Products of the Reaction of 9-Nickelafluorenyllithium Complexes with Water

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Summary: Reactions of 9-nickelafluorenyllithium complexes with water were carried out. Trinickel clusters with aryne ligands were formed (via aromatic C−H bond activation by a nickel atom), whose crystal and molecular structures were determined by single-crystal X-ray analysis.

Introduction

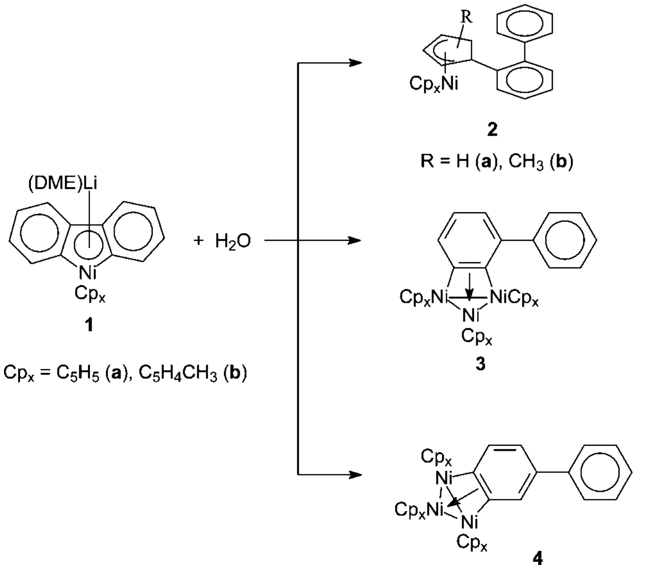
We have recently published the synthesis and structural characterization of 9-nickelafluorenyllithium compounds.[1] To extend our knowledge of their properties, we studied their reactivity toward various reagents. In this paper we present the results of our studies on reactions of these compounds with water. The reaction is not a simple hydrolysis. A C−H bond of the phenyl ring is activated, and trinickel complexes with phenylbenzyne are formed among other products. C−H bond activation by transition metal complexes has been intensively studied in recent years due to its potential applications in synthesis.[2]

Benzyne and its derivatives are a specific type of alkynes derived from benzene. They are very reactive and cannot be isolated as free species,[3] but can be stabilized as complexes with various early and late transition metals, similar to those formed with alkynes, which can be bonded to one or more metal centers in various ways.[4] Several structurally characterized nickel complexes with aryne ligands containing one,[5] two,[6] or three[7] nickel atoms are known.

Results and Discussion

The reactions of compounds **1a** and **1b** with deoxygenated water have been carried out in a mixture of toluene and diethyl ether at temperatures ranging from 0 °C to room temperature. Three types of products were formed in these reactions (Scheme 1).

Scheme 1. Reactions of Complexes 1 with Water



The products were separated by column chromatography on neutral alumina deactivated with 5% water. Three colored bands were collected. The first, green fraction from the reaction of **1a** with water contained traces of nickelocene. The second, red fraction contained π-allyl complex **2a** (yield 28%). It was characterized by EIMS, EI HRMS, and ^1H and ^{13}C NMR spectroscopy. Recrystallization from ethanol afforded crystals of **2a** suitable for X-ray diffraction. The molecular structure of **2a** is presented in Figure 1. Crystal data, data collection, and refinement parameters are given in Table 1. The compound crystallizes in the monoclinic crystal system. The cyclopentenyl ring exhibits an "open envelope" conformation. The nickel atom is bonded to the cyclopentadienyl ring in η^5 mode and to the cyclopentenyl ring in η^3 mode. The hinge angle between the planes C1−C2−C4−C5 and C2−C3−C4 is 26.8°. The bond lengths between the nickel atom and carbon atoms (Ni−C3 1.884(4) Å, Ni−C2 2.062(4) Å, N−C4 1.981(5) Å) are typical for π-allyl-nickel complexes.[8] The third, brown fraction contained a mixture of trinickel clusters **3a** and **4a**. They were unstable and decompose during chromatography, so it was impossible to separate them from each other and to obtain crystals for X-ray measurements. They were identified by the EIMS spectrum of their mixture, which revealed the parent ion at *m/e* 521 (^{58}Ni calc) with an isotopic pattern characteristic for three nickel atoms in the molecule, and by an EI HRMS spectrum.

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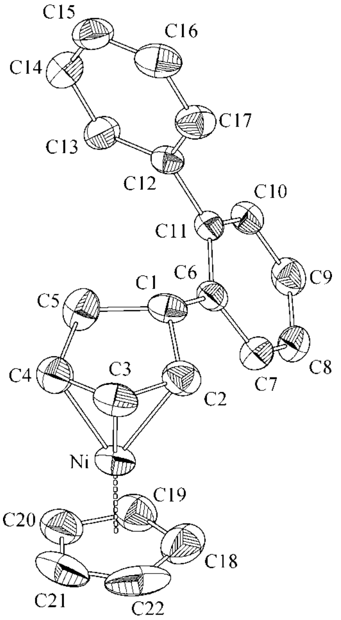

Figure 1. ORTEP view of the molecular structure of **2a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ni−C2 2.062(4), Ni−C3 1.884(4), Ni−C4 1.981(5), Ni−Cg 1.768(2), C1−C2 1.511(5), C2−C3 1.408(7), C3−C4 1.419(7), C4−C5 1.522(6), C1−C5 1.537(6), C2−C3−C4 105.1(4), Ni−C3−C2 76.0(3), Ni−C3−C4 72.1(2), C2−Ni−C4 67.4(2).

Therefore we decided to synthesize complexes with methylcyclopentadienyl ligands. Compound **1b** was synthesized from dilithiobiphenyl and 1,1′-dimethylnickelocene (63% yield). It is much more soluble than **1a** in organic solvents and was characterized on the basis of ^{1}H and ^{13}C NMR spectra. The reaction of **1b** and water was carried out in a mixture of toluene and diethyl ether. The products were separated by column chromatography on neutral alumina deactivated with 5% water. Three colored bands were collected. The first, green fraction contained traces of 1,1′-dimethylnickelocene. The second, red fraction contained π-allyl complex **2b** (yield 16%). It was characterized by EIMS (the parent ion at *m/e* 370 (^{58}Ni calc)), EI HRMS, and ^{1}H and ^{13}C NMR spectra. ^{1}H NMR and ^{13}C NMR spectra of **2b** are difficult to analyze owing to the number of isomers that may be formed during addition of the biphenyl group to the methylcyclopentadienyl ring. The third, brown fraction contained a mixture of trinickel clusters **3b** and **4b**. The mixture was chromatographed again, and two brown fractions of compounds **3b** and **4b** were separated. Their EIMS showed the parent ions at *m/e* 563 (^{58}Ni calc) with an isotopic pattern characteristic for three nickel atoms in the molecules. Compounds **3b** and **4b** are paramagnetic. The EPR spectra of both compounds in benzene and in the solid state were identical. There were no signals in the EPR spectra at room temperature. At 77 K there was an isotropic single Lorentzian line with *g* factor 2.023 and of line width 144 G. Crystals of **3b** and **4b** suitable for X-ray diffraction studies were obtained from hexane solutions. Their molecular structures are presented in Figures 2 and 3, respectively. Crystal data, data collection, and refinement parameters are given in Table 1. Both compounds crystallize in a monoclinic crystal system. Three nickel atoms form a triangle. The phenylbenzyne ligand is bonded to the trinickel core by two σ bonds and one π bond ($2\sigma + \pi$ or μ_3-η^2), which is similar to the bonding mode of alkyne to three nickel atoms in previously described clusters.[9] This type of a bonding mode is commonly found in homo- and heterometallic alkyne clusters and is also common for isonitriles.[5] The Ni−Ni distances (2.38−2.45 Å) are within the range of nickel−nickel single bonds.

The proposed course of the reaction is depicted in Schemes 2 and 3. The formation of clusters **3** and **4** most probably occurs via nickel-mediated aromatic C−H bond activation. It can be assumed that during hydrolysis of **1** an unstable 16 VE species **5** is formed, which is the precursor of cluster **3**. Species **5** isomerizes via nickel-mediated hydrogen transfer to the species **7**, which is the precursor of cluster **4**.

Such isomerization is evidence for C−H bond activation in arenes by nickel. It also demonstrates that the nickel atom can migrate with respect to the aromatic ring. Johnson and coworkers recently postulated that such migration can occur in a difluorobenzynenickel complex.[6a,b]

In conclusion, we have shown that the course of the hydrolysis of 9-nickelafluorenyllithium complexes is complicated, leading to several organonickel products: π-allyl complexes and trinickel clusters with aryne ligands. It appears likely that the formation of these compounds proceeds via aromatic C−H bond activation by nickel.

Experimental Section

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk flask 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. Compound **1a** was synthesized according to the method described previously.[1]

Synthesis of 1b. 2,2′-Dibromobiphenyl (4.00 g, 12.8 mmol) and 150 mL of hexane were placed in a Schlenk flask. Then 25.6 mmol of *n*-butyllithium 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 and dried under vacuum. Then 200 mL of diethyl ether and 2.75 g (12.7 mmol) of 1,1′-dimethylnickelocene were added. The reaction was carried for 2 days at room temperature. The resulting precipitate was allowed to settle, and the clear supernatant solution of **1b** was transferred to another Schlenk flask. A 20 mL amount of dimethoxyethane was added to the solution of **1b**, forming a yellow precipitate. Solvents were removed under reduced pressure, and the solid residue was dissolved in 15 mL of warm dimethoxyethane. Red crystals were obtained after cooling the solution to −15 °C.

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Table 1. Crystal Data and Structure Refinement Parameters[a]

	2a	**3b**	**4b**
empirical formula	$C_{22}H_{20}Ni$	$C_{30}H_{29}Ni_3$	$C_{30}H_{29}Ni_3$
cryst size	0.45 × 0.25 × 0.2 mm	0.5 × 0.4 × 0.1 mm	0.6 × 0.4 × 0.1 mm
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/n$
unit cell dimens	$a = 5.7888(2)$ Å $b = 13.1587(6)$ Å $c = 11.1799(5)$ Å $\beta = 103.979(2)°$	$a = 12.505(2)$ Å $b = 9.792(2)$ Å $c = 19.219(3)$ Å $\beta = 94.32(2)°$	$a = 16.393(2)$ Å $b = 9.319(2)$ Å $c = 17.292(2)$ Å $\beta = 109.71(2)°$
volume	826.44(6) $Å^3$	2346.7(7) $Å^3$	2486.9(7) $Å^3$
Z	2	4	4
fw	343.09	565.66	565.66
density (calcd)	1.379 $Mg \cdot m^{-3}$	1.601 $Mg \cdot m^{-3}$	1.511 $Mg \cdot m^{-3}$
temperature	293(2) K	100(1) K	100(1) K
absorp coeff	1.170 mm^{-1}	2.399 mm^{-1}	2.264 mm^{-1}
$F(000)$	360	1172	1172
radiation	Mo Kα ($\lambda = 0.71073$ Å, graphite monochromator)		
θ range for data collection	1.88–27.86°	3.27–28.39°	3.25–28.52°
index ranges	$-7 \le h \le 7$, $-17 \le k \le 17$, $-14 \le l \le 14$	$-15 \le h \le 16$, $-12 \le k \le 10$, $-25 \le l \le 24$	$-19 \le h \le 21$, $-12 \le k \le 12$, $-18 \le l \le 21$
no. of reflns collected/unique	7324/2037 [$R_{int} = 0.041$]	15 631/5420 [$R_{int} = 0.0287$]	10 034/5434 [$R_{int} = 0.0877$]
refinement method	full-matrix least-squares on F^2		
no. of data/restraints/params	2037/0/208	5420/0/298	5434/0/298
goodness-of-fit on F^2	1.051	1.066	0.955
final R indices [$I > 2\sigma(I)$]	$R = 0.037$, $wR = 0.085$	$R = 0.028$, $wR = 0.065$	$R = 0.065$, $wR = 0.164$
R indices (all data)	$R = 0.049$; $wR = 0.089$	$R = 0.039$; $wR = 0.068$	$R = 0.111$; $wR = 0.188$
largest diff peak and hole	0.411 and −0.497 $e \cdot Å^{-3}$	0.475 and −0.434 $e \cdot Å^{-3}$	0.575 and −0.804 $e \cdot Å^{-3}$

[a] Weighting scheme (where $P = (F_o^2 + 2F_c^2)/3$): For **2a**: $w^{-1} = \sigma^2 (F_o^2 + (0.0362P)^2 - 0.4535P$. For **3b**: $w^{-1} = \sigma^2 (F_o^2 + (0.0385P)^2 + 0.0000P$. For **4b**: $w^{-1} = \sigma^2 (F_o^2 + (0.1015P)^2 + 0.0000P$.

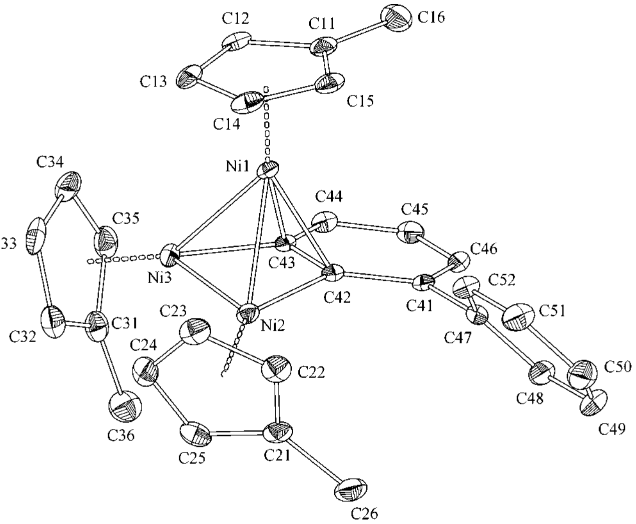


Figure 2. ORTEP view of the molecular structure of **3b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ni1−Ni2 2.3871(5), Ni1−Ni3 2.4071(6), Ni2−Ni3 2.4475(5), Ni1−Cg 1.73(1), Ni2−Cg 1.76(1), Ni3−Cg 1.769(1), Ni1−C42 1.996(2), Ni1−C43 2.003(2), Ni2−C42 1.898(2), Ni3−C43 1.871(2), C42−C43 1.409(3), Ni1−Ni2−Ni3 59.70(2), Ni1−Ni3−Ni2 58.90(2), Ni2−Ni1−Ni3 61.40(1), C42−Ni1−C43 41.27(8).

The crystals were dried under vacuum at 50 °C. **1b** was obtained as a yellow powder (3.12 g, 8.1 mmol, 63%). ^1H NMR (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 (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 $C_{22}H_{25}LiNiO_2$: C, 68.27; H, 6.51. Found: C, 68.10; H, 6.62.

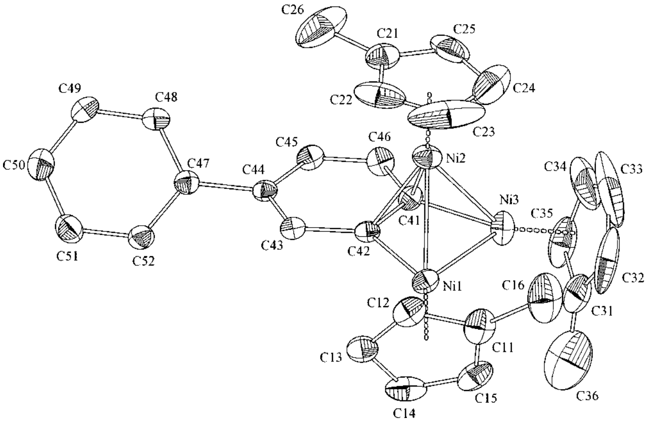
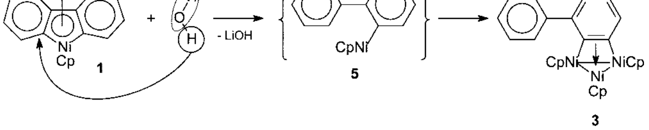


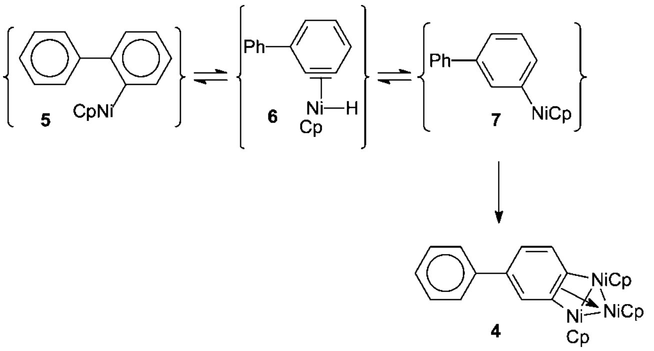
Figure 3. ORTEP view of the molecular structure of **4b**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms were omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ni2−Ni1 2.383(1), Ni2−Ni3 2.403(1), Ni1−Ni3 2.449(1), Ni2−Cg 1.735(3), Ni1−Cg 1.770(2), Ni3−Cg 1.778(9), Ni2−C41 1.983(5), Ni2−C42 2.013(5), Ni1−C42 1.862(5), Ni3−C41 1.884(5), C41−C42 1.403(7), Ni2−Ni1−Ni3 59.62(3), Ni2−Ni3−Ni1 58.83(3), Ni1−Ni2−Ni3 61.54(3), C41−Ni2−C42 41.1(2).

Scheme 2



Reaction of 1a with Water. 1a (1.106 g, 3.0 mmol), toluene (35 mL), and diethyl ether (35 mL) were placed in a Schlenk flask. The solution was cooled to 0 °C. Then 30 mL of deoxygenated water was slowly added. The mixture was stirred for 30 min at 0 °C, then warmed slowly to room temperature and filtered through a bed of alumina. The organic layer solution was concentrated to

Scheme 3



approximately 10 mL. Alumina was added and the solvent was removed under vacuum. The products, absorbed on alumina, were placed at the top of the column and chromatographed on alumina (deactivated with 5% water) with hexane/toluene mixtures as eluents. Three colored bands were separated and collected. The first green fraction (hexane/toluene, 10:1) after evaporation to dryness gave traces of a solid identified by EIMS spectroscopy as nickelocene.

The second, red fraction (hexane/toluene, 5:1) gave a solid identified as **2a** (yield 0.142 g, 0.42 mmol, ca. 28%). Crystals of **2a** suitable for X-ray measurements were obtained from an ethanol solution. EIMS (70 eV) *m*/*e* (rel int) (^{58}Ni): 342 (8%, M$^+$), 304 (26%, $C_{19}H_{18}Ni^+$), 276 (100%, $C_{17}H_{14}Ni^+$), 215 (36%, $C_{17}H_{11}{}^+$), 123 (4%, $C_5H_5Ni^+$). EI HRMS: obsd 342.09298, calcd for $C_{22}H_{20}(^{58}Ni)$ 342.09185. ^{1}H NMR (C_6D_6) δ (ppm) (atom numbering as in Figure 1): 7.07−7.93 (m, 9H, Ph), 5.20 (s, 5H, Cp), 5.06 (m, 1H, CH), 3.87 (m, 1H, CH), 3.59 (m, 1H, CH), 2.60 (m, 1H, CH), 0.95 (m, 2H, CH_2). ^{13}C NMR (C_6D_6) δ (ppm): 142.99 (Ph), 142.94 (Ph), 141.72 (Ph), 130.02 (Ph), 129.49 (Ph), 128.33 (Ph), 126.89 (Ph), 126.78 (Ph), 126.13 (Ph), 89.30 (Cp), 82.37 (CH), 65.71 (CH), 61.38 (CH), 45.08 (CH) (3), 39.80 (CH_2). Anal. Calcd for $C_{22}H_{20}Ni$: C, 77.02 H, 5.88. Found: C, 76.82; H, 6.05. The third, brown fraction (hexane/toluene, 1:1) gave 0.108 g (0.21 mmol, 21%) of a brown solid identified as a mixture of **3a** and **4a**. Repeated chromatography of this fraction did not lead to the separation of these products and caused their decomposition. EIMS (70 eV) *m*/*e* (rel int): (^{58}Ni): 521 (90%, M$^+$), 455 (55%, $C_{22}H_{17}Ni_3{}^+$), 340 (20%, $C_{22}H_{18}Ni^+$), 275 (14%, $C_{17}H_{13}Ni^+$), 215 (28%, $C_{17}H_{11}{}^+$), 188 (37%, $C_{10}H_{10}Ni^+$), 154 (14%, $C_{12}H_{10}{}^+$), 123 (15%, $C_5H_5Ni^+$). EI HRMS: obsd 520.98570, calcd for $C_{27}H_{23}(^{58}Ni)_3$ 520.98602.

Crystal structure determination of **2a**: The crystal was sealed in a glass capillary under a nitrogen stream. X-ray data were collected on a Nonius KappaCCD diffractometer. The diffractometer control program was Collect,[10] unit cell parameters and data reduction was performed with Denzo and Scalepak,[11] and the structure was solved by direct methods with SHELXS-97[12] and refined on F^2 by full-matrix least-squares with SHELXL-97.[13] All hydrogen atoms were placed in calculated positions and refined using a riding model.

Reaction of 1b with Water. The reaction was carried out analogously to the previous one using 2.413 g (6.3 mmol) of **1b**, toluene (30 mL), and diethyl ether (30 mL). Three colored chromatographic bands were separated and collected. The first, green fraction (hexane/toluene, 10:1) after evaporation to dryness gave traces of a solid identified by EIMS spectroscopy as 1,1′-dimethylnickelocene. The second, red fraction (hexane/toluene, 6:1) gave a solid identified as **2b** (yield 0.184 g, 0.5 mmol, ca. 16%). EIMS (70 eV) *m*/*e* (rel int) (^{58}Ni): 370 (13%, M$^+$), 290 (100%, $C_{18}H_{16}Ni^+$), 275 (33%, $C_{17}H_{13}Ni^+$), 215 (14%, $C_{17}H_{11}{}^+$). EI HRMS: obsd 370.12288, calcd for $C_{24}H_{24}(^{58}Ni)$ 370.12315. ^{1}H NMR (C_6D_6) δ (ppm): 6.70−8.10 (m), 4.80−5.15 (m), 3,78 (s), 3.63 (s), 3.45 (s), 2.78 (m), 1.85 (s), 1.83 (s), 1.81 (s), 1.01 (s), 0.85−1.30 (m). ^{13}C NMR (C_6D_6) δ (ppm): 125−144, 82−94, 62−68, 40−46, 12−22. Complex spectra owing to several possible isomers. Anal. Calcd for $C_{24}H_{24}Ni$: C, 77.67 H, 6.52. Found: C, 77.34; H, 6.35. The third, brown fraction (hexane/toluene, 1:1) gave a brown solid identified as a mixture of **3b** and **4b**. This fraction was chromatographed again on a smaller column. Two brown fractions were collected. The first fraction (hexane/toluene, 1:1) gave 0.202 g (0.36 mmol, 17%) of a brown solid identified as **3b**. The second brown fraction (hexane/toluene, 1:1) gave 0.033 g (0.06 mmol, 3%) of a brown solid identified as **4b**. Crystals of **3b** and **4b** suitable for X-ray measurements were obtained from a hexane solution. EIMS of **3b** and **4b** (70 eV) *m*/*e* (rel int) (^{58}Ni): 563 (84%, M$^+$), 481 (29%, $C_{24}H_{19}Ni_3{}^+$), 403 (7%, $C_{18}H_{13}Ni_3{}^+$), 331 (18%, $C_{12}H_{13}Ni_3{}^+$), 288 (5%, $C_{18}H_{14}Ni^+$), 216 (6%, $C_{12}H_{14}Ni^+$), 152 (3%, $C_{12}H_8{}^+$), 136 (4%, $C_6H_6Ni^+$). EI HRMS: obsd 563.03273, calcd for $C_{30}H_{29}(^{58}Ni)_3$ 563.03297. Anal. Calcd for **3b** $C_{30}H_{29}Ni_3$: C, 63.70 H, 5.17. Found: C, 63.54; H, 5.35. Anal. Calcd for **4b** $C_{30}H_{29}Ni_3$: C, 63.70 H, 5.17. Found: C, 63.82; H, 5.32.

Crystal structure determination of **3b** and **4b**: Preliminary examination and intensity data collections were carried out on a KUMA CCD KM-4 κ-axis diffractometer with graphite-monochromated Mo Kα.[14] All data were corrected for Lorentz, polarization, and absorption effects. Data reduction and analysis were carried out with the Oxford Diffraction programs. The structures were solved by direct methods and refined using full-matrix least-squares on all F^2 data with SHELXTL software.[15] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions with isotropic thermal parameters.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of **2a**, **3b**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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