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SYNTHESIS AND REACTIVITY OF HALONITROSYLDICARBONYLCOBALT ANIONS.
NITROSATION OF BENZYL HALIDES

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SUMMARY

Halonitrosyldicarbonylcobalt anions $[CoNO(CO)_2X]^-$ have been obtained from the reaction between nitrosyltricarbonylcobalt and halide ions. Infrared spectra are reported and correlated with those of other nitrosyltricarbonylcobalt derivatives.

Formation of benzaldoximes in the reaction of halonitrosyldicarbonylcobalt anions with benzyl halides is also reported.

We have recently reported the formation of halotricarbonylnickel anions[1] $[Ni(CO)_3X]^-$ in the reaction of tetracarbonylnickel with halide ions. Continuing our investigation on complexes with ligands able to transfer negative charge to metal, we have extended this reaction to the nitrosyltricarbonylcobalt, isoelectronic and isostructural with tetracarbonylnickel. In this series of pseudo-tetracarbonylnickel complexes reactions with halide ions have been reported for dinitrosyldicarbonyliron[2], but nitrosyltricarbonylcobalt[2] seemed to be unreactive. We have now found that the reaction of nitrosyltricarbonylcobalt with halide ions occurs easily in solvents such as acetone, diglyme and dimethoxyethane.

The reaction is analogous to that described for tetracarbonylnickel[1] or dinitrosyldicarbonyliron[2]:

$$CoNO(CO)_3 + MX \rightleftharpoons M[CoNO(CO)_2X] + CO$$
$$X = Cl^-, Br^-, I^-;\ M = \text{ammonium or metallic cation}$$

The halonitrosyldicarbonylcobalt anions obtained are more stable than the halotricarbonylnickel anions. In the case of cobalt, it was in fact possible to isolate the bromo and iodo derivatives, but the chloro derivative was very unstable, and was characterized only in solution. The reaction gives only the monosubstituted products even when a large excess of halide ion is present.

The IR frequencies in the CO and NO stretching region are listed in Table 1 for some of the complexes obtained; these spectra are in agreement with the postulated C_{3v} structure[3]. Previous infrared spectroscopic studies[4] have shown that the CO and NO stretching frequencies are sensitive indicators of the amount of charge back-donated into their antibonding orbitals. The greater the back-donation, the lower the observed CO and NO frequencies. Variation of the back-donation ability of a metal

TABLE 1

CO AND NO STRETCHING FREQUENCIES OF SOME TRICARBONYLNITROSYLCOBALT DERIVATIVES

Compound	ν(CO) (cm⁻¹)		ν(NO) (cm⁻¹)	Solvent
$N(C_4H_9)_4[CoNO(CO)_2I]$	2011	1943	1712	Diglyme
$N(C_4H_9)_4[CoNO(CO)_2Br]$	2013	1940	1707	Diglyme
$N(C_7H_{15})_4[CoNO(CO)_2Cl]$	2012	1938	1703	Diglyme
$K[CoNO(CO)_2CN]$	2019	1952	1726	Diglyme
$Co(NO)(CO)_3$	2104	2035	1800	Diglyme
$Co(NO)(CO)_3$	2110	2042	1802	Toluene[4]
$Co(NO)(CO)_2P(C_6H_5)_3$	2038	1981	1750	Toluene[4]
$Co(NO)(CO)_2P(n\text{-}C_4H_9)_3$	2032	1973	1744	Toluene[4]
$Co(NO)(CO)_2P(C_2H_5)_3$	2032	1969	1747	Toluene[4]

can be easily obtained by replacing one of the ligands in the complex. It has thus been possible to arrange different ligands in a "spectrochemical series"[5] according to the order of their decreasing ability to withdraw charge from the metal or, inversely, to their increasing ability to transfer charge to the metal. One of the complexes used to construct this series was nitrosyltricarbonylcobalt. According to this series the halide ligand, as we have already shown in the case of tetracarbonylnickel[1], causes a charge transfer to the metal, as indicated by the decrease of the CO and NO frequencies, even greater than that brought about by trialkylphosphines (see Table 1). This can be attributed to the fact that the halide ligand is derived from a charged species. Support for this observation can be found in the fact that the cyano group causes a charge transfer similar to that of halide ions although it has antibonding orbitals suitable for back-donation.

In our previous paper[1] we reported that the halotricarbonylnickel anions are good catalysts for the carbonylation of benzyl halides at atmospheric pressure. Consequently, we have examined the reaction of benzyl halides with halonitrosyldicarbonylcobalt anions, and found that an unexpected reaction occurs[6], leading to *syn*- and *anti*-aldoximes according to the following equations:

$$C_6H_5CH_2\text{-}Cl + M[CoNO(CO)_2X] \rightarrow C_6H_5CH_2\text{-}NO + [Co(CO)_2X] + MCl$$

$$C_6H_5CH_2\text{-}NO \rightarrow C_6H_5CH{=}NOH$$

The halonitrosyldicarbonylcobalt anion is transformed into an unknown species, here denoted as $[Co(CO)_2X]$, which is apparently unstable, since CoX_2 is present at the end of the reaction. The reaction is general for benzyl halides; thus the corresponding aldoximes have been obtained from benzyl chloride and bromide, and from *p*-nitro-, *o*-chloro- and *p*-phenylbenzyl chloride. The yields based on the cobalt complex are 30–50%. Among the secondary products phenylacetic acids (5–10%) have been isolated. The reaction is not affected when the carbon monoxide pressure is raised to 5 atm.

An analogous reaction occurs, though with lower yield, when $K[CoNO(CO)_2CN]$ is used, but nitrosyltricarbonylcobalt is unreactive.

The mechanism has not been completely clarified. We think that the first step of the reaction [see eqn. (1)] involves an oxidative addition[7] of the benzyl halide to cobalt. The halide ligand makes this reaction easier by transferring negative charge to the metal[8]. Oxidative additions of complexes containing the nitrosyl group have been reported in the case of iridium[9] and rhodium[14]. A path involving prior dissociation of carbon monoxide to create the necessary vacant coordination site[10] does not seem to be involved, although they would be consistent with the observed second-order kinetics in the substitution reaction of nitrosyltricarbonylcobalt[4,11]:

$$\mathrm{CoNO(CO)_3 + L \rightarrow CoNO(CO)_2L + CO}$$

$$\mathrm{Rate} = K_1 \cdot [\mathrm{CoNO(CO)_3}] + K_2[\mathrm{CoNO(CO)_3}] \cdot [\mathrm{L}]$$

As in the case of the substitution reaction the following explanation could be proposed for the reactions we have described.

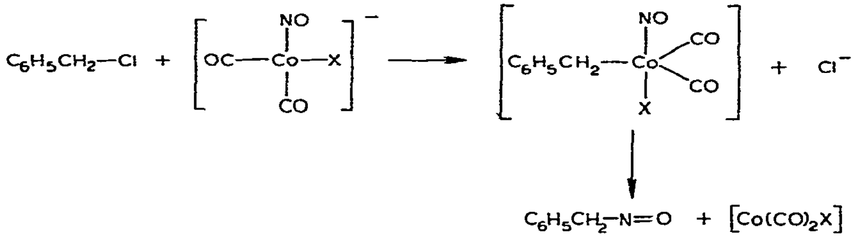
The Co–NO bond can be represented by the following two structures:

$$\overset{-}{\mathrm{Co}}{=}\overset{+}{\mathrm{N}}{=}\mathrm{O} \leftrightarrow \mathrm{Co{-}N{=}O}$$

$$\text{(I) } (d^{10}) \qquad \text{(II) } (d^{8})$$

In structure (II) the cobalt complex has the vacant coordination site necessary for the oxidative addition, and the presence of the charge transfer ligand probably increases the contribution of this structure.

The second step of the reaction probably involves migration of the benzyl group, bonded to cobalt, to the nitrogen of the nitrosyl group, with formation of the aldoxime.



(1)

The extension of the nitrosation reaction to other systems is being examined.

EXPERIMENTAL

All reactions were carried out under nitrogen and all solvents were distilled under nitrogen. IR spectra were measured on Perkin–Elmer 125 spectrophotometer, melting points on Kofler hot stage microscope and conductivities on Conductivity Bridge LKB type 3216 B.

$\mathrm{Co(NO)(CO)_3}$ was prepared from $\mathrm{Co_2(CO)_8}$ and NO[12]; $\mathrm{K[CoNO(CO)_2CN]}$ from $\mathrm{CoNO(CO)_3}$ and KCN[13].

Preparation of $\mathrm{Bu_4N[CoNO(CO)_2I]}$

A suspension of $\mathrm{Bu_4NI}$ (2.98 g) in diglyme (50 ml) and $\mathrm{CoNO(CO)_3}$ (1.4 g) was stirred at 50–60° for 2 h. After CO evolution was complete, a stream of nitrogen was passed through the solution to remove the unreacted $\mathrm{CoNO(CO)_3}$. Petroleum ether was then added to the cooled and filtered solution. The precipitate obtained was filtered, washed with petroleum ether and dissolved in the minimum quantity of ethyl acetate. The solution was filtered and the solvent removed at reduced pressure.

A deep violet solid was obtained (yield 70%), m.p. 73–75°, $\Lambda = 132\ \Omega^{-1} \cdot \text{cm}^{-2}$ in acetone. (Found: C, 42.5; H, 7.24; Co, 11.1; I, 24.71; N, 5.27. $C_{18}H_{36}CoIN_2O_3$ calcd.: C, 42.03; H, 7.05; Co, 11.46; I, 24.67; N, 5.45%.)

Preparation of $Bu_4N[Co(CO)_2Br]$

A suspension of Bu_4NBr (2.46 g) in dimethoxyethane (5 ml) and $CoNO(CO)_3$ (1.32 g) was stirred at 50–60° for 3 h. After CO evolution was complete, a stream of nitrogen was passed through the solution. The cooled solution was filtered and solvent was removed at reduced pressure. The oil thus obtained was dissolved in dimethoxyethane and filtered, then the solvent was removed at reduced pressure. On cooling, a deep violet solid was obtained, m.p. 42–43°. (Found: C, 47.0; H, 7.98; Br, 17.58; Co, 12.24; N, 6.12. $C_{18}H_{36}BrCoN_2O_3$ calcd.: C, 46.26; H, 7.76; Br, 17.1; Co, 12.6; N, 5.99%.)

Reaction between benzyl halides and $Bu_4N[CoNO(CO)_2X]$ ($X = Br^-, I^-$)

A solution of $Bu_4N[CoNO(CO)_2X]$ in acetone was stirred with the stoichiometric quantity of the benzyl halide at 40–50° for 4 h. To the acetone was then added a 1 *N* sulfuric acid solution and the organic products were extracted with diethyl ether. The ether solution was dried over Na_2SO_4 and then evaporated. The residue mainly consisted of benzaldoximes, which were purified by cromatography on silica gel. The benzaldoximes obtained were identical with authentic specimens.

Thus starting from *p*-phenylbenzyl chloride (356 mg) and $Bu_4N[CoNO(CO)_2I]$ (900 mg) in 20 ml of acetone *syn*- and *anti*-*p*-phenylbenzaldoximes (170 mg) were obtained after purification.

Among the secondary products *p*-phenylphenylacetic acid (30 mg) was identified. Some *p*-phenylbenzyl chloride (30 mg) was also recovered.

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