Journal of Organometallic Chemistry, 49 (1973) C57–C58

Preliminary communication

Insertion of carbon dioxide into the Cu–CH_3 bond of methylbis(triphenylphosphine)copper etherate

AKIRA MIYASHITA and AKIO YAMAMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo (Japan)

(Received December 21st, 1972)

In contrast to the many examples of insertions of CO_2 into non-transition metal–carbon bonds, only a few cases of CO_2 insertion into transition metal–carbon bonds are known[1-4].

We now report the insertion of CO_2 into the methyl–copper bond of methylbis(triphenylphosphine)copper etherate[5], (I), to give acetatobis(triphenylphosphine)copper, $(CH_3COO)Cu(PPh_3)_2$, (II), and its CO_2 adduct, acetato(carbon dioxide)bis(triphenylphosphine)copper, $(CH_3COO)Cu(CO_2)(PPh_3)_2$, (III).

(1) $(CH_3COO)Cu(PPh_3)_2$, acetatobis(triphenylphosphine)copper, (II)

A dry CO_2 stream was bubbled through a tetrahydrofuran (THF) solution of I, initially at −40°, with the temperature subsequently being raised gradually to 0°. After a while the yellow brown solution became colourless, and white crystals were slowly precipitated when the mixture was kept below 0°. This solid was recrystallized from toluene or THF to give white prisms of complex II, m.p. 185–186°, which was diamagnetic. Complex II was characterized as $(CH_3COO)Cu(PPh_3)_2$ by elemental analysis, IR, NMR spectroscopy and chemical reactions. The IR spectral properties are as follows: $\nu(OCO_{asym.})$ 1550 vs; $\nu(OCO_{sym.})$ 1413 vs; ν(C–H of $CH_3COO^-{}_{asym.}$) 2975 w; ν(C–H of $CH_3COO^-{}_{sym.}$) 2905 w cm^{-1}. NMR (60 MHz in pyridine): τ 7.65 (s, 3H of CH_3COO^-), *cf.* CH_3COO of free acetic acid τ 7.97 s. Complex II quantitatively gave acetic acid on treatment with HCl in benzene; reactions with CH_3I and C_2H_5I gave methyl acetate and ethyl acetate, respectively. The acetate complex II can also be prepared by treatment of I with acetic acid, and the complex thus produced was proved to be identical with that from the CO_2 insertion by comparison of m.p.'s, elementary analyses, IR spectra, NMR spectra, and chemical reactions.

$$\left.\begin{array}{l} CH_3Cu(PPh_3)_2(ether)_{1/2} + CO_2 \\ CH_3Cu(PPh_3)_2(ether)_{1/2} + CH_3COOH \\ \qquad (I) \end{array}\right] \xrightarrow[-CH_4]{} \begin{array}{c} (CH_3COO)Cu(PPh_3)_2 \\ (II) \end{array}$$

(2) $(CH_3COO)Cu(CO_2)(PPh_3)_2$, acetato(carbon dioxide)bis(triphenylphosphine)copper, (

On prolonged bubbling of CO_2 into the THF solution of I at room temperature (12 h) the complex II which first formed dissolved again and another copper complex, III, precipitated as fleecy white crystals. They were repeatedly washed with dry THF under a CO_2 stream, dried in vacuum, and characterized as $(CH_3COO)Cu(CO_2)(PPh_3)_2$, (III), (nc), m.p. 151–152° (decomp.); the product was diamagnetic and had the correct elemental analyses. III is slightly soluble in benzene, toluene and THF, but attempts to recrystallize III from these solvents resulted in loss of CO_2 and recovery of the acetate complex II. On pyrolysis at 200°, III released CO_2 in an amount agreeing almost quantitatively with the composition of $(CH_3COO)Cu(CO_2)(PPh_3)_2$, and acidolysis with H_2SO_4 also gave CO_2 quantitatively. On treatment with HCl some acetic acid was formed. The IR spectral properties are as follows: ν(OCO of $CH_3COO_{\text{asym.}}$) 1640 s, ν(OCO of $CH_3COO^-{}_{\text{sym.}}$) 1393 s cm^{-1}; there are also 5 bands (2620 w, 1600 vs, 1302 s, 821 m, and 648 w cm^{-1}), which disappear upon heating at 150°. These five bands must be associated with the coordinated CO_2 molecule (after heating at 150°, only CO_2 was detected; the strong absorptions due to the acetato group remained after heating). The absorptions of the acetato group are at higher frequencies in (III) than in II because of the effect of the coordinated CO_2.

Another type of the CO_2 adduct, IV (white fine crystals), has not been fully characterized; it was formed under some experimental conditions in the reaction of I with CO_2. IV differs from II and III in releasing only half a molecule of CO_2 per copper atom on pyrolysis at 200°, acidolysis by H_2SO_4, or reaction with CH_3I.

REFERENCES

1 M.E. Vol'pin, *Pure Appl. Chem.*, 30 (1972) 607.
2 I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Vol'pin, *Chem. Commun.*, (1971) 972.
3 G.N. Schrauzer and J.W. Sibert, *J. Amer. Chem. Soc.*, 92 (1970) 3009.
4 U. Zucchini, E. Albizzati and V. Giannini, *J. Organometal. Chem.*, 26 (1971) 357.
5 A. Yamamoto, A. Miyashita, T. Yamamoto, S. Ikeda, *Bull. Chem. Soc. Japan*, 45 (1972) 583.