Octacarbonylbis{μ-[tris(trimethylsilyl)methyl]indanyl}dimanganese with Two Monoalkyl Indium Groups Bridging the Mn–Mn Bond

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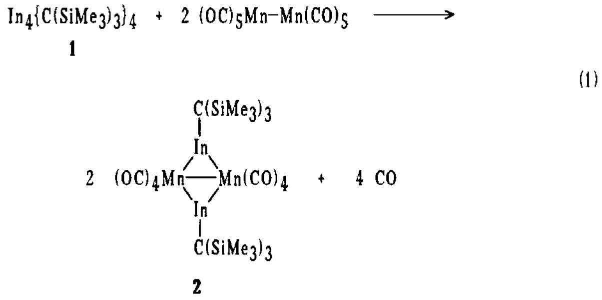
Tetrahedra-tetrakis[tris(trimethylsilyl)methyl]tetraindane(4) (**1**) reacts with decacarbonyldimanganese(0) to yield the bright red crystalline title compound **2**, in which two carbonyl ligands are replaced by two InR fragments. The crystal structure determination of **2** shows two $Mn(CO)_4$ groups (Mn–Mn 313.7 pm) bridged by two monoalkylindium units and a planar Mn_2In_2 molecular center.

Recently, we succeeded in synthesizing and determining the crystal structure of the alkylindium(I) compound $In_4[C(SiMe_3)_3]_4$ (**1**) with a nearly undistorted tetrahedral In_4 skeleton in the solid state[1], which in contrast to the Ga_4 analog[2] remains tetrameric in dilute benzene solutions. In the course of systematic investigations of the chemical properties of **1**[1,3] we found that the monomeric $In-C(SiMe_3)_3$ fragment is able to substitute carbonyl ligands in transition metal carbonyls. In this paper we report on the reaction of **1** with $Mn_2(CO)_{10}$.

Reaction of $In_4[C(SiMe_3)_3]_4$ with $Mn_2(CO)_{10}$

Mixtures of **1** and $Mn_2(CO)_{10}$ in *n*-hexane remain unchanged at room temperature for several days, while in boiling hexane the characteristically deep violet color of **1** disappears within two or three hours, depending on the excess of the manganese carbonyl used. A dark red solution is formed, from which after concentration and recrystallization dark red, very fine needles of the title compound **2** are isolated in 60% yield. The molar mass, cryoscopically determined in benzene solution, and the mass spectrum with a very characteristic isotopic pattern show that two carbonyl groups of the $Mn_2(CO)_{10}$ molecule are replaced by two monoalkylindium fragments [eq. (1)]. Two absorptions are observed in the IR spectrum of **2** at 465 and 519 cm^{-1}, which lie within the region of In–C stretching vibrations. The stretching frequencies for the carbonyl groups reveal six absorptions between 1912 and 2039 cm^{-1}. Similar patterns are observed in compounds with $Mn_2(CO)_8$ fragments and bridged Mn–Mn bonds[4]. For $Mn_2(CO)_{10}$ only a broad absorption is detected with maxima at 1981, 2012, and 2045 cm^{-1}[5].

The trimethylsilyl groups of **2** show one resonance in both the ^1H- and ^{13}C-NMR spectra. Although the molecular structure of **2** exhibits two chemically different carbonyl groups, only one ^{13}C resonance is observed even at $-65\,°C$ with the chemical shift $\delta = 218$. The assignment of the α-carbon atom of the tris(trimethylsilyl)methyl group in the ^{13}C-NMR spectrum is not beyond doubt: there is only one further signal at $\delta = 51.7$ lying more than 25 ppm downfield with respect to the region normally observed for carbon atoms bound to indium[6]. The location of this carbon atom in the nodal plane of the p orbital, which is perpendicular to the molecular plane and can accept π electron density by backdonation, might be responsible for this unusual shift.



$$In_4\{C(SiMe_3)_3\}_4 + 2\ (OC)_5Mn{-}Mn(CO)_5 \longrightarrow 2\ (OC)_4Mn[\mu\text{-}InC(SiMe_3)_3]_2Mn(CO)_4 + 4\ CO \qquad (1)$$

Crystal Structure of 2

Figure 1 shows the molecular structure of **2**. Molecule **2** contains an Mn–Mn bond bridged by two monoalkylindium fragments. Whereas several compounds with bridged Mn–Mn bonds are known[7], only a few examples exhibit a bridging third main group element[8–10]. Indium as a bridging atom is mostly tetracoordinated[9], a lower coordination number is found in a dimanganese compound bridged by an $In-Mn(CO)_5$ group[10]. To our knowledge bridging alkylindium units with tricoordinated In atoms like in **2** have previously not been described. The synthesis according to eq. (1) therefore opens up a route to a new class of compounds, which might lead to special structural and electronic properties in transition metal carbonyls.

The molecule of **2** is located on a crystallographic center of symmetry, so the bicyclic Mn_2In_2 molecular center is planar. The carbonyl groups are not exactly within (C3O3, C5O5) or perpendicular (C2O2, C4O4) to this plane, the angles between the normal of the plane and the C–O bonds are as follows: Mn_2In_2 to C2–O2 1.4°, to C3–O3 81.5°, to C4–O4 169.2°, and to C5–O5 99.8°. The carbonyl carbon atoms C3 and C5 deviate significantly from

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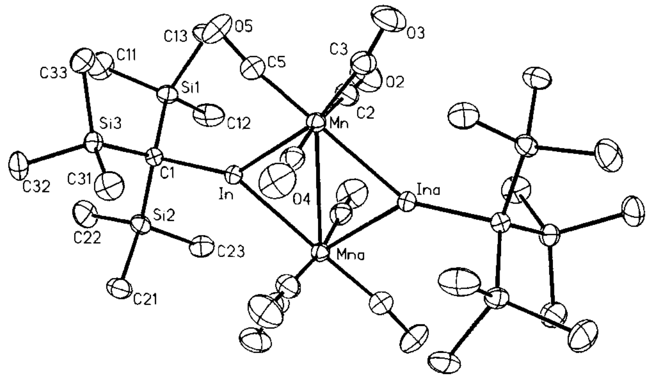
the In_2Mn_2 plane (−21.1 and 23.5 pm) as well as the α carbon atom C1 of the $C(SiMe_3)_3$ group (18.3 pm). The coordination of the In atom is weakly pyramidal with In 9.0 pm above the plane formed by two Mn atoms and C1.

Figure 1. Molecular structure of **2**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are not included; the carbon atom C4 between Mn and O4 is not labelled. Selected bond lengths [pm] and angles [°]: Mn−Mn′ 313.70(6), Mn−In 266.51(4), Mn−In′ 260.62(4), In−C1 220.2(2), Mn−C2 184.8(2), Mn−C3 180.1(2), Mn−C4 184.2(2), Mn−C5 180.2(2); C1−In−Mn 142.10(5), C1−In−Mn′ 144.33(5), Mn−In−Mn′ 73.03(1), In−Mn−In′ 106.97(1), In−Mn−Mn′ 52.62(1), In′−Mn−Mn′ 54.35(1), Mn′ and In′ were calculated by the symmetry operation $1 - x, 1 - y, 1 - z$



The Mn−Mn distance amounts to 313.7 pm, which is considerably longer than in $Mn_2(CO)_{10}$ (292 pm[11]). A similar lengthening is observed in other bridged dimanganese compounds with a strong dependence of the bond length on the size of the bridging atom[7−10]; very small values (266.4 pm) are observed with e.g. a small carbon atom[12] and very large values up to 322.7 pm with In or Tl atoms[8−10]. The Mn−In distances in **2** (260.6 and 266.5 pm) are found within the range usually observed in comparable compounds with the Mn_2In fragment (259.6 to 274.8 pm)[9,10] or with terminal Mn−In bonds (263.6−267.8 pm)[13]. The In−C bond length (220.2 pm) is shortened in comparison with the starting In_4 compound (225 pm[1]), whereas the C−Si bond lengths remain unchanged. The Mn−C distances differ significantly, and with 184.5(2) pm the longer bonds are observed for the *trans*-arranged carbonyl groups (C2 and C4) in comparison with that *trans* to the Mn−In bonds [180.2(2) pm], thus indicating a weaker π-back bonding of the In−R group. The Mn−C−O groups deviate from linearity with angles between 169.4 and 176.3°

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Experimental

All procedures were carried out under purified argon in dried solvents (*n*-hexane with $LiAlH_4$, THF and benzene with Na/benzophenone). Compound **1** was prepared as described in ref.[1]; $Mn_2(CO)_{10}$ from Aldrich Chemical Company was used without further purification.

Synthesis of **2**: A solution of 0.23 g (0.592 mmol) of $Mn_2(CO)_{10}$ in 30 ml of *n*-hexane was added to a solution of 0.41 g (0.296 mmol) of **1** in 30 ml of *n*-hexane at ambient temp. The mixture was heated at reflux for 3 h until the deep violet color of **1** had disappeared and a bright red solution was formed. After filtration of traces of elemental In or Mn, the solution was concentrated in vacuo until crystallization of **2** began. At −50°C the red product crystallized as very fine, fairly airstable needles. Yield 0.38 g (63%), m.p. (closed capillary, argon): 220°C (dec.). − FD MS (70 eV), *m*/*z* (%): 1024.2 (10), 1026.2 (100), 1027.2 (70), 1028.2 (50), 1029.3 (15), 1030.3 (3) [all M^+]. − ^1H NMR (300 MHz, C_6D_6): δ = 0.41. − ^{13}C NMR (75.4 MHz, C_6D_6): δ = 218 (CO); 51.7 (InC?); 6.2 ($SiMe_3$). − IR (paraffin; CsBr): $\tilde{\nu}$ = 2039 cm^{-1} m, 1991 m, 1969 m, 1952 m, 1933 s, 1912 m (νCO); 1462 vs, 1377 vs (paraffin); 1292 w, 1260 m, 1250 sh (δCH_3); 1169 vw, 1160 vw, 1119 vw, 1101 vw, 1071 sh; 1045 m (δCH); 916 w, 856 vs, 839 vs, 774 m, 721 m [$\rho CH_3(Si)$]; 675 m ($\nu_{as}SiC$); 637 s, 631 s, 596 m (ν_sSiC); 565 w, 519 m, 496 w, 465 m (νInC); 421 vw. − UV (*n*-pentane), λ_{max} (lg ε): 207 (4.9), 220 (shoulder, 4.8), 255 (4.6), 325 (shoulder, 3.9), 515 (3.2). − $C_{28}H_{54}In_2Mn_2O_8Si_6$ (1026.8): calcd. C 32.8, H 5.3, In 22.4, Mn 10.7; found C 31.9, H 5.3, In 22.7, Mn 10.8. − Mol. mass: 970 (cryoscopically in benzene).

Crystal Structure Determination: Crystals of **2** from THF; $C_{28}H_{54}In_2Mn_2O_8Si_6$ (1026.8); crystal size 0.4 × 0.4 × 0.3 mm; four-circle diffractometer CAD 4; θ-2θ scan; temperature −60°C; triclinic; $P\bar{1}$ (no. 2[14]); a = 892.6(1), b = 894.3(1), c = 1583.6(2) pm, α = 101.35(1), β = 96.61 (1), γ = 116.87(1)°; $V = 1075 \cdot 10^{-30}$ m^3; $d_{calcd.}$ = 1.586 g/cm³; Z = 1; 2θ range $6 \le 2\theta \le 54°$; μ(Mo-K_α) = 1.84 mm^{-1}; empirical absorption correction (DIFABS)[15]; 4653 independent reflections; 209 parameters; program SHELXL-93 and SHELXTL PLUS[16]; structure solution by direct methods with SIR92[17]; refinement by the full-matrix least-squares method and all independent structure factors; $wR^2 = 0.0546$; $R_1 = 0.0201$ for 4453 $F > 4\sigma(F)$; max./min. residual electron density $0.48/-1.0 \cdot 10^{30}$ e/m³[18].

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