First Structural Characterisation of Penta- and Hexa-phosphorus Analogues of Ferrocene. Synthesis, Crystal and Molecular Structure of the Air-stable, Sublimable Iron Sandwich Compounds $[Fe(\eta^5-C_2R_2P_3)_2]$, and $[Fe(\eta^5-C_3R_3P_2)(\eta^5-C_2R_2P_3)]$ ($R = Bu^t$)

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The first structurally characterised penta- and hexa-phosphorus analogues of ferrocene, bis-(η^5-2,5-di-t-butyl-1,3,4-triphosphacyclopentadienyl)iron and (η^5-2,4,5-tri-t-butyl-1,3-diphosphacyclopentadienyl)-(η^5-2,5-di-t-butyl-1,3,4-triphosphacyclopentadienyl)iron, are described.

The discovery of ferrocene, $[Fe(\eta^5-C_5R_5)_2]$ (**1**) (R = H), the first sandwich compound, is one of the landmarks of organo-transition metal chemistry.[1-4] Subsequently Mathey *et al.*[5] substituted a single CR unit by phosphorus in one or more of the cyclopentadienyl rings of (**1**) to form η^5-phospholyl (**2**) and phospha-ferrocene compounds (**3**), which have been fully structurally characterised.

The recent report by Scherer and Brück[6] of the characterisation of a novel penta-phosphorus ferrocene compound formulated as $[Fe(\eta^5-C_5R_5)(\eta^5-P_5)]$ (**4**) (R = Me) on the basis of elemental analysis, n.m.r. and mass spectroscopic studies prompts us to report syntheses and full single crystal *X*-ray structural characterisation of the novel penta- and hexa-phosphorus compounds $[Fe(\eta^5-C_3R_3P_2)(\eta^5-C_2R_2P_3)]$ (**5**) and $[Fe(\eta^5-C_2R_2P_3)_2]$ (**6**) ($R = Bu^t$).†

The green, air-stable, sublimable (120 °C at 0.01 mmHg) hexa-phosphorus complex (**6**) is the expected major product

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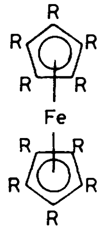
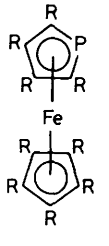
† *Note added in proof:* Adamantyl analogues of (**5**) and (**6**) have also now been synthesised.



(1)



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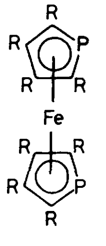

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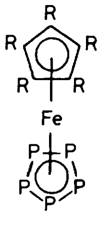

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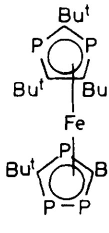

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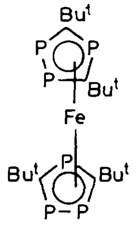

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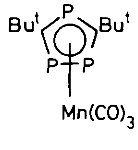

(7)

(*ca.* 30%) of the reaction between $FeCl_2$ and $[Li(dme)_3][C_2R_2P_3]$ ($R = Bu^t$; dme = 1,2-dimethoxyethane) in monoglyme at room temperature, the lithium salt having been made by the method of Becker *et al.*[7] from $Li[P(SiMe_3)_2]$ and the phospha-alkyne $Bu^tC{\equiv}P$. The unexpected minor product (**5**) (*ca.* 10%) which is also green, air-stable, and sublimable can be separated from (**6**) by fractional crystallisation.‡

Confirmation that both (**5**) and (**6**) are indeed phosphorus analogues of ferrocene comes from single-crystal *X*-ray diffraction studies§ and their molecular structures are shown in Figure 1. Compounds (**5**) and (**6**) have sandwich structures; the two η^5-rings are eclipsed in both structures. In both (**5**) and (**6**) the disposition of the rings minimises inter-ring interaction of the Bu^t groups. Bond lengths and bond angles in (**5**) and (**6**) which are summarised in Figure 2 are comparable with data for the $[(CR)_4P]$ rings of 3,4-dimethylphospha-ferrocene.[8] The $^{31}P\{^1H\}$ n.m.r. spectra indicate that the same structures obtain in solution although evidence of some ring rotation is observed for (**6**) above $-40\,°C$.¶

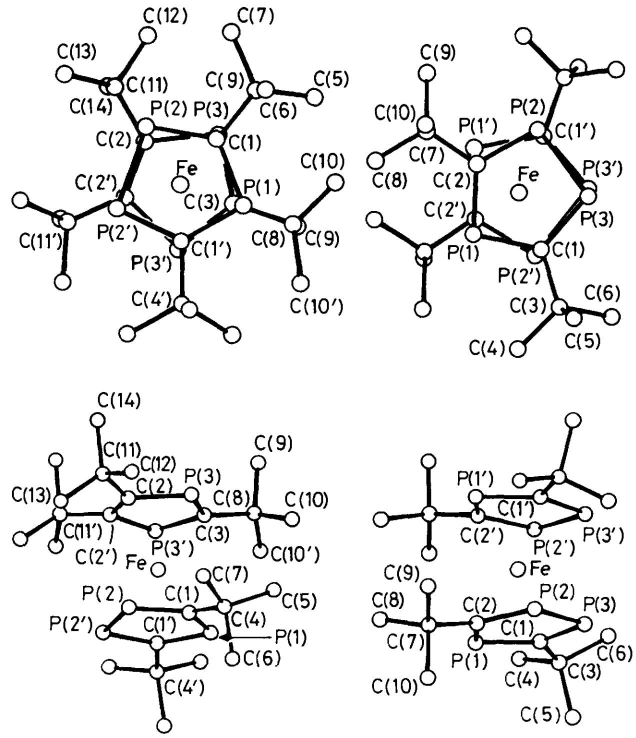

Figure 1. Two views of the molecular structures of (**5**) and (**6**).

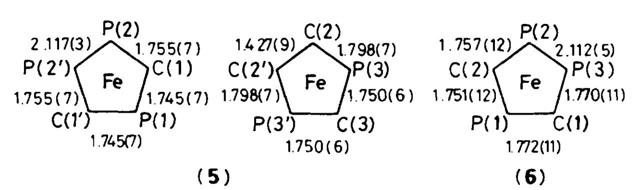

Figure 2. Bond lengths in (**5**) and (**6**) (Å). Bond lengths to iron: (**5**), from P(1) 2.330(3), P(2) 2.360(2), P(3) 2.316(2), C(1) 2.208(7), C(2) 2.192(7), C(3) 2.242(9); (**6**), from P(1) 2.330(3), P(2) 2.358(3), P(3) 2.359(3), C(1) 2.197(11), C(2) 2.222(12) Å.

These results on the $[(RC)_2P_3]$ and $[(RC)_3P_2]$ ring systems further extend the utility of phospha-alkynes as ligands in organotransition metal chemistry,[11] and together with very recent reports of transition metal complexes containing planar

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‡ No preparative details of $[Li(dme)_3][C_2R_2P_3]$ ($R = Bu^t$) are given in ref. 7 but the compound has been fully characterised by ^{31}P n.m.r. spectroscopy and an unpublished single crystal *X*-ray study. Our results suggest that $[Li(dme)_3][C_3R_3P_2]$ is also present in the reaction mixture {a singlet at δ_P + 45 p.p.m. (relative to trimethyl phosphite) can be assigned to the $[C_3R_3P_2]$ anion}. This is currently under further study.

Mass spectra: (**5**): *m/z* 556 (M^+), 418 $[FeP_5C_3Bu^t_3]^+$ 256 $[FeP_2C_2Bu^t_2]^+$, 200 $[P_2C_2Bu^t_2]^+$, 169 $[PC_2Bu^t_2]^+$. 518 (M^+), 380 $[FeP_6C_2Bu^t_2]^+$, 218 $[FeP_3CBu^t]^+$, 156 $[FePCBu^t]^+$.

§ *Crystal data:* (**5**), $C_{25}H_{45}FeP_5$, M = 556.4, orthorhombic, space group *Pnam*, a = 16.629(3), b = 10.379(2), c = 16.844(2) Å, U = 2907.1 Å^3, Z = 4, D_c = 1.27 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 8.0 cm^{-1}. The structure was solved by routine heavy-atom methods and refined by full-matrix least-squares with anisotropic thermal parameters using 1839 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer. Hydrogen atoms were omitted. The final residuals were R = 0.067, R_w = 0.092. The molecule lies on a crystallographic mirror plane.

(**6**), $C_{20}H_{36}FeP_6$, M = 518.2, orthorhombic, space group $C222_1$, a = 11.480(2), b = 16.405(2), c = 13.566(4) Å, U = 2554.8 Å^3, Z = 4, D_c = 1.35 g cm^{-3}, monochromated Mo-K_α radiation, μ = 9.7 cm^{-1}.

The structure analysis was as for (**5**) except that R = 0.064, R_w = 0.077 for 944 reflections with $I > \sigma(I)$. The molecule lies on a crystallographic two-fold rotation axis.

In both molecules the five-membered rings are planar and approximately parallel. In (**5**) the angle between the planes is 1° and in (**6**) it is 8°.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Cystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ N.m.r. spectra: ^1H, (**5**), δ 1.58 (s), 1.56 (s), and 1.27 (s) (relative intensity 2:2:1); (**6**), δ 1.50 (s). $^{31}P\{^1H\}$ (relative to trimethyl phosphite), (**5**), AB_2, δ + 49.0 (P^A) and 48.1 p.p.m. (P^B), $J(P^AP^B)$ 44 Hz; (**6**), AA'BB'CC', δ 79.0 (P^A), 71.0 (P^B), and 32.0 p.p.m. (P^C), ^1J (P^BP^C) 411.2, ^2J (P^AP^B 37.9, ^2J (P^AP^C) 42, ^2J ($P^CP^{C'}$) ~53 Hz; other inter-ring coupling constants are insignificant. This spectrum has been fully analysed and simulated by Dr. A. G. Avent. The temperature dependence of the ^{31}P and ^1H n.m.r. spectra of (**6**) along with the large inter-ring $^2J(P^CP^{C'})$ coupling constant and their implications will be discussed in a later publication.

η^6-P_6,[9] η^5-P_5,[6,10] η^4-$[(CR)_2P_2]$,[10,12] and η^4-$[(CR)_3P]$[13] ring systems strongly suggests to us that families of planar $[(CR)_mP_n]$ rings (n = 4—0, m = 0—4; n = 5—0, m = 0—5: n = 6—0, m = 0—6), stabilised in suitable metal complexes should be capable of synthesis. Routes to planar $[P_4]$, $[(CR)_3P_3]$, and related ring systems are currently under study.

The considerable ligating potential of the $[\eta^5$-$C_2R_2P_3]$ ring system is further suggested by a preliminary study in which $[Li(dme)_3][C_2R_2P_3]$ (R = Bu^t) reacts with $[MnBr(CO)_5]$ to afford a thermally stable orange oil whose mass spectrum exhibits a molecular ion and the expected fragmentation pattern for $[Mn(\eta^5$-$C_2R_2P_3)(CO)_3]$ (R = Bu^t), analogous to $[Mn(\eta^5$-$C_5H_5)(CO)_3]$ and $[Mn(\eta^5$-$C_4R_4E)(CO)_3]$[14] (R = Ph, E = P or As).

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