Neighbouring Group Participation in Oxidative Addition Reactins of Platinum(II) and Rhodium(I)

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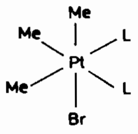
Introduction

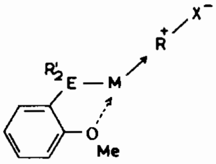
An oxidative addition is often a key and rate-determining step in reactions, including catalytic reactions, of tertiary phosphine- or tertiary arsine-complexes of transition metals, particularly of rhodium, iridium, palladium or platinun. In many of these reactions the metal acts as a nucleophile. However, the introduction of electron releasing substituents acting through the σ- or π-bonding framework of the phosphine (arsine) has a surprisingly small effect on reaction rates, *e.g.* for the addition of methyl iodide to *trans*-$[MCl(CO)\{P(C_6H_4Z\text{-}4)_3\}_2]$ (M = Rh or Ir) [1, 2] the introduction of six *para*-methoxy groups, *i.e.* Z = OMe only increases the rate by a small factor over when Z = H, *e.g.* only 8 times for M = Rh. Chock and Halpern [3] showed that in oxidative additions of alkyl halides to *trans*-$[IrCl(CO)(PPh_3)_2]$, a polar transition state was involved and this suggested to us that such reactions might be promoted by Neighbouring Group Participation (N.G.P.). We confirmed this by a kinetic study of the addition of methyl iodide to the related iridium complexes *trans*-$[IrCl(CO)(PMe_2C_6H_4Z\text{-}2)_2]$ [4] and showed that an *ortho*-methyoxy group, *i.e.* Z = OMe, caused a rate increase of *ca.* 100X compared with Z = H. We now report some studies of oxidative addition reactions of platinum(II) and rhodium(I) with rate enhancements of 100–250X caused by N.C.P. Although an electronic effect due to Neighbouring Group Participation is well recognised, and an important effect, in Organic Chemistry [5], it has not been used in Organometallic/Coordination Chemistry, apart from our previous work.

Results and Discussion

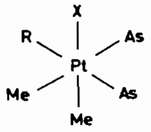
We chose to synthesise the new phosphine PMe_2-(2,4-dimethoxyphenyl). The dichloride, PCl_2(2,4-dimethoxyphenyl) [6], was prepared from 1,3-dimethoxybenzene, phosphorus trichloride and zinc chloride, and treated with methylmagnesium iodide, to give PMe_2(2,4-dimethoxyphenyl). PMe_2-(2-methoxyphenyl) is much more difficult to prepare. We studied the addition of MeBr to *cis*-$[PtMe_2L_2]$ to give $[PtBrMe_3L_2]$ of configuration (1) (L = tertiary phosphine) and followed the conversion by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Using acetone solutions, initially 0.05 *M* in both complex and methyl bromide, the half-lives for reaction at 20 °C were L = PMe_2(2,4-dimethyoxyphenyl), 6 min; PMe_2(4-methoxyphenyl), 10 hours; PMe_2Ph, 14.4 hours. In benzene solution at 20 °C with solutions initially 0.1 *M* in complex and MeBr, the half-lifes were respectively 16.5 min, 30 hours and 50 hours. The relative rates are thus 145:1.45.1 in acetone and 180:1.7.1 in benzene. We explain these rate enhancements in terms of interaction of the *ortho*-methoxy group with the metal, M, in the polar transition state: see (2) E = P, R = R′ = Me, X = Br. Such interactions in polar transition states are well recognised in organic chemistry [5] and were similarly used to explain our results with iridium [4].



(1)



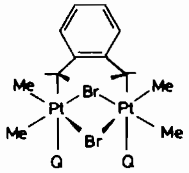
(2)



(3a) X = Br, R = $PhCH_2$

(3b) X = Br, R = CH_2COOEt

(3c) X = Cl, R = CH_2COOMe



(4)

Although an *ortho*-methoxy group, by interacting electronically with the metal, lowers the activation energy it will also slow down reactions because of steric hindrance in a transition such as (2). We anticipated that with the *ortho*-methoxypehnylarsines the steric hindrance due to the R′ groups in (2) would be less with arsenic than with phosphorus, because arsenic is bigger, and that the rate enhancement due to Neighbouring Group Participation would be greater in a 2-methoxyphenylarsine–metal complex than in a corresponding 2-methoxyphenylphosphine complex. We compared the rates of addition of MeBr to *cis*-$[PtMe_2Q_2]$ {Q = $AsMe_2$(2-methoxyphenyl)} or $AsMe_2Ph$ at 20 °C in C_6H_6 and found a rate enhancement of 250X, *e.g.* with solutions initially 0.05 *M* in both reactants the half-

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lives were respectively 7 minutes and 29 hours. The times for 90% conversion were respectively 1 hour and 11 days. These reactions were followed by monitoring the OMe and/or PtMe resonances in an n.m.r. spectrometer. A plot of the ratio [Pt(IV) complex]/[Pt(II)complex] *vs.* time gave a straight line to at least 80% conversion, indicating that the reactions were first-order in both Pt(II) complex and MeBr. Similarly for the phosphine complexes.

We have also used N.G.P. to promote the oxidative addition of $PhCH_2Br$, $BrCH_2COOEt$ or $ClCH_2COOMe$ to *cis*-$[PtMe_2(AsMe_2C_6H_4OMe\text{-}2)_2]$. These and similar halides have not been oxidatively added to platinum(II) previously. However, these three halides add smoothly to *cis*-$[PtMe_2(AsMe_2C_6H_4OMe\text{-}2)_2]$ to give the adducts of configurations (3a), (3b) or (3c) respectively. In benzene at 20 °C, with solutions initially 0.12 *M* in platinum(II) complex, the times for 90% conversion were respectively 30 minutes, 6 minutes and 32 hours; the adducts were readily isolated and characterised. Under similar conditions *cis*-$[PtMe_2(AsMe_2Ph)_2]$ takes an exceedingly long time before adduct formation approaches completion. We have also treated *cis*-$[PtMe_2\{AsMe_2(C_6H_4OMe\text{-}2)\}_2]$ with di(1,2-bromomethyl)benzene. This gave the unusual adduct (4) $\{Q = AsMe_2C_6H_4OMe\text{-}2\}$ with a bridging xylenyl group. This structure follows from analytical, molecular weight and n.m.r. data.

We have also done some preliminary studies on oxidative additions of rhodium(I) promoted by N.G.P. *trans*-$[RhCl(CO)\{PMe_2C_6H_3(OMe)_2\text{-}2,4\}_2]$ reacted with CH_3I very much more rapidly than did *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ but halogen scrambling occurred. It is difficult to do quantitative n.m.r. studies with methyl chloride owing to its volatility and we found that *trans*-$[RhX(CO)\{PMe_2C_6H_3(OMe)_2\text{-}2,4\}_2]$ X = Br or I, were exceedingly reactive and we could not prepare them in a pure state from the chloride by metathesis. However, *trans*-$[RhBr(CO)\{PEt_2C_6H_3(OMe)_2\text{-}2,4\}_2]$ was prepared and found to undergo oxidative addition of methyl bromide very much faster than *trans*-$[RhBr(CO)(PEt_2Ph)_2]$. Using benzene solutions initially 0.05 *M* in both complex and methyl bromide the respective half-lives were 1½ hours and 325 hours, *i.e.* a rate enhancement of approximately 215X.

Thus an ortho-methoxyphenyl group on a tertiary-phosphine or -arsine ligand coordinated to platinum(II) or rhodium(I), promotes oxidative addition by Neighbouring Group Participation, leading to rate enhancements of 145–250X, at ambient temperatures. The effect is therefore even greater than that reported previously for iridium(I) [4], *viz. ca.* 100X. Readily synthesised ligands which show the phenomenon include the new phosphine $PMe_2C_6H_3(OMe)_2\text{-}2,4$ and the arsine $AsMe_2C_6H_4OMe\text{-}2$ and their use should, (i) greatly increase the rates of reactions already observed with more conventional ligands, *e.g.* PMe_2Ph, PEt_3, $AsMe_2Ph$ and, (ii) make possible oxidative addition reactions which are not practicable when conventional phosphines or arsines are used, because they are too slow.

Experimental

Oxidative addition reactions of methyl bromide or other halides to *cis*-$[PtMe_2\{AsMe_2C_6H_4OMe\text{-}2\}_2]$ were most easily monitored by comparing the relative intensities of the OCH_3 n.m.r. resonances of the Pt(II) and Pt(IV) complexes. For studies with $AsMe_2Ph$ the relative intensities of the $PtCH_3$ or $AsCH_3$ resonances of the Pt(II) and Pt(IV) complexes were monitored. Oxidative additions to the tertiary phosphine–platinum(II) complexes were monitored using $^{31}P\text{–}\{^1H\}$ F.T. n.m.r. spectroscopy. Spin–lattice relaxation times (T_1) were measured for $[PtMe_2\{PMe_2C_6H_3(OMe)_2\}_2]$ and $[PtMe_3Br\{PMe_2C_6H_3(OMe)_2\}_2]$ and found to be very similar; 9.4 and 8.6 sec respectively. In following the faster reactions, a single (90°) pulse with a recovery time of at least 50 sec was used. With a standard sample containing both Pt^{II} and Pt^{IV} a gated decoupling experiment showed that N.O.E. differences between Pt^{II} and Pt^{IV} were very small and thus for slower reactions relatively fast pulsing with the flip angle giving optimum S/N ratio were used. We estimate that the error in determining a half-live was not greater than 7%.

Complexes of type (1), (3) or (4) were readily isolated by evaporation of the reaction solution and were readily recrystallised either from light petroleum (b.p. 60–80 °C) containing benzene, or methanol containing a little dichloromethane. They were characterised by elemental analysis (C, H, halogen), and by ^1H and $^{31}P\text{–}\{^1H\}$ n.m.r. spectroscopy (for the tertiary phosphine complexes).

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References

1 I. C. Douek and G. Wilkinson, *J Chem. Soc (A)*, 2604 (1969).
2 R. Ugo, A. Pasini, A. Fusi and S. Cenini, *J. Am. Chem. Soc.*, *94*, 7364 (1972).
3 P. B. Chock and J. Halpern, *J Am. Chem Soc*, *88*, 3511 (1966).
4 E. M Miller and B L Shaw, *J Chem Soc Dalton Transactions*, 480 (1974).
5 'Neighbouring Group Participation', Vol. 1, B. Capon and S. P. McManus, Plenum Press, New York and London, 1976.
6 I. S. Protopopov and M. Ya. Kraft, *Zh Obsch Khim.* (English translation), *34*, 1446 (1964).