Electronic and Steric Effects on the Rate of Oxidative Addition of Methyl Iodide to Diaryl(2,2′-bipyridyl)platinum(II) Complexes

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The rates of oxidative addition of methyl iodide to the complexes [PtR_2(bipy)] [bipy = 2,2′-bipyridyl; R = Me, Ph, 4-XC_6H_4 (X = F, Cl, Me, or OMe), and 3-XC_6H_4 (X = F or OMe) have been studied.

The second-order rate constants follow the series R = Me > 4-$MeOC_6H_4$ > 4-MeC_6H_4 > 3-$MeOC_6H_4$ > Ph > 4-FC_6H_4 > 4-ClC_6H_4 > 3-FC_6H_4, and can be correlated with the energy of a metal-to-ligand charge-transfer transition in the electronic spectra of the platinum(II) complexes. The complexes [Pt(4-$CF_3C_6H_4$)$_2$(bipy)] and [Pt(2-MeC_6H_4)$_2$(bipy)] fail to react with methyl iodide, in the former case due to electronic effects of the CF_3 group and in the latter case due to steric hindrance by the methyl substituents.

THE reactivity of square-planar complexes to oxidative addition reactions with a given reagent may be influenced by both steric and electronic factors. Electron-releasing ligands enhance the rate of oxidative addition by increasing the electron density at the metal centre. For example, oxidative addition of methyl iodide to *trans*-[IrCl(CO){P(4-XC_6H_4)$_3$}$_2$] [1] or to *trans*-[RhCl(CO)-{P(4-XC_6H_4)$_3$}$_2$] [2] takes place more rapidly for complexes with electron-releasing substituents X. More generally, the rates of some oxidative addition reactions to tertiary phosphine complexes of Co^I, Rh^I, and Ir^I have been found to be related to the energies of the lowest-energy electronic transitions in the u.v.–visible spectra. This band has recently been assigned to a metal-to-ligand charge-transfer (MLCT) transition.[3] The band is at lower energy when there is a higher electron density at the metal centre, and the reactivity towards oxidative addition is then also greater. There are exceptions to this general trend when the ligands have a high steric requirement, so that *e.g.* the complex [IrCl(CO){P(2-MeC_6H_4)$_3$}$_2$] is much less reactive than [IrCl(CO){P(4-MeC_6H_4)$_3$}$_2$] although the electronic spectra of the complexes are similar.[4]

The lowest-energy band in the electronic spectra of alkyl- and aryl-(2,2′-bipyridyl)platinum(II) complexes is

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[1] R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Amer. Chem. Soc.*, 1972, **94**, 7364.

[2] I. C. Douek and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 2604.

[3] R. Brady, B. R. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, and L. Vaska, *Inorg. Chem.*, 1976, **15**, 1485.

[4] R. Brady, W. H. de Camp, B. R. Flynn, M. L. Schneider, J. D. Scott, L. Vaska, and W. F. Werneke, *Inorg. Chem.*, 1975, **14**, 2669.

due to a metal-to-ligand charge-transfer transition, involving excitation of an electron from a filled *d* orbital on platinum to the first π^* level of 2,2′-bipyridyl.[5] If this π^* level is assumed to remain constant for platinum(II) complexes, changes in the energy of the band are due to changes of the energies of the *d* orbitals on platinum in different complexes. For the complexes $[Pt(XC_6H_4)_2(bipy)]$ (bipy = 2,2′-bipyridyl) the band energy has been correlated with the Hammett σ values of X. Electron-releasing groups X destabilise the *d* orbitals on platinum and so cause the MLCT band to move to lower energy, and would be expected to cause an increase in the reactivity of the complexes towards oxidative addition.[5,6] To test this hypothesis we have investigated the rate of oxidative addition of methyl iodide to these $[Pt(XC_6H_4)_2(bipy)]$ complexes.

The mechanisms of oxidative addition of alkyl halides to transition-metal complexes have been extensively investigated. The S_N2 mechanism has been proved for oxidative addition of benzyl halides to palladium(0) and platinum(0) complexes,[7,8] while free-radical-chain and non-chain mechanisms operate in oxidative addition of secondary alkyl halides to platinum(0) complexes,[8] and an electron-transfer mechanism is found for some oxidative addition reactions to molybdenum(0) complexes.[9] No definitive evidence has been obtained for the mechanism of oxidative addition of methyl halides. Lappert and his co-workers have proposed a free-radical non-chain mechanism for reactions with platinum(0) complexes on the basis of spin-trapping experiments[10] but most other authors, after the initial work of Chock and Halpern, prefer the S_N2 mechanism.[11,12] The solvent effects on the rate of oxidative addition of methyl iodide to $[PtPh_2(bipy)]$ indicate a polar transition state in the reaction such as is predicted for the S_N2 mechanism,[13] but, provided the platinum atom acts as a nucleophilic centre during the oxidative addition, the precise mechanism of reaction is not of fundamental significance in discussing the substituent effects on the reaction rates.

TABLE 1

Analytical data and melting points of complexes $[PtI(Me)(XC_6H_4)_2(bipy)]$

X	M.p. * (θ_c/°C)	Analysis: Found (calc.)/% C	H	N
4-OMe	226	42.6 (42.4)	3.65 (3.6)	3.8 (4.0)
4-Me	232	44.0 (44.45)	3.7 (3.7)	4.1 (4.1)
H	245	42.65 (42.7)	3.0 (3.2)	4.3 (4.3)
4-F	228	40.0 (40.4)	2.8 (2.8)	4.2 (4.1)
4-Cl	246	38.4 (38.6)	2.8 (2.7)	3.8 (3.9)
3-OMe	224	42.2 (42.4)	3.8 (3.5)	3.8 (4.0)

* All compounds decomposed upon melting.

RESULTS AND DISCUSSION

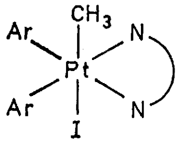
Red, orange, or yellow solutions of $[PtR_2(bipy)]$ (R = 3- or 4-XC_6H_4, X = OMe, Me, H, F, or Cl) in acetone were rapidly decolourised on addition of methyl iodide and the corresponding complexes $[PtI(Me)R_2(bipy)]$ were isolated. Complexes with highly electronegative substituents as in $[Pt(4\text{-}CF_3C_6H_4)_2(bipy)]$ or with large steric effects as in $[Pt(2\text{-}MeC_6H_4)_2(bipy)]$ failed, however, to react with methyl iodide. The complexes were characterised by elemental analysis (Table 1) and by their n.m.r. spectra (Table 2). The n.m.r. spectra indicate that the complexes have structure (1), corresponding to *trans*-oxidative addition. Thus for the 3-methoxy- and 4-methoxy-phenyl and 4-tolyl complexes only one resonance was observed for the methoxy or methyl protons respectively. The only other likely structure is (2), formed by *cis*-oxidative addition, but this contains non-equivalent aryl groups and so is not consistent with the n.m.r. data.

TABLE 2

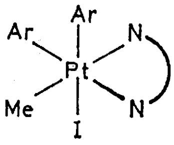
N.m.r. data for the complexes $[PtI(Me)(XC_6H_4)_2(bipy)]$

X	δ(PtMe)/ p.p.m.	^2J(PtH)/ Hz
4-OMe [a]	1.46	72.0
4-CH_3 [b]	1.36	70.8
H	1.44	70.6
4-F	1.54	70.2
4-Cl	1.47	69.0
3-OMe [c]	1.47	72.0

[a] δ(OMe) 3.84 p.p.m., singlet. [b] δ(CMe) 2.36 p.p.m., singlet. [c] δ(OMe) 3.69 p.p.m., singlet.



(1)



(2)

N N = 2,2′-bipyridyl
Ar = Aryl

The course of the reaction was followed by monitoring the decay of the MLCT band of the platinum(II) complexes at *ca.* 450 nm as the reaction progressed. Reactions were carried out at 30 °C in acetone solvent with excess of methyl iodide. Under these conditions the reactions followed pseudo-first-order kinetics and the observed rate constants were proportional to the concentration of methyl iodide (Figure 1). Thus the expected rate law, rate = $k_2[PtAr_2(bipy)][MeI]$, was established. The resulting second-order rate constants, k_2, are given in Table 3 together with similar rate constants for oxidative-addition reactions of methyl iodide to *trans*-

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$[IrCl(CO)\{P(4\text{-}XC_6H_4)_3\}_2]$ [1] and *trans*-$[RhCl(CO)\{P(4\text{-}XC_6H_4)_3\}_2]$.[2] Figure 2 shows the correlation of log k_2 for the reactions with methyl iodide with the energy of the first MLCT band in the u.v.–visible spectra of complexes $[PtR_2(bipy)]$. The observation of this correlation strongly suggests that the rate of oxidative addition in these complexes is primarily dependent on the energy of the filled *d* orbitals on platinum in the platinum(II) complexes. The correlation is good over a wide reactivity range from $[PtMe_2(bipy)]$ with k_2 2 810 dm^3 mol^{-1} min^{-1} to $[Pt(3\text{-}FC_6H_4)_2(bipy)]$ with k_2 2.34 dm^3 mol^{-1} min^{-1} at 30 °C in acetone solution. The correlation of the values of log k_2 with the Hammett σ values of the substituents X in the *meta*- and *para*-substituted derivatives $[Pt(XC_6H_4)_2(bipy)]$ is not so good. The energy of the MLCT bands for $[PtR_2(bipy)]$ has been shown to depend on specific solvation effects, and it is likely that similar effects will influence the rate of oxidative addition. Thus it is not surprising that the correlation of log k_2 with the energy of the MLCT band is better than with the Hammett σ values. The Hammett ρ values for oxidative addition of MeI to $[Pt(4\text{-}XC_6H_4)_2(bipy)]$ and to *trans*-$[IrCl(CO)\{P(4\text{-}XC_6H_4)_3\}_2]$ are −2.6 and −6.4 respectively. The ρ values per aryl group are therefore −1.3 and −1.1 respectively; that is they are only slightly different in the two cases, although the aryl groups are further removed from the metal centre in the iridium(I) complexes. Thus either the electronic effects are transmitted very effectively through the phosphorus atom to iridium, or there is a higher build-up of positive charge in the transition state for the reactions with the iridium(I) compared with the platinum(II) complexes.

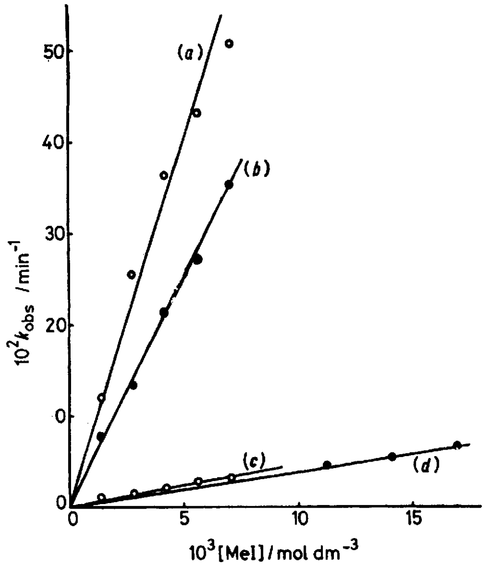

FIGURE 1 Graph of the pseudo-first-order rate constants (k_{obs}) *vs.* concentration of methyl iodide for reaction with $[Pt(4\text{-}XC_6H_4)_2(bipy)]$ in acetone at 30 °C; (*a*) X = OMe, (*b*) X = Me, (*c*) X = F; and (*d*) X = Cl

Activation energies and entropies of activation have been measured for some of the reactions, and these are listed in Table 4. It can be seen that the entropies of activation have large negative values typical of oxidative-addition reactions of methyl iodide.[1,11] The solvent effect on the rate of oxidative addition to $[PtPh_2(bipy)]$ is dominated by the $\Delta S^‡$ term, which is again typical of reactions proceeding through a highly polar transition state.[11,14] The substituent effects on the rate of oxidative addition of MeI to $[Pt(4\text{-}XC_6H_4)_2(bipy)]$ in acetone appear to operate through both the E_a and $\Delta S^‡$ terms. It is presumably this complicating feature, probably resulting from solvation effects, which leads to the rather poor correlation of the rate with the Hammett σ values of the substituents.

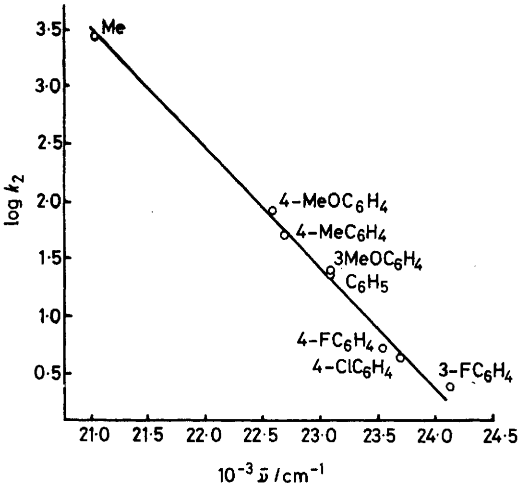

FIGURE 2 Correlation of log k_2 for oxidative addition of methyl iodide at 30 °C with the energy ($\tilde{\nu}$) of the first MLCT band for $[PtR_2(bipy)]$ in acetone solution

TABLE 3

Second-order rate constants, k_2, for reactions of methyl iodide with some complexes

R	$[PtR_2(bipy)]$ [a] k_2/dm^3 mol^{-1} min^{-1}	*trans*-$[IrCl(CO)(PR_3)_2]$ [b] k_2/dm^3 mol^{-1} s^{-1}	*trans*-$[RhCl(CO)(PR_3)_2]$ [c] k_2/dm^3 mol^{-1} s^{-1}
Me	2 810		
4-MeOC$_6$H$_4$	82.5	3.5×10^{-2}	2.8×10^{-4}
4-MeC$_6$H$_4$	50.0	1.5×10^{-2}	
C$_6$H$_5$	22.1	3.3×10^{-3}	3.4×10^{-5}
4-FC$_6$H$_4$	4.96	1.5×10^{-4}	0.75×10^{-5}
4-ClC$_6$H$_4$	4.15	3.7×10^{-5}	
3-MeOC$_6$H$_4$	24.6		
3-FC$_6$H$_4$	2.34		

[a] Solvent acetone at 30 °C. [b] Solvent benzene at 25 °C (ref. 1). [c] Solvent methyl iodide at 25 °C (ref. 2).

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[14] K. B. Wiberg, 'Physical Organic Chemistry,' Wiley, New York, 1964, pp. 379—388.

The high thermal stability of *ortho*-substituted aryl transition-metal complexes compared with the *para*-substituted analogues has often been attributed to steric hindrance. Thus in square-planar complexes the *ortho*-substituent may prevent attack at the metal centre by blocking the co-ordination sites above and below the plane.[15] Some support for this theory is given by the observation that [Pt(2-MeC$_6$H$_4$)$_2$(bipy)] does not react with methyl iodide, although its u.v.–visible spectrum shows that the *d* orbitals are of similar energy as those of [Pt(4-MeC$_6$H$_4$)$_2$(bipy)], which does react. The difference is presumably due to steric hindrance to the approach of methyl iodide to the platinum centre in the *ortho*-substituted derivative.

TABLE 4

Activation parameters for the reaction of methyl iodide with diaryl(2,2′-bipyridyl)platinum(II) complexes *

Complex	Solvent	E_a/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
[PtPh$_2$(bipy)]	Benzene	33.0	−156
	Ethyl acetate	29.2	−162
	Acetone	42.6	−114
	Nitromethane	41.7	−110
[Pt(4-MeC$_6$H$_4$)$_2$(bipy)]	Acetone	40.8	−111
[Pt(4-MeOC$_6$H$_4$)$_2$(bipy)]	Acetone	40.7	−100

* Calculated from at least five values of k_2 covering a temperature range of at least 30 °C.

EXPERIMENTAL

Diaryl(2,2′-bipyridyl)platinum(II) complexes were prepared either by displacement of cyclo-octa-1,5-diene (cod) from the corresponding complex [PtAr$_2$(cod)],[5] or by reaction of (2,2′-bipyridyl)dichloroplatinum(II) with the corresponding Grignard reagent.[16] Complexes were identified by comparison with authentic samples prepared in these laboratories.[5] Products of reaction with methyl iodide were isolated as described previously.[13] The adduct [PtI(Me)(3-FC$_6$H$_4$)$_2$(bipy)] was not isolated (the change in the u.v. spectrum during the reaction was sufficient to identify the product) and attempts to prepare [Pt(3-MeC$_6$H$_4$)$_2$(bipy)] and [Pt(3-ClC$_6$H$_4$)$_2$(bipy)] were unsuccessful. Addition of methyl iodide to [PtMe$_2$(bipy)] gave the known [PtIMe$_3$(bipy)].[17] The following complexes have not been reported previously.

2,2′-*Bipyridylbis*(4-*trifluoromethylphenyl*)*platinum*(II).—To a suspension of [PtCl$_2$(bipy)] (1.0 g) in diethyl ether (30 cm^3) was added a solution of 4-trifluoromethylphenylmagnesium bromide [from Mg (4 g) and 4-CF$_3$C$_6$H$_4$Br (3.5 g) in diethyl ether (40 cm^3)] in an atmosphere of dry nitrogen. The solution was stirred at room temperature for 2 h, then hydrolysed with ammonium chloride solution. The ether layer was separated, and the residue was further extracted with dichloromethane (50 cm^3). The combined organic layers were dried over MgSO$_4$, and evaporated to yield the *product* which was recrystallised from dichloromethane–pentane; yield 71%. A preparation from [Pt(4-CF$_3$C$_6$H$_4$)$_2$(cyclo-octa-1,5-diene)] and 2,2′-bipyridyl gave the same product in 58% yield, m.p. 225—228 °C (Found: C, 43.7; H, 2.7; N, 3.4. Calc. for C$_{24}$H$_{16}$F$_6$N$_2$Pt: C, 44.9; H, 2.5; N, 4.4%).

2,2′-*Bipyridylbis*(3-*methoxyphenyl*)*platinum*(II).— This compound was prepared similarly; m.p. 280 °C (decomp.); n.m.r. in CDCl$_3$: δ (OMe) 3.77 p.p.m. (Found: C, 51.2; H, 4.0; N, 4.6. Calc. for C$_{24}$H$_{22}$N$_2$O$_2$Pt: C, 51.0; H, 3.9; N, 5.0%).

Kinetic Studies.—Standard solutions of methyl iodide and diaryl(2,2′-bipyridyl)platinum(II) in the required solvent were prepared. They were then mixed in the required proportions, and the resultant solution was transferred to a 1-cm quartz u.v. cell held in the sample chamber of a Pye–Unicam SP 30 spectrophotometer. A Techne C-100 circulator was used to maintain the sample at the required temperature in the range 30—80 °C. The decay of the MLCT band of the platinum(II) complexes centred around 450 nm was used to monitor the course of the reactions. The initial concentration of platinum(II) complex was always *ca.* 10^{-4} mol dm^{-3}.

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