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Preliminary communication

FORMATION AND REACTIVITY OF THE NEW COMPLEX $[CNCH_2Co(COOCH_3)(CO)_3]^-$

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Summary

The formation of $[CNCH_2Co(COOCH_3)(CO)_3]^-$ by reaction between sodium methoxide and $CNCH_2Co(CO)_4$ (I) is reported, and some spectroscopic data for this new complex are given. Complexes such as this may be involved in the catalytic carbonylation of organic halides bearing an electron-withdrawing group.

The formation of σ-alkylcobalt tetracarbonyl complexes is a fundamental step in cobalt-catalyzed carbonylation of organic halides [1]. Recently [(alkoxycarbonyl)methyl] cobalt tetracarbonyl complexes have been characterized [2] and some of their reactions investigated [3]. We now report some preliminary observations on the reaction between sodium methoxide and some stable σ-alkylcobalt tetracarbonyl complexes.

Complex $CNCH_2Co(CO)_4$ (I) was synthesized from the reaction of $CNCH_2Br$ with $NaCo(CO)_4$ in diethyl ether at −10°C under argon. The IR and NMR spectral data are shown in Fig. 1 and Table 1, respectively, and agree with the proposed structure and resemble those of similar compounds [2].

A small excess (1.2—1.5 mol per mol) of CH_3ONa in methanol (1.5—2.5 *M*) was added to a solution of I in THF, at −40°C under Ar. The IR spectrum showed the instantaneous and nearly complete disappearance of complex I, while two new bands appeared at 1948 and 1635 cm^{-1} (Fig. 2). The IR spectrum suggests [4] the formation of an anionic alkoxycarbonyl complex according to the following eq. 1. The same behaviour was observed when

$$\underset{(I)}{CNCH_2Co(CO)_4} + CH_3O^- \rightleftharpoons \underset{(II)}{[CNCH_2Co(COOCH_3)(CO)_3]^-} \qquad (1)$$

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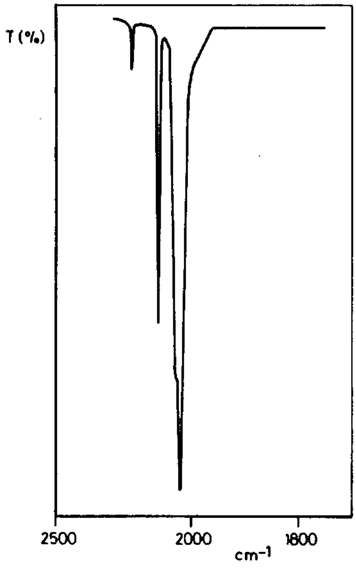
the reaction was carried out in methanol, although it was not possible to observe the band corresponding to the alkoxycarbonyl group. Qualitatively parallel results were obtained using $ROOCCH_2Co(CO)_4$ instead of I, but more CH_3O^- was necessary. To confirm the above hypothesis reaction 1 was monitored by means of ^1H and ^{13}C NMR spectroscopy (Table 1). On adding CH_3ONa to either an ethereal or a methanolic solution of I, the peak for CH_2CN was strongly displaced toward high field in both the ^1H and ^{13}C NMR spectra. This is consistent with the formation of an anionic alkyl complex and rules out the presence of the $CNCH_2COCo$ group of an acyl complex. Furthermore the ^{13}C NMR spectrum shows a peak at 50.3—50.7 ppm which can reasonably be attributed to CH_3OCO. Upon adding a stoichiometric amount of CH_3COOH to solutions of II at −40°C the IR ^1H and ^{13}C



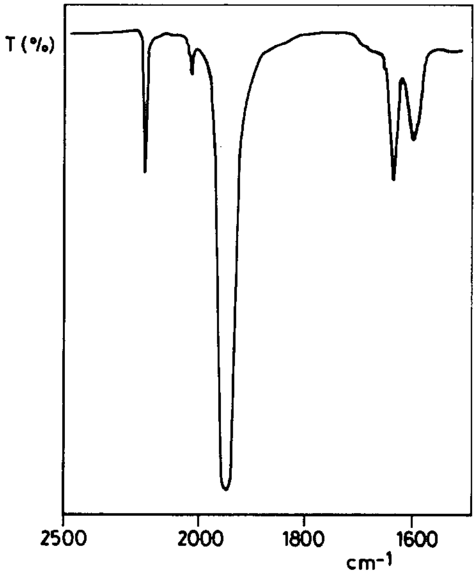


Fig. 1. IR spectrum of I in diethyl ether.

Fig. 2. IR spectrum of II in THF.

TABLE 1

^1H AND ^{13}C NMR CHEMICAL SHIFTS (TMS = 0) RELATIVE TO COMPLEXES I AND II

Complex	Solvent	^1H NMR		^{13}C NMR	
		δ(CH_2CN)	δ(COOCH_3)	δ(CH_2CN)	δ(COOCH_3)
I	THF			−16.1	
I	$(C_2H_5)_2O$			−15.3	
I	CD_3OD	2.09			
II	THF			−26.3	50.3 [a]
II	$(C_2H_5)_2O$			−26.8	50.7 [a]
II	CD_3OD	0.68	n.d. [b]		

[a] The peak of CH_3OH arising from the methoxide solution was found at 49.7 ppm. [b] COOCH_3 group falls under the peaks of the solvent.

NMR spectra of complex I were regenerated in accord with the equilibrium shown in eq. 1 [5].

Finally the behaviour of complex II in methanolic solution under CO was investigated, the temperature being gradually raised from −40 up to 25°C. Only acetonitrile was detected by GLC, while the IR spectrum showed the progressive formation of the $\mathrm{Co(CO)_4}^-$ band.

Similar reactions were also carried out in the presence of $\mathrm{BrCH_2CN}$ and $\mathrm{BrCH_2COOCH_3}$ (2 mol per mol of I).

The compounds $\mathrm{CH_3CN}$ and $\mathrm{CNCH_2COOCH_3}$ (*m/e* = 99, 68, 59, 55, 54, 40) were detected by GLC/MS in the former and $\mathrm{CNCH_2COOCH_3}$ and $\mathrm{CH_2(COOCH_3)_2}$ (*m/e* = 132, 101, 74, 59, 43, 42, 31) in the latter. When $\mathrm{BrCH_2COOCH_3}$ was used the IR spectrum of the methanolic solution showed the presence of both $\mathrm{Co(CO)_4}^-$ and $\mathrm{CH_3OOCCH_2Co(CO)_4}$.

Furthermore the interconversion of complexes I and II, accompanied by the formation of $\mathrm{CNCH_2COOCH_3}$ was observed when $\mathrm{CH_3ONa}$ was gradually added at −5°C under CO to a methanolic solution of complex I and $\mathrm{CNCH_2Br}$ (Fig. 3).

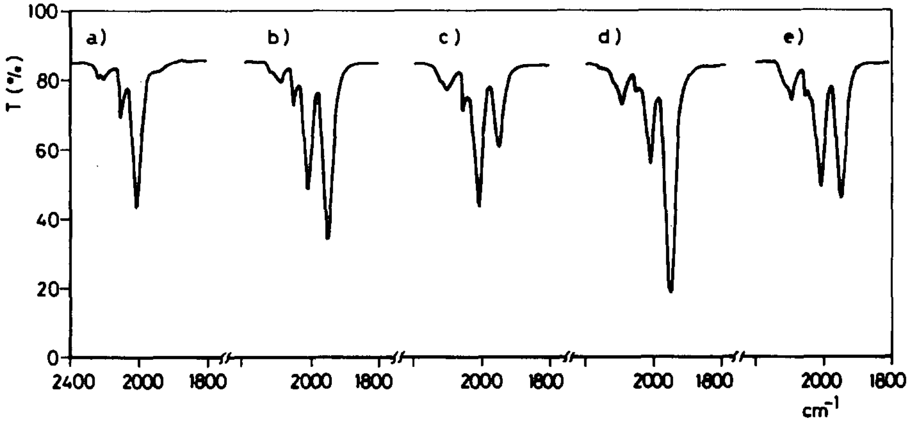


Fig. 3. (a) Complex I and $\mathrm{CNCH_2Br}$ in $\mathrm{CH_3OH}$; (b) a + $\mathrm{CH_3O^-}$ (0.4 mol per mol of I at −5°C; (c) b, 30 min later; (d) + $\mathrm{CH_3O^-}$ (0.4 mol per mol of I; (e) d, 30 min later [10].

The above experiments suggest that complexes of type II are involved as intermediates in carbonylation of organic halides of the form $\mathrm{RCH_2X}$, where R is an electron-withdrawing group. The presence of this group makes the alkyl—acyl transformation very difficult [6], but nevertheless the carbonylation process occurs (see for example the synthesis of diethyl malonate from ethyl chloroacetate [7]). One possible reaction route which accounts for the results is as follows:

$$\mathrm{[CNCH_2Co(COOCH_3)(CO)_3]^- + RCH_2X} \rightarrow$$

$$\mathrm{[CNCH_2Co(COOCH_2)(CH_2R)(CO)_3]} - \begin{cases} \rightarrow \mathrm{NCCH_2COOCH_3 + RCH_2Co(CO)_3} \\ \\ \rightarrow \mathrm{RCH_2COOCH_3 + CNCH_2Co(CO)_3} \end{cases}$$

On this interpretation, complexes of type II interact with RCH_2X to form a Co^{III} complex bearing two alkyl groups [8]. RCH_2COOCH_3 is formed by reductive elimination and the starting complex is regenerated [9]. Obviously when two different alkyl groups are bound to Co^{III} both of the possible carbonylated products are obtained.

Further studies are in progress to confirm this hypothesis. Other catalytic properties of complexes of type II will be reported later.

References and notes

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