

16327-75-6; 8, 486-25-9; 9, 602-15-3; 10, 92-52-4; 11, 90-43-7; 12, 132-64-9; 13, 93644-84-9; 14, 93604-91-2; 15, 641-96-3; 16, 212-74-8; 17, 93604-92-3; Ni, 7440-02-0; nickel(II) acetylacetonate, 3264-82-2; 2,2'-diiodobiphenyl, 2236-52-4; diphenylacetylene, 501-65-5.

**Supplementary Material Available:** Listings of final coordinates, final thermal parameters, and calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

## Functional Trimethylphosphine Derivatives. 21.<sup>†</sup> (Phosphinomethyl)aluminum Compounds: Phosphinomethyl-Bridged Dimers and X-ray Structures of [Me<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub> and [ClAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>‡</sup>

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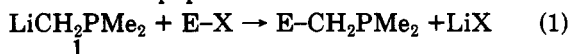
Phosphinomethyl-substituted organoaluminum compounds (Me<sub>2</sub>PCH<sub>2</sub>)<sub>n</sub>AlCl<sub>3-n</sub> (*n* = 1-3) and (Me<sub>2</sub>PCH<sub>2</sub>)<sub>n</sub>AlMe<sub>3-n</sub> (*n* = 1-3) have been prepared by various routes and characterized by analytical and spectroscopic methods. NMR measurements (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>27</sup>Al) in solution reveal an intra- and intermolecular exchange of the CH<sub>2</sub>PMe<sub>2</sub>-, Me-, and Cl- substituents. From these and other measurements, a dimeric structure of the molecules with a central six-membered ring moiety, CH<sub>2</sub>(Me<sub>2</sub>)P(Me<sub>2</sub>)AlCH<sub>2</sub>(Me<sub>2</sub>)P(Me<sub>2</sub>)Al, I, is indicated. In the solid state this central unit adopts a chair conformation with crystallographically imposed centrosymmetry as shown by X-ray structure determinations of [Me<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>, 7, and [ClAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, 3. Both compounds crystallize in the triclinic space group *P* $\bar{1}$  with one (dimeric) formula unit in the unit cell. The lattice constants are as follows. 7: *a* = 6.8850 (4) Å, *b* = 7.8363 (4) Å, *c* = 9.5416 (4) Å,  $\alpha$  = 76.039 (3)°,  $\beta$  = 68.191 (4)°,  $\gamma$  = 65.599 (4)°, *V* = 432.91 Å<sup>3</sup>, *d*<sub>calcd</sub> = 1.014 g/cm<sup>3</sup> for *Z* = 1. 3: *a* = 6.511 (2) Å, *b* = 9.956 (3) Å, *c* = 10.034 (3) Å,  $\alpha$  = 104.98 (2)°,  $\beta$  = 104.48 (2)°,  $\gamma$  = 103.06 (2)°, *V* = 578.27 Å<sup>3</sup>, *d*<sub>calcd</sub> = 1.221 g/cm<sup>3</sup> for *Z* = 1. For 7 full-matrix least-squares refinement of 64 parameters on 1450 observed reflections (*I* > 2.0σ(*I*)) converged at *R* = 0.090 and *R*<sub>w</sub> = 0.109 (*w* = 1/σ<sup>2</sup>(*F*<sub>o</sub>)). For 3 the final agreement indices were *R* = 0.034 and *R*<sub>w</sub> = 0.038 (*w* = *k*/σ<sup>2</sup>(*F*<sub>o</sub>); *k* = 1.33) for 155 refined parameters and 2001 observed reflections. In 3 the terminal phosphinomethyl groups are in the equatorial positions of the six-membered ring. The P-Al bond lengths are 2.451 (2) Å (7) and 2.425 (1) Å (3).

### Introduction

The combination of an electrophilic and a nucleophilic center in one molecule is one of the most attractive prospects for synthetic chemistry. In general, self-association of such molecules, either intra- or intermolecular, may lead to ring systems, and synergetic effects may promote reactivity patterns.

For the combination of R<sub>2</sub>Al and R<sub>2</sub>P groups, connected by an NR linkage, i.e., R<sub>2</sub>AlN(R')PR'<sub>2</sub>, the term "amphoteric ligand" has been used to characterize the utility of these systems in transition-metal and catalytic chemistry.<sup>1</sup> Compounds of the type R<sub>2</sub>AlPR'<sub>2</sub> also have been described.<sup>2</sup>

It is somewhat surprising in this context that the system R<sub>2</sub>AlCH<sub>2</sub>PR'<sub>2</sub> has not received any attention as yet.<sup>3</sup> We have synthesized a variety of phosphinomethyl compounds, Me<sub>2</sub>PCH<sub>2</sub>E (E = Cl,<sup>4</sup> PR<sub>2</sub>,<sup>5</sup> +PR<sub>3</sub>, P(O)R<sub>2</sub>, or P(CR'<sub>2</sub>)R<sub>2</sub>,<sup>6</sup> SiR<sub>3</sub> or SnR<sub>3</sub>,<sup>7</sup> Li,<sup>5</sup> or a transition-metal center<sup>5,8,9</sup>). The most general route is a reaction according to eq 1. The extension of this method to E-X = Me<sub>n</sub>AlCl<sub>3-n</sub>, *n* = 0-2, is described in this paper.<sup>9</sup>



### Results and Discussion

**Preparation and Properties.** The (phosphinomethyl)aluminum compounds 2-4 were obtained in moderate to good yields by stepwise substitution of AlCl<sub>3</sub> with LiCH<sub>2</sub>PMe<sub>2</sub>, 1, according to Scheme I. The reactions were carried out in ether at room temperature, and after removal of the solvent, the products 2-4 were sublimed in vacuo. The colorless, pyrophoric crystals (from toluene, 2 and 3, or pentane, 4) have melting points that increase

(1) Labinger, A. J.; Bonfiglio, J. N.; Grimmet, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* 1983, 2, 733.

(2) Beachley, O. T., Jr.; Tessier-Youngs, C. *Organometallics* 1983, 2, 796.

(3) The X-ray structure of [Et<sub>2</sub>AlCH<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> has been determined, however: Wilke, G.; Gajowski, J.; Krüger, C., personal communication (1983).

(4) Karsch, H. H. *Chem. Ber.* 1982, 115, 823.

(5) Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* 1977, 32B, 762. Karsch, H. H. *Ibid.* 1982, 37B, 284.

(6) Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, 34B, 31. Karsch, H. H. *Chem. Ber.* 1982, 115, 1956.

(7) Karsch, H. H.; Appelt, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1983, 38B, 1399.

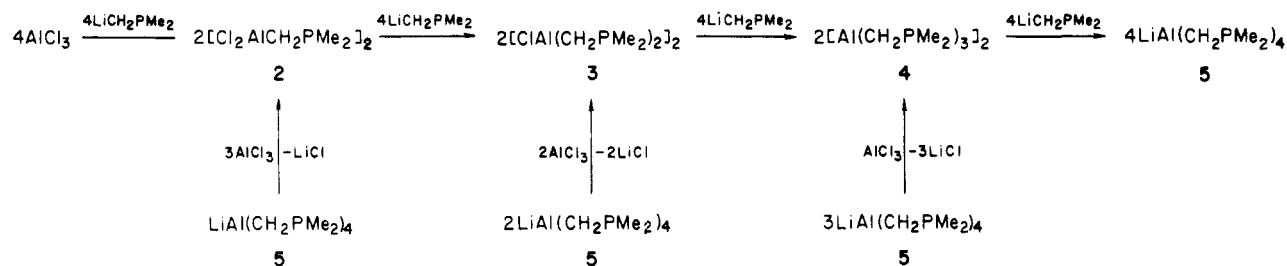
(8) (a) Karsch, H. H. *Chem. Ber.* 1984, 117, 783 and references therein. (b) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* 1984, 273, 195.

(9) Karsch, H. H.; Appelt, A. *Phosphorus Sulfur* 1983, 18, 287. In this paper also preliminary results on the [ >AlCH<sub>2</sub>PMe<sub>2</sub> ]<sub>2</sub> system are described.

<sup>†</sup>Part 20: see ref 12a. Part 19: see ref 8b.

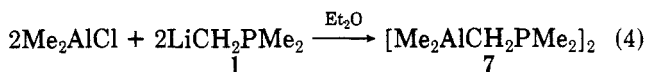
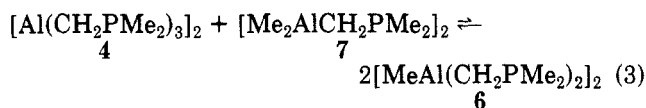
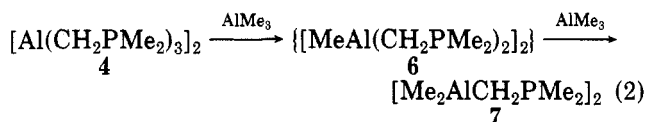
<sup>‡</sup>Dedicated to Prof. Günther Wilke on the occasion of his 60th birthday.

## Scheme I. Preparation of (Phosphinomethyl)aluminum Compounds 2-5

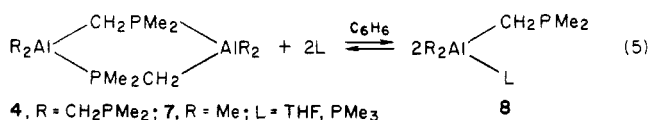


with the number of chlorine substituents. According to spectroscopic and analytical data (vide infra) they are dimeric in hydrocarbon solvents with their solubility increasing with the number of phosphinomethyl substituents from 2 to 4. The dimeric structure corresponds to that of the analogous compound  $[\text{Me}_2\text{BCH}_2\text{PMe}_2]_2$ <sup>10</sup> but seems to be at variance to  $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ .<sup>11</sup> Compound 3 is unique in combining chlorine as well as terminal and bridging phosphinomethyl groups as ligands at the aluminum center, and, therefore, an X-ray structure determination was undertaken to establish its exact molecular geometry (vide infra).

Donor solvents such as tetrahydrofuran are cleaved by reaction with 3, and even more readily with 2, to give unidentified products. Whereas the high synthetic potential of the chlorine-substituted compounds 2 and 3 as valuable precursors for other related (phosphinomethyl)aluminum compounds is evident, the utility of 4 in this respect deserves a comment: the exclusive formation of 7 in the reaction of 4 with the appropriate amount of  $\text{AlMe}_3$  (eq 2) seems to be due to the preference of a sym-



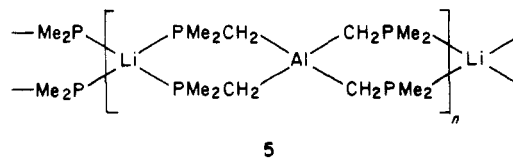
metrical arrangement and to the stability of the six-membered ring, since neither  $\text{AlMe}_3$  nor 6 may be detected in the solutions. Likewise,  $[\text{MeAl}(\text{CH}_2\text{PMe}_2)_2]_2$ , 6, cannot be prepared from a 1:1 mixture of 4 and 7. Although rapid interchange of the substituents in solution is evident from the NMR measurements at +20 °C, at low temperature only 4 and 7 are observed (<sup>31</sup>P NMR), and 7 is isolated by crystallization (eq 3). Compound 7 also may be prepared by the reaction of 1 with  $\text{Me}_2\text{AlCl}$  in high yield (eq 4). 7 forms colorless, extremely air-sensitive crystals (pentane), which proved suitable for X-ray diffraction measurements (vide infra). Donor molecules such as  $\text{PMe}_3$  and, more readily, THF lead to an equilibrium according to eq 5.



4, R =  $\text{CH}_2\text{PMe}_2$ ; 7, R = Me; L = THF,  $\text{PMe}_3$

The equilibrium lies well to the left for L =  $\text{PMe}_3$ , unless

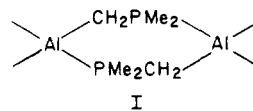
a large excess of  $\text{PMe}_3$  is used. In either case, 8 cannot be isolated from the mixture, since the higher volatility of  $\text{PMe}_3$  and tetrahydrofuran and/or the better crystallinity of 4 and 7 shift the equilibrium to the left on the attempted isolation. Cleavage products may be isolated, however, by the reaction with carbanions.<sup>12</sup> Thus, further reaction of  $[\text{Al}(\text{CH}_2\text{PMe}_2)_3]_2$ , 4, with  $\text{LiCH}_2\text{PMe}_2$  leads to the anionic aluminate 5, which may be regarded as a tetradentate phosphine ligand, i.e., an anionic counterpart of the iso-electronic neutral species  $\text{M}(\text{CH}_2\text{PMe}_2)_4$  (M = Si, Sn).<sup>7</sup> This phosphinomethyl aluminate, also obtained as a by product in the preparation of the covalent compounds 2-4 at low temperature (Scheme I), can be isolated as colorless solid, insoluble in nonpolar solvents but slightly soluble in donor solvents such as THF, DME, or TMEDA. The low solubility leads us to assume that solid 5 is actually



a coordination polymer with lithium bridging the chelating phosphinomethyl groups.<sup>12</sup> Reaction of 5 with appropriate amounts of  $\text{AlCl}_3$  yields the covalent species 2, 3, and 4 (Scheme I). These reactions require an exact stoichiometric ratio and elevated temperatures (+30 °C), i.e., conditions, under which alkyl group exchange is fast. Further details on the preparation and properties of 5 and related aluminates, as well as their structural characteristics, are described in forthcoming papers.<sup>12</sup>

## Spectroscopic Results

The dimeric nature of the new compounds, all containing the six-membered ring moiety I is evident from the



cyroscopic molecular weight determination of  $[\text{Al}(\text{CH}_2\text{PMe}_2)_3]_2$ , 4, and, more conclusive, from the spectroscopic results. These measurements also reveal ring opening on the addition of donors as well as dynamic processes, such as rapid terminal/bridging phosphinomethyl group scrambling and chlorine/alkyl group exchange in solution and in the gas phase.

Mass spectra show the  $\text{M}^+$  peak for  $[\text{Cl}_2\text{AlCH}_2\text{PMe}_2]_2$ , 2, and  $[\text{Me}_2\text{AlCH}_2\text{PMe}_2]_2$ , 7, and the  $\text{M}^+ - 1$  (H) peak for  $[\text{Al}(\text{CH}_2\text{PMe}_2)_3]_2$ , 4. However, more prominent are the  $\text{M}^+ - 15$  ( $\text{CH}_3$ ) peak for 7 and the  $\text{M}^+ - 75$  ( $\text{CH}_2\text{PMe}_2$ ) peaks for 2 and 4. For a crystalline sample of  $[\text{ClAl}(\text{CH}_2\text{PMe}_2)_2]_2$ , 3, the  $\text{M}^+ - 15$  peak has a low intensity and the  $\text{M}^+$  peak

(10) Rathke, J.; Schaeffer, R. *Inorg. Chem.* 1972, 11, 1150.

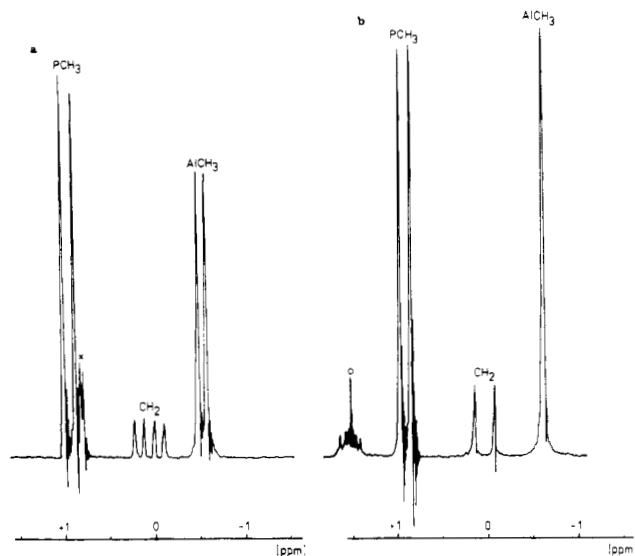
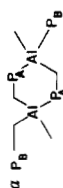
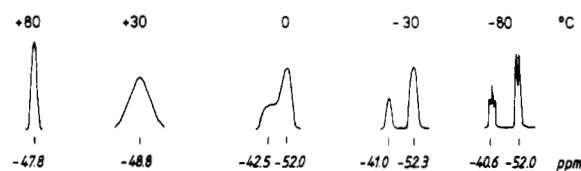
(11) Beachley, O. T., Jr.; Tessier-Youngs, C.; Simmons, R. G.; Hallock, R. B. *Inorg. Chem.* 1982, 21, 1970 and references cited therein.

(12) (a) Karsch, H. H.; Appelt, A.; Müller, G. *J. Chem. Soc., Chem. Commun.* 1984, 1415. (b) Karsch, H. H.; Appelt, A.; Müller, G., to be submitted for publication.

Table I. NMR Data of 2, 3, 4, 5, and 7 (+30 °C, Toluene-*d*<sub>8</sub>;  $\delta$  in ppm, *J* and  $\Delta$  in Hz)

compd	<sup>1</sup> H NMR <sup>a</sup>		<sup>13</sup> C NMR		<sup>27</sup> Al NMR, $\delta$ (Al) ( $\Delta$ expd)
	$\delta$ (PCH <sub>3</sub> ) ( <sup>2</sup> <i>J</i> (PCH <sub>3</sub> ))	$\delta$ (PCH <sub>2</sub> ) ( <sup>2</sup> <i>J</i> (PCH <sub>2</sub> ))	$\delta$ (PCH <sub>3</sub> ) ( <sup>1</sup> <i>J</i> (PC))	$\delta$ (PCH <sub>2</sub> ) ( <sup>1</sup> <i>J</i> (PC))	
[Cl <sub>2</sub> AlCH <sub>2</sub> PMe <sub>2</sub> ] <sub>2</sub> (2)	0.97 (d, 9.8)	0.21 (dd, 16.1/3.8)	10.95 (d, <sup>b</sup> 21.68)	133 (2800)	
[ClAl(CH <sub>2</sub> PMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (3)	1.37 (d, 3.4)	0.47 (d, 8.5)	15.66 (d, 6.89)	144.3 (2100), 128.8 <sup>i</sup> (800)	
[Al(CH <sub>2</sub> PMe <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> (4)	1.15 (s, br) <sup>d</sup>	0.19 (d, br, <sup>d</sup> 5.5)	18.16 (s) <sup>f</sup>	150 (5200)	
LiAl(CH <sub>2</sub> PMe <sub>2</sub> ) <sub>3</sub> (5)	1.23 (s, br)	0.29 (s, br)		147.7 (47)	
[Me <sub>2</sub> AlCH <sub>2</sub> PMe <sub>2</sub> ] <sub>2</sub> (7)	0.95 (d, 7.8)	0.03 (dd, 13.7/6.3)	12.79 (d, 20.51)	160 (200)	

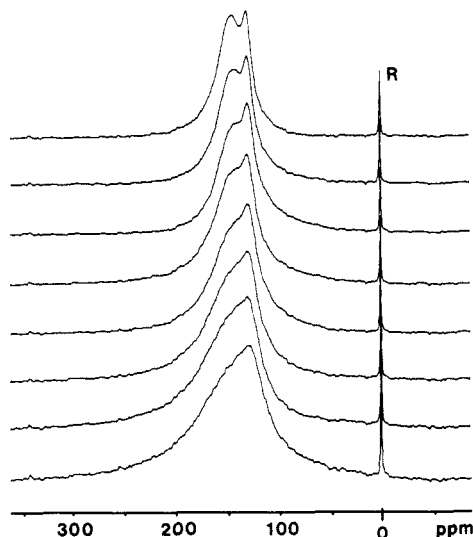
<sup>a</sup>  $\delta$ (P<sub>A</sub>) -40.54 (s, br),  $\delta$ (P<sub>B</sub>) -52.94 (s, br). <sup>b</sup> +80 °C. <sup>c</sup> -80 °C. <sup>d</sup> -80 °C. <sup>e</sup> -80 °C. <sup>f</sup> -70 °C. <sup>g</sup> In C<sub>6</sub>D<sub>6</sub>/DME/TMEDA (mixture of solvents). <sup>h</sup> Mixture of compounds, cf. text. <sup>i</sup> *T* = 100.7 °C.

Figure 1. <sup>1</sup>H NMR of 7 in toluene-*d*<sub>8</sub> (30 °C): (a) in the presence of a small amount of PMe<sub>3</sub> (X); (b) in the presence of a small amount of THF (O).Figure 2. <sup>31</sup>P{<sup>1</sup>H} NMR of 4 in toluene-*d*<sub>8</sub> at different temperatures ( $\delta$  values are relative to external H<sub>3</sub>PO<sub>4</sub>). Idealized curves are shown because of a significant improvement of the signal/noise ratio at low temperature.

is not observed. Instead, the spectrum shows the M<sup>+</sup> - 75 peaks and further fragmentation pattern of {[I]Cl<sub>x</sub>(CH<sub>2</sub>PMe<sub>2</sub>)<sub>4-x</sub>} (x = 1, *m/e* 449/451 (M<sup>+</sup> - 15); x = 3, *m/e* 384/386 (M<sup>+</sup>)). This is indicative of a rearrangement of substituents in the gas phase. A comparable alkyl/chlorine group exchange for 3 is observed also in solution (vide infra).

The NMR spectra (see Table I) are hampered by the quadrupolar broadening of the signals by the <sup>27</sup>Al nucleus. Mainly the <sup>13</sup>C and <sup>31</sup>P nuclei, which are attached directly to the aluminum, are concerned. In certain cases, heating or cooling of the sample solutions improve the recorded spectra to such an extent that detailed information may be obtained.

The dimeric compounds [Cl<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>, 2, and [Me<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>, 7, are rigid on the NMR time scale with respect to ligand exchange and hence show the expected couplings in the <sup>1</sup>H NMR spectrum (Figure 1). Addition of small amounts of PMe<sub>3</sub> (i.e., PMe<sub>3</sub>:7 < 10:1) does not apparently affect the spectrum of 7, whereas a large excess of PMe<sub>3</sub> causes those couplings, which are transmitted through the ring (i.e., <sup>3</sup>*J*(PAICH)), to break down. This effect is also achieved by the addition of only small amounts of donors such as THF or DME (Figure 1). Both the terminal and bridging phosphinomethyl substituents in [ClAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, 3, and [Al(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, 4, show only one resonance for the <sup>31</sup>P nuclei and the PMe<sub>2</sub> and CH<sub>2</sub> protons. Apparently they undergo rapid scrambling at room temperature. At low temperature this process is slow enough to distinguish the bridging and terminal phosphinomethyl groups in the <sup>31</sup>P NMR (3,  $\Delta G^*_{-70^\circ\text{C}}$  = 8.9 kcal/mol; 4,  $\Delta G^*_{0^\circ\text{C}}$  = 12.2 kcal/mol), although the low-temperature limit is not reached for 3. Thus, the <sup>3</sup>*J*(PP) coupling between the two kinds of phosphorus nuclei is observed only in the case of 4 (Figure 2). As



**Figure 3.**  $^{27}\text{Al}$  NMR of **3** in toluene- $d_8$  at different temperatures: 101, 91, 81, 71, 61, 51, 41, 31  $^\circ\text{C}$  (top to bottom). Probe head signals have been subtracted (R = reference  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ).

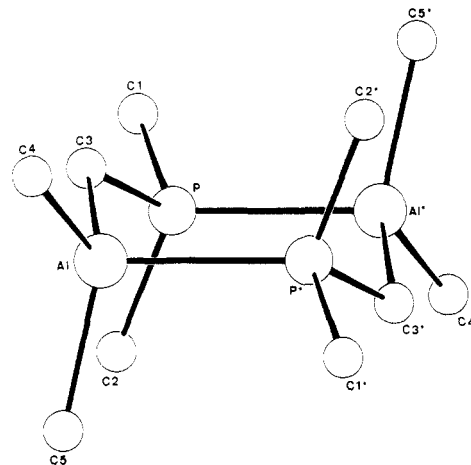
expected, the coordination of the phosphorus to the aluminum atom causes a downfield  $^{31}\text{P}$  shift for the signals of the bridging phosphinomethyl groups.

In principle, equatorial and axial positions of the substituents should be distinguishable for the six-membered ring molecules **2–4** and **7**. In no case could such effects be observed, however, which obviously is due to rapid ring inversion of the six-membered heterocycle, even at low temperature ( $-100\text{ }^\circ\text{C}$ ).

There is no evidence for the existence of  $[\text{MeAl}(\text{CH}_2\text{PMe}_2)_2]_2$ , **6**, in solution. An equimolar mixture of  $[\text{Al}(\text{CH}_2\text{PMe}_2)_3]_2$ , **4**, and  $[\text{Me}_2\text{AlCH}_2\text{PMe}_2]_2$ , **7**, shows a collapse of the  $^3J(\text{PAICH})$  couplings in **7** due to rapid intermolecular interactions, which are obviously induced by the terminal phosphinomethyl groups in **4**. However, separate signals for both compounds are observed in the range of  $-100\text{ }^\circ\text{C}$  to  $+30\text{ }^\circ\text{C}$ . Hence, we assume that **6** is unstable with respect to disproportionation to **4** and **7**.

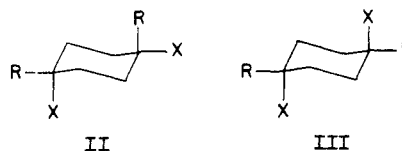
Among the magnetically active nuclei available  $^{27}\text{Al}$  is expected to give the most simple spectra. In fact, compounds **2**, **4**, **5**, and **7** give only one signal: their shifts and line widths,  $\Delta^{\text{exptl}}$ , are included in Table I. The  $^{27}\text{Al}$  signals of **4**, **5**, and **7** appear in a range that is typical<sup>13</sup> for a tetracoordinated aluminum with four carbons or three carbons and one donor ligand next to it. As carbon is replaced by chlorine the signals move to low frequency.  $^{27}\text{Al}$  being a quadrupolar nucleus, the line width depends markedly on the symmetry of the molecules. Hence, for **2**, **4** and **7** with low symmetry we find broad signals that do not allow us to extract  $^{1/2}J(^{31}\text{P}^{27}\text{Al})$ . An exception is **5** which has a narrow signal due to high symmetry. Although  $^2J(^{31}\text{P}^{27}\text{Al})$  is expected to be on the order of 30 Hz,<sup>14</sup> we do not find any fine structure for this signal. We believe that the reason for this is a still unfavorable ratio of line width to coupling constant rather than fast ligand exchange (vide infra).

Compound **3** gives a distorted  $^{27}\text{Al}$  signal at room temperature. As shown in Figure 3, two signals may be re-

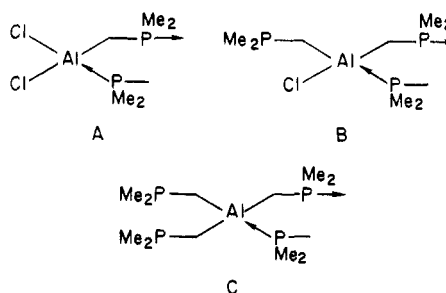


**Figure 4.** Molecular structure (ORTEP) of  $[\text{Me}_2\text{AlCH}_2\text{PMe}_2]_2$ , **7**, with atomic numbering scheme used. Hydrogen atoms have been omitted for clarity. The atoms with an asterisk are related to the atoms without an asterisk by a center of symmetry.

solved on increasing the temperature, indicating that molecular tumbling dominates the line width. The fact that we find more than one signal may not be attributed to the presence of diastereomers, e.g., **II** and **III**, since the



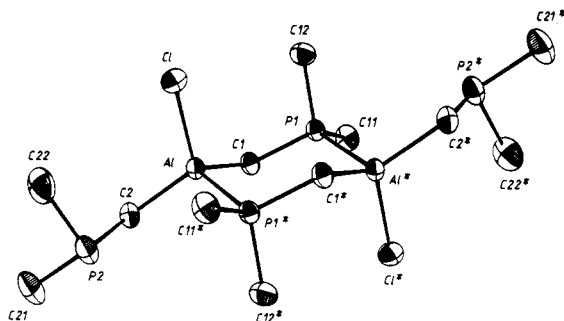
aforementioned rapid terminal/bridging phosphinomethyl group scrambling should interconvert both forms. Instead, the two signals are indicative for a disproportionation in solution by ligand exchange that should lead to aluminum in three different environments, A, B, and C, with the



shifts for A and C being similar to those for **2** ( $\delta(^{27}\text{Al})$  133) and **4** ( $\delta(^{27}\text{Al})$  150). Thus, the relatively narrow high-field signal in Figure 3 ( $\delta(^{27}\text{Al})$  129) may be attributed to A by comparison with the likewise narrow signal of **2**. Furthermore, these data suggest a value of  $\delta(^{27}\text{Al}) \sim 140$  for B. However, the line width observed for **4** indicates that the signals for B and C may not be distinguished and gives a mean shift of 145 ppm. This compares well with the broad resonance at  $\delta(^{27}\text{Al})$  144 for **3** (Figure 3). Although line widths considerably smaller than those shown in Figure 3 are observed at  $205\text{ }^\circ\text{C}$  in 1-methylnaphthalene, the signals for B and C remain unresolved. At this temperature Cl/ $\text{CH}_2\text{PMe}_2$  ligand exchange is still slow enough to yield a separate signal for A. Hence, the  $^{27}\text{Al}$  NMR measurement reveals a similar disproportionation of  $[\text{ClAl}(\text{CH}_2\text{PMe}_2)_2]_2$ , **3**, in solution as it is observed in the gas phase by mass spectroscopy. From the mixture of compounds present in solution (combinations of A, B, and C including **2**, **3**, and **4**) **3** crystallizes most readily and thus may be obtained in a pure state, the crystals being suitable for X-ray measurements.

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**Figure 5.** Molecular structure of  $[\text{ClAl}(\text{CH}_2\text{PMe}_2)_2]_2$ , **3** (ORTEP, thermal ellipsoids at the 50% probability level). Hydrogen atoms have been omitted for clarity. The atoms with an asterisk are related to the atoms without an asterisk by a center of symmetry.

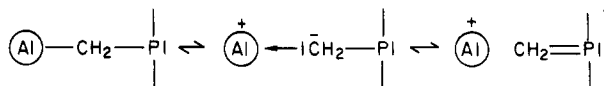
### Description of the Structures and Discussion

The solid-state structures of **7** and **3**, as determined by X-ray diffraction, show both molecules to be dimeric (Figures 4 and 5 and Tables IV–VII). Intermolecular “head to tail” complexation via P–Al donor–acceptor bonds under concomitant formation of a six-membered AlCPAlCP heterocycle in chair conformation accounts for the dimeric nature. The dimers possess crystallographically imposed centrosymmetry. Thus in **3** only one of the  $\text{CH}_2\text{PMe}_2$  substituents at Al is engaged in the ring formation, whereas the other one still possesses an uncomplexed P donor function. As expected, it occupies an equatorial and the Cl substituent an axial position in the six-membered ring. This dimeric nature with crystallographically imposed

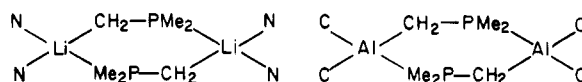
centrosymmetry on a AlCPAlCP heterocycle seems to be a general feature of the solid-state molecular structures of molecules with an  $\text{R}_2\text{AlCH}_2\text{PR}_2$  backbone. The only other example of a structurally characterized compound,  $\text{Et}_2\text{AlCH}_2\text{P}(\text{C}_6\text{H}_{11})_2$ ,<sup>3</sup> also showed a centrosymmetric dimer. All three compounds even crystallize in the same space group, although they are not isomorphous. The P–Al donor–acceptor bonds formed upon dimerization are 2.451 (2) Å in **7** and 2.425 (1) Å in **3**. The significantly shorter P–Al bonds in **3** are most probably due to inductive effects of the different substituents on Al, although steric effects of the larger Cl and  $\text{CH}_2\text{PMe}_2$  substituents might reduce the magnitude of this bond shortening to some extent.<sup>15</sup> In the absence of steric effects, bond lengths of pure dative bonds, especially between donor and acceptor molecules of groups 5B and 3B, respectively, are known to be directly correlated to the inductive effects of the various substituents at the donor and acceptor atoms.<sup>16,17</sup> The Al–C bond lengths both in **7** and in **3** are slightly longer than the Al– $\text{CH}_3$  bonds in uncomplexed, monomeric  $\text{AlMe}_3$  where  $d(\text{Al–C}) = 1.957$  (3) Å was found by electron diffraction.<sup>18</sup> This bond lengthening upon going from a lower to a higher coordination number in group 3B is even more pronounced for the Al–Cl bond length in **3**, 2.176 (1) Å (cf.  $d(\text{Al–Cl}) = 2.06$  (1) Å in monomeric  $\text{AlCl}_3$ <sup>19</sup>). The Al–Cl distance is also longer than those in (nonycyclic)  $\text{AlCl}_3$

(amine) complexes with four-coordinate Al<sup>20</sup> and falls well in the range observed in five-coordinate  $\text{AlCl}_3$ ·(amine)<sub>2</sub> complexes.<sup>21</sup> At the four-coordinate P atom (P1), on the other hand, the substituent bonds are slightly shorter as compared, e.g., to the “free” P atom P2 or uncomplexed  $\text{PMe}_3$  ( $d(\text{P–C}) = 1.846$  (3) Å<sup>22</sup>). Both effects have been observed in a variety of other donor–acceptor complexes of group 3B and 5B molecules as well<sup>15,23</sup> and may be explained on the basis of the VSEPR model<sup>24</sup> or by the differing degree of s-orbital polarization at three- and four-coordinate P and Al atoms.

There exist noteworthy differences between the P– $\text{CH}_3$  and P– $\text{CH}_2$  bond lengths, the latter being shorter by up to 0.024 Å (in **3**). Since the effect is observed with about equal magnitude both for the four-coordinate P atom P1 as well as the three-coordinate, uncomplexed P atom P2 in **3**, steric reasons arising from the six-membered ring formation can almost certainly be ruled out. An explanation might be found in light of structural results obtained on a number of complexes of phosphorus ylides with main-group elements as well as transition metals.<sup>25</sup> In a number of cases distinctly shorter P– $\text{CH}_2$  bonds, the former ylidic bonds, were found, as compared to other P–C bonds in the same molecules.<sup>26</sup> These observations were rationalized in terms of a slight residual double-bond character of the former ylidic  $\text{P}=\text{C}$  bond upon complexation.<sup>26</sup> In **7** and **3** a similar partial double-bond character of the P– $\text{CH}_2$  bond according to the canonical formula



might be envisaged. A similar description has been previously proposed for the mode of bonding in lithium phosphinomethanides to account for their ambivalent nature.<sup>27</sup> In fact,  $\text{LiCH}_2\text{PMe}_2$ <sup>5</sup> has been shown recently to crystallize in the presence of  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$  (TMEDA) in a very similar fashion as in **3** and **7** as a coordination dimer.<sup>28</sup> The main structural feature of  $[(\text{TMEDA})\text{LiCH}_2\text{PMe}_2]_2$  again is a six-membered heterocycle in a chair conformation, the mean P– $\text{CH}_2$  bond length being ca. 0.08 Å shorter than the mean P– $\text{CH}_3$  bond length.<sup>28</sup> Its central skeleton in the solid state may even be regarded as an “isoelectronic”<sup>29</sup> counterpart to **7**:



Such a heterocyclic arrangement, although obscured by

(15) In  $\text{Me}_3\text{P}\cdot\text{AlMe}_3$  an even longer P–Al bond (2.53 (4) Å) was determined by electron diffraction: Almennigen, A.; Fernholt, L.; Haaland, A.; Weidlein, J. *J. Organomet. Chem.* **1978**, *145*, 109.

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(30) It should be kept in mind, however, that the “isoelectronic” centers belong to different periods of the periodic table.

Table II. Preparative Data for Synthesis of 2, 3, and 4 (Method a)

	AlCl <sub>3</sub> , g/mmol	LiCH <sub>2</sub> PMe <sub>2</sub> , g/mmol	yield, g/%
2	1.24/9.39	0.77/9.39	1.54/95.6
3	0.55/4.15	0.68/8.29	0.69/78.2
4	1.87/14.19	3.49/42.56	3.00/83.9

Table III. Preparative Data for Synthesis of 2, 3, and 4 (Method b)

	AlCl <sub>3</sub> , g/mmol	LiAl(CH <sub>2</sub> PMe <sub>2</sub> ) <sub>4</sub> , g/mmol	yield, g/%
2	0.92/6.97	0.78/2.32	1.33/83.2
3	0.54/4.09	1.36/4.09	1.34/77.2
4	0.37/2.80	2.80/8.41	1.75/62.1

additional interactions, has also been found in the solid-state structure of [LiC(PMe<sub>2</sub>)<sub>3</sub>C<sub>4</sub>H<sub>8</sub>O]<sub>2</sub>.<sup>30</sup>

### Experimental Section

All compounds were handled in a dry argon atmosphere employing vacuum line or drybox techniques. Ether solvents were dried, stored, and distilled from sodium/potassium alloy. Hydrocarbon solvents were dried with LiAlH<sub>4</sub>, stored, and distilled immediately prior to their use. Purification of AlCl<sub>3</sub> and AlMe<sub>3</sub> was achieved by sublimation at 180 °C under high vacuum and by room temperature distillation, respectively. AlMe<sub>3</sub> was stored and used as a 3.02 M hexane solution and measured by volume using graduated syringes. The compounds LiCH<sub>2</sub>PMe<sub>2</sub><sup>5</sup> and Me<sub>2</sub>AlCl<sup>31</sup> were prepared and purified by literature procedures. They were judged pure by comparison of their melting and/or boiling points and spectroscopic data with literature values.<sup>5,31</sup>

**Spectra.** IR spectra were run as Nujol mulls between CsI windows on a Perkin-Elmer 577 instrument. Mass spectra (EI) were recorded on a Varian MAT 311A at 70 eV. NMR spectra were recorded on JEOL PMX 60, JEOL C 60 HL, JEOL FX 60, Bruker HX 90, and Bruker CPX 200 instruments at 60 (<sup>1</sup>H), 15.03 (<sup>13</sup>C), 36.43 (<sup>31</sup>P), and 52.12 (<sup>27</sup>Al) MHz. Chemical shifts are reported in parts per million and refer to Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C), 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), or Al(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub> (<sup>27</sup>Al). Negative signs refer to high field. Coupling constants are given in hertz. Double-resonance techniques confirmed the assignments.

**Analyses.** Analyses for C, H (combustion), Cl (potentiometric titration), Al, and Li (AAS) were performed by M. Barth, U. Graf, and G. Schuller, Microanalytical Laboratory, this institute. Whereas the analytical values for H, Cl, Al, and Li are satisfactory, the C values throughout are not.

**Synthesis of [(Me<sub>2</sub>PCH<sub>2</sub>)<sub>n</sub>AlCl<sub>3-n</sub>]<sub>2</sub> (n = 1, 2; n = 2, 3; n = 3, 4).** (a) **From AlCl<sub>3</sub> and LiCH<sub>2</sub>PMe<sub>2</sub>, 1 (General Procedure).** AlCl<sub>3</sub> in 40 mL of diethyl ether was added to a stirred suspension of LiCH<sub>2</sub>PMe<sub>2</sub>, 1, in 40 mL of diethyl ether 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 product was sublimed from the residue and isolated as a colorless, crystalline solid. If the reaction was carried out at low temperature (-50 °C), mainly 5 and LiCl were formed initially as solids of low solubility. The reaction comes to completion (i.e., formation of 2, 3, and 4, respectively) on stirring the resulting mixture for several hours. For preparative data see Table II.

(b) **From LiAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>4</sub>, 5, and AlCl<sub>3</sub> (General Procedure).** A mixture of AlCl<sub>3</sub> with LiAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>4</sub>, 5, in 50 mL of diethyl ether was stirred for 12 h at 30 °C. After the removal of the solvent in vacuo, the residue was sublimed under reduced pressure. For preparative data see Table III.

[(Me<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>AlCl]<sub>2</sub>, 2: mp 190–192 °C; subl pt 150 °C/10<sup>-3</sup> torr; MS, *m/e* (relative intensity) 344/46/48/50 (32.1, M<sup>+</sup>), 309/11/13/15 (13.8, M<sup>+</sup> - 35), 269/71/73/75 (100, M<sup>+</sup> - 75), 268/70/72/74 (62.0, M<sup>+</sup> - 76), 172/74/76 (33.4%, M<sup>+</sup>/2); IR (cm<sup>-1</sup>) ν(AIP) 309 w, ν(AlCl) 441 s, 602 s, ν(AlC) 509 s, 621 s. Anal. Calcd

for C<sub>6</sub>H<sub>16</sub>Al<sub>2</sub>Cl<sub>4</sub>P<sub>2</sub> (345.91): C, 20.83; H, 4.66; Cl, 41.00; Al, 15.60. Found: C, 18.23; H, 4.65; Cl, 40.45; Al, 15.50.

[(Me<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>AlCl]<sub>2</sub>, 3: mp 112–113 °C (recrystallized from toluene); subl pt 260 °C/10<sup>-3</sup> torr; MS, *m/e* (relative intensity) 409/11/13 (4.7, M<sup>+</sup> - 15), 349/51/53 (100, M<sup>+</sup> - 75), 298/91/93 (72.0, M<sup>+</sup> - 135), 449/51 (3.2, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>5</sub>Al<sub>2</sub>Cl - 15), 389/91 (9.4, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>5</sub>Al<sub>2</sub>Cl - 75), 384/86 (1.1, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, M<sup>+</sup>); 309/11/13/15 (49.5, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> - 75), 249/51/53/55 (14.6, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> - 135), 172/74/76 (3.1%, Me<sub>2</sub>PCH<sub>2</sub>AlCl<sub>2</sub>), 212/14 (2.8, (Me<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>AlCl); IR (cm<sup>-1</sup>) ν(AIP) 340 w, ν(AlCl) 418 m, 586 m, ν(AlC) 508 m, 625 s, sh. Anal. Calcd for C<sub>12</sub>H<sub>32</sub>Al<sub>2</sub>Cl<sub>2</sub>P<sub>4</sub> (424.15): C, 33.90; H, 7.59; Al, 12.69. Found: C, 31.61; H, 7.09; Al, 12.70.

[(Me<sub>2</sub>PCH<sub>2</sub>)<sub>3</sub>Al]<sub>2</sub>, 4: mp 69–70 °C; subl. pt 198 °C/10<sup>-3</sup> torr; MS, *m/e* (relative/intensity) 503 (0.28, M<sup>+</sup> - 1), 489 (20.4, M<sup>+</sup> - 15), 429 (100, M<sup>+</sup> - 75), 369 (11.9, M<sup>+</sup> - 135), 237 (12.4, M<sup>+</sup>/2 - 15), 177 (42.0, M<sup>+</sup>/2 - 75); IR (cm<sup>-1</sup>) ν(AIP) 332 w, ν(AlC) 499 m, 590–630 s. Anal. Calcd for C<sub>18</sub>H<sub>48</sub>Al<sub>2</sub>P<sub>6</sub> (504.39): C, 42.86; H, 9.59; mol wt (C<sub>6</sub>H<sub>6</sub>, cryoscopy), 504. Found: C, 41.06; H, 9.48; mol wt, 418.

**Synthesis of LiAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>4</sub>, 5.** A 600-mg (2.38-mmol) sample of [Al(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, 4, in 10 mL of pentane was added at -78 °C to a stirred suspension of 200 mg (2.38 mmol) of LiCH<sub>2</sub>PMe<sub>2</sub>, 1, in 10 mL of pentane. The mixture was allowed to warm to room temperature and stirred for another 12 h. Subsequently, the solvent was removed in vacuo. The solid residue was washed twice with 10 mL of pentane and dried in vacuo. A colorless product was obtained: 730 mg (2.20 mmol, 92.3%); mp 190 °C under decomposition; IR (cm<sup>-1</sup>) ν(LiP) 369 m, 282 m, ν(AlC) 626 s, 760 s. Anal. Calcd for C<sub>12</sub>H<sub>32</sub>AlLiP<sub>4</sub>: C, 43.13; H, 9.65; Al, 80.7; Li, 2.08. Found: C, 41.86; H, 9.28; Al, 8.00; Li, 1.84.

**Synthesis of [Me<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>, 7. (a) From AlMe<sub>3</sub> and [Al(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, 4.** To a stirred solution of 740 mg (2.94 mmol) of [Al(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, 4, in 40 mL of pentane was added 1.92 mL (5.87 mmol) of a 3.05 M solution of AlMe<sub>3</sub> in hexane at -78 °C. The mixture was allowed to warm to room temperature and stirred for another 12 h, and the solvent was removed in vacuo. After sublimation in vacuo (120 °C/10<sup>-3</sup> torr), 560 mg (4.25 mmol) of a colorless solid was obtained.

(b) **From LiCH<sub>2</sub>PMe<sub>2</sub> and AlMe<sub>2</sub>Cl.** To a stirred suspension of 1.32 g (16.10 mmol) of LiCH<sub>2</sub>PMe<sub>2</sub>, 1, in 40 mL of diethyl ether was added 13.4 mL (16.10 mmol) of a 1.2 M solution of AlMe<sub>2</sub>Cl in toluene at -78 °C. The mixture was allowed to warm to room temperature and stirred for 1 h, and the solvent was removed in vacuo. Sublimation in vacuo yielded 1.98 g (14.99 mmol, 93.1%) of a colorless solid: mp 101–102 °C; MS, *m/e* (relative intensity) 264 (0.5, M<sup>+</sup>), 249 (100, M<sup>+</sup> - 15), 132 (4.7, M<sup>+</sup>/2); IR (cm<sup>-1</sup>) ν(AIP) 321 w, ν(AlC) 512 m, 578 s, 660–710 vs. 740 s. Anal. Calcd for C<sub>10</sub>H<sub>28</sub>Al<sub>2</sub>P<sub>2</sub> (264.25): C, 45.45; H, 10.68; Al, 20.42. Found: C, 44.32; H, 10.60; Al, 20.25.

**X-ray Structure Determinations.** [Me<sub>2</sub>AlCH<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>, 7. A suitable single crystal of 7 was grown from pentane and sealed under an atmosphere of argon in a Lindemann glass capillary. According to diffractometer measurements (Enraf-Nonius CAD4) it crystallizes triclinic. The assumed space group *P*1 was later confirmed by the successful refinement of the structure. Reduced cell calculations (TRACER) indicated a monoclinic C-centered cell that could not be confirmed by the respective transformation of the data set and subsequent averaging of symmetry-equivalent reflections (*R*<sub>int</sub> = 0.37). Pertinent crystal data as well as a summary of intensity data collection and structure refinement are given in Table IV. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu Kα radiation and θ-2θ scans. After Lorentz and polarization corrections, reflections with *I* ≥ 2.0σ(*I*) were deemed "observed" and used for all further calculations. The structure was difficult to solve by conventional Patterson methods as well as by direct methods. A solution was finally obtained by a novel random-start multisolution direct method program (SHELX 84<sup>32</sup>) which yielded the position of the monomeric molecule misplaced with respect to the center of symmetry. The correct atom positions could be obtained by calculating a Fourier synthesis in *P*1 over the whole cell phased

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Table IV. Crystallographic Data for 3 and 7

	3	7
formula	C <sub>12</sub> H <sub>32</sub> Al <sub>2</sub> Cl <sub>2</sub> P <sub>4</sub>	C <sub>10</sub> H <sub>28</sub> Al <sub>2</sub> P <sub>2</sub>
M <sub>r</sub>	425.153	264.245
space group	P1	P1
a, Å	6.511 (2)	6.8850 (4)
b, Å	9.956 (3)	7.8363 (4)
c, Å	10.034 (3)	9.5416 (4)
α, deg	104.98 (2)	76.039 (3)
β, deg	104.48 (2)	68.191 (4)
γ, deg	103.06 (2)	65.599 (4)
V, Å <sup>3</sup>	578.27	432.91
Z	1	1
d <sub>calcd</sub> , g/cm <sup>3</sup>	1.221	1.014
μ <sub>calcd</sub> , cm <sup>-1</sup>	6.21	30.74
F(000), e	224	144
T, °C	-40 (±5)	21 (±2)
X radiation	Mo Kα	Cu Kα
λ, Å	0.710 69	1.541 78
scan mode	ω	θ-2θ
scan range, deg	1 ≤ θ ≤ 26	5.0 ≤ θ ≤ 75.6
reflectns unique	2244	1794
reflectns obsd (I ≥ 2.0σ(I))	2001	1450
parameters refined	155	64
R <sup>a</sup>	0.034	0.090
R <sub>w</sub> <sup>b</sup>	0.038	0.109
w	k/σ <sup>2</sup> (F <sub>o</sub> ), k = 1.33	1/σ <sup>2</sup> (F <sub>o</sub> )
Δρ (max), e/Å <sup>3</sup>	+0.64	+1.30
Δρ (min), e/Å <sup>3</sup>	-0.27	-0.56

<sup>a</sup> R = Σ(|F<sub>o</sub> - |F<sub>c</sub>||) / Σ|F<sub>o</sub>|. <sup>b</sup> R<sub>w</sub> = [Σw(|F<sub>o</sub> - |F<sub>c</sub>||)<sup>2</sup> / ΣwF<sub>o</sub><sup>2</sup>]<sup>1/2</sup>.

Table V. X-ray Structure Determination of 7: Final Fractional Atomic Positional Parameters with Esd's in Units of the Last Significant Figure in Parentheses

atom	x/a	y/b	z/c
Al	0.5871 (3)	0.3600 (2)	0.3089 (2)
P	0.5219 (2)	0.3047 (2)	0.6716 (1)
C1	0.6647 (13)	0.1604 (9)	0.8111 (7)
C2	0.2874 (11)	0.2309 (9)	0.7184 (7)
C3	0.6985 (8)	0.2325 (7)	0.4879 (6)
C4	0.8316 (11)	0.3079 (10)	0.1161 (6)
C5	0.3042 (11)	0.3418 (9)	0.3164 (8)

by the atoms taken from the direct method solution. The highest peaks of this map could be arranged in pairs with equal sums of their respective x, y, z coordinates wherefrom the correct origin could be deduced. Since difference Fourier syntheses after anisotropic refinement of the atoms did not reveal reasonable H atom positions, these were introduced at idealized geometrical positions and kept constant in the further refinement cycles (U<sub>iso</sub> = 0.07 Å<sup>2</sup>). The average shift/error ratio in the least cycle was 0.002. The relatively high R values are presumed to originate mainly from the poor crystal quality as judged by the relatively broad reflection profiles. Therefore an absorption correction was not considered worthwhile (μ(Cu Kα) = 30.74 cm<sup>-1</sup>; crystal dimensions ca. 0.3 × 0.5 × 0.5 mm<sup>3</sup>). A final difference map was qualitatively featureless, with the highest four peaks around the heavy atoms P and Al and much smaller values elsewhere. A detailed description of the data collection and refinement procedures including the sources of the atomic scattering factors and a list of the programs used has been published elsewhere.<sup>33</sup> Table V contains the final atomic coordinates of the non-hydrogen atoms. Table VII summarizes important bond lengths and angles.

[ClAl(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, 3. A suitable single crystal of 3 was obtained from toluene and sealed under argon at dry ice temperature in a Lindemann glass capillary. Diffractometer data (Syntex P2) yielded a triclinic unit cell. A monoclinic C-centered cell was again indicated by reduced cell calculations (TRACER) but could not be confirmed by averaging equivalent reflections of the transformed data set (R<sub>int</sub> = 0.34). Intensity data were collected

Table VI. X-ray Structure Determination of 3: Final Fractional Atomic Positional Parameters for the Non-Hydrogen Atoms

atom	x/a	y/b	z/c
Cl	0.3110 (1)	0.5353 (1)	0.2975 (1)
P1	-0.0843 (1)	0.2829 (1)	0.4564 (1)
P2	-0.0946 (1)	0.7968 (1)	0.1838 (1)
Al	-0.0203 (1)	0.5368 (1)	0.3035 (1)
C1	-0.1953 (4)	0.3503 (2)	0.3138 (2)
C2	-0.1871 (4)	0.6022 (2)	0.1541 (2)
C11	-0.2947 (4)	0.1157 (3)	0.4326 (3)
C12	0.1449 (4)	0.2227 (3)	0.4197 (3)
C21	-0.2856 (6)	0.8141 (4)	0.0248 (3)
C22	0.1537 (5)	0.8134 (4)	0.1275 (4)

Table VII. Selected Bond Lengths (Å) and Angles (deg) for 7 and 3

Bond Lengths			
7			
P-Al*	2.451 (2)	Al-C3	2.006 (6)
P-C1	1.829 (7)	Al-C4	1.969 (6)
P-C2	1.804 (8)	Al-C5	1.986 (8)
P-C3	1.788 (5)		
3			
P1-Al*	2.425 (1)	Al-C1	2.176 (1)
P1-C11	1.818 (2)	Al-C2	1.964 (2)
P1-C12	1.813 (2)	P2-C2	1.814 (2)
P1-C1	1.794 (2)	P2-C21	1.835 (3)
Al-C1	1.990 (2)	P2-C22	1.830 (3)
Bond Angles			
7			
Al*-P-C3	114.2 (2)	P*-Al-C3	103.2 (2)
Al*-P-C1	110.3 (2)	P*-Al-C4	105.4 (2)
Al*-P-C2	113.7 (2)	P*-Al-C5	102.9 (2)
C1-P-C2	103.4 (3)	C4-Al-C5	115.6 (3)
C3-P-C1	108.5 (3)	C3-Al-C4	111.5 (3)
C3-P-C2	106.1 (3)	C3-Al-C5	116.3 (3)
P-C3-Al	118.6 (3)		
3			
Al*-P1-C1	111.9 (1)	P1*-Al-C2	110.2 (1)
Al*-P1-C11	112.2 (1)	Cl-Al-C1	112.2 (1)
Al*-P1-C12	113.5 (1)	Cl-Al-C2	114.7 (1)
C11-P1-C12	104.3 (1)	C1-Al-C2	113.4 (1)
C1-P1-C11	107.1 (1)	Al-C2-P2	115.9 (1)
C1-P1-C12	107.3 (1)	C2-P2-C21	103.0 (1)
P1-C1-Al	120.2 (1)	C2-P2-C22	100.9 (1)
P1*-Al-C1	106.0 (1)	C21-P2-C22	99.1 (2)
P1*-Al-C1	99.0 (1)		

in ω scan mode on a Syntex P2, automated four circle diffractometer using graphite-monochromated Mo Kα radiation (Δω = 1°, 0.9 ≤ ω ≤ 29.3°/min). After Lorentz and polarization corrections (Syntex XTL) structure factors with F<sub>o</sub> ≤ 4.0 σ(F<sub>o</sub>) were considered statistically insignificant and excluded from all further calculations. The structure was solved by direct methods (SHELX 76) and completed by Fourier syntheses. After anisotropic refinement of the non-hydrogen atoms all H atoms could be located in difference syntheses and were subsequently refined isotropically (SHELX 76). In the last cycle the maximum ratio of shift to error was less than 0.07. Table IV contains the crystal data and a summary of intensity data collection and refinement. Data collection and refinement procedures followed closely those described in ref 34. This reference contains also the sources of the scattering factors and a list of the programs used. Table VI contains the final atomic coordinates and Table VII selected bond lengths and angles.

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93646-02-7; 5, 93646-03-8; 7, 93646-04-9; AlCl<sub>3</sub>, 7446-70-0; AlMe<sub>3</sub>, 75-24-1; AlMe<sub>2</sub>Cl, 1184-58-3.

**Supplementary Material Available:** Tables of additional crystal structure data, thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes for **3** and **7** (23 pages). Ordering information is given on any current masthead page.

## Reaction of the Phenoxide Ion with Trimethylaluminum. Isolation and Crystal Structure of [K·dibenzo-18-crown-6][Al<sub>2</sub>Me<sub>6</sub>OPh] and K[AlMe<sub>2</sub>(OPh)<sub>2</sub>]

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Potassium phenoxide reacts cleanly with trimethylaluminum in toluene in the presence of a 1:1 ratio of crown ether to salt. The product [K·dibenzo-18-crown-6][Al<sub>2</sub>Me<sub>6</sub>OPh], **1**, was crystallized by cooling from 70 °C to room temperature. In a 1:2 ratio of crown ether to salt, the temperature must be raised to ca. 160 °C for complete reaction. Slow cooling afforded K[AlMe<sub>2</sub>(OPh)<sub>2</sub>], **2**, as the possible decomposition product of [Al<sub>2</sub>Me<sub>6</sub>OPh]<sup>-</sup>. **1** belongs to the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 19.763 (6) Å, *b* = 9.830 (3) Å, *c* = 20.661 (6) Å, β = 116.00 (2)°, and ρ<sub>calcd</sub> = 1.18 g/cm<sup>3</sup> for *Z* = 4. The structure was refined to *R* = 0.088 with 1756 observed reflections. **2** crystallizes in the orthorhombic space group *Pbcn* with *a* = 20.487 (6) Å, *b* = 10.129 (4) Å, *c* = 7.259 (3) Å, and ρ<sub>calcd</sub> = 1.24 g/cm<sup>3</sup> for *Z* = 4. The refinement based on 483 observed reflections led to *R* = 0.031. The anion of **1** has a Y-shaped structure with Al–O–Al = 128.3 (7)° and Al–O = 1.86 (1) Å. The plane of the phenyl ring makes a 77° angle with the Al–O–Al plane. The anion of **2** resides on a crystallographic twofold axis with the Al–O length a short 1.800 (3) Å.

### Introduction

Our recent investigations into the formation and subsequent decomposition behavior of high oxygen content organoaluminum compounds have resulted in isolation of novel anionic species that are based upon four<sup>-1</sup> or six-membered<sup>2</sup> ring systems. These rings consist of alternating Al–O linkages and the anions so formed must represent intermediates to later stages of decomposition of anions of the type [Al<sub>2</sub>Me<sub>6</sub>X]<sup>-</sup> where X is typically oxide,<sup>2</sup> superoxide,<sup>2,3</sup> or high oxygen content anions such as cacodylate,<sup>1,6</sup> sulfate,<sup>4</sup> nitrate,<sup>5</sup> or acetate.<sup>6</sup> In an effort to further elucidate the pathways through which such decomposition may occur and to extend the range of liquid clathrate forming compounds,<sup>7</sup> we have conducted an investigation into the ability of the phenoxide anion to form liquid clathrates in the presence of trimethylaluminum and aromatic liquids. In this contribution we report structural characterization of both the 2:1 adduct of trimethylaluminum with phenoxide and a second compound that

may be the immediate decomposition product of the adduct.

### Results and Discussion

Potassium phenoxide reacts rapidly in the presence of dibenzo-18-crown-6 (1 equiv), trimethylaluminum (2 equiv), and toluene (excess) to yield a liquid clathrate of the composition [K·dibenzo-18-crown-6][Al<sub>2</sub>Me<sub>6</sub>OPh]·*n*C<sub>6</sub>H<sub>6</sub>Me. Heating of this system to 70 °C followed by slow cooling to room temperature yielded crystals of [K·dibenzo-18-crown-6][Al<sub>2</sub>Me<sub>6</sub>OPh], **1**, that were characterized crystallographically. However, the presence of only 0.5 equiv of crown ether, yielded both **1** and its decomposition product K[AlMe<sub>2</sub>(OPh)<sub>2</sub>], **2**, in the liquid clathrate layer. The presence of **2** was confirmed by the observation of two major resonances at ca. 0 ppm in the <sup>1</sup>H NMR spectrum of the liquid clathrate layer and by the subsequent characterization of **2** through a single-crystal X-ray diffraction study. **2** may represent the initial product in the decomposition pathway of **1**, which presumably halts at this early stage (unlike compounds in some of our earlier decomposition studies) because of the relative strength of the O–C bond in the phenoxide anion.

A view of the anion of **1** is given in Figure 1, and it clearly demonstrates adherence to the type of geometry that is typically seen for liquid clathrate parent anions. Similar Y-shaped structures were characterized in the analogous anions derived from azide,<sup>8</sup> superoxide,<sup>3</sup> and chloride.<sup>9</sup> The conformation within the anion is consistent

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