Inorg. Chem. **2007**, *46*, 10749–10753

Inorganic Chemistry
Article

An Unknown Coordination Mode of the Phosphite Unit and a Carbon-Free Heterocycle in Two Different Heterobimetallic Alumophosphites

A. Paulina Gómora-Figueroa, Vojtech Jancik,* Raymundo Cea-Olivares, and Rubén A. Toscano

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior,
Ciudad Universitaria, 04510, México D.F, México

Received August 14, 2007

The unique alumophosphite reagent LAl(SH)(μ-O)P(OEt)$_2$ was prepared and used for the synthesis of the heterobimetallic alumophosphites [{κ^2-*S*,*P*-LAl(S)(μ-O)P(OEt)$_2$}$_2$Zn] and [{κ^4-*S*,*O*,*O*-LAl(SLi)(μ-O)P(OEt)$_2$}$_2$]. The first contains a rare example of two carbon-free five-membered heterocycles (Al–S–Zn–P–O) connected in a spiro fashion through the zinc atom, whereas the second possesses an unknown example of a coordination environment of a phosphite unit M–O–P(μ-OEt)$_2$M with an uncoordinated lone electron pair on the phosphorus center.

Introduction

Recently, we have reported on the preparation of the unique alumosilicate substrates LAl(EH)(μ-O)Si(OH)(O^{t}Bu)$_2$ (E = O, S; L = [HC{C(Me)N(Ar)}$_2$]$^-$, Ar = 2,6-di-^{i}Pr$_2$C$_6$H$_3$) from LAl(SH)$_2$ and (^{t}BuO)$_2$Si(OH)$_2$ and the derivative [LAl(SLi)(μ-O)Si(OLi·thf$_2$)(O^{t}Bu)$_2$]$_2$, a molecular heterobimetallic alumosilicate.[1] Thus, we became interested, if a similar procedure could be used for the preparation of the alumophospite analogue LAl(SH)(μ-O)P(OR)$_2$ (R = alkyl, aryl). Such a complex could be used as a precursor for heterobimetallic alumophosphites LAl(SM)(μ-O)P(OR)$_2$ (M = metal, R = alkyl, aryl), in which the phosphite unit can be coordinated to the metal M via the phosphorus (**a**) or one (**b**) or two (**c**) oxygen atoms (Scheme 1). Despite the fact that such molecular heterobimetallic alumophosphites are not known, they can feature unusual or unknown coordination modes of the PO$_3$ unit. Furthermore, these alumophosphite species could be used as precursors for alumophosphate reagents by oxidizing the phosphorus atom similarly to the synthesis of nucleosides, where the phosphate unit is mostly constructed via a phosphite intermediate.[2] Herein, we report on the first alumophosphite precursor LAl(SH)(μ-O)P(OEt)$_2$ (**1**) prepared from LAl(SH)$_2$[3] and HP(O)(OEt)$_2$ in THF (Scheme 2) and the formation of two heterobimetallic derivatives thereof containing an unknown coordination mode of the phosphite unit and a carbon-free heterocycle, respectively.

Experimental Section

General. All of the manipulations described below were performed under a dried dinitrogen atmosphere using standard Schlenk and glovebox techniques. The solvents were purchased from Aldrich and dried prior to use. Diethylphosphite (Strem Chemicals, 95%) was purified by distillation under reduced pressure and a nitrogen atmosphere. LAl(SH)$_2$ was prepared according to the literature procedure.[3] The dimethylzinc solution 2.0 M in toluene was purchased from Aldrich and used as received. [(Me$_3$Si)$_2$NLi·OEt$_2$]$_2$ was prepared freshly using a butyllithium solution and hexamethyldisilazane in diethylether.

LAl(SH)(μ-O)P(OEt)$_2$ (1). (EtO)$_2$P(O)H (0.27 g, 1.95 mmol) in THF (20 mL) was added dropwise to the solution of LAl(SH)$_2$ (1.00 g, 1.95 mmol) in THF (40 mL) at -78 °C over the period of 35 min. The reaction mixture was allowed to warm up to ambient temperature and stirred for additional 5 h. All of the volatiles were removed in vacuum, the crude product was rinsed with cold hexane ($\sim$5 mL) and dried in a vacuum. **1** was obtained as a white powder. Yield 1.15 g, 1.87 mmol (96%); Mp 94−96 °C. Elemental analysis (%) Calcd for C$_{33}$H$_{52}$AlN$_2$O$_3$PS (614.8 g·mol^{-1}): C 64.47, H 8.53, N 4.56; found: C 64.1, H 8.3, N 4.67. IR (CsI): $\tilde{\nu}$ 2572 cm^{-1} (vw, ν SH). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): $\delta = -0.53$ (s, 2H, S*H*), 0.92 (t, $^3J_{\mathrm{H,H}} = 7.0$ Hz, 6H, CH$_2$C*H*$_3$), 1.11 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.47 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 6H, CH(C*H*$_3$)$_2$), 1.52 (s, 6H, C*H*$_3$), 1.54 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 6H, CH(C*H*$_3$)$_2$), 3.32 (dquart, $^2J_{\mathrm{H,H}} = 16.5$ Hz, $^3J_{\mathrm{H,H}} = 7.0$ Hz, 2H, C*H*$_2$CH$_3$), 3.44 (dquart, $^2J_{\mathrm{H,H}} = 16.5$ Hz,

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* To whom correspondence may be addressed. E-mail: vjancik@servidor.unam.mx, Fax: (+)(52) 55-561-622-17.

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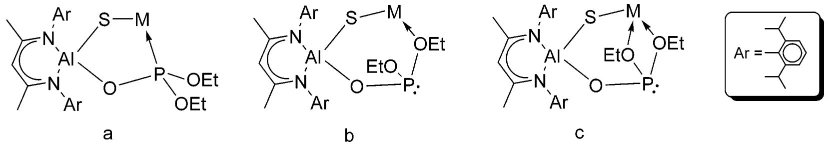
10.1021/ic701614c CCC: $37.00

Scheme 1. Possible Coordination Modes of LAl(SH)(μ-O)P(OR)$_2$

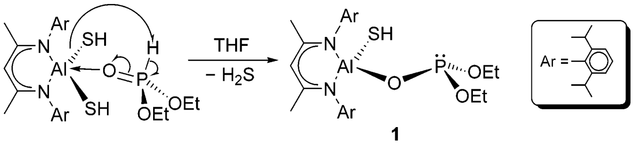


$^3J_{\mathrm{H,H}} = 7.0$ Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 3.46 (sept, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 2H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 3.54 (sept, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 2H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 4.86 (s. 1H, $\mathrm{C}\mathit{H}$), 7.08−7.15 ppm (m, 6H, *m*-, *p*-, H of Ar); ^{13}C NMR (75.6 MHz benzene-d_6, 25 °C, TMS): $\delta = 17.0$ ($\mathrm{CH}_2\mathit{C}\mathrm{H}_3$), 23.3, 24.5, 24.6, 24.7 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 26.4 ($\mathit{C}\mathrm{H}_3$), 28.2, 28.7 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 55.2 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$), 97.9 ($\gamma$-$\mathit{C}\mathrm{H}$), 124.2, 124.3, 124.7, 144.3, 144.6, 144.8, (*i*-, *o*-, *m*-, *p*-C Ar,), 170.9 ppm (C=N); ^{31}P NMR (121.6 MHz, benzene-d_6, 25 °C, 85% $\mathrm{H_3PO_4}$): $\delta = 126.7$ ppm. EI-MS: *m/z* (%) = 614 (26) [M$^+$], 556 (57) [M$^+$ − 2CH$_2$CH$_3$], 476 (100) [M$^+$ − H(O)P(OEt)$_2$].

[{κ^4-*S,O,O*-LAl(SLi)(μ-O)P(OEt)$_2$}$_2$] (2). A solution of **1** (0.30 g, 0.49 mmol) in THF (15 mL) was cooled to −78 °C and then a solution of [(Me$_3$Si)$_2$NLi·OEt$_2$]$_2$ (0.12 g, 0.25 mmol) in THF (10 mL) was added. The reaction mixture was allowed to warm up to ambient temperature and was stirred for additional 3 h. All of the volatiles were removed under a vacuum, leaving a white solid as a product. The crude product was rinsed with cold THF (~5 mL) and dried under a vacuum. **2** was obtained as a white powder. Yield 0.25 g, 0.21 mmol (85%); Mp 160 °C (decomp.). Elemental analysis (%) Calcd for $\mathrm{C_{66}H_{102}Al_2Li_2N_4O_6P_2S_2}$ (1241.5 g·mol^{-1}): C 63.85, H 8.28, N 4.51; found: C 63.5, H 8.1, N 4.62. ^{1}H NMR (300 MHz, THF-d_8, 25 °C, TMS): $\delta = 0.88$ (t, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.03 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.06 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.24 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.30 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.63 (s. 12H, $\mathrm{C}\mathit{H}_3$), 3.07 (dquart, $^2J_{\mathrm{H,H}} = 16.5$ Hz, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 3.22 (dquart, $^2J_{\mathrm{H,H}} = 16.5$ Hz, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 3.64 (sept, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 4H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 3.69 (sept, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 4H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 5.06 (s, 2H, $\mathrm{C}\mathit{H}$), 7.02−7.12 ppm (m, 12H, *m*-, *p*-, H of Ar); ^{13}C NMR (75.6 MHz, THF-d_8, 25 °C, TMS): $\delta = 17.5$ ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 24.1, 24.8, 25.1, 25.8 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 26.9 ($\mathit{C}\mathrm{H}_3$), 28.6, 28.9 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 56.3 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$), 97.8 ($\gamma$-$\mathit{C}\mathrm{H}$), 124.1, 124.6, 126.6, 143.3, 145.9, 146.3, (*i*-, *o*-, *m*-, *p*-C Ar,), 169.0 ppm (C=N); ^{31}P NMR (121.6 MHz, THF-d_8, 25 °C, 85% $\mathrm{H_3PO_4}$): $\delta = 131.7$ ppm; ^{7}Li NMR (116.8 MHz, THF-d_8, 25 °C, LiCl/D$_2$O 1.8 M): $\delta = 1.40$ ppm.

[{κ^2-*S,P*-LAl(S)(μ-O)P(OEt)$_2$}$_2$Zn]·3.5 toluene (3). A solution of **1** (0.26 g, 0.42 mmol) in toluene (15 mL) was cooled to −78 °C and ZnMe$_2$ (2.0 M in toluene, 0.12 mL, 0.24 mmol) was added. The reaction mixture was allowed to warm up to ambient temperature and was stirred for additional 2 h. The product precipitated as a white solid. All of the volatiles were removed under vacuum. The crude product was rinsed with cold toluene (~5 mL) and dried under a vacuum. **3** was obtained as a white powder. Yield 0.31 g, 0.24 mmol (57%); Mp 184−186 °C. Elemental analysis (%) Calcd for $\mathrm{C_{90.5}H_{130}Al_2N_4O_6P_2S_2Zn}$ (1609.5 g·mol^{-1}): C 67.16, H 8.14, N 3.48; found: C 67.0, H 8.2, N 3.6. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): $\delta = 0.93$ (t, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.05 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.21 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.49 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.51 (s. 12H, $\mathrm{C}\mathit{H}_3$), 1.70 (d, $^3J_{\mathrm{H,H}} = 6.0$ Hz, 12H, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.10 (s, 10.5H, $\mathrm{C}\mathit{H}_3$ from toluene), 2.43 (bs, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 3.36 (sept. $^3J_{\mathrm{H,H}} = 6.0$ Hz, 4H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 3.63 (bs, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH}_3$), 3.86 (bs, 4H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 4.82 (s. 2H, $\mathrm{C}\mathit{H}$), 6.97−7.15 ppm (m, 29.5H, *o*-, *m*-, *p*-, H of Ar); ^{13}C NMR (75.6 MHz, benzene-d_6, 25 °C, TMS): $\delta = 16.5$, ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 21.1($\mathit{C}\mathrm{H}_3$ from toluene), 23.4, 23.7, 24.9, 25.0, ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 28.0 ($\mathit{C}\mathrm{H}_3$), 28.0, 28.5 ($\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$), 58.7 ($\mathit{C}\mathrm{H}_2\mathrm{CH}_3$), 97.6 ($\gamma$−$\mathit{C}\mathrm{H}$), 123.5, 124.9, 127.0, 140.0, 144.3, 146.4, (*i*-, *o*-, *m*-, *p*-C Ar), 125.4, 128.2, 129.0, 137.9 (*i*-, *o*-, *m*-, *p*-C toluene,) 169.8 ppm (C=N); ^{31}P NMR (121.6 MHz, benzene-d_6, 25 °C, 85% $\mathrm{H_3PO_4}$): $\delta = 106.9$ ppm.

Scheme 2. Preparation of **1**



X-ray Structure Determination. The crystals were mounted on a nylon loop and a rapidly placed in a stream of cold nitrogen. Diffraction data were collected on a Bruker-APEX three-circle diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The structures were solved by direct methods (*SHELXS-97*[4]) and refined against all of the data by full-matrix least-squares on F^2.[5] The hydrogen atoms of C−H bonds were placed in idealized positions, whereas the hydrogen atom from the SH moiety in **1** was localized from the difference electron-density map and refined isotropically. The disordered toluene molecules as well as the disordered ^{i}Pr and ethoxy moieties were refined using geometry and distance restraints (SAME, SADI) together with the restraints for the U_{ij} values (SIMU, DELU).

Results and Discussion

Formation of Complexes 1−3. The choice of the phosphorus reagent is important because the aluminum precursor is sensitive toward acids and water.[3] Hence, the use of diesters of phosphoric acid in the reaction, which would lead directly to the corresponding alumophosphate, is restricted because of the high acidity of the OH proton and the presence of traces of alcohols or water in the reagent. However, the acidity of the hydrogen in the phosphite is negligible, and the traces of alcohol and water can be conveniently removed by distillation or under a vacuum. Moreover, the HOP ↔ HP(O) tautomeric equilibrium suggests the possibility of the isolation of **1**. The formation of **1** was confirmed by the shift of the signal in the ^{31}P NMR spectra from 7.4 ppm (HP(O)(OEt)$_2$) to 126.7 ppm (**1**). Although the reaction mechanism is simple, great care has to be taken while purifying the starting materials to avoid the formation of the undesired byproducts LAl(OEt)(μ-O)P(OEt)$_2$ (^{31}P NMR δ 126.1 ppm) and LAl(SH)(μ-O)P(S)(OEt)$_2$ (^{31}P NMR δ 58.0 ppm), as all three products have similar solubility and are thus difficult to separate. The first compound is always present in a bulk of **1**, but its amount can be significantly reduced (from more than 30 to less than 3%) by distillation of the phosphite prior to use and by

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Table 1. Crystallographic Data for **1** − **3**

	1	**2**	**3**·3.5 toluene
formula	$C_{33}H_{52}AlN_2O_3PS$	$C_{66}H_{102}Al_2Li_2N_4O_6P_2S_2$	$C_{90.50}H_{130}Al_2N_4O_6P_2S_2Zn$
fw	614.78	1241.42	1615.38
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
temp (K)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073
a (Å)	11.830(3)	27.446(5)	13.004(3)
b (Å)	12.385(3)	16.854(3)	15.672(4)
c (Å)	12.462(3)	16.243(3)	24.766(5)
α (deg)	106.34(3)	90	100.03(3)
β (deg)	94.32(3)	110.82(3)	99.04(3)
γ (deg)	93.73(3)	90	110.02(3)
V (Å^3)	1740(1)	7023(3)	4540(2)
Z	2	4	2
cryst color	colorless	colorless	colorless
no. of data/restraints/params	6351/257/475	6191/0/394	16 046/719/1188
GOF on F^2	1.035	1.041	1.018
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0521, 0.1309	0.0512, 0.1164	0.0507, 0.1148
R1,[a] wR2[b] (all data)	0.0634, 0.1385	0.0751, 0.1271	0.0731, 0.1253
largest diff. peak/hole (e·Å^{-3})	0.547/−0.198	0.268/−0.206	0.529/−0.258

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

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1** − **3**

	1[a]	**2**	**3**·3.5 toluene[b]
Al(1)−N(1)	1.891(2)	1.906(2)	1.907(2), 1.905(2)
Al(1)−N(2)	1.883(2)	1.903(2)	1.895(2), 1.899(2)
Al(1)−S(1)	2.217(1)	2.124(1)	2.160(1), 2.161(1)
Al(1)−O(1)	1.723(2)	1.764(2)	1.773(2), 1.768(2)
P(1)−O(1)	1.564(2)	1.560(2)	1.552(2), 1.551(2)
P(1)−O(2)	1.643(2), 1.65(1)	1.650(2)	1.607(2), 1.599(2)
P(1)−O(3)	1.611(2), 1.65(1)	1.649(2)	1.595(2), 1.595(2)
N(1)−Al(1)−N(2)	99.0(1)	96.4(1)	96.8(1), 96.4(1)
S(1)−Al(1)−O(1)	115.6(1)	116.0(1)	110.5(1), 110.3(1)
Al(1)−O(1)−P(1)	140.7(1)	140.0(1)	125.9(1), 126.4(1)
O(1)−P(1)−O(2)	94.8(1), 99.1(7)	103.6(1)	106.0(1), 106.5(1)
O(1)−P(1)−O(3)	105.1(1), 91.0(8)	103.7(1)	102.0(1), 101.6(1)
O(2)−P(1)−O(3)	103.2(1), 101(1)	86.9(1)	98.8(1), 99.7(1)
	Other selected bond lengths and angles for **2**[c]		
S(1)−Li(1)	2.419(5)	O(2)−Li(1)−O(3)	67.1(2)
S(1)−Li(1A)	2.343(5)	O(2)−Li(1)−S(1)	107.6(2)
Li(1)−O(2)	2.054(5)	O(2)−Li(1)−S(1A)	136.4(2)
Li(1)−O(3)	2.056(6)	O(3)−Li(1)−S(1)	110.5(2)
Al(1)−S(1)−Li(1)	94.5(1)	O(3)−Li(1)−S(1A)	121.7(2)
Al(1)−S(1)−Li(1A)	161.9(1)	S(1)−Li(1)−S(1A)	107.5(2)
Li(1)−S(1)−Li(1A)	72.5(2)		
	Other selected bond lengths and angles for **3**·3.5 toluene		
Zn(1)−S(1)	2.307(1)	S(1)−Zn(1)−P(1)	96.2(1)
Zn(1)−S(2)	2.315(1)	S(1)−Zn(1)−P(2)	112.1(1)
Zn(1)−P(1)	2.429(1)	S(2)−Zn(1)−P(1)	112.1(1)
Zn(1)−P(2)	2.413(1)	S(2)−Zn(1)−P(2)	96.4(1)
S(1)−Zn(1)−S(2)	128.1(1)	P(1)−Zn(1)−P(2)	112.5(1)

[a] The second number belongs to the bond lengths or angles involving the atoms O(2A) and O(3A) from the second position (ca. 39%) of the PO_3 unit. [b] The second number belongs to the bond lengths and angles involving the atoms Al(2), P(2), S(2), N(3), N(4), O(4), O(5), and O(6) from the symmetry independent second position of the molecule (Figure 2 for detailed labeling). [c] The symmetry operation to generate the atoms Li(1A) and S(1A) is $^3/_2 - x$, $^1/_2 - y$, $-z$.

adjusting its rate of addition, whereas the second is a result of the oxidation of **1** by traces of elemental sulfur remaining from the synthesis of $LAl(SH)_2$. **1** is soluble in common organic solvents including pentane and hexane. The acidic proton from the SH moiety can be easily substituted by metal, and thus the reaction of two equivalents of **1** with $[(Me_3Si)_2NLi{\cdot}OEt_2]_2$ in THF results in the precipitation of a microcrystalline dimeric species [{κ^4-*S*,*O*,*O*-LAl(SLi)(μ-O)P(OEt)$_2$}$_2$] (**2**), whereas the reaction of 2 equiv of **1** with $ZnMe_2$ in toluene yielded the unique spirocyclic compound [{κ^2-*S*,*P*-LAl(S)(μ-O)P(OEt)$_2$}$_2$Zn]·3.5 toluene (**3**) (Scheme 3). The amount of the solvating toluene in **3** was determined by ^{1}H NMR spectroscopy and later unambiguously confirmed by an X-ray diffraction experiment. The preparation of **2** and **3** can be conveniently monitored using ^{31}P NMR spectroscopy. The disappearance of the resonance of **1** at 126.7 and presence of the signal at 131.7 (**2**) or 106.9 ppm (**3**), respectively, indicates the end of the reaction. The ^{31}P NMR chemical shifts of **2** and **3** are significantly different and suggest different coordination modes of the PO_3 unit to the metal. The substitution of the acidic proton in **2** and **3** is well evidenced by the disappearance of its resonance in the

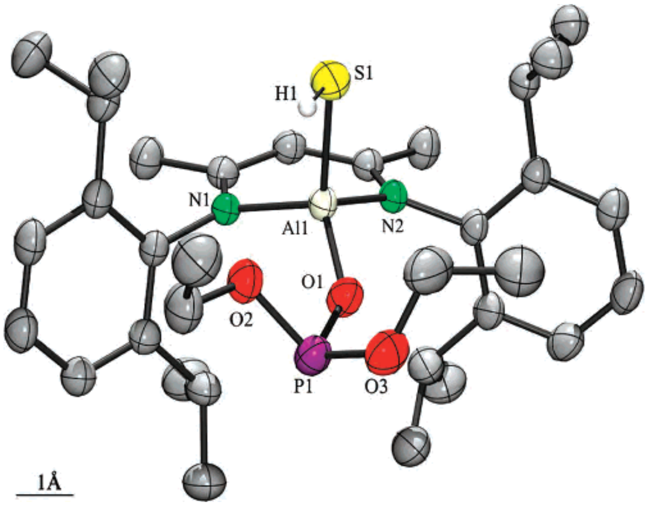


Figure 1. Thermal ellipsoid plot of **1** at the 50% level. Carbon-bound hydrogen atoms are omitted for clarity.

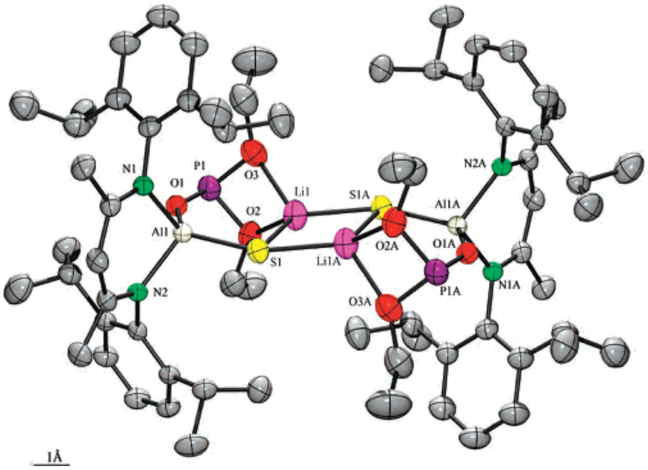


Figure 2. Thermal ellipsoid plot of **2** at the 50% level. All of the hydrogen atoms are omitted for clarity.

^{1}H NMR spectrum at −0.53 ppm as well as the absence of the S−H vibration band at $\tilde{\nu}$ 2572 cm^{-1} in the IR spectra of **2** and **3**. The ^{1}H NMR shifts for the protons of the S−H moiety of related compounds are: −0.88 ppm for LAl(SH)$_2$, −1.00 ppm for [LAl(SH)(SLi•thf$_2$)]$_2$ and −0.45 ppm for LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$, and the IR absorption bands for these compounds can be found at the following wavenumbers: $\tilde{\nu}$ 2549 cm^{-1} for LAl(SH)$_2$, 2552 cm^{-1} for [LAl(SH)(SLi•thf$_2$)]$_2$ and 2560 cm^{-1} for LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$.[3,6] **2** is sparingly soluble in THF but readily soluble in dichloromethane and in chloroform. No reaction was observed between **2** and dichloromethane or chloroform, respectively. **3** is soluble in hot toluene, THF, dichloromethane, and chloroform. The ^{1}H NMR spectrum for **3** revealed a dynamic equilibrium in the solution, resulting in broad singlet signals for the OCH_2CH$_3$ protons (theoretically should be a doublet of quartets) and for one of the two signals for the CH(CH$_3$)$_2$ protons (theoretically should be a septet). These signals remained unresolved even at low temperature.

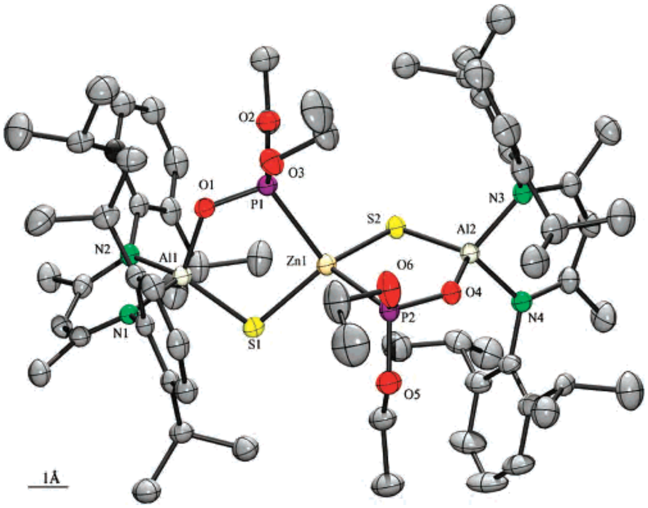
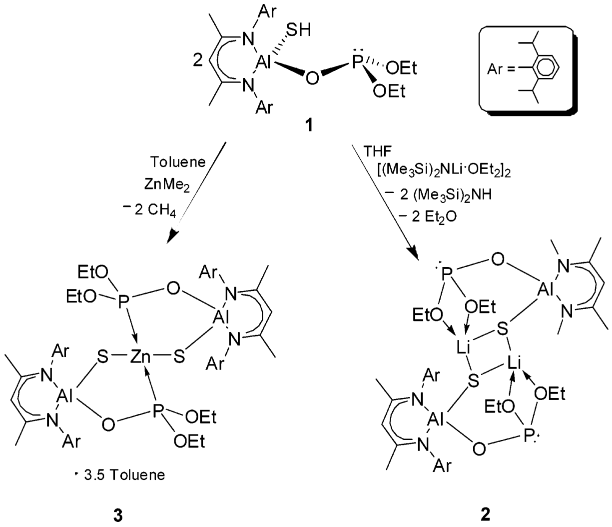


Figure 3. Thermal ellipsoid plot of **3** at the 40% level. All of the hydrogen atoms and solvating toluene molecules are omitted for clarity.

Scheme 3. Preparation of Heterobimetallic Compounds **2** and **3**



This is most probably caused by the dissociation and association of the diethoxy phosphite unit from and to the zinc center. The EI-MS spectrum of **1** contains the molecular peak at m/z 614 (26%), whereas the spectra of **2** and **3** exhibit only low-weight fragments.

X-ray Structural Analyses. The molecular structures of all three compounds were unambiguously determined by single-crystal X-ray diffraction studies. Single crystals of **1** were obtained from the saturated hexane solution at −30 °C, whereas slow cooling of hot saturated solutions of **2** (in THF) and **3** (in toluene) resulted in the growth of X-ray quality monocrystals (Table 1).

1 and **3** crystallize in the triclinic space group $P\bar{1}$ with one molecule (**1**) and 3.5 molecules of toluene (**3**) in the asymmetric unit. **2** crystallizes in a monoclinic space group $C2/c$ with one-half of the molecule in the asymmetric unit. (Figures 1−3). The crystal structure analysis confirmed the different coordination modes of the PO$_3$ unit for **2** and **3**. Thus, the PO$_3$ unit is coordinated to the zinc center in **3** through the phosphorus atom, whereas, the lithium atoms in **2** are coordinated to the two oxygen atoms from the ethoxy

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(6) (a) Jancik, V.; Roesky, H. W. *Inorg. Chem.* **2005**, *44*, 5556−5558 and references cited therein. (b) Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem.* **2004**, *116*, 6318−6322; *Angew. Chem., Int. Ed.* **2004**, *43*, 6192−6196.

groups. Surprisingly, the lone electron pair is free and is also not shielded by the ligand (Figure S1 in the Supporting Information).

To the best of our knowledge, this is the only known example of the M−O−P(μ^y-O)$_2$M (y ≥ 2, M = metal) coordination pattern for the phosphite moiety in which the lone electron pair on the phosphorus atom is not involved in any interaction. In fact, there is only one record in the CSD for such a phosphite environment X−O−P(μ^y-O)$_2$X (y ≥ 2, X = any element) in Ar−O−P(μ-O)$_2$P−O−Ar (Ar = 2,6-di-^{t}Bu-4-MeC$_6$H$_2$) reported in 1987 by Chasar et al.[7] The lithium atom in **2** is coordinated to two sulfur and two oxygen atoms; however, in highly irregular shape with the angles between the atoms ranging from 67.1 (O(2)−Li(1)−O(3)) to 136.4° (O(2)−Li(1)−S(1A)). The central Li$_2$S$_2$ motif is essentially planar due to the crystallographic symmetry, but possesses unequal Li−S bond lengths (Li(1)−S(1) 2.419, Li(1)−S(1A) 2.343 Å), whereas the Li−O bond lengths are identical (2.054 and 2.056 Å) and are significantly longer than the mean value for Li−O(P) bond lengths in the CSD database (1.955 Å).[8] The molecule of **3** is formed by an unusual chain of four rings connected together in a spiro fashion through the aluminum and zinc atoms and contains two carbon-free true heterocycles S−Al−O−P−Zn formed by as many as five different elements.[9] Both S−Al−O−P−Zn rings are almost perfectly planar (sum of the inner angles is in both cases is 539.8°; the theoretical value for a five-membered ring is 540°) and are nearly perpendicular to each other with an interplanar angle of 85.5°. Because the zinc atom is shared by both of these rings, it is coordinated to two phosphorus and two sulfur atoms in a distorted tetrahedral fashion (angles between 96.2° and 128.1°). Such a coordination environment has so far been characterized by X-ray only in [2-Ph$_2$P-6-Me$_3$Si−C$_6$H$_3$S]$_2$Zn·CH$_3$CN).[10] The Al−S bond length in **1** (2.217 Å) is comparable to those in LAl(SH)$_2$ (av 2.220 Å)[3] and in LAl(SH)(μ-O)Si(OH)(O^{t}Bu)$_2$ (2.222 Å),[1] but is longer than that in **2** (2.124 Å) and in **3** (av 2.161 Å); however, longer Al−SH bond lengths have been reported for the salts LAl(SH)(Scat) (cat is cation) (2.268−2.290 Å).[6] The substitution of the SH proton in **2** and **3** led to the elongation of the Al−O bond lengths from 1.723 Å in **1** to 1.764 Å in **2** and finally to 1.768 and 1.773 Å in **3**; however, all these bonds are longer than those reported for LAl(OH)$_2$ (1.711 and 1.695 Å).[11] The Al−O bond length for **1** is comparable to the Al−O(M)bond lengths in LAl(OH)(μ-O)M(SH)Cp$_2$ (M = Ti, 1.719 Å; M = Zr, 1.713 Å).[12] Although the Al−S and Al−O bond lengths follow the same trend in **2** and **3** compared to **1**, the P−O bond lengths depend strongly on the coordination mode of the PO$_3$ unit. The coordination of the metal to the phosphorus atom leads to a slight shortening of all three P−O bonds and a less acute Al−O−P angle, but coordination of the metal to the OEt oxygen atoms has an effect only on the P−O bond lengths: AlO−P 1.564 Å (**1**), av 1.560 Å (**2**), 1.551 Å (**3**); P−OEt av 1.638 Å (**1**), av 1.650 Å (**2**), av 1.601 Å (**3**); Al−O−P 140.7° (**1**), 140.0° (**2**), av 126.2° (**3**). Selected bonds and angles for **1**−**3** are given in Table 2.

Conclusions

To sum up, we have prepared an unusual alumophosphite reagent and used it for the preparation of unprecedented heterobimetalic alumophosphites. Furthermore, the lithium salt **2** features a unique coordination mode of the phosphite unit to two metal atoms via the three oxygen donors, whereas the lone electron pair on phosphorus is free and is not shielded by the organic ligand. Thus, **2** can be used not only as a further reagent but also as a neutral ligand. Reactions to investigate these possibilities are currently underway in our laboratory.

Acknowledgment. The authors wish to thank to PAPIIT for financial support in the form of Grant IN209706. We thank the Consejo Superior de Investigationes Científicas of Spain for the license of the CSD. This article is dedicated to Prof. Ionel Haiduc on the occasion of his 70th birth anniversary.

Supporting Information Available: Figures S1 and S2 (PDF) and the details of the single-crystal X-ray structure determination of **1**−**3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. It is also available as CCDC-637667 (**1**), 637668 (**2**), 637669 (**3**) via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)-1223−336-033; or deposit@ccdc.cam.ac.uk).

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(8) The CSD database contains currently 406 records of Li−O−P units. The analysis of the Li−O(P) bond lengths from these units is shown in Figure S2 in Supporting Information as an histogram.

(9) The true heterocycle term refers to a heterocycle formed by a maximum number of different atoms. There are over 600 compounds reported in the CSD containing such a five-membered heterocycle, where one of the atoms is carbon. However, to the best of our knowledge, the CSD database contains only nine compounds with a five-membered carbon-free true heterocyclic ring. From these nine compounds, only one contains two of such rings connected in a spiro fashion: Valderrama, M.; Lahoz, F. J.; Oro, L. A.; Plou, F. J. *Inorg. Chim. Acta* **1988**, *150*, 157−163.

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(12) Jancik, V.; Roesky, H. W. *Angew. Chem.* **2005**, *117*, 6170−6172; *Angew. Chem., Int. Ed.* **2005**, *44*, 6016−6018.