

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 alkoxy-carbonylcobalt tetracarbonyls, $ROC(O)Co(CO)_4$.

(Keywords: Alkoxides, reaction with dicobalt octacarbonyl; Alkoxy-carbonylcobalt tetracarbonyls; Hydrocarbalkoxylation intermediates)

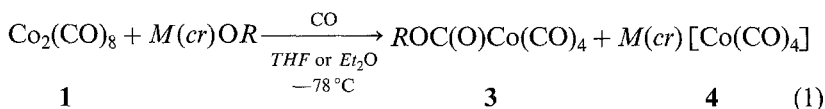
Reaktion von Alkoxiden mit Dicobaltoctacarbonyl: Abfangen des Co(I) Zwischenproduktes in der Disproportionierung („Basen-Reaktion“) mit einer harten Lewis Base (Kurze Mitteilung)

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

The nature of the products of disproportionation of dicobalt octacarbonyl, $Co_2(CO)_8$ (**I**) 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 isonitriles²], 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) salts³. It has been suspected³ that the disproportionation with hard bases proceeds through a Co(I)

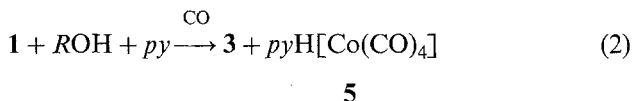
intermediate, like *e.g.* $[\text{Co}(\text{CO})_4\text{L}][\text{Co}(\text{CO})_4]$ (**2**). Only indirect evidence could be obtained, however, for the existence of **2**⁴.

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*:



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 dienes⁵.

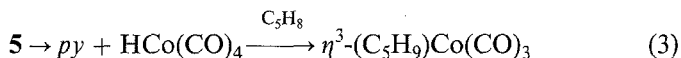


If **1** was treated in alcoholic solutions under conditions (50–95°C, 50–80 bar CO) near to catalytic ones, traces of **3** could be detected by i.r. spectroscopy in samples taken from the autoclave. Under similar conditions, but in the presence of 10 mol% pyridine isolable amounts of **3 a, b, c** were formed (1, 5 and 2% based on **1**, resp.). These low yields are explained by the consecutive reaction between **3** and **5** or $\text{HCo}(\text{CO})_4$ leading to formates⁷, because 46% *EtOC(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 $\eta^3\text{-(C}_5\text{H}_9\text{)Co}(\text{CO})_3$ ** was observed. The appearance of the η^3 -complex can be interpreted in terms of the dissociation of the

* Compounds **3 a**⁵ and **3 b**⁷ were known; our products were identified by comparison of the ν_{CO} spectra with that of an authentic sample. Compounds **3 c–e** were oily substances, which were characterized by ν_{CO} spectra, and through the *PPh*₃-derivatives $\text{ROC(O)Co}(\text{CO})_3\text{PPh}_3$, which could be obtained in analytically pure form. Example for this characterization: **3 c**, ν_{CO} (hexane) 2 116.6 m, 2 052.9 s, 2 041.6 vs, 2 028.6 vs, $\nu_{\text{CO acyl}}$ 1 688.8 m, cm^{-1} ; *PPh*₃-derivative ν_{CO} (hexane) 2 060.2 w, 1 994.4 vs, 1 981.5 vs $\nu_{\text{CO acyl}}$ 1 666.3 m cm^{-1} , ¹H n.m.r. (ppm, CDCl_3) δ 1.15, d, *J* = 6 Hz, 6 H, CH_3 ; 2.13, m, 1 H, CH ; 7.25 s (br), 15 H, $\text{P}(\text{C}_6\text{H}_5)_3$; the compound gave correct elemental analysis. Yields of **3** and **4** were nearly quantitative.

** Characterized by its ν_{CO} spectrum (ethanol), 2 053 m, 1 982 vs⁸.

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



These findings support the most important features of an early suggestion⁹ about the function of alcohols as hydrogen donors in hydrocarbalkoxylation and the recent work¹⁰ 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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