Tetrahedron Letters No.37, pp. 2627-2629, 1964. Pergamon Press Ltd.
Printed in Great Britain.

CARBONYL-OLEFIN COMPLEXES OF THE NOBLE METALS AS REACTION INTERMEDIATES

A. J. CHALK

General Electric Research Laboratory

Schenectady, New York

(Received 10 July 1964)

In a recent communication[1], a reaction was described between olefins, carbon monoxide and palladous chloride to produce β-chloroacyl chlorides. The reaction of carbon monoxide was compared to that of a number of nucleophiles on palladium olefin complexes[2] and it was concluded that carbon monoxide was similarly acting as a nucleophile. However, although carbon monoxide has an affinity for transition metal ions, it is in fact a very poor base and coordinates by virtue of π bonding in a somewhat similar manner to olefins. The most likely reaction path is therefore via nucleophilic attack by chloride ion on either (1) coordinated olefin or (2) coordinated carbon monoxide. Either case could then result in further addition across the alternative unsaturated molecule followed by reduction of the metal ion.

Mechanisms of this type are likely to involve noble metal complexes containing both coordinated olefin and carbon monoxide. A search of the literature revealed no clear cases of this, although Hel'man may have isolated such a mixed complex by passing ethylene through a solution of $(Cl_2PtCO)_2$.[3] Such a preparation requires the initial formation of a complex in which two strongly trans-labilizing groups are located trans, a very unstable situation.[4]

Despite this it has now been found that mixed complexes of carbon monoxide and olefins are formed when carbon monoxide is passed through solutions of halogen-bridged platinum olefin complexes. The preparation is similar to that of the mixed amine-olefin complexes.[5] Similar palladium carbonyl-olefin complexes may be presumed to exist, although it seems likely that they would be somewhat less stable. Thus when carbon monoxide is passed through solutions of dichloro-bis(olefin)-$\mu\mu'$-dichloro diplatinum II, in carbon tetrachloride or the corresponding olefin, (hexene-1, octene-1, styrene), the solutions are decolorized. The resulting platinum complexes precipitated as white solids from concentrated solutions or by the addition of petroleum ether. They were more sensitive to moist air than the corresponding olefin complexes and after washing with petroleum ether, were dried under carbon monoxide or dry nitrogen. Their I.R. spectra showed them to contain coordinated carbon monoxide (bands 2050-2200 cm.$^{-1}$), but were otherwise similar to spectra of the corresponding platinum olefin complexes with bands attributed to C=C stretch at approximately 1500cm.$^{-1}$ Their color and spectra are inconsistent with their formulation as simply mixtures of olefin and carbonyl complexes. The hexene-1 complex showed strong carbonyl absorption at 2110 and 2170 cm.$^{-1}$ (*c.f.* $(PtCOCl_2)_2$ at 2152 cm.$^{-1}$ (6) The relative intensity of these bands changed somewhat with time, the stronger 2110 cm. band increasing at the expense of the 2170 cm.$^{-1}$band. A shift to lower frequency might well be expected for an isomerization from the trans- to the more stable cis-isomer. A small band also appeared at 2050 cm.$^{-1}$ Refluxing the complex in hexene accelerated this change, leaving virtually a single carbonyl absorption at 2110 cm

Attempts were made to use platinum carbonyl olefin complexes as true catalysts. One might expect that the iodination of olefins might be catalyzed by Pt II and that in the additional presence of carbon monoxide, a platinum carbonyl olefin complex might catalyze the formation of β-iodo acyl iodides. Platinum olefin complexes were found to catalyze the iodination of olefins; however, the additional presence of carbon monoxide resulted in no carbonyl insertion at one atmosphere pressure. It was noted, however, that the platinum carbonyl olefin complex formed, catalyzed the iodination more strongly than the olefin complex.

Consideration of the products obtained by Tsuji, et. al., give an indication of the probable course of the reactions they describe.

Mechanism (1), am initial attack of chloride ion on olefin, would be expected to produce preferably primary carbanions, and subsequent addition across carbon monoxide would produce β-chloroacyl chlorides, as found. Reactions of this type are fairly common and are involved in the hydroformylation reaction, where hydride is believed to attack olefin first, followed by alkyl addition to carbon monoxide. The oxidation of olefins in aqueous solution, catalyzed by palladous chloride[7] also appears to involve nucleophilic attack by hydroxide ion on coordinated olefin. Attack on olefin by chloride ion is unusual but might well be affected by the other ligands coordinated to the metal catalyst. Carbon monoxide may promote such an attack as I have found for the iodination of olefins.

Reactions of type (2) are involved in the mechanism of oxidation of carbon monoxide by metal ions[8] and in the case of mercuric salts, intermediates have been isolated to support the proposed mechanism of nucleophilic attack on carbon monoxide.[9] However, for this mechanism to be operating, the formyl group would then be required to add across coordinated olefin. No precedent for such an addition exists to the authors knowledge. The expected products would be α-(chloromethyl)acyl chlorides which were not found.

REFERENCES

1. J.Tsuji, M.Morikawa, J.Kiji, Tetrahedron Letters 16, 1061 (1963).
2. E.W.Stern, M.L.Spector, Proc.Chem.Soc., 370 (1961).
3. Compt. Rend. Acad. Sci., U.R.S.S. 18, 645 (1938) C.A. 32, 5718 (1938).
4. J.Chatt, R.G.Wilkins, J.Chem.Soc., 2622 (1952).
5. J.Chatt, L.M.Venanzi, J.Chem.Soc.,3858 (1955)
6. R.J.Irving, E.A.Magnusson, J.Chem.Soc.,1860 (1956)
7. J.Smidt, Chemistry and Industry 54 (1962).
8. J.Halpern, et.al., J.Amer.Chem.Soc., 83, 1258, 4102 (1961).
9. J.Halpern, S.F.A.Kettle, Chem.Ind., 668 (1961).