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Oxidative Addition to Methylplatinum(II) Complexes: Trapping of a Cationic Intermediate and a Comparison of Reactivities of Mononuclear and Binuclear Complexes

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cis-[$PtMe_2(SMe_2)_2$], **1**, reacts with MeI to give *fac*-[$PtIMe_3(SMe_2)_2$], **3**, but in solvent CD_3CN an intermediate characterized as *fac*-[$PtMe_3(SMe_2)_2(CD_3CN)$]I, **4**, is detected by low-temperature NMR and in acetone saturated with LiCl an intermediate *fac*-[$PtClMe_3(SMe_2)_2$] is detected similarly. The dimer [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **2**, reacts with MeI to give **3** and [$(PtIMe_3)_4$] as major products. Both complexes **1** and **2** react by the S_N2 mechanism, and **1** reacts 20 times faster than **2** at −10 °C in acetone. Both **1** and **2** react with *o*-$C_6H_4(CH_2Br)_2$ to give [$Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(SMe_2)_2$], but in this case the dimer **2** reacts faster than the monomer **1**.

Introduction

Oxidative additions of alkyl halides to binuclear transition-metal complexes are of current interest.[1-3] One aspect of such reactions which has not been studied thoroughly is how the rates of reaction of mononuclear and binuclear complexes compare. In some cases, cooperative effects between two metal centers are thought to enhance reactivity of the binuclear system[4,5] but, in other cases, increased steric hindrance in binuclear systems leads to a decrease in reactivity.[6]

This paper reports a study of mechanism and reactivity in the oxidative addition of methyl iodide to the complexes *cis*-[$PtMe_2(SMe_2)_2$], **1**, and [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **2**.[7] Since both complexes have the *cis*-[$PtMe_2(SMe_2)_2$] coordination environment, it was felt that differences in steric and electronic effects in the ground state of **1** and **2** would be small.[8] The most significant results are that the monomer **1** is more reactive than the dinuclear **2** and that strong evidence for the S_N2 mechanism was found for oxidative addition to **1**, including the trapping of a cationic intermediate.

Results

Reaction of MeI with *cis*-[$PtMe_2(SMe_2)_2$]. The complex *cis*-[$PtMe_2(SMe_2)_2$], **1**, was generated in solution by adding excess Me_2S to a solution of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], **2**.[7] Reaction of **1** with a stoichiometric amount of MeI in acetone rapidly gave *fac*-[$PtIMe_3(SMe_2)_2$], **3**. Complex **3** was readily identified in solution by the ^1H NMR spectrum, but it could not be isolated in pure form due to loss of the labile Me_2S ligands when the solvent was evaporated. Crystals of [$(PtIMe_3)_4$] were formed on slow evaporation of an acetone solution of **3**. Sulfide dissociation from **3** caused broadening of the ^1H NMR signals at room temperature, but good spectra were obtained at −10 °C. Three singlet resonances in a 4:2:1 intensity ratio due *Me*S, *Me*Pt trans to S, and *Me*Pt trans to I, respectively, each with satellites due to coupling to ^{195}Pt (Figure 1)[9,10] observed.

When the reaction of **1** with MeI to give **3** in toluene-d_8 or acetone-d_6 was monitored by ^1H NMR spectroscopy at −10 °C, no intermediates were detected. However, the reaction in CD_3CN did give an intermediate characterized as having structure *fac*-[$PtXMe_3(SMe_2)_2$] by the ^1H NMR spectrum (Figure 1). The methylplatinum groups trans to sulfur gave a normal $^2J(PtH)$ coupling of 70 Hz, but the MePt group trans to X gave $^2J(PtH) = 76$ Hz, showing that the trans group X has a very low trans influence.[10] As the reaction progressed, the peaks due to the intermediate decayed and those due to the product **3** increased (Figure 1). The intermediate is therefore characterized as *fac*-[$PtMe_3(SMe_2)_2(CD_3CN)$]I, **4**. Formation of cationic intermediates such as **4** has long been expected in oxidative addition by the S_N2 mechanism,[11] but this appears to be the first case where the intermediate has been sufficiently longlived to be characterized. Cationic complexes have been formed previously in oxidative addition reactions of 18-electron complexes; for example, [$Ir(\eta\text{-}C_5H_5)(CO)(PPh_3)$] with MeI gives [$IrMe(\eta\text{-}C_5H_5)(CO)(PPh_3)$]I.[12] It is clear that acetonitrile is a good enough ligand for platinum to give **4** and, since **4** then reacts further to give **3**, the complex **4** must be formed as a result of kinetic control. Of the several mechanisms proposed for oxidative addition, only the S_N2 mechanism should give this result.[13] Acetone and toluene are not good enough ligands to give long-lived intermediates. However evidence for cationic intermediates in acetone was obtained by conducting the reaction of **1** with MeI in the presence of LiCl, when *fac*-[$PtClMe_3(SMe_2)_2$] was formed at intermediate stages and the chloride was then substituted slowly by iodide to

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[1] Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75.

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[8] Slightly greater steric effects in **2** are expected due to lack of free rotation about the PtS bonds in μ-SMe_2 complexes and due to probable puckering of the Pt_2S_2 ring of **2**, which will hinder attack on one side of the square-planar platinum centers. It is also probable that a μ-SMe_2 ligand will be a slightly weaker donor than a terminal SMe_2 ligand.

[9] Lashanizadehgan, M.; Rashidi, M.; Hux, J. E.; Puddephatt, R. J.; Ling, S. S. M. *J. Organomet. Chem.* **1984**, *269*, 317.

[10] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. Compare values of $^2J(PtH) = 70$ and 72 Hz when X = I and Cl, respectively.

[11] This suggestion was first made by: Halpern. Chock, P. B.; Halpern J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

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[13] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 7.

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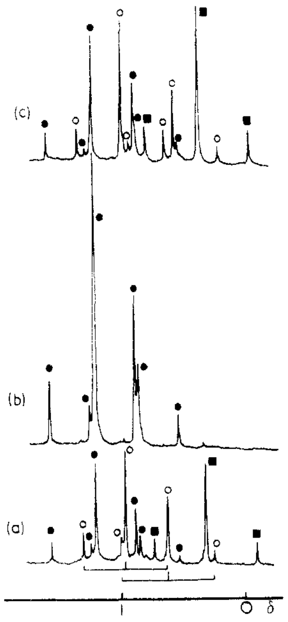


Figure 1. ^{1}H NMR spectra (100 MHz) in the methylplatinum region of reaction mixtures: (a) complex **1** with MeI in CD_3CN after 15 min at -10 °C (platinum satellites of the MePt resonances of intermediate **4** are shown below); (b) same reaction mixture as (a) after 2 h; (c) complex **1** with MeI in $(CD_3)_2CO$ saturated with LiCl. Resonances marked with closed squares are due to starting complex **1**, those marked with closed circles are due to final complex **3**, and those marked with open circles are due to intermediates **4** (spectrum a) or *fac*-$[PtClMe_3(SMe_2)_2]$ (spectrum c).

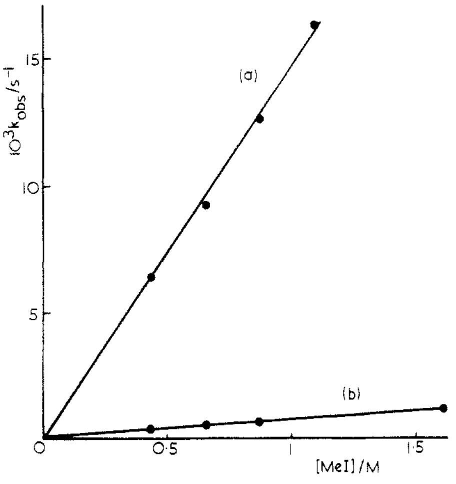
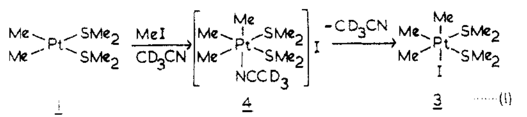


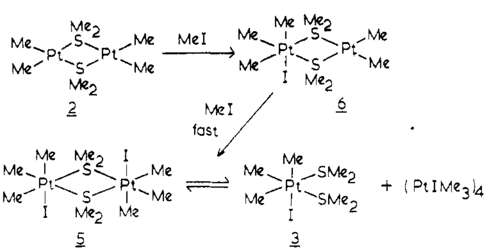
Figure 2. Graphs of first-order rate constants for reactions with MeI at -10 °C in acetone-d_6 vs. concentration of MeI: (a) *cis*-$[PtMe_2(SMe_2)_2]$; (b) $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$.

give only **3** as the final product.[14] The proposed mechanism for oxidative addition in CD_3CN is shown in eq 1.



The kinetics of oxidative addition were measured at -10 °C by monitoring decay of the *Me*Pt resonance of **1** during the reaction with MeI. Good second-order kinetics were observed, first order in both **1** and MeI (Figure 2). The second-order rate constants in toluene, acetone, and acetonitrile were 2.5 × 10^{-3}, 14.5 × 10^{-3}, and 22 × 10^{-3} L mol^{-1} s^{-1}, respectively. The increase in rate with solvent polarity is expected for the S_N2 mechanism.[11-13,15] The concentration of free SMe_2 had no effect on the rate,[16] and the radical scavenger benzoquinone also had no effect.

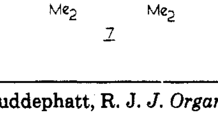
Scheme I



Reaction of MeI with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, 2. This reaction was carried out in acetone solution and gave an equilibrium mixture of $[Pt_2Me_6I_2(\mu\text{-}SMe_2)_2]$, **5**, formed by double oxidative addition of MeI, along with **3** and $[(PtIMe_3)_4]$. The equilibrium strongly favored the latter two products, and **5** was detected only by the very characteristic μ-S*Me*$_2$ resonance in the ^{1}H NMR spectrum. This occurred as a quintet due to coupling to ^{195}Pt with a very low value of ^3J(PtH) as found for $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$.[9,17] The observation of only one MeS resonance strongly suggests the trans-fac structure for **5**.[9,17] No intermediates, such as the expected product **6**, were observed when the reaction was monitored by ^{1}H NMR at -10 °C. Acetonitrile reacted with **2** to give *cis*-$[PtMe_2(SMe_2)(CH_3CN)]$ in solution, thus precluding studies of the binuclear oxidative addition in this solvent.

Kinetic studies were carried out by ^{1}H NMR at -10 °C in acetone solution, monitoring disappearance of **2** with time. Second-order kinetics were observed, first-order in both MeI and complex **2** (Figure 2). The observed second-order rate constant was (7.0 ± 0.4) × 10^{-4} L mol^{-1} s^{-1}; this is approximately 20 times lower than that for reaction with the monomer **1** of (14.5 ± 0.5) × 10^{-3} L mol^{-1} s^{-1}. In the reaction with **2**, the rate-determining step is the initial oxidative addition. The dimer could dissociate at this point followed by rapid oxidative addition to the mononuclear platinum(II) fragment or a rapid second oxidative addition could occur[17] followed by fragmentation to give the observed products. Since no intermediates could be detected, it is not possible to distinguish between these mechanisms. The proposed intermediate and resulting product equilibrium are shown in Scheme I.

Reaction of α,α'-Dibromo-*o*-xylene with 1 or 2. The above reactions occurred readily to give in both cases the binuclear product **7**. A similar product $[Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(\mu\text{-}Ph_2PCH_2PPh_2)]$, **7**, has been charac-



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[14] A related experiment has been reported showing anion exchange on oxidative addition of allyl chloride to Ir(I) in the presence of bromide. The allyl bromide adduct was formed. Pearson, R. G.; Poulos, A. T. *Inorg. Chim. Acta* **1979**, *34*, 67. Oxidative addition of MeI in the presence of chloride to $[IrCl(CO)L_2]$ does not give chloride incorporation but to a rhodium(I) macrocycle it does. Pearson, R. G.; Muir, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5519. Collman, J. P.; MacLaury, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 3019.

[15] Jawad, J. K.; Puddephatt, R. J. *J. Organomet. Chem.* **1976**, *117*, 297.

[16] A high concentrations of Me_2S the reaction with MeI to give insoluble $[Me_3S]I$ occurred and limited the concentration range used. However, dissociation of SMe_2 from **1** prior to oxidative addition is disproved by this observation.

[17] Kuyper, J.; van der Laan, R.; Jeanneaus, F.; Vrieze, K., *Transition Met. Chem.* **1976**, *1*, 199.

terized by Shaw and co-workers.[18] The ^{1}H NMR data for the *Me*Pt and xylene ligands of **6** are very similar to those reported for **7**.[18] An alternative structure in which the bromide and SMe_2 ligands in **6** are interchanged is disproved by the appearance of one quarter intensity satellites due to coupling to ^{195}Pt for the S*Me*$_2$ resonance, as expected for terminal but not for bridging SMe_2 groups.[7,9]

It is of interest that the dimer **2** reacted about twice as fast as the monomer **1** with dibromoxylene. This is presumably the result of a template effect which increases the rate of oxidative addition of the second C–Br bond on reaction with the dimer **2**.[18] The NMR spectra were too complex to allow a kinetic study of the system.

Conclusions

The characterization of the cationic intermediate **4** on reaction of **1** with MeI in CD_3CN is consistent with an S_N2 mechanism for this reaction.[19] The same mechanism is probably involved for the reaction of MeI with **2**, based on the kinetic studies. Since the dimer **2** reacts about 20 times slower than the monomer **1** with MeI, it is clear that the second platinum center in **2** does not enhance the reactivity. In cases where binuclear systems are more reactive than mononuclear ones, the second metal is in a position where it can form a donor–acceptor metal–metal bond trans to the alkyl–metal bond being formed[4,5] and thus provide anchimeric assistance. The geometry of complex **2** prevents such an effect and the lower reactivity of **2** compared to **1** with MeI is then probably due to a combination of minor unfavorable steric and electronic effects.[8]

Experimental Section

^{1}H NMR spectra were recorded by using a Varian XL100 spectrometer. Chemical shifts are given with respect to Me_4Si, but using the ^{1}H impurity in the deuterated solvents as internal reference since Me_4Si interfered with the MePt resonances.

Complexes *cis*-$[PtMe_2(SMe_2)_2]$ and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ were prepared as described previously.[7]

Monitoring of Reactions. To a solution (1 mL) of *cis*-$[PtMe_2(SMe_2)_2]$ (0.0435 M), CH_2Cl_2 (0.0653 M) as reference, and excess SMe_2 (0.0435 M) in acetone-d_6 in an NMR tube cooled to −10 °C was added MeI (0.0435 mmol). NMR spectra were recorded at −10 °C as the reaction proceeded. Concentrations of *cis*-$[PtMe_2(SMe_2)_2]$ at different times were determined by comparing the intensity of the MePt resonance with that of the CH_2Cl_2 reference, after calibration. The only product was *fac*-$[PtIMe_3(SMe_2)_2]$: NMR δ_H 0.68 [s, ^2J(PtH) = 70 Hz, *Me*Pt trans to I], 1.04 [s, ^2J(PtH) = 70 Hz, *Me*Pt trans to SMe_2], 2.20 [s, ^3J(PtH) = 13 Hz, MeS]. In the presence of LiCl, resonances due to *fac*-$[PtClMe_3(SMe_2)_2]$ were observed at intermediate stages: δ_H 0.36 [s, ^2J(PtH) = 72 Hz, *Me*Pt trans to Cl], 0.78 [s, ^2J(PtH) = 70 Hz, *Me*Pt trans to SMe_2], 2.08 [s, ^3J(PtH) = 12 Hz, MeS]. When the reaction was carried out in CD_3CN, resonances due to *fac*-$[PtMe_3(CD_3CN)(SMe_2)_2]I$ were observed at intermediate stages: δ_H 0.65 [s, ^2J(PtH) = 76 Hz, MePt trans to CD_3CN], 1.00 [s, ^2J(PtH) = 70 Hz, *Me*Pt trans to SMe_2], 2.36 [s, ^3J(PtH) = 10 Hz, MeS].

Reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with MeI were monitored similarly. In all solvents studied the major products were *fac*-$[PtIMe_3(SMe_2)_2]$ and $[(PtIMe_3)_4]$, δ_H(acetone) 1.73 [s, ^2J(PtH) = 78 Hz] and $\delta_H(C_6D_6)$ 1.73 [s, ^2J(PtH) = 78 Hz], but some complex tentatively identified as *fac*-$[Pt_2I_2Me_6(\mu\text{-}SMe_2)_2]$ was observed, δ_H(acetone-d_6) 2.66 [s, ^2J(PtH) = 10 Hz, MeS].

Kinetic Studies. These studies were carried out by using excess methyl iodide, monitoring decay of the *Me*Pt resonance of the starting material by NMR as above. For example, MeI (0.435 mmol) was added to a solution of *cis*-$[PtMe_2(SMe_2)_2]$ (0.0435 M) in acetone (1.00 mL) containing CH_2Cl_2 as reference (0.0653 M) in an NMR tube at −10 °C. NMR spectra were recorded at 2–5 min intervals until the reaction was complete. Graphs of $-\ln\ [PtMe_2(SMe_2)_2]$ vs. time gave good straight line plots from which the first-order rate constants were calculated. The linear plots of k_{obsd} vs. [MeI] then gave the second-order rate constants k_2 (Figure 2). The same method was used for reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone with MeI.

Approximate rate constants for reaction of *cis*-$[PtMe_2(SMe_2)_2]$ with MeI in CD_3CN or toluene-d_8 were determined similarly but using $[PtMe_2(SMe_2)_2]$ = [MeI]. Second-order treatment then gave straight line plots from which values of k_2 were calculated.

Preparation of $[Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(SMe_2)_2]$. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.0495 g, 0.0861 mmol) was dissolved in acetone-d_6 (2.0 mL), and to this solution was added 1 equiv of α,α'-dibromo-*o*-xylene (0.0227 g). As monitored by NMR, the reaction was complete within 3 h. The product $[Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(SMe_2)_2]$ was obtained as white crystals from acetone–pentane at 0 °C: yield 88%; mp 195 °C dec. Anal. Calcd for $[Pt_2Me_4(\mu\text{-}Br)_2(\mu\text{-}CH_2C_6H_4CH_2)(SMe_2)_2]$: C, 22.9; H, 3.85. Found: C, 23.0; H, 3.7.

Similarly, α,α'-dibromo-*o*-xylene (0.0227 g) with *cis*-$[PtMe_2(SMe_2)_2]$, prepared from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.0495 g) and SMe_2 in acetone-d_6 (2 mL), gave the same product within 5 h: yield 74% NMR (acetone-d_6) δ_H 0.63 [s, ^2J(PtH) = 78 Hz, *Me*^{a}Pt], 0.73 [s, ^2J(PtH) = 78 Hz, *Me*^{b}Pt], 2.02 [s, ^3J(PtH) = 13 Hz, MeS], 2.23 [m, $^2J(H^aH^b)$ = 9 Hz, ^2J(PtH) = 23 Hz, CH^a], 4.03 [m, $^2J(H^aH^b)$ = 9 Hz, ^2J(PtH) = 122 Hz, ^5J(PtH) = 6 Hz, CH^b]. Assignments for Me^a, Me^b and H^a, H^b may be reversed.

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Registry No. 1, 87145-38-8; 2, 79870-64-7; 3, 96413-69-3; 4, 96427-36-0; 5, 96427-37-1; 7, 96413-70-6; $[(PtIMe_3)_4]$, 18253-26-4; SMe_2, 75-18-3; MeI, 74-88-4; *fac*-$[PtClMe_3(SMe_2)_2]$, 81313-95-3; α,α'-dibromo-*o*-xylene, 91-13-4.

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(18) A less favorable entropy of activation is expected for intramolecular oxidative addition.

(19) This trapping of a cationic intermediate by a donor solvent should be possible for many other oxidative additions to square-planar d^8 complexes, since the octahedral d^6 products are inert to ligand substitution. The ligand substitution is presumably a dissociative process aided by the labilizing effect of the trans methyl group.