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Synthesis and kinetic studies of new bipyridyl platinum(II) phenoxide complexes by phase transfer catalysis: Crystal structure of [(bipy)Pt(OC_6H_4-4-OMe$)_2$]

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ABSTRACT

The synthesis of new platinum bipy (bipy = 2,2′-bipyridyl) complexes containing phenoxide ligands is reported, together with kinetic studies of their oxidative addition reactions with MeI to produce phenoxo platinum(IV) complexes. Complexes of the form [(bipy)Pt(OC_6H_4-4-X$)_2$] (X = OCH_3, CH_3, H, Br, Cl) are prepared by the reaction of the chloro complex [(bipy)$PtCl_2$] with substituted phenols and KOH in a two phase system of water and chloroform in the presence of benzyl triphenylphosphonium chloride. Platinum(IV) complexes are formed by oxidative addition of MeI to the platinum(II) complexes obtained. The complexes are characterized by elemental analysis, UV–Vis, IR, mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy.

The reaction of methyl iodide with [(bipy)Pt(OC_6H_4-4-OMe$)_2$] to give [(bipy)PtMe(I)(OC_6H_4-4-OMe$)_2$] follows the rate law rate = k_2[(bipy)Pt(OC_6H_4-4-OMe$)_2$][MeI]. The values of k_2 increase with increasing polarity of the solvent, suggesting a polar transition state for the reaction.

1. Introduction

An earlier belief that the metal-to-oxygen bond is weak, as a result of the occurrence of antibonding π-interactions between filled metal d-orbitals and oxygen lone pairs [1], may have limited research in this area and reports concerning late transition metal alkoxides and aryloxides are still rare, in particular when the other ligands are mono- or bidentate tertiary amines. It is now recognized, however, that the metal to-oxygen bond may be of comparable strength or even stronger than the metal-to-carbon (sp^3) bond [2].

There has been a steady development of interest in phenoxide and aryloxide transition metal complexes because of their importance in many areas of science, and this area still attracts much attention. The reason for this continuing interest is that such complexes have been postulated as key intermediates in various transition metal-catalysed processes [3]. In biology, for example, metal–phenoxide linkages are formed between a metal and the phenolic side chain of tyrosine. Metal sequestration units often have multiple phenoxide donor atoms for chelation such as enterobactin [4].

Metal centres also bind to phenoxide ligands during oxidation of phenols to ketones as in catecholase [5,6]. Late metal aryloxides had been less well studied than early transition metal derivatives [7], but more recent works [8,9], including this paper, address the disparity [10].

Platinum(II) complexes with phenoxide ligands have been synthesized by many different methods. The phenoxo complexes [M(OPh$)_2$($PPh_3)_2$] (M = Pd, Pt) have reportedly been prepared by reaction of [M($PPh_3)_4$] with phenol [11], and monophenoxo complexes of palladium [12,13] and platinum [13,14] have also been prepared. The preparation of [Pt(OMe$)_2$(dppe)] has been reported [15], as well as the complex [Pt(OPh$)_2$(dppe)] which exhibits quite different reactivity [16]. The complexes of the type [M(EPh$)_2$(dppe)] (M = Pt, Pd; E = O, S, Se) have been prepared previously [16]. The reaction of [PtMe$_2$(bipy)] with phenol affords the complex [Pt(Me)(OPh)(bipy)] [17]. A series of complexes of formula [M(OR)(terpy)]BF_4 (M = Pd, Pt; terpy = 2,2′:6′,2″-terpyridine) have been prepared by reaction of [M(OH)(terpy)]BF_4 with ROH [18]. Recently, some late transition metal fluoroaryloxide complexes have been reported including the platinum complex [(cod)Pt($OC_6F_5)_2$] which was prepared by reaction of [(cod)$PtCl_2$] with KOC_6F_5 in THF [9].

As the chemical industry strives to increase efficiency, improve process safety, and reduce environmental impact, phase transfer catalysis (PTC) has become recognized as a useful tool for achieving these goals [19]. Phase transfer catalysis is useful primarily for performing reactions between anions (and certain neutral molecules and transition metal complexes) and organic substrates. PTC is needed because many anions (in the form of their salts) and neutral compounds are soluble in water but not in organic solvents,

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whereas the organic reactants are not usually soluble in water. The catalyst acts as a shuttling agent by extracting the anion or neutral compound from the aqueous (or solid) phase into the organic reaction phase (or interfacial region) where the anion or neutral compound can freely react with the organic reactant already located in the organic phase. Reactivity is further enhanced, sometimes by orders of magnitude, because once the anion or neutral compound is in the organic phase, it has very little (if any) hydration or solvation associated with it, thereby greatly reducing the energy of activation [20]. It has been shown [21] that there are several advantages in using PTC such as an increased reaction rate, a lower reaction temperature, avoiding the need for expensive anhydrous or aprotic solvents, and the use of water together with an organic solvent as reaction medium.

Inorganic polymers incorporating phosphorus, nitrogen and sulfur as well as silicon and oxygen, are being designed to provide the sophisticated materials of the future [22]. Platinum-containing polymers [23,24] have been prepared by the interfacial polymerization of diamines with potassium tetrachloroplatinate(II) in the absence of a catalyst. We have synthesized [25] some new platinum-containing polymers by phase transfer polymerization between various bisphenolate anions and *cis*-dichlorobis(dimethylphenylphosphine)platinum(II) in a two phase system of water and chloroform in the presence of dibenzo-24-crown-8. Recently, interfacial polycondensation of bisphenols with alkyl(aryl) phosphonic dichlorides using PTC has been shown to be the most important method [26,27] which generates polyphosphonates and polyphosphates, and yields linear, solid and high molecular weight polymers [28]. We have previously reported the synthesis of platinum phosphine complexes containing N-(substituted aryl or benzyl)-γ-mercaptobutyramides using phase transfer catalysis. Complexes of the form $[Pt(PMe_2Ph)_2\{S(CH_2)_3CONHC_6H_4\text{-}4\text{-}X\}_2]$, where X = OCH_3, CH_3, Cl or benzyl, have been synthesized by the reaction of *cis*-dichlorobis(dimethylphenylphosphine)platinum(II) with the corresponding N-(substituted aryl or benzyl)-γ-mercaptobutyramide in a two phase system of water and chloroform in the presence of benzyl triphenylphosphonium chloride [29].

It has been shown [30] 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 also 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 [31], suggesting that it is the energy of the platinum d-orbitals that primarily determines the reactivity [30,32–34], since in such reactions the metal centre acts as a nucleophile [35]. We are examining this effect by studying the oxidative addition of methyl iodide to the complexes $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$ as a function of the substituent X. Steric effects due to X should be negligible in these compounds, and it has already been shown [29] 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 [36]. This is probably due to the greater σ-donor and poorer π-acceptor power of bipy compared to tertiary phosphines and to its lower steric requirements. The oxidative addition reactions of methyl iodide to platinum(II) 2,2′-bipyridyl and 1,10-phenanthroline complexes has been reported [37]. Solvent effects on the rate of oxidative addition of methyl iodide to $[PtPh_2(bipy)]$ have been studied [33] and a polar transition state has been suggested for the reaction such as predicted for the S_N2 mechanism [38] provided the platinum atom acts as a nucleophilic centre during the oxidative addition. Jawad et al. [39] also reported solvent effects on the rate of oxidative addition of MeI to di(4-thiocresolate)(2,2′-bipyridyl)platinum(II) and they concluded that the most likely mechanism of reaction of $[(bipy)Pt(SC_6H_4\text{-}4\text{-}Me)_2]$ with the methyl iodide involves nucleophilic attack by platinum on the carbon atom of MeI to give an intermediate which rapidly rearranges to the final product.

In this work, we demonstrate an alternative approach, namely by using phase transfer catalysis (PTC) as a new method to obtain our new complexes, and we have concentrated on compounds containing the bipy ligand. One reason for this is that aryloxo complexes of this type (containing the bipy ligand) have not, to our knowledge, previously been reported.

2. Results and discussion

In this work bipyridyl platinum(II) phenoxides have been synthesized in two different ways for comparison. Firstly the reaction of the chloro complex $[(bipy)PtCl_2]$ with substituted phenols and KOH in dichloromethane provides precipitates of red solid complexes that, when washed with Et_2O, afford the new platinum(II) phenoxide complexes in good yield. The new compounds were characterized in the usual ways.

The same series of the bipyridyl platinum(II) phenoxides have also been prepared by the reaction of the chloro complex with substituted phenols and KOH in a two phase system of water and chloroform in the presence of benzyl triphenylphosphonium chloride following the general reaction scheme:

$$[PtCl_2(bipy)] + 2KOH + 2(4\text{-}X\text{-}C_6H_4OH) \xrightarrow[CHCl_3/H_2O,\ 30^\circ C]{BTPPC} [(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2] + 2KCl + 2H_2O$$

where X = OCH_3, CH_3, H, Br, Cl; BTPPC = benzyl triphenylphosphonium chloride.

We have found that using phase transfer catalyst (PTC) increased both the reaction rate and the percentage yield, and also allowed a decrease in the required reaction temperature. Thus, treatment of yellow recrystallized dichloro(2,2′-bipyridyl)platinum(II) in chloroform with phenoxides in deionized distilled water containing potassium hydroxide (N.B. precautions should be taken with reactions containing chloroform and a base) and benzyl triphenylphosphonium chloride as a PTC agent under an inert atmosphere at 30 °C gave the red phenoxide complexes which are stable in air and were characterized by elemental analyses, IR, UV–Vis, and NMR spectra.

The elemental analyses of the new complexes were generally in good agreement with theoretical values. Table 1 shows the physical properties of the $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$ complexes, and Table 2 shows the physical properties of the corresponding Pt(IV) complexes $[(bipy)PtMe(I)(OC_6H_4\text{-}4\text{-}X)_2]$.

The UV–Vis spectra were used mainly to characterize the diphenoxo(2,2′-bipyridyl)platinum(II) complexes by comparison with similar samples prepared earlier [30]. As noted earlier, the energies of the two intense MLCT bands in the UV–Vis spectra of (2,2′-bipyridyl)platinum(II) complexes are strongly dependent on the nature of the ligands bound to platinum and on the solvent. In the diphenoxo(2,2′-bipyridyl)platinum(II) complexes studied here, the energy of the MLCT bands was very sensitive to the nature of the phenoxo group bound to platinum. The lowest energy MLCT band for the $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$ complexes was observed as follows: X = OCH_3 (525 nm), CH_3 (500 nm), H (475 nm), Br (462 nm), Cl (457 nm). The same band of these complexes (e.g.: X = OCH_3) in acetonitrile solution was at 502 nm and in acetone the band moved to 516 nm while in dichloromethane it was at 522 nm and in

Table 1
Physical properties of $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$.

Group X	Melting point (°C)	Yield (%)	Colour	CHN	% Calc.	(Found)
				C	H	N
H	252–255d	78	red	49.16	3.38	5.21
				(49.18)	(3.32)	(5.12)
Cl	246–248d	89	red	43.58	2.66	4.62
				(43.57)	(2.67)	(4.67)
Br	236–238d	80	red	38.00	2.32	4.03
				(38.10)	(2.36)	(3.96)
CH_3	245–247d	82	red	50.97	3.92	4.95
				(51.07)	(3.89)	(5.10)
OCH_3	250–252d	90	red	48.24	3.71	4.69
				(48.09)	(3.69)	(4.65)

d = decomposed.

Table 2
Physical properties of Pt(IV) complexes $[(bipy)PtMe(I)(OC_6H_4\text{-}4\text{-}X)_2]$.

Group X	Melting point (°C)	Yield (%)	Colour	CHN	% Calc.	(Found)
				C	H	N
H	242–244d	73	yellow	40.66	3.12	4.12
				(40.76)	(3.10)	(4.09)
Cl	236–238d	80	yellow	36.92	2.56	3.74
				(36.84)	(2.54)	(3.76)
Br	230–232d	81	yellow	33.00	2.29	3.35
				(32.95)	(2.18)	(3.10)
CH_3	238–240d	84	yellow	42.44	3.56	3.96
				(42.22)	(3.50)	(3.94)
OCH_3	240–242d	89	yellow	40.61	3.41	3.79
				(40.58)	(3.36)	(3.72)

Table 3
IR spectra of $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$.

Compound	Wavenumber (cm^{-1})	Intensity	Assignment
H	810[a]	m	Pt–O
	1020	m	C–O
Cl	814[a]	s	Pt–O
	1010	m	C–O
Br	814[a]	s	Pt–O
	1020	m	C–O
CH_3	760[a]	s	Pt–O
	1030	m	C–O
OCH_3	752[a]	s	Pt–O
	1032	s	C–O

Where: m = medium, s = strong.
[a] peak is split into two.

chloroform at 530 nm. We have thus again confirmed that more electronegative substituents on platinum and more polar solvents cause the bands to move to higher energy.

By comparing the IR spectra of diphenoxoplatinum(II) complexes with the starting materials one notices the disappearance of the weak band at 3640–3600 cm^{-1}, which was attributed to the OH stretching peak of the free ligand and the two bands at 300–340 cm^{-1}, which were attributed to the Pt–Cl stretch of the complex $[PtCl_2(bipy)]$. At the same time a new strong band at 752–814 cm^{-1} appeared, which is attributed to the Pt–O bond stretch. This confirms the formation of a new square planar complex with, of necessity, a *cis*-geometry enforced by the bipy ligand. This is confirmed by the formation of one band (split in two) for the Pt–O stretch as well as one medium band at 680–714 cm^{-1} belonging to the Pt–N bond. A strong band at 1010–1032 cm^{-1} is also evident in the spectra of the ligand and the new complex, and is attributed to the C–O vibration, whereas there is no such band in the spectrum of $[PtCl_2(bipy)]$. Table 3 shows assignments of some characteristic frequencies in the IR spectra of $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$ which compared with related complexes [40,41].

Chemical shifts in the ^1H NMR spectra of the starting materials and complexes are tabulated in Table 4, with the corresponding ^{13}C NMR data given in Table 5. Because of some experimental problems due to solubility we report the spectral data of the starting materials and one of the products. Fig. 1 shows the structural formula of the complex $[(bipy)Pt(OC_6H_4\text{-}4\text{-}OMe)_2]$ with the carbon atoms numbered to clarify the chemical shifts in Tables 4 and 5.

Intense red crystals of $[(bipy)Pt(OC_6H_4\text{-}4\text{-}OMe)_2]$ suitable for single crystal X-ray structure determination were grown from $CH_2Cl_2/Et_2O/n$-pentane. The molecular structure of the complex in the crystal is shown in Fig. 2; a summary of the crystallographic details of the X-ray analysis of is given in Table 6. Selected bond distances and angles for $[(bipy)Pt(OC_6H_4\text{-}4\text{-}OMe)_2]$ are compiled in Table 7. Comparison with related structures such as [(bipy)PtMe(OPh)] [17], $[(cod)Pt(OC_6F_5)_2]$ [9], *trans*-$[Pt(H)(OPh)(PEt_3)_2]$ [14] and *trans*-$[Pt(H)(OPh)(PBz_3)_2]$ [13] reveals similar gross features e.g. the Pt–O distances of 2.018(3) and 2.019(3) Å in the current molecule compared with a range of 2.014–2.130 Å in the quoted complexes, and the somewhat enlarged Pt–O–C angles of 119.6(2) and 123.0(3)° in the aryloxide ligands.

In addition to the platinum complex, and because the sample that the crystals were grown from came from the PTC reaction (i.e., not analytically pure complex) the unit cell contains a water molecule, and a molecule of 4-methoxyphenol, the phenolic –OH of which is hydrogen bonded to a second water molecule. This phenol molecule, which was also identified by mass spectroscopy (*m*/*z* 124), is situated on a crystallographic inversion centre and is twofold disordered.

Orange solutions of the $[(bipy)Pt(OC_6H_4\text{-}4\text{-}X)_2]$ complexes in common organic solvents turned yellow on addition of methyl iodide and yellow crystals of $[(bipy)PtMe(I)(OC_6H_4\text{-}4\text{-}X)_2]$ could be isolated. Once formed, the product was very sparingly soluble in common organic solvents, but a satisfactory NMR spectrum

Table 4
Assignment of the characteristic chemical shifts in ^{1}H NMR spectra.

Compound	Chemical shifts of aromatic protons, δ (ppm)	Chemical shifts of non-aromatic protons, δ (ppm)
[(bipy)$PtCl_2$] in DMSO-d_6	8.61 (d, $H_{(3)}$, J = 8.0 Hz), 8.41 (t, $H_{(4)}$, J = 7.8 Hz), 7.89 (t, $H_{(5)}$, J = 6.8 Hz), 9.54 (d, $H_{(6)}$, J = 5.6 Hz)	
4-Methoxyphenol in $CDCl_3$ solution	6.77 (d, 2H), 6.76 (d, 2H)	3.75 (s, 3H, OCH_3), 5.39 (s, 1H, OH)
Complexes in $CDCl_3$ solution: e.g., [(bipy)Pt(OC_6H_4-4-OMe)$_2$]	9.30 (d, 2H, C_6), 8.20 (t, 2H, C_9), 7.57 (t, 2H, C_8), 7.12 (t, 2H, C_7), 6.62 (t, 2H, C_1), 6.60 (t, 2H, C_2)	3.73 (s, 3H, OCH_3)

Table 5
Assignment of the characteristic chemical shifts in ^{13}C NMR spectra.

Compound	Chemical shifts of aromatic carbons, δ (ppm)	Chemical shifts of non-aromatic carbons, δ (ppm)
[(bipy)$PtCl_2$] in $CDCl_3$ solution	157.66, 149.25, 141.42, 128.57, 125.02	
4-Methoxyphenol ($CDCl_3$ solution)	154.07 (C–OH), 149.98 (C–OCH_3), 116.54, 115.39	56.30 (OCH_3)
Complexes in $CDCl_3$ solution: e.g., [(bipy)Pt(OC_6H_4-4-OMe)$_2$]	161.77 (C_5, C_{10}), 151.13 (C_3), 150.10 (C_6), 138.42 (C_8), 122.42 (C_9), 120.12 (C_7), 115.21 (C_1), 114.6 (C_2)	56.17 (C_4)

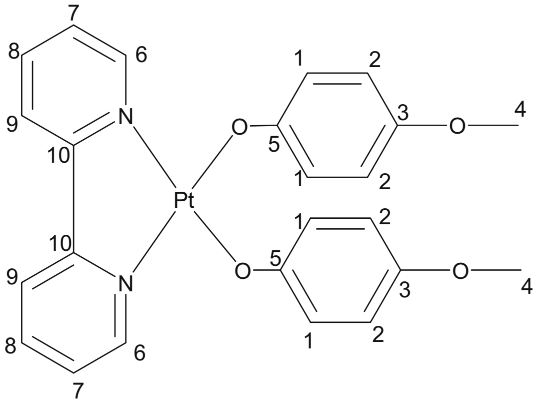


Fig. 1. The structure of the complex [(bipy)Pt(OC_6H_4-4-OMe)$_2$] with numbered carbon atoms.

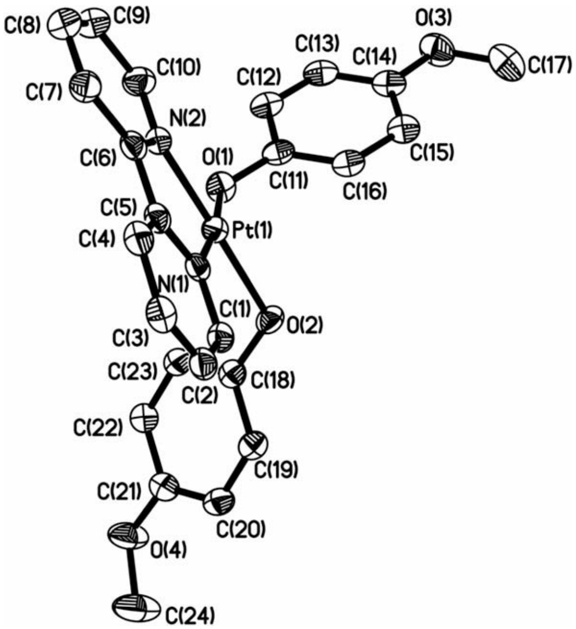


Fig. 2. ORTEP diagram of [(bipy)Pt(OC_6H_4-4-OMe)$_2$] in the crystal.

Table 6
Experimental details for the single crystal structure of [(bipy)Pt(OC_6H_4-4-OMe)$_2$]·0.5HOC_6H_4-4-OMe·1.5H_2O.

Empirical formula	$C_{55}H_{58}N_4O_{13}Pt_2$
Formula weight	1373.23
T (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	12.956(2)
b (Å)	16.309(3)
c (Å)	11.940(2)
α (°)	90
β (°)	90.381(3)
γ (°)	90
Volume (Å^3)	2522.9(7)
Z	2
Density (calculated) (Mg/m^3)	1.808
Absorption coefficient (mm^{-1})	5.610
F(0 0 0)	1352
Crystal size (mm^3)	0.23 × 0.21 × 0.21
θ Range for data collection (°)	1.57–25.00
Index ranges	$-15 \leqslant h \leqslant 15$, $-19 \leqslant k \leqslant 19$, $-14 \leqslant l \leqslant 14$
Reflections collected	23 993
Independent reflections	4445 [R_{int} = 0.0491]
Completeness to θ = 25.00°	100.0%
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.3854 and 0.3586
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4445/184/338
Goodness-of-fit (GOF) on F^2	0.997
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0255, wR_2 = 0.0543
R indices (all data)	R_1 = 0.0368, wR_2 = 0.0573
Largest difference in peak and hole	0.789 and −0.725 (e Å^{-3})

was obtained by adding one drop of methyl iodide to a suspension of [(bipy)Pt(OC_6H_4-4-X)$_2$] in chloroform in an NMR tube and recording the spectrum before the product began to crystallize from the resulting solution.

In the case of X = OMe, the methyl of the 4-methoxy phenol was a singlet at 3.9 ppm and the methyl platinum resonance appeared as a singlet at 2.1 ppm with satellites due to the coupling to ^{195}Pt with $^{2}J(PtH) = 68$ Hz. The magnitude of the coupling constant in such complexes is usually sufficient to determine the stereochemistry [42], but because the *trans*-influence of 2,2′-bipyridyl and iodide are very similar, either stereochemistry **I** or **II** is possible.

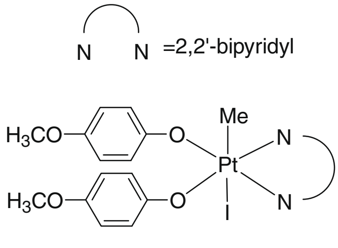
Table 7
Selected bond lengths [Å] and angles [°] for [(bipy)Pt(OC_6H_4-4-OMe)$_2$].

Pt(1)–N(1)	1.994(3)
Pt(1)–N(2)	2.000(3)
Pt(1)–O(1)	2.019(3)
Pt(1)–O(2)	2.018(3)
O(1)–C(11)	1.347(5)
O(2)–C(18)	1.353(5)
O(3)–C(14)	1.379(5)
O(3)–C(17)	1.421(6)
O(4)–C(21)	1.383(5)
O(4)–C(24)	1.413(6)
N(1)–Pt(1)–N(2)	80.96(14)
N(1)–Pt(1)–O(1)	173.48(12)
N(2)–Pt(1)–O(1)	93.23(13)
N(1)–Pt(1)–O(2)	94.00(13)
N(2)–Pt(1)–O(2)	174.95(12)
O(1)–Pt(1)–O(2)	91.82(12)
C(11)–O(1)–Pt(1)	123.0(3)
C(18)–O(2)–Pt(1)	119.6(2)

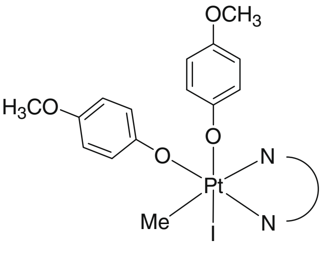
Table 8
Solvent effects on the second order rate constants for reactions with methyl iodide.

Solvent	E_T	(bipy)Pt(SC_6H_4-4-Me)$_2$ k_2 (30 °C) (l mol^{-1} min^{-1})	(bipy)Pt(OC_6H_4-4-OMe)$_2$ k_2 (30 °C) (l mol^{-1} min^{-1})	(bipy)PtPh$_2$ k_2 (40 °C) (l mol^{-1} min^{-1})
Benzene	34.5			6.5
Ethyl acetate	38.1			11.3
Chloroform	39.1	0.14	0.68	
Dichloromethane	41.1	0.71	2.08	21
Acetone	42.2	0.88	4.12	40.5
Acetonitrile	46.0	1.40	8.36	89
Nitromethane	46.3			

The stereochemistry of oxidative addition of methyl iodide to *cis*-[$PtMe_2(PMe_2Ph)_2$] has previously been shown to be *trans* by deuterium labelling studies [38]. The NMR spectrum indicates that the complex has structure **I**, corresponding to *trans*-oxidative addition. Thus for the 4-methoxy group of the 4-methoxy phenol 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.



(I)



(II)

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 the platinum(II) complexes by UV–Vis spectrophotometry.

Graphs of $\log(A_t - A_\infty)$ versus time gave good straight lines, indicating a first order dependence of the rate on the concentration of the platinum(II) complexes, and the pseudo-first order rate constants obtained were proportional to the concentration of methyl iodide for a given solvent.

Thus the reactions are first order in both platinum complex and methyl iodide. The resulting second order rate constants are given in Table 8, which also includes the second order rate constants for oxidative addition of methyl iodide to [(bipy)PtPh$_2$] [33] and [(bipy)Pt(SC_6H_4-4-Me)$_2$] [39] in various solvents together with the polarity parameter E_T [43] for each solvent. This may confirm that there is a simple correlation and simple kinetics between the oxidative addition and these different metal bonds.

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 energies and entropies of activation have been measured, and it was found that the entropy of activation has a large negative value typical of oxidative addition reactions of methyl iodide [44,45]. The mechanism of the reaction of diaryl(2,2′-bipyridyl)platinum(II) complexes with methyl iodide has already been shown [33,34] to involve nucleophilic attack by platinum on the carbon atom of MeI to give [PtMePh$_2$(bipy)]$^+$I$^-$, which rapidly rearranges to [PtIMePh$_2$(bipy)]. Thus by analogy, the most likely mechanism of reaction of [(bipy)Pt(OC_6H_4-4-X)$_2$] with methyl iodide involves nucleophilic attack by platinum on the carbon atom of MeI to give a similar intermediate, which rapidly rearranges to the final product.

3. Experimental

3.1. General information

Unless otherwise stated, all of the starting materials were obtained at the highest levels of purity possible from commercial sources and used as received. All reactions were performed in an atmosphere of nitrogen. The complex [$PtCl_2$(bipy)] was prepared according to a literature procedure [30]. Its ^{1}H NMR spectrum was checked with a recent Ref. [46].

Mass spectra were recorded on a Quattro Ultima Pt Mass Spectrometer (Waters Corp, Milford, USA). Infrared spectra of the complexes were obtained utilizing CsI window (200–4000 cm^{-1}) using a Perkin Elmer 1300 IR spectrophotometer. Electronic absorption spectra were measured using an HP8453 UV–Visible spectrophotometer in the range 200–1100 nm. Microanalyses were performed by the Centre National de la Recherche Scientifique, Service Central D'Analyse, Vernaison, France, or were obtained from the Chemistry Department, University College London, UK. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. TMS was used as standard.

Single-crystal X-ray diffraction data collection and analyses were performed on a Bruker SMART 1 K CCD area detector diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). The crystallographic measurements were carried out at 150 K. Data processing was carried out using SHELX software [47].

3.2. Synthesis of the [(bipy)Pt(OC_6H_4-4-X)$_2$] complexes

The Pt(II) complexes were all prepared in a manner similar to the example given here.

3.2.1. Preparation of [(bipy)Pt(OC_6H_4-4-Cl)$_2$]

Recrystallized dichloro(2,2′-bipyridyl)platinum(II) (0.422 g, 1.0 mmol) in chloroform (15 ml) was added to a magnetically stirred solution of 4-chlorophenol (0.256 g, 2.0 mmol) in deionized distilled water (15 ml) containing potassium hydroxide (0.127 g, 2.2 mmol) and benzyl triphenylphosphonium chloride (0.039 g, 0.1 mmol) at 30 °C in a 100 ml flask, equipped with an N_2 inlet, water-cooled condenser and 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 sulfate. The solution was filtered and the chloroform evaporated under vacuum, to give a red solid. Yield: 89%. MS *m/z* 606.4 $[M+H]^+$.

3.3. Synthesis of the $[(bipy)PtMe(I)(OC_6H_4\text{-}4\text{-}X)_2]$ complexes

The Pt(IV) complexes were all prepared in a manner similar to the example given here.

3.3.1. Preparation of $[(bipy)PtMe(I)(OC_6H_4\text{-}4\text{-}Cl)_2]$

To a suspension of $[(bipy)Pt(OC_6H_4\text{-}4\text{-}Cl)_2]$ (0.606 g, 1 mmol) in dichloromethane (10 ml) was added an excess of methyl iodide. 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 80%. MS *m/z*: 748.3 $[M+H]^+$.

3.4. Kinetic studies

Standard solutions of $[Pt(OC_6H_4\text{-}4\text{-}OMe)_2(bipy)]$ 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 cell compartment of the UV–Visible spectrophotometer. Spectra were then recorded as the reaction proceeded. The concentration of platinum(II) complex was about 10^{-4} M at the start of each reaction.

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Appendix A. Supplementary material

CCDC 696237 contains the supplementary crystallographic data for $[(bipy)Pt(OC_6H_4\text{-}4\text{-}OMe)_2]$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.023.

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