Organometallic Iron Indium Derivatives Prepared by the Reaction of Carbonyliron Compounds with the Alkylindium(I) Derivative $In_4[C(SiMe_3)_3]_4$†

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The monomeric fragment In−C(SiMe$_3$)$_3$ with a monovalent indium atom is isolobal with carbon monoxide. It is probably formed as a reactive intermediate on heating solutions of the tetrahedral cluster compound $In_4[C(SiMe_3)_3]_4$ (**1**) in hexane and reacts with $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ to yield by the substitution of bridging CO ligands three novel iron indium compounds, $Fe_3(CO)_{10}(\mu\text{-InR})_2$ (**2**), $Fe_2(CO)_8(\mu\text{-InR})$ (**3**), and $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-InR})_2$ (**4**), which all were characterized by crystal structure determinations (**2**: $C_{30}H_{54}Fe_3In_2O_{10}Si_6$, monoclinic, $P2_1/n$, $a = 1436.1(2)$ pm, $b = 1992.9(3)$ pm, $c = 1764.8(3)$ pm, $\beta = 107.02(2)°$. **3**: $C_{18}H_{27}Fe_2InO_8Si_3$, monoclinic, $C2/c$, $a = 1527.8(3)$ pm, $b = 960.3(2)$ pm, $c = 3755.4(8)$ pm, $\beta = 90.17(3)°$. **4**: $C_{27}H_{54}Fe_2In_2O_7Si_6$, triclinic, $P\bar{1}$, $a = 959.3(1)$ pm, $b = 1506.7(2)$ pm, $c = 1561.4(1)$ pm, $\alpha = 86.11(1)°$, $\beta = 88.76(1)°$, $\gamma = 73.57(1)°$). While both products **2** and **4** are isostructural with the pure carbonyls with two or three bridging groups, respectively, compound **3** has only one bridging InR group besides eight terminal carbonyl ligands. The Fe−In bond lengths are quite similar (255.9−260.5 pm), but the Fe−Fe distances differ significantly with 286.7(1) pm for the bridged Fe−Fe bond in **2**, 289.3(1) pm in **3**, and 275.87(5) pm in **4**. They all are much elongated compared to the starting carbonyl complexes.

Introduction

The tetraalkyltetraindium(I) derivative $In_4[C(SiMe_3)_3]_4$ (**1**) was recently synthesized in a high yield by our group[1] and the group of Cowley[2] by the reaction of InBr or InCl with LiC(SiMe$_3$)$_3$·2THF. **1** possesses a nearly undistorted tetrahedron of four In atoms in the solid state and remains a tetramer in dilute benzene solutions, while in conventional mass spectra the monomer is observed as the highest mass.[1] The monomeric fragment In−C(SiMe$_3$)$_3$ can be trapped by refluxing solutions of **1** in *n*-hexane in the presence of 1,4-dihetero butadienes like benzil derivatives.[3] It exhibits two empty p orbitals perpendicular to the In−C bond axis and one lone electron pair and is therefore isolobal[4] with carbon monoxide. InR would thus belong to the intensively studied group of CO-analogous compounds like isonitriles or phosphorus trifluoride, which have been successfully applied as σ-donor/π-acceptor ligands in transition metal complexes. Indeed, we succeeded in substituting CO ligands of binuclear transition metal carbonyl complexes by the reaction of **1** with $Co_2(CO)_8$[5] or $Mn_2(CO)_{10}$,[6] but the InR groups occupy exclusively bridging positions between both metal centers in all products. Two derivatives were isolated with octacarbonyldicobalt, in which, depending on the stoichiometric ratio of the components, one or both bridging CO ligands are replaced by InR.[5] These reactions differ significantly from the formerly described reactions of In(I) halides with dinuclear carbonyl complexes, in which an insertion into the metal−metal bond is observed instead of a substitution of CO ligands.[7] Transition metal carbonyl analogues of the Al(I) derivative AlCp* with an η^5-pentamethylcyclopentadienyl group were recently published by Schnöckel et al.[8] and Fischer et al.;[9] a dinickel derivative with two bridging AlCp* moieties similar to CpNi(μ-CO)$_2$NiCp was synthesized by the reaction of dicyclopentadienylnickel with Al$_4$Cp*$_4$,[8] while a terminal AlCp* ligand was observed in Fe(CO)$_4$(AlCp*), which is isostructural with pentacarbonyliron.[9] Theoretical investigations confirm a σ-donor/π-acceptor bonding model in the iron complex with the back-donation of electron density from iron to aluminum.[9] We wish to report here the reactions of **1** with the iron carbonyl complexes $Fe_2(CO)_{12}$ and $Fe_2(CO)_9$, with two or three bridging CO ligands, which we hoped to replace gradually by systematically changing the reaction conditions.

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and cyclopentane over LiAlH$_4$; toluene over Na/benzophenone). **1** was prepared according to the literature,[1] and the carbonyl complexes $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were purchased from ABCR GmbH (Karlsruhe, Germany); while $Fe_3(CO)_{12}$

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† Dedicated to Prof. Dr. M. Weidenbruch on the occasion of his 60th birthday.

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was used without further purification, $Fe_2(CO)_9$ was washed with hydrochloric acid, water, ethanol, and diethyl ether and dried in vacuum.

$Fe_3(CO)_{10}(\mu$-InR$)_2$ (2). A suspension of $In_4[C(SiMe_3)_3]_4$ (**1**) (210 mg, 0.152 mmol) and $Fe_3(CO)_{12}$ (155 mg, 0.308 mmol) in *n*-hexane is refluxed for 4 h. The color changes to deep red. The mixture is filtered to remove traces of a gray powder of elemental indium or iron, and the filtrate is evaporated in vacuo. Recrystallization of the residue from cyclopentane (20 °C/−30 °C) yields the product **2** as deep red crystals. Yield: 270 mg (78% based on **1**). Mp (argon, closed capillary): 150 °C. FD MS: *m*/*z* 1137.4, 1139.5, 1140.4, 1141.5 (all M^+) corresponding with a calculated isotope pattern. ^1H NMR (C_6D_6, 300 MHz): δ 0.36 (s, $SiMe_3$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 212.2 (s, CO), 6.3 (s, $SiMe_3$); InC not detected. IR (paraffin, CsBr plates, cm^{-1}): 2066 s, 2010 s, 1985 m, 1973 vs, 1931 m ν(CO); 1462 vs, 1377 vs paraffin; 1304 w, 1262 m, 1254 m $\delta(CH_3)$; 1169 vw, 1154 vw; 855 vs, 841 sh, 777 w, 721 m $\rho(CH_3(Si))$; 677 w, 652 w ν_{as}(SiC); 610 m, 600 m, 581 w, 565 w ν(FeC); 476 w, 469 w ν(InC); 442 vw, 390 vw, 360 vw δ(SiC). UV/vis (*n*-pentane, nm, (log ϵ)): 210 (br, 5.0), 275 (sh, 4.6), 326 (sh, 4.3), 400 (sh, 3.8). Anal. Calcd for $C_{30}H_{54}Fe_3In_2O_{10}Si_6$: Fe, 14.69; In, 20.14. Found: Fe, 14.72; In, 20.13.

$Fe_2(CO)_8(\mu$-InR) (3) and $Fe_2(CO)_6(\mu$-CO$)(\mu$-InR$)_2$ (4). $In_4[C(SiMe_3)_3]_4$ (**1**) (410 mg, 0.296 mmol) is treated with a 5-fold molar excess of $Fe_2(CO)_9$ (538 mg, 1.48 mmol) in 30 mL of boiling *n*-hexane for 70 min. The solution is concentrated and cooled to precipitate the dark green byproduct $Fe_3(CO)_{12}$. Further concentration and cooling to −30 °C give dark red crystals of compound **4** with two bridging InR groups, which can be further purified by recrystallization from toluene. The dark red compound **3** with only one bridging InR group crystallizes in several fractions from the hexane mother liquor after further concentration and cooling to −30 °C. Yields: 200 mg of **3** (25% based on **1**) and 208 mg of **4** (35% based on **1**).

Characterization of 3. Mp (argon, closed capillary): 123 °C. FD MS: *m*/*z* 682.1 and 683.1 (both M^+) corresponding with a calculated isotope pattern. ^1H NMR (C_6D_6, 300 MHz): δ 0.249 (s, $SiMe_3$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 210.7 (s, CO), 5.6 (s, $SiMe_3$); InC not detected. IR (paraffin, CsBr plates, cm^{-1}): 2076 vs, 2052 sh, 2023 vs, 2010 vs, 1987 vs, 1941 sh ν(CO); 1452 vs, 1377 vs paraffin; 1294 m, 1254 vs $\delta(CH_3)$; 1169 w, 1155 w, 1080 vw, 1042 vw, 1009 w; 856 vs, 777 s, 721 s $\rho(CH_3(Si))$; 675 m, 650 w ν_{as}(SiC); 617 vs, 604 vs ν(FeC); 548 s, 523 m, 503 m ν(InC); 430 w, 392 w δ(SiC). UV/vis (*n*-pentane, nm (log ϵ)): 245 (4.4), 320 (sh, 4.0), 355 (sh, 3.7), 420 (sh, 3.5). Anal. Calcd for $C_{18}H_{27}Fe_2InO_8Si_3$: Fe, 16.37; In, 16.83. Found: Fe, 16.12; In, 16.95.

Characterization of 4. Dec pt (argon, closed capillary): 238 °C. FD MS: *m*/*z* 998.4, 1000.0, 1001.2, 1002.1 (all M^+) corresponding with a calculated isotope pattern. ^1H NMR (C_6D_6, 300 MHz): δ 0.269 (s, $SiMe_3$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 215.7 (s, CO), 49.9 (InC), 5.9 (s, $SiMe_3$). IR (paraffin, CsBr plates, cm^{-1}): 2023 s, 1985 s, 1956 s, 1942 s ν(CO) (terminal); 1786 s ν(CO) (bridge); 1461 vs 1377 vs paraffin; 1298 m, 1262 sh, 1252 vs $\delta(CH_3)$; 1169 w, 1042 w; 856 vs, 841 vs, 775 s, 721 s $\rho(CH_3(Si))$; 677 s, 648 s ν_{as}(SiC); 617 s, 594 vs, 579 vs ν(FeC); 488 s, 473 m ν(InC); 424 w, 401 m δ(SiC). UV/vis (*n*-pentane, nm (log ϵ)): 240 (4.5), 440 (3.4). Anal. Calcd for $C_{27}H_{54}Fe_2In_2O_7Si_6$: Fe, 11.16; In, 22.95. Found: Fe, 11.40; In, 22.72.

Crystal Structure Determinations. Dark red single crystals of compound **2** were obtained by recrystallization from toluene; dark red single crystals of **3** and **4** were obtained from *n*-hexane. The X-ray data collections were performed on the four-circle diffractometers AED 2 (**2**) and CAD 4 (**3** and **4**) with graphite-monochromated Mo Kα radiation. The crystals (**2**, 0.4 × 0.5 × 1.0 mm; **3**, 0.5 × 0.4 × 0.3 mm; **4**, 0.5 × 0.4 × 0.4 mm) were mounted under an atmosphere of argon in glass capillaries, which were then sealed off. The intensity data were collected at room temperature (**2**), 199 K (**3**), and 193 K (**4**) in the 2θ ranges of 3−50° for **2** and 6−52° for **3** and **4**, spanning the respective octants $0 \leq h \leq 17$, $0 \leq k \leq 23$, $-20 \leq l \leq 20$; $-18 \leq h \leq 18$, $-11 \leq k \leq 7$, $-46 \leq l \leq 46$; and $-11 \leq h \leq 11$, $0 \leq k \leq 18$, $-19 \leq l \leq 19$. A total of 8860 reflections was collected for compound **2** (9660 for **3** and 8400 for **4**), from which 8500 independent reflections were used for structure solution and refinement (5313 for **3** and 8393 for **4**). All structures were solved by direct methods using the program system SHELXTL PLUS[11] and refined with the SHELXL-93[11] program via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}$(C). The crystallographic data and details of the final *R* values are provided in Table 1. Conventional *R* factors (R1) are based on *F* using reflections with $F > 4\sigma(F)$ (6515 reflections for **2**, 4321 for **3**, and 7761 for **4**); weighted *R* factors (wR2) are based on F^2. The number of refined parameters was 478 (**2**), 299 (**3**), and 416 (**4**). Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-406859 (**2**), −406858 (**3**), and −406857 (**4**).

Table 1. Crystallographic Data for **2**−**4**

	2	**3**	**4**
empirical formula	$C_{30}H_{54}Fe_3In_2O_{10}Si_6$	$C_{18}H_{27}Fe_2InO_8Si_3$	$C_{27}H_{54}Fe_2In_2O_7Si_6$
fw	1140.46	682.19	1000.58
space group	$P2_1/n$; No. 14[10]	$C2/c$; No. 15[10]	$P\bar{1}$; No. 2[10]
a (pm)	1436.1(2)	1527.8(3)	959.3(1)
b (pm)	1992.9(3)	960.3(2)	1506.7(2)
c (pm)	1764.8(3)	3755.4(8)	1561.4(1)
α (deg)	90.00	90.00	86.11(1)
β (deg)	107.02(2)	90.17(3)	88.76(1)
γ (deg)	90.00	90.00	73.57(1)
V (10^{-30} m^3)	4830(1)	5510(2)	2159.7(4)
Z	4	8	2
temp (K)	293	199	193
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calc} (g cm^{-3})	1.568	1.645	1.539
μ (mm^{-1})	2.012	2.036	1.914
R1[a]	0.0386	0.0465	0.0231
wR2[b]	0.1259	0.1451	0.0644

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ ($F > 4\,\sigma(F)$). [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ (all data).

Results and Discussion

Syntheses. The triiron compound $Fe_3(CO)_{12}$ reacts in boiling *n*-hexane with $In_4[C(SiMe_3)_3]_4$ (**1**) in the stoichiometric ratio of 2:1 (eq 1) to yield only one product (**2**), which is isolated

$$\underset{\mathbf{1}}{In_4[C(SiMe_3)_3]_4} + 2Fe_3(CO)_{12} \rightarrow 2\underset{\mathbf{2}}{Fe_3(CO)_{10}[\mu\text{-}InC(SiMe_3)_3]_2} + 4CO \quad (1)$$

after recrystallization from cyclopentane in a yield of 78% as dark red crystals. The IR spectrum of **2** shows absorptions of the CO stretching vibrations only between 1931 and 2066 cm^{-1}, which is consistent with an exclusively terminal coordination of CO, and both bridging CO ligands of the starting carbonyl complex are replaced by InR groups, as clearly shown by elemental analysis and mass spectroscopy. The $SiMe_3$ groups exhibit sharp singlets in the ^1H and ^{13}C NMR spectra, and only one resonance of the carbonyl carbon atoms is observed, similar to the case of $Fe_3(CO)_{12}$,[12] with a chemical shift of 212.2 ppm. The resonance of the α-carbon atom of the tris(trimethylsilyl)methyl group bonded to indium could, however, not be detected. The UV/vis spectrum shows a very broad absorption at 210 nm with several shoulders up to 400 nm. Reactions with an excess of the iron carbonyl did not yield another derivative with, for instance, one bridging CO and one bridging InR ligand, similar to the reactions of $Co_2(CO)_8$[5] discussed above; instead,

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compound **2** was exclusively formed, and the excess $Fe_3(CO)_{12}$ could quantitatively be recovered as the less soluble component after the concentration and cooling of the reaction mixture in *n*-hexane.

The reaction of $Fe_2(CO)_9$ with **1** is much more complicated. An excess of the iron carbonyl with a molar ratio of at least 5:1 is required to completely consume **1** in boiling *n*-hexane over a period of about 1 h. Two main products (**3** and **4**, eq 2)

$$\underset{\mathbf{1}}{In_4[C(SiMe_3)_3]_4} + Fe_2(CO)_9 \xrightarrow[-CO]{} \underset{\mathbf{3}}{Fe_2(CO)_8[\mu\text{-}InC(SiMe_3)_3]} + \underset{\mathbf{4}}{Fe_2(CO)_6(\mu\text{-}CO)[\mu\text{-}InC(SiMe_3)_3]_2} \quad (2)$$

are formed, which can be separated by recrystallization from *n*-hexane. Some byproducts of the reaction could be isolated or identified: (i) dark green $Fe_3(CO)_{12}$ as the most sparingly soluble component of the reaction mixture, which results from a partial decomposition of $Fe_2(CO)_9$; (ii) a small amount of $HC(SiMe_3)_3$, formed by a decomposition of **1**; and (iii) a further iron indium derivative, which we could, however, isolate only as an impure 1:1 mixture with **4**. The NMR spectroscopically determined yield of the unknown derivative in the crude product in relation to **3** and **4** increases with an increasing excess of $Fe_2(CO)_9$. The ^1H and ^{13}C NMR shifts of the $SiMe_3$ groups ($\delta(^1H) = 0.36$ ppm; $\delta(^{13}C) = 6.3$ ppm) coincide with the resonances of two compounds: the Fe_3In_2 derivative **2**, which could have been formed by the reaction of the byproduct $Fe_3(CO)_{12}$ with **1**, and $(CO)_3Fe(\mu\text{-}InR)_3Fe(CO)_3$, which formally is the product of the replacement of all bridging CO ligands of $Fe_2(CO)_9$ and was recently obtained in our group by the reaction of **1** with $Fe(CO)_3COT$ (COT = cyclooctatetraene).[13] Both compounds differ in the resonances of the carbonyl groups (212.2 compared to 217.6 ppm), but despite changing the recording conditions, we were not able to obtain a clearly resolved ^{13}C NMR spectrum of the mixture in that region; a small resonance at 212 ppm possibly indicates compound **2**. The Fe_2In_3 compound is only sparingly soluble in hexane;[13] thus we believe that, owing to the high solubility of the unknown component of the reaction mixture in hexane and to the higher yield with increasing excess of the iron carbonyl, probably compound **2** has formed as a byproduct.

Elemental analysis and mass spectroscopy show that in the slightly less soluble product (**4**) two CO groups are replaced by two InR ligands, while in the second isolated product (**3**) only one CO group is substituted. Both **3** and **4** exhibit sharp singlets of the $SiMe_3$ substituents in the ^1H and ^{13}C NMR spectra. The carbonyl carbon atoms resonate at 210.7 (**3**) and 215.7 ppm (**4**). The α-carbon atom of the $C(SiMe_3)_3$ group could only be detected for compound **4** at 49.9 ppm; it is shifted to lower field compared to that range usually observed with alkylindium(III) derivatives ($\delta < 30$ ppm).[14] The tetraindium compound **1** with a tetrahedral In_4 molecular center shows a stronger shift to 72 ppm, which is caused by the delocalized molecular orbitals of the cluster as shown by up to now unpublished theoretical calculations. Similar unusual shifts as for **4** occur with the cobalt and manganese derivatives bridged by InR groups (49[5] and 52[6] ppm, respectively); they possibly indicate some electronic π interactions between the iron and the electronically unsaturated indium atoms. Only stretching vibrations of terminal CO groups between 1941 and 2076 cm^{-1} can be determined for product **3**, while the derivative **4** shows an absorption at 1786 cm^{-1}, characteristic of a bridging CO ligand; the vibrations of the terminal groups lie between 1942 and 2023 cm^{-1}.

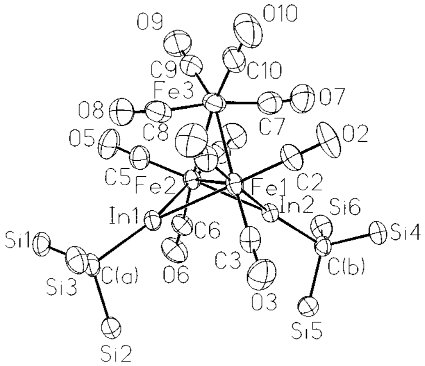

Figure 1. Molecular structure and numbering scheme of **2**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen and methyl carbon atoms are omitted for clarity.

Table 2. Important Bond Lengths (pm) and Angles (deg) for **2**

Fe(1)−Fe(2)	286.7(1)		
Fe(1)−Fe(3)	272.3(1)	In(1)−Fe(1)	260.49(8)
Fe(2)−Fe(3)	270.3(1)	In(1)−Fe(2)	260.47(8)
In(1)−C(A)	220.1(5)	In(2)−Fe(1)	258.91(8)
In(2)−C(B)	219.4(5)	In(2)−Fe(2)	259.00(9)

	$n = 1$	$n = 2$	$n = 3$	
Fe(1)−C(*n*)	177.3(6)	177.2(6)	176.4(6)	
	$n = 4$	$n = 5$	$n = 6$	
Fe(2)−C(*n*)	177.1(6)	178.4(6)	176.1(5)	
	$n = 7$	$n = 8$	$n = 9$	$n = 10$
Fe(3)−C(*n*)	182.5(8)	180.4(8)	179.9(7)	178.9(7)

C(A)−In(1)−Fe(1)	145.3(1)	C(B)−In(2)−Fe(1)	147.9(1)
C(A)−In(1)−Fe(2)	147.7(1)	C(B)−In(2)−Fe(2)	144.6(1)
Fe(1)−In(1)−Fe(2)	66.78(2)	Fe(1)−In(2)−Fe(2)	67.22(2)
In(1)−Fe(1)−C(1)	85.5(2)	In(1)−Fe(2)−C(4)	174.4(2)
In(1)−Fe(1)−C(2)	177.6(2)	In(1)−Fe(2)−C(5)	86.2(2)
In(1)−Fe(1)−C(3)	87.3(2)	In(1)−Fe(2)−C(6)	89.7(2)
In(2)−Fe(1)−C(1)	176.8(2)	In(2)−Fe(2)−C(4)	82.4(2)
In(2)−Fe(1)−C(2)	83.9(2)	In(2)−Fe(2)−C(5)	178.8(2)
In(2)−Fe(1)−C(3)	88.9(2)	In(2)−Fe(2)−C(6)	86.6(2)
In(1)−Fe(1)−In(2)	94.44(2)	In(1)−Fe(2)−Fe(1)	56.62(2)
In(1)−Fe(1)−Fe(3)	94.09(3)	In(2)−Fe(2)−Fe(1)	56.37(2)
In(1)−Fe(1)−Fe(2)	56.61(2)	Fe(1)−Fe(2)−Fe(3)	58.45(3)
In(2)−Fe(1)−Fe(2)	56.41(2)	In(1)−Fe(2)−In(2)	94.43(3)
Fe(3)−Fe(1)−C(1)	86.2(2)	Fe(3)−Fe(2)−C(4)	81.0(2)
Fe(3)−Fe(1)−C(2)	84.1(2)	Fe(3)−Fe(2)−C(5)	90.0(2)
Fe(3)−Fe(1)−C(3)	178.5(2)	Fe(3)−Fe(2)−C(6)	175.2(2)
Fe(2)−Fe(1)−C(1)	121.3(2)	In(1)−Fe(2)−Fe(3)	94.57(3)
Fe(2)−Fe(1)−C(2)	120.9(2)	In(2)−Fe(2)−Fe(3)	90.95(3)
Fe(2)−Fe(1)−C(3)	122.9(2)	Fe(1)−Fe(2)−C(4)	117.9(2)
In(2)−Fe(1)−Fe(3)	90.53(3)	Fe(1)−Fe(2)−C(5)	124.8(2)
Fe(2)−Fe(1)−Fe(3)	57.77(3)	Fe(1)−Fe(2)−C(6)	122.9(2)
Fe(1)−Fe(3)−C(7)	91.1(2)	Fe(2)−Fe(3)−C(7)	91.8(2)
Fe(1)−Fe(3)−C(8)	81.0(2)	Fe(2)−Fe(3)−C(8)	81.9(2)
Fe(1)−Fe(3)−C(9)	160.9(2)	Fe(2)−Fe(3)−C(9)	97.6(2)
Fe(1)−Fe(3)−C(10)	98.7(3)	Fe(2)−Fe(3)−C(10)	162.4(3)
Fe(1)−Fe(3)−Fe(2)	63.78(3)		

Crystal Structures. The molecular structure of compound **2** is shown in Figure 1. The compound is isostructural with the starting carbonyl $Fe_3(CO)_{12}$ and consists of a three-membered ring of iron atoms with one of the Fe−Fe bonds symmetrically bridged by two $In{-}C(SiMe_3)_3$ groups. The Fe−In bond lengths (259.7 pm on average, Table 2) to the axial Fe atoms Fe(1) and Fe(2) are in that range normally observed.[13,15] The lengths of the bonds Fe(1)−Fe(3) and Fe(2)−Fe(3) (271.3

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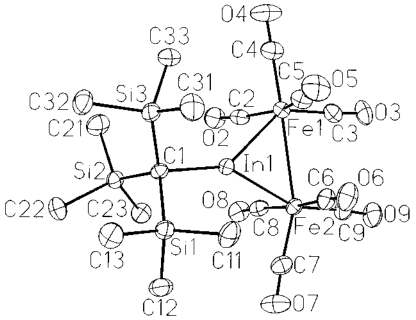

Figure 2. Molecular structure and numbering scheme of **3**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity.

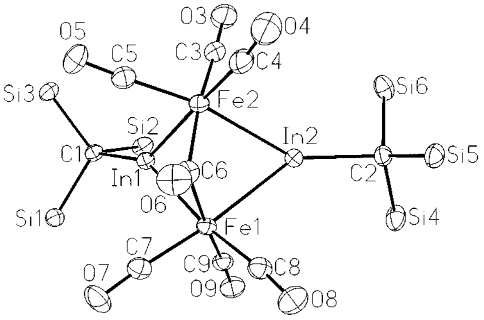

Figure 3. Molecular structure and numbering scheme of **4**. The thermal ellipsoids are drawn at the 40% probability level; hydrogen and methyl carbon atoms are omitted for clarity.

Table 3. Important Bond Lengths (pm) and Angles (deg) for **3**

In(1)−C(1)	218.0(6)	In(1)−Fe(1)	257.4(1)
Fe(1)−Fe(2)	289.3(1)	In(1)−Fe(2)	255.9(1)

	$n = 2$	$n = 2$	$n = 4$	$n = 5$
Fe(1)−C(n)	179.5(8)	181.5(7)	177.5(8)	179.6(7)
	$n = 6$	$n = 7$	$n = 8$	$n = 9$
Fe(2)−C(n)	179.5(7)	176.8(7)	179.7(8)	181.8(7)

	$n = 2$	$n = 3$	$n = 4$	$n = 5$
Fe(2)−Fe(1)−C(n)	90.2(2)	81.8(2)	177.1(3)	94.4(2)
In(1)−Fe(1)−C(n)	80.0(2)	137.2(2)	124.1(3)	80.5(2)
	$n = 6$	$n = 7$	$n = 8$	$n = 9$
In(1)−Fe(2)−C(n)	84.5(2)	100.1(2)	87.1(2)	156.8(2)
Fe(1)−Fe(2)−C(n)	84.9(2)	156.0(2)	89.0(2)	100.9(2)

In(1)−Fe(1)−Fe(2)	55.45(3)	Fe(1)−In(1)−Fe(2)	68.62(3)
In(1)−Fe(2)−Fe(1)	55.93(3)	Fe(1)−In(1)−C(1)	142.6(2)
		Fe(2)−In(1)−C(1)	148.7(2)

Table 4. Important Bond Lengths (pm) and Angles (deg) for **4**

Fe(1)−Fe(2)	275.87(5)	Fe(1)−C(9)	180.0(3)
Fe(1)−In(1)	259.13(5)	Fe(2)−C(3)	179.4(3)
Fe(1)−In(2)	256.36(5)	Fe(2)−C(4)	178.6(3)
Fe(2)−In(1)	257.49(6)	Fe(2)−C(5)	179.6(3)
Fe(2)−In(2)	259.51(5)	Fe(2)−C(6)	197.9(3)
Fe(1)−C(6)	199.2(3)	In(1)−C(1)	217.7(3)
Fe(1)−C(7)	178.9(3)	In(2)−C(2)	217.7(3)
Fe(1)−C(8)	179.0(3)		

	$n = 6$	$n = 7$	$n = 8$	$n = 9$
Fe(2)−Fe(1)−C(n)	45.81(8)	114.9(1)	116.49(9)	127.23(8)
In(1)−Fe(1)−C(n)	89.99(8)	89.02(9)	172.53(9)	84.90(8)
In(2)−Fe(1)−C(n)	86.26(8)	172.5	83.67(9)	88.94
	$n = 3$	$n = 4$	$n = 5$	$n = 6$
Fe(1)−Fe(2)−C(n)	127.8(1)	119.8(1)	112.15(9)	46.19(8)
In(1)−Fe(2)−C(n)	87.1(1)	177.7(1)	82.93(9)	90.76(8)
In(2)−Fe(2)−C(n)	87.9(1)	90.4(1)	169.08(9)	85.65(8)

In(1)−Fe(1)−In(2)	89.12(2)	In(1)−Fe(2)−In(2)	88.79(2)
In(2)−Fe(1)−Fe(2)	58.23(1)	In(1)−Fe(2)−Fe(1)	58.01(2)
In(1)−Fe(1)−Fe(2)	57.44(2)	In(2)−Fe(2)−Fe(1)	57.12(1)
C(1)−In(1)−Fe(2)	144.96(7)	C(2)−In(2)−Fe(1)	144.83(7)
C(1)−In(1)−Fe(1)	150.47(7)	C(2)−In(2)−Fe(2)	150.07(7)
Fe(2)−In(1)−Fe(1)	64.55(2)	Fe(1)−In(2)−Fe(2)	64.65(1)

pm) are quite similar to the corresponding bond lengths in $Fe_3(CO)_{12}$ (268 pm[16]), while the bridged bond Fe(1)−Fe(2) is much elongated from 255 pm in the pure carbonyl to 286.7 pm in **2**. We observed an even larger elongation in $(CO)_3Fe(\mu\text{-InR})_3Fe(CO)_3$ with three bridging InR groups and an Fe−Fe distance of 299.2(2) pm;[13] similar long distances have been observed before in several organometallic diiron complexes.[17] The difference between the starting carbonyl and **2** might strongly depend on steric restrictions, and the much shorter Fe−C bond lengths of carbonyl bridges (205 pm) compared to the Fe−In bonds in the Fe−In−Fe bridges could result in a shorter Fe−Fe distance. The angles on the bridging atoms are more acute in the In derivative (67.0° in **2** and about 77° in $Fe_3(CO)_{12}$[16]). The equatorial $FeIn_2$ triangle is almost equilateral with long interatomic distances of In(1)···In(2) 381.2 pm, Fe(3)···In(1) 390.1 pm, and Fe(3)···In(2) 377.5 pm, which indicate no significant bonding interaction. The angle between the normals of the planes (In(1)Fe(1)Fe(2)) and (In(2)Fe(1)Fe(2)) is 59.8°, and between (In(1)Fe(1)Fe(2)) and (Fe(1)Fe(2)Fe(3)) it is 117.3°. The In−C bond lengths are slightly shortened compared to those of **1** (219.8−225 pm) as often observed before in reaction products of **1**,[5,6,18] and the indium atoms are almost planar, coordinated by their substituents with the In atoms 5.4 and 6.3 pm above the plane (sum of the angles: In(1), 359.8°; In(2), 359.7°).

Figures 2 and 3 show the molecular structures of the diiron compounds **3** and **4**, in which one or two InR ligands occupy a bridging position between both Fe atoms. While compound **4** is isostructural with $Fe_2(CO)_9$ with three bridging groups (one CO and two InR) and a distorted octahedral environment of the Fe atoms, compound **3** exhibits only one bridging InR group besides eight exclusively terminal CO ligands. These ligands occupy almost eclipsed positions with torsion angles between corresponding CO groups of 9.4° (C(2)Fe(1)Fe(2)C(8)), −2.9°

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(C(3) Fe(1)Fe(2)C(9)) and −11.6° (C(5)Fe(1)Fe(2)C(6)). The Fe−Fe distance of **3** (289.3 pm, Table 3) is longer than that in the triply bridged derivative **4** (275.9 pm, Table 4); three bridging InR groups between two $Fe(CO)_3$ fragments as in $(CO)_3Fe(\mu\text{-InR})_3Fe(CO)_3$ give the longest distance of 299.2 pm.[13] The shorter bond in **4** might be caused by the bridging with the small CO group; the Fe−C bond lengths to the bridging CO ligand are similar to that observed in $Fe_2(CO)_9$ (198.6 pm compared to 201.6 pm[19]), but the Fe−C−Fe angle is enlarged to 88.0° compared to 77.6° in the carbonyl complex. The Fe−In−Fe angles amount to 64.6° on average in **4** and 68.6° in **3**. The Fe−In bond lengths (256.7 pm (**3**) and 258.1 (**4**)) are similar to that in compound **2** and lie in the range normally observed.

The In atoms in both compounds **3** and **4** are almost ideally planar coordinated by the α-carbon atom of the $C(SiMe_3)_3$ group and two iron atoms, and deviate from the planes through these three atoms by only 2.9 pm in **3** (sum of the angles 359.9°) and 1.7 (In(1), sum of the angles 360.0°) and 7.6 pm (In(2), sum of the angles 359.6°) in **4**. The normals of the triangular planes around the Fe−Fe axis Fe(1)Fe(2)In(1), Fe(1)Fe(2)In(2), and Fe(1)Fe(2)C(6) include angles of 65.6, 52.1, and 117.7°, so that a slightly distorted trigonal bipyramidal arrangement of the atoms Fe_2In_2C results. As in compound **2**, the equatorial interatomic distances are, however, very long (In(1)···In(2) 361.7 pm, In(1)···C(6) 326.8 pm, In(2)···C(6) 314.2 pm); they are slightly shorter than the sum of the van der Waals radii (InIn 380 pm, InC 360 pm[20]) and indicate no significant bonding interaction. A shorter In−In distance of 336 pm has been observed in the derivative $(CO)_3Co(\mu\text{-InR})_2Co(CO)_3$ with a distorted tetrahedral Co_2In_2 molecular center,[5] which is only 36 pm longer than in the In_4 starting compound **1**.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for $Fe_3(CO)_{10}[\mu\text{-InC(SiMe}_3)_3]_2$ (**2**), $Fe_2(CO)_8[\mu\text{-InC(SiMe}_3)_3]$ (**3**), and $Fe_2(CO)_6(\mu\text{-CO})[\mu\text{-InC(SiMe}_3)_3]_2$ (**4**) are available on the Internet only. Access information is given on any current masthead page.

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