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Organoindium Transition Metal Complexes. Synthesis and Reactivity. Structures of $[(CO)_4Co]_2In[CH_2Si(CH_3)_3](C_4H_8O)$, $(\eta^5\text{-}C_5H_5)(CO)_nM\text{-}In[(CH_2)_3N(CH_3)_2]_2$ (M = Fe, Ni; n = 2, 1), and $(\mu\text{-}CO)\{\mu\text{-}In[(CH_2)_3N(CH_3)_2]\}[(\eta^5\text{-}C_5H_5)(CO)Fe]_2$[†]

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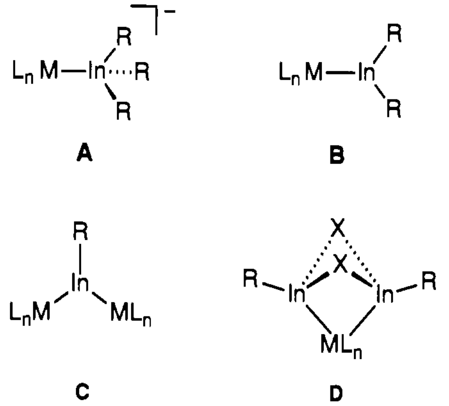
Novel stable and volatile organoindium transition metal complexes of the type $[L(CO)_nM]_a[InR_{3-a}(D)]$ (**1–12**: M = Mo, W, Mn, Re, Fe, Co, Ni; L = η^5-C_5H_5, CO; R = CH_2SiMe_3, $(CH_2)_3NMe_2$; D = O-, N-donor; n = 1–4; a = 1, 2) have been prepared in high yields by the reaction of the alkali metalates $[L(CO)_nM](Na/K)$ with organoindium halides InR_2X (X = Cl, Br), and have been fully characterized by elemental analysis, IR, NMR, and mass spectrometry. The (3-dimethylamino)propyl-substituted alkylindium transition metal complexes are unusually stable toward ligand redistribution equilibria. Depending on the nature of the transition metal fragment, e.g. steric bulk and radical stability, compounds with transition metal to indium ratios of 1:1 and 2:1 are thermodynamically preferred. The transition metal indium bonds in these compounds were shown to be easily cleaved by electrophilic and nucleophilic attack, oxidation and photolysis. Single-crystal data are as follows. $[(CO)_4Co]_2In[CH_2Si(CH_3)_3](C_4H_8O)$, **1**: triclinic, $P\bar{1}$ with a = 932.1(2) pm, b = 1054.2(2) pm, c = 1257.7(3) pm, α = 80.19(2)°, β = 80.55(2)°, γ = 85.05(2)°, $V = 1199 \times 10^6$ pm^3, Z = 2, and R = 0.039 (R_w = 0.025). $[(\eta^5\text{-}C_5H_5)(CO)_n]M\text{-}In[(CH_2)_3N(CH_3)_2]_2$ (**4**, M = Fe, n = 2; **5**, Ni; n = 1): **4**, monoclinic, $P2_1/c$, with a = 1329.1(3) pm, b = 978.4(2) pm, c = 1524.8(3) pm, β = 95.53(1)°, $V = 1974 \times 10^6$ pm^3, Z = 4, and R = 0.032 (R_w = 0.039); **5a** (T = –80 °C), monoclinic, $P2_1/n$ with a = 967.4(5) pm, b = 1507.0(2) pm, c = 1332.0(5) pm, β = 103.69(2)°, $V = 1887 \times 10^6$ pm^3, Z = 4, and R = 0.048 (R_w = 0.030). $(\mu\text{-}CO)\{\mu\text{-}In[(CH_2)_3N(CH_3)_2]\}[(\eta^5\text{-}C_5H_5)(CO)Fe]_2$, **12**: orthorhombic, $Pnma$ with a = 1533.0(2) pm, b = 1253.7(1) pm, c = 1007.2(1) pm, $V = 1936 \times 10^6$ pm^3, Z = 4, and R = 0.041 (R_w = 0.025).

Introduction

Organoindium compounds have been studied extensively,[2] and the continuous interest paid to their chemistry is stimulated in large measure by important applications of these compounds in materials science.[3] Their transition metal substituted derivatives instead have gained only very little attention so far.[2] To the best of our knowledge,[4] prior to this work, only three structurally characterized examples existed, in which organoindium moieties are linked to transition metal fragments by unbridged metal to metal bonds. These compounds are *cis*-$\{[(CH_3)_3Si]_3ClIn(\mu\text{-}Cl)\}_2Fe(CO)_4$ (I),[5] *mer*-$\{[(CH_3)_3P]_3(H)(C_2H_5)Ir\text{-}In(C_2H_5)_2\}$ (II),[6] and *cis*-$\{(Cy_2PCH_2CH_2PCy_2)[(CH_3)_3SiCH_2]Pt\text{-}In[CH_2Si(CH_3)_3]_2\}$ (III; Cy = cyclo-C_6H_{11}).[7] A few other related complexes containing $[R_nIn]$ fragments (n = 1–3; R = CH_3, C_2H_5, t-C_4H_9, $CH_2C(CH_3)_3$, C_6H_5) have been identified spectroscopically.[8,9] The structure typs known for compounds of the general formula $(L_nM)_a[In(X)_mR_l]_b$ (M: transition metal, L: CO, C_5H_5, PR_3 etc., R = alkyl, aryl; $1 \le a, b \le 2$; $0 \le m + l \le 3$) are given in Chart 1.

Chart 1



Type **A** corresponds to Lewis acid/base aducts of $In(C_6H_5)_3$ with transition metal carbonylates, e.g. $[(CO)_4Co\text{-}In(C_6H_5)_3]^-$.[9] Examples of type **B** and **C** are obtained by cophotolysis of InR_3 with $[(C_5H_5)(CO)_3Mo]_2$[8] or by oxidative addition of In–C bonds to unsaturated transition metal centers.[6,7] Type **D** is only known for the $FeIn_2$ complex **I** mentioned above. We were attracted to the organoindium transition metal chemistry since it was recently recognized that heteronuclear organometallics containing certain combinations of transition metals and group 13 metals may serve as "single source" precursors for organometallic chemical vapor

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[†] Part 8 of the series Organo Group 13 Metal Complexes of d-Block Elements. Part 7: See ref 1.

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deposition (OMCVD)[10] of *intermetallic* thin films. However, to be eligible for such an application, an organometallic compound has to meet important requirements[11] including (i) appropriate metal stoichiometry, (ii) volatility (minimum vapor pressure at room temperature around 1–10 Pa), (iii) low heteroatom content in the ligand sphere ("all hydrocarbon precursors"[12]), (iv) facile pyrolysis and controllable deposition chemistry, (v) high purity, (vi) long-term stability, and last but not least (vii) low cost and high-yield synthesis. Most of the reported transition metal indium compounds are oligonuclear or clusters with transition metal to indium ratios greater than one or bearing halides or bulky phosphine ligands.[4] Examples include $[(\eta^5\text{-}C_5H_5)(CO)_mM]_n[In(X)_{3-n}]$ (X = Cl, Br, n = 1, 2; M = Cr, Mo, W, Fe; m = 3, 2),[13] $[(CO)_4Co]InCl_2[P(C_6H_5)_3]$,[14] $Br_3In_3Co_4(CO)_{15}$,[15] and $[Mn_2(CO)_8][\mu\text{-}InMn(CO)_5]_2$.[16] Such features are undesired for OMCVD applications.[10b,12] Still the best chance for OMCVD usefulness might involve type **B** and type **C** compounds of chart 1. Solvent dependent dissociation/association equilibria and ligand redistribution via thermally or photochemically induced homolysis of the transition metal indium bond and/or the indium carbon bond(s) shown in eqs 1–3 contribute to the complex

$$L_nM\text{–}ER_2 \rightleftharpoons [L_nM]^-(\text{solv}) + [ER_2]^+(\text{solv}) \qquad (1)$$

$$2L_nM\text{–}ER_2 \rightleftharpoons ER_3 + [L_nM]_2ER \qquad (2)$$

$$[L_nM]_2ER + L_nM\text{–}ER_2 \rightleftharpoons ER_3 + [L_nM]_3E \qquad (3)$$

chemistry of these compounds. For this reasons attempts to synthesize type **B** and **C** complexes usually gave mixtures which were not amenable to separation.[8]

Most information about these species was therefore gathered by spectroscopic analysis of reaction solutions.[2] Very few organoindium transition metal complexes, namely **I-III**, have been isolated in a pure form. We have thus been led to investigate possibilities to stabilize organoindium fragments at transition metal centers, aiming at sufficiently volatile and stable compounds of type **B** and **C**, which might be suitable for OMCVD of indium containing thin alloy films.[17,18]

Experimental Section

All manipulations were undertaken utilizing standard Schlenk and glovebox techniques under inert gas atmosphere (purified N_2 or argon). Solvents were dried under N_2 by standard methods and stored over molecular sieves (4 Å, Merck; residual water < 3 ppm H_2O, Karl Fischer). Infrared spectra were recorded as thin films (Nujol mull) or solutions between CaF_2 plates with a Nicolet FT-5DX instrument and are reported in reciprocal centimeters. JEOL JNM-GX400 and JNM-GX270 spectrometers were used for NMR spectroscopy. (^1H and ^{13}C NMR spectra were referenced to internal solvent and corrected to TMS). All J values are reported in hertz. All samples for NMR spectra were contained in vacuum-sealed NMR tubes. Mass spectra were recorded using a Varian MAT 311-A instrument (EI spectra) and with a Varian MAT FS-90 instrument (CI spectra; isobutene); m/z values are reported for ^{55}Mn, ^{56}Fe, ^{59}Co, ^{59}Ni, ^{95} Mo, ^{115}In, ^{183}W, and ^{186}Re, and normal isotope distribution was observed. Melting points were observed in sealed capillaries. The starting compounds $BrIn[(CH_2)_3N(CH_3)_2]_2$,[19] $ClIn[CH_2Si(CH_3)_3]_2$,[20] $[^tBu_2InCl]_2$,[21] $K_2[Fe(CO)_4]$,[22] and $(Na/K)[Co(CO)_4]$[23] were prepared as described in the literature. Abbreviations are as follows: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, ^{t}Bu = *tert*-butyl. Elemental analysis were provided by the Microanalytic Laboratory of the Technical University at Munich.

Synthesis of 1. A 1.07-g (3.8 mmol) sample of $Na[Co(CO)_4]\cdot 1.2THF$ was suspended in 50 mL of *n*-pentane at –78 °C. After the addition of 1.20 g (3.8 mmol) of solid $ClIn(CH_2SiMe_3)_2$, the reaction mixture was stirred vigorously and allowed to warm up to room temperature within 1 h. The resulting yellow solution was filtered from the white precipitate and concentrated to a volume of 10 mL. Slow cooling to –78 °C afforded yellow well-shaped crystals of **1** (yield: 920 mg, 79% based upon Co). Mp: 82 °C. ^1H NMR (399.78 MHz, C_6D_6, 25 °C): δ = 0.31 (s, 9 H, CH_3), 0.68 (s, 2 H, $InCH_2$), 1.13 (t, br, 4 H, OCH_2CH_2), 3.42 (t, br, 4 H, CH_2O). ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C.): δ = 2.3 (q, CH_3), 10.5 (t, $InCH_2$), 20.2 (t, OCH_2CH_2), 68.4 (t, CH_2O), 203.2 (s, CoCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 2083 (m), 2067 (vs), 2010 (s), 1997 (vs), 1982 (vs), 1969 (s). Anal. Calcd for $C_{16}H_{19}Co_2InO_9Si$: C, 31.19; H, 3.16; Si, 4.56. Found: C, 30.50; H, 3.32; Si, 4.83.

Synthesis of 4. To 50 mL of a solution of $Na[(\eta^5\text{-}C_5H_5)(CO)_2Fe]$ in tetrahydrofuran, prepared by sodium amalgam reduction of 1.77 g (5.0 mmol) $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$ (freshly recrystallized from *n*-pentane/diethyl ether), 3.67 g (10 mmol) of solid $BrIn[(CH_2)_3NMe_2]_2$ was added. After stirring the reaction mixture at room temperature for 1 h, the solvent was removed in vacuo. The residue was extracted three times with 50 mL of *n*-pentane. The combined pentane solutions were concentrated to a volume of 10 mL. Slow cooling of the solution to –78 °C afforded deep yellow crystals of **4** (yield: 4.50 g, 97% based upon indium). Mp 58 °C; sublimation at 50 °C, (10^{-3} Torr). ^1H NMR (399.75 MHz, toluene-d_8, 25 °C): δ = 0.80 (m; 4 H, $InCH_2$), 1.85 (m; 4 H, NCH_2CH_2), 2.01 (s; 12 H; NCH_3), 2.08 (m; 4 H, NCH_2), 4.31 (s; 5 H, C_5H_5). ^{13}C NMR (100.5 MHz, toluene-d_8, 25 °C): δ = 15.9 (t, br; ^1J(C,H) = 123 Hz, $InCH_2$), 26.0 (t; ^1J(C,H) = 124 Hz, $InCH_2CH_2$), 46.6 (q; ^1J(C,H) = 133 Hz, NCH_3), 64.2 (t; ^1J(C,H) = 131 Hz, NCH_2), 80.1 (d; ^1J(C,H) = 177 Hz, $^nJ(C,H_{ring})$ = 6.9 Hz, C_5H_5), 219.2 (s; FeCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 1958 (sst), 1904 (sst); EI-MS (70 eV): m/z (relative intensity [%]): 464 [M^+] (not observed), 378 (12) [$M^+ - (CH_2)_3N(CH_3)_2$], 322 (3) [$M^+ - 2\ CO - (CH_2)_3N(CH_3)_2$], 287 (89) [$In(CH_2)_3N(CH_3)_2^+$], 236 (5) [$(C_5H_5)FeIn^+$], 202 (34) [$HIn(CH_2)_3N(CH_3)_2^+$], 115 (38) [$In^+$], 86 (27) [$(CH_2)_3N(CH_3)_2^+$], 58 (100) [$H_2CN(CH_3)_2^+$]. Anal. Calcd for $C_{17}H_{29}FeInN_2O_2$: C, 43.99; H, 6.29; N, 6.04; Fe, 12.03; In, 24.74. Found: C, 43.98; H, 6.27; N, 5.86; Fe, 12.37; In, 24.20.

Synthesis of 5. A 2.70-g (20-mmol) sample of potassium graphite, C_8K, was suspended into 100 mL of tetrahydrofuran at –78 °C. At this temperature 3.03 g (10 mmol) of $[(\eta^5\text{-}C_5H_5)(CO)Ni]_2$ (freshly recrystallized from *n*-pentane/diethylether) dissolved into 20 mL of tetrahydrofurane was quickly added in one portion with vigorous stirring. The reaction mixture was allowed to warm up to room temperature within 10 min. After an additional 10 min the the color of the mixture had turned dark brown to black-green. At this point 7.34 g (20 mmol) of solid $BrIn[(CH_2)_3NMe_2]_2$ was added. The color of the mixture immediately changed to deep orange-brown. After stirring the reaction mixture at room temperature for 1 h, the solvent was removed in vacuo. The residue was extracted three times with 50 mL *n*-pentane. The combined pentane solutions were concentrated to a volume of 30 mL. Slow cooling of the solution to –78 °C afforded deep yellow crystals of **5** (yield: 8.64 g, 98% based upon In). Mp: 67 °C; sublimation at 50 °C

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(10^{-3} Torr). ^{1}H NMR (399.78 MHz, toluene-d$_8$, –80 °C): $\delta = 0.50$ (m, br; 4 H, $\mathrm{InCH_2}$), 0.87 (m, br; 4 H, $\mathrm{InCH_2C}H_2$), 1.68 (s, 8 H, $\mathrm{NCH_2}$ and $\mathrm{NCH_3}$ overlapping), 1.83 (s, 8 H, $\mathrm{NCH_2}$ and $\mathrm{NCH_3}$ overlapping), 5.24 (s, 5 H, $\mathrm{C_5H_5}$). ^{13}C{^{1}H} NMR (100.5 MHz, toluene-d$_8$, –80 °C): $\delta =$ 13.2 ($\mathrm{InCH_2}$), 24.7 ($\mathrm{InCH_2}C\mathrm{H_2}$), 46.5 ($\mathrm{NCH_3}$), 46.9 (q, $\mathrm{NCH_3}$), 62.6 ($\mathrm{NCH_2}$), 88.2 ($\mathrm{C_5H_5}$), 194.2 (NiCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 1948 (vs). IR (ν_{CO} cm^{-1}, Nujol mull): 1942 (vs); EI-MS (70 eV) *m/z* (relative intensity [%]): 439 (5) [M$^+$], 352 (2.5) $[\mathrm{M^+ - (CH_2)_3N(CH_3)_2}]$, 287 (41) $[\mathrm{In\{(CH_2)_3N(CH_3)_2\}^+}]$, 202 (15) $[\mathrm{HIn(CH_2)_3N(CH_3)_2^+}]$, 115 (22) [In$^+$], 86 (28) $[\mathrm{(CH_2)_3N(CH_3)_2^+}]$, 58 (100} $[\mathrm{H_2CN(CH_3)_2^+}]$. Anal. Calcd for $\mathrm{C_{16}H_{31}InN_2NiO}$: C, 43.58; H, 7.09; N, 6.35. Found: C, 43.92; H, 7.13; N, 6.15.

Synthesis of 6 and 7. A 1.0-g (2.65-mmol) sample of $\mathrm{Mn_2(CO)_{10}}$ was dissolved into 25 mL of tetrahydrofuran and treated with 20 g of sodium amalgam (1% sodium). After 1 h of vigorous stirring, the nearly colorless, slightly turbid solution was filtered from from the excess amalgam. The solvent was removed from the filtrate in vacuo. The white residue was then suspended in 50 mL of *n*-pentane at room temperature. Then 1.83 g (5.0 mmol) of solid $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$ was added, and the mixture was stirred for 1 h. After this time the colorless solution was filtered from the deposited white residue and concentrated to 10 mL. Slow cooling of the solution to –78 °C afforded colorless to light yellow crystals of **6** (yield: 2.10 g, 87% based upon indium). **7** was prepared analogously from 0.50 g (0.77 mmol) of $\mathrm{Re_2(CO)_{10}}$ and 0.50 g (1.35 mmol) of $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$ (yield: 680 mg, 82% based upon indium).

Characterization Data for 6. Mp: 63 °C. ^{1}H NMR (399.75 MHz, toluene-d$_8$, 25 °C): $\delta = 0.89$ (m, br, 4 H, $\mathrm{InC}H_2$), 1.81 (m, br, 4 H, $\mathrm{InCH_2C}H_2$), 1.99 (s, 12 H, $\mathrm{NCH_3}$), 2.05 (m, br, 4 H, $\mathrm{NCH_2}$). ^{13}C{^{1}H} NMR (100.5 MHz, toluene-d$_8$, 25 °C): $\delta = 17.1$ ($\mathrm{InCH_2}$), 25.4 ($\mathrm{InCH_2}C\mathrm{H_2}$), 46.8 ($\mathrm{NCH_3}$), 63.9 ($\mathrm{NCH_2}$), 202.2 (MnCO). IR ($\nu_{\mathrm{CO}}$ cm^{-1}, *n*-pentane): 2084 (w), 2063 (s), 2046 (w), 2016 (m), 1976 (s), 1961 (vs), 1952 (vs). Anal. Calcd for $\mathrm{C_{15}H_{24}InMnN_2O_5}$: C, 37.37; H, 5.01; N, 5.81; Mn, 11.39; In, 23.82. Found C, 37.48; H, 5.12; N, 5.67; Mn, 11.10; In, 23.40.

Characterization Data for 7. Mp: 78 °C. ^{1}H NMR (399.75 MHz, toluene-d$_8$, 25 °C): $\delta = 0.92$ (m, br, 4 H, $\mathrm{InC}H_2$), 1.86 (m, br, 4 H, $\mathrm{InCH_2C}H_2$), 2.05 (s, 12 H, $\mathrm{NCH_3}$), 2.15 (m, br, 4 H, $\mathrm{NCH_2}$). ^{13}C NMR (100.5 MHz, toluene-d$_8$, 25 °C): $\delta = 17.7$ (t, $\mathrm{InCH_2}$), 26.1 (t, $\mathrm{InCH_2}C\mathrm{H_2}$), 47.1 (q, $\mathrm{NCH_3}$), 64.5 (t, $\mathrm{NCH_2}$), 197.5 (s, ReCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 2099 (w), 2083 (s), 2034 (w), 2017 (m), 1976 (s), 1970 (vs), 1940 (w), 1921 (s). Anal. Calcd for $\mathrm{C_{15}H_{24}InN_2O_5Re}$: C, 29.37; H, 5.01; N, 3.94; Re, 30.35; In, 18.72. Found: C, 28.98; H, 5.12; N, 3.87; Re, 31.10; In, 18.40.

Synthesis of 8. A 2.10-g (10.0-mmol) sample of $\mathrm{K[Co(CO)_4]}$ was suspended in 100 mL of *n*-pentane and the mixture cooled to –78 °C. Then 3.67 g (10.0 mmol) of solid $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$ was added, and the stirred reaction mixture was allowed to warm up to room temperature within 1 h. The nearly colorless solution was filtered from the deposited white precipitate (1.12 g, 94 based upon KBr), and the solvent was removed in vacuo at 0 °C. The resulting colorless oil (4.50 g, 98% yield) proved to be analytically pure. Colorless crystals of **8** could be grown from concentrated *n*-pentane/toluene solutions at –78 °C over several weeks. Mp: 28 °C; sublimation at 20 °C (10^{-3} Torr). ^{1}H NMR (399.75 MHz, toluene-d$_8$, 25 °C): $\delta = 0.95$ (t; 4 H, *J* (H, H) = 7 Hz, $\mathrm{InCH_2}$), 1.69 (quin; 4 H, *J*(H,H) = 6.3 Hz, $\mathrm{NCH_2C}H_2$), 1.89 (s; 12 H; $\mathrm{NCH_3}$), 1.93 (m; 4 H, $\mathrm{NCH_2}$). ^{13}C NMR (100.5 MHz, toluene-d$_8$, 25 °C): $\delta = 17.8$ (t, br; ^1J(C,H) = 130 Hz, $\mathrm{InCH_2}$), 24.5 (t, ^1J(C,H) = 125 Hz, $\mathrm{InCH_2}C\mathrm{H_2}$), 46.1 (q, ^1J(C,H) = 131 Hz, $\mathrm{NCH_3}$), 63.1 (t, ^1J(C,H) = 133 Hz, $\mathrm{NCH_2}$); 207.1 (s, CoCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 2056 (vs), 1986 (vs), 1956 (sh), 1945 (vs); CI-MS (isobutene): *m/z* (relative intensity [%]): 457 (62) [M$^+$ – H], 171 (100) $[\mathrm{(CO)_4Co^+}]$. Anal. Calcd for $\mathrm{C_{14}H_{24}CoInN_2O_4}$: C, 36.70; H, 5.28; N, 6.12; Co, 12.86; In, 25.06. Found: C, 35.78; H, 5.10; N, 6.23; Co, 12.40; In, 25.30.

Synthesis of 9. To a solution of 320 mg (1.3 mmol) of $\mathrm{K_2[Fe(CO)_4]}$ in 25 mL of tetrahydrofuran was added 950 mg (2.6 mmol) of solid $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$. After this mixture was stirred at room temperature for 10 min, the solvent was removed in vacuo and the residue was suspended into 20 mL of toluene. After the mixture was stirred for 2 h, the yellow solution was filtered from the deposited white precipitate. All volatile constituents were then removed in vacuo. The obtained yellow residue was dissolved in the minimum amount of a 1:1 mixture of *o*-xylene/benzene (3 mL) and carefully layered with 10 mL of *n*-pentane. Large yellow crystals of **9** grew within 12 h (yield: 365 mg, 76%, based upon iron). Mp: 85 °C. **9** presumably consists of a 2:3 mixture of two isomers, **9a** and **9b**. ^{1}H NMR (399.75 MHz, toluene-d$_8$, 25 °C): $\delta = 1.41$ (t; 2 H, *J*(H,H) = 7 Hz, $\mathrm{InCH_2}$; **9a**), 1.53 (t; 2 H, *J*(H,H) = 7 Hz, $\mathrm{InCH_2}$; **9b**), 1.66 (m; $\mathrm{NCH_2C}H_2$; **9a** and **9b** overlapping), 1.95–2.02 (m; 2 H, $\mathrm{NCH_2}$; **9b**), 2.09 (m, 2 H, $\mathrm{NCH_2}$, **9a**), 2.17 (s, 6 H; $\mathrm{NCH_3}$; **9b**), 2.30 (s; 6 H, $\mathrm{NCH_3}$; **9a**). ^{13}C NMR (100.5 MHz, toluene-d$_8$, 25 °C): $\delta = 18.9$ (t, br; ^1J(C,H) = 131 Hz, $\mathrm{InCH_2}$; **9b**), 19.1 (t, br; ^1J(C,H) = 130 Hz, $\mathrm{InCH_2}$; **9a**), 24.4 (t, ^1J(C,H) = 125 Hz, $\mathrm{InCH_2}C\mathrm{H_2}$, **9a** and **9b** overlapping), 47.1 (q, ^1J(C,H) = 132 Hz, $\mathrm{NCH_3}$; **9b**), 48.0 (q, ^1J(C,H) = 132 Hz, $\mathrm{NCH_3}$; **9a**), 65.2 (t, ^1J(C,H) = 133 Hz, $\mathrm{NCH_2}$; **9a** and **9b** overlapping), 212.6 (s, br, FeCO; the expected five different resonances for the $\mathrm{CO_{eq}}$ and $\mathrm{CO_{ax}}$ groups in **9a** and **9b** could not be fully resolved). IR (ν_{CO} cm^{-1}, toluene): 2005 (vs), 1953 (vs), 1932 (vs), 1945 (vs). Anal. Calcd for $\mathrm{C_{18}H_{24}Fe_2In_2N_2O_8}$: C, 29.31; H, 3.27; N, 3.79; O, 17.35; Fe, 15.14; In, 31.13. Found: C, 29.24; H, 3.31; N, 3.80; O, 17.69; Fe, 15.08; In, 30.50.

Synthesis of 10 and 11. To 20 mL of a solution of $\mathrm{Na[(\eta^5\text{-}C_5H_5)(CO)_3Mo]}$ in tetrahydrofuran prepared by sodium amalgam reduction of 1.05 g (2.15 mmol) of $\mathrm{[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2}$ was 1.47 g (4,0 mmol) of solid $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$. The solution was heated to reflux and stirred for 5 h. After this time, the mixture was allowed to cool to room temperature and the solvent was removed in vacuo. The off-white residue was suspended into 30 mL of toluene and heated to 80 °C with stirring for a period of 12 h. Then, the solution was filtered from the deposited white residue and brought to dryness in vacuo. The obatined residue was dissolved into the minimum amount of a 1:1 mixture of *o*-xylene/benzene (5 mL), that was carefully layered with 20 mL of *n*-pentane. Over 12 h small, well-shaped yellow crystals of **10** grew at the wall of the Schlenk tube (yield: 890 mg, 65% based upon indium). **11** was prepared analogously from 665 mg (1.0 mmol) of $\mathrm{[(\eta^5\text{-}C_5H_5)(CO)_3W]_2}$ and 650 mg (1.8 mmol) of $\mathrm{BrIn[(CH_2)_3NMe_2]_2}$ (yield: 540 mg, 70% based upon In).

Characterization Data for 10. Mp: >250 °C; sublimation at 180 °C (10^{-3} Torr). ^{1}H NMR (270.2 MHz, toluene-d$_8$, 25 °C): $\delta = 1.41$ (t; 2 H, ^3J(H,H) = 7.3 Hz, $\mathrm{InCH_2}$), 2.06 (quint.; 2 H, ^3J(H,H) = 7.3, $\mathrm{NCH_2C}H_2$), 2.18 (s; 6 H; $\mathrm{NCH_3}$), 2.29 (m; 2 H, $\mathrm{NCH_2}$), 4.91 (s; 10 H, $\mathrm{C_5H_5}$). ^{13}C NMR (100.5 MHz, toluene-d$_8$, 25 °C): $\delta = 24.5$ (t, br; ^1J(C,H) = 125 Hz, $\mathrm{InCH_2}$), 25.8 (t; ^1J(C,H) = 124 Hz, $\mathrm{InCH_2}C\mathrm{H_2}$), 47.3 (q; ^1J(C,H) = 132 Hz, $\mathrm{NCH_3}$), 64.9 (t; ^1J(C,H) = 131 Hz, $\mathrm{NCH_2}$), 89.8 (d; ^1J(C,H) = 178 Hz, $^nJ(\mathrm{C,H_{ring}})$ = 7 Hz, $\mathrm{C_5H_5}$), 229.2 (s; MoCO). IR (ν_{CO} cm^{-1}, *n*-pentane): 1971 (vs), 1889 (s), 1858 (vs). IR (ν_{CO} cm^{-1}, toluene): 1961 (vs), 1879 (s), 1850 (vs); IR (ν_{CO} cm^{-1}, THF): 1962 (vs), 1880 (s), 1852 (vs). EI-MS (70 eV): *m/z* (relative intensity [%]): 693 [M$^+$] (not observed), 607 (1) $[\mathrm{M^+ - (CH_2)_3N(CH_3)_2}]$, 551 (1) $[\mathrm{M^+ - 2\,CO - (CH_2)_3N(CH_3)_2}]$, 495 (0.5) $[\mathrm{M^+ - 4\,CO - (CH_2)_3N(CH_3)_2}]$ 439 (1) $[\mathrm{M^+ - 6\,CO - (CH_2)_3N(CH_3)_2}]$, 448 (10) $[\mathrm{M^+ - \{(\eta^5\text{-}C_5H_5)(CO)_3Mo\}}]$, 246 (10) $[\mathrm{(\eta^5\text{-}C_5H_5)(CO)_3Mo^+}]$, 202 (18) $[\mathrm{HIn(CH_2)_3N(CH_3)_2^+}]$, 115 (100) [In$^+$], 86 (40) $[\mathrm{(CH_2)_3N(CH_3)_2^+}]$, 58 (100} $[\mathrm{H_2CN(CH_3)_2^+}]$. Anal. Calcd for $\mathrm{C_{21}H_{22}Mo_2InNO_6}$: C, 36.50; H, 3.21; N, 2.03; O, 13.89; Mo, 27.76; In, 16.61. Found: C, 36.54; H, 3.27; N, 2.04; O, 14.04; Mo, 28.14; In, 16.25.

Characterization Data for 11. Mp >250 °C; sublimation at 220 °C, (10^{-3} Torr). ^{1}H NMR (270.2 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta = 1.47$ (t; 2 H, ^3J(H,H) = 7.1 Hz, $\mathrm{InCH_2}$), 2.08 (quint.; 2 H, ^3J(H,H) = 7.1, $\mathrm{NCH_2C}H_2$), 2.19 (s; 6 H; $\mathrm{NCH_3}$), 2.29 (m; 2 H, $\mathrm{NCH_2}$), 4.86 (s; 10 H, $\mathrm{C_5H_5}$). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta = 21.3$ (t, br; ^1J(C,H) = 126 Hz, $\mathrm{InCH_2}$), 26.1 (t; ^1J(C,H) = 125 Hz, $\mathrm{InCH_2}C\mathrm{H_2}$), 47.6 (q; ^1J(C,H) = 133 Hz, $\mathrm{NCH_3}$), 65.2 (t; ^1J(C,H) = 131 Hz, $\mathrm{NCH_2}$), 88.4 (d; ^1J(C,H) = 176 Hz, $^nJ(\mathrm{C,_{ring}})$ = 7 Hz, $\mathrm{C_5H_5}$), 218.9 (s; WCO; ^{183}W satellites not observed). IR (ν_{CO} cm^{-1}, *n*-pentane): 1968 (vs), 1883 (s), 1854 (vs). IR (ν_{CO} cm^{-1}, $\mathrm{CH_2Cl_2}$): 1960 (vs), 1883 (vs), 1842 (s); IR (ν_{CO} cm^{-1}, THF): 1961 (vs), 1881 (s), 1852 (vs). EI-MS (70 eV): m/z (relative intensity [%]): 866 (0.3) [M$^+$] (correct isotope pattern), 781 (0.8) $[\mathrm{M^+ - (CH_2)_3N(CH_3)_2}]$, 725 (0.3) $[\mathrm{M^+ - 2CO - (CH_2)_3N(CH_3)_2}]$, 613 (0.5) $[\mathrm{M^+ - 6CO - (CH_2)_3N(CH_3)_2}]$, 534 (12) $[\mathrm{M^+ - \{(\eta^5\text{-}C_5H_5)(CO)_3W\}}]$, 333 (8) $[\mathrm{(\eta^5\text{-}C_5H_5)(CO)_3W^+}]$, 202 (20) $[\mathrm{HIn(CH_2)_3N(CH_3)_2^+}]$, 115 (100) [In$^+$], 86 (38) $[\mathrm{(CH_2)_3N(CH_3)_2^+}]$, 58 (100} $[\mathrm{H_2CN(CH_3)_2^+}]$. Anal. Calcd for $\mathrm{C_{21}H_{22}InNO_6W_2}$: C, 29.09; H, 2.56; N, 1.62; O, 11.07; W, 42.41; In, 13.24. Found: C, 29.04; H, 2.63; N, 1.69; O, 11.50; W, 41.83; In, 12.90.

Reaction of 4 with Electrophiles/Nucleophiles. To a solution of 200 mg (0.43 mmol) of **4** in toluene or tetrahydrofuran were added the stoichiometric amounts of electrophiles or nucloeophiles such as MeI, $\mathrm{Me_3SnCl}$, $\mathrm{HgBr_2}$, $\mathrm{(C_6H_5)_2PCl}$, $\mathrm{CF_3COOH}$, [PPN]Cl, $\mathrm{I_2}$, etc. at room temperature with stirring. After 30 min the reactions proved to be quantitative in every case (IR spectroscopy). The products, namely $\mathrm{[(\eta^5\text{-}C_5H_5)(CO)_2Fe–X]}$ (X = H, I, $\mathrm{Me_3Sn}$, HgBr, $\mathrm{(C_6H_5)_2P}$), $\mathrm{[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2}$, and $\mathrm{Y–In[(CH)_2NMe_3]_2}$ (Y = I, Br, Cl, $\mathrm{CF_3COO}$), were identified by their comparison of their IR and NMR spectra with literature values and/or authentic samples.

Table 1. Crystallographic and Data Collection Parameters

	1	**4**	**5a**	**5b**	**12**
formula	$C_{16}H_{19}Co_2InO_9Si$	$C_{17}H_{29}FeInN_2O_2$	$C_{16}H_{29}InN_2NiO$	$C_{16}H_{29}InN_2NiO$	$C_{18}H_{22}Fe_2InNO_3$
fw	616.1	464.1	438.9	438.9	526.9
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
λ, pm	71.073	71.073	71.073	71.073	71.073
a, pm	932.1(2)	1329.1(3)	967.4(5)	963.4(6)	1533.0(2)
b, pm	1054.2(2)	978.4(2)	1507.0(2)	1501.8(2)	1253.7(1)
c, pm	1257.7(3)	1524.8(3)	1332.0(5)	1331.8(5)	1007.2(1)
α, deg	80.19(2)				
β, deg	80.55(2)	95.53(1)	103.69(2)	103.90(2)	
γ, deg	85.05(2)				
V, 10^6 pm^3	1199	1974	1887	1870	1936
Z	2	4	4	4	4
ρ_{calc} g cm^{-3}	1.706	1.562	1.545	1.559	1.808
μ (Mo Kα), cm^{-1}	23.9	18.9	22.1	22.1	26.6
transm range, %	87.9–100.0		92.1–100.0	91.5–100.0	84.4–100.0
no. of reflns	4477	3871	3602	3568	3905
no. of obsd reflns	3804	2800	3025	3040	1677
cutoff	$I > 0.01$	$I > 3.0^*\sigma(I)$	$I > 0.01$	$I > 0.01$	$I > 0.01$
R^a	0.039	0.032	0.048	0.050	0.041
$R_w{}^b$	0.025	0.039	0.030	0.035	0.025

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of **1**

atom	*x/a*	*y/a*	*z/a*	$B_{eq}{}^a$ Å^2
In	0.22160(3)	0.23654(2)	0.22297(2)	2.619(5)
Co1	0.38090(5)	0.20822(5)	0.03380(4)	3.31(1)
Co2	0.01608(5)	0.42392(5)	0.22241(4)	3.09(1)
Si	0.4171(1)	0.2903(1)	0.4209(1)	4.18(3)
O11	0.3345(3)	0.4869(3)	−0.0265(3)	5.6(1)
O12	0.1568(3)	0.0419(3)	0.0138(3)	7.4(1)
O13	0.5462(4)	0.1778(3)	−0.1793(3)	7.6(1)
O14	0.6049(3)	0.1057(4)	0.1685(3)	7.4(1)
O21	−0.2092(3)	0.6358(3)	0.2198(2)	4.7(1)
O22	0.2589(3)	0.5901(3)	0.1934(3)	6.5(1)
O23	−0.0446(3)	0.2346(3)	0.0326(2)	4.9(1)
O24	−0.0780(3)	0.2835(3)	0.4401(2)	6.3(1)
O41	0.0687(3)	0.0649(2)	0.2624(2)	3.5(1)
C2	0.3179(4)	0.1740(4)	0.3703(3)	3.7(1)
C11	0.3500(4)	0.3878(4)	0.0016(3)	4.1(1)
C12	0.2405(4)	0.1094(4)	0.0259(3)	4.5(1)
C13	0.4851(5)	0.1887(4)	−0.0962(4)	5.0(1)
C14	0.5139(4)	0.1476(4)	0.1182(3)	4.6(1)
C21	−0.1227(4)	0.5530(4)	0.2210(3)	3.6(1)
C22	0.1671(5)	0.5212(4)	0.2050(3)	4.3(1)
C23	−0.0182(4)	0.3608(4)	0.1074(3)	3.6(1)
C24	−0.0386(4)	0.3367(4)	0.3552(3)	4.1(1)
C30	0.5459(5)	0.3778(4)	0.3085(4)	5.6(1)
C31	0.5263(5)	0.2026(5)	0.5271(4)	7.5(1)
C32	0.2840(6)	0.4107(5)	0.4816(4)	6.5(1)
C42	−0.0796(4)	0.0582(4)	0.2413(4)	4.3(1)
C43	−0.1212(5)	−0.0752(4)	0.2885(4)	6.2(1)
C44	0.0189(5)	−0.1530(4)	0.2899(5)	6.4(1)
C45	0.1212(5)	0.0625(4)	0.3099(4)	5.5(1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Photolysis of 4 and Synthesis of 12. A 230-mg (0.50-mmol) sample of **4** was dissolved in 0.5 mL of toluene-d_8 (c = 1.0 mmol/mL) in a quartz NMR tube that was sealed under vacuum. At 15 °C, the yellow solution was irradiated with a water-cooled high-pressure mercury lamp (150 W) for a period of 15 min. After this time the solution had turned black-green. From this solution large black crystals grew within 2 days in the dark at 0 °C. The supernatant solution was then decanted off and the crystals were washed with *n*-pentane (yield: 67 mg, 52%). ^1H NMR (399.5 MHz, C_6D_6, 25 °C): δ = 1.11 (t; 2 H, $^3J(H,H)$ = 7 Hz, $InCH_2$), 1.92 (quint.; 2 H, $^3J(H,H)$ = 7 Hz, NCH_2CH_2), 1,97 (t; 2 H, $^3J(H,H)$ = 7 Hz, NCH_2), 2.11 (s; 6 H, NCH_3), 4.17 (s; 10 H, C_5H_5). ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): δ = 21.9 (t, br; $^1J(C,H)$ = 127 Hz, $InCH_2$), 22.3 (t; $^1J(C,H)$ = 124 Hz, $InCH_2CH_2$), 43.4 (q; $^1J(C,H)$ = 134 Hz, NCH_3), 62.3 (t; $^1J(C,H)$ = 132 Hz, NCH_2), 77.5 (d; $^1J(C,H)$ = 177 Hz, $^nJ(C,H_{ring})$ = 7 Hz, C_5H_5), (the carbonyl C resonances could not be detected). IR (ν_{CO} cm^{-1}, C_6D_6): 1924 (vs), 1885 (m), 1738 (s). IR (ν_{CO} cm^{-1}, CH_2Cl_2): 1920 (vs), 1883 (m), 1735 (s). Anal. Calcd for $C_{21}H_{22}Fe_2InNO_3$: C, 41.03; H, 4.21; N, 2.66. Found: C, 41.08; H, 4.31; N, 2.72.

X-ray Structure Determinations. Crystals of compounds **1**, **4**, **5**, and **12** were grown by standard cooling techniques at low temperature. Preliminary examination and data collection were carried out on an Enraf-Nonius CAD4 diffractometer. Final cell constants were obtained by least-squares refinements of 25 automatically centered high angle reflections. During data collection orientation control reflections were monitored every 200th, and the intensity of three reflections were checked every 3600 s. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 1. The reflection data were corrected for Lorentz and polarization factors. If necessary, corrections for decay, absorption, and/or extinction were applied. Anisotropic temperature parameters were applied for all non-hydrogen atoms excluding disordered atoms. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(|F_o| - |F_c|)^2$. All calculations were performed on a Micro VAX 3100 computer with the STRUX-IV system[24] including the programs CRYSTALS, MULTAN 11/82, ORTEP-II, PLATON, PLUTON, SCHAKAL, SDP, and SHELX-86.

$[(CO)_4Co]_2In[CH_2Si(CH_3)_3](C_4H_8O)$ (1). The complex crystallizes as well-shaped yellow prisms. The structure was solved by heavy-atom methods and subsequent difference Fourier maps. Final positional parameters are given in Table 2, with selected bond angles and distances in Table 3. Hydrogen atoms were included at their calculated positions (d_{C-H} 95 pm) but not refined. Anomalous dispersion is considered. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features.

$(\eta^5-C_5H_5)(CO)_2Fe-In[(CH_2)_3N(CH_3)_2]_2$ (4). The complex crystallizes as well-shaped deep yellow prisms. The structure was solved by heavy-atom methods and subsequent difference Fourier maps. Final positional parameters are given in Table 4, with selected bond angles and distances in Table 5. Hydrogen atoms were included at their calculated positions (d_{C-H} 95 pm) but not refined. Anomalous dispersion is considered. Disorder occured at the Cp position C11–C15. Two split positions with occupation factors of 0.62 and 0.38, respectively, could be refined. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features.

$(\eta^5-C_5H_5)(CO)Ni-In[(CH_2)_3N(CH_3)_2]_2$ (5). The complex crystallizes as well- shaped deep yellow needles. For obvious reasons (see comments and discussion below) the data set was measured twice at different temperatures. The structure was solved by heavy-atom methods and subsequent difference Fourier maps. Final positional parameters are given in Table 6 with selected bond angles and distances in Table 7. Hydrogen atoms were included at their calculated positions (d_{C-H} 95

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(24) Scherer, W.; Kiprof, P.; Herdtweck, E.; Schmidt, R. E.; Birkhahn, M.; Massa, W. STRUX-IV , ein Programmsystem zur Verarbeitung von Röntgendaten, TU Munich and University of Marburg, Germany (1985/1990).

Table 3. Selected Interatomic Distances (pm) and Angles (deg) for Compound **1**

	Distances		
In–Co1	263.83(4)	In–C2	216.8(3)
In–Co2	263.03(4)	Si–C2	184.9(3)
In–O41	233.9(2)		
	Angles		
Co1–In–Co2	117.17(1)	In–Co2–C22	82.5(1)
Co1–In–O41	104.7(1)	In–Co2–C23	81.8(1)
Co1–In–C2	118.3(1)	In–Co2–C24	80.8(1)
Co2–In–O41	97.3(1)	In–Co2–C21	179.3(1)
Co2–In–C2	118.6(1)		
O41–In–C2	92.4(1)		
		In–C2–Si	118.8(1)
In–Co1–C11	84.4(1)		
In–Co1–C12	82.8(1)		
In–Co1–C14	82.3(1)		
In–Co1–C13	178.6(1)		

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of **4**

atom	x/a	y/a	z/a	U_{eq}[a] Å^2
In	0.22180(3)	0.18584(4)	0.12028(3)	0.0336
Fe	0.37867(6)	0.33114(9)	0.08107(5)	0.0369
O1	0.3691(4)	0.1691(6)	–0.0778(3)	0.0690
O2	0.2374(4)	0.5179(5)	–0.0116(4)	0.0743
N3	0.2706(4)	–0.0612(5)	0.0684(4)	0.0527
N4	0.1040(4)	0.3750(6)	0.1927(4)	0.0549
C1	0.3721(4)	0.2305(7)	–0.0128(4)	0.0431
C2	0.2897(5)	0.4420(7)	0.0271(4)	0.0468
C11	0.411(1)	0.352(2)	0.217(1)	0.039
C12	0.430(2)	0.476(2)	0.177(1)	0.048
C13	0.510(1)	0.446(2)	0.121(1)	0.037
C14	0.533(2)	0.316(3)	0.120(2)	0.061
C15	0.472(2)	0.245(2)	0.183(1)	0.050
C21	0.441(1)	0.276(1)	0.211(1)	0.039
C22	0.420(1)	0.417(2)	0.206(1)	0.064
C23	0.482(1)	0.475(2)	0.142(1)	0.058
C24	0.536(1)	0.370(2)	0.108(1)	0.051
C25	0.512(1)	0.244(1)	0.149(1)	0.041
C31	0.221(1)	0.063(1)	0.242(1)	0.065
C32	0.252(1)	–0.086(1)	0.227(1)	0.077
C33	0.220(1)	–0.137(1)	0.134(1)	0.076
C34	0.223(1)	–0.098(1)	–0.022(1)	0.075
C35	0.377(1)	–0.093(1)	0.075(1)	0.070
C41	0.084(1)	0.195(1)	0.028(1)	0.053
C42	0.017(1)	0.310(1)	0.048(1)	0.081
C43	0.011(1)	0.348(1)	0.134(1)	0.112
C44	0.136(1)	0.514(1)	0.189(1)	0.149
C45	0.085(1)	0.344(1)	0.283(1)	0.084

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

pm) but not refined. Anomalous dispersion is considered. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features.

$(\mu\text{-CO})\{\mu\text{-In}[(CH_2)_3N(CH_3)_2]\}[(\eta^5\text{-}C_5H_5)(CO)Fe]_2$ (12). The complex crystallizes as well shaped dark brown plates. The structure were solved by heavy-atom methods and subsequent difference Fourier maps. Final positional parameters are given in Table 8, with selected bond angles and distances in Table 9. Hydrogen atoms were included at their calculated positions (d_{C-H} 95 pm) but not refined. Disorder occurred at the Cp-position C10–C14. Two split positions, with occupation factors 0.58 and 0.42, respectively, could be refined. With respect to the crystallographic mirror plane through O1, C1, In, C3, C4, and N the atoms C5, C6, and C7 are disorderd too. (A refinement of the data set in the acentric space group *Pna*2$_1$ did not resolve the disorder problems satisfactorily. Anomalous dispersion is considered. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features.

Results and Discussion

A. Synthesis and Properties. One of the more general methods to obtain metal to metal bonds involves salt elimination in the course of *formal* nucleophilic substitution reactions.[25] Whereas this principle has been widely used in transition metal indium chemistry, the synthesis of the known organoindium transition metal derivatives followed distinctly different routes, already mentioned in the introduction. The only exception is compound **I**, which was derived from $Na_2[Fe(CO)_4]$ and $\{Li(THF)_3(\mu\text{-Cl})InCl_2[C(SiMe_3)_3]\}$. Following this route, a suspension of $[(CO)_4Co]Na(THF)$ in *n*-pentane was treated with an equimolar amount of $\{[Me_3SiCH_2]_2InCl\}_2$ (scheme 1).

Table 5. Selected Interatomic Distances (pm) and Angles (deg) for Compound **4**

	Distances		
In–Fe	263.9(1)	Fe–C1	173.3(7)
In–N3	264.3(5)	Fe–C2	175.0(7)
In–N4	272.6(5)	O1–C1	115.7(7)
In–C31	220.7(6)	O2–C2	114.2(8)
In–C41	219.5(6)	Fe–Cp[a]	170.9
In···O1	376	In···C1	301
In···O2	384	In···C2	306
	Angles		
Fe–In–N3	101.7(1)	In–Fe–C1	84.4(2)
Fe–In–N4	102.9(2)	In–Fe–C2	85.9(2)
Fe–In–C31	123.6(2)	C1–Fe–C2	89.2(3)
Fe–In–C41	117.4(2)	In–Fe–Cp	118.2
N3–In–N4	155.4(2)		
C31–In–C41	119.0(3)	O1–C1–Fe	175.8(4)
N3–In–C31	77.0(2)	O2–C2–Fe	176.0(4)
N3–In–C41	93.3(2)		
N4–In–C31	88.8(2)		
N4–In–C41	75.9(2)		
	Torsion Angles		
Cp–Fe–In–N3	–98.8	Cp–Fe–In–N4	80.5

[a] Cp denotes the center of the cyclopentadienyl ligand C11–C15.

Within minutes an intense lemon yellow solution over a white precipitate formed. The trinuclear Co_2In complex **1** was isolated upon crystallization in 85% yield. $(Me_3SiCH_2)_3In$ was formed as a byproduct. At room temperature, the ^{1}H-NMR spectra of the filtered reaction mixture (benzene-d_6) revealed broadened signals for the different ((trimethylsilyl)methyl)indium species, indicating alkyl exchange processes under these conditions. The course of this reaction follows eq 2. $\{[Me_3SiCH_2]_2InCl\}_2$ is known to exhibit apparently no acidic properies, e.g. it does not form a THF adduct.[20] It is interesting to note that the very weak nucleophile $[Co(CO)_4^-]$ can break up the dimeric structure of this organoindium halide. However, this ability strongly depends on the reaction conditions. In tetrahydrofuran or acetonitrile as coordinating solvents, no reaction occurred. This was indicated by the single IR absorption at 1888 cm^{-1} of the reaction solution corresponding to unchanged cobalt nucleophile. However, in pentane or toluene as reaction media, where tetracarbonylcobaltate is insoluble, the addition of a donor ligand, e.g. THF, proved to be necessary to get reactivity. When solvent-free $[(CO)_4Co]K$ was used instead of $[(CO)_4Co]Na(THF)$, a yellow precipitate formed, but most of the dialkylindium chloride was left unchanged in solution. Pentane-soluble CoIn species could not be detected by IR spectroscopy. After addition of exactly 1 equiv of THF to this system, rapid formation of **1** took place. In the case of sterically less demanding alkyl substituents at the indium center, e.g. $[^tBu_2InCl]_2$, the tetranuclear complex **3**[26] was the only isolable CoIn compound besides *t*-Bu_3In. The treatment of a toluene solution of $\{[Me_3SiCH_2]_2InCl\}_2$ with 1 equiv of $Me_2NCH_2CH_2NMe_2$ (TMEDA) followed by addition of a stoichiometric amount of tetracarbonylcobaltate gave a pale yellow solution over a white precipitate. The IR pattern of the reaction

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Table 6. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of **5**

atom	x/a	y/a	z/a	B_{eq}[a] Å^2
		Compound **5a**		
In	0.37793(4)	0.17099(2)	0.16790(3)	2.540(6)
Ni	0.55280(7)	0.10766(4)	0.33089(5)	2.98(1)
O	0.4707(6)	0.2680(3)	0.4113(3)	9.3(2)
N1	0.1617(5)	0.0864(3)	0.1970(3)	4.6(1)
N2	0.5590(5)	0.2682(3)	0.1140(4)	5.0(1)
C	0.5032(7)	0.2025(4)	0.3750(4)	5.0(2)
C1	0.2329(7)	0.2788(4)	0.1796(4)	5.1(2)
C2	0.1020(7)	0.2401(5)	0.2187(5)	7.4(2)
C3	0.0538(7)	0.5129(5)	0.1707(5)	8.2(2)
C4	0.1780(6)	0.0576(4)	0.3054(4)	5.1(2)
C5	0.1261(8)	0.0096(5)	0.1271(5)	8.8(2)
C6	0.3831(7)	0.1075(4)	0.0224(4)	5.8(2)
C7	0.4843(9)	0.1660(5)	−0.0310(4)	9.2(2)
C8	0.5998(9)	0.2144(5)	0.0415(6)	11.0(2)
C9	0.4928(7)	0.3512(4)	0.0777(6)	9.2(2)
C10	0.6923(8)	0.2850(6)	0.1906(6)	10.9(3)
C11	0.5675(6)	−0.0270(3)	0.3814(4)	3.9(1)
C12	0.5406(6)	−0.0229(3)	0.2754(4)	4.1(1)
C13	0.6552(6)	0.0214(4)	0.2487(4)	4.3(1)
C14	0.7530(6)	0.0453(4)	0.3394(4)	4.0(1)
C15	0.6970(6)	0.0165(4)	0.4220(4)	4.0(1)
		Compound **5b**		
In	0.37743(5)	0.17214(3)	0.16781(3)	2.162(7)
Ni	0.55348(8)	0.10878(5)	0.33123(5)	2.53(2)
O	0.4746(6)	0.2710(3)	0.4108(3)	7.6(2)
N1	0.1604(5)	0.0888(4)	0.1978(4)	4.0(1)
N2	0.5592(6)	0.2686(4)	0.1139(4)	4.2(1)
C	0.5072(7)	0.2050(4)	0.3754(4)	4.2(2)
C1	0.2336(7)	0.2816(5)	0.1804(5)	4.4(2)
C2	0.1040(8)	0.2436(5)	0.2217(6)	6.5(2)
C3	0.0515(7)	0.1571(5)	0.1744(6)	6.9(2)
C4	0.1788(7)	0.0587(4)	0.3065(4)	4.1(2)
C5	0.1211(9)	0.0121(6)	0.1274(6)	7.9(2)
C6	0.3825(8)	0.1069(5)	0.0222(5)	4.9(2)
C7	0.4811(10)	0.1659(6)	−0.0323(5)	7.9(2)
C8	0.6014(9)	0.2117(5)	0.0413(6)	7.2(2)
C9	0.4906(8)	0.3508(5)	0.0730(6)	7.1(2)
C10	0.6917(8)	0.2882(6)	0.1917(7)	8.8(3)
C11	0.5662(7)	−0.0269(4)	0.3819(4)	3.2(1)
C12	0.5379(7)	−0.0219(4)	0.2751(4)	3.4(1)
C13	0.6549(7)	0.0210(4)	0.2491(4)	3.5(1)
C14	0.7542(6)	0.0448(4)	0.3405(4)	3.3(1)
C15	0.6960(6)	0.0163(4)	0.4228(4)	3.2(1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)$.

Table 7. Selected Interatomic Distances (pm) and Angles (deg) for Compound **5**

	5a	**5b**
	Distances	
In–Ni	259.8(1)	259.7(1)
In–N1	255.7(3)	254.9(3)
In–N2	251.5(3)	250.7(3)
In–C1	217.7(3)	218.1(4)
In–C6	217.3(4)	218.3(3)
Ni–C	165.9(4)	166.1(4)
Ni–Cp[a]	174.9	175.0
C–O	117.4(4)	117.2(4)
In···O	347.5	347.8
In···C	277.8	279.1
	Angles	
Ni–In–N1	94.9(1)	94.8(1)
Ni–In–N2	95.3(1)	95.2(1)
Ni–In–C1	121.2(1)	120.7(1)
Ni–In–C6	115.9(1)	115.5(1)
N1–In–N2	169.7(1)	169.8(1)
C1–In–C6	123.0(1)	123.8(1)
N1–In–C1	78.3(1)	78.4(1)
N1–In–C6	96.2(1)	96.5(1)
N2–In–C1	95.2(1)	95.0(1)
N2–In–C6	80.6(1)	80.7(1)
C–Ni–In	78.1(1)	78.6(1)
In–Ni–Cp	122.8	122.5
C–Ni–Cp	159.1	159.0
Ni–C–O	176.5(3)	176.9(4)
	Torsion Angles	
N1–In–Ni–Cp	85.6	85.4
N2–In–Ni–Cp	−95.8	−96.4

[a] Cp denotes the center of the cyclopentadienyl ligand C11–C15.

Table 8. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of **12**

atom	x/a	y/a	z/a	U_{eq}[a] Å^2
In	0.15230(2)	$^1/_4$	0.14642(4)	0.0404
Fe1	0.10272(3)	0.35702(4)	0.34628(5)	0.0410
O1	0.0082(3)	$^1/_4$	0.5555(4)	0.069
O2	−0.0636(2)	0.3912(3)	0.2225(4)	0.090
N	0.0701(4)	$^1/_4$	−0.0570(5)	0.065
C1	0.0500(3)	$^1/_4$	0.4568(5)	0.050
C2	0.0036(3)	0.3748(3)	0.2697(4)	0.053
C3	0.2584(5)	$^1/_4$	0.0062(7)	0.081
C4	0.2239(6)	$^1/_4$	−0.1328(7)	0.088
C5	0.1360(7)	0.2059(7)	−0.1505(7)	0.078
C6	0.0542(9)	0.1370(9)	−0.0945(11)	0.087
C7	−0.0114(7)	0.1934(11)	−0.0642(10)	0.115
C10	0.1534(7)	0.4392(9)	0.5110(10)	0.057
C11	0.2212(8)	0.3978(9)	0.4451(14)	0.075
C12	0.2250(6)	0.4358(9)	0.3172(11)	0.054
C13	0.1587(7)	0.5089(8)	0.2995(10)	0.056
C14	0.1132(6)	0.5136(8)	0.4210(12)	0.055
C15	0.1274(8)	0.4723(10)	0.4930(12)	0.058
C16	0.1942(7)	0.3885(9)	0.0530(11)	0.053
C17	0.2363(6)	0.3913(8)	0.3822(11)	0.045
C18	0.2009(9)	0.4688(11)	0.2940(12)	0.063
C19	0.1274(8)	0.5181(9)	0.3657(15)	0.063

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

mixture with three strong absorptions at 2053, 1977, and 1955 cm^{-1} was suggestive for $(CO)_4Co$–InR_2(TMEDA) (**2**) as the major reaction product. However no pure compound could be isolated. Similar results were obtained when other transition metal nucleophiles, e.g. $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]^-$ were used. These observations differ from the related organogallium transition metal chemistry. In that case, the corresponding salt elimination reactions between equimolar quantities of dialkylgallium chlorides and transition metal carbonylates do give the one-to-one transition metal gallium compounds, e.g. $[(CO)_4Co$–$GaR_2(THF)]$ (R = CH_2CMe_3) in nearly quantitative yields.[27] The indium chemistry appears to be governed by the weaker indium carbon bonds and the tendency toward higher coordination numbers, which both favor alkyl exchange processes. The behavior of organoindium transition metal complexes with simple alkyl ligands is more closely modeled by the respective organothallium systems, for example $[(CO)_5Mn$–$TlMe_2]$, which also tend to ligand redistribution at the group 13 center.[28]

In this context it should be mentioned that the iridium and platinum complexes *mer*-$\{[Me_3P]_3(H)(Et)Ir$–$In(Et)_2\}$ (**II**), and *cis*-$[(Cy_2PCH_2CH_2PCy_2)(Me_3SiCH_2)Pt$–$In(CH_2SiMe_3)]$ (**III**) constitute very rare examples of low coordinated, trigonal planar R_2In–transition metal systems that are stable against alkyl exchange. This might well be due to steric effects, because the iridium and platinum fragments are considerably bulky. However, since both transition metal centers are very electron rich compared to transition metal carbonyl fragments, some electronic stabilization in a d_π–p_π or d_π–d_π back-bonding fashion may also be important.[6,7] But we have restricted ourselves to volatile and rather heteroatom-free compounds! This rules out systems like **II** or **III**, which both are nonvolatile. With OMCVD applications in mind, only a severely restricted set of ligands is left to be put on the two metals which also guarantees coordinative saturation

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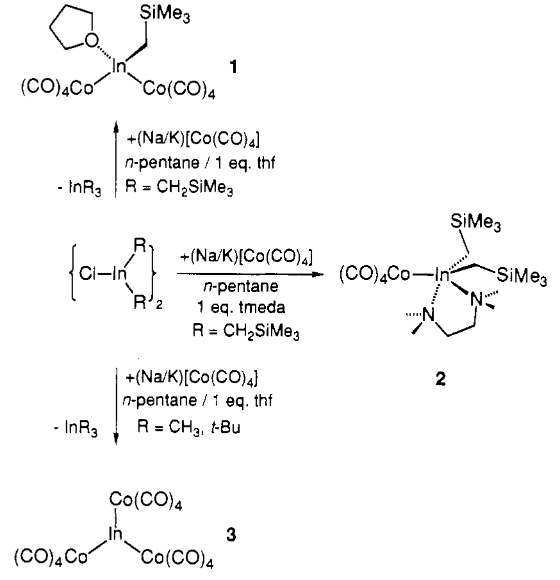
(28) Walther, B.; Albert, H.; Kolbe, A. *J. Organomet. Chem.* **1978**, *145*, 285.

Table 9. Selected Interatomic Distances (pm) and Angles (deg) for Compound **12**[a]

	Distances		
In-Fe	253.6(1)	Fe-C1	192.1(4)
In-N	240.5(5)	Fe-C2	171.9(4)
In-C3	215.3(5)		
Fe-Fe′	268.3(1)	C1-O1	118.3(6)
Fe-Cp[b]	176.6	C2-O2	115.3(5)
	Angles		
Fe-In-Fe′	63.89(3)	Fe-C1-Fe′	88.6(3)
N-In-Fe	121.3(1)	Fe-C1-O1	135.6(4)
N-In-C3	80.6(3)	Fe-C2-O2	176.4(4)
C1-Fe-In	102.5(2)		
C2-Fe-In	88.7(3)		
C1-Fe-C2	88.8(3)		
Cp-Fe-C1	126.4		
Cp-Fe-C2	126.2		
Cp-Fe-Fe′	136.4		
Cp-Fe-In	115.8		

[a] Symmetry operation Fe → Fe′: *x*, 0.5 − *y*, *z*. [b] Cp denotes the center of the cyclopentadienyl ligand C10–C14.

Scheme 1

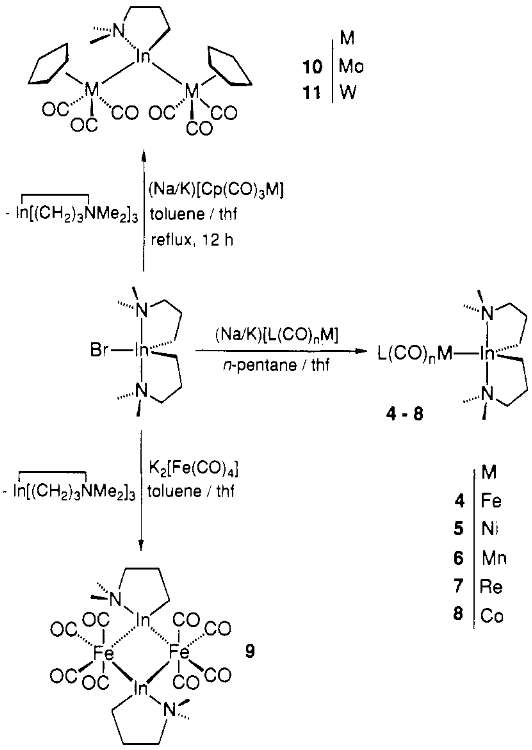


at the critical point, the indium atom. We therefore selected the (3-dimethylamino)propyl group as chelating alkyl substituent to shield the indium center. Following Scheme 2 a variety of transition metal derivatives of $BrIn[(CH_3)_2N(CH_2)_3]_2$ could thus be obtained in almost quantitative yields.

With strong nucleophiles, e.g. $[(\eta^5\text{-}C_5H_5)(CO)_nM]^-$ (M = Fe, Ni;[29] *n* = 2, 1) the reaction was complete within minutes in polar solvents, typically THF, while the reactants remained unchanged in pentane or toluene suspension. **4–5** were obtained simply by extraction of the crude product with pentane and crystallization at low temperatures. No other side products than the expected quantities of alkali bromide were detected. In the case of weaker nucleophiles, e.g. $[(CO)_nM]^-$ (M = Mn, Re, Co; *n* = 5, 4), the synthesis was successful only when carried out in *n*-pentane or toluene suspension. Due to the presence of Lewis base functionality in the alkyl substituent, the addition of a donor equivalent was not necessary in these cases.

The treatment of $K_2[Fe(CO)_4]$ with 2 equiv of $BrIn[(CH_3)_2N(CH_2)_3]_2$ in pentane or toluene was unsuccessful. In THF solution, however, the anionic complex $(CO)_4FeIn[(CH_2)_3NMe_2]^-$ appeared as the dominant carbonyl species. The IR spectrum showed a typical $2A_1 + E$ pattern shifted to lower wavenumbers (1982, 1897, 1869 cm^{-1}). The solvent was then removed and the reaction was continued in toluene suspension. After workup the tetranuclear complex **9** was obtained in 80–90% yield. $In[(CH_2)_3N(CH_3)_2]_3$[30] was found as a byproduct. This reaction presumably proceeds via *cis*-$(CO)_4Fe\{In[(CH_2)_3N(CH_3)_2]_2\}_2$ as an unstable intermediate. The related organotin iron compound *cis*-$[(CO)_4Fe][Sn(CH_3)_3]_2$ is known to eliminate tetramethyltin to give the dimer $\{\mu\text{-}[Sn(CH_3)_2][(CO)_4Fe]\}_2$.[31] It is quite likely that two dialkylindium moieties (i) being in close proximity and (ii) bearing labile bonds to carbon may undergo a similar alkyl group transfer. **9** consists of a mixture of two isomers as could be judged from the NMR spectra. The major one presumably exhibits the two N-donor moieties *trans* to each other. When the comparatively weak nucleophiles $[\eta^5\text{-}(C_5H_5)(CO)_3M]^-$ (M = Cr, Mo, W) were treated with $BrIn[(CH_2)_3N(CH_3)_2]_2$ in boiling tetrahydrofuran/toluene mixtures the trinuclear mixed metal species **10–11** were obtained in good yields, and again, $In[(CH_2)_3N(CH_3)_2]_3$ was produced as byproduct. For M = Cr, a pure product has not been isolated so far.

Scheme 2



The new heterodinuclear complexes **1–11** are moderately air sensitive and soluble in all common hydrocarbon solvents. They can be sublimed unchanged at typically 40–80 °C, 10^{-3} mbar. At 20(±1) °C the vapor pressure of **8**, for example, amounts to 0.020(5) mbar.[17] The trinuclear systems **10-12** are thermally remarkably stable and sublime at 180–220 °C (10^{-3} mbar).

B. Reactivity. Compounds **4** and **5**, which produce very strong transition metal nucleophiles upon dissociation, are entirely undissociated in THF and acetonitrile, wheras **6–11** show some dissociation, especially in acetonitrile. The metal to metal bonds in the compounds **1–11** are all very susceptible toward electrophilic and nucleophilic attack. The reactions compiled in Scheme 3 are typical for this class of compounds. When 1 equiv of triflic acid was added to a solution of **4** in diethyl ether immediate cleavage of the Fe–In bond occurred rather than protolysis of the In–C bonds. The instable primary product $[\eta^5\text{-}(C_5H_5)(CO)_2Fe\text{–}H]$ transformed under the reaction conditions quickly into [η^5-

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(30) Schumann, H.; Seuss, T. D.; Hemling, H. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 81.

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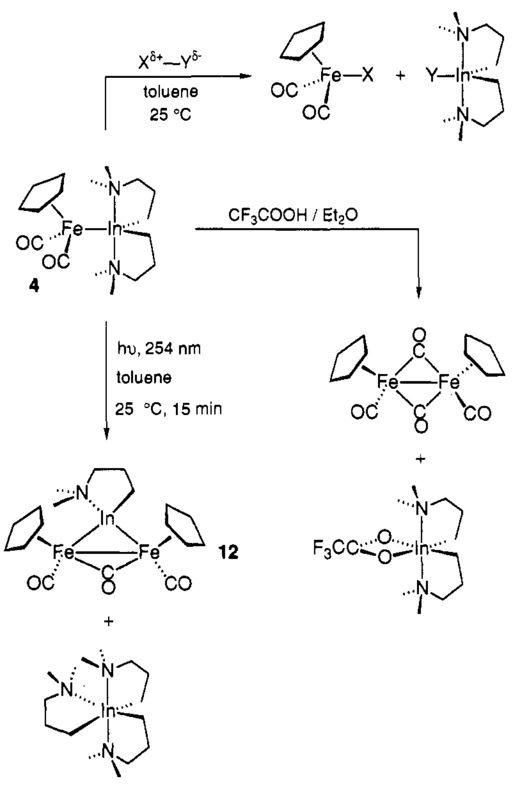
Scheme 3



$(C_5H_5)(CO)_2Fe]_2$, which was observed by infrared spectroscopy. With other electrophiles and nucleophiles such as Me_3SnCl, $(C_6H_5)_2PCl$, MeI, $HgBr_2$, and $\{N[P(C_6H_5)_3]_2\}Cl$ similar observations were made. Rapid oxidative cleavage of the Fe–In bond occurred with iodine.

Interestingly, **4** proved to be much more photosensitive than its Ni analogue **5**. Fairly concentrated ($c = 0.5$ *m*) deep yellow solutions of **4** in toluene change color to pale green upon standing in the light for a couple of days. By irradiation with a mercury lamp at 254 nm, this color change was complete within 15 min. From this solutions green-black well shaped crystals of **12** were obtained. The single-crystal X-ray diffraction study revealed the predicted structure (Scheme 3), which will be discussed later (see section C). The conditions of this photoreaction are very critical to achieve high yields of **12**. In diluted solution ($c = 0.01$ *m*) **4** did not transform to **12** and was left unchanged when irradiated for a short time. Prolonged irradiation of diluted solutions of **4** gave a complex mixture without reasonable quantities of **12** amoung the other unidentified photoproducts.

C. Structures. Structure of 1. An ORTEP diagram of the Co_2In complex **1** is shown in Figure 1. An organoindium moiety bridges two tetracarbonylcobalt fragments. One donor molecule THF completes the distorted tetrahedral coordination sphere around the indium center. Compound **1** represents a base aduct of a trigonal type **C** complex (Chart 1). The average In–Co distance of 263.4 pm is, within standard deviation, equal to the value of 263.4(2) pm found for the related anionic complex $[Br_2In(Co(CO)_4)_2^-]$.[32] This distance lies at the upper end of the range of CoIn bond lengths from 254 to 264 pm with 4-fold-coordinated indium centers. An analysis of the geometry around the indium center resembles the qualitative difference between the dative In–O41 bond and the other three covalent bonds. The sum of the angles which the three atoms Co1, Co2, and C2 form with the In center amounts to 354° and is close to a planar arrangement. In this respect the structure of **1** differs from the related ones of $\{[(CO)_4Co]InX_2\}^-$ (X = Cl, Br)[14,32] with almost tetrahedral geometry around the indium atom. In case of **1** the sterically demanding alkyl group is an important factor in determinig the geometry at the indium center. The trigonal bipyramidal arrangement around the cobalt atom is quite similar to that in compounds such as $In[Co(CO)_4]_3$,[33] minimizing steric interactions of the carbonyl ligands of adjacent cobalt centers.

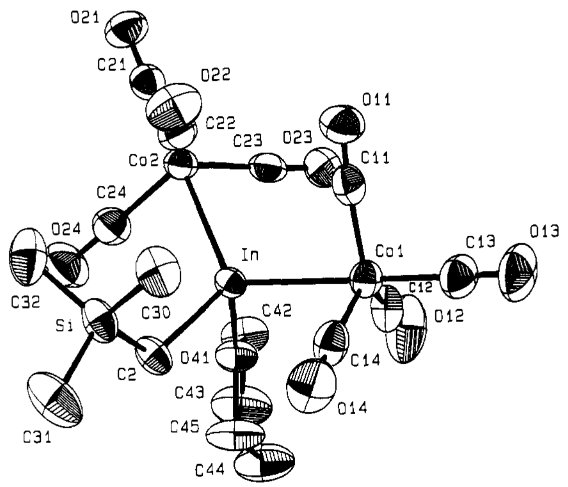


Figure 1. Molecular structure of $[(CO)_4Co]_2In[CH_2Si(CH_3)_3](C_4H_8O)$ (**1**) in the crystal (ORTEP drawing; hydrogen atoms are omitted; non-hydrogen atoms are shown as 50% thermal ellipsoids).

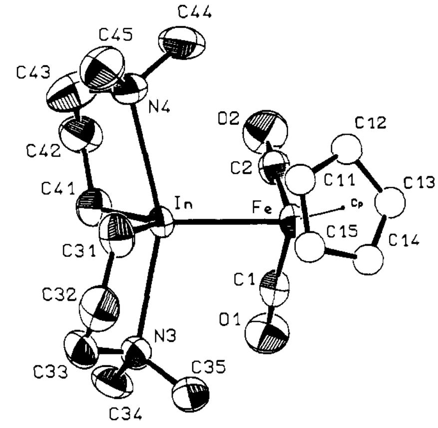


Figure 2. Molecular structure of $(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}In[(CH_2)_3N(CH_3)_2]_2$ (**4**) in the crystal (ORTEP drawing; hydrogen atoms are omitted; non-hydrogen atoms are shown as 50% thermal ellipsoids). Disorder occurred at the Cp position C11–C15; see Experimental Section.

Structures of 4 and 5, a Comparison. ORTEP diagrams of the FeIn compound **4** and the related NiIn compound **5**[34] are shown in Figures 2 and 3. Both compounds resemble the structure of the "parent molecule" $BrIn[(CH_2)_3NMe_2]_2$.[19] The bromide ligand is substituted by the transition metal fragment $[(\eta^5\text{-}C_5H_5)(CO)_nM]$ occupying one equatorial position of a distorted trigonal bipyramidal coordination sphere around the indium atom. In the parent bromo compound the individual molecular units are linked together to form one dimensional chains by long range Br–In···Br interactions (397.5 pm).[19] The transition metal derivatives **4** and **5** do not exhibit any noticably short intermolecular contacts in the solid state.[35] The γ-amino donor functions of the two alkyl substituents are *trans* to each other in the apical positions. Two five-membered heterocyclic rings are produced by intramolecular adduct formation which are joined by the indium center. The envelope conformation of these hetrocycles is not very rigid, which can be seen by the large thermal parameters

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(32) Cradwick, P. D.; Hall, D. *J. Organomet. Chem.* **1970**, *22*, 203.

(33) Robinson, W. R.; Schussler, D. P. *Inorg. Chem.* **1973**, *12*, 848.

(34) The discussion below corresponds to the structural parameters of **5** obtained at -80 °C, denoted as **5a** in Table 7.

(35) Compound **4** exhibits one somewhat short intermolecular contact between O1 and C11 of 323.5 pm, having no significant structural consequences.

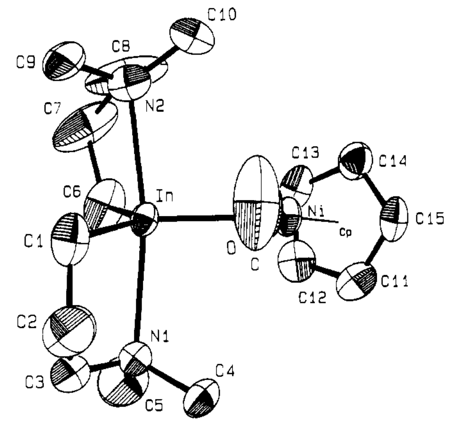

Figure 3. Molecular structure of $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}In[(CH_2)_3N(CH_3)_2]_2$ (**5**) in the crystal (ORTEP drawing; hydrogen atoms are omitted; non-hydrogen atoms are shown as 50% thermal ellipsoids).

(**4**, **5**, and **12**). Compound **5** was selected as a representative example to decide between order/disorder phenomena and solid state fluxionality. A low-temperature single crystal X-ray diffraction experiment at −125 °C was performed (**5b**). Under these conditions the U_{eq} values expectedly reduce, but the U_1/U_3 ratio enlarges compared to the respective values obtained at −80 °C. Consequently the low-temperature *R* values increase. These results agree with an order/disorder model. The corresponding carbon atoms of $BrIn[(CH_2)_3NMe_2]_2$ are in fact disordered at room temperature.[19] In the solid state, the coordination geometry around the indium in **4** and **5** is helical and consequently all carbon atoms of the two (3-dimethylamino)propyl groups are different. Due to the flexibility of the coordination sphere around the indium atom only two out of the possible four signals for the methyl groups could be resolved at −90 °C by NMR.

The observed Fe–In distance of 263.9(1) pm is somewhat *longer* than the respective bond lengths in related compounds such as $(\mu\text{-}InCl)[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with 255.5 pm (average) or $[(\mu\text{-}In(Cl)(PMe_2Ph)[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with 257.6 pm (average).[13c] Because of the lack of structural data on other Ni–In compounds the value of 259.8(1) pm for the σ(Ni–In) bond of **5** can only be related to the sum of the covalent radii of 258(±5) pm,[36,37] which shows good agreement. However, care must be taken in such a comparison. It is well-known, that that $\sigma(M^1\text{–}M^2)$ bond lengths can vary over a large range and are very sensitive toward repulsive interactions of the ligands and weak multiple bonding effects.[38]

One interesting feature in both molecules **4** and **5** is the rather small angles (≤86°) between the metal carbonyl vectors and the metal to metal bond vectors. The carbonyl groups appear to be bent toward the indium center. If one describes the nickel atom in **5** as 3-fold coordinated, one might expect an angle of 120° between each two of the vectors Ni–Cp, Ni–In, and Ni–C to minimize steric interactions. With a value of 122.8° the angle Cp–Ni–In is indeed close to 120°, the other two, Cp–Ni–C and C–Ni–In, are very much different, 159.1 and 78.1(1)°, respectively. In addition, the C–O distance, amounting to 117.4(4) pm, is at the upper end for terminal Ni–CO ligands. Remembering that the indium center in $BrIn[(CH_2)_3NMe_2]_2$ exhibits residual Lewis acidity, as could be judged from the polymeric solid-state structure, it is possible to describe the carbonyl substituent in **5** as linear semibridging. The In–C and In–O distances, amounting to 278 and 348 pm, respectively, are not out of the range of weak bonding interactions. Related examples of transition metal-main group metal complexes exhibiting similar geometric features with small angles $OC\text{–}M^1\text{–}M^2$ include $[(\eta 5\text{-}C_5H_5)(CO)_3W\text{–}GaMe_2]$[39] (average: 64.6°), and $[(\eta 5\text{-}C_5H_5)(CO)_3Mo\text{–}Zn(Cl)(OEt2)]$[40] (average.: 65.6°). In these cases effects of steric crowding at the transition metal center have also be taken into account, which is clearly not necessary for the Ni–In system **5**. However, we do not think that the structural parameters of **4** and **5** are indicative for linear semibridging carbonyls. It is reasonable to consider the intermetallic bonds in **4** and **5** being polarized in a $M^{\delta-}\text{–}In^{\delta+}$ fashion. Crabtree et al.[41] and Hall et al.[42] argue that in such a case the L_nM fragment will not need to rehybridize much on forming the transition metal indium bond. "The structure of the complex as a whole will be very similar to the $[L_nM]^-$ system, typically a *n*-vertex polyhedron".[42] Our preliminary EHMO calculations[43,44] with the model compound $[(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}In(CH_3)_2(NH_3)_2]$ agree with this interpretation and show an energy minimum of the optimized geometry at a OC–Ni–In angle of 85°, which is reasonably close to the observed value of 78.1(1)°. This interpretation agrees with the somewhat short Ni–C contact of 165.9(4) pm ($Ni(CO)_4$: 181.7(2) pm[45]) and the correspondingly long C–O distance of 117 pm. Structural data about $[(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}X]$ species are surprisingly rare. For comparison: in the compounds $[[(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}Mn(CO)_5]$[35a] and $[(\eta^5\text{-}C_5H_5)(CO)Ni][[(\eta^5\text{-}C_5H_5)(CO)_2Fe][(CO)_4Co]SnCl$[46] the related values for *d*(OC–Ni) and *d*(C–O) are 171.0(7) and 113(1) pm and 173.0(0) and 113.0(0) pm, respectively. Also consistent with this view is the position of the ν(CO) absorption of **5** at 1946 cm^{-1}. Other systems in which more electronegative substituents, e.g. halide, or alkyl, occupy the In position, exhibit typical values ≥2000 cm^{-1}. The situation in the Fe–In compound **4** is similar. The same arguments hold for the Co–In compound **1**.

In both molecules **4** and **5** the N–In–N plane and the M–Cp vectors are nearly perpendicular. These particular orientations can be explained by minimization of repulsive interactions between the transition metal fragment and the methyl groups at the two nitrogen atoms. For the Fe–In compound **4** the N3–In–N4 angle of 155.4(2)° is bent and deviates considerably from the values in the Br–In parent molecule of 172.6(5)° and in the Ni–In compound **5** of 169.7(1)°. In addition, the distances In–N3 and In–N4 are unusually long, 264.3(5) and 272.6(5) pm, respectively. The respective values of 255.7(3) and 251.5(3) pm, obtained for the Ni–In compound **5**, lie within the usual range for In–N distances between 214 and 260 pm.[19] They are very similar to the In–N distances of $BrIn[(CH_2)_3NMe_2]_2$ (253(1) and 251(1) pm).[19] As discussed above, the polar $Fe^{\delta-}\text{–}In^{\delta+}$ bond of **4** requires rather small angles C1–Fe–In and C2–Fe–In, which in turn give rise to steric interactions with the methyl substituents bonded to the nitrogen donor atoms at the indium site. The distances O1–C34, O1–C35 and O2–C44 of **4** are indeed within the range of repulsive van der Waals contacts (≤340 pm). Contrasting this the single carbonyl substituent of **5** is far away from the $N\text{–}CH_3$ groups (>400 pm) and has little steric influence. Whether

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(36) The covalent radius of the Ni atom of 121(±5) pm was taken from ref 37a, which agrees well with the Ni–Ni distances in $[(\eta^5\text{-}C_5H_4R)(CO)Ni]_2$ (R = H, CH_3) divided by two. The covalent radius of In of 137(±5) pm was taken as the mean of In–In distances ranging from 266 to 282 referred to in ref 34b.

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(38) (a) Madach, T.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 3235–3244. (b) Pluta, C.; Pörschke, K. R.; Mynott, R.; Betz, P.; Krüger, C. *Chem. Ber.* **1991**, *124*, 1321. (c) Note that σ(Co-Ga) distances for example can vary over a large range from 238 to 260 pm depending on the donor/acceptor properties of the metal fragments. See ref 17 and refserences cited therein.

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(41) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1985**, *25*, 805.

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(43) On the basis of the structural parameters of **5**, the model compound $[(\eta^5\text{-}C_5H_5)(CO)Ni\text{-}In(CH_3)_2(NH_3)_2]$ was constructed. The total energy was calculated with variation in the C–Ni–In angle and in the C–Ni–In–N1 torsion angle using a standard EHMO program.[44]

(44) Calzaferi, G.; Fross, L.; Kamber, I. *J. Phys. Chem.* **1989**, *93*, 5366.

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(46) Carre, F. H.; Corriu, R. J. P.; Henner, B. J. L. *J. Organomet. Chem.* **1982**, *228*, 139.

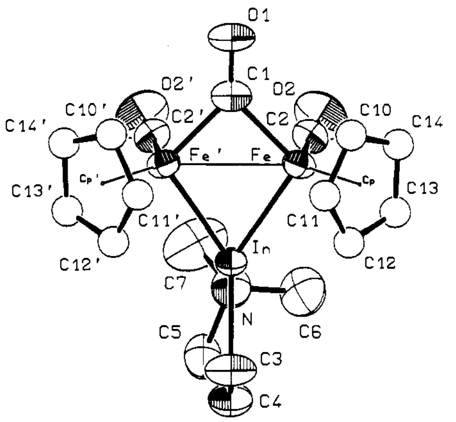


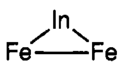
Figure 4. Molecular structure of $(\mu\text{-CO})\{\mu\text{-In}[(CH_2)_3N(CH_3)_2]\}[(\eta^5\text{-}C_5H_5)(CO)Fe]_2$ (**12**) in the crystal (ORTEP drawing; hydrogen atoms are omitted; non-hydrogen atoms are shown as 50% thermal ellipsoids). The molecule has a crystallographic mirror plane defined by O1, C1, In, C3, C4, and N. Disorder occurred at the Cp position C10-C14 and C5-C7; see Experimental Section.

electronic effects, e.g. a d_π–σ^*(In–N) hyperconjugation, may also contribute to the geometric features of **4** and **5** is still a matter of current investigations. For $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}SiF(C_6H_5)_2$ interactions of this kind, e.g. d_π–σ^*(Si-F), had been discussed.[47]

If transition metal fragments like $[(\eta^5\text{-}C_5H_5)(CO)_3M]$ (M = Cr, Mo, W) were bonded to the $In[(CH_2)_3NMe_2]_2$ moiety, the steric repulsions involving the *cis* carbonyl groups outlined above would increase substantially. On the basis of the structures of **4** and **5** and the compound $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_3In$,[13a] a simple molecular model of the hypothetical species $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}Mo\text{–}In[(CH_2)_3NMe_2]_2$ was constructed.[48] The geometric features of the molybdenum and indium parts were then kept constant on rotation around the Mo–In bond axis. With Mo–In distances varying from 280 to 320 pm, the model showed close contacts around 250–300 pm between the *cis* carbonyl groups and the $N\text{–}CH_3$ substituents. The minimization of steric interactions in this hypothetical molecule requires a rather long Mo–In bond, long In–N distances, and a high bending of the N–In–N angle. From this discussion it may be understandable why the Mo and W congeners of **4** and **5** are significantly labilized toward radical induced ligand redistribution processes[8] to give the sterically less crowded[48] trinuclear species **10** and **11** (Scheme 2) with 4-fold coordinated indium. The enhanced photolability of **4** compared to **5**, leading to the Fe_2In species **12** with a lower coordinated indium atom, agrees well with this interpretation.

Structure of 12. An ORTEP diagram of the Fe_2In-complex **12** is shown in Figure 4. Two $[(\eta^5\text{-}C_5H_5)(CO)Fe]$ moieties are bridged by one carbonyl group and the organoindium fragment $[In\{(CH_2)_3NMe_2\}]$. The molecule has a symmetry plane, defined by O1, C1, In, N, C3, and C4. Compound **12** can be formally derived by replacement of one bridging carbonyl group in *cis*-$[(\mu\text{-CO})(\eta^5\text{-}C_5H_5)(CO)Fe]_2$ (*cis*-Fp_2) by the $In[(CH_2)_3NMe_2]$ fragment. The resulting four membered heterocycle Fe, Fe', In, and C1 is nearly planar. The position of the nitrogen donor atom at the indium center is *trans* to the cyclopentadienyl rings. Because of the steric requirements of the bridging indium atom, the value of 268.3(1) pm for the Fe–Fe' distance is significantly longer

Chart 2



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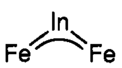

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compared to the value of 253.1(2) pm for *cis*-Fp_2.[49] The Fe–C1 distance of 192.1(4) pm and the angle Fe–C1–Fe' of 88.6(3)° for **12** are instead quite similar to the respective values of 191 pm and 82.5° for *cis*-Fp_2. The Fe–In distance in **12** of 253.6(1) pm is shortened by 10 pm compared to **4**, being in the lower range of bond lengths which have been observed in related systems.[50] The angle Fe–In–Fe' of 63.89(3)° is drastically smaller than those found in other Fe_2In compounds without additional bridging ligands (125–130°).[13c] The angle N–In–C3 of 80.6(3)° is also far from an ideal tetrahedral geometry but quite similar to the respective values in **4**, **5**, and $BrIn[(CH_2)_3NMe_2]_2$. Referring to those latter compounds, it is not surprising that the In–N bond length in **12** is shortened to 240.3(5) pm. This value is close to In–N distances found in related systems such as $[\{(\eta^5\text{-}C_5H_5)(CO)_3\text{-}Cr\}_2In(NC_5H_5)Cl]$ (233.5 pm)[13b] with 4-fold coordinated indium. On the basis of the 18 electron rule and the diamagnetism of **12**, two formal descriptions may represent the bonding in the Fe_2In triangle, which is the central unit of **12** (Chart 2). Form **B** refers to a Fe-In-Fe four electron three center bond, since the $In[(CH_2)_3\text{-}NMe_2]$ moiety can be regarded as isolobal to a stannylene $[SnR_2]$ group. The HOMO of the organo indium fragment at −9.4 eV has σ donor character and the LUMO at −5.6 eV is essentially an empty 5p orbital at the indium, which is correctly orientated to act as a π-acceptor.[51]

Conclusions

(3-Dimethylamino)propyl-substituted alkylindium transition metal carbonyl complexes are remarkably stable toward ligand redistribution equilibria. Depending on the nature of the transition metal carbonyl fragment, e.g. steric bulk and radical stability, compounds with a transition metal to indium ratio of 1:1 and 2:1 are thermodynamically preferred and can be synthesized in very good yields. These materials are stable enough to be volatilized unchanged at moderate conditions. Experiments showing their potential use as novel single source precursors for OMCVD of indium containing thin alloy films, e. g. ϵ-NiIn, have recently been reported elsewhere.[17] The metal–metal bonds in these complexes are strongly polarized and very reactive toward electrophilic/nucleophilic attack and oxidative cleavage. The combination of indium carbon with transition metal carbonyl units as two photoactive types of bonds in one molecule may open up interesting routes to synthesize transition metal indium compounds with new structures.

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Supplementary Material Available: Tables giving positional parameters, calculated hydrogen positions, anisotropic thermal parameters, bond lengths, and bond angles (36 pages). Ordering information is given on any current masthead page. Supplementary material for **1** and **4** including full crystallographic and experimental data, hydrogen positional parameters, thermal parameters, interatomic distances, and bond angles are available from the "Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH", D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-56977, the names of the authors, and the journal citation of ref 17.

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(51) On the basis of the structural parameters of **12**, EHMO calculations[44] were performed on the fragment $In[(CH_2)_3NMe_2]$.