Intramolecular Base Stabilization of Cobalt–Gallium and Cobalt–Indium Compounds

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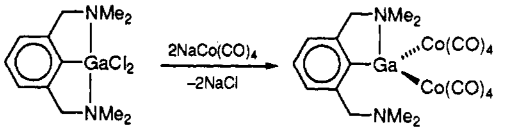
Summary: The intermetallic derivatives $[\{(2,6\text{-}Me_2NCH_2)_2C_6H_3\}M\{Co(CO)_4\}_2]$ *(M = Ga (1); M = In (2)) have been prepared. X-ray analysis reveals that only one of the dimethylamine groups is coordinated to Ga in 1 and as a consequence the* $CGaCo_2$ *moiety is pyramidal; the indium analogue 2 possesses a distorted-trigonal-bipyramidal geometry and a planar* $ClnCo_2$ *unit.*



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Compounds with gallium- or indium–transition-metal bonds are beginning to attract attention as single-source precursors to bimetallic thin films.[1-3] Initial effort has been focused on compounds with 1/1 group 13/transition-metal stoichiometry. However, experience gained in our laboratory with gallium arsenide single-source precursors indicates that the 1/1 stoichiometry of the precursor is not necessarily preserved in the resulting film because of the facile discharge of smaller molecules during the deposition process.[4] As an example, the homoleptic derivative $Ga(As\text{-}t\text{-}Bu_2)_3$ has turned out to be superior to any of the 1/1 stoichiometry precursors. Given the foregoing, we have started to investigate group 13/transition-metal compounds with less common stoichiometries. This communication is concerned with compounds of the type $RGa(ML_n)_2$ and $RIn(ML_n)_2$. Although there are a few examples of such species in the literature,[5] only one gallium and one indium compound have been characterized structurally.[6]

Our first attempts to prepare the desired compounds using simple alkyl or aryl substituents were frustrated by facile donor solvent loss and/or uncontrolled symmetrization reactions. Recognizing that both of these problems can, in principle, be solved by means of intramolecular coordination, we opted to use an *o*-bis(dialkylamino)aryl ligand system.[7] A metathetical reaction of the gallium dichloride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaCl_2$[8] with $NaCo(CO)_4$ in Et_2O solution afforded the corresponding bis(tetracarbonyl) cobalt derivative 1.[9,10] The CI-MS of 1 exhibits a molecular ion at *m/e* 603, followed by peaks at *m/e* 491 and 431, which correspond to the loss of four CO's and a $Co(CO)_4$ group, respectively. The X-ray crystal structure of 1[11] reveals that only one dimethylamine group is coordinated to gallium. The gallium positions are disordered, however, and consequently there are two isomers in the unit cell. The major isomer (67% abundance) features a bond between N(2) and Ga(1) and is illustrated in Figure 1. In the minor isomer (33% abundance) N(1) is bonded to Ga(1A). The Ga–N bond distances (2.405(10) and 2.394(17) Å in the major and minor isomers, respectively) are considerably larger than those in amine–gallane adducts with substituents of comparable steric bulk (range 2.050(7)–2.246(9) Å[12]). The four-coordinate

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(9) A solution of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaCl_2$[8] (1; 0.66 g, 2.0 mmol) in 30 mL of Et_2O solution was treated with $NaCo(CO)_4$ (1.066 g, 5.5 mmol). The resulting red-brown reaction mixture was filtered, following which the solvent and volatiles were removed by evacuation. The residual red oil was extracted with hexane. X-ray-quality yellow crystals of 1 (mp 106 °C dec) were grown by cooling a concentrated hexane solution to −20 °C. HRMS: calcd for $C_{20}H_{20}Co_2GaN_2O_8$ 602.9121, found 602.9139. Compound 2 was prepared similarly by treatment of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]InCl_2$[14] (0.067 g, 0.18 mmol) with $NaCo(CO)_4$ (0.0975 g, 0.5 mmol) in Et_2O solution. Yellow X-ray-quality crystals (mp 132 °C dec) were grown from Et_2O solution at −20 °C. HRMS: calcd for $C_{20}H_{20}Co_2InN_2O_8$ 648.8922, found 648.8909.

(10) ^1H NMR (300 MHz, 295 K, TMS external): 1 (THF-d_8), δ 2.5 (s, 12H, $(CH_3)_2N$), 3.86 (s, 4H, CH_2N), 7.20 (m, 3H, H aryl); 2 (C_6D_6), δ 2.06 (s, 12H, $(CH_3)_2N$), 3.28 (s, 4H, CH_2N), 6.85 (d, 2H, H aryl), 7.08 (t, 1H, H aryl). $^{13}C\{^1H\}$ NMR (75.48 MHz, 295 K, C_6D_6, TMS external): 1, δ 46.3 ($(CH_3)_2N$), 66.7 (CH_2N), 126.3 (C–Ga), 128.5 (*p*-C,Ga-aryl), 129.0 (*m*-C,Ga-aryl), 141.5 (*o*-C,Ga-aryl), 201.5 ($Co(CO)_4$); 2, δ 45.9 ($(CH_3)_2N$), 66.4 (CH_2N), 126.4 (C–Ga), 128.5 (*p*-C,Ga-aryl), 128.6 (*m*-C,Ga-aryl), 143.2 (*o*-C,Ga-aryl), 202.4 ($Co(CO)_4$). IR (KBr pellets): 1, ν_{CO} 2080 s, 2059 s, 2013 m, 1986 s, 1973 s, 1878 m cm^{-1}; 2, ν_{CO} 2077, s, 2062 s, 2057 s, 2011 m, 1992 s, 1974 s, 1959 s cm^{-1}. MS (CI, CH_4): 1, *m/z* 603 [M^+], 491 [$M^+ - 4CO$], 431 [$M^+ - (Co(CO)_4) - H$]; 2, *m/z* 649 [M^+], 477 [$M^+ - (Co(CO)_4) - H$].

(11) Crystal structure data for 1: $C_{20}H_{19}Co_2GaN_2O_8$, monoclinic, space group $P2_1/n$, with $a = 8.926(2)$ Å, $b = 14.257(3)$ Å, $c = 19.356(4)$ Å, $\beta = 100.40(3)°$, $V = 2422.7(9)$ Å^3, $Z = 4$, $d_{calcd} = 1.653$ Mg/m^3, and μ(Mo Kα) = 2.503 mm^{-1}. Crystal structure data for 2: $C_{20}H_{19}Co_2InN_2O_8$: monoclinic, space group $P2_1/n$, with $a = 8.970(1)$ Å, $b = 14.460(1)$ Å, $c = 19.472(1)$ Å, $\beta = 100.66(1)°$, $V = 2482.1(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.734$ Mg/m^3, and μ(Mo Kα) = 2.287 mm^{-1}. Totals of 3033 and 3225 independent reflections were collected for 1 and 2, respectively, on a Siemens P3 diffractometer at 298 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure of 1 was solved by direct methods. Initial refinement of the structure of 1 with an undisordered gallium gave large maximum and minimum difference map peaks (1.78 and −2.10 e/Å^3) near the gallium atom and along the axis of the gallium complex and a thermal parameter that was anomalously large parallel to this axis. Refinement of a model in which the gallium atom is found in two different partially occupied positions with the sum of the two refined site occupancy factors constrained to 1.0 led to a 3.5% drop in R_w and difference map extrema of +0.37/−0.36 e/Å^3. The final R and R_w values for 1 were 0.0412 and 0.0588, respectively. The structure of 2 was solved on the basis of the isostructural relationship with 1. Refinement by full-matrix least-squares methods gave final R and R_w values of 0.0339 and 0.0432, respectively.

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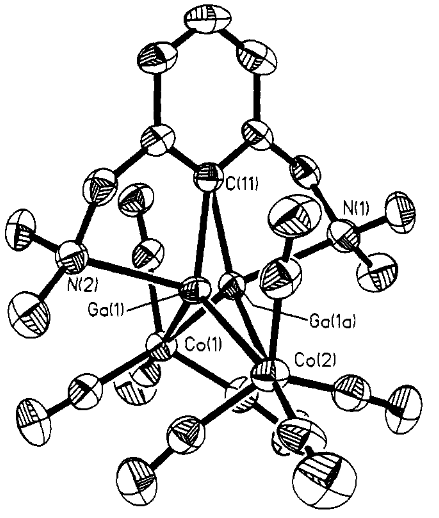
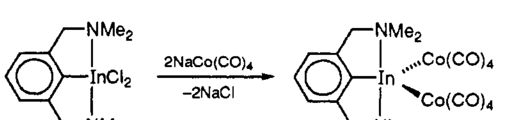


Figure 1. View (ORTEP, 30% ellipsoids) of the major and minor isomers of 1. Important bond distances (Å) and angles (deg): Ga(1a)–Co(1) = 2.602(16), Ga(1a)–Co(2) = 2.536(19), Ga(1a)–N(1) = 2.394(17), Ga(1a)–C(11) = 1.983(14); Co(1)–Ga(1a)–Co(2) = 116.8(5), Co(1)–Ga(1a)–C(11) = 116.2(9), Co(2)–Ga(1a)–C(11) = 118.4(6), N(1)–Ga(1a)–C(11) = 83.0(6).

environment around each gallium is completed by bonds to one carbon and two cobalt atoms. As a consequence of the weak N→Ga dative interaction, the geometry of the $CGaCo_2$ moiety is slightly pyramidal (sums of angles at Ga are 355.1 and 351.4° in the major and minor isomers, respectively). The (few) known gallium–cobalt bond distances span the range 2.38–2.58 Å.[3,5] Although there is a scatter of Ga–Co bond distances in 1, they fit within this range.

Compounds with dynamic N–Si–N bonds have attracted recent attention.[13] In an elegant study of the molecular dynamics of the silylene (silanediyl) complex $[2\text{-}(Me_2NCH_2)C_6H_4]Si{=}Cr(CO)_5$, it was established that the exchange of coordinated and uncoordinated amine donors takes place by a "flip-flop" mechanisn involving a pentacoordinate transition state at silicon. Compound 1 is of particular interest in this context because the termini for such a flip-flop process are both present in the same unit cell. However, in the case of 1, although there are some intensity and peak width changes, the N—Me and N—CH_2 resonances remain equivalent down to −95 °C, hence, the flip-flop inversion barrier is less than that in the silylene complex.

Treatment of the analogous indium dichloride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]InCl_2$[14] with 2 equiv of $NaCo(CO)_4$ in Et_2O solution afforded the intermetallic derivative 2.[9] The spectral properties of 2 are very similar to those of 1.[10] Interestingly, however, the X-ray crystal structure[11] reveals that, in contrast to 1, the group 13 element is pentacoordinate in 2 (Figure 2). The thermal parameters for In(1) are almost isotropic and are of reasonable magnitude, and furthermore, there are no extraneous peaks near this center; hence, there is no evidence of a flip-flop exchange of amines in this case. The geometry at indium is best described as distorted trigonal bipyramidal. Although the $ClnCo_2$ unit is planar (sum of angles 359.9(2)°), the axial N–In–N angle (143.1(2)°) departs considerably from the ideal trigonal-bipyramidal value of 180°. Another conspicuous structural feature is that the nitrogen–indium bonds are unusually long (average 2.706(5) Å), thus implying very weak N→In dative interactions. This value lies between the sums of covalent radii (2.19 Å)[15] and van der Waals radii (3.45 Å)[15] for indium and nitrogen and is considerably longer than the N–In bond distances of typical donor–acceptor complexes, e.g. $C_2H_5InI_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]$ (2.33(1) and 2.44(1) Å)[16] and $Me_3In(t\text{-}BuNH_2)$ (2.363(8) Å).[17] The indium–cobalt bond distances in 2, which average 2.676(1) Å, are close to those in the $[InCl_2\{Co(CO)_4\}_2]^-$ (2.614(4) Å) and $[InI\{Co(CO)_4\}_3]^-$ (2.705(1) Å) anions.[18] As in these cases, there is no vacant 5p orbital available on indium, thus precluding significant Co–In multiple bonding.



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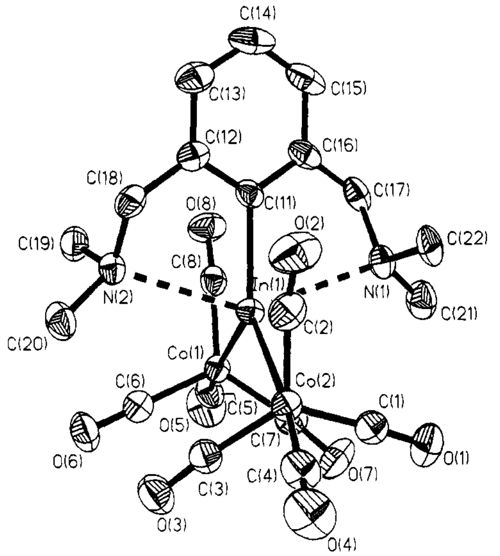

Figure 2. View (ORTEP, 30% ellipsoids) of 2. Important bond distances (Å) and angles (deg): In(1)–Co(1) = 2.674(1), In(1)–Co(2) = 2.679(1), In(1)–C(11) = 2.158(6), In(1)–N(1) = 2.702(5), In(1)–N(2) = 2.711(5); Co(1)–In(1)–Co(2) = 118.6(1), Co(1)–In(1)–C(11) = 120.9(2), Co(2)–In(1)–C(11) = 120.4(2), N(1)–In(1)–C(11) = 71.9(2), N(2)–In(1–C(11) = 71.2(2).

Note Added in Proof. Since the acceptance of this paper, the compound $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}In\{Mn(CO)_5\}_2]$ has been prepared and characterized by X-ray crystallography. Only one of the dimethylamine groups is coordinated to indium, and the $ClnMn_2$ moiety is pyramidal with a sum of bond angles of 355.2(6)° and an average In–Mn bond distance of 2.761(4) Å.

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Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters and figures giving additional views for 1 and 2 (10 pages). Ordering information is given on any current masthead page.

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