

## SOLVENT EFFECTS ON THE RATE OF OXIDATIVE ADDITION OF METHYL IODIDE TO DIPHENYL(2,2'-BIPYRIDINE)PLATINUM(II)

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### Summary

The reaction of methyl iodide with diphenyl(2,2'-bipyridine)platinum(II) to give iodo(methyl)diphenyl(2,2'-bipyridine)platinum(IV) follows the rate law,  $\text{rate} = k_2[\text{PtPh}_2(2,2'\text{-bipyridine})][\text{MeI}]$ . The values of  $k_2$  increase with increasing polarity of the solvent suggesting a polar transition state for the reaction.

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### Introduction

The UV-visible spectra of (2,2'-bipyridine)platinum(II) complexes contain two intense metal to ligand charge transfer (MLCT) bands, whose energies are strongly dependent on the nature of the other ligands bound to platinum and on the solvent. More electronegative substituents on platinum and more polar solvents cause the bands to move to higher energy [1]. The nature of the solvent effect suggests that the platinum centre is electron rich and interacts with the positive dipole of the solvent, so that the excited state (in which an electron has been excited from platinum to bipyridine) is destabilised with respect to the ground state in more polar solvents.

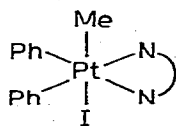
The reactivity of methyl- and ethyl-(2,2'-bipyridine)platinum(II) complexes towards alkenes and alkynes can, in many cases, be correlated with the energy of the lowest energy MLCT band, suggesting that it is the energy of the platinum *d*-orbitals which primarily determines the reactivity [2,3]. A similar correlation would be expected for reactivity of alkyl- and aryl-(2,2'-bipyridine)platinum(II) complexes towards oxidative addition reactions since in such reactions the metal centre acts as a nucleophile [4]. We are looking for this effect by studying the oxidative addition of methyl iodide and benzyl bromide to the complexes  $[(4\text{-XC}_6\text{H}_4)_2\text{Pt}(2,2'\text{-bipyridine})]$  as a function of the substituent X. Thus steric effects due to X should be negligible in these compounds, and it has already been shown [1] that the energy of the first MLCT band (and hence the energy

of the platinum *d*-orbitals) correlates well with Hammett  $\sigma$ -values of X. Preliminary results indicate that there is no correlation however, so that we are undertaking a more detailed study of the factors influencing reactivity in this system. The ability of the arylplatinum(II) complexes to undergo oxidative addition at all is remarkable, since similar complexes stabilised by tertiary phosphine ligands do not give stable arylplatinum(IV) complexes [5]. This is probably due to the greater  $\sigma$ -donor and poorer  $\pi$ -acceptor power of 2,2'-bipyridine with respect to tertiary phosphines and to its lower steric requirements. A preliminary note has been published very recently in which oxidative addition reactions of (2,2'-bipyridine)- and (1,10-phenanthroline)-platinum(II) complexes were reported [6]. This prompts us to report our investigations into the effect of solvent on the rate of reaction of methyl iodide with diphenyl(2,2'-bipyridine)-platinum(II).

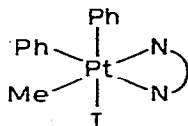
## Results

Yellow solutions of diphenyl(2,2'-bipyridine)platinum(II) in common organic solvents were rapidly decolourised on addition of methyl iodide and colourless crystals of [PtMePh<sub>2</sub>(2,2'-bipyridine)] could be isolated. Once formed the product was very sparingly soluble in common organic solvents, but a satisfactory NMR spectrum was obtained by adding one drop of methyl iodide to a suspension of [PtPh<sub>2</sub>(2,2'-bipyridine)] in dichloromethane in an NMR tube and recording the spectrum before the product began to crystallise from the resulting solution. The methylplatinum resonance appeared as a singlet at  $\delta$  1.44 ppm with satellites due to coupling with <sup>195</sup>Pt with <sup>2</sup>J(PtH) 70.6 Hz. In complexes of this type the magnitude of the coupling constant is usually sufficient to determine the stereochemistry [7], but, because the *trans*-influence of 2,2'-bipyridine and iodide are very similar, the data is consistent with the methyl group being *trans* to either ligand. Hence either stereochemistry I or II is possible.

(N N = 2,2'-bipyridine)



(I)



(II)

The stereochemistry of oxidative addition of methyl iodide to *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] has previously been shown to be *trans* by deuterium labelling studies [8], so that stereochemistry I is expected but not proved.

Since the platinum(IV) product has no MLCT band in the UV-visible spectrum, the kinetics of the reaction could be followed conveniently by monitoring the decay of the MLCT band due to [PtPh<sub>2</sub>(2,2'-bipyridine)] by UV-visible spectrophotometry. The changes in the spectrum during a typical run are shown in

Fig. 1. Graphs of  $\log(A_t - A_\infty)$  vs. time gave good straight lines indicating a first order dependence of the rate on  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  concentration, and the pseudo-first order rate constants obtained were proportional to the concentration of methyl iodide for a given solvent as shown in Fig. 2. Thus the reactions are first order in both platinum complex and methyl iodide. The resulting second order rate constants for five solvents at  $40^\circ\text{C}$  are given in Table 1, which also includes the second order rate constants for oxidative addition of methyl iodide to  $[\text{IrCl}(\text{CO}(\text{PPh}_3)_2)]$  [9] and  $[\text{Co}(\text{C}_5\text{H}_5)\text{CO}(\text{PPh}_3)]$  [10] in various solvents together with the polarity parameter [11]  $E_T$  for each solvent. In each case there is an increase in rate by a factor of 10–15 between the least polar and most polar solvents, suggesting a common mechanism with a polar transition state. Both the energy of the first MLCT band of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  and the second order rate constants for its reaction with methyl iodide give reasonable correlations with the solvent  $E_T$  values as shown in Fig. 3.

For the coordinatively unsaturated iridium(I) and platinum(II) complexes several mechanisms are possible within this framework [4,9,12], but for the coordinatively saturated  $[\text{Co}(\text{C}_5\text{H}_5)\text{CO}(\text{PPh}_3)]$ , which gives  $[\text{Co}(\text{C}_5\text{H}_5)\text{Me}(\text{CO})(\text{PPh}_3)]^+\text{I}^-$  in the rate-determining step the possible mechanisms are very limited. The most likely mechanism involves nucleophilic attack by cobalt on the carbon atom of methyl iodide (an  $S_N2$  reaction), with the only reasonable alternative involving an initial electron transfer to give  $[\text{Co}(\text{C}_5\text{H}_5)\text{CO}(\text{PPh}_3)]^+[\text{MeI}]^-$  followed by rapid rearrangement\*. Thus by analogy, the most likely mechanism of reaction of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  with methyl iodide involves

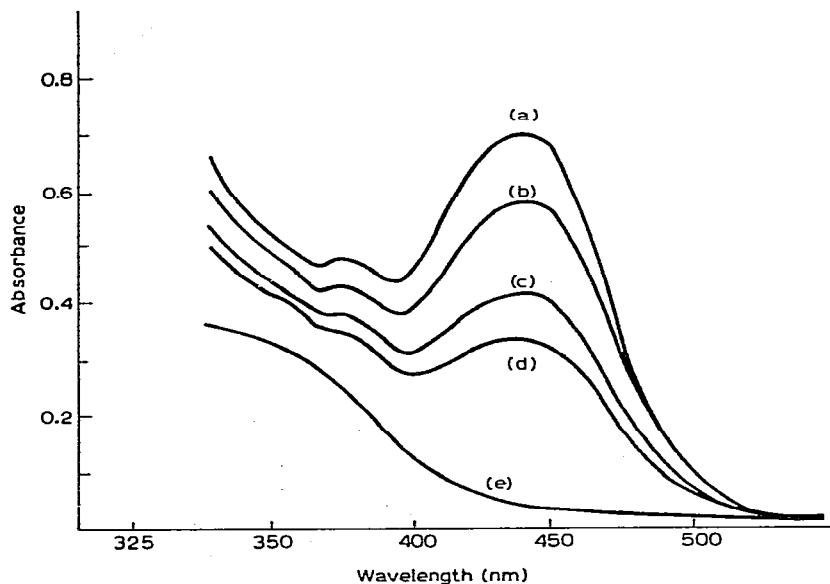


Fig. 1. Changes in the UV-visible spectrum during the reaction in dichloromethane at  $40^\circ\text{C}$  with  $[\text{MeI}] = 2.82 \times 10^{-3} \text{ M}$ : (a)  $t = 0$ , (b)  $t = 4$  min, (c)  $t = 10$  min, (d)  $t = 14$  min, (e)  $t = \infty$ .

\* Compare the mechanism of formation of Grignard reagents [13].

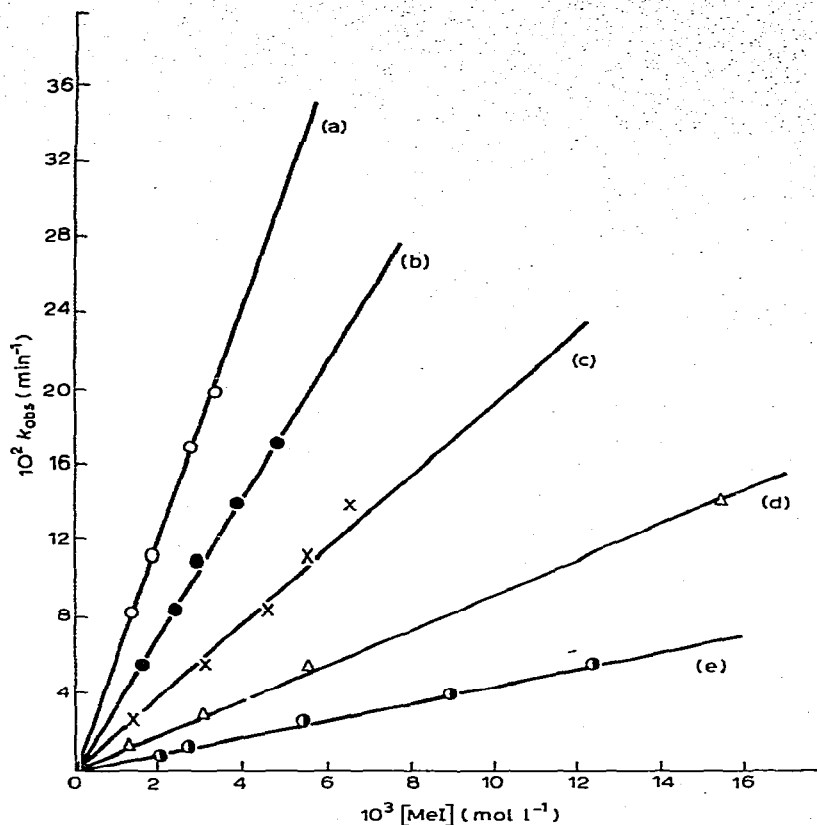


Fig. 2. Graph of the psuedo-first order rate constants ( $k_{obs}$ ) vs. concentration of methyl iodide for the reaction at 40°C in solvents; (a) nitromethane, (b) acetone, (c) dichloromethane, (d) ethyl acetate (e) benzene.

TABLE 1

SOLVENT EFFECTS ON THE SECOND ORDER RATE CONSTANTS FOR REACTIONS WITH METHYL IODIDE

Solvent	$E_T$	[PtPh <sub>2</sub> (bipy)] $k_2$ (40°C) (l mol <sup>-1</sup> min <sup>-1</sup> )	[IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] $k_2$ (25°C) (l mol <sup>-1</sup> min <sup>-1</sup> )	[Co(C <sub>5</sub> H <sub>5</sub> )(CO)(PPh <sub>3</sub> )] $k_2$ (25°C) (l mol <sup>-1</sup> sec <sup>-1</sup> )
Toluene	33.9		0.15	
Benzene	34.5	6.5	0.21	
Tetrahydrofuran	37.4			6
Chlorobenzene	37.5		0.46	
Ethyl acetate	38.1	11.3		
Chloroform	39.1		1.85	
Dichloromethane	41.1	21	1.10	25.7
Acetone	42.2	40.5	1.20	22.2
<i>N,N</i> -Dimethylformamide	43.8		1.70	60
Acetonitrile	46.0			
Nitromethane	46.3	89		

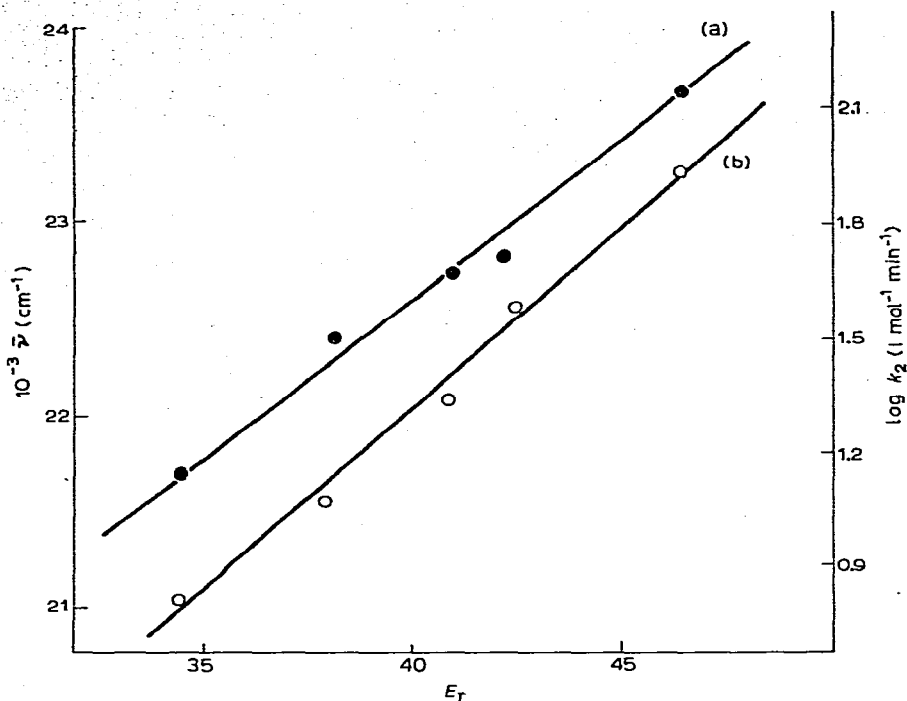


Fig. 3. Correlation of (a) energy of the first MLCT band of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  and (b)  $\log k_2$ , where  $k_2$  is the second order rate constant for reaction with methyl iodide, with the  $E_T$  values of the solvents.

nucleophilic attack by platinum on the carbon atom of MeI to give  $[\text{PtMePh}_2(2,2'\text{-bipyridine})]^+\text{I}^-$  which rapidly rearranges to  $[\text{PtIMEPh}_2(2,2'\text{-bipyridine})]$ .

### Experimental

Diphenyl(2,2'-bipyridine)platinum(II) was prepared as described earlier [1].

#### *Iodo(methyl)diphenyl(2,2'-bipyridine)platinum(IV)*

To a suspension of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  (0.10 g) in dichloromethane (10 ml) was added methyl iodide (0.5 ml). After stirring the mixture for 10 min a clear solution was obtained. Diethyl ether was added dropwise until the solution became cloudy and the mixture was set aside in the refrigerator, when colourless needles of the product crystallised. Yield 0.085 g, m.p. 245°C (dec.) (Found: C, 42.65; H, 3.0; N, 4.3.  $\text{C}_{23}\text{H}_{21}\text{IN}_2\text{Pt}$  calcd.: C, 42.7; H, 3.2; N, 4.3%).

#### *Kinetic studies*

Standard solutions of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  and methyl iodide in the required solvent were prepared. They were then mixed in the required proportions, and the resulting solution transferred to a 1 cm quartz UV cell which was held in the electrically heated thermostatted cell compartment of a Unicam SP 8000 spectrophotometer. Spectra were then recorded as the reaction proceeded. The concentration of  $[\text{PtPh}_2(2,2'\text{-bipyridine})]$  was about  $10^{-4}$  M at the start of each reaction.

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