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Uncommon Solvent Effect in Oxidative Addition of MeI to a New Dinuclear Platinum Complex Containing a Platina(II)cyclopentane Moiety

S. Jafar Hoseini,[a] S. Masoud Nabavizadeh,[a] Sirous Jamali,[b] and Mehdi Rashidi*[a]

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The reaction of the known complex *cis,cis*-[$Me_2Pt^a(\mu\text{-dppm})(\mu\text{-}SMe_2)Pt^b\text{–}CH_2(CH_2)_2C^cH_2(Pt^b\text{–}C^c)$] [dppm = bis(diphenylphosphanyl)methane] with phthalazine (NN) proceeded by replacement of the labile bridging SMe_2 ligand with the bidentate N-donor ligand NN to give *cis,cis*-[$Me_2Pt^a(\mu\text{-dppm})(\mu\text{-NN})Pt^b\text{–}CH_2(CH_2)_2C^cH_2(Pt^b\text{–}C^c)$] (**1**) as a pale red solid in good yield. The complex was fully characterized by multinuclear (^1H, ^{31}P, ^{195}Pt) NMR spectroscopy. The subsequent reaction of complex **1** with excess MeI gave the colorless diplatinum(IV) complex [$Me_3Pt^a(\mu\text{-dppm})(\mu\text{-I})_2Pt^b\{CH_2(CH_2)_2C^cH_2(Pt^b\text{–}C^c)\}Me$], in which the bridging NN ligand is replaced by bridging iodido ligands. The reddish color of complex **1**, which is due to a metal-to-ligand charge transfer (MLCT) band in the visible region, was used to monitor its reaction with MeI in the solvents acetone, CH_2Cl_2, and benzene. The kinetic data revealed that the reactions in nonpolar benzene or slightly polar CH_2Cl_2 proceeded in two steps, each following a common S_N2 mechanism. In the first step, MeI attacked the platina(II)cyclopentane center rather than the dimethylplatinum(II) center, because the first center is more electron-rich than the second center. In the more polar acetone, the reaction proceeded similarly, with the exception that each step was accompanied by a solvolytic reaction, which was suggested to be responsible for the unusually slower reaction rate in acetone than in benzene or CH_2Cl_2. Consistently, the reaction rate in the highly polar solvent CH_3CN was too slow for any meaningful measurement.

Introduction

Oxidative addition of organic halides to mononuclear organoplatinum(II) compounds, especially those containing auxiliary diimine ligands, has extensively been studied during the past several decades.[1,2] This type of reaction plays a fundamental role in many industrially important catalytic reactions.[3] The reactions usually proceeded by a classical S_N2 type mechanism, involving a second-order rate law (rate = k_2[complex][halides]), although reactions following a radical mechanism have also been observed in some occasions.[1] The possibility of a concerted three-center mechanism resulting in a *cis* addition of alkyl halides has also been suggested, although it has never been exclusively demonstrated for any particular system. Factors influencing the rate of the reactions and the kinetic parameters are also established.[1,2] Despite this, similar oxidative addition reactions involving dinuclear organoplatinum(II) complexes have not been investigated much.[4,5] These reactions could be important, as cooperative steric and/or electronic effects between the two adjacent metal centers may give rise to reaction pathways or products that are not possible in the mononuclear analogues.[6] Our recent report of an oxidative addition of MeI to a symmetrical dinuclear dimethyldiplatinum(II) complex containing the bridging diphosphane ligand dppm [= bis(diphenylphosphanyl)methane], which retains the dinuclear integrity of the system during the reaction, indicated a stepwise oxidative addition of the reagent to the platinum(II) centers. The rate of the addition to the second metallic center was significantly slower, by a factor of about 6–10, which suggests that the electronic information is somehow conveyed through the bridging system.[4] However, our next investigation involving the oxidative addition of MeI to an organodiplatinum(II) complex containing 1,1′-bis(diphenylphosphanyl)ferrocene as spacer ligand revealed that some complications occurred after addition of reagent to the first metal center but prior to its addition to the second metal center.[5]

In the case of oxidative addition reactions of alkyl halides, in particular MeI, to square-planar d^8 complexes, it is established that the reaction rate in polar solvents like acetone is faster than that in nonpolar solvents like benzene, which has been attributed to the formation of a polar ionic intermediate during the reaction.[1,3] In continuation of our interest in studying oxidative additions to organo-diplatinum(II) complexes, we have prepared a new unsymmetrical dimethylplatinum(II)–platina(II)cyclopentane complex with the formula *cis,cis*-[$Me_2Pt^a(\mu\text{-dppm})(\mu\text{-NN})Pt^b\text{–}CH_2(CH_2)_2\text{-}C^cH_2(Pt^b\text{–}C^c)$] (**1**) (NN = phthalazine), [dppm = bis(di-

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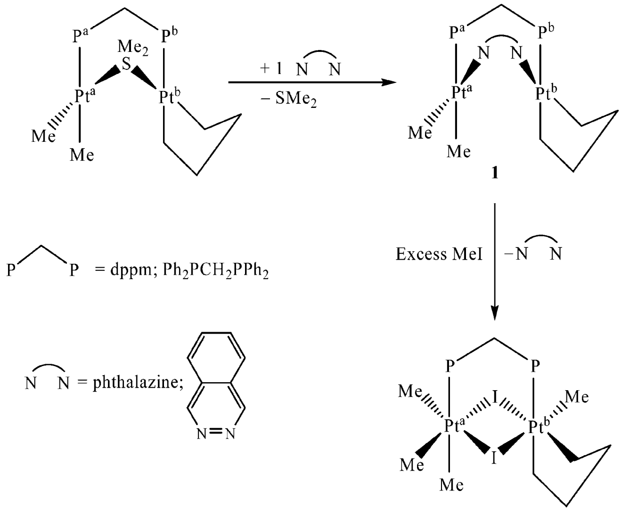
[a] Chemistry Department, College of Sciences, Shiraz University,
Shiraz 71454, Iran
Fax: +98-711-2286008
E-mail: rashidi@chem.susc.ac.ir
[b] Chemistry Department, Persian Gulf University,
Bushehr 75169, Iran

phenylphosphanyl)methane] and fully characterized it by multinuclear NMR spectroscopy. Two interesting aspects of the complex are notable. First, the stepwise oxidative addition of MeI to the two different platinum(II) centers of the complex is useful to confirm directly that the platina(II)-cyclopentane center is rather willing to perform oxidative addition of MeI relative to the dimethylplatinum(II) center. This effect has been quantified by a measurement of the reaction rates. Secondly, we have observed an uncommon solvent effect in that the reaction of complex **1** with MeI was faster in the nonpolar solvent benzene than in the polar solvent acetone. A particular solvent effect has been suggested to explain these results.

Results and Discussion

Preparation and Characterization of the Complexes

The preparative route to the new dinuclear organoplatinum(II) complex **1** and its reaction with excess MeI are described in Scheme 1. Reaction of the known dinuclear precursor *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-SMe_2)Pt^b–$CH_2(CH_2)_2C^cH_2$-(Pt^b–C^c)][7] with NN proceeded by replacement of the labile SMe_2 ligand with the bidentate N-donor ligand NN to give *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(Pt^b–C^c)] (**1**) as a pale red solid in good yield. Subsequent reaction of complex **1** with excess MeI gave the known diplatinum(IV) complex [Me_3Pt^a(μ-dppm)(μ-I)$_2Pt^b${$CH_2(CH_2)_2$-C^cH_2(Pt^b–C^c)}Me],[7] in which the bridging NN ligand is replaced by bridging iodido ligands.



Scheme 1.

Complex **1** was fully characterized by using multinuclear (^1H, ^{31}P, ^{195}Pt) NMR spectroscopy. In the ^{31}P NMR spectrum of **1** at room temperature, which is shown in Figure 1, the signals of the two inequivalent dppm phosphorus atoms P^a (*trans* to the Me ligand) and P^b (*trans* to the CH_2 group of the platinacyclopentane ring) appear as overlapping singlets at δ = 10.9 ppm with $^1J(Pt^aP^a)$ = 1980 Hz and $^1J(Pt^bP^b)$ = 1897 Hz. The first coupling, which has an about 4% larger value than the second coupling, is assigned to P^a, in consistency with previous findings that the CH_2 group of the platinacyclopentane ring exerts a higher *trans* influence than the Me ligand.[2,7,8] As it is depicted in Figure 1, the long-range couplings between the Pt atoms and the corresponding P atoms are observed as overlapping humps close to the central singlet signal, and the ^3J(PtP) values were not measurable. The coupling between P^a and P^b of dppm was measured, however, from the splitting in the satellites, as ^2J(PP) = 65 Hz. In the ^{31}P NMR spectrum of complex **1** at –80 °C (see Figure 1), the two signals for the two different phosphorus atoms P^a and P^b of dppm were resolved as two doublets at δ = 8.8 ppm, with $^1J(Pt^aP^a)$ = 1974 Hz and ^2J(PP) = 61 Hz for P^a, which is *trans* to the Me ligand, and at δ = 10.3 ppm, with $^1J(Pt^bP^b)$ = 1890 Hz and ^2J(PP) = 62 Hz for P^b, which is *trans* to the CH_2 group of the platinacyclopentane ring. It therefore seems that complex **1** has some kind of fluxionality at higher temperatures. We rule out the possibility of any mechanism involving a fast exchange of the P atoms with dissociation of one P atom from the Pt center and reconnection to another Pt center to explain the fluxional behavior, because if this were the case,

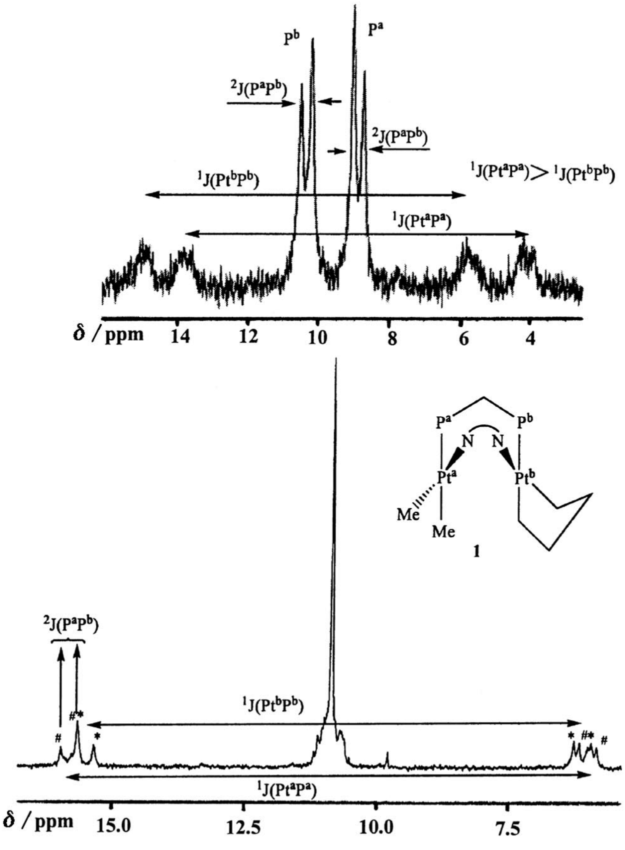
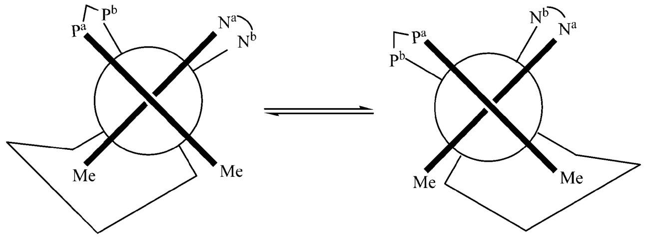


Figure 1. ^{31}P NMR spectra of *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(Pt^b–C^c)] (**1**) at room temperature (bottom view) and at –80 °C (top view).

one would expect the P atoms to become completely equivalent, giving rise to a singlet signal with one set of satellites at room temperature. As two different sets of satellites are actually observed, it is probable that fluxionality of the type shown in Scheme 2 is operative. In agreement with these results, in the ^{195}Pt NMR spectrum of complex **1** two doublets for the two different Pt atoms were observed at δ = –4005 ppm with $^1J(\mathrm{Pt^aP^a})$ = 1970 Hz, for $\mathrm{Pt^a}$, and at δ = –4109 ppm with $^1J(\mathrm{Pt^bP^b})$ = 1894 Hz, for $\mathrm{Pt^b}$. As it can be seen, the coupling values are almost identical with the values obtained from the ^{31}P NMR spectrum.



Scheme 2.

In the ^{1}H NMR spectrum of complex **1**, two doublets at δ = 0.41 ppm [with $^3J(\mathrm{PH})$ = 7.8 Hz and $^2J(\mathrm{PtH})$ = 73.8 Hz, for the Me ligand *trans* to the phosphorus atom] and at δ = 0.52 [with $^3J(\mathrm{PH})$ = 8.0 Hz and $^2J(\mathrm{PtH})$ = 88.6 Hz for the Me ligand *trans* to the nitrogen atom, which has a lower *trans* influence than the phosphorus atom] were observed. The signals of the CH_2 groups of the platinacyclopentane ring appeared as overlapping multiplets around δ = 1–2.5 ppm.[7] Two multiplets at δ = 2.75 and 4.00 ppm were assigned to the two different protons of the CH_2 group of dppm. Two rather broad singlets at δ = 9.4[with $^3J(\mathrm{PtH})$ = 17.5 Hz] and 9.5 ppm [with $^3J(\mathrm{PtH})$ = 20.8 Hz] were observed for the two inequivalent CH groups of the phthalazine ligand adjacent to the N atoms.

The known $\mathrm{Pt^{IV}–Pt^{IV}}$ complex $[\mathrm{Me_3Pt^a(\mu\text{-}dppm)(\mu\text{-}I)_2\text{-}Pt^b\{CH_2(CH_2)_2C^cH_2}(\mathit{Pt^b–C^c})\}\mathrm{Me}]$, obtained from an oxidative addition of MeI to complex **1**, was identified by its NMR spectroscopic data as described previously.[7]

Kinetic Study of the Reaction of *cis,cis*-[Me$_2$Pt^a(µ-dppm)(µ-NN)Pt^b–CH$_2$(CH$_2$)$_2$}C^{c}H$_2$(*Pt^b–C^c*)] (1) with MeI in Different Solvents

The kinetics of the reaction of MeI with the reddish complex *cis,cis*-$[\mathrm{Me_2Pt^a(\mu\text{-}dppm)(\mu\text{-}NN)Pt^b–CH_2(CH_2)_2C^cH_2\text{-}}(\mathit{Pt^b–C^c})]$ (**1**), which contains a MLCT band in the visible region, was studied in different solvents by using UV/Vis spectroscopy. An excess of MeI was used at 25 °C and the disappearance of the MLCT band at λ = 360 nm in benzene and CH_2Cl_2 or at λ = 370 nm in acetone was used to monitor the reaction. The changes in the spectrum during a typical run and a typical set of absorbance–time curves for the reaction are shown in Figure 2 and Figure 3, respectively.

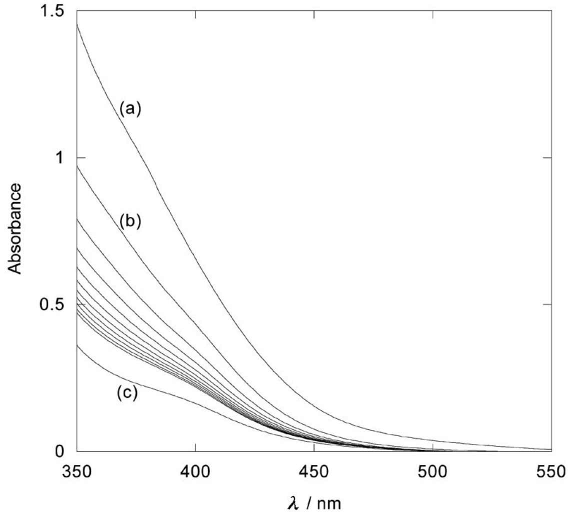


Figure 2. Changes in the UV/Vis spectrum during the reaction of *cis,cis*-$[\mathrm{Me_2Pt^a(\mu\text{-}dppm)(\mu\text{-}NN)Pt^b–CH_2(CH_2)_2C^cH_2}(\mathit{Pt^b–C^c})]$ (**1**) (3×10^{-4} M) and MeI (0.0267 M) in acetone at T = 25 °C: (a) initial spectrum (before adding MeI), (b) spectrum at t = 0; successive spectra were recorded at intervals of 25 s, and (c) final spectrum.

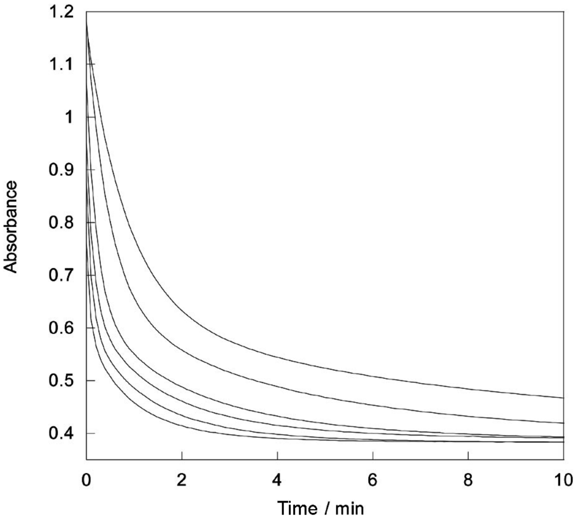


Figure 3. Absorbance–time curves for the reaction of **1** with MeI (0.026–0.33 M, [MeI] increases reading downwards) in benzene at 25 °C.

For all reaction steps studied in this work, the data could not be fitted in Equation (1), which corresponds to a monophasic kinetic behavior. However, the data were successfully fitted in Equation (2) with two exponentials, indicating a clear biphasic kinetic behavior. Thus, the pseudo-first-order rate constants $k_{\mathrm{obs}(1)}$ and $k_{\mathrm{obs}(2)}$ for the two reaction steps were evaluated by nonlinear least-squares fitting of the absorbance-time profiles to the biphasic first order equation [Equation (2)].

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

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

As shown in Figure 4, plots of the first-order rate constants, $k_{obs(1)}$ (for step 1) and $k_{obs(2)}$ (for step 2) vs. [MeI] were linear, showing a first-order dependence of the rate on the concentration of MeI in each step. The slope of each line gave the second-order rate constants (k_2 for the first step and k'_2 for the second step) and the results are collected in Table 1. Note that the plots of the first-order rate constants vs. [MeI] for both steps (Figure 4) in nonpolar benzene as well as in slightly polar CH_2Cl_2 solution (not shown in Figure 4) have zero as intercept. Therefore, each reaction step obeys a simple second-order rate law {Equation (3) for step 1 and Equation (4) for step 2, in which [A] corresponds to the concentration of the Pt^{II}–Pt^{IV} intermediate obtained in first step}, first-order in both the corresponding dimer and MeI.

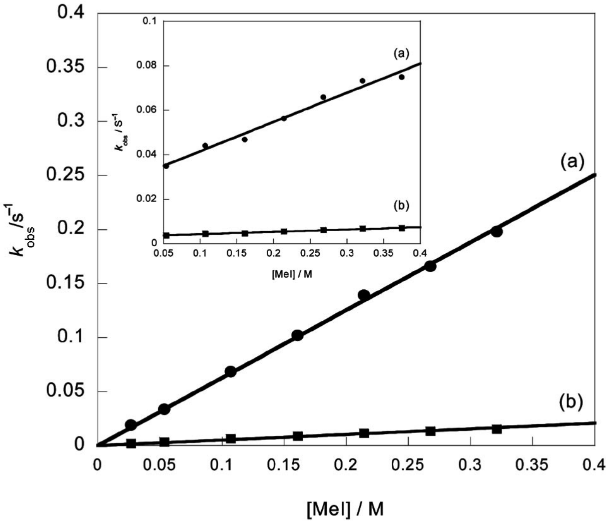


Figure 4. Plots of first-order rate constants [(a) first step, k_{obs}/s^{-1}, and (b) second step, k'_{obs}/s^{-1}] for the reaction of **1** with MeI at 20 °C vs. concentration of methyl iodide in benzene (the inset: in acetone at 25 °C; note the intercept for the two steps).

$$\text{Rate for step 1} = k_2\,[\mathbf{1}][\text{MeI}] \tag{3}$$

$$\text{Rate for step 2} = k'_2[\mathbf{A}][\text{MeI}] \tag{4}$$

However, the corresponding plots for the reactions in acetone (Figure 4) have significant intercepts and, as will be discussed later, the rate constant for each step has contributions from the second-order term (k_2 for the first step and k'_2 for the second step) and also from a term corresponding to a solvolytic reaction (k_1 for the first step and k'_1 for the second step). The rate law obeys Equation (5) for step 1 and Equation (6) for step 2.

$$\text{Rate for step 1} = (k_1 + k_2[\text{MeI}])[\mathbf{1}] \tag{5}$$

$$\text{Rate for step 2} = (k'_1 + k'_2[\text{MeI}])[\mathbf{A}] \tag{6}$$

The reproducibility of the data was remarkable (±4%). The same methods were used at other temperatures, and activation parameters were obtained from Eyring equation [see Equation (7) and Figure 5]. The data are collected in Table 1. For both steps, the observation of large negative values of $\Delta S^{\ddagger}$ is a strong support for the operation of a classical S_N2-type mechanism.

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \tag{7}$$

On the basis of the data obtained from kinetic studies, a mechanism for the two-step oxidative addition of MeI to the dinuclear complex **1** as described in Scheme 3 is suggested. MeI is first oxidatively added to one of the Pt^{II} cen-

Table 1. Rate constants and activation parameters[a] for reaction of the complex *cis,cis*-[$Me_2Pt^a(\mu$-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)] (**1**) with MeI in benzene, CH_2Cl_2, or acetone.

Reaction in benzene	Rate constants at different temperatures					
	5 °C	15 °C	20 °C	25 °C	$\Delta H^{\ddagger}$ [b] /kJ mol^{-1}	$\Delta S^{\ddagger}$ [b]/J K^{-1} mol^{-1}
$k_2 \times 10^2$ /L mol^{-1} s^{-1}	27.8 ± 1.1	50.2 ± 1.1	62.0 ± 0.8	71.2 ± 1.0	30.7 ± 3.1	–144 ± 11
$k'_2 \times 10^2$ /L mol^{-1} s^{-1}	1.4 ± 0.1	3.7 ± 0.2	5.2 ± 0.2	6.4 ± 0.2	50.9 ± 5.1	–96 ± 18
Reaction in CH_2Cl_2	Rate constants at different temperatures					
	5 °C	10 °C	15 °C	25 °C	$\Delta H^{\ddagger}$ [b] /kJ mol^{-1}	$\Delta S^{\ddagger}$ [b]/J K^{-1} mol^{-1}
$k_2 \times 10^2$ /L mol^{-1} s^{-1}	27.4 ± 1.3	36.0 ± 2.6	61.7 ± 2.5	116.5 ± 3.9	63.6 ± 8.6	–27 ± 30
$k'_2 \times 10^2$ /L mol^{-1} s^{-1}	6.1 ± 0.3	8.4 ± 0.6	14.0 ± 0.5	23.6 ± 0.3	59.5 ± 5.4	–54 ± 19
Reaction in acetone	Rate constants at different temperatures					
	10 °C	20 °C	25 °C	30 °C	$\Delta H^{\ddagger}$ [b]/kJ mol^{-1}	$\Delta S^{\ddagger}$ [b]/J K^{-1} mol^{-1}
$k_2 \times 10^2$ /L mol^{-1} s^{-1}	4.3 ± 0.3	8.9 ± 0.8	13.1 ± 0.8	17.6 ± 1.5	48.3 ± 1.1	–100 ± 4
$k_1 \times 10^2$ /s^{-1}	2.1 ± 0.1	3.0 ± 0.2	2.9 ± 0.2	2.1 ± 0.3		
$k'_2 \times 10^2$ /L mol^{-1} s^{-1}	0.19 ± 0.01	0.56 ± 0.04	1.06 ± 0.06	1.40 ± 0.12	71.8 ± 4.8	–44 ± 16
$k'_1 \times 10^2$ /s^{-1}	0.17 ± 0.01	0.31 ± 0.01	0.33 ± 0.01	0.34 ± 0.01		

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

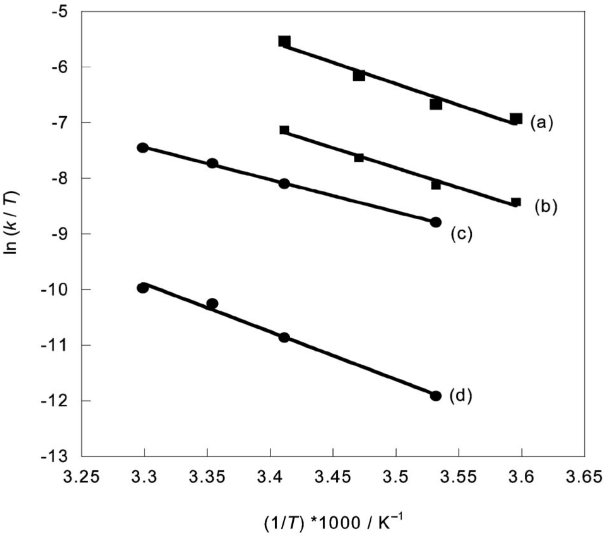
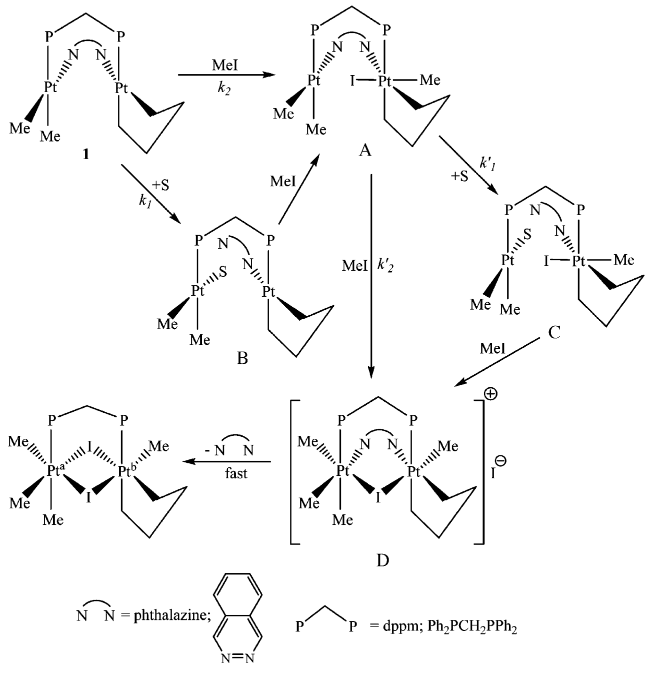


Figure 5. Eyring plots for the reaction of **1** with MeI in acetone [(a) first step, (b) second step] and CH_2Cl_2 [(c) first step, (d) second step].

ters by a classical S_N2 process. Previous studies have established that the metal center of a platina(II)cyclopentane complex is modestly more electron-rich relative to the metal center of a dimethyl platinum(II) complex, provided that the other ligands of both complexes are the same.[2] For example, EtI reacts about three times faster with the platina(II)cyclopentane complex $[Pt^b\{CH_2(CH_2)_2C^cH_2(Pt^b–C^c)\}(NN)]$, in which NN is 2,2′-bipyridine, than with complex $[PtMe_2(NN)]$, both following a S_N2-type mechanism.[2] It is therefore reasonable to assume that, as indicated in Scheme 3, the platina(II)cyclopentane center of complex **1** is first attacked by MeI, with a rate constant k_2, to give a $Pt^{II}–Pt^{IV}$ intermediate probably with structure A. Observation of a second term, k_1, in the overall rate equation [Equation (5)] is best explained by a solvolytic reaction involving formation of intermediate **1**·S; one reasonable possibility may be the replacement of a ligating N atom by a solvent molecule, S, to give an intermediate with structure B shown in Scheme 3. Intermediate B is expected to form by the attack of a solvent molecule on one of the platinum(II) centers of complex **1** to give a pentacoordinate intermediate followed by dissociation of the N leaving group. The attack is probably carried out rather on the dimethylplatinum(II) center than on the platina(II)cyclopentane center, since the latter is more electron-rich. Intermediate B then reacts rather quickly with MeI to give A. Intermediate A subsequently reacts with MeI, with rate constant k'_2, to give a $Pt^{IV}–Pt^{IV}$ intermediate probably with structure D. A second term, k'_1, in the overall rate equation [Equation (6)] is also observed for this second step, which is again attributed to a solvolytic reaction, probably involving the replacement of S with a ligating N atom on the dimethylplatinum(II) center to give intermediate C. Note that this reaction should be preferred to a similar replacement occurring on the Pt^{IV} center of intermediate A, as substitution reactions on Pt^{IV} complexes are much slower than on Pt^{II} complexes. Intermediate C is subsequently converted rather quickly to intermediate D. The suggested mechanism, discussed as follows, is consistent with the kinetic data that are summarized in Table 1.



Scheme 3.

(i) *cis,cis*-$[Me_2Pt^a(\mu\text{-dppm})(\mu\text{-NN})Pt^b–CH_2(CH_2)_2C^cH_2(Pt^b–C^c)]$ (**1**) reacts with MeI in benzene in a two-step process with rate constants (at 25 °C) $k_2 \times 10^2$ = 71.2 ± 1.0 $L\,mol^{-1}\,s^{-1}$ (for the first step) and $k_2 \times 10^2$ = 6.4 ± 0.2 $L\,mol^{-1}\,s^{-1}$ (for the second step). When these values are compared with the rate constant values reported previously for the analogous symmetrical dimethyl–dimethyl complex *cis,cis*-$[Me_2Pt(\mu\text{-dppm})(\mu\text{-NN})PtMe_2]$ (under the same conditions) [$k_2 \times 10^2$ = 39.0 ± 0.5 $L\,mol^{-1}\,s^{-1}$ (for the first step) and $k'_2 \times 10^2$ = 5.6 ± 0.1 $L\,mol^{-1}\,s^{-1}$ (for the second step)],[4] it is found that, as expected, the rate of the reaction of MeI with the platina(II)cyclopentane center of complex **1** (in the first step) is nearly 2 times faster than the rate of the first MeI attack on the analogous dimethyl–dimethyl complex. The rates for the second step of the reaction of MeI with both complexes are almost the same, as MeI in each case attacks a dimethylplatinum(II) center. In the case of the reaction of complex *cis,cis*-$[Me_2Pt^a(\mu\text{-dppm})(\mu\text{-NN})Pt^b–CH_2(CH_2)_2C^cH_2(Pt^b–C^c)]$ (**1**) with MeI, the first step is more than 11 times faster than the second step. This large rate difference is attributed to the considerable electronic information transmitted through the bridging dppm ligand in the $Pt^{II}–Pt^{IV}$ intermediate A.

(ii) When the reaction of complex **1** with MeI is performed in CH_2Cl_2, which is moderately more polar than benzene, the rate of reaction at 25 °C increases by a factor of 1.6 in the first step and by a factor of 3.7 in the second step relative to that in benzene, as expected for S_N2 processes.

(iii) However, when the reaction of complex **1** with MeI was performed in acetone, which has a significantly higher dielectric constant than that of benzene or CH_2Cl_2, the involvement of solvent decreased the rates of both steps of the reaction considerably by a factor of about six at 25 °C. Consistently, the reaction in the much more polar solvent CH_3CN was too slow for any meaningful measurements.

(iv) The $\Delta H^‡/\Delta S^‡$ compensation plots for the two steps of the reaction of complex **1** with MeI in the solvents acetone, CH_2Cl_2, and benzene are shown in Figure 6. For each step a reasonably straight line is obtained and although the number of points is not ample, it may be taken as an evidence for the operation of a common (associative, second-order) mechanism for the reaction in all solvents.[9]

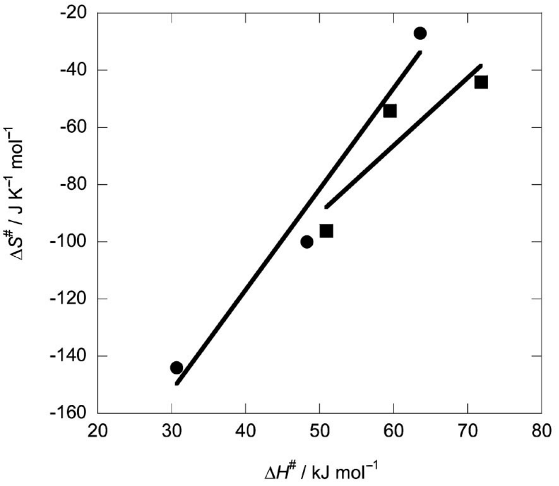


Figure 6. The $\Delta H^‡/\Delta S^‡$ compensation plots of the reaction of complex **1** with MeI: (a) first step (●) and (b) second step (■).

Conclusions

Mechanistic studies of the oxidative addition of alkyl halides to monomeric d^8 complexes, especially organoplatinum(II) complexes, have established that the reactions normally occur by a S_N2-type mechanism. The rate constants of these reactions are sensitive to the polarity of the solvent, in each case an increase in the reaction rate was observed in more polar solvents, as would be expected for a polar transition state.[1,2] The rates for these reactions in nonpolar benzene are normally about 4–10 times slower than those in polar acetone. However, in the present work, the kinetic data for the oxidative addition of MeI to a new dimeric complex *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)](**1**), occurring in a two-step process by a common S_N2 mechanism in each step, show that the opposite has happened: the rate of the reaction is considerably slower in the polar solvent acetone than that in the nonpolar solvent benzene. Consistently, the reaction in the much more polar CH_3CN was too slow for any meaningful measurements. This unusual observation was attributed to an accompanying solvolytic reaction in each step, happening when the reaction of dimeric complex **1** was performed in more polar solvents.

The Pt center of the platina(II)cyclopentane moiety is expected to be more electron-rich than the dimethylplatinum(II) center.[2] In consistency with this assumption, kinetic study of the reaction of complex **1** with MeI in the solvents acetone, CH_2Cl_2, and benzene suggested that the more electron-rich Pt center experienced the oxidative addition of MeI prior to the second one. The observation that the first step of this reaction is about 11 times faster than the second step indicates that a considerable amount of the electronic information is transmitted through bridging dppm and NN ligands in the Pt^{II}–Pt^{IV} intermediate A.

Experimental Section

The NMR spectra were recorded with a Bruker Avance DRX 500 MHz spectrometer. ^1H, ^{31}P, and ^{195}Pt NMR chemical shifts were referenced to TMS, 85% H_3PO_4, and aqueous K_2PtCl_4, respectively. Kinetic studies were carried out with a Perkin–Elmer Lambda 25 spectrophotometer with temperature control by using an EYELA NCB-3100 constant-temperature bath. The microanalysis was performed with a Termofinnigan Eager 300 CHN–O elemental analyzer. The dimeric precursor *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-SMe_2)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)] was prepared by the literature method.[7]

***cis,cis*-[Me_2Pt^a(μ-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)] (1):** A solution of phthalazine (NN) (14.3 mg, 0.11 mmol) in acetone (5 mL) was added to a solution of *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-SMe_2)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)] (100 mg, 0.11 mmol) in acetone (15 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 diethyl ether (3 mL) to give a pale red solid that was separated and dried under vacuum. Yield: 80 mg (74%). M.p.: 118 °C(dec). $C_{39}H_{42}N_2P_2Pt_2$ (990): calcd. 47.2, H 4.2, N 2.8; found C 46.9, H 4.3, N 2.7. ^1H NMR (500 MHz, [D$_6$]acetone): δ = 0.41 [d, ^2J(PtH) = 73.8 Hz, ^3J(PH) = 7.8 Hz, 3 H, Me ligand *trans* to phosphorus], 0.52 [d, ^2J(PtH) = 88.6 Hz, ^3J(PH) = 8.0 Hz, 3 H, Me ligand *trans* to nitrogen], 1–2.5 [overlapping multiplets, CH_2 groups of the platinacyclopentane ring], 2.75 [br., 1 H, CH_2 group of dppm], 4.0 [m, 1 H, CH_2 group of dppm], 9.4 [br. s., ^3J(PtH) = 17.5 Hz, 1 H, CH group of phthalazine adjacent to the N atom], 9.5 [b. s., ^3J(PtH) = 20.8 Hz, 1 H, CH group of phthalazine adjacent to the N atom] ppm. ^{31}P NMR (202 MHz, [D$_6$]acetone, r. t.): δ = 10.9 [s, ^1J(Pt^aP^a) = 1980 Hz, ^1J(Pt^bP^b) = 1897 Hz, ^3J(PtP) = observed but not measured, ^2J(PP) = 65 Hz, P^a and P^b of dppm] ppm. ^{31}P NMR (202 MHz, CD_2Cl_2, –80 °C): δ = 8.8 [d, ^1J(Pt^aP^a) = 1974 Hz, ^2J(PP) = 61 Hz, P^a of dppm], 10.3 [d, ^1J(Pt^bP^b) = 1890 Hz, ^2J(PP) = 62 Hz, P^b of dppm] ppm. ^{195}Pt NMR (107 MHz, [D$_6$]acetone, r. t.): δ = –4005 [d, ^1J(Pt^aP^a) = 1970 Hz, Pt^a], –4109 [d, ^1J(Pt^bP^b) = 1894 Hz, Pt^b] ppm.

Reaction of *cis,cis*-[Me_2Pt^a(μ-dppm)(μ-NN)Pt^b–$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)] (1) with MeI: To a solution of complex **1** (20 mg in 5 mL acetone) was added an excess amount of MeI (40 μL) at room temperature and the mixture was allowed to stand under these conditions for 6 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether (2 × 3 mL). The product was dried under vacuum and identified by its ^1H and ^{31}P NMR spectra as the known diplatinum(IV) complex [Me_3Pt^a(μ-dppm)(μ-I)$_2Pt^b${$CH_2(CH_2)_2C^cH_2$(*Pt^b–C^c*)}Me][7] in pure form.

Kinetic Study: In a typical experiment, a solution of complex **1** in benzene (3 mL, 3×10^{-4}M) in a cuvette was tempered at 25 °C and a known excess of MeI was added by using a microsyringe. After rapid stirring, the absorbance at $\lambda = 360$ nm was monitored with time.

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