807

C(sp³)–N(sp) Bond Cleavage of Isocyanides at a Cationic [CCH] Subunit in a Bisdisphenoidal Eight-atom Tetrairon–Tetracarbon Cluster

Wataru Taniwaki and Masaaki Okazaki*

Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561

(Received April 12, 2013; CL-130337; E-mail: mokazaki@cc.hirosaki-u.ac.jp)

Reaction of $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-NC_4H_4N)]$ -(PF₆)₂ (1) with *tert*-butyl isocyanide led to C(sp³)–N(sp) bond activation to give $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-CN)](PF_6)$ (2). The resulting *tert*-butyl cation was trapped as the adduct with pyrazine. Reactions of 1 with 2,6-dimethylphenyl isocyanide and cyclohexyl isocyanide led to the coordination of the isocyanides to the cationic [CCH] subunit. Thermolysis of $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-CNCy)](PF_6)_2$ (6) yielded 2.

A carbenium ion is stabilized through delocalization of adjacent π electrons over the vacant orbital of the cationic carbon center. Dolby and Robinson reported the reaction between $[Co_3(CO)_9(\mu_3-CCI)]$ and arenes (Ar–H) in the presence of AlCl₃ to give $[Co_3(CO)_9(\mu_3-CAr)]^{1}$ This result implies the possibility for the transient formation of an unprecedented pyramidal carbenium ion, $[Co_3(CO)_9(\mu_3-C^+)]^2$ Back donation of the π electron from the tricobalt core to the electron-deficient carbon atom would enhance its stability. The carbonyl adduct, $[Co_3(CO)_9(\mu_3$ -CCO)], was studied from experimental and theoretical viewpoints.³ Our recent effort has focused on the nature of the cationic [CCH] subunit on the polymetallic core,⁴ generation of which has been assumed in the heterogeneous catalytic reactions.⁵ We have reported the Lewis acid chemistry of the cationic [CCH] subunit in a bisdisphenoidal eight-atom tetrairon-tetracarbon cluster.6 Treatment of [(η5-C5H4Me)4-Fe₄(HCCH)(HCC-Br)](PF₆) with AgPF₆ in the presence of pyrazine gave $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-NC_4H_4N)]$ - $(PF_6)_2$ (1). Coordination of the pyrazine moiety is labile, and the resulting cationic carbon atom activates an acetonitrile molecule to allow deprotonation under very mild conditions (triethylamine or diisopropylethylamine, room temperature, 30 min). We herein report the reaction of 1 with tert-butyl isocyanide, leading to cleavage of the C(sp³)-N(sp) bond to give $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-CN)](PF_6)$ (2). The *tert*-butyl cation was trapped as the adduct with pyrazine. To obtain insight into the reaction mechanism, the reactions of 1 with cyclohexyl isocyanide and 2,6-dimethylphenyl isocyanide were also examined.

The reaction of **1** with *tert*-butyl isocyanide in acetonitrile gave $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-CN)](PF_6)$ (**2**) as dark green crystals in 86% yield (Scheme 1).⁷ From the reaction mixture, a white solid of 1-*tert*-butylpyrazinium salt **3** was isolated in 32% yield. Monitoring of the reaction at room temperature by NMR spectroscopy indicated the instantaneous formation of **2** (quant.), **3** (37%), and isobutene (33%), in which no intermediate was detected.

As expected from the cluster electron count (59 electrons), complex 2 is paramagnetic. For full characterization, the diamagnetic neutral form, $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-$



Scheme 1. Reaction of 1 with *tert*-butyl isocyanide.



Figure 1. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level. The methyl groups on the cyclopentadienyl ligands and hydrogen atoms, except for acetylenic hydrogens, are omitted for clarity. Selected bond lengths (Å) and angles (degree): Fe1–Fe3 2.4871(4), Fe1–Fe4 2.4994(4), Fe2–Fe3 2.4973(4), Fe2–Fe4 2.5032(4), C1–C2 1.519(3), C3–C4 1.497(3), C1–C5 1.437(3), C5–N 1.161(3), C1–C5–N 179.0(3).

CN)] (4), was synthesized by the reaction of 2 with [Cp₂Co] as dark brown crystals in 92% yield. In the downfield region of the ¹H NMR spectrum of 4, two singlet signals were observed at δ 9.92 (2H) and 10.31 (1H), which are assigned to the acetylenic protons of HCCH and HCC–CN, respectively. The ¹³C{¹H} NMR spectrum shows a resonance at δ 130.9 assignable to the cyano group. The infrared (IR) spectrum shows a strong-intensity band at 2160 cm⁻¹, assignable to the C–N stretching vibration mode.

The ¹H NMR spectrum of **3** contains three kinds of signals at δ 1.78 (9H), 8.92 (2H), and 9.39 (2H). The first is assignable to the *tert*-butyl group, and the latter to two aromatic protons. The ESI-MS spectrum shows a peak of *tert*-butylpyrazinium ion at m/z 137.

The single-crystal X-ray diffraction analysis of 4 clearly revealed the introduction of the cyano group at one of the acetylenic carbons (Figure 1).^{7,8} The C1–C5 distance is

Editor's Choice



Scheme 2. A plausible mechanism for formation of 2 and 3.



Scheme 3. Reactions of **1** with 2,6-dimethylphenyl isocyanide and cyclohexyl isocyanide.

1.437(3) Å, which is typical for carbon–carbon single bonds next to a nitrile group (1.466(5) Å).⁹ The C5–N bond distance (1.161(3) Å) and the C1–C5–N bond angle (179.0(3)°) are consistent with the existence of an sp-hybridized cyano group.⁷ The structure of the [4Fe–4C] core is quite similar to that in $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)_2]$.¹⁰

A plausible mechanism for the formation of **2** and **3** involves the substitution of pyrazine by *tert*-butyl isocyanide to generate $[(\eta^5-C_5H_4Me)_4Fe_4(HCCH)(HCC-CN'Bu)](PF_6)_2$ (**A**) (Scheme 2). The related nitrilium complexes have been reported by Casey and his co-workers.¹¹ The reaction of $[(\eta^5-C_5H_5)_2Fe_2-(CO)_2(\mu-CO)(\mu-CR)]^+PF_6^-$ (R = H, Me) with *tert*-butyl isocyanide led to the formation of the thermally stable $[(\eta^5-C_5H_5)_2Fe_2(CO)_2(\mu-CO)(\mu-CR)(\mu-CR)CNC(CH_3)_3)]^+PF_6^-$. The heterolytic cleavage of the carbon–nitrogen bond gives **2** and *tert*-butyl cation. The latter is trapped by pyrazine to give **3**. The driving force for the heterolytic cleavage of the carbon–nitrogen bond is probably related to the high Lewis acidity of the cationic [CCH] subunit compared to the *tert*-butyl cation.

The reactions of **1** with 2,6-dimethylphenyl isocyanide and cyclohexyl isocyanide at room temperature for 3 h afforded the corresponding isocyanide-coordinated compounds **5** and **6** (Scheme 3). These compounds were unequivocally characterized by the results of elemental analysis and spectroscopic data. The IR spectra of **5** and **6** show strong-intensity bands at 2245 and 2274 cm⁻¹, respectively, which are assigned to the C–N stretching vibration mode of the nitrilium CN bond.¹²

The structure of the cationic part of **5** is depicted in Figure 2.^{7,8} The bonding parameter around the nitrilium moiety indicates sp hybridization of the CN unit:¹³ The bond distance of C5–N (1.167(7) Å) is close to that of a typical carbon–nitrogen triple bond. The bond distances of C1–C5 (1.400(7) Å) and



Figure 2. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 30% probability level. The methyl groups on the cyclopentadienyl ligands and hydrogen atoms, except for acetylenic hydrogens, are omitted for clarity. Selected bond lengths (Å) and angels (degree): Fe1–Fe3 2.5042(9), Fe1–Fe4 2.5124(10), Fe2–Fe3 2.4861(10), Fe2–Fe4 2.4741(10), C1–C2 1.538(7), C3–C4 1.484(7), C1–C5 1.400(7), C5–N 1.167(7), C6–N 1.396(7), C1–C5–N 177.6(5). C5–N–C6 176.8(6).



Scheme 4. Thermolysis of 6 in acetonitrile- d_3 .

C6–N (1.396(7)Å) lie in the range expected for the typical single bonds next to the carbon–nitrogen triple bonds.⁹ The bond angles of C1–C5–N and C5–N–C6 are 177.6(5) and $176.8(6)^{\circ}$, respectively.

The thermal stability of 5 and 6 was examined by NMR spectroscopy. Compound 5 in acetonitrile- d_3 was stable at 70 °C. Further heating of 5 in dimethyl sulfoxide- d_6 at 150 °C resulted in decomposition, in which formation of 2 was not confirmed. Heating of 6 in acetonitrile- d_3 at 70 °C allowed the complete transformation to 2, accompanied by the formation of cyclohexene (13%) (Scheme 4). Thermal reaction in the presence of pyrazine enhanced the yield of cyclohexene (57%), although the reaction rate was independent of the concentration of pyrazine. Thus, thermolysis of 6 enhances the heterolytic cleavage of the carbon-nitrogen bond. Pyrazine deprotonates the resulting cyclohexyl cation to form cyclohexene. The tendency in reactivity of the carbon-nitrogen bond cleavage can be explained based on the stability of the resulting carbenium ion. Stability of the carbenium ion, estimated by the heterolytic bond dissociation energies of $D(R^+-H^-)$, is in the following order, *tert*-butyl cation $(233 \text{ kcal mol}^{-1}) > \text{cyclohexyl cation}$ $(243 \text{ kcal mol}^{-1}) > \text{phenyl cation } (294 \text{ kcal mol}^{-1}).^{14}$

Dealkylation of the coordinated *tert*-butyl isocyanide has been reported in some transition-metal complexes, although examples are limited.¹⁵ Jones and his co-workers reported that thermolysis of $[Fe(PMe_3)_2(t-BuNC)_3]$ at 60 °C for 24 h resulted

809

in the formation of [Fe(PMe₃)₂(t-BuNC)₂(H)(CN)] and isobutene. They proposed a mechanism involving homolysis of the C-N bond to generate a tert-butyl radical.16 Activation of secondary alkyl isocyanides was very limited and was reported in the decamethylvanadocene system.^{15b} Tokitoh and his coworkers reported the thermal reaction of Tbt(Mes)Si=Si(Mes)-Tbt {Tbt: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes: mesityl} with tert-butyl isocvanide at 70 °C to form [Tbt(Mes)-SiH(CN)] and isobutene. They proposed a mechanism involving the initial formation of a silvlene-isocyanide complex, followed by the concerted proton migration of the *tert*-butyl group to the silicon atom and elimination of isobutene.¹⁷ Power and his coworkers reported that the isolable germylene $GeAr_2$ {Ar = C_6H_3 -2,6-[C_6H_2 -2,4,6-(CH_3)₃]₂} reacted with *tert*-butyl isocyanide to give a germylene-isocyanide complex, which was further converted to GeAr2H(CN) and isobutene. DFT calculations indicated a concerted pathway similar to the mechanism proposed by Tokitoh.¹⁸ To the best of our knowledge, activation of the carbon-nitrogen bond of isocyanides by the carbocations is unprecedented. In our reaction, the extremely high Lewis acidity of the cationic [CCH] subunit plays a crucial role in the activation of secondary and tertiary alkyl isocyanides under extremely mild conditions.

This research was supported by the funding program for Next Generation World-Leading Researchers and Grant for Hirosaki University Institution Research.

References and Notes

- a) R. Dolby, B. H. Robinson, J. Chem. Soc. D 1970, 1058. b)
 R. Dolby, B. H. Robinson, J. Chem. Soc., Dalton Trans. 1972, 2046.
- 2 D. Seyferth, Adv. Organomet. Chem. 1976, 14, 97.
- 3 a) J. E. Hallgren, C. S. Eschbach, D. Seyferth, J. Am. Chem. Soc. 1972, 94, 2547. b) D. Seyferth, G. H. Williams, J. Organomet. Chem. 1972, 38, C11. c) D. Seyferth, C. N. Rudie, J. Organomet. Chem. 1980, 184, 365. d) M. F. D'Agostino, M. Mlekuz, J. W. Kolis, B. G. Sayer, C. A. Rodger, J.-F. Halet, J.-Y. Saillard, M. J. McGlinchey, Organometallics 1986, 5, 2345.
- 4 Generation and observation of an ethynyl cation have been reported by several groups. a) S. J. Huang, V. Paneccasio, F. DiBattista, D. Picker, G. Wilson, J. Org. Chem. 1975, 40, 124. b) S. I. Miller, J. I. Dickstein, Acc. Chem. Res. 1976, 9,

358. c) P. C. Burgers, J. L. Holmes, A. A. Mommers, J. E. Szulejko, *J. Am. Chem. Soc.* **1984**, *106*, 521. d) R. Helwig, M. Hanack, *Chem. Ber.* **1985**, *118*, 1008. e) R. Glaser, *J. Am. Chem. Soc.* **1987**, *109*, 4237. f) G. Angelini, M. Hanack, J. Vermehren, M. Speranza, *J. Am. Chem. Soc.* **1988**, *110*, 1298.

- 5 a) P. M. Maitlis, V. Zanotti, *Chem. Commun.* 2009, 1619. b)
 Z.-P. Liu, P. Hu, J. Am. Chem. Soc. 2002, 124, 11568.
- 6 M. Okazaki, W. Taniwaki, K. Miyagi, M. Takano, S. Kaneko, F. Ozawa, *Organometallics* 2013, 32, 1951.
- 7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/ index.html.
- 8 Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-933591 (4) and CCDC-933592 (5). Copies of the data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).
- 9 J. G. Speight, *Lange's Handbook of Chemistry*, 16th ed., McGraw-Hill, New York, 2005.
- 10 M. Okazaki, T. Ohtani, S. Inomata, N. Tagaki, H. Ogino, J. Am. Chem. Soc. 1998, 120, 9135.
- 11 C. P. Casey, M. Crocker, G. P. Niccolai, P. J. Fagan, M. S. Konings, J. Am. Chem. Soc. 1988, 110, 6070.
- 12 G. A. Olah, T. E. Kiovsky, J. Am. Chem. Soc. 1968, 90, 4666.
- 13 A. K. Gjøystdal, C. Rømming, Acta Chem. Scand., Ser. B 1977, 31, 56.
- 14 F. P. Lossing, J. L. Holmes, J. Am. Chem. Soc. 1984, 106, 6917.
- 15 a) C. M. Giandomenico, L. H. Hanau, S. J. Lippard, *Organometallics* 1982, *1*, 142. b) S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* 1984, *23*, 1739.
 c) W. D. Jones, W. P. Kosar, *Organometallics* 1986, *5*, 1823.
 d) W. D. Jones, G. P. Foster, J. M. Putinas, *Inorg. Chem.* 1987, *26*, 2120.
- 16 C. L. Tennent, W. D. Jones, Can. J. Chem. 2005, 83, 626.
- 17 N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki, N. Tokitoh, *Chem.*—*Eur. J.* **2003**, *9*, 3530.
- 18 Z. D. Brown, P. Vasko, J. C. Fettinger, H. M. Tuononen, P. P. Power, J. Am. Chem. Soc. 2012, 134, 4045.