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Ligand substitution reaction at a binuclear organoplatinum(II) complex

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Abstract

The ligand substitution reactions of the N-donor ligand in the binuclear dimethylplatinum(II) complex of formula *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$], **1**, in which dppm = bis(diphenylphosphino)methane and NN = phthalazine, by different nucleophilic phosphorous-donors L, L = $P(O\text{–}^iPr)_3$ or PPh_3 and L_2 = dppm, to form the dinuclear complexes **2**, *cis*,*cis*-[$Me_2LPt(\mu$-dppm)$PtLMe_2$] and *cis*,*cis*-[$Me_2Pt(\mu$-dppm)$_2PtMe_2$], respectively, are studied. Complex **1** has a MLCT band in the visible region which was used to easily follow the kinetics of its ligand substitution reactions. These reactions which involve diplatinum(II) complex **1** containing *cis* Pt–C bonds, proceeded by the normal associative mechanism. In associative reactions of the present work, as expected, the rate of the reactions was depended on the concentration and the nature of the entering group. The nucleophilicity of PPh_3 is stronger than $P(O\text{–}^iPr)_3$ on the basis of its stronger σ-donor ability and its lower solvation and is responsible for the observed 3-fold increase of its rate as compared to that of $P(O\text{–}^iPr)_3$. Also, the solvation energy involved is suggested to be responsible for the observation of higher rates in benzene than in acetone. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot gives a straight line which suggests the operation of the same mechanism for all entering nucleophiles.

Keywords: Kinetics; Organoplatinum(II) complexes; Substitution reactions

1. Introduction

Ligand substitution reactions on monomeric square planar platinum(II) complexes have been extensively studied [1]. The especial attention has been due to the exceptionally low rate of their reactions as compared to those of d^8 square planar complexes of other metals such as palladium, nickel, rhodium, iridium and gold. This low rate of ligand exchange is particularly important in the cancer chemotherapy of platinum(II) complexes, e.g. *cis*-platin, $[PtCl_2(NH_3)_2]$, and the second generation analogous, since this allows binding to cellular DNA before inactivation of the Pt(II) center by extracellular binding sites such as S-donor residues [2]. The mechanism of the reported reactions is usually consistent with an associative pathway involving the direct attack of the entering nucleophile on the substrate with the formation of a five-coordinate intermediate [3]. An elegant density functional study of S_N2 ligand substitution at square-planar platinum(II) complexes has recently been reported by Cooper and Ziegler [4]. A typical rate law indicated in Eq. (1) is presented for square planar substitution in which [N] and [M] are the concentrations of the nucleophile and the metal complex, respectively; k_2 term corresponds to a second-order rate constant for bimolecular attack of the nucleophile on the substrate and k_1 term corresponds to either a dissociative path or a solvolytic path, in which a solvent molecule displaces the leaving group and is subsequently displaced by the nucleophile.

$$\text{rate} = (k_1 + k_2[\text{N}])[\text{M}] \quad (1)$$

Pioneered by Romeo et al., during the past two decades, there has been a great interest in ligand substitution reactions of organoplatinum(II) complexes containing one or more Pt–C bonds [5–10], e.g. the ligand substitution or ligand exchange on organometallic substrates of the type

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cis-[PtR_2L_2] (R = Ph or Me; L = thioethers or dimethylsulfoxide). A changeover of mechanism from a "normal" associative substitution to an "abnormal" dissociative substitution is usually observed in the nucleophilic substitution reactions of this type of complexes. The factors influencing this changeover are discussed [7,8].

Despite these extensive studies, nothing is really reported about the kinetics and mechanism of ligand substitution reactions involving binuclear platinum(II) complexes, even though compounds containing two or more metal atoms are of great interest because they can be used as models for mimicking the behaviors of heterogeneous catalytic systems. Also in recent years there has been a great interest in investigating binuclear platinum(II) complexes as a new and exciting area in the effort to improve platinum chemotherapy [11]. The ligand substitution reactions of dinuclear platinum(I) complexes have been briefly investigated by Espenson et al. [12,13]. In the present work, we have studied the ligand substitution reactions of the N-donor ligand in the binuclear dimethylplatinum(II) complex of formula *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$], in which dppm = bis(diphenylphosphino)methane and NN = phthalazine [14], with different phosphorous-donors. This diplatinum(II) complex showed two main advantages in studying its ligand substitution reactions. First, it has a distinct color due to presence of the imine ligand and so its reactions could easily be followed by spectrophotometry in the visible region. Second, the complex contains a robust bridging ligand which prevents fragmentation of the dimer during the reaction, a major problem which is usually encountered when different reactions of binuclear systems are studied.

2. Results

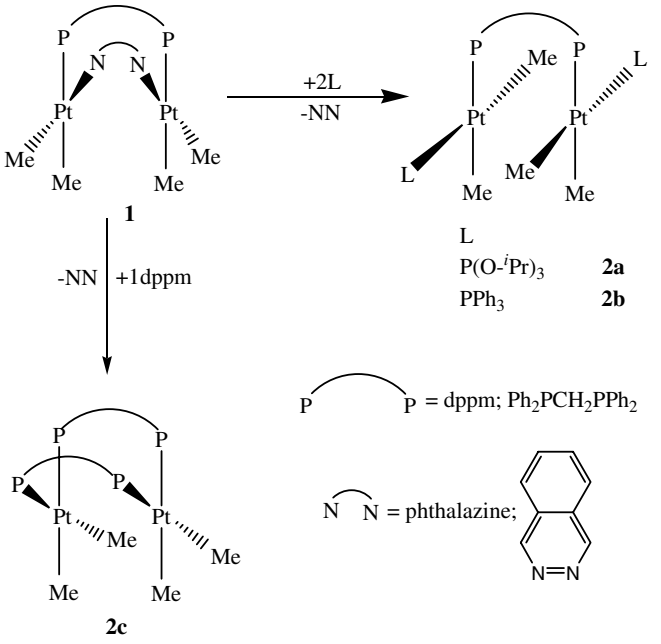
2.1. Reaction of the diplatinum(II) complex with P-donor ligands

The reaction of the diplatinum(II) complex *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$], **1**, in which dppm = bis(diphenylphosphino)methane and NN = phthalazine [14], with 2 equiv. of L, in which L = $P(O-^iPr)_3$ or PPh_3, or 1 equiv. of L_2 = dppm as nucleophile, caused the displacement of the NN ligand in each case and the dinuclear complexes **2** are formed, almost quantitatively in pure form, as depicted in Scheme 1. The reactions with a large excess of L or L_2 gave the same dimers with no fragmentation or other products. Meanwhile, the reactions using 1 equiv. of L or 0.5 equiv. of dppm gave the dimeric complexes **2** with 0.5 equiv. of unreacted starting dimer **1**. The complexes **2** were identified by comparison of their ^1H and ^{31}P NMR spectra with those of the authentic samples [15,16].

2.2. Kinetic study of the substitution reactions

Complex **1** has a strong absorption in its UV–Vis spectrum at $\lambda = 375$ nm (both in acetone and benzene) and this absorption is ascribed to the $5d_\pi(Pt) \rightarrow \pi^*$(imine) MLCT band which is believed to be responsible for the reddish color of the complex [14]. Upon the reaction of the reddish complex **1** with the phosphorus donors, L, the color is gradually faded away and eventually an almost colorless solution is obtained. Thus, an excess of L was used at 25 °C, and the disappearance of the MLCT band at $\lambda = 375$ nm in benzene or acetone solution was used to monitor the reaction. The reactions followed good first-order kinetics (Figs. 1 and 2). Graphs of these first-order rate constants against the concentration of the nucleophile L gave good straight line plots passing through origin, showing a first-order dependence of the rate on the concentration of L (Fig. 3). Thus, the overall second-order rate constants were determined. The activation parameters were also determined from measurement at different temperatures (Fig. 4) and the data are given in Table 1. These reactions followed good second-order kinetics, first order in both the dimer complex and the attacking nucleophile, with remarkable reproducibility (±3%).

Using ^1H NMR spectroscopy, we found that the rate of disappearance of the starting diplatinum(II) complex *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$], **1**, equals the rate of appearance of the free NN ligand. Thus, a 10-fold excess of L = $P(O-^iPr)_3$ was added to a solution of complex **1** in acetone-d_6 in an NMR tube at 27 °C, and the disappearance of the signal at $\delta = 9.35$, for the two equivalent CH groups of phthalazine adjacent to N atoms [14], and the appearance of the corresponding signal for the free NN at $\delta = 9.38$ was used to monitor the reaction. The latter two steps followed good first-order kinetics (Fig. 5) and the k_{obs} values for first step, the disappearance of complex **1**, and for the second step, appearance of free NN, were found to be $1.2(\pm0.1) \times 10^{-3}$ and $1.1(\pm0.1) \times 10^{-3}$ s^{-1}, respectively.



Scheme 1.

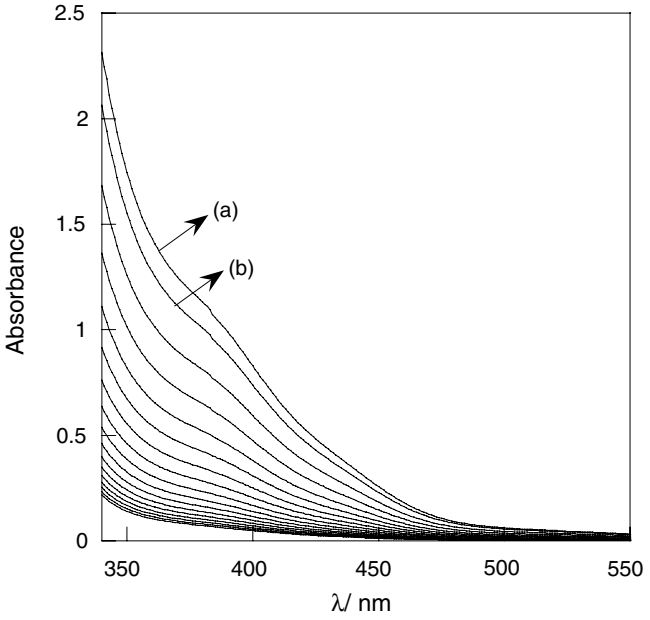


Fig. 1. Changes in the UV–Vis spectrum during the reaction of complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2$], **1**, ($3 \times 10^{-4}$ M) and dppm (0.2 M) in benzene at $T = 25$ °C: (a) initial spectrum (before adding dppm) and (b) spectrum at $t = 30$ s; successive spectra were recorded at intervals of 3 min.

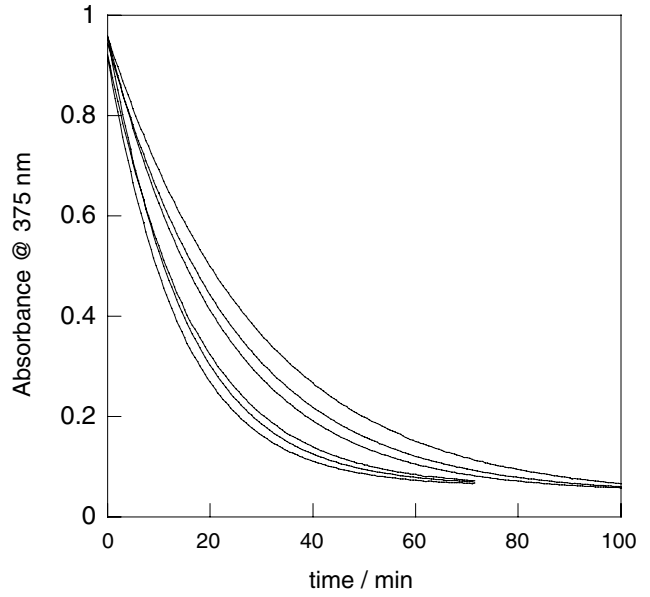


Fig. 2. Absorbance–time curves for the reaction of complex **1** with PPh_3 (0.016–0.42 M, [PPh_3] increases reading downward) in acetone at 35 °C.

3. Discussion

The above studies led us to propose the associative mechanism shown in Scheme 2. A simple second-order rate law (Eq. (2)) was clearly obtained with absolutely no sign of any dissociative or solvolytic paths.

$$-\mathrm{d}[\text{complex } \mathbf{1}]/\mathrm{d}t = k_{\text{obs}}[\text{complex } \mathbf{1}]; \quad k_{\text{obs}} = k_2[\mathrm{L}] \qquad (2)$$

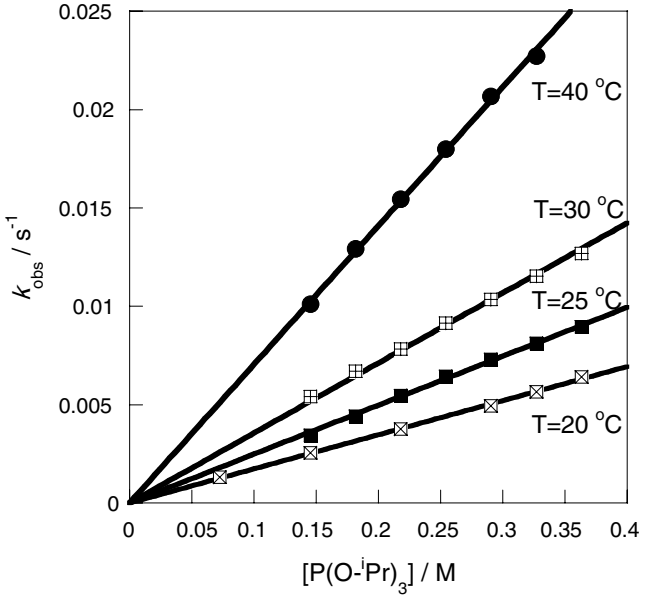


Fig. 3. Plots of first-order rate constants (k_{obs}/s^{-1}) for the reaction of complex **1** with P(O–^{i}Pr)$_3$ in benzene at different temperatures vs. concentration of P(O–^{i}Pr)$_3$.

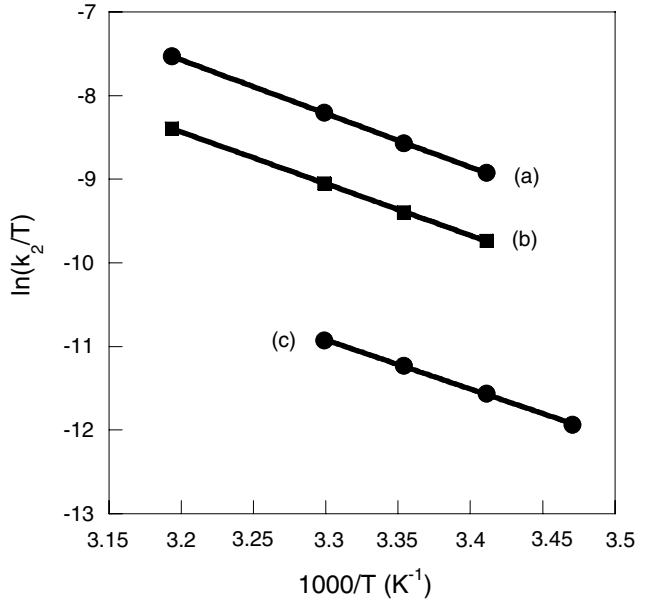


Fig. 4. Eyring plots for the reaction of complex **1** with: (a) PPh_3 in benzene; (b) P(O–^{i}Pr)$_3$ in benzene; (c) P(O–^{i}Pr)$_3$ in acetone.

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. A further support for the proposed associative mechanism comes from the fact that the rate of the reaction is dependent on the nature of the entering group (see Table 1). Thus, for example the rate of the reaction of complex **1** with PPh_3 in acetone at 30 °C is more than 3 times faster than the corresponding rate with P(O–^{i}Pr)$_3$ at the same condition. We therefore suggest that as shown in Scheme 2, the first mole

Table 1
Second-order rate constants and activation parameters[a] for reaction of the complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2$], **1**, with the nucleophile L (L = PPh_3 and $P(O\text{–}^iPr)_3$) or L_2 = dppm in acetone (or benzene)[b]

L or L_2	10^2 k_2 (L mol^{-1} s^{-1}) at different temperatures						$\Delta H^{\ddagger c}$ (kJ mol^{-1})	$\Delta S^{\ddagger c}$ (J K^{-1} mol^{-1})
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C		
dppm		1.01 ± 0.01	1.39 ± 0.02	2.30 ± 0.04	3.48 ± 0.07		60.5 ± 4.2	-77 ± 14
		(5.29 ± 0.12)	(6.86 ± 0.13)	(11.94 ± 0.28)		(27.42 ± 0.86)	(62.3 ± 5.0)	(-57 ± 16)
PPh_3		1.03 ± 0.02	1.38 ± 0.02	1.88 ± 0.03	2.98 ± 0.07		49.9 ± 4.7	-113 ± 16
		(3.90 ± 0.10)	(5.67 ± 0.25)	(8.30 ± 0.49)		(16.81 ± 0.39)	(53.3 ± 0.3)	(-90 ± 1)
$P(O\text{–}^iPr)_3$	0.19 ± 0.01	0.28 ± 0.01	0.40 ± 0.02	0.54 ± 0.02			48.7 ± 1.0	-128 ± 3
		(1.74 ± 0.01)	(2.49 ± 0.02)	(3.56 ± 0.03)		(7.11 ± 0.08)	(51.4 ± 0.4)	(-103 ± 2)

[a] Values given based on 95% confidence limits from least squares regression analysis.
[b] Values in parenthesis are in benzene.
[c] Obtained from the Eyring equation.

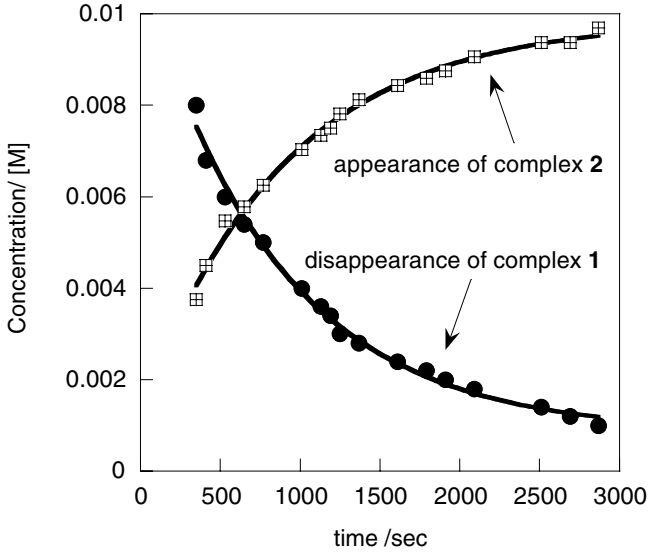


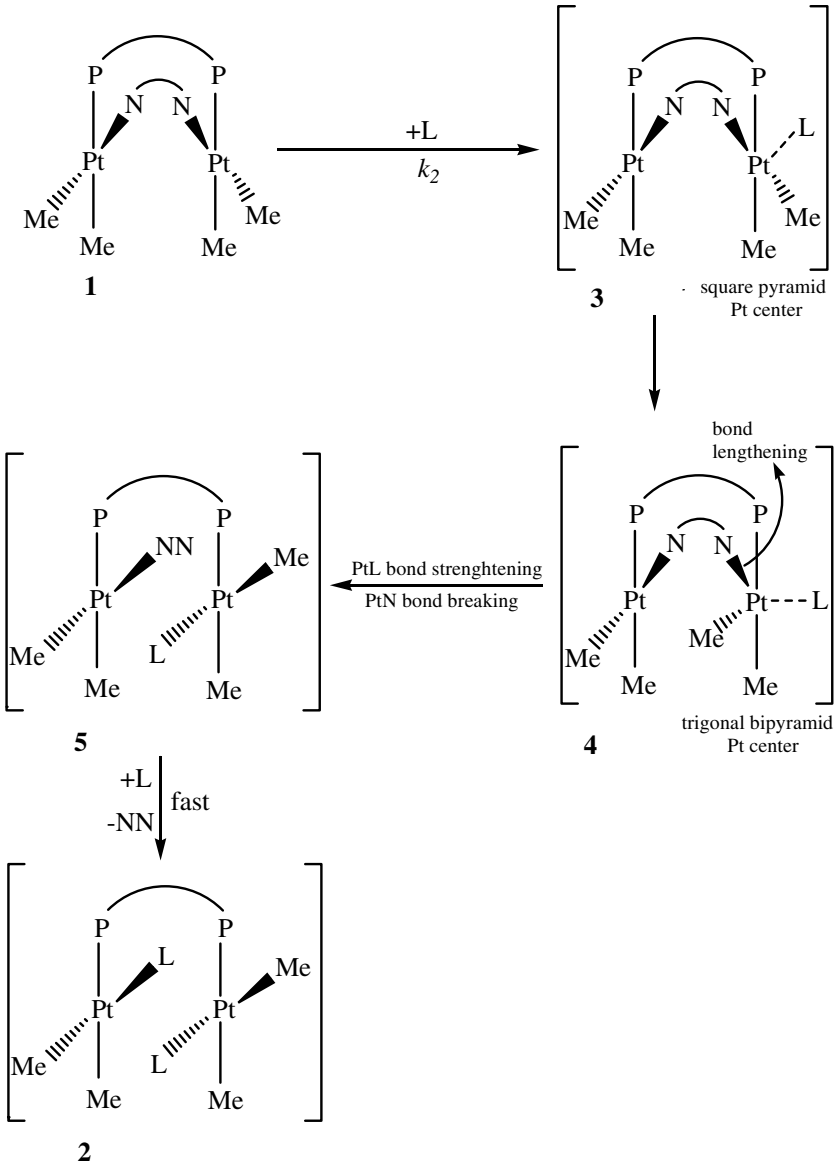
Fig. 5. Concentration–time curves for the reaction of complex **1** (0.01 M) with $P(O\text{–}^iPr)_3$ (0.218 M) in acetone-d_6 at 27 °C, using ^1H NMR spectroscopy.

of L has an associative nucleophilic attack on one of the platinum(II) centers of complex **1**, and the first substitution, which is the rate determining step, is proceeded via the usual five coordinated transition states with a square pyramid and a trigonal bipyramid geometries, **3** and **4**, respectively, to give the intermediate **5**. The dimeric nature of the metallic substrate does not create any restriction for the latter transformation to happen because in **4** the axial P and Me ligands and the equatorial N ligand can stay in the same positions as they were in square pyramid structure **3** while the equatorial monodentate ligands Me and L in **3** can move appropriately to form the trigonal bipyramid geometry in **4**. The second mole of L completely replaces the NN ligand by a rate which is much faster than the rate of replacement of the first L. This is supported by the fact that, as mentioned above, when the reactions are performed using 1 equiv. of L or 0.5 equiv. of dppm, the dimeric complexes **2** with 0.5 equiv. of unreacted starting dimer **1** is obtained.

This suggestion that the rate of the replacement of the second L is faster than that of the first L is in particular confirmed by the results of the kinetic study using ^1H NMR spectroscopy as described above. Thus, for the reaction of the starting complex *cis*,*cis*-[$Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2$], **1**, with excess L = $P(O\text{–}^iPr)_3$ at 27 °C, the k_{obs} value of $1.2(\pm 0.1) \times 10^{-3}$ s^{-1} was obtained for the disappearance of the complex, which is related to rate of replacement of the first L. This value is very close to $k_{obs} = 1.1(\pm 0.1) \times 10^{-3}$ s^{-1} obtained for the reaction at the same condition using UV–Vis spectroscopy (calculated easily from the data in Table 1). The value of k_{obs} for the appearance of signal of product **2** obtained using ^1H NMR spectroscopy, almost equals to the k_{obs} value obtained for replacement of the first L. This result obviously confirms the above conclusion that the rate of the second substitution should be faster than that of the first one.

Note also that the suggested mechanism is consistent with the fact that no signal was observed in the low temperature ^{31}P NMR spectrum for any intermediate such as **5** and also with the observation that the rate of reactions were depended on both the concentration and the nature of the entering ligand.

The above observations are consistent with the fact that substitution reactions of platinum(II) complexes generally proceed associatively, even though complex **1** contains *cis* Pt–C bonds. Note also that in the dissociative substitution reactions of mononuclear complexes, due to the formation of two species from a single molecule of the starting complex in the rate determining step, the entropy of activation has a large positive value. This would obviously compensate significantly for the unfavorable enthalpy due to the necessary bond breaking between the metal center and the leaving ligand. If we assumed a dissociative mechanism for the step 1 of the ligand substitution reactions involving the dinuclear complex **1**, then the dissociated N donor leaving group would still be connected to the other N–Pt bridging arm and therefore no significant positive contribution to the entropy of activation would be expected. One therefore might argue that



Scheme 2.

this entropy effect probably has helped to prevent complex **1**, having *cis* Pt–C bonds, to proceed dissociatively as is observed in complexes such as *cis*-[$PtPh_2(Me_2SO)_2$] [5–10]. However, in order to support the argument, it would be necessary to demonstrate that close analogues having *cis* Pt–C bonds that lack the dppm bridging would react dissociatively. This point is under investigation. The following feathers are also worth noting:

3.1. Nature of the entering group

The rate of substitution reaction of complex **1** depends on the nature of the entering nucleophile (see Table 1), and this has been taken as a strong evidence for the associative nature of the reaction. Thus, the rate for entering ligand PPh_3 at different temperatures is more than three times faster than that of the $P(O–^iPr)_3$. Richens in his recent review [1b] of ligand substitution reactions at inorganic centers, summarizes that two of the factors, among others, affecting the incoming ligand nucleophilicity are polarizability and solvation energy. We rationalize the aforementioned rate increase involving phosphorous-donor entering group, L, in terms of its σ-donor ability rather than its polarizability, as this should be more useful in considering nucleophiles such as halide ions. PPh_3 has a higher σ-donor ability than $P(O–^iPr)_3$, and therefore when the lone pair of electrons of PPh_3 entering ligand is binding to the low lying platinum $6p_z$ orbital to form the initial transition state containing the square-pyramidal metallic center (Scheme 2), it is better able to cope with the electron density already present in the same direction from the filled metal $5d_{z^2}$ orbital [17]. Note that the Tolman cone angle of PPh_3(145°) is significantly greater than that of $P(O–^iPr)_3$ (130°). In

the associative process suggested for the present ligand substitution reactions of complex **1**, one might expect a lower rate for the larger entering group. The fact that PPh_3 is reacted faster than $P(O\text{–}^{i}Pr)_3$ indicates that the dominating factor should be by far electronic; by comparing the observed data in Table 1 for PPh_3 and dppm as entering groups, we conclude that the steric effects of the entering groups do not probably have a significant effect in the reaction rates. It is reasonable to assume that the effective cone angle of each phosphorous donor of dppm, i.e. Ph_2PCH_2– moiety, is smaller than that of PPh_3. However, the data show that they both perform the substitution reaction with almost the same rate at different temperatures. Since the nucleophilicity difference between these two phosphines is small, their similar rates support the suggestion that the steric difference probably has not a considerable effect in the rate constants. The second mentioned factor, i.e. solvation energy that states a more highly solvated ligand will be a poorer nucleophile and will require solvation changes to accompany metal complex formation, is also consistent with the above rate increase. The presence of oxygen on the phosphorus substitutents of $P(O\text{–}^{i}Pr)_3$ would increase the solvation of the ligand's active sites, as compared to that of PPh_3, and thus decreases its nucleophilicity.

The dependence of the nature of the entering nucleophile on the above reactions rates could also be rationalized on the basis of the effective nucleophilicity scale, n^0_{Pt} for the incoming ligands. For the *soft* platinum(II) centers, Tobe and Burgess quote that: "The nucleophilicities of ligands containing a *soft* donor are extremely sensitive to the nature of the substituents and the extent to which its other electrons are involved in bonding", and the reported n^0_{Pt} values for PPh_3 and $P(OMe)_3$ are 8.93 and 7.23, respectively [1a]. Thus, if we assume a similar trend that the phosphite $P(O\text{–}^{i}Pr)_3$ has a lower n^0_{Pt} value than that of the phosphine PPh_3, then it is qualitatively reasonable to accept that in substitution reactions of complex **1**, PPh_3 is more reactive than $P(O\text{–}^{i}Pr)_3$.

3.2. Solvent effect

As can be seen from Table 1, the rate of reaction of the nucleophile L with complex **1** at different temperatures is faster in benzene that in acetone. For example, at 25 °C the reaction of either $P(O\text{–}^{i}Pr)_3$ or PPh_3 with complex **1** is faster in benzene than in acetone by a factor of 6.2 or 4.1, respectively. The above solvation energy argument could also be used here to explain this solvent effect. The active sites of the entering groups L are obviously more solvated in polar acetone solvent than in non-polar benzene solvent and thus a more compensation of the solvation energy is involved in the case of reaction in acetone as compared to that in benzene resulting in a slower rate. The fact that this solvent effect is more pronounced for $P(O\text{–}^{i}Pr)_3$ than for PPh_3 is obviously due to the former having more solvating power than the latter in both solvents.

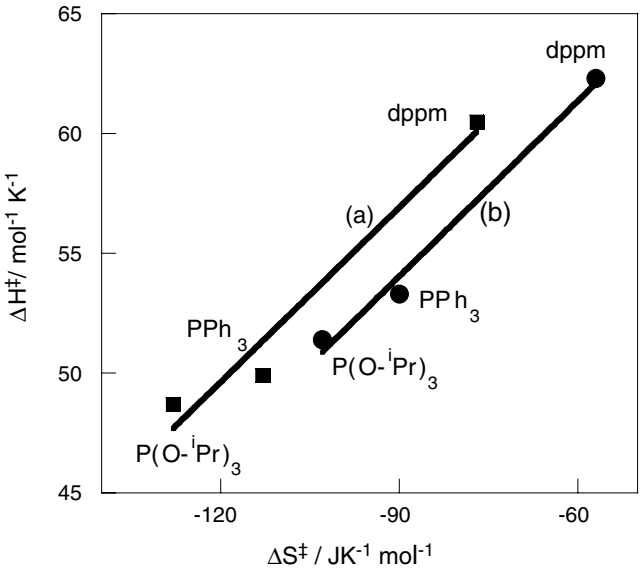


Fig. 6. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plots of reaction of complex **1** with nucleophiles L: (a) in acetone and (b) in benzene.

3.3. Entropy–enthalpy compensation

The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plots for reactions of complex **1** with different nucleophiles in acetone or in benzene are shown in Fig. 6. For each solvent a good straight line is obtained and although the number of the points is not ample, but as it is it may be taken as an evidence for operation of a common (associative, second-order) mechanism in this series of reactions [18]. As can be seen, the two straight lines have almost the same slope. We tentatively suggest that the fact that the lines are parallel confirms that the mechanism operated in both solvents is the same.

4. Experimental

The NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^{1}H (500 MHz, TMS) and ^{31}P (202 MHz, 85% H_3PO_4). Kinetic studies were carried out by using a Perkin–Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath, or a Bruker Avance DPX 250 MHz spectrometer. The dimeric precursor complex **1**, *cis*,*cis*-$[Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2]$ was prepared by the literature method [14]. The final products complexes **2** were fully identified according to their ^{1}H and ^{31}P NMR spectra reported earlier [15,16].

Kinetic study. In a typical experiment, a solution of complex **1** in benzene (3 ml, 3×10^{-4} M) in a cuvette with a 1 cm path length was thermostated at 25 °C and a known excess of PPh_3 (100 μl, 0.5 M in benzene) was added using a micro syringe. After rapid stirring, the absorbance at $\lambda = 375$ nm was monitored with time.

For the experiment using ^{1}H NMR spectroscopy, to a sample of complex **1** (10 mg, 0.01 mmol) in acetone-d_6 (1 mL) in an NMR tube was added P(O–^{i}Pr)$_3$ (50 μl, 0.218 mmol) and the disappearance of signal of the CH groups of phthalazine adjacent to N atoms and the appearance of the same signal for the free NN ligand were used to monitor the reaction.

5. Conclusions

The substitution reactions of the binuclear organoplatinum(II) complex **1**, *cis*,*cis*-[Me$_2$Pt(μ-NN)(μ-dppm)PtMe$_2$], with different phosphane nucleophiles L, L = P(O–^{i}Pr)$_3$ or PPh$_3$, or L$_2$ = dppm, were investigated using UV–Vis spectrophotometry and suggested to proceed via the normal associative pathway. The observation of large negative entropies of activation and the significant dependence of the rate on both concentration and nature of the entering nucleophile, L (Table 1), supported the proposed mechanism. The stronger nucleophile PPh$_3$ is reacted more than three times faster than P(O–^{i}Pr)$_3$. The stronger nucleophilic ability of PPh$_3$ is rationalized on the basis of its higher σ-donor ability (enabling it to better coping with the filled metal 5d$_{z^2}$ orbital of the platinum center) and also on the basis of the lower solvation of its active site, requiring lower solvation energy to accompany metal complex formation. This latter solvation energy also accounts for the 4–6-fold increase of the rate of the reaction on going from the polar acetone solvent to the non-polar benzene media. The effect is of course more pronounced for P(O–^{i}Pr)$_3$ due to the higher solvation of its active site.

The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation plot (Fig. 6) for the substitution reactions is a straight line for each solvent, and the fact that the slopes for both acetone and benzene medias are the same is tentatively assigned to the operation of the same mechanism (i.e. S$_N$2) in both solvents.

Acknowledgements

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