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Aluminium and gallium compounds of salicylic and anthranilic acids: examples of weak intra-molecular hydrogen bonding

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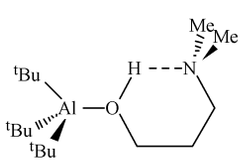
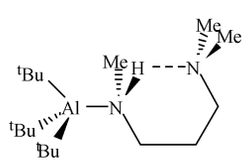
Reaction of $M(^tBu)_3$ with anthranilic, salicylic and *ortho*-toluic acids yields $[(^tBu)_2M(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$, M = Al (**1**), Ga (**2**), $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}OH)]_2$ (**3**), and $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Me)]_2$ (**4**), respectively. Reaction of anthranilic acid with two equivalents of $Al(^tBu)_3$ allows for the isolation of $(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**5**). Compounds **1**–**5** have been characterized by NMR and IR spectroscopy, mass spectrometry, and X-ray crystallography. The presence of intra-molecular hydrogen bonding, in compounds **1**–**3**, is probed by the orientation of the aromatic rings. Compound **5** is proposed to be a Lewis acid stabilized complex of the intermediate in the synthesis of compound **1**.

Introduction

We have recently become interested in the presence of strong intra-molecular hydrogen bonding of alcohol-amines (**I**) and diamines (**II**) upon coordination to a Group 13 Lewis acid.[1]



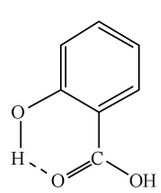
(**I**)



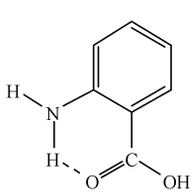
(**II**)

The increase in the hydrogen bond strength in comparison to the "free" compounds is due to a dramatic increase in the acidity of the alcohol or amine proton. We have used this "enhanced" hydrogen bonding strength to create compounds possessing desirable crystallographic architectures.[2]

Based on these results we are interested in determining if hydrogen bonding strength may be increased through activation of the Lewis base termini of the hydrogen bond (*i.e.*, X–H···*X*′), rather than the Brønsted acidic termini (*i.e.*, *X*–H···X′). In this regard, salicylic acid (**III**) and anthranilic acid (**IV**), both of which have intra-molecular hydrogen bonds in the solid state,[3,4] should offer a suitable system of study.

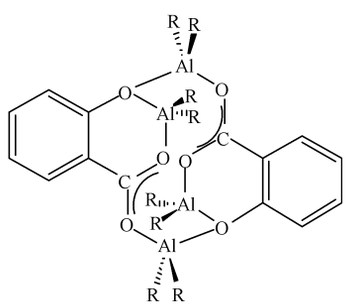


(**III**)



(**IV**)

We have previously reported that the reaction of salicylic acid with AlR_3 (R = Me, Et) yields the tetra-aluminium compound, **V**, due to the reaction of the hydroxide with additional aluminium alkyl.[5,6] We now report the synthesis and characterization of the sterically more demanding *tert*-butyl aluminium and gallium derivatives.



(**V**)

Results and discussion

The reaction of $M(^tBu)_3$ (M = Al, Ga) with one molar equivalent of the *ortho*-substituted carboxylic acids, $HO_2CC_6H_4$-2-X, yields the dimeric carboxylates, $[(^tBu)_2M(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}X)]_2$, in moderate to high yield, where X = NH_2, M = Al (**1**), Ga (**2**) and X = OH, Ga (**3**). Attempts to prepare the aluminium analog of compound **3** were unsuccessful, resulting in a complex mixture of products.

Compounds **1**–**3** have been characterized by IR and NMR spectroscopy (see Experimental section) and the spectra are consistent with the solid state structures as determined by X-ray crystallography. The molecular structures of compounds **2** and **3** are shown in Figs. 1 and 2, respectively; compound **1** is isostructural to compound **2**. Selected bond lengths and angles for compounds **1**–**3** are given in Table 1.

The structures of compounds **1**–**3** consist of centrosymmetric dimers of two $(^tBu)_2M$ units bridged by two carboxylate groups. This is consistent with previous reports of

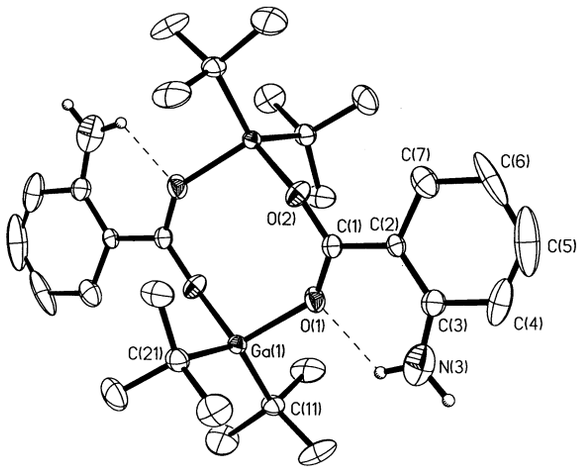


Fig. 1 Molecular structure of $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (**2**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms bound to carbon are omitted for clarity. Hydrogen bonding interactions are denoted by a dashed line.

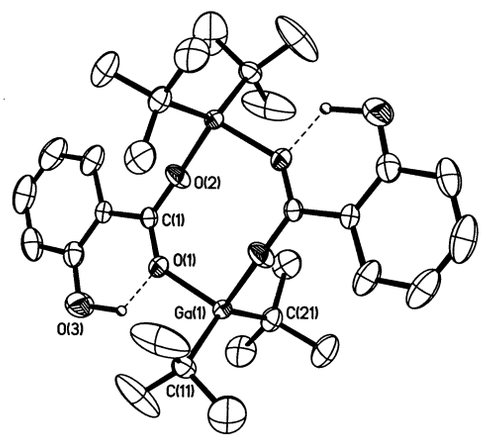


Fig. 2 Molecular structure of $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}OH)]_2$ (**3**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms bound to carbon are omitted for clarity. Hydrogen bonding interactions are denoted by a dashed line.

alkylaluminium and alkylgallium carboxylates.[7–10] The M–O bond lengths to the carboxylate ligands in these dimeric systems (Table 1) are within the range expected for aluminium [1.767(7)–1.837(6) Å][8] and gallium [1.956(7)–1.967(8) Å] carboxylates.[8,9,10,11] The carboxylate's O–C bond lengths in each compound are similar [Δ(O–C) ≈ 0.01 Å], indicative of a symmetrically bound acid group that is unaffected by the carboxylate organic substituents. The bond lengths and angles within the carboxylate unit are typical of such moieties. The ligand bite distances [M(1)···M(1a) = 4.20 Å (**1**), 4.26 Å (**2**), 4.39 Å (**3**)] are comparable to the ranges previously observed for alkylaluminium (3.26–4.18 Å)[12,13] and alkylgallium (4.35–4.68 Å)[10] carboxylates.

As may be seen from Figs. 1 and 2, the NH_2 in **2** and OH in **3** are oriented such that a hydrogen bonding interaction is possible with one of the carboxylate oxygens, O(1). The N(3)···O(1) distance in compounds **1** and **2** (2.73 and 2.72 Å, respectively) are longer than observed in the free ligand [2.688(4) and 2.682(7) Å[4]], but shorter than reported for N–H···O=C interactions (*ca.* 2.85 Å).[14] The O(3)···O(1) distance in compound **3** (2.627 Å) is the same as in the free ligand (2.620 Å).[3] Thus, based upon these distances it appears that although the intra-molecular H-bond remains intact, they are not enhanced by the presence of the Group 13 metal as compared to the free ligand.

It has been previously shown that the intra-molecular hydrogen bonding in anthranilic and salicylic acids results in a near-planar geometry of the arene and carboxylate groups (*e.g.*, the maximum deviation from planarity in salicylic acid is 0.028 Å[3]). Similarly, the phenyl substituents on the anthranilate and salicylate ligands in compounds **1**–**3** are near coplanar with the carboxylate moiety; O(1)–C(1)–C(2)–C(3) = 2.8° (**1**), 9.2° (**2**) and 2.9° (**3**). We have previously reported the molecular structures of $[(^tBu)_2M(\mu\text{-}O_2CPh)]_2$ in which the equivalent torsion angles are 5.9° and 0.12° for M = Al[8] and Ga,[9] respectively. Clearly, the presence of coplanarity within the anthranilate and salicylate ligands is not in itself an indication of the presence of intra-molecular hydrogen bonding and could be an artifact of intra-molecular steric interactions.

In an effort to ascertain the magnitude of such steric effects the molecular structure was determined for the *ortho*-toluic acid derivative, $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Me)]_2$ (**4**), see Experimental section and Table 1. As may be seen from Fig. 3, the aromatic ring is twisted away from co-planarity with the carboxylate group, *i.e.*, O(1)–C(1)–C(2)–C(3) = 42.6°. Thus, if steric factors were dominating in compounds **1**–**3**, a similar twist would be expected due to the comparable steric bulk of CH_3, NH_2 and OH groups. The planarity of the anthranilate and salicylate ligands is therefore a further indication that the orientations of the ligands are due to intra-molecular hydrogen bonding.

The IR spectra for compounds **1** and **2**, both in toluene solution and solid state, show the presence of two bands associated with the amine's ν_{N-H} stretch (*e.g.*, Fig. 4a) consistent with retention of N–H···O bonding on IR time scale. However, variable temperature solution ^1H NMR show single broad resonances [δ 5.02 (**1**) and 5.11 (**2**)], down to −115 °C, indicat-

Table 1 Selected bond lengths (Å) and angles (°) in $[(^tBu)_2M(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}X)]_2$

M X	Al NH_2 (**1**)	Ga NH_2 (**2**)	Ga OH (**3**)	Ga Me (**4**)
M(1)–O(1)	1.801(2)	1.946(3)	1.963(3)	1.966(2)
M(1)–O(2′)	1.817(2)	1.941(3)	1.938(3)	1.954(2)
M(1)–C(11)	1.991(3)	1.988(5)	1.975(4)	1.987(3)
M(1)–C(21)	1.977(3)	1.972(5)	1.968(4)	1.988(3)
O(1)–C(1)	1.261(3)	1.262(5)	1.253(5)	1.262(3)
O(2)–C(1)	1.268(3)	1.255(5)	1.244(4)	1.256(3)
O(1)–M(1)–O(2′)	109.4(1)	107.5(2)	105.2(1)	102.6(1)
O(1)–M(1)–C(11)	105.6(1)	102.1(2)	102.3(2)	102.6(1)
O(1)–M(1)–C(21)	107.2(1)	106.8(2)	105.0(2)	109.0(1)
O(2′)–M(1)–C(11)	104.0(1)	101.8(2)	102.6(2)	103.0(1)
O(2′)–M(1)–C(21)	106.0(1)	106.8(2)	107.5(2)	107.4(1)
C(11)–M(1)–C(21)	124.0(1)	130.3(2)	131.7(2)	129.3(1)

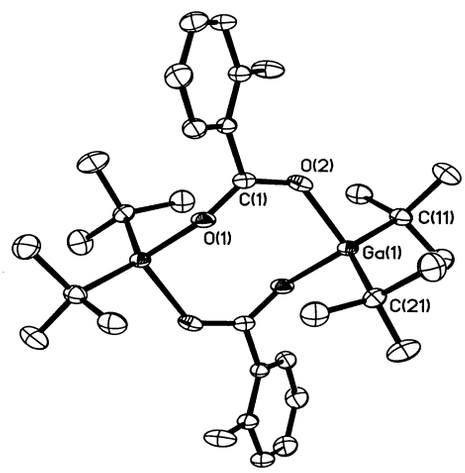


Fig. 3 Molecular structure of $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Me)]_2$ (**4**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

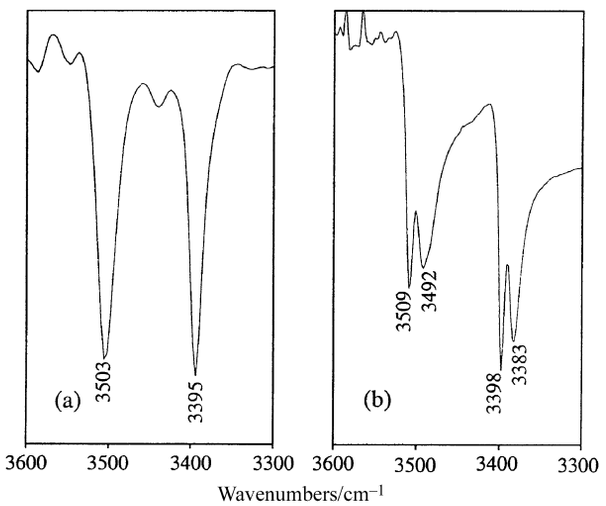


Fig. 4 IR spectra of $[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ in toluene solution (a) and the solid state (b) showing the presence of discreet hydrogen bonded and the non-hydrogen bonded N–H groups.

ing facile rotation about the C(3)–N(3) bond. Thus, we can estimate that the lifetime of the intra-molecular N–H···O bonds in compounds **1** and **2** is between 10^{-5} and 10^{-12} s. In addition, it is worth noting that in the solid state IR spectrum of compound **2** solid state splitting of the ν_{N-H} resonances is observed (see Fig. 4b) with a ν_L of 8 cm^{-1}.

The position of the O–H band in the IR spectra of compound **3** (solid and solution) shows intra-molecular hydrogen bonding to be present in both solid state (3298 cm^{-1}) and solution (3298 cm^{-1}). The ^1H NMR chemical shift of the O–*H* peak is found to be temperature dependent, suggesting fluxionality on the NMR time scale. However, no asymptote was reached down to −115 °C.

In conclusion, we have found that the intra-molecular hydrogen bonds in the anthranilate and salicylate ligands remain present in the Group 13 compounds. However, complexation of a Group 13 metal to the donor (*i.e.*, O–H···*X*–M; where X = N, O) does not appear to enhance the strength of the hydrogen bond as it does when complexed to the acceptor (*i.e.*, M–*O*–H···X). We note, however, that the presence of hydrogen bonding in the anthranilate complex $[Me_2In(O_2CC_6H_4\text{-}2\text{-}NH_2)]_\infty$,[15] leads to a decrease in the indium coordination number as compared to the acetate complex.[16]

Reaction of $Al(^tBu)_3$ with anthranilic acid in a 2 : 1 ratio yields the dialuminium compound, $(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**5**), see Experimental. The molecular structure of compound **5** has been determined by X-ray crystallography (Fig. 5); selected bond lengths and angles are given in Table 2. The Al(2)–O(2) [1.896(2) Å] is slightly longer than Al(1)–O(1) [1.822(2) Å] consistent with the difference in bonding to a neutral $Al(^tBu)_3$ *versus* a cationic $Al(^tBu)_2$ moiety. The Al(1)–N(1) distance [2.003(3) Å] is within the range expected for amine complexes of aluminium (1.94–2.10 Å).[17]

Based upon the isolation of compound **5**, and its conversion to compound **1** during physical grinding (see Experimental section), we propose that the formation of compounds **1** and **2** (and possibly **3**) occurs *via* a chelate species, $(^tBu)_2M(O_2CC_6H_4\text{-}2\text{-}X)$ (**VI**).

The related chelate complexes **VII**[18] and **VIII**[19] have been reported in which the **VI**-like structure is stabilized by an extended hydrogen bond network rather than Lewis acid–base interaction, as we observe in compound **5**.

We have previously demonstrated that, although the chelate binding (**IX**) of a carboxylate to aluminium (or gallium) is highly disfavored (*ca.* 130 kJ mol^{-1}) as compared to bridging (**X**), it is favored (*ca.* 75 kJ mol^{-1}) over the monodentate modes [*i.e.*, eclipsed and staggered (**XI**)].

Table 2 Selected bond lengths (Å) and angles (°) for $(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**5**)

Al(1)–O(1)	1.822(2)	Al(1)–N(1)	2.003(3)
Al(1)–C(11)	1.960(4)	Al(1)–C(21)	1.958(3)
Al(2)–O(2)	1.896(2)	Al(2)–C(31)	2.021(3)
Al(2)–C(41)	2.005(4)	Al(2)–C(51)	2.001(3)
O(1)–C(1)	1.270(3)	O(2)–C(1)	1.250(3)
O(1)–Al(1)–N(1)	89.1(1)	O(1)–Al(1)–C(11)	113.1(1)
O(1)–Al(1)–C(21)	108.9(1)	N(1)–Al(1)–C(11)	108.6(1)
N(1)–Al(1)–C(21)	107.8(1)	C(11)–Al(1)–C(21)	123.7(2)
O(2)–Al(2)–C(31)	98.3(1)	O(2)–Al(2)–C(41)	106.0(1)
O(2)–Al(2)–C(51)	104.6(1)	C(31)–Al(2)–C(41)	115.0(2)
C(31)–Al(2)–C(51)	114.9(2)	C(41)–Al(2)–C(51)	115.4(2)

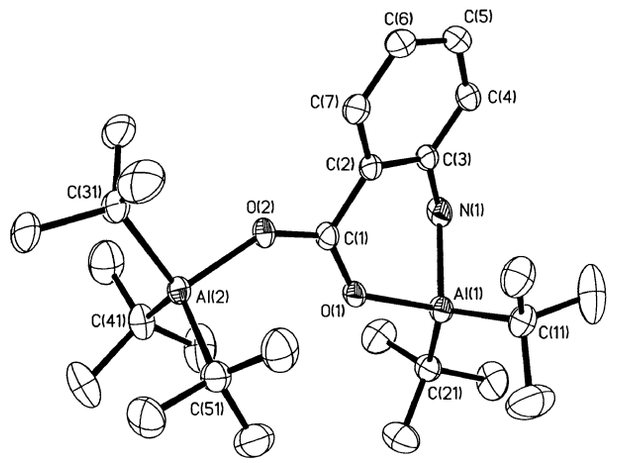
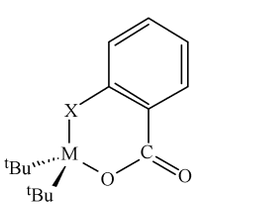
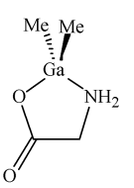


Fig. 5 Molecular structure of $(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**5**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

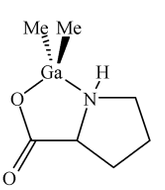


M = Al, X = NH_2: M = Ga, X = OH, NH_2

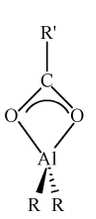
(**VI**)



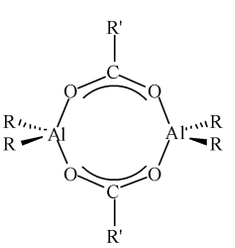
(**VII**)



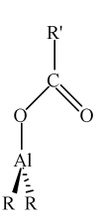
(**VIII**)



(**IX**)



(**X**)



(**XI**)

In the present case, the Lewis base substituents (OH or NH_2) in the *ortho* position on the phenyl ring provide an alternative stabilization to the monomeric derivatives. The stability of **VI** will be dependent on the strength of the M–X interaction.

Based upon known Lewis acid–base bond strength for aluminium alkyls, the interaction is expected to be *ca.* 80 kJ mol^{-1} for X = OH and *ca.* 125 kJ mol^{-1} for X = NH_2. The greater stability of the anthranilate complex (**VI** where X = NH_2) presumably is such to allow **VI** to be "trapped" by the presence of an excess of Al(^{t}Bu)$_3$ and thus forming compound **5**. In contrast, the similarity in stabilization for salicilate between the chelate carboxylate (**IX**) and chelation *via* the hydroxide (**VI** where X = OH), as well as the greater acidity of the hydroxide, may explain the observation that a complex mixture of products is obtained with the reaction of salicylic acid with either an equimolar equivalent or excess of Al(^{t}Bu)$_3$.

Experimental

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400 cm^{-1}) were obtained using an Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as either Nujol mulls between KBr plates or toluene solution (0.1 mM). Due to the partial conversion of compound **5** to compound **1** upon mechanical grinding required for KBr sample preparation, the IR spectrum of compound **5** was determined by a computer subtraction of a reference spectrum of compound **1**. NMR spectra were obtained on Bruker AM-250 and Avance 400 spectrometers using d_8-toluene solutions. Chemical shifts are reported relative to internal solvent resonances. The synthesis of Al(^{t}Bu)$_3$ and Ga(^{t}Bu)$_3$ were performed according to literature methods.[20,21] Salicylic and anthranilic acids were obtained from Aldrich and used without further purification.

[(^{t}Bu)$_2$Al(μ-$O_2CC_6H_4$-2-NH_2)]$_2$ (1)

To a toluene (40 mL) slurry of anthranilic acid (0.693 g, 5.05 mmol) at −78 °C was added Al(^{t}Bu)$_3$ (1.0 g, 5.05 mmol). The yellow reaction mixture was allowed to warm to room temperature and then to stir for three hours. The solution was filtered and placed in a freezer, yielding yellow crystals. Yield: 70%. Mp: 170 °C (decomp.). Anal. (%, calc.): C, 64.9 (64.9); H, 8.58 (8.72); N, 4.29 (5.05). MS (EI,%): *m/z* 497 ($2M^+ - {}^t$Bu, 35), 439 ($2M^+ - 2\ {}^t$Bu − H, 52), 277 (M^+, 10), 220 ($M^+ - {}^t$Bu, 35), 120 ($O_2CC_6H_4$, 30). IR (cm^{-1}): 3513 (w), 3411 (w), 1629 (m), 1577 (m), 1545 (m), 1419 (w), 1301 (w), 1163 (w), 1010 (w), 973 (w), 722 (w), 543 (s). ^{1}H NMR: *δ* 8.19 [2H, dd, *J*(H–H) = 9.1 Hz, *J*(H–H) = 1.7 Hz, 6-C*H*], 6.92 [2H, ddd, *J*(H–H) = 8.4 Hz, *J*(H–H) = 7.2 Hz, *J*(H–H) = 1.5 Hz, 4-C*H*], 6.44 [2H, ddd, *J*(H–H) = 8.2 Hz, *J*(H–H) = 7.0 Hz, *J*(H–H) = 1.1 Hz, 5-C*H*], 6.03 [2H, dd, *J*(H–H) = 8.6 Hz, *J*(H–H) = 0.9 Hz, 3-C*H*], 5.02 (2H, s, NH_2), 1.20 [36H, s, C(CH_3)$_3$]. ^{13}C NMR: *δ* 175.4 (O_2C), 152.5 (1-*C*), 133.6 (2-*C*), 121.5 (6-*C*H), 117.8 (4-*C*H), 117.2 (5-*C*H), 109.8 (3-*C*H), 30.3 [C(*C*H_3)$_3$].

[(^{t}Bu)$_2$Ga(μ-$O_2CC_6H_4$-2-NH_2)]$_2$ (2)

To a toluene (40 mL) solution of anthranilic acid (1.93 g, 7.03 mmol) at −78 °C was added Ga(^{t}Bu)$_3$ (3.40 g, 7.03 mmol). The bright yellow reaction mixture was allowed to warm to room temperature and then to stir for three hours. The solution was filtered and placed in a freezer, yielding yellow crystals. Yield: 60%. Mp: 243 °C (decomp.). Anal. (%, calc.): C, 55.8 (56.3); H, 7.53 (7.56); N, 3.67 (4.38). MS (EI): *m/z* 319 (M^+, 10), 262 ($M^+ - {}^t$Bu, 50), 205 ($M^+ - 2\ {}^t$Bu, 12), 120 ($O_2CC_6H_4$, 100), 92 ($C_6H_4NH_2$, 15), 69 (Ga, 25), 57 (^{t}Bu, 85). IR (cm^{-1}): 3509 (m), 3492 (m), 3398 (m), 3383 (m), 1623 (s), 1580 (s), 1536 (s), 1305 (s), 1255 (s), 1163 (m), 1020 (w), 985 (w), 825 (w), 499 (s). ^{1}H NMR: *δ* 8.25 [2H, dd, *J*(H–H) = 8.1 Hz, *J*(H–H) = 1.5 Hz, 6-C*H*], 6.99 [2H, ddd, *J*(H–H) = 8.4 Hz, *J*(H–H) = 6.9 Hz, *J*(H–H) = 1.6 Hz, 4-C*H*], 6.54 [2H, ddd, *J*(H–H) = 8.1 Hz, *J*(H–H) = 7.1 Hz, *J*(H–H) = 1.0 Hz, 5-C*H*], 6.15 [2H, dd, *J*(H–H) = 8.3 Hz, *J*(H–H) = 0.7 Hz, 3-C*H*], 5.11 (4H, s, NH_2), 1.27 [36H, s, C(CH_3)$_3$]. ^{13}C NMR: *δ* 179.7 (O_2C), 151.3 (1-*C*), 135.3 (2-*C*), 133.3 (6-*C*H), 117.4 (4-*C*H), 116.8 (5-*C*H), 113.2 (3-*C*H), 30.3 (*C*H_3), 25.0 [C(*C*H_3)$_3$].

[(^{t}Bu)$_2$Ga(μ-$O_2CC_6H_4$-2-OH)]$_2$ (3)

To a toluene (40 mL) solution of salicylic acid (1.12 g, 4.04 mmol) at −78 °C was added Ga(^{t}Bu)$_3$ (1.95 g, 4.04 mmol). The clear reaction mixture was allowed to warm to room temperature and then to stir for three hours. The solution was filtered and placed in a freezer, yielding colorless crystals. Yield: 50%. Mp: 150 °C (decomp.). Anal. (%, calc.): C, 55.6 (56.1); H, 6.96 (7.22). MS (EI): *m/z* 320 (M^+, 10), 263 ($M^+ - {}^t$Bu, 38), 206 ($M^+ - 2\ {}^t$Bu, 10), 189 [Ga($O_2CC_6H_4$), 72], 69 (Ga, 28), 57 (^{t}Bu, 100). IR (cm^{-1}): 3324 (w), 3180 (w), 3078 (w), 1613 (s), 1567 (w), 1526 (w), 1398 (s), 1250 (s), 1165 (w), 1147 (m), 1034 (w), 896 (w), 866 (w), 850 (w), 825 (w), 758 (m), 712 (w), 681 (w), 543 (s). ^{1}H NMR: *δ* 10.26 (2H, s, O*H*), 8.04 [2H, d, *J*(H–H) = 6.6 Hz, 6-C*H*], 7.03 [2H, t, *J*(H–H) = 8.4 Hz, 4-C*H*], 6.90 [2H, d, *J*(H–H) = 8.2 Hz, 3-C*H*], 6.60 [2H, t, *J*(H–H) = 6.5 Hz, 5-C*H*], 1.19 [36H, s, C(CH_3)$_3$]. ^{13}C NMR: *δ* 178.2 (O_2C), 168.3 (1-*C*), 138.0 (2-*C*), 133.5 (6-*C*H), 123.1 (4-*C*H), 118.1 (3-*C*H), 112.9 (5-*C*H), 24.8 [*C*(CH$_3$)$_3$], 21.0 [C(*C*H$_3$)$_3$].

[(^{t}Bu)$_2$Ga(μ-$O_2CC_6H_4$-2-Me)]$_2$ (4)

To a hexane (30 mL) slurry of *o*-toluic acid (0.565 g, 4.15 mmol) at −78 °C was added Ga(^{t}Bu)$_3$ (1.0 g, 4.15 mmol). The clear reaction mixture was allowed to warm to room temperature and then to stir for three hours. The solution was filtered and placed in a freezer, yielding colorless crystals. Yield: 75%. Mp: 160 °C. Anal. (%, calc.): C, 60.2 (60.2); H, 7.69 (7.90). MS (EI,%): *m/z* 205 ($M^+ - 2\ {}^t$Bu + H, 30), 91 (C_6H_4Me, 10), 69 (Ga, 40), 57 (^{t}Bu, 100). IR (cm^{-1}): 3336 (w), 3168 (w), 3075 (w), 2730 (w), 2350 (w), 1605 (w), 1585 (m), 1561 (m), 1457 (s), 1413 (m), 1373 (m), 1299 (w), 1166 (w), 1102 (w), 1018 (w), 939 (w), 855 (w), 821 (w), 747 (w), 668 (w). ^{1}H NMR: *δ* 8.27 [2H, dd, *J*(H–H) = 7.6 Hz, *J*(H–H) = 1.5 Hz, 6-C*H*], 7.03 [2H, ddd, *J*(H–H) = 7.4 Hz, *J*(H–H) = 7.4 Hz, *J*(H–H) = 1.6 Hz, 4-C*H*], 6.98 [2H, ddd, *J*(H–H) = 7.6 Hz, *J*(H–H) = 7.4 Hz, *J*(H–H) = 1.7 Hz, 5-C*H*], 6.91 [2H, dd, *J*(H–H) = 7.4 Hz, *J*(H–H) = 0.9 Hz, 3-C*H*], 2.67 (6H, s, CH_3), 1.26 [36H, s, C(CH_3)$_3$]. ^{13}C NMR: *δ* 179.7 (O_2C), 140.6 (2-*C*), 132.9 (4-*C*H), 132.4 (1-*C*), 132.1 (6-*C*H), 128.0 (3-*C*H), 126.2 (5-*C*H), 30.2 [*C*(CH$_3$)$_3$], 24.9[C(*C*H$_3$)$_3$], 23.2 (*C*H$_3$).

(^{t}Bu)$_2$Al(μ-$O_2CC_6H_4$-2-NH_2)Al(^{t}Bu)$_3$ (5)

To a toluene (40 mL) solution of anthranilic acid (0.277 g, 2.0 mmol) at −78 °C was added Al(^{t}Bu)$_3$ (0.8 g, 4.0 mmol). The orange reaction mixture was allowed to warm to room temperature and then to stir for three hours. The solution was filtered and placed in a freezer, yielding yellow crystals. Mechanical grinding of a sample resulted in its slow conversion to compound **1** and Al(^{t}Bu)$_3$ as confirmed by ^{1}H NMR spectroscopy. Yield: 65%. Mp: 80 °C. MS (EI): *m/z* 475 (M^+, 35), 418 ($M^+ - {}^t$Bu, 55), 361 ($M^+ - 2\ {}^t$Bu, 100), 277 [M^+ − Al(^{t}Bu)$_3$, 10]. IR (cm^{-1}): 3513 (w), 3416 (w), 2724 (w), 2366 (w), 2325 (w), 1629 (m), 1577 (m), 1552 (m), 1470 (s), 1413 (m), 1378 (s), 1306 (m), 1255 (m), 1163 (w), 825 (w), 753 (w), 676 (w). ^{1}H NMR: *δ* 8.33 (1H, m, 3-C*H*), 6.64 (2H, m, 6-C*H* and 4-C*H*), 5.61 (1H, m, 5-C*H*), 1.60 [27H, s, C(CH_3)$_3$], 0.84 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: *δ* 170.2 (O_2C), 135.8 (1-*C*), 134.9 (2-*C*), 134.6 (4-*C*H), 133.9 (6-*C*H), 126.2 (3-*C*H), 124.4 (5-*C*H), 34.0 [*C*(CH$_3$)$_3$], 30.8 [*C*(CH$_3$)$_3$] 29.8 [C(*C*H$_3$)$_3$], 24.9 [C(*C*H$_3$)$_3$].

Crystallographic studies

Crystals of all compounds were sealed in glass capillaries under argon.

The cell determination and intensity data for compound **1** were performed using a NONIUS KappaCCD system. The

Table 3 Summary of X-ray diffraction data

Compound	$[(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (**1**)	$[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (**2**)	$[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}OH)]_2$ (**3**)	$[(^tBu)_2Ga(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}Me)]_2$ (**4**)	$(^tBu)_2Al(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**5**)
Empirical formula	$C_{30}H_{48}Al_2N_2O_4$	$C_{30}H_{48}Ga_2N_2O_4$	$C_{30}H_{46}Ga_2O_6$	$C_{32}H_{50}Ga_2O_4$	$C_{34}H_{59}Al_2NO_2$
Formula weight	554.68	640.17	642.14	638.19	567.81
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	9.411(2)	8.927(2)	8.984(2)	8.601(2)	9.008(2)
b/Å	16.601(3)	12.645(3)	17.028(3)	10.433(2)	19.590(4)
c/Å	10.923(2)	14.662(3)	11.064(2)	11.225(2)	21.077(4)
α/°				101.40(3)	
β/°	106.58(3)	101.17(3)	103.35(3)	110.76(3)	93.33(3)
γ/°				108.61(3)	
V/Å^3	1635.6(5)	1623.7(6)	1646.8(6)	835.9(3)	3713.0(1)
Z	2	2	2	1	4
μ/cm^{-1}	1.22	1.693	1.67	1.64	1.10
T/K	293	298	298	298	298
No. collected	7257	7171	7307	3821	16880
No. independent	3717	2321	2372	2392	5321
No. observed	3717	1833 ($\|F_o\| > 4.0\sigma\|F_o\|$)	1806 ($\|F_o\| > 6.0\sigma\|F_o\|$)	2194 ($\|F_o\| > 6.0\sigma\|F_o\|$)	3006 ($\|F_o\| > 6.0\sigma\|F_o\|$)
Weighting scheme (SHELXTL)		0.1017, 0.0834	0.067, 0	0.0625, 0	0.10, 0
R	0.0816	0.0496	0.0397	0.0348	0.0591
R_w	0.2280	0.136	0.1032	0.0918	0.1496
Largest difference peak/e Å^{-3}	0.78	1.80	0.50	0.87	0.24

structure was solved by direct methods[22] and refined by full-matrix least squares on F^2.[22] Hydrogen atoms were added at the final steps of refinement as 'riding' on the respective carbon atoms. The amine hydrogens were ignored. A relatively high residual electron density maximum (*ca.* 2 e Å^{-3}) was found at the position which suggested some orientational disorder of the aromatic ring around the C(9)–C(10) bond. Introducing two 'half nitrogen' atoms at the two possible positions, *i.e.* at C(15) and C(11), led to site occupation factors 0.654 and 0.346(6) respectively. This model was used in the final cycles of refinement; the hydrogens at the nitrogen atom in the two positions being ignored.

Data for compounds **2**–**5** were collected on a Bruker CCD SMART system, equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS[22] and difference Fourier maps and refined by using full-matrix least squares method.[22] Disorder and/or high thermal motion were noted, usually associated with the *tert*-butyl groups. Of particular note were the observations of two positions each for the methyl carbons [C(16)–C(18)] of a *tert*-butyl group in compound **3** (in a 1 : 1 ratio). A peak of unassigned electron density was noted close to the aromatic ring but no rational disodered model could be developed. The toluene of solvation in compound **5** was disordered in a 1 : 1 ratio. The best model that could be developed was one in which both possible sites shared one carbon atom and are related by a small rotation about that atom to present a "V" shaped appearance. The carbon atoms adjacent to the common carbon could not be resolved into two peaks. All other carbons were so resolved and refined. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms involved in hydrogen bonding were found, but not refined. Remaining hydrogen atoms were placed in calculated positions [$U_{iso} = 0.08$; d(C–H) = 0.96 Å] for refinement. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 3).

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