Synthesis and characterization of compounds with the Al–O–X (X = Si, P, C) structural motif†

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The reactions of LAlH_2 ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) (**1**) with diphenylsilanediol, phenylphosphonic acid, diphenylphosphinic acid, and pyrocatechol afford compounds with the Al–O–X (X = Si, P, C) motif of composition $[\text{LAl}(\mu\text{-O})_2\text{Si}(\text{Ph})_2]$ (**2**), $[\text{LAl}(\mu\text{-O})_2\text{PO}(\text{Ph})]$ (**3**), $\text{LAl}[\text{OPO}(\text{Ph})_2]_2$ (**4**), and $\text{LAl}(\mu\text{-O})_2(o\text{-C}_6\text{H}_4)$ (**5**), respectively. Compound **2** contains the Al–O–Si–O–Al heterotrimetallic dioxide chain. Compound **3** features an $\text{Al}(\mu\text{-O})_2\text{P}$ four-membered ring, while compound **4** exhibits a P–O–Al–O–P chain structure. Compound **5** contains the benzo-aluminum-dioxide organic–inorganic hybrid five-membered ring. Complexes **2**, **3**, **4**, and **5** were characterized by NMR, elementary analysis, and single-crystal X-ray diffraction.

Introduction

Owing to the desirable chemical properties and structures, aluminum–nonmetallic oxides with the Al–O–X (X = Si, P, C) core have tremendously increased in recent years. In 1997 Wessel *et al.*¹ and in 2004 Prabusankar *et al.*² reported compounds containing the Al–O–Si moiety which have been shown to have various applications, for example as ion exchangers, catalysts, catalyst supports, and molecular sieves.³ Compounds possessing the Al–O–P core are also associated with far-ranging applications such as flame retardants and sensors.⁴ The molecular aluminum phosphonates containing the Al–O–P motif model some of the naturally occurring minerals and synthetic large-pore zeolitic materials.⁵ Many researchers have reported on organic compounds⁶ and ionic compounds⁷ containing the Al–O–P skeleton. The organic phosphorus acids are versatile building precursors for the synthesis of materials with extended architectures. Thus, we became interested in preparing compounds containing the Al–O–P core by the reactions of organic aluminum compounds with organic phosphorus acids. Meanwhile, aluminosilicates exhibit excellent initiator properties for the ring opening polymerization of lactones.⁸

In 2006 we reported a rare aluminum spirocyclic hybrid with an inorganic B_2O_3 and an organic C_3N_2 core,⁹ and in 2011 a

series of novel structures bearing the Al–O–B unit.¹⁰ Due to the converse polarity of the hydridic hydrogen in LAlH_2 ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) **1** and the protonic one in X–OH (X = Si, P, C), these systems facilitate reactions under hydrogen elimination. Herein, we report on a series of novel structures bearing the Al–O–X moiety by the reaction of **1** with diphenylsilanediol, phenylphosphonic acid, diphenylphosphinic acid, and pyrocatechol, respectively.

Results and discussion

The reaction of **1** with diphenylsilanediol, phenylphosphonic acid, diphenylphosphinic acid, and pyrocatechol (Scheme 1) in a molar ratio of 2 : 1, 1 : 1, 1 : 2, and 1 : 1 resulted in the products $[\text{LAl}(\mu\text{-O})_2\text{Si}(\text{Ph})_2]$ (**2**), $[\text{LAl}(\mu\text{-O})_2\text{PO}(\text{Ph})]$ (**3**), $\text{LAl}[\text{OPO}(\text{Ph})_2]_2$ (**4**), and $\text{LAl}(\mu\text{-O})_2(o\text{-C}_6\text{H}_4)$ (**5**), respectively. During the course of these reactions hydrogen gas evolution was observed, which proceeds under the elimination of 2 equiv. of hydrogen. Compounds **2**, **4**, and **5** were isolated after growing colorless crystals from a concentrated *n*-hexane solution. Crystals of **3** were obtained from a concentrated toluene solution. All compounds are soluble in toluene, benzene, and trichloromethane.

Compounds **2**, **3**, **4**, and **5** were characterized by ^1H NMR investigation in CDCl_3 and C_6D_6 solutions, as well as by elemental analysis. Compounds **3** and **4** were additionally characterized by ^{31}P NMR. The ^1H NMR spectra of **2**, **3**, **4**, and **5** exhibit one set of resonances for the aryl group on silicon, phosphorus, phenyl, and the ligand, indicating a symmetric arrangement. The ^{31}P NMR spectrum of **3** exhibits one resonance at δ 24.26 ppm, and **4** shows one resonance at 20.68 ppm. Those resonances are consistent with the two expected crystallographic phosphorus sites, and the chemical shift values are close to those observed in other aluminum phosphonates.^{11,12}

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Scheme 1 Preparation of compounds.

X-ray quality single crystals of **2**, **4**, and **5** were obtained in *n*-hexane and for **3** in toluene at 0 °C. Compound **2** crystallizes in the monoclinic $P2_1/n$, **3** in the triclinic $P\bar{1}$, **4** in the monoclinic $P2_1/c$, and **5** in the orthorhombic space group $Cmca$. The molecular structures are shown in Fig. 1–4, respectively. Compound **2** consists of the heterotrimeric oxide with the metallic–non metallic chain of (H)Al–O–Si–O–Al(H) as a backbone. There are few examples known of this type: (Me)Al–O–Mg–O–Al(Me),¹³ (Me)Al–O–M–O–Al(Me) (M = Ti, Zr),¹⁴ and (Me)Al–O–Sn–O–Al(Me).¹⁵ The steric effect of diphenylsilanediol with two phenyl groups gives rise to the chain-like structure of **2**. The silicon center in **2** is four coordinated and surrounded by two phenyl groups and two μ -O-bonded oxygen atoms, resulting in a distorted tetrahedral environment. Two aluminum atoms are four coordinated and surrounded by a hydride, a bridging oxygen atom and two nitrogen atoms, respectively. The quasi-tetrahedral configuration of the aluminum center shows the existence of the hydride at the aluminum. The Al(2)–O(2) bond lengths of **2** (av. 1.724 Å) are longer than those of normal Al–OH bond distances (av. 1.705 Å) in $\text{La}(\text{OH})_2$.¹⁶ The Si–O bond distances (av. 1.620 Å) and O–Si–O bond angle (112.51(7)°) are comparable with those reported in the literature.² For the structures of complexes **3** and **4**, **3** features a four-membered AlO_2P ring, and **4** shows a P–O–Al–O–P framework. The Al–O bond lengths in **3** (av. 1.915 Å) are longer when compared with those of **4** (av. 1.724 Å), while the O(1)–Al(1)–O(2) angle of **3** (74.80(6)°) is much smaller than the O(1)–Al(1)–O(3) angle of **4** (113.60(1)°). These differences could be attributed to the AlO_2P ring strain. The sum of the inner angles of the AlO_2P four-membered ring in **3** is 358.67°, which is quite close to the ideal planar ring of 360°. The structure of compound **5** contains a benzoaluminum

Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.9146(15), Al(1)–N(2) 1.9047(16), Al(2)–N(3) 1.9068(16), Al(2)–N(4) 1.9128(16), Al(1)–O(1) 1.7030(14), Al(2)–O(2) 1.7243(13), Si(1)–O(1) 1.6168(13), Si(1)–O(2) 1.6222(13), Al(1)–H(01) 1.50(2), Al(2)–H(02) 1.51(2); O(1)–Si(1)–O(2) 112.51(7), Si(1)–O(1)–Al(1) 156.49(9), Si(1)–O(2)–Al(2) 138.61(8), O(1)–Al(1)–N(1) 114.46(7), O(1)–Al(1)–N(2) 113.96(7), O(2)–Al(2)–N(3) 113.85(6), O(2)–Al(2)–N(4) 114.46(7), N(2)–Al(1)–N(1) 95.80(7).

Fig. 2 Molecular structure of **3**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.9525(16), Al(1)–N(2) 1.9251(17), Al(1)–O(1) 1.8929(15), Al(1)–O(2) 1.9376(14), P(1)–O(1) 1.5387(14), P(1)–O(2) 1.5297(14), P(1)–O(3) 1.5266(14), P(1)–C(30) 1.7832(19); O(1)–Al(1)–N(1) 90.12(7), O(1)–Al(1)–N(2) 147.35(7), O(1)–Al(1)–O(2) 74.80(6), P(1)–O(1)–Al(1) 93.34(7), P(1)–O(2)–Al(1) 91.89(7), O(2)–P(1)–O(1) 98.64(7), O(3)–P(1)–O(1) 114.53(8), O(3)–P(1)–O(2) 115.16(8).

dioxide moiety. It is an organic–inorganic hybrid type. The sum of the inner angles of the C_2AlO_2 five-membered ring in **5** is 549.2°, which is slightly different from the planar pentagonal value of 540°.

Fig. 3 Molecular structure of **4**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.876(2), Al(1)–N(2) 1.866(3), Al(1)–O(1) 1.712(2), Al(1)–O(3) 1.736(2), P(1)–O(1) 1.562(2), P(1)–O(2) 1.472(2), P(2)–O(3) 1.553(2), P(2)–O(4) 1.474(2); O(1)–Al(1)–N(1) 110.12(1), O(1)–Al(1)–N(2) 114.57(1), O(3)–Al(1)–N(1) 110.69(1), O(3)–Al(1)–N(2) 107.58(1), P(1)–O(1)–Al(1) 147.36(1), P(2)–O(3)–Al(1) 150.06(1), O(2)–P(1)–O(1) 115.68(1), O(4)–P(2)–O(3) 115.80(1), O(1)–Al(1)–O(3) 113.60(1).

Fig. 4 Molecular structure of **5**. Thermal ellipsoids are drawn at 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.861(2), Al(1)–N(2) 1.861(2), Al(1)–O(1) 1.764(3), Al(1)–O(2) 1.758(3), O(1)–C(16) 1.380(4), O(2)–C(21) 1.369(5); O(2)–Al(1)–O(1) 94.90(12), O(2)–Al(1)–N(1) 115.24(8), O(2)–Al(1)–N(2) 115.24(8), O(1)–Al(1)–N(1) 117.02(8), O(1)–Al(1)–N(2) 117.02(8), C(16)–O(1)–Al(1) 106.9(2), C(21)–O(2)–Al(1) 106.8(2).

Experimental section

General procedures

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside an Mbraun MB 150-GI glovebox. All solvents were distilled from Na–benzophenone ketyl prior to use. Commercially available chemicals were purchased from Aldrich, Fluka and used as received. LH^{17} and LAH_2^{18} were prepared as described in the literature. Elemental analyses were performed by the Analytical Instrumentation Center of the Peking University. ^1H NMR and ^{31}P NMR spectra were recorded on Bruker AM 400 spectrometers. Melting points were measured in sealed glass tubes.

Preparation of $[\text{LAl}(\mu\text{-O})]_2\text{Si}(\text{Ph})_2$ (**2**)

A solution of **1** (0.446 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a suspension of diphenylsilanediol (0.108 g, 0.5 mmol) in toluene (10 mL) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for 72 h. The solvent was removed *in vacuo*. The solid was extracted with *n*-hexane (15 mL), and the extract was stored at room temperature for 3 d to afford **2** as colorless crystals. An additional crop of **2** was obtained from the mother liquor. Total yield 0.517 g (93.5%), mp 300–302 °C. ^1H NMR (399.13 MHz, C_6D_6 , 25 °C, TMS): δ 7.15–6.73 (m, 22 H, Ar–H), 4.90 (s, 2 H, g–H), 3.39 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4 H, CHMe_2), 3.25 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4 H, CHMe_2), 1.43 (s, 12 H, Me), 1.29 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2), 1.19 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2), 1.08 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2), 0.99 ppm (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2). $\text{C}_{70}\text{H}_{94}\text{Al}_2\text{N}_4\text{O}_2\text{Si}$ (1105.54). Anal. Calcd C, 76.05; H, 8.57; N, 5.07. Found C, 76.59; H, 8.59; N, 5.03%.

Preparation of $[\text{LAl}(\mu\text{-O})]_2\text{PO}(\text{Ph})_2$ (**3**)

A solution of **1** (0.446 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a suspension of phenylphosphonic acid (0.158 g, 1 mmol) in toluene (10 mL) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for 72 h. The solution was filtered to remove any solid impurities and stored at room temperature for crystallization. Compound **3** was isolated as colorless crystals. An additional crop of **3** was obtained from the mother liquor. Total yield 0.479 g (79.7%), mp 165–167 °C. ^1H NMR (399.13 MHz, C_6D_6 , 25 °C, TMS): δ 7.28–6.96 (m, 11 H, Ar–H), 4.89 (s, 2 H, g–H), 3.35 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4 H, CHMe_2), 1.67 (s, 6 H, Me), 1.28 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2), 1.10 ppm (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2). ^{31}P NMR (161.98 MHz, C_6D_6 , 25 °C, H_3PO_4) δ 24.26 ppm. $\text{C}_{35}\text{H}_{46}\text{AlN}_2\text{O}_3\text{P}$ (600.71). Anal. Calcd C, 69.98; H, 7.72; N, 4.66. Found C, 69.55; H, 7.75; N, 4.59%.

Preparation of $\text{LAl}[\text{OPO}(\text{Ph})_2]_2$ (**4**)

Preparation like that of **2** from **1** (0.446 g, 1.0 mmol) in THF (10 mL) and diphenylphosphinic acid (0.436 g, 2.0 mmol) in THF (10 mL). Total yield 0.863 g (87.9%), mp 274–277 °C. ^1H

Table 1 Crystallographic data for compounds **2**, **3**, **4**, and **5**

Compound reference	2	3	4	5
Chemical formula	C ₇₀ H ₉₄ Al ₂ N ₄ O ₂ Si	C ₄₉ H ₆₂ AlN ₂ O ₃ P	C ₅₆₋₅₀ H ₆₅ AlN ₂ O ₄ P ₂	C ₃₈ H ₅₂ AlN ₂ O ₂
Formula mass	1105.54	784.96	925.03	595.80
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
<i>a</i> /Å	21.960(3)	12.875(2)	12.3271(19)	17.191(4)
<i>b</i> /Å	15.053(2)	14.052(3)	42.636(6)	19.749(5)
<i>c</i> /Å	22.295(4)	14.388(3)	10.5983(16)	21.205(5)
α /°	90.00	86.432(9)	90.00	90.00
β /°	117.445(2)	70.108(7)	115.176(2)	90.00
γ /°	90.00	68.574(6)	90.00	90.00
Unit cell volume/Å ³	6540.4(17)	2272.7(7)	5041.1(13)	7199(3)
Temperature/K	93(2)	193(2)	153(2)	153(2)
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>Cmca</i>
No. of formula units per unit cell, <i>Z</i>	4	2	4	8
Radiation type	MoK α	MoK α	MoK α	MoK α
Absorption coefficient, μ /mm ⁻¹	0.109	0.121	0.151	0.089
No. of reflections measured	51 638	22 684	47 321	24 253
No. of independent reflections	14 982	10 305	11 466	3460
<i>R</i> _{int}	0.0328	0.0248	0.1050	0.0606
Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>))	0.0583	0.0579	0.0695	0.0695
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.1423	0.1345	0.1370	0.1298
Final <i>R</i> ₁ values (all data)	0.0736	0.0840	0.1312	0.0893
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1538	0.1478	0.1640	0.1382
Goodness of fit on <i>F</i> ²	0.998	1.001	1.001	0.998
CCDC number	895833	895834	895835	895836

NMR (399.13 MHz, CDCl₃, 25 °C, TMS): δ 7.30–7.08 (m, 26 H, Ar-*H*), 5.82 (s, 1 H, g-*H*), 3.11 (sept, ³*J*_{H-H} = 6.8 Hz, 4 H, CHMe₂), 1.96 (s, 6 H, Me), 1.22 (d, ³*J*_{H-H} = 6.8 Hz, 12 H, CHMe₂), 1.11 ppm (d, ³*J*_{H-H} = 6.8 Hz, 12 H, CHMe₂). ³¹P NMR (161.98 MHz, CDCl₃, 25 °C, H₃PO₄) δ 20.68 ppm. C₅₃H₆₁AlN₂O₄P₂ (878.99). Anal. Calcd C, 72.42; H, 6.99; N, 3.19. Found C, 72.75; H, 7.38; N, 3.07%.

Preparation of LAl(μ-O)₂(*o*-C₆H₄) (**5**)

Preparation like that of **2** from **1** (0.446 g, 1.0 mmol) and pyrocatechol (0.110 g, 1.0 mmol). Product **5** was isolated as colorless crystals. Total yield 0.469 g (84.9%), mp 165–168 °C. ¹H NMR (399.13 MHz, C₆D₆, 25 °C, TMS): δ 7.15–6.73 (m, 10 H, Ar-*H*), 4.90 (s, 1 H, g-*H*), 3.25 (sept, ³*J*_{H-H} = 6.8 Hz, 4 H, CHMe₂), 1.43 (s, 6 H, Me), 1.29 (d, ³*J*_{H-H} = 6.8 Hz, 12 H, CHMe₂), 1.08 ppm (d, ³*J*_{H-H} = 6.8 Hz, 12 H, CHMe₂). C₃₅H₄₅AlN₂O₂ (552.73). Anal. Calcd C, 76.05; H, 8.21; N, 5.07. Found C, 76.35; H, 8.41; N, 4.68%.

Single crystal X-ray structure determination and refinement

Single crystals of **2**, **3**, **4**, and **5** were mounted with glue on a glass fiber and crystal data were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated MoK α radiation (λ = 0.710747 Å). Empirical absorption correction was applied using the SADABS program.¹⁹ Structures were solved by direct methods²⁰ and refined by full-matrix least squares on *F*² using the SHELXL-97 program.²¹ A summary of the crystal data is given in Table 1.

Conclusions

A series of compounds containing the Al–O–X (X = Si, P, C) structural unit have been prepared by the facile reaction of

LAlH₂ with R_nM(OH)_m. Novel chain-like or cyclic structures have been obtained by selecting different functional organic R groups which are attached to silicon, phosphorus or carbon. Presently we are in the process of treating compounds **2–5** with water to generate new hybrid materials at the nanometer level.

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