Journal of Organometallic Chemistry, 154 (1978) C16—C18
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE PHOTOLYSIS OF PLATINACYCLOALKANES IN SOLUTION

DUNCAN C.L. PERKINS, RICHARD J. PUDDEPHATT and CHARLES F.H. TIPPER
Donnan Laboratories, The University, Liverpool (Great Britain)

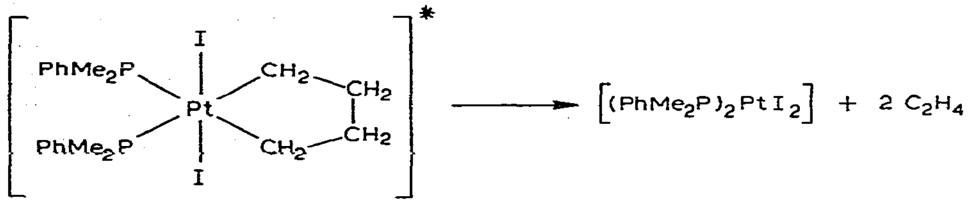
(Received April 20th, 1978)

Summary

The photolysis of $[I_2\overline{PtCH_2CH_2CH_2CH_2}(PMe_2Ph)_2]$ gives ethylene and but-1-ene as volatile products, the latter probably being formed via a five-coordinate platinum intermediate. However, the formation of propene from the photolysis of $[Cl_2\overline{PtCH_2CH_2CH_2}$(1,10-phenanthroline)] appears to involve a direct transfer of a hydrogen atom between neighbouring CH_2 groups in the ring. Other gaseous products, e.g. cyclopropane, ethylene, may be formed via a platinum ion radical.

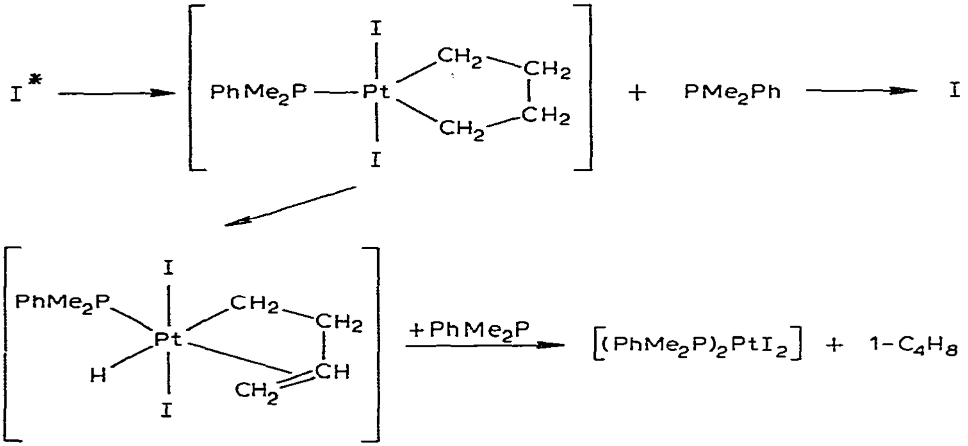
Since an earlier study of the kinetics of the photolysis of platinacyclobutane compounds [1], Ephritikhine and Green [2] have prepared the metallacyclobutane compounds $[\overline{MCH_2CH_2CH_2}(\eta\text{-}C_5H_5)_2]$ (M = Mo, W and C_5H_5 = cyclopentadienyl) and shown that photolysis in hexane solution gives mainly ethylene, with some propene and a little methane. We have recently investigated the photolysis of the platinacyclopentane compound, $[I_2\overline{PtCH_2CH_2CH_2CH_2}(PMe_2Ph)_2]$ (I) and it seemed interesting to find out whether any ethylene or methane were formed in the photolysis of the platinacyclobutane compounds, since they would have been missed in the earlier work [1] because of the method of collecting gaseous products. This communication reports some results which indicate that very different mechanisms operate in the photolyses, depending on the size of the platinacycloalkane ring.

Using a direct gas-sampling method it was found that the photolysis of I in CH_2Cl_2 solution at 25°C under the influence of UV radiation gives ethylene (ca. 70 mol %) and but-1-ene (ca. 30 mol %) as volatile products. Using the mixed solvent (3/2 $CH_2Cl_2/C_6D_5CD_3$ by volume), the olefins contained no deuterium and no ethane or n-butane could be detected. This suggests that free radical type intermediates are not involved since hydrogen abstraction from toluene by radicals is relatively rapid. However, in the presence of excess PMe_2Ph, only ethylene is produced ($<0.1\%$ 1-C_4H_8), indicating that ligand dissociation precedes the formation of but-1-ene. The mechanism, therefore, probably involves two simultaneous processes (Scheme 1): the 1,3-hydrogen shift in the $(CH_2)_4$ moiety involving a vacant coordination site on the platinum as with



(I*)

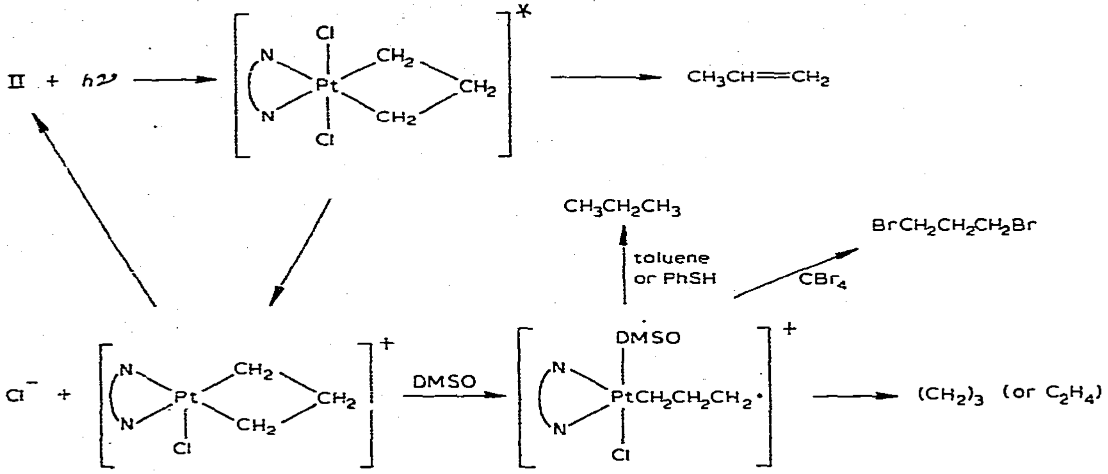
(1)



SCHEME 1

the thermal decomposition [3]. It is interesting to note that the coordinately saturated compounds $L_3\overline{NiCH_2CH_2CH_2CH_2}$ (L = R_3P, Ar_3P) give ethylene on thermolysis, while $L\overline{NiCH_2CH_2CH_2CH_2}$ undergo β-elimination giving but-1-ene [4].

The composition of the volatile products of the photolysis of the platinacyclobutane compound [$Cl_2\overline{PtCH_2CH_2CH_2}$ (1,10-phenanthroline)] (II) varies markedly with conditions (solvent, additive). For example, with CH_2Cl_2 as solvent, propene (ca. 92%), cyclopropane (ca. 7%) and ethylene (ca. 1%) are formed, whereas, with dimethylsulphoxide as solvent, the volatile product composition is; propene (ca. 30%), cyclopropane (ca. 67%), ethylene (ca. 3%). However, with this compound, the addition of even great excess of neutral ligand (i.e. 1,10-phenanthroline) does not appreciably affect the relative yields of products with either solvent, indicating that there is a direct 1,2-hydrogen shift in the $(CH_2)_3$ moiety to give propene. Addition of excess Me_4NCl to the DMSO solution greatly increases the propene/cyclopropene ratio in the products. This suggests that ionisation precedes cyclopropane formation, and, of course, DMSO is a relatively good ionising solvent (dielectric constant, ca. 46 [5]). Ionic species have been proposed as intermediates in the thermal elimination of cyclopropane [6]. With mixed DMSO/toluene and DMSO/benzenethiol solvents (2/1 by volume), appreciable amounts of propane (ca. 1 and 5% respectively) are found in the gaseous products, and 1,3-dibromopropane was detected in solution after photolysis with a DMSO/CBr_4 solvent. Although the possibility that some 1,3-dibromopropane is formed from addition of Br_2 (formed by photolysis to CBr_4) to the C_3H_6 moiety directly cannot be eliminated, it would appear, that cyclization of the C_3H_6 moiety is preceded by homolytic fission of a Pt—C bond to give a substituted propyl radical. Since DMSO can displace cyclopropane from some platinacyclobutane compounds thermally [6], the data suggest that the photolysis mechanism involves the steps shown in Scheme 2. Obviously the formation of ethylene, which becomes a major product (up to 60%) if phosphines are added to the DMSO solution, is accommodated by this scheme.



SCHEME 2

It is intended to extend the work to platinum(IV) compounds with substituted trimethylene moieties, since metallacyclobutanes are thought to be key intermediates in olefin metathesis [7].

Acknowledgements

One of us (D.C.L.P.) thanks the Science Research Council for a maintenance grant.

References

1 G. Phillips, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 131 (1977) 467.
2 M. Ephritikhine and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1976) 926.
3 M.P. Brown, A. Hollings, K.J. Houston, R.J. Puddephatt and M. Rashidi, J. Chem. Soc. Dalton Trans., (1976) 786.
4 R.H. Grubbs and A. Miyashita, J. Amer. Chem. Soc., 100 (1978) 1300.
5 D. Martin and H.G. Hauthal, Dimethyl Sulphoxide, Van Nostrand Reinhold, 1971 (Eng. Trans., 1975).
6 P.W. Hall, R.J. Puddephatt and C.F.H. Tipper, J. Organometal. Chem., 84 (1975) 407.
7 R.J. Puddephatt, M.A. Quyser and C.F.H. Tipper, J. Chem. Soc. Chem. Commun., (1976) 626.