

# Monomeric Group 13 compounds with bidentate (N,O) ligands

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## Abstract

The bidentate ligand, Sal('Bu)H, is prepared by the condensation of one equivalent of a bulky amine with 3,5-di-*tert*-butylsalicylaldehyde. When one equivalent of Sal('Bu)H is added to MR<sub>3</sub> or AlMe<sub>2</sub>Cl, compounds are obtained which have the general form: [Sal('Bu)MR<sub>2</sub>] (with M/R combinations, Al/Me (1), Al/Et (3), Ga/Et (4) and In/Et (5)) and Sal('Bu)AlMeCl (2). The compounds are characterized by melting point, elemental analyses, IR, <sup>1</sup>H-NMR, and in the case of 2 and 3 by single-crystal X-ray analysis. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Aluminum; Gallium; Chelate

## 1. Introduction

It is widely recognized that many bidentate nitrogen-containing ligands form monomeric compounds with the Group 13 elements. In being monomeric and four-coordinate these compounds possess a number of similar features related to a balance of steric effects, chelate ring size, and ligand rigidity [1]. The most common derivatives may be classified into six general categories (Fig. 1 a–f), having one, (a) [2] and (b) [3–6], two, (c) [7–11] or three (d) [12] carbon atoms separating the two nitrogen atoms. For ligands with N and O heteroatoms, two (e) [1,13] and three carbon (f) [14–16] separations are most prevalent. It should be noted that the means by which these ligands take their form in combination with Group 13 elements is often subtle. For example, compounds of type (c) [8] may form through intramolecular alkyl transfer from one of the amine groups or through alkyl transfer from the incoming aluminum reagent (this is also observed in the formation of selected amidinates) [6]. Furthermore, sev-

eral of these bonding arrangements can appear in one molecule [17].

Some unique applications have emerged for these compounds including use in lactone depolymerizations [18], as reagents in the alkylation of unsaturated organic groups [19], the Pd-catalyzed alkylation of aryl substrates [20], and in light-emitting devices [16]. Recently, these compounds have been used to create cationic olefin polymerization catalysts [21].

These applications rely on a fundamental understanding of the chemistry of these compounds, in particular, their degree of association and stability under varying conditions. For aluminum, the pioneering work of Beachley on factors affecting the degree of aggregation of four-coordinate dialkylaluminum amides [7], the structural work of Atwood [22], and more recently, the systematic work of Barron on intramolecular Lewis base coordination with potential chelates [23], have provided a foundation upon which new applications may be developed.

To date, however, Ga and In have not been subjected to the same systematic treatment, although several isolated examples with these heavier congeners are known [24]. The present contribution to this area will describe new Schiff base compounds of Al, Ga, In, and an examination of their hydrolytic stability.

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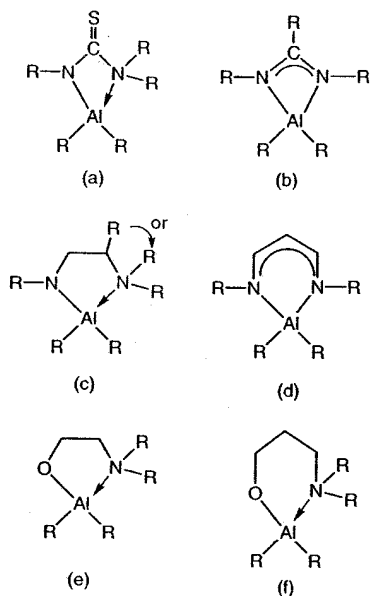
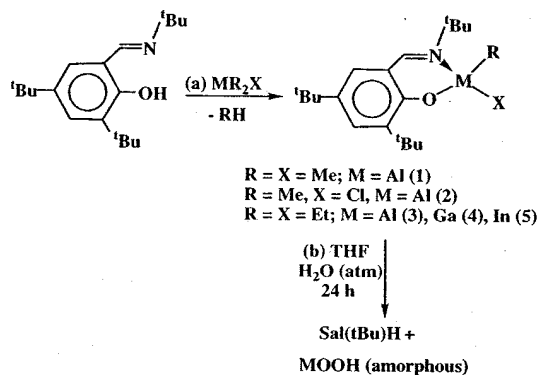


Fig. 1. Six general types of Group 13 compounds with bidentate nitrogen-containing ligands.



Scheme 1. General syntheses and hydrolyses of 1–5.

Table 1  
Selected bond distances (Å) and angles (°) for 2 and 3

Sal(tBu)Al(Me)Cl (2) (two independent molecules in the unit cell, data for only one presented)			
Al(1)–O(1)	1.750 (5)	Al(1)–N(1)	1.938 (6)
Al(1)–C(20)	1.960 (6)	Al(1)–Cl(1)	2.147 (3)
O(1)–C(7)	1.323 (7)	N(1)–C(1)	1.298 (8)
N(1)–C(16)	1.511 (8)		
O(1)–Al(1)–N(1)	97.5 (2)	O(1)–Al(1)–C(20)	112.2 (3)
N(1)–Al(1)–C(20)	117.2 (3)	O(1)–Al(1)–Cl(1)	107.9 (2)
N(1)–Al(1)–Cl(1)	106.0 (2)	C(20)–Al(1)–Cl(1)	114.5 (2)
[Sal(tBu)AlEt <sub>2</sub> ] (3)			
Al–O(1)	1.772 (1)	Al–N(1)	1.976 (2)
Al–C(22)	1.961 (2)	Al–C(20)	1.973 (2)
O(1)–C(1)	1.328 (2)	N(1)–C(15)	1.297 (2)
N(1)–C(16)	1.514 (2)		
O(1)–Al–N(1)	94.97 (6)	O(1)–Al–C(22)	107.47 (8)
O(1)–Al–C(20)	110.51 (8)	C(22)–Al–C(20)	115.61 (9)
C(22)–Al–N(1)	115.38 (8)	C(20)–Al–N(1)	110.83 (8)

## 2. Results and discussion

The reaction between a Group 13 reagent and the Sal(tBu)H ligand in toluene leads to the formation of the monomeric chelate compounds, 1–5, in good yield (Scheme 1). The <sup>1</sup>H-NMR indicates that the tBu groups on the phenol portion of the ligand for each appears in the same position. This is not true for the N-tBu group, which should be more sensitive to the changes in the nature of the metal. It appears at  $\delta$  1.42–1.53 ppm for 1–3, respectively, and  $\delta$  1.46 for the gallium derivative, 4. This serves to indicate that the relative Lewis acidity of the metals in these complexes is similar, even with the chloride present in 2. By contrast this group appears much more shielded in 5 at  $\delta$  1.39 ppm, possibly reflecting the reduced Lewis acidity of In compared to Al and Ga. This electronic effect is also observed for the imine unit. It is found in the narrow range of  $\delta$  8.22–8.38 ppm for 1–3 but more shielded at  $\delta$  8.1 ppm for 4 and 5. The Me group of 1 (–0.72 ppm) and 2 (–0.38 ppm) and the –CH<sub>2</sub> unit in 3 (–0.25 ppm) are much more shielded by comparison to the –CH<sub>2</sub> units in 4 (0.41–0.44 ppm) and 5 (0.65–0.71 ppm). This may be attributed to the greater ionic component in the Al<sup>δ+</sup>–C<sup>δ-</sup> bond by comparison to the Ga and In analogues. These negative Al–Me resonances are very similar to those observed in type (a) and (b) ( $\delta \sim -0.8$  ppm).

Selected bond distances and angles for compounds 2 and 3 are summarized in Table 1 and crystallographic data are presented in Table 2. The aluminum atoms in both compounds are in a distorted Td geometry (see Figs. 2 and 3, respectively). Distortions from ideal geometry are observed in the C–Al–Cl angle of 2 (114.5 (2)°) and 3 (115.6 (9)°). Correspondingly more acute angles are observed in the N–Al–O angles, which for 2 is 97.5 (1)° and for 3 is 94.97 (6)°. This angle in the only other structurally characterized Schiff base compound of a Group 13 element, GaMe<sub>2</sub>{OC<sub>6</sub>H<sub>4</sub>(2-iminopyridine)}, is much smaller, 90.76 (7)° [15]. The angles for 2 and 3 more closely approach the angle observed in AlMe<sub>2</sub>{OC<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6-Me-4}·N–AlMe<sub>3</sub> (94.8 (2)°) [14]. In general, this angle is somewhat flexible in chelates of types (c)–(f) (Fig. 1) and is found in the range of  $\sim 90$ – $100^\circ$ . By comparison the ligand chelate angle in amidinates, types (a) and (b), are  $\sim 70^\circ$ .

There must be a wide range of unique and interesting clusters possible from the hydrolysis of Group 13 chelates. This type of compound appears sporadically in the literature, generally stemming from the adventitious presence of oxygen or water [25]. The most widely studied compounds are those of gallium, for which definitive information has been obtained. Generally, it has been observed that gallium chelates hydrolyze through ligand elimination and the formation of stable Me<sub>2</sub>Ga-containing species (usually [Me<sub>2</sub>GaOH]<sub>3</sub>) [26].

Table 2  
Summary of X-ray data for compounds 2 and 3

Compound	Sal('Bu)Al-(Me)Cl (2)	Sal('Bu)AlEt <sub>2</sub> (3)
Color/shape	Yellow cube	Yellow rectangle
Empirical formula	C <sub>40</sub> H <sub>66</sub> N <sub>2</sub> O <sub>2</sub> Al <sub>2</sub>	C <sub>23</sub> H <sub>40</sub> NOAl
Formula weight	731.81	373.54
Temperature (K)	298	144 (1)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 <sub>1</sub> /c
Unit cell dimensions		
<i>a</i> (Å)	41.043(3)	9.096(1)
<i>b</i> (Å)	12.1369(7)	12.612(1)
<i>c</i> (Å)	29.020 (2)	21.017 (2)
$\beta$ (°)	134.965 (2)	100.90 (1)
<i>V</i> (Å <sup>3</sup> )	10228.2(11)	2367.6(4)
<i>Z</i>	8	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	0.950	1.048
Absorption coefficient (mm <sup>-1</sup> )	0.189	0.096
Diffractometer/scan	Nonius CCD	Nonius CCD
Theta range for data collection (°)	1.4–18	1.89–25.00
Reflections measured	11 762	6979
Independent reflections	3524	4159
	[ <i>R</i> <sub>int</sub> = 0.0567]	[ <i>R</i> <sub>int</sub> = 0.0250]
Data/restraints/parameters	3313/0/434	4159/0/292
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0868, <i>wR</i> <sub>2</sub> = 0.2753	<i>R</i> <sub>1</sub> = 0.0463, <i>wR</i> <sub>2</sub> = 0.1079
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1274, <i>wR</i> <sub>2</sub> = 0.3785	<i>R</i> <sub>1</sub> = 0.0693, <i>wR</i> <sub>2</sub> = 0.1188
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.084	1.018

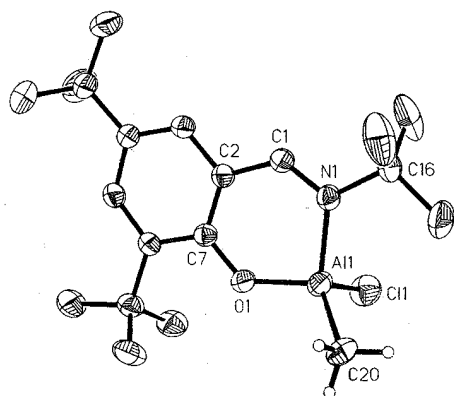


Fig. 2. ORTEP view (30%) of Sal('Bu)Al(Me)Cl (2).

In an effort to isolate stable oxygen-containing cluster compounds with Group 13 chelates the hydrolysis of 1–5 was explored. In a typical experiment a measured amount of the Group 13 chelate was dissolved in THF and then stirred open to air for 24 h. In the case of 1–3 and 5 this led to the precipitation of a pale yellow solid. This solid was washed with hexane to remove the free ligand, Sal('Bu)H. The remaining white material was then subjected to XRD and elemental analyses. The elemental analyses were consistent with the formation of metal-oxides (with low C and H

content). Initially the XRD data for the precipitates was amorphous. These results indicate that oxygen-containing cluster compounds, if formed at all in these hydrolyses, are themselves susceptible to further hydrolysis. In the case of 4 no precipitate was observed. Spectroscopic characterization of a pale yellow solid obtained after solvent removal indicated the presence of free ligand and [Et<sub>2</sub>Ga(OH)]<sub>3</sub>.

### 3. Conclusions

New monomeric chelate compounds are reported for combinations between a Schiff base ligand and Group 13 reagents containing Al, Ga and In. In the structures of the aluminum derivatives the ligand demonstrated a significant range of chelate angle indicating that these ligands may accommodate varying metal geometries. A hydrolysis study demonstrated that the aluminum and indium compounds decompose totally to free ligand and metal-oxide materials, rather than metal-oxide chelate clusters. The gallium compound decomposes to [Et<sub>2</sub>Ga(OH)]<sub>3</sub> and free ligand following the precedent for various diketonate compounds [25].

### 4. Experimental

#### 4.1. General considerations

All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glove box. 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<sub>4</sub> and are in ppm. Elemental analyses were obtained on an Elementar III Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm<sup>-1</sup>. Mass spectral data were

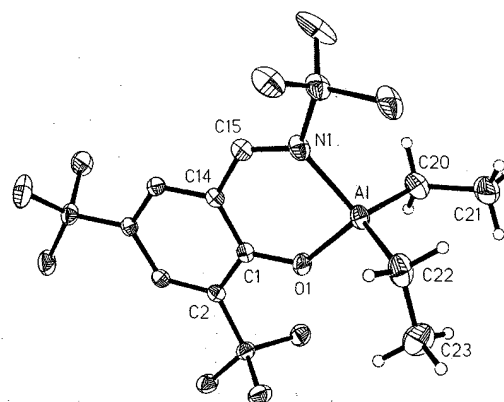


Fig. 3. ORTEP view (30%) of Sal('Bu)AlEt<sub>2</sub> (3).

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 [27].

X-ray diffraction data were collected at 298 K (**2**) and 173 K (**3**) on a Nonius kappa-CCD diffractometer from irregular-shaped crystals [28]. The structures were solved by direct methods (SHELXS-97) [29] and interpretation of difference Fourier maps (SHELXL-97). Refinement was carried out against  $F^2$  by weighted full-matrix least-squares (SHELXL-97). 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 [30]. Spatial variation in the  $R$  value as a function of position in reciprocal space was checked by the R-Tensor method [31]. The refinement of compound **2** was complicated by the presence of two molecules in the asymmetric units.

#### 4.2. Synthesis of *Sal*(*t*-Bu)AlMe<sub>2</sub> (**1**)

Trimethylaluminum (0.25 g, 3.46 mmol) in toluene (5 ml) was added to a stirred solution of *Sal*(*t*-Bu)H (1.00 g, 3.46 mmol) in toluene (15 ml). When gas evolution had ceased, the pale yellow solution was refluxed for 1 h before in vacuo removal of solvent to produce a pale yellow crystalline solid. This was recrystallized from hexane at  $-30^\circ\text{C}$  to yield the title compound as pale yellow blocks suitable for X-ray analysis (1.01 g, 85%), m.p.  $111^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ -*d*, 270 MHz,  $\delta$  ppm):  $-0.72$  (s, 6H, AlCH<sub>3</sub>); 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.40 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.49 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 6.98 (s, 1H, Ph-*H*); 7.49 (s, 1H, Ph-*H*); 8.25 (s, 1H, Ph-*CH*). IR (KBr,  $\text{cm}^{-1}$ ): 2957 (s), 2574 (m), 1614 (s), 1545 (s), 1467 (s), 1411 (m), 1363 (m), 1323 (m), 1257 (m), 1172 (s), 989 (w), 910 (w), 856 (m), 760 (m), 677 (s), 598 (m), 501 (w). Anal. Found: C, 72.86; H, 10.31; N, 3.94. Calc. C, 73.05; H, 10.44; N, 4.06%.

#### 4.3. Synthesis of *Sal*(*t*-Bu)AlMeCl (**2**)

This compound was synthesized by the same general method as that outlined above from dimethylaluminum chloride (0.48 g, 5.19 mmol) and *Sal*(*t*-Bu)H (1.50 g, 5.19 mmol) and isolated, after crystallization from hexane at  $-30^\circ\text{C}$  as large pale yellow blocks suitable for X-ray analysis (1.54 g, 81%), m.p.  $121^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ -*d*, 270 MHz,  $\delta$  ppm):  $-0.38$  (s, 3H, AlCH<sub>3</sub>); 1.31 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.42 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.58 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 7.10 (s, 1H, Ph-*H*); 7.58 (s, 1H, Ph-*H*); 8.38 (s, 1H, Ph-*CH*). IR (KBr,  $\text{cm}^{-1}$ ): 2957 (s), 2914 (m), 2872 (m), 1612 (s), 1547 (s), 1467 (m), 1411 (m), 1363 (w), 1317 (w), 1257 (m), 1176 (s), 912 (w), 864 (m), 783 (w), 671

(m), 588 (w), 507 (w), 441 (w). Anal. Found: C, 65.47; H, 8.89; N, 3.63. Calc. C, 65.67; H, 9.03; N, 3.83%.

#### 4.4. Synthesis of *Sal*(*t*-Bu)AlEt<sub>2</sub> (**3**)

Triethylaluminum (0.795 g, 6.97 mmol) in toluene (10 ml) was added to a stirred solution of *Sal*(*t*-Bu)H (2.00 g, 6.94 mmol) in toluene (30 ml). The pale yellow solution was stirred at room temperature for 30 min, allowing gas evolution to cease, then refluxed under N<sub>2</sub> for 1 h. The solvent was removed in vacuo, leaving a yellow paste. This was dissolved in hexanes and left at  $-30^\circ\text{C}$  for ca. 4 months. The product recrystallized as pale yellow blocks suitable for X-ray analysis, m.p.  $99$ – $102^\circ\text{C}$  (1.34 g, 51.9%).  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ -*d*, 200 MHz,  $\delta$  ppm):  $-0.25$  (m, 4H, AlCH<sub>2</sub>); 0.98 (t, 6H, AlCH<sub>2</sub>CH<sub>3</sub>); 1.29 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.43 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.53 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 6.91 (d, 1H, Ph-*H*); 7.21 (s,  $\text{CHCl}_3$ -*d*); 7.49 (d, 1H, Ph-*H*); 8.22 (s, 1H, HC=N). IR (KBr,  $\text{cm}^{-1}$ ): 2960 (s), 2900 (s), 2860 (s), 1615 (m), 1545 (m), 1319 (w), 1250 (m), 1173 (m), 1050 (w), 1005 (w), 960 (m), 850 (m), 790 (w), 750 (w), 640 (s), 500 (m). Anal. Found: C, 2.86; H, 2.15; N, 3.76. Calc. C, 74.2; H, 10.50; N, 3.76%.

#### 4.5. Synthesis of *Sal*(*t*-Bu)GaEt<sub>2</sub> (**4**)

This compound was synthesized by the same general method as that outlined above from triethylgallium (0.27 g, 1.73 mmol) and *Sal*(*t*-Bu)H (0.50 g, 1.73 mmol) and isolated, after crystallization from hexane at  $-30^\circ\text{C}$ , as pale yellow plates suitable for X-ray analysis (0.60 g, 83%), m.p.  $72^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ -*d*, 270 MHz,  $\delta$  ppm): 0.41–0.44 (m, 4H, GaCH<sub>2</sub>); 1.08 (t, 6H, GaCH<sub>2</sub>CH<sub>3</sub>); 1.29 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.42 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 6.85 (s, 1H, Ph-*H*); 7.43 (s, 1H, Ph-*H*); 8.15 (s, 1H, Ph-*CH*). IR (KBr,  $\text{cm}^{-1}$ ): 2957 (s), 2574 (m), 1614 (s), 1545 (s), 1467 (s), 1411 (m), 1363 (m), 1323 (m), 1257 (m), 1172 (s), 989 (w), 910 (w), 856 (m), 760 (m), 677 (s), 598 (m), 501 (w). Anal. Found: C, 66.10; H, 9.40; N, 3.40. Calc. C, 66.39; H, 9.62; N, 3.37%.

#### 4.6. Synthesis of *Sal*(*t*-Bu)InEt<sub>2</sub> (**5**)

This compound was synthesized by the same general method as that outlined above from triethylindium (0.33 g, 1.62 mmol) and *Sal*(*t*-Bu)H (0.47 g, 1.62 mmol) and isolated, after removal of solvent under reduced pressure as a pale yellow solid in stoichiometric yield, m.p.  $62^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ -*d*, 270 MHz,  $\delta$  ppm): 0.65–0.71 (m, 4H, InCH<sub>2</sub>); 1.21 (m, 6H, InCH<sub>2</sub>CH<sub>3</sub>); 1.27 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.37 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 1.39 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); 6.81 (s, 1H, Ph-*H*); 7.38 (s, 1H, Ph-*H*); 8.13 (s, 1H, Ph-*CH*). IR (KBr,  $\text{cm}^{-1}$ ): 2957 (s), 2574 (m), 1614 (s), 1545 (s), 1467 (s), 1411 (m), 1363 (m),

1323 (m), 1257 (m), 1172 (s), 989 (w), 910 (w), 856 (m), 760 (m), 677 (s), 598 (m), 501 (w). Anal. Found: C, 59.51; H, 8.38; N, 2.91. Calc. C, 59.89; H, 8.68; N, 2.91%.

#### 4.7. Hydrolysis of 1–3, 5

The hydrolyses followed the general procedure for Sal(Bu)AlMeCl (**2**): (0.67 g, 1.84 mmol) was dissolved in THF (100 ml) and allowed to stir exposed to air for 48 h. The THF was then removed under vacuum. <sup>1</sup>H-NMR data on the solid confirmed the presence of free ligand. A mass spectrum of the crude product gave a primary fragment at 289 (the free ligand has a mass of 288). The crude precipitate was washed with hexanes and filtered, leaving behind a white solid. An XRD of this solid showed it to be amorphous. In the case of **4** the hydrolysis yielded [Me<sub>2</sub>Ga(OH)]<sub>3</sub>.

#### 5. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 134947 and 134948, for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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#### References

- [1] J.A. Francis, S.G. Bott, A.R. Barron, *J. Chem. Soc. Dalton Trans.* (1998) 3305.
- [2] W. von Maringele, *Z. Anorg. Allg. Chem.* 473 (1981) 133.
- [3] J. Barker, N.C. Blacker, P.R. Phillips, N.W. Alcock, W. Errington, M.G.H. Wallbridge, *J. Chem. Soc. Dalton Trans.* (1996) 431.
- [4] M.P. Coles, D.C. Swenson, R.F. Jordan, *Organometallics* 16 (1997) 5183.
- [5] S.L. Aeilts, M.P. Coles, D.C. Swenson, R.F. Jordan, *Organometallics* 17 (1998) 3265.
- [6] M.P. Coles, D.C. Swenson, R.F. Jordan, *Organometallics* 17 (1998) 4042.
- [7] O.T. Beachley Jr., K.C. Racette, *Inorg. Chem.* 15 (1976) 2110.
- [8] E. Wissing, J.T.B.H. Jastrzebski, J. Boersma, G. van Koten, *J. Organomet. Chem.* 459 (1993) 11.
- [9] S.J. Trepanier, S. Wang, *J. Chem. Soc. Dalton Trans.* (1995) 2425.
- [10] C. Paek, S.O. Kang, J. Ko, *Organometallics* 16 (1997) 2110.
- [11] V.C. Gibson, C. Redshaw, A.J.P. White, D.J. Williams, *J. Organomet. Chem.* 550 (1998) 453.
- [12] B. Qian, D.L. Ward, M.R. Smith III, *Organometallics* 17 (1998) 3070.
- [13] C.N. McMahon, S.G. Bott, A.R. Barron, *J. Chem. Soc. Dalton Trans.* (1998) 3301.
- [14] M.P. Hogerheide, M. Wesseling, J.T.B.H. Jastrzebski, J. Boersma, H. Kooijman, A.L. Spek, G. van Koten, *Organometallics* 14 (1995) 4483.
- [15] Y.-Z. Shen, H. Gu, Y. Pan, G. Dong, T. Wu, X.-P. Jin, X.-Y. Huang, Hu, Hongwe, *J. Organomet. Chem.* 605 (2000) 234.
- [16] K.A. Higginson, X.-M. Zhang, F. Papadimitrakopoulos, *Chem. Mater.* 10 (1998) 1017.
- [17] C. Paek, S.O. Kang, J. Ko, *Organometallics* 16 (1997) 1503 (see also p. 2110).
- [18] Ph. Dubois, I. Barakat, R. Jermome, Ph. Teyssie, *Macromolecules* 26 (1993) 4407.
- [19] W. Baidossi, A. Rosenfeld, B.C. Wassermann, S. Schutte, H. Schumann, J. Blum, *Synthesis* (1996) 1127.
- [20] J. Blum, D. Gelman, W. Baidossi, E. Shakh, A. Rosenfeld, Z. Aizenshat, *J. Org. Chem.* 62 (1997) 8681.
- [21] (a) M.P. Coles, R.F. Jordan, *J. Am. Chem. Soc.* 19 (1997) 8125. (b) E. Ihara, V.G. Young, R.F. Jordan, *J. Am. Chem. Soc.* 120 (1998) 8277. (c) M. Bruce, V.C. Gibson, C. Redshaw, G.A. Solan, A.J.P. White, D. Williams, *J. Chem. Commun.* (1998) 2523.
- [22] M.J. Zaworotko, J.L. Atwood, *Inorg. Chem.* 19 (1980) 268.
- [23] (a) T. Gelbrich, E. Hecht, K.-H. Thiele, J.J. Sieler, *Organomet. Chem.* 595 (2000) 21. (b) J.A. Francis, S.G. Bott, A.R. Barron, *J. Organomet. Chem.* 597 (2000) 29. (c) J.A. Francis, N. McMahon, S.C. Bott, A.R. Barron, *Organometallics* 18 (1999) 4399. (d) C.N. McMahon, J.A. Francis, S.C. Bott, A.R. Barron, *J. Chem. Soc. Dalton Trans.* (1999) 67.
- [24] For gallium there are type (b): Y. Koide, J.A. Francis, S.G. Bott, A.R. Barron, *Polyhedron* 17 (1998) 983 and (d), (f): R.W. Chesnut, R.R. Cesati III, C.S. Cutler, S.L. Pluth, J.A. Katzenellenbogen, *Organometallics* 17 (1998) 4889.
- [25] Several unique hydrolytic products of Ga and In are reported in: S.-J. Kim, N. Yang, D.-H. Kim, S.O. Kang, J. Ko, *Organometallics*, ASAP.
- [26] R.W. Chesnut, R.R. Cesati III, C.S. Cutler, S.L. Pluth, J.A. Katzenellenbogen, *Organometallics* 17 (1998) 4889.
- [27] G. Casiraghi, G. Casnati, G. Puglia, G. Sartori, G. Terenghi, *J. Chem. Soc. Perkin Trans.* (1980) 1862.
- [28] W. Otwinowski, W. Minor, Processing of X-ray diffraction data collected in oscillation mode, in: C.W. Carter, R.M. Swet (Eds.), *Methods in Enzymology, Macromolecular Crystallography Part A*, Academic Press, New York, 1997, pp. 307–326.
- [29] G.M. Sheldrick, SHELX-97-Programs for Crystal Structure Solution and Refinement University of Göttingen, Germany, 1997.
- [30] *International Tables for Crystallography vol. C: Mathematical, Physical and Chemical Tables*, E. Prince and A.J.C. Wilson (Eds.) (1992) Kluwer, Holland.
- [31] S. Parkin, *Acta Crystallogr. A* 56 (2000) 157.