Two Types of Intramolecular Lewis-Base Adducts with the [2-(Dimethylamino)ethyl]cyclopentadienyl Ligand: Synthesis and Crystal Structures of {η^5:η^1-$C_5H_4[(CH_2)_2NMe_2]$}Ni−I and {η^5-μ-$C_5H_4[(CH_2)_2NMe_2]$}(Me_3P)Ni−InI_2[†,‡]

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The synthesis and reactivity of nickel complexes with the [2-(dimethylamino)ethyl]-cyclopentadienyl ligand (Cp^N) are described. The reaction of $NiBr_2$ with Cp^NLi leads to the new paramagnetic nickelocene derivative $(Cp^N)_2Ni$ (**1**), which has been characterized by ^1H and ^{13}C NMR, elemental analysis, and mass spectroscopy. Synproportionation of this complex with $Ni(CO)_4$ affords quantitatively the dimeric nickel complex $[Cp^N(CO)Ni]_2$ (**2**). Reductive cleavage of **2** with KC_8 and trapping of the anionic intermediate with Me_3SnCl gives the stannyl−nickel complex $Cp^N(CO)Ni-SnMe_3$ (**4**). Reaction of **2** with Ga_2Cl_4 yields the gallium−nickel complex (η^5-μ-Cp^N)(CO)Ni-$GaCl_2$ (**7**) with intramolecular coordination of the dimethylamino group to the gallium center. Oxidative cleavage of **2** with iodine and liberation of CO leads to the intramolecular chelate (η^5:η^1-Cp^N)Ni−I (**3**). The compounds (η^5-μ-Cp^N)(PR_3)Ni−InI_2 with R = C_6H_5 (**5**) and CH_3 (**6**) are obtained in good yields by insertion of low-valent indium halides InX (X = Br, I) into the Ni−I bond of **3**. X-ray diffraction determinations were carried out for **3** and **6**, and for **6**, a comparably short Ni−In distance of 241.80(7) pm was found.

Introduction

The coordination chemistry of functionalized cyclopentadienyl ligands was recently enriched by the introduction of the (dimethylamino)ethyl group at the Cp ring.[1] Jutzi et al. have been studying a number of metal complexes bearing this Lewis base functionalized ligand and its tetramethyl ring-substituted derivative in detail.[2] The benefit of such a ligand, capable of stabilizing both soft and hard metal centers by intramolecular adduct formation, was demonstrated. Our interest is particularly directed toward so-called "all hydrocarbon"[3] (i.e. carbonyl group free) and volatile mixed-metal compounds. Such compounds may be suitable as alternative precursors for organometallic chemical vapor deposition (OMCVD) of the respective mixed-metal thin films. Metallic alloys of selected combinations of group 13 elements with d metals, especially with nickel, e.g. NiGa[4a] and NiIn,[4b] may be of interest as metal contacts to III/V semiconductor surfaces.[4c,d] CO ligands may cause problems in deriving C- and O-free, very pure metallic alloys from organometallic sources if oxophilic and/or carbide-forming metals are involved.[3] We were therefore led to investigate some organonickel complexes with the N-donor functionalized [2-(dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N) and their chemistry with group 13 halides, aiming at novel intramolecular adduct stabilized "CO free" (mixed) metal compounds, which might be suitable for OMCVD studies.

Experimental Section

General Data. All manipulations were undertaken utilizing standard Schlenk and glovebox techniques under an 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). The NMR spectra of a saturated solution of *paramagnetic* **1** in C_6D_6 were recorded on a Bruker MSL 300 NMR spectrometer operating in the low-power mode and equipped with a conventional 5 mm $^1H/^{13}C$ dual probehead. Measurement frequencies of 300 (^1H) and 75.5 (^{13}C) MHz were applied. A dead-time delay of 10 μs and a pulse repetition time of 200

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ms were integrated within the single pulse sequence. The line widths $\nu_{1/2}$ at half height of the signals were obtained by the deconvolution routine of the Bruker Winnmr program. For the numbering of ^{1}H and ^{13}C nuclei, see Figure 1. JEOL JNM-GX400 and JNM-GX270 spectrometers and standard data collection parameters were used for the NMR spectroscopy of the *diamagnetic* compounds **2**−**8** (^{1}H and ^{13}C NMR spectra were referenced to internal solvent and corrected to TMS). All *J* values are reported in Hz. All samples for NMR spectra were kept 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 ^{127}I, and normal isotope distribution was observed. The starting compounds were prepared as described in the literature. Abbreviations are as follows: Cp^N = η^5-$C_5H_4(CH_2CH_2NMe_2)$, Me = CH_3, Ph = C_6H_5. Elemental analyses were provided by the Microanalytic Laboratory of the Technical University of Munich.

Synthesis of Bis{[2-(dimethylamino)ethyl]cyclopentadienyl}nickel(II) (1). A cold THF suspension of 2.18 g (10 mmol) of $NiBr_2$ was added to a stirred solution (THF/*n*-hexane) of Cp^{N}Li (20 mmol) at −78 °C, which was obtained from reaction of 1.6 M *n*-BuLi (12.5 mL, 20 mmol) with $C_5H_5[CH_2CH_2N(CH_3)_2]$ (Cp^{N}H; 2.74 g, 20 mmol). The resulting mixture was warmed to room temperature and stirred for 2 h. After evaporation of the solvent, the residue was extracted with toluene and the crude product was purified by microdistillation at 120 °C (10^{-3} Torr, dynamic vacuum, "flask to flask"). Compound **1** was obtained as a green oil, yield 5.3 g (80%). ^{1}H NMR (300.0 MHz, C_6D_6, 25 °C): δ (^{1}H) {$\nu_{1/2}$ [Hz]} −250.1 {820} (H_b and H_c, C_5H_4); 5.2 {47} (6H, NCH_3); 6.4 {59} (2H, H_β, NCH_2CH$_2$); 187.8 {305} (2H, H_α, NCH$_2$CH_2). ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): δ (^{13}C) {$\nu_{1/2}$ [kHz]} = −557.8 {0.39} (C_α, NCH$_2$CH$_2$); 68.8 {0.17} (NCH$_3$); 691.1 {0.46} (C_β, NCH$_2$CH$_2$); 1426 {5.4} (C_b, C_5H_4); 1567 {5.6} (C_c, C_5H_4); 1642 {5.6} (C_a, C_5H_4). MS (CI): *m*/*z* (%) 330 (0.7) [M$^+$], 136 (1.4) [Cp^{N+}], 58 (100) [$CH_2N(CH_3)_2^+$]. Anal. Calcd for $C_{18}H_{28}N_2Ni$: C, 65.42; H, 8.55; N, 8.48; Ni, 17.55. Found: C, 65.73; H, 8.66; N, 8.60; Ni, 17.43.

Synthesis of Bis[carbonyl{[2-(dimethylamino)ethyl]cyclopentadienyl}nickel(I)] (2). **Method a.** A toluene solution of 1.32 g (4 mmol) of **1** and $Ni(CO)_4$ (1.1 mL, 8 mmol) was heated at 80 °C for 1 h. After evaporation of the solvent, the residue was extracted with *n*-pentane. The nickel carbonyl dimer **2** was obtained quantitatively as a deep red oil, yield 1.75 g (98%).

Method b. At −35 °C $Ni(CO)_4$ (3.5 mL in 15 mL of THF) was added to a solution of Cp^{N}Li, which was obtained from reaction of 1.6 M *n*-BuLi (12 mL, 14.6 mmol) with $C_5H_4[CH_2CH_2N(CH_3)_2]$ (Cp^{N}H; 2.00 g, 14.6 mmol at −78 °C) in 100 mL of THF. The resulting mixture was warmed to room temperature and was heated to reflux for 14 h. At room temperature CuCl (1.45 g, 14.6 mmol) was added, and the mixture was heated to reflux again for 2 h. After evaporation of the solvent, the residue was extracted with *n*-pentane. The nickel carbonyl dimer **2** was obtained as a deep red oil, yield 3.25 g (50%). ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ 2.10 (s, 12H, NCH_3); 2.39−2.41 (2 × m, br, 4 × 4H, NCH_2CH_2); 5.11 (br, 4H, C$_5H_4$); 5.19 (br, 4H, C$_5H_5$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 25.2 (NCH$_2$CH$_2$); 46.3 (NCH$_3$); 59.8 (NCH$_2$CH$_2$); 93.3−94.1 (C_5H_4); 109.2 (C_{ipso} of C_5H_4); 228.3 (CO). IR (*n*-pentane): 1888, 1846 cm^{-1} (ν(CO)). MS (CI): *m*/*z* (%) 445 (not detected) [M$^+$], 389 (5) [M$^+$ − 2(CO)], 388 (24) [Cp$^N_2$Ni$_2^+$], 330 (100) [M$^+$ − Ni(CO)$_2$], 222 (42) [Cp^N(CO)Ni$^+$], 194 (2) [Cp^{N}Ni$^+$], 136 (1) [Cp^{N+}]. Anal. Calcd for $C_{20}H_{28}N_2Ni_2O_2$: C, 53.88; H, 6.33; N, 6.28; Ni, 26.33. Found: C, 54.36; H, 6.52; N, 6.42; Ni, 25.51.

Synthesis of {η^5:η^1-[2-(Dimethylamino)ethyl]cyclopentadienyl}iodonickel(II) (3). A THF solution (20 mL) of 1.02 g (4 mmol) of I_2 was added at −78 °C over a period of 30 min to a stirred THF solution of **2** (1.8 g, 4 mmol). The resulting mixture was warmed to room temperature and stirred for 2 h. After evaporation of the solvent, the residue was washed with 15 mL of *n*-pentane and extracted with toluene. The crude product was purified by crystallization at −30 °C. Complex **3** was obtained as analytically pure brown-violet crystals in 85% yield (2.2 g). ^{1}H NMR (399.78 MHz, CD_2Cl_2, 25 °C): δ 0.42 (m, br, 2H, NCH$_2$CH_2); 2.51 (s, 6H, NCH_3); 3.39 (m, br, 2H, NCH_2CH$_2$); 5.26−5.31 (2 × br, 2 × 2H, C$_5H_4$). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 10.07 (NCH$_2$CH$_2$); 20.3 (NCH$_3$); 70.3 (NCH$_2$CH$_2$); 124.1 (C_{ipso} of C_5H_4); 127.0−127.8 (C_5H_4). MS (CI): *m*/*z* (%) 321 (51) [M$^+$], 194 (48) [M$^+$ − I], 136 (4) [Cp^{N+}]. Anal. Calcd for C_9H_{14}INNi: C, 33.60; H, 4.38; N, 4.35; I, 39.45; Ni, 18.22. Found: C, 34.00; H, 4.45; N, 4.33; I, 38.85; Ni, 18.92.

Synthesis of {η^5-[2-(Dimethylamino)ethyl]cyclopentadienyl}(trimethylstannyl)nickel(II) (4). A THF solution (20 mL) of **2** (0.891 g, 2 mmol) was added to a stirred THF suspension of C_8K (0.540 g, 4 mmol) at −78 °C. The resulting mixture was warmed to room temperature and stirred for 10 min. After the resulting orange solution was cooled to −78 °C, a solution of Me_3SnCl (0.797 g, 4 mmol) in 15 mL of THF was added. The stirred mixture was warmed to room temperature over the course of 1 h. After evaporation of the solvent, the residue was extracted with *n*-pentane. Product **4** was obtained as a yellow-orange oil, yield 1.392 g (90%). ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ 0.46 (s, 9H, SnCH_3); 2.08 (s, 6H, NCH_3); 2.36−2.38 (2 × m, br, 2 × 2H, NCH_2CH_2); 4.72−5.10 (2 × m, br; 2 × 2H, C$_5H_4$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ −2.4 (SnCH$_3$); 28.9 (NCH$_2$CH$_2$); 45.5 (NCH$_3$); 61.1 (NCH$_2$CH$_2$); 85.9−102.1 (C_5H_4); 115.2 (C_{ipso} of C_5H_4). ^{119}Sn{^{1}H} NMR (C_6D_6, 25 °C): δ 107.7. IR (*n*-pentane): 1996 cm^{-1} (ν(CO)). MS (CI): *m*/*z* (%) 387 (67.8) [M$^+$], 388 (24) [Cp$^N_2$Ni$_2^+$], 359 (100) [M$^+$ − CO], 222 (6.33) [M$^+$ − SnMe$_3$], 136 (4) [Cp^{N+}]. Anal. Calcd for $C_{13}H_{23}$NNiOSn: C, 40.37; H, 5.99; N, 3.62; Ni, 15.18. Found: C, 41.13; H, 5.42; N, 3.77; Ni, 14.85.

Synthesis of {η^5-μ-[2-(Dimethylamino)ethyl]cyclopentadienyl}(triphenylphosphino)(diiodoindio)nickel(II) (5) and {η^5-μ-[2-(Dimethylamino)ethyl]cyclopentadienyl}(trimethylphosphino)(diiodoindio)nickel(II) (6). A sample of **3** (0.322 g, 1 mmol), freshly sublimed InBr (0.195 g, 1 mmol), and triphenylphosphine (0.262 g, 1 mmol) were suspended in 20 mL of THF at −78 °C. The brown-violet suspension turned immediately red to give the intermediate {η^5-[2-(dimethylamino)ethyl]cyclopentadienyl}(triphenylphosphino)iodonickel(II) (see Scheme 1). The resulting mixture was warmed to room temperature and stirred for another 3 h. A sample of NaI (0.300 g, 2 mmol) was added to the resulting yellow-green solution. The reaction mixture was stirred for another 2 h, and the solvent was removed in vacuo. The residue was washed with 15 mL of *n*-pentane and extracted with toluene. The crude product was purified by crystallization in toluene at −30 °C. Compound **5** was obtained as yellow-green crystals in 85% yield (0.70 g). The preparation of **6** was analogous to that for **5**. Complex **6** was obtained with 90% yield as dark green crystals.

Characterization data for **5** are as follows. ^{1}H NMR (399.78 MHz, CD_2Cl_2, 25 °C): δ 2.57 (s, 6H, NCH_3), 2.62 (AA′BB′, 2H, NCH$_2$CH_2); 2.93 (AA′BB′, 2H, NCH_2CH$_2$); 4.83 (br, 2H, C$_5H_4$); 5.30 (br, 2H, C$_5H_4$); 7.36−7.61 (m, 15H, PPh$_3$). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 25 °C): δ 24.2 (NCH$_2$CH$_2$); 46.8 (NCH$_3$); 57.0 (NCH$_2$CH$_2$); 90.6 (C_5H_4); 92.4 (C_{ipso} of C_5H_4); 93.0 (C_5H_4); 128.3−136.0 (Ph). ^{31}P{^{1}H} NMR (169.9 MHz, CD_2Cl_2, 25 °C, H_3PO_4 ext.): δ 48.7 (PPh$_3$). MS (CI): *m*/*z* (%) 825 (not detected) [M$^+$], 583 (2.8) [M$^+$ − InI], 456 (12) [M$^+$ − InI$_2$], 369 (4.8) [InI$_2^+$], 321 (12.3) [M$^+$ − {In(I)(PPh$_3$)}], 263 (100) [Ph$_3$PH$^+$], 262 (30.4) [Ph$_3$P$^+$], 136 (2) [Cp^{N+}]. Anal. Calcd for $C_{27}H_{29}I_2$InNNiP: C, 39.24; H, 3.54; N, 1.69; I, 30.74; Ni, 7.11; In, 13.90. Found: C, 38.76; H, 3.55; N, 1.56; I, 30.27; Ni, 6.97; In, 13.10.

Characterization data for **6** are as follows. ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): δ 1.01 (d, $^2J_{H-P}$ = 9.3 Hz, 9H, P(CH_3)$_3$); 1.85 (AA′BB′, 2H, NCH$_2$CH_2); 2.07 (AA′BB′, 2H, NCH_2CH$_2$); 2.18 (s, 6H, NCH_3); 4.90 (m, 2H, C$_5H_4$); 5.00 (m, 2H, C$_5H_4$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 21.0 (d, $^1J_{C-P}$ = 31.2 Hz, P(CH$_3$)$_3$); 24.2 (CH$_2$CH$_2$N); 45.9 (NCH$_3$); 55.9

Table 1. Crystallographic Data for Compounds 3 and 6

	3	6
formula	$C_9H_{14}INNi$	$C_{12}H_{23}I_2InNNiP$
fw	321.8	705.9
cryst color, habit	brown-violet, prism	dark green, column
cryst syst	orthorhombic	orthorhombic
space group	*Pbca* (No. 61)	$P2_12_12_1$ (No. 19)
cryst dimens, mm	0.23 × 0.15 × 0.15	0.32 × 0.32 × 0.24
temp, K	303 ± 1	233 ± 1
a, pm	900.0(1)	928.2(1)
b, pm	1320.6(1)	978.9(1)
c, pm	1891.3(1)	2119.5(2)
V, 10^6 pm^3	2247.9(3)	1925.8(3)
Z	8	4
d_{calcd}, g cm^{-3}	1.902	2.206
μ(Mo Kα), cm^{-1}	44.2	54.5
scan type, mode	image plate, oscillation	image plate, rotation
scan time, s	120 per image	120 per image
θ_{max}, deg; octants	25.1; $\pm h,\pm k,\pm l$	24.9; $\pm h,\pm k,\pm l$
corrections	Lp	Lp; abs
no. of rflns collctd	27224	24201
$R_{(merge)}$	0.032 (F_o^2)	0.032 (F_o^2)
no. of unique data	1864	3096
no. of rflns included (NV)	1864	3096
no. of variables (NO)	109	255
data:variable ratio	17.1	12.1
R1[a]	0.0565	0.0188
wR2[a]	0.1117	0.0449
GOF[a]	0.953	1.164
Flack param	−0.02(2)	
largest shift/error	<0.005	<0.001
max/min resid electron dens, e Å^{-3}	+2.38/−0.81	+0.43/−0.52
weighting scheme	SHELXL (0.0715; 0.00)	SHELXL (0.0147; 3.18)

[a] $R1 = \sum||F_o| - F_c|/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, and $GOF = [\sum w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$.

(CH_2CH_2N); 89.4−89.6 (C_5H_4), 91.2 (C_{ipso} of C_5H_4). $^{31}P\{^1H\}$ NMR (169.9 MHz, C_6D_6, 25 °C, H_3PO_4 ext.): δ −12.4 (PMe_3). MS (CI): *m/z* (%) 639 (not detected) [M^+], 321 (3.3) [M^+ − {In(I)PMe_3}], 136 (100) [Cp^{N+}]. Anal. Calcd for $C_{12}H_{23}I_2InNNiP$: C, 22.53; H, 3.62; N, 2.18; I, 39.68; Ni, 9.17; In, 17.95. Found: C, 21.53; H, 3.42; N, 1.98; I, 38.24; Ni, 8.88; In, 17.4.

Synthesis of Carbonyl{η^5-μ-[2-(dimethylamino)ethyl]cyclopentadienyl}(dichlorogallio)nickel(II) (7). A THF solution (20 mL) of **2** (0.892 g, 2 mmol) was added at −78 °C to a stirred THF solution of 0.844 g (3 mmol) of Ga_2Cl_4. The resulting mixture was warmed to room temperature, and stirred for 3 days. After evaporation of the solvent, the residue was extracted with toluene. The crude product could be purified by crystallization at −30 °C. Compound **7** was obtained as orange crystals in 50% yield (0.727 g). ^1H NMR (399.78 MHz, C_6D_6, 25 °C): δ 1.61 (AA′BB′, 2H, NCH_2CH_2); 1.95 (AA′BB′, 2H, NCH_2CH_2); 1.98 (s, 6H, NCH_3), 4.79 (t, $^3J_{H-H}$ = 2.2 Hz, 2H, C_5H_4); 5.20 (t, $^3J_{H-H}$ = 2.2 Hz, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ 22.8 (CH_2CH_2N); 44.1 (NCH_3); 55.5 (CH_2CH_2N); 89.6−92.0 (C_5H_4), 93.3 (C_{ipso} of C_5H_4). IR (toluene): 2012.8 cm^{-1} (ν(CO)). MS (CI): *m/z* (%) 363 (1) [M^+], 141 (100) [$GaCl_2^+$]. Anal. Calcd for $C_{10}H_{14}Cl_2GaNNiO$: C, 33.03; H, 3.88; N, 3.85; Ga, 19.17; Cl, 19.50; Ni, 16.14. Found: C, 33.26; H, 3.84; N, 3.60; Ga, 19.3; Cl, 19.39; Ni, 15.19.

X-ray Single Crystal Structure Determination of {η^5:η^1-[2-(Dimethylamino)ethyl]cyclopentadienyl}iodonickel(II) (3). Suitable crystals were grown by slow solvent diffusion techniques from toluene/*n*-pentane mixtures at −30 °C. Crystal data together with details of the data collection and structure refinement are listed in Table 1. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (ENRAF-Nonius FR591; 50 kV; 60 mA; 3.0 kW) and graphite-monochromated Mo Kα radiation. The data collection was performed at 303 ± 1 K within the θ range of 1.6° < θ < 25.1° with an exposure time of 2 min per image (oscillating scan modus for φ = 0.0−150.0° and φ = 160−360° with $\Delta\varphi$ = 1°). A total number of 27 224 reflections were collected, from which a sum of 1864 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for intensity decay, absorption μ = 44.2 cm^{-1}, and extinction were not necessary and were not applied. The unit cell parameters were obtained by least-squares refinements of 1571 reflections with the program Cell.[5,6] The structure was solved with direct methods and difference Fourier syntheses.[7,8] All 12 "heavy atoms" of the asymmetric unit were anisotropically refined. All H positions were calculated in ideal geometry riding on the parent carbon atom. The isotropic displacement parameters were kept constant ($U_{iso} = 1.3U_{eq}$(C)). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and stopped at shift/error <0.005: wR2 = 0.1117, and R1 = 0.0565. In the final difference map, the largest peaks, +2.38 and −0.81 e/Å^3, are located around the iodine atom. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 9. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V system,[8] including the programs PLATON-92,[10] PLUTON-92,[10] SIR-92,[7] and SHELX-93.[11] Selected bond lengths and angles are given in Table 2. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-405435, the names of the authors, and the journal citation, or from the author E.H.

Table 2. Selected Bond Distances (pm) and Angles (deg) for Compound 3[a]

I−Ni	250.02(9)	N−C(8)	146.6(8)
Ni−N	196.0(5)	N−C(9)	147.0(8)
Ni−Cp	173.2	C(1)−C(2)	136.8(10)
Ni−C(1)	212.8(6)	C(1)−C(5)	141.1(10)
Ni−C(2)	213.0(5)	C(2)−C(3)	143.3(9)
Ni−C(3)	214.2(7)	C(3)−C(4)	137.2(11)
Ni−C(4)	211.9(7)	C(4)−C(5)	144.1(10)
Ni−C(5)	199.7(7)	C(5)−C(6)	149.2(11)
N−C(7)	151.7(10)	C(6)−C(7)	137.9(14)
I−Ni−N	103.3(2)	C(7)−N−C(8)	104.1(6)
I−Ni−Cp	134.0	C(7)−N−C(9)	111.2(7)
N−Ni−Cp	122.7	C(8)−N−C(9)	109.1(5)
Ni−N−C(7)	107.4(4)	C(5)−C(6)−C(7)	112.1(8)
Ni−N−C(8)	113.3(4)	N−C(7)−C(6)	116.2(8)
Ni−N−C(9)	111.6(4)		

[a] Cp denotes the centre of gravity in the C_5H_4R part of the Cp^N ligand.

X-ray Single Crystal Structure Determination of {η^5-μ-[2-(dimethylamino)ethyl]cyclopentadienyl}(trimethylphosphino)(diiodoindio)nickel(II) (6). Suitable crystals

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(6) Schütt, W.; Herdtweck, E.; Hahn, F.; Kreissl, F. R. *J. Organomet. Chem.* **1993**, *443*, C33 and references cited therein.
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(11) Sheldrick, G. M. *J. Appl. Crystallogr.*, in press; Program SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.

Table 3. Selected Bond Distances (pm) and Angles (deg) for Compound 6[a]

(1)−In	279.82(5)	P−C(2)	182.0(8)
I(2)−In	278.73(6)	P−C(3)	179.6(7)
In−Ni	241.80(7)	N−C(5)	148.2(7)
In−N	233.2(4)	N−C(6)	147.9(8)
Ni−P	211.6(1)	N−C(7)	147.3(8)
Ni−Cp	172.8	C(4)−C(5)	150.7(9)
Ni−C(11)	210.1(4)	C(4)−C(11)	150.0(8)
Ni−C(12)	211.6(6)	C(11)−C(12)	143.5(8)
Ni−C(13)	210.6(7)	C(11)−C(15)	143.4(7)
Ni−C(14)	207.9(6)	C(12)−C(13)	138.7(9)
Ni−C(15)	212.8(5)	C(13)−C(14)	140.7(9)
P−C(1)	181.2(7)	C(14)−C(15)	141.1(8)
I(1)−In−I(2)	98.83(2)	C(1)−P−C(2)	102.0(3)
I(1)−In−Ni	121.64(2)	C(1)−P−C(3)	103.1(3)
I(1)−In−N	99.1(1)	C(2)−P−C(3)	102.6(4)
I(2)−In−Ni	125.93(2)	In−N−C(5)	108.1(3)
I(2)−In−N	96.66(9)	In−N−C(6)	111.5(3)
Ni−In−N	109.1(1)	In−N−C(7)	110.3(3)
In−Ni−P	94.39(4)	C(5)−N−C(6)	108.2(5)
In−Ni−Cp	126.5	C(5)−N−C(7)	110.7(4)
P−Ni−Cp	139.1	C(6)−N−C(7)	108.0(5)
Ni−P−C(1)	119.1(2)	C(5)−C(4)−C(11)	119.5(5)
Ni−P−C(2)	113.3(3)	N−C(5)−C(4)	116.1(5)
Ni−P−C(3)	114.5(2)		

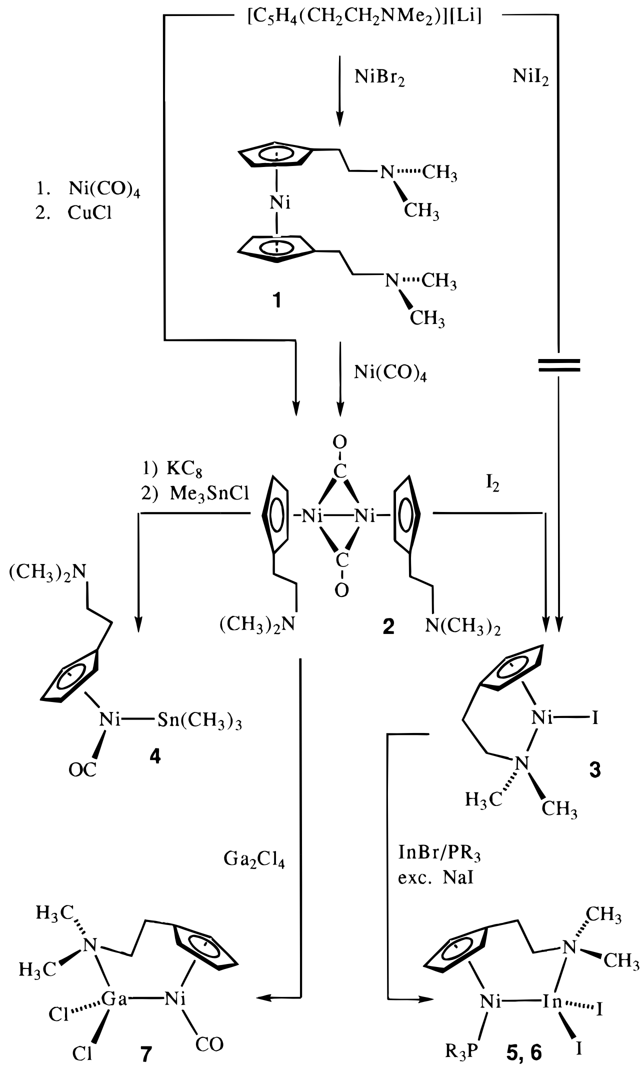
[a] See footnote *a* in Table 2.

were grown by slow solvent diffusion techniques from toluene at −30 °C. Crystal data together with details of the data collection and structure refinement are listed in Table 1. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (ENRAF-Nonius FR591; 50 kV; 80 mA; 4.0 kW) and graphite-monochromated Mo Kα radiation. The data collection was performed at 233 ± 1 K within the θ range of 1.9° < θ < 24.9° with an exposure time of 2 min per image (rotating scan modus for φ = 0.0−360° with $\Delta\varphi$ = 1°). A total number of 24 201 reflections were collected, from which a sum of 3096 independent reflections remained and were used for all calculations. Data were corrected for Lorentz, polarization, and absorption effects (μ = 44.2 cm^{-1}; program Decay[5,6]). Corrections for intensity decay and extinction were not necessary and were not applied. The unit cell parameters were obtained by least-squares refinements of 1805 reflections with the program Cell.[5,6] The structure was solved with direct methods and difference Fourier syntheses.[7,8] All 18 "heavy atoms" of the asymmetric unit were anisotropically refined. All hydrogen positions were found and refined free with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and stopped at shift/error <0.001: wR2 = 0.0449, and R1 = 0.0188. In the final difference map, the largest peaks, +0.43 and −0.52 e/Å^3, are located around the metal atoms. The correct polarity of the crystal is proved by refining Flack's parameter to −0.02(2). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 9. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V system,[8] including the programs PLATON-92,[10] PLUTON-92,[10] SIR-92,[7] and SHELX-93.[11] Selected bond lengths and angles are given in Table 3.

Synthesis and Reactivity

According to Scheme 1, the key compound Cp$^N{}_2$Ni (**1**) is readily available as a green distillable (120 °C, 10^{-2} Torr, dynamic vacuum) oil in very good yield (80%) by the reaction of a suspension of dry $NiBr_2$ in THF with Cp^{N}Li prepared in situ (from Cp^{N}H and ^{n}BuLi). Complex **1** reacts rapidly with excess $Ni(CO)_4$ in toluene at 80 °C to give quantitatively (98%) the nickel carbonyl dimer **2** as a deep red oil. The trinuclear cluster compound Cp$^N{}_3$Ni$_3$(μ_3-CO)$_2$ was not detected in the reaction mixture. This is interesting, because in the case of the *parent* Cp ligand the corresponding nickel cluster is usually formed as a byproduct in 30−40% yield.[12] Alternatively, a one-pot synthesis of **2** is possible (Scheme 1), but the yields are not better. Oxidative cleavage of the Ni−Ni bond of **2** with iodine in THF solution gives the CO-free intramolecular Lewis base adduct **3**. The direct synthesis of **3** from NiI_2 and Cp^N-Li was attempted but could not be carried out successfully.

Scheme 1



Reductive cleavage of the Ni-Ni bond of **2** with potassium graphite (KC_8) in THF yields the anion [Cp^{N}Ni(CO)]$^-$ as a highly reactive species (identified by its infrared ν(CO) absorption) which can be trapped quantitatively by the addition of various electrophiles (Scheme 1). Addition of Me_3SnCl, for example, leads to the Ni−Sn compound **4**. It was not possible to liberate the CO substituent of **4** by heating (110 °C) and to coordinate the amine donor to the Ni center. Irradiation with UV light (250 nm, Hg lamp) quickly gave unspecific decomposition. The reactivity of compound **3** with low-valent group 13 halides illustrates its synthetic potential as a starting material to achieve the

(12) Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725.

desired nickel compounds, free of CO ligands. The new insertion products **5** and **6** are prepared by treatment of **3** with $In^{I}Br$. In order to achieve this insertion of $In^{I}X$ (X = Cl, Br, I) into the Ni−I bond of **3**, however, the presence of PPh_3 or PMe_3 is necessary (Scheme 1). Without this ancillary ligand **3** does not react cleanly with $In^{I}X$. Interestingly, the related chemistry of $Cp(PPh_3)$Ni-Br with $In^{I}Br$ is also very much dependent on the solvent and the presence of Lewis base ligands.[13] Treatment of **3** with $In^{I}Br$ and phosphine ligands immediately gives red solutions, which turn slowly yellow-green as the final color. Apparently, the primary step of this reaction involves the substitution of the amine ligand by the softer phosphine to give intermediates, which then react smoothly with InBr to yield the Ni−In compounds **5** and **6** with the amine ligand now intramolecularly coordinated to the "harder" indium center. The presence of NaI is only necessary to obtain the symmetrically substituted InI_2 complex by salt metathesis.

The mixed-metal nickel gallium complex **7** (Scheme 1) was prepared by insertion of Ga_2Cl_4 into the Ni-Ni bond of **2**, but a suitable crystal for X-ray analysis could not be obtained. A homologous mixed-metal nickel indium complex had been derived from **2** by a similar route.[13a] Compound **7** sublimed unchanged under moderate conditions (10^{-3} Torr, 120 °C). Therefore, it can be used as a precursor for OMCVD of nickel gallium alloy thin films. The synthesis of related "CO-free" nickel gallium complexes similar to the Ni−In compounds **5** and **6** requires "$Ga^{I}I$", which is not known as a pure compound but can be prepared in situ according to Green et al.[14] Work in this direction is currently in progress. The synthetic potential of complex **3** is especially illustrated by the quantitative synthesis of the first structurally characterized intramolecularly adduct stabilized silyl−silylene $\{\eta^5$-μ-$C_5H_4[(CH_2)_2N$-$Me_2]\}[(SiMe_3)_2MeSi]Ni{=}SiMe_2$, which we reported recently.[15]

Spectroscopic Characterization

The presence of a stable intramolecular Lewis base adduct, involving the (dimethylamino)ethyl unit, is indicated in the ^1H NMR spectra by a downfield shift of the methylene protons in a position α to the terminal N atom of the side chain.[1,2] Furthermore, the multiplicity of the spin system of the CH_2CH_2 moiety changes from a simple AB_2 system of the free side chain to a more or less resolved AA′BB′ system upon coordination to the Lewis acid center, because of the restricted conformational freedom.[1,2] The ^1H and ^{13}C NMR data for the noncoordinated ethylamino moiety of **2** are very similar to the values reported for the permethylated derivative $[Cp^{*N}(CO)Ni]_2$ (Cp^{*N} = 1-[2-dimethylamino)-ethyl]-2,3,4,5-tetramethylcyclopentadienyl), the structure of which is known, proving the existence of the free uncomplexed aminoethyl group.[16] The ^1H NMR spectrum of the two methylene groups for **2** shows some unusual temperature dependence. Because of the accidentally very small chemical shift difference of the methylene protons, no simple spin system results at room temperature. A poorly resolved quintet is observed instead of the expected set of two AB_2 spin systems. Cooling did not improve the resolution. Upon stepwise heating to 348 K, however, a very sharp singlet developed gradually with the relative intensity of 4 hydrogen equivalents relative to the $N{-}CH_3$ groups. This effect results from the small temperature dependency of the chemical shift of the hydrogen atoms under consideration, leading to the magnetic equivalence of all the methylene protons. Consequently, the expected AB_2 spin systems collapse to one singlet. An attempt to obtain a simple derivative of **2** to check the NMR spectroscopic properties of **2** somewhat further failed, however: the treatment of **2** with HBF_4 surprisingly led to complete decomposition. This finding contrasts with the behavior of $[Cp^{*N}(CO)Ni]_2$, from which compound the respective protonated derivative is reported.[16]

The ^1H NMR spectra of **5** and **8** clearly show the features indicative of an intramolecular adduct[1,2] involving the indium center in these cases. Compound **8** shows the ν(CO) IR absorption at 2002 cm^{-1}, which compares to the value of 1997 cm^{-1} for the related compound $Cp(CO)Ni$-$InBr_2(NC_7H_{13})$, whose structure was determined.[13a] The ^{31}P NMR shift of **5** is very similar to the respective value for the related compound $Cp(PPh_3)Ni{-}InBr_2(O{=}PPh_3)$, whose structure is also known,[13b] and indicates the presence of a Ni-PPh_3 unit rather than an indium−phosphorus linkage. The preference of In−N over Ni−P follows the HSAB (hard and soft acids and bases) concept.

Compound **4** exhibits a Ni−CO unit (1996 cm^{-1}) similar to **8** and some downfield shift of the α-CH_2 group but a less resolved AA′BB′ spin system at room temperature. A tetracoordinate trialkyltin center is much less Lewis acidic than a tricoordinate dihalogenoindium group. Therefore, it is unlikely that the aminoethyl group is coordinated to the tin atom at room temperature. The ^{119}Sn NMR data for **4** (δ 107.6) is almost identical with the value of 109.7 of the closely related cyclopentadienyl complex $[Cp(CO)Ni$-$SnMe_3]$.[17] It follows that the amino atom of **4** is not coordinated to the tin atom. This situation may change if more Lewis acidic tin centers are employed (e.g. $SnOR_3$).

Compound **3** represents a new member of the series of intramolecularly complexed Cp^N ligands at 3d metals. The ^1H NMR data for **3** are similar to those for other related systems such as $Cp^{*N}CoI_2$.[2e] The formation of **7** is proved by NMR and mass spectroscopy. The ^1H NMR spectra clearly show the features indicative of an intramolecular adduct[1,2] involving the gallium center in these cases. The methylene groups exhibit two partially resolved AA′BB′ spin systems similar to those for complex **5, 6**, and the known complex **8**.[13a] The electron impact mass spectrum of **7** shows the molecular peak.

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(16) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H. G. *J. Organomet. Chem.* **1995**, *498*, 127.

(17) Fischer, R. A.; Behm, J.; Herdtweck, E.; Kronseder, C. *J. Organomet. Chem.* **1992**, *437*, C29 and references cited therein. Spectroscopic data for an authentic sample of $Cp(CO)Ni$-$SnMe_3$ for comparison with the new complex **4** are as follows. (red-orange oil). ^1H NMR (399.78 MHz, C_6D_6, 25 °C): δ 2.42 (s, 9H, $SnCH_3$); 7.00 (C_5H_5). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ −2.7 ($SnCH_3$); 89.9, 93.9, 112.9 (C_5H_5); 192.1 (CO). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 25 °C): δ 109.7. IR (*n*-pentane): 2000 cm^{-1}.

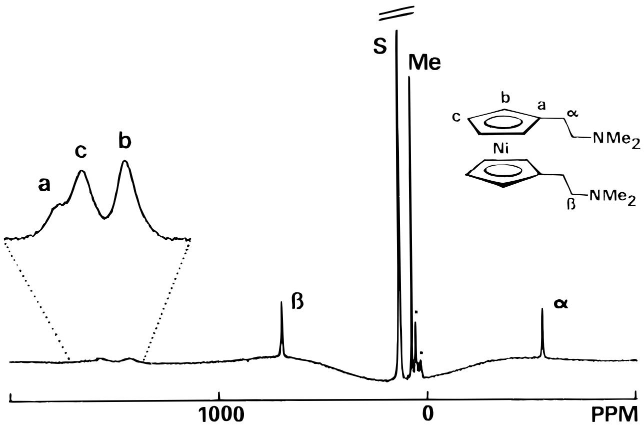

Figure 1. Paramagnetic ^{13}C NMR spectrum of complex **1**.

Although compound **1** is *paramagnetic*, its ^{1}H and ^{13}C NMR spectra can be recorded easily. The ^{13}C NMR spectrum of **1** is displayed in Figure 1. Due to the excellent solubility of **1**, no special equipment is needed as described elsewhere.[18] As expected, the line width of the signals decreases with increasing distance of the corresponding nuclei from the paramagnetic center. The ^{1}H and ^{13}C NMR signal assignments can be made in analogy to the known ones of $[MeCp]_2Ni$,[19] $[EtMe_4Cp]_2Ni$,[20] and $[EtCp]_2Ni$.[21] The chemical shifts of **1** are in good agreement with those reference compounds. (Note, however, that the sign convention has been changed since the earlier publications.[20,21]) The ^{13}C NMR signals of the ring carbon atoms are well resolved (Figure 1, expanded region), while the ring ^{1}H NMR signals are overlapping. The latter could possibly by resolved by switching from ^{1}H to ^{2}H NMR spectroscopy (natural abundance!), which provides narrower lines.[19]

Structure of Compound 3

There are still only a few other CpNi complexes with intramolecular coordination to the Ni center from a side group attached to the Cp ring: for example, [η^5:η^2-2,3,4,5-tetramethyl-1-(4-pentenyl)cyclopentadienyl]bromonickel(II).[22] The overall quality of the structure of **3** (Figure 2) suffers somewhat from a dynamic disorder of the (dimethylamino)ethyl moiety, as indicated by the large anisotropic displacement parameters of C(6) and C(7). This dynamic disorder in the solid state is in full agreement with the conformative flexibility observed by solution NMR.

The Ni−I and Ni−C(1···5) bond lengths are within the expected range. The coordination of the Cp ring is distinctly off-center with the Ni closest to C(5). The Ni−N distance of 196.0(5) pm resembles a comparably short dative amine−Ni(II) bond, which typically range from 200 to 220 pm, depending on the coordination number of the Ni atom.[23] The angle N−Ni−I of 103.3(2)° is at the upper end of the range for the bond angles L−Ni−X of Cp(L)Ni−X compounds found from 78° [24] to about 100°.[13b] The angle N−C(7)−C(6) of 116.2(8)° indicates some distortion of the tetrahedral surroundings of C(7) caused by the Ni−N bond formation. The corresponding N−C−C angles of the related compounds $Cp^NMo(CO)_2I$[1b] and Cp^NML_2 (M = Mn, L = CO;[1a] M = Co, Rh, Ir[2e,h]) are somewhat smaller (110−112°). Those complexes exhibit pentacoordinate (Mo) and tetracoordinate (Mn, Co, Rh, Ir) d metal centers. The aminoethyl unit is apparently conformatively flexible enough to coordinate to various d metal centers of different steric demand and coordination number. In summary, however, a significant stress on the system of **3** is reflected by the structural parameters, i.e. asymmetric coordination of the Cp ring, the “large” angle N−C(6)−C(7), and the comparably large deviation of C(6) from the best Cp-ring plane of 37 pm *toward* the Ni atom. Complex **3** is chiral in the solid state, which is caused by the conformative requirements of the intramolecular adduct ring (zigzag fashion). Due to the disorder of C(6) and C(7), however, the two enantiomers cannot be distinguished. In solution the molecule appears to have C_s symmetry, which is caused by a very fast motion of the side chain, so that only an averaged spectrum is observed.

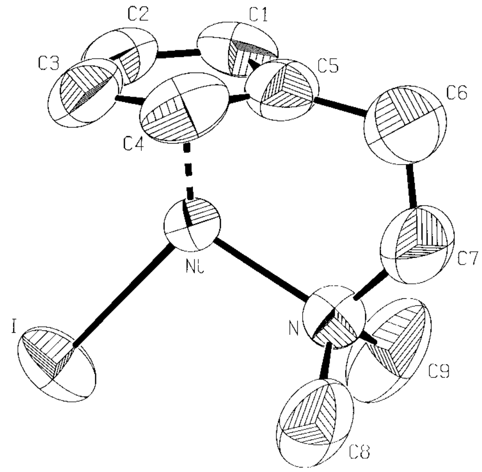

Figure 2. Molecular structure of **3** in the solid state (PLATON drawing; the thermal ellipsoids are represented at a 50% probability level). Hydrogen atoms are omitted for clarity.

Structure of Compound 6

The single-crystal X-ray diffraction study of **6** (Figure 3) unambiguously proves the presence of an intramolecular Lewis base adduct in the solid state. The structure of **6** also confirms the presence of a direct, rather short Ni−In bond of 241.80(7) pm. Ni−In bond lengths range up to 280 pm for hexacoordinate indium.[25] The sum of the covalent radii and the Ni−In distance in intermetallic alloys (e.g. ϵ-NiIn) is around 260 pm, a value which is also found for (η^5-C_5H_5)(CO)Ni−In[$(CH_2)_3$-$NMe_2]_2$ (259.8(1) pm), with a pentacoordinate indium atom.[24] Short σ(Ni−In) distances were found for lower

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(24) Fischer, R. A.; Herdtweck, E.; Priermeier, T. *Inorg. Chem.* **1994**, *33*, 934−943.
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(26) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.*, in press.

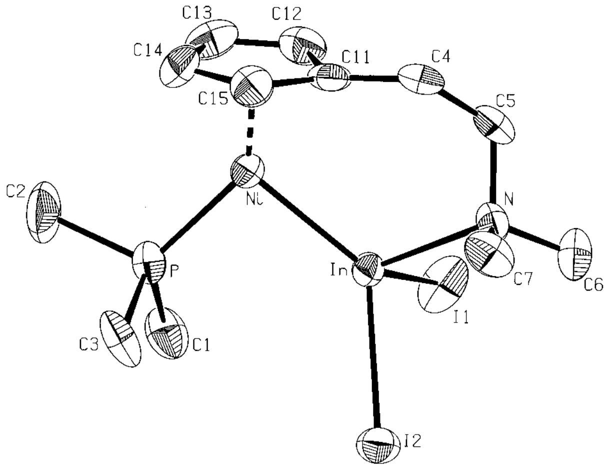

Figure 3. Molecular structure of **6** in the solid state (PLATON drawing; the thermal ellipsoids are represented at a 50% probability level). Hydrogen atoms are omitted for clarity.

coordinated indium centers without steric repulsions and bearing electronegative halide substituents.[13] The Ni−In bond of **6** compares to those in the compounds (η^5-C_5H_5)(CO)Ni−$InBr_2$(NC_7H_{13}) of 246.3(1) pm,[13a] [(η^5-C_5H_5)(CO)Ni−$InBr_3$][HNC_7H_{13}] of 243.7(2) pm,[13a] and (η^5-C_5H_5)(Ph_3P)Ni−$InBr_2$(O=PPh_3) of 244.7(9) pm.[13b] From these comparisons it is clear that the intramolecular bridge exerts only a small influence on the Ni−In bond. Also, it follows that the Ni−In bond length is not affected by a change from CO to PR_3 as supporting ligands at the Ni center or by the type of Lewis base ligand at the In atom. The conformative flexibility of the aminoethyl side group allows an almost stress-free intramolecular complexation of the indium center, which is shown by a comparably normal deviation of C(4) from the best Cp-ring plane of 21 pm *away* from the Ni atom and is best reflected by the central coordination of the Cp ring. The center of gravity of the Cp ring and the atoms P, Ni, and In are almost coplanar. The indium center is coordinated tetrahedrally without unusual distortions. The effect of the intramolecular Lewis base adduct formation on the relative orientation of the two metal fragments can be seen by the torsion angles I(2)−In−Ni−P of 44.54(4)° and I(1)−In−Ni−P of 87.46(4)°, which show that the Ni−In bond vector is not coplanar with the bisector of the angle I(1)−In−I(2). Also, the angle P−Ni−In of 94.39(4)° is slightly smaller than the analogous angle of (η^5-C_5H_5)(Ph_3P)Ni−$InBr_2$(O=PPh_3) of 98.7(1)°. The In−N distance of 233.2(4) pm and the Ni−P distance of 211.6(1) pm are normal.

Conclusions

In summary, it was shown that the [2-(dimethylamino)ethyl]cyclopentadienyl ligand is capable of forming *two types* of intramolecular Lewis-base adducts with electron-deficient metal centers. Either an adjacent electron-deficient metal center can be stabilized by bridging the metal−element bond, e.g. the Ni−In bonds of **6**−**8**, or the nickel center itself is complexed by the amine function, as exemplified by **3**. Compound **3** is thought to be an interesting starting material for CO-ligand-free, "all-hydrocarbon" (i.e. only C, H, N, and metal atoms[3]) single-source precursors for OMCVD of nickel alloy thin films, e.g. NiGa, NiIn, NiSi, NiGe, etc. Complex **3** has the potential of a rich chemistry with low-coordinated CpNi compounds, exemplified by compound **9**. In particular, the presence of the labile intramolecular Lewis acid/base adduct (whose properties can be altered by variation of the N−CH_3 groups) and the nickel−iodide bond, which can be functionalized in various ways as shown, should present interesting opportunities for organonickel chemistry, such as insertion reaction, bridging function, and access to different novel neutral, anionic, and cationic compounds.

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Supporting Information Available: Tables of crystallographic parameters, positional parameters, thermal parameters, interatomic distances, and bond angles for **3** and **6** (12 pages). Ordering information is given on any current masthead page.

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