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Reaction of $[Ga_2(^tBu)_4(neol\text{-}H)]_2$ with early transition metal chlorides and amides

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Abstract

The reaction of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (neol-H_2 = 2,2-dimethylpropane-1,3-diol) with $TiCl_4$, $ZrCl_4$, or VCl_4 in the presence of proton sponge, $C_{10}H_6(NMe_2)_2$, yields $[(^tBu)GaCl_3][C_{10}H_6(NMe_2)_2H]$ (**1**). The reaction of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ with $M(NMe_2)_4$ (M = Ti, Zr) in yields $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (**2**) along with multiple transition metal containing products. In contrast, $Cr(NEt_2)_4$ reacts with $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ to yield $[Ga_3(^tBu)_5(neol)_2]$. For the reaction with $Ti(NMe_2)_4$, the identity of the titanium containing products have been determined as $[(^tBu)_2Ga(neol)_2Ti(NMe_2)]$ (**3**), $[Ti(NMe_2)_2(neol)_2]$ (**4**) and $[Ti(neol)_2]$ (**5**). In addition, following the reaction by ^1H NMR allows for the observation of an additional gallium containing intermediate, $[(^tBu)_2Ga(neol)_2]_2Ti(NMe_2)_2$ (**6**) and $[(^tBu)_2Ga]_2(\mu\text{-}neol)$ (**7**). Compounds **4** and **5** are also made by the direct reaction of $Ti(NMe_2)_4$ with neol-H_2. Reaction of $Ga(^tBu)_3$ with $HNMe_2$ yields $(^tBu)_3Ga(HNMe_2)$ (**8**). Compound **2** is also formed along with $[Ti(NMe_2)_2(O^iPr)_2]$ (**9**) from the reaction of $[(^tBu)_2Ga(\mu\text{-}O^iPr)]_2$ with $Ti(NMe_2)_4$. The formation of compound **6** is implied by the isolation of the hydration product, $[(^tBu)_2Ga(neol)_2Ti(\mu\text{-}O)Ga(^tBu)(HNMe_2)]$ (**10**). The reaction of $CpTi(NMe_2)_3$ with $[(^tBu)_2Ga(neol\text{-}H)]_2$ yields $[(^tBu)_2Ga(neol)_2TiCp]$ (**11**) and **2**.

Keywords: Amide; Chloride; Gallium; Ligand exchange; Titanium

1. Introduction

We have previously reported that the reaction of $Ga(^tBu)_3$ with 2,2-dimethylpropane-1,3-diol (neol-H_2) yields $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ (**I**) and have demonstrated its application as bifunctional (two OH groups) tetradentate (4*O*) ligand towards both divalent and trivalent main group and transition metals (**II** and **III**) [1,2]. As an extension of this work we attempted to incorporate tetravalent transition metal ions, in particular those of the early transition metals, within the bifunctional (two OH groups) tetradentate (4*O*) ligand. Our results in this area are described herein.

2. Experimental

All operations were carried out under inert atmosphere using Schlenk techniques or VAC inert atmosphere dry box. 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 Magna 760 FT IR infrared spectrometer. IR samples were prepared as mulls on KBr plates. NMR spectra were obtained on Bruker Avance 200 and 400 spectrometers using (unless otherwise stated) d_6-benzene solutions. Chemical shifts are reported relative to internal solvent resonances. The syntheses of $[(^tBu)_2Ga(neol\text{-}H)]_2$, $Ti(NMe_2)_4$, and $CpTi(NMe_2)_3$ were performed according to a literature methods [3]. $TiCl_4$, $ZrCl_4$, VCl_4 and Proton Sponge® were commercial samples and were used without further purification. Solvents were distilled and degassed prior to use.

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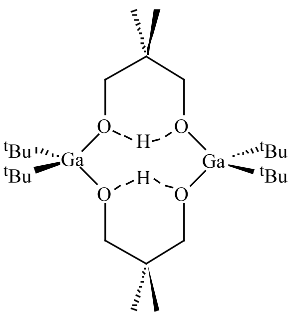
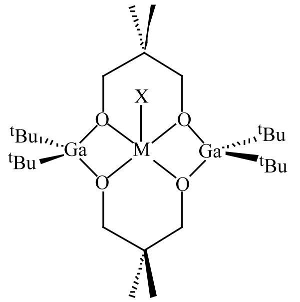
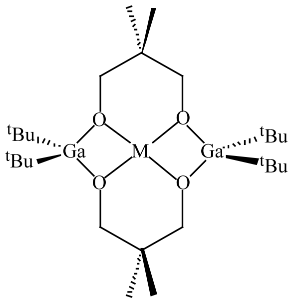


(I)



M = Al, Ga, Fe
X = Cl, ^{t}Bu, Me, H
(II)



M = Co, Ni, Cu

(III)

2.1. *Reaction between MCl_4 and $[(^tBu)_2Ga(neol\text{-}H)]_2$*

A THF solution (100 ml) of VCl_4 (0.167 g, 0.866) was added to a refluxing THF solution (150 ml) of $[(^tBu)_2Ga(neol\text{-}H)]_2$ (0.5 g, 0.871 mmol) and Proton Sponge® (0.373 g, 1.74 mmol). The reaction mixture was allowed to reflux for 5 h. All volatiles were removed under vacuum resulting in a brown powder. The brown powder was dissolved in toluene (50 ml). The solution was filtered and cooled to −30 °C. Yellow crystals suitable for single crystal X-ray diffraction were formed. ^1H NMR (C_6D_6): δ 7.25 [2H, d, J(H−H) = 8.2 Hz, 2-CH], [2H, t, J(H−H) = 7.8 Hz, 3-CH], [2H, d, J(H−H) = 8.5 Hz, 4-CH], 2.72 [6H, d, J(H−H) = 2.5 Hz, 1.71 [9H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 144.7, (1-NC), 135.7 (10-C), 129.4 (2-CH), 127.4 (3-CH), 121.9 (4-CH), 119.4 (5-CH), 46.9 (NCH$_3$), 29.3 [C(CH$_3$)].

2.2. *Reaction between $Ti(NMe_2)_4$ and $[(^tBu)_2Ga(neol\text{-}H)]_2$*

To a cooled (0 °C) hexane (100 ml) solution of $[(^tBu)_2Ga(neol\text{-}H)]_2$ (1.28 g, 2.23 mmol) was added $Ti(NMe_2)_4$ (0.5 g, 2.23 mmol) in hexane (75 ml). The reaction mixture was allowed to warm to room temperature (r.t.) and stirred for 18 h. The resulting yellow solution was concentrated (ca. 100 ml) and cooled to −30 °C. Colorless crystals of $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (**2**) suitable for single crystal X-ray diffraction were formed. In an alternative method, $[(^tBu)_2Ga(neol\text{-}H)]_2$ (0.64 g, 1.19 mmol) was dissolved in hexane (100 ml) and heated to reflux. To this solution was added a hexane solution (30 ml) of $Ti(NMe_2)_4$ (0.26 g, 1.19 mmol) over a period of an hour, after which the solution was refluxed for a further 30 min. All volatiles were removed under vacuum. ^1H NMR in C_6D_6 revealed three soluble products: $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (**2**), $[(^tBu)_2Ga(neol)_2Ti(NMe_2)]$ (**3**), and $[(neol)Ti(NMe_2)_2]$ (**4**). An insoluble product was characterized as $[Ti(neol)_2]$ (**5**) by comparison with a sample prepared by the direct reaction of $Ti(NMe_2)_4$ with neol-H_2.

2.2.1. *$[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (**2**)*

IR (cm^{-1}): 3036 (w), 2980 (m), 2949 (m), 2919 (m), 2833 (s), 2707 (w), 1471 (m, 1349 (w), 1363 (w), 1268 (w), 1225 (w), 1164 (w), 1121 (m), 1078 (w), 1035 (m), 1009 (w), 901 (m), 810 (m). ^1H NMR (C_6D_6): δ 2.60 (6H, s, NCH_3), 1.29 (18H, s, CH_3). ^{13}C NMR (C_6D_6): δ 48.2 (NCH$_3$), 33.87 (CH$_3$).

2.2.2. *$[(^tBu)_2Ga(neol)_2Ti(NMe_2)]$ (**3**)*

^1H NMR (C_6D_6): δ 4.35 [2H, d, J(H−H) = 11.0 Hz, OCH_2], 3.92 [2H, d, J(H−H) = 10.5 Hz, OCH_2], 3.74 [2H, d, J(H−H) = 11.0 Hz, OCH_2], 3.61 [2H, d, J(H−H) = 10.5 Hz, OCH_2], 3.11 (6H, s, NCH_3), 1.26 [9H, s, C(CH_3)$_3$], 1.24 [9H, s, C(CH_3)$_3$], 1.03 (6H, s, CH_3), 0.61 (6H, s, CH_3).

2.2.3. *$[Ti(NMe_2)_2(neol)]$ (**4**)*

^1H NMR (C_6D_6): δ 3.86 (2H, s, OCH_2), 3.37 (6H, s, NCH_3), 0.93 (3H, s, CH_3).

*2.2.3.1. $[Ti(neol)_2]$ (**5**).* MS (EI, %): m/z 501 (2M$^+$, 15), 250 (M$^+$, 15), 145 (M$^+$ −neol, 95).

2.3. *Synthesis of $[Ti(NMe_2)_2(neol)]$ (**4**)*

To a slurry of neol-H_2 (0.064 g, 1.19 mmol) in hexane (30 ml) was added a solution of $Ti(NMe_2)_4$ (0.26 g, 1.19 mmol) in hexane (20 ml). After stirring for 18 h an orange–yellow solution was formed. All volatiles were removed under vacuum yielding an orange powder. Yield: 0.20 g, 71%. MS (EI, %): m/z 234 (M$^+$, 5), 131 [$Ti(NMe_2)_2$, 50], 101 (neol-H, 70). IR (cm^{-1}): 2954 (m), 2884 (m), 2833 (s), 2802 (s), 2755 (s), 1450 (w), 1406 (w), 1389 (w), 1359 (w), 1255 (w), 1234 (w), 1139 (w), 1104 (m), 1065 (s), 1005 (s), 944 (s), 806 (w). ^{13}C NMR (C_6D_6): δ 80.2 (OCH$_2$), 48.6 (NCH$_3$), 37.5 (CCH$_3$), 23.7 (CH$_3$).

2.4. *NMR monitored reaction between $Ti(NMe_2)_4$ and $[(^tBu)_2Ga(neol\text{-}H)]_2$*

$[(^tBu)_2Ga(neol\text{-}H)]_2$ (0.033 g, 0.058 mmol) was dissolved in C_6D_6 (0.57 ml) in a 5 mm NMR tube. To this was added $Ti(NMe_2)_4$ (0.012 g, 0.054 mmol). The contents of the tube were not mixed until just prior to the NMR tube being inserted into the instrument. This was marked as time zero. The reaction was monitored for 41 h.

2.4.1. *[(^{t}Bu)$_2$Ga(neol)$_2$]$_2$Ti(NMe$_2$)$_2$ (**6**)*

^{1}H NMR (C_6D_6): δ 4.05 [2H, s, OC*H*$_2$], 3.83 [2H,s, OC*H*$_2$], 3.16 (6H, s, NC*H*$_3$), 1.31 [9H, s, C(C*H*$_3$)$_3$], 1.29 (3H, s, C*H*$_3$), 1.24 [9H, s, C(C*H*$_3$)$_3$], 0.93 (6H, s, C*H*$_3$).

2.4.2. *[(^{t}Bu)$_2$Ga]$_2$(μ-neol) (**7**)*

^{1}H NMR (C_6D_6): δ 4.49 [2H, d, *J*(H–H) = 10.9 Hz, OC*H*$_2$], 3.39 [2H, d, *J*(H–H) = 10.9 Hz, OC*H*$_2$], 1.24 [36H, s, C(C*H*$_3$)$_3$], 1.21 (3H, s, C*H*$_3$), 0.53 (3H, s, (C*H*$_3$).

2.5. *Synthesis of (^{t}Bu)$_3$Ga(HNMe$_2$) (**8**)*

To a solution of Ga(^{t}Bu)$_3$ (0.25 g, 1.03 mmol) in hexane (50 ml) was added HNMe$_2$ (2 M in THF) (0.5 ml, 1.00 mmol). The reaction mixture was refluxed for 6 h. All volatiles were removed under vacuum yielding a colorless oil. ^{1}H NMR (C_6D_6): δ 1.83 [6H, d, *J*(H–H) = 6.3 Hz, NC*H*$_3$], 1.25 [27H, s, C(C*H*$_3$)$_3$].

2.6. *Reaction of [(^{t}Bu)$_2$Ga(μ-O^{i}Pr)]$_2$ with Ti(NMe$_2$)$_4$*

[(^{t}Bu)$_2$Ga(μ-O^{i}Pr)]$_2$ (0.026 g, 0.054 mmol) was dissolved in C_6D_6 (0.58 ml) in a 5 mm NMR tube. To this was added Ti(NMe$_2$)$_4$ (0.012 g, 0.054 mmol). No reaction was observed at r.t., so the reaction mixture was heated to 90 °C for 1 h. ^{1}H NMR showed starting material and two products: [(^{t}Bu)$_2$Ga(μ-NMe$_2$)]$_2$ and [Ti(NMe$_2$)$_2$(O^{i}Pr)$_2$].

2.6.1. *[Ti(NMe$_2$)$_2$(O^{i}Pr)$_2$] (**9**)*

^{1}H NMR (C_6D_6): δ 4.57 (1H, m, OC*H*), 3.16 (6H, s, NC*H*$_3$), 1.28 [6H, d, *J*(H–H) = 6 Hz, CC*H*$_3$].

2.7. *Synthesis of [(^{t}Bu)$_2$Ga(neol)$_2$Ti(μ-O)Ga(^{t}Bu)$_2$(NMe$_2$)] (**10**)*

To a solution of [(^{t}Bu)$_2$Ga(neol-H)]$_2$ (1.28 g, 2.23 mmol) in wet hexane (100 ml) was added a Ti(NMe$_2$)$_4$ (0.5 g, 2.23 mmol) in hexane (100 ml). The reaction was refluxed 1.5 h. The resulting light yellow solution was concentrated and cooled to −30 °C, yielding colorless crystals suitable for single crystal X-ray diffraction. Yield: 0.474 g, 31%. IR (cm^{-1}): 3209 (w), 2949 (m), 2932 (m), 2872 (m), 2837 (s), 1467 (m), 1398 (w), 1359 (w), 1264 (w), 1203 (w), 1056 (s), 1009 (m), 935 (w), 901 (w), 862 (m), 814 (m). ^{1}H NMR (C_6D_6): δ 4.40 [2H, d, *J*(H–H) = 10.4 Hz, OC*H*$_2$], 4.08 [2H, d, *J*(H–H) = 10.3 Hz, OC*H*$_2$], 3.79 [2H, d, *J*(H–H) = 10.4 Hz, OC*H*$_2$], 3.66 [2H, d, *J*(H–H) = 10.3 Hz, OCH$_2$], 2.14 (6H, br s, NC*H*$_3$), 1.47 (9H, s, C(C*H*$_3$)$_3$], 1.35 [9H, s, C(C*H*$_3$)$_3$], 1.26 [18H, s, C(C*H*$_3$)$_3$], 1.18 (6H, s, C*H*$_3$), 0.67 (6H, s, C*H*$_3$). ^{13}C NMR (C_6D_6): δ 82.1 (O*C*H$_2$), 77.6 (O*C*H$_2$), 37.9 [*C*(CH$_3$)$_2$], 34.3 (N*C*H$_3$), 32.2 [C(*C*H$_3$)$_3$], 31.8 [C(*C*H$_3$)$_3$], 31.4 [C(*C*H$_3$)$_3$], 23.8 (*C*H$_3$), 22.2 (*C*H$_3$).

2.8. *Synthesis of [(^{t}Bu)$_2$Ga(neol)$_2$TiCp] (**11**)*

Dissolution of [(^{t}Bu)$_2$Ga(neol-H)]$_2$ (1.11 g, 1.94 mmol) in pentane (100 ml) was followed by the addition of a pentane solution (30 ml) of CpTi(NMe$_2$)$_3$ (0.52 g, 2.10 mmol). The reaction mixture was allowed to stir for 18 h. Removal of all volatiles and extraction of the brown product into toluene (30 ml) followed by cooling to −30 °C yielding crystals suitable for single crystal X-ray diffraction. Yield: 0.52 g, 46%. MS (EI, %): *m/z* 443 (M$^+$ − ^{t}Bu, 20), 183 [Ga(^{t}Bu)$_2$, 100], 145 [Ti(neol), 85]. IR (cm^{-1}): 3083 (w), 2962 (m), 2928 (m), 2876 (m), 2833 (s), 1463 (w), 1394 (w), 1363 (w), 1260 (m), 1061 (s), 1013 (s), 940 (w), 801 (s), 732 (w). ^{1}H NMR (C_6D_6): δ 6.26 (5H, s, C$_5$*H*$_5$), 4.20 [2H, d, *J*(H–H) = 11.1 Hz, OC*H*$_2$], 3.75 [2H, d, *J*(H–H) = 11.1 Hz, OC*H*$_2$], 3.5 [4H, d of d, *J*(H–H) = 17.1 Hz, OC*H*$_2$), 1.33 [9H, s, C(C*H*$_3$)$_3$], 1.31 (9H, s, C(C*H*$_3$)$_3$], 1.14 (6H, s, C*H*$_3$), 0.51 (6H, s, C*H*$_3$). ^{13}C NMR (C_6D_6): δ 114.5 (Cp), 85.0 (O*C*H$_2$), 77.7 (O*C*H$_2$), 35.5 [*C*(CH$_3$)$_2$], 32.6 [C(*C*H$_3$)$_3$], 31.6 [C(*C*H$_3$)$_3$], 26.2 (*C*H$_3$), 22.5 (*C*H$_3$).

2.9. *X-ray crystallography*

Crystals of compounds **1**, **2**, **10** and **11** were sealed in a glass capillary and mounted on the goniometer of a Bruker CCD SMART system, equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. Data collection and unit cell and space group determination were all carried out in the usual manner [4]. Pertinent details are given in Table 1. The structures were solved by direct methods and the refined using full-matrix least-squares techniques [5]. Disorder was observed in both compounds **10** and **11**. In compound **10**, the amine and one *tert*-butyl group on Ga(1) suffer from rotational disorder about the Ga-group bond. For the amine, this is only about 10° while for the *tert*-butyl group, the usual ‘hexagon’ of positions is observed. The solvent is disorder in both **10** and **11**. In compound **10**, no methyl positions could be resolved and an examination of the cell packing indicates that it is very likely to be disordered over all possible positions. In compound **11**, the disorder is a static one, over two positions such that the *ortho*-carbons are present in both positions, and the methyl carbon in one orientation becomes the *para*-carbon in the second. All hydrogen atoms were placed in calculated positions [$U_{\mathrm{iso}} = 1.3U_{(\mathrm{C})}$; d(C–H) = 0.95 Å] for refinement. Neutral-atom scattering factors were taken from the usual source [6]. Refinement of positional and anisotropic displacement parameters led to convergence (see Table 1).

Table 1
Summary of X-ray diffraction data

Compound	$[(^t\text{Bu})\text{GaCl}_3]$-$[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]$ (**1**)	$[(^t\text{Bu})_2\text{Ga}(\mu\text{-NMe}_2)]_2$ (**2**)	$[(^t\text{Bu})_2\text{Ga(neol)}_2\text{Ti}(\mu\text{-O})\text{Ga}$-$(^t\text{Bu})(\text{HNMe}_2)]\cdot\text{C}_6\text{H}_5\text{Me}$ (**10**)	$[(^t\text{Bu})_2\text{Ga(neol)}_2\text{TiCp}]\cdot$ $1/2\text{C}_6\text{H}_5\text{Me}$ (**11**)
Empirical formula	$C_{18}H_{28}Cl_3GaN_2$	$C_{20}H_{48}Ga_2N_2$	$C_{35}H_{71}Ga_2NO_5Ti$	$C_{26.5}H_{47}GaO_4Ti$
M_w	448.50	456.04	773.27	547.26
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
a (Å)	8.524(2)	8.859(2)	14.376(3)	11.219(2
b (Å)	13.016(3)	12.821(3)	11.992(2)	15.083(3)
c (Å)	19.946(4)	11.211(2)	25.017(5)	17.694(4)
α (°)				77.26(3)
β (°)	98.87(3)	106.46(3)	98.99(3)	88.26(2)
γ (°)				82.05(3)
V (Å^3)	2168.4(8)	1221.1(4)	4260(2)	2892.3(1)
Z	4	2	4	4
D_{calc} (g ml^{-1})	1.362	1.240	1.204	1.257
μ (mm^{-1})	1.63	2.21	1.47	1.23
2θ Range (°)	3.7–46.6	5.0–46.52	3.08–46.58	2.36–46.62
Number collected	10 544	3001	12 722	13 197
Number indicated	3154	1559	4124	8303
Number observed	2793 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$)	1466 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)	1836 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)	5205 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)
Weighting scheme	SHELXTL 0.0428, 0.6721	SHELXTL 0.0589, 0.4041	SHELXTL 0.0382, 0	SHELXTL 0.0261, 0
R [a]	0.0294	0.0292	0.0557	0.0484
R_w [a]	0.0812	0.0795	0.1092	0.0959
Largest difference peak (e Å^{-3})	0.37	0.35	0.33	0.41

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$; $wR = \{\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}\}^{1/2}$.

3. Results and discussion

3.1. Reaction with MCl_4

We have previously shown [2] that the mixed gallium transition metal complexes $[\text{FeCl}\{\text{Ga}_2(^t\text{Bu})_4(\text{neol})_2\}]$ and $[\text{M}\{\text{Ga}_2(^t\text{Bu})_4(\text{neol})_2\}]$ (M = Co, Ni, Cu) may be prepared by the reaction of $[\text{Ga}_2(^t\text{Bu})_4(\text{neol-H})_2]$ (neol-H_2 = 2,2-dimethylpropane-1,3-diol) with the appropriate metal halide in the presence of Proton Sponge® $[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2]$. The reaction of $[\text{Ga}_2(^t\text{Bu})_4(\text{neol-H})_2]$ with MCl_4 (M = Ti, Zr, V) in the presence of Proton Sponge® does not yield any gallium transition metal containing products. Instead the ionic gallium complex $[(^t\text{Bu})\text{GaCl}_3][\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]$ (**1**) is the only gallium containing product isolated, see Section 2. The formation of $[(^t\text{Bu})\text{GaCl}_3][\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]$ presumably occurs by both alkyl–chloride and alkoxide–halide exchange reactions, both of which are well documented for Group 13 metals [7] and gallium in particular [8].

The crystal structure of compound **1** has been confirmed by X-ray crystallography. The structure of the $[(^t\text{Bu})\text{GaCl}_3]^-$ anion is shown in Fig. 1; selected bond lengths and angles are given in Table 2. The structure of $[(^t\text{Bu})\text{GaCl}_3][\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]$ consists of separate cations and anions with the closest inter-ionic distance between a chloride and a methyl group on the Proton Sponge® [Cl(1)···C(81) = 3.63 Å] being close to the sum of the van der Waals' radii (3.8 Å) [9]. The lack of inter-ionic hydrogen bonding, typically observed for ionic Group 13 metal chlorides with ammonium counter ions [10], is due to the steric constraints of the Proton Sponge®.

The coordination environment about Ga(1) is similar to previously characterized anions $[\text{R}_n\text{GaCl}_{4-n}]^-$, $n = 1$ [11,12], 2 [6–13], and 3 [14]. The Ga(1)–Cl bond distances [2.2105(9)–2.2316(9) Å] are within the range previously observed for non-hydrogen bonded gallium chloride anions [6–8]. The parameters for the $[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}]^+$ cation are similar to those observed previously [15].

3.2. Reaction with $M(NMe_2)_4$

The observation of ligand exchange rather than complex formation for the reaction described above prompted our investigation of a more facile leaving group than chloride. In this regard, transition metal amides react readily with protic acids (i.e. O–H) to yield the appropriate complexes with a secondary amine as the readily removed (volatile) side product, Eq. (1).

$$\text{M(NR}_2)_n + n\text{HX} \xrightarrow[\text{X=OH,OR,SR}]{} \text{MX}_n + n\text{HNR}_2 \tag{1}$$

The reaction of $[\text{Ga}_2(^t\text{Bu})_4(\text{neol-H})_2]$ with $\text{M(NMe}_2)_4$ (M = Ti, Zr) in hexane (at or below room temperature) yields $[(^t\text{Bu})_2\text{Ga}(\mu\text{-NMe}_2)]_2$ (**2**) along with multiple transition metal containing products, vide infra. In contrast, the reaction of $\text{Cr(NEt}_2)_4$ with $[\text{Ga}_2(^t\text{Bu})_4(\text{neol-H})_2]$ yields the previously reported trigallium compound, $[\text{Ga}_3(^t\text{Bu})_5(\text{neol})_2]$ [1].

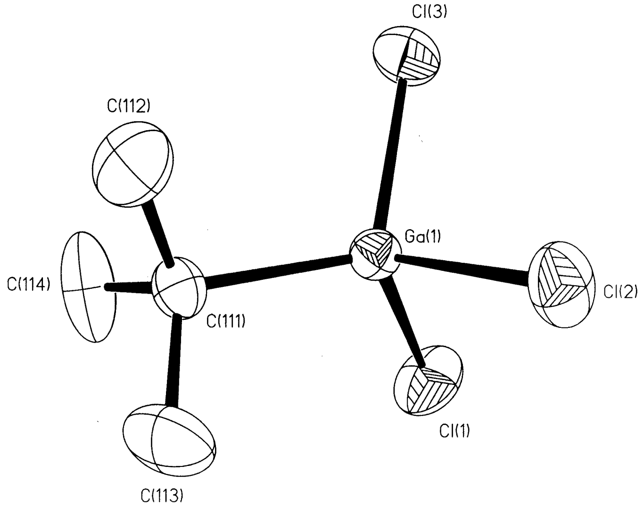


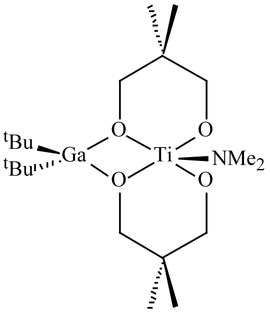
Fig. 1. Structures of the $[(^t\mathrm{Bu})\mathrm{GaCl}_3]^-$ anion in $[(^t\mathrm{Bu})\mathrm{GaCl}_3][\mathrm{C}_{10}\mathrm{H}_6(\mathrm{NMe}_2)_2\mathrm{H}]$ (**1**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for $[(^t\mathrm{Bu})\mathrm{GaCl}_3][\mathrm{C}_{10}\mathrm{H}_6(\mathrm{NMe}_2)_2\mathrm{H}]$ (**1**)

Bond lengths			
Ga(1)–Cl(1)	2.2269(9)	Ga(1)–Cl(2)	2.2316(9)
Ga(1)–Cl(3)	2.2105(9)	Ga(1)–C(111)	1.976(3)
Bond angles			
Cl(1)–Ga(1)–Cl(2)	104.64(4)	Cl(1)–Ga(1)–Cl(3)	104.05(4)
Cl(1)–Ga(1)–C(111)	114.88(8)	Cl(2)–Ga(1)–Cl(3)	105.29(4)
Cl(2)–Ga(1)–C(111)	112.17(8)	Cl(3)–Ga(1)–C(111)	114.76(8)

The molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{NMe}_2)]_2$ (**2**) is shown in Fig. 2; selected bond lengths and angles are given in Table 3. The structure of compound **2** exhibits no unusual bond lengths or angles and all the structural parameters are within the ranges observed previously [16].

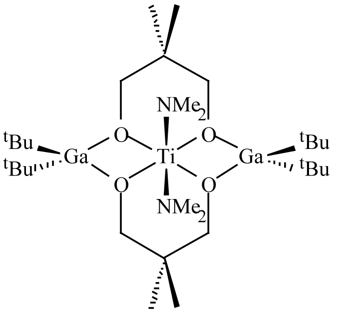
For the reaction with $\mathrm{Ti(NMe_2)_4}$, the identity of the titanium containing products have been determined as $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti(NMe_2)}]$ (**3**), $[\mathrm{Ti(NMe_2)_2(neol)_2}]$ (**4**) and $[\mathrm{Ti(neol)_2}]$ (**5**) from spectroscopic characterization (**3** and **4**) and from comparison with samples prepared directly (**4** and **5**), Eq. (2).



(3)

$$\mathrm{Ti(NMe_2)_4} \xrightarrow[-2\mathrm{HNMe_2}]{+\mathrm{neolH_2}} \underset{(\mathbf{4})}{[\mathrm{Ti(NMe_2)_2(neol)}]} \xrightarrow[-2\mathrm{HNMe_2}]{+\mathrm{neolH_2}} \underset{(\mathbf{5})}{[\mathrm{Ti(neol)_2}]} \quad (2)$$

Although $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{NMe}_2)]_2$ (**2**) is the only gallium containing product isolated in a pure state, and $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti(NMe_2)}]$ (**3**) is observed in the reaction mixture (see Section 2), two additional gallium containing products are observed as intermediates in the reaction: $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2}]_2\mathrm{Ti(NMe_2)_2}$ (**6**) and $[(^t\mathrm{Bu})_2\mathrm{Ga}]_2(\mu\text{-neol})$ (**7**).



(6)

Compound **7** most likely exists as the Lewis acid–base complex, $[(^t\mathrm{Bu})_2\mathrm{Ga(HNMe_2)}]_2(\mu\text{-neol})$, given the presence of an excess of $\mathrm{HNMe_2}$ in solution.

Following the reaction between $[\mathrm{Ga_2}(^t\mathrm{Bu})_4(\mathrm{neol\text{-}H})_2]$ and $\mathrm{Ti(NMe_2)_4}$ by ^{1}H NMR spectroscopy (Fig. 3) provides insight into the reaction pathway for the formation of the various products. The product that is formed is $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2}]_2\mathrm{Ti(NMe_2)_2}$ (**6**) along with $\mathrm{HNMe_2}$, see Scheme 1. Compound **6** rapidly decomposes (Fig. 3, ○) over 700 min by two separate pathways to give either $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti(NMe_2)}]$ (**3**) and $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{NMe}_2)]_2$ (**2**) or $[\mathrm{Ti(NMe_2)_2(neol)}]$ (**4**) and $[(^t\mathrm{Bu})_2\mathrm{Ga}]_2(\mu\text{-neol})$ (**7**). It is worth noting that the

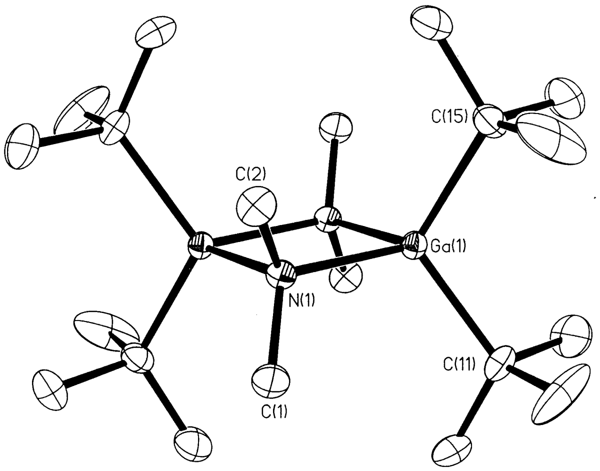


Fig. 2. Molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{NMe}_2)]_2$ (**2**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (**2**)

Bond lengths			
Ga(1)–N(1)	2.059(2)	Ga(1)–N(1)′	2.063(2)
Ga(1)–C(11)	2.069(3)	Ga(1)–C(15)	2.059(4)
Bond angles			
N(1)–Ga(1)–N(1)′	85.65(7)	N(1)–Ga(1)–C(11)	113.3(1)
N(1)–Ga(1)–C(15)	113.5(1)	C(11)–Ga(1)–C(15)	114.6(1)
Ga(1)–N(1)–Ga(1)′	94.35(7)		

formation of compounds **3** and **4** does not occur until all starting material has reacted, therefore, they must be formed as a part of the decomposition of $[Ti(NMe_2)_2Ga_2(^tBu)_4(neol)_2]$ rather than as direct reaction products. Compound **3** appears to be stable and does not undergo any subsequent reaction (Fig. 3, ●). In contrast, the concentration of compounds **4** and **7** both decrease slowly, with the concomitant increase in the concentration of compound **2** and precipitate characterized as $[Ti(neol)_2]$ (**5**). A summary of the reaction pathway is shown in Scheme 1.

While the decomposition of compound **6** to give compounds **4** and **7** is a dissociation of the respective fragments, the formation of compounds **2** and **3** must occur via an alkoxide–amide exchange reaction. A similar reaction must be responsible for the conversion of compound **4** to compound **5** since no 'free' neol-H_2 is observed at any point during the reaction.

In order to preclude alternative routes to the formation of compound **2**, the addition of excess $HNMe_2$ to a solution of $[Ga_2(^tBu)_4(neol\text{-}H)_2]$ was shown not to result in any reaction under the conditions that compound **2** forms (vide supra). This lack of reaction is expected since it is known that Group 13 amides ($M{-}NR_2$) reacts with alcohols to give the Group 13 alkoxide ($M{-}OR$) and the corresponding amine [17]. Conversely, if a simple gallium alkoxide is reacted with $Ti(NMe_2)_4$, then alkoxide–amide exchange occurs slowly at room temperature, but rapidly when heated to 75 °C (Eq. 3). Finally, it is worth noting that direct reaction of $Ga(^tBu)_3$ with $HNMe_2$ does not result in the formation of compound **2**, even upon refluxing for 6 h in toluene. Instead the Lewis acid–base complex is formed $(^tBu)_3Ga(HNMe_2)$ (**8**).

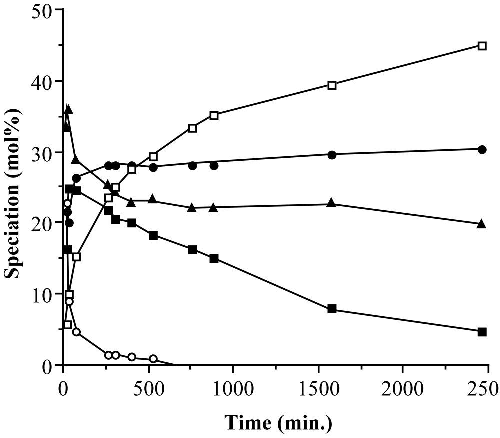


Fig. 3. Plot of speciation (mol%) as a function of reaction time (min) for the reaction of $[(^tBu)_2Ga(neol\text{-}H)]_2$ with $Ti(NMe_2)_4$. $Ti(NMe_2)_2(neol)$ (■), $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$ (□), $[(^tBu)_2Ga(neol)_2Ti(NMe_2)]$ (●), $[(^tBu)_2Ga(neol)_2]_2Ti(NMe_2)_2$ (○), $[(^tBu)_2Ga]_2(\mu\text{-}neol)$ (▲).

$$[(^tBu)_2Ga(\mu\text{-}O^iPr)]_2 + Ti(NMe_2)_4 \rightarrow [(^tBu)_2Ga(\mu\text{-}NMe_2)]_2 + \underset{(\mathbf{9})}{[Ti(NMe_2)_2(O^iPr)_2]} \quad (3)$$

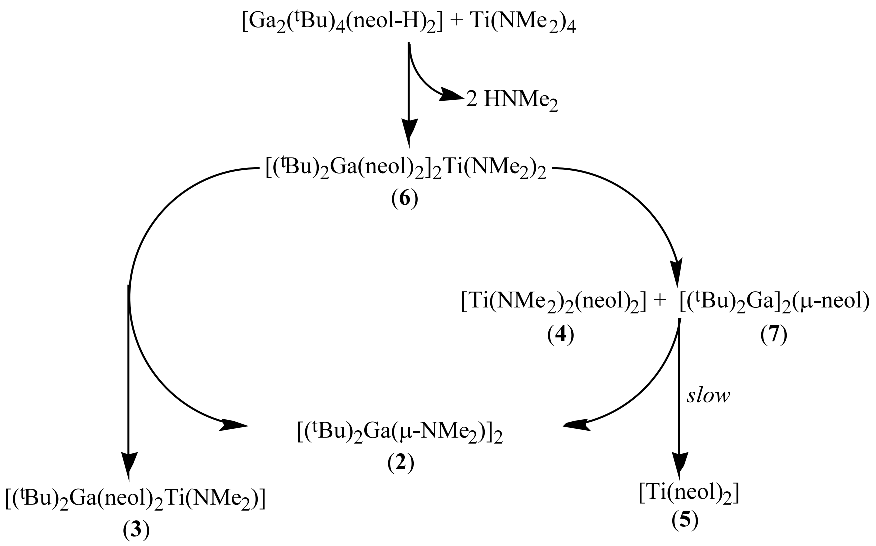
Indirect evidence for the formation of $[(^tBu)_2Ga(neol)_2]_2Ti(NMe_2)_2$ (**6**), is from the isolation of the hydration product, $[(^tBu)_2Ga(neol)_2Ti(\mu\text{-}O)\text{-}Ga(^tBu)(HNMe_2)]$ (**10**). Scheme 2 shows a possible pathway for the formation of compound **10**, from the hydrolysis of compound **6**, followed by a rearrangement to relieve ring strain.

The molecular structure of compound **10** is shown in Fig. 4; selected bond lengths and angles are given in Table 4. The structure consists of a five coordinate square-based pyramidal titanium, chelated by the $[(^tBu)_2Ga(neol)_2]^{3-}$ 'ligand' and bridging a second gallium via an oxide bridge. The bond lengths associated with the oxide bridge are consistent with previously reported galloxanes [18] and titanium μ-oxo compounds to Group 13 elements [19]. The geometry about titanium is similar to other $CpTiO_4$ coordination environments [20]. The methyl groups attached to the quaternary carbons of the neol rings adopt axial and equatorial positions. We have previously observed that in the majority of the Group 13 neol complexes containing a central metal atom, one ring is in the chair conformation and the other in a boat conformation [1,2]. With increased steric bulk or decreased size of the central atom both rings adopt a chair conformation. Both rings in compound **10** adopt a chair conformation (75%).

3.3. Reaction with $CpTi(NMe_2)_3$

Based upon the above reactions, it appears that titanium amides readily undergo reaction with the hydroxides in $[(^tBu)_2Ga(neol\text{-}H)]_2$, to yield compound **6**, however, two alternative decomposition pathways are possible. In an effort to promote the formation of a single gallium–titanium species, we have investigated the reaction of $CpTi(NMe_2)_3$ with $[(^tBu)_2Ga(neol\text{-}H)]_2$.

Reaction of $CpTi(NMe_2)_3$ with $[(^tBu)_2Ga(neol\text{-}H)]_2$ yields a mixture of $[(^tBu)_2Ga(neol)TiCp]$ (**11**) and $[(^tBu)_2Ga(\mu\text{-}NMe_2)]_2$. The formation of compound **11** presumably occurs via the elimination of 2 equiv. of $HNMe_2$ (Eq. (4)), followed by an amides–alkoxide exchange (Eq. (5)).

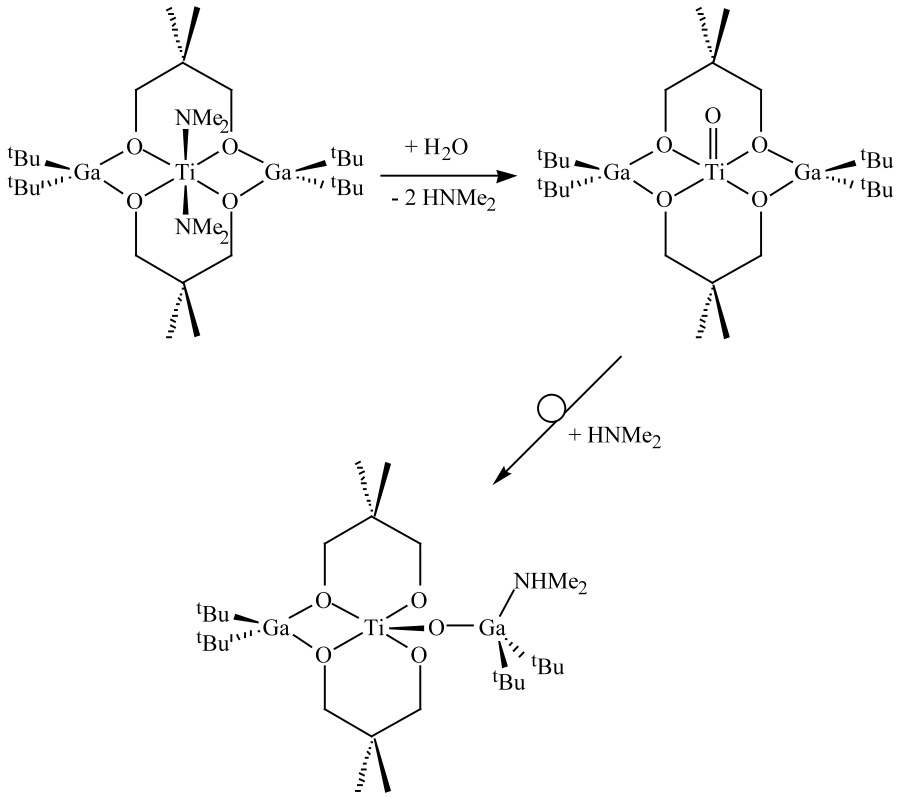


Scheme 1. Proposed pathway for the reaction of $[({}^t\mathrm{Bu})_2\mathrm{Ga(neol\text{-}H)}]_2$ with $\mathrm{Ti(NMe_2)_4}$.

$$\mathrm{CpTi(NMe_2)_3} + [({}^t\mathrm{Bu})_2\mathrm{Ga(neol\text{-}H)}]_2 \rightarrow [({}^t\mathrm{Bu})_2\mathrm{Ga(neol)}]_2\mathrm{Ti(NMe_2)Cp} + 2\mathrm{HNMe_2} \qquad (4)$$

$$[({}^t\mathrm{Bu})_2\mathrm{Ga(neol)}]_2\mathrm{Ti(NMe_2)Cp} \rightarrow [({}^t\mathrm{Bu})_2\mathrm{Ga(neol)_2TiCp}] + 1/2\ [({}^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{NMe_2})]_2 \qquad (5)$$

The molecular structure of compound **11** is shown in Fig. 5; selected bond lengths and angles are given in Table 5. The structure consists of a five coordinate titanium chelated by the $[({}^t\mathrm{Bu})_2\mathrm{Ga(neol)_2}]^{3-}$ 'ligand'. The coordination environment of the titanium is completed by a η^5-cyclopentadienyl ligand.



Scheme 2. Proposed pathway for the formation of $[({}^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti}(\mu\text{-}\mathrm{O})\mathrm{Ga}({}^t\mathrm{Bu})(\mathrm{HNMe_2})]$ (**10**) from the hydration of $[({}^t\mathrm{Bu})_2\mathrm{Ga(neol)_2}]_2\mathrm{Ti(NMe_2)_2}$ (**6**).

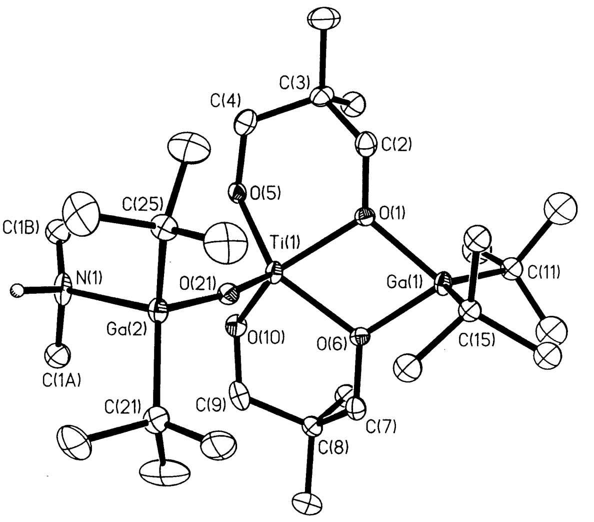


Fig. 4. Molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti}(\mu\text{-O})\mathrm{Ga}(^t\mathrm{Bu})(\mathrm{HNMe_2})]$ (**10**). Thermal ellipsoids are shown at the 10% level and hydrogen atoms are omitted for clarity.

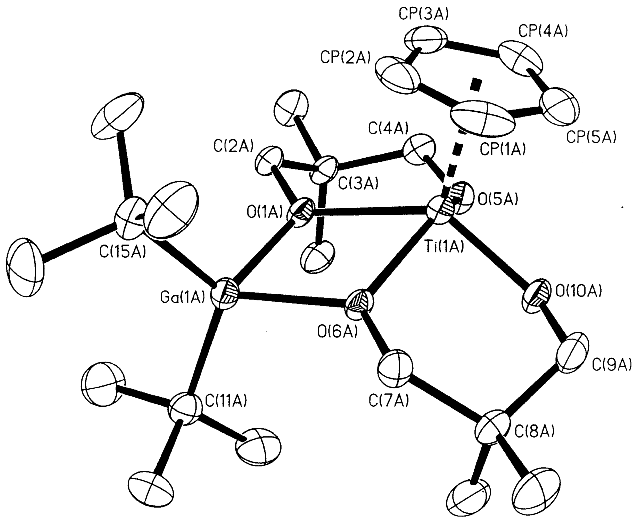


Fig. 5. Molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2TiCp}]$ (**11**). Thermal ellipsoids are shown at the 20% level and hydrogen atoms are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2Ti}(\mu\text{-O})\mathrm{Ga}(^t\mathrm{Bu})(\mathrm{HNMe_2})]$ (**10**)

Bond lengths			
Ga(1)–O(1)	1.921(5)	Ga(1)–O(6)	1.946(6)
Ga(1)–C(11)	1.99(1)	Ga(1)–C(15)	2.00(1)
Ga(2)–O(21)	1.89(1)	Ga(2)–N(1)	2.086(7)
Ga(2)–C(21)	1.94(1)	Ga(2)–C(25)	1.96(1)
Ti(1)–O(1)	2.032(6)	Ti(1)–O(5)	1.811(6)
Ti(1)–O(6)	2.024(6)	Ti(1)–O(10)	1.831(6)
Ti(1)–O(21)	1.725(9)		
Bond angles			
O(1)–Ga(1)–O(6)	75.1(2)	O(1)–Ga(1)–C(11)	112.8(3)
O(1)–Ga(1)–C(15)	110.4(3)	O(6)–Ga(1)–C(11)	112.4(4)
O(6)–Ga(1)–C(15)	110.1(3)	C(11)–Ga(1)–C(15)	125.1(4)
O(21)–Ga(2)–N(1)	96.1(3)	O(21)–Ga(2)–C(21)	110.4(5)
O(21)–Ga(2)–C(25)	121.1(6)	N(1)–Ga(2)–C(21)	108.0(5)
N(1)–Ga(2)–C(25)	107.0(4)	C(21)–Ga(2)–C(25)	121.1(6)
O(1)–Ti(1)–O(5)	87.1(3)	O(1)–Ti(1)–O(6)	71.0(2)
O(1)–Ti(1)–O(10)	142.6(3)	O(1)–Ti(1)–O(21)	107.6(3)
O(5)–Ti(1)–O(6)	144.8(3)	O(5)–Ti(1)–O(10)	95.6(3)
O(5)–Ti(1)–O(21)	107.5(3)	O(6)–Ti(1)–O(10)	86.7(3)
O(6)–Ti(1)–O(21)	105.3(3)	O(10)–Ti(1)–O(21)	107.0(4)
Ga(2)–O(21)–Ti(1)	106.8(3)		

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 184598–184601 for compounds **1**, **2**, **10** and **11**, 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).

Table 5
Selected bond lengths (Å) and angles (°) for $[(^t\mathrm{Bu})_2\mathrm{Ga(neol)_2TiCp}]$ (**11**)

Molecule 1		Molecule 2	
Bond lengths			
Ga(1a)–O(1a)	1.923(3)	Ga(1b)–O(1b)	1.949(3)
Ga(1a)–O(6a)	1.942(3)	Ga(1b)–O(6b)	1.931(3)
Ga(1a)–C(11a)	1.994(6)	Ga(1b)–C(11b)	2.000(6)
Ga(1a)–C(15a)	2.017(5)	Ga(1b)–C(15b)	2.016(5)
Ti(1a)–O(1a)	2.072(3)	Ti(1b)–O(1b)	2.075(3)
Ti(1a)–O(5a)	1.814(3)	Ti(1b)–O(5b)	1.837(3)
Ti(1a)–O(6a)	2.075(3)	Ti(1b)–O(6b)	2.075(3)
Ti(1a)–O(10a)	1.835(3)	Ti(1b)–O(10b)	1.811(3)
Ti(1a)–Cp(1a)	2.400(6)	Ti(1b)–Cp(1b)	2.416(6)
Ti(1a)–Cp(2a)	2.393(6)	Ti(1b)–Cp(2b)	2.412(6)
Ti(1a)–Cp(3a)	2.412(6)	Ti(1b)–Cp(3b)	2.386(6)
Ti(1a)–Cp(4a)	2.394(6)	Ti(1b)–Cp(4b)	2.369(6)
Ti(1a)–Cp(5a)	2.383(6)	Ti(1b)–Cp(5b)	2.383(6)
Bond angles			
O(1a)–Ga(1a)–O(6a)	74.8(1)	O(1b)–Ga(1b)–O(6b)	74.9(1)
O(1a)–Ga(1a)–C(11a)	115.5(2)	O(1b)–Ga(1b)–C(11b)	113.2(2)
O(1a)–Ga(1a)–O(15a)	110.6(2)	O(1b)–Ga(1b)–O(15b)	111.0(2)
O(6a)–Ga(1a)–C(11a)	112.2(2)	O(6b)–Ga(1b)–C(11b)	113.1(2)
O(6a)–Ga(1a)–C(15a)	111.7(2)	O(6b)–Ga(1b)–C(15b)	111.7(2)
C(11a)–Ga(1a)–C(11a)	122.4(2)	C(11b)–Ga(1b)–C(11b)	122.9(2)
O(1a)–Ti(1a)–O(5a)	83.5(1)	O(1b)–Ti(1b)–O(5b)	83.1(1)
O(1a)–Ti(1a)–O(6a)	68.9(1)	O(1b)–Ti(1b)–O(6b)	69.3(1)
O(1a)–Ti(1a)–O(10a)	135.7(1)	O(1b)–Ti(1b)–O(10b)	136.7(1)
O(5a)–Ti(1a)–O(6a)	134.8(1)	O(5b)–Ti(1b)–O(6b)	133.8(1)
O(5a)–Ti(1a)–O(10a)	93.8(2)	O(5b)–Ti(1b)–O(10b)	93.1(2)
O(6a)–Ti(1a)–O(10a)	83.1(1)	O(6b)–Ti(1b)–O(10b)	83.7(1)

Acknowledgements

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