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Reactions of Co-ordinated Phosphines and Arsines. Iron(II)-facilitated Syntheses of 1-Phenylphosphetane and 1-Phenylarsetane

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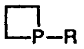
Phenylphosphine in the complex (R^*,R^*)-$(\pm)$-$[Fe(\eta\text{-}C_5H_5)\{C_6H_4(PMePh)_2\text{-}1,2\}(PH_2Ph)]PF_6$ was treated with 1,3-dibromopropane in the presence of KOBu^t to give 1-phenylphosphetane; similarly, $(\pm)$-(3-chloropropyl)phenylarsine was converted into 1-phenylarsetane.

The cyclooligomerization of epoxides by various metal compounds into crown ethers[1] presents the tantalizing prospect of a facile and perhaps stereoselective synthesis of a macrocyclic poly(tertiary phosphine or arsine) by a similar strategy. Macrocycles of this type, which contain pyramidally stable phosphorus or arsenic stereocentres, are difficult to obtain in configurationally homogeneous form by classical methods.[2] Hitherto, however, there has been no experimental evidence concerning the parent phosphorus-substituted phosphetanes **1**,[3] and the synthesis of free arsenic-substituted arsetanes **2** by the previously published procedure[4] is currently being reinvestigated (since deprotonation of free $(\pm)$-(3-chloropropyl)phenylarsine leads to extensive oligomerization of the intermediate arsenide). Accordingly, we have performed metal-template syntheses of 1-phenylphosphetane **1** (R = Ph) and 1-phenylarsetane **2** (R = Ph) with the view to establishing routes to the co-ordinated molecules and the structures of the complexes.

Thus $\mathbf{3}\cdot 0.5CH_2Cl_2$,[5] when treated with 1,3-dibromopropane and 1,8-diazabicyclo[5.4.0]undec-7-ene in tetrahydrofuran (thf), affords complex **4**. The salt was isolated in 85% yield as friable yellow needles of the hemidichloromethane solvate $\mathbf{4}\cdot 0.5CH_2Cl_2$,† or, in considerably lower yield as the fractional mixed solvate $\mathbf{4}\cdot 0.75C_6H_6\cdot 0.25CHCl_3$. Crystals of the latter form of the complex were suitable for X-ray crystallography.‡



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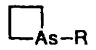

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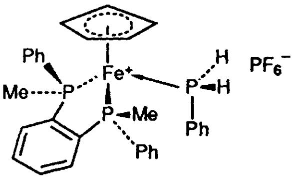

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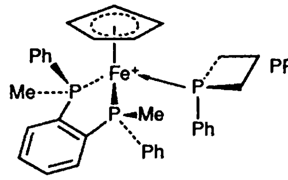

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The phenylarsine analogue of complex **3** could not be prepared by the method used to prepare complex **3** itself, indeed, well characterized transition-metal derivatives of primary arsines are rare.[6] The secondary arsine complex **5**, however, which was prepared from $(\pm)$-(3-chloropropyl)phenylarsine,[7] is readily isolated,§ and deprotonation of **5** with KOBu^t in thf[8] affords complex **6** in high yield.¶ The crystal structure of **6** has been determined.||

The molecular structures of the cations in complexes **4** and **6** are shown in Figs. 1 and 2, respectively. The 1-phenylphosphetane complex crystallizes with two independent molecules of C_1 symmetry in the unit cell. The structural

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† Selected spectroscopic data for $\mathbf{4}\cdot 0.5CH_2Cl_2$. NMR: ^1H (300 MHz, CD_2Cl_2, standard $SiMe_4$) δ 0.85–2.40 (6 H, m, $CH_2CH_2CH_2$), 2.09 [3 H, d, $|^2J(PH)|$ 8.2, PMe], 2.43 [3 H, d, $|^2J(PH)|$ 8.8 Hz, PMe] and 6.70–8.00 (19 H, m, aryl H); ^{13}C (75.43 MHz, $CDCl_3$, standard $SiMe_4$) δ 23.36 [d, $|^2J(PC)|$ 18.5, $CH_2\mathit{C}H_2CH_2$], 25.79 [d, $|^1J(PC)|$ 31.9, $\mathit{C}H_2CH_2CH_2$] and 28.56 [d, $|^1J(PC)|$ 34 Hz, $CH_2CH_2\mathit{C}H_2$]; ^{31}P (121.42 MHz, $CDCl_3$, standard H_3PO_4) $\delta(P_A)$ 79.70, $\delta(P_B)$ 80.73 and $\delta(P_X)$ 99.47 [m, ABX system, $|^2J(P_AP_B)|$ 44.2, $|^2J(P_AP_X)|$ 50.7, $|^2J(P_BP_X)|$ 49.2 Hz].

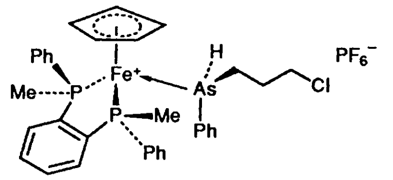
‡ *Crystal data for* $\mathbf{4}\cdot 0.75C_6H_6\cdot 0.25CHCl_3$: $C_{38.75}H_{40.75}Cl_{0.75}F_6FeP_4$, M_r = 826.82, dark brown crystals from benzene–chloroform; space group $P2_1/n$, a = 22.491(14), b = 14.477(14), c = 25.516(17) Å, β = 112.55(5)°, U = 7673(10) Å^3, Z = 8, D_c = 1.431 g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator, μ = 6.6 cm^{-1}. Data were collected at −125 °C on a Nicolet XRD P3 diffractometer. A total of 13 243 unique reflections were recorded in the range $2 \leqslant 2\theta \leqslant 50°$, of which 3484 with $I > 3\sigma(I)$ were regarded as observed. The structure was solved by direct methods and refined by a full-matrix least-squares procedure, R = 0.087.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

§ Complex **5** was obtained as a mixture of two diastereomers from (R^*,R^*)-$(\pm)$-$[Fe(\eta^5\text{-}C_5H_5)\{C_6H_4(PMePh)_2\text{-}1,2\}(NCMe)]PF_6$ (7.95 mmol) and $(\pm)$-$HAs(Ph)[(CH_2)_3Cl]$ (10 mmol) in boiling ethanol. NMR: ^{31}P (121.42 MHz, CD_2Cl_2, standard H_3PO_4) $\delta(P_A)$ 83.3 and $\delta(P_B)$ 80.7 [2 d, AB system, $|^2J(P_AP_B)|$ 44.0], $\delta(P_A)$ 83.0 and $\delta(P_B)$ 81.8 [2 d, AB system, $|^2J(P_AP_B)|$ 43.5 Hz]; fast atom bombardment (FAB) mass spectroscopy m/z 673 ($C_{34}H_{37}As^{35}Cl^{56}FeP_2$, M^+). Satisfactory elemental analysis was obtained.

¶ Selected spectroscopic data for **6**. NMR (CD_2Cl_2): ^1H (300 MHz, standard $SiMe_4$) δ 1.2–2.6 (6 H, m, $CH_2CH_2CH_2$); ^{13}C (75.43 MHz, standard $SiMe_4$, arsetane ring) δ 26.23, 26.14 and 24.41; ^{31}P (121.42 (MHz, standard H_3PO_4) $\delta(P_A)$ 82.1 and $\delta(P_B)$ 80.9 [2 d, AB system, $|^2J(P_AP_B)|$ 44.6 Hz]; FAB mass spectroscopy m/z 637 ($C_{34}H_{36}As^{56}FeP_2$, M^+).

|| *Crystal data for* **6**: $C_{34}H_{36}AsF_6FeP_3$, M_r = 782.34, orange-red prisms from dichloromethane–diethyl ether; space group $P2_12_12_1$; a = 14.021(2), b = 14.846(2), c = 16.504(2); U = 3435.4(7) Å^3; Z = 4; D_c = 1.512 g cm^{-3}; Cu-Kα radiation (λ = 1.5418 Å); μ = 64.6 cm^{-1}; Philips PW 1100/20 diffractometer; θ–2θ scan method. A total of 3211 unique data were collected of which 2221 with $I > 3\sigma(I)$ were refined. The structure was solved by the heavy-atom method and refined anisotropically by a full-matrix procedure; R = 0.058.



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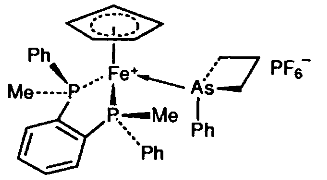

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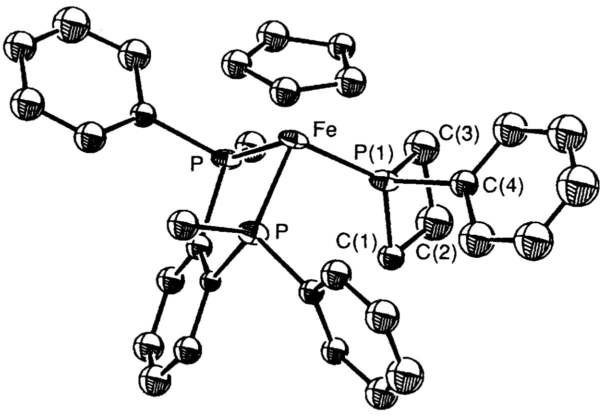

Fig. 1 An ORTEP plot of cation A of the complex $4\cdot0.75C_6H_6\cdot0.25CHCl_3$ with key atoms numbered. Hydrogen atoms have been omitted for clarity. Selected interatomic distances, angles and torsion angles (and the corresponding values of cation B) are Fe–P(1) 2.193(7) [2.184(6)], P(1)–C(4) 1.88(2) [1.87(2)], P(1)–C(1) 1.85(2) [1.86(3)], P(1)–C(3) 1.87(2) [1.90(2)], C(1)–C(2) 1.49(3) [1.60(3)] and C(2)–C(3) 1.58(3) [1.51(4)] Å; Fe–P(1)–C(4) 115.3(6) [115.6(8)], Fe–P(1)–C(1) 128.3(8) [128.9(6)], Fe–P(1)–C(3) 124.6(8) [124.8(8)], P(1)–C(1)–C(2) 92(1) [90(1)], C(1)–C(2)–C(3) 98(2) [98(2)], P(1)–C(3)–C(2) 89(1) [91(1)] and C(1)–P(1)–C(3) 77.6(8) [77(1)]°; C(3)–P(1)–C(1)–C(2) 12(2) [15(1)], C(1)–P(1)–C(3)–C(2) −11(1) [−16(1)], P(1)–C(1)–C(2)–C(3) −14(2) [−19(2)] and C(1)–C(2)–C(3)–P(1) 14(2) [18(2)]°

data agree well with those calculated for phosphetane $(\mathrm{H\overline{PCH_2CH_2CH_2}})$[9] and with those determined for various ring-substituted phosphetane oxides and phosphetanium salts.[10] To our knowledge, compound **6** is the first arsetane complex to be isolated, and there are no other structural data available on the arsacyclobutane ring. Notably, however, substituted phospha- and arsa-cyclobutenes have recently been isolated and structurally characterized.[11] The As–C and C–C distances within the four-membered ring of complex **6** are typical of single bonds. The Fe–As bond is elongated with respect to the sum of the covalent radii (2.28 Å), but is almost identical to that in $[Fe(\eta\text{-}C_5H_5)(CO)_2(AsPh_3)][BF_4]$.[12]

We are presently seeking methods of displacement of the four-membered heterocycles from complexes **4** and **6** and related complexes in order to investigate cyclooligomerization reactions of the monomers under metal-template conditions.

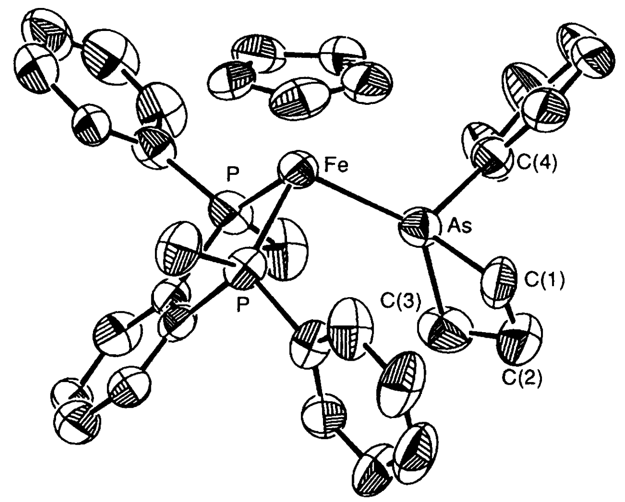

Fig. 2 An ORTEP plot of the cation of complex **6** with key atoms numbered. Hydrogen atoms have been omitted for clarity. Selected interatomic distances, angles and torsion angles are Fe–As 2.326(2), As–C(4) 1.953(12), As–C(1) 1.974(13), As–C(3) 2.004(12), C(1)–C(2) 1.55(2) and C(2)–C(3) 1.52(2) Å; Fe–As–C(4) 113.5(4), Fe–As–C(1) 129.9(4), Fe–As–C(3) 131.4(4), As–C(1)–C(2) 91.0(9), C(1)–C(2)–C(3) 100(1), As–C(3)–C(2) 90.8(9) and C(1)–As–C(3) 72.5(6)°; C(3)–As–C(1)–C(2) 15.6(8), C(1)–As–C(3)–C(2) −15.9(8), As–C(1)–C(2)–C(3) −20(1) and C(1)–C(2)–C(3)–As 20(1)°

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