electronic environments of the metal atoms in the two compounds.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-8420806 to A.W.), Ministero Pubblica Istruzione (Rome), and NATO (through Grant 068.81 to A.W. and M.C.). High-field NMR and FAB mass spectra were obtained at the Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019).

Supplementary Material Available: Listings of structure factors for complexes 1 and 3 (30 pages). Ordering information is given on any current masthead page. Listings of temperature factors and hydrogen atom coordinates for 1 and 3 are given in the supplementary material provided with ref 3.

Functional Trimethylphosphine Derivatives. 24.[†] (Phosphinomethyl)aluminum Compounds: Bis- and Tris(dimethylphosphino)methyl Ligands in Tetrahedral and Octahedral Aluminum Phosphine Complexes and X-ray Structure of $Al[(PMe_2)_2C(SiMe_3)]_3$

Hans H. Karsch,* Armin Appelt, Jürgen Riede, and Gerhard Müller

Anorganisch-chemisches Institut, Technische Universität München,
D-8046 Garching, Federal Republic of Germany

Received April 17, 1986

The bis- and tris(phosphino)methanides $Li[CX(PMe_2)_2]$ (**5a,b**) react with Me_2AlCl to give the tetrahedral, monomeric phosphine complexes $Me_2Al[(PMe_2)_2CX]$ (**6a,b**) (**a**, X = PMe_2; **b**, X = $SiMe_3$) with the four-membered chelate rings AlPCP. **6a,b** disproportionate in solution to $AlMe_3$ and the homoleptic complexes $Al[(PMe_2)_2CX]_3$ (**7a,b**) with hexacoordinated aluminum (AlP_6). **7a,b** are also obtained directly from $AlCl_3$ and **5a,b**. In contrast, the sterically less hindered bis(phosphino)methanide $Li[CX(PMe_2)_2]$ (**2**, X = H) yields $\{Me_2Al[CX(PMe_2)_2]\}_n$ (**4**) with Me_2AlCl. **4** exists in solution as an equilibrium mixture of dimeric (six-membered ring, AlCPAlCP, $n = 2$) and monomeric (three-membered ring, AlCP, $n = 1$) species. **4** forms aluminates with LiMe ($[Me_3AlCH(PMe_2)_2Li(TMEDA)_{3/2}]$ (**8**)) and **2** ($\{Me_2Al[CH(PMe_2)_2]_2Li(OEt_2)_2\}$ (**9**)). In **8**, the aluminate acts as a monodentate phosphine ligand to Li, whereas in **9** each of the two bis(phosphino)methyl groups acts as a monodentate ligand to Li, thus forming a six-membered ring (LiPCAlCP). The characterization of the compounds is based on ^1H, ^{13}C, ^{31}P, and ^{27}Al NMR as well as on an X-ray structure determination of **7b**. Crystals of **7b** are rhombohedral of space group $R\bar{3}c$ with $a = b = 12.964$ (2) Å, $c = 43.575$ (5) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6342.3$ Å^3, and $d_{calcd} = 1.019$ g/cm^3 for $z = 6$ at 22 °C. Crystals of **7b** are rhombohedral of space group $R\bar{3}c$ with $a = b = 12.964$ (2) Å, $c = 43.575$ (5) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6342.3$ Å^3, and $d_{calcd} = 1.019$ g/cm^3 for $Z = 6$ at 22 °C. Refinement converged at $R_w = 0.069$ for 67 refined parameters and 898 observables ($F_o \geqslant 4.0\,\sigma(F_o)$). **7b** is a trischelate with the ligands bound exclusively by Al–P bonds (Al–P = 2.495 (2) Å). Crystallographic D_3 symmetry is imposed on the molecule. The AlP_6 coordination geometry is almost halfway between octahedral and trigonal prismatic as manifested by a trigonal twist angle of 35.9° which compares with 60° for a regular octahedron and 0° for regular TP geometry. The observed distortion is induced by the small ligand bite.

Introduction

The ambidentate nature of phosphinomethanide anions I is well-documented. Depending on the nature of the

$$\underset{\text{I}}{[CH_2PR_2]^-} \qquad \underset{\text{II}}{[CH(PR_2)_2]^-} \qquad \underset{\text{III}}{[C(PR_2)_3]^-}$$

electrophile and on the reaction conditions, reaction is observed at either the carbon or the phosphorus atom or at both ligand sites simultaneously.[1] On going from I to II and III, i.e., with increasing number of phosphino substituents at the carbanion, its nucleophilicity should decrease both for steric and electronic reasons, thus favoring P reactivity. It was this argument, which led to the central role of phosphinomethanides in a new concept for the preparation of main group element phosphine complexes.[2] Within this concept, the anionic charge of the phosphine ligand proved to be a key for the accessibility of neutral, halogen-free and, in some cases, homoleptic phosphine complexes of main group elements. Thus, in the reaction of III with $SnCl_2$, neutral monomeric phosphine complexes of Sn(II) were obtained.[3] These reactions also revealed the dominant role of steric effects in compounds with phosphinomethanide ligands. In contrast to Sn(II) (soft metal/soft P donor), the hard metal center Al(III) is less

---

[†] Part 23: see ref 2. Also part 6 of the series: Phosphine Complexes of Main Group Elements. Part 5: see ref 3b.

(1) Some recent compilations of leading references may be found in: (a) Karsch, H. H.; Weber, L.; Wewers, D.; Boese, R.; Müller, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1518. (b) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783. (c) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195.

(2) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1985**, *4*, 1624.

(3) (a) Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem.* **1985**, *97*, 404; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402. (b) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics*, **1986**, *5*, 1664.

0276-7333/87/2306-0316$01.50/0 © 1987 American Chemical Society

Table I. ^{1}H and ^{31}P NMR Data of Aluminum Bis- and Tris(dimethylphosphino)methanide Complexes 4a,b, 6a,b, 7a,b, 8, and 9^a

		^{1}H NMR^b			^{31}P NMR^b	
compd	no.	δ(PCH$_3$) [^2J(PCH)]	δ(P$_A$CHP$_B$) [^2J(P$_A$CH)/ ^2J(P$_B$CH)]	δ(AlCH$_3$) [^3J(PAlCH)]	δ(P$_A$CH$_3$)	δ(P$_B$CH$_3$)
[Me$_2$AlCH(PMe$_2$)$_2$]$_2$^{c}	**4a**	P$_A$: 1.50 (m)/1.40 (m)^{d,e} P$_B$: 1.28 (m)/1.23 (m)^{d,e}	0.52 (dd, br) [7.5/2.4]	−0.33 (m)	−34.51 (t)	−53.70^f
Me$_2$AlCH(PMe$_2$)$_2$^{c}	**4b**	*g*	0.78 (d, br) [2.7/0]	*g*	−33.34 (d)	−50.47 (d)^h
Me$_2$Al[C(PMe$_2$)$_3$]	**6a**	P$_A$: 1.31 ("t")^i P$_B$: 1.38 (d) [3.6]	...	−0.15 (t) [5.2]	−17.34 (s, br)	−39.04 (s)
Me$_2$Al[C(PMe$_2$)$_2$SiMe$_2$]	**6b**^{j}	1.39 ("t")^i	...	−0.04 (t) [5.2]	−20.52 (s, br)	
Al[C(PMe$_2$)$_3$]$_3$	**7a**	P$_A$: 1.40 (s, br)/1.90 (s, br)^e P$_B$: 1.54 (d) [3.2]	...	...	−0.42 (m, br)^k	−46.83 (s, br)
Al[C(PMe$_2$)$_2$SiMe$_3$]	**7b**^{b}	1.45 (s, br)/1.69 (s, br)^e	...	...	−0.12 (m, br)^k	
{(TMEDA)$_{3/2}$Li[(Me$_2$P)$_2$CH]-AlMe$_3$}	**8**^{m}	1.48 (s)/1.56 (s)^e	0.55 (t) [4.5]	−0.37 (s, br)		−47.08 (s)
{(Et$_2$O)$_2$Li[(Me$_2$P)$_2$CH]$_2$AlMe$_2$}	**9**^{n}	1.42 (s)/1.55 (s)^e	0.70 (t) [3.4]	−0.22 (s, br)		−43.81 (s)

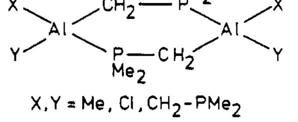
^{a} P$_A$ refers to the phosphorus atom directly bound to the aluminum atom. ^{b} Chemical shift in ppm (positive values refer to low field); Me$_4$Si and H$_3$PO$_4$ as external standards, respectively; coupling constants in Hz. ^{c} Temperature-dependent equilibrium between the two isomers **4a** and **4b** (see text). ^{d} Complex multiplet pattern not resolved. ^{e} Diastereotopic CH$_3$ groups. ^{f} ^2J(P$_A$P$_B$) = 9.2 Hz. ^{g} Superposition with signals of **4a**. ^{h} ^2J(P$_A$P$_B$) = 21.4 Hz. ^{i} X$_6$AA′X$_6$′ spin system: N = 8.8 Hz; cf. ref 17. ^{j} δ(SiCH$_3$) 0.44 (s). ^{k} See text. ^{l} δ(SiCH$_3$) 0.57 (s). ^{m} TMEDA: δ(NCH$_3$) 2.20 (s, 18 H), δ(NCH$_2$) 2.10 (s, 6 H). ^{n} Et$_2$O: δ(CH$_3$) 1.24 (t, 12 H), δ(OCH$_2$) 3.47 (q, 8 H, J(HH) = 6.8 Hz).

Table II. ^{13}C and ^{27}Al NMR Data of Aluminum Bis- and Tris(dimethylphosphino)methanide Complexes 4a,b, 6b, 7a,b, 8, and 9^a

		^{13}C NMR^b			^{27}Al NMR^b
compd	no.	PCH$_3$ [^1J(PC)]	PCP [^1J(PC)]	AlCH$_3$	Al[Δ^{exptl}]
[Me$_2$AlCH(PMe$_2$)$_2$]$_2$	**4a**	P$_A$: 16.60 (m)^c P$_B$: 12.15 ("quin")/9.30 ("q")^e	15.90 (m, br)	−6.50 (m, br)/−9.58 (m, br)^d	160 [3340]
Me$_2$AlCH(PMe$_2$)$_2$	**4b**	P$_A$^{f} P$_B$: 10.90 (dd)/8.54 (dd) [14.7/18.3]/[15.9/29.3]	*g*	−6.46 (m, br)/−8.49 (m, br)^d	156 [1680]^h
Me$_2$Al[C(PMe$_2$)$_2$SiMe$_3$]^i	**6b**^{j}	18.74 ("t")^{j,k}	14.67 (t) [17.7]	−11.25 (s, br)	177 [2300]
Al[C(PMe$_2$)$_3$]$_3$	**7a**	P$_A$: 20.51 (m)^l P$_B$: 18.26 (dt)/17.70 (dt)^m [14.7/1.1]/[14.0/1.7]	13.30 (td), [8.8/1.5]	...	27.6 [20] sept^{h,n}
Al[C(PMe$_2$)$_2$SiMe$_3$]$_3$	**7b**	21.41 (s, br)	16.74 br^o		35.1 [20] sept^p
{(TMEDA)$_{3/2}$Li[(Me$_2$P)$_2$CH]AlMe$_3$}	**8**^{q}	17.19 ("t")^r/17.99 (s)^m	24.00 s, br	−3.69 (s, br)	152 [320]
{(Et$_2$O)$_2$Li[(Me$_2$P)$_2$CH]AlMe$_2$}	**9**^{s}	17.53 (m)^t/18.09 (s)^m	23.64 t [31.7]	−0.36 (s, br)	154 [1800]^h

^{a} P$_A$ refers to the phosphorus atom directly bound to the aluminum atom. ^{b} Chemical shift in ppm (positive values refer to low field); Me$_4$Si and [Al(D$_2$O)$_6$]$^{3+}$ as external standards, respectively; coupling constants in Hz. ^{c} Complex multiplet pattern. ^{d} Diastereotopic AlCH$_3$ groups. ^{e} Two AA′X spin systems for the diastereotopic PCH$_3$ groups; N = distance of the two outermost lines of the multiplets = 29.7 and 40.3 Hz, respectively. ^{f} Superposition with P$_A$ signal of **4a**. ^{g} Signal could not be identified. ^{h} T = 100 °C. ^{i} δ(SiCH$_3$) 4.61 (s). ^{j} AA′X spin system. ^{k} N = distance of the two outermost lines = 37.9 Hz. ^{l} Unsymmetrical multiplet for the diastereotopic PCH$_3$ groups, unresolved. ^{m} Diastereotopic PCH$_3$ groups. ^{n} ^1J(PAl) = 97.7 Hz. ^{o} T = −80 °C, signal not well-resolved. ^{p} T = 90 °C; ^1J(PAl) = 91.6 Hz. ^{q} TMEDA: δ(NCH$_3$) 45.94 (s), δ(NCH$_2$) 56.93 (s). ^{r} AA′X spin system, N = distance of the two outermost lines = 7.3 Hz. ^{s} Et$_2$O: δ(CH$_3$) 15.20 (s), δ(CH$_2$) 66.04 (s). ^{t} AA′X spin system, N = distance of the two outermost lines of the symmetrical multiplet = 14.7 Hz.

likely to give stable phosphine complexes of the type envisaged. Thus, the choice of Al(III) as the coordination center for phosphinomethanides provides a reliable probe for the general validity of the above-mentioned concept. With aluminum as the electrophile, I forms dimeric compounds IV containing a six-membered ring with both C- and P-coordination.[4]



IV

Replacement of I by II, or III, is expected to favor monomeric species and/or the formation of Al–P bonds. With III even hexacoordinate aluminum phosphine species might be envisaged. Another aim of the present work was the preparation of new (phosphinomethyl)aluminates, which likewise have been shown to be useful phosphine ligands for the synthesis of main group element phosphine complexes.[2] With II and III instead of I as substituents at the aluminate center, potentially polydentate, anionic phosphine ligands might become accessible. The preparation and characterization of neutral and anionic phosphinomethyl-substituted aluminum compounds with ligands of type II and III are described in this work.[5]

Experimental Section

A. Preparation and Characterization of Compounds. General procedures and instrumentation followed closely those previously described.[2] All compounds were prepared and handled in a dry argon atmosphere by using conventional vacuum line or Schlenk tube techniques. LiAlH$_4$ (hydrocarbon solvents) and sodium/potassium alloy (ethereal solvents) were employed for drying and storage of the solvents which were redistilled immediately prior to their use. AlCl$_3$ was sublimed in vacuo (180 °C, 10^{-2} torr); Me$_2$AlCl[6] and Li[CX(PMe$_2$)$_2$] (X = PMe$_2$, **5a**;[7] X = SiMe$_3$, **5b**;[8] X = H, **2**[7]) were prepared according to the literature.

---

[4] Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* **1985**, *4*, 231.

[5] Part of this work has been published in a preliminary paper: Karsch, H. H.; Appelt, A. *J. Chem. Soc., Chem. Commun.* **1985**, *1083*.

[6] Marsel, C. L.; Kalil, E. O.; Reidinger, A.; Kramer, L. In *Metallorganic Compounds*; Advances in Chemistry 23; American Chemical Society: Washington, DC, 1959; p 172.

[7] Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1178.

MeLi (ethereal solution) and $AlMe_3$ (hexane solution) were obtained from commercial sources and used without further purification. Toluene-d_8 was used as solvent for the NMR measurements throughout (Table I and II). IR spectra were run as Nujol mulls between CsI windows. Melting points were determined in sealed capillaries by using a Büchi capillary melting point apparatus and are uncorrected.

Microanalytical values were determined by combustion (C, H, N) or AAS (Al). Due to the high air sensitivity of the compounds, satisfying results could not be obtained in all cases. The known effect of Al or P carbide formation may also contribute to this deficiency. However, in all cases, the identity and purity of the compounds could unambiguously deduced from the NMR spectroscopic measurements. Especially diagnostic in this sense are the ^{31}P NMR spectra, which definitely indicate the absence of (P-containing) impurities at least in a 3% range.

$\{Me_2Al[CH(PMe_2)_2]\}_n$ (4). To a stirred suspension of 1.05 g (7.39 mmol) of $LiCH(PMe_2)_2$ (2) in 40 mL of diethyl ether was added 5.64 mL (7.39 mmol) of a 1.31 M solution of Me_2AlCl in toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h. The solvent was removed in vacuo, and the residue was sublimed under reduced pressure. A colorless solid (2.44 g, 6.36 mmol, 86%) was obtained: mp 131 °C; sublimation point 128–131 °C (10^{-3} torr); IR (cm^{-1}) 702–652 (s), 571 (m), 336 (w). Anal. Calcd for $C_{14}H_{38}Al_2P_4$ (384.31): C, 43.75; H, 9.97; Al, 14.04. Found: C, 43.30; H, 9.83; Al, 13.04.

$[Me_3AlCH(PMe_2)_2Li(TMEDA)_{3/2}]$ (8). (a) From $\{Me_2Al[CH(PMe_2)_2]\}_n$ (4) and LiMe. To a solution of 280 mg (1.46 mmol) of 4 in 40 mL of diethyl ether was added with stirring at −78 °C a mixture of 0.89 mL (1.46 mmol) of a 1.64 M solution of LiMe in diethyl ether and 338 mg (2.92 mmol) of TMEDA. The clear solution then was allowed to warm to 0 °C and again cooled to −78 °C. The colorless crystals obtained were washed twice with 20 mL of cold diethyl ether and dried in vacuo (0 °C (10^{-3} torr)): 521 mg (1.34 mmol, 92%).

(b) From $AlMe_3$ and $LiCH(PMe_2)_2$ (2). A 3.05 M solution of $AlMe_3$ in hexane (0.53 mL, 1.62 mmol) was added under stirring to a solution of 230 mg (1.62 mmol) of $LiCH(PMe_2)_2$ (2) and 376 mg (3.24 mmol) of TMEDA in 20 mL of diethyl ether at −78 °C. The reaction mixture was allowed to warm to 0 °C and then cooled to −78 °C. Further manipulations followed closely those described in (a). Colorless crystals (559 mg, 1.44 mmol, 89%) were obtained: mp 28–30 °C; IR (cm^{-1}): 790 (s), 710–670 (vs, br), 441 (m), 342 (w). Anal. Calcd for $C_{17}H_{46}AlLiN_3P_2$ (388.44): C, 52.57; H, 11.94; Al, 6.95; N, 10.82. Found: C, 51.45; H, 12.27; Al, 6.58; N, 11.01.

$\{Me_2Al[CH(PMe_2)_2]_2Li(OEt_2)_2\}$ (9). To a suspension of 178 mg (1.25 mmol) of $LiCH(PMe_2)_2$ (2) in 20 mL of diethyl ether a solution of 240 mg (1.25 mmol) of $\{Me_2Al[CH(PMe_2)_2]\}_n$ (4) in 20 mL of diethyl ether was added with stirring at −78 °C. When the mixture was stirred and warmed to room temperature, a clear colorless solution was obtained. The solution was again cooled slowly to −78 °C. The crystalline solid obtained was washed twice with 10 mL of diethyl ether. After the solid was dried in vacuo, 518 mg (1.08 mmol, 86%) of a colorless crystalline product remained: mp 32–33 °C; IR (cm^{-1}) 710–630 (s, br), 555 (m, sh), 400 (m), 349 (m). Anal. Calcd for $C_{20}H_{52}AlLiO_2P_4$ (482.45): C, 49.79; H, 10.86; Al, 5.59. Found: C, 48.51; H, 10.61; Al, 6.01.

$Al[C(PMe_2)_3]_3$ (7a). (a) To a stirred solution of 720 mg (3.06 mmol) of $LiC(PMe_2)_3$ (**5a**), in 40 mL of diethyl ether was slowly added with stirring at −78 °C a solution of 157 mg (1.19 mmol) of $AlCl_3$ in 40 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h. The solvent was removed under reduced pressure, and the remaining residue was sublimed in vacuo, which gave 670 mg (1.09 mmol, 92%) of a colorless solid.

(b) Following the same procedure with molar ratios of $LiC(PMe_2)_3$ (**5a**) to $AlCl_3$ = 2:1 and 1:1, $Al[C(PMe_2)_3]_3$ (**7a**) was obtained in 82 and 84% yields, respectively (based on **5a**).

(c) **7a** was also formed quantitatively if a solution of **6a** in benzene or pentane was stored at room temperature overnight or warmed to the boiling point of the solvent for some minutes. The reaction may be monitored by NMR spectroscopy. After removal of the solvent in vacuo, $AlMe_3$ and **7a** may be separated and isolated by fractional sublimation at 10^{-3} torr: mp 161–164 °C dec; sublimation point 180 °C (10^{-3} torr); IR (cm^{-1}) 1014 (vs), 972 (s), 937 (s), 748 (m), 701 (m), 670 (m), 457 (m), 401 (m). Anal. Calcd for $C_{21}H_{54}AlP_9$ (612.41): C, 41.91; H, 8.89; Al, 4.41. Found: C, 40.48; H, 8.86; Al, 4.50.

$Al[(PMe_2)_2CSiMe_3]_3$ (7b). (a) $Li(PMe_2)_2CSiMe_3$ (**5b**) (4–6 mmol) was dissolved in 40 mL of THF or alternatively in diethyl ether. Under stirring a solution of $AlCl_3$ in 40 mL of diethyl ether was added at −78 °C, with molar ratios of **5b** to $AlCl_3$ = 3:1, 2:1, and 1:1. The solution was allowed to warm to room temperature, the solvent was removed in vacuo, and the remaining residue was extracted with 40 mL of pentane, filtered, and washed twice with 30 mL of pentane. The combined pentane solutions were dried in vacuo. After sublimation under reduced pressure, a colorless solid was obtained in yields of 92, 88, and 79%, respectively.

(b) Storage of benzene solutions of **6b** for 15 months with subsequent removal of the solvent yields a residue, which on fractional sublimation results in the isolation of an approximately 85% yield of **7b**: mp 169–170 °C; sublimation point 175 °C (10^{-3} torr); IR (cm^{-1}) 1254 (s), 838 (vs), 750 (m), 451 (m), 402 (m). Anal. Calcd for $C_{24}H_{63}AlP_6Si_3$ (648.86): C, 44.43; H, 9.79; Al, 4.16. Found: C, 43.67; H, 9.69; Al, 4.19.

$Me_2Al[C(PMe_2)_3]$ (6a). To a solution of 720 mg (3.86 mmol) of $LiC(PMe_2)_3$ (**5a**) in 40 mL of diethyl ether was added at −78 °C 6.3 mL (3.86 mmol) of a 0.61 M solution of Me_2AlCl in toluene. The stirred mixture was allowed to warm to 0 °C, and the solvent was removed in vacuo. The residue was extracted twice with 40 mL of pentane at 0 °C, and the combined pentane solutions were dried in vacuo. The colorless solid obtained was identified by spectroscopic measurements (see text).

$Me_2Al[C(PMe_2)_2SiMe_3]$ (6b). With stirring and cooling at −78 °C, 11.9 mL (7.24 mmol) of a 0.61 M solution of Me_2AlCl in toluene was added to a solution of 1.55 g (7.24 mmol) of $LiC(PMe_2)_2SiMe_3$ (**5b**) in 40 mL of THF. After the reaction mixture had warmed to room temperature, the now clear solution was stirred for another 12 h. The solvent was removed in vacuo and the remaining residue distilled under reduced pressure. A colorless liquid (1.30 g, 4.92 mmol, 68%) was obtained: bp 37 °C (10^{-2} torr); IR (cm^{-1}) 1243 (s), 843–26 (s), 749 (s), 720–670 (vs), 628 (m), 569 (m), 440 (m), 399 (m). Anal. Calcd for $C_{10}H_{27}AlP_2Si$ (264.34): C, 45.44; H, 10.30; Al, 10.21. Found: C, 44.64; H, 10.14; Al, 9.89.

B. X-ray Structure Determination of $Al[(PMe_2)_2CSiMe_3]_3$ (7b). A colorless single crystal of **7b** (from pentane) was sealed at dry ice temperature into a glass capillary under an atmosphere of argon and immediately transferred to the diffractometer (Enraf-Nonius CAD4). A monoclinic C-centered unit cell was indicated by diffractometer measurements, and the data set was measured in this setting (*hkl* range, ±28,+16,+20). Inspection of the reduced cell and its Niggli matrix indicated a higher symmetric rhombohedral unit cell, with the systematic absences pointing to $R3c$ or $R\bar{3}c$ as possible space groups (Cc or $C2/c$ in monoclinic setting). After appropriate transformation of the data set, solution of the structure was only attempted in $R\bar{3}c$, and this choice of space group was later confirmed by successful refinement. Exact cell constants were determined by least-squares from the Bragg angles of 25 centered reflections ($8.7 \leq \theta \leq 11.5°$) from various parts of reciprocal space. Crystal data and other numbers related to the structure determination are collected in Table III. Intensity data collection and refinement followed previously described procedures.[9]

The intensity data were corrected for Lorentz and polarization effects but not for those of absorption. After equivalent data were merged, structure factors with $F_o \geqslant 4.0\sigma(F_0)$ were considered statistically insignificant and not used in the refinement. The structure was solved in the centrosymmetric space group $R\bar{3}c$ by direct methods (SHELXS-86), which clearly gave the position of the unique SiCPAl fragment with crystallographically imposed D_3 symmetry. (The plausible, calculated density of 1.019 g/cm^3 for $Z = 6$ could not be verified experimentally due to the exceeding air and moisture sensitivity of the single crystals.) Difference Fourier syntheses gave the remainder of the non-H atoms. Location and refinement of the methyl groups at Si were severely

---

(8) Appelt, A. Thesis, Technical University of Munich, 1985.

(9) Schmidbaur, H.; Schier, A.; Frazão, C. M. F.; Müller, G. *J. Am. Chem. Soc.* **1986**, *108*, 976.

Table III. Crystal Structure Data of 7b

formula	$C_{24}H_{63}AlP_6Si_3$
M_r	648.85
cryst system	rhombohedral
space group	$R\bar{3}c$ (No. 167)
$a = b$, Å	12.964 (2)
c, Å	43.575 (5)
$\alpha = \beta$, deg	90
γ, deg	120
V, Å^3	6342.3
Z	6
d_{calcd}, g/cm^3	1.019
μ(Mo Kα), cm^{-1}	3.7
F(000)	2112
T, °C	22
radiatn	Mo Kα
λ, Å	0.710 69
scan type	θ–2θ
scan width (in ω)	$0.5 + 0.35 \tan \theta$
$((\sin \theta)/\lambda)_{max}$, Å	0.639
std reflctns	$\bar{6},3,0$; 0,4,20; $0,3,\overline{12}$
decay, %	2.9
reflctns measd	4964
reflctns unique	1546
R_{int}	0.03
reflctns obsd	898
params refined	67
R^a	0.062
$R_w{}^b$	0.069
(shift/error)$_{max}$	0.06 (1.2 for disordered Me groups)
$\Delta\rho_{fin}$(max/min), e/Å^3	+0.37/–0.22

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, where w = unit weights.

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors of 7b

atom	x/a	y/b	z/c	U(eq)
Al	0.0000	0.0000	0.2500	0.039
P	0.1900 (1)	0.1302 (2)	0.2778 (1)	0.055
Si	0.3818 (3)	0.3818 (3)	0.2500	0.096
C1	0.2404 (6)	0.2404 (6)	0.2500	0.060
C2	0.1791 (6)	0.1844 (6)	0.3156 (1)	0.083
C3	0.2998 (6)	0.0853 (9)	0.2863 (2)	0.098
C4	0.4958 (15)	0.3602 (19)	0.2297 (5)	0.093
C5	0.3846 (19)	0.4864 (19)	0.2198 (6)	0.105
C6	0.4406 (37)	0.4657 (38)	0.2859 (5)	0.142

$^a U(\text{eq}) = (U_1U_2U_3)^{1/3}$, where U_i are the eigenvalues of the U_{ij} matrix.

hampered by extensive disorder. Best results were achieved with a split model consisting of three half-occupied C atoms at a common Si center with the Si–C distances constrained to 1.867 (10) Å. Thereby the alternative sites were generated by the crystallographic twofold symmetry.

The H atoms of the methyl groups at P were included as fixed-atom contributions with U_{iso} = 0.10 Å^2. Two of these had been located in difference maps; four of these were calculated at idealized geometrical positions. The H atoms of the Si–Me groups were neglected. Both the thermal parameters of the silyl carbon atoms as well as the final difference map pointed to further disorder of these atoms. It seems possible that they are virtually randomly distributed on the $-SiMe_3$ cones. Refinement of a model with C_3 symmetry (in $R3c$) led to high correlations with gross differences in equivalent bonding parameters and was not persued further. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ (SHELX 76). The neutral, isolated atom scattering factors used were those of Cromer and Waber.[10] H atom factors, based on a bonded spherical atom model, were those of Stewart, Davidson, and Simpson.[11] All atoms were corrected for $\Delta f'$ and $\Delta f''$.[12] Table IV contains the final atomic coordinates and Table V important distances and angles.

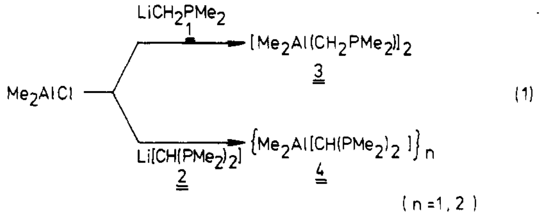
Table V. Selected Interatomic Distances (Å) and Angles (deg) for 7b^a

	Bond Distances		
P1–Al	2.495 (2)	Al···C1	3.117 (8)
P1–C1	1.732 (5)	P1···P4	2.770 (5)
P1–C2	1.826 (7)	P1···P2	3.779 (5)
P1–C3	1.826 (8)		
Si–C1	1.833 (9)		
	Bond Angles		
P1–Al–P4	67.4 (1)	Al–P1–C2	117.3 (3)
P1–Al–P2	98.4 (1)	Al–P1–C3	123.1 (3)
P1–Al–P5	158.9 (1)	C1–P1–C2	112.6 (3)
P1–Al–P6	99.1 (1)	C1–P1–C3	111.8 (4)
C1–P1–Al	93.2 (2)	C2–P1–C3	99.4 (4)
P1–C1–P4	106.1 (4)		
P1–C1–Si	126.9 (2)		

^{a}Estimated standard deviations in units of the last significant figure in parentheses. See Figure 1 for numbering scheme used. P2–P6 are generated from P1 by the following symmetry operations: P2, $-y$, $x - y$, z; P3, $y - x$, $-x$, z; P4, y, x, $0.5 - z$; P5, $-x$, $-x + y$, $0.5 - z$; P6, $-y + x$, $-y$, $0.5 - z$.

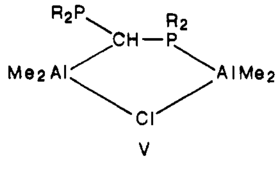
Results and Discussion

$AlCl_3$ is known to react with 3 equiv of $LiCH_2PMe_2$ (1) to give $\{Al(CH_2PMe_2)_3\}_2$, which readily dissolves in hydrocarbon solvents.[4] When $AlCl_3$ is allowed to react with 3 equiv of $Li[HC(PMe_2)_2]$ (2)[7] no soluble compound can be extracted from the reaction mixture with pentane or toluene. Apparently, polymeric species are formed, presumably by means of a bridging function of the anionic ligand. To prevent this polymerization, Me_2AlCl, which likewise gives a dimeric (phosphinomethyl)aluminum compound on reaction with $LiCH_2PMe_2$, was allowed to react with 2 (eq 1). No intermediate could be found. In



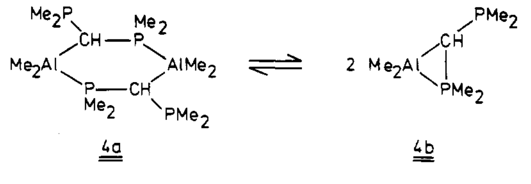
(1)

particular, there was no detectable formation of V (R = Me).[13] In contrast, with R = Ph, V is formed as the only



V

(diphosphinomethyl)aluminum species hitherto known.[14] 4 is shown by NMR spectroscopy to exist as an equilibrium mixture of 4a and 4b in solution. If 4 is dissolved in



(2)

---

[10] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

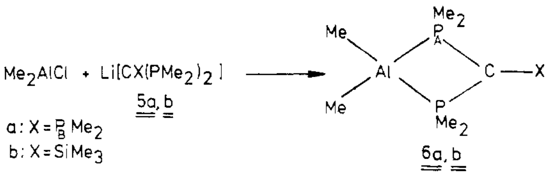
[11] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[12] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[13] Addition of Me_2AlCl to a toluene solution of 4 results in an immediate reaction (NMR), the products could not yet be identified with certainty, however.

[14] Schmidbaur, H.; Lauteschläger, S.; Müller, G. *J. Organomet. Chem.* **1985**, *281*, 33.

toluene, cooled to −78 °C, and kept at this temperature for some hours, only ^{31}P NMR signals, which are attributable to **4a**, are observed, i.e., a degenerate AA′BB′ spectrum (apparently A_2X_2). On warming the solution, these signals gradually decrease and an AB system emerges, which, at room temperature, indicates an approximate 1:1 mixture of **4a** and **4b** (Table I). The ^{27}Al, ^{1}H, and ^{13}C NMR data are in accord with these findings (see Tables I and II). On cooling, the process is reversible. If the spectrum is recorded immediately after **4** is dissolved in toluene at −78 °C, again only **4a** is observed, suggesting that also in the solid state **4** is a dimer, **4a**. **4b** is unique in the sense that an $\overline{\text{MCP}}$ three-membered ring involving a main group metal M is observed for the first time.[15,16] Obviously, the monomer/dimer equilibrium (2), which is not observed for the CH_2PMe_2-bridged dimers IV, is due to the increased steric bulk of the $[CH(PMe_2)_2]^-$ ligand as compared to $[CH_2PMe_2]^-$. Further increase of the steric bulk of the (diphosphino)methanide ligand is achieved by replacing H in $[CH(PMe_2)_2]^-$ by PMe_2 or $SiMe_3$. If Me_2AlCl is allowed to react with $Li[CX(PMe_2)_2]$ (X = PMe_2, **5a**;[7] X = $SiMe_3$; **5b**[8]), **6a** (colorless crystals) and **6b** (distillable liquid) are obtained (eq 3). In **6a,b** the phosphinomethanide ligands span two tetrahedral coordination sites at Al by two equivalent phosphorus atoms, thus forming a four-membered chelate ring. Triplets for the $AlCH_3$ and the PCH_3 groups ($X_nAA'X'_n$ spin system)[17] in the ^{1}H NMR are common features in the spectra of **6a,b** (Table I). Triplets are also observed for the PCH_3 and PCP groups of **6b** in the ^{13}C NMR, whereas the $AlCH_3$ resonance is broad and unresolved, due to the ^{27}Al quadrupolar nucleus (Table II). ^{13}C and ^{27}Al NMR spectra of **6a** could not be recorded, since the compound has only a very limited lifetime in solution ($t_{1/2} \approx 10$ min/20 °C). In fact, **6a** could only be obtained in about 90% purity. **6b** is much more stable ($t_{1/2} \approx 2$ months/20 °C) but also rearranges to the octahedral complexes discussed below (eq 4).



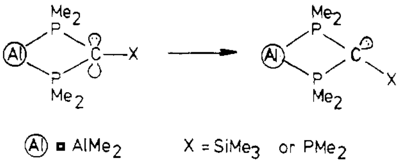
(3)

$$3\,Me_2Al[(PMe_2)_2CX] \xrightarrow[20^\circ C]{toluene} 2\,AlMe_3 + Al[(PMe_2)_2CX]_3 \qquad (4)$$

6a,b **7a,b**

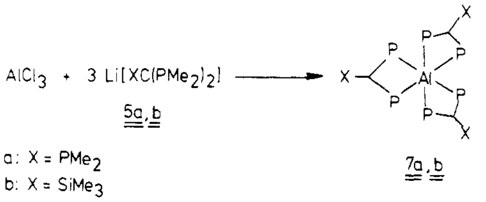
a: X = PMe_2 b: X = $SiMe_3$

Clearly, the "free" phosphino group in **6a** is responsible for the rapid decomposition (probably by intermolecular attack of this group at a second aluminum center and subsequent transfer of the ligand), but the main reason for the relative instability of both compounds very likely is the high ring strain of the four-membered ring. This ring strain should be reduced in a distorted octahedral (**7a,b**) or trigonal-bipyramidal (cf., e.g., $Sn[(PMe_2)_2CX]_2$[3]) coordination. One might furthermore suggest that this ring strain may be released to some extent by a pyramidalization of the carbanionic C atom:



An inequivalence of the PCH_3 groups would serve as a probe for this process. However, even at −100 °C, there is no indication for this inequivalence; the ^{31}P-decoupled ^{1}H NMR signal of PCH_3 in **6b** remains a sharp singlet.

The six-coordinate aluminum phosphine complexes **7a,b** are much more easily prepared (in high yield) by the direct synthesis from $AlCl_3$ and **5a,b** (eq 5). The ready formation of these complexes is also evident from the fact that **7a,b** are also formed nearly quantitatively from $AlCl_3$ and **5a,b** in any other stoichiometric ratio. Though thermally very stable, these complexes, as well as other aluminum phosphinomethanide compounds, are exceedingly air- and moisture-sensitive. They readily dissolve in pentane, and colorless single crystals suitable for X-ray diffraction may be grown from this solvent.



(5)

Their constitution as the first reported homoleptic, neutral, six-coordinate aluminum phosphine complexes is demonstrated by NMR spectroscopy. The most straightforward evidence comes from the ^{27}Al NMR spectrum: the resonances of **7a,b** appear at higher field than that of the tetrahedral complexes (cf. **6b**, +177 ppm; **7b**, + 35 ppm) and lie well in the region reported for octahedral Al complexes.[18] At +100 °C the signals appear as a septet, thus showing ^{1}J(AlP) coupling for the first time, due to the high "local" symmetry at the aluminum nucleus in **7a,b** (Figure 1). At +20 °C, the signal is broad and unresolved in both cases, however (Table II).

The $^{31}P_{Al}$ signal is a sharp single line at −90 °C. On warming to −50 °C, the signal gradually features a broad, unresolved multiplet structure and is unchanged on further warming to +80 °C. Obviously, this broad multiplet again is due to ^{31}P–^{27}Al coupling (Table I). The (distorted) octahedral Al-coordination is evident from the diastereotopic $P_{Al}CH_3$ groups: two 1:1 signals in the ^{1}H spectrum of **7a,b** (Table I) and in the ^{13}C NMR of **7a** (Table II) are easily recognized. For **7b** we could detect only one ^{13}C NMR signal for the PCH_3 groups, probably due to accidental superposition. The expected triplet of doublets structures of the P_XCH_3 and PCP ^{13}C NMR signals in **7a** further support our assignment and indicate that no equilibration process of the P(Al) and P(X) nuclei occurs, as is observed in $Sn[C(PMe_2)_3]_2$.[3]

---

(15) In the transition-metal series, the MCP fragment is now known to be quite common;[1b] the first compounds containing this structural unit have been described a decade ago: Karsch, H. H.; Klein, H.-F.; Kreiter, C. G.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 3692. Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem.* **1975**, *87*, 630; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637.

(16) From the NMR data, a tricoordinated aluminum species, i.e., $Me_2Al–PMe_2CHPMe_2$ (**4c**) has also been taken into consideration instead of **4b**. We prefer the formulation of a three-membered ring because of the coordinative unsaturation of the aluminum in **4c**. Moreover, a cyclic structure (three-membered ring) is predicted as the minimum for $LiCH_2PH_2$: Schleyer, P. v. R.; Clark, T.; Kos, A. I.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(17) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

(18) (a) Benn, R.; Rufińska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem.* **1983**, *95*, 808; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 77. (b) Delpuech, J. J.; Khaddar, M. R.; Pegny, A. A.; Rubini, P. R. *J. Am. Chem. Soc.* **1975**, *97*, 3373.

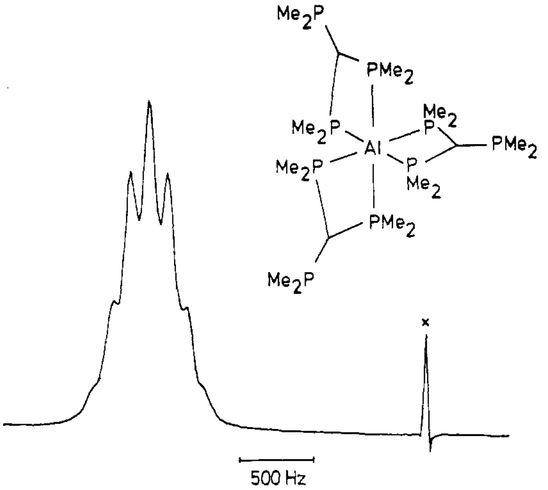


Figure 1. ^{27}Al NMR spectrum of **7a** in toluene-d_8 (100 °C). X is the reference signal (see text).

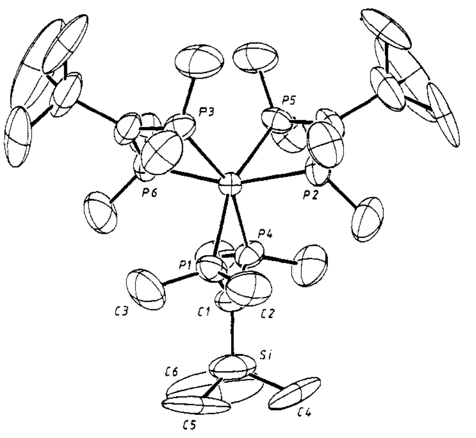


Figure 2. Molecular structure of **7b**, seen approximately down the crystallographic C_3 axis (ORTEP, thermal ellipsoids at the 50% probability level, H atoms omitted for clarity, only one alternative is shown for the disordered SiMe$_3$ groups). Crystallographic C_2 axes pass through the Al, C1, and Si atoms. The trigonal faces of the AlP$_6$ polyhedron, referred to in the discussion, are defined by atoms P1, P2, P3 and P4, P5, P6.

Solid-State Structure of Al[(PMe$_2$)$_2$CSiMe$_3$]$_3$ (7b). As is evident from Figure 2, complexation of the bidentate ligand [(PMe$_2$)$_2$CSiMe$_3$]$^-$ at Al(III) occurs exclusively by formation of Al–P dative bonds. The distances Al···C1 (Table V) are longer than 3 Å and exclude any significant Al–C bonding interaction. The Al–P bond lengths 2.495 (2) Å are noticeably shorter than the Sn–P bond lengths in the Sn(II) complex Sn[C(PMe$_2$)$_3$]$_2$ of the related ligand [C(PMe$_2$)$_3$]$^-$ (Sn–P = 2.598 (2)–2.839 (2) Å) which in this complex likewise acts as a bidentate donor.[3] Apparently the expected bond lengthening due to the higher coordination number of Al(III) is more than counterbalanced by its smaller radius as compared to Sn(II). It should be noted, however that the observed Al–P distances are also shorter than the few determined values for Li–P dative bonds in related Li phosphinomethanide complexes which center around 2.60 Å.[1a,2] In fact, the Al–P bond lengths in **7b** are only slightly longer than in [Me$_2$Al(CH$_2$PMe$_2$)]$_2$ (Al–P = 2.451 (2) Å) and in [ClAl(CH$_2$PMe$_2$)$_2$]$_2$ (Al–P = 2.425 (1) Å) with tetracoordinated aluminum.[4] This, at least in part, may be responsible for the observed stability of the six-coordinate compounds.

The overall geometry of **7b** is characterized by crystallographic D_3 symmetry with the twofold axes passing through Al, C1, Si and the C_3 axis passing perpendicular through their intersection at Al (Figure 2). Quite noticeably, the SiMe$_3$ groups which, if ordered, would reduce this highest attainable symmetry by virtue of their threefold symmetry are found to be extensively disordered in the solid state, thereby resembling the conditions prevailing in solution.

The geometry of the AlP$_6$ coordination sphere is marked by significant distortions from regular octahedral symmetry. Thus the unique bond angles at Al may be divided into three distinct groups (Table V): (a) the small chelate angles P1–Al–P4 which by virtue of the four-membered ring formation are only 67.4 (1)°, (b) the "trans" angles P1–Al–P5 (158.9 (1)°), and (c) the remainder which center around 98.7 (2)°. Quite remarkably, the deviation of the bite angles of 22.6° from the 90° value of a regular octahedron is virtually identical with the deviation of the "trans" angles from 180°: a clear indication that the small ligand bite is predominantly responsible for the observed distortion from octahedral symmetry. Confirmation comes from the trigonal twist angle ϕ, i.e., the relative orientation of the trigonal P$_3$ faces P1, P2, P3 and P4,P5,P6 perpendicular to the C_3 axis (Figure 2).[19] For a regular octahedron ϕ equals 60° while for the other limiting case, the trigonal prism, ϕ equals 0°. In **7b** a value of 35.9° is observed,[20] close to the midpoint between these two idealized polyhedra. If according to Kepert[23] the minimization of interligand repulsion is considered the only driving force for the distortion toward a trigonal prism, one obtains an optimum twist angle of approximately 26° for the ratio of the intraligand P–P distance (the span of the ligand) to the Al–P distance of 2.770/2.495 = 1.11 observed in **7b**. Although at first glance the difference to the observed value might seem quite large, the potential energy minimum given by Kepert[23] is actually quite shallow for a normalized ligand bite of 1.11, thus accounting easily for the discrepancy. Therefore the distortion from regular octahedral geometry in **7b** can be attributed predominantly to the constraints of the ligand bite. This is what is actually expected for phosphine complexation at Al(III) where bonding should be largely ion dipole in character and orbital interactions should only play a minor role in determining the stereochemistry. By comparison, the twist angle of 48° in tris(tropolonato)aluminum(III), Al(O$_2$C$_7$H$_5$)$_3$,[24] likewise is in good agreement with Kepert's values. Closely related to bis(phosphino)methanide ligands, both structurally and electronically should be dithiocarbamates. For group 13 elements, Ga(III)[25] and In(III)[25,26] examples have been structurally characterized. In In(S$_2$CNC$_5$H$_{10}$)$_3$[26] the observed trigonal twist of 33°[27] is in excellent agreement with that in **7b**, clearly a consequence of the similar normalized ligand bite of 1.14. This value results from a slightly longer ligand span, S···S = 2.95 Å, while the In–S distances (2.59 Å) are closer to Al–P in **7b**. Also the bite

---

(19) The bite angle at Al in projection down the C_3 axis.

(20) Calculated according to Dymock and Palenik[21] as the angle between the planes P1, D1, Al and P4, D2, Al, where D1 and D2 are the centroids of the P1, P2, P3 and P4, P5, P6 trigonal faces, respectively. It should be noted that in **7b** by virtue of the crystallographic D_3 symmetry the trigonal faces are parallel and equilateral and that the three ligand bites and the six Al–P distances are equal. Therefore, the relations given by Stiefel and Brown[22] between the trigonal faces, h, and nonbonded contacts, s, hold for **7b**.

(21) Dymock, K. R.; Palenik, G. J. *Inorg. Chem.* **1975**, *14*, 1220.

(22) Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434.

(23) Kepert, D. L. *Inorg. Chem.* **1972**, *11*, 1561.

(24) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 8046.

(25) Dymock, K.; Palenik, G. J.; Slezak, J.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 28.

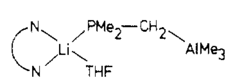
(26) Hauser, P. J.; Bordner, J.; Schreiner, A. F. *Inorg. Chem.* **1973**, *12*, 1347.

(27) Cf. Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

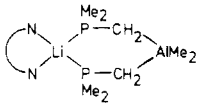
angle (69.4°) in $In(S_2CNC_5H_{10})_3$[26] is directly comparable to that in **7b** as is the overall coordination geometry in both compounds. The geometry of $In(S_2CNEt_2)_3$ is similar,[25] although a larger variation in In–S distances is observed. The latter is also true for $Ga(S_2CNEt_2)_3$,[25] which shows a larger trigonal twist of 41.4°, however. This is clearly a consequence of the larger normalized ligand bite of 1.19 resulting from an average intraligand S···S separation of 2.92 Å and an average Ga–S bond length of 2.44 Å.[25] Thus for dithiocarbamates a generally larger ligand bite is characteristic as compared to those of bis(phosphino)methanides, while the metal ligand distances are more similar for both ligands.

Some other features in the structure of **7b** deserve comment. The P_2CSi skeleton of the phosphinomethanide ligands is planar in complex **7b** as are the planes AlP_2C.[28] The latter observation is at variance with the Sn(II) complex $Sn[C(PMe_2)_3]_2$, where a distinct fold angle was observed which was tentatively attributed to the stereochemical activity of the lone pair at Sn(II).[3] As in the Sn(II) complex, the P–C1 bonds are significantly shorter than P–C single bonds, thus reflecting a high degree of polarity, as is also found in phosphorus ylides.

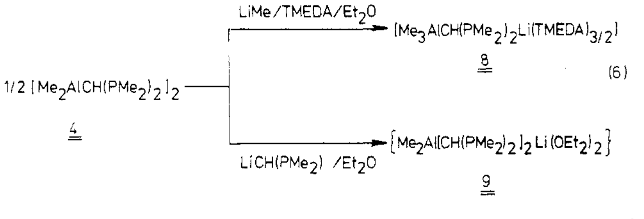
Reactions with Organolithium Reagents ("Ate"-Complex Formation). In the reaction of $[Me_2AlCH_2PMe_2]_2$ with RLi (R = Me, CH_2PMe_2), the only isolable products were $[Li{\cdot}solv][AlMe_4]$ and $Li[Al(CH_2PMe_2)_4]$ in ethereal solvents. Chelating, lithiophilic ligands like TMEDA are necessary to achieve the formation of neutral, soluble lithium (phosphinomethyl)aluminate complexes with tetrahedral Li^+ coordination, as, e.g., VI or VII.[2] In contrast, this type of complexes is readily accessible from $[Me_2AlCH(PMe_2)_2]_2$ (**4**) and $LiCH(PMe_2)_2$, even in diethyl ether (Et_2O). A similar reaction occurs in the system **4**/LiMe/TMEDA (eq 6). Independently, **8** is also obtained from $AlMe_3$ and $LiCH(PMe_2)_2$ (**2**) (eq 6).[9] Both compounds **8** and **9** are isolated as low melting crystals which readily dissolve in aromatic hydrocarbons. Their composition (C, H, Li elemental analysis; relative intensity of the NMR signals) suggests that in **8** the (phosphinomethyl)aluminate acts as a monodentate ligand and in **9** as a bidentate ligand to Li^+, if a tetrahedral Li^+ coordination is also assumed in these cases. Formula **8** implies that the formation of a four-membered chelate ring, LiPCP, is not very favorable, if a sp^3-carbon atom is involved. In contrast, $\{LiC(PMe_2)_3{\cdot}THF\}_2$ exhibits a four-membered chelate ring moiety LiPCP, with a sp^2-carbon atom incorporated in the ring system.[29] Consequently, **9** should adopt a six-membered ring structure, AlCPLiPC, as has been shown for VII.[2] The enhanced stability of **9** with respect to disproportionation, compared to the unisolable analogue with mono(phosphino)methanide ligands, i.e., $Me_2Al(CH_2PMe_2)_2Li(OEt)_2$, probably is due to steric (and perhaps electronic, vide supra) prevention from forming Li–C contacts. Li–C contacts presumably are responsible for alkyl group exchange at aluminum with the consequence of disproportionation in tetramethylaluminate species.[2] Unlike the proposals for the solid-state structures of **8** and **9**, in solution the PCH_3 groups (^1H, ^{13}C, ^{31}P) in both compounds are equivalent down to −90 °C (Tables I and II). Therefore, a rapid exchange process (eq 7) has to be envisaged.



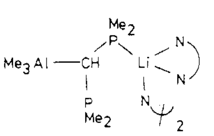
VI



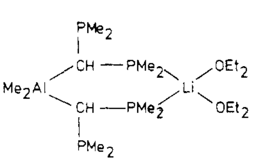
VII



(6)



8



9

(7)

MeLi also reacts with $[Me_2AlC(PMe_2)_2X]$ (**6a**,**b**), but a mixture of several products is obtained, which could not be analyzed, as yet. In contrast, MeLi fails to react with the hexacoordinate aluminum complexes **7a**,**b**, even when a large excess (100:1) is used. Again, the stability of hexacoordination at aluminum is obvious, which prevents disproportionation/redistribution reactions typical for tetrahedral aluminum.

Conclusions

Together with the Sn(II) phosphinomethyl compounds reported previously,[3] the Al(III) phosphinomethyl compounds described in this and previous papers[2,4] enable us to draw some general conclusions with regard to phosphine coordination at main group elements.

Mono(phosphino)methanides $[R_2PCH_2]^-$ and diphosphinomethanides $[(R_2P)_2CH]^-$ may form complexes with C, C⌒P, or P⌒P coordination at main group centers depending mainly on steric effects.

C⌒P coordination is possible by forming either six-membered rings (dimers) or three-membered rings (monomers). The latter is now also met with main group elements (Al), in accord with theory.[16]

Tris(phosphino)methanides $[(R_2P)_3C]^-$ and the corresponding silylsubstituted anions $[(R_2P)_2(Me_3Si)C]^-$ may act as chelating phosphine ligands (P⌒P coordination) in octahedral, trigonal bipyramidal, and tetrahedral complexes. In the latter, it is the ring strain of the four-membered chelate rings which is mainly responsible for the observed limited stability. The Al–P bond lengths in tetrahedral and octahedral aluminum phosphine complexes are almost identical.

The deviations from an idealized coordination geometry, caused by the four-membered chelate rings, are considerable.

The isolation and observed superior stability of the first six-coordinate aluminum phosphine complexes (AlP_6) suggests that high coordination numbers are typical for this type of ligands.

Thus bis- and tris(phosphino)methanides are reminiscent to some extent of dithiocarbamate ligands, which likewise are uninegative ligands, forming four-membered, chelate complexes with high coordination numbers.[25,26]

---

[28] Angle between ligand planes = 81.5°.

[29] Karsch, H. H.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1984**, 569.

In contrast to dithiocarbamate complexes, the possible involvement of the "central" carbon atom in bonding to the metal center in phosphinomethanide complexes promotes dynamic behavior in solution, which adds flexibility and more reaction pathways for these types of complexes.

Registry No. 2, 70355-43-0; **4a,** 104911-10-6; **4b,** 104911-15-1; **5a,** 70377-69-4; **5b,** 102493-28-7; **6a,** 104946-37-4; **6b,** 104946-38-5; **7a,** 99900-56-8; **7b,** 99900-57-9; **8,** 104911-12-8; **9,** 104911-14-0; Me_2AlCl, 1184-58-3; $AlMe_3$, 75-24-1; $AlCl_3$, 7446-70-0.

Supplementary Material Available: Additional crystal structure data and complete tables of atomic positional and thermal parameters (5 pages); a listing of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

Organotransition-Metal Metallacarboranes. 8. Mono-, Di-, and Triiron Polyarene Sandwich Complexes of $Et_2C_2B_4H_4^{2-}$ Containing Fluorene, 9,10-Dihydroanthracene, or [2.2]Paracyclophane Ligands[1]

James T. Spencer and Russell N. Grimes*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

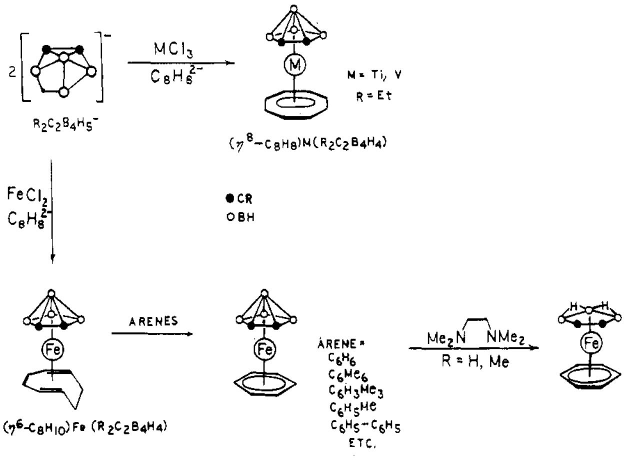
Received April 29, 1986

This paper describes the synthesis of mixed-ligand carborane–iron–polycyclic arene complexes from *nido*-2,3-$Et_2C_2B_4H_6$ together with structural characterization of the products via ^{11}B and ^{1}H NMR, infrared, and mass spectroscopic data. All products reported were isolated as air-stable crystalline solids. The main preparative route utilized displacement of the neutral ligand (L) from $(\eta^6\text{-L})Fe(Et_2C_2B_4H_4)$ (L = C_8H_{10} or $C_{16}H_{18}$) by arenes. In an alternative approach, the previously known naphthalene species $(\eta^6\text{-}C_{10}H_8)\text{-}Fe(Et_2C_2B_4H_4)$ was obtained directly from the $Et_2C_2B_4H_5^-$ ion, $FeCl_2$, and the naphthaleneide dianion. A monoiron fluorene complex $(\eta^6\text{-}C_{13}H_{10})Fe(Et_2C_2B_4H_4)$ (6) was prepared via both routes, employing displacement of C_8H_{10} from $(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)$ (2) as well as direct treatment of $Et_2C_2B_4H_5^-$ with $C_{13}H_{10}^-$ and $FeCl_2$. The thermal reaction of 6 with 2 gave a staggered triple-decker diiron species $(\eta^6,\eta^6\text{-}C_{13}H_{10})Fe_2(Et_2C_2B_4H_4)_2$ (7) and a staggered quadruple-decker triiron complex $Fe[(C_{13}H_{10})Fe(Et_2C_2B_4H_4)]_2$ (8), whose proposed structures are supported by spectroscopic evidence and by X-ray crystallographic data on 6 and 7. "Decapitation" (apex BH removal) of 6 was achieved by treatment with tetramethylethylenediamine giving *nido*-$(\eta^6\text{-}C_{13}H_{10})Fe(Et_2C_2B_3H_5)$.

Introduction

Small *nido*-carboranes of the $R_2C_2B_4H_6$ class (R = alkyl) are emerging as remarkably versatile reagents for the systematic construction of stable transition-metal–organometallic sandwich complexes, including those containing arenes[2] or higher cyclic polyenes[3] coordinated to the metal. Scheme I depicts the main synthetic approaches that have been developed in our laboratory in recent years.[2d-h] Among the compounds that have been prepared by these routes are the first crystallographically defined iron η^6-complexes of naphthalene and phenanthrene,[2h] as well as novel air-stable η^8-C_8H_8 complexes of vanadium and titanium (X-ray structure determinations have been conducted on the latter two species as well[3b]). These compounds, and most of the others reported thus far from our laboratory, utilize the *C,C′*-diethylcarborane ligand $Et_2C_2B_4H_4^{2-}$. The $R_2C_2B_4H_4^{2-}$ group is formally analogous to $C_5H_5^-$ but evidently forms much stronger, more covalent η^5-bonds to transition metals than do either $C_5H_5^-$ or arenes.[4a] The metal–hydrocarbon bonding in many of these species is clearly stabilized by the presence of the carborane unit, as supported by experimental evidence[2,3] and, indi-

Scheme I



---

(1) (a) For part 7 see ref 2h. (b) Presented in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985, paper INOR-295.

(2) (a) Garcia, M. P.; Green, M.; Stone, F. G. A.; Somerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1981, 871. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* 1982, *1*, 77. (c) Micciche, R. P.; Sneddon, L. G. *Organometallics* 1983, *2*, 674. (d) Maynard, R. B.; Swisher, R. G.; Grimes, R. N. *Ibid.* 1983, *2*, 500. (e) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* 1983, *2*, 506. (f) Swisher, R. G.; Sinn, E.; Butcher, R. J.; Grimes, R. N. *Ibid.* 1985, *4*, 882. (g) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* 1985, *4*, 890. (h) Part 7: Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* 1985, *4*, 896. (i) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics*, third of three papers in this issue.

(3) (a) Swisher, R. G.; Sinn, E.; Brewer, G. A.; Grimes, R. N. *J. Am. Chem. Soc.* 1983, *105*, 2079. (b) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Ibid.* 1984, *3*, 599.

(4) (a) Calhorda, M. J.; Mingos, D. M. P. *J. Organomet. Chem.* 1982, *229*, 229. (b) Calhorda, M. J.; Mingos, D. M. P. *Ibid.* 1982, *228*, 309 and references therein.

0276-7333/87/2306-0323$01.50/0