The Addition of Halogenated Olefins to a Platinum Hydride

H. C. CLARK and W. S. TSANG
(*Department of Chemistry, University of Western Ontario, London, Canada*)

THE additions of fluoro-olefins to metal carbonyl hydrides[1,2] and cyanohydrido-metal complexes[3] to form fluoroalkyl derivatives have been recently described. In other instances, it has been reported, also very recently,[3-5] that fluoro-olefins and hexafluorobut-2-yne form π-type complexes with transition-metal derivatives. However, reactions of fluoro-olefins with metal hydrides stabilized by tertiary phosphines, not only follow a very different route to lead to fluorovinyl compounds,[6] but they also provide useful information related to the catalytic activity of metal hydrides.

The reaction of *trans*-bis(triethylphosphine)-hydridochloroplatinum(II) with tetrafluoroethylene in cyclohexane at 120° gives bis(triethylphosphine)-perfluorovinylchloroplatinum(II), $(Et_3P)_2PtCl(CF{=}CF_2)$ and bis(triethylphosphine)-1-difluoromethyldifluorovinylchloroplatinum(II) $(Et_3P)_2PtCl[C(CF_2H){=}CF_2]$. These were separated chromatographically and were formed in almost equal molar yields, even though the tetrafluoroethylene was spectroscopically free of perfluoropropene, so that the origin of this C_3-fragment is not clear and requires further study. The eliminated hydrogen and fluorine were observed only indirectly in the form of the by-product silicon tetrafluoride. There is no evidence that products containing $-CF_2CF_2H$ or $-CF_2H$ groups are formed. In addition to these two new vinyl derivatives, a much smaller amount of a third solid product was isolated. This decomposed on chromatographic columns but was purified from chloroform–cyclohexane solutions. Its infrared spectrum showed strong C–F absorptions as well as a Pt–H absorption at 2090 cm.$^{-1}$, a much lower frequency than that of the original hydride (2200 cm.$^{-1}$). These and the analytical data suggest that it is a five-co-ordinate Pt^{II} complex, containing a π-C_2F_4 group, $(Et_3P)_2PtHCl(C_2F_4)$. This could well be the intermediate from which the perfluorovinyl derivative is formed, and significantly it is the type of intermediate postulated to occur in many catalytic reactions of metal hydrides, *e.g.*, in the homogeneous hydrogenation of ethylene.

Similar reactions of bis(triethylphosphine)-hydridochloroplatinum(II) with perfluoropropene and perfluorocyclobutene lead to the formation of $(Et_3P)_2PtCl(C_3F_5)$ and $(Et_3P)_2PtCl(C_4F_5)$ respectively, and of silicon tetrafluoride. With hexafluorobut-2-yne, addition across the Pt–H bond occurs to form $(Et_3P)_2PtCl[C(CF_3)=CHCF_3]$. All of these new compounds were satisfactorily characterized by analytical and spectroscopic data.

In contrast to the above reactions, tetrachloroethylene reacts with the platinum(II) hydride to form *trans*-bis(triethylphosphine)dichloroplatinum-(II), $(Et_3P)_2PtCl_2$. These results with hexafluorobut-2-yne, fluoro-olefins, and tetrachloroethylene are in marked contrast to those obtained[2] from similar reactions with hydridotetracarbonylcobalt, and for the fluoro-olefins also differ from the reactions with pentacarbonylhydridomanganese,[2] suggesting that different mechanisms may be operative. With the square-planar platinum hydride it seems likely that the reactions proceed *via* a five-co-ordinate, π-olefinic type of intermediate, perhaps stabilized by strong interaction between the hydridic proton and a fluorine (or chlorine) atom of the olefin. In reactions of olefins with the *co-ordinatively saturated* carbonyl hydrides and $HCo(CN)_5^{3-}$ a more direct mechanism involving a four-centre transition state may lead to direct addition across the M–H bond. Further studies of this type should be particularly useful in elucidating the catalytic role of metal hydrides.

(*Received, February 7th,* 1966; *Com.* 073.)

---

[1] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93.
[2] J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519.
[3] M. J. Mayo and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.
[4] R. Cramer and G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 1392.
[5] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356.
[6] H. C. Clark, J. H. Tsai, and W. S. Tsang, *Chem. Comm.*, 1965, 171.