2450 *Inorg. Chem.* **1998,** *37,* 2450−2457

Reactions of Phosphoric Acid Triesters with Aluminum and Gallium Amides[†]

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Received October 16, 1997

Triesters of phosphoric acid $OP(OR)_3$ (R = Me, Et, *n*-Bu, $SiMe_3$) react with $[M(NMe_2)_3]_2$ (M = Al (**1**), Ga (**2**)) in nonaqueous aprotic solvents with the formation of amorphous alumino- and gallophosphates MPO_4 (M = Al, Ga). Triphenyl phosphate, on the other hand, undergoes ligand scrambling with **1** and **2**. Aluminophosphate also results from the reaction of $AlCl_3$ with $OP(OSiMe_3)_3$. The products and mechanisms of these reactions were examined by ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, X-ray powder diffraction (XRD), thermogravimetric methods (TG/DTA), infrared spectroscopy (IR), and elemental analyses. The molecular structure of the first-step model compound $(Me_2N)_3Al{\cdot}OPPh_3$ (**3**) was established by the single-crystal X-ray diffraction experiment. Crystal data for **3** (−70 °C): $a = 8.870(2)$ Å, $b = 10.195(3)$ Å, $c = 14.706(5)$ Å, $\alpha = 90.27(3)°$, $\beta = 94.04(2)°$, $\gamma = 109.61(2)°$, $V = 1249.0(6)$ Å^3, $Z = 2$, triclinic space group $P\bar{1}$ (No. 2). Alumazene $[MeAlNDipp]_3$ (**4**) forms a bis-adduct $[MeAlNDipp]_3{\cdot}2OP(OMe)_3$ (**5**) with trimethyl phosphate. The molecular structure of **5** was also elucidated by X-ray crystallography. Crystal data for **5** (−140 °C): $a = 12.176(2)$ Å, $b = 12.630(3)$ Å, $c = 21.376(4)$ Å, $\alpha = 96.04(3)°$, $\beta = 90.46(3)°$, $\gamma = 115.38(3)°$, $V = 2948(1)$ Å^3, $Z = 2$, triclinic space group $P\bar{1}$ (No. 2).

Introduction

Aluminophosphate molecular sieves[1] are traditionally prepared by hydrothermal synthetic methods[2] where a source of aluminum, such as pseudo-boehmite[3] or Al(O*i*-Pr)$_3$, is combined with aqueous H_3PO_4 in equimolar ratio.[4] The most frequently utilized solvent is water, but recently also nonaqueous systems were successfully studied.[5] Here glycols, alcohols, pyridine, THF, DMSO, DMF, and others serve as the reaction medium. Under these predominantly nonaqueous conditions, water acts as a catalyst and mineralizer, and the water content plays an important role in determining the nature of the products.[6] Careful control of the water concentration in the reactive gel led to the formation of novel chain,[7] sheet,[7b,c,8] and three-dimensional framework[9] structures, and increasing water content promoted higher dimensionality of these networks. The use of HF as a mineralizer was studied in both aqueous and nonaqueous systems and enabled the synthesis of new aluminophosphate structures.[8d,e,10]

Obviously, a minimum amount of water from aqueous H_3PO_4, solvents, and pseudo-boehmite is always present in these reaction mixtures and cannot be excluded. Thus, to study the

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[†] Dedicated to Professor Robert Holmes on the occasion of his 70th birthday.

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S0020-1669(97)01303-7 CCC: $15.00

formation of aluminophosphates under truly nonaqueous conditions and with the help of new mineralizers, different aluminum and phosphate sources must be employed.

Another crucial point in the molecular sieve synthesis which determines the structure of the final products is the addition of usually 1 equiv of a template compound,[11] such as alkylamine, quarternary ammonium salt, amino alcohol, crown ether, or (rarely) a coordination complex, to facilitate the formation of microporous structures. In order to achieve crystallization, the reaction mixture is heated in an autoclave (100−200 °C) under autogenous pressure for several hours to several days. Although many parameters, such as the ratio of reactants, their concentrations, the order of mixing, aging time, agitation, and crystallization time, play an important role in this process and determine the structure and morphology of the resulting molecular sieve, it is true that the most prominent is the function of the structure-directing and templating guests. In spite of their paramount role, the mechanism of the structure-forming action is only poorly understood, and it is expected that discovery of new structures will result from the application of new and nontraditional guest compounds. Currently, the harsh conditions of the hydrothermal synthesis, such as extended periods of heating, presence of water, elevated pressure, and insolubility or reactivity of many categories of chemical compounds in aqueous solutions, severely limit our choice of the structure-directing guests to inert, polar, and water-soluble compounds. In some instances even the traditional organic guests alkylamines and quaternary ammonium cations are known to decompose to smaller fragments.[12] The use of inorganic and organometallic complexes in zeolite and molecular sieve syntheses, which would bring more variability in stereochemical characteristics, coordination number, oxidation state, and charge of the structure-directing agents, has been realized only recently and is limited to a handful of robust and kinetically inert ionic complexes, such as $[Co(diamine)_3]^{3+}$,[13] $[Co(NH_3)_6]^{3+}$,[14] $[Ni(diamine)_3]^{2+}$,[15] $[Co(C_5Me_5)_2]^+$,[16] $[Co(C_5H_4R)_2]^+$ (R = H,[17] Me[13]) $[Fe(C_6H_6)(C_5H_5)]^+$,[18] $M(II)F_{16}Pc$ ($F_{16}Pc$ = perfluorophthalocyanine, M(II) = Cu, Fe, Co, Ru).[19] Therefore, milder and dry alternatives to the hydrothermal synthesis are being intensively sought.

Herein we report our study of novel reactions of $[Al(NMe_2)_3]_2$ (**1**), $[Ga(NMe_2)_3]_2$ (**2**), and $AlCl_3$ with phosphoric acid triesters according to eqs 1 and 1a in rigorously nonaqueous solvents.

$$MX_3 + OP(OR)_3 \rightarrow MPO_4 + 3XR \tag{1}$$
$$(M = Al, Ga; X = NMe_2, N(SiMe_3)_2;$$
$$R = Me, Et, n\text{-Bu}, SiMe_3)$$

$$AlCl_3 + OP(OSiMe_3)_3 \rightarrow AlPO_4 + 3ClSiMe_3 \tag{1a}$$

These reactions provide directly solid aluminum and gallium phosphates without employing phosphoric acid and thus in the absence of water. They can potentially become the basis for strictly nonaqueous synthetic routes which would allow the study of new mineralizers and the use of variety of new templates. Furthermore, we examined the reactivity of alumazene $[MeAlNDipp]_3$ (**4**) toward $OP(OMe)_3$.

Experimental Section

All preparative procedures were performed under a dry nitrogen atmosphere using Schlenk and drybox techniques. Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated solvents were dried over and distilled from Na/K alloy and degassed prior to use. ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments. Mass spectra were obtained on a Finnigan MAT 8230 or MAT 95 mass spectrometer (70 eV, EI). IR spectra (4000−400 cm^{-1}) were recorded on a Bio-Rad FTS-7 instrument. Samples were prepared as KBr pellets or Nujol mulls between KBr disks. X-ray powder diffraction spectra were obtained using a Siemens D 500 diffractometer with monochromated Cu Kα radiation ($\lambda = 1.5416$ Å). A continuous step scan mode with 0.05° 2θ step and counting time 5 s was employed. TG/DTA experiments were run on a Netzsch STA/QMS 409/429-403 system in flowing air (20 mL min^{-1}). The temperature was ramped from room temperature to 800 °C at 5 °C min^{-1}. Elemental analyses were carried out by the Analytisches Labor des Anorganischen Instituts, Göttingen. Melting points were measured in sealed capillaries and are uncorrected.

General Procedure for Reactions of Phosphoric Acid Triesters with Aluminum and Gallium Amides. An amide (4−10 mmol) was dissolved in a dry solvent (50 mL), and the equimolar amount of a triester was added slowly via syringe into the stirred solution at room temperature. When needed, the reaction mixture was heated to reflux until a white precipitate formed. The products were filtered off, washed with the pure solvent, and dried under vacuum for 2 h. Amorphous alumino- and gallophosphates were calcined in oxygen atmosphere in a Heraeus RO 4/25 horizontal furnace equipped with a RE 1-1 temperature controller (±3 °C). Temperature was ramped to the desired value at 5 °C min^{-1}, held constant for 15 h, and then left to decrease slowly to room temperature.

Reactions of 1 and 2 with $OP(OPh)_3$. The amide and ester reagents (0.3 mmol) were weighed into an NMR tube and dissolved in toluene-d_8 (0.6 mL). The solution was degassed by three freeze−pump−thaw cycles, and the tube was flame-sealed. We report here the NMR spectroscopic data for the phosphorus-containing products.

$OP(NMe_2)(OPh)_2$ (6). ^1H NMR (toluene-d_8): δ 2.46 (d, $^3J_{PNCH}$ = 10.3 Hz, NMe_2), 6.7−7.2 (m, OPh). ^{13}C NMR (toluene-d_8): δ 36.42 (d, $^2J_{PNC}$ = 4.0 Hz, NMe_2), 151.73 (d, $^2J_{POC}$ = 6.4 Hz, *ipso*-C), 120.49 (d, $^3J_{PC}$ = 5.2 Hz, *o*-C), 129.75 (d, $^4J_{PC}$ = 1 Hz, *m*-C), 124.74 (d, $^5J_{PC}$= 1 Hz, *p*-C). ^{31}P NMR (toluene-d_8): δ 1.5.

$OP(NMe_2)_2(OPh)$ (7). ^1H NMR (toluene-d_8): δ 2.23 (d, $^3J_{PNCH}$ = 10.5 Hz, NMe_2), 6.7−7.2 (m, OPh). ^{13}C NMR (toluene-d_8): δ 36.04 (d, $^2J_{PNC}$ = 4.7 Hz, NMe_2), 150.16 (d, $^2J_{POC}$ = 7.3 Hz, *ipso*-C), 120.63

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(d, $^3J_{PC} = 4.6$ Hz, *o*-C), 130.17 (d, $^4J_{PC} = 1$ Hz, *m*-C), 125.87 (d, $^5J_{PC} = 1$ Hz, *p*-C). ^{31}PNMR(toluene-d_8): δ 13.8.

$(Me_2N)_3Al\cdot OPPh_3$ (3). Solid $OPPh_3$ (0.65 g, 2.3 mmol) was added to the solution of $Al(NMe_2)_3$ (0.37 g, 2.3 mmol) in toluene (50 mL). The yellow clear solution was stirred at room temperature for 20 min, and then its volume was reduced to 2 mL under vacuum. To the resulting white slurry was added hexane (5 mL), which caused further precipitation of a white solid. Filtration, washing with cold hexane (2 mL), and drying under vacuum afforded 0.70 g (69%) of **3**. Mp: 102−104 °C. ^{1}H NMR (benzene-d_6): δ 3.03 (s, NMe_2), 7.0 (br m, Ph), 7.7 (br m, Ph). ^{13}C NMR (benzene-d_6): δ 41.76 (s, NMe_2), 128.7, 132.4, 133.1 (br m, Ph). ^{31}P NMR (benzene-d_6): δ 38.4. IR (KBr pellet, cm^{-1}): ν 3057 w, 2938 w, 2863 w, 2824 w, 2781 w, 1591 w, 1485 m, 1440 vs (ν_{PC}), 1312 w, 1264 w, 1190 vs ($\nu_{P=O}$), 1121 vs, 1095 w, 1072 m, 1027 m, 996 m, 862 w, 755 s, 722 vs, 698 vs, 542 vs, 505 m, 458 m. Anal. Calcd for $C_{24}H_{33}AlN_3OP$: C, 65.89; H, 7.60; Al, 6.17; N, 9.60; P, 7.08. Found: C, 66.20; H, 7.33; Al, 5.93; N, 9.26; P, 7.11.

$[MeAlNDipp]_3\cdot 2OP(OMe)_3$ (5). $OP(OMe)_3$ (0.42 g, 3.0 mmol) was added dropwise to the solution of **4**[20] (0.98 g, 1.5 mmol) in toluene (60 mL). After addition, the reaction mixture was stirred for 12 h at room temperature and then heated to 70 °C for 30 min. All volatile compounds were removed under vacuum, and the residue was treated with *n*-hexane (20 mL). Compound **5** precipitates as white microcrystals. Yield: 1.25 g (90%). Mp: 140 °C. ^{1}H NMR (benzene-d_6): δ −0.35 (s, $AlCH_3$, 9 H), 1.50 (d, $^3J_{HH} = 6.7$ Hz, CH_3(*i*-Pr), 36 H), 2.60 (s, OCH_3, 12 H), 3.20 (m, CH(*i*-Pr), 6 H), 4.60 (s, OCH_3, 6 H), 6.95 (m, arom. H, 9 H). ^{31}P NMR (benzene-d_6): δ −5.08 (s). IR (Nujol, KBr disks, cm^{-1}): ν 1911 w, 1621 m, 1585 w, 1422 s, 1313 s, 1235 vs ($\nu_{P=O}$), 1188 vs, 1108 m, 1054 vs, 1043 vs, 904 s, 880 s, 852 s, 790 vs, 743 m, 660 m, 632 w, 580 w, 542 w, 522 m, 448 m. Anal. Calcd for $C_{45}H_{78}Al_3N_3O_8P_2$: C, 58.00; H, 8.38; N, 4.51. Found: C, 58.3; H, 8.5; N, 4.6.

Single-Crystal X-ray Diffraction Studies. Intensity data for **3** were collected on a Siemens-Stoe AED2 four-circle diffractometer using a crystal with dimensions 0.8 × 0.4 × 0.4 mm. The cell parameters were determined from randomly chosen and well centered high-angle reflections. Out of 6989 collected reflections ($7 \le 2\theta \le 50°$), 4462 unique data ($R_{int} = 0.0201$) were used for the structure solution and refinement of 277 parameters. The structure solution by direct methods and refinement by full-matrix least-squares on F^2 were carried out using SHELXS-90 and SHELXL-93 programs. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were found and refined isotropically. The minimum/maximum residual electron density was −0.243/0.319 e Å^{-3}.

The data for **5** were collected on a Siemens/Stoe/Huber four-circle diffractometer, equipped with a Siemens CCD area detector, using a crystal with dimensions 0.4 × 0.2 × 0.2 mm. Out of the 41 103 measured reflections ($4 \le 2\theta \le 53°$), 11 980 unique data ($R_{int} = 0.0436$) were used for the structure solution and refinement of 650 parameters. The structure was solved by direct methods using the program SHELXS-90/96,[21] and refined on all data by full-matrix least-squares on F^2 with SHELXL-93/96.[22] All non hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement in idealized positions. The minimum/maximum residual electron density was −0.487/0.350 e Å^{-3}.

Results and Discussion

Aluminum Amides. Firstly we explored the reactions of $[Al(NMe_2)_3]_2$ (**1**)[23] with phosphoric acid esters in dry aprotic solvents as a novel nonaqueous route to the solid aluminophosphate. This type of reaction is a novel mode of aluminum amide reactivity.[24] Depending on the nature of the ester R group, the reactions take two distinct courses. In the case of the alkyl and silyl substituents (eq 2, where R = Me, Et, *n*-Bu, $SiMe_3$), the ester R−O bonds are preferentially cleaved and the corresponding tertiary amines are formed together with the desired aluminophosphate.

Table 1. Comparison of ^{31}P NMR Chemical Shifts (ppm) for the Phenyl Mono- and Bis(alkylamido)phosphates

NR_2	$OP(NR_2)(OPh)_2$	$OP(NR_2)_2(OPh)$
NH_2	2.2	15.2
NHMe	1.2	16.0
NHEt	1.0	
NMe_2	1.5[a]	13.8[a]
	2.63[b]	16.46[c]

[a] This work, in toluene-d_8. [b] Reference 26a, in $OP(OMe)_3$. [c] Reference 26b, in $CDCl_3$.

$$\underset{\mathbf{1}}{{}^{1}/_{2}[Al(NMe_2)_3]_2} + OP(OR)_3 \rightarrow AlPO_4 + 3RNMe_2 \qquad (2)$$

The reactions were conducted in dry hydrocarbon or ether solvents. Trimethyl phosphate reacts instantly, and the reaction is slightly exothermic. Also tris(trimethylsilyl) phosphate reacts within several hours at room temperature. On the other hand, triethyl and tributyl phosphates required higher temperatures and longer reaction times. Tertiary amine byproducts, such as Me_3N, $EtNMe_2$, *n*-$BuNMe_2$, and Me_3SiNMe_2, were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The freshly formed $AlPO_4$ was gel-like, and its volume shrank to $^1/_5$ upon drying under vacuum at room temperature for several hours. The resulting powders were amorphous according to XRD experiments. By elemental analysis and thermogravimetry it was shown to contain 35−50% of occluded solvents, the particular tertiary amine, and possibly some unreacted end groups. These organics were released in two stages upon heating of the powdery samples in air or oxygen atmosphere. The removal starts below 100 °C by evaporation of volatile compounds which is accompanied by an endothermic effect. The second step takes place around 300 °C. Its exothermic nature suggests oxidation of occluded organics by air. Further heating up to 800 °C resulted in the formation of crystalline tridymite-$AlPO_4$ dense phase[25] which was free of organic impurities. The ratio of Al to P in the calcined products is 1:1. However, $AlPO_4$ from the reaction of $OP(OSiMe_3)_3$ with $[Al(NMe_2)_3]_2$ remained amorphous even at 800 °C and required heating up to 1100 °C for crystallization. The resulting tridymite-$AlPO_4$ phase contained 6.5% of silicon.

The replacement of alkyl for aryl group in the phosphoric acid ester changes the course of the reaction. Instead of the clean $AlPO_4$ formation, the ligand scrambling was observed (eq 3, where $n = 1,2$). The reaction progress was monitored by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy in toluene-d_8 and the resulting ester amides of phosphoric acid were identified by comparison of their ^{13}C and ^{31}P NMR chemical shifts with the literature data (Table 1).[26] The starting triphenyl phosphate was completely consumed shortly after the reagents were mixed, and it was not observed in the ^{31}P NMR spectra. At room

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$$\underset{\mathbf{1}}{{}^{1}\!/_{2}[\mathrm{Al(NMe_2)_3}]_2} + \mathrm{OP(OPh)_3} \rightarrow [\mathrm{Al(OPh)}_x(\mathrm{NMe_2})_{3-x}]_y + \mathrm{OP(NMe_2)}_n(\mathrm{OPh})_{3-n} \quad (3)$$

temperature, the reaction mixture consisted of $\mathrm{OP(NMe_2)(OPh)_2}$ (**6**) and $\mathrm{OP(NMe_2)_2(OPh)}$ (**7**) in the ratio of 10:1. Upon heating (95−110 °C), the monoamide **6** was gradually converted to diamide **7**. After 90 h, **7** was observed as the only phosphorus-containing product, but, surprisingly, no $\mathrm{OP(NMe_2)_3}$ could be detected even after 144 h of heating. In contrast, the corresponding reaction of boric acid esters[27] proceeds completely to the trisamide (eq 4, where R = Me, Et, *n*-Bu). The ^{1}H NMR

$${}^{1}\!/_{2}[\mathrm{Al(NMe_2)_3}]_2 + \mathrm{B(OR)_3} \rightarrow \mathrm{Al(OR)_3} + \mathrm{B(NMe_2)_3} \quad (4)$$

spectrum of the reaction mixture demonstrated that half of the $\mathrm{NMe_2}$ groups was still connected to aluminum. However, the aluminum dimethylaminophenoxide products could not be unequivocally identified from their ^{1}H and ^{13}C NMR spectra as they feature only broad overlapping signals in the $\mathrm{NMe_2}$ region. This is indicative of the presence of the equilibria between several oligomeric products ($x = 0$, 1, 2 and $y = 1$, 2 in eq 3) and possible fast chemical exchange of the $\mathrm{NMe_2}$ groups between bridging and terminal positions.

The driving force in these reactions is the bond energy difference between Al−O (585 kJ mol^{-1})[28] and Al−N (280 kJ mol^{-1})[29] resulting in the substantial affinity between aluminum and oxygen. In the case of the alkyl phosphates the scission of the P−O−C moieties takes place preferentially at the C−O bond (355 kJ mol^{-1}) which is weaker than the P−O one (359 kJ mol^{-1}).[30] The thermodynamic advantage of forming $\mathrm{AlPO_4}$ instead of $\mathrm{Al(OMe)_3}$ is in the gain of one extra Al−O bond per molecule by formally transforming P═O (544 kJ mol^{-1}) to P−O and Al−O. Thus, the energetically slightly unfavorable transformation of three C−O links to C−N ones (305 kJ mol^{-1}) is overcome by the benefit gained from the strong Al−O bonds. Phenyl esters differ from their alkyl counterparts in the higher C−O bond strength (D(Et−OH) = 340 kJ mol^{-1}, D(Ph−OH) = 357 kJ mol^{-1})[31] which was manifested in the cleavage of the P−O bond instead of the C−O one and it prevented the formation of $\mathrm{AlPO_4}$. Following the same line of reasoning, the reaction of the tris(trimethylsilyl) phosphate should proceed similarly to the one of the phenyl ester. The Si−O bonds (452 kJ mol^{-1})[32] are certainly stronger than the P−O bonds. However, the transformation of the P═O to P−O−Al moiety apparently outweighs this thermodynamic disadvantage and the reaction proceeds with the cleavage of the Si−O bonds and formation of $\mathrm{AlPO_4}$. The ability of various aluminum compounds, such as $\mathrm{AlCl_3}$,[33] $\mathrm{AlR_3}$ (R = Me,[34] Et[35]), and $\mathrm{Mes^*AlH_2}$,[36] to cleave Si−O bonds is well documented.

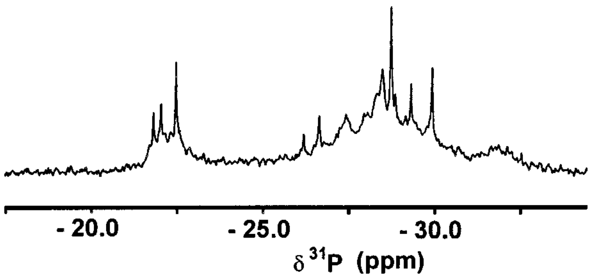

Figure 1. ^{31}P NMR spectrum of the reaction mixture of **1** and $\mathrm{OP(OSiMe_3)_3}$ in benzene-d_6.

Table 2. ^{31}P Solid-State NMR Chemical Shifts for Selected Dense and Microporous Aluminophosphates

compound	δ, ppm	lit.
berlinite	−25.6	47
cristobalite	−27.1	47
tridymite	−29.5	47
$\mathrm{AlPO_4}$−5	−27.8	48
$\mathrm{AlPO_4}$−11	−23.3, −30.2	48
$\mathrm{AlPO_4}$−17	−29.9	48
$\mathrm{AlPO_4}$−31	−29.6	48
$\mathrm{AlPO_4}$−20	−35.2	49
$\mathrm{AlPO_4}$−21	−14.8, −21.4, −26.4	50
VPI−5	−27, −32	51

To compare the ability of **1** to cleave C−O and Si−O bonds, we carried out a reaction with $\mathrm{MeOSiMe_3}$ (eq 5) in benzene-

$$\underset{\mathbf{1}}{{}^{1}\!/_{2}[\mathrm{Al(NMe_2)_3}]_2} + 3\mathrm{MeOSiMe_3} \rightarrow \mathrm{Me_3SiNMe_2} + [\mathrm{Al(OMe)(NMe_2)_2}]_x + 2\mathrm{Me_3SiOMe} \quad (5)$$

d_6. Upon standing at room temperature for 6 h, a white solid was formed and $\mathrm{Me_3SiNMe_2}$ and $\mathrm{MeOSiMe_3}$ in the ratio 1:2 were detected in the volatile reaction products by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The absence of $\mathrm{Me_3N}$ attests to the preferential cleavage of the Si−O bond. The transfer of one relatively small MeO group to aluminum apparently increases the degree of oligomerization of the $[\mathrm{Al(OMe)(NMe_2)_2}]_x$ species, and it in turn lowers their solubility. Diminished reactivity of the insoluble aluminum bis(dimethylamino)methoxide can explain the large amount of the unreacted $\mathrm{MeOSiMe_3}$.

Mechanistic Studies. The nearly instant formation of the solid $\mathrm{AlPO_4}$ in the reaction of the trimethyl phosphate with **1** prevented any solution NMR experiments. On the other hand, the tris(trimethylsilyl)ester reacts much slower and the homogeneous reaction mixture persists for several hours. Therefore the reaction progress (eq 2) was followed by ^{1}H, ^{31}P, and ^{29}Si (INEPT) NMR methods. Shortly after mixing, the starting compounds were completely consumed and absent in the NMR spectra. The expected product $\mathrm{Me_3SiNMe_2}$ was observed in the ^{1}H and ^{29}Si (INEPT) NMR spectra. The other resulting species are evidently oligomeric as they feature broad and overlapping signals in the $\mathrm{Me_3Si}$ and $\mathrm{Me_2N}$ regions. Relatively better resolved were the signals in the ^{31}P NMR spectrum (Figure 1). The series of peaks in the region from −21.5 to −32.5 ppm closely corresponds to the values found for the dense and microporous phases of $\mathrm{AlPO_4}$ in the solid-state ^{31}P NMR experiments (Table 2). Worth noting is also the similarity of these chemical shifts to the values for the molecular dimeric (**8**, −31.4 ppm) and tetrameric (**9**, −28.4 ppm) aluminophos-

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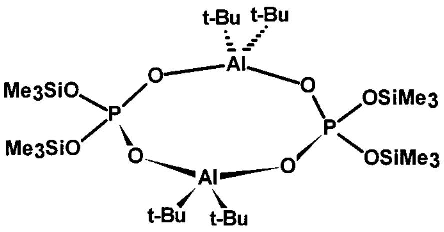
(36) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387.

Chart 1



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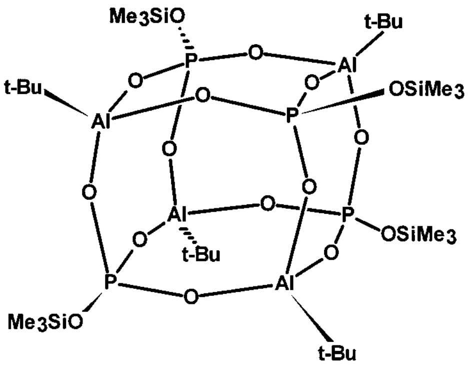

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Scheme 1

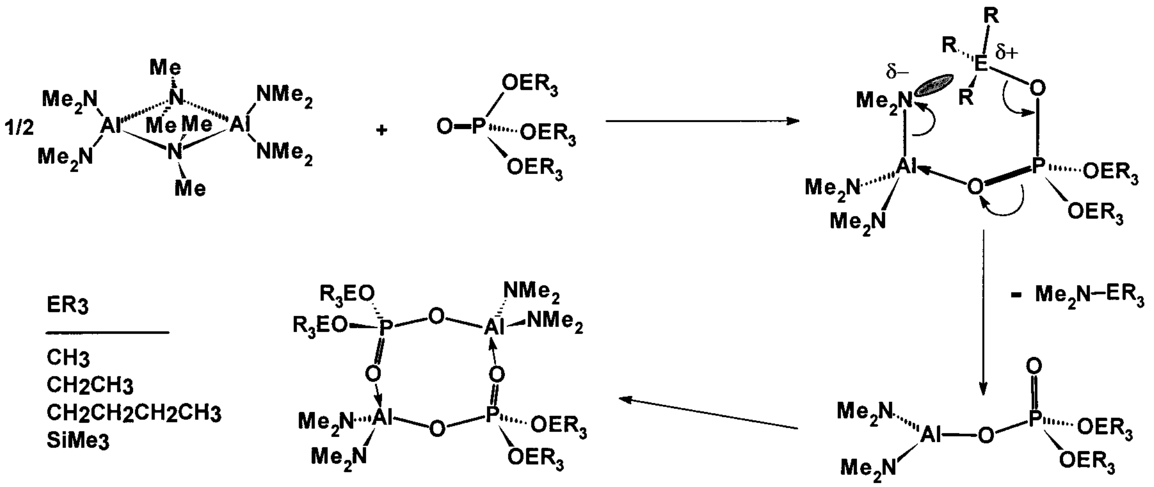

Table 3. Crystal and Structure Refinement Data for $(Me_2N)_3Al{\cdot}OPPh_3$ (**3**) and $[MeAlNDipp]_3{\cdot}2OP(OMe)_3$ (**5**)

	3	**5**
empirical formula	$C_{24}H_{33}AlN_3OP$	$C_{45}H_{78}Al_3N_3O_8P_2$
fw	437.48	932.02
a, Å	8.870(2)	12.176(2)
b, Å	10.195(3)	12.630(3)
c, Å	14.706(5)	21.376(4)
α, deg	90.27(3)	96.04(3)
β, deg	94.04(2)	90.46(3)
γ, deg	109.61(2)	115.38(3)
volume, Å^3	1249.0(6)	2948.3(10)
Z	2	2
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T. °C	−70(2)	−140(2)
wavelength, Å	0.710 73	0.710 73
d_{calcd}, g cm^{-3}	1.163	1.050
μ, cm^{-1}	1.64	1.70
$R1$, $[I > 2\sigma(I)]^a$	0.0357	0.0549
w$R2$ (all data)^b	0.0992	0.1339
GOF on F^2	1.036	1.119

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

phate derivatives (Chart 1).[37] This implies the presence of similar oligomeric species in our reaction mixture.

The breakage of the dimeric structure of **1** followed by the formation of an Al−O−P bonded adduct (Scheme 1) is presumably the initial step in the reaction of **1** with phosphoric acid triesters. This adduct is well suited to form a six-membered ring as a transition state in which an intramolecular nucleophilic attack of the NMe_2 electron lone pair on the alkyl or silyl group can take place. The resulting amine Me_2NER_3 (E = C, Si) is released, and the coordinatively unsaturated aluminum center may be stabilized by the formation of a dimer similar to the crystallographically characterized molecule **8**. Further intermolecular attacks of the NMe_2 group on ER_3 produce higher oligomers, one of them is presumably analogous to the cubane-like tetramer **9**. Progressive condensation and cross-linking of these oligomeric species lead to insoluble polymeric gel and ultimately to the formation of $AlPO_4$.

Obviously, the rapid course of these reactions hinders structural characterization of the intermediates. Therefore, we replaced the phosphoric acid triesters in our system with triphenyl phosphine oxide to model the first step in the described mechanism. Because of the lack of the ester groups, this reaction stops at the stage of the Al−O−P adduct **3** (eq 6).

$$^{1}/_{2}[Al(NMe_2)_3]_2 + OPPh_3 \rightleftharpoons \underset{\mathbf{3}}{(Me_2N)_3Al{\cdot}OPPh_3} \qquad (6)$$

Crystallization from benzene/hexane mixture afforded X-ray-quality crystals and the molecular structure of **3** was elucidated by the single-crystal X-ray diffraction experiment (Table 3, Figure 2). Compound **3** was also characterized by ^1H, ^{13}C, and ^{31}P NMR, IR, and mass spectroscopies and elemental analyses.

The molecule **3** consists of an $Al(NMe_2)_3$ unit connected via the bridging oxygen atom to the phosphorus center. Both NMe_2 and phenyl groups are arranged in a propeller-like geometry

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[37] Mason, M. R.; Matthews, R. M.; Mashuta, M. S.; Richardson, J. F. *Inorg. Chem.* **1996**, *35*, 5756.

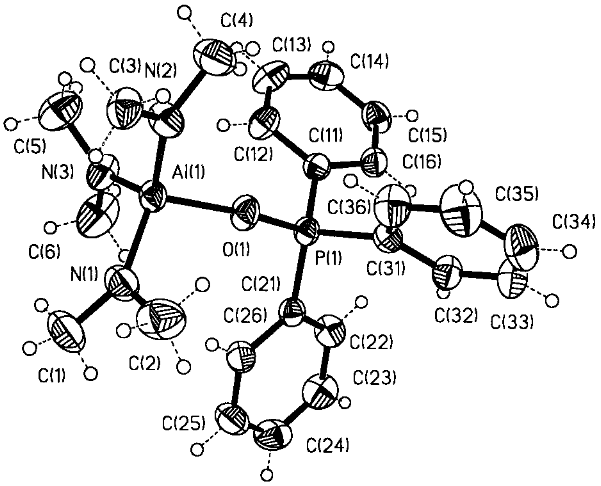

Figure 2. Molecular structure and the atom-numbering scheme of **3**.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) in **3**

Al(1)−O(1)	1.8421(13)	P(1)−O(1)−Al(1)	166.00(9)
P(1)−O(1)	1.5016(12)	O(1)−P(1)−C(11)	110.04(8)
Al(1)−N(1)	1.813(2)	O(1)−P(1)−C(21)	110.42(8)
Al(1)−N(2)	1.814(2)	O(1)−P(1)−C(31)	109.42(8)
Al(1)−N(3)	1.816(2)	N(1)−Al(1)−N(2)	113.42(8)
P(1)−C(11)	1.794(2)	N(1)−Al(1)−N(3)	113.58(8)
P(1)−C(21)	1.796(2)	N(2)−Al(1)−N(3)	114.70(8)
P(1)−C(31)	1.793(2)	N(1)−Al(1)−O(1)	105.79(7)
N(1)−C(1)	1.437(3)	N(2)−Al(1)−O(1)	103.05(7)
N(1)−C(2)	1.446(3)	N(3)−Al(1)−O(l)	104.85(7)
N(2)−C(3)	1.438(2)		
N(2)−C(4)	1.442(2)		
N(3)−C(5)	1.434(3)		
N(3)−C(6)	1.447(3)		

Table 5. Comparison of Selected Geometrical Characteristics and ^{31}P NMR Chemical Shifts for $X_3Al{\cdot}OPPh_3$ Adducts

X	Al−O, Å	P-O, Å	Al−O−P, deg	$\delta^{31}P$, ppm	lit.
Cl	1.733(4)	1.519(4)	180	44.9	52
Br	1.736(4)	1.513(7)	180	45.7	52
$OSiMe_3$	1.807(4)	1.517(4)	146.7(2)	40.6	53
Me	1.837(2)	1.500(2)	180	36.5	53
NMe_2	1.842(1)	1.502(1)	166.0(1)	38.3	this work

and are staggered. The Al−O−P angle is slightly bent to 166.0(1)° (Table 4). The Al−O bond distance is relatively long in comparison with other relevant $OPPh_3$ adducts and is comparable to the Al−O bond length in $Me_3Al{\cdot}OPPh_3$ (Table 5). Also, the P═O stretching vibration of **3** which appeared at 1165 cm^{-1} is very close to 1167 cm^{-1} for $Me_3Al{\cdot}OPPh_3$.[38] Moreover, the nitrogen atoms reside in planar atomic environment, the average sum of angles around them is 359.7(4)°. This suggests some degree of π donation to the aluminum center which in turn decreases its Lewis acidity. This is consistent with the low stability of this complex in solution and the gas phase (see below). The Al−N distances are equal (within 2σ), and their average value 1.814(3) Å is slightly longer than the average terminal bond distance in **1** (1.802(3) Å).[23]

^1H, ^{13}C, and ^{31}P NMR experiments revealed lability of the adduct **3** in benzene-d_6 solution. At room temperature, around 20% of the adduct dissociates. The signal of **3** is shifted to lower field in the ^{31}P NMR spectrum (δ 38.4 ppm) with respect to free $OPPh_3$ (δ 25.3 ppm). Both signals are broadened by slow chemical exchange between bound and free phosphine oxide. Raising the temperature to 70 °C broadens the signals, but coalescence was not attained. Two resonances in the aliphatic region of the ^1H NMR spectrum were assigned to the adduct **3** (δ 3.04 ppm) and to the exchange-averaged signal of bridging and terminal NMe_2 groups of **1** (δ 2.58 ppm). The low stability of **3** was also confirmed by the absence of the molecular peak in the mass spectrum.

To gain further insight into the reaction mechanism, we increased the bulkiness of the amide groups at the aluminum center. $Al[N(SiMe_3)_2]_3$[39] was used in the reactions with $OP(OMe)_3$ and $OP(OSiMe_3)_3$. Only unchanged starting materials were detected in the ^1H, ^{13}C, and ^{31}P NMR spectra of the reaction mixtures, and no formation of an $AlPO_4$ precipitate was observed even after heating to 90 °C for 35 h. Similarly, there was no reaction between $Al[N(SiMe_3)_2]_3$ and $OPPh_3$. Thus, the sterically demanding $SiMe_3$ groups effectively hinder the formation of the initial adducts similar to **3** and thus frustrate further reaction (Scheme 1).

As it was noted above, the most important factor in the syntheses of microporous aluminophosphates is the structure directing ability of the templating agents. We studied the reaction of **1** with $OP(OMe)_3$ (eq 2) in various solvents, such as toluene, cyclohexane, dioxane, and dicyclohexylamine, to assess their templating effect. So far none of these systems provided a crystalline material. The plausible explanation for the amorphous character of these products is the high reaction rate which prevents the formation of ordered structures. We tried to moderate the progress of reaction by carrying it out in a two-layer system at low temperature. The solution of $OP(OMe)_3$ in THF ($d = 0.886$ g cm^{-3}) was carefully covered with the solution of **1** in cyclohexane ($d = 0.779$ g cm^{-3}) in a narrow Schlenk flask and kept at 10 °C. Within a week, a white solid gradually grew at the layer interface. Washing with Et_2O and drying in vacuum afforded 42% of the theoretical yield. This shows that the reaction was slowed down considerably. The white product displays one broad diffraction line ($d = 8.96$ Å, fwhm $= 2.5°$ (2θ)).

Aluminum Chloride. Another route leading to $AlPO_4$ is the reaction of $AlCl_3$ with $OP(OSiMe_3)_3$ (eq 1a). It was carried out in the THF solution, and after 2 days of refluxing, a white gel-like solid was formed. Washing with THF and drying under vacuum afforded a white amorphous powder. Heating of the product to 800 °C in oxygen for 10 h afforded a partially crystalline tridymite-$AlPO_4$ phase. The ratio of Al:P was 1:1.04, and the solid contained 13.6% silicon and 2.3% chloride. In spite of the black color, the CHN contamination was below the detection level. Upon further heating to 1100 °C in air for 15 h, the solid turned white and fully crystallized. The silicon content decreased to 10%, and chloride was removed completely. The total weight loss was 31.6%. The TG/DTA experiment revealed a two-step mass-loss behavior (Figure 3). The first process at 100−140 °C was accompanied with an endothermic effect which is characteristic for the entrapped solvent evaporation (mass loss 23%). The second step at 450−600 °C is exothermic and corresponds to the thermal oxidation of occluded organic species (mass loss 5.5%).

The delayed formation of insoluble materials in this reaction at room temperature allowed ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR observations in the THF-d_8 solution. Shortly after mixing, no starting $OP(OSiMe_3)_3$ could be detected in the reaction mixture. The ^1H NMR spectrum displayed the signal for Me_3SiCl[40] and a broad peak in the $SiMe_3$ region (0.2−0.4 ppm) representing

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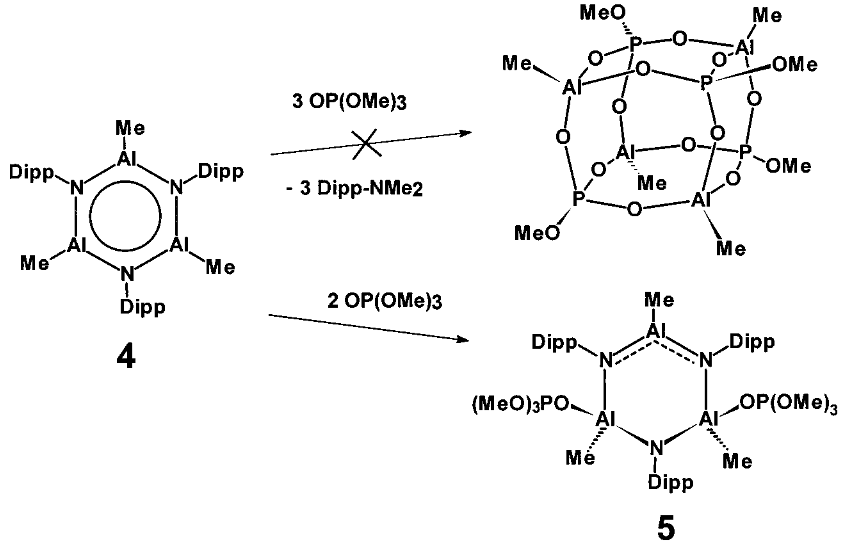
(38) Nykerk, K. M.; Eyman, D. P. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 253.

(39) Bürger, H.; Cichon, J.; Goetze, U.; Wannagat, U.; Wismar, H. J. *J. Organomet. Chem.* **1971**, *33*, 1.

(40) ^1H NMR: δ 0.400 (s, $^2J_{SiCH} = 7.0$ Hz, ^{29}Si satellites, $^1J_{CH} = 120.4$ Hz, ^{13}C satellites).

Scheme 2[a]



[a] Dipp = (2,6-i-$Pr_2C_6H_3$).

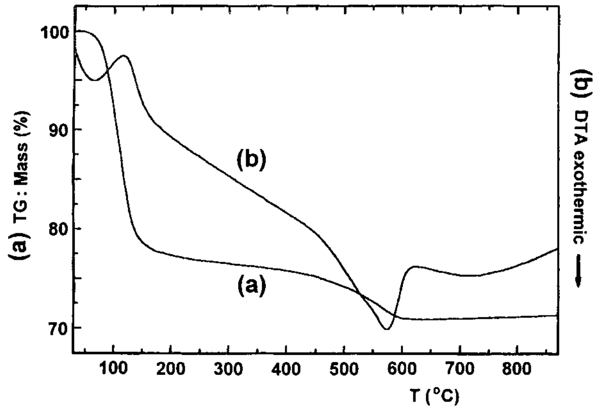


Figure 3. Thermogravimetric experiments (TG/DTA) on aluminophosphate precursor prepared from $AlCl_3$ and $OP(OSiMe_3)_3$.

a mixture of oligomers. Integrated intensities showed that 29.4% of the $OSiMe_3$ groups remained bound to oligomeric species. The ^{31}P NMR spectrum displayed a number of signals in the same region (−22 to −35 ppm) which was observed in the reaction of **1** with $OP(OSiMe_3)_3$ (Figure 1). Interestingly, the reaction mixture remained a homogeneous solution for more than 2 weeks at room temperature, and no apparent changes were observed in the NMR spectra. Precipitation of the $AlPO_4$ gel was induced by heating. Upon standing at room temperature, the gel dissolved suggesting reversibility of the reaction. We are investigating the possibility of using Me_3SiCl as a mineralizer in the preparations of crystalline aluminophosphates. Furthermore, the relative stability of soluble oligomeric species in the reaction mixtures of $OP(OSiMe_3)_3$ with both **1** and $AlCl_3$ can be exploited in spray coating of $AlPO_4$.

Alumazene. To assess the ability of other aluminum−nitrogen compounds to react with phosphoric acid esters, we chose alumazene **4** whose interesting reactivity was recently reported.[41] The reaction of **4**, with $OP(OMe)_3$ in toluene at 70 °C afforded an 1:2 adduct, **5** (Scheme 2). The molecular structure of **5** was elucidated by single-crystal X-ray diffraction experiment and is shown in Figure 4. The molecule of **5** contains a six-membered Al_3N_3 ring in a half-boat conformation. The N(2) atom lies 0.68 Å above the plane formed by the other five atoms (rms deviation 0.014 Å). The coordination of the $OP(OMe)_3$ molecules to the Al(1) and Al(2) atoms causes disruption of the Al_3N_3 ring π-system and loss of its planarity. The Al(1)−N and Al(2)−N bonds (average 1.84 Å) are longer than the Al−N bonds in the starting alumazene **4** (Table 6). The coordination around Al(1) and Al(2) is distorted tetrahedral with bond angles ranging from 105.7 to 109.8°. In contrast, the Al(3) atom maintains its trigonal-planar coordination (N(3)−Al(3)−N(1) angle 118.9°). The Al(3)−N bond distances (2 × 1.784(2) Å) are equal within the experimental error to the corresponding ones in **4**.

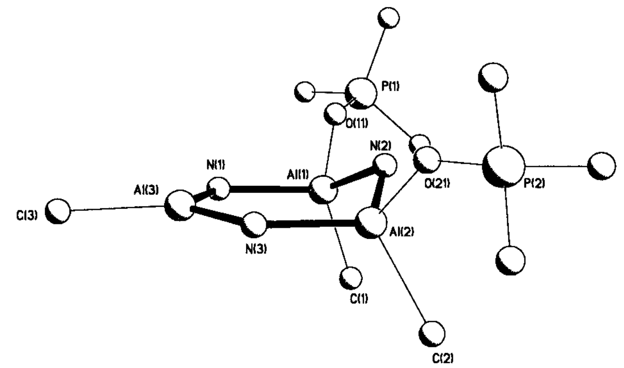


Figure 4. Molecular structure of **5**. For the sake of clarity, only the *ipso*-carbons of the 2,6-i-$Pr_2C_6H_3$ groups are shown and the methyl groups of $OP(OMe)_3$ are omitted.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) in **5**

Al(1)−N(2)	1.831(2)	Al(2)−N(3)	1.852(2)
Al(1)−N(1)	1.855(2)	Al(2)−0(21)	1.8701(18)
Al(1)−O(11)	1.8645(18)	Al(3)−N(3)	1.784(2)
Al(2)−N(2)	1.827(2)	Al(3)−N(1)	1.784(2)
N(2)−Al(1)−N(1)	109.78(9)	N(3)−Al(3)−N(1)	118.87(9)
N(2)−Al(1)−O(11)	107.08(9)	P(1)−O(11)−Al(l)	148.57(12)
N(1)−Al(1)−O(11)	105.70(9)	P(2)−O(21)−Al(2)	141.90(11)
N(2)−Al(2)−N(3)	109.04(9)	Al(3)−N(1)−Al(1)	120.82(11)
N(2)−Al(2)−O(21)	107.83(9)	Al(2)−N(2)−Al(1)	118.84(10)
N(3)−Al(2)−O(21)	105.68(9)	Al(3)−N(3)−Al(2)	122.66(11)

In analogy to **3**, $OP(OMe)_3$ coordinates to the aluminum centers of alumazene **4** through the oxygen atom. However, the further nucleophilic attack to the methyl group by the nitrogen lone pair (Scheme 1) which would provide compounds

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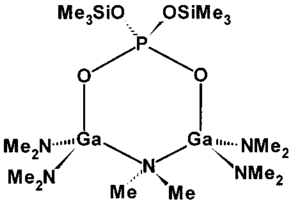
(41) Wessel, H.; Rennekamp, C.; Waezsada, S.-D.; Roesky, H. W.; Montero, M. L.; Usón, I. *Organometallics* **1997**, *16*, 3243.

Chart 2



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with Al−O−P bonds (Scheme 2) is hindered by electron conjugation in the ring. The adduct **5** is labile in solution as two broad signals of the free (δ −3.76 ppm) and coordinated (δ −5.08 ppm) $OP(OMe)_3$ were observed in the ^{31}P NMR spectrum. Also only one broad signal for the $Al-CH_3$ moieties and one doublet for the *i*-Pr groups attest to the fluxional behavior of **5**.

Gallium Amides. Although the gallophosphate molecular sieves[42] are less studied than their aluminum counterparts, their significance can be demonstrated on the fact that one of the largest pore opening was found in gallophosphate cloverite.[43] We examined the reactions of $[Ga(NMe_2)_3]_2$ (**2**)[44] with phosphoric acid esters in anhydrous solvents as a new method leading to gallophosphates (eq 1).

In contrast to amide **1**, its gallium analogue **2** is less reactive. The reaction of **2** with $OP(OMe)_3$, which is nearly instant for **1**, takes several days at room temperature. Washing with Et_2O and drying under vacuum yielded a white powder which was amorphous according to XRD. Heating of the product to 1100 °C in oxygen atmosphere afforded a white solid which was identified by XRD as cristobalite-$GaPO_4$ (JCPDS # 31-0546). The mass loss of 35% accounts for the presence of solvent, amine, and the end groups in the as-prepared material. The ratio of Ga to P (1:0.84) revealed slight excess of gallium. The Me_3N byproduct was identified by ^1H and ^{13}C NMR spectroscopy.

There is no reaction with the higher alkyl ester $OP(O\text{-}n\text{-}Bu)_3$ even after 17 h of heating to 90 °C. The presence of both the bridging and terminal NMe_2 signals of dimeric **2** in the ^1H NMR spectrum of the reaction mixture rules out the formation of an adduct intermediate similar to **3**.

Surprisingly, the reaction of **2** with the trimethylsilyl phosphate is relatively fast in comparison with that of the trimethyl ester. The formation of gel-like products required approximately 10 h. It allowed us to examine the reaction progress by ^1H, ^{29}Si, and ^{31}P NMR spectroscopy. In contrast to the analogous reaction of **1**, both starting reagents, **2** and $OP(OSiMe_3)_3$, were observed after their mixing and an intermediate was gradually formed. On the basis of signal intensities in ^1H NMR spectra (δ 2.94 (s, 30 H, Me_2N), 0.14 (s, 18 H, $SiMe_3$)), we tentatively assign it the cyclic structure $(Me_2N)_5Ga_2O_2P(OSiMe_3)_2$ (**10**, Chart 2) with exchange-averaged Me_2N groups. It appeared in the spectra soon after mixing of reagents and slowly grew in intensity (max. less than 10% intensity of the $OP(OSiMe_3)_3$ signal). At the same time the formation of 1 equiv of Me_3SiNMe_2 was observed. Both ^{31}P (δ −18.0 ppm) and ^{29}Si (δ 22.6 ppm, d, $^2J_{POSi}$ = 5.5 Hz) chemical shifts of **10** are downfield from the free $OP(OSiMe_3)_3$. After 2 h at room temperature, **2** and **10** disappeared from the spectra and signals for Me_3SiNMe_2 and oligomeric species started to grow. The latter show broad signals (δ −11.3 and −11.9 ppm) in the ^{31}P NMR spectrum which correspond well with the chemical shifts found in the solid state for cristobalite−$GaPO_4$ (δ −9.8 ppm)[45] and cloverite PO_4 groups (δ −9.9 and −11.4 ppm).[46]

In analogy to the reaction of **1**, amide **2** also scrambles ligand groups with $OP(OPh)_3$ (eq 7). However, the reaction proceeds only to the monoamide **6** and the starting triphenyl phosphate can be detected in the reaction mixture by ^{31}P NMR spectroscopy even after 40 h of heating to 90 °C.

$$\underset{\mathbf{2}}{{}^1/_2[Ga(NMe_2)_3]_2} + OP(OPh)_3 \rightarrow [Ga(OPh)_x(NMe_2)_{3-x}]_y + \underset{\mathbf{6}}{OP(NMe_2)(OPh)_2} \quad (7)$$

Sterically encumbered $Ga[N(SiMe_3)_2]_3$ is unreactive in reactions with $OPPh_3$ and $OP(OMe)_3$ in analogy to its aluminum counterpart.

Conclusions

As described above, we obtained very promising results in our approach to the preparation of alumina- and gallophosphate materials by novel nonaqueous routes. By using aluminum and gallium amides and triesters of phosphoric acid, we completely excluded water from our reaction system. We found the reactivity of the trimethyl phosphate superior to other alkyl esters. Triphenyl phosphate displays different reaction pathways in these reactions, namely, ligand scrambling. Unfortunately, we have not yet been able to obtain any crystalline materials which could be structurally characterized. By tailoring the reaction conditions and by using various solvents and additive molecules as templating and mineralizing agents, we hope to induce the formation of microporous crystalline phases.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. J.P. thanks the Alexander von Humboldt Stiftung for a research fellowship. H.W. is grateful to the Fonds der Chemischen Industrie for a fellowship.

Supporting Information Available: Complete listings of crystallographic details, atomic coordinates, bond lengths and bond angles, thermal displacement parameters, and hydrogen position parameters for **3** and **5** (14 pages). Ordering information is given on any current masthead page.

IC9713036

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