

Novel N-Nucleophilic Addition to and Ring-Breaking of Coordinated Cyclooctatetraene in Diiron Bridging Carbyne Complexes

Shu Zhang,[†] Qiang Xu^{*,‡} Jie Sun,[†] and Jiabi Chen^{*,†}

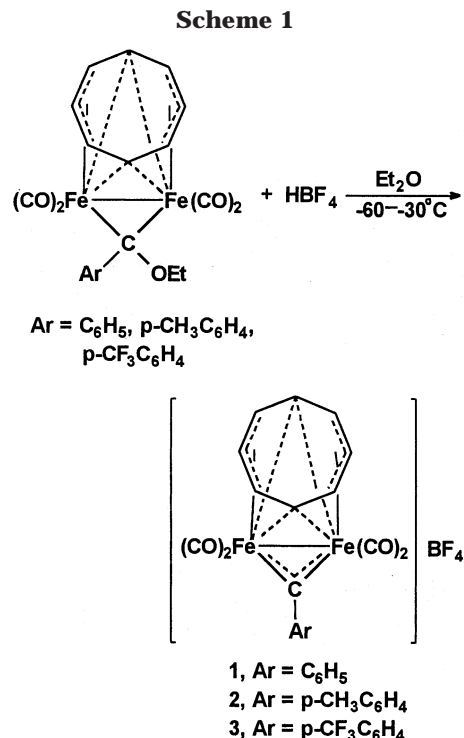
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China, and National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Received August 20, 2002

Summary: The reactions of the diiron cationic carbyne complexes **1–3** with $\text{NaN}(\text{SiMe}_3)_2$ or $\text{LiN}(\text{SiMe}_3)_2$ in THF at low temperature give novel N-nucleophilic addition products, the neutral diiron bridging carbyne complexes **4–6**, while the reactions of **1–3** with LiNEt_2 lead to breaking of the COT ring to produce the diiron bridging carbene inner salts **7–9**, among which the structures of **4** and **7** have been established by X-ray diffraction studies.

The chemistry of transition-metal-promoted nucleophilic attack on unsaturated ligands has been the subject of intensive research.¹ In this field cyclic polyolefin ligands are of great importance, because attack on them has led to the synthesis of many otherwise inaccessible substituted polyolefin complexes.² Cyclooctatetraene (COT), as a medium-ring polyene and the next higher vinyllog of benzene, forms an exceptional variety of complexes with transition metals and plays a notable role in many aspects of organic and organometallic chemistry.³ As an extension of our studies of olefin-coordinated metal carbene and carbyne complexes, we investigated the COT-bridged diiron alkoxy-carbene complexes $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]$, which were prepared by the reaction of $[\text{Fe}_2(\text{CO})_5(\eta^8\text{-C}_8\text{H}_8)]$ with aryllithium reagents, followed by alkylation with $[\text{Et}_3\text{O}]\text{BF}_4$.⁴ The bridging COT ligand in these bridging carbene complexes participates in a novel two-electron–three-center (Fe–C–Fe) interaction, similar to that in $[\text{Fe}_2(\text{CO})_5(\eta^8\text{-C}_8\text{H}_8)]$.^{4,5}

It is well-known that nucleophiles such as amines attack a carbon atom of coordinated alkenes in transition-metal complexes if the metal is sufficiently electropositive to promote such an attack.⁶ While the COT



ligand in $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]$ is not sufficiently electropositive to undergo attack by nucleophiles, we thought that protonation⁷ of the iron centers would make such an attack possible. Thus, we studied the reaction of diiron bridging alkoxy-carbene complexes with acids such as HBF_4 ; they did not give the proton addition product but, rather, the highly electrophilic cationic bridging carbyne complexes $[\text{Fe}_2(\mu\text{-CAr})(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]\text{BF}_4$, whose COT ligand is activated to attack by nucleophiles. In this communication we report novel N-nucleophilic addition and ring-breaking reactions of the coordinated COT ring in the COT-coordinated diiron bridging carbyne complexes, which produced a series of novel N-nucleophilic addition and ring-opening products.

The diiron bridging alkoxy-carbene complexes $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]$ react with 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at low temperature (below -30°C) to give the COT-coordinated diiron cationic bridging carbyne com-

[†] Shanghai Institute of Organic Chemistry.

[‡] National Institute of Advanced Industrial Science and Technology.

(1) (a) McDaniel, K. F. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, New York, 1995; Vol. 12, p 601. (b) Yamamoto, A. *J. Organomet. Chem.* **2000**, 600, 159. (c) Ovchinnikov, M. V.; LeBlanc, E.; Guzei, I. A.; Angelici, R. J. *J. Am. Chem. Soc.* **2001**, 123, 11494.

(2) Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: New York, 1979.

(3) (a) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: Cambridge, U.K., 1978. (b) Lange, G.; Reimelt, O.; Jessen, L.; Heck, J. *Eur. J. Inorg. Chem.* **2000**, 1941.

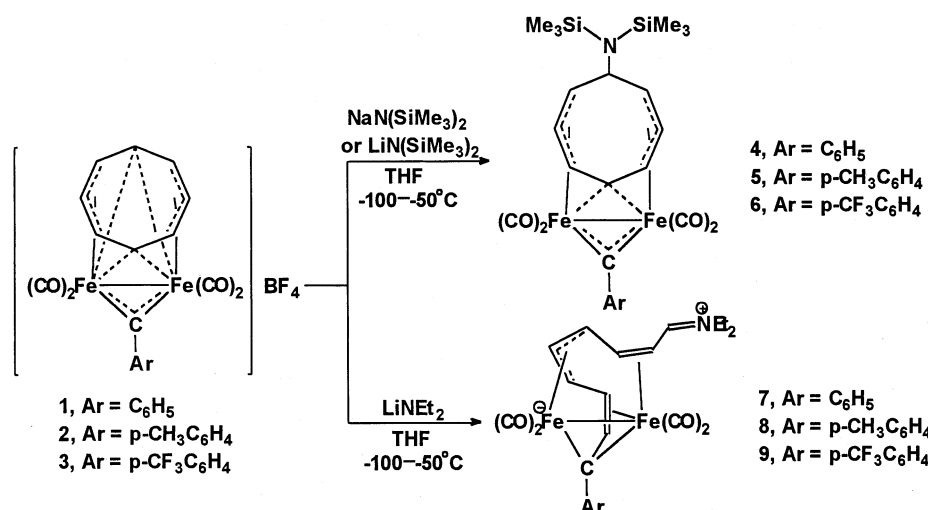
(4) Chen, J.-B.; Li, D.-S.; Yu, Y.; Jin, Z.-S.; Zhou, Q.-L.; Wei, G.-C. *Organometallics* **1993**, 12, 3885.

(5) Fleischer, E. B.; Stone, A. L.; Dewar, R. B. K.; Wright, J. D.; Keller, C. E.; Pettit, R. *J. Am. Chem. Soc.* **1966**, 88, 3158.

(6) Bush, R. C.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, 108, 2735.

(7) (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, 28, 52. (b) Bullock, R. M. *Comments Inorg. Chem.* **1991**, 12, 1.

Scheme 2



plexes [Fe₂(μ-CAr)(CO)₄(η⁸-C₈H₈)]BF₄ (**1**, Ar = C₆H₅; **2**, Ar = p-CH₃C₆H₄; **3**, Ar = p-CF₃C₆H₄) as brick red solids in 93–96% yield (Scheme 1). These cationic complexes **1–3** are novel olefin-coordinated dimetal complexes with bridging carbyne ligands. They are very sensitive to air and moisture and can be stored for only a short time at low temperature (below –65 °C).

The freshly prepared (in situ) diiron cationic carbyne complexes **1–3** react with NaN(SiMe₃)₂ in THF at –100 to –50 °C over 4–5 h to form the novel diiron bridging carbyne complexes [Fe₂(μ-CAr)(CO)₄{η⁷-C₈H₈N(SiMe₃)₂}] (**4–6**) in 60–68% yield (Scheme 2), as air- and temperature-sensitive, purple-red crystals. When cationic **3** was treated with LiN(SiMe₃)₂ under the same conditions, the bridging carbyne complex **6** was also obtained in 61% yield, indicating that the counterions of the [–]N(SiMe₃)₂ anion have no obvious influence in this reaction.

The infrared spectra of **4–6** exhibit three strong bands with a pattern similar to that of [Fe₂(CO)₅(η⁸-C₈H₈)], except for the absent bridging CO band, which is indicative of the high symmetry of these complexes. The ¹H NMR spectra of **4–6** with five signals for the COT ring (at ca. 6.09–5.99 (2H), 5.28–5.20 (2H), 3.76–3.73 (1H), 3.60–3.48 (1H), 2.57–2.46 (2H) ppm) also suggests a high symmetry in the COT ring. This has been confirmed by an X-ray diffraction study⁸ of **4** (Figure 1). The products **4–6** are neutral diiron bridging carbyne complexes with a N(SiMe₃)₂ group added on a central carbon of the COT ring. This site of nucleophilic attack contrasts with reactions^{9,10} of the bridging carbyne complexes [Fe₂(μ-CO)(μ-CAr)(CO)₂(η⁵-C₅H₅)₂]-BBR₄ and [Fe₂(μ-CO)(μ-CAr)(CO)₂{(η⁵-C₅H₄)₂Si(CH₃)₂}]·BBR₄ with nucleophiles, which result in nucleophilic addition to the μ-carbyne carbon to give diiron bridging carbene complexes.

Complex **4** has a mirror plane passing through C(12) and C(16) of the ring, the N atom, and the bridging

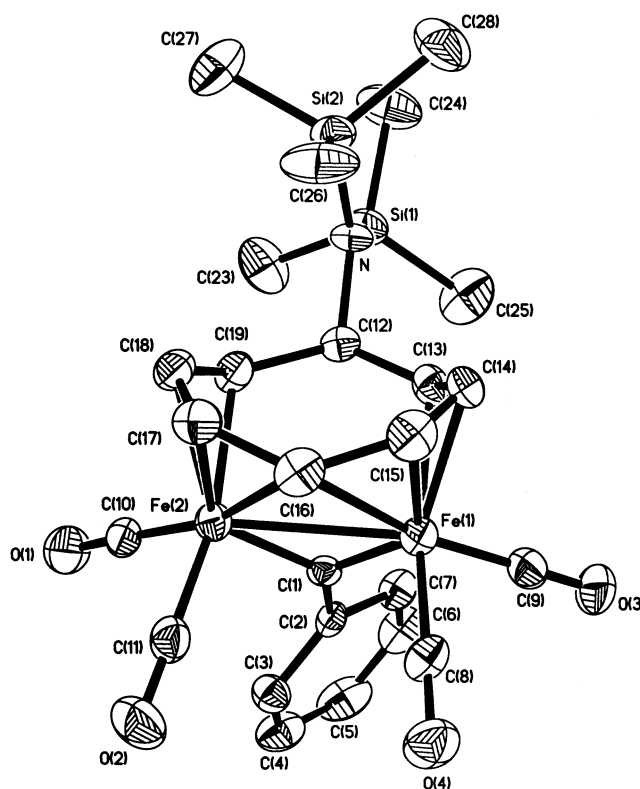


Figure 1. ORTEP diagram of **4**. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(2) = 2.6691(9), Fe(1)–C(1) = 1.818(3), Fe(2)–C(1) = 1.828(3), Fe(1)–C(13) = 2.103(4), Fe(1)–C(14) = 2.083(4), Fe(1)–C(15) = 2.084(4), Fe(1)–C(16) = 2.345(4), C(12)–C(13) = 1.497(5), C(13)–C(14) = 1.398(5), C(14)–C(15) = 1.392(6), C(15)–C(16) = 1.438(6), N–C(12) = 1.506(4); Fe(1)–C(1)–Fe(2) = 94.13(17), Fe(1)–Fe(2)–C(1) = 42.79(11), Fe(2)–Fe(1)–C(1) = 43.08(11).

carbene carbon (C(1)). The two Fe atoms are bridged symmetrically (relative to the mirror) by the C₈ ring; three of the eight ring atoms (C(13)–C(15)) are η³ bonded to Fe(1), and the other three (C(17)–C(19)) are attached in a η³ fashion to Fe(2). The Fe–Fe distance in **4** (2.6691(9) Å) is nearly the same as that in the bridging carbene complex [Fe₂{μ-C(OC₂H₅)C₆H₄CF₃-p}-(CO)₄(η⁸-C₈H₈)] (**A**) (2.686(1) Å).⁴ In **4**, the distances from the Fe atoms to the η³- and μ-bonding carbon atoms of the C₈ ring are very close to those in **A**. The

(8) X-ray data for **4**: C₂₅H₃₁O₄NSi₂Fe₂, triclinic, $\bar{P}1$, $a = 9.3987(12)$ Å, $b = 12.4109(16)$ Å, $c = 12.6069(16)$ Å, $\alpha = 72.015(2)^\circ$, $\beta = 81.607(3)^\circ$, $\gamma = 75.369(3)^\circ$, $V = 1349.6(3)$ Å³, $F(000) = 600$, $R = 0.0383$, $R_w = 0.0479$.

(9) (a) Liu, Y.-J.; Wang, R.-T.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 3498. (b) Liu, Y.-J.; Wang, R.-T.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 3784.

(10) Wang, R.-T.; Xu, Q.; Sun, J.; Song, L.-C.; Chen, J.-B. *Organometallics* **2001**, *20*, 4092.

change from the bridging carbene carbon in **A** to the bridging carbyne carbon in **4** is responsible for the short $\mu\text{-C-Fe}$ bond lengths in **4** (average 2.037 Å in **A**,⁴ 1.823 Å in **4**).

When the N-nucleophile LiNEt_2 was used instead of $\text{NaN}(\text{SiMe}_3)_2$ in the reaction with the cationic carbyne complexes **1–3** under the same conditions, violet-red crystals of $[\text{Fe}_2\{\mu\text{-C}(\text{Ar})\text{C}_8\text{H}_8\text{NEt}_2\}(\text{CO})_4]$ (**7–9**), formulated as diiron bridging carbene inner salts, were obtained in 52–65% yield (Scheme 2). The ^1H NMR spectra of **7–9** with eight proton signals for the COT ring suggest that ring cleavage of the $\text{C}_8\text{H}_8\text{NEt}_2$ ligand has occurred. An X-ray diffraction study¹¹ of **7** also was undertaken, which unequivocally established that opening of the COT ring had occurred.

The crystallographic investigation of **7** reveals a highly unusual structure (Figure 2). The core grouping $\text{Fe}(\text{CO})_2(\mu\text{-C}(\text{Ar}))\text{Fe}(\text{CO})_2$ is retained, but the COT ring has opened to form a $\text{C}(12)\text{--C}(19)$ chain carrying a NEt_2 group on $\text{C}(12)$ with $\text{C}(19)$ directly bonded to the bridging carbene carbon $\text{C}(1)$. Atoms $\text{C}(15)\text{--C}(17)$ form an allyl-type unit η^3 -bonded to $\text{Fe}(1)$, while $\text{C}(13)$, $\text{C}(14)$ and $\text{C}(18)$, $\text{C}(19)$ are η^2 -bonded to $\text{Fe}(2)$. The terminal carbon ($\text{C}(12)$) of the C_8 chain links to the NEt_2 unit to form a $\text{C}=\text{N}$ double bond with a positive charge on the N atom, whereas the $\text{Fe}(1)$ atom bears a negative charge, thereby satisfying the 18-electron rule. The Fe-Fe distance (2.6326(12) Å) is somewhat shorter than that of **4**. The average $\mu\text{-C}(1)\text{--Fe}$ bond length in **7** is 2.018 Å, which is significantly longer than that in **4**.

Although a mechanism for the COT ring opening in Scheme 2 has not yet been established, it seems possible that the Et_2N^- anion first attacks the COT ring, giving an intermediate similar to **4–6**. Then $\text{C}=\text{N}$ bond formation and cleavage of a C--C bond bearing the N substituent ($\text{C}(12)\text{--C}(19)$) could occur at the same time. The resulting electron-rich carbon ($\text{C}(19)$) could then attack the electrophilic bridging carbyne carbon atom to produce **7** or **8** and **9**. To the best of our knowledge, there is no precedent for such activation leading to ring opening of the COT ligand in a metal complex at very low temperature. There is only one example of a COT ring-opening reaction, and that occurs in the Si-substituted C_8 ring of the diruthenium complex $[\text{Ru}_2(\text{CO})_4(\text{SiMe}_3)(\eta^7\text{-C}_8\text{H}_8\text{SiMe}_3)]$ in boiling octane.¹²

In summary, we have developed novel reactions involving N-nucleophilic attack on coordinated COT rings in dimetal cationic bridging carbyne complexes, giving COT ring addition products **4–6** or ring-opening

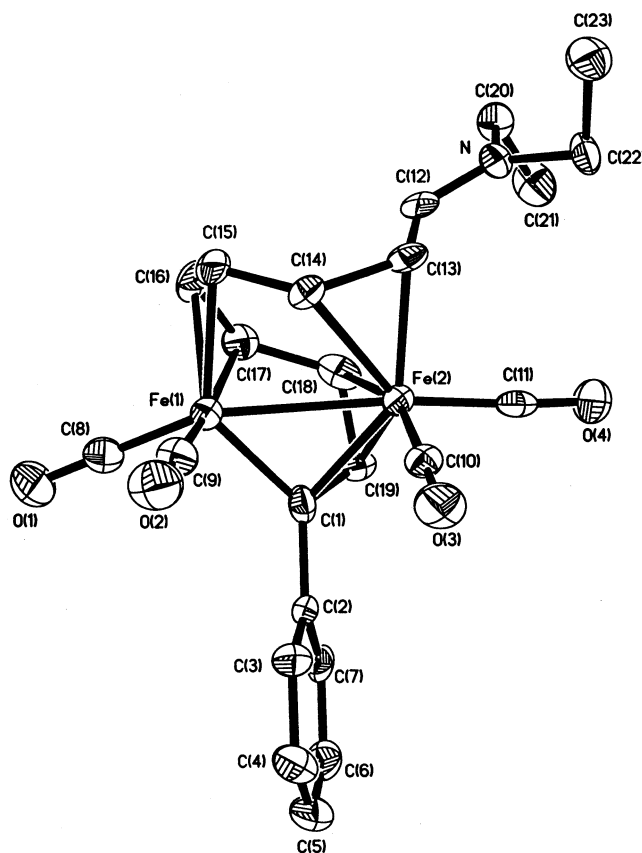


Figure 2. ORTEP diagram of **7**. Selected bond lengths (Å) and angles (deg): $\text{Fe}(1)\text{--Fe}(2) = 2.6326(12)$, $\text{Fe}(1)\text{--C}(1) = 1.953(6)$, $\text{Fe}(2)\text{--C}(1) = 2.082(6)$, $\text{Fe}(1)\text{--C}(15) = 2.061(6)$, $\text{Fe}(1)\text{--C}(16) = 2.079(6)$, $\text{Fe}(1)\text{--C}(17) = 2.097(6)$, $\text{Fe}(2)\text{--C}(13) = 2.068(5)$, $\text{Fe}(2)\text{--C}(14) = 2.195(6)$, $\text{Fe}(2)\text{--C}(18) = 2.044(7)$, $\text{Fe}(2)\text{--C}(19) = 2.039(6)$, $\text{C}(12)\text{--C}(13) = 1.406(6)$, $\text{C}(13)\text{--C}(14) = 1.477(8)$, $\text{C}(14)\text{--C}(15) = 1.444(9)$, $\text{C}(15)\text{--C}(16) = 1.395(9)$, $\text{C}(16)\text{--C}(17) = 1.392(8)$, $\text{C}(17)\text{--C}(18) = 1.486(9)$, $\text{C}(18)\text{--C}(19) = 1.395(8)$, $\text{N}\text{--C}(12) = 1.317(5)$; $\text{Fe}(1)\text{--C}(1)\text{--Fe}(2) = 81.4(2)$, $\text{Fe}(1)\text{--Fe}(2)\text{--C}(1) = 47.18(16)$, $\text{Fe}(2)\text{--Fe}(1)\text{--C}(1) = 51.43(17)$.

products **7–9**. Further studies on reactions with other nucleophiles and their applications in organic and organometallic synthesis are underway.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the NEDO of Japan is gratefully acknowledged.

Supporting Information Available: Text giving full experimental details and characterization data for complexes **1–9** and tables giving the X-ray crystallographic data for **4** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020683M

(11) X-ray data for **7**: $\text{C}_{23}\text{H}_{24}\text{O}_4\text{NFe}_2$, orthorhombic, $Pna2_1$, $a = 19.301(7)$ Å, $b = 11.224(4)$ Å, $c = 9.918(4)$ Å, $V = 2148.6(14)$ Å³, $F(000) = 1012$, $R = 0.0359$, $R_w = 0.0424$.

(12) Edwards, J. D.; Goddard, R.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1975**, 828.