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

**Justin Wolf,[a] Matthias Manger,[a] Ulrich Schmidt,[a] Guido Fries,[a] Dietmar Barth,[a] Birgit Weberndörfer,[a] David A. Vicic,[b] William D. Jones[b] and Helmut Werner*[a]**

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: helmut.werner@mail.uni-wuerzburg.de*
[b] *Department of Chemistry, University of Rochester, Rochester, New York 14627-0216, USA*

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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 $R'_2PCl$ or $R'_2AsCl$, 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 $R_2PCl$ or $R'_2PCl$ in the absence of solvent. The bis(cyclooctene) derivative $[RhCl(C_8H_{14})_2]_2$ **26** reacted with excess $Pr^i_2PCH_2PPr^i_2$ to give $[Rh(\kappa^2P,P'\text{-}Pr^i_2PCH_2PPr^i_2)_2]Cl$ **27**, while treatment of **26** with $Ph_2PCH_2PPr^i_2$ yielded the chloro-bridged dimer $[RhCl(\kappa^2P,P'\text{-}Ph_2PCH_2PPr^i_2)]_2$ **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 $[(\eta^6\text{-}C_6H_6)Rh(\kappa^2P,P'\text{-}Cy_2PCH_2PPr^i_2)]PF_6$ **30**, $[(\eta^6\text{-}C_6H_5CH_3)Rh(\kappa^2P,P'\text{-}Cy_2PCH_2PPr^i_2)]PF_6$ **31**, of which the latter was characterized by X-ray crystallography.

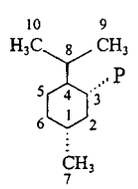
Ditertiary phosphines containing two phosphorus atoms which are linked together by a chain of $CH_2$ moieties are of major interest as mono- and bi-dentate ligands in transition-metal chemistry.[1] Since the coordination mode of these phosphines and therefore the reactivity of the complexes obtained 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**, **7**,[5] **26**,[36] **29**,[37] $R_2PCl$ (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




**$Men_2PCH_2SnPh_3$ 3.** A solution of **1** (21.27 g, 43.32 mmol) in toluene (200 $cm^3$) was treated at −55 °C dropwise (over *ca.* 20 min) with a 2.73 M solution of $Bu^nLi$ (16.00 $cm^3$, 43.32 mmol) in hexane. The solution was stirred for 30 min and then a solution of $Men_2PCl$ (14.94 g, 43.32 mmol) in toluene (60 $cm^3$) was added over *ca.* 10 min. The reaction mixture was slowly brought to room temperature and treated with water (50 $cm^3$). The organic phase was separated, washed twice with 50 $cm^3$ 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 $cm^3$). The extract was concentrated to *ca.* 40 $cm^3$ *in vacuo*. Upon storing the solution at −25 °C for 18 h, white crystals precipitated, which were separated from the mother-liquor, washed twice with 10 $cm^3$ portions of pentane

(−40 °C) and dried: yield 20.18 g (69%); mp 121 °C (Found: C, 69.24; H, 9.09. $C_{39}H_{55}PSn$ requires C, 69.55; H, 8.88%). NMR ($C_6D_6$): $\delta_C$ (50.3 MHz) 139.5 [d, *J*(PC) 1.8, *J*($^{119/117}$SnC) 485.6, *ipso*-C of $C_6H_5$], 137.6 [d, *J*(PC) 1.3, *J*($^{119/117}$SnC) 35.9, *ortho*-C of $C_6H_5$], 129.2 (s, *para*-C of $C_6H_5$), 128.8 [s, *J*($^{119/117}$SnC) 50.1, *meta*-C of $C_6H_5$], 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, $CH_2$(2)], 35.3, 35.2 [both s, $CH_2$(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, $CH_2$(5)], 25.5 [d, *J*(PC) 6.3, $CH_2$(5)], 23.2, 23.0 [both s, $CH_3$(7)], 22.2, 22.0 [both s, $CH_3$(10)], 16.1, 15.7 [both s, $CH_3$(9)], 0.5 [d, *J*(PC) 45.6 Hz, $PCH_2Sn$]; $\delta_P$(162.0 MHz) 31.8 [s, *J*($^{119/117}$SnP) 115.5 Hz].

**$Men_2PCH_2SnMe_3$ 4.** This compound was prepared as described for **3**, from **2** (3.95 g, 12.95 mmol), a 1.83 M solution of $Bu^nLi$ (6.80 cm$^3$, 12.44 mmol) in hexane and $Men_2PCl$ (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. $C_{24}H_{49}PSn$ requires C, 59.15; H, 10.14%). NMR ($CDCl_3$): $\delta_H$(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, $CH_2$ and $CH_3$ of $PMen_2$ and $PCH_2Sn$), 0.74, 0.66 [3 H each, both d, *J*(HH) 6.8, $CH_3$ of $PMen_2$], 0.13 [9 H, s, *J*($^{119}$SnH) 53.6, *J*($^{117}$SnH) 51.2 Hz, $SnCH_3$]; $\delta_C$ (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, $CH_2$(2)], 36.0, 35.2 [both s, $CH_2$(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, $CH_2$(5)], 25.4 [d, *J*(PC) 7.0, $CH_2$(5)], 22.9, 22.7 [both s, $CH_3$(7)], 22.0, 21.7 [both s, $CH_3$(10)], 15.7, 15.4 [both s, $CH_3$(9)], −0.3 [d, *J*(PC) 42.3, *J*($^{119}$SnC) 328.7, *J*($^{117}$SnC) 246.5, $PCH_2Sn$], −8.4 [d, *J*(PC) 4.7, *J*($^{119}$SnC) 334.5, *J*($^{117}$SnC) 320.4 Hz, $SnCH_3$]; $\delta_P$ (162.0 MHz) −29.9 [s, *J*($^{119/117}$SnP) 125.5 Hz].

**$Mes_2PCH_2SnPh_3$ 5.** A solution of **1** (4.22 g, 8.60 mmol) in toluene (80 cm$^3$) was treated at −55 °C dropwise (over *ca.* 10 min) with a 2.73 M solution of $Bu^nLi$ (3.15 cm$^3$, 8.60 mmol) in hexane. The solution was stirred for 20 min and then TMEDA (3.70 cm$^3$, 24.52 mmol) was added. After the reaction mixture was cooled to −80 °C, it was treated with a suspension of a mixture of $Mes_2PBr$ and $Mes_2PCl$ (ratio *ca.* 6:1; 2.88 g, *ca.* 8.53 mmol) in toluene (20 cm$^3$) and stirred for 30 min. The solution was slowly brought to room temperature and treated with water (15 cm$^3$). The organic phase was separated, washed three times with 5 cm$^3$ portions of water, carefully dried with $Na_2SO_4$ and then filtered. The filtrate was brought to dryness *in vacuo*, the oily residue was dissolved in pentane (5 cm$^3$), and the solution was chromatographed on $Al_2O_3$ (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 cm$^3$ portions of ethanol and dried: yield 3.50 g (65%); mp 130 °C (Found: C, 70.74; H, 6.13. $C_{37}H_{39}PSn$ requires C, 70.16; H, 6.21%). NMR ($C_6D_6$): $\delta_H$(200 MHz) 8.03–7.65 (15 H, m, $C_6H_5$), 7.01 [2 H, d, *J*(PH) 2.4 Hz, $C_6H_2$], 2.78 (2 H, br s, $PCH_2Sn$), 2.71 (12 H, s, 2,6-$H_3$C-$C_6H_2$), 2.56 (6 H, s, 4-$H_3$C-$C_6H_2$); $\delta_C$ (50.3 MHz) 141.4 [d, *J*(PC) 13.9, *ortho*-C of $C_6H_2$], 138.7 [d, *J*(PC) 2.8, *ipso*-C of $C_6H_5$], 137.1 (s, *para*-C of $C_6H_2$), 136.7 [s, *J*($^{117/119}$SnC) 38.4, *ortho*-C of $C_6H_5$], 134.8 [d, *J*(PC) 23.1, *ipso*-C of $C_6H_2$], 129.8 [d, *J*(PC) 2.3, *meta*-C of $C_6H_2$], 128.4 (s, *para*-C of $C_6H_5$), 128.2 (s, *meta*-C of $C_6H_5$), 23.0 [d, *J*(PC) 3.9, 2,6-$H_3C$-$C_6H_2$], 20.7 (s, 4-$H_3C$-$C_6H_2$), 10.3 [d, *J*(PC) 37.9 Hz, $PCH_2Sn$]; $\delta_P$ (81.0 MHz, $CDCl_3$) −25.1 [s, *J*($^{119}$SnP) 122.1, *J*($^{117}$SnP) 116.3 Hz].

**$Men_2PCH_2PMen_2$ 8.** A solution of **1** (13.20 g, 19.60 mmol) in diethyl ether (200 cm$^3$) was treated with a 1.73 M solution of PhLi (11.04 cm$^3$, 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 $Men_2PCl$ (6.59 g, 19.10 mmol) in diethyl ether (100 cm$^3$) 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 cm$^3$), and the extract was evaporated to dryness *in vacuo*. Recrystallization of the residue from propan-1-ol (170 cm$^3$) gave, at −25 °C, white crystals, which were separated from the mother-liquor, washed three times with 10 cm$^3$ portions of propan-1-ol (−40 °C) and dried: yield 7.84 g (65%); mp 162 °C (Found: C, 77.42; H, 12.53. $C_{41}H_{78}P_2$ requires C, 77.80; H, 12.42%). NMR ($C_6D_6$): $\delta_C$ (50.3 MHz) 46.8 (vt, *N* 20.5, CH), 44.8 (vt, *N* 11.2, CH), 40.5 (s, $CH_2$), 40.1 (vt, *N* 9.8, CH), 36.8, 35.4, 35.3 (all s, $CH_2$), 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, $CH_2$), 25.6 (vt, *N* 6.1 Hz, $CH_2$), 23.2, 23.0, 22.4, 21.8, 15.7, 15.6 (all s, $CH_3$), 11.8 [t, *J*(PC) 28.5 Hz, $PCH_2P$]; $\delta_P$ (81.0 MHz, $CDCl_3$) −36.7 (s).

**$Men_2PCH_2PPr^i_2$ 9.** *Method A.* A solution of **2** (1.56 g, 3.20 mmol) in diethyl ether (35 cm$^3$) was treated with a 1.48 M solution of MeLi (2.27 cm$^3$, 3.26 mmol) in diethyl ether and stirred for 5 h at room temperature. The solution was cooled to −60 °C and $Pr^i_2PCl$ (0.51 cm$^3$, 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 cm$^3$). The extract was evaporated to dryness *in vacuo*. The remaining product was dissolved in ethanol–methanol (8 cm$^3$, 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 cm$^3$ 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 cm$^3$, 20.96 mmol) in cyclohexane–diethyl ether (1:1) and $Pr^i_2PCl$ (3.37 cm$^3$, 22.00 mmol): yield 7.00 g (76%); mp 84 °C (Found: C, 73.28; H, 12.56. $C_{27}H_{54}P_2$ requires C, 73.59; H, 12.35%). NMR ($C_6D_6$): $\delta_C$ (100.6 MHz) 46.0 [dd, *J*($P^1$C) 18.9, *J*($P^2$C) 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*($P^1$C) 18.6, *J*($P^2$C) 7.0, CH(3)], 36.4 [d, *J*(PC) 1.4, $CH_2$(2)], 35.1, 35.0 [both s, $CH_2$(6)], 33.9, 33.7 [both s, CH(1)], 33.0 [dd, *J*($P^1$C) 22.9, *J*($P^2$C) 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, $CH_2$(5)], 25.2 [d, *J*(PC) 7.6, $CH_2$(5)], 24.6 [dd, *J*($P^2$C) 14.2, *J*($P^1$C) 5.4, P*C*HCH$_3$], 24.0 [dd, *J*($P^2$C) 13.5, *J*($P^1$C) 6.2, P*C*HCH$_3$], 22.8, 22.7 [both s, $CH_3$(7)], 21.7, 21.5 [both s, $CH_3$(10)], 19.9 [dd, *J*($P^2$C) 12.3, *J*($P^1$C) 1.5, PCH*C*H$_3$], 19.8 [dd, *J*($P^2$C) 12.2, *J*($P^1$C) 2.2, PCH*C*H$_3$], 19.3 [dd, *J*($P^2$C) 10.2, *J*($P^1$C), PCH*C*H$_3$], 19.2 [dd, *J*($P^2$C) 9.6, *J*($P^1$C) 1.4, PCH*C*H$_3$], 15.4, 15.3 [both s, $CH_3$(9)], 12.4 [dd, *J*($P^1$C) 30.6, *J*($P^2$C) 27.0 Hz, $PCH_2P$]; $\delta_P$ (81.0 MHz, $CDCl_3$) −3.4 [d, *J*(PP) 102.4, $Pr^i_2P$], −34.0 [d, *J*(PP) 102.4 Hz, $Men_2P$].

**$Cy_2PCH_2PMen_2$ 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 cm$^3$, 0.86 mmol) in diethyl ether and $Cy_2PCl$ (0.177 cm$^3$, 0.83 mmol). White crystals: yield 0.35 g (82%); mp 57 °C (Found: C, 76.17; H, 11.50. $C_{33}H_{62}P_2$ requires C, 76.11; H, 12.00%). NMR ($CDCl_3$): $\delta_H$ (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, $PCH_2P$ and CH and $CH_2$ of $Cy_2P$ and $PMen_2$), 0.86 (12 H, m, $CH_3$), 0.75, 0.66 [3 H each, both d, *J*(HH) 6.8 Hz, $CH_3$]; $\delta_C$ (100.6 MHz, $C_6D_6$) 45.9 [d, *J*(PC) 18.5, CH(4)], 44.9 [d, *J*(PC) 12.2, CH(4)], 39.1 [br s, $CH_2$(2)], 37.9 [dd, *J*($P^2$C) 20.7, *J*($P^1$C) 7.5, CH(3)], 36.5 [s, $CH_2$(2)], 35.2, 35.1 [both s, $CH_2$(6)], 34.6 [dd, *J*($P^1$C) 15.1, *J*($P^2$C) 6.1, P*C*HCH$_2$], 34.3 [dd, *J*($P^1$C) 15.1, *J*($P^2$C) 7.1, P*C*HCH$_2$], 34.0, 33.8 [both s, CH(1)], 33.1 [dd, *J*($P^2$C) 25.2, *J*($P^1$C) 5.0, CH(3)], 30.2 [d, *J*(PC) 12.5, PCH*C*H$_2$], 29.5 (m,

PCH*C*H$_2$), 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, CH$_2$ of PCy$_2$), 25.8 [d, *J*(PC) 8.5, CH$_2$(5)], 25.3 [d, *J*(PC) 7.1, CH$_2$(5)], 22.9, 22.8 [both s, CH$_3$(7)], 21.7, 21.6 [both s, CH$_3$(10)], 15.4, 15.3 [both s, CH$_3$(9)], 11.7 [dd, *J*(P$^2$C) 30.2, *J*(P$^1$C) 26.4 Hz, PCH$_2$P]; $\delta_P$ (162.0 MHz, CDCl$_3$) −11.5 [d, *J*(PP) 108.5, Cy$_2$P], −34.1 [d, *J*(PP) 108.5 Hz, Men$_2$P]. For an alternative preparative procedure for **10** see ref. 11.

**Men$_2$PCH$_2$PPh$_2$ 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 cm$^3$, 3.10 mmol) in diethyl ether and Ph$_2$PCl (0.549 cm$^3$, 3.10 mmol). White crystals: yield 1.34 g (85%); mp 72 °C (Found: C, 77.72; H, 9.95. C$_{33}$H$_{50}$P$_2$ requires C, 77.92; H, 9.91%). NMR (CDCl$_3$): $\delta_H$ (400 MHz) 7.46–7.36 (4 H, m, C$_6$H$_5$), 7.26–7.19 (6 H, m, C$_6$H$_5$), 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, PCH$_2$P and CH and CH$_2$ of PMen$_2$), 0.77 (12 H, m, CH$_3$), 0.63, 0.58 [3 H each, both d, *J*(HH) 6.8 Hz, CH$_3$]; $\delta_C$ (100.6 MHz) 140.5 [dd, *J*(P$^2$C) 15.7, *J*(P$^1$C) 9.1, *ipso*-C of C$_6$H$_5$], 139.8 [dd, *J*(P$^2$C) 14.8, *J*(P$^1$C) 6.2, *ipso*-C of C$_6$H$_5$], 133.3 [d, *J*(PC) 20.0, *ortho*-C of C$_6$H$_5$], 132.4 [d, *J*(PC) 17.2, *ortho*-C of C$_6$H$_5$], 128.7, 128.3 (both s, *para*-C of C$_6$H$_5$), 128.2 [d, *J*(PC) 2.9, *meta*-C of C$_6$H$_5$], 128.1 [d, *J*(PC) 1.9, *meta*-C of C$_6$H$_5$], 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, CH$_2$(2)], 38.1 [dd, *J*(P$^2$C) 20.0, *J*(P$^1$C) 6.7, CH(3)], 36.6 [br s, CH$_2$(2)], 35.0, 34.9 [both s, CH$_2$(6)], 32.6, 32.7 [both s, CH(1)], 33.4 [dd, *J*(P$^2$C) 24.3, *J*(P$^1$C) 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, CH$_2$(5)], 24.2 [d, *J*(PC) 8.6, CH$_2$(5)], 21.8, 21.7, 20.8, 20.5 [all s, CH$_3$(9) and CH$_3$(10)], 18.7 [dd, *J*(P$^2$C) 31.5, *J*(P$^1$C) 20.0 Hz, PCH$_2$P], 14.3, 14.2 [both s, CH$_3$(7)]; $\delta_P$ (81.0 MHz) −19.8 [d, *J*(PP) 148.0, Ph$_2$P], −30.7 [d, *J*(PP) 148.0 Hz, Men$_2$P].

**Cy$_2$PCH$_2$PPr$^i_2$ 12.** *Method A*. A solution of **7** (4.75 g, 8.46 mmol) in diethyl ether (100 cm$^3$) was treated with a 1.82 M solution of PhLi (6.80 cm$^3$, 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 cm$^3$, 8.37 mmol) and subsequently Pr$^i_2$PCl (1.27 cm$^3$, 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 cm$^3$), and the extract was evaporated to dryness *in vacuo*. The remaining oily product was suspended in pentane (3 cm$^3$), and the suspension was chromatographed on Al$_2$O$_3$ (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 ($\rho$ 1.16 g cm$^{-3}$): yield 1.70 g (62%).

*Method B*. A mixture of **6** (1.28 g, 2.66 mmol) and Cy$_2$PCl (0.59 cm$^3$, 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 Pr$^i_2$PCl (0.25 cm$^3$, 1.60 mmol): yield 0.40 g (76%) (Found: C, 69.39; H, 11.81. C$_{19}$H$_{38}$P$_2$ requires C, 69.47; H, 11.66%). NMR (CDCl$_3$): $\delta_H$ (200 MHz) 1.72–1.53 (12 H, br m, PC*H*CH$_3$ and PCHCH$_2$), 1.35 (2 H, br s, PCH$_2$P), 1.19 (12 H, br m, CH$_2$ of PCy$_2$), 1.09 [6 H, dd, *J*(PH) 11.2, *J*(HH) 7.1, PCHC*H*$_3$], 1.07 [6 H, dd, *J*(PH) 13.6, *J*(HH) 7.0 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz) 34.2 [dd, *J*(P$^1$C) 15.7, *J*(P$^2$C) 6.0, P*C*HCH$_2$], 29.8 [dd, *J*(P$^1$C) 12.6, *J*(P$^2$C) 1.4, PCH*C*H$_2$], 27.2 [d, *J*(PC) 10.4, CH$_2$ of PCy$_2$], 27.1 [d, *J*(PC) 8.0, CH$_2$ of PCy$_2$], 26.4 (s, CH$_2$ of PCy$_2$), 24.2 [dd, *J*(P$^2$C) 14.3, *J*(P$^1$C), 6.0, P*C*HCH$_3$], 19.6 [dd, *J*(P$^2$C) 13.8, *J*(P$^1$C) 1.7, PCH*C*H$_3$], 19.0 [dd, *J*(P$^2$C) 10.9, *J*(P$^1$C) 1.4, PCH*C*H$_3$], 13.1 [dd, *J*(PC) 27.3, *J*(PC) 27.0 Hz, PCH$_2$P]; $\delta_P$ (81.0 MHz) −1.9 [d, *J*(PP) 100.0, Pr$^i_2$P], −10.1 [d, *J*(PP) 100.0 Hz, Cy$_2$P].

**Mes$_2$PCH$_2$PPr$^i_2$ 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 cm$^3$, 0.83 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.13 cm$^3$, 0.83 mmol) and Pr$^i_2$PCl (0.132 cm$^3$, 0.83 mmol). Colorless, oily liquid ($\rho$ 1.18 g cm$^{-3}$): yield 285 mg (85%) (Found: C, 75.41; H, 10.00. C$_{25}$H$_{38}$P$_2$ requires C, 74.97; H, 9.56%). NMR (CDCl$_3$): $\delta_H$ (200 MHz) 6.86 [4 H, br d, *J*(PH) 2.6, C$_6$H$_2$], 2.59 [2 H, dd, *J*(P$^1$H) 4.9, *J*(P$^2$H) 1.7, PCH$_2$P], 2.47 (12 H, s, 2,6-*H*$_3$C-C$_6$H$_2$), 2.31 (6 H, s, 4-*H*$_3$C-C$_6$H$_2$), 1.86 (2 H, m, PC*H*CH$_3$), 1.17 [6 H, dd, *J*(PH) 20.8, *J*(HH) 6.8, PCHC*H*$_3$], 1.09 [6 H, dd, *J*(PH) 22.6, *J*(HH) 7.0 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz) 141.6 [d, *J*(PC) 13.4, *ortho*-C of C$_6$H$_2$], 137.1 (s, *para*-C of C$_6$H$_2$), 133.8 [dd, *J*(P$^1$C) 23.6, *J*(P$^2$C) 7.9, *ipso*-C of C$_6$H$_2$], 129.7 [d, *J*(PC) 2.8, *meta*-C of C$_6$H$_2$], 24.3 [dd, *J*(P$^2$C) 15.5, *J*(P$^1$C) 8.2, P*C*HCH$_3$], 23.3 [dd, *J*(P$^1$C) 12.8, *J*(P$^2$C) 2.7, 2,6-H$_3$*C*-C$_6$H$_2$], 21.3 [dd, *J*(P$^2$C) 26.9, *J*(P$^1$C) 22.9, PCH$_2$P], 20.7 (s, 4-H$_3$*C*-C$_6$H$_2$), 19.2 [br d, *J*(PC) 14.6, PCH*C*H$_3$], 18.7 [br d, *J*(PC) 11.1 Hz, PCH*C*H$_3$]; $\delta_P$ (81.0 MHz) −1.5 [d, *J*(PP) 149.7, Pr$^i_2$P], −25.1 [d, *J*(PP) 149.7 Hz, Mes$_2$P].

**Cy$_2$PCH$_2$PMes$_2$ 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 cm$^3$, 0.47 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.072 cm$^3$, 0.47 mmol) and Cy$_2$PCl (0.105 cm$^3$, 0.47 mmol). Colorless, oily solid: yield 170 mg (74%) (Found: C, 77.89; H, 10.04. C$_{31}$H$_{46}$P$_2$ requires C, 77.46; H, 9.65%). NMR (CDCl$_3$): $\delta_H$ (200 MHz) 6.79 [4 H, br d, *J*(PH) 2.3, C$_6$H$_2$], 2.53 [2 H, dd, *J*(P$^2$H) 3.9, *J*(P$^1$H) 1.4 Hz, PCH$_2$P], 2.32 (12 H, br s, 2,6-*H*$_3$C-C$_6$H$_2$), 2.24 (6 H, br s, 4-*H*$_3$C-C$_6$H$_2$), 1.85–1.47 (10 H, br m, PCHCH$_2$), 1.30–1.15 (12 H, br m, CH$_2$ of PCy$_2$); $\delta_C$ (50.3 MHz) 141.7 [d, *J*(PC) 13.9, *ortho*-C of C$_6$H$_2$], 137.2 (s, *para*-C of C$_6$H$_2$), 134.0 [dd, *J*(P$^2$C) 23.6, *J*(P$^1$C) 7.9, *ipso*-C of C$_6$H$_2$], 129.8 [d, *J*(PC) 2.3, *meta*-C of C$_6$H$_2$], 34.3 [dd, *J*(P$^1$C) 16.2, *J*(P$^2$C) 8.3, P*C*HCH$_2$], 29.4 [d, *J*(PC) 12.3, PCH*C*H$_2$], 27.3 [d, *J*(PC) 9.7, CH$_2$ of PCy$_2$], 26.5 (s, CH$_2$ of PCy$_2$), 23.4 [dd, *J*(P$^2$C) 12.7, *J*(P$^1$C) 2.5, 2.6-H$_3$*C*-C$_6$H$_2$], 20.9 [dd, *J*(P$^1$C) 25.9, *J*(P$^2$C) 22.7 Hz, PCH$_2$P], 20.7 (s, 4-H$_3$*C*-C$_6$H$_2$); $\delta_P$ (81.0 MHz) −8.4 [d, *J*(PP) 153.0, Cy$_2$P], −25.5 [d, *J*(PP) 153.0 Hz, Mes$_2$P].

**Bu$^t_2$PCH$_2$PCy$_2$ 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 cm$^3$, 0.60 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.090 cm$^3$, 0.59 mmol) and Bu$^t_2$PCl (0.109 cm$^3$, 0.58 mmol). Colorless liquid: yield 130 mg (64%). NMR (CDCl$_3$): $\delta_H$ (200 MHz) 1.82–1.58 (10 H, br m, PCHCH$_2$), 1.43 (2 H, br s, PCH$_2$P), 1.22–1.16 (12 H, br m, CH$_2$ of PCy$_2$), 1.13 [18 H, d, *J*(PH) 10.8 Hz, PCCH$_3$]; $\delta_C$ (50.3 MHz) 34.4 [dd, *J*(P$^2$C) 15.5, *J*(P$^1$C) 6.2, P*C*HCH$_2$], 32.1 [dd, *J*(P$^1$C) 22.9, *J*(P$^2$C) 5.1, P*C*CH$_3$], 29.9 [dd, *J*(P$^1$C) 13.0, *J*(P$^2$C) 2.1, PC*C*H$_3$], 29.4 [br d, *J*(PC) 10.2, PCH*C*H$_2$], 27.3 [br d, *J*(PC) 9.5, CH$_2$ of PCy$_2$], 26.6 (s, CH$_2$ of PCy$_2$), 12.7 [dd, *J*(P$^1$C) 31.8, *J*(P$^2$C) 26.7 Hz, PCH$_2$P]; $\delta_P$ (81.0 MHz) 20.1 [d, *J*(PP) 107.8, Bu$^t_2$P], −4.4 [d, *J*(PP) 107.8 Hz, Cy$_2$P].

**Bu$^t_2$PCH$_2$PPr$^i_2$ 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 cm$^3$, 1.55 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.23 cm$^3$, 1.55 mmol) and Bu$^t_2$PCl (0.29 cm$^3$, 1.53 mmol). Colorless liquid: yield 210 mg (50%). NMR (C$_6$D$_6$): $\delta_H$ (400 MHz) 1.79 [2 H, dsept, *J*(PH) 2.4, *J*(HH) 7.2, PC*H*CH$_3$], 1.43 (2 H, br s, PCH$_2$P), 1.14 [18 H, d, *J*(PH) 10.8, PCCH$_3$], 1.13 [6 H, dd, *J*(PH) 12.4, *J*(HH) 7.2, PCHC*H*$_3$], 1.09 [6 H, dd, *J*(PH) 12.0, *J*(HH) 6.8 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz, CDCl$_3$) 31.8 [dd, *J*(P$^1$C) 22.9, *J*(P$^2$C) 4.6, P*C*CH$_3$], 29.7 [dd, *J*(P$^1$C) 13.0, *J*(P$^2$C) 2.0, PC*C*H$_3$], 24.1 [dd, *J*(P$^2$C) 15.3, *J*(P$^1$C) 6.5, P*C*HCH$_3$], 19.7 [d, *J*(PC) 13.9, PCH*C*H$_3$], 19.1 [d, *J*(PC) 11.1, PCH*C*H$_3$], 13.4 [dd, *J*(P$^1$C) 33.1, *J*(P$^2$C) 27.3 Hz, PCH$_2$P]; $\delta_P$ (162.0 MHz, CDCl$_3$) 19.0 [d, *J*(PP) 98.3, Bu$^t_2$P], 2.7 [d, *J*(PP) 98.3 Hz, Pr$^i_2$P].

**$Pr^i_2PCH_2PPr^i_2$ 17.** This was prepared as described for **12** (method B), from **6** (3.70 g, 7.69 mmol) and $Pr^i_2PCl$ (1.22 $cm^3$, 7.68 mmol); colorless liquid: yield 1.52 g (80%). NMR ($CDCl_3$): $\delta_P$ (81.0 MHz) 1.3 (s). For other data see ref. 13.

**$Cy_2PCH_2PCy_2$ 18.** This was prepared as described for **12** (method B), from **7** (0.50 g, 0.89 mmol) and $Cy_2PCl$ (0.198 $cm^3$, 0.89 mmol); colorless solid: yield 0.29 g (80%). For analytical and spectroscopic data see ref. 14.

**$Ph_2PCH_2PPr^i_2$ 19.** This was prepared as described for **12** (method B), from **6** (0.85 g, 1.76 mmol) and $Ph_2PCl$ (0.317 $cm^3$, 1.76 mmol). Colorless, oily liquid: yield 0.41 g (74%). NMR ($CDCl_3$): $\delta_C$ (50.3 MHz) 139.5 [dd, $J(P^1C)$ 14.8, $J(P^2C)$ 6.5, *ipso*-C of $C_6H_5$], 132.7 [d, $J$(PC) 18.7, *ortho*-C of $C_6H_5$], 128.4 (br s, *para*-C of $C_6H_5$), 128.2 [d, $J$(PC) 7.2, *meta*-C of $C_6H_5$], 24.1 [dd, $J(P^2C)$ 14.3, $J(P^1C)$ 7.2, P*C*HCH$_3$], 20.7 [dd, $J(P^2C)$ 29.1, $J(P^1C)$ 21.3, $PCH_2P$], 19.6 [br d, $J$(PC) 15.0, PCH*C*H$_3$], 18.8 [dd, $J(P^2C)$ 10.1, $J(P^1C)$ 1.5 Hz, PCH*C*H$_3$]; $\delta_P$ (81.0 MHz, $CDCl_3$) −3.7 [d, $J$(PP) 119.5, $Pr^i_2P$], −19.1 [d, $J$(PP) 119.5 Hz, $Ph_2P$]. For other data see ref. 15.

**$Cy_2PCH_2PPh_2$ 20.** This was prepared as described for **12** (method B), from **7** (0.92 g, 1.64 mmol) and $Ph_2PCl$ (0.303 $cm^3$, 1.64 mmol); colorless, oily solid: yield 0.38 g (58%) (Found: C, 76.05; H, 8.90. $C_{25}H_{34}P_2$ requires C, 75.73; H, 8.65%). NMR ($CDCl_3$): $\delta_H$ (200 MHz) 7.54–7.25 (10 H, m, $C_6H_5$), 2.13 [2 H, br d, $J(P^2H)$ 2.2 Hz, $PCH_2P$], 1.77, 1.24 (22 H, both br m, $C_6H_{11}$); $\delta_C$ (50.3 MHz) 139.6 [dd, $J(P^2C)$ 14.6, $J(P^1C)$ 6.3, *ipso*-C of $C_6H_5$], 132.7 [d, $J$(PC) 18.7, *ortho*-C of $C_6H_5$], 128.3 [d, $J$(PC) 7.6, *meta*-C of $C_6H_5$], 128.1 (s, *para*-C of $C_6H_5$), 34.1 [dd, $J(P^1C)$ 14.7, $J(P^2C)$ 6.6, P*C*HCH$_2$], 29.8 [d, $J$(PC) 13.6, PCH*C*H$_2$], 29.1 [d, $J$(PC) 8.6, PCH*C*H$_2$], 27.3 [d, $J$(PC) 4.8, $CH_2$ of $PCy_2$], 27.1 (br s, $CH_2$ of $PCy_2$), 26.4 (s, $CH_2$ of $PCy_2$), 20.4 [dd, $J(P^1C)$ 28.4, $J(P^2C)$ 21.2 Hz, $PCH_2P$]; $\delta_P$ (81.0 MHz) −11.6 [d, $J$(PP) 120.6, $Cy_2P$], −19.1 [d, $J$(PP) 120.6 Hz, $Ph_2P$].

**$Pr^i_2AsCH_2PPr^i_2$ 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 $cm^3$, 2.46 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.37 $cm^3$, 2.45 mmol) and a solution of $Pr^i_2AsCl$ (476 mg, 2.42 mmol) in diethyl ether. Colorless liquid ($\rho$ 1.15 g $cm^{-3}$): yield 477 mg (67%); MS (CI, isobutane, 70 eV): *m*/*z* 294 [100, $\{Pr^i_2AsCH_2PPr^i_2\}^+ + H$]. NMR ($CDCl_3$): $\delta_H$ (200 MHz) 1.78 (4 H, br m, AsC*H*CH$_3$ and PC*H*CH$_3$), 1.34 (2 H, br s, $AsCH_2P$), 1.12 (24 H, br m, AsCHC*H*$_3$ and PCHC*H*$_3$); $\delta_C$ (50.3 MHz) 24.6 [d, $J$(PC) 5.5, As*C*HCH$_3$], 24.4 [d, $J$(PC) 13.4, P*C*HCH$_3$], 20.5, 20.2 (both s, AsCH*C*H$_3$), 19.8 [br d, $J$(PC) 13.9, PCH*C*H$_3$], 19.1 [br d, $J$(PC) 10.2, PCH*C*H$_3$], 11.6 [d, $J$(PC) 31.4 Hz, $AsCH_2P$]; $\delta_P$ (81.0 MHz) −0.7 (s).

**$Bu^t_2AsCH_2PPr^i_2$ 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 $cm^3$, 5.08 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.76 $cm^3$, 5.04 mmol) and a solution of $Bu^t_2AsCl$ (1.11 g, 4.94 mmol) in diethyl ether. Colorless liquid: yield 1.16 g (73%). MS (CI, isobutane, 70 eV): *m*/*z* 321 [8.3, $\{Bu^t_2AsCH_2PPr^i_2\}^+ + H$]; NMR ($CDCl_3$): $\delta_H$ (200 MHz) 1.70 [2 H, dsept, $J$(PH) 2.2, $J$(HH) 7.2, PC*H*CH$_3$], 1.35 (2 H, s, $AsCH_2P$), 1.11 (18 H, s, AsCCH$_3$), 1.05 [6 H, dd, $J$(PH) 11.7, $J$(HH) 6.9, PCHC*H*$_3$], 1.03 [6 H, dd, $J$(PH) 12.8, $J$(HH) 6.9 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz) 33.0 [d, $J$(PC) 4.7, As*C*CH$_3$], 30.1 [d, (PC) 1.8, AsC*C*H$_3$], 24.7 [d, $J$(PC) 13.4, P*C*HCH$_3$], 19.7 [d, $J$(PC) 11.1, PCH*C*H$_3$], 19.5 [d, $J$(PC) 12.0, PCH*C*H$_3$], 12.1 [d, $J$(PC) 35.2 Hz, $AsCH_2P$]; $\delta_P$ (81.0 MHz) 1.6 (s).

**$Cy_2AsCH_2PPr^i_2$ 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 $cm^3$, 3.67 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.70 $cm^3$, 3.58 mmol) and $Cy_2AsCl$ (0.70 $cm^3$, 3.58 mmol). Colorless liquid ($\rho$ 1.17 g $cm^{-3}$): yield 1.10 g (82%) (Found: C, 60.88; H, 10.52. $C_{19}H_{38}AsP$ requires C, 61.28; H, 10.29%). NMR ($CDCl_3$): $\delta_H$ (200 MHz) 1.77–1.60 (12 H, br m, AsCHC$H_2$ and PC*H*CH$_3$), 1.34 (2 H, br s, $AsCH_2P$), 1.29–1.19 (12 H, br m, $CH_2$ of $AsCy_2$), 1.08 [12 H, br dd, $J$(PH) 12.3, $J$(HH) 7.0 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz) 34.7 [d, $J$(PC) 6.0, As*C*HCH$_2$], 30.8, 30.2 (both s, AsCH*C*H$_2$), 27.7, 26.5 (both s, $CH_2$ of $AsCy_2$), 24.5 [d, $J$(PC) 13.8, P*C*HCH$_3$], 19.8 [d, $J$(PC) 13.8, PCH*C*H$_3$], 19.1 [d, $J$(PC) 10.2, PCH*C*H$_3$], 10.7 [d, $J$(PC) 31.0 Hz, $AsCH_2P$]; $\delta_P$ (81.0 MHz) −0.7 (s).

**$Cy_2AsCH_2PCy_2$ 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 $cm^3$, 3.65 mmol) in cyclohexane–diethyl ether (1:1), TMEDA (0.56 $cm^3$, 3.70 mmol) and $Cy_2AsCl$ (0.70 $cm^3$, 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. $C_{25}H_{46}AsP$ requires C, 66.34; H, 10.24%). NMR ($CDCl_3$): $\delta_H$ (200 MHz) 1.74–1.46 (20 H, br m, AsCHC$H_2$ and PCHC$H_2$), 1.35 (2 H, br s, $AsCH_2P$), 1.36–1.22 (24 H, br m, $CH_2$ of $AsCy_2$ and $PCy_2$); $\delta_C$ (50.3 MHz) 34.7 [d, $J$(PC) 6.0, As*C*HCH$_2$], 34.6 [d, $J$(PC) 14.6, P*C*HCH$_2$], 30.8, 30.2 (both br s, AsCH*C*H$_2$), 30.1 [br d, $J$(PC) 14.3, PCH*C*H$_2$], 29.2 [d, $J$(PC) 8.8, PCH*C*H$_2$], 27.7 (s, $CH_2$ of $AsCy_2$), 27.5–27.2 (m, $CH_2$ of $PCy_2$), 26.6 (br s, $CH_2$ of $AsCy_2$ and $PCy_2$), 10.3 [d, $J$(PC) 30.8 Hz, $AsCH_2P$]; $\delta_P$ (81.0 MHz) −8.9 (s).

**$Cy_2AsCH_2PMen_2$ 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 $cm^3$, 3.50 mmol) in cumene–THF (9:1) and $Cy_2AsCl$ (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. $C_{33}H_{62}AsP$ requires C, 70.18; H, 11.07%). NMR ($CDCl_3$): $\delta_H$ (200 MHz) 2.73, 2.47 (1 H each, both m, CH), 1.71, 1.50–0.81 (42 H, all br m, $PCH_2P$ and CH and $CH_2$ of $Cy_2P$ and $PMen_2$), 0.87 [6 H, br d, m, $J$(HH) 6.6, $CH_3$], 0.75 [3 H, d, $J$(HH) 6.7, $CH_3$], 0.66 [3 H, d, $J$(HH) 6.9 Hz, $CH_3$]; $\delta_C$ (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, $CH_2$(2)], 38.5 [d, $J$(PC) 20.1, CH(3)], 36.4 [s, $CH_2$(2)], 35.1 [br s, $CH_2$(6)], 34.8 [d, $J$(PC) 6.5, As*C*HCH$_2$], 34.5 [d, $J$(PC) 6.9, As*C*HCH$_2$], 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, $CH_2$ of $AsCy_2$), 27.9–27.6 [m, $CH_2$ of $AsCy_2$ and CH(8)], 27.3 [d, $J$(PC) 19.2, CH(8)], 26.7 (s, $CH_2$ of $AsCy_2$), 25.8 [d, $J$(PC) 8.3, $CH_2$(5)], 25.2 [d, $J$(PC) 7.4, $CH_2$(5)], 22.9, 22.8 [both s, $CH_3$(7)], 21.7, 21.6 [both s, $CH_3$(10)], 15.4 [br s, $CH_3$(9)], 9.8 [d, $J$(PC) 33.8 Hz, $AsCH_2P$]; $\delta_P$ (81.0 MHz) −32.5 (s).

**[Rh($\kappa^2P,P'$-$Pr^i_2PCH_2PPr^i_2$)$_2$]Cl 27.** A suspension of 85 mg (0.12 mmol) of **26** in benzene (6 $cm^3$) was treated with a solution of 179 mg (0.72 mmol) of **17** in hexane (3 $cm^3$) 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 $cm^3$ portions of pentane and dried: yield 135 mg (90%); mp 90 °C (decomp.) (Found: C, 49.55; H, 10.00. $C_{26}H_{60}ClP_4Rh$ requires C, 49.18; H, 9.52%). $\Lambda$ ($MeNO_2$) 111.5 $cm^2\ \Omega^{-1}\ mol^{-1}$. NMR ($C_6D_6$–$CDCl_3$): $\delta_H$ (400 MHz) 2.79 (4 H, m, $PCH_2P$), 1.85 (8 H, m, PC*H*CH$_3$), 1.05 [24 H, m, in $^1$H-{$^{31}$P} d, $J$(HH) 7.1, PCHC*H*$_3$], 0.97 [24 H, m, in $^1$H-{$^{31}$P} d, $J$(HH) 6.8 Hz, PCHC*H*$_3$]; $\delta_C$ (50.3 MHz, $CDCl_3$) 27.0 [t, $J$(PC) 9.7 Hz, $PCH_2P$], 26.3 (vt, *N* 11.1 Hz, P*C*HCH$_3$), 19.8, 18.2 (both s, PCH*C*H$_3$); $\delta_P$ (81.0 MHz, $CDCl_3$) −8.4 [d, $J$(RhP) 111.5 Hz].

**[{RhCl($\kappa^2P,P'$-$Ph_2PCH_2PPr^i_2$)}$_2$] 28.** A suspension of 891 mg (1.24 mmol) of **26** in toluene (30 $cm^3$) was treated at −20 °C with a solution of 800 mg (2.52 mmol) of **19** in toluene (45 $cm^3$). 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 $cm^3$ portions of pentane and

extracted with diethyl ether (50 $cm^3$). The extract was concentrated to *ca.* 10 $cm^3$ *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 $cm^3$ portions of pentane (−30 °C) and dried: yield 745 mg (75%); mp 98 °C (decomp.) (Found: C, 50.21; H, 6.01. $C_{38}H_{52}Cl_2P_4Rh_2$ requires C, 50.18; H, 6.76%). MS (DCI, isobutane, 70–100 eV): *m/z* 489 [0.1, $\{RhCl_2(Ph_2PCH_2PPr^i_2)\}^+$], 454 [0.1 $\{RhCl(Ph_2PCH_2PPr^i_2)\}^+$], 419 [0.4, $\{Rh(Ph_2PCH_2PPr^i_2)\}^+$], 316 [0.9, $Ph_2PCH_2PPr^i_2{}^+$]. NMR ($C_6D_6$): $\delta_H$ (200 MHz) 8.19 (8 H, m, *ortho*-H of $C_6H_5$), 7.09 (12 H, m, *meta*-H and *para*-H of $C_6H_5$), 2.74 (4 H, br m, $PCH_2P$), 1.81 (4 H, m, $PCHCH_3$), 1.34, 0.97 (24 H, both br m, $PCHCH_3$); $\delta_C$ (50.3 MHz) 137.2 [d, *J*(PC) 34.4, *ipso*-C of $C_6H_5$], 134.0 [d, *J*(PC), 12.7, *ortho*-C of $C_6H_5$], 129.3 (br s, *para*-C of $C_6H_5$), 128.2 [d, *J*(PC) 5.1, *meta*-C of $C_6H_5$], 37.1 (br m, $PCH_2P$), 25.4 [d, *J*(PC) 18.7, $PCHCH_3$], 25.3 [d, *J*(PC) 18.5 Hz, $PCHCH_3$], 19.3, 19.2, 18.3 (all s, $PCHCH_3$); $\delta_P$ (81.0 MHz) 3.9 [dd, *J*(RhP) 164.2, *J*(PP) 125.7, $Pr^i_2P$], −27.5 [dd, *J*(RhP) 176.6, *J*(PP) 125.7, $Ph_2P$], −28.2 [dd, *J*(RhP) 177.3, *J*(PP) 125.7 Hz, $Ph_2P$].

**$[(\eta^6\text{-}C_6H_6)Rh(\kappa^2P,P'\text{-}Cy_2PCH_2PPr^i_2)]PF_6$ 30.** A solution of 90 mg (0.15 mmol) of **29** in benzene–acetone (6 $cm^3$, 2:1) was treated with a solution of 65 mg (0.20 mmol) of **12** in benzene (3 $cm^3$) 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 $cm^3$) and stirred for 30 min in an ultrasonic bath. A yellow-brown solid precipitated, which was filtered off and washed with pentane (20 $cm^3$) and dried: yield 79 mg (78%); mp 50 °C (decomp.) (Found: C, 46.16; H, 6.92. $C_{25}H_{44}F_6P_3Rh$ requires C, 45.88; H, 6.78%). NMR ($CD_2Cl_2$): $\delta_H$ (200 MHz) 6.35 (6 H, s, $C_6H_6$), 2.66 (2 H, m, $PCH_2P$), 2.17–1.63 (12 H, br m, $PCHCH_3$ and $PCHCH_2$), 1.35–1.21 (12 H, br m, $CH_2$ of $C_6H_{11}$), 1.13, 1.12 [12 H, both dd, *J*(PH) 17.5, *J*(HH) 7.0 Hz, $PCHCH_3$]; $\delta_C$ (50.3 MHz) 98.5 [d, *J*(RhC) 2.0, $C_6H_5$], 38.1 [d, *J*(PC) 21.3, $PCHCH_2$], 29.2 [br d, *J*(PC) 3.5, $PCHCH_2$], 27.6 [d, *J*(PC) 21.5, $PCHCH_3$], 26.9 [d, *J*(PC) 3.2, $CH_2$ of $PCy_2$], 26.7 [d, *J*(PC) 2.6 Hz, $CH_2$ of $PCy_2$], 26.2 (m, $PCH_2P$), 26.0 (s, $CH_2$ of $C_6H_{11}$), 18.8 (s, $PCHCH_3$); $\delta_P$ (81.0 MHz, $C_6D_6$–$CDCl_3$) 0.9 [dd, *J*(RhP) 171.5, *J*(PP) 98.8, $Pr^i_2P$], −8.4 [dd, *J*(RhP) 171.1, *J*(PP) 98.8, $Cy_2P$], −143.9 [sept, *J*(FP) 711.4 Hz, $PF_6^-$].

**$[(\eta^6\text{-}C_6H_5CH_3)Rh(\kappa^2P,P'\text{-}Cy_2PCH_2PPr^i_2)]PF_6$ 31.** This was prepared as described for **30**, from **29** (110 mg, 0.19 mmol) in toluene–acetone (6 $cm^3$, 2:1) and **12** (65 mg, 0.20 mmol) in toluene (3 $cm^3$). Yellow solid: yield 114 g (90%); mp 105 °C (Found: C, 46.50; H, 6.47; Rh, 15.85. $C_{26}H_{46}F_6P_3Rh$ requires C, 46.71; H, 6.94; Rh, 15.39%). NMR ($CD_2Cl_2$): $\delta_H$ (400 MHz) 6.55–6.35 (5 H, m, $C_6H_5$), 2.62 [2 H, dt, *J*(RhH) 2.2, $J(P^1H) = J(P^2H)$ 10.0, $PCH_2P$], 2.41 (3 H, s, $C_6H_5CH_3$), 1.98–1.70 (12 H, br m, $PCHCH_3$ and $PCHCH_2$), 1.40–1.17 (12 H, br m, $CH_2$ of $C_6H_{11}$), 1.12, 1.10 [12 H, both dd, *J*(PH) 17.6, *J*(HH) 7.2 Hz, $PCHCH_3$]; $\delta_C$ (50.3 MHz) 118.7 (s, *ipso*-C of $C_6H_5CH_3$), 100.8 (s, *ortho*-C of $C_6H_5CH_3$), 100.1 (s, *para*-C of $C_6H_5CH_3$), 98.2 (s, *meta*-C of $C_6H_5CH_3$), 38.7 [d, $J(P^1C)$ 20.8, $PCHCH_2$], 30.9 [br d, *J*(PC) 8.8, $PCHCH_2$], 29.2 [d, *J*(PC) 20.8, $PCHCH_3$], 28.6 [d, $J(P^1C)$ 6.0, $CH_2$ of $C_6H_{11}$], 28.4 [d, $J(P^1C)$ 5.1 Hz, $CH_2$ of $C_6H_{11}$], 27.7 (s, $CH_2$ of $C_6H_{11}$), 27.6 (m, $PCH_2P$), 23.0 (s, $C_6H_5CH_3$), 20.5 (s, $PCHCH_3$); $\delta_P$ (81.0 MHz, $C_6D_6$–$CDCl_3$) 0.9 [dd, *J*(RhP) 171.7, *J*(PP) 100.5, $Pr^i_2P$], −8.4 [dd, *J*(RhP) 170.9, *J*(PP) 100.5, $Cy_2P$], −143.9 [sept, *J*(FP) 710.8 Hz, $PF_6^-$].

### Crystallography

Single crystals of **25** were grown from $Pr^iOH$ (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 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.

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

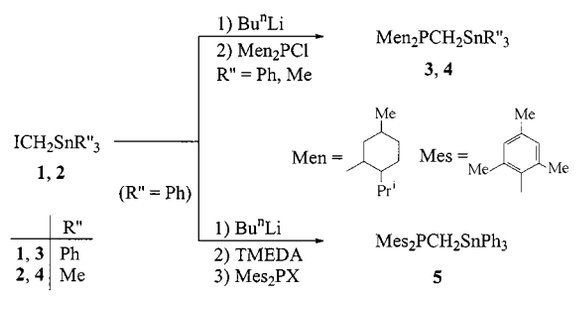
| Formula | $C_{33}H_{62}AsP$ **25** | $C_{26}H_{46}F_6P_3Rh$ **31** |
|---|---|---|
| *M* | 564.72 | 668.45 |
| Crystal system | Trigonal | Monoclinic |
| Space group | $P3_12_1$ (no. 152) | *Cc* (no. 9) |
| *a*/Å | 10.0640(4) | 18.8181(6) |
| *b*/Å | — | 10.8572(3) |
| *c*/Å | 57.716(4) | 29.2564(10) |
| *β*/° | — | 96.7910(10) |
| *V*/Å$^3$ | 5062.5(4) | 5935.5(3) |
| *T*/K | 173(2) | 223(2) |
| *Z* | 6 | 8 |
| $D_c$/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 [*R*(int) = 0.0430] | 7016 [*R*(int) = 0.0536] |
| *R*1 [a] | 0.0418 | 0.0262 [c]<br>0.0320 [d] |
| *wR*2 [b] | 0.0955 | 0.0633 [c]<br>0.0661 [d] |
| Residual electron density/e Å$^{-3}$ | 0.373/−0.410 | 1.406/−0.404 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = [\sigma^2(F_o^2) + (0.040P)^2 + 1.2636P]$ **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**.

## Results and discussion

### Preparation of the bis(phosphino)methanes

Following our recent work on the synthesis of phosphino(stibino)methane derivatives $R_2PCH_2SbR'_2$ 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 $Ph_2AsCH_2AsPh_2$.[8] Using one of the bifunctional compounds $ICH_2SnR''_3$ **1**, **2** (Scheme 1) as the starting material, metalation by $Bu^nLi$ in toluene–hexane at low temperature affords the lithiated species



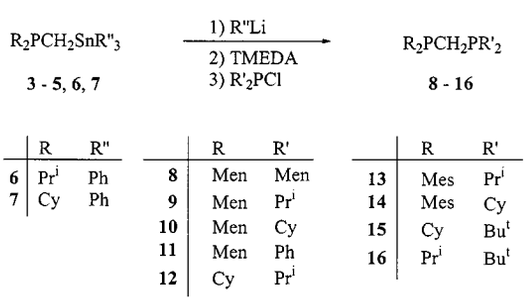

**Scheme 1**

$LiCH_2SnR''_3$ 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 $LiCH_2SnR''_3$ at the triphenyl- or trimethyl-stannyl group of the desired product $R_2PCH_2SnR''_3$,[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 $LiCH_2SnR''_3$, $R_2PX$ 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 $ICH_2SnMe_3$ with $Bu^nLi$ and $R_2PCl$ (R = $Pr^i$, Cy), even at −90 °C in the presence of TMEDA, leads to a mixture of products which contains the phosphines $R_2PCH_2SnMe_3$, $R_2PCH_2PR_2$ and the bis(stannyl)methane $Me_3SnCH_2SnMe_3$ in a ratio of approximately 2:1:1. Attempts to separate the P–Sn product from the other components failed.

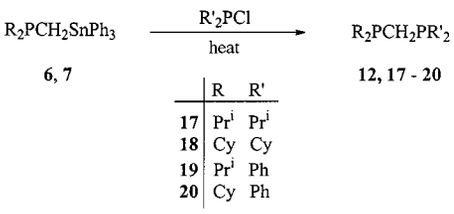
Similarly to $Pr^i_2PCH_2SnPh_3$ **6** and $Cy_2PCH_2SnPh_3$ **7**,[5] compounds **3**–**5** are quite thermally stable and soluble in most organic solvents. The $^{31}P$ NMR spectra of **3**–**5** display a singlet at high field which is partially split into a doublet due to $^{119/117}Sn$–P coupling. The resonance of the bridging $CH_2$ carbon atom appears as a doublet in the $^{13}C$ NMR spectra at $\delta \approx 0$ (for **3** and **4**) and $\delta$ 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 $PMen_2$ 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 stannane $SnR''_4$, the lithiated phosphine $R_2PCH_2Li$ is formed. This reacts with the chlorophosphine $R'_2PCl$ 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 $R_2PCH_2PR'_2$ 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 $Bu^t_2PCH_3$ by deprotonation with $Bu^tLi$ and subsequent addition of $R_2PCl$ (R = Cy, $Pr^i$) to the lithiated intermediate.[11,12] While the $^{31}P$ NMR spectrum of **8** displays only a singlet, the spectra of the unsymmetrically substituted compounds **9**–**16** show two doublets with $^{31}P$–$^{31}P$ 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 $^{13}C$ 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 $R_2PCH_2SnPh_3$ with $R'_2PCl$ can occur even in the absence of PhLi. Whereas treatment of $R_2PCH_2SnPh_3$ with $R'_2PCl$ 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 $R_2PCH_2PR'_2$ by elimination of $Ph_3SnCl$ (Scheme 3). Chromatographic work-up of the 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 Ph(R)P-$CH_2PR_2$ (R = Ph, Me) from $Ph(R)PCH_2SiMe_3$ and $R_2PCl$ in comparable yields.[16]



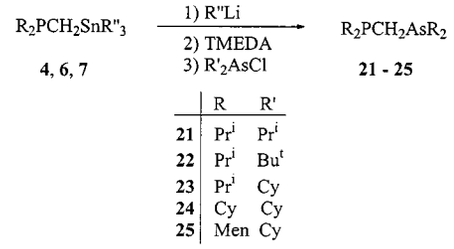

**Scheme 2**




**Scheme 3**

### Synthesis and structure of arsino(phosphino)methanes

The tetraphenyl derivative $Ph_2AsCH_2PPh_2$ is, to the best of our knowledge, the only compound of general composition $R_2AsCH_2PR'_2$ which has been described in the literature.[16,17] The related arsino(phosphino)methanes **21**–**25** (Scheme 4) reported 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 $R_2PCH_2SbR'_2$ and need no further comment.




**Scheme 4**

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 ORTEP[18] plot (Fig. 1) reveals that the molecule of **25** has no crystallographic symmetry. The relative orientation of the $P(Men)_2$ and $AsCy_2$ 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 $CH_2$ 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 $Bu^t_2SbCH_2PCy_2$ [119.17(8)°][5] and P–C–P of $Cy_2PCH_2PCy_2$ [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) | | |

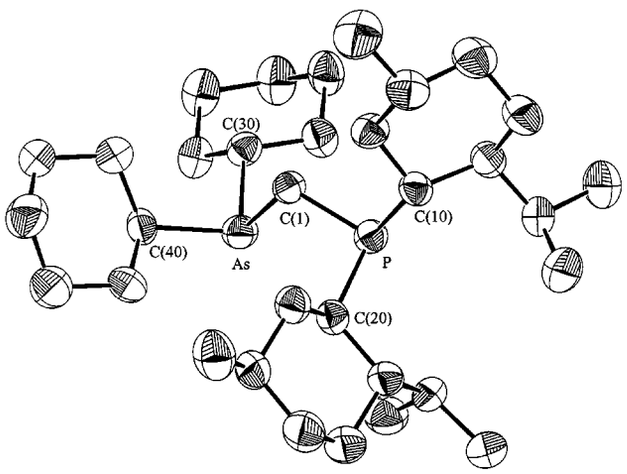
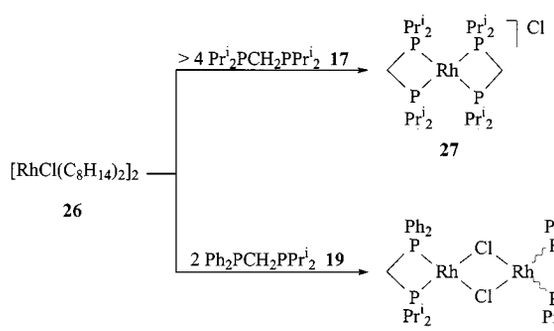



**Fig. 1** An ORTEP plot of compound **25**.

$Bu^t_2SbCH_2PCy_2$ [1.842(2) Å][5] and $Ph_2PCH_2PPh_2$ [1.848(5) Å],[20] and differs only slightly from that in $Cy_2PCH_2PCy_2$ [1.858 Å].[19]

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

In contrast to $Ph_2PCH_2PPh_2$ (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 $R_2PCH_2PR_2$ 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



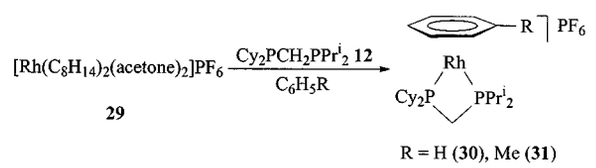

**Scheme 5**

$Bu^t_2PCH_2PBu^t_2$ to give the chloro-bridged dimer [RhCl($\kappa^2P,P'$-$Bu^t_2PCH_2PBu^t_2$)]$_2$,[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 $^1$H and the $^{13}$C 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 $^1$H as well as the $^{13}$C 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 [RhCl($\kappa^2P,P'$-$Bu^t_2PCH_2P$-$Bu^t_2$)]$_2$.[23] The most noteworthy spectroscopic features of **28** are the slightly broadened resonance at $\delta$ 3.9 for the phosphorus atoms of the $PPr^i_2$ moieties and the appearance of two separate signals at $\delta$ −27.5 and −28.2 for the $^{31}$P nuclei of the $PPh_2$ units in the $^{31}$P NMR spectrum. Owing to these data we assume that compound **28** consists of a mixture of two diastereoisomers (both with a planar P′PRhCl$_2$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 [RhCl($\kappa^2P,P'$-$Bu^t_2PCH_2PBu^t_2$)]$_2$, 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 [MCl($\kappa^2P,P'$-$Pr^i_2PCH_2$-$CH_2PPr^i_2$)]$_2$, 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 [Rh($\kappa^2P,P'$-$Cy_2PCH_2PPr^i_2$)(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 $^{31}$P NMR spectra of **30** and **31**, the phosphorus atoms of the two different $PR_2$ units give rise to two doublets of doublets, the $^{103}$Rh–$^{31}$P coupling constants of which (171–172 Hz) are nearly the same as for the neutral complex [($\eta^5$-$C_5H_5$)Rh($\kappa^2P,P'$-$Ph_2PCH_2PPh_2$)] (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 $PPr^i_3$,[28] a cationic intermediate [Rh($\kappa^2P,P'$-$Cy_2PCH_2PPr^i_2$)(Me$_2$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 [($\eta^6$-arene)-Rh{$\kappa^2P,P'$-$Ph_2P(CH_2)_nPPh_2$}]$BF_4$ ($n$ = 2–4) using [Rh($\eta^4$-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) |

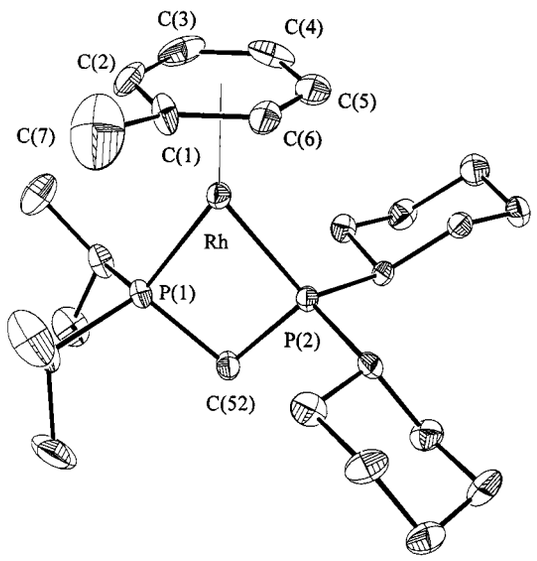



**Fig. 2** An ORTEP plot of the cation of complex **31**.

$\{\kappa^2P,P'$-$Ph_2P(CH_2)_nPPh_2\}]BF_4$ (dien = norbornadiene 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 $\eta^6$-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 dppe 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 $[RhCl(\kappa^2P,P'$-$Bu^t_2PCH_2Bu^t_2)]_2$ [75.8(1)°], $[RhCl(PMe_3)(\kappa^2P,P'$-$Bu^t_2PCH_2PBu^t_2)]$ [75.47(4)°] and $[Rh(\eta^3$-$C_3H_5)(CO)(\kappa^2P,P'$-$Pr^i_2PCH_2PPr^i_2)]$ [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 alkyl 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 laboratory[5] 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 Leitner[24] which indicates that in contrast to $Ph_2PCH_2PPh_2$ (dppm) the more sterically demanding derivatives $Bu^t_2PCH_2PBu^t_2$ 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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