

## SOME OBSERVATIONS ON THE SYSTEMS $\text{Co}_2(\text{CO})_8$ /SODIUM AMALGAM AND $\text{Hg}[\text{Co}(\text{CO})_4]_2$ /SODIUM AMALGAM, AND THE EFFECT OF ADDED $\text{LiBr}$

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(Received May 24th, 1982)

### Summary

$\text{Co}_2(\text{CO})_8$  and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  react with sodium amalgam and/or mercury in ethereal solvents to give a variety of products. On treatment with aqueous  $\text{M}(o\text{-phen})_3\text{Cl}_2$  ( $\text{M} = \text{Fe}, \text{Ni}$ ), the anions  $[\text{Co}(\text{CO})_4]^-$ ,  $[\text{Co}_3(\text{CO})_{10}]^-$ ,  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  and  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{Cl}\}^-$  could be isolated as their  $[\text{M}(o\text{-phen})_3]^{2+}$  salts. The effect of  $\text{LiBr}$  on the reacting systems was also investigated and the anion  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{Br}\}^-$  isolated.

### Introduction

Although the reaction of sodium amalgam with ethereal solutions of dimeric metal carbonyls is a standard preparation of metal carbonyl anions [1] some confusion still surrounds this possible route to the tetracarbonylcobaltate(−1)-ion,  $[\text{Co}(\text{CO})_4]^-$ . The reaction is said to fail in rigorously dried THF\* [2] but was quite recently reported as a route to  $[\text{Co}(\text{CO})_4]^-$  in ether [3]! In our own hands it has proved slow and erratic in both solvents. After our discovery that lithium bromide promotes the disproportionation of dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$ , in THF [4], it occurred to us to investigate its possible effect on the  $\text{Co}_2(\text{CO})_8$ /sodium amalgam reaction in this solvent. We extended the investigation to the effect of sodium amalgam, and of mercury itself, on the system  $\text{Co}_2(\text{CO})_8/\text{LiBr}$  in ether, in the hope of reducing its apparent complexity. (We have since shown [5] that this system contains  $\text{LiCo}(\text{CO})_4$  and  $\text{LiCo}_3(\text{CO})_{10}$  in solution, and that these both function as an effective and convenient source of the  $[\text{Co}(\text{CO})_4]^-$  nucleophile.) For completeness, we also investigated the reaction of bis(tetracarbonylcobaltato)mercury,  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , with sodium amalgam in ether, and re-investigated the reaction in THF.

\* In this paper THF = tetrahydrofuran, ether = diethyl ether.

The anion  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  was first recorded by Markó et al. [6] (erroneously formulated as  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\}^-$ ), and further investigated by Burlitch et al. [7] who reported it to show strong IR bands at 2035 and 1969  $\text{cm}^{-1}$ , very similar to the related absorptions of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  but shifted to lower frequencies. The anion was found to react with halides which displace  $[\text{Co}(\text{CO})_4]^-$  to give  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  with IR carbonyl absorptions at 2052 and 1983  $\text{cm}^{-1}$  [7] indicating that the  $\text{Co}(\text{CO})_4$  groups bear a fractional negative charge.

## Experimental

$\text{Co}_2(\text{CO})_8$  was used as supplied by Strem Chemicals Inc., without further purification.  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  was prepared as described in the literature [6]. Lithium halides were dried overnight in vacuo at 100°C. Gases (Air Products or B.O.C. carbon monoxide and "oxygen free" nitrogen) were dried with dried silica gel, concentrated  $\text{H}_2\text{SO}_4$  and phosphorus(V)oxide, before passing into the reaction vessel. Reactions were performed at room temperature in a 3-necked flask, with run-off, equipped with a mechanical stirring device for the mercury layer, as recommended by King [8]. THF was dried using sodium wire and benzophenone [9]; ether ("anhydrous") was dried over sodium. All apparatus was baked out at 120°C and solvents were distilled into the reaction vessel under nitrogen immediately before use.

IR spectra of solids were run on KBr discs (Perkin—Elmer 580 spectrometer). Solution IR spectra were obtained using Perkin—Elmer 337, 257 and 577 spectrometers and sealed, 0.1 mm pathlength cells with sapphire windows to prevent interference by halide.

All reactions were carried out under carbon monoxide unless stated otherwise.

### (a) $\text{Co}_2(\text{CO})_8$ and sodium amalgam in ether

Typically 1.21 g ( $3.54 \times 10^{-3}$  mol)  $\text{Co}_2(\text{CO})_8$  was added to 100 ml ether containing 150 g fresh sodium amalgam (1% sodium present). This gave an orange-brown solution over a few days.

### (b) $\text{Co}_2(\text{CO})_8$ and mercury in ether, followed by LiBr

0.514 g ( $1.50 \times 10^{-3}$  mol)  $\text{Co}_2(\text{CO})_8$  was placed with 70 g (0.35 mol) mercury in 70 ml ether, forming some  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . Addition of 0.17 g ( $1.93 \times 10^{-3}$  mol) LiBr 4 h later, resulted in a dark orangy-brown solution with formation of  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ , X =  $\text{Co}(\text{CO})_4$  or Br. ( $\nu(\text{CO})$  2060s, 2035s, 2010 shoulder, 1970—1950vs, broad.) If LiBr was added at an earlier stage in the reaction,  $\text{LiCo}(\text{CO})_4$  was also detected.

The mercury layer was run off and the anions were isolated as their iron(II) tris(*o*-phenanthroline) salts. Solutions were filtered under carbon monoxide into 70 ml aqueous 0.025 mol  $\text{dm}^{-3}$   $\text{Fe}(\textit{o}\text{-phen})_3\text{Cl}_2$  solution and stirred for 20 min. The mixture so formed was decanted into a separating funnel and the resulting oily layer extracted and treated with 20 ml ethanol to give a red solid and a red solution. The solid proved to be the simple salt  $[\text{Fe}(\textit{o}\text{-phen})_3][\text{Co}(\text{CO})_4]_2$ . Another solid was isolated from the sides of the separating funnel; this contained a mixture of the anions  $[\text{Co}(\text{CO})_4]^-$  and  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ .

*(c) Co<sub>2</sub>(CO)<sub>8</sub>, LiBr and mercury in THF*

2.09 g ( $6.12 \times 10^{-3}$  mol) Co<sub>2</sub>(CO)<sub>8</sub> and 155.15 g (0.77 mol) mercury were added to 50 ml THF. 0.70 g ( $8.05 \times 10^{-3}$  mol) LiBr was added after 30 min and the reaction was left for 3 h. Treatment with aqueous Fe(*o*-phen)<sub>3</sub>Cl<sub>2</sub> yielded a red solution and a dark solid. The solution on standing separated to give a red oil. This was dissolved in 20 ml ethanol then 100 ml water was added to precipitate the product. A mixture of {Hg[Co(CO)<sub>4</sub>]<sub>2</sub>X}<sup>-</sup>, X = Cl and/or Br and Co(CO)<sub>4</sub>, resulted. If LiBr was added at the same time as Co<sub>2</sub>(CO)<sub>8</sub> and mercury, {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> was the major anion in the product with some {Hg[Co(CO)<sub>4</sub>]<sub>2</sub>X}<sup>-</sup>, X = Br and/or Cl, present. A similar experiment using nickel in place of iron led to the anions [Co(CO)<sub>4</sub>]<sup>-</sup>, {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> and {Hg[Co(CO)<sub>4</sub>]<sub>2</sub>X}<sup>-</sup>, X = Br and/or Cl, all being present, as well as Hg[Co(CO)<sub>4</sub>]<sub>2</sub>.

*(d) Hg[Co(CO)<sub>4</sub>]<sub>2</sub> and sodium amalgam in ethereal solvents*

Typically 1.98 g ( $3.65 \times 10^{-3}$  mol) freshly prepared Hg[Co(CO)<sub>4</sub>]<sub>2</sub> was added to 50 ml solvent, under nitrogen, and 6 g sodium amalgam poured in. The solution was stirred for 3 h and then filtered under nitrogen, into 70 ml aqueous M(*o*-phen)<sub>3</sub>Cl<sub>2</sub>, M = Fe or Ni. THF solutions were treated as described in sections (b) and (c) above but for ether solutions the {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> salt precipitated from the aqueous solution without further work being necessary.

*(e) Hg[Co(CO)<sub>4</sub>]<sub>2</sub> and allyl bromide in THF*

To 50 ml carbon monoxide saturated THF 0.814 g ( $1.50 \times 10^{-3}$  mol) Hg[Co(CO)<sub>4</sub>]<sub>2</sub> was added, while stirring, followed by 170 μl ( $1.96 \times 10^{-3}$  mol) allyl bromide. The green-yellow solution showed no change over the next 5 days (expanded scale of IR spectrum is necessary; the IR spectrum of independently prepared ( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Co(CO)<sub>3</sub> is fortuitously very similar to that of Hg[Co(CO)<sub>4</sub>]<sub>2</sub>.)

**Results**

The investigation of the Co<sub>2</sub>(CO)<sub>8</sub>/mercury/LiBr/ether system was originally undertaken in the hope of intercepting intermediates of the Co<sub>2</sub>(CO)<sub>8</sub>/LiBr/ether system which at that time was not understood. (Since then enlightenment has dawned, see ref. 5.) Anomalies in the results led to the study of Hg[Co(CO)<sub>4</sub>]<sub>2</sub> itself with sodium amalgam.

*(a) Co<sub>2</sub>(CO)<sub>8</sub> and sodium amalgam in ether*

Our attention was first drawn to the reaction of Co<sub>2</sub>(CO)<sub>8</sub> with sodium amalgam in ether while attempting to reduce the cobalt compound to [Co(CO)<sub>4</sub>]<sup>-</sup>. Under carbon monoxide a complicated mixture of [Co<sub>3</sub>(CO)<sub>10</sub>]<sup>-</sup>, [Co(CO)<sub>4</sub>]<sup>-</sup>, {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> and an unidentified species was obtained (see Fig. 1(a), (b) and (c)). The anions were identified by comparison to literature values [5,7]. This mixture was reasonably stable with respect to time, the only change noted being in the relative intensities of the different species. A plausible reaction sequence is outlined in Scheme 1. The broad, very strong signals at 1900 and 1830 cm<sup>-1</sup> are reminiscent of the [Co(CO)<sub>4</sub>]<sup>-</sup> signal and its side band when the anion is perturbed by Na<sup>+</sup> in dry ether [5]. Addition of a few drops of water at

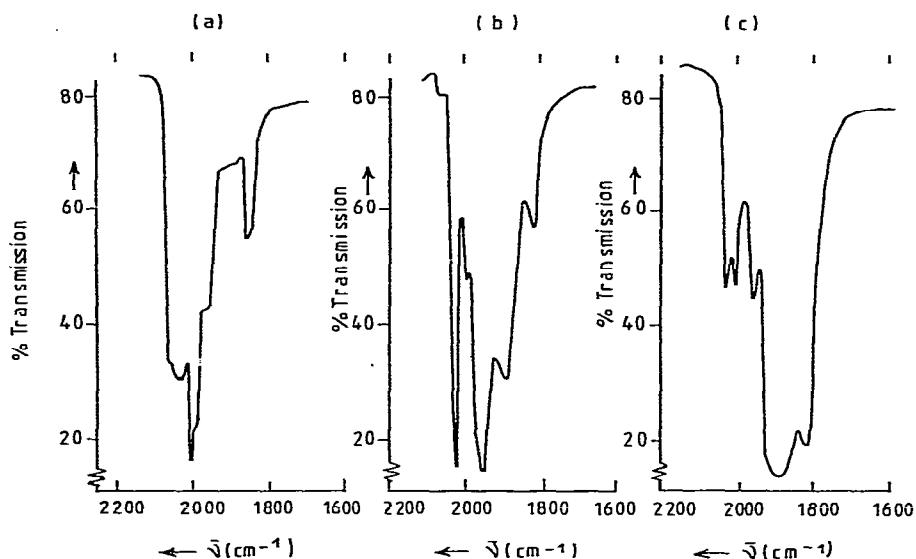
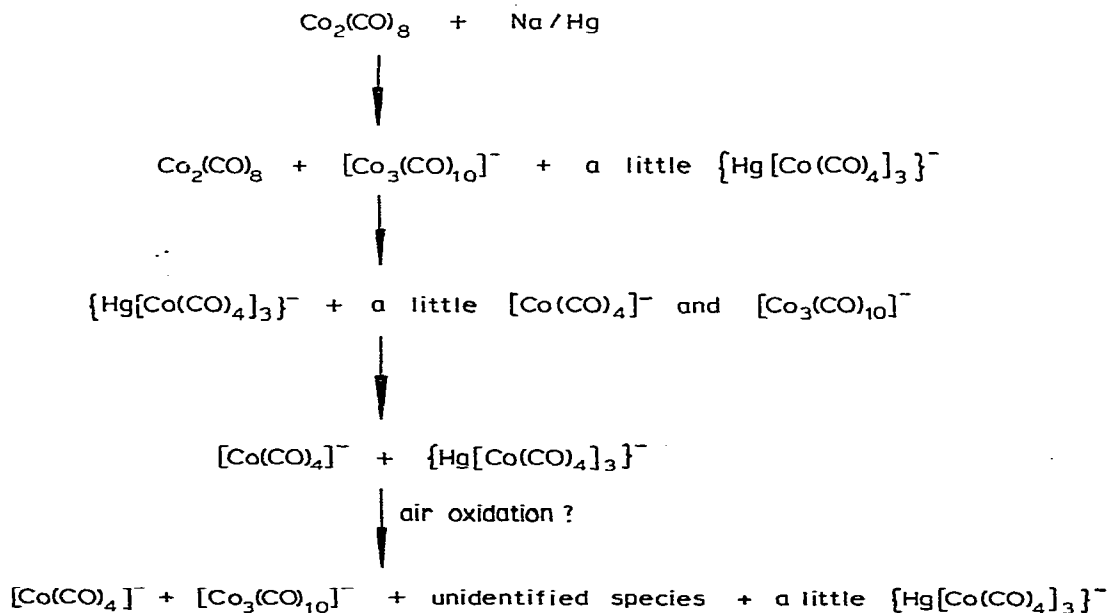


Fig. 1.  $\text{Co}_2(\text{CO})_8$  + sodium amalgam in ether (a) after 3 h; (b) after 6½ h and (c) after 30 h.

this stage led to the expected IR spectrum of "free"  $[\text{Co}(\text{CO})_4]^-$  ions. In wet ether only  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{Co}_3(\text{CO})_{10}]^-$  are present at the intermediate stage.

*(b)  $\text{Co}_2(\text{CO})_8$ , mercury and LiBr in ether*

To verify that reaction was due to the sodium part of the amalgam, mercury was added to  $\text{Co}_2(\text{CO})_8$  in ether and only a mixture of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and



SCHEME 1. Possible reaction sequence for  $\text{Co}_2(\text{CO})_8$  and sodium amalgam in ether.

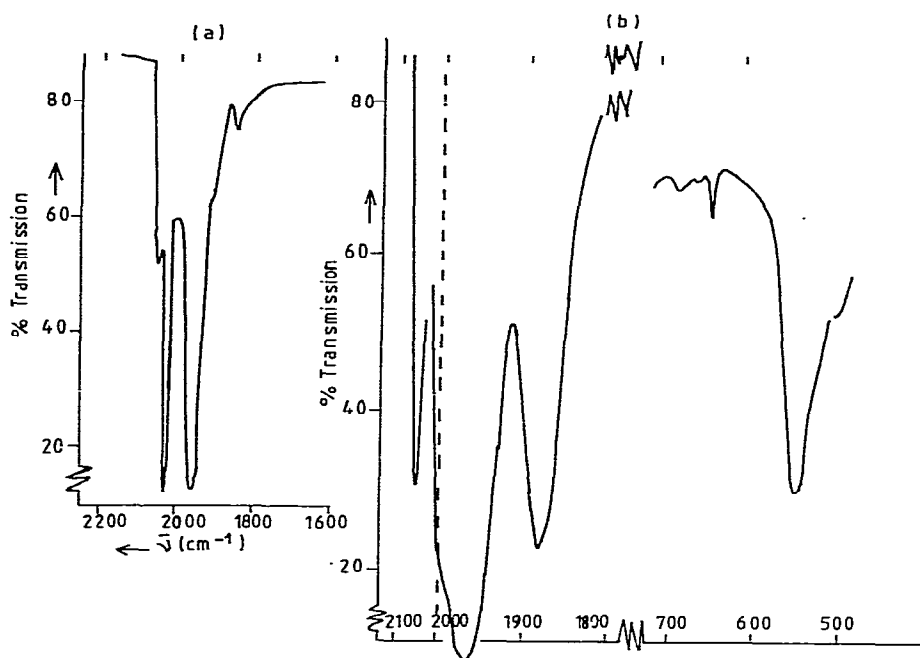


Fig. 2. (a)  $\text{Co}_2(\text{CO})_8$  + mercury in ether 10 min after LiBr added; (b)  $\text{Co}_2(\text{CO})_8$  + mercury + LiBr in THF, solid isolated, mixture of anions  $[\text{Co}(\text{CO})_4]^-$  and  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ).

$\text{Co}_2(\text{CO})_8$  resulted after 5 h. Adding LiBr at this stage resulted in formation of an orange solution and an IR spectrum (Fig. 2(a)) which was provisionally assigned to  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  although the possibility of  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{Br}\}^-$  cannot be ruled out.

Adding LiBr before the mercury had interacted with  $\text{Co}_2(\text{CO})_8$  to any noticeable degree led to formation of  $[\text{Co}_3(\text{CO})_{10}]^-$  and  $[\text{Co}(\text{CO})_4]^-$  as well as some mercury-cobalt species. The only anion isolated, as the  $[\text{Fe}(\text{o-phen})_3]^{2+}$  salt, was  $[\text{Co}(\text{CO})_4]^-$ , along with some impure  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ .

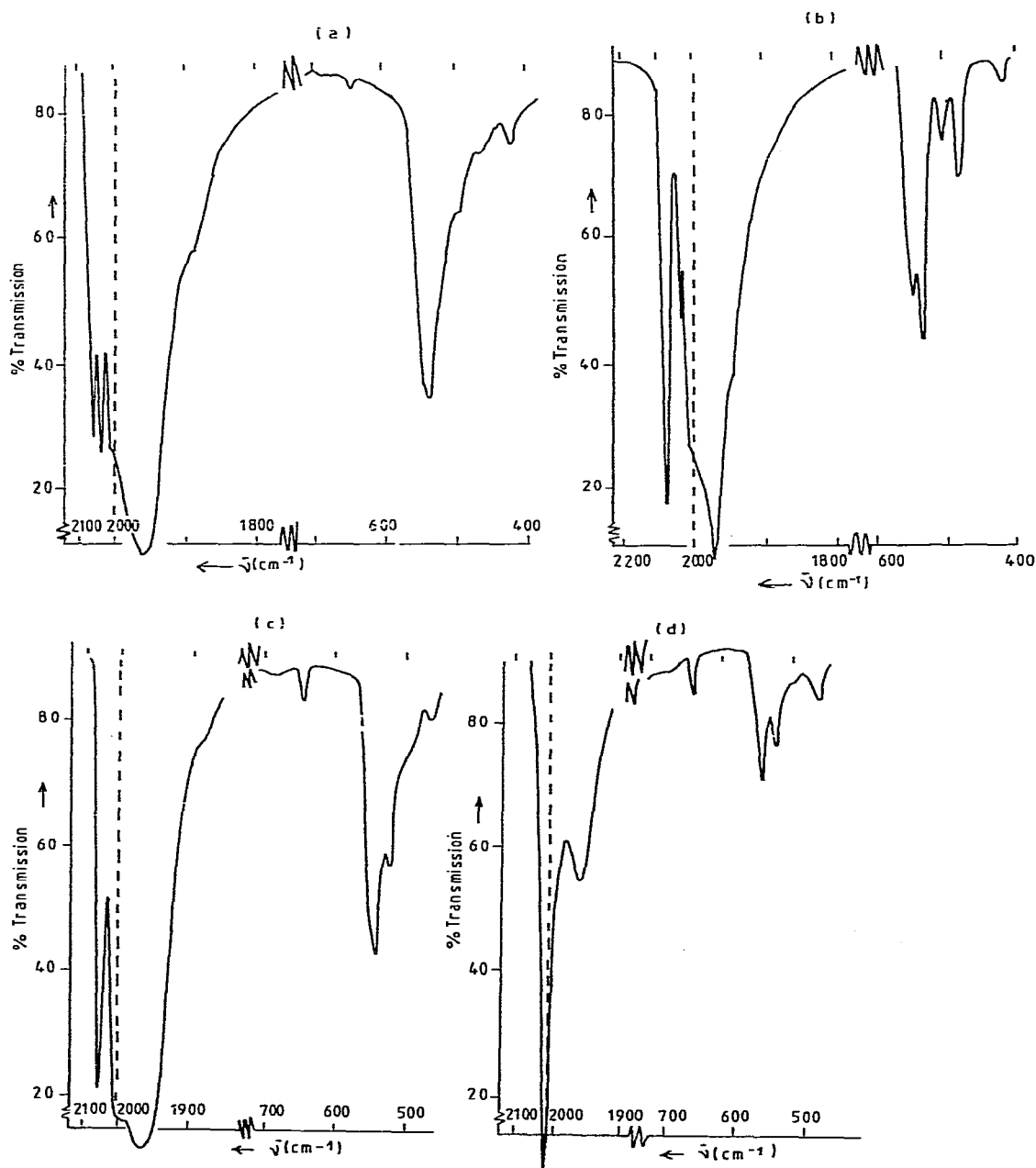
#### (c) $\text{Co}_2(\text{CO})_8$ , mercury and LiBr in THF

When repeated in THF the mixture allowed us to isolate  $[\text{Co}(\text{CO})_4]^-$  and  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ,  $\text{X} = \text{Cl}$  and  $\text{Br}$ , as the  $[\text{Fe}(\text{o-phen})_3]^{2+}$  salts (see Fig. 2(b)). If the amount of mercury present and the rate of stirring are both increased, the  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  salt is the major product isolated with a little  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  present. Using  $[\text{Ni}(\text{o-phen})_3]^{2+}$  instead of the iron analogue gave a mixture of  $[\text{Co}(\text{CO})_4]^-$ ,  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{Co}(\text{CO})_4$ , and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  at various stages of the work-up.

#### (d) $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and sodium amalgam in ethereal solvents

To check the above observations, and in some instances to try and interpret the results, the work of Markó et al. [6] was repeated and extended. The IR spectrum of the solid isolated, when THF was the solvent, is shown in Fig. 3(a). By comparison with earlier work [6,7] the signals at 2040 and 1965  $\text{cm}^{-1}$  are of the anion  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ . Burlitch tentatively assigned the signal at 2068

$\text{cm}^{-1}$  in his work to  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ; in the present work it was found that the higher frequency signal was at  $2060 \text{ cm}^{-1}$  and did not correspond closely to the solid IR spectrum of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  (Fig. 3(b)) and there were further differences in the  $\nu(\text{MC})-\delta(\text{MC})$  region (see Fig. 3). Rather this has been cautiously assigned to a separate species,  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  where  $\text{X} = \text{Cl}$ . Presumably this is formed by the reaction of aqueous  $\text{Cl}^-$  with  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$



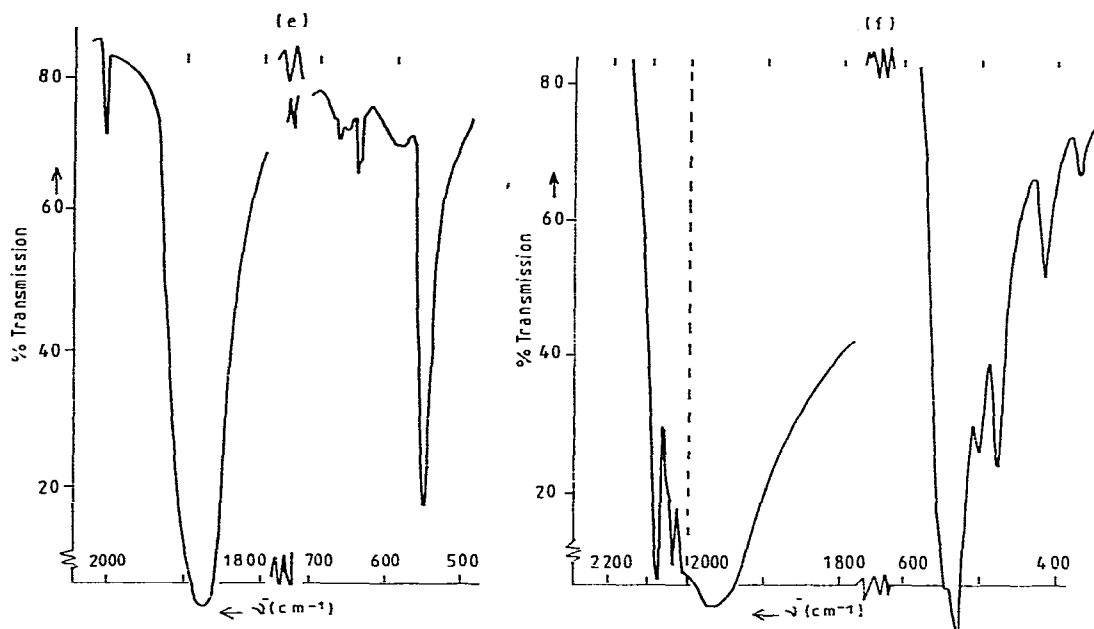


Fig. 3. (a)  $\text{Hg}[\text{Co}(\text{CO})_4]_2 + \text{Na}/\text{Hg}$  in THF, solid isolated, mixture of  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  anions ( $\text{X} = \text{Co}(\text{CO})_4, \text{Cl}$ ); (b)  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , solid; (c)  $\text{Hg}[\text{Co}(\text{CO})_4]_2 + \text{Na}/\text{Hg}$  in THF, solid isolated during work-up,  $[\text{Fe}(\text{o-phen})_3] \{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{Cl}\}_2$ ; (d)  $\text{Hg}[\text{Co}(\text{CO})_4]_2 + \text{Na}/\text{Hg}$  in THF, solid isolated from aqueous phase  $[\text{Fe}(\text{o-phen})_3][\text{Co}_3(\text{CO})_{10}]_2$ ; (e)  $\text{Hg}[\text{Co}(\text{CO})_4]_2 + \text{Na}/\text{Hg}$  in THF, solid product  $[\text{Ni}(\text{o-phen})_3]^-[\text{Co}(\text{CO})_4]_2$ ; (f)  $\text{Hg}[\text{Co}(\text{CO})_4]_2 + \text{Na}/\text{Hg}$  in ether, solid isolated, mixture of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and  $[\text{Ni}(\text{o-phen})_3] \{\text{Hg}[\text{Co}(\text{CO})_4]_3\}_2$ .

or indeed with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . This complex, and that of the Br species, has been reported [10] and the solution IR spectra of these complexes in THF are:

$\text{X} = \text{Cl}$ , 2075w, 2051s, 1979vs, 1896vw  $\text{cm}^{-1}$ ;  $\text{X} = \text{Br}$ , 2071w, 2048s, 1979vs, 1896vw  $\text{cm}^{-1}$ .

The signal at 1896  $\text{cm}^{-1}$  is due to  $[\text{Co}(\text{CO})_4]^-$ , that around 2070  $\text{cm}^{-1}$  is too weak to be observed in this example and the signal at 1979  $\text{cm}^{-1}$  appears as a shoulder, at slightly higher frequency, of the main  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  signal. With hindsight, it would have been preferable to use  $[\text{M}(\text{o-phen})_3]^{2+}$  salts containing non-coordinating counteranions; indeed it is ironic that heeding Burlitch's advice in avoiding halide containing cell materials [11], we should (again following the same author) have added halides during work-up.

During the work-up of the solution, a solid was deposited on the sides of the reaction flask which apparently consisted of the  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{Cl}\}^-$  salt, (Fig. 3(c)). The aqueous layer also surrendered a solid compound whose IR spectrum was identical to that of  $[\text{Co}_3(\text{CO})_{10}]^-$  (Fig. 3(d)). When repeated similar results were obtained with only the ratio of the mercury containing anions being slightly altered. Using aqueous  $\text{Ni}(\text{o-phen})_3\text{Cl}_2$  again gave both mercury containing anionic species along with the simple salt  $[\text{Ni}(\text{o-phen})_3][\text{Co}(\text{CO})_4]_2$  (Fig. 3(e)).

A change of solvent was now introduced (ether) giving a similar reddish solid whose IR spectrum indicated the presence of both  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  and unreacted  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  (Fig. 3(f)).

*(e) Hg[Co(CO)<sub>4</sub>]<sub>2</sub> and allyl bromide in THF*

To establish (i)  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  did not react with all halides (cf. the experiment with  $\text{LiBr}$ ) and (ii) to mop up any free  $[\text{Co}(\text{CO})_4]^-$ , the reaction of allyl bromide ( $\text{CH}_3\text{CH}=\text{CHBr}$ ) and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in THF was studied. This showed no change after 5 days of stirring; proof of this being furnished by running expanded IR spectra of the reaction solution and of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in THF.

**Discussion**

Reaction of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  itself with lithium halides in THF has been reported to give  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  anions ( $\text{X} = \text{halide}$ ). These anionic species can be precipitated from solution by large organic cations. Solutions of these species tend to be unstable [10]. In our hands products detected depended upon the solvent used and the means of isolation, proving that  $\text{Co}_2(\text{CO})_8$  and mercury containing compounds do not react to give just one or two simple products. The mixture of products obtained is subject to the exact point at which the reaction was halted, or in the experiments involving  $\text{LiBr}$ , when this reagent was added. The products of reaction are tabulated in Table 1 and the IR frequencies of the various species in Table 2.

In ether it is not surprising that large cations, such as  $[\text{M}(\text{o-phen})_3]^{2+}$  ( $\text{M} = \text{Ni}$  or  $\text{Fe}$ ), should cause solid salts of  $[\text{Co}(\text{CO})_4]^-$  to come out of solution. The small solvation energy of such salts makes them insoluble in solution, as has previously been illustrated [5,12].

Elsewhere a mixture of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  and the species assigned to  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  ( $\text{X} = \text{Cl}$  or  $\text{Cl}$  and  $\text{Br}$ ) was found, with these

TABLE 1  
PRODUCTS OF REACTIONS

Reactants	Solvent	Metal cation <sup>a</sup>	Products <sup>b</sup>
$\text{Co}_2(\text{CO})_8, \text{Hg}, \text{LiBr}$	THF	Fe	$\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ( $\text{X} = \text{Co}(\text{CO})_4, \text{Cl}, \text{Br}$ ); $[\text{Co}(\text{CO})_4]^-$ ; unknown species;
$\text{Co}_2(\text{CO})_8, \text{Hg}, \text{LiBr}$	THF	Ni	$\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ( $\text{X} = \text{Co}(\text{CO})_4, \text{Cl}, \text{Br}$ ); $[\text{Co}(\text{CO})_4]^-$ ; $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ;
$\text{Co}_2(\text{CO})_8, \text{Hg}, \text{LiBr}$	ether	— <sup>c</sup>	$\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ( $\text{X} = \text{Co}(\text{CO})_4$ or $\text{Cl}$ and $\text{Br}$ );
$\text{Co}_2(\text{CO})_8, \text{Hg}, \text{LiBr}$	ether	Fe	$\text{Hg}[\text{Co}(\text{CO})_4]_2$ ; $[\text{Co}(\text{CO})_4]^-$ ; traces of $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ ?
$\text{Co}_2(\text{CO})_8, \text{Na}/\text{Hg}$	ether	— <sup>c</sup>	$\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ ; $[\text{Co}(\text{CO})_4]^-$ ; $[\text{Co}_3(\text{CO})_{10}]^-$ ; unidentified species;
$\text{Co}_2(\text{CO})_8, \text{Na}/\text{Hg}, \text{LiBr}$	ether	— <sup>c</sup>	$[\text{Co}(\text{CO})_4]^-$ ; $[\text{Co}_3(\text{CO})_{10}]^-$ ;
$\text{Hg}[\text{Co}(\text{CO})_4]_2, \text{Na}/\text{Hg}$	THF	Fe	$\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ( $\text{X} = \text{Co}(\text{CO})_4$ and $\text{Cl}$ ); $[\text{Co}_3(\text{CO})_{10}]^-$ ;
$\text{Hg}[\text{Co}(\text{CO})_4]_2, \text{Na}/\text{Hg}$	THF	Ni	$\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ ( $\text{X} = \text{Co}(\text{CO})_4$ and $\text{Cl}$ ); $[\text{Co}(\text{CO})_4]^-$ ;
$\text{Hg}[\text{Co}(\text{CO})_4], \text{Na}/\text{Hg}$	ether	Ni	$\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ ;

<sup>a</sup> Metal cation in  $\text{M}(\text{o-phen})_3^{2+}$ . <sup>b</sup> Solid products after work-up unless stated otherwise. <sup>c</sup> Solution mixture.



TABLE 2  
IR FREQUENCIES OF PRODUCTS (SOLID FORM)

Compound <sup>a</sup>	IR absorptions <sup>b</sup> (cm <sup>-1</sup> )
[Co(CO) <sub>4</sub> ] <sup>-</sup>	2005w, 1880vs
[Co <sub>3</sub> (CO) <sub>10</sub> ] <sup>-</sup>	2015vs, 1960m
Hg[Co(CO) <sub>4</sub> ] <sub>2</sub>	2075s, 2040m, 2010 shoulder, 1970vs
{Hg[Co(CO) <sub>4</sub> ] <sub>3</sub> } <sup>-</sup>	2035s, 1970—1950vs, broad
{Hg[Co(CO) <sub>4</sub> ] <sub>2</sub> X} <sup>-</sup> (X = Cl, Br)	2060s, 2010 shoulder, 1970vs

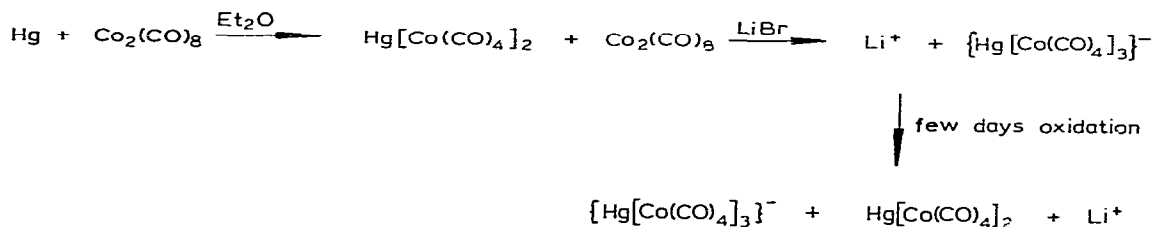
<sup>a</sup> Cation of the anionic compounds is Fe(*o*-phen)<sub>3</sub><sup>2+</sup>. <sup>b</sup> In the carbonyl region 2200—1800 cm<sup>-1</sup>.

anionic species being isolated on separate occasions as the only complex present (from THF solutions). {Hg[Co(CO)<sub>4</sub>]<sub>2</sub>X}<sup>-</sup> was only isolated in reactions using THF as the solvent. Ether gave a more complicated system; apart from [Co(CO)<sub>4</sub>]<sup>-</sup> coming out of solution, there was never one species only in any product isolated. Because these species are closely related, no attempt was made to separate them.

The other interesting solid isolated was [Fe(*o*-phen)<sub>3</sub>][Co<sub>3</sub>(CO)<sub>10</sub>]<sub>2</sub>, from the aqueous layer of the work-up of a THF reaction solution. Since it was not in evidence at earlier stages of the reaction it is presumed that air oxidation of [Co(CO)<sub>4</sub>]<sup>-</sup>, which is soluble in water, has occurred and the large cation present has stabilised [Co<sub>3</sub>(CO)<sub>10</sub>]<sup>-</sup> by precipitation. In ether itself any [Co(CO)<sub>4</sub>]<sup>-</sup> present crashes out of solution upon addition of Fe(*o*-phen)<sub>3</sub>Cl<sub>2</sub> but in THF it is dispersed between both phases and so salts of the anion or its derivative(s) are obtained from the aqueous phase. Using aqueous Ni(*o*-phen)<sub>3</sub>Cl<sub>2</sub> instead of the iron compound appears to favour [Co(CO)<sub>4</sub>]<sup>-</sup> being present in the aqueous phase.

For the reaction of Co<sub>2</sub>(CO)<sub>8</sub> and mercury in ether, a simple reaction sequence has been constructed and is shown in Scheme 2.

The presence of {Hg[Co(CO)<sub>4</sub>]<sub>2</sub>X}<sup>-</sup> was noted in THF solutions with the appearance of an unexplained signal at 2060 cm<sup>-1</sup>. This coincided with a shoulder, around 2005 cm<sup>-1</sup>, on the very intense broad signal of {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> at 1950—1970 cm<sup>-1</sup>. Although the literature values are not in perfect agreement [10], it would seem reasonable that a species intermediate between Hg[Co(CO)<sub>4</sub>]<sub>2</sub> and {Hg[Co(CO)<sub>4</sub>]<sub>3</sub>}<sup>-</sup> is the cause of this extra signal at 2060 cm<sup>-1</sup>, which happens to be intermediate between the 2070 and 2040 cm<sup>-1</sup>

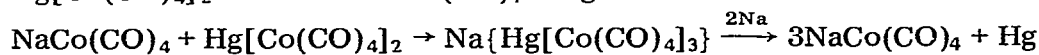
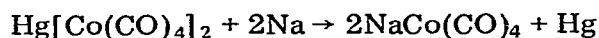


SCHEME 2. Possible reaction sequence for Co<sub>2</sub>(CO)<sub>8</sub> and mercury in ether.

signals of these two respective species; hence our assignment to  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$ . A  $[\text{Co}(\text{CO})_4]^-$  group of  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  has been replaced by a halide, either  $\text{Cl}^-$  from  $\text{Fe}(o\text{-phen})_3\text{Cl}_2$ , or  $\text{Br}^-$  from  $\text{LiBr}$  when this is present. The halogen is more electron withdrawing than the  $\text{Co}(\text{CO})_4$  group and so will perpetrate a shift to higher wavenumber with respect to  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$ .

For the simple reaction of sodium amalgam with  $\text{Co}_2(\text{CO})_8$  in ether the IR spectra were not very conclusive, because of the initial high concentration of  $\text{Co}_2(\text{CO})_8$  giving rise to too intense absorptions. By comparing the spectra with similar experiments discussed elsewhere [5] it was obvious that the same type of species in solution were being observed viz. when  $[\text{Co}(\text{CO})_4]^-$  is dominating the spectrum in a very dry solution it is strongly perturbed as shown by the pronounced shoulder (virtually a separate signal in its own right) of the main signal.

From these results it can be seen that  $[\text{Co}(\text{CO})_4]^-$  can be displaced, to some extent, from  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  by  $\text{X}^-$  ( $\text{X} =$  halide), especially during work-ups of THF solutions. In ether, formation of  $[\text{Co}_3(\text{CO})_{10}]^-$  instead of  $[\text{Co}(\text{CO})_4]^-$  is highly likely [5]; this may function as a source of  $[\text{Co}(\text{CO})_4]^-$ . In view of Fachinetti's results, the formation, in the presence of excess unreacted  $\text{Co}_2(\text{CO})_8$ , of  $[\text{Co}_3(\text{CO})_{10}]^-$  rather than  $[\text{Co}(\text{CO})_4]^-$  is not surprising [13]. The subsequent formation of  $\{\text{Na}^+[\text{Co}(\text{CO})_4]^- \}$  indicated that water is not essential to the reaction of  $\text{Co}_2(\text{CO})_8$  and sodium amalgam in ether. It is, however, quite possible that adventitious sodium hydroxide [14], rather than sodium amalgam itself, is the effective reagent. The  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  species formed may originate either from reduction of  $\text{Hg}[\text{Co}(\text{CO})_4]_2^*$  or from the known reaction [16] of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with  $[\text{Co}(\text{CO})_4]^-$  formed more directly from  $\text{Co}_2(\text{CO})_8$ , i.e.:



We do not recommend the attempted preparation of  $[\text{Co}(\text{CO})_4]^-$  by sodium amalgam reduction of  $\text{Co}_2(\text{CO})_8$  under anhydrous conditions. Contamination by mercury compounds seems unavoidable and if, as we suspect,  $\text{NaOH}$  is the actual reagent, there seems no reason not to add it as such.

We repeat our point about the avoidance of halides during work-up. The point may be of quite general importance in the chemistry of polynuclear metal carbonyl derivatives from which anionic fragments could be displaced by halides.

Finally, we draw attention to the use of the  $700\text{--}400\text{ cm}^{-1}$  region as a fingerprint for metal carbonyls in difficult cases. Thus both  $\{\text{Hg}[\text{Co}(\text{CO})_4]_3\}^-$  and  $\{\text{Hg}[\text{Co}(\text{CO})_4]_2\text{X}\}^-$  anions differ clearly from neutral  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in this region in the intensity patterns of the bands as well as in their position.

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\* We verified, in ether, the claim [15] that mercury reacts with  $\text{Co}_2(\text{CO})_8$  in solution to give this species.

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