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Some Observations on Nitrogen and Hydrogen Complexes of Cobalt. Preparation of $Co(N_2)(PPh_3)_3$ and $H_2Co(PPh_3)_3$

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Paramagnetic $H_2Co(PPh_3)_3$ and $Co(N_2)(PPh_3)_3$ were prepared from cobaltous acetylacetonate and diethyl aluminium ethoxide in H_2 or N_2 atmosphere, respectively. $H_2Co(PPh_3)_3$ reacts reversibly with N_2 at room temperature and atmospheric pressure to yield $Co(N_2)(PPh_3)_3$. Both complexes are transformed by carbon monoxide to $Co_2(CO)_2(PPh_3)_6$. $H_2Co(PPh_3)_3$ hydrogenates n-heptene-1 in a stoichiometric reaction to n-heptane.

Introduction

Three research groups have observed the formation of cobalt complexes with molecular nitrogen and the products obtained were formulated as $Co(N_2)(PPh_3)_3$[1-4] and $HCo(N_2)(PPh_3)_3$.[4,5]. X-Ray structure determination[6] furnished evidence for the latter formulation. As the crystals used in this investigation were prepared by the method[1] described to yield $Co(N_2)(PPh_3)_3$, the existence of the nitrogen complex containing no hydrogen seemed doubtful. The complexes $H_2Co(PPh_3)_3$ and $Co(N_2)(PPh_3)_3$ were further questioned by a recent report,[7] reformulating these substances as $H_3Co(PPh_3)_3$ and $HCo(N_2)(PPh_3)_3$.

It was now found that pure crystalline $H_2Co(PPh_3)_3$ and $Co(N_2)(PPh_3)_3$ can be prepared under an atmosphere of hydrogen or nitrogen, respectively from cobalt*ous* acetylacetonate and $EtOAlEt_2$ in diethyl ether as solvent. As to our experience, it is essential to use cobalt*ous* instead of cobalt*ic*[1-4,6,7] acetyl acetonate in order to obtain a pure, easily crystallisable product. This difference can be attributed partly to the good solubility of the cobaltous compound in diethyl ether. Perhaps even more important, however, is the fact that using the cobaltous compound as starting material no reduction is necessary to obtain as a primary product the *di*hydride, an intermediate also in the formation of the nitrogen complex.

The formulation of the nitrogen complex obtained by our method as $Co(N_2)(PPh_3)_3$ is based on the following observations:

a: elementary analysis;

b: liberation of 0.98 - 1.02 mole of gas containing 98-99% N_2 and 1-2%H_2, by thermal decomposition at 100-150°;

c: a strong infrared absorption band at 2092.8 cm^{-1} in tetrahydrofuran as solvent due to the $N{\equiv}N$ stretching vibration (this band is split in a nujol mull — probably because of crystal field effects — into a double band at 2102 and 2085 cm^{-1});

d: paramagnetism ($\chi_g = 1.7 \times 10^{-6}$) which shows the substance to be monomeric;

e: reaction with CCl_4, which yields *no* $HCCl_3$, showing the absence of a hydridic hydrogen;

f: reaction with CO, which yields mainly $Co_2(CO)_2(PPh_3)_6$[8] as shown by elemental analysis and IR spectrum.

That our compound is not identical with $HCo(N_2)(PPh_3)_3$ is most clearly shown by the gas liberated on thermal decomposition, the paramagnetism of the complex,* the reaction with CCl_4** and by the reaction with CO, which was found in the case of the hydrogen containing nitrogen complex to yield $HCo(CO)(PPh_3)_3$,[7,9] $HCo(CO)_2(PPh_3)_2$[7] and $Co_2(CO)_6(PPh_3)_2$.[7] The complex $Co_2(CO)_2(PPh_3)_6$, formed in our experiments, is also not identical with $[Co(CO)(PPh_3)_3]_x$, a by-product of the reaction between $HCo(N_2)(PPh_3)_3$ and CO_2.[7,9]

According to our measurements, $HCo(N_2)(PPh_3)_3$ in THF solution shows absorption at 2093.8 cm^{-1}. Thus the difference in the position of the ν_{N_2} bands is rather small, though definite (1.0 cm^{-1}). In both instances the correct determination of wavenumbers was aided by the simultaneous registration of a DCl gas spectrum.

The method used for the preparation of $Co(N_2)(PPh_3)_3$ yields in an atmosphere of H_2 the corresponding dihydride $H_2Co(PPh_3)_3$. The monomeric formula-

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(1) A. Yamamoto, S. Kitazume, L. S. Pu and S. Ikeda, *Chem. Comm.*, 79 (1967).
(2) A. Misono, Y. Uchida, T. Saito and K. M. Song, *Chem. Comm.*, 419 (1967).
(3) A. Yamamoto, L. S. Pu, S. Kitazume and S. Ikeda, *J. Am. Chem. Soc.*, *89*, 3071 (1967).
(4) A. Misono, Y. Uchida and T. Saito, *Bull. Chem. Soc. Japan*, *40*, 700 (1967).
(5) A. Sacco and M. Rossi, *Chem. Comm.* 316 (1967); *Inorg. Chim. Acta*, *2*, 127 (1968).
(6) P. H. Enemark, B. R. Davis, J. A. McGinety and J. A. Ibers, *Chem. Comm.*, 96 (1968).
(7) A. Misono, Y. Uchida, M. Hidai and T. Kuse, *Chem. Comm.*, 981 (1968).

* $HCo(N_2)(PPh_3)_3$ is reported to be diamagnetic.[5]
** In the reaction of CCl_4 with $HCo(N_2)(PPh_3)_3$, $HCCl_3$ is formed.[5]
(8) A. Simon, Z. Nagy-Magos, J. Palágyi, G. Pályi, G. Bor and L. Markó, *J. Organometal. Chem.*, *11*, 634 (1968).
(9) L. S. Pu, A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, *90*, 3896 (1968).

tion is supported by the paramagnetism ($\chi_g = +1.6 \times 10^{-6}$) of the complex. The presence of two hydrogen atoms per cobalt atom is shown by thermal decomposition and by the ability of the complex to hydrogenate one mole of heptene–1 in an atmosphere of argon.

$H_2Co(PPh_3)_3$ reacts at room temperature and atmospheric pressure both in solution or suspension with N_2 to yield $Co(N_2)(PPh_3)_3$. This reaction was followed by infrared spectroscopy, using the intense ν_{N_2} band of the latter complex at 2093 cm^{-1}. The reaction was found to be reversible and could be repeated several times. No efforts were made, however, to separate pure complexes, or to determine equilibrium data during these qualitative investigations.

Both $Co(N_2)(PPh_3)_3$ and $H_2Co(PPh_3)_3$ are relatively stable in air, in sharp contrast to $HCo(N_2)(PPh_3)_3$ and $H_3Co(PPh_3)_3$, which instantaneously decompose, if exposed to air. Thus a sample of solid $H_2Co(PPh_3)_3$ turns reddish-brown in air in a few minutes and if at this stage a THF solution of the substance is prepared, it shows the ν_{N_2} band at 2093 cm^{-1}, characteristic for the nitrogen complex. $H_2Co(PPh_3)_3$, therefore, is probably more reactive towards N_2 than O_2.

The reaction of $H_2Co(PPh_3)_3$ with CO yields $Co_2(CO)_2(PPh_3)_6$ in contrast to the hydride $H_3Co(PPh_3)_3$ from which according to our experience mainly $Co_2(CO)_6(PPh_3)_2$ is formed.

Since the complex $Co_2(CO)_2(PPh_3)_6$ was first prepared[8] by the reaction of CO with a solution obtained from cobalt stearate, alkyl Grignard reagents and triphenyl phosphine, $H_2Co(PPh_3)_3$ seems to be present in these solutions too. This is in accordance with the postulated formation of a complex cobalt dihydride L_xCoH_2 in the solutions obtained from cobalt stearate and alkyl Grignard reagents,[10] which solutions catalyse the hydrogenation[11] and isomerization[12] of olefins.

It could be shown that in the presence of triphenyl phosphine this latter catalyst solution too reacts with molecular nitrogen at 1 atm and room temperature as evidenced by the strong infrared absorption band at 2093 cm^{-1} observed in an atmosphere of nitrogen. Following this line, several other similar cobalt-containing solutions were found to have hydrogenating catalytic and nitrogen fixing properties. The study of these catalysts is being continued.

Experimental Section

1. *Preparation of $Co(N_2)(PPh_3)_3$.* Through a solution of 2.6 g (10 mmoles) cobaltous acetyl acetonate and 7.8 g (30 mmoles) triphenyl phosphine in 200 ml absolute diethyl ether nitrogen gas was bubbled for a few minutes at 0°. Following this 3 ml (about 20 mmoles) of diethyl aluminium ethoxide were added dropwise under stirring to the solution which turned gradually deep red and successively the formation of red crystals could be observed. Stirring was continued for about 2 hrs, and the reaction mixture was left standing overnight. The red crystalline product was filtered, washed with ether and dried in vacuum. Yield 5.8 g (66%). (Found: Co, 6.7; P, 10.5. $C_{54}H_{45}CoN_2P_3$ calcd.: Co, 6.75; P, 10.63%).

2. *Preparation of $H_2Co(PPh_3)_3$.* This complex can be prepared by the method given above for the nitrogen compound, using an atmosphere of hydrogen instead of nitrogen. Light brown crystals, yield 6.3 g (74%). (Found: Co, 6.9; P, 11.0. $C_{54}H_{47}CoP_3$ calcd.: Co, 6.95; P, 10.96 %).

3. *Thermal decomposition of $Co(N_2)(PPh_3)_3$.* 1.35 g (1.55 mmoles) of $Co(N_2)(PPh_3)_3$ was heated in an atmosphere of CO_2 to 100-150°. 34.8 normal ml (1.56 mmole) of gas was evolved, which was analysed by gas chromatography (active charcoal, carrier gas CO_2, room temp.) and found to contain 1,3% H_2, the rest being N_2.

To ascertain the possible influence of CO_2,[7,9] the decomposition was also carried out under Ar. In this experiment 0.566 g (0.65 mmole) of complex yielded 14.2 normal ml (0.64 mmole) of gas, showing that the thermal decomposition of the complex is not influenced by an atmosphere of CO_2.

4. *Thermal decomposition of $H_2Co(PPh_3)_3$.* 0.485 g (0.57 mmole) of $H_2Co(PPh_3)_3$ was heated under CO_2 to 100-150°. The formation of 12.3 normal ml (0.55 mmole) gas was observed. Analysed according to section 3 it was found to contain 2.1 % N_2, the rest was H_2.

The decomposition of 0.394 g (0.46 mmole) $H_2Co(PPh_3)_3$ under Ar yielded 9.66 normal ml (0.43 mmole) of gas, again proving the decomposition of this complex also not being influenced by CO_2.

5. *Reaction of $Co(N_2)(PPh_3)_3$ with CO.* 0.87 g (1.0 mmole) of $Co(N_2)(PPh_3)_3$ was suspended in 50 ml absolute hexane and the mixture stirred under CO for 2 hrs. The red crystals of the nitrogen complex gradually disappeared and yellow crystals separated, which were filtered and washed with hexane. Yield 0.75 g. (Found: Co, 6.4. $Co_2(CO)_2(PPh_3)_6$ calcd.: Co, 6.74%). The IR-spectrum of the product in KBr showed one strong band at 1904 cm^{-1}, due to $Co_2(CO)_2(PPh_3)_6$,[8] and a broad band of much lower intensity at 1960-1950 cm^{-1}, which has to be attributed to some contamination by $Co_2(CO)_6(PPh_3)_2$.[13]

6. *Reaction of $Co(N_2)(PPh_3)_3$ with CCl_4.* To 0.12 g (0.14 mmole) of $Co(N_2)(PPh_3)_3$ about 0.3 ml CCl_4 was added. A vigorous reaction took place, and a light blue precipitate separated. The liquid part of the reaction product contained no $HCCl_3$, as analysed by gas chromatography.

7. *Reaction of $H_2Co(PPh_3)_3$ with CO.* 1.13 g (1.33 mmole) of $H_2Co(PPh_3)_3$ was reacted with CO in the manner described in section 5. Yield 0.92 g. (Found: Co, 6.4. $Co_2(CO)_2(PPh_3)_6$ calcd.: Co, 6.74 %). The IR-spectrum of this product was essentially identical with that obtained in section 5.

8. *Hydrogenation of heptene–1 with $H_2Co(PPh_3)_3$.* 0.250 g (0.294 mmole) of $H_2Co(PPh_3)_3$ was dissolved in

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(10) F. Ungváry, B. Babos and L. Markó, *J. Organometal. Chem. 8*, 329 (1967).

(11) B. Babos, F. Ungváry, L. Papp and L. Markó, *Magy. Kém. Folyóirat*, in the press.

(12) B. Babos, J. Kovács, L. Papp and L. Markó, *Magy. Kém. Folyóirat*, in the press.

(13) O. Vohler, *Chem. Ber.*, *91* 1235 (1958).

2 ml benzene and chilled under Ar to –78°. 0.10 ml (0.71 mmole) n-heptene-l and 0.10 ml (0.69 mmole) 2,3-dimethyl-pentane (as a gas chromatographic reference substance) were added and the reaction mixture rapidly warmed to room temperature. Samples were taken at different time intervals and analyzed by gas chromatography:

time,	n-heptane formed	
min	mmole	mmole/mmole of complex
5	0.146	0.50
15	0.266	0.91
37	0.268	0.92
72	0.304	1.04
192	0.306	1.05

9. *Reaction of $H_3Co(PPh_3)_3$ with CO.* 1.32 g (1.55 mmole) of $H_3Co(PPh_3)_3$[5] was suspended in 50 ml hexane and the mixture stirred under CO for 2 hrs. The product was filtered and washed with hexane. Yield 1.13 g (Found: Co, 13.8 . $Co_2(CO)_6(PPh_3)_2$ calcd.: Co, 14.53%).

The IR-spectrum of the product in KBr showed one broad and strong band at 1960-1950 cm^{-1}, as reported[13] for $Co_2(CO)_6(PPh_3)_2$.

10. *Reaction of N_2 with cobalt stearate and butyl magnesium bromide.* 0.63 g (1.0 mmole) cobalt stearate and 0.78 g (3.0 mmole) triphenyl phosphine were dissolved under N_2 in 8.5 ml absolute tetrahydrofuran. To this solution 4.4 ml of Grignard reagent in THF (containing 4 mmole n-butyl magnesium bromide) was added and the reaction mixture shaken under N_2 for 10 min. The dark red solution showed a strong IR absorption band at 2093 cm^{-1}.

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