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Journal of Organometallic Chemistry 599 (2000) 166–169

Solvent effects on the rate of oxidative addition of methyl iodide to di(4-thiocresol)(2,2′-bipyridyl) platinum(II)

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Received 24 November 1998; received in revised form 9 December 1999

Abstract

The reaction of methyl iodide with di(4-thiocresol)(2,2′-bipyridyl) platinum(II) to give iodo (methyl) di(4-thiocresol)(2,2′-bipyridyl) platinum(IV) follows the rate law, rate = K_2[Pt-(4-thiocresol)$_2$ (2,2′-bipyridyl)] [MeI]. The values of K_2 increase with increasing polarity of the solvent, suggesting a polar transition state for the reaction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxidative addition; Platinum; Solvent effects

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1. Introduction

It has been shown [1] that the UV–vis spectra of bipyridyl 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.

The reactivity of alkyl and aryl-(2,2′-bipyridyl) platinum(II) complexes towards oxidative addition reactions can be correlated with the energy of the lowest-energy MLCT band [2], suggesting that it is the energy of the platinum d-orbitals that primarily determines the reactivity [1,3–5], and since in such reactions the metal centre acts as a nucleophile [6]. We are looking for this effect by studying the oxidative addition of methyl iodide to the complexes [4X-$C_6H_4S)_2$ Pt(2,2′-bipyridyl)] 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 σ-values of X.

The ability of the aryl platinum(II) complexes to undergo oxidative addition at all is remarkable since similar complexes stabilized by tertiary phosphine ligands do not give stable aryl platinum(IV) complexes [7]. This is probably due to the greater σ-donor and poorer π-acceptor power of 2,2′-bipyridyl with respect to tertiary phosphines and to its lower steric requirements. The oxidative-addition reactions of methyl iodide to (2,2′-bipyridyl) and (1,10-phenanthroline) platinum (II) complexes has been reported [8]. 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 [16], provided the platinum atom acts as a nucleophilic centre during the oxidative addition.

Bipyridine platinum (II) thiolates have been synthesized and characterized [9]. Some transition-metal thiolate complexes have been synthesized recently [10–14]. This prompted us to report the solvent effects on the rate of oxidative addition of methyl iodide to di(4-thiocresol) (2,2′-bipyridyl) platinum(II).

2. Results

Orange solutions of di(4-thiocresol)(2,2′-bipyridyl) platinum(II) in common organic solvents turned yellow

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PII: S0022-328X(99)00759-7

on addition of methyl iodide and yellow crystals of [PtIMe(4-thiocresol)$_2$(2,2′-bipyridyl)] 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 [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] in chloroform in an NMR tube and recording the spectrum before the product began to crystallize from the resulting solution. The methyl of the 4-thiocresol appeared as a singlet at 2.34 ppm, and the methyl platinum resonance appeared as a singlet 1.34 ppm with satellites due to coupling of ^{195}Pt with 2_j(PtH) 70.6 Hz. The magnitude of the coupling constant in such complexes is usually sufficient to determine the stereochemistry [15], but because the *trans*-influences of 2,2′-bipyridyl and iodide are very similar, either stereochemistry I or II is possible.

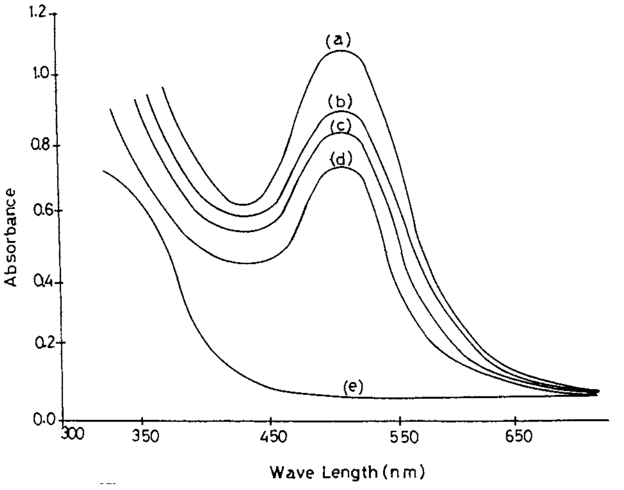


Fig. 1. Changes in the UV–vis spectrum during the reaction in chloroform at 30°C with [MeI]: (a) $t = 0$; (b) $t = 20$ min; (c) $t = 40$ min; (d) $t = 60$ min; (e) $t = \infty$.

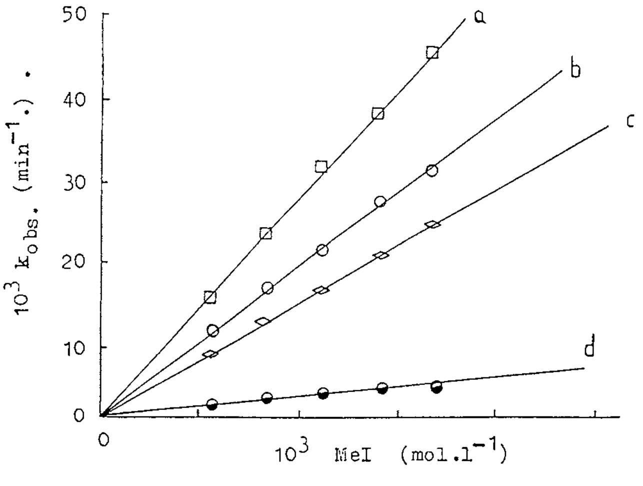
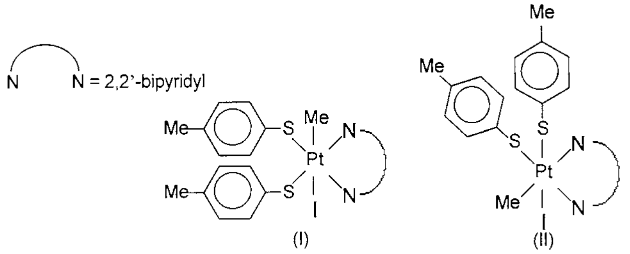


Fig. 2. Graph of the psuedo-first-order rate constants ($k_{obs.}$) vs. concentration of methyl iodide of the reaction at 30°C in solvents: (a) methyl cyanide; (b) acetone; (c) dichloromethane; (d) chloroform.



The stereochemistry of oxidative addition of methyl iodide to *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] has previously been shown to be *trans* by deuterium labelling studies [16]. The NMR spectrum indicates that the complex has structure I, corresponding to *trans*-oxidative addition. Thus for the 4-methyl group of the thiocresol only one resonance was observed for the methyl protons. The only other likely structure is II, formed by *cis*-oxidative addition, but this contains non-equivalent aryl groups and so is not consistent with the NMR spectrum.

Since the platinum(IV) product has no MLCT band in the UV–vis spectrum, the kinetics of the reaction could be followed conveniently by monitoring the decay of the MLCT band due to [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] by UV–vis spectrophotometry. The changes in the spectrum during a typical run are shown in Fig. 1. Graphs of $\log(A_t - A_\infty)$ versus time gave good straight lines, indicating a first-order dependence of the rate on [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] 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 four solvents at 30°C are given in Table 1, which also includes the second-order rate constants for oxidative addition of methyl iodide to [PtPh$_2$(bipy)] [4] and [IrCl(CO)PPh$_3$)$_2$] [17] in various solvents together with the polarity parameter [18] E_T for each solvent. In each case there is an increase in rate by a factor of about 10–15 between the least-polar and most-polar solvents, suggesting a common mechanism with a polar transition state. Activation energy and entropy of activation have been measured for the reaction, and they are 55 kJ mol^{-1} and -140 J mol^{-1} K^{-1}, respectively. It can be seen that the entropy of activation has a large negative value typical of oxidative-addition reactions of methyl iodide [19,20]. The mechanism of the reaction of diaryl (2,2′-bipyridyl) platinum (II) complexes with methyl iodide has already been shown [4,5] to involve nucleophilic attack by platinum on the carbon atom of MeI to give [PtMePh$_2$(2,2′-bipyridyl)]$^+$I$^-$, which rapidly rearranges to [PtIMePh$_2$(2,2′-bipyridyl)]. Thus by analogy, the most likely mechanism of reaction of [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] with methyl iodide involves nucleophilic attack by platinum on the carbon

Table 1
Solvent effects on the second-order rate constants for reactions with methyl iodide

Solvent	E_T	$Pt(4\text{-thiocresol})_2(bipy)$ k_2 (30°C) ($l\ mol^{-1}\ min^{-1}$)	$PtPh_2(bipy)$ k_2 (40°C) ($l\ mol^{-1}\ min^{-1}$)	$IrCl(CO)(PPh_3)_2$ k_2 (25°C) ($l\ mol^{-1}\ min^{-1}$)
Toluene	33.9		0.15	
Benzene	34.5		6.5	0.112
Tetrahydrofuran	37.4			
Chlorobenzene	37.5		0.46	
Ethyl acetate	38.1		11.3	
Chloroform	39.1	0.14		1.85
Dichloromethane	41.1	0.71	21	1.10
Acetone	42.2	0.88	40.5	1.20
N,*N*-Dimethyl-formamide	43.8		1.70	
Acetonitrile	46.0	1.40		
Nitromethane	46.3		89	

atom of MeI to give the intermediate, which rapidly rearranges to the final product.

3. Experimental

Di(4-thiocresol)(2,2′-bipyridyl) platinum(II) was prepared as shown below.

Recrystallized dichloro (2,2′-bipyridyl) platinum(II) (1.0 mmol) in chloroform (15ml) was added to a magnetically stirred solution of 4-thiocresol (2.0 mmol) in deionized distilled water (15 ml) containing potassium hydroxide (2.2 mmol) and benzyl triphenyl phosphonium chloride (PTC) (0.1 mmol) at 30°C in a 100 ml flask, equipped with an N_2 inlet, water-cooled condensor and a thermometer. After stirring for 1 h under N_2, the organic layer was separated and the aqueous layer extracted (three times) with chloroform.

The chloroform fractions were dried over anhydrous magnesium sulphate. The solution was filtered and the chloroform evaporated under vacuum, to give a red solid.

Yield (80%). M.p. 336°C (dec.) found: C, 48.06; H, 3.64; N, 4.62. Anal. Calc. for $C_{24}H_{22}N_2S_2$: C, 48.23; H, 3.71; N, 4.69%.

The comparison of IR spectra shows the disappearance of the weak band at (2600–2620) cm^{-1}, which was attributed to the stretching peak of (S–H) of the free ligand the two bands at (300, 340) cm^{-1}, which was attributed to the (Pt–Cl) stretch of dichlorobipyridyl–platinum (II). At the same time a new strong band at 485 cm^{-1} appeared, which was attributed to the (Pt–S) bond stretch. This may confirm the formation of a new complex, which may be a square-planar *cis*-complex because the bonding of the stabilizing ligand (bipy) is in the *cis*-form. This suggestion is confirmed by the formation of one band for the bond (Pt–S) as well as one medium band at 402 cm^{-1} belonging to the band (Pt–N). Also a strong band at 1000 cm^{-1} appears, which is attributed to the (C–S) vibration in the spectra of the ligand and the new complex formed, whereas there is no such band in the spectrum of dichlorobipyridyl platinum(II).

The UV–vis spectra of (2,2′-bipyridyl) platinum(II) complexes contain two intense MLCT bands, whose energies are strongly dependent on the nature of the 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]. We have found this to be so.

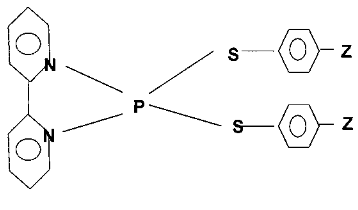
Similar assignment can be made for the dithiolato (2,2′-bipyridyl) platinum(II) complexes studied here, though the energy of the MLCT bands was very sensitive to the nature of the thiolato group bound to platinum.

The lowest energy MLCT band for $[Pt(p\text{-}ZC_6H_4)_2(bipy)]$ complexes was as follows: Z = CH_3 (522 nm), H (475 nm), Br (462 nm), Cl (457 nm). The same band of these complexes in methylcyanide solution was at 502 nm and in acetone the band had moved to 516 nm while in dichloromethane it was at 522 nm and in chloroform the band had moved to 530 nm.

The UV–vis spectra were used mainly to characterize the dithiolato (2,2′-bipyridyl) platinum(II) complexes by comparison with similar samples prepared earlier [1].

The elemental analyses of the new complexes were generally in good agreement with theoretical values.

The IR, UV–vis spectra and elemental analyses are consistent with complexes of the form:



Iodo (methyl) di(4-thiocresol)(2,2′-bipyridyl) platinum-(IV): To a suspension of [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] (1 mmol) in dichloromethane (10 ml) was added methyl iodide (excess). After stirring the mixture for 10 min a yellow solution was obtained. Diethyl ether was added dropwise until the solution became cloudy and the mixture was set aside in the refrigerator, when yellow crystals of the product crystallized. Yield 85%, m.p. 267°C (dec.) Found: C, 40.34; H, 3.39; N, 3.64. Anal Calc. for $C_{25}H_{25}IN_2S_2Pt$: C, 40.59; H, 3.40; N, 3.78%.

4. Kinetic studies

Standard solutions of [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] and MeI 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 Philips pu 8620 UV/VIS/NIR spectrophotometer. Spectra were then recorded as the reaction proceeded. The concentration of [Pt(4-thiocresol)$_2$(2,2′-bipyridyl)] was about 10^{-4} M at the start of each reaction.

References

[1] N. Chaudhury, R.J. Puddephatt, J. Organomet. Chem. 84 (1975) 105.

[2] R. Brady, B.R. Flynn, G.L. Geoffory, H.B. Gray, J. Peone, L. Vaska, Inorg. Chem. 15 (1976) 1485.

[3] N. Chaudhury, M.G. Kekre, R.J. Puddephatt, J. Organomet. Chem. 73 (1979) C17.

[4] J.K. Jawad, R.J. Puddephatt, J. Organomet. Chem. 117 (1976) 297.

[5] J.K. Jawad, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1977) 1466.

[6] A.J. Deeming, M.T.P. International Review of Science, Inorganic Chemistry, series one, Butterworth, London, 1972, Chapter 4.

[7] T.G. Appleton, H.C. Clark, L.E. Manzer, J. Organomet. Chem. 65 (1974) 275.

[8] R. Uson, J. Fronies, P. Espinet, J. Garin, Syn. React. Inorg. Met. Org. Chem. 7 (1977) 211.

[9] J.A. Hammud, MSc. Thesis, 1989, University of Salahaddin, Erbil, Iraq.

[10] D. Cruz-Garritz, P. Sosa, H. Torrens, A. Hill, D.L. Hughes, R.L. Richards, J. Chem. Soc. Dalton Trans. 3 (1989) 419.

[11] S. Dev, K. Imagawa, Y. Mizobe, G. Cheng, Y. Wakatsuki., H. Yamazaki, M. Hidai, Organometallics 8 (1989) 1232.

[12] A. Shaver, R.D. Lai, Inorg. Chem. 27 (1988) 4664.

[13] C. Xu, J.W. Sirice, G.K. Anderson, Inorg. Chim. Acta 206 (1993) 123.

[14] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinsa, J. Chem. Soc. Dalton Trans. 10 (1993) 1509.

[15] D.E. Clegg, J.R. Hall, G.A. Swile, J. Organomet. Chem. 38 (1972) 403.

[16] M.P. Brown, R.J. Puddephatt, C.E.E. Upton, J. Chem. Soc. Dalton Trans. (1974) 2457.

[17] H. Stieger, K. Kelm, J. Phys. Chem. 77 (1973) 29.

[18] C. Reichardt, Angew. Chem. Int. Ed. 4 (1965) 29.

[19] R. Ugo, A. Pasini, A. Fusi, S. Cenini, J. Am. Chem. Soc. 94 (1974) 7364.

[20] P.B. Chock, J. Halpern, J. Am. Chem. Soc. 88 (1966) 3511.