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Substitution reactions involving cyclometalated platinum(II) complexes: Kinetic investigations

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ABSTRACT

Substitution reaction of the labile SMe_2 ligand in the cyclometalated platinum(II) complexes of general formula [PtAr(ppy)(SMe_2)], **1**, in which ppy = deprotonated 2-phenylpyridyl and Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$, by several N or P donor reagents were studied; the N-donors, N, are pyridine (Py) and substituted pyridines, N = 4-MePy, Py, Py-d_5, 2-MePy, 3-PhPy, 3,4-Me_2Py, 4-^{t}BuPy or 3-C(O)OMePy, and the P-donors, L, are phosphines or phosphites, L = $P(OPh)_3$, $P(O\text{-}^iPr)_3$, PPh_3, PPh_2Me and L_2 = $Ph_2PCH_2PPh_2$, bis(diphenylphosphino)methane (dppm). The products were identified by multinuclear NMR studies as [PtAr(ppy)(N)], **2**, or [PtAr(ppy)(L)], **3**, respectively. Complexes **1** have a MLCT band in the visible region which was used to easily follow the kinetics of the ligand substitution reactions by UV–vis spectroscopy. Although the complexes **1** contain two *cis* Pt–C bonds, the substitution reactions followed a normal associative mechanism. The rates of reactions were depended on the concentration and the nature of the entering group. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot gave a straight line suggesting the operation of the same mechanism for all entering nucleophiles.

1. Introduction

Ligand substitution reaction involving a transition metal complex is usually considered as a key step in many catalytic reactions [1]. The related reactions on square planar platinum(II) complexes have been extensively studied [2–7] and shown to proceed usually via an associative process, implying direct attack of the entering nucleophile on substrate with the formation of 18e five-coordinated intermediates [8–10]. However, to the best of our knowledge, such reactions have rarely been studied on cyclometalated platinum complexes [11–16]. Kinetic studies of ligand substitution on the cyclometalated platinum(II) complexes [Pt(N–N–C)Cl] (N–N–CH = 6-(1-methylbenzyl)-2,2′-bipyridine) [13] and [Pt(N–C)(N)(H_2O)] (N–CH = *N*,*N*-dimethylbenzylamine, N = $pySO_3$-3) [14,15] and on the cationic complex $[Pt(N–C–N)(H_2O)]^+$ (N–CH–N = 2,6-bis((dimethylamino)methyl) phenyl) [16], each containing only one monodentate ligand for substitution, have shown that the activation mode is associative in nature. On the other hand, SMe_2 substitution reactions in the complexes [Pt(bph)(SMe_2)$_2$] (bph = 2,2′-biphenyl dianion) and [$PtPh_2$(SMe_2)$_2$], each bearing two Pt–C bondings, with reagents potentially having bidentate donor abilities such as bipyridine, phenanthroline or 1,2-(diphenylphosphino)ethane, have been shown to occur through a dissociative path [12].

Transition metal cyclometalated complexes, in particular those involving platinum, are of interest due to their potential applications in many areas, such as chemosensors [17,18], photocatalysts [19,20], and luminescent [21,22]. Square planar cyclometalated platinum complexes have also been used as "building blocks" for complex systems such as self-assembly [23], and dendrimers [24,25]. As such we prompted to study the kinetics and mechanism of the ligand substitution reactions concerning the lability of sulfur-bonded dimethylsulfide in the cyclometalated platinum(II) complexes of general formula [PtAr(ppy)(SMe_2)], **1**, in which ppy = deprotonated 2-phenylpyridyl and Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$, with different nitrogen and phosphorous-donors. Despite the presence of two *cis*-Pt–C bondings in the starting complexes **1**, the kinetic investigations comply with the substitution reactions proceeding via an associative mechanism.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

The general route used to prepare the cyclometalated organoplatinum complexes are described in Scheme 1. The reaction of 2-

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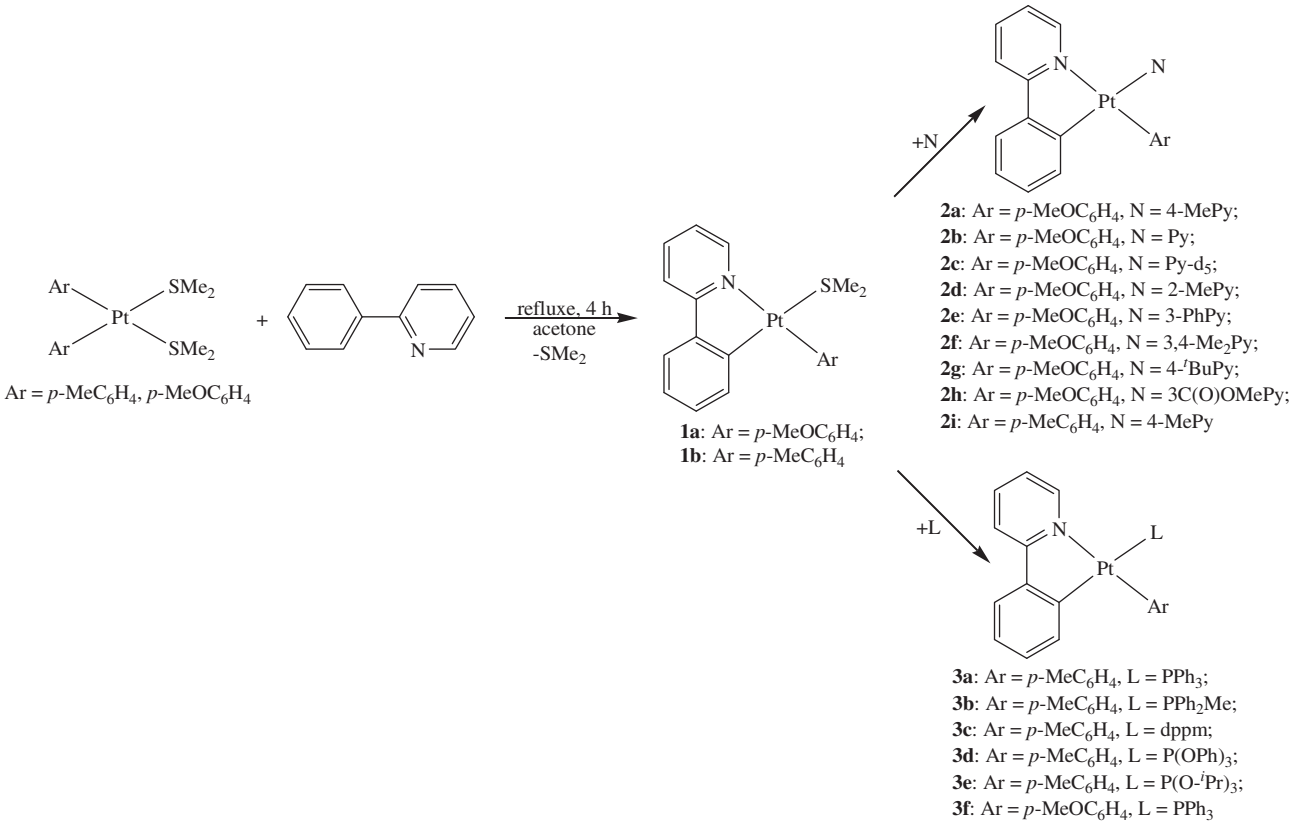

Scheme 1.

phenylpyridine (ppyH) with the starting complexes $[PtAr_2(SMe_2)_2]$ (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) led to formation of the monoarylplatinum complexes $[PtAr(ppy)(SMe_2)]$, **1**, believed to occur by coordination of the nitrogen atom of the pyridyl group followed by subsequent cyclometalation, as described elsewhere for other similar reactions involving C–H bond activation and formation of a new metal–carbon bond [26–30].

Reaction of the complexes $[PtAr(ppy)(SMe_2)]$, **1** (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$), with 1 equiv of either the nitrogen nucleophiles N (N = 4-MePy, Py, Py-d_5, 2-MePy, 3-PhPy, 3,4-Me_2Py, 4-^{t}BuPy or 3-C(O)OMePy) or the phosphorous nucleophiles L (L = PPh_3, PPh_2Me, $P(OPh)_3$, $P(O\text{-}^iPr)_3$, or $L_2 = Ph_2PCH_2PPh_2$, dppm) proceeded via displacement of the labile SMe_2 ligand to give the complexes $[PtAr(ppy)(N)]$ or $[PtAr(ppy)(L)]$, as depicted in Scheme 1.

The complexes $[Pt(p\text{-}MeOC_6H_4)(ppy)(N)]$, **2**, were characterized by ^{1}H NMR spectroscopy. Typically, in the ^{1}H NMR spectrum of complex $[Pt(p\text{-}MeOC_6H_4)(ppy)(4\text{-}MePy)]$, **2a**, the methyl groups on 4-MePy and anisole ligands were observed at $\delta = 2.30$ and 3.70, respectively. A doublet signal at $\delta = 8.61$ (with $^3J_H{}^m{}_H{}^o = 6.0$ Hz), that is accompanying by platinum satellites with $^3J_{PtH}{}^o = 24.6$ Hz, is assigned to the two equivalent H^o protons of the 4-MePy ligand. Notice that a similar doublet signal at $\delta = 8.87$ (with $^3J_H{}^m{}_H{}^o = 6.3$ Hz) is assigned to the two equivalent H^o protons of the Py ligand in the ^{1}H NMR spectrum of the complex $[Pt(p\text{-}MeOC_6H_4)(ppy)(Py)]$, **2b**, which as expected was missed in the spectrum of related deuterated complex $[Pt(p\text{-}MeOC_6H_4)(ppy)(Py\text{-}d_5)]$, **2c**. This indicates that the H^o of the N ligand in complexes **2** is expected to appear close to $\delta = 8.70$ and this should not be misassigned with the signal for *ortho* hydrogen of ppy ligand (i.e. proton of C–H group locating adjacent to coordinated nitrogen atom) which seems to be overlapped under the aromatic protons. The equivalency of the two H^o of the N ligand in complexes **2** confirms that the pyridine ligands in the complexes **2** should be oriented perpendicular to the square planar geometry of the platinum centers.

The complexes $[Pt(p\text{-}MeC_6H_4)(ppy)(L)]$, **3**, were characterized using NMR (^{1}H, ^{31}P, ^{195}Pt) spectroscopy as typically described for $[Pt(p\text{-}MeC_6H_4)(ppy)(PPh_3)]$, **3a**. In the ^{31}P NMR spectrum of complex **3a**, the phosphorous atom appeared as a singlet signal at $\delta = 31.8$ which was coupled to platinum atom to give satellites with $^1J_{PtP} = 2041$ Hz. Consistent with this, in the ^{195}Pt NMR spectrum of **3a**, a doublet at −2435 with $^1J_{PtP} = 2035$ Hz was observed. In the ^{1}H NMR spectrum of complex **3a**, a singlet signal was observed at 2.10 ppm for the Me group of the *para*-tolyl ligand. The *ortho* and *meta* protons of the *para*-tolyl ligand appeared as two doublets at $\delta = 6.43$ and 6.99, respectively, each with $^3J_H{}^m{}_H{}^o = 7.5$ Hz; the *ortho* protons further coupled to platinum to give satellites with $^3J_{PtH} = 65.0$ Hz. A doublet signal at $\delta = 6.50$, accompanied by platinum satellites, with $^3J_{HH} = 1.5$ Hz and $^3J_{PtH} = 12.5$ Hz was attributed to the hydrogen atom of C–H group adjacent to the coordinated C atom of ppy ligand.

2.2. Kinetics and mechanism of the reactions

As was mentioned above, reactions of the complexes $[PtAr(ppy)(SMe_2)]$, **1**, with 1 equiv of either of the nitrogen or phosphorus nucleophiles proceeded via displacement of the labile SMe_2 ligand to give the final complexes **2** or **3**, respectively. This was typically demonstrated by monitoring the reaction of complex $[Pt(p\text{-}MeOC_6H_4)(ppy)(SMe_2)]$, **1a**, with 3-PhPy in $CDC1_3$ by using ^{1}H NMR spectroscopy and the results are shown in Fig. 1S. Thus the singlet signal at 2.20 ppm with platinum satellites with $^3J_{PtH} = 25.0$ Hz due to coordinated dimethylsulfide protons was disappeared while the corresponding signal for the free SMe_2 ligand at 2.05 ppm was appeared.

The complexes **1** contain a band in the visible region which is ascribed to the $5d_{\pi}(Pt) \rightarrow \pi^*$(imine) metal-to-ligand charge-transfer (MLCT) absorption and is believed to be responsible for the color of the complex [5,31]. This was used to monitor the reactions of complexes with donor nucleophiles in order to investigate the kinetics of reactions by using UV–vis spectroscopy, as will be described below.

2.2.1. Kinetics of the reaction of complex *1a* with N-donor nucleophiles

Typically, the reaction of complex [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, and 4-MePy is described. As can be seen in Fig. 2S, the complex **1a** has a maximum absorption band at 367 nm (spectrum 2b), while the N-donor reagent 4-MePy contains no absorption band at this point (spectrum 2a). The product complex [Pt(*p*-MeC_6H_4)(ppy)(4-MePy)], **2a**, has a maximum absorption band at 380 nm (spectra 2c and 2d). Thus, an excess of 4-MePy was used at 25 °C and the change of the MLCT band at $\lambda = 380$ nm in a CH_2Cl_2 solution was used to monitor the reaction. The change in the spectrum during a typical run is shown in Fig. 1.

The time-dependence curves of the spectra of the reaction in CH_2Cl_2 at this condition are shown in Fig. 3S. Thus, the pseudo-first-order rate constants k_{obs} were evaluated by nonlinear least-squares fitting of the absorbance–time profiles to the monophasic first-order equation (Eq. (1)):

$$A_t = A_\infty + (A_0 - A_\infty)[\exp(-k_{obs}t)] \quad (1)$$

Plots of the first-order rate constants, k_{obs}, versus [N-donor ligands] was linear (Fig. 4S), showing a first-order dependence of the rate on the concentration of N-donor ligands. The slope in each case gave the second-order rate constant, and the results are collected in Table 1. Therefore, the reaction obeys a simple second-order rate law, first order in both the corresponding complex and N-donor ligands. The same method was used at other temperatures, and activation parameters were obtained from the Eyring equation (see Eq. (2) and Fig. 5S). The data are collected in Table 1.

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \quad (2)$$

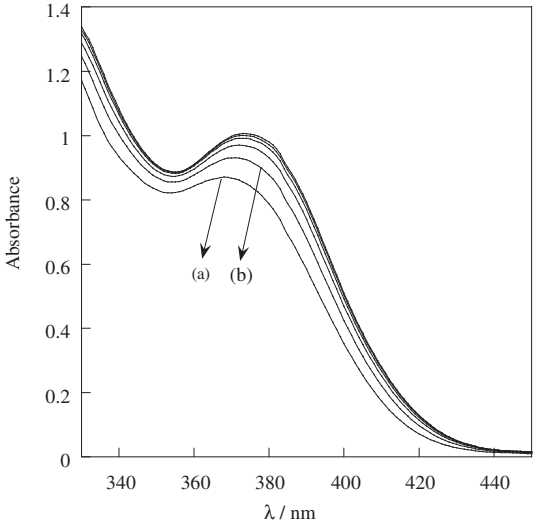

Fig. 1. Changes in the UV–vis spectrum during the reaction of complex [Pt(*p*-$MeOC_6H_4$)(ppy)SMe_2], **1a** (2×10^{-4} M) and 4-MePy (0.1 M) in CH_2Cl_2 at $T = 25$ °C: (a) initial spectrum (before adding 4-MePy) and (b) spectrum at $t = 30$ s; successive spectra were recorded at intervals of 1 min.

The above results led us to propose an associative mechanism. A second-order rate law (Eq. (3)), k_2, was clearly obtained with solvolytic path, k_1, but no sign of any involvement of dissociative processes was observed. The rather large negative values of $\Delta S^{\ddagger}$ (see Table 1) for all the reactions strongly confirm the associative nature of the ligand displacement.

$$-d[\text{complex } \mathbf{1a}]/dt = k_{obs}[\text{complex } \mathbf{1a}]; k_{obs} = k_1 + k_2[N] \quad (3)$$

The kinetic investigation using ^1H NMR spectroscopy in $CDCl_3$ was also performed typically for the reaction of complex [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, with N = 3-PhPy at 27 °C (see Fig. 1S and the above description) and the k_2 value was obtained as 6.1×10^{-2} L mol^{-1} s^{-1}, which is related to rate of replacement of the labile SMe_2 ligand with 3-PhPy. This value is very close to the value of $k_2 = = 5.8 \times 10^{-2}$ L mol^{-1} s^{-1}, measured for the same reaction in CH_2Cl_2 solvent by using UV–vis technique at 27 °C and the value $k_2 = 6.5 \times 10^{-2}$ L mol^{-1} s^{-1} obtained at the same condition (at 27 °C, in $CHCl_3$) using UV–vis spectroscopy (see Table 1).

Rates of the reactions proceeding by an associative mechanism must somehow be dependent on the nature of the entering group. The rate of addition of N-donor ligands to [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, is expected to be governed by both electronic and steric effects [32]. Plot of the rate constants, k_2, versus basicity of N-donor nucleophile (each in logarithm scale), shown in Fig. 2, is almost linear suggesting that increasing the basicity of entering group has caused increasing the rate of reaction. Consistently when the donor is 2-MePy, the related point is significantly off, confirming that the steric factor of Me group in *ortho* position of 2-MePy is greatly influential in decreasing the rate of reaction. Therefore, although the nucleophilicity of 2-MePy is greater than that of Py, the rate of reaction of complex **1a** with Py is more than 7 times faster than that with 2-MePy at the same condition (see Table 1). Besides, the rate of the reaction of complex **1a** with 4-MePy, for example, at 10 °C is more than 2 times faster than the corresponding rate with Py at the same condition, confirming that the dominating factor should be basicity of the 4-MePy (see Fig. 2).

The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot for reactions of complex **1a** with N-donor ligands in dichloromethane is shown in Fig. 3. A good straight line is obtained that could probably be taken as an evidence for operation of the same (associative, second-order) mechanism in this series of reactions [33].

2.2.2. Kinetics of the reaction of complex *1b* with P-donor nucleophiles

The rates of reactions of complex **1b** with phosphorus donor reagents were found to be rather fast and it was not convenient to measure the rates by common pseudo-first order technique. Therefore, an equal molar of L was used at 25 °C and the change of the MLCT band at $\lambda = 364$ nm in dichloromethane solution was used to monitor the reaction; see Fig. 4 for a typical example of the reaction of complex [Pt(*p*-MeC_6H_4)(ppy)SMe_2], **1b**, with dppm. The reactions followed good second-order kinetics and the rate constants, k_2, were evaluated from the time-dependence curves of the spectra of the reaction by fitting of the absorbance–time profiles to Eq. (4) [34,35]. The activation parameters were also determined from measurement at different temperatures (see Eq. (2) and Fig. 6S) and the data are given in Table 2. These reactions followed good second-order kinetics, first order in both the cyclometalated complex and the attacking nucleophile.

$$A = A_\infty + (A_0 - A_\infty)/(1 + [\text{complex}]_0 \times k \times t) \quad (4)$$

The compensation between the enthalpic and entropic contributions for reactions of complex **1b** with P-donor reagents in dichloromethane gave a good straight line as shown in Fig. 5. This

Table 1
Second-order rate constants (L mol^{-1} s^{-1})[a] and activation parameters[b] for reaction of the complex [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, with the N-donor nucleophiles, N, in dichloromethane.

N	pK_a	10^2 k_2 (10^5 k_1) at different temperatures						$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
		10 °C	15 °C	20 °C	25 °C	30 °C	35 °C		
3,4-Me_2Py	6.46	2.9 (0.07)	5.1 (0.05)	8.1 (0.06)	10.5 (0.18)			57.1 ± 0.7	−71 ± 2
4-MePy	5.94	3.6	5.2	7.6	10.8 11.9[c]			54.2 ± 0.3	−81 ± 1
4-^{t}BuPy	5.8		4.5 (0.06)	6.8 (0.11)	8.9 (0.24)	14.1 (0.36)		50.5 ± 0.4	−95 ± 1
2-MePy	5.9			0.5 (0.13)	0.9 (0.18)	1.2 (0.40)	3.3 (0.55)	82.3 ± 0.9	−7.4 ± 2
3C(O)OMePy	3.13			3.1 (0.07)	4.1 (0.18)	5.4 (0.35)	8.7 (0.64)	48.8 ± 0.6	−107 ± 2
Py	5.23	1.7	3.2 (0.12)	4.2 (0.13)	6.3 (0.21)	8.6 (0.39)		53.8 ± 0.5	−87 ± 2
3-PhPy	4.85		3.6 (0.02)	5.3 (0.07)	6.4 (0.22) 6.5[d] (0.24)	9.9 (0.37)		44.2 ± 0.6	−118 ± 2

[a] Values in parentheses are k_1, estimated errors in rate constants values are ±5%.
[b] Activation parameters were calculated from the temperature dependence of the second-order rate constant in the usual way using Eyring equation.
[c] k_2 for the reaction of complex [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, with 4-MePy in CH_2Cl_2 at 25 °C.
[d] k_2 at 27 °C.

may be taken as an evidence for operation of the same (associative, second-order) mechanism in this series of reactions.

The available experimental data support a rate law of the form given in Eq. (5) for the substitution reactions involving complex **1b**, where [L] represents the concentration of the nucleophile and [M] that of the cyclometalated platinum complex.

$$\text{rate} = k_2[\text{L}][\text{M}] \quad (5)$$

The rate constant k_2 corresponds to a direct S_N2 substitution by the nucleophile, with no any contribution from the solvent path, k_1. The large negative values of $\Delta S^{\ddagger}$ (see Table 2) for all the reactions strongly confirm the associative nature of the ligand displacement. Consistent with the proposed associative mechanism, the reactions are dependent on the nature of the entering group (see Table 2). Thus, for example the rate of the reactions of complex **1b** with PPh_3 at different temperatures is more than two times faster than those with $P(OPh)_3$. PPh_3 has a higher σ-donor ability than $P(OPh)_3$, and therefore when the lone pair of electrons of PPh_3 entering ligand is binding to the low lying platinum 6 p_z orbital to form the initial transition state containing the square-pyramidal metallic center, it is better able to cope with the electron density already present in the same direction from the filled metal $5d_z^2$ orbital [3]. It is interesting to note that the Tolman cone angle of PPh_3 (145°) is significantly greater than that of $P(OPh)_3$ (128°) [36]. In the associative process suggested for the present ligand substitution reactions of complex **1b**, one might expect a lower rate for the larger entering group. The fact that PPh_3 is reacted faster than $P(OPh)_3$ (see Table 2) indicates that the dominating factor should be by far electronic. The nucleophile $P(O\text{-}^iPr)_3$ has a lower σ-donor ability and Tolman cone angle (130°) [36] than PPh_3 and the related rate concerning $P(O\text{-}^iPr)_3$ at different temperatures is rather faster than that of the PPh_3 (see Table 2), suggesting that the dominating factor should be by far steric (see Table 2).

3. Conclusions

Substitution reaction of the cyclometalated complex [Pt(*p*-$MeOC_6H_4$)(ppy)SMe_2], **1a**, with pyridine and some other substituted pyridine reagents, as revealed by using UV–vis spectroscopy, is suggested to proceed by an associative S_N2 mechanism, and therefore the reaction rates should be dependent on the nature of the entering nucleophile. As summarized in Table 1 and indicated in Fig. 2, the rate of reactions involving N-donors are correlated rather well with the basicity (pK_a) of the entering group with the following trend:

$$4-\text{MePy} \approx 3,4-\text{Me}_2\text{Py} > 4-{}^t\text{BuPy} > 3-\text{PhPy} > \text{Py} > 3-\text{C(O)OMePy}$$

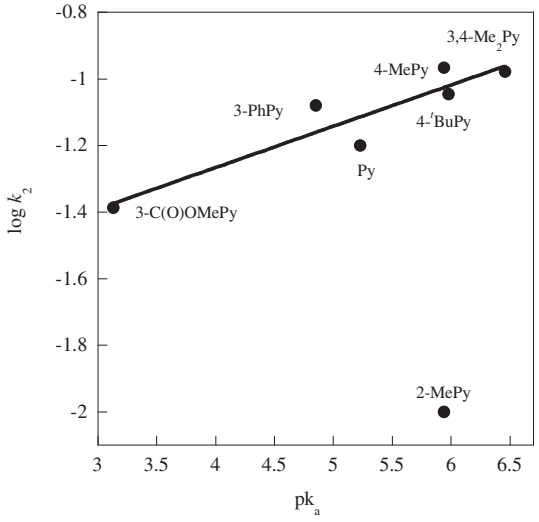

Fig. 2. The plot of log k_2 versus pk_a of entering ligand. 2-MePy was omitted form the linear fit.

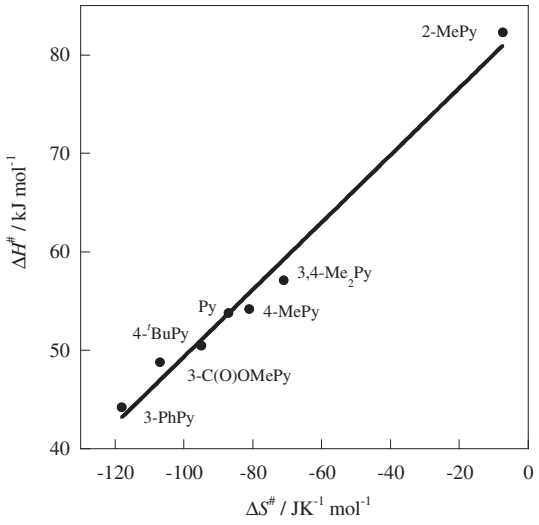

Fig. 3. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plots of reaction of complex **1a** with nucleophiles N in CH_2Cl_2.

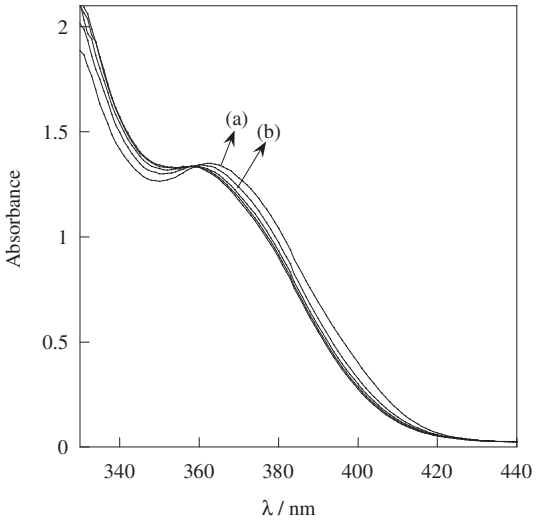

Fig. 4. Changes in the UV–vis spectrum during the reaction of complex [Pt(*p*-MeC_6H_4)(ppy)SMe_2], **1b** (2.6×10^{-4} M) and dppm, under second-order 1:1 stoichiometric conditions, in CH_2Cl_2 at $T = 25$ °C: (a) initial spectrum (before adding dppm) and (b) spectrum at $t = 30$ s; successive spectra were recorded at intervals of 1 min.

However, when the donor is 2-MePy, the steric factor of Me group in *ortho* position of 2-MePy is greatly influential in decreasing the rate of reaction.

The substitution reactions of the complex [Pt(*p*-MeC_6H_4)(py)(SMe_2)], **1b**, with phosphorus nucleophiles are generally proceeded much faster than those involving the nitrogen nucleophiles. This observation complies well with the phosphorus donors being soft (as compared with the nitrogen donors that are hard) when they react with the platinum center of complex that is soft. Thus, rates of the related substitution reactions involving phosphorus donors, using UV–vis spectroscopy, were too fast to be studied by more traditional pseudo-first order method and so second-order technique was used to measure the rate constants by employing 1:1 molar ratio of the complex: reagent. The following trend was observed for rates of reactions of the phosphorus donors with complex **1b**:

$$P(O-{}^{i}Pr)_3 > PPh_3 > P(OPh)_3 \approx dppm$$

Steric and electronic effects have been responsible for the trend. The reaction rates of complex **1b** with PPh_3 at different temperatures are more than two times faster than those with $P(OPh)_3$, having a rather lower Tolman cone angle (128°) as compared to that of PPh_3 with its Tolman cone angle being considerably bigger (145°). Here the electronic effect has been dominating as PPh_3 has a higher σ-donor ability (enabling it to better coping with the filled metal $5dz^2$ orbital of the platinum center) than $P(OPh)_3$. In contrast, the reaction rates involving $P(O\text{-}{}^{i}Pr)_3$ nucleophile (having a Tolman cone angle of 130°, which is smaller than that of PPh_3) are significantly higher than those involving PPh_3 despite of the fact that $P(O\text{-}{}^{i}Pr)_3$ has a lower σ-donor ability than PPh_3, indicating that here the steric factor has been quite dominating. The reaction rates involving $P(O\text{-}{}^{i}Pr)_3$ nucleophile are significantly higher than those involving $P(OPh)_3$, with both having almost similar Tolman cone angles. The reason here ought to be electronic; it is reasonable to believe that the $P(O\text{-}{}^{i}Pr)_3$ has a stronger σ-donor ability than $P(OPh)_3$, due to electron donating ability of ^{i}Pr groups in the former in contrast to electron withdrawing nature of Ph groups in the latter. The reaction rates involving PPh_3 nucleophile are nearly 2 times faster than those concerning the biphosphine nucleophile bis(diphenylphosphino)methane, dppm, although it is reasonable to assume that cone angle of the attacking part of dppm, i.e. Ph_2PCH_2–, is smaller than that of PPh_3. It is possible that when one of the dppm phosphorus atoms is reacting with the complex **1b** to form the penta-coordinate intermediate containing a dangling dppm ligand [Pt(*p*-MeC_6H_4)(ppy)$(SMe_2)(\eta^1$-dppm)], the other rather electronegative free phosphorus atom withdraws electron from the connecting phosphorus atom making it having a lower σ-donor ability than PPh_3, indicating that the electronic factor has been dominating.

In order to compare the abilities of the complexes [Pt(*p*-$MeOC_6H_4$)(ppy)SMe_2], **1a**, and [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, with each other in terms of the above mentioned substitution reactions, kinetics of reaction of the latter complex with 4-MePy was also studied at 25 °C (see Table 1). The results indicate that although the metallic center of complex **1a** is expected to be more electrophilic as compared with that of the complex **1b**, the reaction rates of both complexes with 4-MePy at 25 °C are almost the same within the experimental errors. It is therefore concluded that the nature of aromatic ligand, Ar, in complexes [PtAr(ppy)(SMe_2)], **1**, does not seem to be significantly effective in the rates of their reactions with the nitrogen donor entering reagents N. However, the related reactions involving phosphine entering groups act differently. Thus, complex **1b** reacts some 70% faster (as compared to complex **1a**) with PPh_3 at 25 °C (see Table 2). The metallic center in complex **1b** is expected to be more electron rich as compared to that in complex **1a**; the *p*-MeC_6H_4 ligand is considerably more electron donating than the *p*-$MeOC_6H_4$ ligand. Therefore, in the penta-coordinate intermediate formed through associative attack by the entering ligand, PPh_3, the extent of back donation from the filled *d* orbitals of platinum is expected to be bigger in the reaction involving the starting complex **1b** (as compared with complex **1a**). This is suggested to make the related intermediate more stable and thus causing its reaction rate faster than that for the related reaction involving the starting complex **1a**.

The complexes **1** have two Pt–C bonds that should labilize the Pt–S bond significantly to enable a dissociative substitution mechanism. However, the in plane pyridine ligand can cause a significant pi-back bonding with the metal center, which will decrease the electron density on the metal center and make it more electrophilic to enable an associative attack by the entering ligands.

Table 2
Second-order rate constants[a] and activation parameters[b] for reaction of the complex [Pt(*p*-MeC_6H_4)(ppy)(SMe_2)], **1b**, with the P-donor nucleophiles, L, in dichloromethane.

L	k_2(L mol^{-1} s^{-1}) at different temperatures							$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C		
PPh_3	84.6	100.8	122.0	147.8	169.8 104.3[c]	186.4	204.6	19.1 ± 0.1	−139 ± 1
dppm	31.2	42.2	59.8	78.1	101.8	122.6	140.3	34.2 ± 0.2	−92 ± 1
$P(OPh)_3$	37.0	46.5	58.3	75.7	94.6	108.7	124.7	27.3 ± 0.1	−116 ± 1
$P(O\text{-}{}^{i}Pr)_3$	96.7	114.6	137.6	163.5	197.7	233.1	263.2	22.0 ± 0.1	−127 ± 1

[a] Estimated errors in k_2 values are ±3%.
[b] Activation parameters were calculated from the temperature dependence of the second-order rate constant in the usual way using Eyring equation.
[c] k_2 from reaction of the complex [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, with PPh_3 in CH_2Cl_2 at 25 °C.

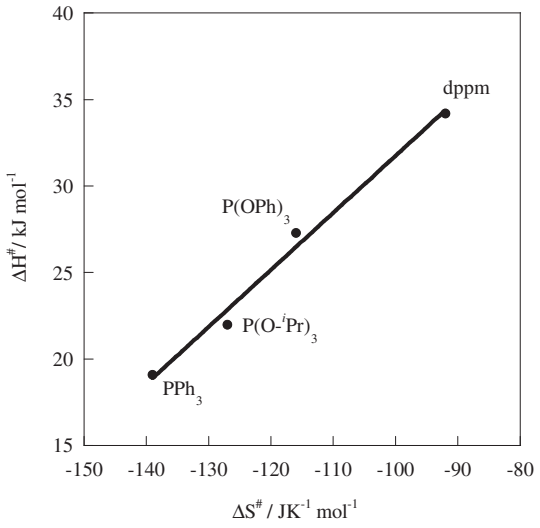

Fig. 5. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plots of reaction of complex **1b** with the P-donor nucleophiles L in CH_2Cl_2.

4. Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer and the ^{31}P and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^1H (250 MHz, TMS), ^{13}C (69 MHz, TMS), ^{31}P (202 MHz, 85% H_3PO_4), and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). The chemical shifts and coupling constants are in ppm and Hz, respectively. The microanalyses were performed using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. Kinetic studies were carried out by using a Perkin–Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. 2-phenylpyridine was purchased from Aldrich, and the monomeric precursors *cis*-[$PtAr_2(SMe_2)_2$] (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) were made by the known methods [37]. The complexes [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, [Pt(*p*-MeC_6H_4)(py)(SMe_2)], **1b**, and [Pt(*p*-MeC_6H_4)(ppy)(η^1-dppm)], **3c**, were prepared as reported [27]. For **1a:** ^{13}C NMR: $\delta = 20.2$ (s, Me of SMe_2 ligand, 2 C), 55.0 (s, OMe group on the *p*-anisol ligand, 1 C), 114.0 (s, $^2J_{PtC^o} = 83$ Hz, C^o of *p*-anisol ligand, 2 C), 136.9 (s, $^3J_{PtC^m} = 20$ Hz, C^m of *p*-anisol ligand, 2 C), 139.0 (s, C^p of *p*-anisol ligand, 1 C), 147.0 (s, C atom of the *p*-anisol ligand connected to Pt atom, 1 C), ppy carbons, 123.0 (s, C atom which is connected to Pt atom, 1 C), 119.0 (s, 1 C), 122.3 (s, 1 C), 123.8 (s, 1 C), 130.0 (s, 1 C), 137.0 (s, 1 C). For **1b:** ^{13}C NMR: $\delta = 20.2$ (s, Me of SMe_2 ligand, 2 C), 21.0 (s, Me group on the *p*-tolyl ligand, 1 C), 128.0 (s, $^2J_{PtC^o} = 74$ Hz, C^o of *p*-tolyl ligand, 2 C), 136.8 (s, $^3J_{PtC^m} = 17$ Hz, C^m of *p*-tolyl ligand, 2 C), 138.0 (s, C^p of *p*-tolyl ligand, 1 C), 146.7 (s, $^1J_{PtC} = 538$ Hz, C atom of the *p*-tolyl ligand connected to Pt atom, 1 C), ppy carbons, 123.4 (s, $^1J_{PtC} = 538$ Hz, C atom which is connected to Pt atom, 1 C), 119.0 (s, $J_{PtC} = 17$ Hz, 1 C), 122.3 (s, $J_{PtC} = 6$ Hz, 1 C), 123.8 (s, $J_{PtC} = 6$ Hz, 1 C), 130.2 (s, $J_{PtC} = 79.3$ Hz, 1 C), 137.4 (s, $J_{PtC} = 74$ Hz, 1 C).

4.1. Synthesis

4.1.1. Preparation of the complex [Pt(*p*-$MeOC_6H_4$)(ppy)(4-MePy)], **2a**

To a solution of [Pt(*p*-$MeOC_6H_4$)(ppy)(SMe_2)], **1a**, (20 mg, 0.04 mmol) in acetone (20 ml) was added 4-MePy (4 μL, 0.04 mmol), and the solution was stirred for 3 h. A green solution was formed, then the solvent was removed under reduced pressure and the residue was triturated with cold acetone (2 × 3 mL). The product as a green solid was dried under vacuum. Yield 18 mg; 84%, mp = 218 °C (decomp.). Anal. Calcd. for $C_{24}H_{22}N_2OPt$: C, 52.5; H, 4.0; N, 5.1; Found: C, 52.8; H, 4.0; N, 5.2. ^1H NMR data in $CDCl_3$: $\delta = 2.30$ (s, Me group on the 4-MePy ligand, 1 Me), 3.68 (s, OMe group on the *p*-anisol ligand, 1 Me), 6.58 (d, $^3J_{H^mH^o} = 8.6$ Hz, H^m of *p*-anisol ligand, 2 H), 7.12 (d, $^3J_{H^mH^o} = 6.0$ Hz, H^m of 4-MePy ligand, 2 H), 7.34 (d, $^3J_{H^oH^m} = 8.6$ Hz, $^3J_{PtH^o}$ = not resolved, H^o of *p*-anisol ligand, 2 H), 7.62 (d, $^3J_{HH} = 5.3$ Hz, $^3J_{PtH} = 19.1$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 6.91–7.73 (aromatic protons), 8.61 (d, $^3J_{H^oH^m} = 6.0$ Hz, $^3J_{PtH^o} = 24.6$ Hz, H^o of 4-MePy ligand, 2 H).

The following complexes were made similarly by using the appropriate N-donor nucleophiles:

4.1.1.1. [Pt(p-MeOC$_6$H$_4$)(ppy)(Py)], ***2b***. Yield 16 mg; 77%, mp = 225 °C (decomp.). Anal. Calcd. for $C_{23}H_{20}N_2OPt$: C, 51.6; H, 3.8; N, 5.2; Found: C, 52.0; H, 3.9; N, 5.4. ^1H NMR data in $CDCl_3$: $\delta = 3.76$ (s, OMe group on the *p*-anisol ligand, 1 Me), 6.66 (d, $^3J_{H^mH^o} = 8.3$ Hz, H^m of *p*-anisol ligand, 2 H), 7.23 (dd, $^3J_{H^mH^o} = 6.3$ Hz, H^m of Py ligand, 2 H), 7.41 (d, $^3J_{H^oH^m} = 8.3$ Hz, $^3J_{PtH^o} = 69.7$, H^o of *p*-anisol ligand, 2 H), 7.01–7.65 (aromatic protons), 7.80 (d, $^3J_{HH} = 6.1$ Hz, $^3J_{PtH} = 18.6$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 8.87 (d, $^3J_{H^oH^m} = 6.3$ Hz, $^3J_{PtH^o} = 23.1$ Hz, H^o of Py ligand, 2 H).

4.1.1.2. [Pt(p-MeOC$_6$H$_4$)(ppy)(Py-d$_5$)], ***2c***. ^1H NMR data in $CDCl_3$: $\delta = 3.69$ (s, OMe group on the *p*-anisol ligand, 1 Me), 6.59 (d, $^3J_{H^mH^o} = 8.2$ Hz, H^m of *p*-anisol ligand, 2 H), 7.36 (d, $^3J_{H^oH^m} = 8.2$ Hz, $^3J_{PtH^o} = 68.4$, H^o of *p*-anisol ligand, 2 H), 6.91–7.60 (aromatic protons), 7.72 (d, $^3J_{HH} = 5.9$ Hz, $^3J_{PtH} = 18.1$, CH group adjacent to coordinated N atom of ppy ligand, 1 H).

4.1.1.3. [Pt(p-MeOC$_6$H$_4$)(ppy)(2-MePy)], ***2d***. Yield 15 mg; 71%, mp = 221 °C (decomp.). Anal. Calcd. for $C_{24}H_{22}N_2OPt$: C, 52.5; H, 4.0; N, 5.1; Found: C, 52.1; H, 3.9; N, 5.4. ^1H NMR data in $CDCl_3$: $\delta = 2.95$ (s, Me group on the 2-MePy ligand, 1 Me), 3.74 (s, OMe group on the *p*-anisol ligand, 1 Me), 6.64 (d, $^3J_{H^mH^o} = 8.4$ Hz, H^m of *p*-anisol ligand, 2 H), 7.45 (d, $^3J_{H^oH^m} = 8.4$ Hz, $^3J_{PtH^o} = 67.2$ Hz, H^o of *p*-anisol ligand, 2 H), 7.02–7.80 (aromatic protons), 8.97 (d, $^3J_{H^oH^m}$ = 5.1 Hz, $^3J_{PtH^o} = 21.6$ Hz, H^o of 2-MePy ligand, 1 H).

4.1.1.4. [Pt(p-MeOC$_6$H$_4$)(ppy)(3-PhPy)], ***2e***. Yield 19 mg; 80%, mp = 223 °C (decomp.). Anal. Calcd. for $C_{29}H_{24}N_2OPt$: C, 57.0; H, 4.0; N, 4.6; Found: C, 57.4; H, 4.1; N, 4.8. ^1H NMR data in $CDCl_3$: $\delta = 3.76$ (s, OMe group on the *p*-anisol ligand, 1 Me), 6.68 (d, $^3J_{H^mH^o} = 8.6$ Hz, H^m of *p*-anisol ligand, 2 H), 7.44 (d, $^3J_{H^oH^m} = 8.6$ Hz, $^3J_{PtH^o}$ = not resolved, H^o of *p*-anisol ligand, 2 H), 7.00–7.81 (aromatic protons), 7.98 (d, $^3J_{HH} = 5.4$ Hz, $^3J_{PtH} = 19.3$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 8.83 (d, $^3J_{H^6H^5} = 4.6$ Hz, $^3J_{PtH^6} = 20.3$, H^6 of 3-PhPy ligand, 1 H), 9.15 (s, $^3J_{PtH^2} = 21.6$ Hz, H^o of 3-PhPy ligand, 1 H).

4.1.1.5. [Pt(p-MeOC$_6$H$_4$)(ppy)(3,4-Me$_2$Py)], ***2f***. Yield 12 mg; 56%, mp = 196 °C (decomp.). Anal. Calcd. for $C_{25}H_{24}N_2OPt$: C, 53.3; H, 4.3; N, 5.0; Found: C, 53.8; H, 4.4; N, 5.2. ^1H NMR data in $CDCl_3$: $\delta = 2.20$ (s, Me group on the 3,4-MePy ligand in *para* postion, 1 Me), 2.32 (s, Me group on the 3,4-MePy ligand in *meta* postion, 1 Me), 3.63 (s, OMe group on the *p*-anisol ligand, 1 Me), 6.39 (d, $^3J_{H^mH^o} = 8.1$ Hz, H^m of *p*-anisol ligand, 2 H), 7.62 (d, $^3J_{H^oH^m} = 8.1$ Hz, $^3J_{PtH^o}$ = not resolved, H^o of *p*-anisol ligand, 2 H), 6.83–8.14 (aromatic protons), 8.32 (d, $^3J_{HH} = 6.1$ Hz, $^3J_{PtH} = 18.1$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 8.66 (s, $^3J_{PtH^2} = 19.4$ Hz, H^2 of 3,4-MePy ligand, 1 H), 9.90 (d, $^3J_{H^6H^5} = 5.6$ Hz, $^3J_{PtH^6} = 20.8$ Hz, H^6 of 3,4-MePy ligand, 1 H).

4.1.1.6. [Pt(p-MeOC$_6$H$_4$)(ppy)(4-^{t}BuPy)], ***2g***. Yield 17 mg; 75%, mp = 238 °C (decomp.). Anal. Calcd. for $C_{27}H_{28}N_2OPt$: C, 54.9; H, 4.8;

N, 4.7; Found: C, 55.0; H, 4.8; N, 4.6. ^{1}H NMR data in $CDCl_3$: $\delta = 1.33$ (s, ^{t}Bu group on the 4-^{t}BuPy ligand, 3 Me), 3.81 (s, OMe group on the *p*-anisol ligand, 1 Me), 6.65 (d, $^3J_H{}^mH^o = 8.5$ Hz, H^m of *p*-anisol ligand, 2 H), 7.36 (d, $^3J_H{}^mH^o = 5.1$ Hz, H^m of 4-^{t}BuPy ligand, 2 H), 7.43 (d, $^3J_H{}^oH^m = 8.5$ Hz, $^3J_{PtH}{}^o = 63.4$ Hz, H^o of *p*-anisol ligand, 2 H), 7.54 (d, $^3J_{HH} = 5.6$ Hz, $^3J_{PtH} = 18.4$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 7.00–7.80 (aromatic protons), 8.74 (d, $^3J_H{}^oH^m = 5.1$ Hz, $^3J_{PtH}{}^o = 22.3$ Hz, H^o of 4-^{t}BuPy ligand, 2 H).

4.1.1.7. [Pt(p-MeOC$_6$H$_4$)(ppy)(3C(O)OMePy)], ***2h***. Yield 19 mg; 83%, mp = 232 °C (decomp.). Anal. Calcd. for $C_{25}H_{22}N_2O_3Pt$: C, 50.6; H, 3.7; N, 4.7; Found: C, 50.1; H, 3.6; N, 4.5. ^{1}H NMR data in $CDCl_3$: $\delta = 3.75$ (s, s, OMe group on the *p*-anisol ligand, 1 Me), 3.96 (s, OMe group of 3C(O)OMePy ligand, 1 Me), 6.66 (d, $^3J_H{}^mH^o = 8.6$ Hz, H^m of *p*-anisol ligand, 2 H), 7.50 (d, $^3J_H{}^oH^m = 8.6$ Hz, $^3J_{PtH}{}^o = 62.6$ Hz, H^o of *p*-anisol ligand, 2 H), 7.81 (d, $^3J_{HH} = 5.5$ Hz, $^3J_{PtH} = 18.1$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 7.00–8.44 (aromatic protons), 8.98 (d, $^3J_H{}^6H^5 = 4.3$ Hz, $^3J_{PtH}{}^6 = 21.3$ Hz, H^6 of 3C(O)OMePy ligand, 1 H), 9.56 (s, $^3J_{PtH}{}^2 = 22.7$ Hz, H^2 of 3C(O)OMePy ligand, 1 H).

4.1.1.8. [Pt(p-MeC$_6$H$_4$)(ppy)(4-MePy)], ***2i***. Yield 17 mg; 80%, mp = 238 °C (decomp.). Anal. Calcd. for $C_{24}H_{22}N_2Pt$: C, 54.0; H, 4.2; N, 5.3; Found: C, 54.3; H, 4.3; N, 5.1. ^{1}H NMR data in $CDCl_3$: $\delta = 2.24$ (s, Me group on the *p*-anisol ligand, 1 Me), 2.37 (s, Me group on the 4-MePy ligand, 1 Me), 6.83 (d, $^3J_H{}^mH^o = 7.2$ Hz, H^m of *p*-tolyl ligand, 2 H), 7.20 (d, $^3J_H{}^mH^o = 5.0$ Hz, H^m of 4-MePy ligand, 2 H), 7.41 (d, $^3J_H{}^oH^m = 7.2$ Hz, $^3J_{PtH}{}^o = 61.9$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.78 (d, $^3J_{HH} = 4.8$ Hz, $^3J_{PtH} = 19.6$, CH group adjacent to coordinated N atom of ppy ligand, 1 H), 6.95–7.67 (aromatic protons), 8.72 (d, $^3J_H{}^oH^m = 5.0$ Hz, $^3J_{PtH}{}^o = 22.8$ Hz, H^o of 4-MePy ligand, 2 H).

4.1.2. Preparation of the complex [Pt(p-MeC$_6$H$_4$)(ppy)(PPh$_3$)], ***3a***

To a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], **1b**, (20 mg, 0.04 mmol) in acetone (20 ml) was added PPh_3 (11 mg, 0.04 mmol), and the solution was stirred for 1 h. A green solution was formed, then the solvent was removed under reduced pressure and the residue was triturated with cold acetone (2 × 3 mL). The product as a green solid was dried under vacuum. Yield 23 mg; 82%, mp = 250 °C (decomp.). Anal. Calcd. for $C_{36}H_{30}NPPt$: C, 61.6; H, 4.3; N, 2.0; Found: C, 61.8; H, 4.5; N, 1.9. NMR data in $CDCl_3$: ^{1}H NMR: $\delta = 2.10$ (s, Me group on the *p*-tolyl ligand, 1 Me), 6.43 (d, $^3J_H{}^mH^o = 7.5$ Hz, H^m of *p*-tolyl ligand, 2 H), 6.50 (d, $^3J_{HH} = 1.5$ Hz, $^3J_{PtH} = 12.5$ Hz, CH group adjacent to coordinated C atom, 1 H), 6.99 (d, $^3J_H{}^oH^m = 7.5$ Hz, $^3J_{PtH}{}^o = 65.0$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.06–7.84 (aromatic protons); ^{31}P NMR: $\delta = 31.8$ (s, $^1J_{PtP} = 2041$ Hz, 1 P); ^{195}Pt NMR: $\delta = -2435$ (d, $^1J_{PtP} = 2035$ Hz, 1 Pt).

The following complexes were made similarly by using the appropriate P-donor nucleophile:

4.1.2.1. [Pt(p-MeC$_6$H$_4$)(ppy)(PPh$_2$Me)], ***3b***. Yield 19 mg; 75%, mp = 218 °C (decomp.). Anal. Calcd. for $C_{31}H_{28}NPPt$: C, 58.1; H, 4.4; N, 2.2; Found: C, 57.6; H, 4.4; N, 1.9. NMR data in $CDCl_3$: ^{1}H NMR: $\delta = 1.40$ (d, $^2J_{PH} = 8.8$ Hz, $^3J_{PtH} = 35.0$ Hz, Me group of the PPh_2Me ligand, 1 Me), 2.24 (s, Me group on the *p*-tolyl ligand, 1 Me), 6.53 (d, $^3J_{HH} = 1.7$ Hz, $^3J_{PtH} = 13.2$ Hz, CH group adjacent to coordinated C atom, 1 H), 6.79 (d, $^3J_H{}^mH^o = 7.5$ Hz, H^m of *p*-tolyl ligand, 2 H), 7.31 (d, $^3J_H{}^oH^m = 7.5$ Hz, $^3J_{PtH}{}^o = 60.0$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.08–7.82 (aromatic protons); ^{31}P NMR: $\delta = 14.5$ (s, $^1J_{PtP} = 1997$ Hz, 1 P); ^{195}Pt NMR: $\delta = -2413$ (d, $^1J_{PtP} = 1990$ Hz, 1 Pt).

4.1.2.2. [Pt(p-MeC$_6$H$_4$)(ppy)[P(OPh)$_3$)], ***3d***. Yield 21 mg; 73%, mp = 167 °C. Anal. Calcd. for $C_{36}H_{30}NO_3PPt$: C, 57.6; H, 4.0; N, 1.9; Found: C, 57.2; H, 4.0; N, 1.8. NMR data in $CDCl_3$: ^{1}H NMR: $\delta = 2.25$ (s, Me group on the *p*-tolyl ligand, 1 Me), 6.75 (d, $^3J_H{}^mH^o = 7.5$ Hz, H^m of *p*-tolyl ligand, 2 H), 7.11 (d, $^3J_H{}^oH^m = 7.5$ Hz, $^3J_{PtH}{}^o = 61.4$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.16–7.87 (aromatic protons), 9.24 (d, $^3J_{HH} = 4.5$ Hz, $^3J_{PtH} = 17.8$ Hz, CH group adjacent to coordinated N atom, 1 H); ^{31}P NMR: $\delta = 116.0$ (s, $^1J_{PtP} = 3517$ Hz, 1 P).

4.1.2.3. [Pt(p-MeC$_6$H$_4$)(ppy)[P(O-^{i}Pr)$_3$)], ***3e***. Yield (as yellowish oil), almost quantitative. NMR data in $CDCl_3$: ^{1}H NMR: $\delta = 1.23$[d, $^3J_{HH}$ = not resolved, 12Me groups of ^{i}Pr, 36H], 2.28 (s, Me group on the *p*-tolyl ligand, 1 Me), 4.82 [m, 6CH groups of ^{i}Pr, 6H], 6.87 (d, $^3J_H{}^mH^o = 7.2$ Hz, H^m of *p*-tolyl ligand, 2 H), 7.38 (d, $^3J_H{}^oH^m = 7.2$ Hz, $^3J_{PtH}{}^o = 66.5$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.06–7.90 (aromatic protons), 9.33 (d, $^3J_{HH} = 4.8$ Hz, $^3J_{PtH} = 18.3$ Hz, CH group adjacent to coordinated N atom, 1 H); ^{31}P NMR: $\delta = 125.6$ (s, $^1J_{PtP} = 3485$ Hz, 1 P); ^{195}Pt NMR: $\delta = -2429$ (d, $^1J_{PtP} = 3476$ Hz, 1 Pt).

4.1.2.4. [Pt(p-MeOC$_6$H$_4$)(ppy)(PPh$_3$)], ***3f***. Yield 22 mg; 82%, mp = 233 °C (decomp.). Anal. Calcd. for $C_{36}H_{30}NOPPt$: C, 60.2; H, 4.2; N, 2.0; Found: C, 60.6; H, 4.3; N, 2.1. NMR data in $CDCl_3$: ^{1}H NMR: $\delta = 3.67$ (s, OMe group on the *p*-anisol ligand, 1 Me), 6.30 (d, $^3J_H{}^mH^o = 8.6$ Hz, H^m of *p*-tolyl ligand, 2 H), 6.50 (d, $^3J_{HH} = 2.4$ Hz, $^3J_{PtH} = 13.7$ Hz, CH group adjacent to coordinated C atom, 1 H), 7.01 (d, $^3J_H{}^oH^m = 8.6$ Hz, $^3J_{PtH}{}^o = 65.8$ Hz, H^o of *p*-tolyl ligand, 2 H), 7.08–7.85 (aromatic protons); ^{31}P NMR: $\delta = 30.7$ (s, $^1J_{PtP} = 2029$ Hz, 1 P).

4.2. Kinetic studies

For the reactions with N-donors: in a typical experiment, a solution of [Pt(*p*-MeOC$_6$H$_4$)(ppy)(SMe$_2$)], **1a**, in dichloromethane (3 ml, 2 × 10^{-4} M) in a cuvette was thermostated at 25 °C and a known excess of a solution of 4-MePy in dichloromethane (30 μl, 1 M) was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 380$ nm was monitored with time. The same method was used at other temperatures.

For the reaction with P-donors: in a typical experiment, a solution of [Pt(*p*-MeC$_6$H$_4$)(ppy)(SMe$_2$)], **1b**, in dichloromethane (3 ml, 2.6 × 10^{-4} M) in a cuvette was thermostated at 25 °C and a solution of dppm in dichloromethane (78 μl, 0.01 M) was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 364$ nm was monitored with time. The same method was used at other temperatures.

4.3. ^{1}H NMR study of reaction of [Pt(p-MeOC$_6$H$_4$)(ppy)(SMe$_2$)], 1a, with N-donor ligand

For the experiment using ^{1}H NMR spectroscopy, to a sample of complex [Pt(*p*-MeOC$_6$H$_4$)(ppy)(SMe$_2$)], **1a**, (10 mg, 0.02 mmol) in $CDCl_3$ (0.75 mL) in an NMR tube was added 3-PhPy ligand (30 μl, 0.02 mmol) and the disappearance of signal of the SMe_2 ligand connected to platinum center atom and the appearance of the signal for the free SMe_2 ligand were used to monitor the reaction.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.08.005.

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry. University Sciences Books, Mill Valley, California, 1987.

[2] M.L. Tobe, J. Burgess, Inorganic Reaction Mechanism. Longman, Essex, UK, 1999.
[3] D.T. Richens, Chem. Rev. 105 (2005) 1961–2002.
[4] M. Rashidi, K. Kamali, M.J. Jennings, R.J. Puddephatt, J. Organomet. Chem. 690 (2005) 1600–1605.
[5] S.J. Hoseini, S.M. Nabavizadeh, S. Jamali, M. Rashidi, J. Organomet. Chem. 692 (2007) 1990–1996.
[6] A.R. Esmaeilbeig, H.R. Samouei, Mehdi Rashidi, J. Organomet. Chem. 693 (2008) 2519–2526.
[7] M. Rashidi, S.M. Nabavizadeh, A. Zare, S. Jamali, R.J. Puddephatt, Inorg. Chem. 49 (2010) 8435–8443.
[8] R.G. Wilkins, Kinetics and Mechanisms of Reactions of Transition Metal Complexes. VCH, Weinheim, Germany, 1991.
[9] F. Basolo, Coord. Chem. Rev. 154 (1996) 151–161.
[10] R.J. Cross, Chem. Soc. Rev. 14 (1985) 197–223.
[11] S.M. Nabavizadeh, H. Amini, H.R. Shahsavari, M. Namdar, M. Rashidi, R. Kia, B. Hemmateenejad, M. Nekoeinia, A. Ariafard, F. Niroomand Hosseini, A. Gharavi, A. Khalafi-Nezhad, M.T. Sharbati, F. Panahi, Organometallics 30 (2011) 1466–1477.
[12] M.R. Plutino, L. Monsú Scolaro, R. Romeo, A. Grassi, Inorg. Chem. 39 (2000) 2712–2720 (and references therein).
[13] R. Romeo, M.R. Plutino, L. Monsú Scolaro, S. Stoccoro, Inorg. Chim. Acta 265 (1997) 225–233.
[14] M. Schmülling, A.D. Ryabov, R. van Eldik, J. Chem. Soc. Chem. Commun. (1992) 1609–1611.
[15] M. Schmülling, A.D. Ryabov, R. van Eldik, J. Chem. Soc. Dalton Trans. (1994) 1257–1263.
[16] M. Schmülling, D.M. Grove, G. van Koten, R. van Eldik, N. Veldman, A.L. Spek, Organometallics 15 (1996) 1384–1391.
[17] M. Albrecht, R.A. Gossage, U. Frey, A.W. Ehlers, E.J. Baerends, A.E. Merbach, G. van Koten, Inorg. Chem. 40 (2001) 850–855.
[18] M. Albrecht, R.A. Gossage, M. Lutz, A.L. Spek, G. van Koten, Chem. Eur. J. 6 (2000) 1431–1445.
[19] D. Zhang, L.-Z. Wu, L. Zhou, X. Han, Q.-Z. Yang, L.-P. Zhang, C.-H. Tung, J. Am. Chem. Soc. 126 (2004) 3440–3441.
[20] M. Hissler, J.E. McGarrah, W.B. Connick, D.K. Geiger, S.D. Cummings, R. Eisenberg, Coord. Chem. Rev. 208 (2000) 115–137.
[21] H. Jude, J.A.K. Bauer, W.B. Connick, Inorg. Chem. 44 (2005) 1211–1220.
[22] S.W. Lai, T.C. Cheung, M.C.W. Chan, K.K. Cheung, S.M. Peng, C.M. Che, Inorg. Chem. 39 (2000) 255–262.
[23] M. Lopez-Torres, A. Fernandez, J.J. Fernandez, A. Suarez, S. Castro-Juiz, J.M. Vila, M.T. Pereira, Organometallics 20 (2001) 1350–1353.
[24] P.A. Chase, R.J.M. Klein Gebbink, G. van Koten, J. Organomet. Chem. 689 (2004) 4016–4054.
[25] H.P. Dijkstra, C.A. Kruithof, N. Ronde, R. van der Coevering, D.J. Ramón, D. Vogt, G.P.M. van Klink, G. van Koten, J. Org. Chem. 68 (2003) 675–685.
[26] M. Golbon Haghighi, M. Rashidi, S.M. Nabavizadeh, S. Jamali, R.J. Puddephatt, Dalton Trans. 39 (2010) 11396–11402.
[27] S.M. Nabavizadeh, M. Golbon Haghighi, A.R. Esmaeilbeig, F. Raoof, Z. Mandegani, S. Jamali, M. Rashidi, R.J. Puddephatt, Organometallics 29 (2010) 4893–4899.
[28] S. Jamali, Z. Mazloomi, S.M. Nabavizadeh, D. Milić, R. Kia, M. Rashidi, Inorg. Chem. 49 (2010) 2721–2726.
[29] S. Jamali, S.M. Nabavizadeh, M. Rashidi, Inorg. Chem. 47 (2008) 5441–5452.
[30] T. Yagyu, J.-I. Ohashi, M. Maeda, Organometallics 26 (2007) 2383–2891.
[31] S. Jamali, S.M. Nabavizadeh, M. Rashidi, Inorg. Chem. 44 (2005) 8594–8601.
[32] D.R. Lide, Editor-in-Chief (Eds.), CRC Handbook of Chemistry and Physics, 81st ed. CRC Press, Boca Raton, FL, 2000.
[33] L. Liu, Q.-X. Guo, Chem. Rev. 101 (2001) 673–696.
[34] J.H. Espenson, Chemical Kinetics and Reaction Mechanisms, second ed., McGraw-Hill, New York, 1995.
[35] S. Habibzadeh, M. Rashidi, S.M. Nabavizadeh, L. Mahmoodi, F. Niroomand Hosseini, R.J. Puddephatt, Organometallics 29 (2010) 82–88.
[36] K.A. Bunten, L. Chen, A.L. Fernandez, A.J. Poe, Coord. Chem. Rev. 233 (2002) 41–51.
[37] M. Rashidi, M. Hashemi, M. Khorasani-Motlagh, R.J. Puddephatt, Organometallics 19 (2000) 2751–2755.