

Halide Ion-induced Disproportionation of Cobalt Carbonyls; Formation of $[\text{Co}(\text{CO})_4]^-$ and Subsequent Cyclic Ketone Synthesis†

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Summary Free or complexed halide ions catalyse the disproportionation of $[\text{Co}_2(\text{CO})_8]$ and $[\text{Co}_4(\text{CO})_{12}]$ to give $[\text{Co}(\text{CO})_4]^-$ (I) in ethers or, using $[\text{K}(\text{crown})]_2[\text{CoX}_4]$ (crown = dicyclohexyl-18-crown-6), in benzene; (I) reacts with *o*-xylylene dihalides (IIa,b), 2,3-bis(bromomethyl)naphthalene (III), or sebacyl chloride to give indan-2-one (IV), 1*H*-benz[*f*]inden-2-(3*H*)-one (V), or $[(\text{OC})_4\text{CoCO}[\text{CH}_2]_8\text{COCO}(\text{CO})_4]$, benzene being the preferred solvent for the latter two reactions.

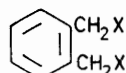
BOTH $[\text{Co}_2(\text{CO})_8]$ and $[\text{Co}_4(\text{CO})_{12}]$ disproportionate slowly in dry ethers to give $[\text{Co}(\text{CO})_4]^-$ (I) and solvated Co^{2+} .¹ Strong bases (*e.g.*, OH^- and amines) induce more rapid disproportionation,² but can interfere with subsequent reactions. We now report our quite unexpected discovery that halide ions (free or complexed) powerfully catalyse the reaction, thus giving a convenient synthesis of (I) from readily available precursors. For example, $3.55 \times 10^{-2}\text{M}$ of $[\text{Co}_4(\text{CO})_{12}]$ in diglyme under N_2 was fully disproportionated by 0.45 M LiCl in 2.5 min at 293 K, while in the absence of a catalyst the disproportionation (monitored by i.r. spectroscopy using sapphire cell windows) was incomplete after 6 h. Complex halides are probably catalysts in their own right, since $[\text{CoX}_4]^{2-}$ ($\text{X} = \text{halogen}$) salts are effective and there is no sign of self-poisoning.

We have also found that salts of solubilised cations in solvents of low polarity can cause disproportionation; thus the anion (I) is obtained in solution in benzene or toluene by the action of $[\text{K}(\text{crown})]_2[\text{CoX}_4]$ or $\text{K}(\text{crown})\text{OH}$ (crown = dicyclohexyl-18-crown-6) on $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}_4(\text{CO})_{12}]$ at room temperature. The resultant solutions show the familiar³ nucleophilicity of (I) towards organic halides, but reactions are, if anything, slightly slower than in ethers, presumably because the expulsion of X^- increases charge localisation. Despite this, such solutions are useful where polar solvents interfere. For instance, we have found that the reaction of acyl halides with (I) to give cobalt acyls is complicated in tetrahydrofuran (THF) by side-production of $\text{RCO}_2[\text{CH}_2]_4\text{Cl}$. The reaction can, however, be perfectly well carried out under CO in benzene, in which we have observed production of $[(\text{OC})_4\text{CoCO}[\text{CH}_2]_8\text{COCO}(\text{CO})_4]$ (from sebacyl chloride) and $[\text{Me}_2\text{CHCH}_2\text{COCO}(\text{CO})_4]$ (from isovaleryl chloride). The latter decomposes thermally under 1 atm CO at 333 K to give di-isobutyl ketone and cobalt carbonyls, without significant isomerisation or side-product formation.

It follows that the salts $[\text{K}(\text{crown})]_2[\text{CoX}_4]$ should promote the reactions of $[\text{Co}_2(\text{CO})_8]$ in hydrocarbons with organic halides, through a combination of disproportionation and nucleophilic attack, to give the overall stoichiometry shown in equation (1). In agreement with this $2\text{RX} + \frac{3}{2}[\text{Co}_2(\text{CO})_8] \rightarrow \text{CoX}_2 + 2[\text{RCo}(\text{CO})_n] + (12-2n)\text{CO}$ (1)

prediction, freshly distilled benzyl bromide ($1.7 \times 10^{-2}\text{M}$) in benzene showed no reaction at 293 K with $[\text{Co}_2(\text{CO})_8]$ ($1.35 \times 10^{-2}\text{M}$) in benzene over 24 h but was completely converted into $[\text{PhCH}_2\text{Co}(\text{CO})_4]$ and $[\text{PhCH}_2\text{COCO}(\text{CO})_4]$ in 30 min in the presence of $5 \times 10^{-3}\text{M}$ of $[\text{K}(\text{crown})]_2[\text{CoBr}_4]$. Equation (1) understates the usefulness of the reaction, since the conversion of $\text{RCo}(\text{CO})_n$ into organic products will regenerate cobalt carbonyls.

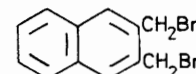
We have also discovered that (I) reacts with (IIa) or (IIb) in benzene or THF at 343 K to give (IV) in 80% yield [based on (II); yields by quantitative ^1H n.m.r. spectroscopy after removal of paramagnetic species]; σ -organo-cobalt intermediates are formed at 273 K. The reaction thus compares favourably with that between (IIb) and $[\text{Fe}(\text{CO})_4]^{2-}$ followed by CO in the presence of AlCl_3 to give (IV) (overall yield 20%).⁴ The reaction of (I) with (III) in THF gives an allylic species (not isolated) which we formu-



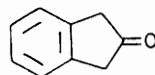
(II)

a; X = Cl

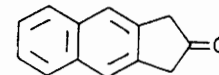
b; X = Br



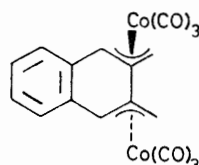
(III)



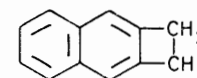
(IV)



(V)



(VI)



(VII)

late as (VI) from the stoichiometry of its formation and the simplicity⁵ of its i.r. spectrum $\{\nu(\text{CO}) 2047$ (s, v, sharp) and 1991 (s) cm^{-1} in THF; we find 2062 and 1989 cm^{-1} for $[(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3]$ in the same solvent}. This difference between (II) and (III) serves to illustrate the ease with which, in naphthalene, one of the rings may be withdrawn from aromatic conjugation. Heating the solution to 240 K under CO for 12 h gives the novel species (V) [m.p. 358–360 K (decomp.), $\nu(\text{CO}) 1758$ cm^{-1} in THF; ^1H n.m.r.

† Information protected by U.K. Patent application nos. 6432 and 12802, 1977.

(60 MHz, CDCl_3) τ 2.1—2.8 with peaks at τ 2.37 and 2.59 (ArH) and 6.38 (s) with relative intensities 6:4; M^+ and $(M - 28)^+$ peaks observed in the 70 eV mass spectrum]. The yield of (V) is 40%, dimethylnaphthalene being formed in 60% yield. In benzene under CO, the reaction between (I) and (III) proceeds similarly, but there is an improvement in the overall yield of (IV) to 55%, and the main side-

product (25%) is now (VII). We relate these differences to the poorer hydrogen atom donor ability of benzene.

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¹ W. Hieber and J. Sedlmeier, *Chem. Ber.*, 1954, **87**, 25.

² W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, 1960, **72**, 795, and references therein; W. Hieber, F. Mühlbauer, and E. A. Ehmann, *Ber. Deut. Chem. Gesell.*, 1932, **65**, 1090; W. Hieber and H. Schulten, *Z. anorg. Chem.*, 1937, **232**, 17.

³ See, e.g. R. F. Heck, 'Organometallic Chemistry, a Mechanistic Approach,' Academic Press, New York and London, 1974.

⁴ B. F. G. Johnson, J. Lewis, and D. J. Thompson, *Tetrahedron Letters*, 1974, 3789.

⁵ P. S. Braterman and D. T. Thompson, *J. Chem. Soc. (A)*, 1968, 1454; P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, New York and London, 1975.