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Group 13 Cation Formation with a Potentially Tridentate Ligand

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A potentially tridentate ligand, Phensal(tBu)H_3, was prepared by the condensation of 1 equiv of phenylenediamine with 3,5-di-*tert*-butylsalicylaldehyde. When 1 equiv of this new ligand is added to $AlMe_3$, [[Phensal(tBu)HAlMe]]$_2$ (**1**) results. In contrast, this reaction with $GaMe_3$ produces [Phensal(tBu)H_2]$GaMe_2$ (**2**). When 1 or 2 equiv of Phensal(tBu)H_3 is combined with Et_2AlCl, the complex [Phensal(tBu)]$_2$AlCl (**3**) forms. However the same reaction with Me_2GaCl leads to [Phensal(tBu)H_2]Ga(Me)Cl (**4**). A cationic complex, {[Phensal(tBu)]$_2$Al}$^+$Cl$^-$ (**5**), is formed when **3** is dissolved in MeOH. The MeOH apparently mediates the formation of the cation but does not coordinate the cationic metal. When the solvent is removed, **5** reverts back to neutral **3**. When **3** is combined with $GaCl_3$ in toluene, another cationic complex, {[Phensal(tBu)H_2]$_2$Al}$^+$$GaCl_4^-$ (**6**), is formed. In a similar manner, {[Phensal(tBu)H_2]$_2$Al}$^+$$Me_2AlCl_2^-$ (**7**) is formed by adding Me_2AlCl to **3**. The compounds were characterized by mp, elemental analyses, IR, ^1H and ^{27}Al NMR, and in the case of **2**, **5**, and **6** single-crystal X-ray analysis.

Introduction

The Salen[1] class of ligands (Figure 1) have utility in the isolation of higher coordinate monometallic group 13 complexes. Some examples include those incorporating boron,[2] aluminum,[3,4] gallium,[5] and indium[6,7] and aluminum amides,[8] alkoxides,[9] siloxides,[10] and chelated higher coordinate cations.[11−15] Under appropriate conditions bimetallic compounds can also be formed.[16−18] Beyond their fundamental interest the cations have potential as initiators in the cationic oligomerization of propylene oxide.[11] More recently it has been found that lower coordinate group 13 cations are active as olefin polymerization agents.[19] This has focused attention on the possible utility of anionic single-charged ligands with two or three coordinating heteroatoms.

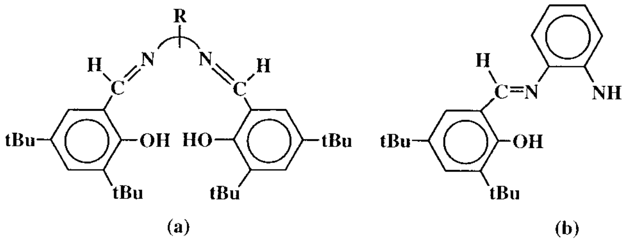

Figure 1. (a) General view of the Salen(tBu)H_2 ligands (R = *N*,*N*′-alkylene or phenylene and (b) the ligand, Phensal(tBu)H, used in this study.

Herein is presented work toward examining the reaction chemistry of three-coordinate ligands in forming cationic aluminum compounds while still taking advantage of the low cost, variability, and ease of synthesis inherent to the components that make up the Salen ligands. This will be attempted using a tridentate ligand, Phensal(tBu)H_3 (where Phensal(tBu)H = salicylidene(1-iminophenylene-2-amine)), which is similar to the Salen ligands but contains only one phenol unit (see Figure 1). Non-*tert*-butylated versions of the ligands have been used previously to prepare interesting transition metal complexes[20−23] and a few organoantimony

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[1] "Salen" is the name that has historically been used to describe the entire class of such ligands possessing various diamino backbones. However, it is also the specific name of the ethyl derivative, SalenH_2. The Salen(tBu)H_2 ligands possess tBu groups at the 4- and 6-positions of the phenol portion of the ligand.

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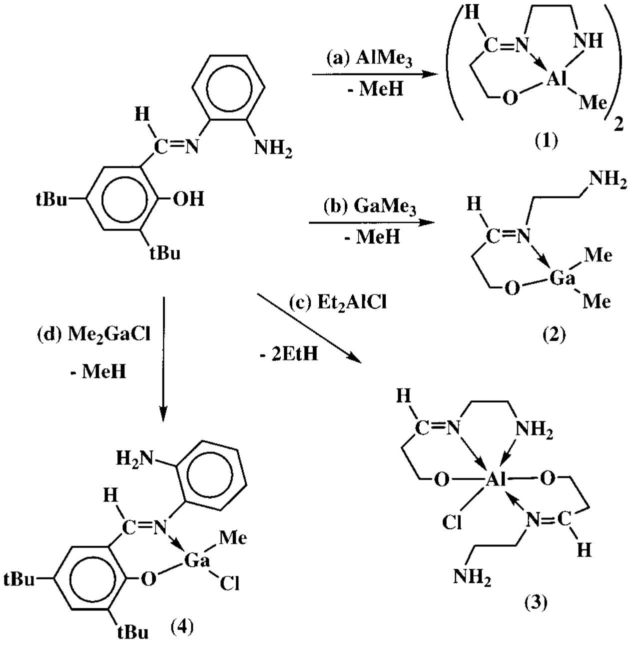
Scheme 1. General Syntheses of Compounds 1−4 (the Phensal ligand is generalized for the structure of 1 and simply named "L" in the formulas of 2 and 3)



compounds.[24] However, no group 13 complexes have yet been prepared with these ligands.

Results and Discussion

When AlMe$_3$ is mixed with Phensal(tBu)H$_3$ (Scheme 1a) 2 mol of methane are eliminated and the red-colored [[Phensal(tBu)H]AlMe]$_2$ (**1**) is formed. The ^{1}H NMR supports this formulation with an integration of 3H for the Al−Me group (δ −0.91 ppm) and 18H for the tBu groups of the ligand. The remaining NH is observed in the NMR (δ 2.85 ppm) and the IR (3332 cm^{-1}). However, the ^{27}Al NMR peak at 20 ppm is difficult to interpret. Resonances for six-coordinate aluminum generally appear at ~10 ppm, while those for four-coordinate aluminum appear at ~150 ppm.[25] The more rare five-coordinate aluminum resonances generally appear at ~100 ppm.[26] Thus, the resonance observed for **1** is best interpreted as being six-coordinate, although it is hard to visualize how this occurs since any dimerization would lead to a maximum of five-coordination.

A different product is observed when the same reaction is conducted with GaMe$_3$ (Scheme 1b). Only 1 mol of methane is lost and the product [Phensal(tBu)H$_2$]-GaMe$_2$ (**2**) results. There is one resonance for the Ga−Me groups (δ −0.28 ppm) at lower field than was observed for the Al−Me group in **1**. The NH$_2$ protons are manifested as a broad singlet in the ^{1}H NMR (δ 3.69 ppm) and as two peaks (3472 and 3388 cm^{-1}) in the IR. The crystal structure reveals that the pendant amine is oriented away from the four-coordinate, distorted tetrahedral, gallium atom (Figure 2). The Ga−C distances are equivalent (1.947 Å) and longer than the Ga−O (1.893(2) Å) and Ga−N (2.028(2) Å) distances (Table 1). Distortions from an ideal T_d geometry are observed in the O−Ga−N angle, which is more narrowed (91.30(8)°) (a common feature in bidentate ligands containing N or O), and in the C−Ga−C angle, which is more obtuse (127.4(2)°).

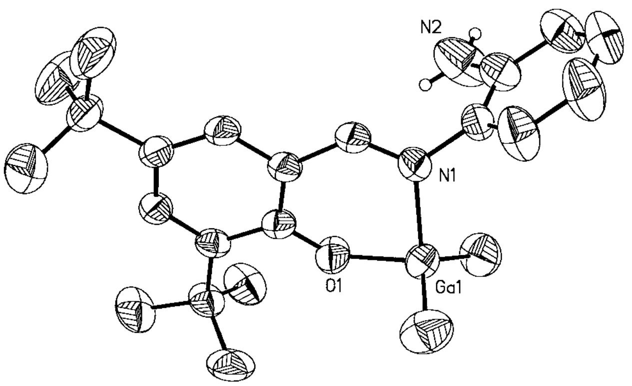


Figure 2. Molecular structure of [Phensal(tBu)H$_2$]-GaMe$_2$ (2).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Phensal(tBu)H$_2$]GaMe$_2$ (2)

Ga(1)−O(1)	1.893(2)	Ga(1)−N(1)	2.028(2)
Ga(1)−C(1)	1.947(3)	Ga(1)−C(2)	1.947(4)
O(1)−C(3)	1.316(3)	N(1)−C(9)	1.290(3)
O(1)−Ga(1)−C(1)	107.2 (1)	O(1)−Ga(1)−C(2)	109.6(1)
C(1)−Ga(1)−C(2)	127.4 (2)	O(1)−Ga(1)−N(1)	91.30(8)
C(1)−Ga(1)−N(1)	109.0 (1)	C(2)−Ga(1)−N(1)	106.4 (1)

It is more difficult to remove the second alkyl group from gallium by comparison with aluminum. This has been observed in a related compound, [SalenH]GaMe$_2$, in which the Ga−C bond coexists with a phenol proton.[27] This is not a unique occurrence. It has been demonstrated previously that the [GaMe$_2$]$^+$ fragment can remain stable in aqueous sulfuric acid.[28] Apparently, increasing the electronegativity of gallium, either by making the atom cationic or by substituting a Ga−C bond for a Ga−O bond (as occurs in **2**), has the effect of making the remaining Ga−C bonds less ionic and thereby less reactive with protic reagents. Gallium is like boron in this regard.

Combination of 2 equiv of Phensal(tBu)H with Et$_2$-AlCl in toluene leads to the formation of **3** in high yield (Scheme 1c). Interestingly, this is the product, albeit in lower yield, when the reaction is conducted in a 1:1 stoichiometry. The ^{27}Al NMR data (δ 17 ppm) was indicative of a six-coordinate geometry around aluminum. This would imply the presence of a free amine (NH$_2$) group. In fact, there are two widely spaced resonances in the ^{1}H NMR which can be attributed to these groups (δ ~3.7 and 8.0 ppm). The more deshielded resonance is assumed to be the one that is not coordinated. Moreover, the resonance at higher field corresponds closely with what is observed in the free ligand

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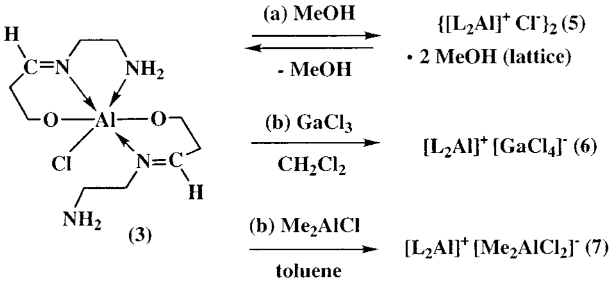
Scheme 2. Formation of the Cationic Products Starting with Compound 3



(see Experimental Section). Noncoordinated NH_2 groups are a rather rare situation when "half-unit" ligands derived from salicylaldehyde and diamines are used. For example, the only crystal structure known so far that features a free pendant NH_2 is the one found in $[PPh_4]_2$-$[Mo(CN)_3O(Ensal)]\cdot 5.5H_2O$ (where Ensal = salicylidene-(1-iminoethylene-2-amine).[29] In the other crystal structures known with similar ligands, the NH_2 groups are coordinating the metal.[30-32] Therefore, on the basis of the spectroscopic evidence and the crystal structures obtained for the derivatives **5** and **6** (see discussion below), compound **3** may be the first example of a complex showing a tridentate and bidentate coordination with the same kind of ligand. Substituting Me_2GaCl into this reaction, conducted under the same conditions, leads to the more traditional product, $[Phensal(tBu)H_2]$-$Ga(Me)Cl$ (**4**) (Scheme 1d). The Me resonance in the ^1H NMR appears as a singlet (δ −0.14 ppm), and there is no reason to suppose that the molecule is dimeric in solution.

Dissolution of **3** in MeOH leads to the formation of a compound having a six-coordinate aluminum and equivalent imine (HC=N) groups (Scheme 2a). Furthermore, removal of the solvent causes **3** to re-form, as shown by the ^1H NMR. It is likely that the compound in solution is the cation, $[\{Phensal(tBu)\}_2Al]^+ Cl^-$ (**5**). The cation **5** in CD_3OD does not show NH_2 resonances in the ^1H NMR, which might be a consequence of hydrogen bonding or due to exchange of the amine protons with deuterium of the NMR solvent. The ^{27}Al NMR data (δ 20.34 ppm) are consistent with a six-coordinate arrangement about aluminum. It definitely is six-coordinate in the solid (Figure 3).

We have previously demonstrated that group 13 cations can be formed through the base-promoted displacement of halide.[33] This occurred when the base was H_2O, MeOH, and, proving that hydrogen bonding was not critical, with $Ph_3P(O)$.[34] In these examples the added base remained on the group 13 element after departure of the halide. In **5**, however, this is not the case, and also contrasting with past results, hydrogen bonding is implicated. The MeOH must facilitate removal of the halide through hydrogen bonding. The Lewis basicity of the MeOH is not sufficient to allow it to compete for a coordination site with internal solvation of an amine. Although there is MeOH in the crystal lattice, it is not involved in hydrogen bonding with the resulting cation. Rather, there is hydrogen bonding between the chlorides and the amine groups. These organize two cations into a dimeric structure (Figure 4).

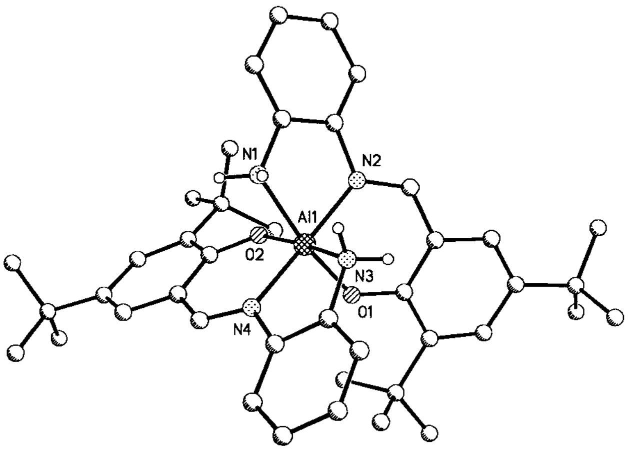


Figure 3. Molecular structure of $\{[Phensal(tBu)H_2]_2Al\}^+Cl^-$ (**5**).

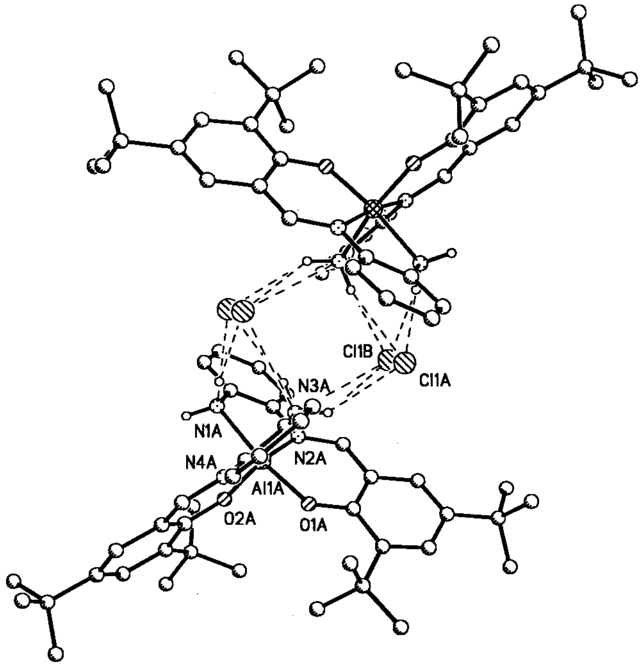


Figure 4. Dimeric structure of $\{[Phensal(tBu)H_2]_2Al\}^+Cl^-$ (**5**) resulting from hydrogen bonding (HN−H- - -Cl^-).

The chloride of **3** can be permanently displaced by the addition of $GaCl_3$ in CH_2Cl_2 (Scheme 1f). The resulting cationic complex, $[Phensal(tBu)\}Al]^+GaCl_4^-$ (**6**), still features two NH_2 resonances, but they are now more closely spaced (δ ~4.0 and 4.8 ppm). The ^{27}Al NMR confirms the six-coordinate nature of **6** in solution (δ 18 ppm). The compound is also cationic in the solid (Figure 5). The same cation can be prepared by adding Me_2AlCl to **3** to form the ion pair $[Phensal(tBu)\}Al]^+Me_2AlCl_2^-$ (**7**). This serves to demonstrate the general utility of this cation-forming reaction.

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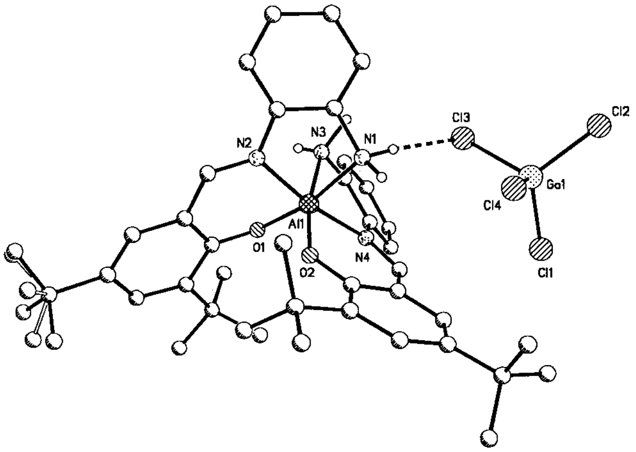

Figure 5. Molecular structure of $\{[\mathrm{Phensal(tBu)}]_2\mathrm{Al}\}^+$-$\mathrm{GaCl_4}^-$ (**6**) showing the hydrogen bonding HN−H- - -$\mathrm{ClGaCl_3}^-$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5 and 6

	5	6
Al(1)−O(1)	1.799(4)	1.804(6)
Al(1)−O(2)	1.816(5)	1.799(5)
Al(1)−N(1)	2.073(6)	2.114(8)
Al(1)−N(2)	1.961(6)	1.970(6)
Al(1)−N(3)	2.059(7)	2.061(8)
Al(1)−N(4)	1.972(6)	1.971(6)
O(1)−Al(1)−O(2)	95.6(2)	97.4(3)
N(1)−Al(1)−O(1)	171.1(2)	168.0(3)
N(1)−Al(1)−O(2)	88.3(2)	88.9(3)
N(1)−Al(1)−N(2)	80.7(2)	79.1(3)
N(1)−Al(1)−N(3)	86.9(3)	87.1(4)
N(1)−Al(1)−N(4)	94.9(2)	93.8(3)
N(2)−Al(1)−N(3)	92.3(2)	93.5(3)
N(2)−Al(1)−N(4)	171.9(3)	170.9(3)
N(2)−Al(1)−O(1)	91.0(2)	90.1(3)
N(2)−Al(1)−O(2)	95.2(2)	95.1(3)
N(3)−Al(1)−O(1)	90.3(2)	88.3(4)
N(3)−Al(1)−O(2)	170.4(2)	169.7(3)
N(4)−Al(1)−O(1)	92.9(2)	96.4(3)
N(4)−Al(1)−O(2)	91.5(2)	90.5(3)

Adequate crystals of **5** and **6** for X-ray diffraction were obtained from MeOH and CH_2Cl_2, respectively. Several crystals were coated with a dense oil (Paraton-N), and data for the best looking ones were collected at −100 °C. The final crystal structures show residual disordered solvent that adversely affects the *R* values. Additionally, **5** always produced twinned crystals, even under variable crystal growth conditions. However, the connectivity of compounds **5** and **6** is unambiguous, and no exceptional claims are being made for the bond distances or angles within the structures.

Selected bond distances and angles for compounds **5** and **6** are summarized in Table 2, and crystallographic data are presented in Table 3. Although it was not possible to obtain ideal data on crystals of these two compounds, the molecular structures of compounds **5** and **6** (Figures 3 and 4) confirm the six-coordinate environment of the aluminum atoms. The ligands are arranged in a meridional configuration about aluminum. The overall geometry around the metallic center can be described as distorted octahedral. The amine groups of the ligands are coordinated to the metal with distances in the range of 2.059(7)−2.114(8) Å, which are longer than the imine nitrogen distances, 1.961(6)−1.972(6) Å. These latter distances are similar to what is observed in the $[\mathrm{SalenAl(base)_2}]^+\mathrm{Cl}^-$. These distances are similar to what is observed in $[\{\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}_2\mathrm{Al}]^+[\mathrm{AlCl_4}]^-$ (where the distances fall in the range 1.951(9)−2.066(8) Å.[35] The oxygen distances are shorter yet, 1.799(4)−1.816(5) Å. The greater deviations from an O_h geometry in **5** and **6** are the result of the rigidity of the ligand imposed by the phenylene ring. (e.g., compound **6**: N(1)−Al(1)−O(1), 168.0(3)°, and N(3)−Al(1)−O(2), 169.7(3)°). The molecular structures of cations **5** and **6** are similar to the cationic complexes $[(\mathrm{Ensal})_2\mathrm{M}]^+\mathrm{X}^-\cdot n\mathrm{H_2O}$ (where M = Cr, Fe, Co; X = Cl, I).[14b] Coordination of the NH_2 groups is also observed in dimeric $[(1,2\text{-Pnsal})\mathrm{VO_2}]_2$ (where 1,2-Pnsal = salicylidene(1-iminopropylene-2-amine).[14c]An interesting feature in both structures is the hydrogen bonding. These bonds are made with the amine groups and the anions. In **5**, these contacts form a dimer (which contrasts with **6**, which remains monomeric).

Conclusions

New tridentate ligand complexes of aluminum were formed, three of which were cationic. It was demonstrated that one of the cations was formed through a new route: hydrogen-bond-mediated halide displacement.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. All solvents were rigorously dried 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 $SiMe_4$ in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. Mass spectral data were obtained on a Kratos CONCEPT IH instrument at 70 eV. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[36]

X-ray diffraction data were collected at 173 K on a Nonius kappa-CCD diffractometer from irregularly shaped crystals.[37] The structure(s) was solved by direct methods (SHELXS97)[38] and difference Fourier (SHELXL97) techniques. Refinement was carried out against F^2 by weighted full-matrix least-squares (SHELXL97) methods. Hydrogen atoms were either found in difference maps or placed at calculated positions, and refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.[39] The best data obtained on multiple crystals for compounds **5** and **6** were poor. Compound **5** crystallizes twinned from MeOH regardless of crystal growth conditions. Compound **6** produces weakly diffracting crystals in CH_2Cl_2. Attempts to grow X-ray quality crystals from other solvents was unsuccessful. Consequently, no undo claims are being

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Table 3. Crystallographic Data for Structurally Characterized Compounds 2, 5, and 6

	2	5	6
formula	$C_{23}H_{33}GaN_2O$	$C_{47}H_{54}AlClN_4O_7$	$C_{45}H_{59}AlCl_{13}GaN_4O_2$
fw	423.23	849.37	1245.51
cryst size (mm)	0.8 × 0.4 × 0.3	0.3 × 0.4 × 0.4	0.43 × 0.29 × 0.24
cryst syst	monoclinic	monoclinic	triclinic
a (Å)	12.540(1)	15.065(3)	12.485(1)
b (Å)	9.380(1)	18.004(4)	14.1770(1)
c (Å)	20.3240(2)	17.825(4)	17.509(1)
α (deg)	90.0	90.0	85.90(1)
β (deg)	99.77(1)	90.91(3)	84.88(1)
γ (deg)	90.0	90.0	74.33(1)
V (Å$^{3)}$	2356.0(4)	4834.07(2)	2968.4(4)
Z	4	4	2
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
D_{calc} (g/cm^3)	1.193	1.167	1.394
abs coeff (mm^{-1})	1.181	0.148	1.101
radiation, Kα; λ (Å)	Mo; 0.71073	Mo; 0.71073	Mo; 0.71073
temp (K)	173	173	173
2θ range (deg)	4.80−50.0	5.34−41.48	3.70−44.98
reflns collected	8285	8954	13 075
ind reflns	4075	4665	7590
no. of reflns used	3925 [$F > 4.0\sigma(F)$]	4653 [$F > 4.0\sigma(F)$]	7578 [$F > 4.0\sigma(F)$]
no. of params	244	545	660
R	0.0401	0.1219	0.1043
R_w	0.0894	0.2927	0.2524
GOF	1.056	1.122	1.091
electron density (e/Å^3)	0.310 and −0.224	0.434 and −0.357	1.571 and −0.804

made for the bond distances and angles within these structures; they are only presented to verify the molecular connectivity. The data are sufficient for this purpose. Spatial variation in the R value as a function of position in reciprocal space was checked by the R-tensor method.[40] For **5** the fit is noticeably anisotropic, which is consistent with twinning. This analysis indicated that the solution for **6** was correct, but the quality was reduced by the weakness of the data. Further details of the structure analyses are given in Table 3.

Preparation of Phensal(tBu)H$_3$. To a solution of phenylendiamine (5.12 g, 85.34 mmol) disolved in EtOH (100 mL) was added 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (10 g, 42.7 mmol) in EtOH (150 mL). The reaction mixture was heated to reflux for 4 h and then concentrated to ∼100 mL by distillation. Storage at −30 °C deposited yellow crystals of Phensal(tBu)H$_3$, which were filtered by suction filtration and washed twice with cold EtOH (10 mL). Yield: 12.1 g, 87%. Mp: 126−127 °C. ^{1}H NMR (199.97 MHz, CDCl$_3$): δ 1.14 [s, 9H, C(CH_3)$_3$], 1.28 [s, 9H, C(CH_3)$_3$], 3.81 [s (br), 2H, NH_2], 6.61 [m, 2H, C$_6H_4$], 6.88 [m, 2H, C$_6H_4$], 7.05 [d, 1H, C$_6H_2$], 7.25 [d, 1H, C$_6H_2$], 8.44 [s, 1H, CHN]. IR (cm^{-1}): 3487 (m), 3290 (m), 2958 (m), 2943 (m), 2909 (w), 2866 (w), 2364 (w), 2333 (w), 1615 (s), 1492 (m), 1461 (m), 1434 (m), 1392 (w), 1353 (m), 1311 (m), 1268 (m), 1245 (m), 1160 (s), 1025 (w), 975 (w), 929 (w), 875 (w), 751 (s), 685 (w), 635 (w), 574 (w). Anal. Calcd (found) for $C_{21}H_{27}N_2O$: C, 77.96 (77.84); H, 8.36 (8.41).

[[Phensal(tBu)H]AlMe]$_2$ (1). A solution of trimethylaluminum (1.11 g, 15.4 mmol) in toluene (25 mL) was added slowly at room temperature to a quickly stirred solution of Phensal(tBu)H$_3$ (5.0 g, 15.4 mmol) in toluene (150 mL). The resulting red solution was stirred for 5 h. Removal of the solvent left a red solid. The solid was washed with 10 mL of hexanes twice and then dried under vacuum to yield 3.4 g (78%). Mp: 182 °C (dec). ^{1}H NMR (CDCl$_3$): δ −0.91 [s, 3H, AlCH_3], 0.99 [s, 18H, C(CH_3)$_3$], 2.85 [s, 1H, PhNH], 6.41−7.12 [m, 6H, C$_6H_2$+C$_6H_4$], 7.99 [s, 1H, CHN]. ^{27}Al (CDCl$_3$): 20.14 ($w_{1/2}$ = 190.1 Hz). IR: 3332 (w), 3225 (w), 2977 (s), 2900 (m), 2865 (m), 1619 (s), 1614 (m), 1593 (m), 1537 (s), 1489 (m), 1464 (m), 1436 (s), 1412 (w), 1387 (m), 1362 (w), 1328 (w), 1258 (w), 1203 (m), 1169 (m), 751 (m). MS (EI$^+$): 728.7 (8%) M$^+$, 713.7 (32%) M$^+$ − CH$_3$, 671.6 (100%) M$^+$ − tBu. Anal. Calcd (Found) for $C_{22}H_{29}AlN_2O$: C, 72.50 (71.96); H, 8.02 (7.92).

[Phensal(tBu)H$_2$]GaMe$_2$ (2). A solution of trimethylgallium (1.05 g, 9.2 mmol) in toluene (15 mL) was added slowly at room temperature to a quickly stirred solution of Phensal(tBu)H (3.0 g, 9.2 mmol) in toluene (40 mL). The resulting orange solution was stirred for 5 h. Removal of the solvent left an orange solid, which was recrystallized from 30 mL of hexanes, affording adequate crystals for X-ray analysis. Yield: 3.2 g (82%). Mp: 118 °C. ^{1}H NMR (CDCl$_3$): δ −0.28 [s, 6H, GaCH_3], 1.30 [s, 9H, C(CH_3)$_3$], 1.44 [s, 9H, C(CH_3)$_3$], 3.69 [s, 2H, PhNH_2], 6.79−7.54 [m, 6H, C$_6H_2$+C$_6H_4$], 8.15 [s, 1H, CHN]. IR: 3472 (w), 3388 (m), 3004 (s), 2962 (s), 2908 (m), 2867 (m), 1624 (s), 1615 (m), 1600 (s), 1593 (m), 1535 (s), 1499 (m), 1459 (m), 1431 (m), 1386 (m), 1256 (m), 1203 (m), 1189 (m), 1165 (s), 751 (m). MS (EI$^+$): 421.3 (5%) M$^+$ − H, 407.3 (100%) M$^+$ − CH$_3$. Anal. Calcd (Found) for $C_{23}H_{33}GaN_2O$: C, 65.37 (65.21); H, 7.88 (7.92).

Preparation of [Phensal(tBu)H]$_2$AlCl (3). X-ray quality crystals of **3**, in ∼40% yield, were obtained from a reaction employing a ligand-to-metal ratio of 1:1. A higher yield preparation requires a 2:1 ligand-to-metal ratio. Accordingly, a solution of diethylaluminum chloride (2.79 g, 23.11 mmol) in toluene (25 mL) was added at room temperature to a quickly stirred solution of Phensal(tBu)H$_3$ (15.0 g, 46.23 mmol) in toluene (150 mL). The resulting yellow solution was stirred for 5 h. Removal of the solvent left a yellow-greenish powder of Phensal(tBu)AlCl, which was washed twice with hexanes (20 mL) and then dried under vacuum. Yield: 15.6 g (95%). Mp: 291−292 °C. ^{1}H NMR (CDCl$_3$): δ 0.66 [s, 18H, C(CH_3)$_3$], 1.11 [s, 18H, C(CH_3)$_3$], 3.68 [d, 2H, PhNH_2], 6.99−7.40 [m, 12H, C$_6H_2$+C$_6H_4$], 8.03 [d, 2H, PhNH_2], 8.65 [s, 2H, CHN]. ^{27}Al-{^{1}H} NMR (CDCl$_3$): δ 17.13 ($w_{1/2}$ = 198.5 Hz). The NMR spectra taken in CD$_3$OH match those for **5**. IR (cm^{-1}): 3297 (m), 2945 (s), 2341 (w), 1712 (w), 1621 (s), 1603 (s), 1497 (m), 1461 (s), 1434 (s), 1389 (s), 1358 (m), 1320 (m), 1278 (w), 1258 (s), 1176 (s), 1139 (m), 1097 (w), 1041 (w), 936 (m), 841 (m), 751 (s), 607 (m), 501 (w), 478 (w). MS (EI$^+$): 671.4 (100%) M$^+$ − Cl − 2H. Anal. Calcd (Found) for $C_{42}H_{54}AlClN_4O_2$: C, 70.93 (71.23); H, 7.96 (7.92).

[Phensal(tBu)H$_2$]GaMeCl (4). A solution of dimethylgallium chloride (1.24 g, 9.2 mmol) in toluene (15 mL) was added slowly at room temperature to a quickly stirred solution of Phensal(tBu)H$_3$ (3.0 g, 9.2 mmol) in toluene (40 mL). The resulting green solution was stirred for 5 h. Removal of the solvent left a yellow solid, which was washed several times

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with hexanes and then dried under vacuum to afford 2.8 g (69%) of **4**. Mp: 71 °C. ^{1}H NMR (CDCl$_3$): δ −0.14 [s, 3H, GaCH_3], 1.04 [s, 9H, C(CH_3)$_3$], 1.21 [s, 9H, C(CH_3)$_3$], 3.79 [s, 2H, PhNH_2], 6.57−7.38 [m, 6H, C$_6H_2$+C$_6H_4$], 8.16 [s, 1H, CHN]. IR: 3374 (w), 3336 (w), 3299 (w), 2965 (s), 2950 (m), 2936 (m), 2895 (m), 1613 (s), 1588 (s), 1537 (s), 1461 (m), 1426 (m), 1389 (m), 1251 (m), 1173 (m). MS (EI$^+$) 442.3 (10%) M$^+$, 427.2 (85%) M$^+$ − CH$_3$, 406.3 (100%) M$^+$ − HCl, 391.3 (100%) M$^+$ − HCl − CH$_3$. Anal. Calcd (Found) for C$_{22}$H$_{30}$ClGaN$_2$O: C, 59.71 (59.66); H, 6.84 (6.72).

Preparation of {[Phensal(tBu)H$_2$]$_2$Al}$^+$Cl$^-$ (5). A solution of Phensal(tBu)AlCl (0.5 g) in MeOH (20 mL) was stored at −30 °C, and after several weeks adequate crystals for X-ray analysis of {[Phensal(tBu)]$_2$Al}Cl were obtained. When the crystals are dried in a vacuum, the cation goes back to [Phensal(tBu)Al]$_2$Cl (**3**) (as determined by ^{1}H and ^{27}Al NMR in CDCl$_3$). This occurs partially on exposure to nitrogen within a drybox. ^{1}H NMR (CD$_3$OD): δ 0.90 [s, 18H, C(CH_3)$_3$], 1.25 [s, 18H, C(CH_3)$_3$], 7.21−7.93 [m, 12H, C$_6H_2$+C$_6H_4$], 9.17 [s, 2H, CHN]. ^{27}Al{^{1}H} NMR (CD$_3$OD): δ 20.34 ($w_{1/2}$ = 148.9 Hz).

Preparation of {[Phensal(tBu)]$_2$Al}$^+$GaCl$_4^-$ (6). A solution of GaCl$_3$ (0.13 g, 0.71 mmol) in CH$_2$Cl$_2$ (10 mL) was added at room temperature to a quickly stirred solution of Phensal(tBu)AlCl (0.5 g, 0.71 mmol) in CH$_2$Cl$_2$ (30 mL). The resulting orange solution was stirred for 3 h and concentrated in a vacuum to ~10 mL. Storage of the solution at −30 °C for several weeks and separation by cannula filtration afforded crystlline {[Phensal(tBu)]$_2$Al}GaCl$_4$ adequate for X-ray analysis. Yield: 0.46 g (72%). Mp: 268−271 °C. ^{1}H NMR (CDCl$_3$): δ 0.67 [s, 18H, C(CH_3)$_3$], 1.03 [s, 18H, C(CH_3)$_3$], 4.04 [d, 2H, PhNH_2], 4.78 [d, 2H, PhNH_2], 6.89−7.43 [m, 12H, C$_6H_2$+C$_6H_4$], 8.64 [d, 2H, CHN]. ^{27}Al{^{1}H} NMR (CDCl$_3$): δ 17.63 ($w_{1/2}$ = 62.52 Hz). IR (cm^{-1}): 3293 (m), 3236 (s), 2963 (s), 2908 (s), 2869 (s), 2723 (w), 2356 (w), 1822 (w), 1605 (s), 1538 (s), 1496 (s), 1462 (s), 1434 (s), 1412 (s), 1388 (s), 1361 (s), 1324 (m), 1276 (m), 1257 (s), 1229 (m), 1174 (s), 1132 (m), 1088 (m), 1027 (w), 979 (w), 927 (w), 886 (w), 847 (m), 824 (m), 787 (m), 755 (s), 726 (m), 695 (w), 620 (m). Anal. Calcd for C$_{42}$H$_{54}$AlCl$_4$GaN$_4$O$_2$: C, 71.12 (70.98); H, 7.67 (7.72).

{[Phensal(tBu)]$_2$Al}$^+$Me$_2$AlCl$_2^-$ (7). A solution of dimethylaluminum chloride (0.29 g, 3.08 mmol) in toluene (10 mL) was added at room temperature to a quickly stirred solution of Phensal(tBu)H (1.0 g, 3.08 mmol) in toluene (30 mL). The resulting yellow solution was stirred for 3 h, and the solvent was removed in vacuo. The resulting solid was washed twice with hexanes and dried under vacuum to afford 1.13 g (78%) of **7**. Mp: 176−180 °C (dec). ^{1}H NMR (CDCl$_3$): δ −0.97 [s, 6H, Al(CH_3)$_2$], 0.65 [s, 18H, C(CH_3)$_3$], 1.04 [s, 18H, C(CH_3)$_3$], 3.83 [d, 2H, PhNH_2], 6.10 [d, 2H, PhNH_2], 6.97−7.40 [3m, 12H, C$_6H_2$+C$_6H_4$], 8.62 [s, 2H, CHN]. ^{27}Al{^{1}H} NMR (CDCl$_3$): δ 16.91 ($w_{1/2}$ = 708.8 Hz); 101.08 ($w_{1/2}$ = 104.2 Hz). IR (cm^{-1}): 3289 (w), 3192 (w), 2970 (s), 2908 (m), 2873 (m), 1617 (s), 1603 (m), 1593 (s), 1537 (s), 1494 (m), 1460 (s), 1433 (s), 1361 (m), 1257 (m), 1193 (m), 1174 (s), 754 (s). Anal. Calcd (Found) for C$_{42}$H$_{54}$AlCl$_4$GaN$_4$O$_2$: C, 71.12 (71.35); H, 7.67 (7.48).

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Supporting Information Available: Crystallographic data for compounds **2**, **5**, and **6**, which includes full tables of bond lengths and angles, full atom-labeled ORTEP views, and unit cell views. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available upon request. This data may also be obtained at the Cambridge Crystallographic Database (CCDC 139436, 139437, 139438).

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