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REACTION OF DICOBALT OCTACARBONYL WITH SECONDARY AMINES: $R_2NCOCo(CO)_4$ DERIVATIVES

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SUMMARY

Secondary aliphatic amines were found to react with dicobalt octacarbonyl in hexane solution to form (*N*-dialkylcarbamoyl)cobalt carbonyl derivatives. Compounds of the type $R_2NCOCo(CO)_3(PPh_3)$ were isolated from the reaction products.

The reaction of metal carbonyls and amines frequently leads to the formation of *N*-formyl derivatives and substituted ureas; furthermore, metal carbonyls can act as catalysts in the reaction between amines and carbon monoxide yielding the same products[1]. Dicobalt octacarbonyl is especially active in this respect[2]. These reactions are generally regarded as proceeding through cobalt carbonyl derivatives containing the $Co{-}CO{-}N\textless$ group[1,3], but such intermediates have not previously been isolated.

When piperidine was treated with a hexane solution of dicobalt octacarbonyl, gas was evolved and a violet-coloured oil separated. This oil showed a very intense infrared absorption band at about 1890 cm^{-1}, characteristic of the $Co(CO)_4^-$ anion, and was therefore regarded as the end product of the well-known reaction of $Co_2(CO)_8$ with bases[4]:

$$3\,Co_2(CO)_8 + 12\,B \rightarrow 2[CoB_6][Co(CO)_4]_2 + 8\,CO$$

This oil was not investigated further.

The reddish-brown hexane solution showed 6 sharp IR absorption bands in the 2200–1900 cm^{-1} region (2108, 2052, 2024, 2001, 1981 and 1952 cm^{-1}) and one broader band at 1585 cm^{-1}. The relative intensities of the six bands varied with the $C_5H_{10}NH/Co_2(CO)_8$ molar ratio in a way which suggests that they arise from two separate compounds, referred to hereafter as (A) and (B). The amount of compound (A), to which the bands at 2108, 2024, 2001 and (partly) 2052 cm^{-1} belong, was decreased by increasing the $C_5H_{10}NH/Co_2(CO)_8$ ratio from 3/1 to 4/1, and at even higher ratios its concentration became very low. The formation of compound (B), as shown by its bands at 1981, 1952 and (partly) 2052 cm^{-1}, was favoured by higher $C_5H_{10}NH/Co_2(CO)_8$ ratios. A large excess of piperidine transformed both (A) and (B) to the oily product containing $Co(CO)_4^-$. At $C_5H_{10}NH/Co_2(CO)_8$ ratios below 3/1, some unreacted $Co_2(CO)_8$ remained in the products.

Compounds (A) and (B) could not be isolated in a pure form but addition of triphenylphosphine to the hexane solution gave $C_5H_{10}NCOCo(CO)_3(PPh_3)$ (I) as a yellow, finely crystalline precipitate.

Similar results were obtained with di-n-propylamine, and $(n\text{-}C_3H_7)_2NCOCo(CO)_3(PPh_3)$ (II) was isolated. In the reaction of $Co_2(CO)_8$ with n-propylamine, n-butylamine, *N*-methylaniline or diphenylamine however, no hexane-soluble complexes were formed. The violet-coloured oils, which separated from the reaction mixtures, contained the $Co(CO)_4^-$ anion and were not investigated.

The identification of complexes (I) and (II) is based on their elementary composition and infrared spectra in the C–O stretching region which is characteristic for $RCOCo(CO)_3L$ type compounds (Table 1). For purposes of comparison, Table 1 also lists data for the structurally similar $C_6H_5CH_2COCo(CO)_3(PPh_3)$[5].

TABLE 1

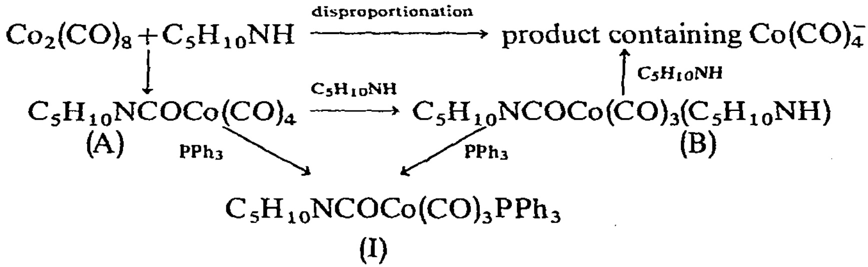
C–O STRETCHING FREQUENCIES OF $C_5H_{10}NCOCo(CO)_3(PPh_3)$ (I), $(n\text{-}C_3H_7)_2NCOCo(CO)_3(PPh_3)$ (II) AND $C_6H_5CH_2COCo(CO)_3(PPh_3)$ (III)

Compound	Stretching frequencies (cm^{-1})
(I)[a]	2050 (m), 1983 (vs), 1952 (vs), 1591 (m)
(II)[a]	2050 (m), 1983 (vs), 1949 (vs), 1598 (m)
(III)[b]	2049 (m), 1985 (vs), 1965 (vs), 1698 (m), 1680 (m)

[a] In tetrahydrofuran solution. [b] In diethyl ether solution.

As can be seen from these data, the spectra of compounds (I) and (II) in the ν(CO) region are very similar to that of the phenylacetyl derivative, the only significant difference being the lower wavenumber attributable to the "organic" carbonyl group which can be associated with mesomeric interaction between the N atom and the CO group. Furthermore, the position of this band is consistent with the values, found for $(C_5H_5)Fe(CO)(PPh_3)CONHR$ compounds[6].

The reactions leading to the formation of (I) can be represented by the following scheme



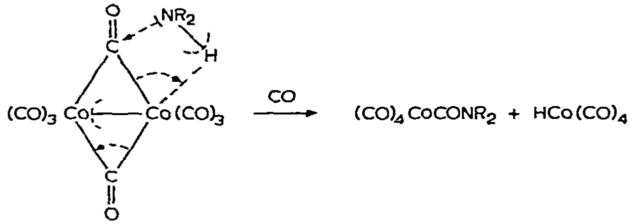
The formulation of the intermediates (A) and (B) as $C_5H_{10}NCOCo(CO)_4$ and $C_5H_{10}NCOCo(CO)_3(C_5H_{10}NH)$ is based on: (*a*) their reaction with triphenylphosphine [formation of (I)]; (*b*) their infrared spectra, which show great similarity to the spectra of acylcobalt tetracarbonyls[7] and their monosubstituted derivatives[5], respectively; (*c*) their reaction with HCl, by which both are transformed to $HCo(CO)_4$, as evidenced by infrared spectroscopy.

The formation of (A) and (B) may start with the rupture of the N–H bond by dicobalt octacarbonyl (a process already observed with the S–H bond[8]), followed by carbon monoxide insertion into the nitrogen–cobalt bond of the (dialkylamido)cobalt carbonyl derivative thus formed. This CO insertion may lead to both (A) or (B), depending on whether carbon monoxide or piperidine fills up the coordination sphere of the cobalt atom:

$$C_5H_{10}NH + Co_2(CO)_8 \rightarrow C_5H_{10}NCo(CO)_4 + HCo(CO)_4$$

$$C_5H_{10}NCo(CO)_4 \rightleftarrows C_5H_{10}NCOCo(CO)_3 \begin{cases} \xrightarrow{CO} & (A) \\ \xrightarrow[C_5H_{10}NH]{} & (B) \end{cases}$$

An alternative mechanism involves the nucleophilic attack of the amine at the carbon atom of one bridging carbonyl group of $Co_2(CO)_8$. In this case, the formation of the C–N and Co–H bonds may take place almost simultaneously and a definite CO-insertion reaction is not involved:



Cobalt carbonyl hydride (which is formed from mercaptans[7]) could not be detected in the reaction products, presumably because it is transformed into its piperidinium salt.

EXPERIMENTAL

1. *Preparation of $C_5H_{10}NCOCo(CO)_3(PPh_3)$ (I)*

To a solution of 2.83 g (8.2 mmole) of $Co_2(CO)_8$ in 60 ml hexane, 2.79 g (32.8 mmole) of piperidine in 30 ml hexane was slowly added in a stream of carbon monoxide. The dark brown solution gradually became deep red and a violet oily precipitate separated. Agitation of the mixture was continued for 2 h. After filtration, the cobalt content of the hexane solution was determined and found to be 5.4 mmole. After addition of 1.42 g (5.4 mmole) triphenylphosphine in 30 ml hexane to this solution, yellow crystals separated, these were filtered and washed with hexane. Yield 2.8 g (5.4 mmole), 33% based on cobalt. (Found: Co, 11.6; P, 6.1. $C_{27}H_{25}CoNO_4P$ calcd.: Co, 11.39; P, 5.99%.)

2. *Preparation of $(n\text{-}C_3H_7)_2NCOCo(CO)_3(PPh_3)$ (II)*

This complex was prepared analogously to compound (I) from 3.65 g (10.6 mmole) $Co_2(CO)_8$ and 10.7 g (106 mmole) di-n-propylamine. Yield 2.8 g (5.3 mmole), 25% based on cobalt. (Found: Co, 10.7; N, 2.7; P, 5.6. $C_{28}H_{29}CoNO_4P$ calcd.: Co, 11.05; N, 2.63; P, 5.82 %.)

3. *Reaction with HCl*

The hexane solution obtained from the reaction of $Co_2(CO)_8$ and piperidine as described in section 1 was chilled to $-30°$ and dry HCl gas was bubbled through the reaction mixture for 30 min. The solution was allowed to warm to room temp. and investigated by infrared spectroscopy. Strong absorption bands were found at 2116, 2052 and 2030 cm^{-1}, characteristic for $HCo(CO)_4$[9].

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