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Ligand–Tetrahydrofuran Coupling in Chelated Aluminum Phosphinates

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When the reagents LAlMe (L = *N*,*N*′–(alkylene or arylene)bis(3,5-di-*tert*-butyl)salicylideneimine (alkylene = ethylene (Salen(*t*Bu)) (**1**), propylene (Salpen(*t*Bu)) (**2**), and butylene (Salben(*t*Bu)) (**3**); arylene = phenylene (Salophen(*t*Bu) (**4**), 3,4-dimethylphenylene (Salomphen(*t*Bu) (**5**)) are combined with Ph(H)P(O)OH in tetrahydrofuran (thf) the unique aluminophosphinate compounds, $[L(t\text{Bu})Al\{O_2P(H)Ph\}]_n$ with L, *n* = Salen, ∞ (**6**), Salpen, 2 (**7**), Salben, 2 (**8**), Salophen, ∞ (**9**) and Salomphen, ∞ (**10**) are produced. The yields for the latter two reactions are low, and it was subsequently found that the unique thf-coupled compounds appear in the thf filtrates of the original reaction mixture. These compounds are, $[L–thf(t\text{Bu})Al\{O_2P(H)Ph\}]_2$, L = Salophen (**13**) and Salomphen (**14**). The thf connects through an α-carbon to only one of the two possible imine carbons of the ligand. While trying to determine how this coupling proceeds, the six-coordinate, solution-state species LAlMe(thf) (L = Salophen (**11**) and Salomphen (**12**) were discovered and implicated as intermediates. All of the compounds are characterized by melting point, NMR, IR, and X-ray analyses for **5**–**8**, **13,** and **14**. A possible mechanism for the thf coupling event is presented.

Introduction

There are three general classes of compounds which possess an Al−O−P linkage: phosphates, phosphonates, and phosphinates (Figure 1). In materials chemistry, nanoporous and open-framework[1] group 13 phosphates have far-ranging applications[2] in catalysis,[3] in separations,[4] and in many other areas.[5,6] Synthetic chemistry is responsible for the majority of these materials since there are relatively few that are naturally occurring. One noteworthy example is turquoise $(CuAl_6(PO_4)_4(OH)_8{\cdot}4H_2O)$. The vast majority of these solid-state materials contain aluminum in a four-coordinate geometry. This is true, also, for molecular aluminum phosphonates that model some of the naturally occurring minerals and synthetic large-pore zeolitic materials.[7−10]

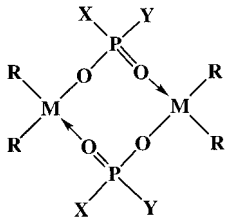

Figure 1. General representation and example of a group 13 phosphinate (X, Y = alkyl), phosphonate (*X* = alkyl; Y = alkoxide), and phosphate (X = Y = alkoxide).

Such materials containing six-coordinate aluminum are extremely rare. This coordination number may be observed, for example, in $KAl_2(PO_4)_2(OH){\cdot}nH_2O$ [11] and in phosphonate composite materials containing both an inorganic and an organic component.[12] Furthermore, there are relatively few *molecules* containing higher coordinate aluminum bound to

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either a phosphate, phosphonate, or phosphinate. Group 13 phosphinates, $[R_2MO_2P(X)(Y)]_2$ (R = alkyl; X, Y = halide, alkyl, etc.; M = Al,[13,16,18] Ga,[14−19] In,[15,16,18] Tl[18]), the most developed class of these molecular species, for example, are predominantly four-coordinate and dimeric (as shown generally in Figure 1). In a unique example, a five-coordinate aluminum atom is found in $[Al(OiPr)_2O_2P(OtBu)_2]_4$.[20]

The present work will demonstrate that molecular six-coordinate aluminum phosphinates may be readily obtained using tetradentate Salen chelate ligands. In these chelated phosphinates, $[Salen(tBu)AlO_2P(H)Ph]_n$, the degree of aggregation may be manipulated by changing the length of the ligand "backbone". This is observed, for instance, in the formation of a dimer having $n = 2$ with the ligands containing a two-carbon backbone, while polymeric compounds result when the backbone contains three or more carbon atoms between the nitrogens.

In the course of the preparation of these compounds, an unprecedented thf coupling reaction between the α-carbon of tetrahydrofuran (thf) and an imine carbon of the ligand was discovered. These reactions and the means by which they proceed will be described in the context of traditional inorganic characterization techniques including X-ray crystallography.

Results and Discussion

Six-Coordinate Aluminum Phosphinates. The combination of $AlMe_3$ with the appropriate ligand leads to the formation of the five-coordinate compounds, **1**−**5**.[21] This coordination number is evident in solution, as demonstrated by ^{27}Al NMR: the spectra of all five compounds contain a single resonance at ∼50 ppm, the appropriate region for five-coordinate aluminum. There is a structural difference in these starting materials. The Salpen(*t*Bu) and Salben(*t*Bu) derivatives are trigonal bipyramidal, and the others are square pyramidal. As a square pyramidal representative the structure of compound **5** is shown in Figure 2. Selected bond lengths and angles are listed in Table 1.

These compounds readily undergo alkane elimination reactions when combined with protic reagents. Thus, the addition of phenylphosphinic acid to **1**−**5** leads to the formation of **6**−**10** (respectively; Scheme 1). Compounds **7** and **8** feature a single ^{27}Al NMR resonance in the vicinity expected for six-coordinate aluminum (∼0 ppm). No peak could be detected for compounds **6**, **9**, and **10**, even with prolonged acquisition times on the spectrometer (48 h). This is a partial indication that these compounds are polymeric. Remarkably, however, compounds **6**−**10** were of similar solubility in organic solvents. Nevertheless, the solubility of **6**, **9**, and **10** was not sufficient to homogenize the aluminum environments.

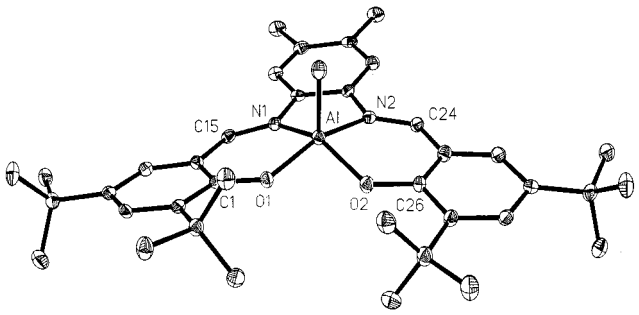

Figure 2. Molecular structure of Salomphen(*t*Bu)AlMe (**5**).

Single ^{1}H NMR resonances for the *t*Bu groups and the imine proton indicated a symmetric solution state geometry for the compounds.[22] The P−H group appeared in the range 6.66−7.30 ppm with a coupling constant of 500−550 Hz. By comparison, the phosphorus atom in phosphinates ($[O_2PR_2]^-$, R = alkyl or aryl) bridging either titanium (37.1 ppm)[22] or antimony (57.7 ppm)[23] appear more deshielded. This may be due to the presence of alkyls in these systems as opposed to the phenyl/hydride combination in **6**−**10**. Interestingly, the ^{31}P NMR resonances increased from δ 7.08 to 7.81 ppm for **6**−**8** in step with the increasing length of the backbone connection between the two nitrogens. An even more pronounced increase was observed for **9** and **10**, 7.97 and 9.16 ppm, respectively.

The mass spectral data (EI, positive) contained a highest molecular weight peak attributable to a dimer for **6**−**10**. However, the distinction between dimeric or polymeric structures in the native compounds could not be made. From past work it is clear, however, that the Salen, Salophen, and Salomphen ligands adopt planar geometries around a central metal,[21] while the Salpen and Salben ligands are more variable due to the flexibility inherent to the ligand backbone.

Through a crystallographic study of **6**−**8** the distinction between dimer and polymer for **6**−**10** could be made. Details of the study and selected bond lengths and angles are located in Tables 1 and 2, respectively. Compound **6** was found to consist of polymeric chains of −[LAl(OP{(H)Ph}O]− units (Figure 3). The −[O−Al−O−P]− backbones are not linear but curved at the O−P−O junctions with angles in the range ∼ 119.1(3)°. Adjacent ligand−*t*Bu groups are arranged in a staggered conformation to reduce steric contacts. The effect of this arrangement is to make the polymer appear as columns in the packing diagram (see figure in Supporting Information). These columns are arranged so that the *t*Bu groups point inward toward channels containing thf molecules. In this manner the structure of **6** is loosely comparable to the structures of other inorganic phosphate solid-state materials.[12]

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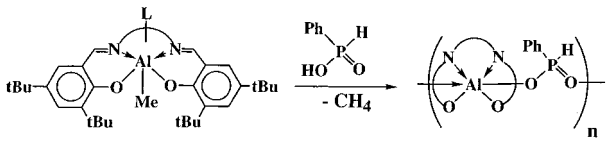
Table 1. Selected Bond Lengths and Angles for **5**−**7**, **8a**, **13**, and **14**

[Salomphen(*t*Bu)AlMe·2thf] (**5**)							
Al(1)−O(1)	1.812(3)	Al(1)−O(2)	1.811(4)	Al(1)−N(1)	2.023(4)	Al(1)−N(2)	2.038(4)
Al(1)−C(39)	1.962(5)						
O(1)−Al(1)−O(2)	89.4(2)	O(2)−Al(1)−C(39)	111.1(2)	O(1)−Al(1)−C(39)	107.5(2)	O(2)−Al(1)−N(1)	141.6(2)
O(1)−Al(1)−N(1)	88.3(2)	C(39)−Al(1)−N(1)	106.1(2)	O(2)−Al(1)−N(2)	87.5(2)	O(1)−Al(1)−N(2)	153.0(2)
C(39)−Al(1)−N(2)	98.6(2)	N(2)−Al(1)−N(1)	77.7(2)				
[Salen(*t*Bu)AlO$_2$P(H)Ph]$_\infty$ (**6**)							
Al(1)−O(1)	1.816(3)	Al(1)−O(2)	1.821(3)	Al(1)−O(3)	1.896(3)	Al(1)−O(4)	1.895(3)
Al(1)−N(1)	2.004(3)	Al(1)−N(2)	2.008(3)	P(1)−O(3)	1.444(4)	P(1)−O(4)	1.476(3)
O(1)−Al(1)−O(2)	97.8(1)	O(1)−Al(1)−O(4)	91.4(1)	O(2)−Al(1)−O(4)	92.3(1)	O(1)−Al(1)−O(3)	93.4(1)
O(2)−Al(1)−O(3)	90.5(1)	O(4)−Al(1)−O(3)	174.1(1)	O(1)−Al(1)−N(1)	90.8(1)	O(2)−Al(1)−N(1)	171.2(1)
O(4)−Al(1)−N(1)	89.6(1)	O(3)−Al(1)−N(1)	86.9(1)	O(1)−Al(1)−N(2)	170.9(1)	O(2)−Al(1)−N(2)	91.1(1)
O(4)−Al(1)−N(2)	86.1(1)	O(3)−Al(1)−N(2)	88.7(1)	N(1)−Al(1)−N(2)	80.4(1)	O(3)−P(1)−O(4)	119.1(3)
P(1)−O(3)−Al(1)	158.5(2)	P(1)−O(4)−Al(1)	160.8(3)				
[Salpen(*t*Bu)AlO$_2$P(H)Ph]$_2$ (**7**)							
Al(1)−O(2)	1.830(2)	Al(1)−O(1)	1.830(2)	Al(1)−O(4)	1.890(2)	Al(1)−O(3)	1.917(2)
Al(1)−N(2)	2.034(2)	Al(1)−N(1)	2.052(2)	P(1)−O(4)	1.507(2)	P(1)−O(3)	1.507(2)
P(1)−C(34)	1.801(2)	O(1)−C(1)	1.313(2)	O(2)−C(21)	1.316(2)	N(1)−C(15)	1.290(3)
N(1)−C(16)	1.474(3)	N(2)−C(19)	1.286(3)	N(2)−C(18)	1.478(3)		
O(2)−Al(1)−O(1)	92.09(7)	O(2)−Al(1)−O(4)	93.59(7)	O(1)−Al(1)−O(4)	90.28(7)	O(2)−Al(1)−O(3)	93.18(7)
O(1)−Al(1)−O(3)	174.68(7)	O(4)−Al(1)−O(3)	90.19(7)	O(2)−Al(1)−N(2)	90.08(7)	O(1)−Al(1)−N(2)	93.16(7)
O(4)−Al(1)−N(2)	174.87(7)	O(3)−Al(1)−N(2)	86.03(7)	O(2)−Al(1)−N(1)	174.07(7)	O(1)−Al(1)−N(1)	87.71(7)
O(4)−Al(1)−N(1)	92.33(7)	O(3)−Al(1)−N(1)	86.97(7)	N(2)−Al(1)−N(1)	84.01(7)	O(4)−P(1)−O(3)	116.81(8)
P(1)−O(3)−Al(1)	140.6(1)	P(1)−O(4)−Al(1)	140.56(9)				
[Salben(*t*Bu)AlO$_2$P(H)Ph]$_2$ (**8**)							
Al(1)−O(1)	1.835(2)	Al(1)−O(2)	1.839(2)	Al(1)−O(3)	1.890(2)	Al(1)−O(4)	1.906(2)
Al(1)−N(2)	2.061(2)	Al(1)−N(1)	2.065(2)	P(1)−O(4)	1.508(2)	P(1)−O(3)	1.512(2)
P(1)−C(35)	1.792(2)	O(1)−C(1)	1.323(3)	O(2)−C(22)	1.306(3)	N(1)−C(15)	1.289(3)
N(1)−C(16)	1.484(3)	N(2)−C(20)	1.292(3)	N(2)−C(19)	1.482(3)		
O(1)−Al(1)−O(2)	92.92(7)	O(1)−Al(1)−O(3)	89.52(7)	O(2)−Al(1)−O(3)	177.42(8)	O(1)−Al(1)−O(4)	92.81(7)
O(2)−Al(1)−O(4)	90.19(7)	O(3)−Al(1)−O(4)	90.52(7)	O(1)−Al(1)−N(2)	176.16(8)	O(2)−Al(1)−N(2)	89.32(7)
O(3)−Al(1)−N(2)	88.20(7)	O(4)−Al(1)−N(2)	90.30(7)	O(1)−Al(1)−N(1)	89.07(7)	O(2)−Al(1)−N(1)	88.13(7)
O(3)−Al(1)−N(1)	91.07(7)	O(4)−Al(1)−N(1)	177.55(8)	N(2)−Al(1)−N(1)	87.89(8)	O(4)−P(1)−O(3)	116.16(9)
P(1)−O(3)−Al(1)	132.7(1)	P(1)−O(4)−Al(1)	136.4(1)				
[Salophen(thf)(*t*Bu)AlO$_2$P(H)Ph]$_2$ (**13**)							
Al(1)−O(1)	1.835(5)	Al(1)−O(2)	1.812(5)	Al(1)−O(3)	1.860(5)	Al(1)−O(4)	1.942(5)
Al(1)−N(1)	2.100(6)	Al(1)−N(2)	2.023(6)	P(1)−O(3)	1.491(5)	P(1)−O(4)	1.494(5)
P(1)−C(37)	1.798(8)	O(1)−C(1)	1.337(9)	O(2)−C(24)	1.312(8)	N(1)−C(15)	1.51(1)
N(1)−C(16)	1.451(9)	N(2)−C(21)	1.423(9)	N(2)−C(22)	1.286(9)	O(5)−C(43)	1.43(1)
O(5)−C(46)	1.51(2)						
O(1)−Al(1)−O(2)	93.9(2)	O(2)−Al(1)−O(3)	97.8(2)	O(1)−Al(1)−O(3)	93.0(2)	O(2)−Al(1)−O(4)	93.0(2)
O(1)−Al(1)−O(4)	173.0(2)	O(3)−Al(1)−O(4)	87.0(2)	O(1)−Al(1)−N(2)	94.5(2)	O(2)−Al(1)−N(2)	90.0(2)
O(3)−Al(1)−N(2)	168.8(2)	O(4)−Al(1)−N(2)	84.6(2)	O(2)−Al(1)−N(1)	169.5(3)	O(1)−Al(1)−N(1)	90.5(2)
O(3)−Al(1)−N(1)	91.5(2)	O(4)−Al(1)−N(1)	82.6(2)	N(2)−Al(1)−N(1)	80.2(3)	O(4)−P(1)−O(3)	119.1(3)
P(1)−O(3)−Al(1)	146.8(3)	P(1)−O(4)−Al(1)	138.8(3)				
[Salomphen(thf)(*t*Bu)AlO$_2$P(H)Ph]$_2$ (**14**)							
Al(1)−O(1)	1.828(2)	Al(1)−O(2)	1.820(2)	Al(1)−O(3)	1.927(2)	Al(1)−O(4)	1.839(2)
Al(1)−N(1)	2.042(3)	Al(1)−N(2)	2.085(3)	P(1)−O(3)	1.501(2)	P(1)−O(4)	1.495(2)
P(1)−C(43)	1.793(3)	O(1)−C(1)	1.309(4)	O(2)−C(26)	1.335(4)	N(1)−C(15)	1.296(4)
N(1)−C(16)	1.424(4)	N(2)−C(23)	1.454(4)	N(2)−C(24)	1.513(4)	O(5)−C(42)	1.368(5)
O(5)−C(39)	1.444(4)						
O(2)−Al(1)−O(1)	93.1(1)	O(2)−Al(1)−O(4)	92.0(1)	O(1)−Al(1)−O(4)	95.8(1)	O(2)−Al(1)−O(3)	172.3(1)
O(1)−Al(1)−O(3)	94.5(1)	O(4)−Al(1)−O(3)	88.4(1)	O(2)−Al(1)−N(1)	95.5(1)	O(1)−Al(1)−N(1)	91.1(1)
O(4)−Al(1)−N(1)	169.6(1)	O(3)−Al(1)−N(1)	83.3(1)	O(2)−Al(1)−N(2)	89.6(1)	O(1)−Al(1)−N(2)	171.8(1)
O(4)−Al(1)−N(2)	91.9(1)	O(3)−Al(1)−N(2)	82.7(1)	N(2)−Al(1)−N(1)	80.9(1)	O(4)−P(1)−O(3)	118.6(1)
P(1)−O(3)−Al(1)	143.2(1)	P(1)−O(4)−Al(1)	151.5(1)	C(42)−O(5)−C(39)	110.8(3)		

Scheme 1. General Synthesis of Compounds **6**−**10**



n = ∞; L = Salen (6), Salophen (9), Salomphen (10)
n = 2; L = Salpen (7), Salben (8)

The structures of **7** and **8** (from either CH_2Cl_2 or toluene) were found to be dimeric (Figures 4 and 5 (for the core of **8**)). Apparently the flexible nature of the ligand backbones in these compounds allows for dimerization to occur rather than polymerization. In all three structures the aluminum atoms are in an octahedral environment. The Al−O(ligand) distances, ∼1.83 Å, are marginally shorter than the Al−O−P distances, ∼1.93 Å. These are the first structurally characterized phosphinates of aluminum but similar to the analogous Ga and In compounds which are also dimeric.[24] The bond distances in **7** and **8** are similar to that observed in an aluminum phenylphosphonate (O_3PR) with Al−O distances in the range 1.786(6)−1.951(6) Å. By comparison, these distances are just slightly shorter in derivatives containing

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Table 2

	compd **5**	compd **6**	compd **7**	compd 8	compd **13**	compd **14**
formula	$C_{47}H_{69}AlN_2O_4$	$C_{142}H_{209.5}Al_3N_6O_{19}P_3$	$C_{82}H_{116}Al_2Cl_8N_4O_8P_2$	$C_{42}H_{60}AlCl_4N_2O_4P$	$C_{50.2}H_{64.8}AlN_2O_5P$	$C_{49}H_{66}AlCl_2N_2O_5P$
fw	753.06	2478.51	1685.29	856.67	834.22	891.89
color	yellowish red	pale yellow	yellow	yellow	yellow	yellow
cryst size (mm^3)	0.05 × 0.08 × 0.25	0.25 × 0.20 × 0.18	0.40 × 0.38 × 0.28	0.24 × 0.18 × 0.16	0.24 × 0.11 × 0.11	0.34 × 0.30 × 0.18
cryst system	monoclinic	monoclinic	Triclinic	triclinic	triclinic	orthorhombic
space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Pbca
a (Å)	35.539(6)	16.6500(10)	9.3370(10)	12.101(2)	13.214(5)	21.384(2)
b (Å)	10.2870(15)	27.518(2)	16.245(2)	12.533(2)	13.480(5)	18.039(2)
c (Å)	27.986(5)	31.149(2)	16.297(2)	16.136(2)	15.347(5)	25.375(3)
α (deg)	90	90	66.953(10)	91.552(10)	109.56(3)	90
β (deg)	119.965(4)	92.280(10)	73.913(10)	106.656(10)	96.48(3)	90
γ (deg)	90	90	78.892(10)	104.090(10)	93.56(3)	90
V ($Å^3$)	8864(2)	14260.4(16)	2175.6(4)	2261.6(6)	2544.8(16)	9788.3(18)
Z	8	4	1	2	2	8
F (000)	3264	5358	892	908	983	3808
D(calcd) (g cm^{-3})	1.123	1.154	1.286	1.258	1.199	1.210
(mm^{-1})	0.087	0.124	0.370	0.357	0.121	0.229
unique data measd	5782	18627	7657	7954	5473	8617
obsd data, *n* [$F \geq 4\sigma(F)$]	4498	13676	5785	6280	3895	6777
no. of variables, *p*	489	1730	481	516	577	542
R1	0.0908	0.0765	0.0425	0.0507	0.1112	0.0747
wR2	0.2042	0.1896	0.1031	0.1179	0.3087	0.1595
S (goodness of fit)	1.12	1.04	1.03	1.04	1.13	1.11

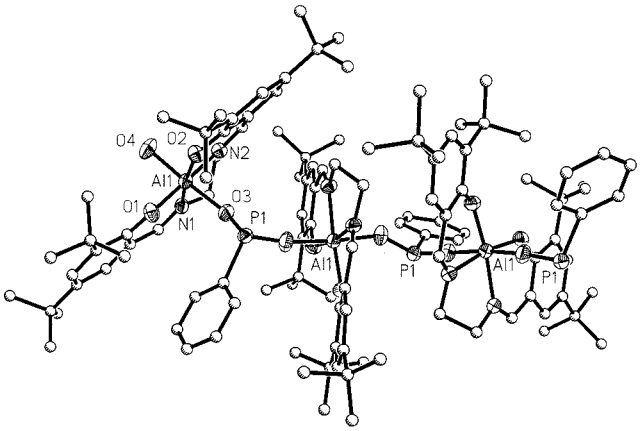

Figure 3. Molecular structure of [Salen(*t*Bu)Al{O_2P(H)Ph}]$_\infty$ (**6**).

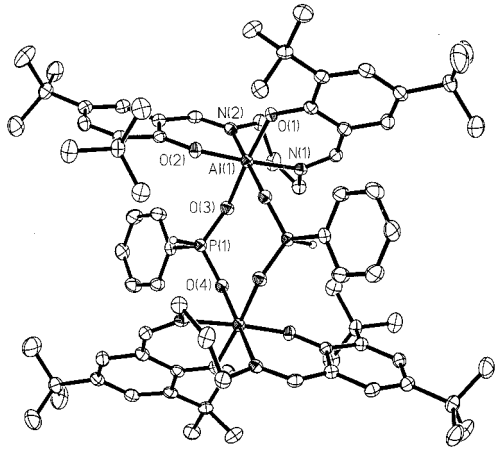

Figure 4. Molecular structure of [Salpen(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**7**).

four-coordinate aluminum such as $[Me_2AlO_2P(OtBu)_2]_2$ (Al−O ∼ 1.77 Å). The dimerization of **7** and **8** follows the precedent set with the previously reported compounds which have most often been dimeric, including, $[Me_2Al(O_2PPh_2)]_2$, first reported by Coates in 1964.[25] Although the bonding within compounds **7** and **8** are not unusual, the compounds

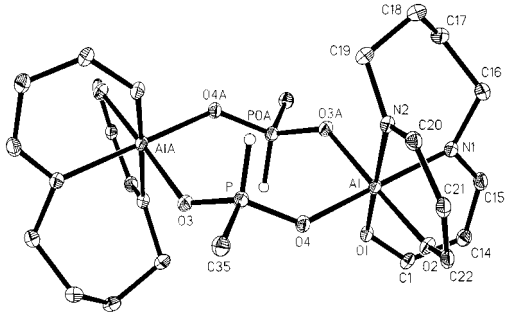

Figure 5. Molecular structure of [Salben(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**8**) emphasizing the coordination environment around the aluminum atoms.

still serve to demonstrate that molecular phosphinates of six-coordinate aluminum can be obtained.

A similar arrangement to **6** is observed in the carboxylate, $[SalenMn(O_2CPr)]_n$ while the Salpen derivative is monomeric, $SalpenMn(O_2CnBu)$.[26] Thus, both carboxylate and phosphinate follow the same general trend in oligomerization for Salen-chelated metals: for Salen, Salophen, and Salomphen, polymers are observed. With ligands having more than two carbons in the backbone, lower oligomers, either dimers (for the phosphinates) or monomers (for the carboxylates), are observed.

Thf−Salen Ligand Coupling. One of the main reasons for the popularity of the Salen ligands is the fact that they are stable under a broad range of conditions.[27] The ligands do not decompose or undergo side reactions. Indeed, the only known instances where an inorganic or organometallic compound undergoes a reaction at the ligand is in the coupling of two ligands following reduction in thf.[28−30]

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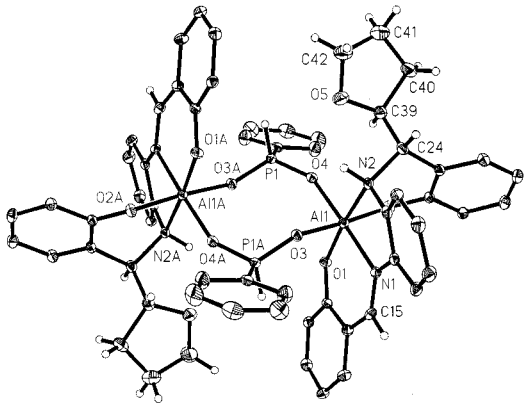

Figure 6. Molecular structure of [Salophen(thf)(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**13**).

However, it was found that when **4** or **5** are combined with phenylphosphininc acid in thf, one molecule of thf adds to the imine carbon of the ligand forming [Salophen(thf)-(*t*Bu)AlO_2P(H)Ph]$_2$ (**13**) and [Salomphen(thf)(*t*Bu)AlO_2P(H)-Ph]$_2$ (**14**). The presence of the newly formed amine linkage is signaled by a new IR resonance at ∼3260 cm^{-1}. One imine remains at ∼1620 cm^{-1}. In the ^{1}H NMR there are two sets of resonances attributable to a cyclic ether: one for free thf (1.85 and 3.76 ppm) and one for the coupled thf (broadened peaks in the ranges 1.60−1.85 and 3.50−4.60 ppm). Otherwise, the spectroscopic data for **13** and **14** are very similar to those of **6**−**10**.

X-ray analyses confirm the formulations for **13** and **14** (the two are isostructural; only **13** is shown in Figure 6). The degree of oligomerization of both compounds is no longer dictated by the nature of the ligand backbone. The increased flexibility in the ligand resulting from the thf coupling apparently allows dimerization to occur rather than polymerization, as observed for compounds **9** and **10**. Thus, the structures of **7**, **8**, **13**, and **14**, as dimers, are very similar.

The C−C bond to the coupled thf is ∼1.5 Å. The distance in the newly formed amine is lengthened (∼1.6 Å) compared to the imine. Otherwise, the structures of **7**, **8**, **13**, and **14** differ very little. Compounds **6**−**8** do not produce the thf-coupled products.

Imines have been known to undergo one or both of either C−C or C-solvent coupling. For example, both occur when *N*-benzylideneaniline is reduced with Na.[31] Furthermore, thf coupling to benzaniline occurs photolytically. In this process the thf is ionized and the resulting benzaniline radical anion couples with the thf.[32] A common feature of the literature on this reaction (and for the known Salen coupling reactions),[29−31] then, is that an anionic substrate undergoes the coupling. For **13** and **14**, however, it is not clear how an anion might be produced during the course of the reaction.

There must be an electronic consideration, however, since only those compounds having an aryl backbone produce the coupled product. Furthermore, the presence of one coupled thf is apparently sufficient to deactivate the compound to a second coupling reaction. Thus, conjugation throughout the compound must play a role. Another consideration is the fact that ^{27}Al NMR studies indicate that **4** and **5** exist as the six-coordinate thf−solvates (compounds **11** and **12**) in solution. They feature ^{27}Al resonances at 18.01 ppm ($W_{1/2}$ = 1094 Hz) and 17.06 ppm ($W_{1/2}$ = 2396 Hz), respectively. However, thf coordination (and attendant activation) is not sufficient alone, otherwise coupled products would have been observed in the now commonplace cations, [SalenAl-(base)$_2$]$^+$X$^-$ (where base = H_2O,[33] MeOH,[34] thf,[35] etc.).

To explore the possibility that protic reagents, in general, effect the thf coupling, Ph_3SiOH was employed in place of phenylphosphinic acid. It had already been demonstrated that silanol could induce alkane elimination and form compounds of the type SalenAlOSiPh_3 in toluene.[22] When this reagent is combined with **1**−**5** in thf, however, the same product is obtained.

Thus, for thf coupling to occur two components appear to be necessary: an aryl backbone on the ligand (providing an extended resonance structure and allowing the coordination of thf) and phenylphosphinic acid. Moreover, the acid is not simply a proton donor but must operate in another capacity. It is known that compounds containing a P═O bond can undergo a variety of hydrogen bonding interactions.[36−39] Additionally, the hydrogen of the α-carbon on thf is sufficiently protic to be involved in this type of interaction[40] and can be readily activated.[41] One scenario then is that the phosphinic acid serves to activate the coordinated thf through a hydrogen bonding interaction (Scheme 2b). The same interaction could be made with the imine nitrogen and the acid proton. The last step would be coupling of the thf carbanion with the ligand carbocation (Scheme 2d).

Conclusion

It has been demonstrated that six-coordinate phosphinates of aluminum can be prepared when utilizing Salen-based starting materials. These phosphinates are polymeric when the "backbone" of the ligand contains two carbon atoms (as Salen or Salophen, for example). With "backbones" containing long-chain alkanes, the resulting compounds are dimeric.

In the presence of thf the formation of these phosphinates occurs concurrently to the coupling of thf to the Salen ligand. In this coupling it appears that phosphinic acid is ideally

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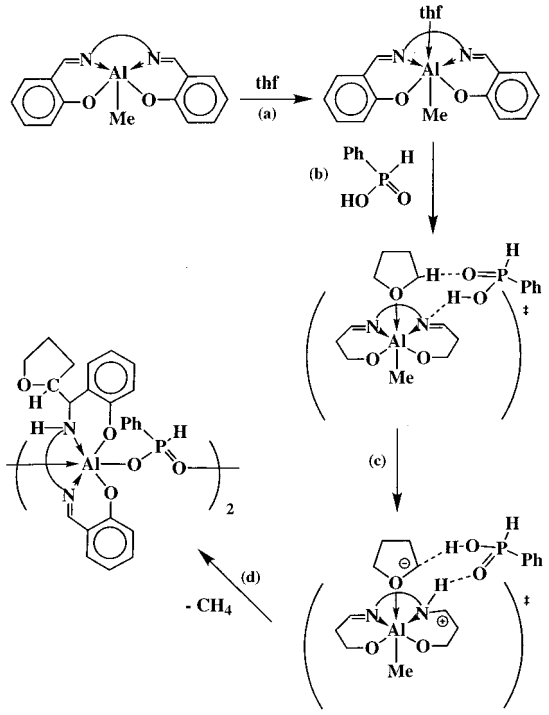
Scheme 2. General Route for the Formation of Compounds **11** and **12** (a) and a Proposed Mechanism (b, c) for the Formation of **13** and **14** (d)



suited to activate both the thf and the imine of the ligand through hydrogen bonding contacts. This is an unprecedented reaction and differs from other coupling reactions involving these ligands in that an anion or radical is not involved.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. Solvents were dried over activated alumina or iron and dispensed under pressure into the drybox prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments operating at 270.17 and 399.78 MHz and are reported relative to $SiMe_4$ and are in ppm. ^{27}Al NMR data were obtained in $CDCl_3$ at 52.1 MHz. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[42] The ligands were prepared by combining various diamines with the aldehyde following the literature precedent. The reagents, L(tBu)AlMe (L = Salen, Salpen, Salben, Salophen, and Salomphen), were prepared as described previously.[22] X-ray data were collected on a Nonius Kappa-CCD unit using Mo Kα radiation. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Further details of the structure analyses are given in Table 2.

The structures were solved using Shelxs and refined using Shelxl from the Shelx-97 program package. Molecular fragment editing, including the construction of suitable disorder models, was performed using the XP program of Siemens Shelxtl 5.0. With the exception of a few minor component atoms of some disordered groups, all non-hydrogen atoms were refined with anisotropic displacement parameters. The majority of hydrogen atoms were found in difference Fourier maps, but some belonging to disordered groups could not be found. All hydrogens were subsequently placed at calculated positions and refined using an appropriate riding model. Absorption corrections were not strictly applied, but the data-reduction program Scalepack (Otwinowski & Minor, 1997) effectively provides a satisfactory correction for the gross effects of anisotropic absorption in cases where absorption is not severe. Further details of the structure analyses are given in Table 2. The high *R*-values for these refinements are largely a consequence of poor crystal quality. This is a perennial problem for compounds of salen-type ligands, especially those that contain occluded solvent, where extensive disorder is common. In such cases the spatial quality of the fit, as obtained by the **R**-tensor (Parkin, 2000), can be invaluable in distinguishing between poor counting statistics and an inadequate model as the source of high *R*-values. For the structures presented here, the anisotropy of the fit clearly implicates poor counting statistics, which are a direct consequence of crystal quality. An X-ray analysis of compound **8** was obtained in both CH_2Cl_2 (data for **8**·2CH_2Cl_2 presented herein) and from toluene (data for **8**·toluene in Supporting Information). The dimeric aluminum-containing units of each were found to be identical.

[Salomphen(*t*Bu)AlMe]·2thf (5). Salomphen(*t*Bu)AlMe (0.500 g, 0.766 mmol) was dissolved in a mixed solution of thf (20 mL) and CH_2Cl_2 (10 mL). Storage of it at −30 °C for 1 week yielded orange needle crystals suitable for X-ray analysis. Yield: 0.487 g, 79%. Mp: 304−307 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ −1.25 (s, 3H, AlCH_3), 1.31 (s, 18H, C(CH_3)$_3$), 1.53 (s, 18H, C(CH_3)$_3$), 1.83 (m, thf), 2.34 (s, 6H, PhCH_3), 3.73 (m, thf), 7.13−7.54 (m, 6H, Ph*H*), 8.73 (s, 2H, PhC*H*). IR(KBr; ν, cm^{-1}): 2960(s), 2905(m), 2869(m), 1619(vs), 1592(m), 1559(m), 1539(s), 1520(w), 1472(m), 1387(m), 1256(m), 1202(w), 1177(s), 1089(m), 1022(m), 845(m), 788(m), 750(m).

[Salen(tBu)AlO$_2$P(H)Ph]$_\infty$ (6). To a stirring solution of Salen(*t*Bu)AlMe (0.540 g, 1.01 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.144 g, 1.01 mmol) in 20 mL of thf at −78 °C. After 3 h of stirring, the solution stand at ambient temperature overnight to yield clear and yellow crystals. Yield: 0.529 g, 79%. Mp: The color of the crystal became darker at 340 °C, and the crystal melt at 361−362 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.19 (s, 18H, C(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 3.05(br, 4H, NCH_2), 6.66 (d, $^1J_{PH}$ = 552 Hz, 1H, P*H*), 6.51, 6.70, 6.92, 7.43 (m, 9H, Ph*H*), 7.28 (s, 2H, PhC*H*). ^{31}P{^{1}H}NMR ($CDCl_3$, 80.9 MHz): δ 7.08 (s). IR(KBr; ν, cm^{-1}): 3054(w), 2954(s), 2905(m), 2867(m), 2385(w), 1656(s), 1548(m), 1536(m), 1477(m), 1462(m), 1441(s), 1416(m), 1390(m), 1335(m), 1197(s), 1171(s), 1141(m), 1080(m), 1021(w), 970(m), 875(m), 770(m), 760(m), 610(m). MS(EI, positive): 1317.7 (2.1%, Dimer$^+$), 658.3 (100%, M$^+$). Anal. Calcd: C, 69.28; H, 7.96. Found: C, 69.27; H, 8.17.

[Salpen(tBu)AlO$_2$P(H)Ph]$_2$ (7). To a stirring solution of Salpen(*t*Bu)AlMe (0.500 g, 0.91 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.129 g, 0.91 mmol) in 20 mL of thf at −78 °C. After 3 h of stirring, the thf was removed under vacuum yielding a yellow solid which was dissolved in CH_2Cl_2 (20 mL) and allowed to stand for several days at room temperature during which time yellow crystals formed. Yield: 0.450 g, 73%. Mp: >400 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.06 (s, 36H, C(CH_3)$_3$), 1.31 (s, 36H, C(CH_3)$_3$), 2.14(m, 4H, $CH_2CH_2CH_2$), 3.25, 3.49 (m, 8H, NCH_2), 7.25 (d, $^1J_{PH}$ = 556 Hz, 2H, P*H*), 6.61, 6.96, 7.20, 7.42 (m, 18H, Ph*H*), 7.91 (s, 4H, PhC*H*). ^{31}P{^{1}H}NMR ($CDCl_3$, 80.9 MHz): δ 7.24 (s). ^{27}Al NMR ($CDCl_3$, 52.1 MHz): δ 0.53 ($W_{1/2}$ = 1615 Hz). IR (KBr; ν, cm^{-1}): 3053(m), 2956(s),

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2902(s), 2867(s), 2420(w), 1632(s), 1548(s), 1536(s), 1475(s), 1462-(s), 1440(s), 1416(s), 1386(s), 1360(s), 1341(m), 1327(s), 1277-(m), 1259(s), 1234(s), 1207(s), 1172(s), 1140(s), 1087(m), 1071(s), 1018(w), 974(s), 841(m), 787(m), 750(m). MS (EI, positive): 1346.5 (8.2%, Dimer$^+$), 672.0 (9.1%, M$^+$). Anal. Calcd: C, 69.62; H, 8.09. Found: C, 69.64; H, 8.30.

[Salben(tBu)AlO$_2$P(H)Ph]$_2$ (8). Two routes were used: (1) To a stirring solution of salben(*t*Bu)AlMe (1.000 g, 1.78 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.253 g, 1.78 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 3 h. The solution was brought to room temperature slowly and stirred overnight. The thf was removed under vacuum yielding a yellow solid which was dissolved in toluene (10 mL) and refluxed for 30 min. The resulting solution was allowed to stand for 1 week during which time yellow crystals formed. Yield: 0.850 g, 69%). (2) To a stirring solution of salben-(*t*Bu)(AlMe$_2$)$_2$ (1.000 g, 1.58 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.225 g, 1.58 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 3 h. The solution was brought to room temperature slowly and stirred overnight. The thf was removed under vacuum yielding a yellow solid which was dissolved in CH_2Cl_2 (15 mL) and allowed to stand for 1 week at room temperature during which time yellow crystals formed. Yield: 0.900 g, 83%. Mp: 316−319 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ1.29 (s, 36H, C(C*H*$_3$)$_3$), 1.43 (s, 36H, C(C*H*$_3$)$_3$), 1.79 (m, 8H, C*H*$_2$), 3.61(m, 8H, C*H*$_2$), 7.15(d, $^1J_{PH}$ = 553 Hz, 2H, P*H*), 7.06, 7.18, 7.24, 7.36 (m, 18H, Ph*H*), 8.35 (s, 4H, PhC*H*). ^{31}P{^{1}H}NMR ($CDCl_3$, 80.9 MHz): δ 7.81 (s). ^{27}Al NMR ($CDCl_3$, 52.1 MHz): δ 3.10 ($W_{1/2}$ = 1824 Hz). IR (KBr; ν, cm^{-1}): 2959(s), 2910(m), 2867(m), 2424(w), 1628(s), 1554(m), 1539(m), 1476(m), 1457(m), 1438(m), 1419(m), 1360(m), 1276-(m), 1258(m), 1233(m), 1182(s), 1139(s), 1080(m), 1060(m), 1037-(w), 1022(m), 983(m), 875(m), 841(m), 787(m), 596(m). MS (EI, positive): 1372.4 (2.4%, Dimer$^+$), 686.4 (5.1%, M$^+$). Anal. Calcd: C, 69.95; H, 8.22. Found: C, 70.39; H, 8.41.

[Salophen(tBu)AlO$_2$P(H)Ph]$_\infty$ (9). To a stirring solution of salophen(*t*Bu)AlMe (1.000 g, 1.72 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.245 g, 1.72 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 24 h. The solution was brought to room temperature slowly and stirred overnight, after which the thf was filtered off to leave a yellow solid. Yield: 0.365 g (30%). Mp: melt and decomposed at 316−320 °C. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.32 (s, 18H, C(C*H*$_3$)$_3$), 1.51 (s, 18H, C(C*H*$_3$)$_3$), 6.89 (d, $^1J_{PH}$ = 511 Hz, 1H, P*H*), 6.97, 7.22, 7.46, 8.04 (m, 13H, Ph*H*), 9.06 (s, 2H, PhC*H*). ^{31}P{^{1}H}NMR (DMSO-d_6, 80.9 MHz): δ 7.97. IR (KBr; ν, cm^{-1}): 2964(s), 2903(s), 2870(m), 2387(w), 1619(s), 1586(s), 1546(s), 1532(s), 1488(m), 1473(s), 1445(m), 1414(m), 1389(s), 1359(s), 1263(m), 1238(m), 1198(s), 1175(s), 1140(s), 1111(m), 1096(m), 1070(w), 1025(w), 845(m), 788(m), 744(s), 693(m). MS (EI, positive): 1412.0 (2.0%, Dimer$^+$), 706.4 (91.8%, M$^+$). Anal. Calcd: C, 71.37; H, 7.42. Found: C, 71.36; H, 7.62.

[Salomphen(tBu)AlO$_2$P(H)Ph]$_\infty$ (10). To a stirring solution of salomphen(*t*Bu)AlMe (1.000 g, 1.64 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.233 g, 1.64 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 24 h. The solution was brought to room temperature slowly and stirred overnight, after which the thf was filtered off to leave a yellow solid. Yield: 0.484 g, 40%. Mp: melt and decomposed at 342−344 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.34 (s, 18H, C(C*H*$_3$)$_3$), 1.48 (s, 18H, C(C*H*$_3$)$_3$), 2.35(s, 6H, PhC*H*$_3$), 7.07(d, $^1J_{PH}$ = 546 Hz, 1H, P*H*), 6.95, 7.13, 7.21, 7.40, 7.58 (m, 11H, Ph*H*), 8.58 (s, 2H, PhC*H*). ^{31}P{^{1}H}NMR ($CDCl_3$, 80.9 MHz): δ 9.16. IR (KBr; ν, cm^{-1}): 3051(w), 3011(w), 2951(s), 2903(s), 2866(s), 2361(w), 2340(w), 1653(w), 1621(s), 1595(s), 1532(s), 1505(m), 1474(s), 1444(s), 1418(m), 1386(s), 1359(s), 1331(w), 1279(m), 1255(m), 1234(s), 1197(s), 1138(s), 1087(m), 1073(w), 1018(w), 1003(w), 981(s), 868(m), 847(m), 788(m), 743-(m), 693(m), 597(m), 561(m), 509(m), 419(s), 409(m). MS (EI, positive): 1468.1(2.6%, Dimer$^+$), 734.2 (100%, M$^+$). Anal. Calcd: C, 71.91; H, 7.68. Found: C, 71.46; H, 7.97.

[Salophen(thf)(tBu)AlO$_2$P(H)Ph]$_2$ (13). To a stirring solution of salophen(*t*Bu)AlMe (1.000 g, 1.72 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.245 g, 1.72 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 24 h. The solution was brought to room temperature slowly and stirred overnight, after which the thf was filtered off. For the filtered solution, the thf was removed under vacuum yielding an orange solid. It was then dissolved in toluene (15 mL) and allowed to stand for 7 days at room temperature during which time yellow crystals formed. Yield: 0.511 g, 38%. Mp: melt and decomposed at 273−277 °C. ^{1}H NMR (toluene-d_8, 200 MHz): δ 1.19 (s, 18H, C(C*H*$_3$)$_3$), 1.21 (s, 18H, C(C*H*$_3$)$_3$), 1.38 (s, 18H, C(C*H*$_3$)$_3$), 1.41 (s, 18H, C(C*H*$_3$)$_3$), 1.68−1.85 (m, 8H, thf), 3.52−4.30 (m, 8H, thf and PhC*H*(thf)), 6.38 (d, $^1J_{PH}$ = 544 Hz, 2H, P*H*), 6.30, 6.50, 6.71, 7.32 (m, 26H, Ph*H*), 8.14 (s, 2H, PhC*H*). ^{31}P{^{1}H}NMR (toluene-d_8, 80.9 MHz): δ 4.71. ^{27}Al NMR (toluene-d_8, 52.1 MHz): δ 3.08 ($W_{1/2}$ = 721.4 Hz). IR (KBr; ν, cm^{-1}): 3260-(w), 2953(s), 2903(m), 2866(m), 2361(m), 2344(m), 1621(s), 1589(m), 1534(s), 1496(s), 1438(s), 1414(m), 1388(m), 1258(m), 1215(s), 1169(s), 1142(s), 1086(m), 1072(w), 1021(m), 975(s), 842-(m), 749(M), 693(m), 668(m), 566(m). MS (MALDI-TOF, positive): 1274 (100%, [dimer − 2thf − P(H)(Ph)O$_2$]$^+$), 778 (3.0%, M$^+$), 638 (81.5%, [M − P(H)(Ph)O$_2$]$^+$). Anal. Calcd: C, 70.93; H, 7.76. Found: C, 71.41; H, 7.91.

[Salomphen(thf)(*t*Bu)AlO$_2$P(H)Ph]$_2$ (14). To a stirring solution of salomphen(*t*Bu)AlMe (1.000 g, 1.64 mmol) in thf (40 mL) was added a solution of phenylphosphinic acid (0.233 g, 1.64 mmol) in 20 mL of thf at −78 °C. The reaction was allowed to proceed at −78 °C for 24 h. The solution was brought to room temperature slowly and stirred overnight, after which the thf was filtered off. For the filtered solution, the thf was removed under vacuum yielding an orange solid. It was then dissolved in dichloromethane (10 mL) and allowed to stand for 1 day at room temperature during which time yellow crystals formed. Yield: 0.426 g, 32%. Mp: melt and decomposed at 278−280 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.18 (s, 18H, C(C*H*$_3$)$_3$), 1.20 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (s, 18H, C(C*H*$_3$)$_3$), 1.40 (s, 18H, C(C*H*$_3$)$_3$), 1.60−1.85 (m, 8H, thf), 2.09 (s, 6H, PhC*H*$_3$), 2.10 (s, 6H, PhC*H*$_3$), 3.60−4.60 (m, 8H, thf and PhC*H*-(thf)), 7.30 (d, $^1J_{PH}$ = 550 Hz, 2H, P*H*), 6.31−7.35 (m, 22H, Ph*H*), 8.38 (s, 2H, PhC*H*). ^{31}P{^{1}H}NMR ($CDCl_3$, 80.9 MHz): δ 11.59 (s). ^{27}Al NMR ($CDCl_3$, 52.1 MHz): δ 4.86 ($W_{1/2}$ = 938 Hz). IR (KBr; ν, cm^{-1}): 3264(w), 2953(s), 2904(m), 2866(m), 2378 (w), 1621(s), 1601(m), 1534(m), 1479(s), 1463(s), 1415(m), 1388(m), 1359(m), 1255(m), 1233(s), 1170(s), 1143(s), 1085(m), 1067(m), 1021(m), 1001(w), 978(m), 872(m), 807(m), 788(m), 710(m), 694-(w), 614(w), 557(m). MS (EI, positive): 1330 (2.7%, [dimer − 2thf − P(H)(Ph)O$_2$]$^+$), 807 (2.0%, M$^+$), 664 (24.0%, [M − P(H)-(Ph)O$_2$]$^+$). Anal. Calcd: C, 71.44; H, 7.99. Found: C, 71.29; H, 7.89.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic parameters for (Salomphen(*t*Bu)AlMe (**5**), [Salen(*t*Bu)Al{O_2P(H)Ph}]$_\infty$ (**6**), [Salpen(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**7**), [Salben(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**8**), [Salophen−thf(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**13**), and [Salomphen−thf(*t*Bu)Al{O_2P(H)Ph}]$_2$ (**14**). This material is available free of charge via the Internet at http://pubs.acs.org.

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