

A new synthetic route to ligands of the general composition $R_2PCH_2ER'_2$ ($E = P, As$) and some rhodium complexes derived thereof

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Symmetrical and unsymmetrical bis(phosphino)methanes $R_2PCH_2PR'_2$ (**8–16**) as well as the arsino(phosphino) analogues $R'_2AsCH_2PR_2$ (**21–25**) with bulky alkyl, cycloalkyl or aryl groups R and R' were prepared from the stannylated phosphines $R_2PCH_2SnR''_3$ (**3–5**, **6**, **7**) via metalation with MeLi or PhLi in the presence of tetramethylethylenediamine and subsequent treatment with R'_2P Cl or R'_2As Cl, respectively. Compound **25** [$R' = Cy$, $R = (R)$ -menthyl] is the first arsino(phosphino)methane which has been structurally characterized. The bis(phosphino)methanes $R_2PCH_2PR_2$ ($R = Pr^i$ **17**, Cy **18**) and $R_2PCH_2PR'_2$ (**12**, **19**, **20**) were also obtained by thermal reaction of $R_2PCH_2SnPh_3$ and the corresponding chlorophosphine R_2P Cl or R'_2P Cl in the absence of solvent. The bis(cyclooctene) derivative $[RhCl(C_8H_{14})_2]$ **26** reacted with excess $Pr^i_2PCH_2PPr^i_2$ to give $[Rh(\kappa^2P, P'-Pr^i_2PCH_2PPr^i_2)_2]Cl$ **27**, while treatment of **26** with $Ph_2PCH_2PPr^i_2$ yielded the chloro-bridged dimer $[RhCl(\kappa^2P, P'-Ph_2PCH_2PPr^i_2)_2]$ **28**. The reaction of the cationic species $[Rh(C_8H_{14})_2(OCMe_2)_2]PF_6$ **29** with $Cy_2PCH_2PPr^i_2$ in benzene or toluene afforded the half-sandwich-type complexes $[(\eta^6-C_6H_6)Rh(\kappa^2P, P'-Cy_2PCH_2PPr^i_2)]PF_6$ **30**, $[(\eta^6-C_6H_5CH_3)Rh(\kappa^2P, P'-Cy_2PCH_2PPr^i_2)]PF_6$ **31**, of which the latter was characterized by X-ray crystallography.

Ditertiary phosphines containing two phosphorus atoms which are linked together by a chain of CH_2 moieties are of major interest as mono- and bi-dentate ligands in transition-metal chemistry.¹ Since the coordination mode of these phosphines and therefore the reactivity of the complexes obtained thereof are strongly dependent on both the substituents at phosphorus and the length of the carbon bridging unit, a great variety of diphosphine ligands have been prepared.² Despite the large number of publications on their coordination chemistry,¹ only a few synthetic routes allowing the unrestricted variation of structural features are established for the preparation of ligands of the general composition $R_2P(CH_2)_nPR'_2$.^{2,3}

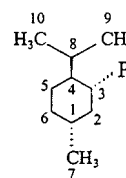
In the course of our continuous studies concerning the coordination capabilities of bifunctional (possibly hemilabile) phosphines,⁴ we recently set out to prepare sterically hindered donor systems in which one PR_2 unit is connected to an AsR_2 or SbR_2 fragment only by one methylene bridge.^{5,6} In order to introduce different elements of Group 15 as well as a variety of different organic substituents, we were particularly interested in developing a general methodology for bis(phosphino)methanes as well as their P–As and P–Sb analogues. Here we describe the preparation of a series of symmetrical and unsymmetrical compounds of the type $R_2PCH_2ER'_2$ ($E = P, As$) from the stannylated iodomethanes $ICH_2SnR''_3$ as starting materials, the molecular structure of one representative and with a few examples of how the bis(phosphino)methanes behave as ligands to rhodium(I) are illustrated. Some preliminary results of these studies have already been communicated.⁷

Experimental

All experiments were carried out under an atmosphere of argon using Schlenk techniques. The starting materials **1**, **2**,³⁵ **6**,⁵ **26**,³⁶ **29**,³⁷ R_2P Cl ($R = Pr^i$, Cy , Bu^t ,³⁸ $R = Men$ ³⁹), Mes_2PX ($X = Br, Cl$)⁴⁰ and R_2AsCl ($R = Pr^i$, Bu^t , Cy)^{41,42} were prepared

as described in the literature. Tetramethylethylenediamine (TMEDA) was a commercial product from Fluka. It was dried over CaH_2 and distilled prior to use. NMR spectra were recorded at room temperature on Bruker AC 200 and AMX 400 instruments. Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal; v, virtual signal [$N = J(PC) + J(P'C)$]. Melting points were measured by DTA. For the assignment of C(1)–C(10) in the menthyl derivatives see the procedure for the preparation of compound **3**. The phosphorus nuclei in bis(phosphino)methanes are assigned to the R_2P (P^1) and PR'_2 (P^2) fragments.

Preparations



Men₂PCH₂SnPh₃ 3. A solution of **1** (21.27 g, 43.32 mmol) in toluene (200 cm³) was treated at $-55^\circ C$ dropwise (over ca. 20 min) with a 2.73 M solution of Bu^tLi (16.00 cm³, 43.32 mmol) in hexane. The solution was stirred for 30 min and then a solution of Men_2P Cl (14.94 g, 43.32 mmol) in toluene (60 cm³) was added over ca. 10 min. The reaction mixture was slowly brought to room temperature and treated with water (50 cm³). The organic phase was separated, washed twice with 50 cm³ portions of water, carefully dried with Na_2SO_4 and then filtered. The filtrate was brought to dryness *in vacuo* and the residue was extracted with pentane (200 cm³). The extract was concentrated to ca. 40 cm³ *in vacuo*. Upon storing the solution at $-25^\circ C$ for 18 h, white crystals precipitated, which were separated from the mother-liquor, washed twice with 10 cm³ portions of pentane

(−40 °C) and dried: yield 20.18 g (69%); mp 121 °C (Found: C, 69.24; H, 9.09. C₃₉H₅₅PSn requires C, 69.55; H, 8.88%). NMR (C₆D₆): δ_C (50.3 MHz) 139.5 [d, J(PC) 1.8, J(^{119/117}SnC) 485.6, *ipso*-C of C₆H₅], 137.6 [d, J(PC) 1.3, J(^{119/117}SnC) 35.9, *ortho*-C of C₆H₅], 129.2 (s, *para*-C of C₆H₅), 128.8 [s, J(^{119/117}SnC) 50.1, *meta*-C of C₆H₅], 45.8 [d, J(PC) 19.2, CH(4)], 44.8 [d, J(PC) 9.4, CH(4)], 40.2 [d, J(PC) 19.1, CH(3)], 39.1, 36.3 [both s, CH₂(2)], 35.3, 35.2 [both s, CH₂(6)], 33.9, 33.7 [both s, CH(1)], 33.7 [d, J(PC) 23.8, CH(3)], 27.9 [d, J(PC) 20.7, CH(8)], 27.8 [d, J(PC) 27.1, CH(8)], 26.1 [d, J(PC) 8.4, CH₂(5)], 25.5 [d, J(PC) 6.3, CH₂(5)], 23.2, 23.0 [both s, CH₃(7)], 22.2, 22.0 [both s, CH₃(10)], 16.1, 15.7 [both s, CH₃(9)], 0.5 [d, J(PC) 45.6 Hz, PCH₂Sn]; δ_P(162.0 MHz) 31.8 [s, J(^{119/117}SnP) 115.5 Hz].

Men₂PCH₂SnMe₃ 4. This compound was prepared as described for **3**, from **2** (3.95 g, 12.95 mmol), a 1.83 M solution of BuⁿLi (6.80 cm³, 12.44 mmol) in hexane and Men₂PCL (4.26 g, 12.37 mmol). Recrystallization from acetone gave at −25 °C white crystals: yield 3.60 g (60%); mp 32 °C (Found: C, 59.54; H, 9.99. C₂₄H₄₉PSn requires C, 59.15; H, 10.14%). NMR (CDCl₃): δ_H(400 MHz) 2.70, 2.47 (1 H each, both m, CH), 1.83, 1.69, 1.40–0.92, 0.86, 0.80 (34 H, all br m, CH, CH₂ and CH₃ of PMen₂ and PCH₂Sn), 0.74, 0.66 [3 H each, both d, J(HH) 6.8, CH₃ of PMen₂], 0.13 [9 H, s, J(¹¹⁹SnH) 53.6, J(¹¹⁷SnH) 51.2 Hz, SnCH₃]; δ_C (100.6 MHz) 45.7 [d, J(PC) 19.4, CH(4)], 44.6 [d, J(PC) 9.5, CH(4)], 40.5 [d, J(PC) 18.5, CH(3)], 38.9, 38.8 [both s, CH₂(2)], 36.0, 35.2 [both s, CH₂(6)], 34.1, 33.6 [both s, CH(1)], 33.1 [d, J(PC) 26.1, CH(3)], 27.6 [d, J(PC) 15.1, CH(8)], 27.4 [d, J(PC) 19.8, CH(8)], 25.8 [d, J(PC) 8.5, CH₂(5)], 25.4 [d, J(PC) 7.0, CH₂(5)], 22.9, 22.7 [both s, CH₃(7)], 22.0, 21.7 [both s, CH₃(10)], 15.7, 15.4 [both s, CH₃(9)], −0.3 [d, J(PC) 42.3, J(¹¹⁹SnC) 328.7, J(¹¹⁷SnC) 246.5, PCH₂Sn], −8.4 [d, J(PC) 4.7, J(¹¹⁹SnC) 334.5, J(¹¹⁷SnC) 320.4 Hz, SnCH₃]; δ_P (162.0 MHz) −29.9 [s, J(^{119/117}SnP) 125.5 Hz].

Mes₂PCH₂SnPh₃ 5. A solution of **1** (4.22 g, 8.60 mmol) in toluene (80 cm³) was treated at −55 °C dropwise (over ca. 10 min) with a 2.73 M solution of BuⁿLi (3.15 cm³, 8.60 mmol) in hexane. The solution was stirred for 20 min and then TMEDA (3.70 cm³, 24.52 mmol) was added. After the reaction mixture was cooled to −80 °C, it was treated with a suspension of a mixture of Mes₂PBr and Mes₂PCL (ratio ca. 6:1; 2.88 g, ca. 8.53 mmol) in toluene (20 cm³) and stirred for 30 min. The solution was slowly brought to room temperature and treated with water (15 cm³). The organic phase was separated, washed three times with 5 cm³ portions of water, carefully dried with Na₂SO₄ and then filtered. The filtrate was brought to dryness *in vacuo*, the oily residue was dissolved in pentane (5 cm³), and the solution was chromatographed on Al₂O₃ (basic, activity grade III, height of column 10 cm). With pentane a colorless fraction was eluted, from which upon removal of the solvent a colorless oily solid was obtained. Recrystallization from hexane–ethanol (2:1) gave at −78 °C a colorless solid, which was separated from the mother-liquor, washed twice with 5 cm³ portions of ethanol and dried: yield 3.50 g (65%); mp 130 °C (Found: C, 70.74; H, 6.13. C₃₇H₃₉PSn requires C, 70.16; H, 6.21%). NMR (C₆D₆): δ_H(200 MHz) 8.03–7.65 (15 H, m, C₆H₅), 7.01 [2 H, d, J(PH) 2.4 Hz, C₆H₂], 2.78 (2 H, br s, PCH₂Sn), 2.71 (12 H, s, 2,6-H₃C-C₆H₂), 2.56 (6 H, s, 4-H₃C-C₆H₂); δ_C (50.3 MHz) 141.4 [d, J(PC) 13.9, *ortho*-C of C₆H₂], 138.7 [d, J(PC) 2.8, *ipso*-C of C₆H₅], 137.1 (s, *para*-C of C₆H₂), 136.7 [s, J(^{117/119}SnC) 38.4, *ortho*-C of C₆H₅], 134.8 [d, J(PC) 23.1, *ipso*-C of C₆H₂], 129.8 [d, J(PC) 2.3, *meta*-C of C₆H₂], 128.4 (s, *para*-C of C₆H₅), 128.2 (s, *meta*-C of C₆H₅), 23.0 [d, J(PC) 3.9, 2,6-H₃C-C₆H₂], 20.7 (s, 4-H₃C-C₆H₂), 10.3 [d, J(PC) 37.9 Hz, PCH₂Sn]; δ_P (81.0 MHz, CDCl₃) −25.1 [s, J(¹¹⁹SnP) 122.1, J(¹¹⁷SnP) 116.3 Hz].

Men₂PCH₂PMen₂ 8. A solution of **1** (13.20 g, 19.60 mmol) in diethyl ether (200 cm³) was treated with a 1.73 M solution of PhLi (11.04 cm³, 19.10 mmol) in cyclohexane–ether (1:1) and

stirred for 6 h at room temperature. During the time of reaction, a white solid precipitated. The reaction mixture was cooled to −50 °C, and then a solution of Men₂PCL (6.59 g, 19.10 mmol) in diethyl ether (100 cm³) was added over a period of 45 min. After the solution was stirred for 60 min at −25 °C, it was warmed to room temperature. The solvent was removed, the residue was extracted with pentane (250 cm³), and the extract was evaporated to dryness *in vacuo*. Recrystallization of the residue from propan-1-ol (170 cm³) gave, at −25 °C, white crystals, which were separated from the mother-liquor, washed three times with 10 cm³ portions of propan-1-ol (−40 °C) and dried: yield 7.84 g (65%); mp 162 °C (Found: C, 77.42; H, 12.53. C₄₁H₈P₂ requires C, 77.80; H, 12.42%). NMR (C₆D₆): δ_C (50.3 MHz) 46.8 (vt, N 20.5, CH), 44.8 (vt, N 11.2, CH), 40.5 (s, CH₂), 40.1 (vt, N 9.8, CH), 36.8, 35.4, 35.3 (all s, CH₂), 34.2 (s, CH), 33.1 (vt, N 22.7, CH), 28.0 (vt, N 22.3, CH), 27.7 (vt, N 26.1, CH), 26.3 (vt, N 7.9, CH₂), 25.6 (vt, N 6.1 Hz, CH₂), 23.2, 23.0, 22.4, 21.8, 15.7, 15.6 (all s, CH₃), 11.8 [t, J(PC) 28.5 Hz, PCH₂P]; δ_P (81.0 MHz, CDCl₃) −36.7 (s).

Men₂PCH₂PPr₂ 9. *Method A.* A solution of **2** (1.56 g, 3.20 mmol) in diethyl ether (35 cm³) was treated with a 1.48 M solution of MeLi (2.27 cm³, 3.26 mmol) in diethyl ether and stirred for 5 h at room temperature. The solution was cooled to −60 °C and Pr₂PCL (0.51 cm³, 3.20 mmol) was added. After the solution was slowly warmed to room temperature, the solvent was removed *in vacuo* and the oily residue was extracted with hexane (40 cm³). The extract was evaporated to dryness *in vacuo*. The remaining product was dissolved in ethanol–methanol (8 cm³, 1:1; 50 °C) and the solution was slowly cooled to −25 °C. After 18 h, white crystals precipitated which were separated from the mother-liquor, washed twice with 3 cm³ portions of methanol (−40 °C) and dried: yield 1.17 g (83%).

Method B. As described for method A, from **1** (13.64 g, 20.97 mmol), a 1.60 M solution of PhLi (13.10 cm³, 20.96 mmol) in cyclohexane–diethyl ether (1:1) and Pr₂PCL (3.37 cm³, 22.00 mmol): yield 7.00 g (76%); mp 84 °C (Found: C, 73.28; H, 12.56. C₂₇H₅₄P₂ requires C, 73.59; H, 12.35%). NMR (C₆D₆): δ_C (100.6 MHz) 46.0 [dd, J(P¹C) 18.9, J(P²C) 1.7, CH(4)], 44.8 [d, J(PC) 12.2, CH(4)], 39.1 [d, J(PC) 2.6, CH(2)], 38.0 [dd, J(P¹C) 18.6, J(P²C) 7.0, CH(3)], 36.4 [d, J(PC) 1.4, CH₂(2)], 35.1, 35.0 [both s, CH₂(6)], 33.9, 33.7 [both s, CH(1)], 33.0 [dd, J(P¹C) 22.9, J(P²C) 4.1, CH(3)], 27.6 [d, J(PC) 19.5, CH(8)], 27.4 [d, J(PC) 23.6, CH(8)], 25.8 [d, J(PC) 8.5, CH₂(5)], 25.2 [d, J(PC) 7.6, CH₂(5)], 24.6 [dd, J(P²C) 14.2, J(P¹C) 5.4, PCHCH₃], 24.0 [dd, J(P²C) 13.5, J(P¹C) 6.2, PCHCH₃], 22.8, 22.7 [both s, CH₃(7)], 21.7, 21.5 [both s, CH₃(10)], 19.9 [dd, J(P²C) 12.3, J(P¹C) 1.5, PCHCH₃], 19.8 [dd, J(P²C) 12.2, J(P¹C) 2.2, PCHCH₃], 19.3 [dd, J(P²C) 10.2, J(P¹C), PCHCH₃], 19.2 [dd, J(P²C) 9.6, J(P¹C) 1.4, PCHCH₃], 15.4, 15.3 [both s, CH₃(9)], 12.4 [dd, J(P¹C) 30.6, J(P²C) 27.0 Hz, PCH₂P]; δ_P (81.0 MHz, CDCl₃) −3.4 [d, J(PP) 102.4, Pr₂P], −34.0 [d, J(PP) 102.4 Hz, Men₂P].

Cy₂PCH₂PMen₂ 10. This was prepared as described for **9** (method A), from **4** (0.40 g, 0.83 mmol), a 1.48 M solution of MeLi (0.58 cm³, 0.86 mmol) in diethyl ether and Cy₂PCL (0.177 cm³, 0.83 mmol). White crystals: yield 0.35 g (82%); mp 57 °C (Found: C, 76.17; H, 11.50. C₃₃H₆₂P₂ requires C, 76.11; H, 12.00%). NMR (CDCl₃): δ_H (400 MHz) 2.74, 2.47 (1 H each, both m, CH), 1.87–1.50, 1.43–0.98 (42 H, all br m, PCH₂P and CH and CH₂ of Cy₂P and PMen₂), 0.86 (12 H, m, CH₃), 0.75, 0.66 [3 H each, both d, J(HH) 6.8 Hz, CH₃]; δ_C (100.6 MHz, C₆D₆) 45.9 [d, J(PC) 18.5, CH(4)], 44.9 [d, J(PC) 12.2, CH(4)], 39.1 [br s, CH₂(2)], 37.9 [dd, J(P²C) 20.7, J(P¹C) 7.5, CH(3)], 36.5 [s, CH₂(2)], 35.2, 35.1 [both s, CH₂(6)], 34.6 [dd, J(P¹C) 15.1, J(P²C) 6.1, PCHCH₂], 34.3 [dd, J(P¹C) 15.1, J(P²C) 7.1, PCHCH₂], 34.0, 33.8 [both s, CH(1)], 33.1 [dd, J(P²C) 25.2, J(P¹C) 5.0, CH(3)], 30.2 [d, J(PC) 12.5, PCHCH₂], 29.5 (m,

PCHCH₂), 27.9 [d, *J*(PC) 21.2, CH(8)], 27.7 [d, *J*(PC) 25.7, CH(8)], 27.5, 27.3, 26.6 (all s, CH₂ of PCy₂), 25.8 [d, *J*(PC) 8.5, CH₂(5)], 25.3 [d, *J*(PC) 7.1, CH₂(5)], 22.9, 22.8 [both s, CH₃(7)], 21.7, 21.6 [both s, CH₃(10)], 15.4, 15.3 [both s, CH₃(9)], 11.7 [dd, *J*(P²C) 30.2, *J*(P¹C) 26.4 Hz, PCH₂P]; δ_p (162.0 MHz, CDCl₃) -11.5 [d, *J*(PP) 108.5, Cy₂P], -34.1 [d, *J*(PP) 108.5 Hz, Men₂P]. For an alternative preparative procedure for **10** see ref. 11.

Men₂PCH₂PPh₂ 11. This was prepared as described for **9** (method A) from **4** (1.50 g, 3.10 mmol), a 1.74 M solution of MeLi (1.78 cm³, 3.10 mmol) in diethyl ether and Ph₂PCl (0.549 cm³, 3.10 mmol). White crystals: yield 1.34 g (85%); mp 72 °C (Found: C, 77.72; H, 9.95. C₃₃H₅₀P₂ requires C, 77.92; H, 9.91%). NMR (CDCl₃): δ_H (400 MHz) 7.46–7.36 (4 H, m, C₆H₅), 7.26–7.19 (6 H, m, C₆H₅), 2.56, 2.29 (1 H each, both m, CH), 2.19–2.08, 1.78–1.52, 1.42–1.20 (20 H, all br m, PCH₂P and CH and CH₂ of PMen₂), 0.77 (12 H, m, CH₃), 0.63, 0.58 [3 H each, both d, *J*(HH) 6.8 Hz, CH₃]; δ_C (100.6 MHz) 140.5 [dd, *J*(P²C) 15.7, *J*(P¹C) 9.1, *ipso*-C of C₆H₅], 139.8 [dd, *J*(P²C) 14.8, *J*(P¹C) 6.2, *ipso*-C of C₆H₅], 133.3 [d, *J*(PC) 20.0, *ortho*-C of C₆H₅], 132.4 [d, *J*(PC) 17.2, *ortho*-C of C₆H₅], 128.7, 128.3 (both s, *para*-C of C₆H₅), 128.2 [d, *J*(PC) 2.9, *meta*-C of C₆H₅], 128.1 [d, *J*(PC) 1.9, *meta*-C of C₆H₅], 45.6 [d, *J*(PC) 17.2, CH(4)], 45.0 [d, *J*(PC) 12.4, CH(4)], 39.1 [d, *J*(PC) 3.8, CH₂(2)], 38.1 [dd, *J*(P²C) 20.0, *J*(P¹C) 6.7, CH(3)], 36.6 [br s, CH₂(2)], 35.0, 34.9 [both s, CH₂(6)], 32.6, 32.7 [both s, CH(1)], 33.4 [dd, *J*(P²C) 24.3, *J*(P¹C) 8.1, CH(3)], 26.7 [d, *J*(PC) 20.0, CH(8)], 26.4 [d, *J*(PC) 25.8, CH(8)], 24.7 [d, *J*(PC) 8.6, CH₂(5)], 24.2 [d, *J*(PC) 8.6, CH₂(5)], 21.8, 21.7, 20.8, 20.5 [all s, CH₃(9) and CH₃(10)], 18.7 [dd, *J*(P²C) 31.5, *J*(P¹C) 20.0 Hz, PCH₂P], 14.3, 14.2 [both s, CH₃(7)]; δ_p (81.0 MHz) -19.8 [d, *J*(PP) 148.0, Ph₂P], -30.7 [d, *J*(PP) 148.0 Hz, Men₂P].

Cy₂PCH₂PPrⁱ₂ 12. *Method A.* A solution of **7** (4.75 g, 8.46 mmol) in diethyl ether (100 cm³) was treated with a 1.82 M solution of PhLi (6.80 cm³, 12.44 mmol) in cyclohexane–diethyl ether (1 : 1) and stirred for 5 h at room temperature. A white solid precipitated during the time of reaction. The reaction mixture was cooled to -78 °C, and then TMEDA (1.33 cm³, 8.37 mmol) and subsequently Prⁱ₂PCl (1.27 cm³, 8.34 mmol) were added. After the solution was stirred for 30 min at -78 °C, it was slowly warmed to room temperature. The solvent was removed, the residue was extracted with hexane (40 cm³), and the extract was evaporated to dryness *in vacuo*. The remaining oily product was suspended in pentane (3 cm³), and the suspension was chromatographed on Al₂O₃ (basic, activity grade I, height of column 12 cm). With pentane a colorless fraction was eluted, from which upon removal of the solvent a colorless liquid was obtained (ρ 1.16 g cm⁻³): yield 1.70 g (62%).

Method B. A mixture of **6** (1.28 g, 2.66 mmol) and Cy₂PCl (0.59 cm³, 2.66 mmol) was stirred vigorously for 20 min at 240 °C. After cooling to room temperature, extraction of the reaction mixture with pentane and chromatographic work-up as described above gave a colorless liquid: yield 0.64 g (73%).

Method C. As described for method B, from **7** (0.90 g, 1.60 mmol) and Prⁱ₂PCl (0.25 cm³, 1.60 mmol): yield 0.40 g (76%) (Found: C, 69.39; H, 11.81. C₁₉H₃₈P₂ requires C, 69.47; H, 11.66%). NMR (CDCl₃): δ_H (200 MHz) 1.72–1.53 (12 H, br m, PCHCH₃ and PCHCH₂), 1.35 (2 H, br s, PCH₂P), 1.19 (12 H, br m, CH₂ of PCy₂), 1.09 [6 H, dd, *J*(PH) 11.2, *J*(HH) 7.1, PCHCH₃], 1.07 [6 H, dd, *J*(PH) 13.6, *J*(HH) 7.0 Hz, PCHCH₃]; δ_C (50.3 MHz) 34.2 [dd, *J*(P¹C) 15.7, *J*(P²C) 6.0, PCHCH₂], 29.8 [dd, *J*(P¹C) 12.6, *J*(P²C) 1.4, PCHCH₂], 27.2 [d, *J*(PC) 10.4, CH₂ of PCy₂], 27.1 [d, *J*(PC) 8.0, CH₂ of PCy₂], 26.4 (s, CH₂ of PCy₂), 24.2 [dd, *J*(P²C) 14.3, *J*(P¹C) 6.0, PCHCH₃], 19.6 [dd, *J*(P²C) 13.8, *J*(P¹C) 1.7, PCHCH₃], 19.0 [dd, *J*(P²C) 10.9, *J*(P¹C) 1.4, PCHCH₃], 13.1 [dd, *J*(PC) 27.3, *J*(PC) 27.0 Hz, PCH₂P]; δ_p (81.0 MHz) -1.9 [d, *J*(PP) 100.0, Prⁱ₂P], -10.1 [d, *J*(PP) 100.0 Hz, Cy₂P].

Mes₂PCH₂PPrⁱ₂ 13. This was prepared as described for **12** (method A), from **5** (0.54 g, 0.85 mmol), a 1.75 M solution of PhLi (0.485 cm³, 0.83 mmol) in cyclohexane–diethyl ether (1 : 1), TMEDA (0.13 cm³, 0.83 mmol) and Prⁱ₂PCl (0.132 cm³, 0.83 mmol). Colorless, oily liquid (ρ 1.18 g cm⁻³): yield 285 mg (85%) (Found: C, 75.41; H, 10.00. C₂₅H₃₈P₂ requires C, 74.97; H, 9.56%). NMR (CDCl₃): δ_H (200 MHz) 6.86 [4 H, br d, *J*(PH) 2.6, C₆H₂], 2.59 [2 H, dd, *J*(P¹H) 4.9, *J*(P²H) 1.7, PCH₂P], 2.47 (12 H, s, 2,6-*H*₃C-C₆H₂), 2.31 (6 H, s, 4-*H*₃C-C₆H₂), 1.86 (2 H, m, PCHCH₃), 1.17 [6 H, dd, *J*(PH) 20.8, *J*(HH) 6.8, PCHCH₃], 1.09 [6 H, dd, *J*(PH) 22.6, *J*(HH) 7.0 Hz, PCHCH₃]; δ_C (50.3 MHz) 141.6 [d, *J*(PC) 13.4, *ortho*-C of C₆H₂], 137.1 (s, *para*-C of C₆H₂), 133.8 [dd, *J*(P¹C) 23.6, *J*(P²C) 7.9, *ipso*-C of C₆H₂], 129.7 [d, *J*(PC) 2.8, *meta*-C of C₆H₂], 24.3 [dd, *J*(P²C) 15.5, *J*(P¹C) 8.2, PCHCH₃], 23.3 [dd, *J*(P¹C) 12.8, *J*(P²C) 2.7, 2,6-*H*₃C-C₆H₂], 21.3 [dd, *J*(P²C) 26.9, *J*(P¹C) 22.9, PCH₂P], 20.7 (s, 4-*H*₃C-C₆H₂), 19.2 [br d, *J*(PC) 14.6, PCHCH₃], 18.7 [br d, *J*(PC) 11.1 Hz, PCHCH₃]; δ_p (81.0 MHz) -1.5 [d, *J*(PP) 149.7, Prⁱ₂P], -25.1 [d, *J*(PP) 149.7 Hz, Mes₂P].

Cy₂PCH₂PMes₂ 14. This was prepared as described for **12** (method A), from **5** (305 mg, 0.48 mmol), a 1.74 M solution of PhLi (0.275 cm³, 0.47 mmol) in cyclohexane–diethyl ether (1 : 1), TMEDA (0.072 cm³, 0.47 mmol) and Cy₂PCl (0.105 cm³, 0.47 mmol). Colorless, oily solid: yield 170 mg (74%) (Found: C, 77.89; H, 10.04. C₃₁H₄₆P₂ requires C, 77.46; H, 9.65%). NMR (CDCl₃): δ_H (200 MHz) 6.79 [4 H, br d, *J*(PH) 2.3, C₆H₂], 2.53 [2 H, dd, *J*(P²H) 3.9, *J*(P¹H) 1.4 Hz, PCH₂P], 2.32 (12 H, br s, 2,6-*H*₃C-C₆H₂), 2.24 (6 H, br s, 4-*H*₃C-C₆H₂), 1.85–1.47 (10 H, br m, PCHCH₂), 1.30–1.15 (12 H, br m, CH₂ of PCy₂); δ_C (50.3 MHz) 141.7 [d, *J*(PC) 13.9, *ortho*-C of C₆H₂], 137.2 (s, *para*-C of C₆H₂), 134.0 [dd, *J*(P²C) 23.6, *J*(P¹C) 7.9, *ipso*-C of C₆H₂], 129.8 [d, *J*(PC) 2.3, *meta*-C of C₆H₂], 34.3 [dd, *J*(P¹C) 16.2, *J*(P²C) 8.3, PCHCH₂], 29.4 [d, *J*(PC) 12.3, PCHCH₂], 27.3 [d, *J*(PC) 9.7, CH₂ of PCy₂], 26.5 (s, CH₂ of PCy₂), 23.4 [dd, *J*(P²C) 12.7, *J*(P¹C) 2.5, 2,6-*H*₃C-C₆H₂], 20.9 [dd, *J*(P¹C) 25.9, *J*(P²C) 22.7 Hz, PCH₂P], 20.7 (s, 4-*H*₃C-C₆H₂); δ_p (81.0 MHz) -8.4 [d, *J*(PP) 153.0, Cy₂P], -25.5 [d, *J*(PP) 153.0 Hz, Mes₂P].

Bu^t₂PCH₂PCy₂ 15. This was prepared as described for **12** (method A), from **7** (0.34 g, 0.60 mmol), a 1.52 M solution of PhLi (0.38 cm³, 0.60 mmol) in cyclohexane–diethyl ether (1 : 1), TMEDA (0.090 cm³, 0.59 mmol) and Bu^t₂PCl (0.109 cm³, 0.58 mmol). Colorless liquid: yield 130 mg (64%) (Found: C, 77.89; H, 10.04. C₃₁H₄₆P₂ requires C, 77.46; H, 9.65%). NMR (CDCl₃): δ_H (200 MHz) 1.82–1.58 (10 H, br m, PCHCH₂), 1.43 (2 H, br s, PCH₂P), 1.22–1.16 (12 H, br m, CH₂ of PCy₂), 1.13 [18 H, d, *J*(PH) 10.8 Hz, PCCH₃]; δ_C (50.3 MHz) 34.4 [dd, *J*(P²C) 15.5, *J*(P¹C) 6.2, PCHCH₂], 32.1 [dd, *J*(P¹C) 22.9, *J*(P²C) 5.1, PCCH₃], 29.9 [dd, *J*(P¹C) 13.0, *J*(P²C) 2.1, PCCH₃], 29.4 [br d, *J*(PC) 10.2, PCHCH₂], 27.3 [br d, *J*(PC) 9.5, CH₂ of PCy₂], 26.6 (s, CH₂ of PCy₂), 12.7 [dd, *J*(P¹C) 31.8, *J*(P²C) 26.7 Hz, PCH₂P]; δ_p (81.0 MHz) 20.1 [d, *J*(PP) 107.8, Bu^t₂P], -4.4 [d, *J*(PP) 107.8 Hz, Cy₂P].

Bu^t₂PCH₂PPrⁱ₂ 16. This was prepared as described for **12** (method A), from **6** (754 mg, 1.57 mmol), a 1.66 M solution of PhLi (0.93 cm³, 1.55 mmol) in cyclohexane–diethyl ether (1 : 1), TMEDA (0.23 cm³, 1.55 mmol) and Bu^t₂PCl (0.29 cm³, 1.53 mmol). Colorless liquid: yield 210 mg (50%). NMR (C₆D₆): δ_H (400 MHz) 1.79 [2 H, dsept, *J*(PH) 2.4, *J*(HH) 7.2, PCHCH₃], 1.43 (2 H, br s, PCH₂P), 1.14 [18 H, d, *J*(PH) 10.8, PCCH₃], 1.13 [6 H, dd, *J*(PH) 12.4, *J*(HH) 7.2, PCHCH₃], 1.09 [6 H, dd, *J*(PH) 12.0, *J*(HH) 6.8 Hz, PCHCH₃]; δ_C (50.3 MHz, CDCl₃) 31.8 [dd, *J*(P¹C) 22.9, *J*(P²C) 4.6, PCCH₃], 29.7 [dd, *J*(P¹C) 13.0, *J*(P²C) 2.0, PCCH₃], 24.1 [dd, *J*(P²C) 15.3, *J*(P¹C) 6.5, PCHCH₃], 19.7 [d, *J*(PC) 13.9, PCHCH₃], 19.1 [d, *J*(PC) 11.1, PCHCH₃], 13.4 [dd, *J*(P¹C) 33.1, *J*(P²C) 27.3 Hz, PCH₂P]; δ_p (162.0 MHz, CDCl₃) 19.0 [d, *J*(PP) 98.3, Bu^t₂P], 2.7 [d, *J*(PP) 98.3 Hz, Prⁱ₂P].

Prⁱ₂PCH₂PPrⁱ₂ 17. This was prepared as described for **12** (method B), from **6** (3.70 g, 7.69 mmol) and Prⁱ₂PCl (1.22 cm³, 7.68 mmol); colorless liquid: yield 1.52 g (80%). NMR (CDCl₃): δ_p (81.0 MHz) 1.3 (s). For other data see ref. 13.

Cy₂PCH₂PCy₂ 18. This was prepared as described for **12** (method B), from **7** (0.50 g, 0.89 mmol) and Cy₂PCl (0.198 cm³, 0.89 mmol); colorless solid: yield 0.29 g (80%). For analytical and spectroscopic data see ref. 14.

Ph₂PCH₂PPrⁱ₂ 19. This was prepared as described for **12** (method B), from **6** (0.85 g, 1.76 mmol) and Ph₂PCl (0.317 cm³, 1.76 mmol). Colorless, oily liquid: yield 0.41 g (74%). NMR (CDCl₃): δ_c (50.3 MHz) 139.5 [dd, *J*(P¹C) 14.8, *J*(P²C) 6.5, *ipso*-C of C₆H₅], 132.7 [d, *J*(PC) 18.7, *ortho*-C of C₆H₅], 128.4 (br s, *para*-C of C₆H₅), 128.2 [d, *J*(PC) 7.2, *meta*-C of C₆H₅], 24.1 [dd, *J*(P²C) 14.3, *J*(P¹C) 7.2, PCHCH₃], 20.7 [dd, *J*(P²C) 29.1, *J*(P¹C) 21.3, PCH₂P], 19.6 [br d, *J*(PC) 15.0, PCHCH₃], 18.8 [dd, *J*(P²C) 10.1, *J*(P¹C) 1.5 Hz, PCHCH₃]; δ_p (81.0 MHz, CDCl₃) -3.7 [d, *J*(PP) 119.5, Prⁱ₂P], -19.1 [d, *J*(PP) 119.5 Hz, Ph₂P]. For other data see ref. 15.

Cy₂PCH₂PPh₂ 20. This was prepared as described for **12** (method B), from **7** (0.92 g, 1.64 mmol) and Ph₂PCl (0.303 cm³, 1.64 mmol); colorless, oily solid: yield 0.38 g (58%) (Found: C, 76.05; H, 8.90. C₂₅H₃₄P₂ requires C, 75.73; H, 8.65%). NMR (CDCl₃): δ_H (200 MHz) 7.54–7.25 (10 H, m, C₆H₅), 2.13 [2 H, br d, *J*(P²H) 2.2 Hz, PCH₂P], 1.77, 1.24 (22 H, both br m, C₆H₁₁); δ_c (50.3 MHz) 139.6 [dd, *J*(P²C) 14.6, *J*(P¹C) 6.3, *ipso*-C of C₆H₅], 132.7 [d, *J*(PC) 18.7, *ortho*-C of C₆H₅], 128.3 [d, *J*(PC) 7.6, *meta*-C of C₆H₅], 128.1 (s, *para*-C of C₆H₅), 34.1 [dd, *J*(P¹C) 14.7, *J*(P²C) 6.6, PCHCH₂], 29.8 [d, *J*(PC) 13.6, PCHCH₂], 29.1 [d, *J*(PC) 8.6, PCHCH₂], 27.3 [d, *J*(PC) 4.8, CH₂ of PCy₂], 27.1 (br s, CH₂ of PCy₂), 26.4 (s, CH₂ of PCy₂), 20.4 [dd, *J*(P¹C) 28.4, *J*(P²C) 21.2 Hz, PCH₂P]; δ_p (81.0 MHz) -11.6 [d, *J*(PP) 120.6, Cy₂P], -19.1 [d, *J*(PP) 120.6 Hz, Ph₂P].

Prⁱ₂AsCH₂PPrⁱ₂ 21. This was prepared as described for **12** (method A), from **6** (1.19 g, 2.47 mmol), a 1.54 M solution of PhLi (1.60 cm³, 2.46 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.37 cm³, 2.45 mmol) and a solution of Prⁱ₂AsCl (476 mg, 2.42 mmol) in diethyl ether. Colorless liquid (ρ 1.15 g cm⁻³): yield 477 mg (67%); MS (CI, isobutane, 70 eV): *m/z* 294 [100, {Prⁱ₂AsCH₂PPrⁱ₂}⁺ + H]. NMR (CDCl₃): δ_H (200 MHz) 1.78 (4 H, br m, AsCHCH₃ and PCHCH₃), 1.34 (2 H, br s, AsCH₂P), 1.12 (24 H, br m, AsCHCH₃ and PCHCH₃); δ_c (50.3 MHz) 24.6 [d, *J*(PC) 5.5, AsCHCH₃], 24.4 [d, *J*(PC) 13.4, PCHCH₃], 20.5, 20.2 (both s, AsCHCH₃), 19.8 [br d, *J*(PC) 13.9, PCHCH₃], 19.1 [br d, *J*(PC) 10.2, PCHCH₃], 11.6 [d, *J*(PC) 31.4 Hz, AsCH₂P]; δ_p (81.0 MHz) -0.7 (s).

Bu^t₂AsCH₂PPrⁱ₂ 22. This was prepared as described for **12** (method A), from **6** (2.45 g, 5.09 mmol), a 1.35 M solution of PhLi (3.77 cm³, 5.08 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.76 cm³, 5.04 mmol) and a solution of Bu^t₂AsCl (1.11 g, 4.94 mmol) in diethyl ether. Colorless liquid: yield 1.16 g (73%). MS (CI, isobutane, 70 eV): *m/z* 321 [83, {Bu^t₂AsCH₂PPrⁱ₂}⁺ + H]; NMR (CDCl₃): δ_H (200 MHz) 1.70 [2 H, dsept, *J*(PH) 2.2, *J*(HH) 7.2, PCHCH₃], 1.35 (2 H, s, AsCH₂P), 1.11 (18 H, s, AsCCH₃), 1.05 [6 H, dd, *J*(PH) 11.7, *J*(HH) 6.9, PCHCH₃], 1.03 [6 H, dd, *J*(PH) 12.8, *J*(HH) 6.9 Hz, PCHCH₃]; δ_c (50.3 MHz) 33.0 [d, *J*(PC) 4.7, AsCCH₃], 30.1 [d, *J*(PC) 1.8, AsCCH₃], 24.7 [d, *J*(PC) 13.4, PCHCH₃], 19.7 [d, *J*(PC) 11.1, PCHCH₃], 19.5 [d, *J*(PC) 12.0, PCHCH₃], 12.1 [d, *J*(PC) 35.2 Hz, AsCH₂P]; δ_p (81.0 MHz) 1.6 (s).

Cy₂AsCH₂PPrⁱ₂ 23. This was prepared as described for **12** (method A), from **6** (1.78 g, 3.70 mmol), a 1.67 M solution of PhLi (2.20 cm³, 3.67 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.70 cm³, 3.58 mmol) and Cy₂AsCl (0.70 cm³, 3.58

mmol). Colorless liquid (ρ 1.17 g cm⁻³): yield 1.10 g (82%) (Found: C, 60.88; H, 10.52. C₁₉H₃₈AsP requires C, 61.28; H, 10.29%). NMR (CDCl₃): δ_H (200 MHz) 1.77–1.60 (12 H, br m, AsCHCH₂ and PCHCH₃), 1.34 (2 H, br s, AsCH₂P), 1.29–1.19 (12 H, br m, CH₂ of AsCy₂), 1.08 [12 H, br dd, *J*(PH) 12.3, *J*(HH) 7.0 Hz, PCHCH₃]; δ_c (50.3 MHz) 34.7 [d, *J*(PC) 6.0, AsCHCH₂], 30.8, 30.2 (both s, AsCHCH₂), 27.7, 26.5 (both s, CH₂ of AsCy₂), 24.5 [d, *J*(PC) 13.8, PCHCH₃], 19.8 [d, *J*(PC) 13.8, PCHCH₃], 19.1 [d, *J*(PC) 10.2, PCHCH₃], 10.7 [d, *J*(PC) 31.0 Hz, AsCH₂P]; δ_p (81.0 MHz) -0.7 (s).

Cy₂AsCH₂PCy₂ 24. This was prepared as described for **12** (method A), from **7** (2.06 g, 3.67 mmol), a 1.63 M solution of PhLi (2.24 cm³, 3.65 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.56 cm³, 3.70 mmol) and Cy₂AsCl (0.70 cm³, 3.60 mmol). Recrystallization from ethanol–hexane (3:1) gave at -30 °C colorless crystals: yield 1.15 g (71%); mp 62 °C (Found: C, 65.92; H, 10.22. C₂₅H₄₆AsP requires C, 66.34; H, 10.24%). NMR (CDCl₃): δ_H (200 MHz) 1.74–1.46 (20 H, br m, AsCHCH₂ and PCHCH₃), 1.35 (2 H, br s, AsCH₂P), 1.36–1.22 (24 H, br m, CH₂ of AsCy₂ and PCy₂); δ_c (50.3 MHz) 34.7 [d, *J*(PC) 6.0, AsCHCH₂], 34.6 [d, *J*(PC) 14.6, PCHCH₂], 30.8, 30.2 (both br s, AsCHCH₂), 30.1 [br d, *J*(PC) 14.3, PCHCH₂], 29.2 [d, *J*(PC) 8.8, PCHCH₂], 27.7 (s, CH₂ of AsCy₂), 27.5–27.2 (m, CH₂ of PCy₂), 26.6 (br s, CH₂ of AsCy₂ and PCy₂), 10.3 [d, *J*(PC) 30.8 Hz, AsCH₂P]; δ_p (81.0 MHz) -8.9 (s).

Cy₂AsCH₂PMen₂ 25. This was prepared as described for **12** (method A), from **4** (1.70 g, 3.50 mmol), a 1.05 M solution of MeLi (3.33 cm³, 3.50 mmol) in cumene–THF (9:1) and Cy₂AsCl (0.97 g, 3.50 mmol). Recrystallization from ethanol–hexane (10:1) gave at 4 °C colorless crystals: yield 1.36 g (69%); mp 67 °C (Found: C, 70.37; H, 11.32. C₃₃H₆₂AsP requires C, 70.18; H, 11.07%). NMR (CDCl₃): δ_H (200 MHz) 2.73, 2.47 (1 H each, both m, CH), 1.71, 1.50–0.81 (42 H, all br m, PCH₂P and CH and CH₂ of Cy₂P and PMen₂), 0.87 [6 H, br d, m, *J*(HH) 6.6, CH₃], 0.75 [3 H, d, *J*(HH) 6.7, CH₃], 0.66 [3 H, d, *J*(HH) 6.9 Hz, CH₃]; δ_c (50.3 MHz) 45.8 [d, *J*(PC) 18.0, CH(4)], 45.0 [d, *J*(PC) 12.3, CH(4)], 39.0 [d, *J*(PC) 2.9, CH₂(2)], 38.5 [d, *J*(PC) 20.1, CH(3)], 36.4 [s, CH₂(2)], 35.1 [br s, CH₂(6)], 34.8 [d, *J*(PC) 6.5, AsCHCH₂], 34.5 [d, *J*(PC) 6.9, AsCHCH₂], 34.0, 33.7 [both s, CH(1)], 33.2 [d, *J*(PC) 24.3, CH(3)], 30.9, 30.4, 30.2 (all s, CH₂ of AsCy₂), 27.9–27.6 [m, CH₂ of AsCy₂ and CH(8)], 27.3 [d, *J*(PC) 19.2, CH(8)], 26.7 (s, CH₂ of AsCy₂), 25.8 [d, *J*(PC) 8.3, CH₂(5)], 25.2 [d, *J*(PC) 7.4, CH₂(5)], 22.9, 22.8 [both s, CH₃(7)], 21.7, 21.6 [both s, CH₃(10)], 15.4 [br s, CH₃(9)], 9.8 [d, *J*(PC) 33.8 Hz, AsCH₂P]; δ_p (81.0 MHz) -32.5 (s).

[Rh(κ²P,P'-Prⁱ₂PCH₂PPrⁱ₂)₂]Cl 27. A suspension of 85 mg (0.12 mmol) of **26** in benzene (6 cm³) was treated with a solution of 179 mg (0.72 mmol) of **17** in hexane (3 cm³) and stirred for 10 min at room temperature. A yellow solid precipitated which was separated from the mother-liquor and washed three times with 4 cm³ portions of pentane and dried: yield 135 mg (90%); mp 90 °C (decomp.) (Found: C, 49.55; H, 10.00. C₂₆H₆₀ClP₄Rh requires C, 49.18; H, 9.52%). *λ* (MeNO₂) 111.5 cm² Ω⁻¹ mol⁻¹. NMR (C₆D₆-CDCl₃): δ_H (400 MHz) 2.79 (4 H, m, PCH₂P), 1.85 (8 H, m, PCHCH₃), 1.05 [24 H, m, in ¹H-³¹P} d, *J*(HH) 7.1, PCHCH₃], 0.97 [24 H, m, in ¹H-³¹P} d, *J*(HH) 6.8 Hz, PCHCH₃]; δ_c (50.3 MHz, CDCl₃) 27.0 [t, *J*(PC) 9.7 Hz, PCH₂P], 26.3 (vt, *N* 11.1 Hz, PCHCH₃), 19.8, 18.2 (both s, PCHCH₃); δ_p (81.0 MHz, CDCl₃) -8.4 [d, *J*(RhP) 111.5 Hz].

[[RhCl(κ²P,P'-Ph₂PCH₂PPrⁱ₂)₂]] 28. A suspension of 891 mg (1.24 mmol) of **26** in toluene (30 cm³) was treated at -20 °C with a solution of 800 mg (2.52 mmol) of **19** in toluene (45 cm³). After stirring for 30 min, a dark red solution was formed which was evaporated to dryness *in vacuo*. The remaining oily solid was washed twice with 5 cm³ portions of pentane and

extracted with diethyl ether (50 cm³). The extract was concentrated to ca. 10 cm³ *in vacuo*, and the concentrate was stored at 78 °C for 24 h. An orange-yellow solid precipitated, which was filtered off and washed twice with 5 cm³ portions of pentane (−30 °C) and dried: yield 745 mg (75%); mp 98 °C (decomp.) (Found: C, 50.21; H, 6.01. C₃₈H₅₂Cl₂P₄Rh₂ requires C, 50.18; H, 6.76%). MS (DCI, isobutane, 70–100 eV): *m/z* 489 [0.1, {RhCl₂(Ph₂PCH₂PPR₂)⁺}, 454 [0.1 {RhCl(Ph₂PCH₂PPR₂)⁺}, 419 [0.4, {Rh(Ph₂PCH₂PPR₂)⁺}, 316 [0.9, Ph₂PCH₂PPR₂⁺]. NMR (C₆D₆): δ_H (200 MHz) 8.19 (8 H, m, *ortho*-H of C₆H₅), 7.09 (12 H, m, *meta*-H and *para*-H of C₆H₅), 2.74 (4 H, br m, PCH₂P), 1.81 (4 H, m, PCHCH₃), 1.34, 0.97 (24 H, both br m, PCHCH₃); δ_C (50.3 MHz) 137.2 [d, *J*(PC) 34.4, *ipso*-C of C₆H₅], 134.0 [d, *J*(PC), 12.7, *ortho*-C of C₆H₅], 129.3 (br s, *para*-C of C₆H₅), 128.2 [d, *J*(PC) 5.1, *meta*-C of C₆H₅], 37.1 (br m, PCH₂P), 25.4 [d, *J*(PC) 18.7, PCHCH₃], 25.3 [d, *J*(PC) 18.5 Hz, PCHCH₃], 19.3, 19.2, 18.3 (all s, PCHCH₃); δ_P (81.0 MHz) 3.9 [dd, *J*(RhP) 164.2, *J*(PP) 125.7, PrⁱP], −27.5 [dd, *J*(RhP) 176.6, *J*(PP) 125.7, Ph₂P], −28.2 [dd, *J*(RhP) 177.3, *J*(PP) 125.7 Hz, Ph₂P].

[(η⁶-C₆H₆)Rh(κ²P,P'-Cy₂PCH₂PPR₂)]PF₆ **30**. A solution of 90 mg (0.15 mmol) of **29** in benzene–acetone (6 cm³, 2:1) was treated with a solution of 65 mg (0.20 mmol) of **12** in benzene (3 cm³) and stirred for 30 min at room temperature. The yellow solution was evaporated to dryness *in vacuo*, and the oily residue was treated with diethyl ether (30 cm³) and stirred for 30 min in an ultrasonic bath. A yellow-brown solid precipitated, which was filtered off and washed with pentane (20 cm³) and dried: yield 79 mg (78%); mp 50 °C (decomp.) (Found: C, 46.16; H, 6.92. C₂₅H₄₄F₆P₃Rh requires C, 45.88; H, 6.78%). NMR (CD₂Cl₂): δ_H (200 MHz) 6.35 (6 H, s, C₆H₆), 2.66 (2 H, m, PCH₂P), 2.17–1.63 (12 H, br m, PCHCH₃ and PCHCH₂), 1.35–1.21 (12 H, br m, CH₂ of C₆H₁₁), 1.13, 1.12 [12 H, both dd, *J*(PH) 17.5, *J*(HH) 7.0 Hz, PCHCH₃]; δ_C (50.3 MHz) 98.5 [d, *J*(RhC) 2.0, C₆H₅], 38.1 [d, *J*(PC) 21.3, PCHCH₂], 29.2 [br d, *J*(PC) 3.5, PCHCH₂], 27.6 [d, *J*(PC) 21.5, PCHCH₃], 26.9 [d, *J*(PC) 3.2, CH₂ of PCy₂], 26.7 [d, *J*(PC) 2.6 Hz, CH₂ of PCy₂], 26.2 (m, PCH₂P), 26.0 (s, CH₂ of C₆H₁₁), 18.8 (s, PCHCH₃); δ_P (81.0 MHz, C₆D₆–CDCl₃) 0.9 [dd, *J*(RhP) 171.5, *J*(PP) 98.8, PrⁱP], −8.4 [dd, *J*(RhP) 171.1, *J*(PP) 98.8, Cy₂P], −143.9 [sept, *J*(FP) 711.4 Hz, PF₆[−]].

[(η⁶-C₆H₅CH₃)Rh(κ²P,P'-Cy₂PCH₂PPR₂)]PF₆ **31**. This was prepared as described for **30**, from **29** (110 mg, 0.19 mmol) in toluene–acetone (6 cm³, 2:1) and **12** (65 mg, 0.20 mmol) in toluene (3 cm³). Yellow solid: yield 114 g (90%); mp 105 °C (Found: C, 46.50; H, 6.47; Rh, 15.85. C₂₆H₄₆F₆P₃Rh requires C, 46.71; H, 6.94; Rh, 15.39%). NMR (CD₂Cl₂): δ_H (400 MHz) 6.55–6.35 (5 H, m, C₆H₅), 2.62 [2 H, dt, *J*(RhH) 2.2, *J*(P¹H) = *J*(P²H) 10.0, PCH₂P], 2.41 (3 H, s, C₆H₅CH₃), 1.98–1.70 (12 H, br m, PCHCH₃ and PCHCH₂), 1.40–1.17 (12 H, br m, CH₂ of C₆H₁₁), 1.12, 1.10 [12 H, both dd, *J*(PH) 17.6, *J*(HH) 7.2 Hz, PCHCH₃]; δ_C (50.3 MHz) 118.7 (s, *ipso*-C of C₆H₅CH₃), 100.8 (s, *ortho*-C of C₆H₅CH₃), 100.1 (s, *para*-C of C₆H₅CH₃), 98.2 (s, *meta*-C of C₆H₅CH₃), 38.7 [d, *J*(P¹C) 20.8, PCHCH₂], 30.9 [br d, *J*(PC) 8.8, PCHCH₃], 29.2 [d, *J*(PC) 20.8, PCHCH₃], 28.6 [d, *J*(P¹C) 6.0, CH₂ of C₆H₁₁], 28.4 [d, *J*(P¹C) 5.1 Hz, CH₂ of C₆H₁₁], 27.7 (s, CH₂ of C₆H₁₁), 27.6 (m, PCH₂P), 23.0 (s, C₆H₅CH₃), 20.5 (s, PCHCH₃); δ_P (81.0 MHz, C₆D₆–CDCl₃) 0.9 [dd, *J*(RhP) 171.7, *J*(PP) 100.5, PrⁱP], −8.4 [dd, *J*(RhP) 170.9, *J*(PP) 100.5, Cy₂P], −143.9 [sept, *J*(FP) 710.8 Hz, PF₆[−]].

Crystallography

Single crystals of **25** were grown from PrⁱOH (40–0 °C), those of **31** from toluene–acetone (1:1). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects for **25** and **31**. Data reduction was performed for **25** with Stoe IPDS software and

Table 1 Crystallographic data for **25** and **31**

Formula	C ₃₃ H ₆₂ AsP 25	C ₂₆ H ₄₆ F ₆ P ₃ Rh 31
<i>M</i>	564.72	668.45
Crystal system	Trigonal	Monoclinic
Space group	<i>P</i> 3 ₂ 1 (no. 152)	<i>C</i> c (no. 9)
<i>a</i> /Å	10.0640(4)	18.8181(6)
<i>b</i> /Å	—	10.8572(3)
<i>c</i> /Å	57.716(4)	29.2564(10)
β/°	—	96.7910(10)
<i>V</i> /Å ³	5062.5(4)	5935.5(3)
<i>T</i> /K	173(2)	223(2)
<i>Z</i>	6	8
<i>D</i> _c /g cm ^{−3}	1.111	1.496
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm ^{−1}	1.071	0.789
No. of reflections measured	10185	14637
No. of unique reflections	5402 [<i>R</i> (int) = 0.0430]	7016 [<i>R</i> (int) = 0.0536]
<i>R</i> 1 ^a	0.0418	0.0262 ^c 0.0320 ^d
<i>wR</i> 2 ^b	0.0955	0.0633 ^c 0.0661 ^d
Residual electron density/e Å ^{−3}	0.373/−0.410	1.406/−0.404

^a $R = \sum |F_o - F_c| / \sum F_o$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]$; $w^{-1} = [\sigma^2(F_o^2) + (0.040P)^2 + 1.2636P]$ **25**, $[\sigma^2(F_o^2) + (0.031100P)^2 + 33.270599P]$ **31**, where $P = [F_o^2 + 2F_c^2]/3$; for all data reflections, respectively. ^c Molecule A. ^d Molecule B.

for **31** with XPREP.⁴³ The structures were solved by direct methods (SHELXS-86 for **25** and SHELX-95 for **31**).⁴⁴ For **31** two independent molecules (**A** and **B**) were found in the asymmetric unit. In Fig. 2 only molecule **A** is shown. Table 1 contains the crystallographic data of each whole asymmetric unit (molecule **A** and **B**), the chemical formula and formula weight shown in Table 1, however, belong to one molecule only. Atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL-93 for **25** and SHELX-95 for **31**).⁴⁴

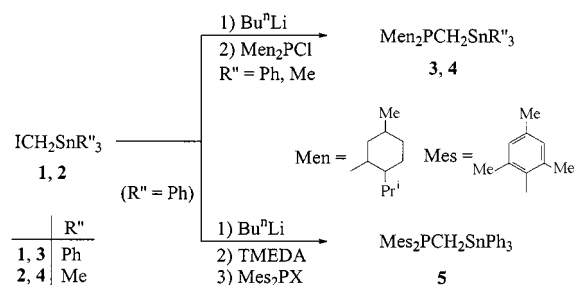
CCDC reference number 186/1427.

See <http://www.rsc.org/suppdata/dt/1999/1867/> for crystallographic files in .cif format.

Results and discussion

Preparation of the bis(phosphino)methanes

Following our recent work on the synthesis of phosphino(stibino)methane derivatives R₂PCH₂SbR'₂ with bulky substituents R and R',⁵ the corresponding bis(phosphino)methanes **8–16** were prepared similarly to a procedure reported by Kauffmann *et al.* for the preparation of Ph₂AsCH₂AsPh₂.⁸ Using one of the bifunctional compounds ICH₂SnR''₃ **1**, **2** (Scheme 1) as the starting material, metalation by BuⁿLi in toluene–hexane at low temperature affords the lithiated species

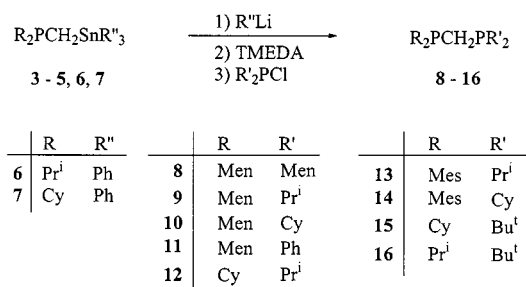


Scheme 1

$\text{LiCH}_2\text{SnR}''_3$ in virtually quantitative yield. This *in situ* generated intermediate is a strong nucleophile and reacts with chloro- or bromo-phosphines (R_2PX) even at temperatures between -80 and -55 °C. However, in order to avoid side reactions, mainly by nucleophilic attack of $\text{LiCH}_2\text{SnR}''_3$ at the triphenyl- or trimethyl-stannyl group of the desired product $\text{R}_2\text{PCH}_2\text{SnR}''_3$,^{8,9} TMEDA (tetramethylethylenediamine) was added to the reaction mixture. This is particularly important for those phosphines R_2PX in which the R substituents are less bulky than Men [Men = (*R*)-menthyl]. After the reaction mixture obtained from $\text{LiCH}_2\text{SnR}''_3$, R_2PX and TMEDA was warmed to room temperature, it was treated with water to remove the excess of the substituted methyllithium derivative. Finally, recrystallization of the crude product from pentane, acetone or a mixture of hexane and ethanol gave the phosphino(stannyl)methanes **3–5** as moderately air-sensitive white solids in 60–70% yield. It should be mentioned that the reaction of $\text{ICH}_2\text{SnMe}_3$ with Bu^nLi and R_2PCL (R = Prⁱ, Cy), even at -90 °C in the presence of TMEDA, leads to a mixture of products which contains the phosphines $\text{R}_2\text{PCH}_2\text{SnMe}_3$, $\text{R}_2\text{PCH}_2\text{PR}_2$ and the bis(stannyl)methane $\text{Me}_3\text{SnCH}_2\text{SnMe}_3$ in a ratio of approximately 2:1:1. Attempts to separate the P–Sn product from the other components failed.

Similarly to $\text{Pr}^i_2\text{PCH}_2\text{SnPh}_3$, **6** and $\text{Cy}_2\text{PCH}_2\text{SnPh}_3$, **7**,⁵ compounds **3–5** are quite thermally stable and soluble in most organic solvents. The ³¹P NMR spectra of **3–5** display a singlet at high field which is partially split into a doublet due to ^{119/117}Sn–P coupling. The resonance of the bridging CH₂ carbon atom appears as a doublet in the ¹³C NMR spectra at $\delta \approx 0$ (for **3** and **4**) and δ 10.3 (for **5**). Moreover, each diastereotopic carbon atom of the chiral menthyl substituents of **3** and **4** exhibits a separate signal which can be assigned by comparison of its chemical shift and P–C coupling constant with that of related compounds containing a PMen₂ unit.¹⁰

The second step of the synthesis of **8–16** is the transmetalation of **3–5** or **6, 7** with PhLi or MeLi, which proceeds smoothly at room temperature (Scheme 2). Besides the stan-

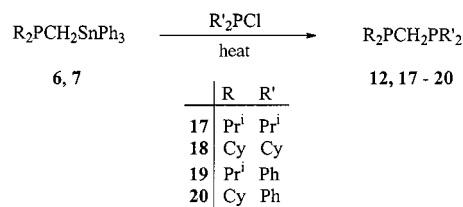


Scheme 2

nane SnR''_4 , the lithiated phosphine $\text{R}_2\text{PCH}_2\text{Li}$ is formed. This reacts with the chlorophosphine $\text{R}'_2\text{PCL}$ in the presence of TMEDA (provided that the groups R and R' are not Men) to give, after recrystallization of the crude product or chromatographic work-up, the bis(phosphino)methanes $\text{R}_2\text{PCH}_2\text{PR}'_2$ as air-sensitive white solids (**8–11**) oily solid (**14**) or colorless liquids (**12, 13, 15, 16**) in good to excellent yield. The *tert*-butyl derivatives **15** and **16** can also be obtained from $\text{Bu}^t_2\text{PCH}_3$ by deprotonation with Bu^tLi and subsequent addition of $\text{R}'_2\text{PCL}$ (R = Cy, Prⁱ) to the lithiated intermediate.^{11,12} While the ³¹P NMR spectrum of **8** displays only a singlet, the spectra of the unsymmetrically substituted compounds **9–16** show two doublets with ³¹P–³¹P coupling constants in the range from 98 Hz for the peralkylated compound **16** to 153 Hz for the partially arylated derivative **14**. The ¹H and ¹³C NMR spectra of **8–16** are in full agreement with the proposed structure and deserve no further comment.

In the course of our investigations of the synthesis of the bis(phosphino)methanes *via* the two step procedure illustrated

in Schemes 1 and 2 we observed that the cleavage of the Sn–C bond of the stannylated derivatives $\text{R}_2\text{PCH}_2\text{SnPh}_3$ with $\text{R}'_2\text{PCL}$ can occur even in the absence of PhLi. Whereas treatment of $\text{R}_2\text{PCH}_2\text{SnPh}_3$ with $\text{R}'_2\text{PCL}$ in solution under reflux leads only to a low degree of conversion, the reaction of the substrates at 240 °C *without any solvent* affords quantitatively the corresponding bis(phosphino)methanes $\text{R}_2\text{PCH}_2\text{PR}'_2$ by elimination of Ph_3SnCl (Scheme 3). Chromatographic work-up of the

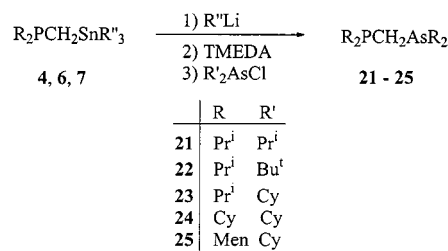


Scheme 3

resulting reaction mixture gives the symmetrically (**17, 13, 18**¹⁴) as well as the unsymmetrically substituted ditertiary phosphines (**12, 19, 15, 20**) in 58–80% isolated yield. We assume that the driving force for this reaction (which appears to be kinetically hindered) is the thermodynamically favored formation of both the P–C and the Sn–Cl bond. By an analogous route, Appel *et al.* prepared the arylated bis(phosphino)methanes $\text{Ph(R)PCH}_2\text{PR}'_2$ (R = Ph, Me) from $\text{Ph(R)PCH}_2\text{SiMe}_3$ and $\text{R}'_2\text{PCL}$ in comparable yields.¹⁶

Synthesis and structure of arsino(phosphino)methanes

The tetraphenyl derivative $\text{Ph}_2\text{AsCH}_2\text{PPh}_2$ is, to the best of our knowledge, the only compound of general composition $\text{R}_2\text{AsCH}_2\text{PR}'_2$ which has been described in the literature.^{16,17} The related arsino(phosphino)methanes **21–25** (Scheme 4) reported



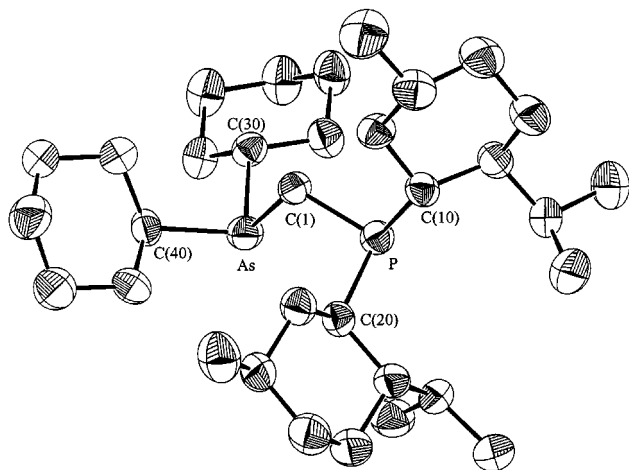
Scheme 4

in this work, with bulky substituents at both the arsenic and the phosphorus atom, were prepared in the same way as their P–P counterparts. The isolated yield of the colorless liquids (**21–23**) or solids (**24, 25**) is 60–80%. Although these arsino(phosphino)methanes are exceedingly air- and light-sensitive, they can be stored, even in pentane, at -20 °C under argon for weeks. The NMR spectra of **21–25** are quite similar to those of the related compounds $\text{R}_2\text{PCH}_2\text{SbR}'_2$ and need no further comment.

The molecular structure of compound **25**, of which single crystals were obtained from ethanol–hexane at 4 °C, was determined by X-ray crystallography. The ORTEP¹⁸ plot (Fig. 1) reveals that the molecule of **25** has no crystallographic symmetry. The relative orientation of the P(Men)₂ and AsCy₂ moieties at the methylene bridge is such that the lone pairs at the arsenic and phosphorus atoms, the menthyl and cyclohexyl groups, and the hydrogen atoms of the CH₂ unit adopt staggered conformations. The most noteworthy structural detail (see Table 2) is the bond angle As–C(1)–P of 108.2(2)° which is considerably smaller than the Sb–C–P bond angles of $\text{Bu}^t_2\text{SbCH}_2\text{PCy}_2$ [119.17(8)°]⁵ and P–C–P of $\text{Cy}_2\text{PCH}_2\text{PCy}_2$ [120.5(1)°],¹⁹ respectively. In contrast to this, the bond length P–C(1) of **25** [1.839(4) Å] is almost identical to that of

Table 2 Selected bond lengths (Å) and angles (°) for compound **25**

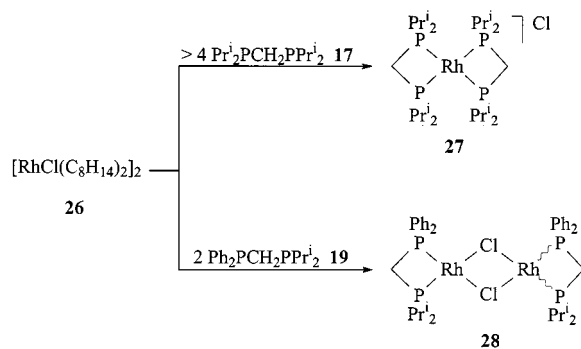
As–C(1)	1.986(4)	P–C(1)	1.839(4)
As–C(30)	1.965(4)	P–C(10)	1.894(4)
As–C(40)	1.966(4)	P–C(20)	1.870(5)
As–C(1)–P	108.2(2)	C(1)–P–C(10)	105.5(2)
C(30)–As–C(40)	101.2(2)	C(1)–P–C(20)	98.7(2)
C(1)–As–C(30)	96.6(2)	C(10)–P–C(20)	103.4(2)
C(1)–As–C(40)	100.2(2)		

**Fig. 1** An ORTEP plot of compound **25**.

$\text{Bu}^t_2\text{SbCH}_2\text{PCy}_2$ [1.842(2) Å]⁵ and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ [1.848(5) Å],²⁰ and differs only slightly from that in $\text{Cy}_2\text{PCH}_2\text{PCy}_2$ [1.858 Å].¹⁹

Square-planar and half-sandwich-type rhodium(i) complexes with bis(phosphino)methanes as chelating ligands

In contrast to $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), which as the best-known bis(phosphino)methane binds to d^8 and d^{10} metal centres preferably in a bridging coordination mode,^{1,3,21} analogous compounds $\text{R}_2\text{PCH}_2\text{PR}_2$ with sterically demanding substituents R such as cyclohexyl or *tert*-butyl behave mainly as chelating ligands.^{14,22–24} Studies by Hofmann *et al.* have shown that the cyclooctene rhodium(i) complex **26** (Scheme 5) reacts with

**Scheme 5**

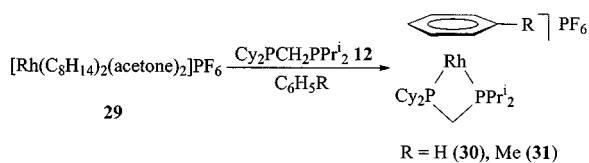
$\text{Bu}^t_2\text{PCH}_2\text{PBu}^t_2$ to give the chloro-bridged dimer $[\text{RhCl}(\kappa^2\text{P}, \text{P}'\text{-Bu}^t_2\text{PCH}_2\text{PBu}^t_2)]_2$,²³ for which an X-ray crystal structure analysis was carried out. The less bulky bis(phosphino)methane **17** behaves differently. While treatment of complex **26** with two equivalents of **17** affords a mixture of products containing the ionic species **27** as a minor component, the reaction of **26** with **17** in a molar ratio of *ca.* 1:6 leads to the formation of compound **27** in nearly quantitative yield. The proposed structure for the bis(chelate) complex is supported by elemental analysis, conductivity measurements and NMR spectroscopy. In both the ¹H and the ¹³C NMR spectrum of **27**, the resonances for the

protons of the CH_2 group and for the corresponding carbon atom are significantly shifted to lower field compared to the free ligand. The methyl groups of the isopropyl units of the chelating ligands in **27** are diastereotopic and therefore give rise to two signals in the ¹H as well as the ¹³C NMR spectrum.

The cyclooctene complex **26** reacts with the unsymmetrical bis(phosphino)methane **19** (in a molar ratio of 1:2) in a different way. Treatment of the starting material **26** with **19** in toluene at -20°C results in the formation of a dark orange-red solution from which, after removal of the solvent and recrystallization of the residue from diethyl ether, an orange-yellow solid was isolated in 75% yield. The elemental analysis as well as the mass spectrum confirmed that the neutral dinuclear complex **28** was obtained. In contrast to the cationic species **27**, compound **28** is quite air-sensitive and thermally much less stable than the *tert*-butyl-substituted derivative $[\text{RhCl}(\kappa^2\text{P}, \text{P}'\text{-Bu}^t_2\text{PCH}_2\text{PBu}^t_2)]_2$.²³ The most noteworthy spectroscopic features of **28** are the slightly broadened resonance at δ 3.9 for the phosphorus atoms of the PPr_2 moieties and the appearance of two separate signals at δ -27.5 and -28.2 for the ³¹P nuclei of the PPh_2 units in the ³¹P NMR spectrum. Owing to these data we assume that compound **28** consists of a mixture of two diastereoisomers (both with a planar $\text{P}'\text{PRhCl}_2\text{RhPP}'$ skeleton)²⁵ in which the two identical PR_2 fragments of each of the two chelating ligands are either *cis* or *trans* disposed.

In contrast to $[\text{RhCl}(\kappa^2\text{P}, \text{P}'\text{-Bu}^t_2\text{PCH}_2\text{PBu}^t_2)]_2$, the related dinuclear complex **28** is quite inert and does not react with an excess of pyridine, even at 40°C , by cleavage of the chloro bridges. In this respect, compound **28** behaves similarly to the rhodium and iridium complexes $[\text{MCl}(\kappa^2\text{P}, \text{P}'\text{-Pr}^i_2\text{PCH}_2\text{-CH}_2\text{PP}^i_2)]_2$, which are also inert toward pyridine.^{26,27}

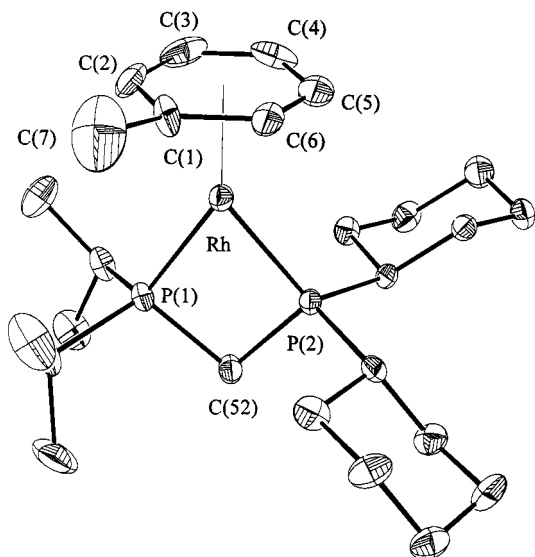
Attempts to prepare cationic chelate rhodium complexes by using the four-coordinate bis(cyclooctene) species **29** and the bulky bis(phosphino)methane **12** as the starting materials led to an unexpected result. From recent studies in our laboratory it was known that the four-coordinate compound **29** does not only react with various alkynes to give either cationic alkyne- or vinylidene-rhodium(i) complexes,²⁸ but that it is also catalytically active in the reactions of olefins with diazoalkanes.²⁹ Despite this activity, we failed to generate a cationic species $[\text{Rh}(\kappa^2\text{P}, \text{P}'\text{-Cy}_2\text{PCH}_2\text{PP}^i_2)(\text{L})_2]^+$ (L = C_8H_{14} or acetone) upon treatment of a solution of **29** with **12** in acetone. If, however, a mixture of acetone–benzene or acetone–toluene is used instead of acetone as the solvent, the reaction of **29** with **12** proceeds cleanly and gives the half-sandwich-type complexes **30** and **31** (Scheme 6) in 78–90% yield. These compounds are yellow-

**Scheme 6**

brown or yellow air-stable solids respectively which were characterized by elemental analysis and NMR spectroscopy. In the ³¹P NMR spectra of **30** and **31**, the phosphorus atoms of the two different PR_2 units give rise to two doublets of doublets, the ¹⁰³Rh–³¹P coupling constants of which (171–172 Hz) are nearly the same as for the neutral complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\kappa^2\text{P}, \text{P}'\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ (163.4 Hz).³⁰ With regard to the mechanism of formation of **30** and **31** we assume that in the initial step, in analogy to the reaction of **29** with PPr_3 ,²⁸ a cationic intermediate $[\text{Rh}(\kappa^2\text{P}, \text{P}'\text{-Cy}_2\text{PCH}_2\text{PP}^i_2)(\text{Me}_2\text{CO})_2]^+$ is formed which reacts with excess benzene or toluene to yield the more stable half-sandwich-type product. We note that quite recently Mirkin and co-workers reported the synthesis of a series of compounds of general composition $[(\eta^6\text{-arene})\text{Rh}\{\kappa^2\text{P}, \text{P}'\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]\text{BF}_4$ ($n = 2\text{--}4$) using $[\text{Rh}(\eta^4\text{-dien})$

Table 3 Selected bond lengths (Å) and angles (°) for cationic complex **31** (there are two independent molecules **A** and **B** in the unit cell)

	A	B		A	B
Rh–P(1)	2.235(3)	2.234(3)	Rh–C(4)	2.332(13)	2.318(14)
Rh–P(2)	2.217(3)	2.223(3)	Rh–C(5)	2.265(12)	2.268(12)
Rh–C(1)	2.392(14)	2.38(2)	Rh–C(6)	2.302(13)	2.349(12)
Rh–C(2)	2.291(13)	2.305(12)	P(1)–C(52)	1.850(10)	1.795(12)
Rh–C(3)	2.327(13)	2.316(13)	P(2)–C(52)	1.846(11)	1.840(10)
P(1)–Rh–P(2)	72.8(1)	72.6(1)	Rh–P(2)–C(52)	98.3(3)	96.7(4)
Rh–P(1)–C(52)	97.6(3)	97.6(3)	P(1)–C(52)–P(2)	91.3(5)	93.1(5)

**Fig. 2** An ORTEP plot of the cation of complex **31**.

$\{\kappa^2P,P'-Ph_2P(CH_2)_nPPh_2\}^+BF_4^-$ (dien = nornbornadiene or cycloocta-1,5-diene) as the starting material.³¹

To obtain information about the detailed structural aspects of the cationic arenerhodium(I) complexes with **12** as ligand, an X-ray diffraction study of **31** was carried out. There are two independent molecules **A** and **B** in the unit cell, of which **A** is shown in Fig. 2. The toluene moiety is almost planar and symmetrically coordinated (in an η^6 -bonding mode) to the metal center. The distance between rhodium and the center of the ring is about 1.84 Å, which is slightly shorter than in the dppf derivative $[(\eta^6-C_6H_2Me_4-1,2,4,5)Rh(\kappa^2P,P'-Ph_2PCH_2CH_2PPh_2)]^+BF_4^-$ (1.87 Å).³¹ The Rh–P bond lengths (Table 3) lie in the expected range. The four-membered chelate ring Rh–P(1)–C(52)–P(2) is perfectly planar with an intra-ligand angle P(1)–C(52)–P(2) of 91.3(5)° (for **A**) and 93.1(5)° (for **B**), respectively. The bond angle P(1)–Rh–P(2) is rather small [72.8(1)° for **A** and 72.6(1)° for **B**] and has one of the smallest 'bite-angles' in a series of chelating rhodium(I) complexes containing examples such as $[RhCl(\kappa^2P,P'-Bu^t_2PCH_2PPh_2)_2]$ [75.8(1)°], $[RhCl(PMe_3)(\kappa^2P,P'-Bu^t_2PCH_2PPh_2)]$ [75.47(4)°] and $[Rh(\eta^3-C_3H_3)(CO)(\kappa^2P,P'-Pr^i_2PCH_2PPh_2)]$ [72.42(2)°], all of which contain bulky bis(phosphino)methanes as ligands.^{23,32}

Conclusions

In this work, we have successfully demonstrated that a series of symmetrical and unsymmetrical bis(phosphino)methanes $R_2PCH_2PR'_2$ as well as their arsino(phosphino) counterparts $R'_2AsCH_2PR_2$ with bulky alkyl, cycloalkyl or aryl groups **R** and **R'** can be readily prepared from the stannylated phosphines $R_2PCH_2SnMe_3$ or $R_2PCH_2SnPh_3$ via metalation with MeLi or PhLi in the presence of TMEDA and subsequent treatment with R'_2PCl or R'_2AsCl , respectively. An alternative route to some of the bis(phosphino)methanes consists of the thermal reaction of $R_2PCH_2SnPh_3$ with the corresponding

chlorophosphine R_2PCl or R'_2PCl in the absence of solvent. If we take these results and those recently reported from our laboratory⁵ into consideration, it should be possible to obtain a great variety of compounds of the general composition $R_2ECH_2E'R_2$ and $R_2ECH_2ER'_2$ [**E** or **E'** = P, As, Sb (**E** ≠ **E'**)] via the methodology that uses the stannylated iodomethane Ph_3SnCH_2I as the starting material.

With regard to the coordination capabilities of the ligands $R_2PCH_2PR'_2$, we have shown by the preparation of complexes **27**, **28**, **30** and **31** that the bulky bis(phosphino)methanes bind to rhodium(I) preferentially in a chelating coordination mode. This observation is in agreement with earlier work by Hofmann^{22,23} and Leitner²⁴ which indicates that in contrast to $Ph_2PCH_2PPh_2$ (dppm) the more sterically demanding derivatives $Bu^t_2PCH_2PPh_2$ and $Cy_2PCH_2PCy_2$ are less prone to behave as bridging ligands. It should be mentioned that although the coordination of benzene and other arenes to cationic rhodium(I) centers is known,^{31,33} both the ease of formation and the stability of the complexes **30** and **31** is rather surprising. In this respect, our results complement recent work by Bargon *et al.* which illustrates that the cleavage of the ring-to-metal bond in cationic species $[(\eta^6-C_6H_5R)Rh\{\kappa^2P,P'-Ph_2P(CH_2)_4PPh_2\}]^+$, formed as intermediates in the rhodium-catalyzed hydrogenation of styrene, is less favored than previously assumed.³⁴

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