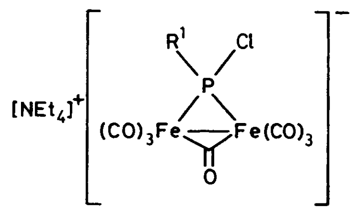


(**11**), with ^{31}P n.m.r. signal at δ +377. A proton-coupled spectrum revealed no attached hydrogens while mass spectroscopy indicated the presence of NEt_4^+ together with R^1 and $Fe(CO)_x$ fragments. Since suitable single crystals of (**11**) could not be obtained, a definitive structural assignment cannot be made. However a structure consistent with the spectroscopic observations is represented below. A similar mono-phosphido anion has been reported previously;[12] moreover, a structure such as (**11**) is chemically reasonable as a reaction product and in accord with observed solubility properties.



(11)

Thus the reactions of $[Fe_2(CO)_8]^{2-}$ with either $(Me_3Si)_2CHPCl_2$ or R^1PCl_2 both produce a large number of products and in each case no spectroscopic evidence for a phosphinidene complex exists. Whether or not such species are present as reactive intermediates is unclear.

X-Ray Crystallographic Studies.—The results of the *X*-ray analysis for (**3**) are illustrated in Figures 1 and 2. Selected bond lengths and angles are collected in Table 1 and atomic positional parameters are presented in Table 2. The structure consists of a 2,4,6-$Bu^t_3C_6H_2P$ phosphinidene ligand bonded to two $Co(CO)(\eta-C_5H_5)$ fragments. The phosphorus atom adopts a trigonal-planar geometry [sum of angles at P = 359.9(4)°] and the two cobalt atoms are separated by a distance (3.89 Å) well outside the usual bonding range. These two factors establish (**3**) as an 'open' type (**A**) complex. The precise geometry at

Table 1. Selected bond distances (Å) and angles (°) for $[Co_2(CO)_2(\eta-C_5H_5)_2\{\mu-P(C_6H_2Bu^t_3-2,4,6)\}]$ (**3**)*

Co(1)–P(1)	2.115(4)	Co(2)–P(1)	2.105(3)
P(1)–C(1)	1.852(13)	Co(1)–C(24)	1.71(2)
Co(2)–C(25)	1.70(2)		
Co(1)–P(1)–Co(2)	134.0(2)	Co(1)–P(1)–C(1)	109.5(4)
Co(2)–P(1)–C(1)	116.4(4)	P(1)–Co(1)–C(24)	95.6(6)
P(1)–Co(2)–C(25)	92.9(4)	Co(1)–C(24)–O(1)	173(2)
Co(2)–C(25)–O(2)	177(1)		

* Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent Tables.

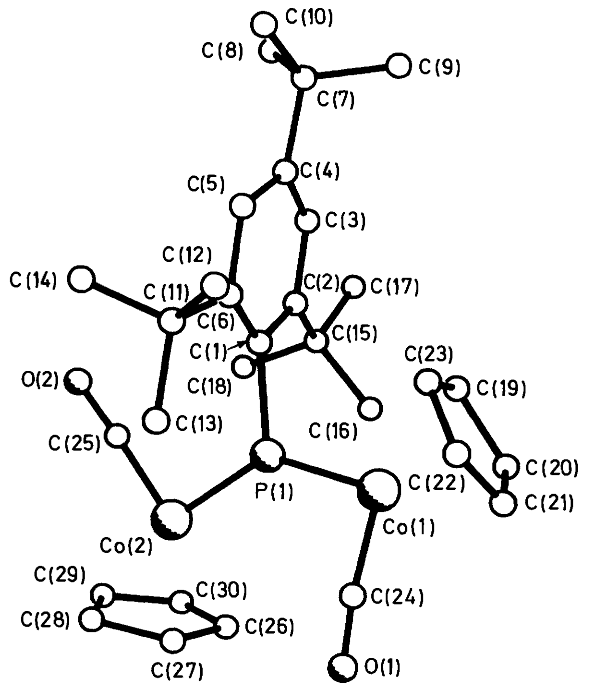


Figure 1. The molecular structure of (**3**) showing the atom numbering scheme adopted

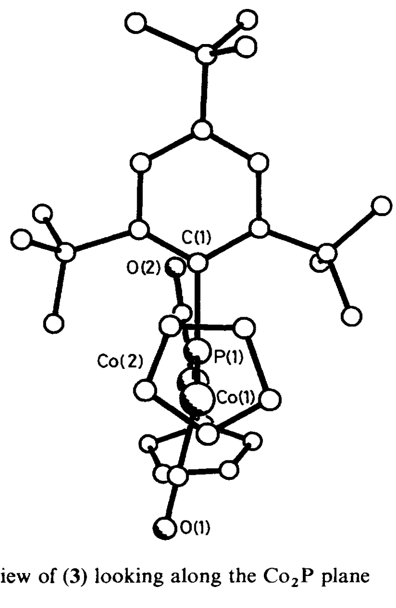


Figure 2. A view of (**3**) looking along the Co_2P plane

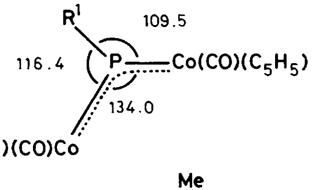
Table 2. Atomic co-ordinates for $[Co_2(CO)_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ (**3**)

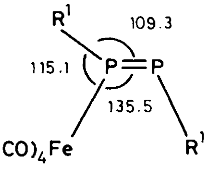
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.793 8(2)	0.404 1(1)	0.602 7(2)	C(14)	1.035(2)	0.210(1)	0.248(2)
Co(2)	0.548 3(2)	0.302 7(1)	0.179 3(2)	C(15)	0.649(1)	0.162(1)	0.604(2)
P(1)	0.716 8(4)	0.313 7(2)	0.422 1(4)	C(16)	0.584(2)	0.232(1)	0.651(3)
O(1)	0.630(2)	0.523 6(7)	0.399(2)	C(17)	0.657(2)	0.104(1)	0.729(2)
O(2)	0.642(1)	0.156 7(7)	0.110(1)	C(18)	0.540(2)	0.133(1)	0.430(3)
C(1)	0.834(1)	0.229 6(7)	0.500(1)	C(19)	0.900(2)	0.350(1)	0.826(2)
C(2)	0.800(1)	0.175 2(8)	0.598(2)	C(20)	0.822(2)	0.417(1)	0.853(2)
C(3)	0.911(1)	0.124 9(7)	0.692(1)	C(21)	0.884(2)	0.476(1)	0.812(2)
C(4)	1.043(1)	0.122 7(7)	0.690(1)	C(22)	0.996(2)	0.455(1)	0.766(3)
C(5)	1.072(1)	0.171 4(8)	0.584(2)	C(23)	1.003(2)	0.377(1)	0.774(2)
C(6)	0.968(1)	0.225 5(7)	0.490(1)	C(24)	0.691(2)	0.473(1)	0.472(2)
C(7)	1.159(1)	0.066 0(8)	0.802(2)	C(25)	0.607(1)	0.216 2(9)	0.142(2)
C(8)	1.090(2)	−0.014 2(9)	0.768(2)	C(26)	0.408(2)	0.386 5(9)	0.188(2)
C(9)	1.200(2)	0.089(1)	0.989(2)	C(27)	0.483(2)	0.412 4(9)	0.093(2)
C(10)	1.294(2)	0.066(1)	0.768(2)	C(28)	0.450(2)	0.360 4(9)	−0.049(2)
C(11)	1.025(1)	0.269 6(8)	0.375(2)	C(29)	0.353(2)	0.304 2(9)	−0.035(2)
C(12)	1.174(2)	0.305(1)	0.484(2)	C(30)	0.326(1)	0.322(1)	0.106(2)
C(13)	0.932(2)	0.336(1)	0.273(2)				

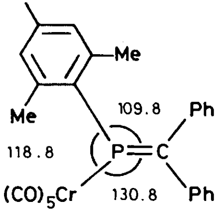
Table 3. Selected bond distances (Å) and angles (°) for $[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$ (**5**) and $[Fe_2(CO)_7(\mu\text{-}H)\{\mu\text{-}P(OH)[CH(SiMe_3)_2]\}]$ (**6**)

Compound (**5**)				Compound (**6**)			
Fe(21)–Fe(22)	2.465(1)	Fe(21)–P(2)	2.236(1)	Fe(11)–Fe(12)	2.573(1)	Fe(11)–P(1)	2.235(1)
Fe(22)–P(2)	2.235(1)	Fe(21)–O(27)	1.989(2)	Fe(12)–P(1)	2.231(1)	Fe(11)–C(17)	1.955(3)
Fe(22)–O(27)	1.990(2)	O(27)–H(27)	0.620(20)	Fe(12)–C(17)	1.976(3)	Fe(11)–H(12)	1.646(37)
P(2)–H(2)	1.316(28)			Fe(12)–H(12)	1.686(34)	P(1)–O(1)	1.597(3)
				O(1)–H(1)	0.700(27)		
Fe(21)–P(2)–Fe(22)	66.9(1)	P(2)–Fe(21)–Fe(22)	56.5(1)	Fe(11)–P(1)–Fe(12)	70.3(1)	P(1)–Fe(11)–Fe(12)	54.8(1)
P(2)–Fe(22)–Fe(21)	56.6(1)	Fe(21)–O(27)–Fe(22)	76.6(1)	P(1)–Fe(12)–Fe(11)	54.9(1)	Fe(11)–C(17)–Fe(12)	81.8(1)
Fe(21)–P(2)–H(2)	111.1(13)	Fe(22)–P(2)–H(2)	115.0(12)	Fe(11)–H(12)–Fe(12)	101.1(19)	Fe(11)–C(17)–O(17)	139.6(2)
Fe(21)–P(2)–C(28)	129.4(1)	Fe(22)–P(2)–C(28)	129.7(1)	Fe(12)–C(17)–O(17)	138.7(2)	Fe(11)–P(1)–O(1)	119.1(1)
H(2)–P(2)–C(28)	102.2(12)	Fe(21)–O(27)–H(27)	114.4(21)	Fe(12)–P(1)–O(1)	118.5(1)	Fe(11)–P(1)–C(18)	123.7(1)
Fe(22)–O(27)–H(27)	107.2(23)			Fe(12)–P(1)–C(18)	126.8(1)	O(1)–P(1)–C(18)	98.9(1)
				P(1)–O(1)–H(1)	116.5(24)		

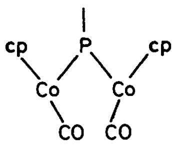
phosphorus is, however, not symmetric as evidenced by the three interbond angles, Co(1)–P(1)–C(1) 109.5(4), Co(2)–P(1)–C(1) 116.4(4), and Co(1)–P(1)–Co(2) 134.0(2)°. The last angle between the two cobalt atoms lies within the range found for other 'open' phosphinidene complexes, *i.e.* 130—140°.[2a,b] The two angles to the *ipso* carbon, C(1), of the arene ring differ by almost 7°; the precise reason for this asymmetry is unclear. Such an effect is not usually observed in other type (**A**)[2a,b] complexes but comparison with related diphosphene[13] and phospha-alkene[14] complexes (which are formally derived from replacement of one metal fragment by either an isobal PR or CR_2 fragment respectively) is instructive as shown below.



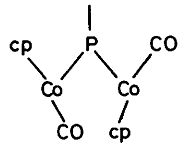




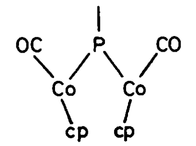
Whether this angle asymmetry in (**3**) reflects a difference in the bonding of the phosphorus to each cobalt is unclear. However, any possible difference is not apparent in the P–Co bond lengths [Co(1)–P(1) 2.115(4) and Co(2)–P(1) 2.105(3) Å] which are very similar although they are in the range expected for P–Co multiple bonding.* The geometry of the aryl, cyclopentadienyl, and carbonyl groups is normal and not worthy of special comment. However, the orientation of the metal fragments merits brief mention. As described in the following section, the bonding requirements in (**3**) are such that the CO ligands are required to lie in the Co_2P plane. This requirement gives rise to three possible isomers, (**I**)—(**III**) (cp = $\eta\text{-}C_5H_5$). Isomer (**II**) is, in fact, the one observed in the solid-state structure (Figure 2) and this appears to represent the most sterically acceptable option. Rather severe intramolecular steric interactions involving the cyclopentadienyl ligands seem



(**I**)



(**II**)



(**III**)

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* A P–Co bond length of *ca.* 2.05 Å has been taken to imply strong multiple bond character.[15]

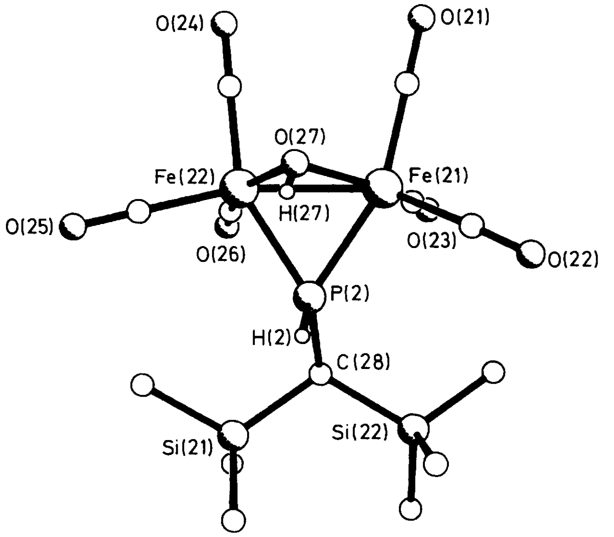


Figure 3. The molecular structure of (**5**) showing the atom numbering scheme adopted

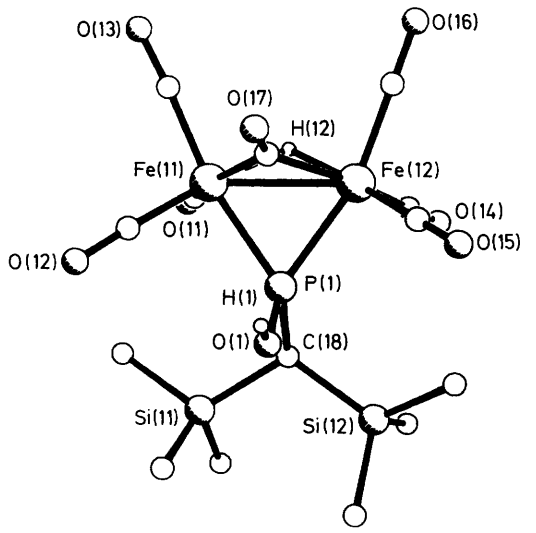


Figure 4. The molecular structure of (**6**) showing the atom numbering scheme adopted

to occur either between themselves as in isomer (**III**) or with the bulky aryl ligand in isomer (**I**). The asymmetric form adopted, *i.e.* (**II**), is possibly associated with the difference in Co–P(1)–C(1) angles. In solution, however, only a broad cyclopentadienyl resonance is observed in the ^1H n.m.r. spectrum thus making distinction between isomers difficult.

The structures of (**5**) and (**6**) are shown in Figures 3 and 4 respectively. Selected bond length and angle data are presented in Table 3 and atomic positional parameters are listed in Table 4. The structure of (**5**) consists of a central di-iron unit with each iron bonded to three terminal carbonyl ligands of normal geometry. In addition, the Fe–Fe bond is bridged by a primary phosphido group, $P(H)CH(SiMe_3)_2$, and a hydroxide. These moieties are positioned such that the Fe_2PO core adopts a butterfly geometry with the hinge angle (*i.e.* that between the Fe_2P and Fe_2O planes) equal to 102.1°. Electron counting procedures require that both the hydroxide and phosphido ligands each donate three electrons to the dimetal centre. Thus formally, a single Fe–Fe bond is required which is consistent with the observed distance [Fe(21)–Fe(22) 2.465(1) Å]. The two Fe–P and the two Fe–O bond lengths are the same within experimental error (Table 3). The two unique hydrogens, H(2) bonded to P(2) and H(27) bonded to O(27), were directly located and freely refined. In the latter case a pyramidal geometry at O(27) is revealed with a sum of angles of 298(2)°. Complex (**5**) is formally analogous to the known di-iron complexes, $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]$[16] and $[Fe_2(CO)_6(\mu\text{-}X)(\mu\text{-}PXR)]$ (X = halide),[17] which adopt similar butterfly structures.

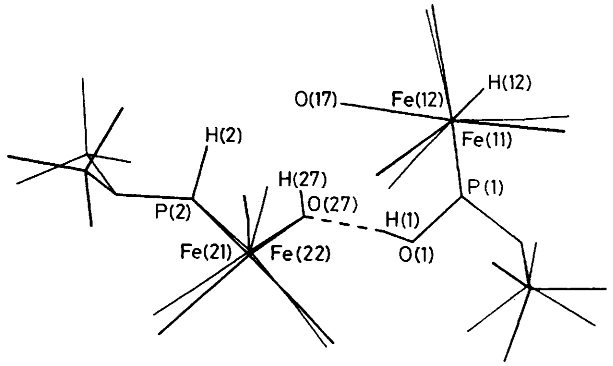


Figure 5. A view of (**5**) and (**6**) showing the intermolecular hydrogen bonding described in the text

Complex (**6**) also contains a $Fe_2(CO)_6$ core similar to that found in (**5**). In this case, however, the iron–iron vector is triply bridged by a carbonyl, a hydride, and a $P(OH)CH(SiMe_3)_2$ phosphido ligand. The geometry around each iron is approximately octahedral and the Fe–Fe distance of 2.573(1) Å is consistent with a bond order of unity as required by electron-counting procedures. Each ligand possesses a normal geometry and the two unique hydrogens, H(1) bonded to O(1) and H(12) bonded to Fe(11) and Fe(12), were directly located and refined without difficulty. The angle at O(1), *i.e.* P(1)–O(1)–H(1), is 117(2)°. The structure of (**6**) is therefore analogous to a recently reported di-iron phosphido anion, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$,[12] protonation of which would presumably yield a neutral hydride similar to (**6**).

As described in the previous section, compounds (**5**) and (**6**) cocrystallise. Moreover, a hydrogen-bonded interaction is apparent from the structure as illustrated below and shown in Figure 5. The interaction occurs between the hydrogen in the OH group in (**6**) and the oxygen in the OH group in (**5**) and is approximately linear (see below): O(1)–H(1)–O(27) 171(3)°; O(1)–H(1) 0.70(3), O(27)–H(1) 1.95(8) Å.

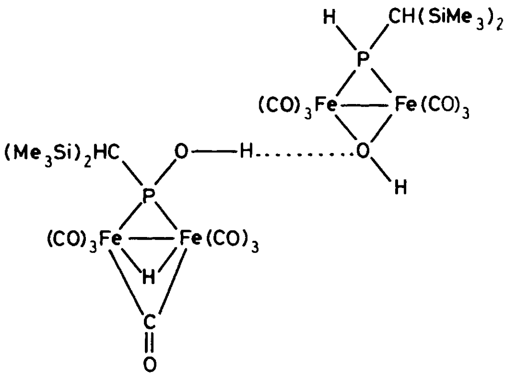
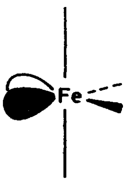


Table 4. Atomic co-ordinates for $[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$ (**5**) and $[Fe_2(CO)_7(\mu\text{-}H)\{\mu\text{-}P(OH)[CH(SiMe_3)_2]\}]$ (**6**)

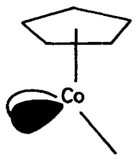
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(11)	0.487 5(1)	0.648 9(1)	−0.186 8(1)	C(123)	−0.054 1(4)	0.793 1(3)	−0.425 0(3)
Fe(12)	0.253 7(1)	0.575 3(1)	−0.154 3(1)	Fe(21)	0.130 3(1)	0.788 6(1)	0.094 0(1)
H(12)	0.407 4(35)	0.565 1(22)	−0.206 3(21)	Fe(22)	0.359 4(1)	0.852 9(1)	0.062 7(1)
C(11)	0.532 0(3)	0.661 5(2)	−0.298 8(2)	C(21)	0.018 1(4)	0.854 0(3)	0.004 5(2)
O(11)	0.561 4(3)	0.664 6(2)	−0.367 5(2)	O(21)	−0.051 3(3)	0.896 3(2)	−0.050 0(2)
C(12)	0.548 5(3)	0.743 8(2)	−0.158 2(2)	C(22)	0.034 8(4)	0.690 0(3)	0.127 2(2)
O(12)	0.584 0(3)	0.806 4(2)	−0.141 3(2)	O(22)	−0.025 3(3)	0.628 6(2)	0.152 8(2)
C(13)	0.644 0(3)	0.570 5(2)	−0.151 2(2)	C(23)	0.054 9(4)	0.854 7(2)	0.161 5(2)
O(13)	0.745 5(2)	0.525 2(2)	−0.130 0(2)	O(23)	0.010 8(3)	0.899 2(2)	0.204 8(2)
C(14)	0.162 7(3)	0.559 3(2)	−0.247 5(2)	C(24)	0.299 2(4)	0.943 2(2)	−0.029 5(2)
O(14)	0.106 1(3)	0.549 8(2)	−0.305 9(2)	O(24)	0.260 8(3)	1.001 4(2)	−0.084 7(2)
C(15)	0.113 2(4)	0.593 7(2)	−0.084 2(2)	C(25)	0.546 6(4)	0.836 9(2)	0.040 2(2)
O(15)	0.025 8(3)	0.606 1(2)	−0.038 5(2)	O(25)	0.664 7(3)	0.829 3(2)	0.027 2(2)
C(16)	0.292 4(4)	0.455 6(2)	−0.106 1(3)	C(26)	0.371 4(4)	0.930 4(2)	0.126 9(2)
O(16)	0.315 9(3)	0.380 7(2)	−0.076 3(2)	O(26)	0.377 0(3)	0.978 4(2)	0.170 7(2)
C(17)	0.396 3(3)	0.602 9(2)	−0.078 0(2)	O(27)	0.277 2(2)	0.762 4(1)	0.012 0(1)
O(17)	0.415 6(2)	0.594 8(1)	−0.004 3(1)	H(27)	0.314 3(23)	0.726 1(14)	0.024 6(14)
P(1)	0.269 9(1)	0.722 2(1)	−0.208 9(1)	P(2)	0.322 7(1)	0.744 4(1)	0.178 7(1)
O(1)	0.218 9(2)	0.791 7(1)	−0.152 6(1)	H(2)	0.376 6(29)	0.662 7(18)	0.175 8(18)
H(1)	0.238 0(30)	0.778 7(19)	−0.109 2(17)	C(28)	0.344 6(3)	0.742 5(2)	0.290 9(2)
C(18)	0.204 0(3)	0.788 3(2)	−0.311 9(2)	Si(21)	0.539 6(1)	0.728 7(1)	0.326 8(1)
Si(11)	0.294 7(1)	0.896 2(1)	−0.356 7(1)	C(211)	0.659 0(4)	0.781 1(3)	0.241 5(2)
C(111)	0.489 7(4)	0.877 6(2)	−0.373 6(2)	C(212)	0.553 6(5)	0.787 9(3)	0.413 4(3)
C(112)	0.275 5(5)	0.976 2(2)	−0.287 5(3)	C(213)	0.606 0(5)	0.607 5(3)	0.361 7(4)
C(113)	0.220 9(5)	0.947 7(3)	−0.465 4(2)	Si(22)	0.229 4(1)	0.661 6(1)	0.364 0(1)
Si(12)	−0.000 3(1)	0.810 0(1)	−0.320 4(1)	C(221)	0.039 1(4)	0.706 3(3)	0.353 8(3)
C(121)	−0.093 7(4)	0.731 8(3)	−0.237 4(3)	C(222)	0.277 4(5)	0.649 5(3)	0.478 7(2)
C(122)	−0.069 4(4)	0.924 0(3)	−0.309 0(3)	C(223)	0.247 2(5)	0.550 1(3)	0.337 9(3)

Theoretical Studies

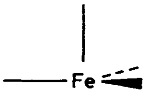
In order to gain an understanding of various properties of the μ-phosphinidene and related species reported here we have carried out extended Hückel molecular orbital (EHMO) calculations on a model complex $[Fe_2(CO)_8(\mu\text{-}PH)]$. In all calculations the local symmetry at iron was constrained to C_{2v} [as in (**E**) below] with C–Fe–C angles 180 or 90°, all Fe–C–O angles 180°, and bond lengths fixed at Fe–C 1.75, C–O 1.15, Fe–P 2.20, and P–H 1.44 Å, with Hückel parameters taken from ref. 18.



(**E**)



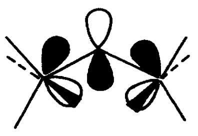
(**F**)



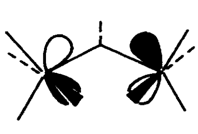
(**G**)

The frontier orbitals of the d^8 ML_4 [here $Fe(CO)_4$] fragment are well known[18] and show a σ-acceptor lowest unoccupied molecular orbital (l.u.m.o.), with the highest occupied molecular orbital (h.o.m.o.) [(**E**)] a well hybridised π-donor orbital in the plane orthogonal to the axial carbonyls, at higher energy than the *d*-block t_{2g}-type orbitals. The frontier orbitals of the closely related $Co(L)(\eta\text{-}C_5H_5)$ fragment [(**F**)] have also been described[19] and are qualitatively very similar to those of $Fe(CO)_4$. These fragments are therefore isolobal with one another and with CH_2.[20] As a result, fragments (**E**) and (**F**) engage in bonding preferentially in one plane [that perpendicular to the axial carbonyls in (**E**), and that perpendicular to the sole carbonyl in (**F**)]. A second possible geometry for the $Fe(CO)_4$ fragment having C_{3v} local symmetry at Fe, namely (**G**), shows no such orientational preference for π bonding to a two-electron donor ligand in the axial site; indeed π-bonding to that site is rather poor.[19]

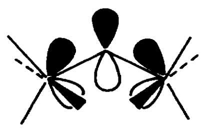
Given that the PR fragment is isolobal with CR^-, the 'open' and 'closed' forms (**A**) and (**B**) may be supposed to be isolobal with the allyl anion and cyclopropyl anion respectively. Our EHMO calculations bear out this analysis well.[6] In particular the model $Fe_2(CO)_8(PH)$ in a geometry corresponding to (**A**) (Fe–P–Fe 135°, planar at P) shows a h.o.m.o. and l.u.m.o. which are qualitatively identical to π_2 and π_3 of the allyl anion [see (**H**) and (**I**) below] with the π_1 equivalent, (**J**), at lower energy. The l.u.m.o., (**H**), is isolated in energy from the other virtual orbitals and is substantially located on phosphorus (*ca.* 53%). These characteristics are the cause of both the unusually large low-field chemical shifts observed for μ-PR ligands[8] and the reactivity of such μ-PR complexes towards nucleophiles.[2a,b] Thus nucleophilic attack on these species will proceed at phosphorus under orbital control. As in the analogous allyl anion the occupancy of orbitals (**I**) and (**J**) leads to an Fe–P bond order greater than unity.



(**H**)

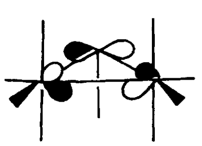


(**I**)

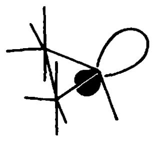


(**J**)

The frontier orbitals of $[Fe_2(CO)_8(\mu\text{-}PH)]$ in a geometry of type (**B**) (Fe–P–Fe 75, Fe–P–H 110°) show a marked resemblance to those of the cyclopropyl anion. Thus the l.u.m.o. is essentially a ring system σ* orbital and the h.o.m.o. a lone pair on phosphorus [see (**K**) and (**L**) respectively]. The ability of the μ-PR ligand in this geometry to form σ-adducts with further metals using orbital (**L**) is well known.[2c]

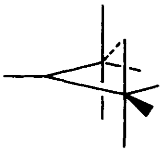


(K)

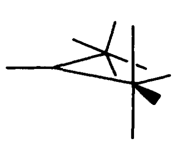


(L)

The isolobal relationships between the CH_2 and C_{2v} $Fe(CO)_4$ [and $Co(CO)(\eta-C_5H_5)$] fragments implies a strong orientational preference in the binding of the metal–ligand fragments in the allyl anion analogues of type (A). This preferred geometry has the metal orbitals [(E), (F)] having their nodal planes coincident with the Fe_2P plane [as in (H)—(J)]. This conformation is adopted in (3) and we find it to be more stable, for the model [$Fe_2(CO)_8(\mu-PH)$], by *ca.* 23 kcal mol^{-1} than one in which the metal fragments are rotated by 90° [*e.g.* as in (M)]. This is undoubtedly a substantial overestimate of the barrier to rotation of the metal fragment about the P–M bond. Indeed the energy of the asymmetric geometry (N) lies only 6 kcal mol^{-1} above that of the favoured geometry [(H)—(J)], indicating a pathway with non-synchronous rotation is likely to be favoured since it allows greater retention of Fe–P π-bonding [partly localised in (N) in one Fe–P bond]. This relatively low barrier is consistent with the observation of a single C_5H_5 signal in the room-temperature ^1H n.m.r. spectrum of (3).



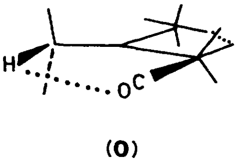
(M)



(N)

As judged by the 'total energy' (*i.e.* the sum of occupied one-electron wavefunction energies) the open geometry [type (A)] is always favoured over the closed geometry [type (B)] for [$Fe_2(CO)_8(PH)$] by *ca.* 35 kcal mol^{-1} for optimum geometries [(H)—(J) *vs.* (K), (L)]. The overall preference can be traced largely to greater stabilisation resulting from enhanced Fe–P bonding in (A) as compared with the Fe–Fe present in (B). In overlap terms, while Fe–P net overlap populations increase from 0.67 to 0.94 on going from (A) to (B), those of Fe–Fe fall from only 0.085 to −0.009. The question therefore arises as to what circumstances will favour the adoption of a 'closed' geometry. While kinetic isolation of the 'closed' form is an obvious possibility, the symmetry allowed conrotatory ring-closure reaction known for the analogous dimethylene-phosphorane, $CH_2P(R)CH_2$, species[21] indicates that there will be no significant symmetry-based electronic barriers to the 'closed'-to-'open' rearrangement. Therefore a means of reversing the thermodynamic preference for the open geometry must be sought. In [$Fe_2(CO)_8\{\mu-SbCH(SiMe_3)_2\}$] (**1**), which does adopt the closed geometry, two different factors may be at work. The known preference of the heavier congeners of phosphorus for pyramidal geometry in three-co-ordination should encourage a type (**B**) structure. In part this is due to enhanced stabilisation of the h.o.m.o. (L) associated with increased pnicogen *s* character of this orbital. In addition, π-bonding, the factor driving the preference for open geometries, is likely to be less significant for Sb than for its lighter congeners, although substitution of Sb for P is not of itself sufficient to force a closed geometry, as witnessed by the open complex [$W_2(CO)_{10}\{\mu-SbCH(SiMe_3)_2\}$] (**12**).[22]

Perhaps more important are the steric properties of the substituent at Sb in (**1**). Models of (**1**) in an open geometry for which the $Fe(CO)_4$ units are in the electronically favoured geometry, (H)—(J), as in (O), show severe steric problems in CO···CO and CO···$HC(SiMe_3)_2$ contacts in the Fe_2Sb plane. This is despite allowing the $CH(SiMe_3)_2$ group to adopt the 'best' conformation with the $SiMe_3$ groups out of this plane. Similar effects have been recognised in the complex [$\{Fe(CO)_4\}_2\{P_2[CH(SiMe_3)_2]_2\}$],[23] dictating a conformation in which the axial carbonyls are forced out of the $Fe_2P_2C_2$ plane. In contrast other bulky substituents, R, in μ-PR complexes may favour an open geometry [*e.g.* R^1 as in (3)] since they can be oriented so as to place their bulk out of the M_2P plane. An alternative, less sterically demanding, geometry in which the $Fe(CO)_4$ units adopt geometry (G) may be possible (as seen in [$Fe_2(CO)_8\{\mu-PH(OMe)\}]^-$),[24] but undoubtedly Fe–P π-bonding would be significantly diminished.

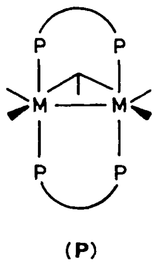


(O)

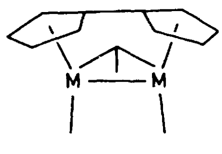
Conclusions

A search for phosphinidene complexes has been successful in the synthesis of the dicobalt complex, (3), which adopts an 'open' type (A) structure. However, attempted preparations designed to synthesise other examples featuring dicobalt and di-iron centres proved unsuccessful resulting, especially in the di-iron systems, in a plethora of products.

Theoretical studies indicate that, when formed, the open type (A) form should be the most stable for electronic reasons. However, a strategy for forming closed [$(ML_n)_2(\mu-PR)$] species of type (B) should concentrate on reducing M–P π-bonding and one way of doing this is to force the ML_n units into conformation(s) minimising such bonding. The use of appropriate bulky substituents represents one possible approach as seen, for example, in (**1**). However this cannot work where ML_n has no orientational preference, *e.g.* $W(CO)_5$ as seen in (**12**). Alternative approaches could involve changing the electronic properties of R to reduce M–P π-bonding or enforcing the desired ML_n conformations by linking the metal co-ordination spheres by bridging ligands [*e.g.* $Ph_2PCH_2PPh_2$ as in (P), or fulvalene as in (Q)].



(P)



(Q)

Experimental

General Procedures.—All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were freshly distilled over Na–benzophenone immediately prior to use.

Spectroscopic Measurements.—Proton and ^{13}C n.m.r. spectra were recorded on Bruker WP200 or Bruker WM300 spectrometers operating at 200.13 and 300.13 MHz respectively for ^1H, and 50 and 75.47 MHz for ^{13}C. Phosphorus-31 n.m.r. spectra were recorded on Varian FT80A and Bruker WM300 spectrometers operating at 32.38 and 121.49 MHz respectively. Proton and ^{13}C spectra were referenced to $SiMe_4$ (0.0 p.p.m.) and ^{31}P spectra to 85% H_3PO_4, with positive values to high frequency in all cases. Infrared spectra were recorded in solution on a Perkin-Elmer 1330 spectrophotometer.

Starting Materials.—The organometallic anions $Na[Co_2(CO)_2(\eta\text{-}C_5H_5)_2]$[25] and $[NEt_4]_2[Fe_2(CO)_8]$,[26] and the dichlorophosphines $2,4,6\text{-}Bu^t_3C_6H_2PCl_2$[7] and $(Me_3Si)_2CHPCl_2$[27] were prepared according to literature methods. All other materials were procured commercially and used as supplied.

Preparation of $[Co_2(CO)_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ (**3**).—A solution of R^1PCl_2 (1.737 g, 5 mmol) in thf (25 cm^3) was added dropwise to a solution of $Na[Co_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (10 mmol) in thf (100 cm^3) at −78 °C. This caused an immediate colour change to blue and the resulting reaction mixture was allowed to warm to room temperature with stirring overnight. Removal of the solvent followed by column chromatography (silica gel, hexane eluant) afforded the diphosphene (**2**) (0.3 g, 22% yield) as the first orange fraction followed by a blue fraction containing (**3**) (1.3 g, 45% yield). Crystals of (**3**) were obtained from hexane, m.p. 135—138 °C; i.r. (CH_2Cl_2), $\nu_{C\equiv O}$ 1 945 cm^{-1}; $^{31}P\text{-}\{^1H\}$ n.m.r. (toluene), δ +612.

Preparation of $[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$ (**5**) *and* $[Fe_2(CO)_7(\mu\text{-}H)\{\mu\text{-}P(OH)[CH(SiMe_3)_2]\}]$ (**6**).—$[NEt_4]_2[Fe_2(CO)_8]$ (0.5 g, 0.84 mmol) was added to thf (20 cm^3) and the resulting dark red suspension stirred at room temperature. To this, a solution of $(Me_3Si)_2CHPCl_2$ (0.22 g, 0.84 mmol) in thf (2 cm^3) was added and the mixture allowed to stir for 2 h. At the end of this time the reaction contained a yellow solution and an off-white precipitate. Filtration through Florisil and removal of the solvent *in vacuo* gave a dark red oil. This was redissolved in hexane and purified by column chromatography on Florisil. Elution with a 1:1 mixture of hexane and Et_2O gave a dark yellow solution. Recrystallisation at −20 °C from concentrated hexane or methylcyclohexane solution afforded a low yield of orange crystals [shown by *X*-ray diffraction to be (**5**) and (**6**)] together with varying quantities of a white solid. Further attempts at purification were unsuccessful and all crystallisations were hampered by the extreme solubility of all products. Relevant ^1H and ^{31}P n.m.r. data are given in the Results and Discussion section. Satisfactory mass spectra and microanalysis on bulk samples could not be obtained.

Reaction of $[NEt_4]_2[Fe_2(CO)_8]$ *with* $2,4,6\text{-}Bu^t_3C_6H_2PCl_2$.—$[NEt_4]_2[Fe_2(CO)_8]$ (2.98 g, 5 mmol) was suspended in thf (180 cm^3) and stirred at room temperature. To this, a solution of R^1PCl_2 (1.74 g, 5 mmol) in thf was added and the reaction mixture stirred for a further 10 h. The thf was then removed *in vacuo* and the resulting dark residue extracted with hexane (100 cm^3) which afforded a green solution. Column chromatography (silica gel; hexane eluant) gave several fractions which contained mixtures of the complexes (**7**), ^{31}P n.m.r. (toluene) δ +75; (**8**), δ +17; (**9**), δ −45; (**10**), δ −61. Further extraction of the crude reaction mixture with CH_2Cl_2 gave a red solution. This was purified by column chromatography (silica gel; 1:1 toluene–CH_2Cl_2 eluant) which afforded a red oily fraction containing (**11**). Spectroscopic details for (**11**) are given in the Results and Discussion section.

Table 5. Crystallographic and intensity data collection parameters for (**3**) and (**5**)/(**6**)

	(**3**)	(**5**)/(**6**)
Formula	$C_{30}H_{39}Co_2O_2P$	$C_{14}H_{21}Fe_2O_8PSi_2$/ $C_{13}H_{21}Fe_2O_7PSi_2$
M	580.5	1 004.3
Crystal size (mm)	0.4 × 0.4 × 0.5	0.6 × 0.6 × 0.5
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.184(3)	9.461(1)
b/Å	17.643(6)	15.318(2)
c/Å	8 790(5)	16.140(2)
α/°	92.21(4)	76.13(1)
β/°	114.89(3)	89.48(1)
γ/°	89.13(3)	84.43(1)
U/Å^3	1 432	2 259.9
Z	2	2
F(000)	608	1 028
D_c/g cm^{-3}	1.35	1.476
Radiation	Mo-K_α	Mo-K_α
μ(Mo-K_α)/cm^{-1}	12.3	14.9
2θ Range/°	3.0—46.0	3.0—50.0
Reflections measured	4 278	8 415
Reflections observed	1 764	6 124
Data omission factor	$I > 3.0\sigma(I)$	$F > 4.0\sigma(F)$
R	0.0641	0.0333
R'	0.0759	0.0369
Goodness of fit	4.29	1.81
Max. shift/e.s.d.	0.220	0.095
Max. peak in difference map (e Å^{-3})	0.47	0.40
No. of parameters	311	485

X-Ray Analysis of $[Co_2(CO)_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ (**3**).—A suitable single crystal of (**3**) was sealed in a Lindemann capillary and mounted on an Enraf–Nonius CAD4-F diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centred reflections, $15 \leqslant 2\theta \leqslant 25°$, and subsequently refined using higher angle data. These indicated a triclinic lattice. Data were collected for one independent half, $+h \pm k \pm l$, using the ω–2θ scan mode. The final scan speed for each reflection was determined from the net intensity gathered in an initial prescan and ranged from 2 to 7° min^{-1}. The ω-scan angle and aperture settings were determined as described in ref. 5*b*. Crystal stability and orientation were monitored every 30 min throughout data collection by means of two check reflections.

Data were corrected for the effects of Lorentz, polarisation and decay but not for absorption. Pertinent data collection and structure refinement parameters are collected in Table 5. The structure was solved by direct methods (MULTAN)[28] which revealed the positions of the cobalt and phosphorus atoms. All other non-hydrogen atoms were located from subsequent difference Fourier maps. All atoms were refined using anisotropic thermal parameters except for C(16) which was refined isotropically. Final refinement converged smoothly to give residuals shown in Table 5.

X-Ray Analysis of $[Fe_2(CO)_6(\mu\text{-}OH)\{\mu\text{-}PH[CH(SiMe_3)_2]\}]$ (**5**) *and* $[Fe_2(CO)_7(\mu\text{-}H)\{\mu\text{-}P(OH)[CH(SiMe_3)_2]\}]$ (**6**).—Measurements were made on a Siemens AED2 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å). Lattice parameters were refined from 2θ values of 32 reflections measured on both sides of the direct beam ($20 < \theta < 22°$). Intensity data were collected for the unique hemisphere with $h \leqslant 0$ in the ω–θ scan mode with scan range 0.85° below α_1 to 0.85° above α_2 and a scan time of 17.5—52.5 s. A decay of about 5% in the intensities of three standard reflections was corrected in data reduction, together with semi-empirical absorption corrections (transmission 0.35—0.38).[29] The structure was solved by heavy-atom methods and refined with anisotropic thermal parameters and with C–H hydrogen atoms in calculated positions [C–H 0.96 Å, H–C–H 109.5°, $U(\mathrm{H}) = 1.2\, U_{\mathrm{eq}}(\mathrm{C})$]; other H atoms were refined freely with isotropic thermal parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.000\,08F^2$. No significant features were found in a final difference synthesis. Other information is given in Table 5.

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

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References

1 A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.*, 1986, **34**, 1.

2 (*a*) G. Huttner and K. Evertz, *Acc. Chem. Res.*, 1986, **19**, 406; (*b*) G. Huttner, *Pure Appl. Chem.*, 1986, **58**, 585; (*c*) G. Huttner and K. Knoll, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 743.

3 L. Weber, R. Reizig, D. Bungardt, and R. Boese, *Organometallics*, 1987, **6**, 110.

4 A. M. Arif, A. H. Cowley, and M. Pakulski, *J. Chem. Soc., Chem. Commun.*, 1985, 1707; A. M. Arif, A. H. Cowley, M. Pakulski, and G. J. Thomas, *Polyhedron*, 1986, **5**, 1651; A. M. Arif, A. H. Cowley, N. C. Norman, A. G. Orpen, and M. Pakulski, *Organometallics*, in the press.

5 (*a*) A. H. Cowley, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, 1984, **106**, 6844; (*b*) A. H. Cowley, N. C. Norman, M. Pakulski, D. L. Bricker, and D. H. Russell, *ibid.*, 1985, **107**, 8211.

6 A. M. Arif, A. H. Cowley, N. C. Norman, A. G. Orpen, and M. Pakulski, *J. Chem. Soc., Chem. Commun.*, 1985, 1267.

7 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587; 1982, **104**, 6167.

8 G. Huttner, *J. Organomet. Chem.*, 1986, **308**, C11.

9 A. M. Arif, A. H. Cowley, M. Pakulski, M. B. Hursthouse, and A. Karauloz, *Organometallics*, 1985, **4**, 2227.

10 D. H. Champion and A. H. Cowley, *Polyhedron*, 1985, **4**, 1791.

11 A. H. Cowley, J. E. Kilduff, J. G. Lasch, S. K. Mehrotra, N. C. Norman, M. Pakulski, B. R. Whittlesey, J. L. Atwood, and W. E. Hunter, *Inorg. Chem.*, 1984, **23**, 2582.

12 E. P. Kyba, R. E. Davis, C. N. Clubb, S-T. Liu, H. O. A. Palacios, and J. S. McKennis, *Organometallics*, 1986, **5**, 869.

13 A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, and T. C. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 7751; *Organometallics*, 1984, **3**, 1044.

14 T. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, and A. van Herk, *J. Organomet. Chem.*, 1982, **210**, 211.

15 L. D. Hutchins, R. W. Light, and R. T. Paine, *Inorg. Chem.*, 1982, **21**, 266.

16 Y-F. Yiu, J. Gallucci, and A. Wojcicki, *J. Am. Chem. Soc.*, 1983, **105**, 4826 and refs. therein.

17 K. Evertz and G. Huttner, *Chem. Ber.*, 1987, **120**, 937.

18 T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.

19 D. L. Thorn and R. Hoffmann, *Nouv. J. Chim.*, 1979, **3**, 39.

20 M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711; F. G. A. Stone, *ibid.*, 1984, **23**, 89.

21 W. W. Schoeller and J. Niemann, *J. Am. Chem. Soc.*, 1986, **108**, 22.

22 A. M. Arif, A. H. Cowley, N. C. Norman, and M. Pakulski, *Inorg. Chem.*, 1986, **25**, 4836.

23 K. M. Flynn, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 2085.

24 A-M. Caminade, J-P. Majoral, M. Sanchez, R. Mathieu, S. Attali, and A. Grand, *Organometallics*, 1987, **6**, 1459.

25 N. E. Schore, C. S. Llenda, and R. G. Bergman, *J. Am. Chem. Soc.*, 1977, **99**, 1781.

26 K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1969, 2339.

27 M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, and H. Goldwhite, *J. Chem. Soc., Dalton Trans.*, 1980, 2428.

28 P. Main, MULTAN, University of York, 1982.

29 G. M. Sheldrick, SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, 1978.

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