*Organometallics* 1992, *11*, 2339–2341 2339

length of C(2)–C(3) is 1.334 (11) Å, which shows its double-bond character. The length of Co–P [2.136 (2) Å] is much shorter than that of the trimethyl phosphite–cobalt complex $[Co\{P(OMe)_3\}_4(S_2CNC_5H_{10})](BF_4)_2$ [Co–P = 2.206 and 2.244 Å (average)][6] and is shortest among those of the several trialkylphosphine–cobalt complexes (Co–P = 2.138–2.292 Å).[7]

Complex **3** undergoes facile photodissociation under irradiation with a high-pressure mercury lamp in benzene to regenerate the ring-contracted complex **2**. Complex **2** is stable against irradiation under these conditions. This photodissociation occurs both under argon and in the presence of air; a $^1H$ NMR study showed that the photoreaction did not give methyl phosphate. This is different from the photodissociation of a phosphine adduct[8] or a phosphite adduct via the elimination of the coordinated phosphine by singlet oxygen to give the phosphine oxide or the phosphate, respectively.

Complex **2**, therefore, causes reversible ring expansion and contraction in the processes of reaction with phosphite and during photoirradiation, as shown in Scheme I. These ring conversions occur so as to keep the coordinative saturation of the central cobalt(III) atoms and therefore so as to keep the 18-electron rule through the addition and dissociation.

An investigation involving preparing related compounds of the six-membered metallacycles is in progress.

**Acknowledgment.** This work was supported in part by Grant-in-Aid for Scientific Research on Priority Areas on Organic Unusual Valency No. 02247102 and by Grant-in-Aid for Scientific Research No. 03640464 from the Ministry of Education, Science and Culture and by the Asahi Glass Foundation.

**Supplementary Material Available:** For **2** and **3**, text giving full details of the preparation and characterization of the compounds and details of the structure determination, listings of crystal data, positional and thermal parameters, and bond distances and angles, and a figure showing atom numbering (23 pages). Ordering information is given on any current masthead page.

OM920174S

---

[6] Matsui, H.; Kita, M.; Kashiwabara, K.; Fujita, J. Presented at The 41st Symposium on Coordination Chemistry of Japan, 2A06, Okayama, Japan, 1991; Abstract 2A06.

[7] Orpen, A. G. *Organometallics* **1990**, *9*, 1206.

[8] Hatano, H.; Kajitani, M.; Akiyama, T.; Sakaguchi, Y.; Nakamura, J.; Hayashi, H.; Sugimori, A. *Chem. Lett.* **1990**, 1089.

---

# $Et_3NH^+Co(CO)_4^-$: Hydrogen-Bonded Adduct or Simple Ion Pair? Single-Crystal Neutron Diffraction Study at 15 K

Lee Brammer* and Melinda C. McCann

*Department of Chemistry, University of Missouri—St. Louis,*
*8001 Natural Bridge Road, St. Louis, Missouri 63121-4499*

R. Morris Bullock and Richard K. McMullan

*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973*

Paul Sherwood

*SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.*

*Received March 18, 1992*

*Summary:* $Et_3NH^+Co(CO)_4^-$ contains a short N–H···Co contact, which provides the closest approach between the anion and cation. Accurate structural characterization by neutron diffraction at 15 K shows the N–H···Co interaction to be linear with a long N–H bond length and a relatively short Co···H separation (Co···H = 2.613 (2) Å, N–H = 1.054 (1) Å, N–H···Co = 180.0°). This evidence is consistent with the presence of a three-center–four-electron hydrogen-bond-like N–H···Co interaction, though it does not rule out simple electrostatic attraction as the principal driving force behind association of the $Et_3NH^+$ and $Co(CO)_4^-$ ions.

It has recently been proposed[1] that certain electron-rich transition-metal centers may be able to participate in interactions with hydrogen atoms to form three-center–four-electron (3c–4e) Z–H···M (Z = C, N) hydrogen bridges. Such interactions appear to be analogous to those of hydrogen bonds involving main-group elements, i.e., attractive interactions involving both an orbital contribution (the 3c–4e interaction) and an electrostatic contribution. The unusual aspect of these interactions is that a transition-metal atom acts as the hydrogen bond acceptor. It has been previously noted that the characteristics of such Z–H···M interactions are as follows: (i) the bridging hydrogen is reasonably protonic in nature (typically belonging to a N–H or X–C–H group, where X is an electron-withdrawing substituent), facilitating an electrostatic component to the interaction; (ii) the metal atom involved is electron-rich with filled d orbitals suitably oriented to facilitate the 3c–4e interaction involving the hydrogen atom; (iii) the $^1H$ NMR chemical shift of the bridging hydrogen atom is *downfield* of TMS and shifted *downfield* relative to the signal for the free ligand of which the hydrogen atom in question is a part; (iv) intermolecular Z–H···M linkages have an approximately linear geometry. These characteristics are analogous to those of conventional hydrogen bonds but are unlike those of three-center-two-electron (3c–2e) interactions involving transition metals, such as agostic[2] C–H→M bridges. Most examples of apparent 3c–4e Z–H···M interactions previously cited[1] have involved square-planar $d^8$ metal centers. Here we

---

[1] Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, A. G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.

[2] (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

0276-7333/92/2311-2339$03.00/0 © 1992 American Chemical Society

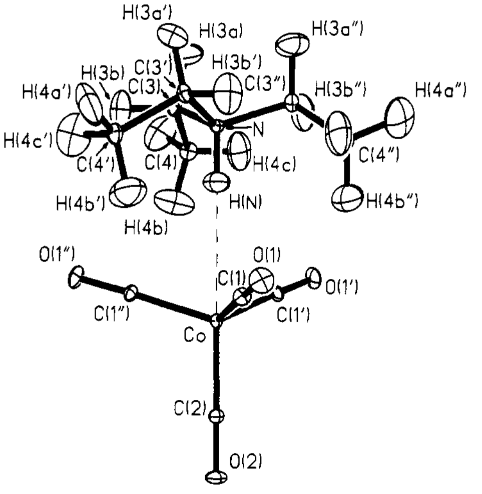

**Figure 1.** Molecular structure of $Et_3NH^+Co(CO)_4^-$, shown with 70% probability ellipsoids. Selected interatomic distances (Å): Co–C(1) = 1.777 (1), Co–C(2) = 1.781 (1), Co···H(N) = 2.613 (2), N–H(N) = 1.054 (1), C(1)–O(1) = 1.157 (1), C(2)–O(2) = 1.154 (1). Selected bond angles (deg): Co···H(N)–N = 180.00, C(1)–Co–C(1') = 112.32 (6), C(1)–Co–C(2) = 106.44 (7), C(1)–Co···H(N) = 73.56 (6), C(2)–Co···H(N) = 180.00, Co–C(1)–O(1) = 178.36 (9), Co–C(2)–O(2) = 180.00, C(3)–N–H(N) = 108.38 (6).

consider the nature of the interaction of the $Et_3NH^+$ cation with the anion $Co(CO)_4^-$, which contains a $d^{10}$ metal center. In particular, the role of the short N–H···Co contact, which provides the closest approach between the cation and anion moieties, is examined. Norton, Sweany, and co-workers have studied[3] the related issue of hydrogen bonding between the cobalt carbonyl hydride complex $HCo(CO)_4$ and various bases, including $R_3N$ (R = H, Me). They conclude, on the basis of IR and Raman studies of Co–H stretching frequencies, that although such hydrogen bonding is not present, a Co–H deformation mode may play a role in proton transfer to strong bases such as $Me_3N$. No comment is made about the nature of interactions between the resultant ammonium cation and the $Co(CO)_4^-$ anion.

$Et_3NH^+Co(CO)_4^-$ (1) was prepared using the method described by Calderazzo et al.,[4] and spectroscopic data are in accord with their observations. Most notably, the $^1H$ NMR signal for the ammonium hydrogen appears downfield of TMS, at $\delta$ 8.31 in $C_6D_6$. Pale green crystals suitable for single-crystal neutron diffraction were grown from toluene at 7 °C under an argon atmosphere. A crystal of volume ca. 15.6 mm$^3$ was selected for neutron data collection. Neutron intensity measurements were made at 15 K on a four-circle diffractometer, equipped with a closed-cycle helium refrigerator,[5] at the H6S beam line of the High Flux Beam Reactor, Brookhaven National Laboratory. Full-matrix least-squares refinement[6] of atomic positional and displacement parameters was conducted, using parameters obtained from the previous room-temperature X-ray diffraction study[4] as the starting refinement model. The resulting molecular structure and atomic displacement parameters are depicted in Figures 1 and 2, together with pertinent interatomic distances and angles.

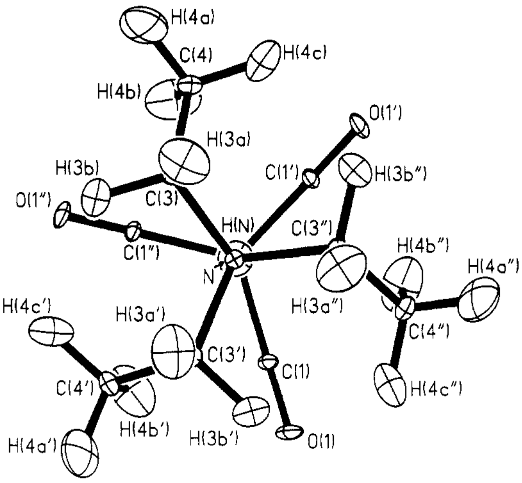

**Figure 2.** Molecular structure of $Et_3NH^+Co(CO)_4^-$, shown with 70% probability ellipsoids, viewed down the crystallographic and molecular $C_3$ axis.

Both the cation and anion have crystallographically imposed $C_3$ symmetry, as seen most readily in Figure 2. The $Co(CO)_4^-$ unit is distorted from the idealized $T_d$ to approximate $C_{3v}$ symmetry as a result of accommodating the anion–cation interactions. The N–H(N) bond of the cation lies along the crystallographic 3-fold axis directed toward the center of the triangular "face" of the anion bounded by symmetry-related oxygen atoms O(1), O(1'), and O(1''). As a result, the tetrahedron flattens with widening of the C(1)–Co–C(1') angle to 112.32 (6)°, as compared to 106.44 (7)° for C(1)–Co–C(2). However, the carbonyl ligands deviate very little from linearity (Co–C(1)–O(1) = 178.36 (9)° and Co–C(2)–O(2) = 180.00°). The anion exhibits Co–C distances typical of terminal carbonyls bonded to cobalt;[7] the C–O distances of 1.157 (1) and 1.154 (1) Å are ca. 0.01 Å longer than the mean value (1.145 Å) reported in the survey by Orpen et al.[7] This lengthening is perhaps to be anticipated, as cobalt is formally in oxidation state −1, which should give rise to substantial $\pi$-back-donation to the carbonyl ligands. A survey of data available for crystal structures[8] which contain the $Co(CO)_4^-$ anion shows the mean C–O distance for these anions to be 1.156 Å, consistent with those reported here (C(1)–O(1) = 1.157 (1), C(2)–O(2) = 1.154 (1) Å).

The geometry of the cation shows no unusual features other than the notably long N–H(N) distance of 1.054 (1) Å. This value is significantly greater than the mean distance 1.033 Å given by Allen et al.[9] from a survey of structures of quaternary nitrogen compounds determined by neutron diffraction. Fewer than 10% of the N–H distances listed in the Cambridge Structural Database (CSD, July 1991 version) exceed 1.05 Å. The only distance

---

(3) Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357.

(4) Calderazzo, F.; Fachinetti, G.; Marchetti, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1981**, 181.

(5) (a) Air Products and Chemicals, Inc., DISPLEX Model CS-202, calibrated with respect to the magnetic phase transition of $FeF_2$ at 78.4 K.[5b] (b) Hutchings, M. T.; Schulhof, M. P.; Guggenheim, H. J. *Phys. Rev.* **1972**, *B5*, 154.

(6) Crystal data: $[Et_3NH][Co(CO)_4]$, $C_{10}H_{16}NO_4Co$, $M_r$ = 273.17, cubic, space group $Pa\bar{3}$ (No. 205), $a$ = 13.567 (7) Å, $V$ = 2497 (4) Å$^3$, $Z$ = 8, $D_c$ = 1.453 g cm$^{-3}$, $\lambda$ = 1.1586 (1) Å (Ge(220) monochromated neutrons), $\mu_N$ = 2.34 cm$^{-1}$. A total of 3238 recorded intensities ($(\sin\theta)/\lambda \le 0.71$ Å$^{-1}$) yielded 1234 independent data, for which final $R(F^2)$ = 0.055, $R_w(F^2)$ = 0.062, and $S(F^2)$ = 1.274 after absorption and extinction corrections. Anisotropic displacement parameters were refined for all atoms. A more detailed summary of data collection and structure refinement (Table S1) is given in the supplementary material.

(7) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(8) (a) Data were obtained from the Cambridge Structural Database[8b] for 16 structures, refcodes CUGWOQ, DOXFUR, FOGNIY, FUBYOQ, FUBYUW, FUBZAD, FUBZEH01, FUBZIL01, FUBZOR01, GAJHOO, KARSAX, KARSEB, MSIPCO, SALCNA, SAWPOV, TPCPCO20. Data for $Et_3NH^+Co(CO)_4^-$ and $Me_3NH^+Co(CO)_4^-$ were excluded. (b) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331.

(9) Allen, F. H.; Kennard, O.; Watson, D. G.; Orpen, A. G.; Brammer, L.; Taylor, R., *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

to exceed 1.10 Å is one which occurs in the strong symmetrical N···H···N hydrogen bond of hydrogen diquinuclidin-3-one perchlorate.[10] Lengthening of the covalent bond of the donor group is recognized as one characteristic effect of hydrogen bonding;[11] the stronger the hydrogen bond, the greater the effect on N–H bond lengths, as amply illustrated by the survey of the CSD for N–H hydrogen-bonding interactions. Thus, the unusually long N–H distance observed in 1 is consistent with the presence of a localized 3c–4e hydrogen-bond-like N–H···Co interaction. That the proton is localized along the N···Co vector by bonding is indicated by the probability ellipsoids (Figures 1 and 2) computed from the $U_{ij}$ displacement parameters obtained in this study: the 70% probability surface of H(N) is markedly smaller than those of the methylene and methyl hydrogens, and the components transverse to the N···Co vector show no notable effects due to static or dynamic disorder. Thus, this study offers a clear characterization of the N–H···Co interaction as linear, a conclusion which could not be drawn from the previous X-ray diffraction study.

As noted above, the closest cation–anion contact is the Co···H(N) separation of 2.613 (2) Å,[12] which, by our best estimates, is less than the sum of the van der Waals radii of H and Co.[13] It suggests the effect of a substantial attractive force between anion and cation. Consistent with this assertion is the fact that the cation and anion adopt a conformation in which the three ethyl groups of the cation and three carbonyl groups of the anion are staggered with respect to each other (Figure 2), thus minimizing steric repulsions. The nature of the attractive force between cation and anion is of particular interest, especially the question of whether this is simply an interaction between two ions or whether, as we have suggested in a previous paper,[1] this may be in part due to a 3c–4e hydrogen-bond-like N–H···Co interaction.

The experimental structural data, therefore, show that the $Co(CO)_4^-$ anion is distorted from an idealized $T_d$ geometry to $C_{3v}$ due to the cation–anion interaction; the Co···H(N) separation is quite short, and the N–H(N) distance is unusually long, consistent with the presence of a hydrogen-bond-like N–H···Co interaction. However, it should be noted that one could also postulate that the elongation of the N–H(N) bond is due to a simple electrostatic attraction of the overall negative charge of the anion, i.e., involving no orbital component to the interaction. We hope to address this question by future theoretical studies.[15]

Of some relevance to our discussion of the interaction between the $Et_3NH^+$ and $Co(CO)_4^-$ moieties are EHMO calculations[16] by Cecconi et al. on the model complex $\{[NH_4][Ni(CO)(PH_3)_3]\}^+$, using a $C_{3v}$ geometry comparable with that in 1. The authors discuss an orbital analysis of the Ni···H···N interaction for a range of H positions and see strong mixing of the filled Ni $d_{z^2}$ orbital and the N–H $\sigma$ and $\sigma^*$ orbitals, clearly providing a mechanism for an energetically favorable 3c–4e interaction. However, they note that for long Ni···H separations, comparable to that seen in 1, the net Ni···H overlap population is very small. Similarly, EHMO calculations on 1 using standard parameters[17] suggest little net Co···H bonding arises from orbital overlap. However, the relative importance of orbital interaction and electrostatic effects cannot be assessed from non-self-consistent EHMO calculations, as used by Cecconi et al. and ourselves. The method is not capable of reflecting the changes in donor–acceptor behavior that arise from charge separation unless the parameters are adjusted accordingly. We would obviously expect the donor ability of an electron-rich metal center to be enhanced by a partial negative charge and the acceptor capabilities of the N–H $\sigma^*$ orbital to be strengthened by the cationic nature of the nitrogen center, and we suspect that any orbital interaction effects will have been underestimated by these calculations. Thus, in order to investigate the anion–cation interaction in 1 in greater detail, taking into account the electrostatic effects, we are currently conducting experimental electron density and ab initio theoretical studies of the title compound.[15]

**Acknowledgment.** We thank the University of Missouri—St. Louis Improved Research Quality Fund and the HFBR Faculty-Student Support Program, Brookhaven National Laboratory, for support, Mr. Thomas Langdon for technical assistance, and Dr. Kathleen Barkigia for helpful discussions. This work was conducted in part at Brookhaven National Laboratory under contract DE-AC02-76CH0016 with the U.S. Department of Energy, supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

**Supplementary Material Available:** A detailed summary of data collection and structure refinement (Table S1), together with interatomic distances and angles (Table S2) and atomic positional and anisotropic displacement parameters (Table S3) (4 pages). Ordering information is given on any current masthead page.

OM920141C

---

(10) N···H = 1.317 Å: Roziere, J.; Belin, C.; Lehmann, M. S. *J. Chem. Soc., Chem. Commun.* **1982**, 388.

(11) Newton, M. D. *Trans. Am. Crystallogr. Assoc.* **1986**, *22*, 1 and references therein.

(12) This is over 0.2 Å less than that determined in the previous X-ray diffraction study[4] (Co···H = 2.85 (7) Å); the discrepancy reflects the systematic inaccuracy of hydrogen atom positions determined by conventional X-ray diffraction methods.

(13) The van der Waals radius of H is ca. 1.20 Å,[14] which means that, unless the corresponding value for Co is as low as ca. 1.41 Å, the Co···H separation in 1 must be less than the sum of H and Co van der Waals radii. Definitive data on the van der Waals radius of Co are not available, though we presume that its value would be ca. 1.8 Å, and certainly greater than 1.41 Å. Values given by Bondi[14] for Cu and Ni are 1.4 and 1.63 Å, respectively. It is assumed that the van der Waals radius for Co would be greater than these values, particularly in 1, where the Co atom is formally in the −1 oxidation state.

(14) Bondi, A. J. *J. Chem. Phys.* **1964**, *68*, 441.

(15) Brammer, L.; Sherwood, P. Work in progress.

(16) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

(17) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3179. (c) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2872. (d) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.