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Oxidative Addition of Methyl Iodide to a New Type of Binuclear Platinum(II) Complex: a Kinetic Study

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A new organodiplatinum(II) complex *cis,cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$] (**1**), in which NN = phthalazine and dppm = bis(diphenylphosphino)methane, is synthesized by the reaction of *cis,cis*-[$Me_2Pt(\mu$-SMe_2)(μ-dppm)$PtMe_2$] with 1 equiv of NN. Complex **1** has a $5d_\pi$(Pt) → π^*(imine) metal-to-ligand charge-transfer band in the visible region, which was used to easily follow the kinetics of its reaction with MeI. Meanwhile, the complex contains a robust bridging dppm ligand that holds the binuclear integrity during the reaction. A double MeI oxidative addition was observed, as shown by spectrophotometry and confirmed by a low-temperature ^{31}P NMR study. The classical S_N2 mechanism was suggested for both steps, and the involved intermediates were suggested. Consistent with the proposed mechanism, the rates of the reactions at different temperatures were slower in benzene than in acetone and large negative $\Delta S^\ddagger$ values were found in each step. However, some abnormalities were observed in the related rate constants and $\Delta S^\ddagger$ values, which were demonstrated to be due to the associative involvement of the polar acetone molecules in the reactions. The rates are almost 6 times slower in the second step as compared to the first step because of the electronic effects transmitted through the ligands and the steric effects.

Introduction

Oxidative addition is a fundamental reaction and often serves as the critical activation step in many homogeneous catalytic processes.[1] Recently, oxidative addition reactions have been used in preparing supramolecular and polymeric materials.[2] Oxidative addition of alkyl halides or other reagents to mononuclear transition-metal complexes has been extensively studied. In particular, oxidative addition of a wide variety of reagents to monomeric organoplatinum(II) complexes, especially those containing diimine ligands, has been extensively studied.[3,4] These diimine complexes are colored and contain characteristic sharp metal-to-ligand charge-transfer (MLCT) bands in the visible region, and therefore kinetics of their reactions can usually be investigated easily using spectrophotometry.[5] The reactions involving the addition of alkyl halides are shown to proceed normally by the classical S_N2 mechanism, although in some relatively rare cases, the reactions proceed by a radical mechanism.[6] Another alternative mechanism involves a concerted three-center transition state that has been proposed in the oxidative addition of C−H[7] or O−O[4c] bonds to diimineorganoplatinum(II) complexes. Despite these, the related reactions with binuclear complexes are scarce.[8] The addition to the binuclear

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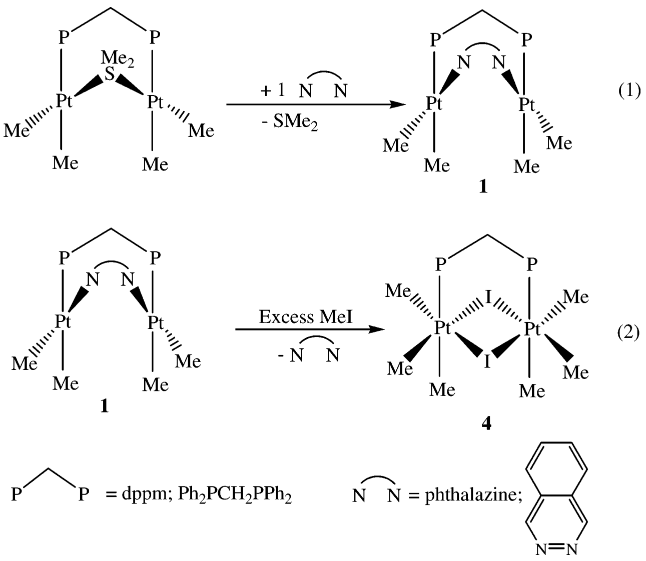
transition-metal complexes is particularly interesting because cooperative steric or electronic effects between the two adjacent metal centers can give rise to reaction pathways or products not possible in the mononuclear analogues.[9] In some cases, cooperative effects between two metal centers are thought to enhance the reactivity of binuclear systems,[8i,j] but in other cases, increased steric hindrance in binuclear complexes leads to a decrease in reactivity.[8d] One main problem faced in such investigations is that binuclear integrity is usually broken up during the reactions, and therefore the reactions are complicated by the parallel reactions involving the monomeric complexes formed by the binuclear fragmentation. One way to tackle the problem is to lock the metallic centers by suitable bidentate phosphine ligands such as bis(diphenylphosphino)methane, dppm, or its amine analogue bis(diphenylphosphino)amine, dppa. These ligands are known to easily bridge between a wide range of transition-metal centers in many binuclear or polynuclear complexes and at the same time strongly hold the molecular integrity during different reactions.[10] The corresponding binuclear complexes are held together by usually two such bridging ligands and as such are normally experiencing a great steric bulk for any oxidative addition to occur.[8d] However, recently a new series of unusual organodiplatinum(II) complexes with a general formula *cis*,*cis*-[R$_2$Pt(μ-SMe$_2$)(μ-PP)PtR$'_2$], in which PP is either dppm or dppa and R and R$'$ are methyl or simple aryl ligands, have been reported in which the labile bridging SMe$_2$ ligand can easily be replaced by other phosphine ligands.[11] In the present study, in an attempt to study the oxidative addition of MeI to a suitable binuclear system, we have used the methyl analogue, *cis*,*cis*-[Me$_2$Pt(μ-SMe$_2$)(μ-dppm)PtMe$_2$], and replaced the bridging SMe$_2$ ligand by phthalazine, represented by NN, to produce *cis*,*cis*-[Me$_2$Pt(μ-NN)(μ-dppm)PtMe$_2$]. This new diplatinum(II) complex showed two main advantages in the study of its reaction with MeI. First, it has a distinct color because of the 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 strongly prevents fragmentation of the dimer during the reaction.

Scheme 1



Results and Discussion

Synthesis and Characterization of Complex *cis*,*cis*-[Me$_2$Pt(μ-NN)(μ-dppm)PtMe$_2$] (1). When a solution of the binuclear complex *cis*,*cis*-[Me$_2$Pt(μ-SMe$_2$)(μ-dppm)PtMe$_2$] was treated with 1 equiv of phthalazine, NN, the color of the reacting mixture turned red and the product *cis*,*cis*-[Me$_2$Pt(μ-NN)(μ-dppm)PtMe$_2$] (**1**) was formed by displacement of the bridging SMe$_2$ ligand by NN (reaction 1 in Scheme 1). The product was separated in good yield in an analytically pure form as a stable pale red solid. Complex **1** is stable in an acetone solution for several hours and was fully characterized by multinuclear (^{1}H, ^{31}P, and ^{195}Pt) NMR spectroscopy. It is to be noted that phthalazine and its derivatives have been used before as ligand-forming mono- and binuclear complexes.[12]

The presence of a single bridging dppm ligand in complex **1** was demonstrated simply by its ^{195}Pt NMR spectrum, which showed a doublet due to the coupling ^1J(PtP) $= 1912$ Hz, although the long-range coupling ^3J(PtP) was not resolved.

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Consistent with this, a singlet at $\delta = 9.1$ was observed in the ^{31}P NMR spectrum of the complex, which has short-range platinum satellites with $^1J(PtP) = 1910$ Hz as well as long-range platinum satellites with $^3J(PtP) = 59$ Hz.[11a] The ^1H NMR spectrum of complex **1** was also very useful in structure determination. Thus, two equal-intensity doublets at $\delta = 0.54$ [with $^2J(PtH) = 70.0$ Hz and $^3J(PH) = 7.5$ Hz] and $\delta = 0.67$ [with $^2J(PtH) = 88.6$ Hz and $^3J(PH) = 7.7$ Hz] were assigned to the Me ligands trans to phosphorus and the Me ligands trans to nitrogen, respectively. Note that the latter signal has a significantly higher $^2J(PtH)$ value because nitrogen has a considerably lower trans influence than phosphorus; the $^3J(PH)$ values are, however, similar for both types of Me ligands.[13] A singlet at $\delta = 9.60$, which is coupled to platinum with $^3J(PtH) = 10.9$ Hz, was easily assigned to two CH groups of phthalazine adjacent to the coordinating N atoms. The presence of only one such signal confirms that the phthalazine ligand has symmetrically bridged between the two metal centers. The overall relative integration of protons also confirmed the presence of one of each of the phthalazine and dppm ligands in the molecule (see the Experimental Section). The UV−vis spectrum of complex **1** contained a series of very strong absorptions below $\lambda = 300$ nm, which are due to the phthalazine intraligand transitions;[14] there was also a strong absorption appearing as a shoulder at $\lambda = 375$ nm (in both acetone and benzene). 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 and is used to study the kinetics of its reaction with MeI (see below).

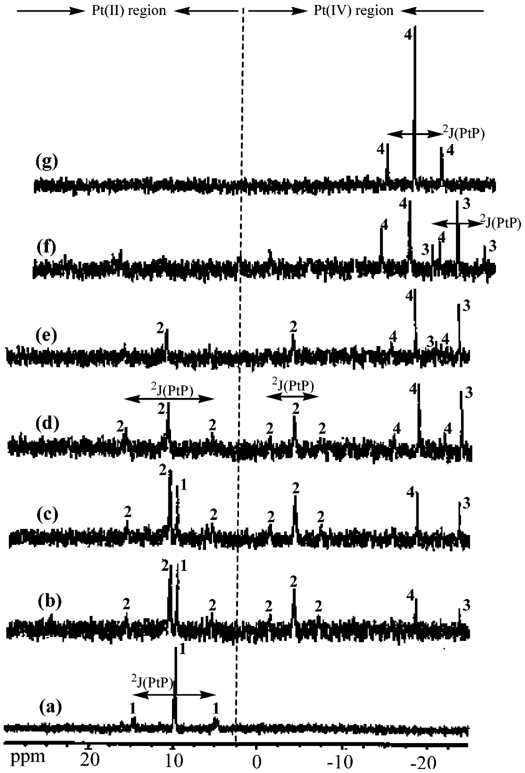

Figure 1. ^{31}P NMR spectra of a mixture of complex **1** and excess MeI in acetone at −40 °C: (a) spectrum of pure complex **1** before adding MeI; (b) spectrum immediately after the addition of MeI; (c−f) successive spectra during 15-min intervals; (g) spectrum after 4 h. As can be seen, upon the addition of MeI, complex **1** is rather quickly converted to intermediate **2**, while the latter is converted to intermediate **3** considerably slower; intermediate **3** is very rapidly converted to the final Pt(IV)−Pt(IV) dimer **4**. The assignments are shown.

Reaction of Complex 1 with MeI. MeI was oxidatively added to both platinum(II) centers of complex **1**, which was then followed by displacement of the NN ligand by iodide ligands to give the known Pt(IV)−Pt(IV) binuclear complex **4** as shown in Scheme 1 (reaction 2). Complex **4** had been prepared previously either by reaction of *cis*,*cis*-[$Me_2Pt(\mu-SMe_2)(\mu$-dppm)$PtMe_2$] with MeI[11b] or by a reaction involving the mixture *cis*,*cis*-[$Me_4Pt_2(\mu-SMe_2)_2$]/MeI/dppm.[15] Reaction 2 in Scheme 1 was slow enough at −40 °C to be monitored by ^{31}P NMR spectroscopy, as shown in Figure 1. The results are described in Scheme 2. Immediately after the addition of MeI, a mixture of complex **1** and an intermediate formulated as **2** in Scheme 2 was detected. This intermediate showed a singlet signal with parameters similar to those of diplatinum(II) complex **1** [$\delta = 10.6$ and $^1J(PtP) = 2029$ Hz] and another singlet signal further upfield at $\delta = -4.2$ with $^1J(PtP) = 1243$ Hz [close to the value of 1060 Hz obtained for the Pt(IV)−Pt(IV) binuclear complex **4**; note that, in complex **2**, the Pt(IV) center is adjacent to a Pt(II) center, and thus a higher $^1J(PtP)$ value is expected]. Intermediate **2** is, therefore, depicted as a rare case of a mixed-valence Pt(II)−Pt(IV) binuclear complex[8f] having structure **2**; the signals are rather broad because of the unresolved P−P coupling of the two chemically inequivalent ^{31}P nuclei.[11a] The formation of any complex with structure **2a** as an alternative for intermediate **2** in Scheme 2 is ruled out because, in contrast to the expectation based on the kinetic date discussed in the next section, structure **2a** is not expected to contain any $5d_\pi(Pt) \rightarrow \pi^*$(imine) MLCT band. Also, on the basis of the ^{31}P NMR spectra in Figure 1, no fragmentation to monomeric forms occurred at this stage; the parameters expected for the presumed Pt(IV) monomer [$PtMe_3I$(dppm)][16] are far more different from the data obtained for the Pt(IV) signal at this stage in Figure 1.

The intermediate **2** was then reacted with MeI, albeit at a rate rather slower than that for the first step, and a singlet with platinum satellites at $\delta = -23.5$ [with $^1J(PtP) = 1035$ Hz] gradually formed. The latter signal is attributed to a cationic symmetrical Pt(IV)−Pt(IV) intermediate binuclear complex with structure **3** in Scheme 2. Note that the two alternative structural possibilities for **3**, i.e., [$Me_3Pt(\mu$-NN)(μ-dppm)$PtMe_3]^{2+}[I^-]_2$ or [$Me_3IPt(\mu$-NN)(μ-dppm)$PtIMe_3$], each of which is expected to give a similar ^{31}P signal, are ruled out because the former contains coordinatively unsatur-

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(13) Similar trends of $^2J(PtH)$ and $^3J(PH)$ values for the Me ligands trans to phosphorus and the Me ligands trans to nitrogen have been observed in the binuclear methylplatinum(II) complex [$MePt(\mu$-PN)(μ-NP)-$PtMe_2](CF_3CO_2)$, where PN = 2-$Ph_2PC_5H_4N$. See: Rashidi, M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 2612.

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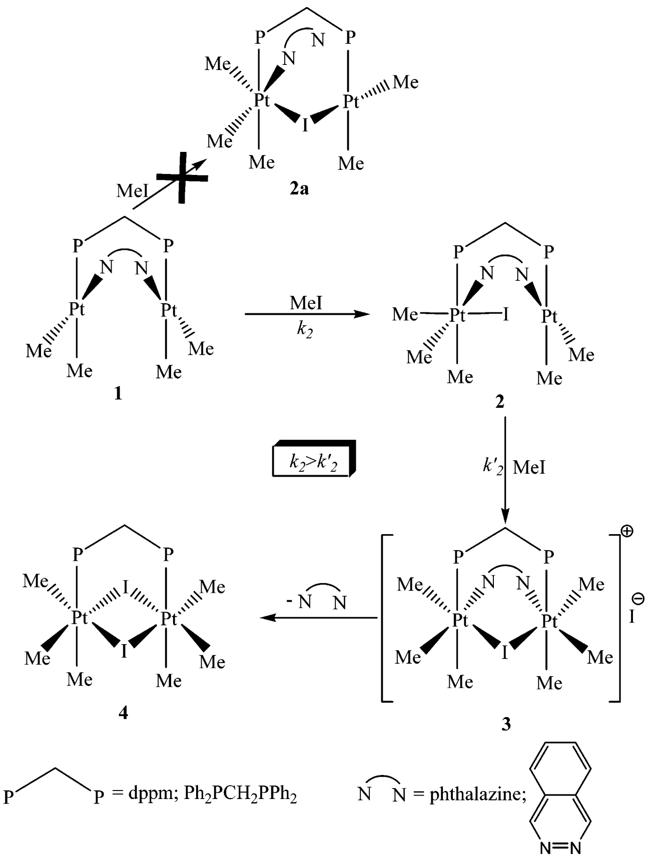
Scheme 2



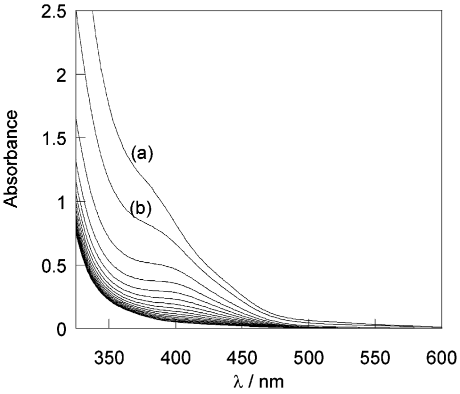


Figure 2. Changes in the UV−vis spectrum during the reaction of complex **1** (3×10^{-4} M) and MeI (0.106 M) in benzene at $T = 25$ °C: (a) initial spectrum (before adding MeI); (b) spectrum at $t = 0$. Successive spectra were recorded at intervals of 30 s.

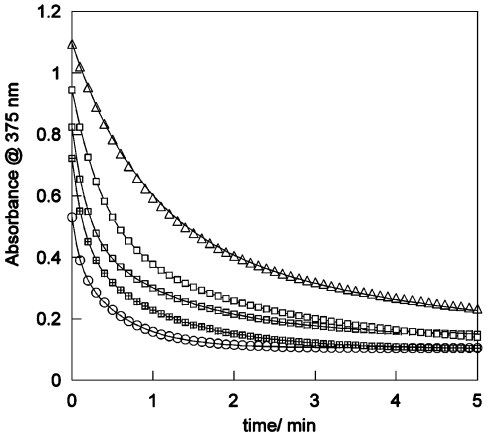


Figure 3. Absorbance−time curves for the reaction of complex **1** with MeI (0.053−0.53 M; [MeI] increases reading downward) in benzene at 25 °C. The solid lines were obtained by fitting the (A, t) data into eq 2.

ated platinum centers and the latter is too crowded. The displacement of NN with iodide ligands in the last step gave the final Pt(IV)−Pt(IV) binuclear complex **4**. Complex **4** was easily characterized by its known NMR data.[11b]

Conductivity measurement was carried out to investigate the possible formation of the ionic species during the reaction of complex **1** with MeI. Thus, the molar conductivity of a 10^{-3} solution of the neutral complex **1** in acetone at −25 °C sharply increased upon the addition of excess MeI and then significantly decreased after 2 h. This observation supports the formation of the ionic intermediate for **3** $[Me_3Pt(\mu\text{-NN})(\mu\text{-dppm})(\mu\text{-I})PtMe_3]^+I^-$, as was also shown above by ^{31}P NMR spectra.

Kinetic Study of the Reaction of Complex 1 with MeI in Benzene. As mentioned before, the reddish complex **1** contains a MLCT band in the visible region that could be used to monitor its reaction with MeI and study the kinetics of the reaction by using UV−vis spectroscopy. Thus, an excess of MeI was used at 25 °C, and the disappearance of the MLCT band at $\lambda = 375$ nm in a benzene solution was used to monitor the reaction. The change in the spectrum during a typical run is shown in Figure 2.

The time-dependence curves of the spectra of the reaction in benzene at this condition are shown in Figure 3. The data failed to fit properly in eq 1, which corresponds to a monophasic kinetic behavior. However, the data were successfully fitted in eq 2 with two exponentials, showing a clear biphasic kinetic behavior. Thus, the pseudo-first-order rate constants $k_{obs(1)}$ and $k_{obs(2)}$ for the two steps of the reaction were evaluated by nonlinear least-squares fitting of the absorbance−time profiles to the biphasic first-order equation (eq 2).

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

$$A_t = \alpha[\exp(-k_{obs(1)}t)] + \beta[\exp(-k_{obs(2)}t)] + A_\infty \qquad (2)$$

Plots of the first-order rate constants, $k_{obs(1)}$ (for step 1) and $k_{obs(2)}$ (for step 2), versus [MeI] in both cases were linear with no intercepts (Figure 4), showing a first-order dependence of the rate on the concentration of MeI in each step. The slope in each case gave the second-order rate constant (k_2 for the first step and k'_2 for the second step), and the results are collected in Table 1. The findings seem to be consistent with the two-step sequence indicated above based on the ^{31}P NMR data (see Figure 1) for the reaction of complex **1** with MeI. Therefore, each step of the reaction (see Scheme 2) obeys a simple second-order rate law (eq 3 for step 1 and eq 4 for step 2), first order in both the corresponding dimer and MeI; note that $k_2 > k'_2$ and the reproducibility of the data was remarkable (±5%). The same method was used at other temperatures, and activation parameters were obtained from the Eyring

Table 1. Rate Constants and Activation Parameters[a] for the Reaction of Complex **1** with MeI in Acetone or Benzene

Reaction in Acetone

	rate constants at different temperatures						
	5 °C	10 °C	15 °C	20 °C	25 °C	$\Delta H^{\ddagger b}$/(kJ mol^{-1})	$\Delta S^{\ddagger b}$/(J K^{-1} mol^{-1})
10^2k_2/(L mol^{-1} s^{-1})	26.4 ± 2.5	37.0 ± 2.2	41.1 ± 2.3	65.6 ± 4.6	85.6 ± 2.4	25.1 ± 2.0	−165 ± 7
10^2k_1/s^{-1}	1.9 ± 0.4	1.5 ± 0.4	2.8 ± 0.4	1.7 ± 0.6	1.1 ± 0.2		
$10^2k'_2$/(L mol^{-1} s^{-1})	5.6 ± 0.2	7.3 ± 0.2	9.2 ± 0.3	12.9 ± 0.4	15.8 ± 0.4	22.1 ± 2.1	−188 ± 7

Reaction in Benzene

	rate constants at different temperatures					
	5 °C	15 °C	25 °C	35 °C	$\Delta H^{\ddagger b}$/(kJ mol^{-1})	$\Delta S^{\ddagger b}$/(J K^{-1} mol^{-1})
10^2k_2/(L mol^{-1} s^{-1})	13.9 ± 0.2	22.4 ± 1.1	39.0 ± 0.5	62.2 ± 3.6	33.5 ± 1.1	−140 ± 4
$10^2k'_2$/(L mol^{-1} s^{-1})	1.4 ± 0.1	3.6 ± 0.1	5.6 ± 0.1	11.1 ± 0.5	45.3 ± 4.4	−116 ± 15

[a] Values given based on 95% confidence limits from least-squares regression analysis. [b] Obtained from the Eyring equation.

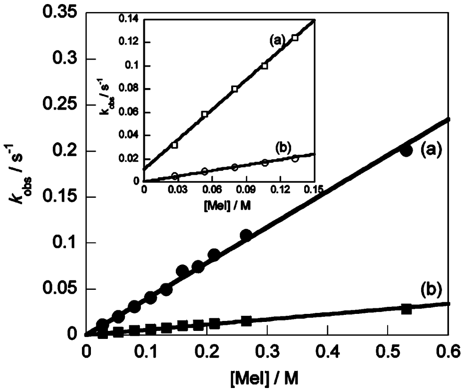


Figure 4. Plots of first-order rate constants [(a) first step, k_{obs}/s^{-1}, and (b) second step, k'_{obs}/s^{-1}] for the reaction of complex **1** with MeI at 25 °C versus the concentration of MeI in benzene (the inset shows plots in acetone; note the intercept for the first step in part a).

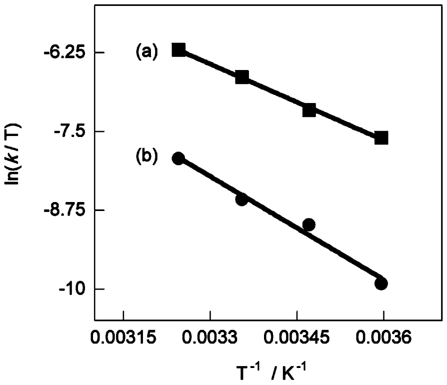


Figure 5. Eyring plots for the reaction of complex **1** with MeI in benzene: (a) first step; (b) second step.

equation (see eq 5 and Figure 5). The data are collected in Table 1.

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_2[\mathbf{1}][\mathrm{MeI}] \tag{3}$$

$$-\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k'_2[\mathbf{2}][\mathrm{MeI}] \tag{4}$$

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \tag{5}$$

Large negative values of $\Delta S^{\ddagger}$, which are in favor of a classical S$_N$2-type mechanism, were observed for both steps. On the basis of these NMR and kinetic data, we suggest that, as is indicated in Scheme 2, MeI first performs an electrophilic attack on one of the electron-rich platinum(II) centers of diplatinum(II) complex **1** with an S$_N$2-type mechanism with the rate constant k_2 and the mixed-valence Pt(II)−Pt(IV) binuclear intermediate **2** (Scheme 2) is formed. The assignment of the alternative structure **2a** to this intermediate is ruled out because **2a** cannot have any 5d$_\pi$-(Pt) → π^*(imine) MLCT band in order to contribute to the absorption changes in the next step. Intermediate **2** was then reacted with MeI in step 2 again by an S$_N$2-type mechanism, with the rate constant k'_2, which is nearly 6−10 times smaller than the corresponding value for k_2 (see Table 1).

In a two-step oxidative addition reaction of this type in which none of the components of the reaction contains any metal−metal bond and yet the metallic centers are not too far from each other, it is suggested that the first addition occurs faster than the second.[8k,9e] In the present study, we strongly believe that this has actually been the case. First, as expected based on the qualitative ^{31}P NMR investigations, vide supra, step 2 appears to be slower than step 1. Second, in step 1, MeI attacks the platinum(II) center of a Pt(II)−Pt(II) complex, **1**, while in step 2, MeI reacts with the platinum(II) center of a Pt(II)−Pt(IV) species (complex **2**). As such, the reaction should be slower in the second step because, in contrast to complex **1**, in species **2** the adjacent Pt(IV) moiety not only creates a more severe steric hindrance for the attacked Pt(II) center but also reduces its nucleophilicity through the bridging ligating groups. Despite these, however, to confirm that the higher rate constant, k_2, actually belongs to the first step in the above sequence and the second step is proceeded with the slower rate constant, k'_2, we considered Espenson's approach, in which the biphasic equation (eq 6) was used in evaluating the two rate constants[17] and it was predicted that the method might be of general applicability.

$$A_t - A_\infty = a_f[\exp(-k_f t) + a_s[\exp(-k_s t)] \tag{6}$$

In this equation, k_f and k_s are the rate constants for the fast and slow steps, respectively, but do not identify a

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(17) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 4069.

Table 2. Rate Constants (k_2 and k'_2) and Calculated ϵ_i Values at 375 nm for Cases 1 and 2[a]

			$10^{-3}\epsilon_i/(M^{-1}\ cm^{-1})$	
10^2[MeI]/M	10^3k_s/(L mol^{-1} s^{-1})	10^3k_f/(L mol^{-1} s^{-1})	case 1	case 2
2.6	2.24	10.79	3.22	−13.49
5.3	3.49	19.95	3.33	−16.75
7.9	5.22	30.76	3.36	−17.42
10.6	6.42	40.59	3.39	−18.97
13.2	7.62	49.63	3.41	−19.64
15.9	10.48	69.19	3.42	−19.99
18.5	10.87	74.15	3.44	−20.78
21.2	12.51	86.97	3.45	−21.25
26.5	15.60	108.14	3.45	−21.17
53.0	28.35	200.97	3.46	−21.75

[a] The values of the extinction coefficient (ϵ_i) at 375 nm were determined by the method of nonlinear least squares (the program KaleidaGraph 3.6).

particular reaction step. Thus, we now consider the two cases pertaining to a sequence of reactions:

Case 1: $k_2 = k_f > k'_2 = k_s$

Case 2: $k_2 = k_s < k'_2 = k_f$

If we consider ϵ_d, ϵ_i, and ϵ_p as the molar absorptivities of starting dimer **1**, intermediate **2**, and the final product (complex **4**), respectively, then ϵ_i can be calculated from the following equations, depending upon which case is applicable:

Case 1: $\epsilon_i = (\epsilon_d - a_f)(1 - k_s/k_f) + \epsilon_p k_s/k_f$

Case 2: $\epsilon_i = (\epsilon_d - a_s)(1 - k_f/k_s) + \epsilon_p k_f/k_s$

The calculated ϵ_i values from the experimental data for different presumed cases are listed in Table 2. As an example, in a benzene solvent at 25 °C and $\lambda = 375$ nm, the end results are as follows:

Before the MeI addition:

$$[\text{complex } \mathbf{1}]_0 = 3.0 \times 10^{-4}\ \text{M and Abs} = 1.192 \Rightarrow \epsilon_d = \text{Abs}/[\text{complex } \mathbf{1}]_0 = 3973.3$$

End of reaction:

$$[\text{complex } \mathbf{4}]_0 = 3.0 \times 10^{-4}\ \text{M and Abs} = 0.103 \Rightarrow \epsilon_p = \text{Abs}/[\text{complex } \mathbf{4}]_0 = 344$$

The data for case 1 are preferable for two reasons. First, in case 1, the value of ϵ_i for the 10 experiments at 375 nm is almost constant; $\epsilon_i = 3.33 \times 10^3$ M^{-1} cm^{-1} (±5% standard deviation), whereas large scatter and negative values are obtained for ϵ_i when case 2 was assumed. Second, the value of ϵ_i at 375 nm in case 1 lies close to ϵ_d (3.97×10^3 M^{-1} cm^{-1}), in which both of the related complexes have MLCT bands, and far from ϵ_p, as one would expect for the final product **4** with no MLCT band in the visible region.

Kinetic Study of the Reaction of Complex 1 with MeI in Acetone. A similar UV−vis spectroscopic method was used at $\lambda = 375$ nm to study the kinetic behavior of the reddish complex **1** with MeI in an acetone solvent. The results are collected in Table 1. A two-step sequence, similar to the one mentioned in the last section for the reaction in benzene, was also observed for the reaction in acetone. Thus, the second-order rate constant for the first step, k_2, is again nearly 6 times larger than the second-order rate constant for the second step, k'_2. However, two abnormalities are seen when the results are compared with the results usually reported for the reaction of MeI with electron-rich transition-metal complexes operated by a classical S_N2-type mechanism:

(i) The reactions in both steps at different temperatures are nearly 2 times faster in acetone than in benzene. This, of course, strongly supports the operation of the S_N2-type mechanism in the reactions because in the latter mechanism, in which after each MeI attack a polar transition state is expected, the rate should be faster in a more polar acetone solvent than in benzene with a significantly lower dielectric constant. Usually, however, a rather higher rate increase is expected. For example, [Pt(p-MeC$_6$H$_4$)$_2$(NN)], in which NN = 4,4′-di-*tert*-butyl-2,2′-bipyridine, reacts with MeI at 25 °C faster in acetone than in benzene by a factor of 7.5,[4e] and the factor for the reaction of MeI with [PtPh$_2$(2,2′-bipyridine)] is 6.2 at 40 °C.[5a] Also, the rate of the reaction of Vaska's complex [IrCl(CO)(PPh$_3$)$_2$] with MeI at 25 °C is 6 times faster in acetone than in benzene.[18]

(ii) It is believed that in S_N2-type reactions, where a highly polar transition state is formed, less negative $\Delta S^\ddagger$ values are obtained in more polar solvents, and this is attributed to decreasing order in the transition state relative to the ground state.[19] In the three reactions of MeI just mentioned in (i), $\Delta S^\ddagger$ values in benzene and acetone, respectively, are −161 and −123 J mol^{-1} K^{-1} for the first reaction[4e] and −156 and −114 J mol^{-1} K^{-1} for the second reaction;[5a] for the third reaction, $\Delta S^\ddagger$ values of −213 and −49 J mol^{-1} K^{-1} in benzene and DMF, respectively, were found. As is shown in Table 1, a reversed trend is actually observed for the system studied in the present work. Thus, $\Delta S^\ddagger$ in each step has a larger negative value in acetone (−165 J mol^{-1} K^{-1} in step 1 and −183 J mol^{-1} K^{-1} in step 2) than in benzene (−140 J mol^{-1} K^{-1} in step 1 and −116 J mol^{-1} K^{-1} in step 2).

To explain these abnormalities, we suggest that, in each step of the reaction, the more polar acetone solvent would unusually lower the entropy of the ground state as compared to the excited state. In fact, we have observed a two-term rate law for the first step of the reaction in acetone (see the inset of Figure 4):

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathbf{1}], \quad \text{where } k_{\mathrm{obs}} = k_1 + k_2[\text{MeI}]$$

Thus, in addition to second-order term k_2 for step 1, which is suggested for the simple associative S_N2-type mechanism, a much smaller term, k_1, is also observed for associative substitutions by solvent in this step. All of the rate constants are shown in Table 1. The associative substitution by acetone, S, in step 1 is suggested to involve a transition state with

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(18) Stieger, H.; Kelm, H. *J. Phys. Chem.* **1973**, *77*, 290.

(19) (a) Wiberg, K. B. *Physical Organic Chemistry*; John Wiley & Sons: New York, 1964; pp 381−387. (b) Levy, C. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 10127.

structure [$Me_2(\eta^1$-NN)Pt(μ-dppm)Pt(S)Me_2], in which one S molecule displaces one of the N donor atoms and the binuclear integrity is held by only one bridging dppm ligand. This structure is based on a recent report that the labile SMe_2 ligand in *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$] can be replaced with monodentate P donor ligands such as PPh_3, L, to form the stable complexes *cis*,*cis*-[$Me_2LPt(\mu$-dppm)-$PtLMe_2$], in which the two platinum(II) moieties are bridged by only one dppm with no metal−metal bonding; each platinum center also bears a monodentate ligand L and two methyl groups.[11e]

We believe that this kind of associative solvent involvement by acetone molecules could most probably be responsible for the above-mentioned abnormalities observed in the kinetics of the reaction of complex **1** with MeI. Thus, in the first step of the MeI reaction in acetone, the association of starting complex **1** with solvent molecules will lower the entropy of the ground state relative to the cationic exited state (not shown in the scheme) more than is usually observed in the absence of such an extra solvent involvement. This makes the $\Delta S^\ddagger$ value in the acetone solvent more negative than usual, to the extend that it abnormally becomes more negative than the $\Delta S^\ddagger$ value in benzene. This entropy effect should also be responsible for an abnormally lower rate increase (nearly 2 times as compared to the usual 6−10 times) observed in the present study in going from the acetone solvent to the nonpolar benzene solvent. The intermediate **2**, which is now the reactant for the reaction with MeI in the second step, would similarly act to make the $\Delta S^\ddagger$ value for step 2 more negative than usual. The magnitude of the effect on $\Delta S^\ddagger$ values is more pronounced in the second step; the $\Delta S^\ddagger$ value difference on going from acetone to benzene is -25 J K^{-1} mol^{-1} for step 1, while it is -72 J K^{-1} mol^{-1} for step 2. We believe that this is because, in the second step, the associative substitution by acetone is only taking place with reactant complex **2** and not with the final kinetic product complex **3** (or more precisely with the preceding polar transition state not shown in Scheme 2) in which both platinum centers are Pt(IV); note that, in the first step, both reactant complex **1** and the product complex **2** (or, more precisely, with the preceding polar transition state not shown in the Scheme 1) are involved in the associative substitution by acetone and so a more modest entropy effect is expected for step 1.

Experimental Section

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: ^1H (500 MHz, TMS), ^{31}P (202 MHz, 85% H_3PO_4), and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). All of the chemical shifts and coupling constants are in ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The conductivity study was carried out using a Metrohm 660 conductometer. The microanalysis was performed using a Termofinnigan Eager 300 CHN−O elemental analyzer. The dimeric precursor *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$] was prepared by the literature method.[11b]

Preparation of *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$] (1). To a solution of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$] (100 mg, 0.11 mmol) in acetone (15 mL) was added phthalazine, NN (14.6 mg, 0.11 mmol), in acetone (5 mL) at room temperature. The mixture was stirred for 1 h, the solvent was then removed under reduced pressure, and the residue was triturated with ether (3 mL) to give a pale red solid, which was separated and dried under vacuum. Yield: 70 mg, 65%. Mp: 170 °C (dec). Anal. Calcd for $C_{37}H_{40}N_2P_2$-Pt_2: C, 46.0; H, 4.1; N, 2.9. Found: C, 45.9; H, 4.1; N, 2.6. ^1H NMR data in acetone-d_6: δ 0.54 [d, $^2J(PtH) = 70.0$ Hz, $^3J(PH) = 7.5$ Hz, 6H, 2 Me ligands trans to phosphorus], 0.67 [d, $^2J(PtH) = 88.6$ Hz, $^3J(PH) = 7.7$ Hz, 6H, 2 Me ligands trans to nitrogen], 2.61 [m, 1H of dppm], 3.90 [m, 1H of dppm]; phthalazine protons, 8.00 [m, 2H], 8.15 [m, 2H], 9.60 [s, $^3J(PtH) = 10.9$ Hz, 2H, 2 CH groups of phthalazine adjacent to N atoms]; dppm phenyl groups, 7.00, 7.10, 7.30, 7.90 [20 H]. ^{31}P NMR in $CDCl_3$: δ 9.1 [s, $^1J(PtP) = 1910$ Hz, $^3J(PtP) = 59$ Hz, dppm]. ^{195}Pt NMR in $CDCl_3$: δ 262 [d, $^1J(PtP) = 1912$ Hz].

Reaction of 1 with MeI. An excess of MeI (40 μL) was added to a solution of complex **1** (20 mg in 5 mL of acetone) at room temperature. The mixture was allowed to stand at this condition for 6 h, then the solvent was removed under reduced pressure, the residue was washed twice with ether (2 × 3 mL), and the product was dried under vacuum and identified by its ^1H and ^{31}P NMR spectra as the known diplatinum(IV) complex [$\{PtMe_3(\mu$-$I)\}_2(\mu$-dppm)] (**4**)[11b,15] in a high yield.

This reaction was also monitored by ^{31}P NMR spectroscopy at −40 °C in an NMR tube as follows: a small sample (10 mg) of **1** was dissolved in acetone-d_6 (0.3 mL) in a sealed NMR tube, and while the tube was cooled by liquid N_2, an excess of MeI (20 μL) was added. The NMR spectra were recorded several times at −40 °C over about 4 h until the mixture was gradually converted to complex **4** in solution (see Figure 1).

Kinetic Study. In a typical experiment, a solution of complex **1** in benzene (3 mL, 3×10^{-4}M) in a cuvette was thermostated at 25 °C and a known excess of MeI was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 375$ nm was monitored with time.

Conclusions

A new binuclear complex, *cis*,*cis*-[$Me_2Pt(\mu$-NN)(μ-dppm)-$PtMe_2$], **1**, in which NN = phthalazine and dppm = bis(diphenylphosphino)methane, was synthesized, and its two-step reaction with MeI was investigated in detail by spectrophotometry in the visible region. The results are consistent with the qualitative results obtained from the study of the reaction by ^{31}P NMR spectroscopy at −40 °C. Both steps proceed by the classical S_N2-type mechanism, as shown in Scheme 2, with large negative $\Delta S^\ddagger$ values in both acetone and benzene, and the rates were faster in acetone than in benzene. An associative substitution by an acetone solvent was suggested as being responsible for some abnormalities observed in the trends of the quantitative kinetic measurements. In the first step, MeI attacks the electron-rich platinum centers of the Pt(II)−Pt(II) starting complex **1** to form the intermediate **2**, which is suggested to have a Pt(II)−Pt(IV) skeleton. The rate of the reaction of the platinum(II) center in complex **2** with MeI is therefore considerably slower (by a factor of 6) than that of the platinum(II) center in the starting complex **1**, for a combination of steric hindrances and the electronic effects transmitted through the ligands.

MeI in the first step reacts with complex **1** (in which each metallic center is bonded to one P donor and one N donor) in acetone at 25 °C with a rate constant $k_2 = 0.86 \pm 0.02$ L mol^{-1} s^{-1}, some 50 times slower than that with the mononuclear complex [PtPh$_2$(2,2′-bipyridine)] (with the metal center bonded to two N donors) at the same condition for which $k_2 = 47$ L mol^{-1} s^{-1}.[8k] This significant rate decrease is to be expected for the reaction of complex **1** in which each of the metallic centers is connected to a P atom with a large π-back-bonding that considerably reduces the electron density on the platinum centers as compared with that in the monomeric complexes with two strong N donor atoms. However, it would be of great interest to have more experimental data on the oxidative addition to the binuclear complexes of this type and also the same oxidative additions to some monomeric complexes with P and N donors (designed to have suitably similar overall structures to the corresponding dimers) to actually substantiate any possible "neighboring group effect" of the adjacent metal center in the binuclear complexes.

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