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Reactions of haloolefins with tetrakis(diphenylmethylphosphine)platinum(0)

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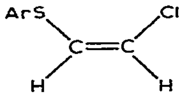
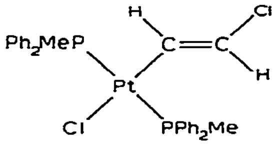
Zerovalent platinum phosphine complexes of the type PtL_4 (L = tertiary phosphine) dissociate in solution to coordinatively unsaturated species PtL_3 and PtL_2[1] which may function as nucleophilic reagents. The way in which such nucleophiles react with haloolefins may be contrasted to other nucleophiles, for example, the *p*-toluenethiolate anion. Truce and coworkers[2] have demonstrated that nucleophilic substitution takes place when *cis*-1,2-dichloroethylene is treated with the *p*-toluenethiolate anion, in the presence of a strong base, giving the arylmercaptoethene (I) as initial product. *trans*-1,2-dichloroethylene does not undergo a similar reaction even in the presence of a base.



(I)

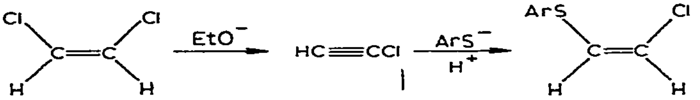
$(Ph_3P)_2PtCl(CH{=}CHCl)$

(II)



(III)

This difference in reactivity has been explained in terms of an elimination-addition mechanism[2]. Strong base is necessary for the reaction with the *cis* olefin to promote *trans* elimination of hydrogen chloride to give chloroacetylene (IV). This undergoes subsequent addition of both the thiolate anion and a proton to give the substituted product (I) (Eqn. 1). For *trans*-1,2-dichloroethylene the *cis* elimination of hydrogen chloride is generally recognised as more difficult.



(1)

More recently Bland *et al.*[3] have reported that in contrast to the behaviour of the β-toluenethiolate anion the zerovalent platinum complex, tetrakis(triphenylphosphine)platinum, reacts with *trans*-1,2-dichloroethylene to give the monochlorovinyl complex (II), while reaction with *cis*-1,2-dichloroethylene occurs only under more forcing conditions to give *cis*-bis(triphenylphosphine)platinum dichloride, $(Ph_3P)_2PtCl_2$.

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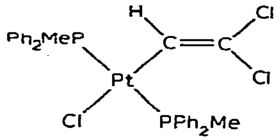
These observations have led to our examination of the reaction of *cis*-1,2-dichloroethylene with tetrakis(diphenylmethylphosphine)platinum(0) in the presence of strong bases such as the ethoxide ion. We have employed diphenylmethylphosphine in these studies as an aid to the structural assignment of the new complexes. By employing this ligand in the reaction described by Bland and his coworkers we have also been able to demonstrate that in the vinyl complex (III) the phosphine ligands take up a *trans* arrangement and that there is retention in the configuration of the olefin. In a typical experiment *cis*-1,2-dichloroethylene was reacted with tetrakis(diphenylmethylphosphine)-platinum in the presence of ethoxide ions in ethanol under reflux. The product of this reaction was the acetylide (V). We consider that in this reaction the ethoxide ions serve to promote the formation of chloroacetylene which then undergoes an oxidative-addition reaction with the platinum(0) complex.

$CH{\equiv}CCl$

(IV)

$(Ph_2MeP)_2PtCl(C{\equiv}CH)$

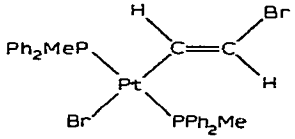
(V)



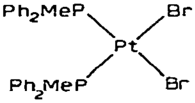
(VI)

$$L_4Pt + ClC{\equiv}CH \longrightarrow L_2Pt(Cl)(C{\equiv}CH) + 2L \qquad (L = Ph_2MeP) \tag{2}$$

As there is a significant variation in the stability of carbon–chlorine and carbon–bromine bonds it was of interest to also examine the reaction of *trans*-1,2-dibromoethylene with the same platinum nucleophile. The reaction of *trans*-1,2-dibromoethylene with $(Ph_2Me)_4Pt$ gave the expected derivative (VII), but in contrast to the thermal stability exhibited by the chloro derivative, this bromo complex readily eliminates acetylene under ambient conditions (Eqn. 3).



(VII)

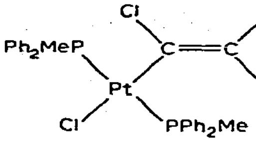


(VIII)

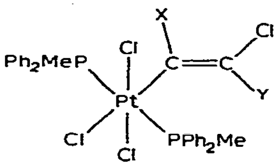
$$L_2Pt(Br)(CH{=}CHBr) \xrightarrow[CHCl_3/20^\circ]{-C_2H_2} L_2PtBr_2 + CH{\equiv}CH \tag{3}$$

A possible reaction path for this reaction is a process involving direct interaction of the bromo atom with platinum analogous to the β-hydrogen effect encountered with certain platinum-alkyl compounds[5].

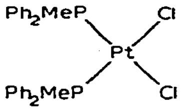
The oxidation of the chlorovinyl complexes (III), (VI) and (IX) with stoichiometric amounts of chlorine produces the new platinum(IV) vinyl complexes Xa, Xb and Xc, respectively. The geometry of these complexes was established directly from ^1H NMR studies. Further reaction of complex (Xb) with a second mole of chlorine led to the substitution of the vinylic hydrogen atom by chlorine to give complex (Xc).



(IX)



(Xa, X=Y=H;
Xb, X=H, Y=Cl;
Xc, X=Y=Cl)



(XI)

trans-$(Ph_2MeP)_2PtCl(CCl{=}CHCl)$

(XII)

trans-$(Ph_2MeP)_2PtCl(CHCl{-}CHCl_2)$

(XIII)

Reaction of complex (III) with hydrogen chloride led to the elimination of vinyl chloride and formation of the *cis*-dichloroplatinum derivative (XI). The reaction of complex (VI) with hydrogen chloride produces an equilibrium involving a mixture of two isomeric vinylic species one of which we consider to be the starting material (VI) and the other complex (XII) in which there has been, in effect, a migration of the vinylic hydrogen atom along the carbon chain. One possible explanation may be that hydrogen chloride adds to complex (VI) to give the saturated σ bonded complex (XIII), which is not isolable, but which then eliminates hydrogen chloride in one of two ways to produce either complex (VI) or complex (XII). In contrast complex (IX) was recovered unchanged from prolonged exposure to hydrogen chloride.

ACKNOWLEDGEMENTS

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REFERENCES

1 J.P. Birk, J. Halpern, and A.L. Pickard, *J. Amer. Chem. Soc.*, 90 (1968) 4491.
2 W.E. Truce, M.M. Boudakian, R.F. Heine and R.J. McManimie, *J. Amer. Chem. Soc.*, 78 (1956) 2743.
3 W.J. Bland and R.D.W. Kemmitt, *J. Chem. Soc. (A)*,(1968) 1278.
4 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc. (A)*, (1966) 770.