Synthesis and Structural Characterization of Functionalized Dimeric Aluminophosphonates and a Monomeric Gallophosphonate Anion[†]

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Reaction of t-BuP(O)(OSiMe$_3$)(OH) with Me$_3$Al leads to the formation of [Me$_2$Al(μ-O)$_2$P(OSiMe$_3$)(t-Bu)]$_2$ (**1**) whereas Me$_2$AlCl reacts with Ph$_2$P(O)(OH) to yield [(Cl)(Me)Al(μ-O)$_2$PPh$_2$]$_2$ (**2**). These compounds represent the first examples of functionalized dimeric four-ring type aluminophosphonate systems. The double four-ring type gallophosphonate, namely, [t-BuPO$_3$GaMe]$_4$, reacts with n-Bu$_4$NHF$_2$ under ambient conditions, resulting in the formation of a monomeric gallophosphonate [n-Bu$_4$N][MeGa{t-BuPO$_2$(OH)}$_3$] (**3**). These derivatives have been adequately characterized using various spectroscopic techniques and X-ray diffraction studies.

Introduction

Aluminophosphates, gallophosphates, and their transition metal derivatives have been the subject of current interest in zeolitic systems,[1] due to their use as size- and shape-selective catalysts,[2] molecular sieves, adsorbents, and ion exchangers.[3] These compounds have been implemented as precursors for the synthesis of alumino- and gallophosphate materials[4] on the account of exceptional properties exhibited by a new group of aluminophosphate-based molecular sieves.[5,6] The conventional mode of syntheses of such materials is based on the hydrothermal route. In the recent years, our aim has been to synthesize model compounds that can be thought to mimic one or more secondary building units (SBU) found in the zeolite library.[7] We were interested in developing synthetic routes leading to microporous materials employing nonaqueous routes and consequently used the building-block strategy to pursue this goal[8,9] relying upon the soft chemical routes or the molecular routes for the synthesis of advanced materials.[10,11] Concerning soluble metallophosphonate assemblies of group 13 metals, to the previously known model compounds, mimicking a single four-ring (4R)[12,13] and a double four-ring (D4R),[13,14] we have added examples which resemble a double six-ring (D6R),[15] a single

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[†] Dedicated to Professor Rafael Uson on the occasion of his 75th birthday.

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six-ring (6R),[16] and a tricyclic unit (6≡1).[17] We have reported new synthetic strategies for 4R type alumino- and gallophosphonate compounds of the type $[R_2M(\mu\text{-}O)_2P(OSiMe_3)_2]_2$ (R = Me, Et; M = Al, Ga) based upon dealkylsilylation and dechlorosilylation using appropriate precursors.[9,18] This report describes the preparation and structural characterization of neutral aluminophosphonates possessing the $Al_2P_2O_4$ core along with the first monomeric gallophosphonate anion.

Results and Discussion

The objective of producing functionalized aluminophosphonates with an $Al_2P_2O_4$ core may be thought to be achieved if new species could be produced with a functionalized phosphorus or an aluminum center.

Viewing the perspective of functionalization of the phosphorus center, it was decided to explore the possibility of introducing an additional substituent like Me_3Si in $t\text{-}BuP(O)(OH)_2$ so as to obtain $t\text{-}BuP(O)(OSiMe_3)(OH)$ and its subsequent reaction with Me_3Al with the anticipation to produce $[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2$ (**1**) (eqs 1 and 2). Interestingly, these speculations have been realized in practice. Purely based on solubility reasons, it was decided to use $t\text{-}BuP(O)(OH)_2$ as the initial synthon. The starting material $t\text{-}BuP(O)(OSiMe_3)(OH)$ was prepared from an equimolar reaction between $t\text{-}BuP(O)(OH)_2$ and Me_3SiCl in the presence of Et_3N, employing high-dilution techniques at low temperatures.[19] The progress of the reaction was revealed through the formation of Et_3NHCl in copious amounts.

$$t\text{-}BuP(O)(OH)_2 + Me_3SiCl + Et_3N \xrightarrow[-Et_3NHCl]{} t\text{-}BuP(O)(OSiMe_3)(OH) \quad (1)$$

$$2\ t\text{-}BuP(O)(OSiMe_3)(OH) + 2Me_3Al \xrightarrow[-2CH_4]{} \underset{\mathbf{1}}{[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2} \quad (2)$$

Starting from $t\text{-}BuP(O)(OSiMe_3)(OH)$ it was possible to synthesize **1** (eq 2). The progress of the reaction was indicated by the evolution of methane. Pure **1** was obtained in 80% yield through crystallization from toluene at −6 °C over a period of 1 week.

The ^1H NMR spectrum of compound **1** indicates two sets of signals for each proton moiety in the ratio 20:1 which is attributed to the trans and the cis isomers. The MeAl moieties are observed as singlets (−0.34 ppm and −0.36 ppm) for the trans and the cis isomers. The Me_3Si groups are observed as singlets (0.28 and 0.27 ppm, respectively) for the corresponding isomers along with two closely spaced doublets for the t-Bu group (1.09 and 1.10 ppm, $^3J_{P-H} = 17.8$ Hz). In the ^{31}P NMR spectrum, two closely spaced signals are observed at 14.6 ppm (cis) and 14.7 ppm (trans) varieties. In addition, these observations are supported by the appearance of two doublets (21.9 ppm, trans, and 22.0 ppm, cis, with $^2J_{PSi} = 11.5$ Hz) (Figure 1) in the ^{29}Si NMR spectrum. The NMR assignments of the cis and the trans isomers are based on the conformational stability of the two species. The nature of the spectra remained unchanged for the crude reaction mixture and the crystallized product, suggesting an equilibrium between the two isomers in solution. No significant changes were observed in the temperature dependent NMR spectra. In the EI-MS spectrum, the peaks due to the fragments $M^+ - CH_3$ (m/z 502, 100%) and $M^+ - C_4H_9$ (m/z 460, 60%) were observed, which provide additional evidence to the dimeric composition of **1**.

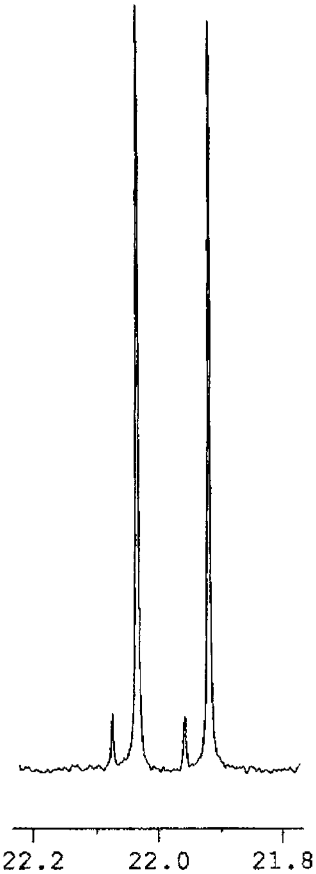

Figure 1. ^{29}Si NMR spectrum of $[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2$.

Recently Mason et al. reported the synthesis of an analogous gallium derivative.[20] However, our method involved a different synthetic strategy and could be extended to group 13 metals in general.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. The molecular structure is shown in Figure 2. The core of the structure consists of an eight-membered $Al_2P_2O_4$ ring composed of two aluminum centers bridged by two $O_2P(OSiMe_3)(t\text{-}Bu)$ moieties. Two methyl groups on each aluminum center complete the distorted tetrahedral environment. The two $Me_2AlO_2P(OSiMe_3)(t\text{-}Bu)$ monomeric units are related by a crystallographic inversion center. The geometry within the eight-membered ring, including Al−O bond lengths (1.787(3) and 1.813(3) Å), the P−O bond distances (1.503(3) and 1.513(3) Å), and the P−O−Al angles (144.9(2)° and 158.2(2)°), fits well in the range reported for related compounds.[9,13a] The extracyclic P−O bond length (1.533(3) Å) is also in agreement with the literature precedents.[9,13a] The substituents on the phosphorus centers are in a trans orientation. Important structural parameters are summarized in Table 1.

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Table 1. Crystal Data and Structure Refinement Details for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{18}H_{48}Al_2O_6P_2Si_2$	$C_{26}H_{26}Al_2Cl_2O_4P_2$	$C_{29}H_{69}GaNO_9P_3$
fw	532.64	589.27	738.48
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/c$
a (Å)	9.460(7)	11.157(9)	12.971(3)
b (Å)	16.789(12)	15.047(12)	14.927(3)
c (Å)	9.963(9)	17.689(12)	22.122(4)
α (deg)	90	90	90
β (deg)	93.797(17)	105.648(17)	103.40(3)
γ (deg)	90	90	90
V (Å^3)	1579	2860	4166.8
T (°C)	−140	−140	−70
λ (Å)	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.120	1.369	1.177
μ (mm^{-1})	0.295	0.431	0.818
F(000)	576	1216	1592
cryst size (mm)	0.20 × 0.40 × 0.30	0.30 × 0.30 × 0.30	1.00 × 0.30 × 0.20
θ range (deg)	2.38−21.95	2.33−21.96	3.51−22.52
index range	$-9 \leq h \leq 9$, $0 \leq k \leq 17$, $0 \leq l \leq 10$	$-11 \leq h \leq 11$, $0 \leq k \leq 15$, $0 \leq l \leq 18$	$-13\ h \leq 13$, $-15 \leq k \leq 16$, $-23 \leq l \leq 23$
no. of reflns colld	15519	17803	7571
no. of indep reflns	1923	1748	5428
R(int)	0.0662	0.0719	0.0605
no. of data	1923	1748	5418
no. of params	144	183	402
no. of restraints	0	160	0
GOF on F^2	1.060	1.073	1.036
R1^a [$I > 2\sigma(I)$]	0.0516	0.0389	0.0564
wR2^a (all data)	0.1418	0.0948	0.1543
largest diff peak and hole (e Å^{-3})	0.992, −0.357	0.282, −0.255	0.399, −0.459

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

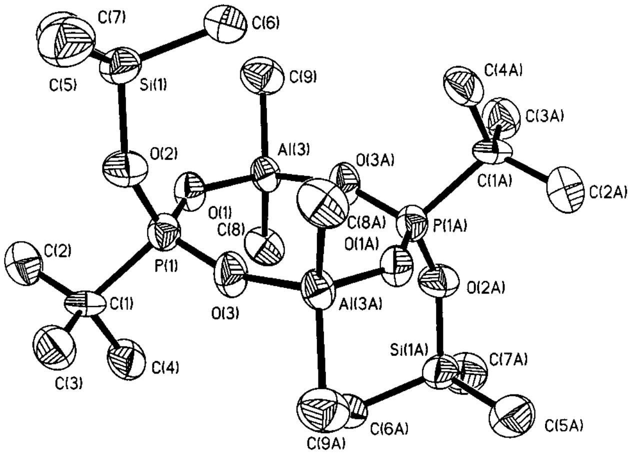

Figure 2. Molecular structure of $[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2$.

The literature quotes a report about the reaction of $EtAlCl_2$ with $Ph_2P(O)(OH)$ investigated by Robinson et al.[12e] However, our intention has been in the development of a rational strategy that would lead to a product possessing the $Al_2P_2O_4$ core and bearing an alkyl group along with a halogen on each aluminum center (eq 3). The desired product $[(Cl)(Me)Al(\mu\text{-}O)_2PPh_2]_2$ (**2**) was obtained in 60% yield.

$$2Me_2AlCl + 2Ph_2P(O)(OH) \xrightarrow[-2CH_4]{} [(Cl)(Me)Al(\mu\text{-}O)_2PPh_2]_2 \quad (3)$$

2

The presence of cis and trans isomers was documented from the ^{1}H and ^{31}P NMR spectra. In the ^{1}H NMR spectrum, two distinct signals are observed for the CH_3Al protons (−0.62 and −0.64 ppm, respectively) for the two isomers whereas the signals corresponding to the C_6H_5 groups were distinctly observed (7.79 and 7.51 ppm) as multiplets. The ^{31}P NMR spectrum reveals the presence of two closely spaced singlets (26.9 and 27.0 ppm) in the ratio 3:2 which could be attributed to the trans and the cis isomers. In the EI-MS spectrum the peaks due to the fragments $M^+ - CH_3$ (m/z 573, 100%) and $M^+ - Cl$ (m/z 553, 40%) are observed, which is an additional evidence for the dimeric nature of **2**.

Compound **2** crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. The core of **2** is an eight-membered $Al_2P_2O_4$ ring. The asymmetric unit contains half a molecule, the rest being generated by an inversion center. The methyl group and chlorine atom on each aluminum center are disordered in the structure, indicating that the crystal also contains a mixture of the trans and cis isomers, despite the apparent centrosymmetrical average molecule reflected in the crystal structure. The proximity does not permit the resolution of the partially occupied disordered sites of chlorine and methyl carbon atoms, so that tight geometric restraints had to be imposed on the Al−Cl and Al−C bond distances to allow convergence of the refinement. The average Al−O (1.77 Å) and P−O (1.51 Å) bond distances are concordant with the literature reports, but their values could be affected by the disorder.[9] Figure 3 depicts the molecular structure of **2** in the trans disposition.

To our surprise the reaction of n-Bu_4NHF_2 with $[t\text{-}BuPO_3\text{-}GaMe]_4$ results in the formation of $[n\text{-}Bu_4N][MeGa\{t\text{-}BuPO_2\text{-}(OH)\}_3]$ (**3**) in moderate yields, representing the first example of a monomeric gallophosphonate. We expected the formation of a gallophosphonate containing fluorine.[18] Compound **3** was characterized on the basis of its spectral properties and X-ray diffraction studies. In the ^{1}H NMR spectrum, signals corre-

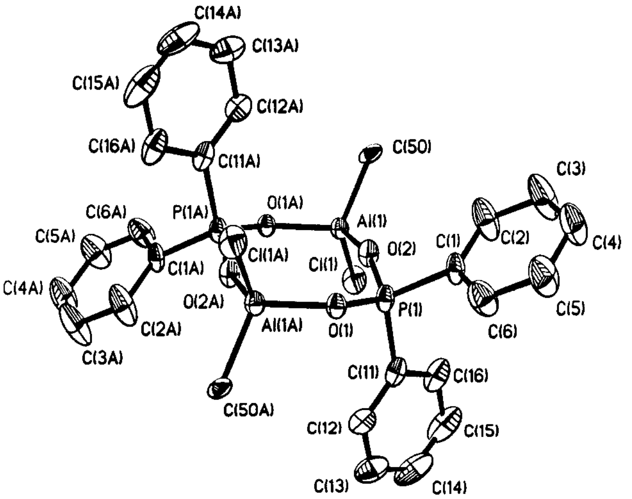

Figure 3. Molecular structure of $[(Cl)(Me)Al(\mu\text{-}O)_2PPh_2]_2$ in the trans isomer. The second disordered component has been omitted for clarity. It is not possible to distinguish in the crystal between a disordered trans structure and a mixture of cis and trans isomers.

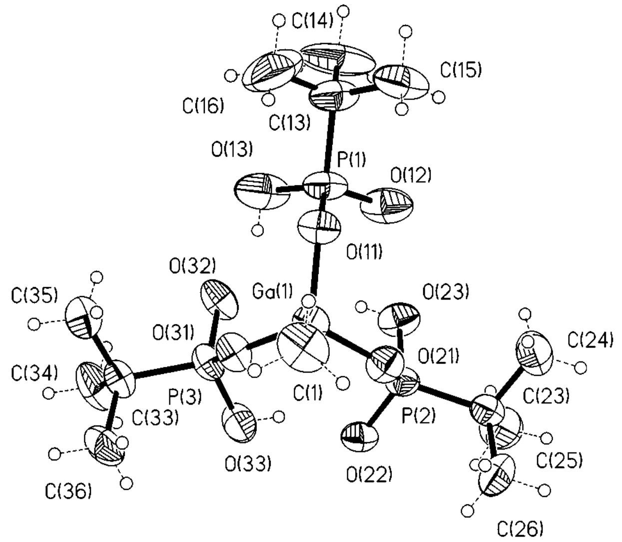

Figure 4. Molecular structure of $[MeGa\{t\text{-}BuPO_2(OH)\}_3]^-$.

sponding to the anionic moiety are observed in the appropriate ratios of intensities. The *t*-Bu- groups are observed as a doublet (1.03 ppm, $^3J_{P-H} = 15.7$ Hz) whereas the CH_3 moiety on the gallium center is located at -0.39 ppm. The P−OH groups are observed as a sharp singlet (13.2 ppm). In the ^{31}P NMR spectrum, a sharp signal appears at 30.9 ppm, indicating that all the phosphorus centers are in an identical environment. There is considerable deshielding in the ^{31}P NMR chemical shift as compared to the dimeric and tetrameric gallophosphonates reported.[13b,14c,20] In the IR spectrum of **3**, broad bands observed at 3165 and 1672 cm^{-1} indicate the presence of residual P−OH groups involved in intramolecular hydrogen bonding interactions. Mass spectrometric techniques do not provide further insight.

Single crystals of **3** were obtained from a saturated solution of THF/hexane over a period of 5 days. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structure of the anion of **3** is depicted in Figure 4. The gallium center in the anion $[MeGa\{t\text{-}BuPO_2(OH)\}_3]^-$ assumes a distorted tetrahedral geometry. The Ga−O bond distances are in the range 1.847(4)−1.855(4) Å and correspond well to those reported for neutral and ionic gallium phosphonates.[13b,20,21] The methyl carbon atom is at a distance of 1.944(6) Å from the central gallium atom. The P═O bond length is found in the range 1.521(5)−1.527(4) Å, which is in agreement with those observed in the case of aluminum[18] and transition metal phosphonates.[19,22] The average P−OH bond distance of 1.523 Å is in the expected range.[19] The structural parameters of **3** are gathered in Table 1.

In summary, we have effectively demonstrated new synthetic routes leading to the generation of functionalized 4R type aluminophosphonates along with the first example of a monomeric gallophosphonate anion. These compounds could be visualized as precursors for the studies of their transformation to three-dimensional phosph(on)ate materials using nonaqueous routes.[9]

Experimental Section

General Information. All manipulations were carried out under a dry, prepurified argon or nitrogen atmosphere, using Schlenk techniques and rigorously excluding moisture and air.[23] The samples for spectral measurements were prepared in a drybox. Solvents were dried over Na/K alloy and distilled freshly prior to use. ^1H and ^{31}P NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments. The chemical shifts are reported in parts per million with reference to Me_4Si (external) for ^1H and ^{29}Si and 85% H_3PO_4 (external) for ^{31}P nuclei. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. *t*-BuP(O)(OSiMe$_3$)(OH)[19] and [*t*-BuPO$_3$GaMe]$_4$[14c] were prepared using the literature procedures. Trimethylaluminum (Witco), dimethylaluminum chloride (Witco), trimethylgallium (Strem), $Ph_2P(O)OH$ (Aldrich), and *n*-Bu_4NHF_2 (Fluka) were used as received.

Preparation of $[Me_2Al(\mu\text{-}O)_2P(OSiMe_3)(t\text{-}Bu)]_2$ (1). To a stirred solution of *t*-BuP(O)(OH)(OSiMe$_3$) (0.42 g, 2 mmol) in hexane (25 mL) at 0 °C was added a solution containing Me_3Al (0.18 g, 2.5 mmol) in hexane (10 mL). The progress of the reaction was marked by the evolution of CH_4 through an oil bubbler. The reaction mixture was slowly allowed to warm to room temperature and stirred for an additional period of 6 h. The solvent was removed in vacuo, and the solid obtained was crystallized from toluene (5 mL) over a period of 7 days at −6 °C yielding 0.42 g (80%) of the product. Mp: 221 °C. ^1H NMR (400 MHz, benzene-d_6): δ −0.36 (s, AlCH$_3$, 12 H, cis), −0.34 (s, AlCH$_3$, 12H, trans), 0.27 (s, SiCH$_3$, 6 H, cis), 0.28 (s, SiCH$_3$, 6 H, trans), 1.09 (d, C(CH$_3$), 18 H, $^3J_{P-H} = 17.8$ Hz, cis), 1.10 (d, C(CH$_3$), 18 H, $^3J_{P-H} = 17.8$ Hz, trans). ^{31}P NMR (101 MHz, benzene-d_6): δ 14.6 (s, cis), 14.7 (s, trans). ^{29}Si NMR (49.5 MHz, benzene-d_6): δ 22.0 (d, $^2J_{P-Si}$ =11.5 Hz, cis), 21.9 (d, $^2J_{P-Si} = 11.5$ Hz, trans). MS (EI): *m/z* (%) 502 ($M^+ - CH_3$, 100). IR (Nujol, cm^{-1}): 1479 w, 1379 w, 1259 vs, 1210 m, 1094 s, 1019 m, 945 m, 849 s, 801 s, 759 m, 692 m, 679 vs, 605 w, 548 w, 506 m, 381 w. Anal. Calcd for $C_{18}H_{48}Al_2O_6P_2Si_2$: C,40.59; H, 9.08; P,11.6; Si, 10.6. Found: C, 40.5; H, 9.0; P, 11.4; Si, 10.5.

Preparation of $[(Cl)(Me)Al(\mu\text{-}O)_2PPh_2]_2$ (2). To a stirred suspension of $Ph_2P(O)(OH)$ (0.44 g, 2 mmol) in toluene (40 mL) at −40 °C was added a solution containing Me_2AlCl (0.20 g, 2.2 mmol) in toluene (10 mL). The progress of the reaction was marked by the slow evolution of CH_4 through an oil bubbler. The reaction mixture was slowly allowed to warm to room temperature over a period of 8 h until the evolution of CH_4 had ceased completely. The reaction mixture was filtered. From the filtrate, the solvent was removed in vacuo and the solid obtained was washed with cold toluene (5 mL portions) repeatedly and

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crystallized from a THF/hexane mixture (1:1) over a period of 14 days at −6 °C yielding 0.24 g (60%) of the product. Mp: 152−155 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ −0.64 (s, $AlCH_3$, 6 H, trans), −0.62 (s, $AlCH_3$, 6 H, cis), 7.51 (m, C_6H_5, 10 H), 7.79 (m, C_6H_5, 10 H). ^{31}P NMR (101 MHz, benzene-d_6): δ 26.9 (s, trans), 27.0 (s, cis). MS (EI): *m*/*z* (%) 573 ($M^+ - CH_3$, 100), 553 ($M^+ - Cl$, 40). IR (Nujol, cm^{-1}): 1593 m, 1487 w, 1440 s, 1397 s, 1261 vs, 1205 s, 1085s, 629 w, 799 vs, 755 s, 733 s, 692 vs, 570 s, 546 vs, 478 m, 446 m, 390 w. Anal. Calcd for $C_{26}H_{26}Al_2Cl_2O_4P_2$: C, 52.99; H, 4.45; Cl, 12.0; P, 10.5. Found: C, 52.8; H, 4.4; Cl, 11.8; P, 10.2.

Preparation of [*n*-Bu$_4$N][MeGa{*t*-BuPO$_2$(OH)}$_3$] (3). To a stirred solution of [*t*-BuPO$_3$GaMe]$_4$ (0.30 g, 0.34 mmol) in THF (40 mL) at 0 °C was slowly added *n*-Bu$_4$NHF$_2$ (0.57 g, 1.02 mmol, 50% in CH_2Cl_2). The reaction mixture was stirred overnight and filtered. The filtrate was concentrated to 15 mL in vacuo, and hexane (30 mL) was layered onto it. The resulting homogeneous mixture was allowed to stand at room temperature for 5 days to produce 0.17 g (68%) of **3**. Mp: 209 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ -0.39 (s, $GaCH_3$ 3 H), 0.93 (t, NCH_2, 12 H), 1.03 (d, $C(CH_3)$, 27 H, $^3J_{P-H} = 15.7$ Hz), 1.32 (m, CH_2, 8 H), 1.58 (m, CH_2, 8 H), 3.08 (m, CH_2, 8 H), 13.2 (s, OH, 3 H). ^{31}P NMR (101 MHz, benzene-d_6): δ 30.9 (s). IR (Nujol, cm^{-1}): 3165 m, 2359 m, 1672 m, 1303 s, 1141 vs, 1021 sh, 945 vs, 832 s, 656 s, 508 s. Anal. Calcd for $C_{29}H_{69}GaNO_9P_3$: C, 47.16; H, 9.42; N, 1.90; P, 12.6. Found: C, 46.8; H, 9.3; N, 2.0; P, 12.2.

X-ray Structure Determination. Crystal data for **1** and **2** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens CCD area detector using the φ-scan mode. Data for **3** were collected on a Stoe-Siemens-AED four-circle diffractometer using a learned-profile method.[24] The structures were solved by direct methods (SHELXS-90/96)[25] and refined on all data by full-matrix least squares on F^2 with the program SHELXL.[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions and refined using a riding model. Severe disorder in the core of **2** between the chlorine and methyl group on aluminum was modeled with the help of geometric restraints on the Al−Cl and Al−C bond distances obtained from similar structures in the CSD.[27] Similarity and rigid bond restraints on the anisotropic thermal displacement parameters were also used in this structure. The crystal data and structure refinement details for **1**, **2**, and **3** are given in Table 1.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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