$(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P[=C(SiMe_3)_2]_2\}$, the First Three-co-ordinate Metallo–Bis(methylene)phosphorane

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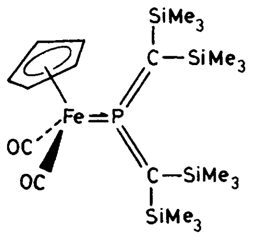
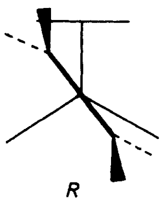
The reaction of $ClP[=C(SiMe_3)_2]$ with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]K$ affords $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P[=C(SiMe_3)_2]_2\}$, the first example of a three-co-ordinate metallo-bis(methylene)phosphorane (metallophospha-allene).

Several examples of λ^5-metallophosphoranes of the type R_4PML_n have been reported.[1] However, to the best of our knowledge metallophosphoranes with lower co-ordination numbers have not been prepared. We report the preparation and characterisation of the first example of a three-co-ordinate metallophosphorane (metallophospha-allene).

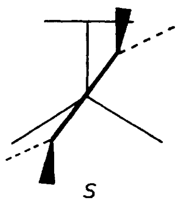
A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]K$ (2.13 mmol) and $ClP[=C(SiMe_3)_2]_2$[2] (2.09 mmol) in tetrahydrofuran (50 ml) was refluxed for 12 h. Removal of the solvent, followed by vacuum sublimation of the residue (40 °C, 0.1 Torr), afforded orange, crystalline (**1**) in 83% yield [m.p. 78 °C (decomp.)]. Unfortunately, crystals of (**1**) were unsuitable for *X*-ray diffraction study because of twinning problems. However, the composition $C_{21}H_{41}FeOPSi_4$ was established by high-resolution mass spectroscopy (calcd. for M^+, 524.7258; found, *m/z* 524.7251). In addition to the parent ion (*m/z* 524), prominent peaks were detected in the medium-resolution mass spectrum at *m/z* 436 and 384 which are due to the loss of Me_4Si and $(C_5H_5)Fe(CO)_2$, respectively.



(**1**)



R
(i)



S
(ii)

Previous experimental work by Appel *et al.*[3] has demonstrated that the $(Me_3Si)_2C$ groups of $XP[=C(SiMe_3)_2]_2$ molecules are twisted out of the XPC_2 plane. *Ab initio* M.O. calculations on model three-co-ordinate phosphoranes[4] suggest that this twisting is due to steric, and to a lesser extent, electronic effects. Furthermore, the vacant $3p_z$ orbital on phosphorus twists in response to rotation of the *P*-methylene units thereby resulting in an overall propeller-like arrangement. Such a conformation has, in fact, been observed[5] for the anion $\{(\text{fluoren-9-yl})P[=C(SiMe_3)_2]_2\}^-$, which exists as *R*- and *S*-stereoisomers. As shown [(i) and (ii)], a similar situation exists for (**1**).

N.m.r. data† are in accord with the existence of *R*- and *S*-stereoisomers. Thus four Me_3Si groups are apparent in the $^{13}C\text{-}\{^1H\}$ spectrum and the ^1H spectrum is somewhat complex in the Me_3Si region. Note also that the $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shift of (**1**) is 220 p.p.m. *upfield* of that of $ClP[=C(SiMe_3)_2]_2$. We attribute this observation to a donor–

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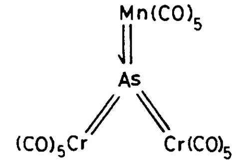
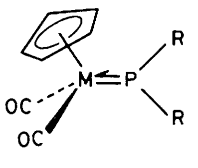
† N.m.r. spectra, values in p.p.m., relative to $SiMe_4$ (^1H and ^{13}C) and 85% H_3PO_4 external (^{31}P) in $[^2H_6]$benzene: ^1H (300 MHz) δ 4.08 (5H, d, $J_{P\text{-}H}$ 48.0 Hz, C_5H_5) and 0.25 (36H, m, SiMe); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 124.0 (d, $J_{P\text{-}C}$ 26.3 Hz, C_5H_5), 69.8 (d, $J_{P\text{-}C}$ 83.0 Hz, P=C), 2.52, 2.48, 2.43, and 2.38 (s, SiMe); $^{31}P\text{-}\{^1H\}$ (32.2 MHz) δ −81.6(s).



(2)



(3) M = Cr, Mo, W

acceptor interaction between the a'' HOMO of the $C_5H_5Fe(CO)_2$ fragment[6] and the vacant phosphorus $3p_z$ orbital.

Further support for the foregoing arguments is provided by the i.r. spectrum of (**1**) (toluene solution) which exhibits two CO stretching frequencies (1979 and 2040 cm^{-1}).[‡] Moreover, use of these vibrational spectroscopic data leads to a computed inter-carbonyl angle[7] of 78 ± 2°. This angle is *ca.* 95° when phosphorus is singly bonded to an $(\eta^5\text{-}C_5H_5)M(CO)_2$ fragment. More acute angles are associated with the presence of phosphorus–metal multiple bonding.[8]

Finally, we draw attention to the fact that (**1**) is related to (**2**)[9] on the basis of the isolobal principle.[10] Moreover, (**1**) is isoelectronic with three-electron donor phosphido complexes (**3**).[6] Both (**2**) and (**3**) have been shown to feature metal–group 15 multiple bonding.[§]

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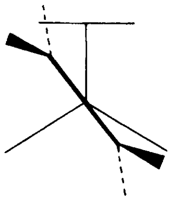
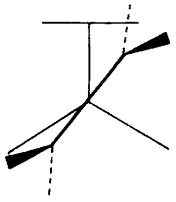
[‡] In the solid state (Nujol mull) low-intensity shoulders are detected at 1963 and 2060 cm^{-1}. Tentatively this observation is attributed to the existence of the two high energy conformers (iii) and (iv). Note that in these conformers the vacant phosphorus $3p_z$ orbital is orthogonal to the a'' donor orbital of the $(C_5H_5)Fe(CO)_2$ group.



(iii)



(iv)

[§] Compound (**1**) also bears a resemblance to cationic iron alkylidene complexes. See M. D. Johnson in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, p. 331.