

Preparation and Crystal and Molecular Structure of Two Trialkylamine Adducts of $\text{HCo}(\text{CO})_4$ showing a Preferential $\text{NR}_3\text{H}^+ \cdots [(\text{OC})_3\text{Co}(\text{CO})]^-$ Interaction

By FAUSTO CALDERAZZO, GIUSEPPE FACHINETTI, and FABIO MARCHETTI

(Istituto Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy)

and PIER FRANCESCO ZANAZZI

(Istituto di Mineralogia, University of Perugia, Piazza Università, 06100 Perugia, Italy)

Summary $\text{HCo}(\text{CO})_4$ and trialkylamines in hydrocarbon solution form 1:1 adducts, which may be described as $\text{NR}_3\text{H}^+ \cdots [\text{Co}(\text{CO})_4]^-$ ion pairs; *X*-ray crystal structure determinations show that in the solid state the interacting unit $\text{NEt}_3\text{H}^+ \cdots [\text{Co}(\text{CO})_4]^-$ has an $\text{N} \cdots \text{Co}$ contact of 3.72 Å with the nitrogen hydrogen on the threefold axis of rotation interacting with the C_3Co part of the $[\text{Co}(\text{CO})_4]^-$ anion, in a sort of 'elongated' $\text{HCo}(\text{CO})_4$ structure, and a substantially similar molecular structure was found for $\text{NMe}_3\text{H}^+ \cdots [\text{Co}(\text{CO})_4]^-$, the $\text{N} \cdots \text{Co}$ contact being reduced to 3.39 Å.

Ion pairs are of considerable interest in discussions of chemical reactivity.¹ As far as anionic metal carbonyl complexes are concerned, their alkali-metal ion pairs have been studied extensively and evidence for the existence of contact- and solvent-separated ion pairs has been obtained

by i.r. spectroscopy.² Also solid-state studies have revealed the existence of contact interactions involving the spherical alkali-metal cations.³

We have found what we believe to be the first direct evidence of the interaction between a co-ordinated proton and a carbonyl metallate anion, the result being of interest *per se* and also for its relevance to hydrogen transfer from metal hydrides to organic substrates.⁴ $\text{HCo}(\text{CO})_4$ is known to undergo heterolytic Co-H bond fission in the presence of nitrogen bases to give the corresponding ammonium⁵ and pyridinium⁶ derivatives of the tetracarbonylcobaltate anion, $[\text{Co}(\text{CO})_4]^-$, but no information about the intimate nature of these compounds is available in the literature. It is also well known that $\text{HCo}(\text{CO})_4$ behaves as a strong acid in water.⁷

By direct combination of the amine and metal carbonyl components under argon in hexane at -78°C , the adducts

$\text{NR}_3\cdot\text{HCo}(\text{CO})_4$ ($\text{R} = \text{Me}$ or Et), were formed within the time of mixing and isolated as colourless solids, sensitive to air and moisture, and slightly soluble in hydrocarbons. Recrystallization from toluene ($\text{R} = \text{Et}$) and from toluene-hexane ($\text{R} = \text{Me}$) afforded crystals suitable for X -ray studies. *Crystal data* for $\text{NEt}_3\cdot\text{HCo}(\text{CO})_4$: $M = 273.17$, cubic, space group $Pa\bar{3}$, $a = 13.881(2)$ Å, $U = 2674.6$ Å³, $D_c = 1.355$ g cm⁻³, $Z = 8$, Mo- K_α radiation ($\lambda = 0.71069$ Å) with a graphite monochromator, $\mu(\text{Mo-}K_\alpha) = 12.6$ cm⁻¹. Reflections which were equivalent by threefold symmetry were measured and averaged and 322 unique reflections having $I \geq 2.5\sigma(I)$ were considered observed. The structure was solved by direct methods and by difference Fourier techniques and refined to a conventional R value of 0.032.⁸ The positions of the hydrogen atoms, located from a difference Fourier synthesis, were included.†

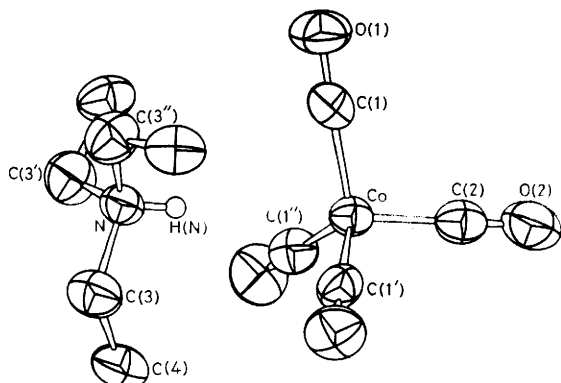


FIGURE 1. ORTEP view of the structure of $\text{NEt}_3\cdot\text{HCo}(\text{CO})_4$. Hydrogen atoms bonded to carbon are omitted. Relevant bond distances, contacts, and angles (e.s.d.s in parentheses) are: Co-C(1), 1.761(5); Co-C(2), 1.774(12); C(1)-O(1), 1.149(7); C(2)-O(2), 1.129(11); C(3)-N, 1.516(6); N-H(N), 0.87(7); Co...N, 3.720(6); Co...H, 2.85(7); C(1)...H, 2.91(8) Å; \angle C(3)-N-C(3'), 110.6(4); C(1)-Co-C(1'), 112.8(3); C(1)-Co-C(2), 105.9(3)°.

The molecular structure of $\text{NEt}_3\cdot\text{HCo}(\text{CO})_4$ (Figure 1) consists of discrete pair units formed by the NEt_3H^+ and $[\text{Co}(\text{CO})_4]^-$ ions, with the nitrogen hydrogen located on the threefold axis of symmetry of the pair, coincident with the threefold crystallographic axis.

The molecular structure of the corresponding methyl derivative was solved similarly. *Crystal data* for $\text{NMe}_3\cdot\text{HCo}(\text{CO})_4$: $M = 231.09$, orthorhombic, space group $Pbca$, $a = 26.491(4)$, $b = 13.659(3)$, $c = 12.540(3)$ Å, $U = 4537.5$ Å³, $D_c = 1.308$ g cm⁻³, $Z = 16$, $\mu(\text{Mo-}K_\alpha) = 14.7$ cm⁻¹. Owing to the poor quality of the crystal only 497 of the independent reflections had $I \geq 3\sigma(I)$ and were considered observed. The structure was refined to a conventional R value of 0.077.† The molecular structure of $\text{NMe}_3\cdot\text{HCo}(\text{CO})_4$ (Figure 2) is similar to that of the ethyl derivative, the main differences being that the $[\text{Co}(\text{CO})_4]^-$ moiety deviates slightly from C_{3v} symmetry and the N...Co contact is shortened to 3.39 Å, as a result of the smaller steric hindrance of the methyl groups.

In view of the fact that in the ethyl derivative the nitrogen hydrogen is effectively equidistant from the cobalt atom and from the three carbon atoms of the CO groups related by the threefold axis, the bonding within each $\text{NEt}_3\text{H}^+ \cdots [\text{Co}(\text{CO})_4]^-$ unit may be regarded as arising from the interaction of the amine-co-ordinated proton with the CoC_3 moiety of the $[\text{Co}(\text{CO})_4]^-$ anion, presumably the site of larger electron density. The data for the less accurately determined structure of the methyl derivative support this conclusion. This is similar to the Na^+ interaction^{3a} with the C-Fe-C system of the $[\text{Fe}(\text{CO})_4]^{2-}$ anion.

$\text{HCo}(\text{CO})_4$ itself⁹ is a C_{3v} molecule, the interaction with the triethylamine therefore causing the following two main modifications: elongation of the Co-H bond along the C_3 axis from 1.56 to 2.85 Å and increase of the $C_{ax}\text{-Co-C}_{eq}$ angle [C(1)-Co-C(2) in the present notation] from 99.7 to 105.9°. The average $C_{ax}\text{-Fe-C}_{eq}$ angle in the isoelectronic¹⁰ $[\text{HFe}(\text{CO})_4]^-$ anion is 99.1°.

That the interactions within the $\text{NR}_3\text{H}^+ \cdots [\text{Co}(\text{CO})_4]^-$ unit persist in hydrocarbon solution with formation of the corresponding contact ion pairs is strongly supported by the following evidence: the adducts showed three carbonyl stretching bands in toluene ($\text{R} = \text{Et}$: 2015w, 1931s, and 1895vs cm⁻¹; $\text{R} = \text{Me}$: 2015w, 1934s and 1899vs cm⁻¹) consistent with the C_{3v} symmetry ($2A_1 + E$) of the $[\text{Co}(\text{CO})_4]^-$ anion; the more soluble trimethylamine adduct had a freezing point depression in benzene showing no dissociation in solution (M : Found 251; Calcd, 231.1); and, finally, the two adducts had ¹H n.m.r. absorptions

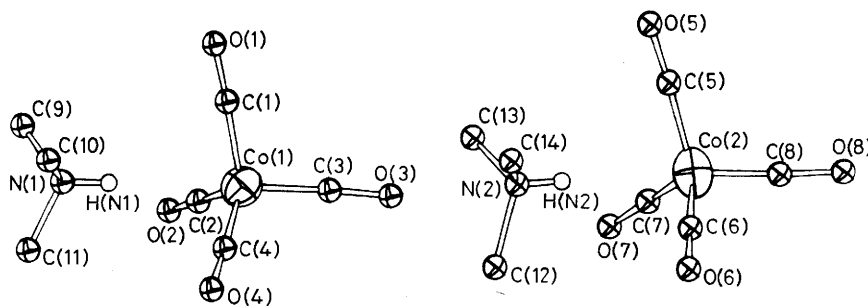


FIGURE 2. ORTEP view of the structure of $\text{NMe}_3\cdot\text{HCo}(\text{CO})_4$. Average bond distances, contacts, and angles are: Co-C, 1.69; C-O, 1.18; C-N, 1.51; Co...N, 3.39(6) Å; \angle C-N-C, 109°; angles at Co(1) with C(3) and: C(1), 106(3); C(2), 103(2); C(4), 110(3)°; angles at Co(2) with C(8) and: C(5), 108(2); C(6), 103(3); C(7), 106(3)°. H(N1) and H(N2) were placed at calculated positions.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor tables are available from the British Library as supplementary publication No. SUP 23010. For details of obtaining this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, Index issue.

consistent with the protonic character of the unique nitrogen-bonded hydrogen (C_6D_6 , shift from Me_3Si in p.p.m.: $R = Et$, -8.1 ; $R = Me$, -9.1). The i.r. spectrum of $HCo(CO)_4$ in the carbonyl stretching region (toluene as solvent: $2100w$, $2040s$, and $2010vs\text{ cm}^{-1}$) is similar to those of the tertiary amine adducts, in both number of bands and their relative intensities. The wavenumber shift may

be attributed to heterolytic Co-H bond splitting induced by the base.

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