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Reactions of Elemental Indium and Indium(I) Bromide with Nickel−Bromine Bonds: Structure of $(\eta^5\text{-}C_5H_5)(Ph_3P)Ni{-}InBr_2(O{=}PPh_3)$[†]

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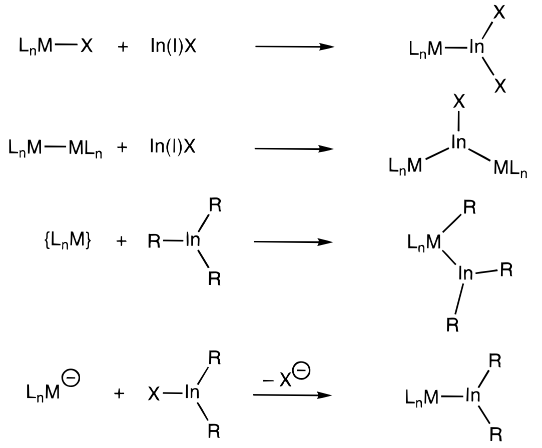
The reactions of elemental indium and In^IBr with the carbonyl-free organonickel complexes $(\eta^5\text{-}C_5H_5)(PR_3)Ni{-}Br$ (R = CH_3, C_6H_5) have been studied in some detail. Either redox reactions to yield the ionic products $[(\eta^5\text{-}C_5H_5)(PR_3)_2Ni][InBr_4]$ (**2a**,**b**) occurred or the Ni−In bound systems $(\eta^5\text{-}C_5H_5)(PPh_3)Ni{-}InBr_2(OPPh_3)$ (**3a**) and $[(\eta^5\text{-}C_5H_5)(PPh_3)Ni]_2InBr$ (**4**) were obtained in good yields. The new compounds were characterized by elemental analysis, NMR, and mass spectrometry. A short Ni−In bond of 244.65(9) pm was found for **3a**. Single crystal data for $(\eta^5\text{-}C_5H_5)(PPh_3)Ni{-}InBr_2(OPPh_3)\cdot THF$ (**3a**): triclinic, *P*1 with $a = 1124.9(3)$, $b = 1353.2(4)$, $c = 1476.4(4)$ pm, $\alpha = 94.74(2)°$, $\beta = 101.78(2)°$, $\gamma = 109.64(1)°$, $V = 2044(1) \times 10^6$ pm^3, $Z = 2$, $R = 0.053$ ($R_w = 0.063$).

Introduction

Transition metal indium compounds have been studied in the past starting with W. Hieber's early work on $In[Co(CO)_4]_3$[1] in 1942 up to the present with N. C. Norman's contributions, namely, on group-6 indium complexes, e.g., $[(\eta^5\text{-}C_5H_5)(CO)_3M]_n\text{-}InX_{3-n}(L)$ (M = Cr, Mo, W; *n* = 2, 3; L = THF, py or other Lewis donors).[2−9] Almost all known systems of the type $(L_mM)_nInX_{3-n}$, which can be viewed as derivatives of trimethylindium or indiumtrihalides, exhibit *carbonyl* transition metal fragments. Rather few compounds exist which do not carry carbonyl ligands at the transition metal center, only two of which have been structurally characterized: *mer*-$\{[(CH_3)_3P]_3(H)(C_2H_5)Ir{-}In(C_2H_5)_2\}$[10] and *cis*-$\{(Cy_2PCH_2CH_2PCy_2)[(CH_3)_3SiCH_2]Pt{-}In[CH_2Si(CH_3)_3]_2\}$ (Cy = cyclo-C_6H_{11}).[11] Some early reports of Mays and Hsieh[12,13] and Chatt et al.[14] do exist also, claiming the compounds $(Et_3P)_2Pt(InCl_2)_2$, $[(Et_3P)_2(p\text{-}MeOC_6H_4NC)Pt{-}InCl_2][ClO_4]$, *trans*-$[Pt(InCl_2)(SiPh_3)(PMe_2Ph)_2]$, and $(Ph_3P)Au{-}InCl_2$ on the basis of elemental analysis and IR ν(In−Cl) data only. The structure of a novel Au−In cluster compound was recently reported by Gabbaï et al.[14b] These compounds were synthesized either by the formal insertion of low-valent indium halides into transition metal halide bonds and metal metal bonds or by a formal oxidative addition of indium carbon bonds to coordinatively unsaturated transition metal fragments. The otherwise widely used salt elimination reaction between anionic transition metal nucleophiles and indium halides cannot be employed in these cases (Scheme 1), because of the lack of suitable "carbonyl-free" transition metal nucleophiles.

Scheme 1



Our interest in the transition metal indium chemistry originates from the potential of heteronuclear organometallics containing certain combinations of transition metals and group-13 metals to serve as "single source" precursors for organometallic chemical vapor deposition (OMCVD) of *intermetallic* thin films. Recently, we have reported on the synthesis and structural properties of the first examples of volatile organoindium transition metal carbonylate compounds and their use in OMCVD to deposit NiIn and CoIn phases.[15,16] Aiming at new

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[†] Part XIII of the series Organometallic Group-13 Metal Complexes of d-Block Elements; for part XII, see ref 31.

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and *carbonyl-free* precursors for indium alloys of the late transition metals, e.g., NiIn, Ni_2In, and AuIn, we had been led to investigate the reactivity of elemental indium and low valent indium halides with organonickel complexes.

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). JEOL JNM-GX400 and JNM-GX270 spectrometer 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 Hz (hertz). All samples for NMR spectra were contained in vacuum-sealed NMR tubes. Mass spectra were recorded with a Finnigan MAT90 instrument (FD spectra); *m/z* values are reported for ^{59}Ni and ^{115}In, normal isotope distribution observed. Melting points were observed in sealed capillaries and are not corrected. The starting compounds In^IBr[17] and $Cp(PR_3)Ni-Br$ (**1a**,**b**)[18] were prepared as described in the literature. Abbreviations are as follows: Cp = η^5-C_5H_5, Me = CH_3, Ph = C_6H_5). Elemental analyses were provided by the Microanalytic Laboratory of the Technical University at Munich.

Syntheses of $[Cp(PPh_3)_2Ni][InBr_4]$ (2a). A 1.0-g (2.15 mmol) sample of $Cp(PPh_3)NiBr$ and 0.42 g (2.15 mmol) of freshly sublimed and finely powdered In^IBr were suspended in 30 mL of dichloromethane and stirred 12 h at room temperature. The color of the mixture changed within this time from dark wine red to dark red−brown. The reaction mixture was filtered and the solvent was removed in vacuo. Dark brown crystals of **2a** could be obtained by slow solvent diffusion (*n*-pentane) from the solvent mixture dichloromethane/*n*-pentane (1:3 volume parts). Yield: 0.64 g, 27.5% based upon indium.

Characterization Data of 2a. ^1H NMR (399.75 MHz, $CDCl_3$, 25 °C): $\delta = 5.19$ (s; 5 H, Cp), 7.32 (m; 30 H, $P(C_6H_5)_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 98.1$ (t; $^nJ(C, H_{Ring}) = 1.65$ Hz, Cp), 129.0 (t; $^nJ(C, P) = 5.51$ Hz, $P(C_6H_5)_3$), 130.2 (d; $^nJ(C, P) = 25.34$ Hz, $P(C_6H_5)_3$), 130.5 (d; $^nJ(C, P) = 25.34$ Hz, $P(C_6H_5)_3$), 131.4 (m; $P(C_6H_5)_3$), 133.6 (t; $^nJ(C, P) = 5.51$ Hz, $P(C_6H_5)_3$). $\{^1H\}^{31}P$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $= 37.2$ (s; NiP). FD-MS: *m/z* (rel int) = 647 $[CpNi(PPh_3)_2^+$, 59], 582 $[Ni(PPh_3)_2^+$, 17], 385 $[CpNi(PPh_3)^+$, 100]. Anal. Calcd for $C_{41}H_{35}Br_4InNiP_2$: C, 45.48; H, 3.26; Br, 29.52; In, 10.60; Ni, 5.42; P, 5.72. Found: C, 45.12; H, 3.42; Br, 29.40; In, 11.5; Ni, 6.52; P, 6.65.

Syntheses of $[Cp(PMe_3)_2Ni][InBr_4]$ (2b). A 0.5 g (1.79 mmol) sample of $Cp(PMe_3)NiBr$ and 0.35 g (1.79 mmol) of freshly sublimed and finely powdered In^IBr were suspended in 20 mL of dichloromethane and stirred for 7 days at room temperature. The color of the mixture changed within this time from intensively red violet to dark brown. The reaction mixture was filtered and the solvent was removed in vacuo. This crude product was first recrystallized from dichloromethane/*n*-pentane and then purified by slow solvent diffusion from the solvent mixture dichloromethane/*n*-pentane (1:3 volume parts). Yield: 0.22 g, 17% based upon indium.

Characterization Data of 2b. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.56$ (d; 3.2 Hz, $P(CH_3)_3$), 1.59 (d; 5.4 Hz, $P(CH_3)_3$), 5.43 (s; 5 H, Cp). ^{13}C NMR (62.0 MHz, $CDCl_3$, 25 °C): $\delta = 36.9$ (s; $P(CH_3)_3$), 87.9 (s; Cp). $\{^1H\}^{31}P$ NMR (101.0 MHz, $CDCl_3$, 25 °C): $\delta = -4.5$ (s; NiP). Anal. Calcd for $C_{11}H_{23}Br_4InNiP_2$: C, 18.60; H, 3.26. Found: C, 18.58; H, 2.87.

Synthesis of $Cp(PPh_3)Ni-InBr_2(OPPh_3)$ (3a). A 0.5-g (1,073 mmol) sample of $Cp(PPh_3)NiBr$, 0.21 g (1.073 mmol) of freshly sublimed and finely powdered In^IBr, and 0.3 g (1.073 mmol) of $O{=}PPh_3$ were suspended in a mixture of 20 mL of toluene and 2 mL of tetrahydrofuran and stirred for 12 h at room temperature. The color of the mixture changed within this time from dark wine red to green. The solvent was removed in vacuo and the residue was washed with toluene and tetrahydrofuran. From these crude product, dark green single crystals of **3a** could be obtained by slow solvent diffusion (*n*-heptane) from the solvent mixture dichloromethane/tetrahydrofuran/*n*-heptane (10:1:10 volume parts). Yield: 0.88 g, 87% based upon indium.

Characterization Data of 3a. ^1H NMR (399.75 MHz, C_6D_6, 25°C): $\delta = 5.19$ (s; 5 H, Cp), 6.98 (m; 20 H, $P(C_6H_5)_3$), 7.68 (m; 10 H, $P(C_6H_5)_3$). $\{^1H\}^{31}P$ NMR (161.9 MHz, C_6D_6, 25 °C): $\delta = 36.0$ (s; InOP), 48.5 (s; NiP). Anal. Calcd for $C_{41}H_{35}Br_2InNiOP_2$: C, 52.45; H, 3.76; Br, 17.02; In, 12.23; Ni, 6.25; O, 1.70; P, 6.60. Found: C, 51.55; H, 3.95; Br, 17.05; In, 11.09; Ni, 6.10; O, 3.3; P, 5.79.

Synthesis of $Cp(PPh_3)Ni-InBr_2(PPh_3)$ (3b). A 0.5 g (1.073 mmol) sample of $Cp(PPh_3)NiBr$, 0.21 g (1.073 mmol) of freshly sublimed and finely powdered In^IBr and 0.28 g (1.073 mmol) of PPh_3 were suspended in a mixture of 20 mL of toluene and 2 mL of tetrahydrofuran and stirred for 12 h at room temperature. The color of the mixture changed within this time from dark wine red to dark green. The reaction mixture was filtered, solvent was removed in vacuo, and the residue was washed with toluene and n-pentane. Yield: 0.89 g, 90% based upon indium.

Characterization Data of 3b. ^1H NMR (399.75 MHz, C_6D_6, 25 °C): $\delta = 5.21$ (s; 5 H, Cp), 7.47 (m; 30 H, $P(C_6H_5)_3$). $\{^1H\}^{31}P$ NMR (161.9 MHz, CD_2Cl_2, 25 °C): $\delta = 37.1$ (s; InP), 49.5 (s; NiP). Anal. Calcd for $C_{41}H_{35}Br_2InNiP_2$: C, 53.35; H, 3.82. Found: C, 51.89; H, 3.91.

Synthesis of $Cp(PPh_3)Ni-InBr_2(NC_7H_{13})$ (3c). Compound **3c** was synthesized according to the above procedures from a 0.5-g (1.07 mmol) sample of $Cp(PPh_3)NiBr$, 0.21 g (1.07 mmol) of freshly sublimed and finely powdered In^IBr, and 0.12 g (1.07 mmol) of quinuclidine. Yield: 0.67 g, 80% based upon indium.

Characterization Data of 3c. $\{^1H\}^{31}P$ NMR (161.9 MHz, CD_2Cl_2, 25 °C): $\delta = 45.6$ (s; NiP).

Syntheses of $[Cp(PPh_3)Ni]_2InBr$ (4). A 0.5-g (1.073 mmol) sample of $Cp(PPh_3)NiBr$ and 0.62 g (5,38 mmol) of finely powdered Indium were suspended in a mixture of 10 mL of diethyl ether and 10 mL of tetrahydrofuran and stirred for 3 days at room temperature. Within this time the color of the reaction mixture changed from red violet to dark orange brown. The reaction mixture was filtered and the solvent was removed in vacuo. Dark brown crystals of **4** could be obtained by slow solvent diffusion (*n*-pentane) using the solvent mixture toluene/tetrahydrofuran/*n*-pentane (1:1:4 volume parts). Yield: 0.5 g, 48.2% based upon nickel.

Characterization Data of 4. ^1H NMR (399.75 MHz, C_6D_6, 25 °C): $\delta = 4.46$ (s; 5 H, Cp), 6.84 (m; 20 H, $P(C_6H_5)_3$), 7.49 (m; 10 H, $P(C_6H_5)_3$). $\{^1H\}^{31}P$ NMR (161.9 MHz, C_6D_6, 25 °C): $\delta = 43.8$ (s; NiP). Anal. Calcd for $C_{46}H_{40}BrInNi_2P_2$: C, 57.14; H, 4.17; Br, 8.26; In, 11.88; Ni, 12.14; P, 6.41. Found: C, 56.11; H, 4.15; Br, 9.1; In, 11.5; Ni, 12.22; P, 5.43.

X-ray Structure Determination of (η^5-C_5H_5)(PPh_3)$Ni-InBr_2$($OPPh_3$) (3a). Crystals of the compound **3a** were grown by slow solvent diffusion techniques from toluene/*n*-pentane/tetrahydrofuran mixtures at room 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 $40.0 < 2\Theta < 48.4°$ with the programs "SET4" and CELDIM".[20] During data collection, orientation control reflections were monitored every 100th, and the intensity of three reflections were checked every 3600 s. Crystal data and intensity collection parameters together with details of the refinement are summarized in Table 1. The reflection data were corrected for Lorentz and polarization factors. During 113.1 h of exposure the three control reflections lost 1.8% of their intensity. An empirical absorption correction was made on the basis of ψ-scan data. Corrections for decay and/or extinction were not applied. Anisotropic temperature parameters were applied for all non-hydrogen atoms. The 35 hydrogen atoms of the complex **3a** were found in the difference Fourier synthesis and were refined freely. The eight hydrogen positions of the tetrahydrofuran solvent molecule were placed in ideal geometry and were included into the structure refinement with isotropic temperature factors but not refined. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(|F_o| - |F_c|)^2$. All calculations were

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Table 1. Crystallographic and Data Collection Parameters for **3a**

formula	$C_{41}H_{35}Br_2InNiOP_2{\cdot}C_4H_8O$
fw	1011.1
space group	$P\bar{1}$ (No. 2)
λ, pm	71.07
a, pm	1124.9(3)
b, pm	1353.2(4)
c, pm	1476.4(4)
α, deg	94.74(2)
β, deg	101.78(2)
γ, deg	109.64(1)
V, 10^6 pm^3	2044(1)
Z	2
D_{calcd}, g cm^{-3}	1.643
μ(Mo Kα), cm^{-1}	3.9
transm range, %	90.33−99.99
no. of reflns	7509
no. of obsd reflns	6363
cutoff	$I > 1{,}0*(I)$
R^a	0.0526
$R_w{}^b$	0.0625

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

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms of **3a**

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
In1	0.07081(4)	0.21041(4)	0.19745(3)	0.0174
Br1	0.0252(1)	0.30981(9)	0.33333(7)	0.0504
Br2	−0.0416(1)	0.01929(8)	0.22043(8)	0.0552
Ni1	0.01084(8)	0.25546(7)	0.04176(6)	0.0155
P1	0.1949(2)	0.3636(1)	0.0377(1)	0.0160
P2	0.3813(2)	0.2196(2)	0.3381(1)	0.0204
C1	−0.1758(7)	0.1545(6)	0.0335(5)	0.0257
C2	−0.1230(8)	0.1053(7)	-0.0292(6)	0.0281
C3	−0.0927(8)	0.1703(7)	-0.0938(6)	0.0334
C4	−0.1293(8)	0.2597(8)	-0.0739(7)	0.0376
C5	−0.1858(7)	0.2470(6)	0.0018(6)	0.0302
C6	0.206(1)	0.8307(8)	0.3649(7)	0.0486
C7	0.069(1)	0.812(1)	0.3521(9)	0.0731
C8	0.036(1)	0.765(1)	0.4378(8)	0.0689
C9	0.128(1)	0.716(1)	0.461(1)	0.0884
C11	0.2707(6)	0.4914(5)	0.1173(5)	0.0187
C12	0.2238(8)	0.5087(6)	0.1948(5)	0.0240
C13	0.2801(9)	0.6046(6)	0.2553(6)	0.0306
C14	0.384(1)	0.6835(8)	0.2381(7)	0.0340
C15	0.4303(8)	0.6691(6)	0.1616(6)	0.0295
C16	0.3741(7)	0.5731(6)	0.1011(6)	0.0255
C21	0.3176(6)	0.3019(5)	0.0490(5)	0.0195
C22	0.2769(7)	0.1971(6)	0.0040(6)	0.0265
C23	0.3651(8)	0.1464(7)	0.0049(6)	0.0318
C24	0.4933(8)	0.1973(7)	0.0519(6)	0.0319
C25	0.5342(8)	0.3002(7)	0.0991(6)	0.0312
C26	0.4472(7)	0.3527(6)	0.0970(5)	0.0233
C31	0.1929(6)	0.4077(6)	−0.0768(5)	0.0200
C32	0.1266(7)	0.4758(6)	−0.1012(6)	0.0270
C33	0.1212(8)	0.5099(7)	−0.1877(6)	0.0349
C34	0.1816(9)	0.4761(8)	−0.2498(6)	0.0409
C35	0.245(1)	0.4097(9)	−0.2264(7)	0.0449
C36	0.2510(8)	0.3755(7)	−0.1406(6)	0.0315
C41	0.4605(7)	0.1439(6)	0.2839(5)	0.0211
C42	0.3822(8)	0.0434(6)	0.2326(5)	0.0274
C43	0.4368(9)	−0.0195(7)	0.1921(6)	0.0312
C44	0.5697(9)	0.0152(7)	0.2039(6)	0.0327
C45	0.6488(8)	0.1141(7)	0.2537(6)	0.0305
C46	0.5938(8)	0.1781(7)	0.2934(5)	0.0269
C51	0.3378(7)	0.1554(5)	0.4345(5)	0.0213
C52	0.4226(8)	0.1172(6)	0.4916(5)	0.0254
C53	0.3899(8)	0.0713(6)	0.5676(6)	0.0305
C54	0.2738(9)	0.0631(7)	0.5881(6)	0.0356
C55	0.1884(9)	0.0998(8)	0.5317(6)	0.0381
C56	0.2203(8)	0.1453(7)	0.4560(6)	0.0286
C61	0.4975(7)	0.3512(6)	0.3862(5)	0.0222
C62	0.6067(7)	0.3687(6)	0.4582(5)	0.0254
C63	0.6926(9)	0.4712(7)	0.4939(6)	0.0323
C64	0.6682(9)	0.5561(7)	0.4601(6)	0.0332
C65	0.5602(9)	0.5400(7)	0.3908(7)	0.0347
C66	0.4741(8)	0.4376(7)	0.3527(6)	0.0296
O1	0.2653(5)	0.2240(5)	0.2700(4)	0.0297
O2	0.2388(7)	0.7669(7)	0.4294(5)	0.0613

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

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

Distances

In1−Ni1	244.65(9)	In1−O1	217.0(5)	P1−Ni1	211.2(2)
In1−Br1	255.7(1)	In1−Br2	255.4(1)	P2−O1	149.8(5)

Angles

Br1−In1−Br2	99.51(4)	Br1−In1−Ni1	117.06(4)
In1−Ni1−P1	98.73(6)		
Br1−In1−O1	96.4(1)	Br2−In1−Ni1	117.50(4)
P2−O1−In1	165.0(3)		
Br2−In1−O1	95.7(1)	O1−In1−Ni1	125.4(1)

performed on a Micro VAX 3100 computer with the STRUX-IV system,[21] including the programs CRYSTALS, MULTAN 11/82, ORTEP-II, PLATON, PLUTON, SCHAKAL, SDP, and SHELX-86. The structure was solved by heavy-atom methods and subsequent difference Fourier techniques. Final positional parameters are given in Table 2, selected bond angles and distances in Table 3. The refinements stopped at shift/err < 0.0001, and final difference Fourier maps showed no significant features. Supplementary material 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, on quoting the depository number CSD-59209, the names of the authors, and the journal citation.

Results and Discussion

A. Synthesis and Properties. The treatment of a deep wine red solution of Cp(PPh$_3$)Ni−Br (**1a**) in dichloromethane with an equimolar amount of freshly sublimed and finely powdered In^{I}Br at room temperature for 12 h gave a dark red-brown solution over a precipitate of unidentified insoluble side products. Prolonged stirring over several days at room temperature did not change the reaction mixture any further. From the filtrated and concentrated solution, well-shaped large green-black crystals of the ionic compound **2a** could be grown by slow solvent diffusion techniques in ca. 30% yield (based upon indium; Scheme 2). Other conditions, like different solvents such as tetrahydrofuran or toluene and various reaction temperatures from dry ice to room temperature or a large excess of In^{I}Br, did altogether not change the result. The trimethylphosphane-substituted analogue of **1a**, Cp(Me$_3$P)NiBr (**1b**), gave similar results when treated with In^{I}Br (Scheme 2). Compound **2a** was independently synthesized in 90% yield from **1a** by addition of equimolar quantities of PPh$_3$ and InBr$_3$ in dichloromethane. This latter reaction is simply a ligand substitution reaction at the nickel center, which is thermodynamically controlled (HSAB principle).

Apparently In(I) is oxidized to In(III) during the interaction of **1a**,**b** with In^{I}Br. A redox disproportionation of In(I) into In(0) and In(III) or reduction of the Ni(II) center could be involved. The reaction medium was checked for organic redox products, e.g., cyclopentadienyl coupling products, free PPh$_3$, nickelocene and other possible products (phenyl derivatives which could arise by some degradation of the PPh$_3$ ligand, e.g., P−C bond splitting), which were, however, not detected by GC-

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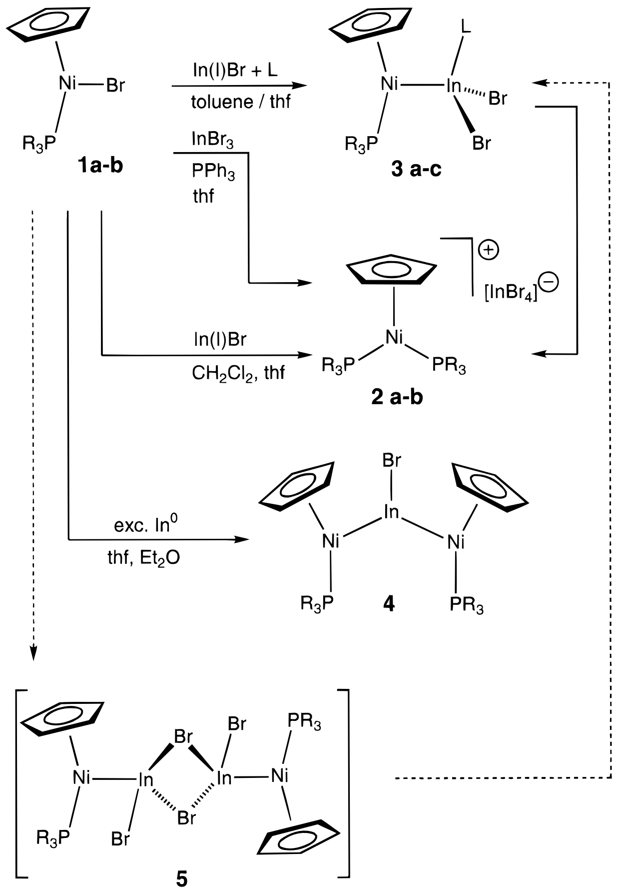
Scheme 2



MS and NMR. The insoluble residue showed a Ni:In ratio of 1:1 by elemental analysis. On the basis of the mass balance and the elemental analysis, we suggest that the insoluble fraction of the reaction mixture consists of a Ni/In cluster compound. As expected, **2a** also forms from 2 equiv of **1a** with $InBr_3$ in nearly quantitative yield (based upon indium). In this reaction an insoluble, nickel-containing residue was obtained again. This latter reaction is similar to the reaction of **1a** with $(Ph_3P)InBr_3$ mentioned above.

The reaction system **1a**,**b** with In^IBr proved to be rather complex and did not give easily the Ni−In bonded insertion products as desired (Scheme 1). However, by addition of exactly 1 equiv of $Ph_3P{=}O$ to a mixture of **1a** and In^IBr in a solvent mixture of toluene/tetrahydrofuran (10:1 vol parts) the Ni−In complex **3a** was obtained reproducibly and quantitatively as well shaped large crystals (Scheme 2). The type of the added Lewis base is crucial for the success of the synthesis. With quinuclidine the corresponding derivative **3c** was obtained also. Tetrahydrofuran, however, only gave traces of the Ni−In insertion compound as juged from the ^{31}P-NMR spectra of the reaction solution. With weaker donors and other solvent mixtures the ionic complex **2a** always was the dominant product. Interestingly, the phosphanoxide ligand of **3a** could not be replaced by another strong σ-donors, e.g., quinuclidine, as was indicated by the unchanged ^{31}P NMR spectra of the reaction solutions. The treatment of **1a** with 1 equiv PPh_3 and In^IBr under the same conditions employed for the synthesis of **3a** and **3c** did also give an analogous Ni−In complex **3b**. But this material proved to be less stable in solution, compared to **3a** and **3c**. The green solutions of **3b,** especially in dichloromethane, but also in toluene, change color to yellow−brown upon standing for several hours, which is accompanied by the formation of an insoluble precipitate. The ionic compound **2a** was identified in these cases by NMR as the major component (≤60−70%, by ^{31}P NMR) in solution. To explain the complex reaction system we suggest, that in the first step In^IBr (formally) inserts into the Ni−Br bond of **1a-b**, giving some intermediate of the type **5**, which has much literature precedence in the case of carbonyl complexes.[7, 9] Depending on the conditions and especially on the presence of other Lewis-basic ligands L, subsequent reactions involve transfer of the phosphane ligand and the bromine residues to build the products **2a**,**b**. In the case of $Ph_3P{=}O$ or quinuclidine as base ligand to stabilize the indium center, a similar ligand transfer of the rather hard base to the soft nickel center is not likely. For example, there is no organometallic nickel compound known which bears a $Ph_3P{=}O$ ligand. But there are several examples of transition metal indium compounds with a $Ph_3P{=}O$ ligand coordinated at the indium center, e.g., $(Ph_3P{=}O)In[Co(CO)_4]_3$ or $(Ph_3P{=}O)In[Co(CO)_3(PPh_3)]_3$.[22] The Lewis-base donor properties of $Ph_3P{=}O$ have been thoroughly studied by N. Burford et al.[23]

As mentioned above, elemental In(0) could be involved in the reaction system. We thus studied the interaction of elemental indium with **1a**,**b**. When a solution of **1a** in diethyl ether/tetrahydrofuran was treated with an excess of indium powder over several days at room temperature, the indium-bridged heteronuclear complex **4** was obtained after workup in ca. 50% yield based upon nickel (Scheme 2). This reaction can be rationalized in the following way. Reductive dehalogenation of **1a** in the presence of excess In(0) may give the tetranuclear species $[Cp(PPh_3)Ni]_3In$ (**5**) and $InBr_3$, which subsequently undergo ligand exchange reactions to give the product **4**. This latter type of reactivity is rather typical for $[L_nM]_3In$ complexes.[7,9] Another possibility would be that indium first inserts into the Ni−Br bond giving an unstable In(II) intermediate. Disproportionation then gives the In(III) species **4** and insoluble In^IBr. This reaction scheme is comparable to the formation of $Cp(PPh_3)Ni{-}MgBr(THF)$ from **1a** and elemental Mg reported by Felkin and Knowles.[24] Wilke et al. have recently shown, that $Cp(PEt_3)Ni{-}Cl$ is reductively dechlorinated by activated Mg to the dimer $[Cp(PEt_3)Ni]_2$. This nickel dimer contains a very reactive Ni−Ni bond into which $SnCl_2$ rapidly inserts to give $(\mu^2\text{-}SnCl_2)[Cp(PEt_3)Ni]_2$.[25] We could, however, not isolate the corresponding Ni−Ni intermediates $[Cp(PR_3)Ni]_2$ from our reaction solutions. With **1b** instead of **1a**, the reaction with elemental indium was surprisingly different. A toluene insoluble new Ni and In containing product of apparently ionic character was obtained, which is currently under investigation.

In the reaction systems of **1a**,**b** with In^IBr to give **2a**,**b** or **3**, depending on the conditions, neither **4** nor **5** were isolated from the reaction solutions. Traces of **4** however, could be identified by NMR.

B. ^{31}P NMR Spectroscopic Characterization of 3a−c and 4. The $\{^1H\}^{31}P$ NMR signals of the triphenylphosphane ligand in the complexes of the general formula $Cp(PPh_3)Ni{-}X$ (X = Cl, Br, I) show a high-field shift with increasing electronegativity of X. This effect was explained by the increasing covalent radii of X in the series.[26] With X = $InBr_n$ (n = 1, 2) π-donor effects of the indium moiety can be ruled out. The indium

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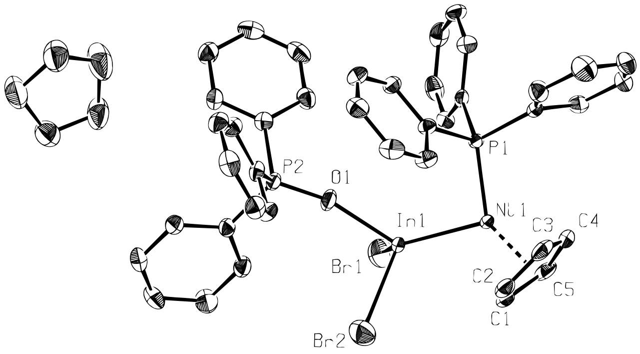

Figure 1. Molecular structure of (η^5-C_5H_5)(Ph_3P)Ni−$InBr_2$($OPPh_3$)·THF (**3a**) in the solid state (PLUTON drawing; hydrogen atoms are omitted for clarity; thermal ellipsoids of non-hydrogen atoms are shown at 50% probability).

substituent may exhibit significant π-acceptor properties which may be due to some Ni(d_π) > σ^*(In-Br) hyperconjugative backbonding. A low-field shift of the resonance for **3a**,**b** and **4** relative to the starting complex **1a** is thus understandable. For **3a**,**b** it has to be decided which of the two ^{31}P resonances corresponds to which phosphorus ligand. By comparison of **4**, which shows a ^{31}P resonance at 43.8 ppm, with an authentic sample of $InBr_3(O{=}PPh_3)$, which exhibits a resonance at 37.6 ppm, and with the **3c** (45.6 ppm), it appears quite clear to assign the resonance at 48.6 ppm of **3a** to the PPh_3 ligand bound to the nickel center and the resonance at 36.0 ppm to the $InBr_2$($O{=}PPh_3$) moiety.

C. Structure. Compound **3a** was structurally characterized by X-ray single-crystal diffraction. The positional parameters and selected bond lengths and angles are compiled in Tables 2 and 3. Figure 1 shows the molecular structure of **3a** in the solid state.

The structure solution of **3a** confirms the presence of a direct unsupported Ni−In bond. The complex Cp(CO)Ni−In[$(CH_2)_3$-NMe_2]$_2$ (**6**) [16] and **3a** are the only structurally characterized examples of this kind of transition metal main group metal bonds to date. The structure also confirms the coordination of the $O{=}PPh_3$ ligand at the indium center. Interestingly, the tetrahydrofuran molecule which is included into the crystal upon crystallization out of toluene/tetrahydrofuran mixtures is not coordinated to the indium center. (If dichloromethane is also a constituent of the solvent mixture then it is incorporated into the crystal lattice, too.) The indium center is nearly tetrahedrally coordinated. The sum of the six angles around the indium is 651.6°, which is close to the ideal value of 657.12°. The coordination geometry at the nickel atom can be described as distorted trigonal planar, if one counts the cyclopentadienyl ligand as one coordination site. The angle In(1)−Ni(1)−P(1) of 98.73(6)° is significantly larger than the corresponding angle (OC)−Ni−In of **7**, which amounts to 78.1(1)° and is, within the accuracy of the measurements, closely similar to the value of 100.69(7)° measured for Cp(Ph_3P)Ni−$GeCl_3$.[27] These angles indirectly show the somewhat different electronic situations at the bent d^{10}-[$CpNiL^-$] fragment for ligands L of different π-acceptor capabilities. The charge polarization of **7** should be more pronounced than for **3a**.[16] The increased stability of the Ni−In bond of **3a** against polar attack, for example toward hydrolysis, agrees with this view. The most significant difference between **3a** and **7** is the much shorter Ni−In bond of 244.65(9) pm of **3a** compared with the value of 259.8(1) pm of the dialkyl derivative **7**. The latter distance corresponds well with the sum of the covalent radii of Ni and In (258 ± 5 pm), the Ni−In distances in intermetallic alloys (262−265 pm),[28a] and the range of Ni−In distances from 257.4(4) to 280.9(4) pm found in Ni/In cluster compounds such as $[Ni_6(\mu^3\text{-}InBr_3)(\eta^2\text{-}\mu^6\text{-}In_6Br_5)(CO)_{11}]^{3-}$ (**8**).[28b] However in these systems the coordination numbers of the indium atom are five (**7**) and six (**8**), respectively. Consequently, the Ni−In distances are longer than in **3a**, which is only fourfold coordinated. Generally, short σ-bonds between transition metal fragments and fourfold-coordinated indium or gallium fragments result, if the transition metal acts as a strong σ/π-donor, e.g., bears few or only weak π-accepting ligands, and/or the group 13 center is substituted by electronegative ligands (halide groups or amide-type functions).[31] The In−O bond length of 217.0(5) pm is expectedly within the range of rather strong dative In−O bonds.[32] The angle In-O-P is close to 180°. The Ni−P bond length of **3a** of 211.2(2) pm is comparable to the value of 215.2(2) pm of Cp(PPh_3)Ni−$GeCl_3$,[27] for example.

Conclusions

Elemental indium and indium(I) halides insert into nickel halogen bonds of carbonyl group free organonickel complexes. The success of these strategy to synthesize Ni−In bound species in acceptable yields depends strongly on the reaction conditions, such as the solvent mixture and the presence and type of added Lewis base ligands to stabilize the formed In(III) center.

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Supporting Information Available: Tables giving positional parameters, calculated hydrogen positions, anisotropic thermal parameters, bond lengths and bond angles (10 pages). Ordering information is given on any current masthead page.

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