C-H Bond Activation by Cobalt(I) Macrocycles: Rapid H/D Exchange between Macrocycle and Acetonitrile Solvent

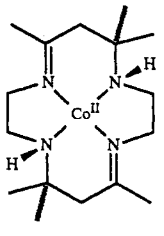
Etsuko Fujita* and Carol Creutz*

Chemistry Department, Brookhaven National Laboratory,
P.O. Box 5000, Upton, New York 11973-5000

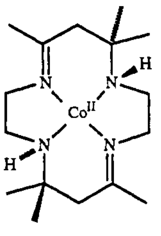
Received November 30, 1993

Despite extensive studies of proton-transfer thermodynamics and kinetics in acetonitrile solution,[1] proton exchange between solute and solvent has rarely been encountered.[2] Here, rapid (20-min $t_{1/2}$ at room temperature) proton exchange between the N-H groups of a cobalt(I) macrocycle and CD_3CN solvent is reported. The reaction is anomalously rapid for a "simple" proton-transfer process and may signal reactivity of the metal center toward C-H activation.

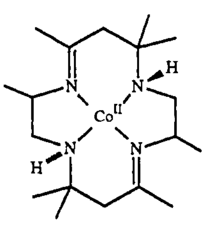
Tetraazamacrocyclic complexes of cobalt and nickel catalyze the electrochemical[3-5] and photochemical reduction of H_2O[6] and CO_2.[4,7] While the binding of CO_2 to low-spin d^8 CoL^+ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been characterized in organic solvents[8-11] and in water,[12,13] the highly nucleophilic CoL^+ complex[14,15] has itself been less well characterized because of its high reactivity.



N-rac-$Co^{II}L^{2+}$



N-meso-$Co^{II}L^{2+}$



$Co^{II}L'^{2+}$

Immediately following preparation of 0.07-0.09 M solutions of $Co^{I}L^+$ by[9] sodium amalgam (Na-Hg) reduction of anhydrous *rac*-$Co^{II}L(ClO_4)_2$ in CD_3CN, the macrocycle ν_{NH} (3201 cm^{-1}) and $\nu_{C=N}$ (1571 cm^{-1}) bands of perprotio $Co^{I}L^+$ lie at their usual positions, as shown in Figure 1. Over the next 1 h H/D exchange of the N-H with the solvent is observed: the ν_{NH} intensity decreases, $\nu_{C=N}$ shifts to 1556 cm^{-1}, and weak bands appear at 1650 cm^{-1} and ~2400 (ν_{ND}) cm^{-1}.[16] The decrease of the 3201-cm^{-1} absorbance is first order in [$Co^{I}L^+$] with a rate constant (k_{obs}) of (5 ± 1) × 10^{-4} s^{-1} at (23 ± 1) °C. About half as rapidly, exchange of macrocycle C-H occurs, as well: the 1571-cm^{-1} band shifts toward 1556 cm^{-1} and then decreases in intensity.[17] Similar results are obtained starting with the meso cobalt(II) isomer[18] (k_{obs} = (6 ± 1) × 10^{-4} s^{-1}; initial [$Co^{I}L^+$] = 0.061 M). The less reducing octamethyl derivative $Co^{I}L'^{+}$ undergoes H/D exchange about a factor of 20 more slowly (k_{obs} = (3 ± 0.5) × 10^{-5} s^{-1} for N-H/N-D exchange). By contrast, with C_3H_7CN as solvent, the intensities of the 1570- and 3200-cm^{-1} bands did not change over 3 h. $Co^{I}L^+$ prepared by ≥1-h bulk electrolysis (Pt electrode, 0.1 M tetrapropylammonium perchlorate) in CD_3CN also undergoes deuteration ($\nu_{C=N}$ = 1556 cm^{-1}).

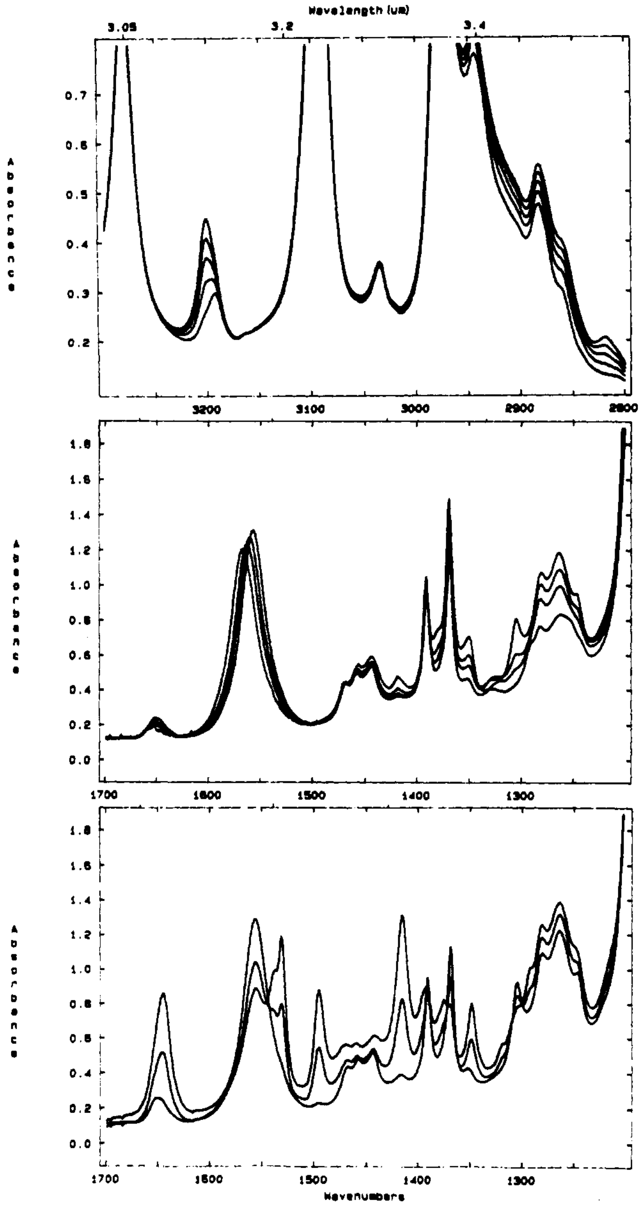


Figure 1. Infrared spectrum of $Co^{I}L^+$ prepared from *N-rac*-$Co^{II}L^{2+}$ (0.09 M, 0.5-mm path length) in CD_3CN as a function of time. Top: Both ν_{NH} and ν_{CH} bands decrease in intensity with time because of H/D exchange with the solvent. The spectra were obtained 15, 23, 31, 49, and 89 min after solution preparation. The 3192-cm^{-1} peak is due to the solvent. Center: C-H/C-D exchange is implicated by (1) the shift of ν_{CN} to lower energy, (2) the decrease of δ_{CH} intensity in the 1320-1200-cm^{-1} region, and (3) the increase in δ_{CD} intensity in the 1500-1320-cm^{-1} region. The times are the same as for the top frame. Bottom: The same solution after 4, 24, and 56 h. The 1645-cm^{-1} band increases, the 1556-cm^{-1} band decreases, and new peaks appear at 1538, 1531, and 1495 cm^{-1} due to decomposition of d_{12}-$Co^{I}L^+$.

---

(1) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45-92.

(2) For hydroxide-ion catalyzed H/D exchange of acetonitrile with water, the bimolecular rate constant 3 × 10^{-5} M^{-1} s^{-1} has been estimated for 25 °C: Reitz, O. Z. *Phys. Chem. A* **1939**, *183*, 371. Bonhoefer, K. F.; Geib, K. H.; Reitz, O. *J. Chem. Phys.* **1939**, *7*, 664.

(3) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.

(4) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. M. W. H.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 288.

(5) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(6) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

(7) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans* **1987**, 2105.

(8) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870-4871.

(9) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343-353.

(10) Schmidt, M. H.; Miskelly, G. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 3420-3426.

(11) Summers, J. S. Ph.D. Thesis, Georgia Institute of Technology, 1989.

(12) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153-4.

(13) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361-3371.

(14) Vasilevskis, J.; Olson, D. C. *Inorg. Chem.* **1971**, *10*, 1228.

(15) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86-93.

0020-1669/94/1333-1729$04.50/0

H/D exchange is also evident in the ^{1}H NMR spectra. ^{1}H NMR spectra of cobalt(I) solutions generated from *rac*-$Co^{II}L(ClO_4)_2$ and *meso*-$Co^{II}L(ClO_4)_2$ in CD_3CN are identical because of rapid formation of an (85 ± 5)%:(15 ± 1)% equilibrium mixture of two isomers.[9] At room temperature the Co^IL^+ imine methyl resonance at 1.45 ppm is broad and overlaps the N–H signal at 1.47 ppm but sharpens when the temperature is reduced to 260 K. Starting within 15 min after the reduction of *rac*-$Co^{II}L(ClO_4)_2$ in CD_3CN, the ^{1}H NMR spectra were monitored for 1 h at room temperature. The intensity of the N–H proton decreased, while the intensity of the CHD_2CN peak increased by 2.2 ± 0.6 protons per Co^IL^+ as estimated from the peak integration. The intensity of the 1.45-ppm methyl resonance decreased more slowly. H/D exchange was confirmed in experiments in which 2,2′-bipyridine (bpy) was used as calibrant. After ^{1}H NMR measurement of the CHD_2CN integral with 0.07 M bpy as internal standard, the solvent was vacuum-transferred into a known amount of $Co^{II}L^{2+}$ and Na–Hg. The $Co^{II}L^{2+}$ was reduced to Co^IL^+ (0.08 M) and filtered as always[9] from the Na–Hg, and 6 h later, the solvent was back-transferred to the original NMR tube containing bpy for another NMR measurement. The solvent CHD_2CN peak had increased by 11 ± 1 protons per cobalt in intensity.

While the N–H groups of Co(II) and -(III) macrocycles readily exchange with D_2O neither *rac*-, *meso*-$Co^{II}L$ nor $Co^IL–CO_2$ undergoes N–H proton exchange with CD_3CN. The rapid exchange of the two N–H protons, followed by slower exchange of C–H protons, is reminiscent of behavior found for NiL^{2+}: for NiL^{2+}, the imine methyl and the 6- and 13-methylene protons are readily deuterated in basic D_2O.[19–21] A sample of d_{12}-$Ni^{II}L(ClO_4)_2$ prepared in basic D_2O showed no ν_{NH} intensity (ν_{ND} = 2363 cm^{-1}), and $\nu_{C=N}$ was shifted from 1660 to 1651 cm^{-1}. The shift of $\nu_{C=N}$ from 1571 to 1556 cm^{-1} for Co^IL^+ is also attributed to deuteration of the imine methyl and 6- and 13-methylene positions of the macrocycle, consistent with the exchange of 11 ± 1 protons determined by NMR.

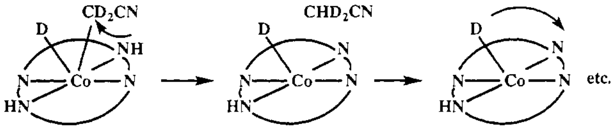
H/D exchange of CoL^+ with CD_3CN is particularly striking because acetonitrile is such a weak acid: the pK_a of CH_3CN in CH_3CN is 29.1.[22] In CoL^+ there are both basic and acidic sites which could be relevant in the exchange pathway. Protonation of *rac*-CoL^+ in water gives hydride complexes with pK_a values of ~11.5,[12,13] which corresponds to a pK_a of ca. 20 in acetonitrile.[23] Thus the equilibrium constant for deprotonation of CD_3CN by CoL^+ (eq 1)could be 10^{-9} M. The pK_a of the macrocycle amine N–H group (eq 2; conjugate base $CoL(-H)^+$) is not known but could be as low as 13 in water, perhaps 19–20 in CH_3CN.[24] Since the reactivity of CoL^+ toward metal-centered proton transfer from neutral nitrogen and oxygen acids in aqueous media is great,[12,13,15] a simple proton-transfer mechanism initiated in eq 1 would seem possible. However, if exchange simply involves an equilibrium deprotonation, other bases of similar basicity would be expected to induce exchange between the conjugate acid (*e.g.* $CpRe(CO)_2H_2$ or $H(CH_3)Os(CO)_4$[24]) and acetonitrile. Such exchange has not been reported.

$$CoL^+ + CD_3CN \rightleftharpoons CoL(D)^{2+} + CD_2CN^- \qquad K_H \quad (1)$$

$$CoL^+ + CD_3CN \rightleftharpoons CoL(-H)^+ + CD_3CNH^+ \qquad (2)$$

To test this issue, we sought evidence for proton exchange of CD_3CN with an acid/base pair with a p*K* comparable to that of the cobalt macrocycle. The pK_a of 1,1,3,3-tetramethylguanidinium ion ($TMGH^+$) (pK_a = 13.6 in water) is 23.3 in acetonitrile,[25] and like other nitrogen-centered systems, this pair exhibits high proton-transfer reactivity. However, no exchange between CD_3CN and 20 mM $TMGH^+$/100 mM TMG or 0.2 M $TMGH^+$/1.3 M TMG was found at 23 ± 1 °C over 1 month. The failure of CD_3CN to exchange with TMG/$TMGH^+$ and other B/BH^+ pairs of high basicity undoubtedly reflects the high intrinsic barrier of CH_2CN^-/CH_3CN with respect to proton transfer. The intrinsic reactivity of CoL^+ with respect to proton transfer is high but no greater than that of N-centered species such as TMG. Thus exchange with CoL^+ must involve another mechanism.

One possibility is suggested by studies of C–H activation.[26,27] Acetonitrile is readily metalated by electron-rich $[Ir(PMe_3)_4]Cl$ to form *cis*-$[Ir(H)(CH_2CN)(PMe_3)_4]Cl$ with $t_{1/2}$ ~ 10 min.[28] Oxidative addition of the methyl group of CH_3CN to the Co(I) complex would result in the formation of the cobalt–carbon bond in the metalated $Co^{III}L(D)(CD_2CN)^+$ species, and H/D exchange could occur via a sequence such as that shown as follows:[29]

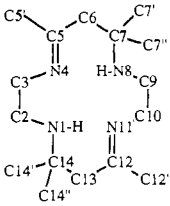


Hopefully, future mechanistic studies of the cobalt systems will clarify the nature of the exchange mechanism for these complexes.

Acknowledgment. We thank Drs. M. Andrews, B. Brunschwig, R. M. Bullock, J. R. Norton, and N. Sutin for helpful discussions. This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

---

(16) Our observations are in fair agreement with those of Summers, who also measured IR spectra of the perprotio Co^IL^+ complex in CD_3CN.[11] The macrocycle numbering scheme is as follows:



(17) Over several hours the 1650-cm^{-1} band increases, the 1556-cm^{-1} band decreases, and new peaks appear at 1538 and 1531 cm^{-1} due to decomposition of Co^IL^+. Complete decomposition takes more than 1 day under these conditions.

(18) Szalda, D. J.; Schwarz, C. L.; Endicott, J. F.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1989**, *28*, 3214–3219.

(19) Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1968**, *90*, 6938–6946.

(20) Barefield, E. K.; Busch, D. H. *Inorg. Chem.* **1971**, *10*, 108.

(21) Ito, T.; Busch, D. H. *Inorg. Chem.* **1974**, *13*, 1770.

(22) Bordwell, F. G.; Mathews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1216–1217.

(23) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005–5010.

(24) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 309–359.

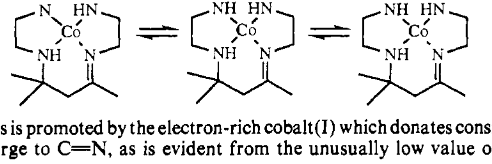
(25) Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28.

(26) Reviews: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. Papers: Crabtree, R. H.; Mellrea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632.

(27) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577–7585.

(28) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648.

(29) "Intramolecular" exchange of N–H protons with those bonded to carbon atoms α to the imine could occur through the following isomerization:



This is promoted by the electron-rich cobalt(I) which donates considerable charge to C=N, as is evident from the unusually low value of ν_{CN}.