Nucleophilic Carbene Complexes of Manganocene

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Received May 14, 2001

*Summary: The reaction of the sterically demanding nucleophilic carbenes 1,3-bis(2,6-dimethyl-4-bromophenyl)imidazol-2-ylidene (**1**) and 1,3-dimesitylimidazol-2-ylidene (**3**) with manganocene resulted in complexes of the type (η^2-C_5H_5)(η^4-C_5H_5)Mn(carbene) (**2** and **4**). The reaction of equimolar amounts of the less sterically demanding nucleophilic carbene tetramethylimidazol-2-ylidene (**5**) afforded the bis(carbene)complex (η^1-C_5H_5)(η^2-C_5H_5)Mn(carbene)$_2$ (**6**). The structures of these complexes were determined by single-crystal X-ray diffraction.*

Recently, we have described the reactions of stable nucleophilic carbenes with chromocene, cobaltocene, and nickelocene.[1] Surprisingly, the various carbene complexes formed by these metallocenes are isostructural. Manganocene is atypical among the transition-metal metallocenes in terms of the large degree of ionic character along with anomalous magnetic and structural properties.[2] Previously reported manganocene complexes of unidentate tertiary phosphines (PMe_3, $PMePh_2$) and tetrahydrofuran all adopt a "ring-tilted" (η^5-C_5H_5)$_2$MnL structure.[3,4] The bidentate phosphine dmpe (1,2 bis(dimethylphosphino)ethane) forms a complex with a similar bis(η^5) "ring-tilted" structure; however, the bidentate amine, tmeda (*N,N,N',N'*-tetramethylethylenediamine) forms an (η^1-C_5H_5)(η^5-C_5H_5)MnL complex.[5] We were, therefore, interested in extending our investigation of transition-metal metallocene-carbene complexes to include those of manganocene. Herein, we report the novel bonding features of the first examples of manganocene-carbene complexes.

The reaction of 1,3-bis(2,6-dimethyl-4-bromophenyl)imidazol-2-ylidene (**1**)[1] with manganocene in toluene solution at room temperature gave a 78% yield of highly air-sensitive, colorless crystals of the carbene complex **2**[6] (Scheme 1). According to an X-ray crystal structure analysis,[7] the C(1)−Mn(1) bond length is 2.227(3) Å. Within experimental error, the Cp rings are both essentially planar and delocalized and are bonded to Mn in an η^2- and an η^4-fashion (Figure 1), which is in contrast to the η^1-and η^5-Cp bonding modes in the analogous nickel and chromium compounds.[1] The aryl groups of the carbene ligand in **2** are twisted with respect to each other by 34.9(5)° to minimize steric interactions with the Cp ligands. The ^{1}H NMR spectrum of **2** displayed broad resonances typical of a paramagnetic species. To gain further insight into this system, 1,3-dimesitylimidazol-2-ylidene (**3**)[11] was treated with manganocene under identical conditions. Highly air-sensitive, colorless crystals of **4**[6] were obtained in 70% yield (Scheme 1). X-ray diffraction showed **4** to be isostructural to **2**,[7] and pertinent metrical parameters

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(6) Synthetic Procedures: **2**. An orange solution of **1** (0.43 g, 1.0 mmol) in tetrahydrofuran (10 mL) was added to a brown solution of manganocene (0.185 g, 1.0 mmol) in tetrahydrofuran (30 mL). The reaction mixture was stirred at ambient temperature for 24 h. The volume of the solution was reduced to 30 mL, and the solution was left to stand at −30 °C for 24 h. Colorless crystals of **2** (mp: 140 °C (dec)) were collected by filtration and washed with ice-cold pentane (0.48 g, 0.78 mmol, 78% yield). The crystals slowly turned pale brown on standing for a few days under an argon atmosphere. No molecular ion was observed with either CI or EI mass spectroscopy. The mass spectra obtained from crystals of **2** consisted of peaks corresponding to those of manganocene and **1**. Anal. Calcd for $C_{29}H_{28}Br_2MnN_2$: C, 56.24; H, 4.56; Br, 25.80; N, 4.52. Found: C, 56.02; H, 4.42; Br, 23.94; N, 4.39. Compound **4** (mp: 110 °C (dec)) was prepared analogously to **2** in 70% yield. These crystals also turned pale brown on standing under an argon atmosphere for several days. No molecular ion was observed with either CI or EI mass spectroscopy. The mass spectra obtained from crystals of **4** consisted of peaks corresponding to manganocene and **2**. Anal. Calcd for $C_{31}H_{34}MnN_2$: C, 76.06; H, 7.00; N, 5.72. Found: C, 75.70; H, 6.97; N, 5.80. Compound **6** (mp: 58 °C (dec)) was prepared analogously to **2** in 90% yield (based on carbene). The X-ray crystal structure revealed that, in the crystals obtained, one molecule of tetrahydrofuran was present for every molecule of **6**. This was confirmed by the microanalysis. Anal. Calcd for $C_{28}H_{42}MnN_4O$: C, 66.52; H, 8.37; N, 11.08. Found: C, 67.10; H, 8.50; N, 10.35. MS (CI, CH_4): *m/e* 434 ($M^+ + H$), 368 ($M^+ - Cp$), 309 ($M^+ -$ carbene).

(7) The X-ray data for **2** and **4** were collected on a Nonius KAPPA CCD diffractometer at 153(2) K; those for **6** were collected on a Siemens P4 diffractometer at 193(2) K. **2**: $C_{29}H_{28}Br_2MnN_2$, monoclinic, $P2_1/n$, $a = 8.7950(18)$ Å, $b = 17.105(3)$ Å, $c = 17.864(4)$ Å, $\beta = 99.89(3)°$, $V = 2647.5(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.554$ g cm^{-3}, μ(Mo Kα) = 3.537 mm^{-1}, 7573 unique reflections measured in the range $6.46° < 2\theta < 60.10°$, $wR_2 = 0.0940$, $R_1 = 0.0507$. **4**: $C_{31}H_{34}MnN_2$, monoclinic, $P2_1/n$, $a = 8.6290(17)$ Å, $b = 17.265(4)$ Å, $c = 17.636(4)$ Å, $\beta = 98.03(3)°$, $V = 2601.7(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.250$ g cm^{-3}, μ(Mo Kα) = 0.528 mm^{-1}, 5881 unique reflections collected in the range $6.08° < 2\theta < 54.92°$, $wR_2 = 0.0902$, $R_1 = 0.0451$. **6**: $C_{28}H_{42}MnN_4O$, tetragonal, $P4_3$, $a = 8.6867(12)$ Å, $b = 8.6867(12)$ Å, $c = 36.057(7)$ Å, $V = 2720.8(8)$ Å^3, $Z = 4$, $D_{calcd} = 0.511$ mm^{-1}, μ(Mo Kα) = 0.511 mm^{-1}, 4114 unique reflections collected in the range $4.52° < 2\theta < 60.00°$, $wR_2 = 0.0673$, $R_1 = 0.0321$. All structures were solved and refined using the Siemens SHELX PLUS 5.0 (PC) software package.[8] In the case of **6**, the presence of highly disordered THF molecule could not be modeled satisfactorily and was dealt with by use of the SQUEEZE routine in PLATON 98.[9]

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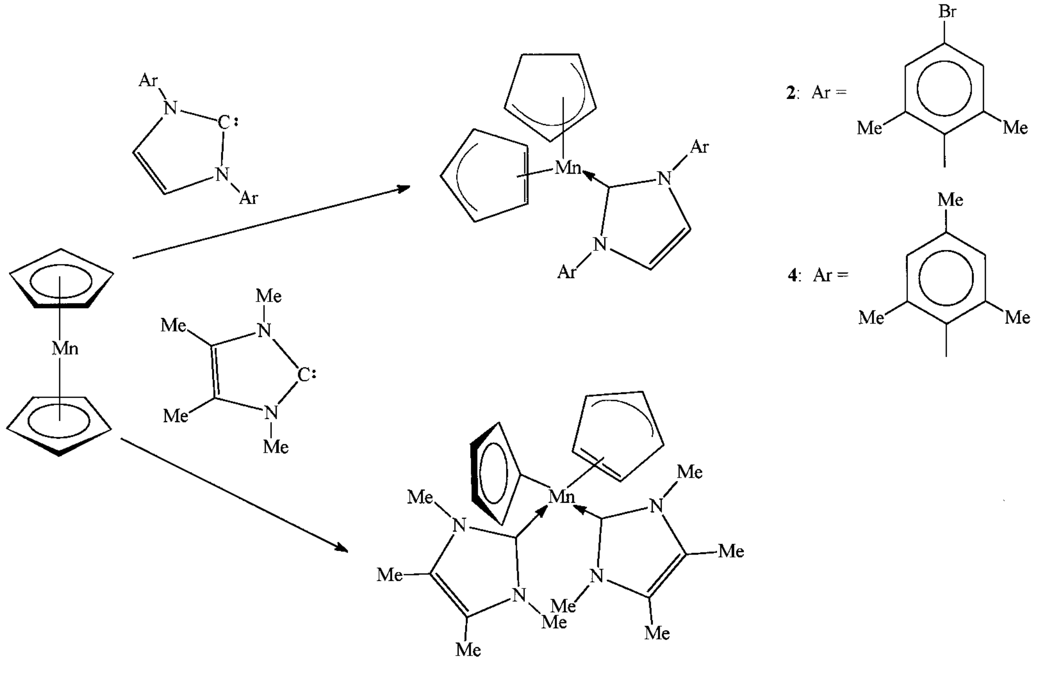
10.1021/om0103916 CCC: \$20.00

Scheme 1



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are listed in the Figure 1 caption. The paramagnetism of this formally 15e$^-$ complex was confirmed by a solid state variable-temperature magnetic moment determination. Complex **4** behaved as a simple paramagnet with three unpaired electrons.[10]

The difference in reactivity of manganocene from that of other transition-metal metallocenes is illustrated further by the reaction of equimolar quantities of manganocene and tetramethylimidazol-2-ylidene (**5**).[12] A bis(carbene) complex of manganocene (**6**) was formed in 90% yield based on the amount of carbene (Scheme 1).[6] The X-ray crystal structure of **6**[7] (Figure 2) revealed that the coordination geometry about the metal center is distorted tetrahedral. One of the Cp rings is bonded to Mn in an η^1-fashion with a Mn(1)$-$C(21) bond length of 2.337(3) Å. The second Cp ligand is disordered over two orientations, with occupancy factors of 52 and 48%, separated by a rotation of 36°. In one orientation the Cp ligand is bonded to Mn in an η^2-fashion with Mn(1)$-$C(31) and Mn(1)$-$C(32) bond lengths of 2.530(10) and 2.496(13) Å, respectively. The corresponding bond lengths for the second orientation are asymmetric (2.342(8) and 2.64(2) Å), which indicates that the Cp ligand in this orientation is intermediate between an η^1- and η^2-bonding mode. As expected, the Mn$-$C(carbene) distances (av 2.218(2) Å) are similar to those in **2** and **4**. Magnetic susceptibility measurements indicate that **6**

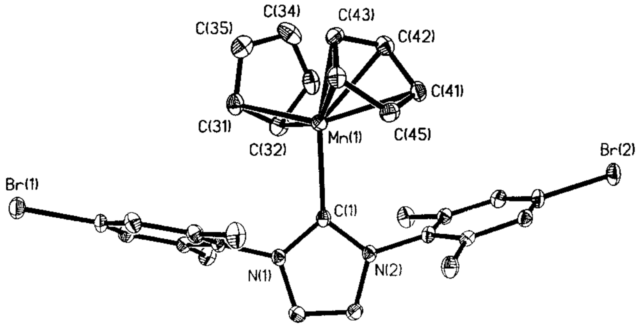

Figure 1. Molecular structure of **2** (thermal ellipsoids at the 30% probability level). Important structural parameters (corresponding values for **4** shown in parentheses): Mn(1)$-$C(1) 2.227(3) Å (2.222(2)), Mn(1)$-$C(31) 2.475(4) Å (2.533(2)), Mn(1)$-$C(32) 2.340(4) Å (2.327(2)), Mn(1)$-$C(41) 2.592(4) Å (2.607(2)), Mn(1)$-$C(42) 2.359(4) Å (2.386(2)), Mn(1)$-$C(43) 2.348(4) Å (2.333(2)), Mn(1)$-$C(44) 2.562(4) Å (2.530(2)). Nonbonded distances: Mn(1)⋯C(33) 2.717(5) Å (2.660(3)), Mn(1)⋯C(34) 3.057(5) Å (3.035(3)), Mn(1)⋯C(35) 2.907(5) Å (2.969(3)), Mn(1)⋯C(45) 2.716(4) Å (2.701(3)).

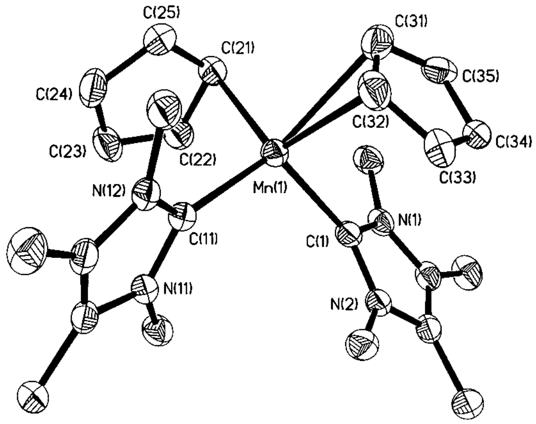

Figure 2. Molecular structure of **6** (thermal ellipsoids at the 30% probability level). Important structural parameters (corresponding values for the second orientation of the disordered Cp ligand shown in parentheses): Mn(1)$-$C(1) 2.215(2) Å, Mn(1)$-$C(11) 2.220(2) Å, Mn(1)$-$C(21) 2.337(3) Å, Mn(1)$-$C(31) 2.53(1) Å (2.64(2)), Mn(1)$-$C(32), 2.49(1) Å (2.342(8)). Nonbonded distances: Mn(1)⋯C(22) 2.742(3) Å, Mn(1)⋯C(23) 3.311(3) Å, Mn(1)⋯C(24) 3.342(3) Å, Mn(1)⋯C(25) 2.806(3) Å, Mn(1)⋯C(33) 3.102(2) Å, Mn(1)⋯C(34) 3.407(7) Å, Mn(1)⋯C(35) 3.119(1) Å.

is paramagnetic with two unpaired electrons.[10] The formation of this formally 14-electron (η^1-C_5H_5)(η^2-C_5H_5)Mn(carbene)$_2$ complex contrasts with the ionic bis(carbene) species of formula [(η^5-C_5H_5)M(carbene)$_2$]$^+$-[C_5H_5]$^-$, formed by the reaction of **5** with chromocene, cobaltocene, and nickelocene.[1] Presumably, compounds of type **6** are precursors to these ionic bis(carbene) derivatives.

A full study of the electronic and magnetic properties and theoretical aspects of these and other transition-metal metallocene-carbene complexes is in progress and will be published in due course.[13]

Acknowledgment. We are grateful to the Science and Technology Center Program of the National Science Foundation (CHE-08920120), the National Science Foundation (CHE-96299088), the Robert A. Welch Foundation, and the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Tables of crystallographic data for **2**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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