# Reaction of the Alkylindium(I) Compound $In_4[C(SiMe_3)_3]_4$ with Octacarbonyldicobalt: Bridging of the Co–Co Bond by One or Two In–$C(SiMe_3)_3$ Groups☆

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*tetrahedra*-Tetrakis[tris(trimethylsilyl)methyl]tetraindane(4) (**1**) reacts with octacarbonyldicobalt to yield two products, depending on the stoichiometric ratio of the starting compounds: By replacement of one bridging carbonyl group a dicobalt monoindium derivative **2** is formed, which contains a Co–Co bond [256.81(5) pm] bridged by one carbonyl and one monoalkylindium group. While **2** is a monomer in benzene solutions, it dimerizes in the solid state by an interaction of the oxygen atom of the bridging carbonyl group to the coordinatively unsaturated In atom of a second molecule across a center of symmetry. Another compound (**3**) is formed by the replacement of both bridging carbonyl ligands, which exhibits a strongly distorted $Co_2In_2$ tetrahedron with normal Co–In bond lengths of 253.44(6) pm, but long Co–Co [280.14(6) pm] and In–In distances [336.18(6) pm].

*tetrahedra*-Tetrakis[tris(trimethylsilyl)methyl]tetraindane(4) (**1**)[1,2] with the In atoms in an oxidation state of +1 shows a nearly undistorted $In_4$ tetrahedron in the solid state. In contrast to the $Ga_4$ analog[3], **1** remains a tetramer in dilute benzene solutions, but becomes a monomer on characterization by conventional mass spectrometry. The monomeric fragment In–$C(SiMe_3)_3$ exhibits a similar pattern of frontier orbitals at the indium centers like a carbonyl group at the carbon atoms: an occupied $\sigma$ donor orbital with the lone electron pair and two vacant p or $\pi^*$ orbitals perpendicular to the molecular axis. This led us to the assumption that In–$C(SiMe_3)_3$ as well as the Ga analog could replace carbonyl ligands in transition metal carbonyl complexes. As a first example of this type of chemistry we recently published the reaction of decacarbonyldimanganese with **1** yielding $Mn_2(CO)_8[\mu\text{-}InC(SiMe_3)_3]_2$, in which after replacement of two CO ligands the Mn–Mn bond is bridged by two In atoms[4]. In the course of systematic investigations we now applied $Co_2(CO)_8$ as a starting compound and hoped to replace the bridging carbonyl groups gradually by one or two monoalkylindium groups.

## Reactions of $Co_2(CO)_8$ with $In_4[C(SiMe_3)_3]_4$ (1)

When a deep violet solution of the tetraindane(4) **1** in boiling *n*-hexane is treated with $Co_2(CO)_8$ in a molar ratio of about 1:4, a dark red solution is formed within two hours, from which after evaporation of the solvent and recrystallization of the residue dark red crystals of compound **2** can be isolated in almost 65% yield (eq. 1). Elemental analysis and the molar mass cryoscopically determined in benzene solution show that as originally intended only one carbonyl group of the Co compound is replaced by a monoalkylindium ligand. When the $In_4$ cluster is treated with $Co_2(CO)_8$ under similar conditions in a molar ratio of about 1:2, a bright red solution is formed. After concentration of the reaction mixture red platelets of compound **3** were isolated on cooling to −20°C in 80% yield (eq. 2), in which two carbonyl groups are replaced by monoalkylindium ligands as revealed by analytical results.

Though both compounds **2** and **3** differ significantly in the intensity of their color, they show nearly indistinguishable UV/Vis spectra with maxima at 255, 285, and 385 nm, of which the last one can be assigned to the metal-metal bonds[1,3]. The IR spectra differ significantly in the region of the C–O stretching vibrations: **3** shows seven absorptions between 1917 and 2035 $cm^{-1}$ for its exclusively terminal CO groups, while in the spectrum of **2** five bands are observed for the terminal CO ligands between 1987 and 2074 $cm^{-1}$ and one band at 1829 $cm^{-1}$ for the carbonyl bridge similar to the IR spectrum of the starting compound $Co_2(CO)_8$[5]. Additionally, there is a very broad absorption in the spectrum of **2** at about 1680 $cm^{-1}$ which might be due to the $\mu_3$-bridging function of the bridging CO group between both Co atoms and a coordinatively unsaturated In atom of a neighboring molecule in the solid state (see discussion of the crystal structure below). Similar effects are observed in complexes of hard acids like $AlR_3$ with the carbonyl groups of transition-metal carbonyl complexes[6].

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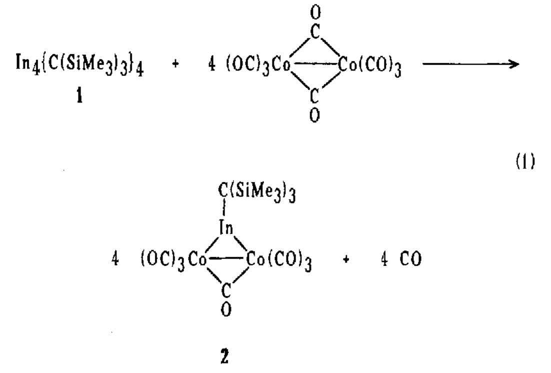
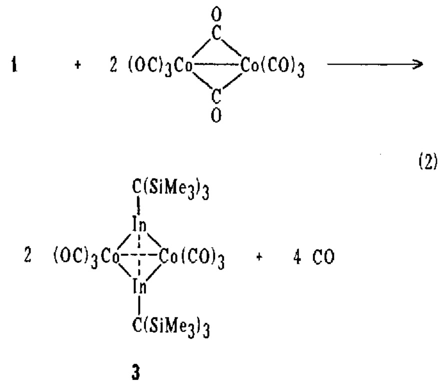
The $^{13}$C-NMR spectra of both compounds **2** and **3** exhibit remarkable chemical shifts of the carbon atoms bound to In, which in alkylindium derivatives usually resonate at about $\delta$ = 15 to 30[7]. In contrast, the In−C resonances in **2** and **3** are observed at $\delta$ = 48.4 and 49.3, respectively, and are very similar to the value found for the manganese derivative $Mn_2(CO)_8[\mu\text{-}InC(SiMe_3)_3]_2$ ($\delta$ = 51.7)[4]. These unusual shifts might be due to the situation of the carbon atom in the nodal plane of the p orbital perpendicular to the $InCo_2C$ plane and possibly indicate some π back donation of electron density from the transition metal centers to the indium atoms.



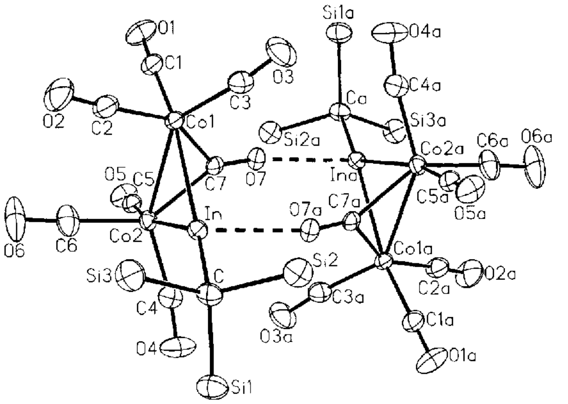


### Crystal Structures of 2 and 3

Figure 1 shows the molecular structure of the dicobalt monoindium derivative **2**. The Co−Co bond is bridged by one carbonyl group and one monoalkylindium ligand. Some indium derivatives of the carbonyl cobalt compound are described in the literature[8,9], but to our knowledge no one has a similar structure with an indium atom bridging the Co−Co bond. Surprisingly, the reactions of indium monohalides with dimetal compounds usually lead to insertion into the metal−metal bond[10] instead of the replacement of carbonyl groups observed for the reactions of the monoalkylindium derivative **1**.

While the Co−Co distance [256.81(5) pm] in **2** is lengthened by 4 pm with respect to $Co_2(CO)_8$ [252.90(8) pm][11], the Co−C distances are shortened: Co1−C7 192.2(2) and Co2−C7 190.1(2) pm for the bridging carbonyl group and 179.9(3) pm on average for the terminal carbonyl groups in **2** compared to 193.9(2) and 182.8(2) pm, respectively, for $Co_2(CO)_8$[11]. The bonds Co1−C3 [177.9(3) pm] and Co2−C4 [177.4(3) pm] having no CO ligand in *trans* position show a significant shortening compared to the mean value of the terminal CO groups, which is a consequence of a more effective π back donation and similarly observed in the pure carbonyl complex[11]. As usual, the shorter C−O bonds with a mean value of 113.6 pm are observed for the terminal CO ligands, while in the bridging CO group the CO distance is lengthened to 118.5(3) pm.

Figure 1. Molecular structure of a dimeric molecule of **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°]: Co1−Co2 256.81(5), In−Co1 257.03(6), In−Co2 259.30(5), In−C 219.3(2), In−O7a 248.7(2); In−Co1−Co2 60.61(1), In−Co2−Co1 59.74(1), Co1−In−Co2 59.65(2), Co1−In−C 148.39(7), Co2−In−C 145.60(7), Co1−C7−Co2 84.4(1), Co1−Co2−C7 48.15(7), Co2−Co1−C7 47.44(7). The atoms labeled with the letter a are calculated by the symmetry operation $-x$, $1-y$, $1-z$

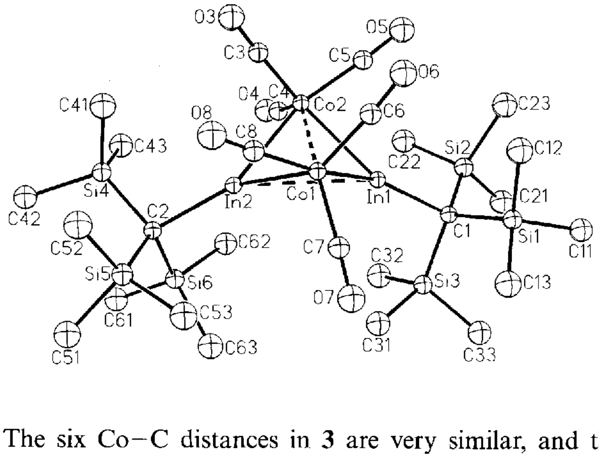


The Co−In distances [258.17(6) pm] in **2** lie in that region normally observed for Co−In bonds[8,9]. The In−C bond length [219.3(2) pm] is shortened by 5 pm compared to the starting compound $In_4[C(SiMe_3)_3]_4$ (**1**)[1] and resembles those values found for alkylindium derivatives with indium in its normal oxidation state +III[7]. The In atom in **2** does not lie in the plane formed by the three directly bound atoms (Co1, Co2, C), but deviates 28.6 pm from this plane due to the dimerization of the compound in the solid state by an interaction of the In atom with the oxygen atom of the bridging CO group of a second molecule; the dimer is located on a crystallographic center of symmetry. The In−O7a distance [248.7(2) pm] indicates a weak coordinative bonding; much shorter distances of 226 and 233.9 pm are observed in THF complexes with $InCl_3$[12] or with an alkylindium octacarbonyl dicobalt derivative[9]. Comparable compounds with a carbonyl oxygen atom acting as a Lewis base are known in few examples with hard Lewis acids like triethyl- or trialkoxyaluminium[6].

Figure 2 shows the molecular structure of the $Co_2In_2$ derivative **3**. Comparable compounds are to our knowledge unknown. The structure is similar to that of $Co_2(CO)_8$[11], and the $Co_2$ unit is bridged by two monoalkylindium ligands in a butterfly arrangement. The In−Co bonds [mean value 253.44(6) pm] are smaller than for compound **2**, but still lie within in the region normally observed for Co−In bond lengths[8,9]. In contrast, the Co−Co distance

[280.14(6) pm] is very long compared to $Co_2(CO)_8$[11] or the $Co_2In$ derivative **2** (see above). The In–In distance of 336.18(6) pm is intermediate between the value in the tetrahedral **1** [300.1(1) pm][2] with multicenter In–In bonding and compounds with negligible In–In bonds like the pseudodimer of $In[C_5(CH_2C_6H_5)_5]$[13] [In–In 363.1(2) pm] or the pseudohexamer of $InC_5Me_5$[14] [In–In 395.3(1) pm] and indicates only a weak In–In interaction. Thus, the molecular structure of **3** can be described as a four-membered heterocycle with a butterfly structure or as a strongly distorted $Co_2In_2$ tetrahedron with weak homonuclear bonding. A threefold degenerate LUMO was calculated for the neutral tetrahedral clusters of the third-main group elements[15]. By the addition of two further electrons a Jahn-Teller distortion should deform the clusters to lower the symmetry[16]. A $Co_2In_2$ tetrahedron with the $Co(CO)_3$ fragment acting as a three-electron donor has two cluster electrons more than the $In_4$ derivative, which might lead to the elongation of the homonuclear bonds and to the strong distortion from regular tetrahedral geometry. The In atoms are not planarly surrounded by one carbon atom (C1 or C2) and both Co atoms, but a trigonal pyramide results with the In atoms 9.8 (In1) and 9.9 (In2) pm above the basal plane and the apices of both pyramides pointing to each other.

Figure 2. Molecular structure of **3**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are not included. Selected bond lengths [pm] and angles [°]: Co1–Co2 280.14(6), In1–In2 336.18(6), Co1–In1 253.92(5), Co1–In2 252.83(5), Co2–In1 252.94(6), Co2–In2 254.06(6), In1–C1 218.1(3), In2–C2 218.4(3); In1–Co1–In2 83.12(2), Co1–In1–Co2 67.10(2), In1–Co2–In2 83.07(2), Co1–In2–Co2 67.10(2), Co1–In1–C1 148.05(7), Co2–In1–C1 144.13(7), Co1–In2–C2 144.10(7), Co2–In2–C2 148.05(7)



The six Co–C distances in **3** are very similar, and the mean value [177.3(3) pm] is smaller by 2.5 pm compared to compound **2**, which indicates a more effective π back donation and more electron-rich Co atoms. The mean C–O bond length amounts to 114.2(4) pm. The In–C bonds [218.3(3) pm] are shortened in comparison with the starting compound **1** [225(1) pm], while the C–Si bonds to the α-carbon atoms [189.7(3) pm] remain unchanged[1].

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## Experimental

All procedures were carried out under purified argon in dried solvents (*n*-hexane and *n*-pentane with $LiAlH_4$). Compound **1** was prepared as described in ref.[1]; $Co_2(CO)_8$ from Ventron GmbH was used without further purification.

*Synthesis of [$Co_2(CO)_7InC(SiMe_3)_3$]* (**2**): A solution of 358 mg (1.047 mmol) of $Co_2(CO)_8$ in 20 ml of *n*-hexane is added to a solution of 330 mg (0.239 mmol) of the tetraindane(4) **1** (molar ratio 4.4:1) in 20 ml of the same solvent. The mixture is refluxed for 4 h, and its color changes from deep violet to dark red. After filtration of small amounts of precipitated metal, concentration of the filtrate and cooling the residue to −20°C the product **2** crystallizes as dark red platelets. Yield: 400 mg (64% based on **1**), m.p. (closed capillary, argon): 92°C (dec.). – $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 0.18$. – $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 207.6$ (CO), 48.4 (InC), 5.2 ($SiMe_3$). – IR (paraffine, CsBr): $\tilde{\nu} = 2074\ cm^{-1}$ vs, 2037 vs, 2010 vs, 1996 sh, 1987 vs νCO; 1829 s, 1680 m, br. νCO (bridge); 1456 vs, 1377 vs (paraffine); 1304 w, 1269 w, 1262 w, 1254 w $\delta CH_3$; 1169 w, 1155 w; 855 s, 843 s, 775 w, 721 s $\rho CH_3$; 677 w, 650 w $\nu_{as}SiC$; 617 vw $\nu_sSiC$; 596 w, 569 w, 557 vw, 532 m, 517 m, 480 vw, 451 w, 434 w νInC; 378 w, 363 vw δSiC; an identical IR spectrum is obtained for the solid in KBr. – UV (*n*-pentane), $\lambda_{max}$ (lg ε): 226 (sh, 3.9), 254 (4.3), 287 (4.3), 385 (3.5). – $C_{17}H_{27}Co_2InO_7Si_3$ (660.3): calcd. C 30.9, H 4.1, In 17.4; found C 30.3, H 4.1, In 17.2. – Mol. mass: 701 g/mol (cryoscopically in benzene).

*Synthesis of {$Co_2(CO)_6[InC(SiMe_3)_3]_2$}* (**3**): A solution of 115 mg (0.336 mmol) of $Co_2(CO)_8$ in 20 ml of *n*-hexane is added to a solution of 260 mg (0.188 mmol) of the tetraindane(4) **1** (molar ratio 1.8:1) in 20 ml of the same solvent. The mixture is heated at reflux for 4 h, and the color changes from deep violet to bright red. After filtration of a small amount of a grey and finely divided precipitate the solution is concentrated. **3** crystallizes on cooling to −20 °C as red crystals. Yield 290 mg (79% based on **1**), m.p. (closed capillary, argon): 199°C. – $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 0.31$. – $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta = 207.6$ (CO); 49.3 (InC); 5.9 ($SiMe_3$). – IR (paraffine, CsBr): $\tilde{\nu} = 2035\ cm^{-1}$ s, 1998 s, 1989 s, 1975 s, 1958 s, 1948 s, 1917 m νCO; 1462 vs, 1377 vs (paraffine); 1300 w, 1260 s, 1252 s $\delta CH_3$; 1169 w, 1159 w, 1049 w; 856 vs, 837 vs, 775 s, 723 vs $\rho CH_3(Si)$; 675 s, 669 s $\nu_{as}SiC$; 648 s, 623 vw, 602 m $\nu_sSiC$; 554 s, 544 s, 527 s, 498 m νInC; 467 m; 385 w δSiC. – UV (*n*-pentane), $\lambda_{max}$ (lg ε): 225 (sh, 3.6), 254 (4.1), 280 (4.1), 304 (sh, 4.0), 349 (sh, 3.7), 385 (3.4). – $C_{26}H_{54}Co_2In_2O_6Si_6$ (978.7): calcd. C 31.9, H 5.6, In 23.5; found C 31.5, H 5.6, In 23.6. – Mol. mass: 974 g/mol (cryoscopically in benzene).

*Crystal Structure Determination of* **2**: Crystals of **2** by crystallization from *n*-hexane; $C_{17}H_{27}Co_2InO_7Si_3$; crystal size 0.5 × 0.5 × 0.4 mm; four-circle diffractometer CAD-4; Θ-2Θ scan; temperature −68°C; triclinic; $P\bar{1}$ (Nr. 2[17]); $a = 933.7(1)$, $b = 994.3(1)$, $c = 1590.6(1)$ pm, $\alpha = 90.60(1)$, $\beta = 105.05(1)$, $\gamma = 111.37(1)°$; $V = 1319 \cdot 10^{-30}\ m^3$; $d_{calcd.} = 1.663\ g/cm^3$; $Z = 2$; 2Θ range $6 \leq 2\Theta \leq 54°$; $-11 \leq h \leq 10$, $0 \leq k \leq 10$, $-20 \leq l \leq 20$; $\mu(Mo\text{-}K_\alpha) = 2.28\ mm^{-1}$; absorption correction by DIFABS[18]; 5285 independent reflections; 334 parameters; programs SHELXTL PLUS and SHELXL-93[19]; structure solution by direct methods; refinement by the full-matrix least-squares method with all independent structure factors; $wR^2 = 0.063$; $R_1 = 0.025$ for 5001 $F > 4\sigma(F)$; max./min. residual electron density $0.64/-0.76 \cdot 10^{30}\ e/m^3$. The $C(SiMe_3)_3$ group is statistically disordered with the silicon atoms in two positions, while the methyl carbon atoms except C13, C22, C32, and C33 occupy identical positions[20].

*Crystal Structure Determination of* **3**: Crystals of **3** by crystallization from diisopropyl ether; $C_{26}H_{54}Co_2In_2O_6Si_6$; crystal size 0.5

× 0.3 × 0.3 mm; four-circle diffractometer CAD 4; Θ-2Θ scan; temperature −68 °C; triclinic (the orthorhombic symmetry could not be verified by systematic control of equivalent reflections); $P\bar{1}$ (Nr. 2[17]); $a$ = 902.2(1), $b$ = 903.0(2), $c$ = 2734.6(4) pm, $\alpha$ = 89.76(1), $\beta$ = 90.24(1), $\gamma$ = 111.81(1)°; $V$ = 2068 · $10^{-30}$ m$^3$; $d_{calcd.}$ = 1.572 g/cm$^3$; $Z$ = 2; 2Θ range $6 \leqslant 2\Theta \leqslant 54°$; $0 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 10$, $-34 \leqslant l \leqslant 34$; $\mu$(Mo-$K_\alpha$) = 2.10 mm$^{-1}$; absorption correction by DIFABS[18]; 8909 independent reflections; 398 parameters; programs SHELXTL PLUS and SHELXL-93[19]; structure solution by direct methods; refinement by the full-matrix least-squares method with all independent structure factors; $wR^2$ = 0.061; $R_1$ = 0.024 for 7848 $F > 4\sigma(F)$; max./min. residual electron density 0.47/−0.75 · $10^{30}$ e/m$^3$[20].

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☆ Dedicated to Prof. Dr. *Kurt Dehnicke* on the occasion of his 65th birthday.

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