Journal of Organometallic Chemistry, 67 (1974) C75—C76

Preliminary communication

PHOTOCHEMICAL REACTIONS OF $Ru_3(CO)_{12}$ INVOLVING METAL—METAL BOND FISSION

BRIAN F.G. JOHNSON, JACK LEWIS and MARTYN V. TWIGG
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received January 31st, 1974)

Summary

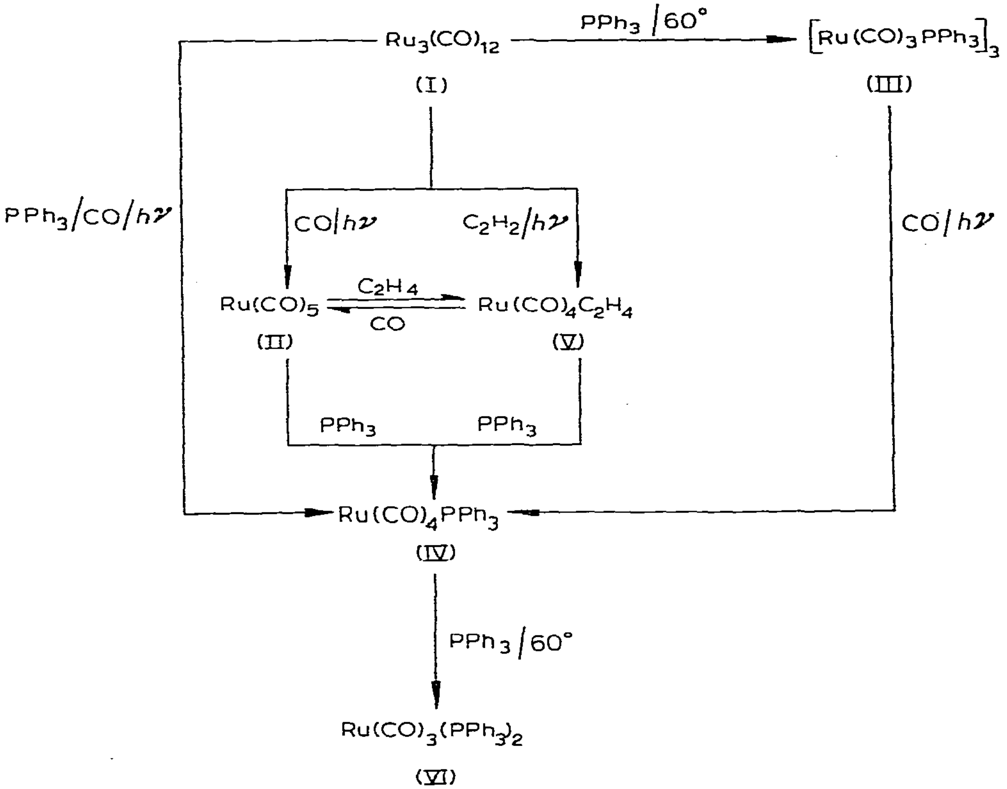
Photolysis of $Ru_3(CO)_{12}$ in the presence of donor ligands rapidly produces monomeric ruthenium species.

The strength of the Ru—Ru bond, relative to the Ru—CO bond, in $Ru_3(CO)_{12}$ (I) is demonstrated by the triangle of ruthenium atoms normally remaining intact after thermal reactions with donor ligands [1]. Carbonyl substitution, rather than metal—metal bond fission, takes place to give complexes of the type $[Ru(CO)_3L]_3$. Indeed, carbonylation of (I) to produce $Ru(CO)_5$ (II) requires a high temperature and pressure (80—100°C, 150 atm.) [2]. Similar conditions (150°C, 80 atm.) are necessary for the carbonylation of $[Ru(CO)_3PPh_3]$ (III) to give $Ru(CO)_4PPh_3$ (IV) [3].

Here we report that irradiating n-heptane solutions of (I) under carbon monoxide (10 psi), with pyrex filtered sun-light or light from fluorescent tubes ($\lambda \approx 390$ nm)* at room temperature rapidly (ca. 5 min) leads to quantitative yields of (II), which was readily identified by its characteristic IR spectrum [4]. Further irradiation of this compound in the presence of carbon monoxide has no effect. Similar experiments using ethylene in place of carbon monoxide produced colourless solutions having IR absorptions at 2104 m, 2021 vs, and 1995 s cm^{-1} thought to be due to $Ru(CO)_4C_2H_4$ (V). Irradiation of (I) and PPh_3 in n-heptane under argon produced a mixture of monomers: (IV) and *trans*-$Ru(CO)_3(PPh_3)_2$ (VI) in a molar ratio ~ 2/1. However, in the presence of carbon monoxide (10 psi) the major product was (IV) together with small amounts of (II) and (VI). Since no reaction between (VI) and CO was observed under the conditions used in these experiments, it appears likely that two photochemical reactions of (I) are operative. One producing only (IV), and the other, involving co-dissociation from (I) and the formation of a monosubstituted intermediate that readily undergoes

---

*The lowest energy absorption maximum of $Ru_3(CO)_{12}$ in the UV visible region is at 391 nm.



further reaction to give (VI) and (IV). Formation of this intermediate being inhibited by carbon monoxide. Compound (IV) was also obtained in good yield by irradiating benzene solutions of the deep-red (III) under an atmosphere of carbon monoxide with a quartz-iodine lamp.

Although it is possible that these reactions involve vibronically excited molecules, it seems more likely that they take place via an electronically excited state. Unfortunately information concerning the lowest unfilled molecular orbital in (I) and (IV) is not available. It is however, noteworthy that the first electronic transition of $Mn_2(CO)_{10}$ is a $\sigma \to \sigma^*$ transition within the metal—metal bond [5], leading to dissociation.

Attempts to produce other monomeric species by irradiation of (I) in the presence of dienes led to the formation of several products. Further studies on these and related reactions are in progress.

We thank the Science Research Council for a Fellowship (to M.V.T.).

References

1 F. Piacenti, M. Bianchi, E. Benedetti and G. Sbrana, J. Inorg. Nucl. Chem., 29 (1967) 1389; M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 2094.
2 F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, Inorg. Chem., 10 (1971) 2759.
3 F. Piacenti, M. Bianchi, E. Benedetti and G. Braca, Inorg. Chem., 7 (1968) 1815; R. Whyman, J. Organometal. Chem., 56 (1973) 339.
4 F. Calderazzo and F. L'Eplattenier, Inorg. Chem., 6 (1967) 1220.
5 R.A. Levenson, H.B. Gray and G.P. Ceasar, J. Amer. Chem. Soc., 90 (1970) 3653.