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Communications

Reactions of a Bulky Arylgallium Dichloride with Organometallic Monoanions. Formation of a Digalloxane with Organometallic Substituents

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Transition metal/group 13 organometallic compounds are beginning to attract attention as precursors for the gas-phase epitaxy of intermetallic phases such as β-CoGa and ϵ-NiIn.[2] Although it would seem that such precursors should necessarily feature a transition metal/group 13 mole ratio of 1/1, developments with other materials systems indicate that different stoichiometries can be employed.[3] The objective of the present work was to prepare organometallic gallium/transition metal complexes of the type $RGa(ML_n)_2$. There are, in fact, a few compounds of this genre in the literature;[4] however, only one (intramolecularly base-stabilized) compound has been characterized structurally.[5] In principle, base-free precursors obviate the possibility of contamination via thermal decomposition of the donor molecule(s). In order to obtain derivatives of this type, it was desirable to employ a bulky organo substituent, R. Accordingly, $Ar'GaCl_2$ ($Ar' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$)[6] was treated with 2.2 equiv of $Na[Co(CO)_4]$ in Et_2O solution at 25 °C.[7] Formulation of the yellow crystalline product as $[Ga(Ar')\{Co(CO)_4\}_2]$ (**1**) was based on elemental analysis,[8] NMR and IR data,[9] and the observation of the $[M - CO]^+$ peak in the high-resolution mass spectrum (*m/z*: calcd, 627.9794; found, 627.9833). Confirmation was provided by an X-ray diffraction study (Figure 1),[10] which revealed that the crystal consists of discrete isolated molecules of **1**. The Ar′ and $Co(CO)_4$ groups are arranged around gallium in a trigonal planar fashion (sum of angles = 360.0(2)°), although the angles are markedly distorted from idealized values. Moreover, the plane of the aryl ring is inclined 17° away from the Ga–C(1) axis. The average Ga–Co bond length (2.497(2) Å) falls within the range of 2.38–2.58 Å reported for the few compounds that feature this linkage.[5,11]

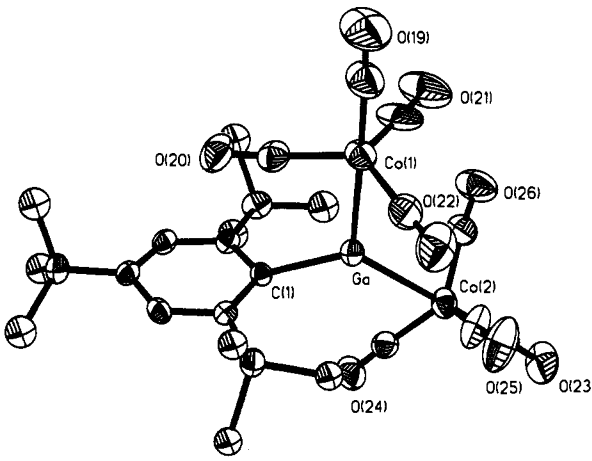

Figure 1. Structure of **1** in the crystal showing the atom numbering scheme. Important bond lengths (Å) and angles (deg): Ga–Co(1) 2.514(2), Ga–Co(2) 2.481(2), Ga–C(1) 2.013(8); Co(1)–Ga–Co(2) 122.2(2), C(1)–Ga–Co(1) 109.4(2), C(1)–Ga–Co(2) 128.4(2).

Interestingly, in the case of the corresponding reaction of $Ar'GaCl_2$ with 2.2 equiv of $Na[Mn(CO)_5]$ in Et_2O solution,[7] the

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(7) A mixture of $[2,4,6\text{-}t\text{-}Bu_3C_6H_2]GaCl_2$[6] (0.206 g, 0.53 mmol) and $NaCo(CO)_4$ (0.228 g, 1.18 mmol) in 30 mL of Et_2O was stirred for 2 h at 25 °C. The resulting red-purple reaction mixture was filtered, following which the solvent and volatiles were removed under reduced pressure. The residual red oil was extracted with hexane. X-ray-quality yellow crystals of **1** were grown in 32% yield by cooling a concentrated hexane solution to −20 °C. Compounds **2**/**3** were prepared similarly by treatment of $[2,4,6\text{-}t\text{-}Bu_3C_6H_2]GaCl_2$[6] (0.155 g, 0.4 mmol) with $NaMn(CO)_5$ (0.191 g, 0.88 mmol) in 40 mL of Et_2O at 25 °C. After it had been stirred for 15 h, the pale green reaction mixture was filtered. Yellow X-ray-quality crystals were grown in 48% yield by storage of the concentrated filtrate at −20 °C. Compound **4** was obtained by treatment of $[2,4,6\text{-}t\text{-}Bu_3C_6H_2]GaCl_2$[6] (0.385 g, 1.0 mmol) with $NaMn(CO)_5$ (0.48 g, 2.2 mmol) in 30 mL of Et_2O at 25 °C. After it had been stirred for 2.5 h, the yellow reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. Toluene (10 mL) was added to the resulting yellow residue. Yellow-orange X-ray-quality crystals of **4** were grown by storage of toluene solution at −20 °C. The properties of **4** were identical to those described in the literature.[16]

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elemental analysis and NMR and IR data for the product[8,9] were inconsistent with the formulation [Ga(Ar′){Mn(CO)$_5$}$_2$]. Moreover, the CI mass spectrum of the crystals showed that a mixture of two compounds, [Ga(Ar′){Mn(CO)$_5$}]$_2$O (**2**) and [Ga(Ar′)(Cl){Mn(CO)$_5$}] (**3**), was present (respective high-resolution mass spectra, *m/z*: calcd, 1037.1321; found, 1037.1313; calcd, 544.0339; found, 544.0307). Further identification of the products demanded an X-ray crystal structure determination.[10] Interestingly, crystals grown from ether solution revealed that the solid state comprises an equimolar mixture of [Ga(Ar′){Mn(CO)$_5$}]$_2$O (**2**) and [Ga(Ar′)(Cl){Mn(CO)$_5$}] (**3**). There are no unusually short intermolecular contacts. To our knowledge, **2** represents the first example of a digalloxane. In the context of the heavier group 13 elements, the closest analogue of **2** is the thia–aluminum derivative [Al{CH(SiMe$_3$)$_2$}$_2$]$_2$S.[12] However, a distinctive feature of **2** is the significantly wider metal–chalcogen–metal bond angle (150.2(5)° *vs* 117.5(3)°). Moreover, the gallium–oxygen bond length (1.786(11) Å) is appreciably shorter than any which have been reported previously. Collectively, these data might be interpreted in terms of dative π-bonding from oxygen lone pairs into formally vacant Ga(4p) orbitals, but an alternative, and probably more realistic, view is that these structural features arise from the partially ionic character of the Ga$^{\delta+}$–O$^{\delta-}$ bonds which stems from the large electronegativity difference between gallium and oxygen. As far as we are aware, only two previous compounds with gallium–manganese bonds have been characterized structurally. The average Ga–Mn bond length in **2** (2.533(4) Å) is similar to Ga–Mn bond lengths which have been reported[13,14] for [Mn$_2$(CO)$_8${μ-GaMn(CO)$_5$}$_2$] (2.455(1) Å) and [Mn$_3$(CO)$_{12}$(μ-GaCl$_2$)]$^{2-}$ (2.691(4) Å). The sum of bond angles at both gallium centers of **2** is 360°, although the angles depart significantly from the idealized values (Figure 2 caption), as seen in **1**.

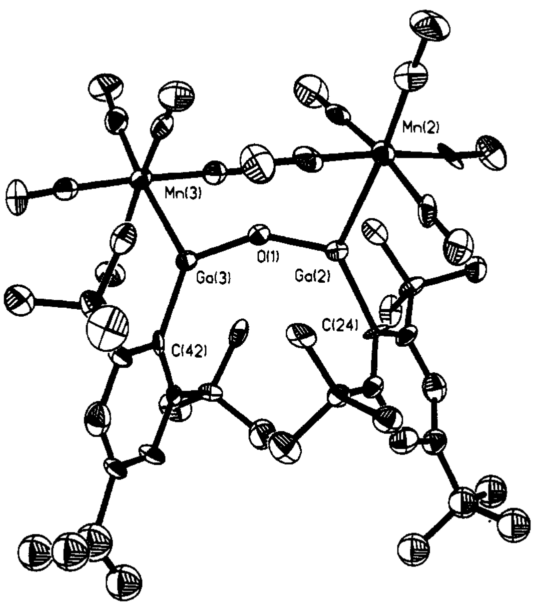

Figure 2. Structure of **2** in the crystal showing the atom-numbering scheme. Important bond lengths (Å) and angles (deg): Ga(2)–O(1), 1.784(11), Ga(3)–O(1) 1.789(10), Ga(2)–Mn(2) 2.530(3), Ga(3)–Mn(3) 2.536(4); Ga(2)–O(1)–Ga(3) 150.2(5), O(1)–Ga(2)–Mn(2) 109.7(3), Mn(2)–Ga(2)–C(24) 130.4(4), O(1)–Ga(2)–C(24) 119.9(5), O(1)–Ga(3)–C(42) 119.0(6), O(1)–Ga(3)–Mn(3) 108.7(3).

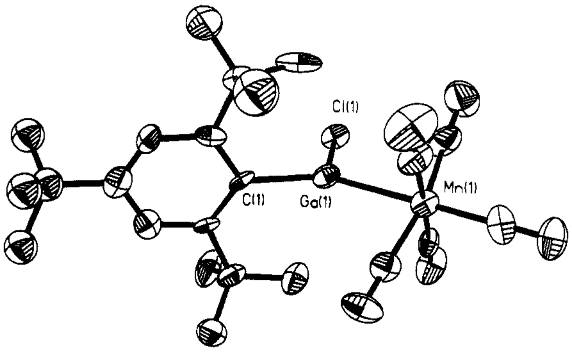

Figure 3. Structure of **3** in the crystal showing the atom-numbering scheme. Important bond lengths (Å) and angles (deg): Ga(1)–Mn(1) 2.495(4), Ga(1)–C(1) 1.986(21), Ga(1)–Cl(1) 2.278(6); Mn(1)–Ga(1)–Cl(1) 110.8(2), Mn(1)–Ga(1)–C(1) 140.9(6), Cl(1)–Ga(1)–C(1) 108.3(6).

Compound **3** represents a rare example of a tricoordinate gallium compound bearing three different substituents (Figure 3).[15] The sum of bond angles at Ga is 360°, and as in the case of **2**, the large C–Ga–Mn bond angle (140.9(6)°) is indicative of steric interactions between the Ar′ and Mn(CO)$_5$ groups. The Ga–Mn bond length (2.495(4) Å) is similar to those in **2**. The reason that the reactions of Ar′GaCl$_2$ with [Co(CO)$_4$]$^-$ and [Mn(CO)$_5$]$^-$ take different courses presumably relates to the larger steric bulk of the latter, which favors the formation of **3**. Inferentially, the conversion of **3** to **2** involves the intermediacy of the hydroxy species [Ar′Ga(OH){Mn(CO)$_5$}], which could arise via the reaction of **3** with adventitious H$_2$O and/or NaOH. However, further work will be necessary to confirm this hypothesis.

In a different experiment,[7] the crude Ar′GaCl$_2$/Na[Mn(CO)$_5$] reaction mixture was recrystallized from toluene, resulting in [Ga{Mn(CO)$_5$}$_3$] (**4**) as the sole isolated product (high-resolution mass spectrum for [M − CO]$^+$, *m/z*: calcd, 625.6685; found, 625.6664. This compound was prepared previously via the metathetical reaction of GaCl$_3$ with Na[Mn(CO)$_5$],[16] although the crystals obtained were not suitable for X-ray diffraction because of facile solvent (Et$_2$O) loss. This problem was overcome

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(8) Anal. Calcd for **1** (mp 112–3 °C), C$_{26}$H$_{29}$Co$_2$GaO$_8$: C, 47.52; H, 4.45. Found: C, 47.79; H, 4.83. Calcd for **2/3** (mp 132–5 °C), 50% abundance of C$_{46}$H$_{58}$Ga$_2$Mn$_2$O$_{11}$ and 50% abundance of C$_{23}$H$_{29}$ClGaMnO$_5$: C, 49.32; H, 5.69. Found: C, 47.51; H, 5.97.

(9) ^{1}H NMR (300 MHz, 295 K): **1** (C$_6$D$_6$) δ 1.25 (s, 9H, *p*-(CH$_3$)$_3$C), 1.54 (s, 18H, *o*-(CH$_3$)$_3$C), 7.44 (s, 2H, aryl H); **2** (C$_6$D$_6$) δ 1.27 (s, 18H, *p*-(CH$_3$)$_3$C), 1.54 (s, 36H, *o*-(CH$_3$)$_3$C), 7.50 (s, 4H, aryl H); **3** (C$_6$D$_6$) δ 1.26 (s, 9H, *p*-(CH$_3$)$_3$C), 1.46 (s, 18H, *o*-(CH$_3$)$_3$C), 7.40 (s, 2H, aryl H). ^{13}C{^{1}H}NMR (75.48 MHz, 295 K): **1** (C$_6$D$_6$) δ 31.25 (*p*-(*C*H$_3$)$_3$C), 34.81 (*p*-(CH$_3$)$_3$*C*), 33.88 (*o*-(*C*H$_3$)$_3$C), 38.87 (*o*-(CH$_3$)$_3$*C*), 122.91 (aryl *m*-C), 136.52 (*ipso*-C), 151.19 (aryl *p*-C), 154.41 (aryl *o*-C), 200.28 (Co(CO)$_4$); **2** (C$_6$D$_6$) δ 31.36 (*p*-(*C*H$_3$)$_3$C), 34.29 (*p*-(CH$_3$)$_3$*C*), 33.84 (*o*-(*C*H$_3$)$_3$C), 38.12 (*o*-(CH$_3$)$_3$*C*), 122.80 (aryl *m*-C), 140.75 (*ipso*-C), 149.83 (aryl *p*-C), 155.07 (aryl *o*-C), 216.06 (Mn(CO)$_5$); **3** (C$_6$D$_6$) δ 31.32 (*p*-(*C*H$_3$)$_3$C), 33.91 (*p*-(CH$_3$)$_3$*C*), 33.25 (*o*-(*C*H$_3$)$_3$C), 38.50 (*o*-(CH$_3$)$_3$*C*), 122.83 (aryl *m*-C), 140.14 (*ipso*-C), 150.86 (aryl *p*-C), 155.49 (aryl *o*-C), 215.98 (Mn(CO)$_5$). IR (KBr) (cm^{-1}): **1** υ_{CO} 2092 s, 2076 s, 2017 m, 2002 s, 1993 s, 1982 s, 1964 m; **2/3** υ_{CO} 2098 m, 2040 m, 2035 m, 2021 m, 2009 m, 2001 s, 1987 vs.

(10) Crystal data for **1**, C$_{26}$H$_{29}$Co$_2$GaO$_8$: M = 657.1, triclinic space group $P\bar{1}$, $Z = 2$, a = 8.632(2) Å, b = 10.561(2) Å, c = 17.204(3) Å, α = 87.97(3)°, β = 82.87(3)°, γ = 70.85(3)°, V = 1470.1(7) Å^3, D_c = 1.484 g cm^{-3}, Mo Kα radiation, λ = 0.710 73 Å, μ(Mo Kα) = 20.7 cm^{-1}. Crystal data for **2** (50% abundance) and **3** (50% abundance): **2**, C$_{46}$H$_{58}$Ga$_2$Mn$_2$O$_{11}$, M = 1036.2; **3**, C$_{23}$H$_{29}$ClGaMnO$_5$, M = 545.6; triclinic space group $P\bar{1}$, $Z = 2 + 2$, a = 11.736(1) Å, b = 16.880(2) Å, c = 20.876(2) Å, α = 109.60(1)°, β = 92.79(1)°, γ = 99.17(1)°, V = 3822(1) Å^3, D_c = 1.405 g cm^{-3}, Mo Kα radiation, λ = 0.710 73 Å, μ(Mo Kα) = 16.3 cm^{-1}. Totals of 5173 and 13,405 independent reflections were collected for **1** and **2/3**, respectively, on an Enraf-Nonius CAD 4 diffractometer at 298 K. The data were corrected for Lorentz and polarization effects but not for absorption. Both structures were solved by direct methods and refined by least-squares analysis using the Siemens SHELXTL PLUS (PC Version) software. The final residuals were R = 0.0666 and R_w = 0.0771 for **1** and R = 0.0870 and R_w = 0.0740 for **2/3**.

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by recrystallization of **4** from toluene, and details of the X-ray analysis, the first for any complex of the form E$\{M(CO)_5\}_3$ (E = Ga, In, Tl; M = Mn, Re), will be published elsewhere. As expected, ligand redistribution is more facile in toluene than in the more basic solvent Et_2O.

Finally, we note that all M–M-bonded compounds of the heavier group 13 elements isolated thus far feature hydrocarbyl or nitrogen substituents.[17] The digalloxane, **2**, can be regarded as the product of oxygen insertion into the as-yet unknown digallane [(Ar′)$\{(CO)_5Mn\}$GaGa$\{Mn(CO)_5\}$(Ar′)], thus encouraging the search for M–M-bonded compounds bearing organometallic substituents.

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Supplementary Material Available: Tables of X-ray crystallographic data, bond lengths, atomic coordinates, and thermal parameters for **1** and **2/3** (21 pages). Ordering information is given on any current masthead page.

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