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Observation of an unusual amine oxidation reaction during the oxidation and hydrolysis of $[(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$: molecular structures of $(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)(\mu\text{-}OH)\text{-}Ga(^{t}Bu)[o\text{-}C_6H_4N(O)Me_2]$ and $(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)(O{=}PPh_3)$†

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Abstract—Reaction of $[(^{t}Bu)_2Ga(\mu\text{-}Cl)]_2$ with $Li(o\text{-}C_6H_4NMe_2)$ yields $[(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2]_2$ (**1**). The atmospheric oxidation/hydrolysis of **1** results in the isolation of $(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)(\mu\text{-}OH)Ga(^{t}Bu)[o\text{-}C_6H_4N(O)Me_2]$ (**2**). The structure of compound **2** (as determined by X-ray crystallography) consists of a gallium dimer in which one of the *ortho*-(dimethylamino)phenyl ligands is oxidized and the other exhibits strong intramolecular O—H···N hydrogen bonding ($\Delta G^{\ddagger} = 57.3$ kJ mol^{-1}) to the hydroxide bridge. A pathway for the formation of **2** is proposed. Reaction of compound **1** with $O{=}PPh_3$ results in the formation of the Lewis acid-base complex $(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)(O{=}PPh_3)$ (**3**), whose structure has been confirmed by X-ray crystallography. © 1997 Elsevier Science Ltd

Keywords: gallium; oxidation; hydrolysis; amine; hydrogen bonding.

Over the past ten years there has been an increasing number of reports of compounds of the Group 13 metals containing bidentate potentially chelating ligands [1]. Potential applications proposed in the literature include: chiral reagents in organic synthesis [2], MOCVD precursors [3], and model compounds for the intermediate stage of an S_N2-like process [4]. Our interest in this class of compound is in their use as models for the alkylalumoxane latent Lewis acid catalysts [5]. During our investigations we observed that one of these compounds, $[(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$, repeatedly underwent a clean decomposition in the presence of humid air to give a single isolable species. Given our previous studies concerning the oxidation and hydrolysis of Group 13 compounds we have undertaken an investigation of this decomposition product [6–8].

RESULTS AND DISCUSSION

Reaction of *ortho*-(dimethylamino)phenyl lithium with $[(^{t}Bu)_2Ga(\mu\text{-}Cl)]_2$ [9], in hexane, yields $[(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$ (**1**), whose structure based upon mass spectrometry and literature precedent [10], is a dimer. Full spectroscopic characterization of compound **1** is given in the Experimental section.

Compound **1** is air and moisture sensitive and decomposes readily in hexane solution upon exposure to humid air to give $(^{t}Bu)_2Ga(o\text{-}C_6H_4NMe_2)(\mu\text{-}OH)Ga(^{t}Bu)[o\text{-}C_6H_4N(O)Me_2]$ (**2**). Compound **2** has been characterized by NMR and IR spectroscopy, mass spectrometry, and X-ray crystallography.

The molecular structure of $(^{t}Bu)_2Ga(o\text{-}C_6H_4$

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† Dedicated to the memory of Sir Geoffrey Wilkinson for his contributions to inorganic chemistry.

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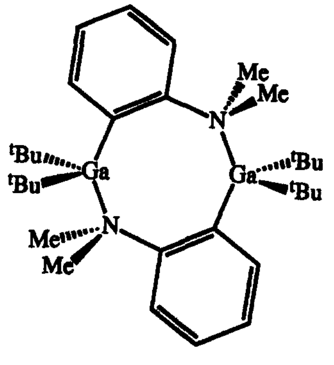


(1)

$\overline{\mathrm{NMe_2)(\mu\text{-}OH}}\overline{\mathrm{Ga(^tBu)[\mathit{o}\text{-}C_6H_4N(O}}\mathrm{)Me_2]}$ **2** is shown in Fig. 1: selected bond lengths and angles are given in Table 1. The structure consists of an asymmetric digallium dimer in which the two 4-coordinate gallium centers are bridged by a single hydroxide bridge, see below. The coordination environment of Ga(1) is completed by one *tert*-butyl ligand and a chelating *ortho*-(dimethylamino-*N*-oxide)phenyl ligand. In contrast, Ga(2) coordination environment includes two *tert*-butyl ligands and an *ortho*-(dimethylamino)phenyl ligand. It should be noted that the *ortho*-(dimethylamino-*N*-oxide)phenyl ligand is isolobal with the *ortho*-(dimethylamino)methylphenyl ligand, which has been demonstrated to chelate to gallium [10].

The unoxidized *ortho*-(dimethylamino)phenyl ligand is positioned coplanar with the Ga(1)—O(1)—Ga(2) plane and the O(1)···N(27) distance (2.80 Å) is within the range suitable for a hydrogen bonding interaction [11]. The hydroxide hydrogen was located in the electron difference map, and the IR spectrum contains a broad band at 3400 cm^{-1} characteristic of a hydrogen bonded O—H group. Both these experimental measurements, and the low acidities previously observed for gallium hydroxides [12] are consistent with the O—H···N representation. However, it is worth noting that since the Ga(1)—O(1) bond distance [1.868(8) Å] is shorter than would be expected for a gallium hydroxide (*ca* 2.00 Å) but similar to that observed for gallium oxide (1.87–1.89 Å) [13], some component of the Zwitter ionic O$^-$···H—N$^+$ form should be considered.

The retention of the O—H···N hydrogen bond at room temperature in solution is confirmed from the ^{1}H NMR spectrum (see Experimental), which indicates that each of the *tert*-butyl groups on Ga(2) and the methyl groups on N(7) are magnetically inequi-

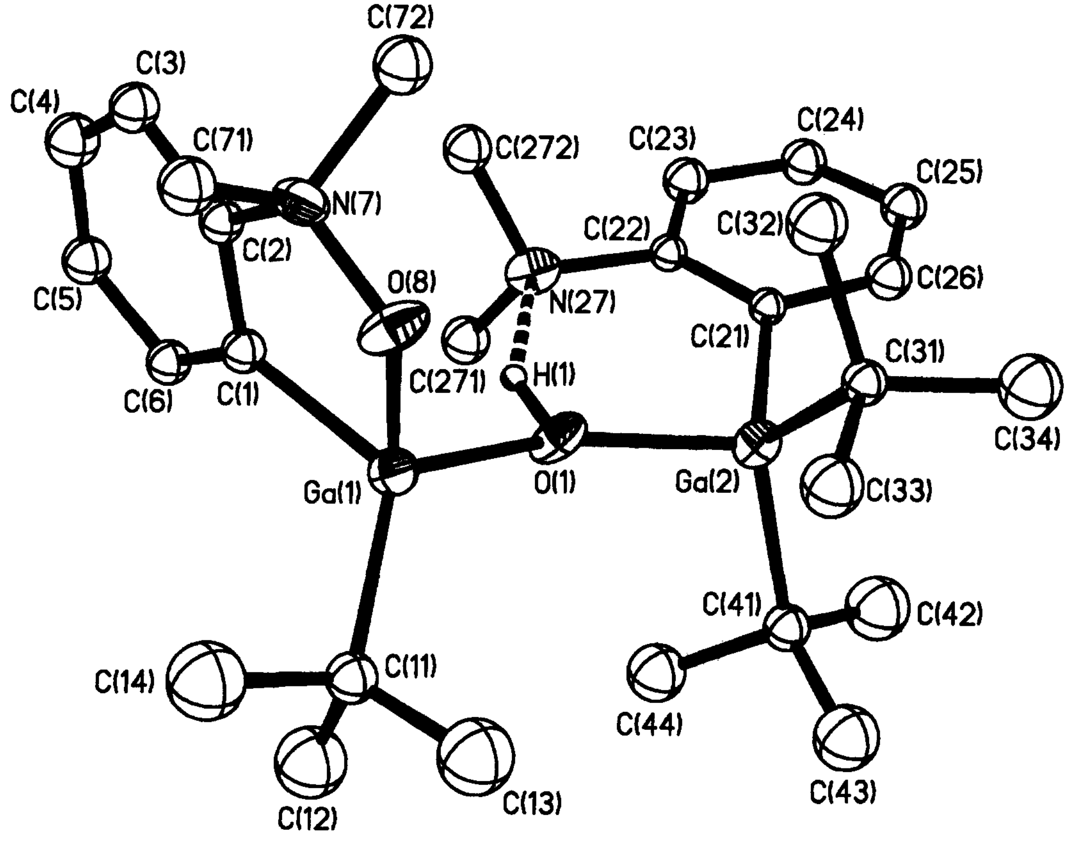


Fig. 1. The molecular structure of $\mathrm{(^tBu)_2Ga(\mathit{o}\text{-}}\overline{\mathrm{C_6H_4NMe_2)(\mu\text{-}OH}}\overline{\mathrm{Ga(^tBu)[\mathit{o}\text{-}C_6H_4N(O}}\mathrm{)Me_2]}$ (**2**). Thermal ellipsoids are shown at the 30% level and organic hydrogen atoms are omitted for clarity.

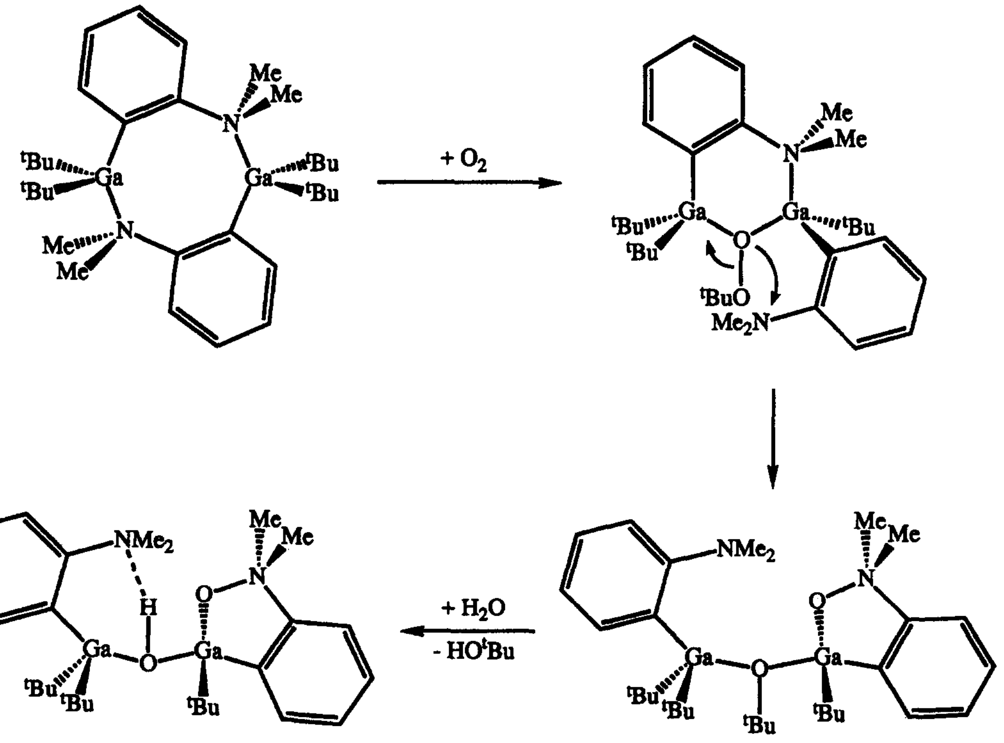
Table 1. Selected bond lengths (Å) and angles (°) for $(^{t}\mathrm{Bu})_2\mathrm{Ga}(o\text{-}\mathrm{C_6H_4NMe_2})(\mu\text{-}\mathrm{OH})\mathrm{Ga}(^{t}\mathrm{Bu})[o\text{-}\mathrm{C_6H_4N(O)Me_2}]$ (2)

Ga(1)—O(1)	1.868(8)	Ga(1)—O(8)	1.919(8)
Ga(1)—C(1)	1.97(1)	Ga(1)—C(11)	2.00(2)
Ga(2)—O(1)	1.977(7)	Ga(2)—C(21)	2.01(1)
Ga(2)—C(31)	2.01(1)	Ga(2)—C(41)	2.03(1)
O(8)—N(7)	1.38(1)		
O(1)—Ga(1)—O(8)	105.9(4)	O(1)—Ga(1)—C(1)	108.4(4)
O(1)—Ga(1)—C(11)	118.7(4)	O(8)—Ga(1)—C(1)	85.5(4)
O(8)—Ga(1)—C(11)	110.2(5)	C(1)—Ga(1)—C(11)	121.9(6)
O(1)—Ga(2)—C(21)	102.2(4)	O(1)—Ga(2)—C(31)	104.9(4)
O(1)—Ga(2)—C(41)	106.1(5)	C(21)—Ga(2)—C(31)	112.4(6)
C(21)—Ga(2)—C(41)	107.8(5)	C(31)—Ga(2)—C(41)	121.5(5)
Ga(1)—O(1)—Ga(2)	153.6(4)	Ga(1)—O(8)—N(7)	115.6(6)

valent. Upon warming the resonances for the *tert*-butyl ligands coalesce ($T_c = 32°C$), indicating free rotation about Ga(2)—O(1). The $\Delta G^{\ddagger}$ for breaking the intramolecular hydrogen bond is thus calculated, by the method of Shanan-Atidi and Bar-Eli [14] to be 57.3 kJ mol^{-1}.

The observation that hydrolysis of compound **1** results in the formation of $[(^{t}\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{OH})]_3$ and dimethylanaline (see Experimental) indicates that during the formation of compound **2**, oxidation must precede hydrolysis. Based upon literature precedent, and the scoping reactions described below, we propose that compound **2** is formed *via* the following reaction sequence outlined in Scheme 1 : (1) auto-oxidation of one of the *tert*-butyl ligands to give a *tert*-butylperoxide ligand. (2) Intramolecular oxidation of the *ortho*-(*N*,*N*-dimethylamino)phenyl ligand and the concurrent formation of an alkoxide ligand. (3) Hydrolysis of the *tert*-butoxide ligand to a hydroxide.

Supporting evidence for this proposal includes the following : (1) Oxidation of $\mathrm{Ga}(^{t}\mathrm{Bu})_3$ yields the alkylperoxide compound, $[(^{t}\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{OO}^{t}\mathrm{Bu})]_2$ [7]. (2) Dimeric $[(^{t}\mathrm{Bu})_2\mathrm{Ga}(o\text{-}\mathrm{C_6H_4NMe_2})]_2$ (**1**) is cleaved by oxygen donor ligands such as O═PPh$_3$ to give $(^{t}\mathrm{Bu})_2$

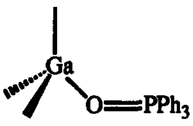


Scheme 1. Proposed reaction pathway for the formation of $(^{t}\mathrm{Bu})_2\mathrm{Ga}(o\text{-}\mathrm{C_6H_4NMe_2})(\mu\text{-}\mathrm{OH})\mathrm{Ga}(^{t}\mathrm{Bu})[o\text{-}\mathrm{C_6H_4N(O)Me_2}]$ (2) from $[(^{t}\mathrm{Bu})_2\mathrm{Ga}(o\text{-}\mathrm{C_6H_4NMe_2})]_2$ (1).

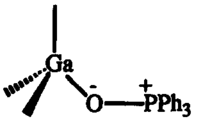
$Ga(o\text{-}C_6H_4NMe_2)(O{=}PPh_3)$ (**3**), whose structure has been confirmed by X-ray crystallography, see below. (3) $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ readily oxidizes phosphines to give a coordinated phosphine oxide and an alkoxide, i.e., $[(^tBu)_2Ga(O^tBu)(O{=}PR_3)$ [8]. (4) Hydrolysis of $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ yields $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ and ^{t}BuOH [15].

It is interesting to note that while $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ oxidizes phosphines to give $(^tBu)_2Ga(O^tBu)(O{=}PR_3)$ [8], we were unable to observe a similar reaction for the oxidation of dimethylanaline. Perhaps this is not surprising since *N*,*N*-dimethylanaline (and other tertiary amines, NR_3) are only readily oxidized with strong oxidizing reagents, such as hydrogen peroxide [16] and Caro's acid ($H_2SO_4/H_2SO_5/H_2O$) [17]. Thus, the formation of compound **2** would therefore suggest that intra-molecular oxidation reactions of gallium alkylperoxides are more facile than their inter-molecular counterparts. This is consistent with the report that the rate of oxidation of dimethylanaline by Caro's acid [18] is proportional to the concentration of both reagents. Since the local concentration of the peroxide is maximized in an intra-molecular reaction the rate is also increased.

The molecular structure of $(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)(O{=}PPh_3)$ (**3**) is shown in Fig. 2: selected bond lengths and angles are given in Table 2. The large Ga(1) ··· N(1) distance (3.25 Å) clearly precludes any Ga—N bond from the *ortho*-dimethylamino phenyl ligand. The P—O bond in **3** [1.494(3) Å] is within experimental error of that in uncoordinated $O{=}PPh_3$ [1.483(2) [19], and within the range of distances reported for phosphorylic complexes (1.49–1.52 Å) [20]. The P—O distance is therefore consistent with the mode of phosphine oxide coordination described as depicted in **I**, without significant contribution of the resonance from **II**. The Ga(1)—O(1)—P(1) angle in compound **3** [161.7(2)°] is smaller than that observed in $Cl_3Ga(O{=}PPh_3)$ (180°) [21], but comparable to that reported for $(Ph_3P{=}O)[AlO_{12}(SiPh)_7]$ [160.0(4)°] [22].



(I)



(II)

EXPERIMENTAL

All operations were carried out using Schlenk techniques or in an argon atmospheric VAC glovebox. The synthesis of $[(^tBu)_2Ga(\mu\text{-}Cl)]_2$, $[(^tBu)_2Ga(\mu\text{-}OO^tBu)_2$, and $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ are reported elsewhere [7,9], ^{1}H and ^{13}C NMR analysis was carried out on a Bruker WM-250 MHz spectrometer. Mass spectra analysis was obtained on a Finnegan MAT95 mass spectrometer with an electron beam energy of 70 eV for EI mass spectra. IR analysis was carried out on a Perkin Elmer 1600 Series FT-IR spectrometer using Nujol mulls.

$[(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$ (1)

To a hexane solution (20 cm^{-3}) of $[(^tBu)_2Ga(\mu\text{-}Cl)]_2$ (0.5 g, 1.1 mmol) was added a hexane solution (20 cm^3) of $Li(o\text{-}C_6H_4NMe_2)$ (0.29 g, 2.3 mmol) at room temperature. The reaction was stirred for 16 h and the LiCl precipitate removed by filtration. The solvent was removed *in vacuo* resulting in a colorless oil. Yield: *ca* 40%. MS (%): *m/z* 608 ($2M^+$, 10), 520 ($2M^+{-}2NMe_2$, 4), 246 ($M^+{-}^tBu$, 100), 120 ($C_6H_4NMe_2$, 50). IR (cm^{-1}): 3051 (m), 2953 (s), 2833 (s), 1601 (m), 1565 (m), 1507 (m), 1465 (s), 1359 (m), 1259 (s), 1106 (m), 1022 (s), 933 (s), 809 (s), 772 (s) 558 (w). ^{1}H NMR (C_6D_6): 6.61–7.51 (8H, m, C_6H_4), 2.34 [12H, s, $N(CH_3)_2$], 1.26 [36H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): 159.57 (Ga—C, C_6H_4), 136.7, 129.6, 128.5, 117.4, 117.2 (C_6H_4), 49.2 [$N(CH_3)_2$], 31.8 [$C(CH_3)_3$].

$(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2(\mu\text{-}OH)(Ga(^tBu)[o\text{-}C_6H_4N(O)Me_2]$ (2)

A hexane (20 cm^3) solution of $[(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$ (0.2 g, 0.3 mmol) was exposed to humid air. Colorless crystals were then grown upon cooling to −16°C. Yield: *ca* 25%. M.p: 132–135°C. MS (%): *m/z* 278 [$Ga(O)(^tBu)\{o\text{-}C_6H_4N(O)Me_2\}$ 40], 262 [$Ga(^tBu)\{o\text{-}C_6H_4N(O)Me_2\}$, 30], 246 [$Ga(^tBu)(o\text{-}C_6H_4NMe_2)$, 10), 205 [$Ga\{o\text{-}C_6H_4N(O)Me_2\}$, 25], 189 [$Ga)o\text{-}C_6H_4NMe_2)$, 10], ^{1}H NMR ($C_6D_6$): 6.13–7.88 (8H, m, C_6H_4), 2.69 [3H, br, s, $ON(CH_3)_2$], 2.58 [6H, s, $N(CH_3)_2$], 2.34 [3H, br, s, $ON(CH_3)_2$], 1.59 [9H, br, s, $C(CH_3)_3$], 1.37 [9H, s, $C(CH_3)_3$], 1.17 [9H, br, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): 156.77 (Ga—C, C_6H_4), 160.55 (Ga—C, C_6H_4), 139.1, 137.7, 129.7, 127.2, 125.6, 119.9, 116.5, (C_6H_4), 61.4 [$ON(CH_3)_2$], 61.1 [$ON(CH_3)_2$], 47.8 [$N(CH_3)_2$], 32.6 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$].

Hydrolysis of $[(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$

To a hexane solution (20 cm^3) of $[(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$ (0.35 g, 0.58 mmol) was added H_2O (0.1 cm^3). The reaction was stirred overnight, after which time colorless crystals of $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ deposited. The ^{1}H NMR, IR, and MS were identical to those of a genuine sample [7].

$(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)(O{=}PPh_3)$ (3)

To a toluene solution (20 cm^3) of $[(^tBu)_2Ga(o\text{-}C_6H_4NMe_2)]_2$ (0.10 g, 0.15 mmol) was added a toluene

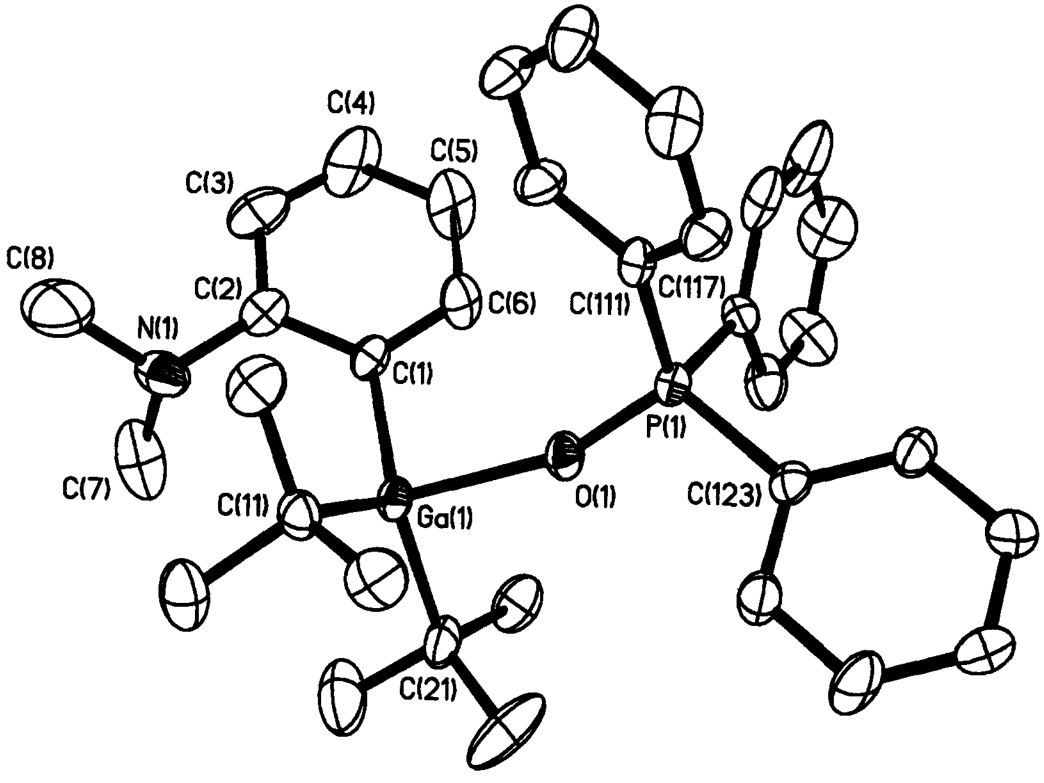


Fig. 2. The molecular structure of (^{t}Bu)$_2$Ga(o-C$_6$H$_4$NMe$_2$)(O=PPh$_3$) (3). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for (^{t}Bu)$_2$Ga(o-C$_6$H$_4$NMe$_2$)(O=PPh$_3$) (3)

Ga(1)—O(1)	2.091(3)	Ga(1)—C(1)	2.029(5)
Ga(1)—C(11)	2.020(4)	Ga(1)—C(21)	2.033(6)
P(1)—O(1)	1.494(3)		
O(1)—Ga(1)—C(1)	97.8(2)	O(1)—Ga(1)—C(11)	100.6(2)
O(1)—Ga(1)—C(21)	96.0(2)	C(1)—Ga(1)—C(11)	117.9(2)
C(1)—Ga(1)—C(21)	115.9(2)	C(11)—Ga(2)—C(21)	120.3(2)
Ga(1)—O(1)—P(1)	161.7(2)		

solution (20 cm^3) of O=PPh$_3$ (0.09 g, 0.32 mmol) at room temperature. The reaction was stirred overnight, and the resulting solution was filtered, concentrated and cooled (−16°C) to give colorless crystals. Yield: 34%. M.p.: 159–163°C. MS (%): m/z 525 (M$^+$—^{t}Bu, 35), 480 (M$^+$—^{t}Bu—NMe$_2$, 36), 346 [Ga(O=PPh$_3$), 100], 328 [(^{t}Bu)Ga(O=PPh$_2$), 60], 308 [Ga(^{t}Bu)$_2$(O=PPh), 91], 278 (O=PPH$_3$, 100), 247 [(^{t}Bu)Ga(o-C$_6$H$_4$NMe$_2$)], 100), 203 [Ga(o-C$_6$H$_4$NMe$_2$), 100), IR (cm^{-1}): 1591(w), 1570(w), 1558(w), 1160(m), 1118(m), 1091(m), 813(m), 772(m), 746(s), 722(s), 694(s), 537(s), 453(m). ^{1}H NMR (CDCl$_3$): 6.99—7.65 (19H, m, C$_6$$H_4$, PPh$_3$), 2.75 [6H, s, N(C$H_3$)$_2$], 0.98 [18H, s, C(C$H_3$)$_3$]. ^{13}C NMR (C$_6D_6$): 161.0 (Ga—$C$, C$_6H_4$), 152.5, 138.2, 126.1, 126.0 (C_6H$_4$), 132.8 [J(P—C) = 106.5 Hz, P—C], 133.0 [d, J(C—P) = 9.9 Hz, o-CH], 132.4 [d, J(C—P) = 2.2 Hz, p-CH], 128.9 [d, J(C—P) = 12.3 Hz, m-CH], 48.7 [N(CH$_3$)$_2$], 32.4 [C(CH$_3$)$_3$]. ^{31}P NMR (C$_6$D$_6$): 25.4.

Crystallographic studies

Crystals of compounds **2** and **3** were sealed in a glass capillary under argon and mounted on the goniometer of a Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described [23], using the $\theta/2\theta$ scan technique. Pertinent details are given in Table 3. The structures were solved by direct methods (SHELX86) [24]. The

Table 3. Summary of X-ray diffraction data

Compound	**2**	**3**
Empirical form	$C_{28}H_{48}Ga_2N_2O_2$	$C_{34}H_{43}GaNOP$
Crystal size (mm)	0.11 × 0.13 × 0.41	0.12 × 0.14 × 0.42
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	10.1212(6)	9.404(1)
b(Å)	12.412(1)	11.087(2)
c(Å)	14.194(2)	16.666(1)
α(°)	65.514(9)	95.97(1)
β(°)	82.989(8)	104.603(9)
γ(°)	73.549(6)	106.86(1)
V(Å^3)	1556.3(3)	1579.5(4)
Z	2	2
D(calcd)(g cm^{-3})	1.246	1.225
μ(mm^{-1})	1.748	0.971
Radiation	Mo-K$_\alpha$(λ = 0.71073 Å) graphite monochrometer	
Temp(K)	298	298
2θ range (°)	2.0–44.0	3.0–44.0
No. collected	3799	3851
No. ind	3799	3851
No. obsd	1528 ($\lvert F_o \rvert > 6\sigma \lvert F_o \rvert$)	2865($\lvert F_o \rvert > 6\sigma \lvert F_o \rvert$)
Weighting scheme	$w^{-1} = 0.04(\lvert F_o \rvert)^2 + \sigma(\lvert F_o \rvert)^2$	$w^{-1} = 0.04(\lvert F_o \rvert)^2 + \sigma(\lvert F_o \rvert)^2$
R	0.0512	0.0395
R_w	0.0606	0.0441
Largest diff peak (eÅ^{-3})	0.43	0.36

models were refined using full-matrix least squares techniques. Ga, N, and O atoms were refined anisotropically for compound **2**, while all non-hydrogen atoms were refined anisotropically for compound **3**. Except for the hydroxide hydrogen, hydrogen atoms were included and constrained to "ride" upon the appropriate atoms [d(C—H) = 0.95 Å, U(H) = 1.3 B_{eq}(C)]. The hydroxide hydrogen was located in the difference map, and its isotropic thermal parameter was allowed to "ride" upon that of O(1) [U(H) = 1.3 B_{eq}(O)]. All computations other than those specified were performed using MolEN [25]. A summary of cell parameters, data collection, and structure solution is given in Table 3. Scattering factors were taken from [26].

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