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# The Reaction of Alkoxides with Dicobalt Octacarbonyl: Trapping of the Co(I) Intermediate in the Disproportionation ("Base Reaction") with a Hard *Lewis* Base

## Short Communication

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Dicobalt octacarbonyl reacts with alcoholates ($RO^-$) yielding alkoxycarbonylcobalt tetracarbonyls, $ROC(O)Co(CO)_4$.

*(Keywords: Alkoxides, reaction with dicobalt octacarbonyl; Alkoxycarbonylcobalt tetracarbonyls; Hydrocarbalkoxylation intermediates)*

*Reaktion von Alkoxiden mit Dicobaltoctacarbonyl: Abfangen des* Co(I) *Zwischenproduktes in der Disproportionierung („Basen-Reaktion") mit einer harten Lewis Base (Kurze Mitteilung)*

Dicobaltoctacarbonyl reagiert mit Alkoxiden ($RO^-$) zu Alkoxycarbonylcobalt tetracarbonylen, $ROC(O)Co(CO)_4$.

The nature of the products of disproportionation of dicobalt octacarbonyl, $Co_2(CO)_8$ (**1**) with *Lewis* bases depends on the nature of the base. Soft bases (like phosphines, arsines, etc.) yield the Co(I) complexes, $[CoL_5][Co(CO)_4]$ [where $L_5 = (CO)_3(ER_3)_2$ for phosphines, etc.[1] or $L_5 = (RNC)_5$ for isonitriles[2]], while oxygen or nitrogen containing hard bases (like alcohols, ketones, amines, etc.) generate $[CoL_6][Co(CO)_4]_2$ ($L = ROH$, pyridine, etc.) type Co(II) salts[3]. It has been suspected[3] that the disproportionation with hard bases proceeds through a Co(I) intermediate, like *e.g.* $[Co(CO)_4L]\,[Co(CO)_4]$ (**2**). Only indirect evidence could be obtained, however, for the existence of **2**[4].

We supposed that if $L$ were an anionic hard base, the Co(I) ion in **2** could be stabilized as a neutral derivative. In fact, reacting **1** with alkali alkoxides in the presence of crown ethers as solid/liquid phase transfer agents, reaction (1) was observed[*]:

$$\underset{\mathbf{1}}{Co_2(CO)_8} + M(cr)OR \xrightarrow[\substack{THF\text{ or }Et_2O\\ -78\,^{\circ}C}]{CO} \underset{\mathbf{3}}{ROC(O)Co(CO)_4} + \underset{\mathbf{4}}{M(cr)\,[Co(CO)_4]} \tag{1}$$

$M$ = Na, K; $R$ = (a) *Me*, (b) *Et*, (c) *iPr*, (d) *cHx*, (e) $CH_2Ph$.

Beyond its theoretical interest, reaction (1) may be directly related to catalytic problems[5,6]. Thus, for example, reaction (2) was postulated recently as a possible way to compounds **3**, regarded as intermediates in the catalytic hydrocarbalkoxylation of dienes[5].

$$\mathbf{1} + ROH + py \xrightarrow{CO} \mathbf{3} + \underset{\mathbf{5}}{pyH[Co(CO)_4]} \tag{2}$$

If **1** was treated in alcoholic solutions under conditions (50–95 °C, 50–80 bar CO) near to catalytic ones, traces of **3** could be detected by i.r. spectroscopy in samples taken from the autoclave. Under similar conditions, but in the presence of 10 mol% pyridine isolable amounts of **3a**, **b**, **c** were formed (1, 5 and 2% based on **1**, resp.). These low yields are explained by the consecutive reaction between **3** and **5** or $HCo(CO)_4$ leading to formates[7], because 46% *Et*OC(O)H (GLC) based on **1** was found; e.g. in the product obtained from ethanol. If the experiment was repeated in the presence of a high excess (100-fold) of isoprene, the formation of **3** and $\eta^3$-$(C_5H_9)Co(CO)_3$[**] was observed. The appearance of the $\eta^3$-complex can be interpreted in terms of the dissociation of the

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[*] Compounds **3a**[5] and **3b**[7] were known; our products were identified by comparison of the $\nu_{CO}$ spectra with that of an authentic sample. Compounds **3c–e** were oily substances, which were characterized by $\nu_{CO}$ spectra, and through the $PPh_3$-derivatives $ROC(O)Co(CO)_3PPh_3$, which could be obtained in analytically pure form. Example for this characterization: **3c**, $\nu_{CO}$ (hexane) 2116.6 m, 2052.9 s, 2041.6 vs, 2028.6 vs, $\nu_{CO\,acyl}$ 1688.8 m, $cm^{-1}$; $PPh_3$-derivative $\nu_{CO}$ (hexane) 2060.2 w, 1994.4 vs, 1981.5 vs $\nu_{CO\,acyl}$ 1666.3 m $cm^{-1}$, $^1H$ n.m.r. (ppm, $CDCl_3$) $\delta$ 1.15, d, $J = 6$ Hz, 6 H, $CH_3$; 2.13, m, 1 H, CH; 7.25 s (br), 15 H, $P(C_6H_5)_3$; the compound gave correct elemental analysis. Yields of **3** and **4** were nearly quantitative.

[**] Characterized by its $\nu_{CO}$ spectrum (ethanol), 2053 m, 1982 vs[8].

pyridinium salt **5**, and the reaction of the resulting $HCo(CO)_4$ with the diolefine:

$$\mathbf{5} \rightarrow py + HCo(CO)_4 \xrightarrow{C_5H_8} \eta^3\text{-}(C_5H_9)Co(CO)_3 \qquad (3)$$

These findings support the most important features of an early suggestion[9] about the function of alcohols as hydrogen donors in hydrocarbalkoxylation and the recent work[10] on the reaction of (1) with water in *THF* as well as the observations on the promoting role of bases in the reactions of **1**[11].

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