Direct Syntheses of 1-Phenylphosphetane and 1-Phenylphosphirane. Crystal and Molecular Structures of Cyclotrimerisation Precursor Complexes *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2CH_2)_3}]$ and *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2)_3}]$

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Dilithium phenylphosphide reacts with 1,3-dichloropropane or 1,2-dichloroethane to give 1-phenylphosphetane or 1-phenylphosphirane, respectively; the free phosphines have been used to prepare the cyclotrimerisation precursor complexes *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2CH_2)_3}]$ and *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2)_3}]$.

Strained three- and four-membered phosphorus heterocycles are potential building blocks for macrocyclic poly(tertiary phosphines) by cyclooligomerisation on metal templates. For such syntheses, which are known for the conversion of oxirane into crown ethers,[1] *P*-substituted phosphiranes and phosphetanes are required with minimal substitution in the rings to facilitate oligomerisation and to reduce the number of product diastereoisomers. Two ideal molecules for attempted cyclooligomerisation under metal template conditions are 1-phenylphosphetane **1** and 1-phenylphosphirane **2**. Hitherto, however, there is no reported synthesis of free **1** and the literature synthesis of **2** produces 1 equiv. of phenylphosphine as byproduct,[2] which is difficult to remove without decomposition of the otherwise stable heterocycle. Previously,[3] we reported the synthesis of **1** in the complex (R^*,R^*)-($\pm$)-$[(\eta^5\text{-}\mathrm{C_5H_5})\{1,2\text{-}\mathrm{C_6H_4(PMePh)_2}\}\mathrm{Fe(PhPCH_2CH_2CH_2)}]\mathrm{PF_6}\cdot 0.5\,\mathrm{CH_2Cl_2}$, **3**; we are not aware of the synthesis of a coordination complex of **2**. A number of di- to penta-methyl-substituted 1-phenylphosphetanes have been isolated following reduction of the corresponding highly substituted phosphine oxides,[4] and 3-*tert*-butyl-1-phenylphosphetane has been prepared by heteroatom transfer between a 3-*tert*-butyltitanacyclobutane and dichlorophenylphosphine.[5] 2-Methyl-1-*tert*-butylphosphirane was prepared in low yield by a direct synthesis involving dilithium *tert*-butylphosphide and 1,2-dichloropropane.[6] We now report that both **1** and **2** can be prepared by direct syntheses between dilithium phenylphosphide and the respective dichloroalkane, and that the distilled products can be used to prepare potential cyclotrimerisation precursor complexes.

Thus, treatment of a suspension of dilithium phenylphosphide, which was prepared from phenylphosphine (97 mmol) and 2.2 equiv. *n*-butyllithium in THF, with 1,3-dichloropropane (89 mmol) at −78 °C, followed by stirring of the reaction mixture at room temp. for 18 h, gave a *ca.* 1 : 3 mixture of **1** and poly(phenylphosphino)propane **4**.[7] (It had been noted previously that this reaction gave **4** only, the ^{31}P NMR spectrum showing a resonance at δ −27.[5]) Removal of solvent, followed by extraction of the residue with light petroleum (bp 40–60 °C) and subsequent distillation, gave **1** as a colourless oil, bp 63 °C (0.05 mmHg). The yield based on 1,3-dichloropropane was 13%.† Pure **1** rearranges rapidly to **4**, but the rate of polymerisation is reduced substantially by quickly diluting the distillate with benzene, whereupon a solution of **1** : **4** *ca.* 4 : 1 of considerable stability is obtained. The ^{31}P NMR spectrum of the mixture in $\mathrm{C_6D_6}$ contains a sharp singlet at δ 13.9 for the phosphetane and a singlet at δ −27.2 for the poly(phenylphosphino)propane. A similar reaction between dilithium phenylphosphide and 1,2-dichloroethane afforded **2** in 21% yield after distillation, bp 48 °C (1 mmHg), δ_P −236 [Lit.[2] bp 44–48 °C (1.5 mmHg), δ_P −234] and some higher boiling 1,4-diphenyl-1,4-diphosphirane[8] and 1,2,3-triphenyl-1,2,3-triphospholane.[9] 1-Phenylphosphorinane can be stored at 0 °C for 1 month without signs of polymerisation. It is noteworthy that the chemical shift values for the phosphorus nuclei in the heterocycles $\mathrm{PhP{-}(CH_2)}_n$ (rel. to 85% aq. $\mathrm{H_3PO_4}$) are maximum for the phosphetane ($n = 3$), *viz.* δ −236 ($n = 2$), 13.9 ($n = 3$), −15.3 ($n = 4$),[10] and −34.3 ($n = 5$).[10]

Benzene solutions of **1** and **2** react with tricarbonyl(η^6-mesitylene)molybdenum(0) to give high yields of *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2CH_2)_3}]$ **5** and *fac*-$[\mathrm{Mo(CO)_3(PhPCH_2CH_2)_3}]$ **6** respectively,‡ both of which were isolated as colourless crystals suitable for X-ray crystallography.§ Complex **6** is the first coordination complex of **2** to be isolated to our knowledge. The molecular structure of **5** and **6**, are shown in Figs. 1 and 2, respectively. Both molecules have C_3 symmetry in the solid state. The thermal ellipsoid for the central carbon C(3) of each phosphetane ring in **5** is elongated perpendicular to the C(2)–P–C(4) plane, consistent with conformational disorder over two sites. Calculations on phosphetane ($\mathrm{HPCH_2CH_2CH_2}$) indicated a similarity in energies between two conformers of C_s symmetry, with a pucker angle of 155.63° and a barrier to ring flipping of 5.81 kJ mol^{-1}.[11] The precision of the data for the phosphetane ligands in **5** is greater than those obtained for corresponding ligand in **3**.[3] X-Ray crystal structure determinations have also been performed on the complexes *cis*-dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum(II)[5] and tricarbonylbis(*trans*-2,2,3,4,4-pentamethyl-1-phenylphosphetane)iron(0).[12] An interesting feature of the structures of **5** and **6** is that the phenyl groups in **5** are arranged *anti* to the carbonyl ligands, whereas in **6** the phenyl groups form a belt around the middle of the molecule *syn* to the carbonyls. The reason for the disparity is unclear, but it emphasises the effect small differences in ligand constitution can have on the structure of a

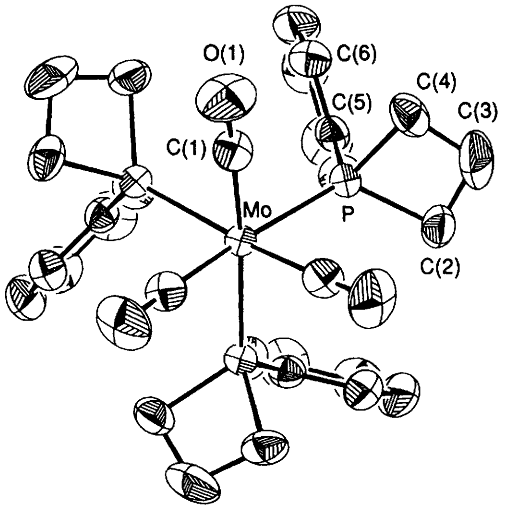

Fig. 1 An ORTEP plot of complex **5** with key atoms numbered. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°), and torsion angles (°), are as follows: Mo–P 2.502(1), P–C(2) 1.850(6), P–C(4) 1.861(6), P–C(5) 1.830(4), C(2)–C(3) 1.481(10), C(3)–C(4) 1.528(10); Mo–P–C(2) 120.84(17), Mo–P–C(4) 118.36(18), Mo–P–C(5) 123.83(14), C(2)–P–C(4) 77.2(2), C(2)–C(3)–C(4) 100.6(6), P–C(4)–C(3) 89.1(4), P–C(2)–C(3) 90.9(4); C(4)–P–C(2)–C(3) −10.4(4), P–C(2)–C(3)–C(4) 12.6(5), C(2)–C(3)–C(4)–P −12.5(5), C(2)–P–C(4)–C(3) 10.1(4).

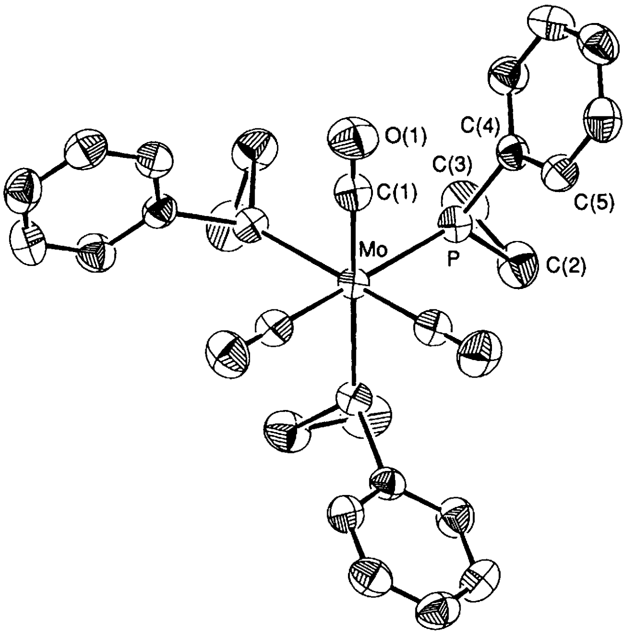

Fig. 2 An ORTEP plot of complex **6** with key atoms numbered. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) are as follows: Mo–P 2.4945(6), P–C(2) 1.826(3), P–C(3) 1.820(2), P–C(4) 1.818(2), C(2)–C(3) 1.509(5); Mo–P–C(2) 130.36(9), Mo–P–C(3) 132.95(12), Mo–P–C(4) 117.22(7), C(2)–P–C(3) 48.88(16), P–C(2)–C(3) 65.36(18), P–C(3)–C(2) 65.75(15).

complex. It is evident from the structural data for **5** and **6** that the three small heterocycles in each case are arranged correctly for cyclotrimerisation into highly desirable face-capping tridentates under suitable conditions.

Received, 24th September 1993; Com. 3/05784D

Footnotes

† *Selected spectroscopic data* for **1**: ^{1}H NMR (200.04 MHz, CD_2Cl_2) δ 1.8–2.8 (m, 6 H, $CH_2CH_2CH_2$), 7.15–7.60 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (50.31 MHz, CD_2Cl_2) δ 22.41 (d, $^1J_{CP}$ 7.04 Hz, α-CH_2), 24.75 (d, $^2J_{CP}$ 3.02 Hz, β-CH_2); $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6, ref. H_3PO_4) δ 13.9.

‡ *Selected spectroscopic data* for **5**: ^{1}H NMR (299.95 MHz, CD_2Cl_2) δ 1.89–2.50 (m, 18 H, $CH_2CH_2CH_2$), 7.23–7.42 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (125.70 MHz, CD_2Cl_2) δ 24.46 (m, $CH_2\mathit{C}H_2CH_2$), 28.52 (m, $\mathit{C}H_2CH_2\mathit{C}H_2$); $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, ref. H_3PO_4) δ 64.25; IR ν_{CO}/cm^{-1} (CH_2Cl_2: 1848, 1941; FAB MS *m/z* 630 ($C_{30}H_{33}{}^{96}MoO_3P_3$, M$^{\cdot+}$). Satisfactory elemental analyses were obtained.

For **6**: ^{1}H NMR (200.04 MHz, CD_2Cl_2) δ 0.89–1.48 (m, 12 H, CH_2CH_2) 7.15–7.50 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (125.70 MHz CD_2Cl_2) δ 10.31 (m, CH_2CH_2); $^{31}P\{^1H\}$ NMR (80.98 MHz, CD_2Cl_2, ref. H_3PO_4) δ −163.60; IR ν_{CO}/cm^{-1} (CH_2Cl_2) 1856, 1950; FAB MS *m/z* 588 ($C_{27}H_{27}{}^{96}MoO_3P_3$, M$^{\cdot+}$). Satisfactory elemental analyses were obtained.

§ *Crystal data* for **5**: $C_{30}H_{33}MoO_3P_3$, M_r = 630.46 g mol^{-1}; colourless, nearly spherical crystals from THF–diethyl ether; space group $I\bar{4}3d$; a = 22.966(2) Å; U = 12113(2) Å^3; Z = 16; D_c = 1.382 g cm^{-3}; μ(Mo-Kα) = 6.2 cm^{-1}; Phillips PW 1100/20 diffractometer; ω–2θ scan method. A total of 1377 unique data were collected in the range $4 \leqslant 2\theta \leqslant 57°$ of which 1075 $[I > 3\sigma(I)]$ were refined. The structure was solved by the heavy-atom method and refined anisotropically by a full-matrix procedure; R = 0.028.

For **6**: $C_{27}H_{27}MoO_3P_3$, M_r = 588.37 g mol^{-1}; colourless rhombohedral crystals from THF–diethyl ether; space group $P\bar{3}$; a = 14.321(1), c = 7.506(1) Å; U = 1333.2(2) Å^3; Z = 2; D_c = 1.456 g cm^{-3}; μ(Mo-Kα) = 7.0 cm^{-1}; Phillips PW 1100/20 diffractometer; ω-2θ scan method. A total of 2242 unique data were collected in the range $4 \leqslant 2\theta \leqslant 57°$ of which 1831 $[I > 3\sigma(I)]$ were refined. The structure was solved by the heavy-atom method and refined anisotropically by a full-matrix procedure; R = 0.024.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. Dale and K. Daasvatn, *J. Chem. Soc., Chem. Commun.*, 1976, 295; P. G. Jones, T. Gries, H. Grützmacher, H. W. Roesky, J. Schimkowiak and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 376; K. Meier and G. Rihs, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 858.
2 S. Chan, H. Goldwhite, H. Keyzer and D. G. Rowsell, *Tetrahedron*, 1969, **25**, 1097; G. A. Gray, S. E. Cremer and K. L. Marsi, *J. Am. Chem. Soc.*, 1976, **98**, 2109.
3 A. Bader, D. D. Pathak, S. B. Wild and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1992, 1751.
4 S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066.
5 W. Tumas, J. C. Huang, P. E. Fanwick and C. P. Kubiak, *Organometallics*, 1992, **11**, 2944.
6 M. Baudler and J. Germeshausen, *Chem. Ber.*, 1985, **118**, 4285.
7 S. Kobayashi, M. Suzuki and T. Saegusa, *Polym. Bull. (Berlin)*, 1982, **8**, 417.
8 P. J. Brooks, M. J. Gallagher, A. Sarroff and M. Bowyer, *Phosphorus Sulfur Silicon*, 1989, **44**, 235.
9 M. Baudler, J. Vesper and H. Sandmann, *Z. Naturforsch., Teil B*, 1972, **27**, 1007.
10 L. D. Quin, *The Heterocyclic Chemistry of Phosphorus*, Wiley, New York, 1981, p. 212.
11 S. M. Bachrach, *J. Phys. Chem.*, 1989, **93**, 7780.
12 D. W. Bennett, D. S. Grubisha, S. E. Cremer and A. C. Peterson, *J. Crystallogr. Spectrosc. Res.*, 1992, **22**, 83.