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Novel 9-Nickelafluorenyl Sandwich Complexes of Nickel(II) and Cobalt(II)

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Summary: (9-Nickelafluorenyl)lithium was found to react with Ni(II) and Co(II) salts to form novel complexes in which the Ni or Co central metal atom is bonded to two nickelafluorenyl ligands. The crystal and molecular structures of the products were determined by single-crystal X-ray analysis.

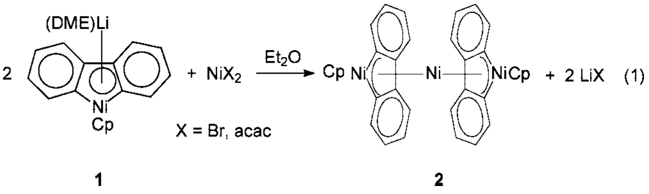
Recently there has been considerable interest in the aromatic properties of cyclic π-systems containing heteroatoms, mainly because of their potential ability to act as multielectron ligands. A well-known preparation of metal−cyclopentadienyl complexes involves the reaction of an appropriate cyclopentadienyllithium complex with with a metal salt.[1] Such reactions also can be carried out with heterocyclopentadienyllithium complexes.[2] Although the synthesis of heterofluorenyl−alkali-metal complexes containing main-group elements[3] and transition metals (zirconium)[4] have been reported, they were not employed in the formation of the compounds in which the metal atom is bonded to the heterocyclic ring.

Recently we have reported the synthesis of (9-nickelafluorenyl)lithium complexes,[5] novel metallafluorenyl−alkali-metal compounds that contain a transition metal in the five-membered metallacyclic ring.

We report here the reactions between metal bromides or acetylacetonates of nickel and cobalt and the (9-nickelafluorenyl)lithium species **1**, in which acetylacetonate or bromide ligands are displaced by the 9-nickelafluorenyl group to form complexes in which the nickel or cobalt atom is bonded to two 9-nickelafluorenyl ligands in a sandwich-type complex.

Results and Discussion

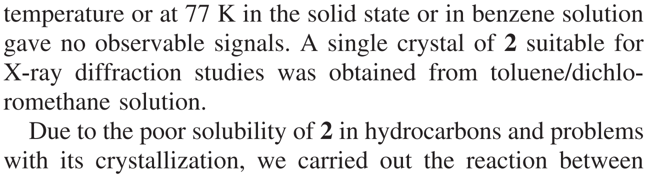
The nickel complex **2** was obtained using nickel(II) acetylacetonate in 48% yield or nickel(II) bromide in 56% yield (eq 1).



The EIMS spectrum of **2** showed the parent ion at *m/e* 608 (^{58}Ni calcd) with an isotopic pattern characteristic of three nickel atoms in the molecule. The magnetic moment of **2** in toluene solution at 294 K is 2.34 μ_B, which indicates that the compound is paramagnetic with two unpaired electrons per molecule. Attempted measurement of the EPR spectrum of **2** at room temperature or at 77 K in the solid state or in benzene solution gave no observable signals. A single crystal of **2** suitable for X-ray diffraction studies was obtained from toluene/dichloromethane solution.

Due to the poor solubility of **2** in hydrocarbons and problems with its crystallization, we carried out the reaction between cobalt(II) acetylacetonate and a 9-nickelafluorenyllithium complex, **1′**, with the methylcyclopentadienyl ligand bonded to the nickel atom (eq 2).

Complex **3′** was synthesized from the (9-nickelafluorenyl)lithium species **1′** and cobalt acetylacetonate (25% yield) in diethyl ether.



The EIMS spectrum of **3′** showed the parent ion at *m/e* 637 (^{58}Ni calcd) with an isotopic pattern characteristic for two nickel atoms. The magnetic moment of **3′** in toluene solution at 295 K is 3.704 μ_B, which indicates that the compound is paramagnetic with three unpaired electrons per molecule. Complex **3′**

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(1) See for example: Elschenbroich, C. *Organometallics*; Wiley-VCH: Weinheim, Germany,2005; p 486.

(2) See for example: (a) Ashe, A. J., III; Kampf, J. W.; Pilotek, S.; Rousseau, R. *Organometallics* **1994**, *13*, 4067. (b) Ashe, A. J., III; Kampf, J. W.; AI-Taweel, S. M. *Organometallics* **1992**, *11*, 1491. (c) Ashe III, A. J.; Kampf, J. W.; Puranik, D. B.; AI-Taweel, S. M. *Organometallics* **1992**, *11*, 2743. (d) Ashe, A. J., III; Diephouse, T. R.; Kampf, J. W.; AI-Taweel, S. M. *Organometallics* **1991**, *10*, 2068. (e) Freeman, W. P.; Dysard, J. M.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **2002**, *21*, 1734. (f) Nief, F.; Turcitu, D.; Ricard, L. *Chem. Commun.* **2002**, 1646. (g) Bazan, G. C.; Rodriguez, G. *Polyhedron* **1995**, *14*, 93. (h) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 8245. (i) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097. (j) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 2671. (k) Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17.

(3) See for example: (a) Grisby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981. (b) Wehmschulte, R. J.; Khan, M. A.; Twamley, B.; Schiemenz, B. *Organometallics* **2001**, *20*, 844. (c) Liu, Y.; Ballweg, D.; Müller, T.; Guzei, I. A.; Clark, R. W.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 12174. (d) Liu, Y.; Stringfellow, T. C.; Ballweg, D.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 49. (e) Bock, H.; Sievert, M.; Bogdan, C. L.; Kolbesen, B. O.; Wittershagen, A. *Organometallics* **1999**, *18*, 2387. (f) Ballweg, D.; Liu, Y.; Guzei, I. A.; West, R. *Silicon Chem.* **2002**, *1*, 57.

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10.1021/om8002834 CCC: $40.75

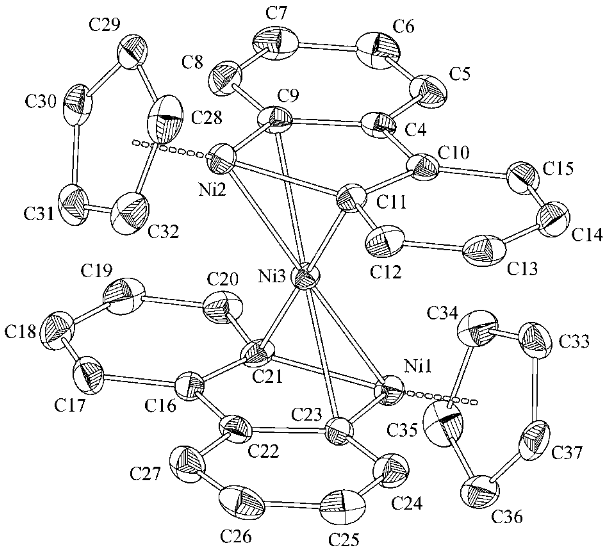

Figure 1. ORTEP view of the molecular structure of **2**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ni1−Ni3 = 2.3981(5), Ni2−Ni3 = 2.3995(5), Ni1−C21 = 1.910(3), Ni1−C23 = 1.911(3), Ni2−C9 = 1.908(3), Ni2−C11 = 1.908(3), Ni3−C9 = 2.201(3), Ni3−C11 = 2.165(3), Ni3−C21 = 2.159(3), Ni3−C23 = 2.187(3), Ni3−C4 = 2.331(3), Ni3−C10 = 2.342(3), Ni3−C16 = 2.335(3), Ni3−C22 = 2.330(3); Ni1−Ni3−Ni2 = 178.55(3), C9−Ni2−C11 = 84.8(1), C9−Ni3−C11 = 72.2(1), C21−Ni1−C23 = 84.4(1), C21−Ni3−C23 = 72.4(1).

is EPR silent at room temperature in benzene and at 77 K in the solid state.

Compounds **2** and **3′** were each characterized by single-crystal X-ray analysis. The molecular structures of **2** and **3′** are shown in Figures 1 and 2, respectively. Crystal data and data collection and refinement parameters are collected in Table 1.

There are three nickel atoms in complex **2**. The Ni1−Ni2−Ni3 angle is 178.6°. The central nickel atom (Ni3) is bonded to two five-membered nickelacyclic rings, each formed by four carbon atoms and one nickel atom (Ni1, C16, C21, C22, C23 and Ni2, C4, C9, C10, C11). The heterocyclic rings are not planar. The nickel atoms deviate from planes formed by four carbon atoms by 0.227 Å (Ni1) and 0.209 Å (Ni2). There are two independent molecules (**A** and **B**) in an asymmetric unit cell of **3′**. The angle between the three metal atoms (Ni, Co, and Ni) is 180°. The two nickelafluorenyl rings are parallel to each other. The nickelafluorenyl rings are not flat. The nickel atom deviates from the plane formed by four carbon atoms (C11, C12, C17, C18) by 0.30 Å in molecule **A** and 0.31 Å in molecule **B**. The dihedral angle between the planes (C11, C12, C17, C18 and C12, Ni, C18) is 12.3° (molecule **A**) and 12.7° (molecule **B**).

We have determined the degree of slip-fold distortion, using parameters as described earlier.[6] The slip parameter $\Delta_{\mathrm{M-C}}$ for the Ni3 atom in **2** is ca. 0.16 Å (for the nickelacyclic ring containing the Ni1 atom) and ca. 0.15 Å (for the nickelacyclic ring containing the Ni2 atom). The slip parameter $\Delta_{\mathrm{M-C}}$ for the Co atom in **3′** is ca. 0.25 Å in molecule **A** and 0.28 Å in molecule **B**. These values indicate that the bonding modes of the central metal atoms, in both complexes **2** and **3′**, to the nickelacyclic rings are between η^3 and η^5.

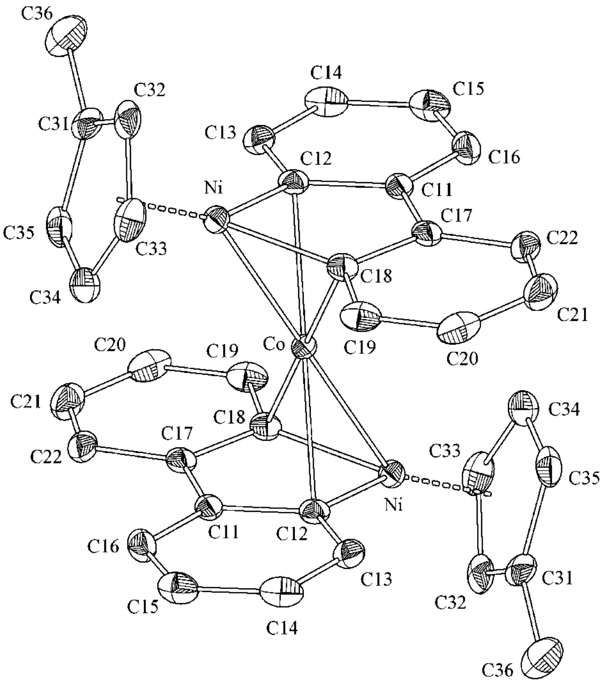

Figure 2. ORTEP view of the molecular structure of **3′**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg) for molecules **A** and **B**, respectively: Ni−Co = 2.3711(8) and 2.379(1), Ni−C12 = 1.926(3) and 1.933(3), Ni−C18 = 1.920(3) and 1.921(3), Co−C12 = 2.220(3) and 2.203(3), Co−C18 = 2.205(3) and 2.199(3), Co−C11 = 2.485(3) and 2.449(3), Co−C17 = 2.493(3) and 2.451(3), C11−C12 = 1.423(4) and 1.423(4), C11−C17 = 1.473(4) and 1.476(4), C17−C18 = 1.416(4) and 1.415(4), Ni−Cg = 1.741(4) and 1.750(9); Ni−Co−Ni = 180.0 and 180.0, C12−Ni−C18 = 84.3(1) and 84.3(1), C12−Co−C18 = 71.3(1) and 72.0(1), Co−Ni−Cg = 140.29(3) and 141.45(3).

Experimental Section

All reactions were carried out under an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury 400BB instrument. Mass spectra were recorded on an AMD-604 spectrometer. EPR spectra were measured on a Bruker ESP 300 spectrometer in X-band. Magnetic susceptibility was determined by NMR measurements at 298 K by the Evans method[7] from differences in chemical shifts of methyl group protons of toluene used as solvent and as external standard. Magnetic moments were calculated from the measurements of magnetic susceptibility. Nickel bromide was synthesized using a literature procedure.[8] The synthesis of compound **1** was described earlier.[5]

Reaction of Compound 1 with Nickel(II) Bromide. Compound **1** 0.435 g (1.17 mmol) and 50 cm^3 of diethyl ether were placed in a Schlenk flask and cooled to −40 °C. Then NiBr$_2$·2DME (0.265 g, 0.67 mmol) was added. The reaction mixture was stirred at room temperature overnight. After the reaction was completed, the solvent was removed, and the solid residue was chromatographed on alumina (deactivated with 5% of water). One violet fraction was collected (toluene/hexane 2/1). After evaporation to dryness it gave 0.202 g (0.33 mmol, 56%) of a black solid identified as **2**. Black crystals appropriate for X-ray measurements were grown from

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Table 1. Crystal Data and Structure Refinement Parameters

	2	3′
empirical formula	$C_{34}H_{26}Ni_3$	$C_{36}H_{30}CoNi_2$
cryst size (mm)	0.48 × 0.32 × 0.24	0.13 × 0.06 × 0.03
cryst syst	orthorhombic	triclinic
space group	$Pna2_1$	$P\bar{1}$
unit cell dimens		
a (Å)	18.3002(3)	9.256(5)
b (Å)	9.1160(3)	9.305(5)
c (Å)	14.8054(6)	17.278(5)
α (deg)		96.93(1)
β (deg)		98.93(1)
γ (deg)		114.74(1)
V (Å^3)	2469.9(1)	1306(1)
Z	4	2
formula wt	610.68	638.95
density (calcd) (Mg m^{-3})	1.642	1.624
temp (K)	150(2)	100(2)
abs coeff (mm^{-1})	2.286	2.080
F(000)	1256	658
radiation	Mo Kα (λ = 0.710 73 Å, graphite monochromator)	
θ range for data collecn (deg)	3.15−27.46	2.97−28.05
scan type	φ and ω	ω
index ranges	$-23 \le h \le 23$, $-11 \le k \le 11$, $-19 \le l \le 19$	$-12 \le h \le 12$, $-11 \le k \le 12$, $-22 \le l \le 22$
no. of collected/unique rflns	16 524/5370 (R_{int} = 0.040)	17 504/6292 (R_{int} = 0.0471)
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	5370/1/335	6292/0/355
goodness of fit on F^2[a]	1.04	1.02
R indices ($I > 2\sigma(I)$)		
R1[b]	0.031	0.041
wR2[c]	0.065	0.084
R indices (all data)		
R1	0.039	0.072
wR2	0.068	0.091
largest diff peak and hole (e Å^{-3})	0.28 and −0.33	0.67 and −0.50

[a] Weighting scheme (where $P = (F_o^2 + 2F_c^2)/3$): for **2**, $w^{-1} = \sigma^2(F_o^2) + (0.0306P)^2 + 0.9983P$; for **3′**, $w^{-1} = \sigma(F_o^2) + (0.0418P)^2 + 0.0000P$. [b] $R1 = \sum(F_o - F_c)/\sum F_o$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)/\sum[w(F_o^2)^2]\}^{1/2}$.

toluene/dichloromethane solution. EIMS of **2** (70 eV; *m*/*e* (relative intensity); ^{58}Ni): 608 (53%, M$^+$), 542 (57%, $C_{29}H_{20}Ni_3^+$), 398 (59%, $C_{22}H_{18}Ni_2^+$), 362 (59%, $C_{24}H_{16}Ni^+$), 338 (38%, $C_{22}H_{16}Ni^+$), 275 (46%, $C_{17}H_{13}Ni^+$), 215 (89%, $C_{17}H_{11}^+$), 154 (100%, $C_{12}H_{10}^+$), 123 (27%, $C_5H_5Ni^+$). The magnetic moment in toluene solution at 294 K is 2.34 μ_B. EI HR MS (*m*/*e*) obsd 608.008 67, calcd for $C_{34}H_{26}{}^{58}Ni_3$ 608.009 49. Anal. Calcd for **2** ($C_{34}H_{26}Ni_3$): C, 66.88; H, 4.29. Found: C, 66.73; H, 4.41.

Crystal Structure Determination of 2. The crystal was sealed in a glass capillary under a nitrogen stream. X-ray data were collected on a Nonius KappaCCD diffractometer at 150 K. The diffractometer control program used was Collect,[9] unit cell parameters and data reduction were carried out with Denzo and Scalepak,[10] and the structure was solved by direct methods with SHELXS-97[11] and refined on F^2 by full-matrix least squares with SHELXL-97.[12] All the hydrogen atoms were placed in calculated positions and refined using a riding model.

Reaction of Compound 1 with Nickel(II) Acetylacetonate. Compound **1** (0.572 g, 1.54 mmol) and 50 cm^3 of diethyl ether were placed in a Schlenk flask and cooled to −40 °C. Then a solution of nickel acetylacetonate (0.205 g, 0.8 mmol) in 50 cm^3 of diethyl ether was added. The reaction mixture was stirred at room temperature overnight. After the reaction was completed, the solvent was removed, and the solid residue was chromatographed on alumina (deactivated with 5% of water). One violet fraction was collected (toluene/hexane 2/1). After evaporation to dryness it gave 0.223 g (0.37 mmol, 48%) of a black solid identified as **2**. Black crystals appropriate for X-ray measurements were grown from toluene/dichloromethane solution.

Synthesis of Compound 1′. A 4 g amount (12.8 mmol) of 2,2′-dibromobiphenyl and 150 cm^3 of hexane were placed in a Schlenk flask. A 25.6 mmol portion of *n*-butyllithium (1.51 M solution in hexane) was added at room temperature. The reaction was carried out for 4 days. The white precipitate of 2,2′-dilithiobiphenyl was washed three times with hexane (to remove bromobutane) and dried under vacuum. Then 200 cm^3 of diethyl ether and 2.75 g (12.7 mmol) of bis(methylcyclopentadienyl)nickel were added to the Schlenk flask. The reaction was carried out for 2 days at room temperature. Then the precipitate was allowed to settle and the clear solution of **1′** was transferred to another Schlenk flask. A 20 cm^3 amount of dimethoxyethane was added to the solution of **1′**. An orange precipitate was formed. Solvents were removed under vacuum, and the solid residue was dissolved in 15 cm^3 of warm dimethoxyethane. Red crystals were obtained after cooling the solution to −15 °C. They were dried under vacuum at approximately 50 °C. A yellow powder of compound **1′** was obtained: yield 3.12 g (8.1 mmol, 63%). ^{1}H NMR of **1′** (C_6D_6; δ (ppm)): 7.76 (d, ^3J = 7.2 Hz, 2H, Ph), 7.55 (d, ^3J = 7.2 Hz, 2H, Ph), 7.09 (t, ^3J = 7.2 Hz, 2H, Ph), 6.87 (t, ^3J = 7.2 Hz, 2H, Ph), 5.38 (t, ^3J = 2.4 Hz, 2H, Ph), 5.27 (t, ^3J = 2.4 Hz, 2H, Ph), 2.50 (s, 6H, CH_3 (DME)), 2.33 (s, 4H, CH_2 (DME)), 2.21 (s, 3H, CH_3 (MeCp)). ^{13}C NMR of **1′** (C_6D_6; δ (ppm)): 167.51 (Ph), 153.80 (Ph), 145.21 (Ph), 123.72 (Ph), 122.69 (Ph), 120.95 (Ph), 103.65 (C, MeCp), 91.32 (CH, MeCp), 88.93 (CH, MeCp), 68.84 (CH_2, DME), 58.90 (CH_3, DME), 13.87 (CH_3, MeCp). Anal. Calcd for **1′** ($C_{22}H_{25}LiNiO_2$): C, 68.27; H, 6.51. Found: C, 68.10; H, 6.62.

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Reaction of Compound 1′ with Cobalt(II) Acetylacetonate. Compound **1′** (0.765 g, 1.98 mmol) and 40 cm^3 of diethyl ether were placed in a Schlenk flask and cooled to −30 °C. A solution of cobalt(II) acetylacetonate (0.260 g, 1.01 mmol) in 30 cm^3 of diethyl ether was slowly added. The reaction mixture was stirred for 1 h at −30 °C and then at room temperature overnight. After the reaction was completed, the solvent was evaporated to dryness. The black solid residue was extracted with 25 cm^3 of toluene, filtered, concentrated to about 10 cm^3, and placed in the refrigerator. After 24 h the solution was removed and a black solid of **3′** was dried under vacuum (0.162 g, 0.25 mmol, 25%). Black crystals appropriate for X-ray measurements were grown from dichloromethane solution. EIMS of **3′** (70 eV; *m*/*e* (relative intensity); ^{58}Ni): 637 (19%, M$^+$), 427 (10%, $C_{24}H_{22}CoNi^+$), 289 (11%, $C_{18}H_{15}Ni^+$), 217 (54%, $C_{17}H_{13}{}^+$), 154 (100%, $C_{12}H_{10}{}^+$). The magnetic moment in toluene solution at 295 K is 3.704 μ_B. EI HR MS (*m*/*e*): obsd 637.034 13, calcd for $C_{36}H_{30}Co^{58}Ni_2$ 637.038 64. Anal. Calcd for **3′** ($C_{36}H_{30}CoNi_2$): C, 67.67; H, 4.73. Found: C, 67.82; H, 4.92.

Crystal Structure Determination of 3′. Preliminary examination and intensity data collection were carried out on a KUMA KM4CCD Diffraction κ-axis diffractometer. All data were corrected for Lorentz, polarization, and absorption effects. Data reduction and analysis were carried out with the Oxford Diffraction programs.[13] The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL_NT V5.1 software.[14] Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL97 default parameters. Other hydrogen atoms were located in a difference map and refined isotropically without any restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of **2** and **3′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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