

Mono- and Bimetallic (NacNac)Ni Cyclopentadienyl Complexes[†]

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Complexes of the form (Nacnac)Ni(η^5 -L) (L = Cp (**3**), indenyl (**4**)) are readily prepared and have been protonated to generate the corresponding cationic species [(HNacnac)Ni(η^5 -L)][B(C₆F₅)₄] (L = Cp (**5**), indenyl (**6**)). While the symmetric compound **3** is paramagnetic, disruption of the symmetry in **4–6** results in diamagnetism. The species [(Nacnac)Ni]₂(μ - η^5 : η^5 -Cp)][B(C₆F₅)₄] (**7**) was prepared in an unusual fashion from the reaction of [(Nacnac)Ni]₂(η^6 : η^6 -C₆H₅Me) (**2**) with [Ph₃C][B(C₆F₅)₄] and Cp₂ZrMe₂, while compound **3** serves as a synthon to the neutral bimetallic Ni(II)/Ni(I) species [(Nacnac)Ni]₂(μ - η^2 : η^2 -Cp)] (**8**). Compounds **7** and **8** are readily interconverted electrochemically. Consideration of the molecular orbitals reveals that the unpaired electron in **8** prompts alteration of the nature of the bridging cyclopentadienyl ligand between the metal centers. Crystal structures of **3–5**, **7**, and **8** are reported.

Introduction

β -Diketiminato ligand complexes continue to draw considerable attention. Main-group complexes,^{1–8} as well as lanthanide^{3,9–12} and transition-metal compounds,^{7,13–46} have been the focus of numerous recent studies. Our interests in such species have focused on Ni(I),⁴⁷ Fe(I),⁴⁸ and Ti(III)⁴⁹ β -diketiminato com-

plexes. In the case of Ni(I) synthons we described the complex [(Nacnac)Ni]₂(μ - η^3 : η^3 -C₆H₅Me)] (Nacnac = HC(CMe)NC₆H₃i-

[†] This paper is dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

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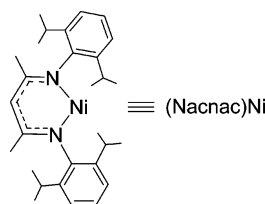
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Chart 1. The (Nacnac)Ni fragment



Pr₂); Chart 1), which proved to act as a synthon for β -diketiminato Ni(I) complexes.⁴⁷ The bridging nature of the toluene fragment in this complex prompted us to consider (β -diketiminato)Ni cyclopentadienyl complexes. While transition-metal complexes containing cyclopentadienyl ligands have been known since the genesis of organometallic chemistry in the 1950s, the vast majority of compounds containing Cp ligands involve a metal–Cp interaction that is η^5 in nature. In addition, a number of examples of complexes containing bridging cyclopentadienyl ligands have also been characterized. Such a “triple-decker” complex, [(CpNi)₂(μ - η^5 -Cp)][BF₄],^{50,51} was first reported in 1974. Since then, related symmetric homobimetallic complexes, including [(CpFe)₂(μ - η^5 -Cp)]PF₆,⁵² [(η -C₆Me₆)Co-(μ - η^5 -Cp)NiCp]PF₆,⁵³ and [(η -9-Me₂S-7,8-C₂B₉H₁₀Ni)₂(μ - η^5 -Cp)]X (X = PF₆, BF₄),⁵⁴ have also been described. In addition, dissymmetric, cyclopentadienyl-bridged, heterobimetallic complexes such as [Cp**M*(μ -Cp)RuCp*]CF₃SO₃ (M = Ru, Fe)⁵⁵ and [(Cp**Ru*(μ - η^5 -Cp*)Ru(η -9-Me₂S-7,8-C₂B₉H₁₀)]PF₆⁵⁴ were also reported. In this report we describe the synthesis and characterization of both monometallic and bimetallic Ni- β -diketiminato complexes that incorporate cyclopentadienyl ligands. The nature of the Cp–metal interaction is probed with structural and electronic perturbations.

Experimental Section

General Data. All preparations were performed under an atmosphere of dry O₂-free N₂, employing either Schlenk-line techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were purified by employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N₂. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers operating at 300 and 500 MHz, respectively. Deuterated benzene and toluene were purchased from Cambridge Isotopes Laboratories, freeze–pump–thaw-degassed (three times), and vacuum-distilled from the appropriate drying agents. Trace amounts of protonated solvents were used as references, and ¹H and ¹³C{¹H} NMR chemical shifts are reported relative to SiMe₄. ³¹P{¹H}, ¹¹B{¹H}, and ¹⁹F NMR spectra were referenced to external 85% H₃PO₄, BF₃·Et₂O, and CFCl₃, respectively. Magnetic moments were determined by employing the Evans method.⁵⁶ Cyclic voltammetry was carried

out under an atmosphere of N₂ using a BAS potentiostat, with a Ag/AgCl reference electrode, a Pt working electrode, 0.1 M [Bu₄N][PF₆] as the supporting electrolyte, and a scan rate of 50 mV s⁻¹. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. Combustion analyses were performed at the University of Windsor Chemical Laboratories employing a Perkin-Elmer CHN analyzer. (Nacnac)Ni(μ -Br)₂Li(THF)₂ (**1**) and [(Nacnac)Ni]₂(η^6 : η^6 -C₆H₅Me) (**2**) were prepared as previously reported.⁴⁷

Synthesis of (Nacnac)Ni(η^5 -Cp) (3**).** THF (40 mL) was added to a mixture of **1** (6.30 g, 8.0 mmol) and LiCp (0.576 g, 8.0 mmol) at 25 °C, and the mixture was stirred overnight. THF was removed in vacuo, leaving a deep red solid, which was then dissolved in toluene (20 mL) and the solution stirred for 20 min at 25 °C. After filtration and subsequent concentration in vacuo, the deep red solution was stored at –35 °C for 1 week to isolate dark red crystals of **3** (3.05 g). Yield: 70%. Magnetic susceptibility: $\mu = 2.05 \mu_B$. IR (Nujol): 1940 (w), 1922 (w), 1865 (w), 1804 (w), 1729 (m), 1701 (w), 1655 (w), 1624 (m), 1548 (s), 1528 (s), 1464 (s), 1435 (s), 1400 (s), 1257 (s), 1229 (m), 1178 (s), 1102 (s), 1056 (m), 1026 (s), 935 (s), 885 (m), 854 (m), 796 (s), 779 (s), 763 (s), 717 (m), 629 (w), 599 (w), 530 (m), 458 (m) cm⁻¹. ¹H NMR (C₆D₆): δ 15.54 (s, 4 H, Ar), 14.11 (br s, 4 H, CHMe₂), 4.32 (br s, 12 H, CHMe₂), 2.69 (br s, 2 H, Ar), 2.08 (br s, 12 H, CHMe₂), –24.75 (s, 6 H, CMe), –66.8 (s, 1 H, γ -CH), –105.40 (br s, 5 H, Cp). ¹³C NMR (C₆D₆): δ 237.3, 159.4, 127.0, 123.7, 85.0, 47.1, 44.2, 28.5, –8.0, –154.4; Anal. Calcd for C₃₄H₄₆N₂Ni (541.5): C, 75.4; H, 8.6; N, 5.2. Found: C, 75.5; H, 8.9; N, 5.2.

Synthesis of (Nacnac)Ni(η^3 -Ind) (4**).** LiBu (1.6 M in hexanes; 2.5 mL, 4.0 mmol) was added to a solution of indene (0.46 g, 4.0 mmol) in toluene (20 mL) at 25 °C, and the reaction mixture was stirred overnight. **1** (3.14 g, 4.0 mmol) was subsequently added, resulting in an intense red mixture which was stirred for an additional 24 h. After filtration and subsequent concentration in vacuo, the resulting deep red solution was kept at –35 °C for 2 days to isolate dark red crystals of **4** (2.2 g). Yield: 92%. IR (Nujol): 1914 (w), 1859 (w), 1795 (w), 1718 (w), 1690 (w), 1657 (w), 1582 (w), 1527 (s), 1500 (m), 1463 (s), 1431 (s), 1403 (s), 1383 (s), 1337 (m), 1310 (s), 1252 (s), 1220 (m), 1176 (s), 1110 (m), 1059 (m), 1046 (s), 1024 (s), 936 (m), 919 (m), 892 (m), 859 (m), 794 (s), 758 (s), 735 (s), 644 (w), 601 (w), 522 (m), 457 (m), 431(m) cm⁻¹. ¹H NMR (C₆D₆): δ 7.92 (t, ³J_{HH} = 3 Hz, 1 H, Ind H²), 7.21–7.06 (m, Ar), 6.61 (m, ³J_{HH} = 5 Hz, ⁴J_{HH} = 3 Hz, 2 H, Ind H^{4,7}), 6.24 (m, ³J_{HH} = 5 Hz, ⁴J_{HH} = 3 Hz, 2 H, Ind H^{5,6}), 5.03 (s, 1 H, γ -CH), 3.63 (sept, ³J_{HH} = 7 Hz, 4 H, CHMe₂), 3.25 (d, ³J_{HH} = 3 Hz, 2 H, Ind H^{1,3}), 1.57 (s, 6 H, CMe), 1.35 (d, ³J_{HH} = 7 Hz, 12 H, CHMe₂), 1.15 (d, ³J_{HH} = 7 Hz, 12 H, CHMe₂). ¹³C{¹H} NMR (C₆D₆): δ 160.5 (NC), 152.4, 141.7 (Ar), 141.3 (Ind C²), 125.3 (Ind C^{3a,7a}), 125.2, 123.9 (Ar), 119.5 (Ind C^{4,7}), 108.9 (Ind C^{5,6}), 100.3 (γ -C), 73.8 (Ind C^{1,3}), 28.3 (CHMe₂), 24.8, 24.4 (CHMe₂), 23.0 (NCMe). Anal. Calcd for C₃₈H₄₈N₂Ni (591.5): C, 77.1; H, 8.2; N, 4.7. Found: C, 77.3; H, 8.5; N, 4.6.

Synthesis of [(HNacnac)Ni(η^5 -L)][B(C₆F₅)₄·C₇H₈ (L = Cp (5**), Ind (**6**)).** These compounds were prepared in a similar fashion, and thus only one preparation is detailed. [PhMe₂NH][B(C₆F₅)₄] (0.320 g, 0.4 mmol) was added to the solution of **3** (0.216 g, 0.4 mmol) in toluene (10 mL). The solution immediately turned orange, and an orange precipitate was formed. After it was stirred for 2 h, the solution was allowed to stand at 25 °C for 2 days. The orange crystalline compound **5** (0.51 g) was isolated. Yield: 96%. IR (Nujol): 1944 (w), 1877 (w), 1800 (w), 1732 (m), 1640 (s), 1559 (w), 1512 (s), 1461 (s), 1406 (m), 1376 (s), 1319 (m), 1271 (s), 1207 (m), 1162 (m), 1086 (s), 1055 (m), 1029 (m), 975 (s), 914 (m), 834 (m), 794 (s), 772 (m), 754 (m), 726 (s), 684 (m), 661 (s), 607 (m), 573 (m), 466 (m) cm⁻¹. ¹H NMR (C₆D₅Br): δ 7.24–7.10 (m, PhMe and Ar), 4.27 (s, 5 H, Cp), 3.90 (s, 2 H, γ -CH₂), 3.13 (sept, ³J_{HH} = 7 Hz, 4 H, CHMe₂), 2.26 (s, PhMe), 1.67 (s, 6

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H, *CMe*), 1.30 (d, $^3J_{\text{HH}} = 6$ Hz, 12 H, *CHMe*₂), 0.99 (d, $^3J_{\text{HH}} = 6$ Hz, 12 H, *CHMe*₂). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): δ 179.0 (NC), 148.1 (d(m), $^1J_{\text{CF}} = 245$ Hz, *o*- $\text{C}(\text{C}_6\text{F}_5)$), 146.8 (*Ar*), 138.3 (d(m), $^1J_{\text{CF}} = 247$ Hz, *p*- $\text{C}(\text{C}_6\text{F}_5)$), 137.3 (*Ar*), 137.2 (*PhMe*), 136.4 (d(m), $^1J_{\text{CF}} = 245$ Hz, *m*- $\text{C}(\text{C}_6\text{F}_5)$), 128.9 (*PhMe*), 128.6 (*Ar*), 128.1 (*PhMe*), 125.2 (*PhMe*), 124.7 (*Ar*), 96.3 (*Cp*), 49.0 (γ -*C*), 28.1 (*CHMe*₂), 26.5, 24.1 (*CHMe*₂), 23.5 (*NcMe*), 21.3 (*PhMe*). ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$): δ -54.1 (8F, *o*-*F*), -84.5 (s br, 4F, *p*-*F*), -88.3 (s br, 8F, *m*-*F*). $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): δ -16.7 (s). Anal. Calcd for $\text{C}_{65}\text{H}_{55}\text{BF}_{20}\text{N}_2\text{Ni}$ (1313.67): C, 59.4; H, 4.2; N, 2.1. Found: C, 59.6; H, 4.2; N, 2.1. **6**: Yield: 93%. IR (Nujol): 1945 (w), 1877 (w), 1807 (w), 1733 (m), 1641 (s), 1617 (m), 1513 (s), 1465 (s), 1377 (s), 1317 (m), 1278 (s), 1210 (m), 1164 (m), 1088 (s), 979 (s), 935 (m), 916 (m), 879 (w), 815 (m), 797 (m), 774 (m), 755 (m), 730 (m), 685 (m), 662 (m), 608 (m), 573 (m), 470 (m), 431 (w) cm^{-1} . ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): δ 7.17–6.94 (m, *Ar*, *Ind H*^{2,7}), 6.65 (m, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.1$ Hz, 2 H, *Ind H*^{4,7}), 5.75 (m, $^3J_{\text{HH}} = 6$ Hz, $^4J_{\text{HH}} = 3$ Hz, 2 H, *Ind H*^{5,6}), 3.82 (d, $^3J_{\text{HH}} = 3$ Hz, 2 H, *Ind H*^{1,3}), 3.48, 3.46 (ds, 2 H, γ -*CH*₂), 2.77 (sept, $^3J_{\text{HH}} = 7$ Hz, 2 H, *CHMe*₂), 2.28 (sept, $^3J_{\text{HH}} = 7$ Hz, 2 H, *CHMe*₂), 2.17 (s, 1 H, *PhMe*), 1.53 (s, 6 H, *CMe*), 1.18 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H, *CHMe*₂), 1.08 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H, *CHMe*₂), 0.90 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H, *CHMe*₂), 0.70 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H, *CHMe*₂). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): δ 177.7 (NC), 148.5 (d(m), $^1J_{\text{CF}} = 243$ Hz, *o*- $\text{C}(\text{C}_6\text{F}_5)$), 145.3 (*Ar*), 138.3 (d(m), $^1J_{\text{CF}} = 245$ Hz, *p*- $\text{C}(\text{C}_6\text{F}_5)$), 137.7 (*Ar*), 137.5 (*PhMe*), 137.3 (*Ind*, *C*²), 136.4 (d(m), $^1J_{\text{CF}} = 248$ Hz, *m*- $\text{C}(\text{C}_6\text{F}_5)$), 133.3 (*Ar*), 128.9 (*PhMe*), 128.8, 128.2 (*Ar*), 128.0 (*PhMe*), 125.4 (*Ind*, *C*^{3a,7a}), 125.2 (*PhMe*), 124.2, 123.9 (*Ar*), 119.8 (*Ind*, *C*^{4,7}), 107.5 (*Ind*, *C*^{5,6}), 78.5 (*Ind*, *C*^{1,3}), 47.4 (γ -*C*), 29.0, 27.6 (*CHMe*₂), 26.7, 24.4, 24.3, 23.5 (*CHMe*₂), 23.5 (*NcMe*), 21.3 (*PhMe*). $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): -16.7 (s). ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$): δ -54.20 (s, 8F, *o*-*F*), -84.57 (t, 4F, $^3J_{\text{FF}} = 21.1$ Hz, *p*-*F*), -88.40 (t, 8F, $^3J_{\text{FF}} = 17.3$ Hz, *m*-*F*). Anal. Calcd for $\text{C}_{69}\text{H}_{57}\text{BF}_{20}\text{N}_2\text{Ni}$ (1363.73): C, 60.8; H, 4.2; N, 2.1. Found: C, 60.5; H, 4.4; N, 2.2.

Synthesis of $[(\text{Nacnac})\text{Ni}]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-Cp})[\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{C}_6\text{H}_6$ (7**).** $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.184 g, 0.20 mmol) was added to a solution of Cp_2ZrMe_2 (0.050 g, 0.20 mmol) in toluene (10 mL) at room temperature. Stirring was continued for 20 min, after which **2** (0.208 g, 0.20 mmol) was added to the resulting pale yellow solution at 25 °C. Stirring was continued for 12 h. After concentration (to 3 mL) in vacuo, the resulting brown solution was kept at -35 °C for 1 week to isolate orange crystals of **7** (0.15 g). Yield: 42%. X-ray crystals were obtained from benzene solution. IR (Nujol): 1936 (w), 1872 (w), 1810 (w), 1733 (s), 1642 (s), 1584 (m), 1533 (s), 1513 (s), 1464 (s), 1374 (s), 1317 (s), 1277 (s), 1259 (s), 1193 (m), 1175 (m), 1089 (s), 1058 (m), 1026 (m), 979 (s), 936 (m), 906 (m), 843 (m), 797 (s), 771 (s), 761 (s), 731 (s), 701 (m), 684 (m), 662 (m), 637 (m), 607 (m), 574 (m), 525 (m), 452 (m) cm^{-1} . ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): δ 7.24–7.10 (m, *PhMe* and *Ar*), 4.56 (s, 2 H, γ -*CH*), 3.21 (s, 5 H, *Cp*), 2.90 (sept, $^3J_{\text{HH}} = 7$ Hz, 8 H, *CHMe*₂), 2.18 (s, *PhMe*), 1.46 (s, 12 H, *CMe*), 1.17 (d, $^3J_{\text{HH}} = 6$ Hz, 24 H, *CHMe*₂), 0.86 (d, $^3J_{\text{HH}} = 6$ Hz, 24 H, *CHMe*₂). ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$): δ -53.6 (s, 8F, *o*-*F*), -83.9 (s br, 4F, *p*-*F*), -87.7 (s br, 8F, *m*-*F*). $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): δ -16.0 (s). Anal. Calcd for $\text{C}_{94}\text{H}_{95}\text{BF}_{20}\text{N}_4\text{Ni}_2$ (1789.03): C, 63.1; H, 5.4; N, 3.1. Found: C, 62.9; H, 5.6; N, 3.1.

Synthesis of $[(\text{Nacnac})\text{Ni}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-Cp})\cdot 2\text{C}_7\text{H}_8$ (8**).** Toluene (10 mL) was added to a mixture of **2** (0.208 g, 0.200 mmol) and **3** (0.216 g, 0.400 mmol) at 25 °C, and the mixture was stirred overnight. The solution was concentrated in vacuo to give a deep green solution, which was then kept at -35 °C overnight to isolate dark green crystals of **8** (0.39 g). Yield: 95%. Magnetic susceptibility: $\mu = 2.74 \mu_{\text{B}}$. IR (Nujol): 1918 (w), 1868 (w), 1843 (w), 1795 (w), 1774 (w), 1739 (m), 1684 (m), 1650 (m), 1530 (s), 1458 (s), 1408 (s), 1258 (s), 1176 (s), 1099 (s), 1026 (s), 933 (m), 859 (m), 796 (s), 758 (m), 719 (m), 669 (m), 524 (m) cm^{-1} . EPR ($\text{C}_6\text{H}_5\text{Me}$): 2.0638. Cyclic voltammetry: $E_{1/2} = 0.186$ V ($\Delta E_p =$

0.076 V). Anal. Calcd for $\text{C}_{63}\text{H}_{87}\text{N}_4\text{Ni}_2$ (1017.8): C, 74.3; H, 8.6; N, 5.5. Found: C, 73.8; H, 8.9; N, 5.5.

Molecular Orbital Computations. All DFT calculations were performed using the Gaussian 03 suite of programs.⁵⁷ The basis set consisted of the LANL2DZ basis set on Ti in combination with the 6-31G(d) basis set^{58–61} on the all other atom types. The geometries for the computational models were based on the crystallographic results presented herein.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2 -free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data ($4.5^\circ < 2\theta < 45\text{--}50.0^\circ$) were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and SHELXTL processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.⁶² The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F , minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C–H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Crystallographic data for **3**, **4**, **5**· C_7H_8 , **7**· C_6H_6 , and **8**· $2\text{C}_7\text{H}_8$ are given in Table 1.

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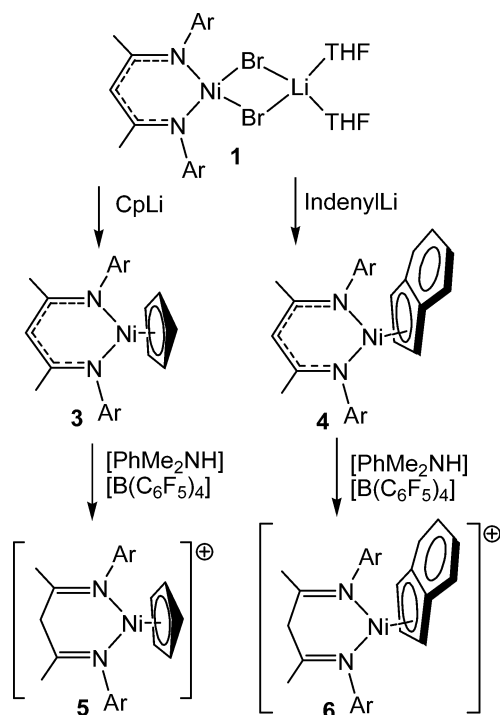
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(62) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, pp 71–147.

Table 1. Crystallographic Data

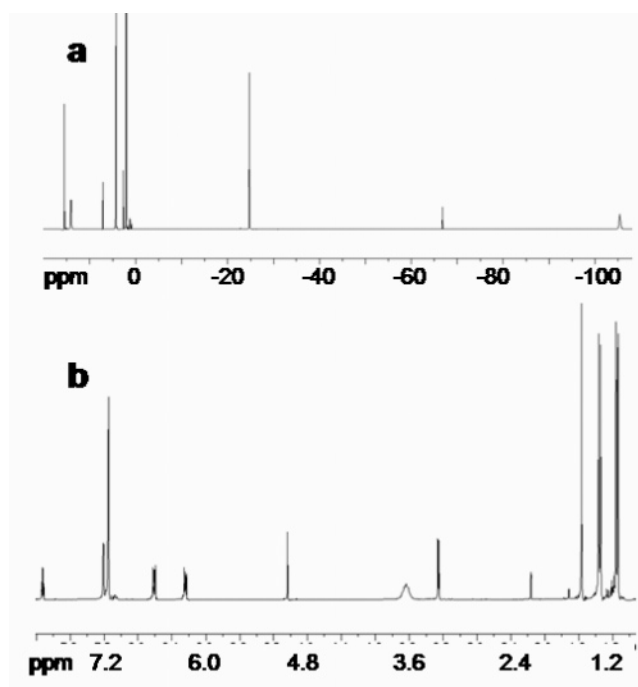
	3	4	5·C ₇ H ₈	7·C ₆ H ₆	8·2C ₇ H ₈
formula	C ₆₈ H ₉₂ N ₄ Ni ₂	C ₃₈ H ₄₈ N ₂ Ni	C ₆₅ H ₅₅ BF ₂₀ N ₂ Ni	C ₉₃ H ₉₃ BF ₂₀ N ₄ Ni ₂	C ₇₇ H ₁₀₃ N ₄ Ni ₂
formula wt	1082.88	591.49	1313.63	1774.94	1202.05
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>P2₁/m</i>	<i>P1</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> (Å)	15.9906(8)	9.1721(10)	12.9531(6)	16.4974(5)	26.558(3)
<i>b</i> (Å)	20.2397(10)	20.653(2)	16.1270(8)	24.8888(8)	13.5604(14)
<i>c</i> (Å)	19.3992(10)	9.4619(10)	17.2826(9)	21.5075(7)	20.873(2)
α (deg)			115.0140(10)		
β (deg)	90.1420(10)	116.5660(10)	90.7370(10)	92.0440(10)	109.646(2)
γ (deg)			110.5410(10)		
<i>V</i> (Å ³)	6278.4(5)	1603.1(3)	3007.8(3)	8825.4(5)	7079.5(12)
<i>Z</i>	4	2	2	4	4
<i>d</i> (calcd) (g cm ⁻³)	1.146	1.225	1.450	1.336	1.128
abs coeff, μ (cm ⁻¹)	0.641	0.633	0.427	0.516	0.575
no. of data collected	24 198	10 838	10 123	31 748	16 955
no. of data $F_o^2 > 3\sigma(F_o^2)$	7863	2335	5812	10 366	5077
no. of variables	667	190	802	1101	340
<i>R</i>	0.0401	0.0469	0.0428	0.0393	0.0844
<i>R_w</i>	0.0871	0.1224	0.1218	0.0796	0.2219
GO _F	0.818	0.989	0.847	0.826	0.947

Scheme 1. Synthesis of (Nacnac)NiCp complexes 3–6



Results and Discussion

Monometallic Species. Reaction of the previously reported species (Nacnac)Ni(μ -Br)₂Li(THF)₂ (**1**) with LiCp proceeds in THF to give the new red crystalline solid **3** in 70% yield after workup (Scheme 1). The ¹H NMR spectra (Figure 1a) show paramagnetically shifted resonances at chemical shifts ranging from 15.5 to –105 ppm. The resonances were assigned on the basis of integrations. It is noteworthy that two resonances at 4.32 and 2.08 ppm, attributable to the isopropyl methyl groups, were observed. In addition, resonances attributed to the aromatic protons were observed at 15.54 and 2.69 ppm, while resonances at 14.11 and –24.75 ppm were attributed to the isopropyl methine and backbone methyl groups of the Nacnac ligand. Resonances at –66.8 and –105.40 ppm were assigned to the backbone methine protons of the Nacnac and Cp ligands, respectively. Similarly, the ¹³C{¹H} NMR spectrum of **3** gave rise to corresponding resonances ranging from 237.3 to –154.4 ppm. These data suggest the formulation of **3** as a paramagnetic

Figure 1. NMR spectra of (a) **3** and (b) **4**.

Ni(II) complex containing Cp and Nacnac ligands. Indeed, an X-ray crystallographic study confirmed the formulation of **3** as (Nacnac)Ni(η -Cp) (Figure 2). The Ni center in **3** is coordinated to the Nacnac ligand as well as to the cyclopentadienyl ligand in a π fashion. The Ni–N distances were found to be 1.937(3) and 1.948(3) Å with a N–Ni–N angle of 94.19(11)°. The Ni–C bond lengths were found to fall in two ranges: three Ni–C bond lengths were between 2.185(5) and 2.189(5) Å, while the remaining two were found to be 2.197(5) and 2.202(5) Å. The plane of the cyclopentadienyl ligand is oriented at an angle of 90.8° with respect to the NiN₂ plane. The Ni–C distances are similar to those seen in η^2 -bound Ni(II)-cyclopentadienyl complexes CpNi(L)Cl (L = carbene, phosphine).⁶³ However, it is noteworthy that the observation of two significantly longer Ni–C bond lengths in **3** suggests a distortion toward an η^3 -bonding mode.

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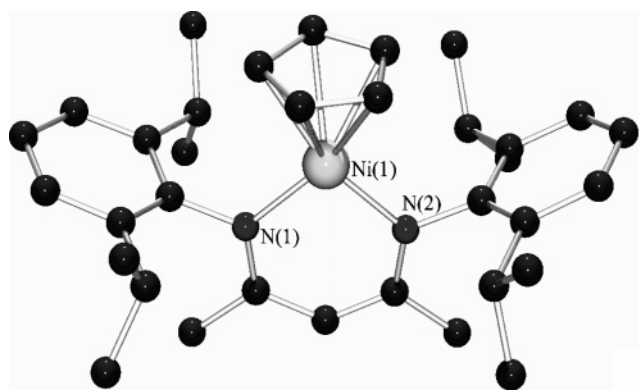


Figure 2. Grayscale POV-ray drawing of **3**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.937(3), Ni(1)–N(2) = 1.948(3), Ni(1)–C(34) = 2.185(5), Ni(1)–C(31) = 2.189(5), Ni(1)–C(33) = 2.188(5), Ni(1)–C(32) = 2.197(5), Ni(1)–C(30) = 2.202(5); N(1)–Ni(1)–N(2) = 94.19(11).

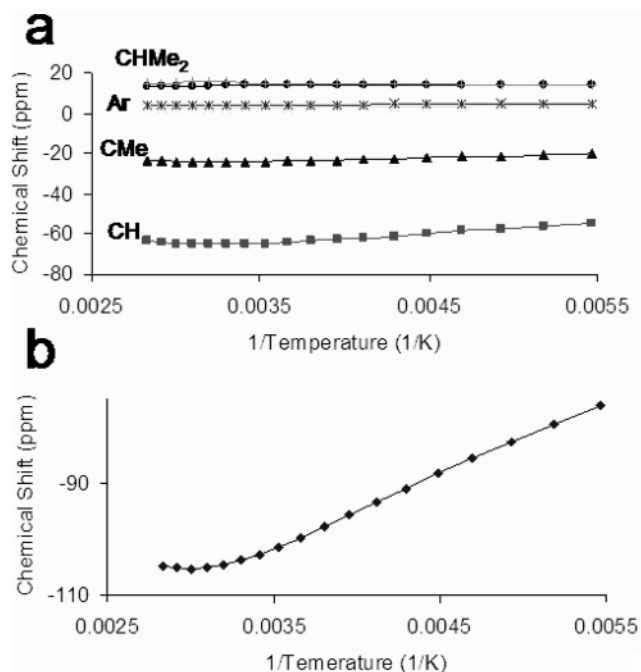


Figure 3. Plots of δ vs T^{-1} for the ^1H spectrum of **3**: (a) Nacnac ligand resonances; (b) Cp ligand resonance.

The paramagnetic behavior of **3** was investigated via variable-temperature ^1H NMR experiments. Over the temperature range from -90 to 80 °C, there were relatively small shifts in the positions of the resonances associated with the Nacnac ligand, while the Cp resonance shifted from -105 to -76 ppm (Figure 3). These data for **3** show a trend similar to that reported for $(\text{Acac})\text{NiCp}^*$, although in this latter case decreasing temperature results in a change in the chemical shift of the Cp* protons from almost 90 ppm into the diamagnetic region, consistent with a triplet to singlet high-spin to low-spin crossover.⁶⁴ While the smaller shift for **3** suggests that **3** may approach diamagnetism at very low temperature, it remains paramagnetic above -90 °C.

In a similar fashion the Ni synthon **1** was reacted with indenyllithium (Scheme 1). This ultimately afforded the related dark red crystalline complex **4** in 92% yield. In marked contrast

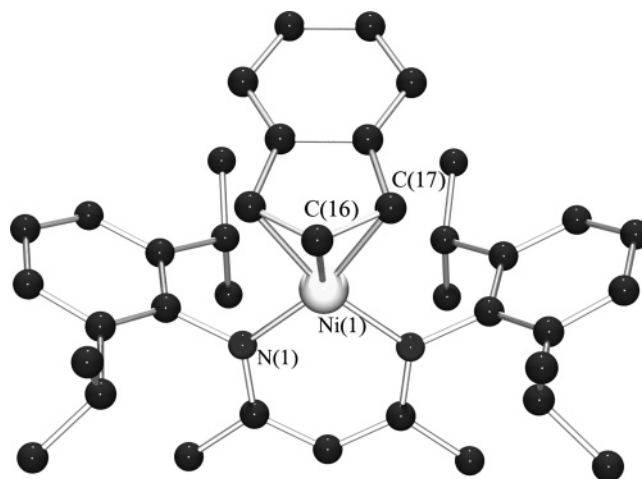


Figure 4. Grayscale POV-ray drawing of **4**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.919(2), Ni(1)–C(16) = 2.007(5), Ni(1)–C(17) = 2.108(3); N(1)–Ni(1)–N(1') = 95.33(3).

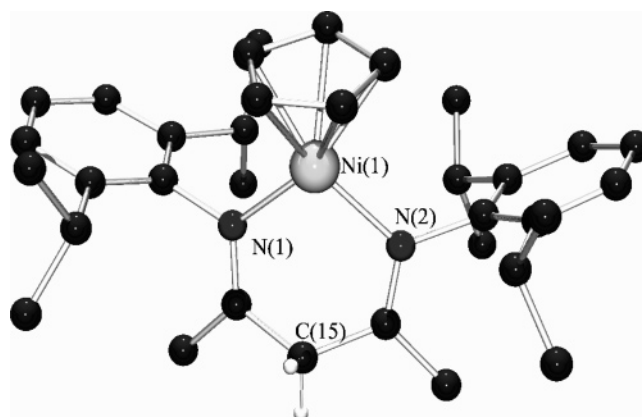


Figure 5. Grayscale POV-ray drawing of the cation of **5**. Hydrogen atoms, with the exception of those on the central methylene carbon of the protonated Nacnac ligand, are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.928(3), Ni(1)–N(2) = 1.942(3), Ni(1)–C(30) = 2.069(4), Ni(1)–C(31) = 2.154(5), Ni(1)–C(32) = 2.155(4), Ni(1)–C(33) = 2.092(4), Ni(1)–C(34) = 2.143(3), C(13)–C(15) = 1.516(5), C(15)–C(16) = 1.487(5); N(1)–Ni(1)–N(2) = 95.50(12).

to **3**, compound **4** exhibited ^1H NMR resonances typical of a diamagnetic species (Figure 4). Of particular interest are the resonances at 7.92 and 3.25 ppm, which were attributed to the protons on the C₅ ring of the indenyl ligand. The backbone methine proton of the Nacnac ligand was observed at 5.03 ppm, while the methine protons of the isopropyl substituents gave rise to a multiplet at 3.63 ppm. These data, together with the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, were consistent with the formulation of **4** as $(\text{Nacnac})\text{Ni}(\eta^3\text{-Ind})$. This was subsequently confirmed by X-ray diffraction (Figure 4). The overall geometry of **4** is similar to that seen for **3**, as the Ni–N distance was found to be 1.919(2) Å, with a chelate bite angle of 95.33(13)°. The indenyl ligand adopts an η^3 coordination mode with Ni–C distances of 2.007(5) and 2.108 Å. The other two carbons of the C₅ ring reside 2.570 and 2.676 Å away from Ni. The closer approach of three of the carbons of the C₅ ring of the indenyl ligand to Ni in **4** is also reflected in the angle of 79.7° between the C₅ plane and the NiN₂ plane. The orientation of the indenyl ring directs the 1,3-protons toward the center of the arene rings of the Nacnac ligand at distances of 2.77 and 2.74 Å from the

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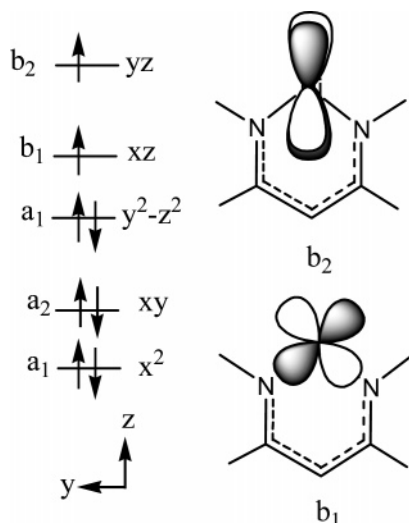


Figure 6. Frontier orbitals of (Nacnac)MCl.²⁶

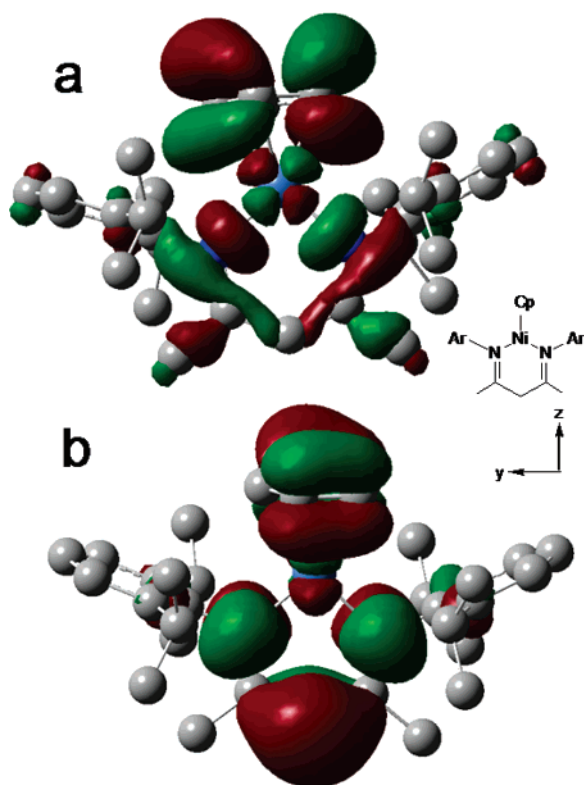


Figure 7. Gaussview depictions of (a) the higher energy SOMO and (b) the lower energy SOMO for the triplet state of **3**.

arene planes. It is this geometry that presumably accounts for the upfield resonance described above and attributed to these protons.

Compounds **3** and **4** were found to react rapidly with 1 equiv of [PhMe₂NH][B(C₆F₅)₄], affording the orange crystalline compounds **5** and **6** in 96% and 93% yield, respectively (Scheme 1). Both compounds displayed poor solubility in toluene compared to their precursors; nonetheless, NMR data typical of diamagnetic species were obtained for **5** and **6** in C₆D₅Br. In the case of **5**, resonances observed were as expected, with the addition of a resonance at 3.90 ppm, attributable to a methylene group derived from protonation of the central carbon of the Nacnac ligand. Similarly, resonances at 3.48 and 3.46 ppm are attributable to the similar but inequivalent protons in **6**. X-ray crystallographic data were obtained for **5** (Figure 5).

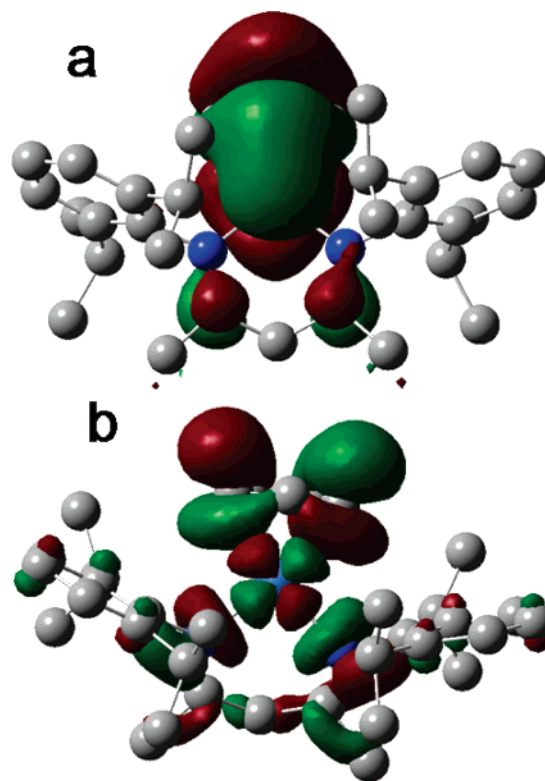
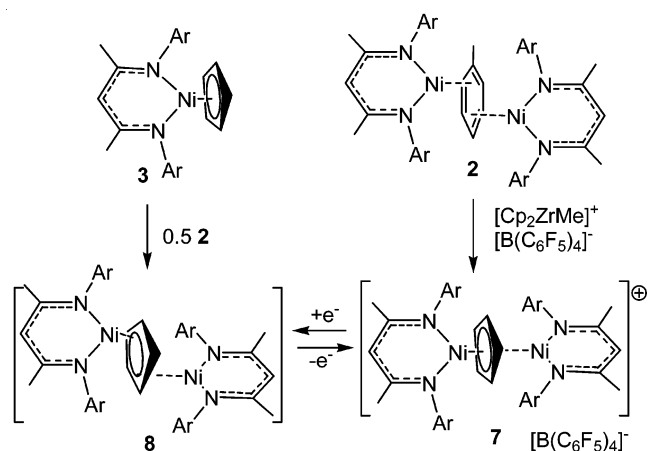


Figure 8. Gaussview depictions of (a) the HOMO and (b) the LUMO of **5**.

Scheme 2. Synthesis of Bimetallic Complexes **7** and **8**



The structural data confirm the η^5 -binding mode of the cyclopentadienyl ligand and the puckered nature of the protonated Nacnac ligand backbone. Such puckering has been previously described for the species (HNacnac)NiBr₂.⁶⁵ Similar to that seen in **3**, the angle between the NiN₂ and the C₅ planes in **5** is 90.5°. The Ni–N distances were found to be 1.928(3) and 1.942(3) Å, slightly longer than those reported above for **3**, consistent with the protonation of the Nacnac ligand and, thus, poorer donor ability. Nonetheless, the N–Ni–N bite angle in **5** is 95.50(12)°, similar to that seen in **3**. Protonation of the central carbon of the Nacnac ligand is further evidenced by the increase in the C–C bond lengths of the ligand backbone, as the C(13)–C(15) and C(15)–C(16) bond lengths were found to be 1.516(5) and 1.487(5) Å, respectively. The Ni–C bond lengths for the Ni–Cp fragment ranged from 2.069(4) to 2.155-

(65) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514–1516.

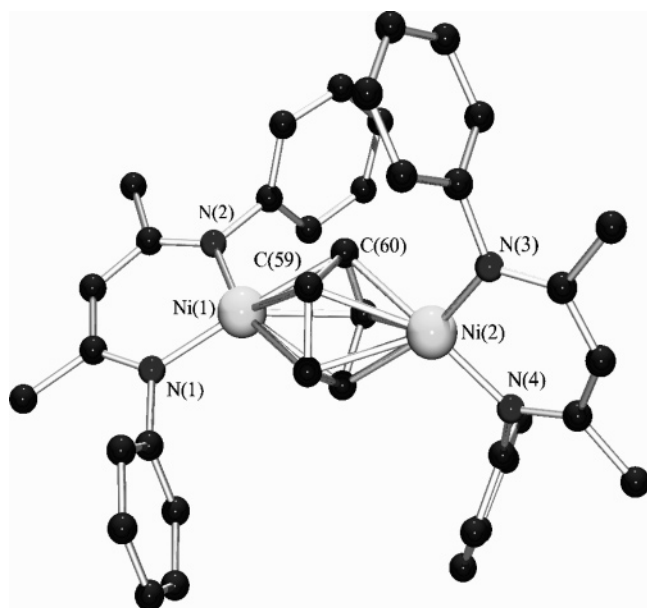


Figure 9. Grayscale POV-ray drawing of the cation of **7**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.903(3), Ni(1)–N(2) = 1.916(3), Ni(1)–C(59) = 2.246(4), Ni(1)–C(60) = 2.229(4), Ni(1)–C(61) = 2.212(4), Ni(1)–C(62) = 2.240(4), Ni(1)–C(63) = 2.252(4), Ni(2)–N(4) = 1.906(3), Ni(2)–N(3) = 1.908(3), Ni(2)–C(61) = 2.207(4), Ni(2)–C(62) = 2.214(4), Ni(2)–C(60) = 2.240(4), Ni(2)–C(63) = 2.260(4), Ni(2)–C(59) = 2.271(4), N(1)–C(13) = 1.335(4), N(1)–C(1) = 1.451(4), N(2)–C(16) = 1.322(4), N(2)–C(18) = 1.451(4), N(3)–C(42) = 1.335(4), N(3)–C(30) = 1.449(4), N(4)–C(45) = 1.338(4), N(4)–C(47) = 1.447(4); N(1)–Ni(1)–N(2) = 95.62(12), N(4)–Ni(2)–N(3) = 96.43(11).

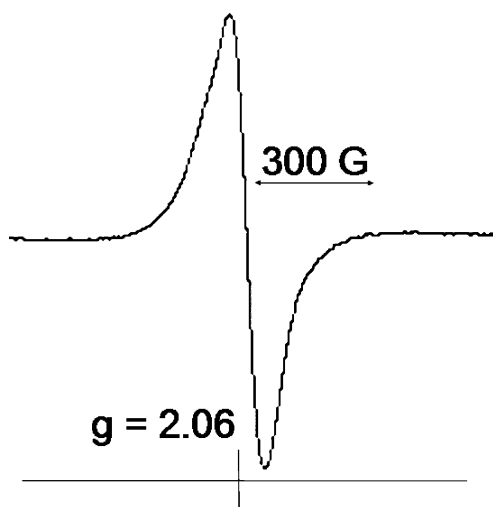


Figure 10. EPR spectrum of **8**.

(4) Å. These distances are considerably shorter than those observed in **3**, reflecting the cationic charge on the Ni center.

The frontier orbitals for a series of complexes of the form (Nacnac)MCl have been described by Holland, Cundari, and co-workers (Figure 6).²⁶ In these cases, the computed orbitals were found to be primarily (~90%) metal in character, with minor contributions from the diketiminate N ligand. To consider the nature of the present complexes, single-point molecular orbital calculations were performed using the Gaussian software package employing DFT methods and geometries based on the crystallographic structural data. Comparative computations of the high- and low-spin states for **3** were consistent with the experimental observation that the high-spin state is lower in

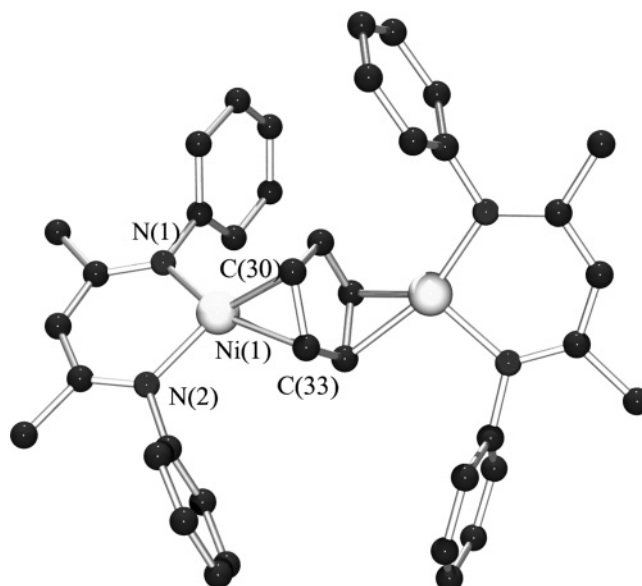


Figure 11. Grayscale POV-ray drawing of **8**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)–N(1) = 1.936(7), Ni(1)–N(2) = 1.930(7), Ni(1)–C(30) = 2.050(11), Ni(1)–C(33) = 2.138(10), Ni(1)–C(31) = 2.343(6); N(2)–Ni(1)–N(1) = 96.1(3).

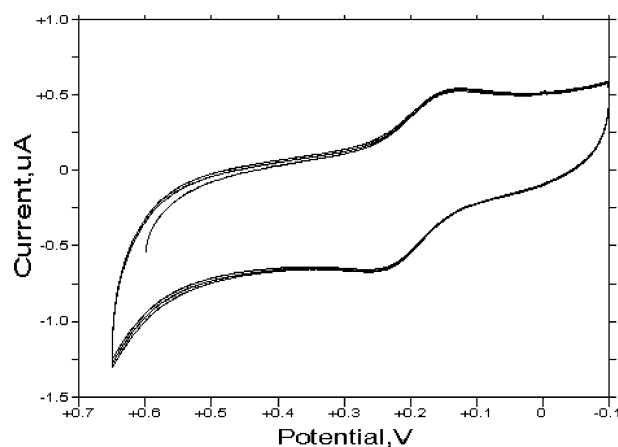


Figure 12. Cyclic voltammogram of **8**.

energy. The singly occupied orbitals (SOMOs) in **3** (Figure 7) have significant contributions from the π orbitals of Cp and Nacnac ligands; the metal-based contributions are best described as d_{xz} and d_{yz} in character, consistent with the MO analysis of Holland, Cundari, and co-workers.²⁶ Analogous calculations performed for the singlet states of **4** and **5** showed the HOMOs were comprised of a significant interaction between the metal d_{xz} orbital with π orbitals of the Cp ligand. The metal contribution to the LUMOs is best described as being derived from the Ni d_{yz} orbital (Figure 8). The HOMO–LUMO gaps in both cases were found to be greater than 300 kJ/mol, consistent with the experimentally observed diamagnetism of **4** and **5**. It appears that disruption of the symmetry of (Nacnac)–NiL either by the nature of L or by protonation of the Nacnac ligand results in the a stabilization of the MO involving the Ni d_{xz} orbital, thus prompting the observed diamagnetism.

Bimetallic Systems. Reaction of **2** with a toluene solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Cp_2ZrMe_2 afforded a brown solution that gave orange crystals of **7** in 42% yield (Scheme 2). Compound **7** proved to be sparingly soluble in most nonreactive solvents; however, it persisted for a couple of hours in $\text{C}_6\text{H}_5\text{-Br}$. ^1H NMR data suggested a 2:1 ratio of the Nacnac and Cp

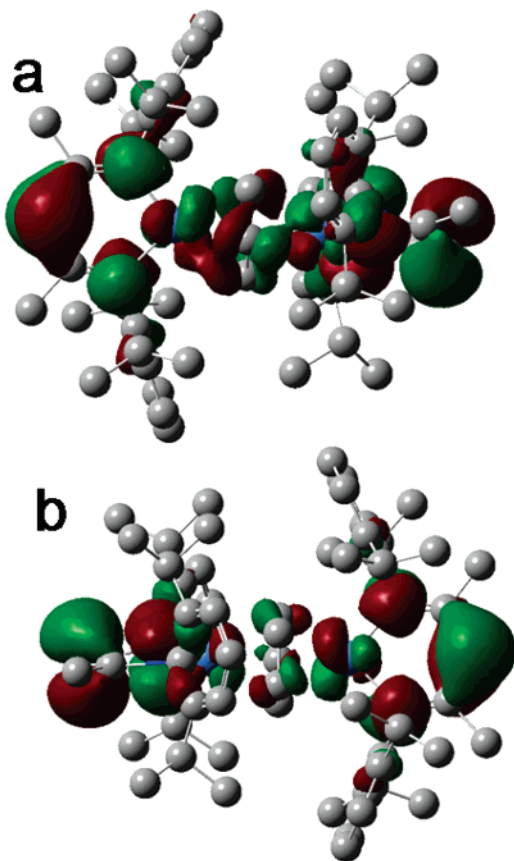


Figure 13. Gaussview depictions of the HOMO of **7**.

ligands, while the ^{19}F and $^{11}\text{B}\{^1\text{H}\}$ NMR data were consistent with the presence of the borate anion. The nature of **7** was ultimately identified by X-ray crystallography to be $[(\text{Nacnac})\text{Ni}]_2(\mu\text{-}\eta^5\text{-Cp})][\text{B}(\text{C}_6\text{F}_5)_4]\text{C}_6\text{H}_6$ (Figure 9). The cation of **7** is comprised of two (Nacnac)Ni units bridged by a cyclopentadienyl ligand. The Ni–N distances were found to range from 1.903(3) to 1.916(3) Å, with N–Ni–N bite angles of 95.62(12) and 96.43(11)°. The angle between the two NiN_2 planes is 73.8°. The cyclopentadienyl ligand binds to the two Ni centers in η^5 fashions with Ni–C distances focused between 2.212(4) and 2.271(4) Å, somewhat longer than the Ni–C distances for the bridging Cp of 2.166(17) and 2.162(10) Å in $[(\text{CpNi})_2(\mu\text{-}\eta^5\text{-}\eta^2\text{-Cp})][\text{BF}_4]$.^{50,51} The approximate 2-fold symmetry of this interaction is also reflected in the angles of 88.1 and 93.1° between the two NiN_2 planes and the C_5 plane.

In the above formation of **7**, the reaction mechanism, as well as the fate of the Zr fragment, is unknown. Nonetheless, it is reasonable to speculate that exchange of the bridging toluene in **2** for a bridging cyclopentadienyl–Zr fragment could initiate the Cp ligand transfer from Zr to Ni. In an effort to probe related reactions, the species **2** was reacted with **3**. This gave a deep green solution and ultimately dark green crystals of **8** in 95% yield (Scheme 2). This paramagnetic compound gave a single resonance in the EPR spectrum with $g = 2.0638$ (Figure 10). X-ray crystallographic analysis identified **8** as $[(\text{Nacnac})\text{Ni}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-Cp})\cdot 2\text{C}_7\text{H}_8$ (Figure 11), confirming the bimetallic nature of **8**. Although **8** is generally similar in structure to that seen in the cation of **7**, it is a neutral species consistent with a formal mixed-valence Ni(II)/Ni(I) formulation. The Ni–N distances to each Ni are 1.930(7) and 1.936(7) Å. The chelate bite angle was 96.1(3)°, while the angle between the NiN_2 planes was 49.7°, significantly smaller than the corresponding angle in the cation of **7**. The bridging cyclopentadienyl ligand also

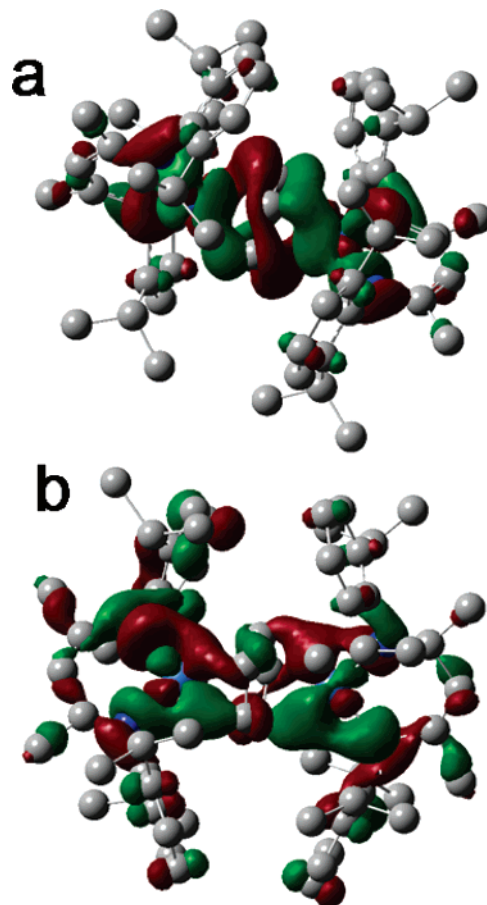


Figure 14. Gaussview depictions of (a) the LUMO of **7** and (b) the SOMO of **8**.

forms a dissymmetric bridge. The Ni(1)–C(30), Ni(1)–C(34), and Ni(1)–C(31) distances were found to be 2.050(12), 2.138(10), and 2.343(6) Å. This affirms the best description of the bridging ligand is as a bridging $\eta^2\text{:}\eta^2$ -cyclopentadienyl group.

The neutral species **8** exhibits a reversible oxidation at $E_{1/2} = 0.186$ V in a cyclic voltammetric experiment in CH_2Cl_2 using $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. The peak-to-peak separation is 0.076 V, consistent with a one-electron process (Figure 12). Moreover, this suggests the electrochemical generation of **7**. This was unambiguously confirmed by an analogous cyclic voltammetric study of **7**, which showed the expected reversible redox at the same potential. These data confirm the facile electrochemical interconversion of **7** and **8** (Scheme 2).

Single-point molecular orbital calculations were performed using the Gaussian software package employing DFT methods and the basis sets based on the crystallographic structural data for **7** and **8**. The HOMO and HOMO-1 orbitals for **7** (Figure 13) are admixtures of metal d orbitals with the Cp and Nacnac π systems. Conceptually, one can consider these the products of the interactions of the SOMOs of **3** with the frontier orbitals of a (Nacnac)Ni⁺ fragment. The LUMO of **7** is a similarly symmetric admixture of d orbitals on both metal centers and the Cp π system orbitals (Figure 14). The corresponding SOMO of **8** shows an MO with similar character. Thus, the presence of the additional electron in the SOMO of **8** is consistent with the observed structural perturbation to the Ni–Cp interactions.

In summary, both monometallic and bimetallic cyclopentadienyl and related derivatives of (Nacnac)Ni^{II} are readily prepared. The magnetic properties of monometallic species appear to be strongly linked to the symmetry of the molecule.

It is also clear that steric and electronic perturbations to (Nacnac)Ni impact the nature and symmetry of bridging cyclopentadienyl ligands of the bimetallic derivatives. The reactivity of the Nacnac–metal complexes continues to be an area of fruitful study in our laboratories. Further results will be reported in due course.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged.

Note Added after ASAP Publication. In the version of this paper published on the Web October 24, 2006, compound **7** was reported in the text with the wrong solvate, although the

correct solvate, C₆H₆, appears in Table 1. The correct solvate now appears in the text. Also, space groups for **4** and **8** have been altered to the centrosymmetric *P2₁/m* and *C2/c*, respectively. In the case of **8** this results in slightly higher *R* factors as a consequence of poor crystal quality. Details of the refinements now appear in the Supporting Information in revised CIF files.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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