Functional Trimethylphosphine Derivatives. 23.[†] (Phosphinomethyl)aluminum Compounds: (Phosphinomethyl)aluminates as a Novel Type of Phosphine Ligands and X-ray Structures of $[(TMEDA)(THF)Li(Me_2PCH_2)AlMe_3]$ and $[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]$

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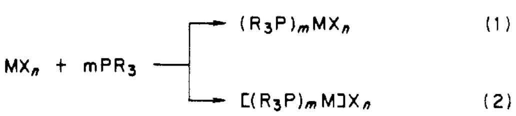
The reaction of $AlMe_3$, $[Me_2Al(CH_2PMe_2)]_2$, and $[Al(CH_2PMe_2)_3]_2$ with LiMe and $LiCH_2PMe_2$, respectively, in hydrocarbon solvents gives white precipitates, which in diethyl ether disproportionate to $Li[AlMe_4]$ and $[Li(Me_2PCH_2)_2Al(CH_2PMe_2)_2]_x$, **5a**. In the presence of tetramethylethylenediamine (TMEDA) and tetrahydrofuran (THF) low melting, toluene-soluble aluminates of the type $[(TMEDA)_x(THF)_yLi(Me_2PCH_2)_nAlMe_{4-n}]$ are isolated for $n = 1$ ($x = {}^3/_2$, $y = 0$, **5d**; $x = 1$, $y = 1$, **5e**; $x = 1$, $y = 0$, **5f**) and $n = 2$ ($x = 1$, $y = 0$, **5c**), whereas for $n = 4$, again **5a** ($x = y = 0$) is obtained as a high melting solid of low solubility. For $n = 3$, a rapid disproportionation dominates and **5c** and **5a** are obtained. Slow disproportionation via alkyl exchange is also observed for $n = 1$. Likewise, $[(TMEDA)_{3/2}Li(Me_2PCH_2)Al(t\text{-}Bu)Me_2]$, **4**, slowly decomposes in solution. Reaction of **5d** with MeI gives the ylide complex $Me_3AlCH_2PMe_3$. The results are explained by the nature of the (phosphinomethyl)aluminates acting as anionic phosphine ligands to Li^+, which is demonstrated unambiguously by X-ray crystal structure determinations of $[(TMEDA)(THF)Li(Me_2PCH_2)AlMe_3]$, **5e**, and $[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]$, **5c**. Crystals of **5e** are monoclinic of space group $P2_1$ with $a = 8.602$ (2) Å, $b = 15.511$ (3) Å, $c = 9.239$ (2) Å, $\beta = 111.80$ (2)°, $V = 1144.56$ Å^3, and $d_{calcd} = 0.993$ g/cm^3 for $Z = 2$. Refinement of 198 parameters on 2110 reflections with $F_o \geq 4.0\sigma(F_o)$ converged at $R_w = 0.052$, $w = k/\sigma^2(F_o)$ and $k = 2.44$. In addition to one THF and one TMEDA molecule, the Li atom is clearly coordinated by the P donor function of the aluminate ligand in a distorted tetrahedral coordination geometry. The Li–P distance is 2.593 (7) Å. No other close contacts of Li are observed. Crystals of **5c** are orthorhombic of space group $Cmc2_1$ with $a = 10.652$ (3) Å, $b = 16.209$ (5) Å, $c = 12.761$ (4) Å, $V = 2203.29$ Å^3, and $d_{calcd} = 0.996$ g/cm^3 for $Z = 4$. Refinement of 110 parameters on 954 reflections produced $R_w = 0.040$. A distorted tetrahedral geometry around Li consists of one TMEDA ligand and both P atoms of the aluminate with Li–P distances of 2.606 (5) Å. The six-membered LiPCAlCP ring formed upon complexation is in a pseudoenvelope conformation with an almost planar $Li(PC)_2$ arrangement.

Introduction

Phosphine ligands play a predominant role in transition-metal coordination chemistry. Examples of main-group element phosphine complexes, however, are by far less frequently encountered, which is especially true for homoleptic species. This difference may be attributed, at least in part, to the fact that phosphines, although forming certain adducts with main-group compounds (eq 1), show little tendency to displace anionic ligands from the main group acceptor (eq 2).



$$MX_n + mPR_3 \longrightarrow (R_3P)_mMX_n \quad (1)$$

$$MX_n + mPR_3 \longrightarrow [(R_3P)_mM]X_n \quad (2)$$

$$MX_n + mPR_3 + nNaY \rightarrow [(R_3P)_mM][Y]_n + nNaX \quad (3)$$

M = main-group element, X = halide,
Y = noncoordinating anion

This difficulty may be overcome by replacing the coordinating anions (e.g., halides) by noncoordinating ones (e.g., $Y = AsF_6^-$ in eq 3). However, the resulting cationic phosphine complexes are usually insoluble in nonpolar solvents, and in more polar solvents decomposition often takes place due to the competition of the solvent molecules for a coordination site at the main-group cation. As a consequence, the introduction of *anionic* phosphine ligands into main group element complexes seems to be a reasonable alternative. In this way the competition by other ligands for a coordination site may be effectively eliminated. Ring formation by chelating or bridging phosphine ligand systems should support the coordination. The resulting neutral, molecular phosphine complexes with betaine-like structures are expected to be far more stable and should exhibit a much more favorable solubility. For the sake of simplicity and because alkali-metal phosphine complexes are scarcely encountered in the literature,[1,2] we chose the Li cation as a model to test our hypotheses. It has been shown recently that phosphine-substituted carbanions, i.e., phosphinomethanides I, fulfill the above-mentioned criteria and in fact may coordinate effectively to Li^+ by both their carbanionoid and their phosphorus donor centers. Thus in $\{Li[C(PMe_2)_3](THF)\}_2$, the tris-

$$\underset{\textstyle\mathrm{I}}{[(R_2P)_nCH_{3-n}]^-}$$

(phosphino)methanide ligand acts via two phosphorus atoms as a chelating donor to Li^+.[1] Due to the ambidentate nature of phosphinomethanides,[1b,3,4] the coordination is

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[†] Part 22: see ref 1b. Part 3 of the series: Phospine Complexes of Main Group Elements. Part 2: see ref 6.

(1) (a) Karsch, H. H.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1984**, 569. (b) Karsch, H. H.; Weber, L.; Wewers, D.; Boese, R.; Müller, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1518.

(2) Engelhardt, L. M.; Jacobson, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.

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Table I. NMR Data of Compounds 4, 5a, 5c, 5d, 5f, 7, and $[LiAlMe_4]_n$ (+30 °C, Toluene-d_8)

		^{1}H NMR δ (*J*, Hz)					^{31}P NMR
compound	no.	δ(PCH_3)	δ(PCH_2)	δ($AlCH_3$)	δ(NCH_3)	δ(NCH_2)	δ(P)
$[(TMEDA)_{3/2}Li(Me_2PCH_2)Al(t\text{-}Bu)Me_2]$[a]	4	1.39 (d, 1.9, 6 H)	0.50 (d, 5.5, 2 H)	−0.40 (s, 6 H)	2.15 (s, 24 H)		−50.43 (s)
$[Li(Me_2PCH_2)_2Al(CH_2PMe_2)_2]_x$[b]	5a	1.23 (s, br, 24 H)	0.29 (s, br, 8 H)				−50.17 (s)
$[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]$	5c	1.20 (s, 12 H)	0.42[c] (t, *N* = 7.4, 4 H)	−0.20 (s, br, 6 H)	1.93 (s, 16 H)		−50.76 (s)
$[(TMEDA)_{3/2}Li(Me_2PCH_2)AlMe_3]$	5d	1.57 (s, 6 H)	0.59 (d, 5.0, 2 H)	−0.18 (s, 9 H)	2.20 (s, 24 H)		−48.84 (s)
$[(TMEDA)(THF)Li(Me_2PCH_2)AlMe_3]$[d]	5e	1.35 (d, 1.8, 6 H)	0.42 (d, 6.2, 2 H)	−0.36 (s, 9 H)	2.15 (s, 12 H)	2.10 (s, 4 H)	−49.17 (s)
$[(TMEDA)Li(Me_2PCH_2)AlMe_3]$	5f	1.39 (d, 1.8, 6 H)	0.50 (d, 6.2, 2 H)	−0.28 (s, 9 H)	2.14 (s, 12 H)	2.02 (s, 4 H)	−51.02 (s)
$[(TMEDA)_2Li][AlMe_4]$	7			−0.33 (s, 12 H)	2.05 (s, 32 H)		
$[LiAlMe_4]_n$[b]				−0.30 (s)			

[a] δ(*t*-Bu) 1.66 (s, 9 H). [b] In toluene-d_8/THF-d_8. [c] $X_2AA'X'_2$ spin system. [d] δ(THF) 1.78 (m, 4 H), 3.71 (m, 4 H).

complicated by additional Li···C interactions, which is not unlike the situation observed in the related compound $[LiCH_2PMe_2(TMEDA)]_2$.[2] As a consequence, bridged dimers are formed in both cases. Therefore, it seemed desirable to design anionic phosphine ligands, where the negatively charged atom is not likely to compete with the phosphorus atom for electrophilic metal centers. Furthermore, the location of the anionic charge in a more remote position with respect to the phosphorus donor atom was expected to yield ligands, which resemble more closely "ordinary" phosphines in their coordination behavior. (Phosphinomethyl)aluminates II seem to be suitable candidates as they fulfill both requirements. Suitable precursors for these aluminates, viz., neutral (phosphinomethyl)aluminum compounds of type III, have been described only recently.[5]

$$\underset{\text{II}}{[(R_2PCH_2)_nAlR'_{4-n}]^-} \qquad \underset{\text{III}}{[(R_2PCH_2)_nAlR'_{3-n}]_2}$$

We report here the preparation, properties, and the spectroscopic and structural characterization of type II aluminates and their coordination to Li^+. Preliminary results have been reported previously.[6]

Experimental Section

A. Preparation and Characterization of Compounds. General procedures, instrumentation, and the preparation of $[Me_2AlCH_2PMe_2]_2$, **2**, and $[Al(CH_2PMe_2)_3]_2$, **3**, followed closely previously described procedures.[5] All compounds were prepared and handled in a dry argon atmosphere employing conventional vacuum line or Schlenk tube techniques. Sodium/potassium alloy (ether solvents, TMEDA) or $LiAlH_4$ (hydrocarbon solvents) were employed for drying, storage, and redistillation immediately prior to their use. $AlMe_3$ (pentane solution), $LiCH_3$ (ethereal solution, and LiC_4H_9-*t* (hexane solution) were obtained from commercial sources and used without further purification. $LiCH_2PMe_2$ was prepared according to ref 3a.

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.

I. Attempted Preparation of Type II Aluminates According to Scheme I. (a) Reaction of $AlMe_3$, 2, or 3 with $LiCH_3$. A 2–5-mmol sample of the aluminum compound was dissolved in 30–80 mL of pentane. With cooling (−78 °C) and stirring, the appropriate amount of $LiCH_3$ in diethyl ether was added and the mixture was allowed to come to room temperature and stirred for 12 h. The resulting precipitate then was filtered, washed three times with 20 mL of ether, dried in vacuo, and identified as **5a** (vide infra). The solvent was removed from the combined ethereal solutions in vacuo, and the crystalline solid residue was identified as $LiAlMe_4$. This compound also is obtained quantitatively from $AlMe_3$ and $LiCH_3$ (^{1}H NMR see Table I; IR ref 7).

(b) Reaction of $AlMe_3$, 2, or 3 with $LiCH_2PMe_2$. A 2–5-mmol sample of the aluminum compound in 20–50 mL of pentane was added dropwise at −78 °C to a stirred suspension of the appropriate amount of $LiCH_2PMe_2$ in 20–50 mL of diethyl ether. The mixture was warmed to room temperature and stirred for 12 h. The further procedure follows method Ia above. From the reaction of **3** and $LiCH_2PMe_2$, **5a** was obtained quantitatively as a colorless solid: mp 190 °C dec; IR (cm^{-1}) 626 (s), 533 (w), 369 (m), 282 (m). Anal. Calcd for $C_{12}H_{32}AlLiP_4$ (334.20): C, 43.13; H, 9.65; Al, 8.07; Li, 2.08. Found: C, 42.57; H, 9.28; Al, 8.00; Li, 1.80.

II. Synthesis of (Phosphinomethyl)aluminates in the Presence of TMEDA According to Scheme II. Synthesis of $[Li(Me_2PCH_2)_2Al(CH_2PMe_2)_2]_n$, 5a. **5a** also was obtained by adding 754 mg (6.50 mmol) of TMEDA to a suspension of 820 mg (3.25 mmol) of $[Al(CH_2PMe_2)_3]_2$, **3**, and 267 mg (3.25 mmol) of $LiCH_2PMe_2$ in diethyl ether and removal of the volatile components of the mixture in vacuo.

Synthesis of $[(TMEDA)_{3/2}Li(Me_2PCH_2)Al(t\text{-}Bu)Me_2]$, 4. A solution of 470 mg (3.56 mmol) of $[Me_2AlCH_2PMe_2]_2$, **2**, in 40 mL of pentane was combined at −78 °C under stirring with a mixture of 826 mg (7.12 mmol) of TMEDA and 2.39 mL (3.56 mmol) of a 1.489 M solution of Li-*t*-Bu in hexane. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuo. The residue was washed twice with 20 mL of pentane and dried in vacuo. Crystallization from diethyl ether yielded 1147 mg (3.10 mmol, 87%) of a colorless solid: mp 90–91 °C; IR (cm^{-1}) 660–680 (vs, br), 586 (m), 541 (m), 442 (m), 340 (m, sh), 289 (w). Anal. Calcd for $C_{18}H_{47}AlN_3LiP$ (370.49): C, 58.35; H, 12.79; Al, 7.28; N, 11.34. Found: C, 58.20; H, 12.93; Al, 7.50; N, 11.08.

Synthesis of $[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]$, 5c. To a stirred solution of 950 mg (7.20 mmol) of $[Me_2AlCH_2PMe_2]_2$, **2**, in 40 mL of diethyl ether was added a mixture of 590 mg (7.20 mmol) of $LiCH_2PMe_2$ and 1670 mg (14.40 mmol) of TMEDA in 40 mL of diethyl ether at −78 °C. With stirring, the reaction mixture was allowed to warm to room temperature and after 1 h again cooled to −78 °C. The colorless crystals obtained were washed twice with 20 mL of diethyl ether and dried in vacuo. Recrystallization from diethyl ether gave 1910 mg (5.90 mmol, 81%) of a colorless solid: mp 124–125 °C; IR (cm^{-1}) 763 (s, sh), 632 (s), 560 (m), 474 (m), 410 (w), 368 (m), 298 (m). Anal. Calcd

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(3) (a) Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1977, *32B*, 762. (b) Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, *34B*, 1171, 1178. (c) Karsch, H. H. *Chem. Ber.* 1982, *115*, 1956.

(4) (a) Appel, R.; Wander, W.; Knoll, F. *Chem. Ber.* 1979, *112*, 1093. (b) Appel, R.; Haubrich, G.; Knoch, F. *Chem. Ber.* 1984, *117*, 2063.

(5) Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* 1985, *4*, 231.

(6) Karsch, H. H.; Appelt, A.; Müller, G. *J. Chem. Soc., Chem. Commun.* 1984, 1415.

(7) Yamamoto, J.; Wilkie, C. A. *Inorg. Chem.* 1971, *10*, 1129.

for $C_{14}H_{38}AlLiN_2P_2$ (330.34): C, 50.90; H, 11.60; N, 8.48. Found: C, 50.77; H, 11.58; N, 8.45.

Synthesis of [(TMEDA)$_{3/2}$Li(Me_2PCH_2)$AlMe_3$], 5d. (a) From [$Me_2AlCH_2PMe_2$]$_2$, 2, and $LiCH_3$. To a solution of 620 mg (4.70 mmol) of [$Me_2AlCH_2PMe_2$]$_2$, **2**, in 40 mL of diethyl ether was added a mixture of 1090 mg (9.40 mmol) of TMEDA and 2.95 mL (4.70 mmol) of a 1.595 M solution of $LiCH_3$ in diethyl ether at −78 °C. The stirred reaction mixture was allowed to warm to room temperature and the solvent removed in vacuo. The solid residue was washed twice with 20 mL of diethyl ether and dried in vacuo. A 1151-mg (3.51 mmol, 75%) sample of a colorless solid was obtained.

(b) From $AlMe_3$ and $LiCH_2PMe_2$. To a stirred solution of 434 mg (5.30 mmol) of $LiCH_2PMe_2$ and 1230 mg (10.60 mmol) of TMEDA in 40 mL of diethyl ether was added 1.74 mL (5.30 mmol) of a 3.05 M solution of $AlMe_3$ in hexane at −78 °C. The reaction mixture was allowed to warm to room temperature and the solvent removed in vacuo. The residue was then washed twice with 25 mL of diethyl ether and dried in vacuo. A 1450-mg (4.42 mmol, 83%) sample of colorless crystals was obtained: mp 141–142 °C; IR (cm^{-1}) 680 (s, br), 600 (m), 558 (m), 442 (m), 342 (m, sh), 291 (w). Anal. Calcd for $C_{15}H_{41}AlLiN_3P$ (328.41): C, 54.86; H, 12.58; Al, 8.22; N, 12.80. Found: C, 54.84; H, 12.80; Al, 8.70; N, 14.63.

Synthesis of [(TMEDA)(THF)Li(Me_2PCH_2)$AlMe_3$], 5e. To a solution of 1280 mg (15.61 mmol) of $LiCH_2PMe_2$ and 2710 mg (23.41 mmol) of TMEDA in a mixture of 50 mL of diethyl ether and 10 mL of tetrahydrofuran was added 5.12 mL (15.61 mmol) of a 3.05 M solution of $AlMe_3$ in hexane at −78 °C. The reaction mixture was allowed to warm to 0 °C with stirring. The clear solution was again cooled slowly to −78 °C. Colorless crystals separated, were washed twice with 25 mL of diethyl ether, and were dried in vacuo at 0 °C: 5072 mg (14.83 mmol, 95%); mp 63–65 °C; IR (cm^{-1}) 660–710 (vs. br), 554 (s), 446 (s), 332 (s), 303 (m), 252 (m). Anal. Calcd for $C_{16}H_{41}AlLiN_2OP$ (342.41): C, 56.12; H, 12.07; Al, 7.88; N, 8.18. Found: C, 56.16; H, 12.05; Al, 8.09; N, 8.64.

Synthesis of [(TMEDA)Li(Me_2PCH_2)$AlMe_3$], 5f. A flask containing 2025 mg (5.92 mmol) of [(TMEDA)(THF)Li(Me_2PCH_2)$AlMe_3$], **5e**, was attached to a vacuum system (0 °C, 10^{-4} torr) and maintained under these conditions for 3 days. A 1598-mg (5.92 mmol, 110%) sample of a colorless solid was obtained: mp 65–70 °C; IR (cm^{-1}) 650–740 (vs, br), 568 (s, br). Anal. Calcd for $C_{12}H_{33}AlLiN_2P$ (270.30): C, 53.32; H, 12.31; Al, 9.98; N, 10.36. Found: C, 52.34; H, 12.17; Al, 10.25; N, 10.71.

Synthesis of [$(TMEDA)_2Li$][$AlMe_4$], 7. A 10-mL sample of a 3.05 M solution of $AlMe_3$ in hexane (30.50 mmol) was diluted with 40 mL of diethyl ether and combined with 19 mL of a 1.595 M solution of $LiCH_3$ in diethyl ether and 7080 mg (71.00 mmol) of TMEDA at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h, and the solvent was removed in vacuo. A 9519-mg (29.20 mmol, 96%) sample of a colorless solid was obtained: mp 161–163 °C dec; IR (cm^{-1}) 694 (vs), 590 (m), 556 (s), 345 (m, sh). Anal. Calcd for $C_{16}H_{44}AlN_4Li$ (326.48): C, 58.86; H, 13.59; Al, 8.26; N, 17.16. Found: C, 58.15; H, 13.39; Al, 8.40; N, 16.89.

The volatile constituents of the reaction mixtures were shown to contain TMEDA in all cases (^1H NMR), except in the case of the preparation of 7, were no excess TMEDA was found.

III. Reactions and Thermolysis of Lithium (Phosphinomethyl)aluminates. Reaction of [(TMEDA)$_{3/2}$Li(Me_2PCH_2)$AlMe_3$], 5d, with MeI. To a stirred suspension of 980 mg (2.99 mmol) of [(TMEDA)$_{3/2}$Li(Me_2PCH_2)$AlMe_3$], **5d**, in 20 mL of diethyl ether was added 425 mg (2.99 mmol) of MeI at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h, and the solvent was removed in vacuo. The residue was distilled at reduced pressure, and 350 mg (2.16 mmol, 72%) of a colorless solid was obtained: bp 130–132 °C (1.0 torr); mp 60–61 °C, identified as $Me_3AlCH_2PMe_3$;[8] ^1H NMR (C_6D_6) δ (PCH_3) 0.39 (d, ^2J(PCH) = 13.0 Hz), δ (PCH_2) −0.42 (d, ^2J(PCH) = 17.0 Hz), δ ($AlCH_3$) −1.04 (s); ^{13}C NMR (C_6D_6) δ (PCH_3) 13.61 (d, J(PC) = 55.7 Hz), δ ($AlCH_3$) −4.81 (s, vbr).

Disproportionation of 5d, 5e, 5f, and 4. In separate experiments solutions of 5.00 mmol of **5d**, **5e**, **5f**, and **4**, respectively, in 40 mL of diethyl ether were stirred for 2 days at room temperature. Subsequently, the ether solvent was decantated from the precipitate, and the precipitate was washed twice with 20 mL of diethyl ether, dried in vacuo, and analyzed by means of ^1H NMR and IR spectroscopy. The ethereal mother liquid was cooled to −78 °C. The colorless crystals obtained were washed twice with 20-mL portions of cold diethyl ether and dried in vacuo. They were characterized by comparison of the ^1H NMR and IR spectra with those of an authentic sample of **5c** (vide supra).

Thermolysis of [(TMEDA)$_{3/2}$Li(Me_2PCH_2)$AlMe_3$], 5d. A 820-mg (2.50-mmol) sample of **5d** was heated in vacuo (112 °C, 10^{-2} torr). A colorless, crystalline solid sublimed and was identified as $2AlMe_3$·TMEDA by means of its ^1H NMR spectrum (C_6D_6) δ ($AlCH_3$) −0.31 (s, br, 18 H), δ (NCH_3) 1.82 (s, br, 12 H), δ (NCH_2) 2.05 (s, br, 4 H).[9] The residue was identified as $LiCH_2PMe_2$·TMEDA by comparison (IR) with an authentic sample prepared from $LiCH_2PMe_2$[3a] and TMEDA in diethyl ether (cf. ref 2).

Thermolysis of "[(TMEDA)$_{1/2}$Li(Me_2PCH_2)$_3$AlMe]", 5b. A mixture of 175 mg (1.51 mmol) of TMEDA, 761 mg (3.02 mmol) of [$Al(CH_2PMe_2)_3$]$_2$, **3**, and 1.9 mL of a 1.595 M solution of $LiCH_3$ in diethyl ether was heated in vacuo (120 °C, 10^{-3} torr). A colorless solid sublimed, which was identified spectroscopically as **2**.[5] The residue was washed twice with diethyl ether and identified as **5a**. The ethereal solution was dried in vacuo. The colorless solid obtained was identified as $LiCH_2PMe_2$·TMEDA (vide supra).

B. X-ray Structure Determinations. [(TMEDA)(THF)Li(Me_2PCH_2)$AlMe_3$], 5e. Colorless single crystals were obtained by crystallization from tetrahydrofuran/diethyl ether (10/50 volume ratio) and sealed under an atmosphere of argon at dry-ice temperature into a Lindemann glass capillary. According to diffractometer measurements (Syntex $P2_1$) the compound crystallizes in the monoclinic space group $P2_1$, as indicated by $Z = 2$ and the systematic absences. Reduced cell calculations (TRACER[10]) did not reveal any higher symmetry. The exact cell dimensions were obtained by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 centered high order reflections from various parts of reciprocal space. Pertinent crystal data as well as a summary of intensity data collection and refinement procedures are given in Table II.

The integrated intensities of the reflections were measured on a computer-controlled four-circle diffractometer (Syntex $P2_1$) using graphite-monochromated Mo Kα radiation. A multispeed moving crystal–stationary counter technique was used where the peak height at the calculated peak position served to determine the final scan speed. The time spent measuring the background intensities at each end of the scan interval was half that taken to measure the peak. A monitor reflection, examined after every 50 reflections, served as a check on the centering and stability of the crystal and diffractometer system, and there was no significant change in its intensity variation. The intensity of a reflection and its standard deviation were calculated as $I = k(S - B/\beta)$ and $\sigma(I) = k(S + B/\beta^2)^{1/2}$, where S is the total scan counts, B the total background counts, β the time ratio of total background to scan, and k a constant which depends on the scanning speed. After Lorentz and polarization corrections ($F_o = (I/Lp)^{1/2}$; $\sigma(F_o) = \sigma(I)/(2F_oLp)$) structure factors with $F_o < 4.0\sigma(F_o)$ were deemed "unobserved" and not used in all further calculations. An absorption correction was not applied.

The structure was solved by direct methods (MULTAN 80[11]) which yielded the C_3AlCPC fragment. Subsequent Fourier syntheses gave the remainder of the molecule. After anisotropic refinement of the non-hydrogen atoms a difference Fourier synthesis revealed 17 of the 41 hydrogen atom positions. All others were calculated

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[8] The preparation of 8 from $AlMe_3$ and Me_3PCH_2 has been described, but only ^1H NMR data have been reported: (a) Schmidbaur, H.; Tronich, W. *Chem. Ber.* **1968**, *101*, 595. (b) Schmidbaur, H.; Füller, H.-J.; Köhler, F. H. *J. Organomet. Chem.* **1975**, *99*, 353.

[9] $2AlMe_3$·TMEDA has been described previously, but NMR data are not reported: Brüser, W.; Thiele, K.-H.; Müller, H. K. *Z. Chem.* **1962**, *2*, 342.

[10] Lawton, S. L.; Jacobson, R. A. TRACER, A General Fortran Lattice Transformation-Cell Reduction Program, Iowa State University, 1965.

[11] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, England, and University of Louvain, Belgium, 1980.

Table II. Crystal Structure Data of 5e and 5c

	5e	5c
formula	$C_{16}H_{41}AlLiN_2OP$	$C_{14}H_{38}AlLiP_2N_2$
M_r	342.412	330.341
space group	$P2_1$	$Cmc2_1$
a, Å	8.602 (2)	10.652 (3)
b, Å	15.511 (3)	16.209 (5)
c, Å	9.239 (2)	12.761 (4)
α, deg	90	90
β, deg	111.80 (2)	90
γ, deg	90	90
V, Å^3	1144.56	2203.29
Z	2	4
d_{calcd}, g/cm^3	0.993	0.996
μ(Mo Kα)$_{calcd}$, cm^{-1}	1.57	2.26
F(000)	380	728
T, °C	−35 ± 5	−35 ± 5
radiatn	Mo Kα	Mo Kα
λ, Å	0.71069	0.71069
scan mode	ω	ω
$\Delta\omega$, deg	0.9	1.0
scan rate, deg/min	0.9–29.3	0.9–29.3
std reflctns	020	040
$((\sin\vartheta)/\lambda)_{max}$, Å^{-1}	0.617	0.595
hkl range	+10,+19,±11	+12,+19,+15
reflctns measd	2504	1249
reflctns unique	2349	1082
R_{int}^{a}	0.022	0.044
reflctn obsd	2110	954
param ref.	198	110
max shift/error (last cycle)	0.003	0.15
R^b	0.053/0.053^d	0.040/0.040^d
R_w^{c}	0.052/0.052^d	0.040/0.040^d
k (last cycle)	2.44/2.44^d	2.04/2.05^d
$\Delta\rho_{fin}$(max/min)	+0.33/−0.25	+0.23/−0.22

^{a} $R_{int} = [\sum(n\sum_n w(\langle F\rangle - F)^2)/\sum_n((n-1)\sum_n wF^2)]^{1/2}$, where n is the number of reflections averaged. ^{b} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{c} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF^2]^{1/2}$; $w = k/\sigma^2(F_o)$. ^{d} The second value results from refinement of the inverse structure (all coordinate signs inverted).

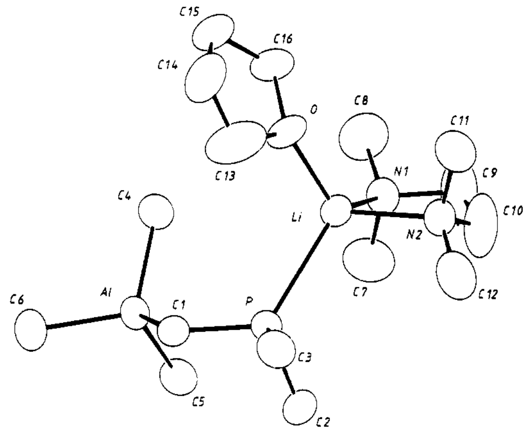

Figure 1. Perspective view of the molecular structure of **5e** and atomic numbering scheme used (ORTEP, thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity.

at idealized geometrical positions (d(C–H) = 0.975 Å; XANADU[12]). Thereby located hydrogen atoms served to determine the conformations of all methyl groups except C7 where the hydrogen atoms where placed in an arbitrary conformation. In further refinement cycles the hydrogen atoms were kept constant (U_{iso} = 0.05 Å^2). All other atoms were allowed anisotropic thermal motion. Relatively high thermal parameters of atoms C13/C14 of the THF molecule and atoms C9/C10 of the TMEDA ligand indicated partial disorder of these atoms, i.e., the fractional occupation of alternative sites. As a result of the anisotropic treatment of these atoms the bonds C9–C10 and C13–C14 are artificially shortened. The refinement of the enantiomorphic structure (all coordinate signs inverted) did not result in significantly different R values nor were the differences between the derived bonding parameters of both refinements larger than one esd. It was not considered worthwhile, however, to improve the significance by collecting another data set of the Friedel opposites because of the relatively small Δf (Mo Kα) contributions to structure factor calculations. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = k/\sigma^2(F_o)$ (SHELX 76[13]). Scattering factors for neutral, isolated non-hydrogen atoms were

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 5e^a

atom	x/a	y/b	z/c	U(eq), Å^2
P	0.9741 (1)	0.4730 (0)	0.2799 (1)	0.033
Al	0.8239 (2)	0.3479 (1)	0.4893 (1)	0.034
O	0.6465 (4)	0.6366 (2)	0.2226 (3)	0.042
N1	0.5044 (4)	0.4803 (3)	−0.0577 (4)	0.043
N2	0.7411 (5)	0.6077 (3)	−0.0913 (4)	0.044
C1	0.9937 (5)	0.4334 (3)	0.4686 (5)	0.035
C2	1.0403 (6)	0.3811 (3)	0.1939 (5)	0.047
C3	1.1572 (6)	0.5438 (3)	0.3182 (6)	0.047
C4	0.6008 (6)	0.4073 (3)	0.4186 (5)	0.046
C5	0.8035 (6)	0.2409 (3)	0.3598 (6)	0.046
C6	0.9071 (6)	0.3198 (3)	0.7177 (5)	0.048
C7	0.5601 (9)	0.3921 (4)	−0.0442 (6)	0.075
C8	0.3390 (6)	0.4805 (5)	−0.0503 (6)	0.064
C9	0.4938 (9)	0.5164 (6)	−0.2096 (6)	0.070
C10	0.6403 (11)	0.5523 (5)	−0.2152 (6)	0.077
C11	0.6767 (8)	0.6953 (4)	−0.1099 (6)	0.060
C12	0.9086 (9)	0.6101 (6)	−0.0917 (6)	0.079
C13	0.7704 (6)	0.6677 (5)	0.3645 (8)	0.066
C14	0.6968 (8)	0.7268 (4)	0.4326 (3)	0.065
C15	0.5178 (6)	0.7058 (4)	0.3739 (6)	0.058
C16	0.4872 (6)	0.6560 (4)	0.2278 (6)	0.047
Li	0.7042 (8)	0.5514 (5)	0.1028 (8)	0.036

^{a} U(eq) = $(U(1)U(2)U(3))^{1/3}$, where $U(1)$,$U(2)$, and $U(3)$ are the eigenvalues of the U(ij) matrix. Esd's in parentheses.

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(12) Roberts, P.; Sheldrick, G. M. XANADU, University of Cambridge, England, 1975.

(13) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.

Table IV. Bond Lengths (Å) and Angles (deg) for 5e and Some Torsion Angles (deg)[a]

		Bond Lengths			
Li-P	2.593 (7)	Al-C4	2.007 (5)	N2-C11	1.453 (7)
Li-N1	2.116 (8)	Al-C5	2.015 (5)	N2-C12	1.443 (7)
Li-N2	2.121 (8)	Al-C6	2.008 (5)	N2-C10	1.436 (8)
Li-O	1.904 (8)	Al···Li	4.588 (7)	O-C13	1.432 (6)
P-C1	1.796 (4)	N1-C7	1.441 (8)	O-C16	1.422 (5)
P-C2	1.824 (5)	N1-C8	1.450 (6)	C13-C14	1.391 (8)
P-C3	1.843 (5)	N1-C9	1.482 (7)	C14-C15	1.467 (8)
Al-C1	2.035 (4)	C9-C10	1.396 (9)	C15-C16	1.491 (8)
		Bond Angles			
P-Li-O	108.9 (3)	Li-P-C2	116.3 (2)	C1-Al-C4	107.7 (2)
P-Li-N1	120.1 (4)	Li-P-C3	110.1 (2)	C1-Al-C5	112.8 (2)
P-Li-N2	110.3 (3)	C1-P-C2	102.9 (2)	C1-Al-C6	104.6 (2)
O-Li-N1	116.7 (4)	C1-P-C3	104.6 (2)	C4-Al-C5	108.8 (2)
O-Li-N2	111.1 (4)	C2-P-C3	99.6 (2)	C4-Al-C6	111.5 (2)
N1-Li-N2	87.7 (3)	P-C1-Al	120.2 (2)	C5-Al-C6	111.3 (2)
Li-P-C1	120.8 (2)				
		Torsion Angles			
Al-C1-P-Li	57.5	P-C1-Al-C4	-64.1	C1-P-Li-O	48.1
Al-C1-P-C2	-74.2	P-C1-Al-C5	56.0	C1-P-Li-N1	-90.3
Al-C1-P-C3	-177.8	P-C1-Al-C6	177.2	C1-P-Li-N2	170.3

[a] Esd's in units of the last significant figure in parentheses.

taken from Cromer and Waber.[14] Those of the H atoms were based on a bonded spherical atom model as given by Stewart, Davidson, and Simpson.[15] Corrections for $\Delta f'$ and $\Delta f''$ were applied to all atoms.[16] Table III lists the final atomic coordinates and equivalent, isotropic temperature factors for the non-hydrogen atoms; Table IV contains principal distances and angles. Figure 1 gives a perspective view of the molecule (ORTEP[17]).

[(TMEDA)Li(Me_2PCH_2)$_2$AlMe_2], 5c. Colorless single crystals were obtained from diethyl ether. Diffractometer data indicated an orthorhombic cell with *Cmcm* (No. 63), *Cmc*2$_1$ (No. 36), and *C*2*cm* (nonstandard setting of *Ama*2, No. 40) as possible space groups. The orthorhombic symmetry was confirmed by axial photographs. A reasonable calculated density of 0.996 g/cm^3 for $Z = 4$ gave *mm* or 2/*m* as possible site symmetries in *Cmcm* which was rejected on chemical grounds. (Experiments to determine the density of the crystals by flotation failed due to their exceeding air and moisture sensitivity.) In the alternative space groups this number of molecules per unit cell necessitates site symmetries *m* in *Cmc*2$_1$ and *m* or 2 in *C*2*cm*. It was in the former space group that the structure was successfully solved and refined. Since the derived structural parameters are chemically reasonable, *C*2*cm* was not tried as an alternative. Data collection and refinement procedures followed closely those described for **5e**. A summary of the crystal structure data is given in Table II.

The AlCP fragment of the molecule was found by direct methods using MULTAN 80.[11] Several subsequent Fourier syntheses yielded the remainder of the molecule. The crystallographic mirror plane bisecting the molecule and containing the atoms Al, C4, C5, Li, N1, N2, and C6 necessitates twofold positional disorder of atoms C7, C9, and C10 of the (nonplanar) TMEDA fragment with the alternative sites related by mirror symmetry. Resolution of the latter two atoms proved difficult, however, since C9 is approximately only 1 Å, from the mirror image of C10 and vice versa. Therefore, C9 and C10 were placed at idealized geometrical positions (d(N–C) = 1.45 Å) and refined isotropically as rigid groups (with calculated H atoms) in different blocks. At convergence the alternatives were about 0.7 Å apart and the N–C bonds were artificially somewhat shortened or elongated. All other non-hydrogen atoms were refined anisotropically. All H atoms were located in difference Fourier syntheses with the exception of those at C6, C7, C9, and C10 which were calculated. They were kept constant in the refinement (U_{iso} = 0.05 Å^2). Refinement of the coordinate set of opposite polarity (all coordinates inverted) did not result in significantly different R values or bonding parameters. The final positional parameters of the non-hydrogen atoms together with their equivalent isotropic temperature factors are given in Table V. Table VI contains important distances and angles. Figure 2 shows the molecular structure.

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 5c

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
P	0.1951 (1)	0.0547 (1)	0.2754 (0)	0.030
Al	0.0000 (0)	−0.0948 (1)	0.3294 (2)	0.029
N1	0.0000 (0)	0.2599 (3)	0.1971 (4)	0.032
N2	0.0000 (3)	0.2280 (3)	0.4218 (4)	0.036
C1	0.3197 (4)	0.0786 (3)	0.1806 (4)	0.048
C2	0.2944 (5)	0.0446 (3)	0.3924 (4)	0.049
C3	0.1499 (4)	−0.0506 (2)	0.2483 (3)	0.033
C4	0.0000 (0)	−0.0563 (4)	0.4791 (5)	0.042
C5	0.0000 (0)	−0.2183 (4)	0.3204 (6)	0.045
C6	0.0000 (0)	0.3254 (3)	0.2753 (6)	0.043
C7	−0.0570 (8)	0.3055 (5)	0.3766 (6)	0.034
C8	0.1120 (5)	0.2664 (3)	0.1308 (5)	0.051
C9	−0.0997 (8)	0.2025 (5)	0.5041 (8)	0.043
C10	0.1123 (10)	0.2353 (6)	0.4706 (9)	0.056
Li	0.0000 (0)	0.1511 (5)	0.2892 (8)	0.028

Table VI. Bond Lengths (Å) and Angles (deg) for 5c

	Bond Lengths		
Li-P	2.606 (5)	Al-C5	2.005 (6)
Li-N1	2.12 (1)	Al···Li	4.020 (6)
Li-N2	2.10 (1)	N1-C8	1.466 (7)
P-C3	1.806 (4)	N1-C6	1.458 (9)
P-C1	1.838 (5)	C6-C7	1.46 (1)
P-C2	1.837 (5)	N2-C9	1.55 (1)
Al-C3	2.033 (4)	N2-C10	1.35 (1)
Al-C4	2.010 (7)	N2-C7	1.509 (9)
	Bond Angles		
P-Li-P*	105.7 (3)	C3-P-C2	103.0 (2)
P-Li-N1	117.5 (3)	C1-P-C2	97.9 (2)
P-Li-N2	114.2 (3)	P-C3-Al	116.4 (2)
N1-Li-N2	87.3 (4)	C3-Al-C3*	103.5 (3)
Li-P-C3	111.6 (2)	C3-Al-C4	112.0 (2)
Li-P-C1	119.6 (3)	C3-Al-C5	108.9 (2)
Li-P-C2	117.2 (3)	C4-Al-C5	111.4 (3)
C3-P-C1	105.4 (2)		

Results and Discussion

Phosphinomethyl derivatives of phosphorus and silicon IV are easily deprotonated at the methylene carbon atom by organolithium reagents (eq 4).[3,4,18,19] However, for

(4)

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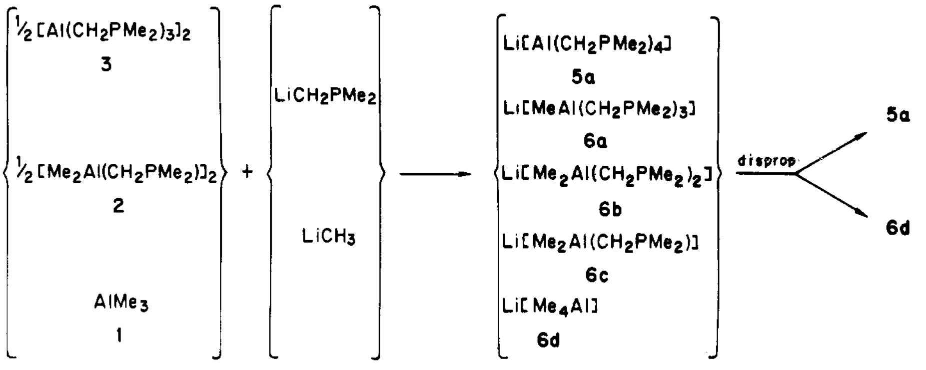
(14) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(16) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1974; Vol. IV.

(17) Johnson, C. K. ORTEP II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Scheme I. Attempted Preparation of Type II Aluminates[22]



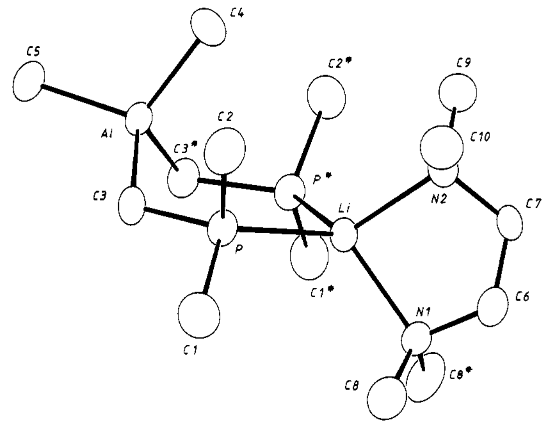
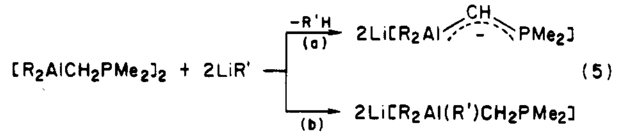


Figure 2. Molecular structure of **5c** under omission of hydrogen atoms (ORTEP, thermal ellipsoids 50%). Crystallographic mirror symmetry relates the atoms with an asterisk to the atoms without an asterisk. The mirror plane bisecting the molecule and containing atoms Al, C4, C5, Li, N1, N2, and C6 necessitates twofold positional disorder of atoms C7, C9, and C10 of the TMEDA ligand. Only one alternative is shown.

analogous compounds IV of aluminum (Ⓔ = AlR_2), addition of the nucleophile to Al also has to be considered (eq 5). One would expect eq 5b to be highly favored over

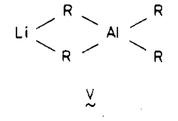


$$[R_2AlCH_2PMe_2]_2 + 2LiR' \begin{cases} \xrightarrow[(a)]{-R'H} 2Li[R_2Al\overset{CH}{\cdots}PMe_2] \\ \xrightarrow[(b)]{} 2Li[R_2Al(R')CH_2PMe_2] \end{cases} \quad (5)$$

the metalation route eq 5a. In order to allow a clear-cut distinction between the two routes, eq 5a and 5b, $[Me_2AlCH_2PMe_2]_2$, **2**, was allowed to react with Li-*t*-Bu. Thereby the steric bulk and the high basicity of Li-*t*-Bu was expected to promote the metalation. On the other hand, the *tert*-butyl group, if incorporated in an aluminate according to eq 5b, should be easily detectable by NMR spectroscopy. For reasons discussed below, TMEDA was added to the reaction mixture (eq 6). The highly air-sensitive, colorless crystalline solid obtained exhibited a signal at 1.66 ppm in the ^1H NMR spectrum in toluene solution (Table I), which is attributed to the presence of a *tert*-butyl group. This result is confirmed by the elemental analysis of **4** and by the similar formation of all other aluminate compounds, described below. The relative intensities of the NMR signals of **4** and the related compounds, although less reliable, are also in accord with these findings. At least for the systems studied in this work, the deprotonation route (5a) may thus be effectively ruled out.[20]

$$[Me_2AlCH_2PMe_2]_2 + 2Li\text{-}t\text{-}Bu \xrightarrow[-78\ °C]{TMEDA/ether} \underset{\mathbf{4}}{[(TMEDA)_{3/2}Li(Me_2PCH_2)Al(t\text{-}Bu)Me_2]} \quad (6)$$

Due to exchange reactions of the carbanionic substituents in aluminates,[21] the number of isolable mixed-ligand aluminates, i.e., $LiAlR_2R'_2$, is restricted. The attempted preparation of aluminates of type II with mixed CH_2PMe_2/CH_3 aluminum substituents also failed. According to Scheme I, none of the aluminates **6a–c** could be isolated. The reason for this failure obviously is the low solubility of $\{Li[Al(CH_2PMe_2)_4]\}_n$, **5a**, which along with $LiAlMe_4$, **6d**, is the only isolated product in the absence of tetramethylethylenediamine (TMEDA). Substituent exchange of this sort can, in principle, occur via alkyl-bridged associates V. Therefore, the effective complexation of Li^+ with strong donors should prevent these aluminates from taking part in such exchange reactions. For this purpose, TMEDA, which is known to be an excellent ligand for Li^+, was added to the reaction mixtures in a 2:1 molar ratio. Most noticeably, it turns out that the aluminate anions **5a–d** may effectively compete with TMEDA for the Li^+ cation (Scheme II). As shown by elemental analysis and the intensity ratio of the ^1H NMR signals of the obtained products (Table I), only in the case of $[(TMEDA)_2Li][AlMe_4]$, **7**, is all the TMEDA used in Li^+ complexation as inferred from quantitative formation of the $[(TMEDA)_2Li]^+$ cation.



V

R = Me, CH_2PMe_2

In all other cases, represented by compounds **4** (vide supra) and **5a–d**, the TMEDA is replaced in part (**4**, **5b–5d**) or completely (**5a**) by the respective phosphinomethyl groups of the aluminate anion and free TMEDA could be

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(18) (a) Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 284. (b) Karsch, H. H.; Appelt, A. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1983**, *38B*, 1399.

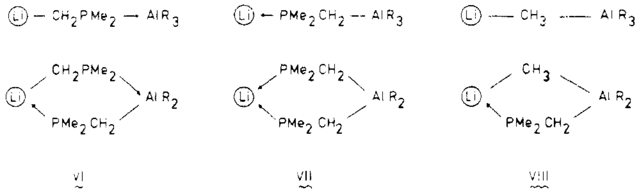
(19) (a) Peterson, D. J. *J. Organomet. Chem.* **1967**, *8*, 199. (b) Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456.

(20) An "Al(III)-ate" complex formation has also been found in the system $M(CH_2SiMe_3)_3/KH$ (M = Al, Ga, In); a previous report of $KM(CH_2SiMe_3)_2$ formation has been rejected: (a) Beachley, O. T., Jr.; Tessier-Youngs, C.; Simmons, R. G.; Wallock, R. B. *Inorg. Chem.* **1982**, *21*, 1970. (b) Wallock, R. B.; Beachley, O. T., Jr.; Li, Y.-J.; Sanders, W. M.; Churchill, M. R.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1983**, *22*, 3683. Therefore, we do not consider the formation of Al(I)-ate compounds in this study, but our results confirm the presence of Al(III)-ate compounds.

(21) Kieft, R. L.; Brown, T. L. *J. Organomet. Chem.* **1974**, *77*, 289.

(22) $[MeAl(CH_2PMe_2)_2]_2$ has been shown to be unstable with respect to disproportionation into **2** and **3**[5] and therefore was not employed in this study.

detected in the volatile constituents of the reaction mixtures. In principle, this type of Li^+ coordination by mixed CH_3/CH_2PMe_2-substituted aluminates may be achieved in three different ways, as indicated by formulas VI–VIII (R = CH_3, CH_2PMe_2). A distinction should be possible by infrared spectroscopy. Unfortunately, the expected region for Li–C, Li–P, Al–C, and Al–P vibrations (700–250 cm^{-1}) is in most cases obscured by additional absorptions. Thus, on the basis of the IR spectra, we were not able to make a clear distinction between these bonding modes. However, from the observed NMR spectra, a coordination of type VII was made likely, as expected.[23] Only one ^{31}P NMR signal is observed for **5a**, **5c**, and **5d** (and **5e**), even at −90 °C. Likewise, only one signal is observed for the $AlCH_3$ and respective CH_2PMe_2 protons of these compounds in the ^1H NMR spectra at −100 °C, and no $^3J(^{31}PAlC^1H)$ coupling is observed for the $AlCH_3$ and $AlCH_2P$ resonances, even at −100 °C, for **5a**, **5c**, **5d**, and **5e** (cf. $^3J(^{31}PAlC^1H)$ in **2**[5]). It was this coordination mode VII, i.e., that with exclusive AlCP→Li bridging, which was observed in the X-ray structure determination of **5e** and **5c** (vide infra). Therefore in the following discussion concerning the type of coordination in **4**, and **5a–e**, only type VII is considered.



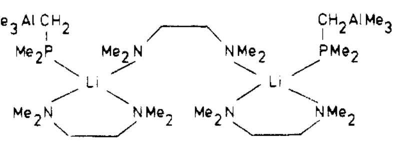
VI VII VIII

(Li = Li^+ with additional ligands)

With the assumption of a tetrahedral coordination of Li^+, the composition of **5d** (and **4**) suggests that the aluminate acts as a monodentate phosphine ligand to Li^+. In principle, two formulations **5d′** and **5d″** are reasonable.

$$[(TMEDA)_2Li]^{\oplus}\quad[(Me_3AlCH_2PMe_2)_2Li(TMEDA)]^{\ominus}$$

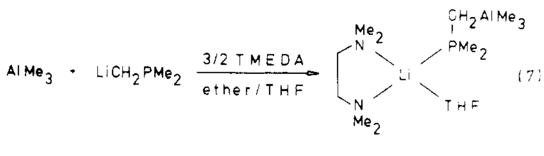
5d′



5d″

Low-temperature NMR spectra do not show a splitting of the TMEDA signals, expected (at least) for **5d″**. On the other hand, chelating and bridging binding modes of the TMEDA ligand might exchange rapidly on the NMR time scale or have the same shift values accidentally. Since conclusive evidence for the nature of **5d** (and **4**) proved elusive, we tried to substitute the (possibly) bridging TMEDA ligand of **5d″** by a monodentate donor (a chelating TMEDA ligand should be more stable with respect to substitution). Thus, according to eq 7, **5e** could actually be isolated as low melting, colorless crystals (ether/THF), which were suitable for an X-ray structure determination (vide infra).

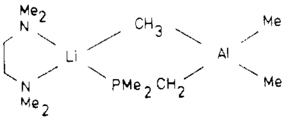
The tetrahydrofuran ligand in solid **5e** is lost in vacuo (0 °C/10^{-4} torr). The resulting solid analyzed correctly for



(7)

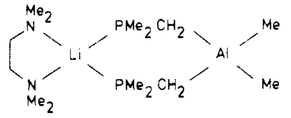
5e

$[(TMEDA)Li(Me_2PCH_2)AlMe_3]$, **5f**, and it is easily soluble in toluene and shows the correct signal intensities in the ^1H NMR spectrum. As derived from inspection of a suitable model and confirmed by the X-ray structure determination, in **5e** one methyl group at the aluminum atom approaches the Li^+ cation and thus may be responsible for the easy loss of THF. At present, coordination of type IX seems to be an adequate discription for **5f**. This suggestion implies that alkyl bridging (as, for instance, in solid $LiAlMe_4$[7]) also may be important in these compounds (cf. formula VIII), but less so than phosphinomethyl or TMEDA coordination to Li^+.

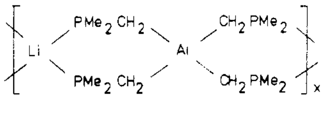


IX

In **5c** and **5a**, the aluminate acts as a mono or doubly chelating phosphine ligand, respectively. Whereas the molecular structure of **5c** could be substantiated by an X-ray structure determination (vide infra), that of **5a** is still tentative, since the low solubility of **5a** in hydrocarbon solvents precludes a more precise characterization. We consider **5a** to be a coordination polymer in the solid state.[5] When an excess of THF or TMEDA is added to **5a** in toluene, the solubility is enhanced to such an extent that NMR spectra may be recorded, obviously due to an equilibrium according to eq 8. The correct signal ratio for the respective PCH_3 and PCH_2 protons in the ^1H NMR spectrum is thus observed.



5c



5a

$$\underset{\mathbf{5a}}{[Li(Me_2PCH_2)_2Al(CH_2PMe_2)_2]_x} + nxL \rightleftharpoons \underset{\mathbf{5a'}}{x[L_nLi][Al(CH_2PMe_2)_4]} \quad (8)$$

L = THF, TMEDA

The aluminate ion $[MeAl(CH_2PMe_2)_3]^-$ is exceptional, since no simple coordination mode may be envisaged in the Li^+/TMEDA system. Not surprisingly, therefore, **5b** could not be isolated. Instead, **5a** and **5c** are obtained by a rapid disproportionation (Scheme II). The favored formation of the more stable chelating phosphine in **5a** and **5c** obviously also is the driving force for the slow decomposition of **5d** in ethereal solution (25 °C, $t_{1/2} \approx$ 2 days) with **5c** and **7** as the isolated products of this disproportionation (eq 9). An analogous decomposition occurs for

$$\mathbf{5d} \rightarrow \underset{\mathbf{5c}}{[(TMEDA)Li(Me_2PCH_2)_2AlMe_2]} \; ; \; \mathbf{5d} \rightarrow \underset{\mathbf{7}}{[(TMEDA)_2Li][AlMe_4]} \quad (9)$$

5e (25 °C, $t_{1/2} \approx$ 1 day) and **4** (25 °C, $t_{1/2} \approx$ 10 h) (see

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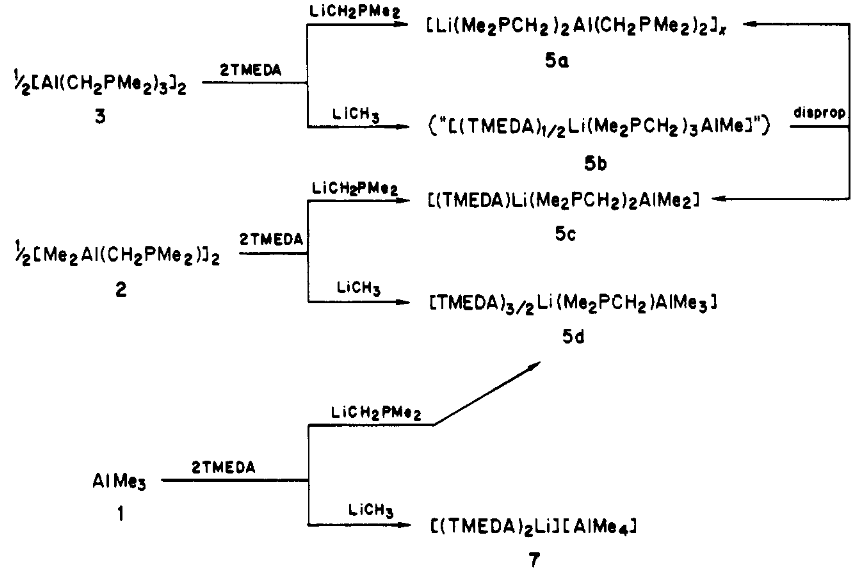
[23] A lithium "ate" coordination is known for only one example (linear C–Li–C)[24] and may be ruled out by similar arguments.

[24] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827.

Scheme II. Reaction of Alkylaluminum Compounds 1-3 with Organolithium Reagents $LiCH_3$ and $LiCH_2PMe_2$ in the Presence of 2 Equiv of Tetramethylethylenediamine (TMEDA)[22]



TMEDA = $Me_2NCH_2CH_2NMe_2$

Experimental Section). These disproportionation reactions may be initiated by the loss of one TMEDA (4, **5d**) or THF (**5e**) ligand. The intermediate is expected to be closely related to formula V and IX. Indeed, **5f**, which probably adopts type IX structure, also disproportionates easily, even in the solid state (0 °C, several weeks). The products of these disproportionations are **5c**, $[(TMEDA)_2Li][AlMe_4]$, and/or, in the case of **5d**, **5e**, and **5f**, $Li[AlMe_4]$, but in the case of 4, the products have not yet been identified. A generally labile coordination of the ligands to the Li^+ cation also may be inferred from the reversibility of the complex formation and redistribution of the ligands upon heating the (phosphinomethyl)aluminates in vacuo. Thus, from **5d** or a mixture representing the composition of **5b**, the most volatile "components" are sublimed away (eq 10 and 11). Equation 10 implies a transfer of the

$$\underset{\textbf{5d}}{2[(TMEDA)_{3/2}Li(Me_2PCH_2)AlMe_3]} \xrightarrow{\Delta T} 2AlMe_3{\cdot}TMEDA + [(TMEDA)LiCH_2PMe_2]_2 \quad (10)$$

$$\underset{\textbf{5b}}{2\text{“}[(TMEDA)_{1/2}Li(Me_2PCH_2)_3AlMe]\text{”}} \xrightarrow{\Delta T} \underset{\textbf{2}}{{}^1/_2[Me_2AlCH_2PMe_2]_2}\uparrow + \underset{\textbf{5a}}{[Li(Me_2PCH_2)_2Al(CH_2PMe_2)_2]_n} + [(TMEDA)LiCH_2PMe_2]_2 \quad (11)$$

carbanionic phosphinomethyl group from aluminum to lithium. The reversibility of the coordination also is evident from the reaction with MeI (eq 12). The easy

$$\underset{\textbf{5d}}{[(TMEDA)_{3/2}Li(Me_2PCH_2)AlMe_3]} + MeI \xrightarrow{\text{ether}} \underset{\textbf{8}}{Me_3AlCH_2PMe_3} \quad (12)$$

quaternization of the phosphorus atom in these reactions establishes a novel access to coordination compounds of phorphorus ylides from phosphinomethyl compounds.[8] For (phosphinomethyl)lithium compounds (lithium phosphinomethanides), a corresponding reaction pathway with electrophiles (P attack), yielding phosphorus ylides, has been described previously,[3] but a "C attack" also is possible.[1b] The phosphinomethyl group in transition-metal complexes, e.g., in $(Me_3P)_3(H)FeCH_2PMe_2$, also is attacked at the carbanionic center by MeI to give $(Me_3P)_3(Me_2PEt)(H)FeI$.[25]

All the aluminates 4, **5c**, **5d**, **5e**, **5f**, and **7** are extremely air-sensitive, colorless solids, soluble in aromatic hydrocarbons such as benzene or toluene. Their NMR spectra are essentially temperature independent in the range −100 to +60 °C. Mixtures of different compounds, e.g., **5c**, **5d**, and **7**, give separate signals for every component, indicating that exchange processes are slow on the NMR time scale. The spectra are hampered by line broadening due to the ^{27}Al quadrupolar nucleus, however. Therefore, intensity ratios from the ^1H NMR spectra are the most valuable information obtainable. The broad ^{13}C NMR signals are scarcely useful for structural assignments and therefore are omitted from Table I. The ^{31}P NMR signals are broad single lines in all cases, and the chemical shifts are very similar for all compounds. Nevertheless, individual signals are observed for all compounds, thus enabling the ^{31}P NMR to be a diagnostic tool.

Description of the Structures of 5e and 5c

As Figure 1 shows, the Li^+ cation in **5e** clearly is coordinated to the donor atoms of the aluminate and the TMEDA and THF ligands in a slightly distorted tetrahedral coordination geometry. Not surprisingly, the largest deviation from the standard tetrahedral angle is found in the five-membered ring formed by the small-bite chelating TMEDA ligand with Li^+. Also, all other geometrical details of this part of the molecule agree closely with previously published examples[26] and are not discussed explicitly here.

The Li–P distance is 2.593 (7) Å which fits nicely into the pattern of the few Li–P distances described in the literature.[1,2] All atoms of the C_3AlCPC_2 skeleton of the novel aluminate ligand exhibit familiar tetrahedral geometries. The valence angle at the bridging C1 is opened to 120.2 (2)°. Most noticeably, the P–C1 distance in the Al–C–P bridge is slightly shorter than the P–methyl bonds, whereas Al–C1 is somewhat longer than the respective

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[25] Karsch, H. H. *Chem. Ber.* **1978**, *111*, 1650.

[26] Amstutz, R.; Laube, Th.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 224.

Al–methyl bonds. This is also observed in **5c** and will be commented on later. All other Al–C and P–C bond lengths do not differ significantly from standard values.[5]

The conformation of the aluminate with respect to the central P–C1 bond is gauche as manifested by a torsion angle, Al–C1–P–Li, of 57.5°. This allows the positively charged Li atom to approach the aluminate center to 4.588 (7) Å, whereas the nonbonded Li–C4/C5 distances are 4.029 (8) and 5.298 (8) Å. Most interestingly, the observed gauche conformation is the same as that predicted by ab initio calculations[27] for the free $[H_2\bar{P}-\bar{C}H_2]^-$ anion. In **5e** the aluminate may be considered formally as $[Me_2\bar{P}-\bar{C}H_2]^-$ whose lone pairs at C and P are complexed by the strong Lewis acids $AlMe_3$ and Li^+, respectively! It cannot be ruled out completely, however, that in **5e** a further approach of Li and Al, which would be feasible in a eclipsed *syn* conformation, is prevented effectively by the steric requirements of the other ligands around Li^+.[28] In any event, the close approach of C4 and Li might explain the easy loss of THF upon heating, with concomitant formation of a $Al-CH_3-Li$ bridge, as described earlier.

In **5c** the Li^+ cation is embedded as a spiro center upon coordination into a five- and six-membered ring system formed by the chelating TMEDA ligand and the bifunctional aluminate, respectively (Figure 2). Again, the $(TMEDA)Li^+$ portion of the molecule shows little deviation from standard geometries. However, the geometry of the six-membered $Al(CP)_2Li$ heterocycle is unusual as it contains an almost planar $(CP)_2Li$ fragment: the Li atom deviates only 0.14 Å from the plane through the other four atoms. This pseudoenvelope conformation is also seen in the angles between the planes AlC3C3*/C3C3*PP* and C3C3*PP*/PP*Li which are 66.7° and 5.0°, respectively. Since no unusual bonding parameters are observed in the aluminate ligand, the reason for this flattening most probably lies in the chelate formation of both P donor centers with the Li^+ cation. The accommodation of two Li–P dative bonds (d(Li–P) = 2.606 (5) Å; ∠(P–Li–P*) = 105.7 (3)°) in the six-membered ring leads to a nonbonding P–P* distance of 4.155 (3) Å, whereas the C3–C3* distance only is 3.193 (8) Å. Apparently, the observed pseudoenvelope conformation best minimizes the strain resulting from these discrepancies. As a further consequence of the six-membered-ring formation the Al center comes closer to Li^+ than in **5e**: 4.020 (6) Å. The Li–C4 distance is 4.15 Å. The $P-CH_2$ distance (1.806 (4) Å) is again slightly shorter than the $P-CH_3$ bonds (1.838 (5) and 1.837 (5) Å) whereas $Al-CH_2$ is slightly longer than $Al-CH_3$. Although sometimes at the margin of significance, this shortening of the $P-CH_2$ bond (relative to standard P–C distances) also was observed in neutral (phosphinomethyl)aluminum compounds III[5] and lithium phosphinomethanides, as, e.g., in the cyclic dimer $[Me_2PCH_2Li(TMEDA)]_2$.[2] It also is a common feature in the structural chemistry of complexes of phosphorus ylides with a wide variety of metal centers. This gives a hint as to the probable origin of this effect, since phosphinomethyl complexes such as **5e** and **5c** also contain a four-coordinate phosphonium center adjacent to a CH_2 group which might be formally regarded as complexed ylidic carbanion. Thus the $P-CH_2$ bond shortening, as well as the concomitant $Al-CH_2$ elongation, should reflect a slight residual ylide character or, in other words, an inherent polarity of the $P-CH_2$ bond.

The structural results on **5e** and **5c** show clearly that the (phosphinomethyl)aluminates form complexes with Li^+ under exclusive formation of P–Li bonds. The observed P–Li distances of ca. 2.60 Å are in accord with the few previously found values[1,2] and might thus be taken as standard values for P–Li donor–acceptor bonds. Since no abnormally short distances between Li and methyl groups at Al are observed, additional weak $Li-CH_3-Al$ interactions can be excluded in these complexes for the solid state. Furthermore, the Coulombic attraction between the anionic Al and the cationic Li centers should be fairly small, as inferred from their long separation in complexes **5e** and **5c**. Nevertheless, complex formation between anion and cation should minimize effectively the electrostatic potential in this system, thus rendering Coulomb forces important as the driving force for the complex formation. This should be especially true for **5e**, whereas in **5c** the chelate effect also is expected to play a role.

These preparative and structural observations may be summarized as follows: a) phosphinomethyl-substituted aluminates may act effectively as donor ligands even to such inherently weak acceptor centers as Li^+ and compete for a coordination site even with classical "lithiophilic" donor ligands such as amines or ethers; (b) ring formation (chelating coordination mode) promotes this type of phosphine complexation considerably; (c) complex formation occurs exclusively via P–Li dative bonds in the case of Li^+; (d) 2.60 Å has to be taken as the standard bond length for P–Li dative bonds. An extension of these findings to other main-group metals lies at hand. We expect phosphinomethyl-substituted aluminates to be especially valuable organometallic ligands for the formation of homoleptic phosphine complexes of main-group metals, as has already been shown for phosphinomethanides.[29]

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Registry No. **2**, 93646-04-9; **3**, 93646-02-7; **4**, 97416-55-2; **5a**, 93646-03-8; **5c**, 95099-95-9; **5d**, 97416-57-4; **5e**, 95099-94-8; **5f**, 97416-58-5; **7**, 97416-59-6; TMEDA, 110-18-9; $LiAlMe_4$, 14281-94-8; $Me_3AlCH_2PMe_3$, 18307-49-8; $2AlMe_3\cdot TMEDA$, 30471-04-6; $LiCH_2PMe_2\cdot TMEDA$, 97416-60-9; $AlMe_3$, 75-24-1; $LiCH_3$, 917-54-4; $LiCH_2PMe_2$, 64065-06-1; Li-*t*-Bu, 594-19-4; MeI, 74-88-4.

Supplementary Material Available: Additional crystal structure data and lists of anisotropic temperature factors, H atom coordinates, and observed and calculated structure factors for **5e** and **5c** (25 pages). Ordering information is given on any current masthead page.

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(27) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(28) E.g., d(C4–C8) = 4.23 Å, d(C4–C16) = 4.20 Å d(C4–O) = 4.08 Å, and d(C5–C7) = 4.24 Å. This idea is also borne out by the relatively large P–C1–Al valence angle.

(29) Karsch, H. H.; Appelt, A. Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402.