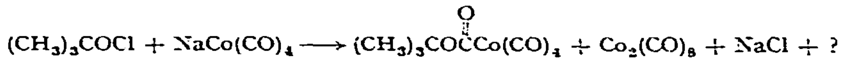
Alkoxycarbonylcobalt tetracarbonyl derivatives

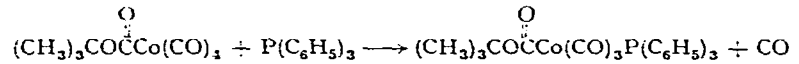
Only two examples of alkoxycarbonylmetal derivatives (RO–CO–M) have been reported, alkoxycarbonylmercury(II) acetates[1] (and other similar salts) and a bicyclic iron carbonyl derivative, *endo*-1-hydroxymethyl-π-allyl(carboxy)-iron(II)tricarbonyl lactone[2]. Alkoxycarbonylcobalt tetracarbonyls have been suggested as intermediates in the side reaction in which formate esters are formed during the hydroformylation reaction, but no evidence for their existence has been obtained[3].

An authentic alkoxycarbonylcobalt carbonyl complex has now been prepared by the reaction of *tert*-butyl hypochlorite with sodium cobalt tetracarbonyl at —80° in ether solution. Even at —80° the reaction is extremely rapid.



$$(CH_3)_3COCl + NaCo(CO)_4 \longrightarrow (CH_3)_3CO\overset{\overset{O}{\|}}{C}Co(CO)_4 + Co_2(CO)_8 + NaCl + ?$$

Evaporation of the solvent in vacuum and extraction of the *tert*-butoxy compound from the major product, cobalt octacarbonyl, with ether at —80°, led to the isolation of about a 10 % yield of yellow oil with infrared bands at 2120 (m), 2035 (vs), and 1695 (m) cm^{-1}. The compound is stable at room temperature under nitrogen but is oxidized by air. The compound reacts rapidly with triphenylphosphine to yield a monotriphenylphosphine derivative with evolution of about a mole of carbon monoxide.

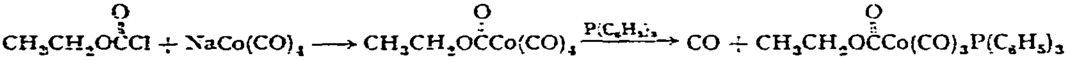


$$(CH_3)_3CO\overset{\overset{O}{\|}}{C}Co(CO)_4 + P(C_6H_5)_3 \longrightarrow (CH_3)_3CO\overset{\overset{O}{\|}}{C}Co(CO)_3P(C_6H_5)_3 + CO$$

The triphenylphosphine derivative is easily obtained directly from the *tert*-butyl hypochlorite–NaCo(CO)$_4$ reaction mixture by adding excess triphenylphosphine, filtering off the insoluble $Co_2(CO)_6[P(C_6H_5)_3]_2$ formed from the cobalt octacarbonyl, evaporating the filtrate in vacuum, and recrystallizing the product from a mixture of ether and pentane at dry ice temperature. The triphenylphosphine complex forms tan prisms which decompose on heating above 100° without melting. The compound is fairly stable in air but does oxidize slowly. The purified product has carbonyl bands in the infrared region in carbon tetrachloride solution at 2060 (w), 1995 (vs), 1935 (vs), and 1715 (m) cm^{-1}. Analyses confirmed the formula as $C_{26}H_{24}O_5PCo$. (Found: C, 61.97; H, 4.63; P, 6.05. $C_{26}H_{24}CoO_5P$ calcd.: C, 61.67; H, 4.77; P, 6.12 %.)

The mechanism of formation of the *tert*-butoxycarbonylcobalt tetracarbonyl from *tert*-butyl hypochlorite and sodium cobalt carbonyl probably involves two steps. In the first step, *tert*-butoxycobalt tetracarbonyl, which for steric reasons is likely quite unstable[4], is formed, and then, in the second step, this compound undergoes a carbon monoxide insertion reaction (or it may decompose into cobalt octacarbonyl). The carbon monoxide required for the insertion step probably comes from decomposition of some of the *tert*-butoxycobalt tetracarbonyl. Unexpectedly, carrying out the reaction under carbon monoxide at one atmosphere pressure did not increase the yield of the *tert*-butoxycarbonylcobalt tetracarbonyl. Similar carbon monoxide insertion reactions of metal alkoxide groups appear to be involved in the preparation of the other two known alkoxycarbonylmetal complexes mentioned above[1,2].

Alkoxycarbonylcobalt tetracarbonyls were also prepared by the reaction of chloroformate esters with sodium cobalt carbonyl. The reactions are very slow and the desired products are produced in low yields. An impure crystalline triphenylphosphine derivative was obtained from ethyl chloroformate by this reaction. The crude product had infrared bands at 2035 (w), 1965 (vs), 1945 (s), and 1640 (m) cm^{-1}, providing good evidence that ethoxycarbonylcobalt tricarbonyl triphenylphosphine had indeed been formed.



$$CH_3CH_2O\overset{O}{\overset{\|}{C}}Cl + NaCo(CO)_4 \longrightarrow CH_3CH_2O\overset{O}{\overset{\|}{C}}Co(CO)_4 \xrightarrow{P(C_6H_5)_3} CO + CH_3CH_2O\overset{O}{\overset{\|}{C}}Co(CO)_3P(C_6H_5)_3$$

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