position of furan itself,[17] and (iii) the opinions of Schmid regarding pyrazole and indazole photolyses.[1]

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[17] Srinivasan[9] also isolated in the parent furan case an adduct believed to be derived from Δ^2-cyclopropenaldehyde (i) and furan, while an unstable "dimethyl derivative corresponding to the aldehyde (i)," but of otherwise unspecified structure, was detected as a product from 2,5-dimethylfuran.

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A Carbon Dioxide Insertion Reaction into the Co–H Bond of Nitrogentris(triphenylphosphine)cobalt Hydride

Sir:

The discovery of the reaction of a tris(triphenylphosphine)cobalt complex with molecular nitrogen under mild conditions[1–3] led us to examine the reactions of the complex with other "inert" gases including carbon dioxide. The insertion reactions of CO_2 into metal–carbon bonds of organo non-transition metal compounds are well known, but very few reports have been made on the reaction of CO_2 with transition metal compounds. Recently reactions of CO_2 with platinum and palladium complexes[4,5] were reported, but the reactions require the presence of oxygen, and carbonato complexes were formed. We wish to report here a novel insertion reaction of CO_2 into a cobalt–hydride bond.

When a CO_2 stream was bubbled through a benzene or tetrahydrofuran solution of $H(N_2)Co[P(C_6H_5)_3]_3$[6] (**1**) containing triphenylphosphine at room temperature, the original red color changed to brownish green with a loss of molecular nitrogen from the complex, as proved by mass spectroscopy. On concentration of the solution, green crystals were obtained which were repeatedly washed with diethyl ether and dried *in vacuo;* mp 217–220° dec; yield about 45% as $HCOOCo[P(C_6H_5)_3]_3$ (**3**). *Anal.* Calcd for $C_{55}H_{46}O_2P_3Co$: C, 74.2; H, 5.2. Found: C, 73.6; H, 5.2. The same complex was obtained in a similar manner by the reaction of $H_3Co[P(C_6H_5)_3]_3$[6] (**2**) with CO_2. This complex is soluble in aromatic hydrocarbons or tetrahydrofuran, but attempts to recrystallize the complex in these solvents always resulted in partial decomposition of the complex. Presumably the complex dissociates in solution accompanied by irreversible decomposition.

The green crystals **3** were characterized as a formate complex of cobalt on the following basis. The infrared spectrum of the complex indicates two strong bands at 1620 and 1300 cm⁻¹ which can be assigned to antisymmetric and symmetric stretching vibrations of a $HCOO^-$ group attached to cobalt. The treatment of the green complex with concentrated sulfuric acid released 1 mol of CO and 0.5 mol of H_2 per mol of the cobalt complex. Thermal decomposition of the complex *in vacuo* at 200–250° liberated CO_2 with a small amount of CO and H_2, as proved by mass spectrometry. The amount of CO_2 and CO evolved corresponded to about 0.85 mol/Co. The reaction of **3** with methyl bromide led to the formation of methyl formate which was identified by infrared spectroscopy after the separation of the ester from the reaction mixture by preparative gas chromatography. The reaction of **3** with dry hydrogen chloride gas at 20° gave HCOOH, as proved by infrared spectroscopy.

The formation of the formate complex **3** by the reaction of cobalt hydrides **1** and **2** with CO_2 can be interpreted as the insertion of CO_2 into the cobalt–hydride bond.

$$\underset{\mathbf{1}}{H(N_2)Co[P(C_6H_5)_3]_3} + CO_2 \longrightarrow \underset{\mathbf{3}}{HCOOCo[P(C_6H_5)_3]_3} + N_2$$

This reaction provides, to our knowledge, the first example of CO_2 insertion among transition metal complexes.

The formate complex **3** can also be prepared by the reaction of **1** with formic acid in a yield of about 65%. In this case the evolution of nitrogen and hydrogen in a molar ratio of about 1:1 was observed. The melting point and the infrared spectrum of the complex obtained by this reaction were identical with those of the complex **3** prepared by the reaction of **1** or **2** with CO_2.

$$H(N_2)Co[P(C_6H_5)_3]_3 + HCOOH \longrightarrow HCO_2Co[P(C_6H_5)_3]_3 + N_2 + H_2$$

When the reaction of **1** with CO_2 was carried out in the absence of tripenylphosphine, a small amount of yellow crystals was obtained. The complex can be formulated as $\{Co(CO[P(C_6H_5)_3]_3\}_x$ (**4**) (probably $x = 2$), mp 158–160° dec. *Anal.* Calcd for $C_{55}H_{45}OP_3Co$: C, 75.6; H, 5.2. Found: C, 75.3; H, 5.8. Iodolysis and pyrolysis of **4** released 1 mol of CO/mol of cobalt complex, and the evolution of hydrogen was not detected by mass spectroscopy.

The same product was also prepared by the reaction of **1** with benzyl isocyanate. The infrared spectrum of complex **4** shows a strong band at 1877 cm⁻¹ which may be assigned to the CO stretch of bridged cobalt carbonyl groups as compared with the CO stretch at 1915 cm⁻¹ of $H(CO)[P(C_6H_5)_3]_3$ which was prepared by the reaction of **1** with carbon monoxide.[7]

The insertion reaction of CO_2 into a cobalt–carbon bond is now under investigation and will be reported later.

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[1] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

[2] A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967); A. Misono, Y.Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967).

[3] A. Sacco and M. Rossi, *ibid.*, 316 (1967).

[4] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *ibid.*, 407 (1967); F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967).

[5] S. Takahashi and N. Hagihara, presented at the 19th Annual Meeting of Chemical Society, Tokyo, Japan, April 1966.

[6] We have proposed the structures $N_2Co[P(C_6H_5)_3]_3$ and $H_2Co[P(C_6H_5)_3]_3$ in our previous communications.[1] We consider now the structures shown here with one more hydride to be more reasonable for various reasons which will be published later and wish to revise our previously proposed structures.

[7] Unpublished results.

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