

## Reactions of Transition-Metal Metallocenes with Stable Carbenes

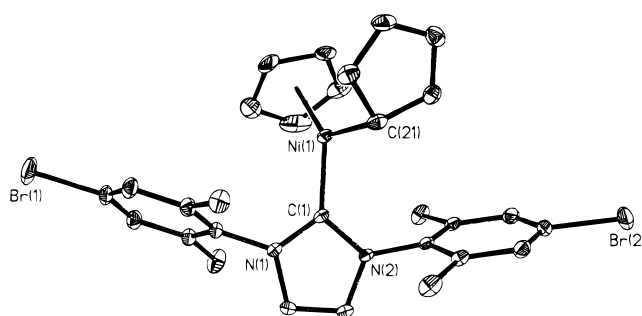
Colin D. Abernethy, Jason A. C. Clyburne,  
Alan H. Cowley,\* and Richard A. Jones\*

Department of Chemistry and Biochemistry  
The University of Texas at Austin  
Austin, Texas 78712

Received October 29, 1998

The reactivity of stable carbenes toward lanthanide<sup>1</sup> and main-group<sup>2</sup> metallocenes has been described recently. However, we are not aware of comparable studies with transition-metal metallocenes.<sup>3</sup> Herein we report (i) a facile one-step synthetic route to d-block metallocene–carbenes, (ii) the first thermally stable non-ansa chromocene adduct, and (iii) novel heterolytic reactions of a stable carbene with metallocenes, which, in the case of chromium, affords a 14-electron cation.

The reaction of equimolar quantities of nickelocene and the new stable carbene, 1,3-bis(2,6-dimethyl-4-bromo)imidazol-2-ylidene (**1**),<sup>4</sup> in toluene solution at  $-30\text{ }^{\circ}\text{C}$  afforded a 45% yield of deep red crystals of carbene complex, **2**<sup>6</sup> (Scheme 1). The <sup>1</sup>H NMR spectrum of **2**<sup>7</sup> indicated the presence of one  $\eta^1$ -bonded Cp ring, one  $\pi$ -bonded Cp ring, and one carbene moiety, a composition consistent with elemental analytical and HRMS data and the observation that the medium-resolution CI-MS fragmentation pattern exhibited peaks corresponding to the loss of the carbene or one Cp ligand. Further structural insights were provided by an X-ray analysis<sup>8</sup> (Figure 1), which confirmed the presence of  $\eta^1$ - and  $\eta^5$ -bonded Cp rings. The angle C(21)–Ni(1)– $\eta^5$ -Cp ring centroid is  $129.7(3)^{\circ}$  and the C(1)–Ni(1) bond length of



**Figure 1.** Molecular structure of **2**. Important structural parameters (corresponding values for **3** shown in parentheses). Ni(1)–C(1) 1.885(4) Å (2.127(5)), Ni(1)–C(21) 2.021(5) Å (2.263(5)), Ni(1)– $\eta^5$ -Cp ring centroid 1.776(6) Å (2.001(6)), C(1)–Ni(1)–C(21)  $95.3(2)^{\circ}$  ( $95.1(2)^{\circ}$ ), C(1)–Ni(1)– $\eta^5$ -Cp ring centroid  $134.9(3)^{\circ}$  ( $128.6(2)^{\circ}$ ).

1.885(4) Å is somewhat shorter than that reported<sup>9</sup> for the carbene complex  $(\eta^2\text{-C}_2\text{H}_4)_2\text{NiC(Ph)NH-}t\text{-Bu}$  (2.008(1) Å). The main structural change accompanying coordination of the carbene in **2** is twisting of the aryl rings by  $55.8(5)^{\circ}$  in a manner that minimizes steric interactions with the  $\eta^5$ -Cp ligand.

Interestingly, there was no evidence of reaction when chromocene was treated with **1**. However, the carbene complex **3** (Scheme 1) was formed in good (72%) yield via the reaction of chromocene with 1,3-dimesitylimidazol-2-ylidene (**4**),<sup>5</sup> thus highlighting the sensitivity of carbene reactivity to subtle substituent changes. The HRMS data for **3**<sup>6</sup> are very similar to those for **2**; however, the former is paramagnetic, and it was not possible to record structurally diagnostic NMR spectra. It was therefore necessary to confirm the  $(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Cr(carbene)}$  structure by X-ray crystallography.<sup>8</sup> The Cr(1)–C(1) bond length of 2.127(5) Å falls in the range observed for Fischer-type carbene complexes.<sup>10</sup> Compound **3**, a 14-electron species, is noteworthy in that it represents the first thermally stable  $(\text{C}_5\text{H}_5)_2\text{CrL}$  complex. Previously, it was necessary to employ intramolecularly bridged Cp ligands to isolate e.g. a monocarbonyl complex.<sup>11</sup>

The reaction of tetramethylimidazol-2-ylidene (**5**)<sup>12</sup> with nickelocene or chromocene afforded 70–80% yields of the cationic bis(carbene) derivatives **6** and **7** (Scheme 1). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6**<sup>7</sup> revealed the presence of a cyclopentadienide anion and a putative cationic Ni(II) complex with an  $\eta^5$ -Cp and two carbene ligands. It was not possible to record useful NMR spectra

(1) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1733.

(2) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375.

(3) For a review of the coordination of stable carbenes to other transition-metal entities, see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(4) 1,3-Bis(2,6-dimethyl-4-bromo)imidazol-2-ylidene (**1**) was prepared in 55% yield by deprotonation of 1,3-(2,6-dimethyl-4-bromo)imidazolium chloride (12.23 g, 26 mmol) by potassium-*tert*-butoxide (2.92 g, 26.0 mmol) in THF solution at  $0\text{ }^{\circ}\text{C}$  following the literature procedure for 1,3-dimesitylimidazol-2-ylidene.<sup>5</sup> Compound **1** was recrystallized from toluene (mp  $138\text{--}141\text{ }^{\circ}\text{C}$ ); the X-ray crystal structure will be described elsewhere.

(5) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(6) Synthetic procedures. **2**: An orange solution of **1** (0.43 g, 1.0 mmol) in toluene (5 mL) was layered with a green solution of nickelocene (0.19 g, 1.0 mmol) in toluene (30 mL). After 48 h at ambient temperature, the solution turned deep red. The volume of the solution was reduced to 10 mL, following which it was overlaid with hexane (30 mL). The resulting red powder was recrystallized from a saturated toluene solution at  $-20\text{ }^{\circ}\text{C}$  to afford 0.28 g (0.45 mmol, 45% yield) of red, crystalline **2** (mp  $140\text{--}5\text{ }^{\circ}\text{C}$ ). Red, crystalline **3** (mp  $63\text{ }^{\circ}\text{C}$  dec) was prepared analogously in 72% yield; however, in this case recrystallization from toluene was unnecessary. HRMS (CI,  $\text{CH}_4$ ) calcd for  $\text{C}_{29}\text{H}_{28}\text{Br}_2\text{N}_2\text{Ni}$ , 619.9973; found 619.9982; calcd for  $\text{C}_{31}\text{H}_{34}\text{N}_2\text{Cr}$ , 486.2127; found 486.2135. Anal. Calcd for  $\text{C}_{29}\text{H}_{28}\text{Br}_2\text{N}_2\text{Ni}$ : C, 55.91; H, 4.53; N, 4.50. Found C, 54.20; H, 5.00; N, 4.15; calcd for  $\text{C}_{31}\text{H}_{34}\text{CrN}_2$ : C, 76.52; H, 7.04; N, 5.76. found C, 74.72; H, 6.90; N, 5.45. Compounds **6** and **7** were prepared by layering a yellow solution of **5** (0.24 g, 2.0 mmol) in toluene (30 mL) with 2.0 mmol of nickelocene or chromocene in toluene (20 mL). Yellow **6** (powder) and **7** (crystals) formed upon mixing of the carbene and metallocene solutions. X-ray quality crystals of **6** (mp  $190\text{--}5\text{ }^{\circ}\text{C}$  dec) and **7** (mp  $111\text{--}5\text{ }^{\circ}\text{C}$  dec) were formed by layering THF solutions with hexane. Yields: **6** (0.35 g, 80%); **7** (0.30 g, 70%).

(7) NMR data. **2**: <sup>1</sup>H NMR (300 MHz, 295 K,  $\text{C}_6\text{D}_6$ )  $\delta$  1.85 (s, 12 H, *o*-Me), 4.22 (s, 5 H,  $\eta^5$ -Cp), 5.73 (s (br), 5 H,  $\eta^1$ -Cp), 6.25 (s, 2 H, CH(carbene)), 7.06 (s, 4 H, CH(arene)). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, 295 K,  $\text{C}_6\text{D}_6$ )  $\delta$  16.3 (Me), 93.6 ( $\eta^5$ -Cp), 113.3 ( $\eta^1$ -Cp), 121.6 (carbene C=C), 122.3 (*p*-C(arene)), 131.8 (*m*-C(arene)), 137.9 (*o*-C(arene)), 140.3 (*ipso*-C(arene)), 160.8 (C(carbene)). **6**: <sup>1</sup>H NMR (300 MHz, 295 K,  $\text{C}_6\text{D}_6$ )  $\delta$  2.17 (s, 12 H, C(CH<sub>3</sub>)), 3.68 (s, 5 H, Cp<sup>-</sup>), 3.98 (s, 12 H, NCH<sub>3</sub>), 5.45 (s, 5 H,  $\eta^5$ -Cp). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, 295 K,  $\text{C}_6\text{D}_6$ )  $\delta$  9.8 (C(CH<sub>3</sub>)), 36.6 (NCH<sub>3</sub>), 106.2 (Cp<sup>-</sup>), 126.3 (carbene C=C), 158.9 (C(carbene)).

(8) Crystal data. Single crystals of **2**, **3**, **6**, and **7** were covered with mineral oil and mounted on a Siemens P4 diffractometer at 178(2) K. All data sets were collected using Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) and each structure was solved by direct methods. **2**:  $\text{C}_{29}\text{H}_{28}\text{Br}_2\text{N}_2\text{Ni}$ , triclinic,  $P1$ ,  $a = 9.456(2)\text{ \AA}$ ,  $b = 12.088(3)\text{ \AA}$ ,  $c = 13.020(3)\text{ \AA}$ ,  $\alpha = 78.44(2)^{\circ}$ ,  $\beta = 72.55(2)^{\circ}$ ,  $\gamma = 69.80(2)^{\circ}$ ,  $V = 1324.5(5)\text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.562\text{ g cm}^{-3}$ ,  $\mu$  (Mo K $\alpha$ ) =  $3.77\text{ mm}^{-1}$ , 7623 unique reflections collected in the range  $3.3 < 2\theta < 60.0^{\circ}$ ;  $wR2 = 0.1822$ ,  $R = 0.0759$ . **3**:  $\text{C}_{31}\text{H}_{34}\text{CrN}_2$ , monoclinic,  $P2_1/n$ ,  $a = 8.569(1)\text{ \AA}$ ,  $b = 17.253(2)\text{ \AA}$ ,  $c = 17.754(2)\text{ \AA}$ ,  $\beta = 97.19(1)^{\circ}$ ,  $V = 2604.1(5)\text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.241\text{ g cm}^{-3}$ ,  $\mu$  (Mo K $\alpha$ ) =  $4.60\text{ cm}^{-1}$ ; 4185 unique reflections collected in the range  $3.3 < 2\theta < 50.0^{\circ}$ ;  $wR2 = 0.1369$ ,  $R = 0.0664$ . **6**(THF):  $\text{C}_{28}\text{H}_{32}\text{N}_4\text{NiO}$ , monoclinic,  $P2_1/n$ ,  $a = 11.165(3)\text{ \AA}$ ,  $b = 9.693(2)\text{ \AA}$ ,  $c = 23.201(5)\text{ \AA}$ ,  $\beta = 95.82(2)^{\circ}$ ,  $V = 2497.9(10)\text{ \AA}^3$ ,  $Z = 4$ ;  $D_{\text{calcd}} = 1.354\text{ g cm}^{-3}$ ,  $\mu$  (Mo K $\alpha$ ) =  $0.80\text{ mm}^{-1}$ , 5726 unique reflections collected in the range  $3.52 < 2\theta < 55.7^{\circ}$ ;  $wR2 = 0.1735$ ,  $R = 0.0550$ . **7**(THF)<sub>0.5</sub>:  $\text{C}_{52}\text{H}_{76}\text{Cr}_2\text{N}_8\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 25.839(5)\text{ \AA}$ ,  $b = 9.501(2)\text{ \AA}$ ,  $c = 21.716(5)\text{ \AA}$ ,  $\beta = 107.06(1)^{\circ}$ ,  $V = 5097(2)\text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.216\text{ g cm}^{-3}$ ,  $\mu$ (Mo K $\alpha$ ) =  $4.70\text{ cm}^{-1}$ ; 11, 642 unique reflections collected in the range  $3.3 < 2\theta < 55.0^{\circ}$ ;  $wR2 = 0.1111$ ,  $R = 0.0450$ .

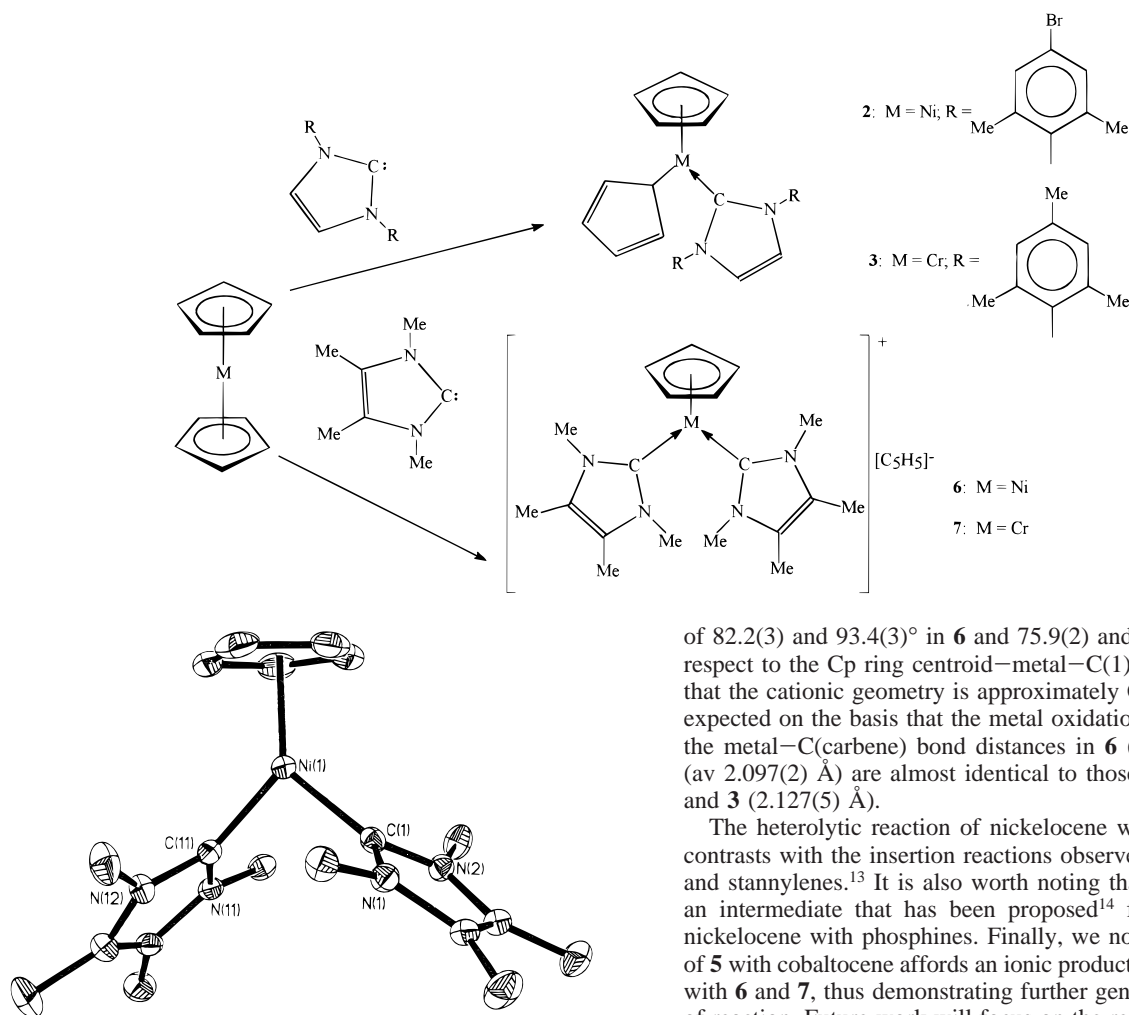
(9) Gabor, B.; Krüger, C.; Marczinke, B.; Mynott, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666.

(10) Fischer, H.; Kreissl, F. R.; Schubert, V.; Hofmann, P.; Dötter, K. H.; Weiss, K. *Transition Metal Carbene Complexes*; VCH Publishers: Weinheim, 1984.

(11) Schwemlein, H.; Zsolnai, L.; Huttner, G.; Brintzinger, H. *J. Organomet. Chem.* **1983**, *256*, 285; Schaper, F.; Rentzsch, M.; Prosenec, M.-H.; Rief, U.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1997**, *534*, 67.

(12) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

## Scheme 1



**Figure 2.** Structure of the cation of **6**. Important structural parameters (corresponding values for **7** shown in parentheses). Ni(1)–C(1) 1.883(2) Å (2.103(2)), Ni(1)–C(11) 1.883(2) Å (2.091(2)), Ni(1)–Cp ring centroid 1.758(4) Å (1.966(3)), C(1)–Ni(1)–C(11) 97.07(2)° (97.42(9)), C(1)–Ni(1)–Cp ring centroid 130.8(2)° (133.7(2)), C(11)–Ni(1)–Cp ring centroid 132.0(2)° (128.8(2)).

for paramagnetic **7**, and the CI-mass spectra of **6** and **7** were uninformative due to extensive fragmentation. The X-ray crystal structures of **6**<sup>8</sup> and **7**<sup>8</sup> are very similar (Figure 2). In neither case is there evidence of close cation–anion contacts, and the geometry at each metal center is trigonal planar (sums of bond angles (using Cp ring centroids) = 359.9(3)° and 359.9(2)° for **6** and **7**, respectively). The carbene ligands are inclined at dihedral angles

of 82.2(3) and 93.4(3)° in **6** and 75.9(2) and 79.3(2)° in **7** with respect to the Cp ring centroid–metal–C(1)–C(11) plane such that the cationic geometry is approximately C<sub>2</sub> in each case. As expected on the basis that the metal oxidation states are all +2, the metal–C(carbene) bond distances in **6** (1.883(2) Å) and **7** (av 2.097(2) Å) are almost identical to those in **2** (1.885(4) Å) and **3** (2.127(5) Å).

The heterolytic reaction of nickelocene with stable carbenes contrasts with the insertion reactions observed with germylenes and stannylenes.<sup>13</sup> It is also worth noting that **2** corresponds to an intermediate that has been proposed<sup>14</sup> for the reaction of nickelocene with phosphines. Finally, we note that the reaction of **5** with cobaltocene affords an ionic product that is isostructural with **6** and **7**, thus demonstrating further generality for this type of reaction. Future work will focus on the reactivities of **2**, **3**, **6**, and **7**.

**Acknowledgment.** We are grateful to the Science and Technology Center Program of the National Science Foundation (CHE-08920120), the National Science Foundation (CHE-9629088), and the Robert A. Welch Foundation for financial support.

**Supporting Information Available:** X-ray experimental details with positional parameters and full bond distances and angles for **2**, **3**, **6**, and **7** (PDF) and an X-ray file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA983772S

(13) Veith, M.; Stahl, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 106.  
(14) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: 1974; p 100.