Notes

$Fe_2(CO)_6[In{-}C(SiMe_3)_3]_3$ with a Trigonal-Bipyramidal Fe_2In_3 Cluster[†]

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Summary: $In_4[C(SiMe_3)_3]_4$ (**1**) *reacts with the tricarbonyliron cyclooctatetraene adduct to yield the dark red organoindium iron compound* $Fe_2(CO)_6[In{-}C(SiMe_3)_3]_3$ (**2**), *which is one of the very rare examples of a compound with two* $Fe(CO)_3$ *fragments symmetrically bridged by three main-group elements.* **2** *exhibits a trigonal-bipyramidal* Fe_2In_3 *molecular center with all indium atoms in equatorial positions. The Fe−In bond lengths are as expected (258.2(2) pm), while the equatorial In−In distances of 364.8(1) pm indicate no significant bonding interaction.*

Introduction

The monoalkylindium(I) derivative $In_4[C(SiMe_3)_3]_4$ (**1**) exhibits a nearly undistorted tetrahedron of four In atoms in the solid state[1,2] and remains a tetramer even in dilute benzene solutions,[1] in contrast to the Ga_4 analog, which gradually dissociates to give a monomer with decreasing concentration.[3] However, the monomeric InR fragment is observed as the highest mass in conventional mass spectroscopy and is often found in products of chemical reactions of **1**. InR has a lone electron pair and two empty p orbitals perpendicular to the In−C bond axis and is therefore isolobal[4] with carbon monoxide. The substitution of CO ligands of transition-metal carbonyls by InR groups indeed succeeds by the reaction of In_4R_4 with $Co_2(CO)_8$,[5] $Fe_2(CO)_9$,[6] $Fe_3(CO)_{12}$,[6] and $Mn_2(CO)_{10}$,[7] but these reactions are restricted to complexes with at least two metal centers and the InR fragments exclusively occupy bridging positions above metal−metal bonds. In addition to CO, the monomeric InR moiety is isolobal to the fragment $Fe(CO)_3$,[8] and the treatment of **1** with different amounts of the $Fe(CO)_3$ donor (cyclooctatetraene)tricarbonyliron(0)[9] should result in the formation of mixed iron−indium clusters either by the substitution of InR groups of the In_4 tetrahedron or by the enlargement of the cluster by the addition of iron carbonyl groups.

Results and Discussion

The title compound **2** was formed by the treatment of the tetraindane(4) species **1** with $Fe(CO)_3(COT)$ (COT = cyclooctatetraene) in a stoichiometric ratio of 3:8 in boiling *n*-hexane over a period of 15 min (eq 1).

$$\underset{\mathbf{1}}{3In_4[C(SiMe_3)_3]_4} + 8Fe(CO)_3(COT) \rightarrow \underset{\mathbf{2}}{4(OC)_3Fe[\mu\text{-}InC(SiMe_3)_3]_3Fe(CO)_3} + 8COT \quad (1)$$

The color of the reaction mixture changed from the violet shade for **1** to orange with the partial precipitation of the product (**2**) as an orange powder. Compound **2** was isolated after recrystallization from warm *n*-hexane in a yield of 60%. Only singlets of the $SiMe_3$ groups were observed in the NMR spectra, and the IR spectrum showed CO stretching vibrations exclusively between 1910 and 1990 cm^{-1}, so that bridging CO groups could be excluded. In the FD mass spectrum a molecular peak of *m*/*e* 1320.7 was found, which is consistent with the formula $Fe_2(CO)_6[InC(SiMe_3)_3]_3$. **2** sublimes in vacuo at 240 °C and decomposes slowly above 295 °C. It is sparingly soluble in hexane or benzene but dissolves readily in diethyl ether or THF. Further products of the reaction of **1** with the iron compound could not be detected, although we systematically changed the stoichiometric ratio of the starting compounds, and in each of these reactions the excess component could be isolated by recrystallization.

The molecular structure of **2** in the solid state is shown in Figure 1. The molecule is located on a crystallographic $\bar{6}$ axis. It consists of a trigonal-bipyramidal Fe_2In_3 molecular center with both Fe atoms in axial positions on the rotation axis and all In atoms in equatorial positions in the mirror plane. Although several compounds with Fe−In bonds have been characterized by crystal structure determinations,[10] a similar structure with indium has not been observed before, and only very few examples with three identical main-group elements bridging two $Fe(CO)_3$ fragments, such as three $GeMe_2$ moieties, have been reported in the literature.[11] Owing to the isolability of InR and CO the

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[†] Dedicated to Prof. Dr. G. Huttner on the occasion of his 60th birthday.

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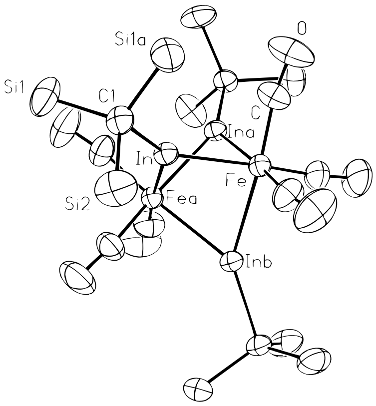

Figure 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity.

Table 1. Crystal Data and Data Collection Parameters for Compound 2

formula	$C_{36}H_{81}Fe_2In_3O_6Si_9$
fw	1318.96
cryst syst	hexagonal
space group	$P6_3/m$
a, pm	1482.9(2)
b, pm	1482.9(2)
c, pm	1579.3(3)
V, 10^{-30} m^3	3007.6(8)
Z	2
D_{calcd}, g/cm^3	1.456
cryst dimens, mm	0.3 × 0.3 × 0.4
μ, mm^{-1}	1.817
temp, K	293
radiation	Mo Kα
2θ range, deg	3−48
scan mode	$\omega-2\theta$
index ranges	$-14 \le h \le 0$, $0 \le k \le 16$, $0 \le l \le 18$
refinement method	full-matrix least squares based on F^2
no. of unique rflns	1630
no. of restraints	18
no. of params	88
R1 ($I > 2\sigma(I)$; 1267)	0.069
wR2 (all data)	0.126
max residual electron density, 10^{30} e/m^3	0.967
min residual electron density, 10^{30} e/m^3	−0.583

Table 2. Important Bond Lengths (pm) and Angles (deg) for Compound 2[a]

Fe−In	258.2(2)	Fe−C	174(1)
In···In	364.8(2)	In−C1	221(1)
Fe···Fe	299.2(2)		
Fe−In−Fe^a	70.83(9)	In−Fe−C	86.1(4)
In−Fe−In^b	89.79(7)	In^b−Fe−C	174.2(4)
Fe−In−C1	144.58(5)	In^c−Fe−C	86.2(4)
C−Fe−C^b	97.6(5)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $x, y, -z + 1/2$; (b) $-x + y, -x + 1, z$; (c) $-y + 1, x - y + 1, z$.

molecule can be described as an analog of $Fe_2(CO)_9$,[12] but the Fe−Fe distance in compound **2** (299.2(2) pm, Table 2) is much elongated in comparison to the pure iron carbonyl (252.2(1) pm);[12] comparably long distances have been observed before in several organometallic diiron derivatives.[13] The Fe−Fe distances in $Fe_2(CO)_6(\mu\text{-}X)_3$ complexes (X = main-group element) seem to be determined by the Fe−X bond lengths ($SiMe_2$ bridges, Fe−Si = 232.2 pm, Fe−Fe = 270.5 pm; $GeMe_2$ bridges, Fe−Ge = 239.8 pm, Fe−Fe = 275.0 pm[11]), while the angle at the bridging atom deviates, with the exception of $Fe_2(CO)_9$ (78°),[12] only slightly from an average value of 70° (**2**: 70.83(9)°). The Fe−In bond lengths of **2** (258.2(2) pm) lie in that region usually observed,[10] while the In−In distances are very long (364.8 pm), indicating no significant In−In bonding interaction. In−In bond lengths of 300.1(1)[1] and 274−292 pm,[14] respectively, have been detected for the cluster compound **1** and for single bonds of organometallic derivatives. Cyclopentadienides with monovalent indium atoms such as the pseudodimeric $In[C_5(CH_2C_6H_5)_5]$[15] or the pseudohexameric $In(C_5Me_5)$[16] show In−In distances of 363.1(2) pm or 395 pm on average; the significance of such weak contacts has been a source of controversy in the literature.[17] Remarkably, the derivative $Co_2(CO)_6[In{-}C(SiMe_3)_3]_2$ with two bridging In−R groups shows an In−In distance of 336.2(1) pm,[5] which is intermediate between the tetraindane(4) species **1** and the negligible interactions of the cyclopentadienyl derivatives.

The iron atoms are surrounded by six ligands in a distorted-octahedral environment, but only the In−Fe−In angles (89.79(7)°) approach the ideal value of 90°. The C−Fe−C angles are enlarged (97.6(5)°), while two of the In−Fe−C angles are smaller at 86.2(4)°; as expected, the third one is almost linear (174.2(4)°). The Fe−C−O groups deviate from linearity with an angle of 167(1)°. The In−C bond lengths are shortened to 221(1) pm compared to the starting compound **1** (226(1) pm),[1] which has often been detected in its reaction

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products and is possibly caused by the change of the oxidation state of the In atoms.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane over $LiAlH_4$, THF over Na/benzophenone). **1** was prepared according to the literature,[1] and $Fe(CO)_3(COT)$ from Aldrich Chemical Co. was used without further purification.

$Fe_2(CO)_6[In-C(SiMe_3)_3]_3$. A 120 mg (0.087 mmol) amount of the tetraindane(4) species **1** and 56 mg (0.23 mmol) of $Fe(CO)_3(COT)$ are dissolved in 30 mL of *n*-hexane. The mixture is heated under reflux for 15 min; the color changes from violet to orange, and the product partially crystallizes on cooling to room temperature. The solution is concentrated, the solid is dissolved in the heat, and the solution is cooled to −30 °C. Yield: 92 mg (60%), red, slightly air-sensitive crystals; in solution rapid decomposition is observed on contact with air. Anal. Calcd for $C_{36}H_{81}Fe_2In_3O_6Si_9$ (1318.96): In, 26.1; Fe, 8.5. Found: In, 25.9; Fe, 8.6. FD MS: *m*/*e* 1320.7, $M^+ + H$. Dec pt: 295 °C (closed capillary, argon). ^1H NMR (THF-d_8, 300 MHz): δ 0.35 (s). ^{13}C NMR (diethyl ether-d_{10}, 75 MHz): δ 217.6 (s, CO), 6.5 (s, $SiMe_3$); In−C not found. IR (paraffin, CsBr, cm^{-1}): 1987 vw, 1960 m, 1921 s, 1910 m (ν(CO)); 1606 br, vw, 1304 w, 1269 sh, 1252 m $\delta(CH_3)$); 1169 w, 1155 w, 1047 w, 858 vs, 841 vs, 774 m, 721 s ($\rho(CH_3(Si))$; 675 m, 650 w (ν(SiC)), 610 m, 598 m, 584 s, 534 w (ν(FeC), ν(InC)). UV/vis (*n*-hexane) (log ϵ): 240 (4.9), 420 nm (3.8).

Crystal Structure. Single crystals of **2** were obtained from a saturated solution in THF on slow cooling to 0 °C. Relevant crystal and data collection parameters are given in Table 1. The structure was solved by direct methods and refined with the program SHELXL-93[18] by a full-matrix least-squares method based on F^2. **2** crystallizes in the hexagonal space group $P6_3/m$ (No. 176[19]) with two molecules in each unit cell. The molecule is located on a $\bar{6}$ axis with a 3-fold rotation axis through both axial Fe atoms and a mirror plane through the three equatorial In atoms. One $SiMe_3$ group of the $C(SiMe_3)_3$ substituent is located in the mirror plane, while the remaining groups above and below the plane are equivalent by symmetry. They show a disorder, which could be described as a rotation of the CSi_3 group by 60°; the ratio of both positions amounts to 0.76:0.24. In addition, the methyl groups at Si2 are statistically disordered across the mirror plane, giving six positions with occupancy factors of 0.5. All carbon atoms of the methyl groups were isotropically refined with the restriction of the Si−C bond lengths (188 pm) and C···C distances (301 pm); hydrogen atoms were fixed on ideal positions.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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