Synthesis and Molecular Structure of $(^{t}Bu)_2Ga(OCPh_3)$: An Example of a Possible Intramolecular π-Interaction

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Summary: Reaction of tri-tert-butylgallium with triphenylmethanol affords the monomeric product $(^{t}Bu)_2Ga(OCPh_3)$*, in which the gallium is three-coordinate. The presence of a short Ga···phenyl intramolecular contact may be explained by the possible donation of electron density from the* π *orbital of one phenyl group to the vacant p orbital of tricoordinate gallium. The compound crystallizes in the monoclinic space group* $P2_1/n$*, with* $a = 9.533(2)$ Å, $b = 17.030(4)$ Å, $c = 14.289(4)$ Å, $\beta = 90.57(2)°$, $Z = 4$*, 2541 observed data,* $R = 0.049$*, and* $R_w = 0.059$*.*

Recent work in our laboratory has been concerned with the synthesis and reactivity of *tert*-butyl derivatives of gallium.[1] Despite the steric bulk of the *tert*-butyl groups the only monomeric compounds with a three-coordinate gallium we have been able to isolate are the hybrid alkyls $GaMe_2(^{t}Bu)$ and $GaMe(^{t}Bu)_2$.[1a] Recently, Power and coworkers have reported[2] the synthesis and crystallographic characterization of the monomeric aryloxide compound $(^{t}Bu)_2Ga(OC_6H_2\text{-}2,4,6\text{-}^{t}Bu_3)$. We now report that the sterically hindered triphenylmethoxide ligand also allows for the isolation of a monomeric three-coordinate gallium alkoxide, with an unusual intramolecular π-interaction.

The reaction of $Ga(^{t}Bu)_3$ with $HOCPh_3$ leads, in addition to the evolution of butane, to a single product, $(^{t}Bu)_2Ga(OCPh_3)$,[3] which has been characterized by IR, NMR,[4] and mass spectrometry.[5] The mass spectrum indicates $(^{t}Bu)_2Ga(OCPh_3)$ to be monomeric in the gas phase;[5] this structure has been confirmed for the solid state by X-ray crystallography.[6]

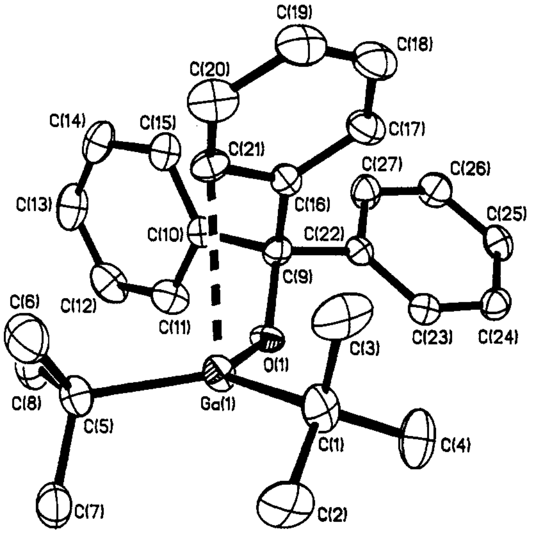

Figure 1. Molecular structure of $(^{t}Bu)_2Ga(OCPh_3)$. Thermal ellipsoids are shown at the 50% probability level. Hydrogens have been omitted for clarity.

The molecular structure of $(^{t}Bu)_2Ga(OCPh_3)$ is shown in Figure 1. The structure consists of discrete monomeric units with the gallium atom in a distorted-trigonal-planar configuration. As is observed in the structure of $(^{t}Bu)_2Ga(OC_6H_2\text{-}2,4,6\text{-}^{t}Bu_3)$,[2] the angles about the gallium associated with the oxygen (O(1)–Ga(1)–C(1) = 115.0(2)°, O(1)–Ga(1)–C(5) = 118.2(2)°) are slightly asymmetric and smaller than the angle between the two *tert*-butyl groups (C(1)–Ga(1)–C(5) = 126.1(2)°). While the Ga(1)–O(1) distance in $(^{t}Bu)_2Ga(OCPh_3)$ (1.831(4) Å) is, by comparison to previously characterized four-coordinate compounds,[7] within the range expected for a terminal alkoxide on a three-coordinate gallium, the Ga(1)–O(1)–C(1) angle (127.5(3)°) is more acute than has been previously observed for terminal gallium alkoxides (132.3(4)°).[7] Furthermore, the orientation of the CPh_3 fragment is such as to preclude a π-type interaction between the oxygen lone pairs and the vacant p_z orbital on gallium (z perpendicular to the C_2GaO plane) and enhance detrimental intermolecular

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(3) A hexane solution (40 mL) of $Ga(^{t}Bu)_3$ (4.43 g, 18.2 mmol) was added to a suspension of $HOCPh_3$ (4.75 g, 18.2 mmol) in hexane (30 mL). The mixture was heated to reflux for 12 h, at which point all solid had dissolved. After the mixture was cooled, the solvent volume was reduced in vacuo and the remaining solution cooled (−24 °C) to yield colorless crystals: yield 79%; mp 128 °C.

(4) ^{1}H NMR (C_6D_6, 25 °C, δ): 7.54 [6H, d, J(H–H) = 8.0 Hz, o-C*H*], 7.11 [6H, t, J(H–H) = 8.0 Hz, m-C*H*], 7.01 [3H, d, J(H–H) = 8.0 Hz, p-C*H*], 0.95 [18H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6, 25 °C, δ): 151.60, 150.51, 127.51, 125.97 (C_5H_5), 29.77 [$C(CH_3)_3$], 28.98 [$C(CH_3)_3$]. IR (KBr pellet, cm^{-1}): 2950 (m), 2926 (m), 2840 (s), 1491 (m), 1468 (m), 1445 (m), 1025 (m), 1015 (m), 760 (s), 701 (s).

(5) MS (EI; m/z (%)): 385 ($M^+ - {}^{t}Bu$, 100). MS (CI, isobutane; m/z (%)): 385 ($M^+ - {}^{t}Bu$, 100).

(6) Crystal data for $(^{t}Bu)_2Ga(OCPh_3)$: monoclinic, $P2_1/n$, $a = 9.533(2)$ Å, $b = 17.030(4)$ Å, $c = 14.289(4)$ Å, $\beta = 90.57(2)°$, $V = 2319.7(9)$ Å^3, $Z = 4$, D(calcd) = 1.269 g cm^{-3}, λ(Mo Kα) = 0.710 73 Å (graphite monochromator), T = 193 K. A Nicolet R3m/V diffractometer, equipped with an LT-1 low-temperature device, was used to collect 3484 reflections (4° < 2θ < 45°) on a white crystal (0.73 × 0.55 × 0.54 mm). Of these, 3029 were independent (R_{int} = 1.76%) and 2541 were observed ($F_o > 4\sigma(F_o)$). Lorentz and polarization corrections were applied to the data. All the heavy atoms were located by direct methods. One of the gallium *tert*-butyl groups shows rotational disorder about the Ga(1)–C(1) bond. The two sets of methyl groups were initially included in the refinement such that equivalent atoms were treated with linked thermal parameters and the group occupancies were constrained to total 1. The latter converged at values of 0.81 and 0.19 and were subsequently fixed as such in subsequent refinements. The thermal parameters of the major isomer were found to be refined freely and anisotropically; however, those of the minor isomer were fixed (U(iso) = 0.05 Å^2). All Ga, O, and C atoms (other than those of the minor disordered component) were refined anisotropically. The hydrogen atoms were placed in calculated positions (U_{iso}(H) = 0.08 Å^2, d_{C-H} = 0.96 Å) for refinement. $R = 0.049$; $R_w = 0.059$. All computations used SHELXTL-PLUS: Sheldrick, G. Nicolet Corp., Madison, WI, 1987.

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Ph···${}^tBu$ interactions. However, the acute Ga(1)–O(1)–C(9) angle does allow for the gallium to have rather short *intra*molecular contacts with the carbon atoms of one of the phenyl groups. The shortest interaction (Ga(1)···C(21) = 2.894(6) Å) is shown as a dotted line in Figure 1. Values for the van der Waals radius of Ga(III) are not available, but previous workers[8] have assumed a value between 1.7 and 2.0 Å. If these values are combined with that of the half-thickness of a benzene ring (1.7 Å),[9] then a Ga···C distance of 3.4–3.7 Å is expected. Clearly in the present case both Ga(1)···C(21) and Ga(1)···C(16) (3.081(6) Å) are significantly shorter. It is reasonable to propose the presence of a possible interaction involving donation of electron density from the π system of the phenyl group into the vacant p orbital of the gallium.[10] If there exists a bonding interaction between the phenyl and the gallium, then some distortion of the C_2GaO plane and/or pyramidalization at C(21) is expected.[11] Indeed, the gallium atom lies ca. 0.09 Å above the C_2O plane, toward the phenyl group. Similar distortions from planarity have been observed for three-coordinate aluminum compounds with intramolecular C–H···Al interactions.[12] In addition, the phenyl ring (C(16)–C(21)) is tilted toward the gallium atom (i.e., C(9)–C(16)–C(21) = 118.8(5)°, C(9)–C(16)–C(17) = 123.5(5)°), counter to steric effects.

In solution, at room temperature the three phenyl rings are equivalent, indicating free rotation about the Ga–O and O–C bonds. Cooling an NMR sample of $({}^tBu)_2Ga(OCPh_3)$ results in decoalescence of the signal due to the meta ring protons ($T_c = -12$ °C) to two resonances centered at 7.11 (2H) and 7.06 (4H) ppm, consistent with cession of free rotation of the $OCPh_3$ moiety. The activation energy ($\Delta G^\ddagger$) associated with this process is calculated from the NMR data to be 13.4 (±0.2) kJ mol^{-1}, which is lower than the value observed previously for the rotation of the triphenylsiloxide groups in $Al(OSiPh_3)_3(H_2O)\cdot 2THF$ (16.5 (±0.3) kJ mol^{-1}).[13] However, this difference is most probably steric in origin rather than a consequence of significant Si–O π-interactions. No further changes in the ^1H NMR spectrum of 1 are observed upon cooling to −70 °C.

While π-complexes of aryl groups with Ga(I) are common,[14] and are in general η^6, those with Ga(III) are rare. To the best of our knowledge the only other example to be crystallographically characterized is $GaPh_3$, in which each tricoordinate gallium makes short *inter*molecular (3.42 Å) contacts with a phenyl group of centrosymmetrically related molecules in the layers above and below. The larger Ga···C distance in $GaPh_3$ compared to $({}^tBu)_2Ga(OCPh_3)$ may be due to the presence of two π-interactions in the former as opposed to one in the latter. Finally, we note that while $({}^tBu)_2Ga(OCPh_3)$ exhibits a possible *intra*molecular arene···gallium interaction, structural evidence has been presented for other group 13 "agostic"[15] interactions, namely C–H···Al,[2,16] C–H···In,[17] and C–F···In.[18]

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Supplementary Material Available: Tables of positional parameters, bond distances and angles, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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[10] We note that the monomeric nature of $({}^tBu)_2Ga(OCPh_3)$ is undoubtedly dictated by the steric bulk of the *tert*-butyl and triphenylmethoxide ligands and not the presence of the *intra*molecular π-interaction.

[11] In response to the comments of one of the reviewers, the hydrogen atom attached to C(21), i.e., H(21a), was located in the X-ray difference map and freely refined. Convergence occurred with H(21a) 0.15 Å out the phenyl C_6 plane, indicative of pyramidalization at C(21).

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