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Preliminary communication

STRONG INTERACTIONS BETWEEN $[Co(CO)_4]^-$ AND Li^+ OR Na^+ IN DIETHYL ETHER; THE SYSTEM $LiBr/Co_2(CO)_8$/DIETHYL ETHER

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Summary

Infrared spectra show $[Co(CO)_4]^-$ to be strongly distorted by Na^+ and especially Li^+ in dry diethyl ether. Lithium bromide with dicobalt octacarbonyl in dry diethyl ether gives $Li^+[Co_3(CO)_{10}]^-$ and $Li^+[Co(CO)_4]^-$.

The distortions of $[Co(CO)_4]^-$ [1a] and $[Mn(CO)_5]^-$ [1b] from idealised symmetry due to ion pairing with Na^+ have been studied spectroscopically in tetrahydrofuran (THF) and in more powerfully donating solvents. In addition, solvent and cation effects on metal carbonyl anion reactivity are matters of current interest to both organic [2] and inorganic [3] preparative chemists, and such effects on the system $Co_2(CO)_8/[Co_3(CO)_{10}]^-/[Co(CO)_4]^-$ have recently been shown to be considerable [3].

We now report our findings for systems containing $[Co(CO)_4]^-$ in diethyl ether.

(1) $[Co(CO)_4]^-$ and Na^+. Water-containing NaOH pellets (ground down) disproportionated $Co_2(CO)_8$ in diethyl ether, under carbon monoxide, to give a pink precipitate (presumably cobalt(II) carbonate [4]) and a solution A, absorbing at 1890s and 1830(sh) cm^{-1}, as expected for weakly distorted, near tetrahedral $[Co(CO)_4]^-$ (Fig. 1a), together with a small amount of $[Co_3(CO)_{10}]^-$, detectable by bands at 2005m and 1995w cm^{-1} and a characteristic red-purple colour in solution. Adding sodium wire, under argon, to form the dried solution B, caused a change in the 1890 cm^{-1} band with the development of a high frequency shoulder, and a separately, clearly resolved band at 1825 cm^{-1} (Fig. 1b). We attribute these changes to tighter ion pairing between cation and anion once the ligand water has been removed.

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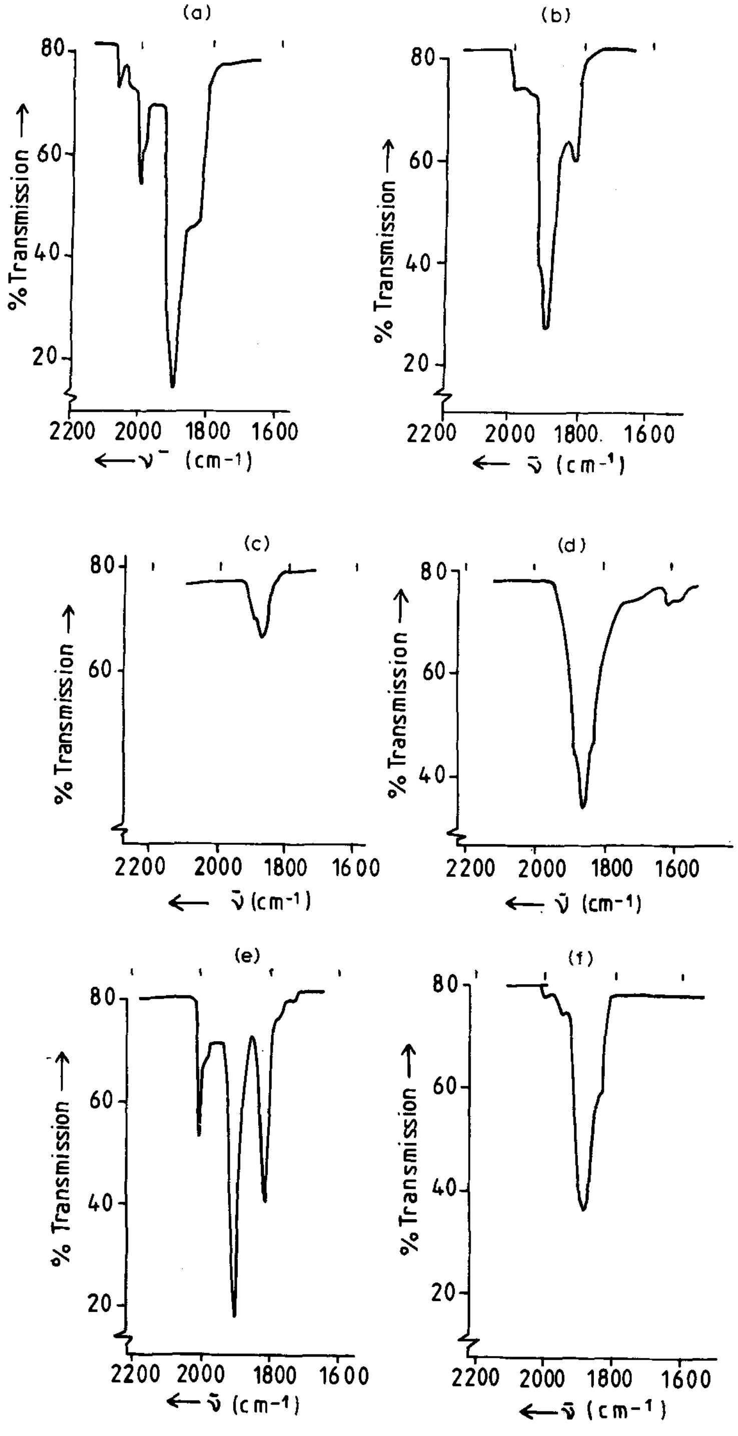
Spectra resembling 1b were also obtained in the system $Co_2(CO)_8$/sodium amalgam/diethyl ether (together with bands for $Hg[Co(CO)_4]_2$ and



$\{Hg[Co(CO)_4]_3\}^-$ [5]) and, after some hours, in the system $Co_2(CO)_8$/sodium wire/wet diethyl ether.

(2) $[Co(CO)_4]^-$ and $n\text{-}Bu_4N^+$. Addition of tetrabutylammonium iodide $[(n\text{-}C_4H_9)_4N]I$ to solution B caused a change in the spectrum to that of Figure 1c, with a single band, due to tetrahedral $[Co(CO)_4]^-$, at 1875 cm^{-1} and a weak band at 1890 cm^{-1}, due to the Na^+-distorted anion. These both rapidly disappear as a pale green solid is precipitated from solution. An infrared spectrum of a Nujol mull of this solid showed it to be $[(n\text{-}C_4H_9)_4N]^+$-$[Co(CO)_4]^-$ (Fig. 1d). It is not unknown for large counterions to precipitate $[Co(CO)_4]^-$ from ether solutions; we find that $[(n\text{-}C_4H_9)_4P]^+$ and $[(C_6H_5)_4P]^+$ have the same effect. These ionic solids are soluble if a more polar solvent, e.g. THF, is used.

(3) $[Co(CO)_4]^-$ and Li^+. Addition of anhydrous lithium iodide to solution B led to precipitation of a white solid, presumably sodium iodide, and a new spectrum (Fig. 1e, Table 1), which we ascribe to $Li^+[Co(CO)_4]^-$ contaminated with some $Li^+[Co_3(CO)_{10}]^-$. There is no free $[Co(CO)_4]^-$ at this stage; the more marked shift and splitting (compared with Fig. 1b) show more electron withdrawal and greater distortion by the smaller cation. The form of 1e is more consistent with a structure $[(OC)_3CoCO\cdots Li]$ than with doubly bridged or Li—Co bonded forms. Removal of free Li^+ from the solution by *N,N,N′,N′*-tetramethylethylenediamine (TMED) gave rise to the spectrum

TABLE 1

EFFECT OF CATION ON INFRARED CARBONYL STRETCHING FREQUENCIES, $\bar{\nu}(CO)$

Sanple[a]	$\bar{\nu}(CO)$ (cm^{-1}) (Species present)	Figure
Solution A	2005m, 1995m $[NaCo_3(CO)_{10}]$; 1890s, 1830(sh) $[NaCo(CO)_4]$	1a
Solution B	1920(sh), 1890s, 1830m [dried $NaCo(CO)_4$]	1b
$[(n\text{-}C_4H_9)_4N][Co(CO)_4]$	1890w $[NaCo(CO)_4]$: 1875m $[\{(n\text{-}C_4H_9)_4N\}\{Co(CO)_4\}]$	1c
Solid $[(n\text{-}C_4H_9)_4N][Co(CO)_4]$[b]	1885(sh), 1865s, 1840(sh) $[\{(n\text{-}C_4H_9)_4N\}\{Co(CO)_4\}]$	1d
$Li^+[Co(CO)_4]^-$	2005m, 1995w $[LiCo_3(CO)_{10}]$; 1905s, 1815m $[LiCo(CO)_4]$	1e
TMED complex	1885s, 1860(sh), 1835(sh) [TMED complex of $Co(CO)_4^-$]	1f
Solution C	2070m, 2040m $[Co_2(CO)_8]$; 2005s, 1995s, 1970m $[Co_3(CO)_{10}^-]$; 1910s $[Co(CO)_4^-]$; 1860m $[Co_2(CO)_8$ and $Co_3(CO)_{10}^-]$; 1820m $[Co(CO)_4^-]$	2

[a] Solutions in diethyl ether, corrected for solvent background, 0.1 mm cell, sapphire windows. [b] Nujol mull, NaCl plates.

Fig. 1. (a) Solution A: NaOH treated $Co_2(CO)_8$ in wet diethyl ether. Note $[Co_3(CO)_{10}]^-$ bands and modified $[Co(CO)_4^-]$ band.

(b) Solution B: as A, after drying and reduction with sodium wire.

(c) As B, after addition of $(n\text{-}C_4H_9)_4NI$. Note presence of both free and modified $[Co(CO)_4]^-$.

(d) Solid $[(n\text{-}C_4H_9)_4N][Co(CO)_4]$, Nujol mull.

(e) $LiCo(CO)_4$ ($+LiCo_3(CO)_{10}$) from addition of LiI to solution B.

(f) As e, after addition of TMED. Note disappearance (base induced disproportionation) of $[Co_3(CO)_{10}]^-$, and near-normal $[Co(CO)_4]^-$ band.

shown in Fig. 1f. As expected, this closely resembled the spectrum in 1b, but with the main anion band at slightly lower frequency. Unexpectedly, however, this reaction is not immediate and a gradual change over a few hours is observed.

TMED was also added to solution B (after removal of sodium wire) and similar results and spectra were obtained.

(4) $Co_2(CO)_8$/LiBr/diethyl ether system. While addition of solid lithium bromide to $Co_2(CO)_8$ in dried THF led to full disproportionation within ten minutes (eq. 1) [6], the systems solid lithium bromide or lithium iodide/ $Co_2(CO)_8$ in diethyl ether under either nitrogen or carbon monoxide give deep red-purple solutions C whose spectra (Fig. 2, Table 1) for some time defied our analysis.

$$\tfrac{3}{2}Co_2(CO)_8 + 2LiX \rightarrow 2[Co(CO)_4]^- + CoX_2 + 2\,Li^+ \qquad (1)$$

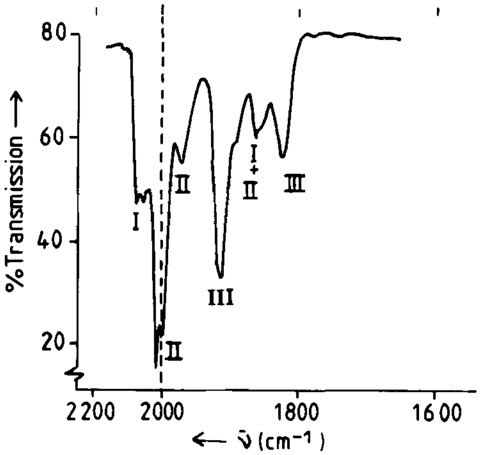


Fig. 2. Solution C: $Co_2(CO)_8$ in diethyl ether treated with solid LiBr. I = $Co_2(CO)_8$, II = $LiCo_3(CO)_{10}$, III = $LiCo(CO)_4$.

Nonetheless solutions C function as a source of $[Co(CO)_4]^-$ giving, with allyl bromide, ($CH_2{=}CHCH_2Br$), ($(\eta^3\text{-}C_3H_5)Co(CO)_3$ (characterised by its infrared spectrum and those of its PPh_3 and $P(OPh)_3$ derivatives) and no other carbonyl containing species. It is clear with hindsight that Fig. 2 shows the spectrum of $Li^+[Co_3(CO)_{10}]^-$ superposed on that of $Li^+[Co(CO)_4]^-$. Removal of $[Co(CO)_4]^-$ by allyl bromide upsets the equilibrium [3] between $Li^+[Co_3(CO)_{10}]^-$ on the one hand and $Co_2(CO)_8$ (trace) together with $Li^+[Co(CO)_4]^-$ on the other:

$$Co_2(CO)_8 + Li^+[Co(CO)_4]^- \rightleftharpoons Li^+[Co_3(CO)_{10}]^- + 2CO \qquad (2)$$

(5) $Co_2(CO)_8$ + lithium wire. $Li^+[Co(CO)_4]^-$ in diethyl ether was also generated by the action of lithium wire on $Co_2(CO)_8$ in wet diethyl ether. This method is slow but reaction does occur to give $Li^+[Co_3(CO)_{10}]^-$ and $Li^+[Co(CO)_4]^-$. Addition of distilled, deoxygenated water gives rise to a rapid

reaction, with gas being evolved, presumably hydrogen. The rapid reaction is no doubt due to the formation of finely divided lithium hydroxide in situ. The infrared spectrum is that of the weakly perturbed anion $[Co(CO)_4]^-$, resembling Fig. 1a, which as the solution dries out (due to the action of lithium wire) changes to the spectrum of $Li^+[Co(CO)_4]^-$ (Fig. 1e).

We interpretate these changes as follows: in the wet solution the spectrum is of $[Co(CO)_4]^-$ (tetrahedral) with Li^+ being hydrated by water and thus unable to participate in tight ion pairing. As water is removed from the solution by lithium wire, the Li^+ indulges in tight ion pairing and so the spectrum of $Li^+[Co(CO)_4]^-$ is observed.

The experiment was repetaed using lithium hydroxide with $Co_2(CO)_8$ in diethyl ether, but there was no reaction, presumably because of the lattice stability of lithium hydroxide.

Since weakly donating solvents and small cations enhance the activity of weakly nucleophilic metal carbonyl anions [2b], the system $Co_2(CO)_8$/LiBr/diethyl ether, which effectively provides $Li^+[Co(CO)_4]^-$ without the difficult reduction of $Co_2(CO)_8$ in diethyl ether, should repay examination.

Infrared spectra were recorded on a PE 257 or 577 spectrophotometer, using sapphire cell windows to avoid the possibility [7] of adventitious halide induced reactions. Solutions were handled, in glassware baked out immediately before use, under dry carbon monoxide or nitrogen. Solid reactants and gases were purified and dried by standard procedures before use. Diethyl ether was dried over magnesium sulphate ($MgSO_4$), and for critical experiments further dried by distillation, from $MgSO_4$, under dry nitrogen.

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