2,6-Bis(2,4,6-triisopropylphenyl)phenyl as an extraordinarily bulky ligand in organometallic chemistry. Synthesis and molecular structure of $[(Mes^*{}_2C_6H_3)MCl_2]_2$ (M = Ga, In; Mes* = $C_6H_2Pr^i{}_3$-2,4,6)

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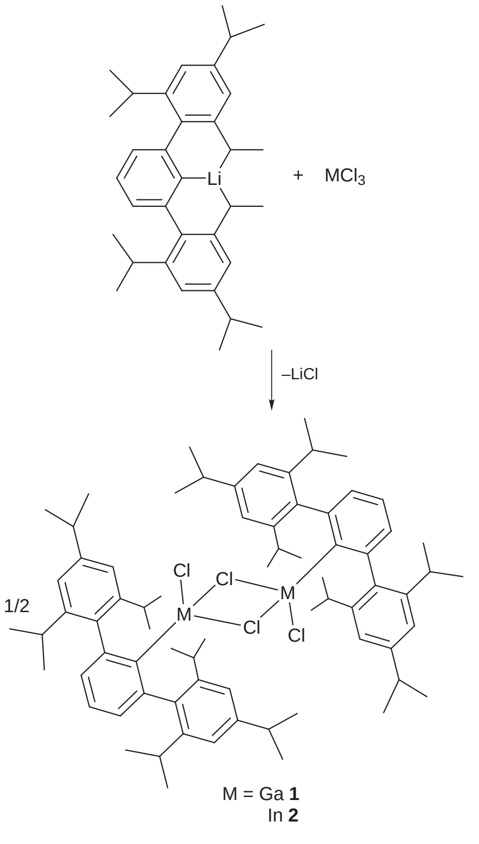
Gallium chloride or indium chloride interacts with 2,6-bis(2,4,6-triisopropylphenyl)phenyllithium, $(Mes^*{}_2C_6H_3)Li$ (Mes* = $C_6H_2Pr^i{}_3$-2,4,6), affording $[(Mes^*{}_2C_6H_3)MCl_2]_2$ (M = Ga 1, In 2), interesting group 13 organometallic crystalline dimers, characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction.

The utilization of bulky ligands in organometallic chemistry is a proven means to compounds which may be particularly sensitive, reactive, or otherwise unstable. This practice has achieved great prominence in the organometallic chemistry of the heavier group 13 elements, particularly where aryl ligands are concerned. The simplest aryl derivatives, triphenylaluminium and triphenylgallium, have been known for decades while the bulkier trimesityl derivatives of aluminium[1] and gallium[2] were first reported in 1986. Herein we report the synthesis† and molecular structure‡ of gallium (**1**) and indium (**2**) derivatives of the very sterically demanding 2,6-bis(2,4,6-triisopropylphenyl)phenyl ligand, $Mes^*{}_2C_6H_3$ (Mes* = $C_6H_2Pr^i{}_3$-2,4,6),[3] $[(Mes^*{}_2C_6H_3)MCl_2]_2$, isolated from reaction of $(Mes^*{}_2C_6H_3)Li$ with the respective metal chloride [eqn. (1)].



(1)

The title compounds, characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction, are noteworthy as they represent interesting organometallic group 13 halide derivatives of the sterically demanding 2,6-bis(2,4,6-triisopropylphenyl)phenyl ligand. The molecular structure of $[(Mes^*{}_2C_6H_3)MCl_2]_2$ (M = Ga **1**, In **2**) is shown in Fig. 1.

Sterically demanding arylgallium dihalides have been shown to play a critical role in the preparation of novel low-valent organometallic gallanes containing Ga–Ga bonds. For example, 2,6-dimesitylphenylgallium dichloride, upon alkali metal reduction, has been shown to afford $Ga_3{}^{2-}$ three-membered dianionic metalloaromatic rings.[4–7] Conversely, the gallium dichloride of 2,6-bis(2,4,6-triisopropylphenyl)phenyl, $(Mes^*{}_2C_6H_3)_2GaCl_2$, prepared *in situ* and allowed to interact with sodium, has recently been shown by this laboratory to give an unprecedented gallium–gallium triple bond in $Na_2[Mes^*{}_2C_6H_3Ga{\equiv}GaC_6H_3Mes^*{}_2]$—the first gallyne, a dianionic organogallium congener of acetylene.[8,9] That adjusting the steric demands of an arylgallium halide may afford such interestingly

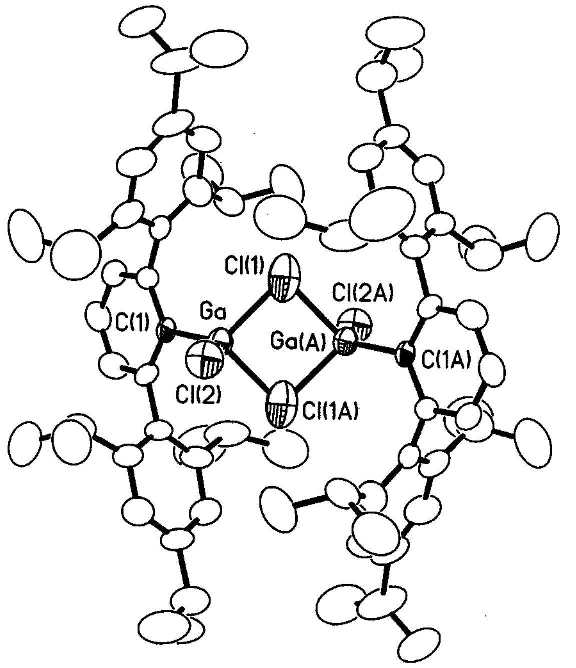


Fig. 1 Molecular structure of **1**. Selected bond distances (Å) and angles (°): for **1**: Ga–C(1) 1.949(8), Ga–Cl(1) 2.196(5), Ga–Cl(1A) 2.201(5), Ga–Cl(2) 2.230(3), Ga(A)–Cl(1) 2.201(5); C(1)–Ga–Cl(1) 112.3(3), C(1)–Ga–Cl(1A) 114.0(3), Cl(1)–Ga–Cl(1A) 90.3(2), C(1)–Ga–Cl(2) 127.3(3), Cl(1)–Ga–Cl(2) 104.0(2), Cl(1A)–Ga–Cl(2) 102.3(2), Ga–Cl(1)–Ga(A) 89.7(2). For **2** (the atom numbering scheme is the same as that for **1**): In–C(1) 2.129(5), In–Cl(1A) 2.233(4), In–Cl(1) 2.236(4). In(A)–Cl(1) 2.233(4); C(1)–In–Cl(1A) 115.3(2), C(1)–In–Cl(1) 114.0(2), Cl(1A)–In–Cl(1) 81.6(2), C(1)–In–Cl(2) 130.7(3), Cl(1A)–In–Cl(2) 103.2(2), Cl(1)–In–Cl(2) 100.7(2), In–Cl(1)–In(A) 98.4(2).

diverse products is sufficiently intriguing to warrant examination of the structural dynamics of this sterically demanding aryl with group 13 metal halides.

Compounds **1** and **2**, soluble in diethyl ether, hexane, and aromatics, assume isostructural dimeric structures possessing two μ_2-bridging chlorine atoms. The bridging chlorine atoms and the metal atoms constitute a planar four-membered M_2Cl_2 ring about a center of symmetry with the two aryl ligands and the two terminal chlorine atoms residing alternately above and below this ring. The environment about the metal centers may be described as distorted tetrahedral as the bond angles about gallium range from 90.3(2) to 127.3(3)°. Considering the steric bulk of the given ligand it is somewhat surprising that these complexes are not monomeric. The most convenient comparison relative to the title compounds concerns the respective 2,6-dimesitylphenyl derivatives. Although the structure of **1** compares with the bis[(dimesitylphenyl)gallium dichloride] derivative, $[(Mes_2C_6H_3)GaCl_2]_2$,[10] it is noteworthy that in **1** the $Ga–Cl_{bridging}$ bond distances [2.196(5) and 2.201(5) Å] are shorter than the $Ga–Cl_{terminal}$ bond distance [2.230(3) Å]. By contrast, for $[(Mes_2C_6H_3)GaCl_2]_2$, the $Ga–Cl_{bridging}$ bond distance [2.334(5) Å] is considerably longer than the $Ga–Cl_{terminal}$ distance [2.172(5) Å]. This trend is also observed for **2** wherein the $In–Cl_{bridging}$ distances [2.236(4) and 2.233(4) Å] are shorter than the $In–Cl_{terminal}$ bond distance [2.448(7) Å]. In $[(Mes_2C_6H_3)InCl_2]_2$[11] the situation is just the opposite with the $In–Cl_{bridging}$ bond distances [2.519(2) and 2.514(2) Å] being considerably longer than the $In–Cl_{terminal}$ bond distances [2.344(3) Å]. Thus, it is interesting to note that for both gallium and indium the bridging M–Cl bonds are shorter than the terminal M–Cl bonds where the sterically more demanding ligand is involved. Indeed, it is noteworthy that the bridging In–Cl distance in **2** of 2.233(4) Å appears to be the shortest In–Cl distance on record. Lastly, it is significant that **2** represents only the third example of a dimeric organoindium halide: $[(Mes_2C_6H_3)InCl_2]_2$ and $[Mes_2InCl]_2$[12] being the other two examples.

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Notes and References

† *Syntheses*: in a dry box a 100 ml flask was charged with $GaCl_3$ (0.88 g, 5 mmol) or $InCl_3$ (1.11 g, 5 mmol) and ether (30 ml). To this solution at −78 °C a diethyl ether solution (30 ml) of $(Mes^*{}_2C_6H_3)Li\cdot OEt_2$ (2.81 g, 5 mmol) was added dropwise with vigorous stirring. The mixture was stirred for 3 h at this temperature and then allowed to warm slowly to room temp. After stirring for one day the solvent was removed from the mixture *in vacuo*. The residue was extracted with hexane (60 ml) and the white precipitate (LiCl) was separated by filtration. The volume of the colorless filtrate was reduced and placed in a freezer (−20 °C) for 2 days to give cubic colorless crystals. Both **1** and **2** crystallize with one unit of hexane in the unit cell. For **1**: 2.2 g, 65% yield; melting point, 256 °C; Anal. Calc. (found) for $C_{72}H_{98}Cl_4Ga_2$ (E + R Microanalytical Laboratories, Corona, NY): C, 69.50 (68.69); H, 7.90 (8.43%). ^1H NMR (300 MHz, 297 K, C_4D_8O), δ 0.89 [d, 12H, CH_3 (Pr^i)], 1.03 [d, 12H, CH_3 (Pr^i)], 1.09 [d, 12H, CH_3 (Pr^i)], 1.22 [d, 12H, CH_3(Pr^i)], 1.26 [d, 12H, CH_3 (Pr^i)], 1.42 [d, 12H, CH_3 (Pr^i)], 2.81 [m, 12H, CH(Pr^i)], 6.61–7.37 [m, 6H, CH (aromatic)], 6.94 [s, 4H, CH (aromatic)], 6.99 [s, 4H, CH (aromatic)]. ^{13}C NMR (300 MHz, 297 K, C_4D_8O), δ 27.67, 33.58, 33.98, 34.12, 37.85, 38.29 (Pr^i); 123.3, 123.9, 130.1, 131.2, 131.6, 150.2, 150.3, 151.7 (aromatic). For **2**: 2.66 g, 75% yield; melting point, 233 °C; Anal. Calc. (found) for $C_{72}H_{98}Cl_4In_2$: C, 64.80 (62.20); H, 7.40 (7.87%). ^1H NMR (300 MHz, 297 K, C_4D_8O), δ 0.90 [d, 12H, CH_3(Pr^i)], 1.04 [d, 12H, CH_3(Pr^i)], 1.09 [d, 12H, CH_3(Pr^i)], 1.22 [d, 12H, CH_3 (Pr^i)], 1.27 [d, 12H, CH_3(Pr^i)], 1.43 [d, 12H, CH_3(Pr^i)], 2.82 [m, 12H, CH(Pr^i)], 6.63–7.39 [m, 6H, CH (aromatic)], 6.96 [s, 4H, CH (aromatic)], 7.01 [s, 4H, CH (aromatic)]. ^{13}C NMR (300 MHz, 297 K, C_4D_8O), δ 28.15, 34.03, 34.46, 34.59, 38.31, 38.77 (Pr^i); 123.8, 124.4, 130.5, 131.8, 132.1, 150.6, 150.8, 152.3 (aromatic). The solvent present in the crystal lattice contributes to the less than ideal elemental analyses.

‡ *Molecular structures*: crystals were mounted in glass capillaries under an atmosphere of nitrogen and sealed. X-Ray intensity data were collected at 22 °C on a Siemens P4 diffractometer (Mo-Kα radiation; λ = 0.710 73 Å) using ω-scan technique to a maximum 2θ value of 45°. Both structures were solved by direct methods using the SHELXTL 5.0[13] system of programs. Non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in ideal positions with their coordinates and thermal parameters riding on the attached carbon atoms. These two crystalline compounds are isostructural: monoclinic, space group $P2_1/c$ (no. 14). The asymmetric unit contains one half $[(Mes^*{}_2C_6H_3)MCl_2]_2$ (M = Ga, In) and one half hexane molecule situated on inversion centers, thereby generating the other half molecules.

Crystallographic data: $[(Mes^*{}_2C_6H_3)GaCl_2]_2$ **1**: a = 13.863(8), b = 15.775(9), c = 18.02(1) Å, β = 106.04(4)°, V = 3789(4) Å^3, Z = 2, R = 0.077, $wR2$ = 0.235 for 2613 [$I > 2\sigma(I)$]. $[(Mes^*{}_2C_6H_3)InCl_2]_2$, **2**: a = 14.273(3), b = 15.671(3), c = 18.048(3) Å, β = 106.45(1)°, V = 3872(1) Å^3, Z = 2, R = 0.039, $wR2$ = 0.122 for 3226 [$I > 2\sigma(I)$]. A slight disorder was observed for the terminal chlorine [Cl(2)] atom in **2**. CDCC 182/959.

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