The NaCl Adduct of the Iron-Indium Compound
Fe2(CO)6(µ-CO)(µ-InR)2 [R = C(SiMe3)3] – a One-Dimensional Coordination Polymer with Sodium Oxygen Bridges

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The organoindium subhalide [R(Cl)In-In(Cl)R]2 [R = C(SiMe3)3] 1 reacts with Na2[Fe2(CO)8] to form an iron-indium coordination compound which was isolated as the sodium chloride adduct [Na(THF)4][Fe2(CO)6(µ-CO)(µ-InR)2Cl] 2. The iron atoms of 2 are bridged by a CO ligand and two InR groups, the indium atoms of which are further connected by the µ2-bridging chlorine atom. Four THF molecules and two oxygen atoms of terminal CO ligands of different anions span the coordination sphere of the sodium cations to give a one-dimensional coordination polymer in the solid state.

Key words: Indium, Iron, Coordination Compound

Introduction

The tetrahedral tetraindium cluster In4[C(SiMe3)3]4 is easily available by the reaction of indium(I) bromide with the corresponding alkyl lithium compound [1]. It shows a remarkable chemical reactivity. For instance, subhalides such as In2Cl2R2 1 and In4Br2R4 [2,3] were synthesized upon oxidation of the cluster with hexachloroethane, 1,2-dibromoethane or mixtures of bromine with aluminum tribromide, respectively. Furthermore, following the isolobal relationship between the monomeric cluster fragments InR and carbon monoxide, transition metal carbonyl analogous compounds were isolated in which bridging or terminal CO ligands are replaced by InR [4 – 8]. The most fascinating products of that type are the Ni(CO)4 analogues M(ER)4 (M = Ni, Pt; E = Ga, In), which possess exclusively terminally coordinated E-R groups. Their bonding situation is quite similar to that of the corresponding binary carbonyl complexes with a strong π-back bonding of electron density from the central nickel or platinum atoms into empty p-orbitals of the third main-group elements [5 – 7]. We hoped to isolate more of these carbonyl analogous compounds by the reaction of the subhalide 1 with carbonylate anions.

Preparative Results

A solution of R(Cl)In-In(Cl)R 1 in n-pentane was treated with an excess of solid Na2[Fe2(CO)8]·4THF. The carbonylate is insoluble under these conditions, and the resulting suspension therefore was stirred for two weeks at room temperature. As was shown by NMR spectroscopy, mixtures of unstable and unknown intermediates were formed. However, we did not succeed in isolating any of these products by interrupting the reaction at an earlier stage. After filtration and concentration orange crystals of the product 2 (eq. (1)) were isolated in 55% yield. 2 decomposes above 127 °C with gas evolution. It was identified by a crystal structure determination as [Na(THF)4][Fe2(CO)6(µ-CO)(µ-InR)2Cl] (see below). Owing to the lability of compound 2 the NMR spectra were recorded at low temperature in D8-THF, but it was not possible to assign all resonances unambiguously. In the 13C NMR spectrum one resonance was observed at δ = 221.2 for carbonyl groups, and a poorly resolved further signal of low intensity was detected at δ = 221.4, which, however, may be caused by decomposition products. Seven CO absorptions were found in the IR spec-
The NaCl Adduct of the Iron-Indium Compound \( \text{Fe}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{InR})_2 \) \( [R = \text{C(SiMe}_3)_3] \)

Fig. 1. Molecular structure of compound 2. The ellipsoids are drawn at the 40% probability level; methyl groups are omitted; the sodium atoms reside on special positions, only the coordinating oxygen atoms of the THF molecules are shown. Selected bond lengths [pm] and angles [°]: Fe1–Fe2 274.8(2), Fe1–C3 180(1), Fe1–C4 176(1), Fe1–C5 176(1), Fe1–C9 195(1), Fe1–In1 263.6(2), Fe1–In2 263.9(2), Fe2–C6 176(1), Fe2–C7 177(1), Fe2–C8 177(1), Fe2–C9 202(1), Fe2–In1 263.1(2), Fe2–In2 264.3(2), In1–C1 221(1), In1–C11 272.2(3), In2–C2 226(1), In2–C11 272.0(3), Na1–O7 257.7(8), Na2–O5 255.3(9), Na–O(THF) 229.6(9)–235.9(9), In1–Cl1–In2 73.64(8), Fe1–In1–Fe2 62.90(5), Fe1–In2–Fe2 62.70(5), Fe1–C9–Fe2 87.7(5), C7–O7–Na1 144.7(9), C7–O7–Na1 144.7(9), C5–O5–Na2 151.0(9).

Crystall Structure

The molecular structure and numbering scheme of compound 2 is depicted in Fig. 1. It contains a diiron moiety in its molecular center which is bridged by one carbon monoxide and two InR ligands. Each iron atom is further attached to three terminal carbonyl groups. This part of the molecule is quite similar to that of the compound \( [\text{Fe}_2(\text{CO})_6(\mu-\text{CO})(\mu-\text{InR})_2] \) (3), which was obtained by the reaction of enneacarbonyldiiron with the tetraindium cluster [8] and which is isostructural with the starting carbonyl complex. The Fe-Fe separation in 2 [274.8(2) pm] is quite similar to that observed for 3, but strongly elongated compared to the Fe-Fe distance in the isostructural pure carbonyl \( \text{Fe}_2(\text{CO})_9 \).
[252.2(1) pm] [9]. This difference may simply be caused by the different Fe-C and Fe-In bond lengths. The Fe-In distances of 2 [263.1(2) to 264.3(2) pm] are slightly lengthened by about 5 pm compared to those of 3. They are in the range usually observed for Fe-In complexes [4, 8, 10]. The most interesting difference between 2 and 3 is the presence of one equivalent of sodium chloride in the structure of 2. The chloride anion is in a bridging position between both indium atoms, which have distorted tetrahedral coordination spheres. The In-Cl distances are 272.1 pm on average, which correspond to weak bonding. In-Cl distances between 241 and 282 pm have been observed for dimeric or polymeric R2InCl or RnInCl2 compounds, the longer ones belonging to weak In-Cl interactions in polymeric dichlorides possessing pentacoordinated indium atoms with the corresponding chlorine atoms in axial positions [11, 12]. The angle In-Cl-In is rather acute with values of 73.64(8)°. By that bridging the indium atoms approach each other more closely to 326.2(1) pm compared to an In-In separation of 362 pm in 3 [8]. The smaller value is near the range of significant In-In interactions in cluster compounds of the monovalent element, in which distances of 300 to 315 pm have been detected [1]. Owing to the steric shielding by the bulky substituents the halide anion is not attached to sodium cations, which are located on inversion centers and possess a quite remarkable distorted octahedral coordination sphere consisting of six oxygen atoms. Four of these are in the equatorial plane and belong to THF molecules with normal Na-O distances in the range of 229.6(9) and 235.9(9) pm. Two longer distances to opposite oxygen atoms of 257.7(8) and 255.3(9) pm indicate an interaction between sodium and oxygen atoms of terminal CO ligands (O7 and O5). By these interactions one-dimensional coordination polymers are formed in the solid state. A similar coordination of terminal CO ligands by sodium has been observed for the starting dianion [Na(THF)2]2[Fe2(CO)8] [13], which forms a layer structure.

**Experimental Section**

All procedures were carried out under purified argon in dried solvents (n-pentane over LiAlH4). Dimeric dialkyldindium dichloride 1 and [Na(THF)2]2[Fe2(CO)8] were synthesized according to literature procedures [3, 14].

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\text{[Na(THF)2]2[Fe2(CO)8](µ-CO)(µ-InR)2Cl} \quad (2)
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A solution of the subhalide 1 (0.398 g, 0.522 mmol) in 30 ml of n-pentane was treated with an excess of [Fe(CO)4]2 and allowed to react for two weeks. After that filtration the solution was concentrated in vacuum to 8 ml and cooled to 5 °C. Orange crystals of 2 precipitated within two days (0.385 g, 55%). Dec. p. (under argon, sealed capillary): 127 °C. – IR (cm⁻¹): paraffin; CsBr plates: 2001 s, 1461 vs, 1377 vs paraffin; 1759 m vCO (Fe2CO bridge); 1461 vs, 1407 vs paraffin; 1293 w, 1259 s, 1251 s δCH2; 1170 w, 1051 m THF; 857 vs, 840 vs, 776 w vCH3; 723 w paraffin; 677 w v5SiC3; 633 s, 608 m, 592 m v5SiC3, vFeC. – 1H NMR (400 MHz, D8-THF, 253 K): δ = 0.30 (54 H, s, SiMe3), 1.82 (16 H, m, CH2 of THF), 3.66 (16 H, m, OCH2 of THF). – 13C NMR (100.6 MHz, D8-THF, 253 K): δ = 6.5 (SiMe3), 26.3 (THF). – 68.1 (THF), 221.2 (Fe-CO); InC not detected.

**Crystal structure determination**

Single crystals of compound 2 were obtained by cooling of a saturated solution in n-pentane to 5 °C. Data collection was performed on a STOE IPDS diffractometer employing graphite-monochromated Mo-Kα radiation. The structure
The NaCl Adduct of the Iron-Indium Compound Fe$_2$(CO)$_6$($\mu$-CO)($\mu$-InR)$_2$ [R = C(SiMe$_3$)$_3$] was solved by direct methods and refined by a full matrix least-squares calculation based on $F^2$ [15]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. Crystallographic data for the structure (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC-199450. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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