REACTION OF A COBALT-CONTAINING ZIEGLER-TYPE SYSTEM WITH CARBON MONOXIDE

DIRECT SYNTHESIS OF DICOBALT OCTACARBONYL AND AN ACYLCOBALT TETRACARBONYL AT ROOM TEMPERATURE

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(Received October 12th, 1964)

The properties of various Ziegler-type systems, *i.e.*, products obtained by reaction of transition-metal compounds and metal alkyls, have been widely investigated in recent years. The synthesis of chromium, molybdenum, tungsten, and manganese carbonyls from the appropriate transition-metal compounds and carbon monoxide in the presence of Grignard reagents or aluminum alkyls[1] is but one of the numerous examples of the great reactivity and applicability of these substances. The success of this method—referred to as "reductive carbonylation"—is principally attributed to the intermediate presence of unstable and reactive transition-metal alkyls. Until now, however, little has been known about the mechanism of metal carbonyl formation in such systems. Moreover, no similar studies on Group VIIIB metal compounds have been reported so far.

We have undertaken a study of the reaction of carbon monoxide with a cobalt-containing Ziegler-type system, with the object of obtaining information on the mechanism of these "reductive carbonylation" reactions.

On the addition of triethylaluminium, dissolved in hexane, to a hexane solution of cobalt stearate, approximately 1 mole of ethane was evolved per cobalt atom and the initial deep violet colour of the cobalt stearate solution changed to black. Shortly after its formation this homogeneous reaction product was found to absorb (at room temperature and atmospheric pressure) up to 2 moles of carbon monoxide per cobalt atom. The highest rates and amounts of carbon monoxide absorption were obtained with aluminum/cobalt ratios from 1:1 to 6:1. As a result of an ageing process, the reactivity of this cobalt- and aluminum-containing solution gradually diminished and disappeared in 24 hours.

The course of the reaction with carbon monoxide could be followed by observation of the infrared spectrum of the reaction mixture in the 2200–1700 cm^{-1} wave-number region. First, a relatively broad unresolved absorption band appeared at about 2020–2010 cm^{-1}. This could not be identified as a band of any of the cobalt carbonyl complexes previously encountered in our work. Later, absorption bands characteristic of $Co_4(CO)_{12}$ (2063, 2054 and 1867 cm^{-1})[2], $Co_2(CO)_8$ (2069, 2042, 2023 and 1857 cm^{-1})[2] and an acylcobalt tetracarbonyl, $RCOCo(CO)_4$ (2105, 2046, 2024 and 2005 cm^{-1})[3] appeared and the band of the unidentified complex gradually vanished.

After methanolysis and extraction of the reaction product with aqueous sulphuric acid, the acylcobalt tetracarbonyl could be separated from the hexane solution as the crystalline triphenylphosphine derivative[4]. This compound was shown by its elementary composition and melting point to be the mono-substituted triphenylphosphine derivative of propionylcobalt tetracarbonyl $[C_2H_5COCo(CO)_3P(C_6H_5)_3]$, (I). The acyl compound originally present in the reaction mixture was therefore propionylcobalt tetracarbonyl $C_2H_5COCo(CO)_4$, (II).

In experiments using an Al:Co ratio of about 1:1, (II) was usually formed as the chief product, $Co_2(CO)_8$ constituting the second major product and $Co_4(CO)_{12}$ appearing only in minor amounts. The formation of (II) suggests intermediates containing the C_2H_5Co group. The course of the carbon monoxide absorption may thus be shown as follows:

$$\mathrm{Co(stear)_2} + \mathrm{Al(C_2H_5)_3} \longrightarrow \mathrm{C_2H_5CoX} + \mathrm{C_2H_6} \xrightarrow{n\mathrm{CO}} \underset{A}{\mathrm{C_2H_5Co(CO)}_n\mathrm{X}} \xrightarrow{(5-n)\mathrm{CO}} \mathrm{(II)}$$

Intermediates of type *A* are presumably responsible for the absorption band appearing at 2020–2010 cm^{-1} in the early stages of the reaction. The composition of group X in this complex is uncertain, it may contain some fragment(s) of the triethylaluminum molecule. The direct conversion of an alkylcobalt group into an acylcobalt group by carbon monoxide is a well-known reaction in metal carbonyl chemistry.

To our knowledge, this is the first reported example of a transiently-formed transition-metal alkyl being stabilized by carbon monoxide addition in the form of a metal carbonyl derivative, and still retaining a metal–carbon σ-bond. This is, therefore, the first *direct* route to acylmetal carbonyl derivatives, previously obtainable only indirectly from carbonylmetalate anions or metal carbonyl hydrides.

In experiments, where the Al:Co ratio was about 3:1, dicobalt octacarbonyl was the chief product, (II) being formed in much smaller amounts. At higher Al:Co ratios (6–12:1) no definite cobalt carbonyls were formed, although carbon monoxide was absorbed and the broad band at 2020–2010 cm^{-1} appeared in the reaction product.

Under similar conditions, but using iron or nickel stearate, iron pentacarbonyl and nickel tetracarbonyl, respectively, were formed, as shown by the infrared spectra of the products. With these metal compounds, however, no intermediates could be detected by the methods employed. Reaction mixtures containing manganese stearate did not react with carbon monoxide at atmospheric pressure.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of purified nitrogen and all solvents were de-aerated before use.

Cobalt stearate (58.0 g, 0.093 mole) dissolved in 1200 ml of hexane was placed in a flask fitted with stirrer and dropping funnel and connected to a gas burette. A solution of 12.5 g (0.11 mole) of triethylaluminum in 1200 ml of hexane was added gradually with stirring. Gas (2280 ml, 0.102 mole) was evolved in a few minutes. Gas chromatographic analysis of a gas sample showed ethane and traces of ethylene to be present as well as nitrogen.

After purging with carbon monoxide, gas absorption started and 3760 ml (0.168

mole) was absorbed in 16 h (provision should be made for efficient stirring during this time). The infrared absorption spectrum of the product showed the presence of (II) and $Co_2(CO)_8$. The product was treated with 180 ml of methanol (a strong evolution of gas was observed) and extracted first with 300 ml of 20 % sulphuric acid and then with 500 ml of water.

The amount of (II) and $Co_2(CO)_8$ present in the clear hexane solution (790 g) was determined by analysis for cobalt (0.237 % = 1.87 g = 31.6 mg-atoms). This represents a 34 % conversion of the cobalt initially introduced into carbonyl complexes. Conversion of both cobalt carbonyls to their triphenylphosphine derivatives was made by the addition of the calculated amount of triphenylphosphine (8.3 g, 31.6 mmole) dissolved in 40 ml of benzene. The di-substituted, insoluble triphenylphosphine derivatives of dicobalt octacarbonyl[5] immediately formed as a brown precipitate. The reaction mixture was agitated for 4 h to complete the formation of (I). This was monitored by infrared spectroscopy*. After filtration, the filtrate was cooled to −70°, when (I) mixed with organic compounds, crystallized out. (I) could be easily separated from the organic contaminants by allowing the whole product to come to room temperature, when the organic material quickly dissolved again, leaving the slowly dissolving (I) in pure form (yield 0.8 g). By evaporating about 50 % of the filtrate and repeating the cooling process, an additional 0.5 g of (I) of equal purity could be obtained. The overall yield was 1.3 g (2.8 mmole), m.p. 101.5–102.5° (lit.[4] m.p. 98–100°). (Found: C, 62.14; H, 4.62; Co, 12.67. $C_{24}H_{20}CoO_4P$ calcd.: C, 62.33; H, 4.36; Co, 12.76 %.)

ACKNOWLEDGEMENT

We thank Dr. G. Bor for valuable discussions and help with the infrared spectroscopic investigations.

SUMMARY

Propionylcobalt tetracarbonyl and dicobalt octacarbonyl are formed at room temperature from triethylaluminum and cobalt stearate containing hexane solutions by reacting with carbon monoxide. The formation of the acylcobalt tetracarbonyl complex proves the presence of ethylcobalt groups in this Ziegler-type system and is the first direct synthesis of an acylmetal carbonyl derivative. Nickel and iron containing analogous solutions give nickel tetracarbonyl and iron pentacarbonyl, respectively.

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* The infrared spectrum of $C_2H_5COCo(CO)_3P(C_6H_5)_3$ was taken from unpublished work of G. Bor.