

Preliminary communication

FLASH-VACUUM PYROLYSIS OF η^5 -CYCLOPENTADIENYL-DICARBONYLCOBALT. FORMATION OF COBALTOCENE

JEAN-CLAUDE FIAUD *, REMI CHAUVIN

Laboratoire de Synthèse asymétrique, U.A. 255, bât. 420, Université Paris-Sud, Centre d'Orsay, 91405 Orsay (France)

and ROBERT BLOCH

Laboratoire des Carbocyles, U.A. 478, bât. 420, Université Paris-Sud, Centre d'Orsay, 91405 Orsay (France)

(Received July 30th, 1986)

Summary

Flash-vacuum pyrolysis (350°C, 0.1 Torr) of cyclopentadienyldicarbonylcobalt [$\text{CpCo}(\text{CO})_2$] afforded cobaltocene (85% yield) at the end of the pyrolysis tube. This compound is formed in a bimolecular reaction in the hot zone of the tube between species from which CO ligands have been lost.

Flash-vacuum pyrolysis (fvp) has proved to be useful in synthetic organic chemistry [1]. Fvp of metal carbonyl complexes has been carried out only recently, but has enabled detection of metastable intermediates [2] and observed to induce ligand rearrangements [3,4]. The studies showed that organometallic complexes can be produced and survive at temperatures well above their decomposition temperatures [4].

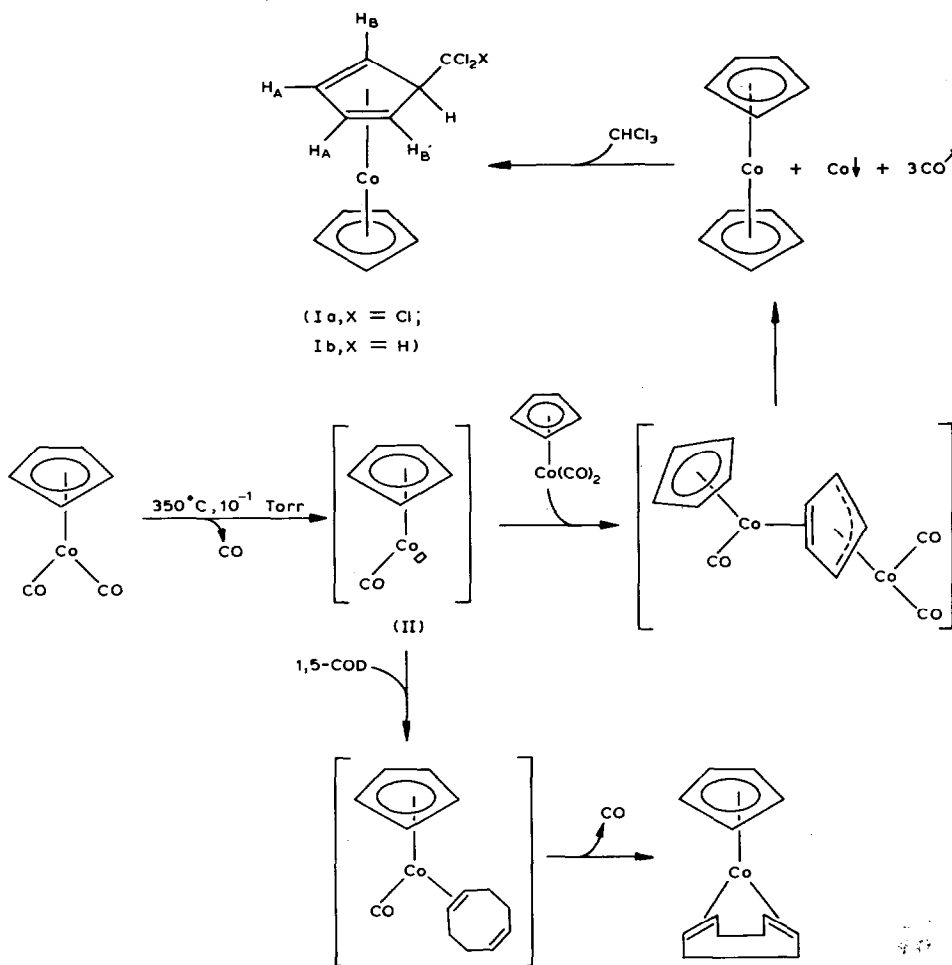
We have now investigated the use of fvp of transition metal complexes for the production of coordinatively unsaturated species that could [5] be involved in catalytic reactions.

Metal carbonyl complexes give catalytic species through photochemically or thermally induced loss (decoordination) of one or several carbonyl ligands. $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$) catalyzes the isomerization of olefins or diolefins, through production of $\text{M}(\text{CO})_5$ by decoordination of a CO ligand [6]. $\text{Fe}(\text{CO})_4$ has been shown (by IR observations) to be the catalytic intermediate of the $\text{Fe}(\text{CO})_5$ -catalyzed isomerization and hydrosilylation of alkenes [7]. Trimerization of acetylenes and co-dimerization of acetylenic compounds with nitriles is catalyzed by $\text{CpCo}(\text{CO})_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) probably through intermediate complexes produced by decoordination of one or two CO ligands, viz. CpCoCO or CpCo [8]. The photolysis of $\text{CpCo}(\text{CO})_2$ has been shown to give, through successive losses of CO ligands, bi-, tri-, and tetranuclear cluster complexes [9].

We studied the fvp of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{CpCo}(\text{CO})_2$ in the hope of trapping coordinatively unsaturated species produced by ligand dissociation, and finding out whether they would show catalytic activity. Pyrolysis was carried out in a 30 cm \times 2.5 cm glass (Pyrex) or silica (quartz) tube heated in a furnace and attached to a cold (liquid N_2) trap located between the oven and the pumping system.

Products arising from fvp of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$) at ca. 0.1 Torr from 600 to 200°C were collected in a matrix of 1-hexene or 1,5-COD previously deposited on the cold trap. Analyses of the organic material recovered after warming up revealed no isomerization (i.e. 2- or 3-hexene or 1,3-COD was detectable by GLC).

Pyrolysis of $\text{CpCo}(\text{CO})_2$ at temperatures above 400°C at 0.1 Torr resulted in the complete decomposition of the complex: a cobalt mirror was deposited in the tube, and no material was recovered on the trap. At temperatures below 300°C at ca. 0.1



SCHEME 1

Torr, $\text{CpCo}(\text{CO})_2$ distilled out and was collected in the cold trap. However, at 350°C and ca. 0.1 Torr, metallic cobalt was deposited in the hot zone of the pyrolysis tube and black crystals were produced at the end of the tube. This crystalline compound, which could even be sublimed in an ice-cooled trap, contained no coordinated CO (lack of IR absorption between 1800 and 2000 cm^{-1}). It reacted with degassed CHCl_3 to give a pentane-soluble orange complex Ia [10], characterized by its $^1\text{H NMR}$ (CDCl_3 , δ (ppm)): 3.0 (bs, 2H_b), 3.8 (bs, H *endo*), 4.85 (s, 5H), 5.3 (bs, 2H_a) and MS ((70 eV, m/e^+ , rel.%): 311 (16.5), 309 (53), 307 (56), 275 (25), 273 (99.6), 271 (100), 190 (85), 189 (100)) spectra. Cobaltocene has been previously reported to react with chloroform only at 60°C to give cyclopentadienyl-1-*exo*-(dichloromethyl)cyclopentadienylcobalt (Ib) [11]. The black compound showed catalytic activity in the trimerization of phenylacetylene to 1,3,5- and 1,2,4-triphenylbenzene. The physical data and reactions indicate that the black compound was cobaltocene, produced in 85% (isolated) yield according to eq. 1:



Production of cobaltocene from $\text{CpCo}(\text{CO})_2$ is indicative of a bimolecular reaction involving cyclopentadienyl-containing cobalt species. Absence of any deposited metallic cobalt outside the pyrolysis tube indicated that the CO-decoordinated cobalt species such as (II) [12] did not decompose after emerging from the tube but reacted further in the hot tube, probably as in Scheme 1. Such a species could be trapped by co-evaporation and pyrolysis (370°C , ca. 0.1 Torr) of a 1/1 mixture of $\text{CpCo}(\text{CO})_2$ (b.p. $158^\circ\text{C}/757$ Torr) and 1,5-cyclooctadiene (1,5-COD) (b.p. $140^\circ\text{C}/710$ Torr), and gave a mixture of Cp_2Co , 1,5-COD and $\text{CpCo}(\text{COD})$ [13] (characterized by vpc and $^1\text{H NMR}$). The pressure (ca. 0.1 Torr) in the tube was evidently too high to prevent intermolecular reactions. Experiments at lower pressure (10^{-3} – 10^{-4} Torr) are in progress with the objective of isolating intermediates such as II, and then investigating their catalytic properties.

Acknowledgements. The C.N.R.S. is thanked for financial support (I.C.M.O.-A.T.P. grant). The authors are indebted to Professor H. Kagan for helpful discussions.

References

- 1 E. Hedaya, Acc. Chem. Res., 2 (1969) 367. G. Seybold, Angew. Chem. Int. Ed. Engl., 16 (1977) 365. R.F.C. Brown, Pyrolytic Methods in Organic Chemistry, Academic Press, New York, 1980. E. Wiersum, Rec. Trav. Chim. Pays-Bas, 101 (1982) 365. E. Wiersum, Aldrichimica Acta, 17 (1984) 31.
- 2 H.Y. Parker, C.E. Klopfenstein, R.A. Wilesek and T. Koenig, J. Am. Chem. Soc., 107 (1985) 5276.
- 3 N.T. Allison, J.R. Fritch, K.P.C. Vollhardt and E. Walborsky, J. Am. Chem. Soc., 105 (1983) 1384.
- 4 J.S. Drage and K.P.C. Vollhardt, Organometallics, 1 (1982) 1545.
- 5 J. Halpern, Acc. Chem. Res., 3 (1970) 186. J.P. Collman, *ibid.*, 1 (1968) 136.
- 6 M.S. Wrighton, G.S. Hammond and H.B. Gray, J. Organomet. Chem., 70 (1974) 283. G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979 p. 171.
- 7 J.C. Mitchener and M.S. Wrighton, J. Am. Chem. Soc., 103 (1981) 975.
- 8 K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl., 23 (1984) 539.
- 9 K.P.C. Vollhardt, J.E. Bercaw and R.G. Bergman, J. Organomet. Chem., 97 (1975) 283.
- 10 S. Katz, J.F. Weiher and G. Wilkinson, J. Am. Chem. Soc., 80 (1958) 6459. M.L.H. Green, L. Pratt and G. Wilkinson, J. Chem. Soc., (1959) 3753.
- 11 G.E. Herberich, E. Bauer and J. Scharzer, J. Organomet. Chem., 17 (1969) 445.
- 12 D.W. Slocum, T.R. Engelman, R.L. Fellows, M. Moronski and S. Duraj., J. Organomet. Chem., 260 (1984) C21.
- 13 R.B. King, P.M. Treichel and F.G.A. Stone, J. Am. Chem. Soc., 83 (1961) 3593.