

Protonation Studies of the New Iron Carbonyl Cyanide *trans*-[Fe(CO)₃(CN)₂]²⁻: Implications with Respect to Hydrogenases

Ajay Kayal and Thomas B. Rauchfuss*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received April 30, 2003

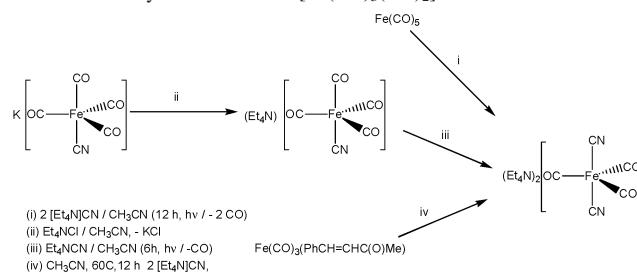
The new iron carbonyl cyanide *trans*-[Fe(CN)₂(CO)₃]²⁻, [2]²⁻, forms in high yield via photosubstitution of Fe(CO)₅ with 2 equiv of Et₄N₃CN. Protonation of [2]²⁻ generated [HFe(CN)₂(CO)₃]⁻, [2H]⁻, the first H–Fe–CN–CO species. Further protonation gives dihydrogen. This simple system provides insights into hydrogen evolution by the hydrogenase enzymes, which also feature H–Fe–CN–CO centers.

Iron carbonyl cyanide complexes^{1–7} have assumed special importance in light of the discovery of Fe–CO–CN motifs in the active sites of both Fe-only and [Ni–Fe] hydrogenases, the enzymes responsible for virtually all bioprocessing of dihydrogen.^{8–10} Thus, Fe–CO–CN–H species may be considered as minimalist biomimetic models of Fe-only and possibly the [Ni–Fe] hydrogenases. Although several Fe–CO–CN species have been described, none features hydro- genic ligands, the sine qua non of hydrogenases.¹¹ Herein, we describe the synthesis of the first hydrides of iron carbonyl cyanides and the conversion of these hydrides into dihydrogen. The development of functional analogues^{12,13} of the hydrogenase enzymes could lay the foundation for new fuel cell and related clean-energy applications.^{14,15}

* Author to whom correspondence should be addressed. E-mail: rauchfuz@uiuc.edu.

- Jiang, J.; Koch, S. A. *Inorg. Chem.* **2002**, *41*, 158–160.
- Jiang, J. F.; Acunzo, A.; Koch, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12109–12110.
- Jiang, J. F.; Koch, S. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2629–2631.
- Rauchfuss, T. B.; Contakes, S. M.; Hsu, S. C. N.; Reynolds, M. A.; Wilson, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 6933–6934.
- Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 770–775.
- Ruff, J. K. *Inorg. Chem.* **1969**, *8*, 86–89.
- Contakes, S. M.; Hsu, S. C. N.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2002**, *41*, 1670–1678.
- Frey, M. *ChemBioChem* **2002**, *3*, 153–160.
- Darensbourg, M. Y.; Lyon, E. J.; Smece, J. J. *Coord. Chem. Rev.* **2000**, *206–207*, 533–561.
- Fontecilla-Camps, J. C.; Ragsdale, S. W. *Adv. Inorg. Chem.* **1999**, *47*, 283–333.
- Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chim. Acta* **1999**, *294*, 240–254.
- Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476–9477.
- Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3683–3688.
- Cammack, R. *Nature* **1999**, *397*, 214–215.

Scheme 1. Synthesis of *trans*-[Fe(CO)₃(CN)₂]²⁻



Initial studies examined the protonation of the well-known Fe(0) complex K[Fe(CO)₄CN] (K[1]).^{5,6} Treatment of K[1] with 1 equiv of HCl (2.0 M solution in Et₂O) in MeCN solution (–30 °C) leads to an 1:8 mixture of HFe(CO)₄CN (**1H**, δ –9.67) and Fe(CO)₄CNH (broad, δ 8.50). This mixture readily decomposes to, inter alia, Fe(CO)₅. The instability of **1H** can be attributed to the facile elimination and lability of HCN, which is facilitated by the four electron-withdrawing CO groups. The Fe sites of both families of hydrogenases feature donor ligands (thiolates) in addition to CO and CN⁻; furthermore, the Fe site in [NiFe] hydrogenase features two CN⁻ ligands.⁸ This logic suggested that the replacement of a further CO by CN⁻ might stabilize the Fe–H bond.

The Et₄N⁺ salt of [Fe(CN)₂(CO)₃]²⁻ ([2]²⁻) can be synthesized on a gram scale from Fe(CO)₅ by photosubstitution with 2 equiv of Et₄N₃CN (Scheme 1). The product was isolated as colorless crystals from Et₂O–MeCN (70% yield). The same salt can also be generated by stepwise photosubstitution from [1]⁻ as well as by thermal displacement of bda from [Fe(CO)₃(bda)]¹⁶ (bda = PhCH=CHCOCH₃). The salt (Et₄N)₂[Fe(CN)₂(CO)₃] air oxidizes to give a mixture of [Fe(CN)₅CO]³⁻ and *trans*-[Fe(CN)₄(CO)₂]²⁻.^{2,3,7}

Crystallographic analysis of (Et₄N)₂[2] reveals the expected trigonal bipyramidal (*D*_{3h}) arrangement of the CN⁻ and CO ligands (Figure 1). The Fe–CO (1.779(2) Å) and Fe–CN (1.925(2) Å) distances indicate extensive π-back-bonding in the Fe–CO bond and the predominantly σ-bond character

- Hydrogen as a Fuel: Learning from Nature*; Cammack, R., Ed.; Taylor and Francis Inc.: New York, 2001.
- Domingos, A. J. P.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1976**, *16*, 103–107.

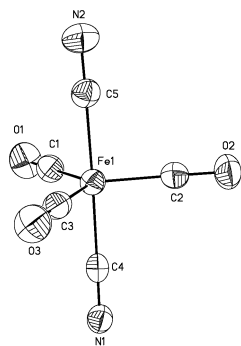
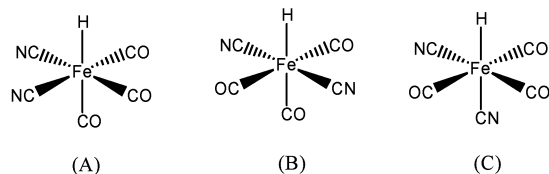


Figure 1. Structure of the dianion ($[2]^{2-}$) in $(\text{Et}_4\text{N})_2[\text{Fe}(\text{CO})_3(\text{CN})_2]$ with thermal ellipsoids (50% probability) and selected atom labels; hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg): Fe(1)–C(1), 1.785(2); Fe(1)–C(2), 1.780(2); Fe(1)–C(3), 1.773(2); Fe(1)–C(4), 1.921(2); Fe(1)–C(5), 1.929(2); C–O(av), 1.161(2); C–N(av), 1.160(2); C(4)–Fe(1)–C(5), 177.7(1); Fe(1)–C–O(av), 178.9(2); Fe(1)–C–N(av), 178.4(2); OC–Fe–CO(av), 120.0(1); NC–Fe–CO(av), 90.0(1).

Scheme 2. Isomers of $[\text{HFe}(\text{CO})_3(\text{CN})_2]^-$, $[2\text{H}]^-$



of the Fe–CN bond. In octahedral and square planar cyanocarbonyls, CO is typically trans to the strong donor CN^- .

The IR spectrum of $(\text{Et}_4\text{N})_2[2]$ in MeCN, displaying ν_{CN} and ν_{CO} bands at 2059 and 1844 cm^{-1} , respectively, is consistent with the solid state structure as is the ^{13}C NMR spectrum. The cyclic voltammogram of $(\text{Et}_4\text{N})_2[2]$ shows an irreversible oxidation at -400 mV; in contrast, $[1]^-$ oxidizes, again irreversibly, at $+150$ mV (all potentials vs Ag/AgCl in MeCN). The 550 mV shift in the E_{ox} and the ca. 175 cm^{-1} shift in ν_{CO} both indicate that $[2]^{2-}$ is substantially more electron-rich than $[1]^-$.

Protonation of $[2]^{2-}$ with 1 equiv of *p*-TsOH (or NH_4PF_6) gave the hydride $[\text{HFe}(\text{CO})_3(\text{CN})_2]^-$ ($\text{Et}_4\text{N}[2\text{H}]$), three isomers of which are possible (Scheme 2).

Low temperature (-30 to 0 °C, MeCN solution) protonations revealed the formation of two major isomers (δ -7.90 , -8.33) with a third minor isomer (δ -11.2). Protonation is complete at 10 °C with the three isomers at δ -7.90 , -8.30 , -11.2 in the ratio of 10:6:1, regardless of the solvent used for the protonation (MeNO_2 , CH_2Cl_2 , MeCN).

The ^1H -coupled ^{13}C NMR spectrum (Figure 2) of $[2\text{H}^*]^-$ at 10 °C consists of two intense doublets in the CN region (δ 135.2 ($J = 16$ Hz), 132.9 ($J = 13$ Hz)) consistent with the predominance of isomers A and B (Scheme 2), both of which have similar coupling to ^{13}C as observed in the ^{13}C NMR spectra of enriched samples. It proved difficult to separate a pure sample of $[2\text{H}]^-$ from the co-formed conjugate salt; however, a solid sample, analytically found to be a 1:1 mixture of (K)[2H] and co-formed [K(18-c-6)]-Cl was obtained by the protonation of [K(18-c-6)] $[2]$ with anhydrous HCl in MeCN at 0 °C followed by precipitation with diethyl ether.

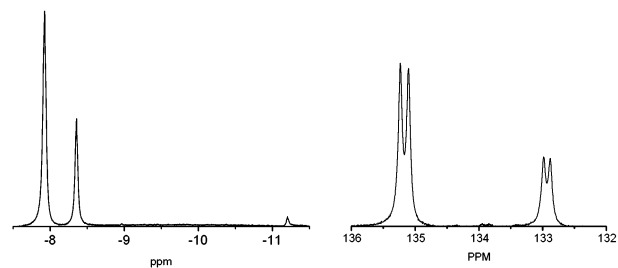


Figure 2. ^1H NMR (500 MHz, CD_3CN) spectrum (hydride region) (left) and ^{13}C NMR (125 MHz, CD_3CN) spectrum (CN region) (right) of $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_3(\text{CN})_2]$.

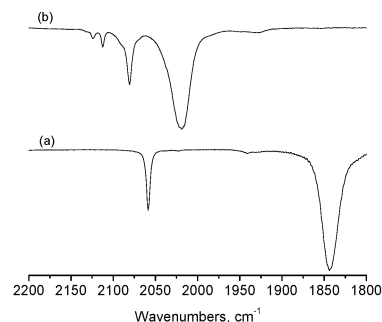


Figure 3. IR spectra of $(\text{Et}_4\text{N})_2[2]$ (a) and $(\text{Et}_4\text{N})[2\text{H}]$ (b) (CH_3CN).

The most notable feature of the IR spectrum of $[2\text{H}]^-$ is the ca. 175 cm^{-1} shift of the $(\nu_{\text{CO}})_{\text{av}}$ stretching frequency upon protonation (Figure 3), indicative of substantial electronic rearrangement associated with conversion of the five-coordinate zerovalent metal center to the divalent octahedral derivative. The shift is comparable to the $\Delta(\nu_{\text{CO}})_{\text{av}}$ shift of 166 cm^{-1} previously recorded for the protonation of $[\text{Co}(\text{CH}_3\text{CN})_6][\text{Co}(\text{CO})_4]_2$ in MeCN.¹⁷ Although splitting of the ν_{CO} bands is not observed, ν_{CO} and ν_{CN} bands in the IR spectra of $[2\text{H}]^-$ in MeCN and $[\text{Fe}(\text{CO})_3(\text{CN})_2\text{Br}]^-$ in THF, which adopts isomer B (in Scheme 2), are very similar.¹⁸ $(\text{Et}_4\text{N})_2[2]$ is protonated by NH_4PF_6 ($\text{p}K_{\text{a}} = 16$ in MeCN), whereas 1H is fully deprotonated by $\text{C}_6\text{H}_5\text{NH}_2$ ($\text{p}K_{\text{a}} = 11$). Thus, 1H is $> 10^5$ more acidic than $[2\text{H}]^-$. These data further establish that the protonation in $[2]^{2-}$ occurs at the Fe(0) center and not at the CN^- to yield the hydride, $[2\text{H}]^-$, although protonation at the metal center in cyanometalates is rare.^{19,20}

Further protonation of $[2\text{H}]^-$ in principle should afford $\text{Fe}(\text{CN})_2(\text{CO})_3(\text{H}_2)$, which would be of obvious relevance to the H_2 -evolution function of the hydrogenases. Treatment of $[2\text{H}]^-$ with excess *p*-TsOH ($\text{p}K_{\text{a}} = 8$) at room temperature completely consumed the hydride and gave 67% yield H_2 , analyzed by ^1H NMR spectroscopy and gas chromatography. The evolution of H_2 is associated with an equimolar evolution of CO (analyzed by gas chromatography) and the formation of a yet unidentified Fe-containing product (ν_{CN} and ν_{CO}

(17) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.

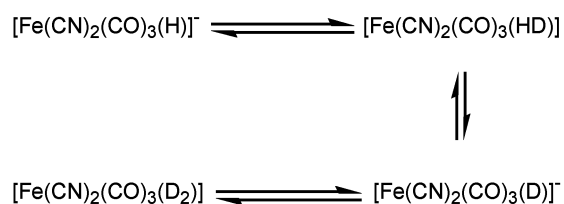
(18) Liaw, W. F.; Lee, J. H.; Gau, H. B.; Chen, C. H.; Jung, S. J.; Hung, C. H.; Chen, W. Y.; Hu, C. H.; Lee, G. H. *J. Am. Chem. Soc.* **2002**, *124*, 1680–1688.

(19) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Inorg. Chem.* **2002**, *41*, 6573–6582.

(20) Bianchini, C.; Laschi, F.; Ottaviani, M. F.; Peruzzini, M.; Zanello, P.; Zanolini, F. *Organometallics* **1989**, *8*, 893–899.

COMMUNICATION

Scheme 3



bands at 2108 and 2069 cm^{-1} in MeCN). Interestingly, treatment of $[\mathbf{2H}]^-$ with excess *p*-TsOD gave mainly D_2 , identified by ^2H NMR spectroscopy. This finding can be rationalized by the occurrence of a rapid protonation–deprotonation equilibrium of the proposed intermediate, $\text{Fe}(\text{CN})_2(\text{CO})_3(\text{H}_{2-x}\text{D}_x)$ (Scheme 3).

In summary, a minimalist, purely inorganic representation of the Fe site in the metallo hydrogenases has been prepared via the synthon $[\text{Fe}(\text{CN})_2(\text{CO})_3]^{2-}$, the newest and most reactive member of the growing iron carbonyl cyanide family.^{1–7} The new dianion gives rise to the first Fe–CN–H–CO species and further connects to the formation of dihydrogen via a pathway that implicates an Fe^{II}–CN–CO–H₂ intermediate.

Acknowledgment. This research was supported by the NIH and DOE.

Supporting Information Available: Crystallographic information file (CIF) for $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC034455B