

STUDY OF CARBON MONOXIDE INSERTION INTO THE CARBON-COBALT BOND

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SUMMARY

(Triphenylphosphine)benzylcobalt tricarbonyl can be carbonylated at atmospheric pressure and room temperature to form (triphenylphosphine)(phenylacetyl)cobalt tricarbonyl. Using $^{13}\text{C}^{18}\text{O}$ as carbonylating agent it was shown, that the acyl group is formed by incorporation of a carbonyl ligand, whereas the carbon monoxide from the gas phase enters the coordination sphere of the cobalt atom as a new ligand. The acyl complex can be easily decarbonylated at somewhat elevated temperatures.

INTRODUCTION

The mechanism of the carbon monoxide insertion reaction has been studied in detail for alkylmanganese pentacarbonyls¹. Despite the fact that the now generally accepted mechanism for the hydroformylation of olefins in presence of cobalt carbonyls as catalysts involves the insertion of carbon monoxide into the carbon-cobalt bond of alkylcobalt carbonyls**, no similar studies have been performed with alkylcobalt carbonyls. Indirect evidence³ made it seem probable that with alkylcobalt carbonyls the insertion of CO follows the same route as with the manganese complexes.

RESULTS AND DISCUSSION

Preparation of (triphenylphosphine)benzylcobalt tricarbonyl and (triphenylphosphine)(phenylacetyl)cobalt tricarbonyl

In the preparation of several acylcobalt carbonyl derivatives it was observed, in contrast to literature reports⁴, that the IR spectrum of the product formed from benzyl chloride and sodium tetracarbonylcobaltate in argon atmosphere differed appreciably from the products obtained with simple alkyl halides⁵. If, however, the reaction was carried out under an atmosphere of carbon monoxide, new bands appeared in the IR spectrum, but their intensity fell rapidly in the IR absorption cell.

The observations suggested, that the primary product of the reaction was benzylcobalt tetracarbonyl (I), which at 20° and 1 atm reacts with carbon monoxide

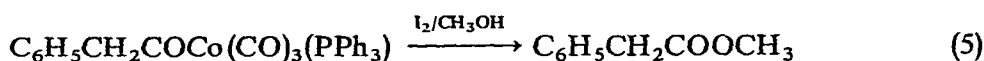
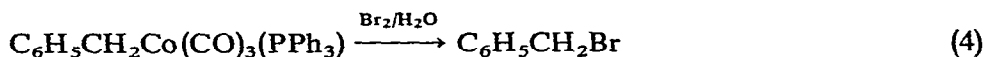
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** For a recent review of literature about hydroformylation mechanism see ref. 2.

phosphinic ligand occupying the axial positions *trans* to each other. Compound (IV) has additionally to the three fundamental metal carbonyl bands a "ketonic" C=O stretching band near 1700 cm^{-1} . The molecule can possess not higher than C_s symmetry as evidenced by the "splitting" of the two lower carbonyl bands by 24 cm^{-1} .

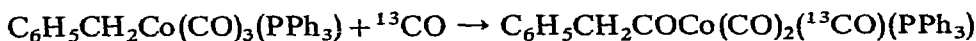
The observations, that in the spectra of the pure compound (IV): (a) the "ketonic" band has always two components separated by about 18 cm^{-1} , (b) in diethyl ether solvent the lowest metal carbonyl band is considerably broadened, and (c) the highest band at 2051.5 cm^{-1} has a shoulder on its *high*-frequency wing, *i.e.* not to be considered as a ^{13}CO -satellite, suggest the presence of two or more rotational isomers of this compound in solution.

Takegami and co-workers reported that under special conditions benzylcobalt carbonyl or (phenylacetyl)cobalt carbonyl (neither of which was isolated) isomerize to the respective *o*-tolyl derivatives⁶. In order to prove that complexes (III) and (IV) [and thus also (I) and (II)] were benzyl and phenylacetyl derivatives respectively they were decomposed by known methods and found to yield only benzyl bromide and phenylacetic acid methyl ester respectively:



Mechanism of carbon monoxide insertion

(III) reacted in ether solution at 20° and 1 atm smoothly with ^{13}CO enriched carbon monoxide. The IR spectrum of the reaction product showed that the entering ^{13}CO had not taken part in the formation of the phenylacetyl group (the position of the double band at $1680\text{--}1698\text{ cm}^{-1}$ not being effected by using ^{13}CO) but that it had occupied the position of one of the carbonyl ligands



This is shown by the considerable strengthening of the ^{13}CO band at 1931 cm^{-1} (*cf.* Table 1) alongside the bands of $\text{C}_6\text{H}_5\text{CH}_2\text{COCO}(^{12}\text{CO})_3\text{PPh}_3$.

Our data thus show, that the mechanism of carbon monoxide insertion is essentially the same both in case of the cobalt-carbon and manganese-carbon bonds¹, a not unexpected result. The insertion obviously needs some kind of activation of carbon monoxide, which is most easily furnished by incorporating it as a carbonyl ligand into the coordination sphere of the transition metal.

The experimental evidence in our case is not sufficient to decide whether the insertion takes place by benzyl migration or not, since the precise structure of the acyl compound (IV) can not be unequivocally assigned on the basis of its IR spectrum.

It is not quite clear at present, why the reaction of the benzyl complexes with carbon monoxide is an equilibrium reaction at room temperature whereas the analogous complexes containing alkyl groups are so reactive towards carbon monoxide^{5,7} under the same conditions. It is noteworthy, however, that under conditions of hydroformylation benzyl alcohols are hydrogenated to a large extent to toluene derivatives⁸ whereas simple aliphatic alcohols are converted into homologous

alcohols⁹. This observation also points to the "reluctance" of the benzyl group to form a new carbon-carbon bond by carbon monoxide insertion.

EXPERIMENTAL

All reactions were carried out in an atmosphere of argon, except where noted.

Preparation of $C_6H_5CH_2Co(CO)_3(PPh_3)$ (III)

0.26 ml (2 mmoles) benzylchloride were added to 16 ml ethereal sodium tetracarbonylcobaltate solution (prepared from dicobalt octacarbonyl with sodium amalgam under diethyl ether) containing 1 mmole cobalt and reacted at room temperature for 3 h. The solution gradually turned reddish-brown. Following this 0.26 g (1 mmole) triphenylphosphine were dissolved in the reaction mixture by shaking. After two h some light brown precipitate was removed by filtration and the liquid product was gradually chilled to -70° . Yellow crystals were obtained (0.16 g, yield: 32% based on cobalt), melting point 135° . (Found: C, 67.4; H, 4.6; Co, 11.5. $C_{28}H_{22}CoO_3P$ calcd.: C, 67.73; H, 4.47; Co, 11.88%.)

Preparation of $C_6H_5CH_2COCO(CO)_3(PPh_3)$ (IV)

This complex was prepared analogously to complex (III) except that all manipulations were performed in an atmosphere of carbon monoxide and that this gas was bubbled for 30 min through the filtrate obtained after removal of the first precipitate formed after the addition of triphenylphosphine. Light yellow crystals were precipitated (0.20 g, yield: 39% based on cobalt), melting point 123° . (Found: C, 65.4; H, 5.2; Co, 10.9. $C_{29}H_{22}CoO_4P$ calcd.: C, 66.40; H, 4.23; Co, 11.25%.)

Decarbonylation of (IV)

A few crystals of (IV) were dissolved in dibutyl ether and the solution heated in Ar-atmosphere to 50° . After 30 min the IR spectrum of the solution showed only the bands characteristic for complex (III).

Reaction of (III) with ^{13}CO

About 8–10 ml of a saturated hexane solution of (III) was placed into a small Schlenk-tube having about 15 ml gas space. The tube was filled with carbon monoxide containing 22 per cent of ^{13}CO , and the sample was shaken for 30 min. The spectra showed that after this period the insertion reaction was completed. Similar experiment has been performed also with an ethereal solution of (III).

Decomposition of (III) with bromine water

A few crystals of (III) were decomposed by adding 2 ml water saturated with bromine and the excess of bromine was neutralised by sodium thiosulphate solution. The oily drops collecting on the water surface were dissolved in ether and investigated by gas chromatography (tricresyl phosphate, 123°). Apart from ether, the gas chromatogram showed the presence of only a single compound, which was proved by an authentic sample to be benzylbromide.

Decomposition of (IV) with I_2 and CH_3OH

A few crystals of (IV) were dissolved in 5 ml methanol and 2 ml of iodine

containing methanol added to the solution. After disappearance of the colour of iodine the solution was investigated by gas chromatography (Apiezon L, 186°). The product was found to be identical with phenylacetic acid methyl ester.

The IR spectra were recorded by a double-beam spectrometer (UR-10 Carl Zeiss, Jena) using a LiF prism.

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