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Synthesis And NMR Investigation of 1-Phenyl-1,2-propanedione-2-oxime Complexes of Trimethylplatinum(IV).

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Abstract.

The ionised monoxime, 1-phenyl-1,2-propanedione-2-oxime (ppdm) reacts smoothly with trimethylplatinum(IV) sulfate in aqueous acetone, to form the complex *fac*-[PtMe₃(ppdm)(H₂O)] **1** in high yield. **1** Reacts with 3,5-lutidine and 2,2'-bipyridine to form stable 1:1 adducts, *viz.* *fac*-[PtMe₃(ppdm)(3,5-lut)] **2** and *fac*-[PtMe₃(ppdm)(bipy)] **3**. In complexes **1** and **2**, the ionised monoxime behaves in a N/O bidentate chelate fashion, whereas in **3**, ppdm is co-ordinated to the metal moiety in a monodentate fashion, via the oximate N donor atom. The parent complex, **1**, dissolves in polar solvents to form species of general formulae *fac*-[PtMe₃(ppdm)(solv)] (solv = DMSO, methanol or acetone), which undergo an intramolecular "windscreen-wiper" fluxional rearrangement. The stereodynamics of the fluxional process have been measured in CD₃OD and [D₆]DMSO solution by two-dimensional exchange spectroscopy; ΔG^\ddagger (298 K) is 73.6 kJ mol⁻¹ and 88.5 kJ mol⁻¹, respectively. The effects of the solvent on the energetics and a possible mechanism for the fluxional process are discussed.

Introduction.

In a previous study¹ of trimethylplatinum(IV) complexes of the physiologically active monoxime butane-2,3-dione monoxime (Hbdm),² it was shown that, in the three complexes prepared, *viz.* [PtMe₃(bdm)]₂, [PtMe₃(bdm)(py)] and [PtMe₃(bdm)(bipy)], the ionised ligand (bdm) adopted three different modes of co-ordination. Furthermore, in the parent complex, [PtMe₃(bdm)]₂, the oximate ligand appears to display two different configurations; an ionised hydroxy-oxime configuration in the solid-state and in protic solvents, and a carbonyl-oxime configuration in aprotic solvents (Figure 1).

The parent complex, [PtMe₃(bdm)]₂, is soluble only in co-ordinating solvents, in which it dissociates into solvent-bonded monomeric species, [PtMe₃(bdm)(solv)] (solv = co-ordinating solvent). The resulting complexes (solv = dimethyl sulfoxide, methanol or acetone) were shown to undergo a novel "windscreen-wiper" fluxional rearrangement. The energetics of the rearrangement were measured by two-dimensional exchange spectroscopy (EXSY) in [D₄]methanol; ΔG^\ddagger (298 K) was *ca.* 74 kJ mol⁻¹. It was therefore of interest to study the behaviour of the related monoxime, 1-phenyl-1,2-propanedione-2-oxime (Hppdm), which can only adopt a carbonyl-oxime configuration when ionised. As with Hbdm, few complexes of Hppdm have been reported hitherto. Aromatic carbonyl oximes are generally regarded as poor chelating agents, and the complexes, if formed at all, are usually unstable.^{3,4} The X-ray crystal structure of the cobalt(III) complex, [Co(ppdm)₃], has been reported,⁴ and is presumably the same compound as that described as the characterisation product of the ligand.⁵

In contrast, like Hbdm, the ionised ligand 1-phenyl-1,2-propanedione-2-oximate (ppdm) reacts readily with trimethylplatinum(IV) sulfate in aqueous media, to form a stable Pt-N=C-C=O chelated complex. The parent complex, [PtMe₃(ppdm)] **1**, which is monomeric (with a water molecule occupying the sixth co-ordination site), reacts readily with 3,5-lutidine and 2,2'-bipyridine in benzene, to form the 1:1 adducts, [PtMe₃(ppdm)(3,5-lut)] **2** and [PtMe₃(ppdm)(bipy)] **3**, respectively.

Experimental.

Materials.- 1-Phenyl-1,2-propanedione-2-oxime was purchased from Aldrich Chemical Company and used without further purification. Trimethylplatinum(IV) sulphate was prepared by our previously published procedure.¹

Synthesis of [PtMe₃(ppdm)(H₂O)] 1.- 1-Phenyl-1,2-propanedione-2-oxime (800 mg, 0.49 mmol) was added as a solid to a stirred aqueous acetone solution (50:50 v/v) of trimethylplatinum(IV) sulfate, [(PtMe₃)₂SO₄.4H₂O], (500 mg, 0.77 mmol). Sodium acetate trihydrate (0.50 g, 3.67 mmol) was added to the resulting clear orange solution. The reaction mixture was stirred for ca. 0.5 h, during which time an orange coloured solid precipitated. The solid product was isolated by filtration, washed with water and dried *in vacuo*. Recrystallisation from acetone-hexane gave 390 mg (60%) of pure, orange [PtMe₃(ppdm)(H₂O)].

Synthesis of [PtMe₃(ppdm)(3,5-lut)] 2.- 3,5-Lutidine (0.20 cm³) was added to a stirred suspension of [PtMe₃(ppdm)(H₂O)] (100 mg, 0.24 mmol) in 10 cm³ of benzene. The reaction mixture was stirred for ca. 1.5 h. The resulting pale pink solution was then evaporated to dryness *in vacuo* and the solid residue crystallised from benzene-hexane to yield a red-pink solid. Yield; 78 mg, 64%.

Synthesis of [PtMe₃(ppdm)(bipy)] 3.- 2,2'-Bipyridine (0.150 mg, 0.64 mmol) was added to a stirred suspension of [PtMe₃(ppdm)(H₂O)] (150 mg, 0.37 mmol) in 15 cm³ of benzene. After ca. 3 h. stirring at ambient temperature, a clear yellow solution was obtained. Concentration of the mother liquor to ca. 5 cm³ *in vacuo*, and addition of hexane yielded crystalline, yellow [PtMe₃(ppdm)(bipy)]. Yield; 162 mg, 81%.

Physical methods.- Hydrogen-1 NMR spectra were recorded in [D₆]dimethyl sulfoxide (DMSO), [D₄]methanol, [D₆]acetone or CDCl₃ solution, on either a

Bruker AC300 or a Bruker AC400 Fourier Transform spectrometer, operating at 300.13 and 400.13 MHz, respectively. Chemical shifts are quoted in ppm, relative to tetramethyl silane as an internal standard. NMR probe temperatures were controlled by a standard B-VT 2000 unit; temperatures were checked periodically against a standard sample of methanol in [D₄]methanol, and are considered accurate to within ± 1 °C. Two-dimensional exchange spectra were obtained using the Bruker NOESYPH program,⁶ which generates the pulse sequence D1-90°-D0-90°-D9-90°-free induction decay. Spectra were typically recorded with 512 words of data in f_1 and f_2 , and transformed with 1024 words of data. The initial delay, D0, was set at 3 μ s and the relaxation delay, D1, was 2.0 s. The mixing time, D9, was varied according to the complex under investigation, and the experimental temperature. Signal intensities were obtained from the resulting two-dimensional spectra by volume integration. Integrations were performed five times; mean values were used to determine the exchange rates from the program D2DNMR.⁷ The activation parameters were calculated from a least-squares fit of the linearised Eyring and Arrhenius equations. Errors quoted are those defined by Binsch and Kessler.⁸

Infrared spectra were recorded as pressed CsI discs on a Nicolet Magna 550 FT-IR spectrometer, operating in the region 4000 - 200 cm^{-1} . Fast atom bombardment (FAB) mass spectra were obtained on a VG AutoSpec instrument using Cs⁺ ion bombardment at 25 kV energy, on samples of the complexes dissolved in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were carried out at Butterworth Laboratories Ltd., Teddington, Middlesex.

Results and Discussion.

The three complexes, [PtMe₃(ppdm)(H₂O)] **1**, [PtMe₃(ppdm)(3,5-lut)] **2** and [PtMe₃(ppdm)(bipy)] **3**, were prepared in high yields as described (*vide supra*). The analytical data (*vide infra*) indicate that the complexes have the structures shown in Figure 2. Attempts to prepare the dimer, [PtMe₃(ppdm)]₂, by dehydration of **1** were unsuccessful, as were attempts to prepare the pyridine

adduct, [PtMe₃(ppdm)(py)].

The infra-red spectrum of [PtMe₃(ppdm)(H₂O)], **1**, showed a strong, broad band at 3243 cm⁻¹ ($\Delta\sigma = 220 \text{ cm}^{-1}$), which shifted to 2360 cm⁻¹ ($\Delta\sigma = 880 \text{ cm}^{-1}$) on deuteration of the complex. Since no N-OH configuration is possible for the ionised monoxime ligand, this indicates the presence of a co-ordinated water molecule. Three bands were observed in the C-H stretching region;⁹⁻¹² two due to C-H stretching modes and one due to the overtone of the C-H deformation at ca. 1408 cm⁻¹. One Pt-N and three Pt-C stretching modes were also tentatively assigned. The strong band at 1552 cm⁻¹ was assigned to the C=O stretch of the co-ordinated oximate carbonyl group. These data are consistent with **1** having the structure shown in Figure 2. Infra-red data are reported in Table 1.

The infra-red spectrum of the 3,5-lutidine adduct, **2**, displayed three bands in the C-H stretching region, together with one Pt-N and three Pt-C stretching bands. The signal at 1520 cm⁻¹ was assigned to the oximate carbonyl stretching mode. Complex **3** displayed three bands in the C-H stretching region, three Pt-C and two Pt-N stretching bands. The presence of a band at 1622 cm⁻¹, assigned to the stretching mode of a free carbonyl group, indicates that the monoximate oxygen donor atom is unco-ordinated. The infra-red data for **2** and **3** (Table 1) thus indicate that the complexes have the structures depicted in Figure 2.

Fast atom bombardment (FAB) mass spectrometry was performed on the three complexes, **1** - **3**. The parent complex, **1**, displayed an intense peak at m/z^+ 403, which corresponds to the species [M-OH]⁺; this presumably arises from protonation of [PtMe₃(ppdm)], *i.e.* M-OH₂. Strong fragmentation peaks were also observed at m/z^+ 357 {[Pt(ppdm)]} and 240 {[PtMe₃]}. The 3,5-lutidine adduct, **2**, displayed a molecular ion at m/z^+ 509, [M], with further strong peaks at m/z^+ : 464, [Pt(ppdm)(3,5-lut)]; 347, [PtMe₃(3,5-lut)]; 317 [PtMe(3,5-lut)]; 302, [Pt(3,5-lut)]. Complex **3**, [PtMe₃(ppdm)(bipy)], displayed intense signals at m/z^+ 581, 559, 396, 366 and 350, attributable to the species [M+Na], [M], [PtMe₃(bipy)], [PtMe₂(bipy)]

and [PtMe(bipy)], respectively. In *all* cases the observed isotope distribution patterns were in accord with those calculated for the formulated species.

The elemental analyses obtained for **1** - **3** were generally consistent with the formation of analytically pure complexes; however, the somewhat anomalous C and H analyses for the 2,2'-bipyridyl adduct, **3**, were difficult to rationalise. Data obtained for the elemental analyses are reported in Table 1.

NMR Studies on [PtMe₃(ppdm)(H₂O)] 1.- Complex **1** dissolves in polar solvents, forming a solvent co-ordinated species, *viz.* [PtMe₃(ppdm)(solv)] (solv = co-ordinating solvent). In [D₆]DMSO solution, the ambient temperature (298 K) ¹H NMR spectrum shows well-resolved signals. The platinum-methyl region of the spectrum (*ca.* δ = 0.6 - 1.1) displayed three signals, with ¹⁹⁵Pt satellites, in a 1:1:1 intensity ratio. On the basis of their ²J_{PtH} scalar coupling constants,^{1,13-16} these signals were assigned to methyls *trans* O (oximate), *trans* N (oximate) and *trans* S (DMSO), respectively from high- to low-frequency. The low magnitude for the ²J_{PtH} scalar coupling constant for the *trans* N (oximate) methyl group {64.3 Hz, *cf.* 66.5 Hz in [PtMe₃(bipy)(H₂O)]⁹} indicates the presence of a strong Pt-N interaction. The ligand-methyl region (Pt-N=C-CH₃) showed a single resonance, with ¹⁹⁵Pt coupling. The signals due to the ligand-phenyl ring (Pt-O=C-C₆H₅), could also be fully assigned (Table 2). Hydrogen-1 NMR data are reported in Table 2; the spectrum of **1** in [D₆]DMSO at 298 K is shown in Figure 3.

On warming the solution, a number of reversible band shape changes occurred, indicating the onset of dynamic exchange processes at a measurable rate on the NMR chemical shift time scale. Firstly, the signal due to the Pt-Me group *trans* S (DMSO) broadened and shifted slightly to higher frequency; this was accompanied by a small increase in the ²J_{PtH} coupling, indicating a lengthening and weakening of the Pt-solvent interaction. This signal then sharpens again, as the complex attains a rapid pre-equilibrium (which probably involves solvent exchange). On warming further, the signals *trans* O (oximate) and *trans* S (DMSO) displayed dynamic line broadening, due to the expected¹ windscreen-

wiper fluxional rearrangement (Figure 4). Line shape changes characteristic of platinum-methyl scrambling, a well established feature of fluxional trimethylplatinum(IV) complexes,¹² also occurred at elevated temperatures. No changes were observed in the other regions of the spectra; the $^4J(\text{Pt-N}=\text{C-CH}_3)$ scalar coupling (ca. 4 Hz) was unaffected by the dynamic processes, indicating that the Pt-N remains intact at all times.

The energetics of the windscreen-wiper fluxion were measured by two-dimensional exchange spectroscopy (EXSY). Five EXSY experiments were performed¹⁷ at temperatures at which the pre-equilibrium had been attained, but the Pt-Me scrambling was of negligible rate on the NMR magnetisation transfer time scale. Reliable rate data were obtained (Table 3), and the activation parameters for the windscreen-wiper rearrangement determined (Table 4). The 2D EXSY spectrum of **1** in $[\text{D}_6]\text{DMSO}$ at 323 K is shown in Figure 5.

The ambient temperature (298 K) spectrum of **1** in $[\text{D}_4]\text{methanol}$ revealed slightly exchange broadened signals; this broadening disappeared on cooling to ca. 273 K and a well resolved spectrum was obtained. The "static" spectrum was exactly analogous to that of **1** in $[\text{D}_6]\text{DMSO}$. Hydrogen-1 NMR data are reported in Table 2. On warming, changes in the Pt-Me band shapes consistent with (i) the attainment of a pre-equilibrium, followed by (ii) the expected windscreen-wiper fluxion and (iii) Pt-Me scrambling (*vide supra*), were observed. The energetics of the windscreen-wiper fluxional rearrangement were measured by two-dimensional exchange spectroscopy; five EXSY experiments were performed¹⁷ in the temperature range 297 - 313 K, and reliable rate data obtained (Table 3). The Eyring and Arrhenius activation parameters are reported in Table 4.

In $[\text{D}_6]\text{acetone}$, the ambient temperature (298 K) spectrum of **1** showed extensive line broadening. On cooling to 243 K, the band shapes sharpened to reveal a total of six platinum-methyl signals (with ^{195}Pt satellites), resulting from two solution-state species; each species displayed three signals in a 1:1:1 intensity

ratio. The relative populations of the two species are highly temperature dependant. The two sets of signals are believed to arise from the presence of both an acetone co-ordinated complex and a water co-ordinated complex. The presence of a water co-ordinated species in acetone solution was not totally unexpected, because **1** is crystallised as the H₂O adduct from acetone (*vide supra*). The addition of excess D₂O to the [D₆]acetone solution of **1** at 238 K resulted in a single set of Pt-Me signals, which presumably arise from the D₂O adduct, [PtMe₃(ppdm)(D₂O)] **1b**. The chemical shift and scalar coupling data for [PtMe₃(ppdm)(D₂O)] (Table 2) were more closely analogous to the data for the major isomer at that temperature. This suggests that the major solution-state species is the H₂O adduct, [PtMe₃(ppdm)(H₂O)]; the spectrum of **1** was assigned on this basis. The ligand-methyl and ligand-phenyl regions of the spectra each displayed two sets of overlapping signals due to the two species, *viz.* [PtMe₃(ppdm)(H₂O)] and [PtMe₃(ppdm)([D₆]acetone)]; as a result, the chemical shifts and scalar coupling constants could not be measured with confidence. Hydrogen-1 NMR data are reported in Table 2. The spectrum of **1** in [D₆]acetone at 243 K is shown in Figure 6.

On warming the [D₆]acetone solution of **1**, the two sets of Pt-Me signals broadened. The ¹H NMR band shape changes indicated the onset of both an intermolecular exchange between the two solution-state species, and the expected windscreen-wiper rearrangement (in both species). Attempts to obtain accurate rate data were frustrated. The presence of four independent rate constants (*vide infra*), plus Pt-Me scrambling at elevated temperatures, renders simulation of standard one-dimensional NMR spectra unreliable; the band shape changes cannot be fitted to a unique set of rate constants in such circumstances. Also the large difference in the magnitudes of the rate constants prevented their accurate measurement by 2D EXSY; there was no mixing time which enabled the four independent rate processes (Figure 7) to be measured simultaneously at a given temperature. However, from the 2D EXSY experiments, it was found that the magnitudes for the four rate processes are in the order: $k_1 > k_3 \approx k_4 > k_2$ (see Figure 7).

The magnitude for the free energy of activation for windscreen-wiper fluxional rearrangement of **1** in [D₄]methanol (Table 4) is, within experimental error, the same as that obtained for the complex [PtMe₃(bdm)] in [D₄]methanol.¹ Thus changing the nature of the monoxime has a negligible effect on the energy barrier of the process. In contrast, the effect of the different solvents is very marked. The rates of the windscreen-wiper fluxion for the complex species [PtMe₃(bdm)(solvent)] were shown qualitatively to be in the order:¹ $k(\text{DMSO}) < k(\text{methanol}) < k(\text{acetone})$. Comparison of the magnitudes for ΔG^\ddagger (298 K) obtained for **1** in [D₆]DMSO and [D₄]methanol (Table 4), enables a quantitative estimate of the effect of the solvent on the windscreen-wiper rearrangement to be made. The trend in the free energy of activation, *viz.* $\Delta G^\ddagger(\text{DMSO}) > \Delta G^\ddagger(\text{acetone})$, is in accord with the trend expected from the relative strengths of the Pt-E(solvent) interactions (E = S or O). A qualitative comparison of the relative strengths of these interactions can be made by inspection of the ²J_{PtH} scalar couplings^{18,19} for the Pt-Me signals *trans* solvent; the larger the scalar coupling constant, the weaker the *trans* Pt-solvent interaction. The magnitudes for the ²J_{PtH} scalar couplings are (Table 2) 69.2 Hz {*trans* S(DMSO)} and 83.1 Hz {*trans* O(methanol)}; this lends support to the hypothesis that the mechanism of the rearrangement (*vide infra*) involves cleavage of the Pt-solvent bond. While it was not possible to obtain a value for the free energy of activation for the windscreen-wiper fluxion in [D₆]acetone (*vide supra*), the (much) broader ¹H NMR band shapes observed at ambient temperature (298 K) clearly indicate that the rate of the rearrangement is more rapid in this solvent. The ²J_{PtH} scalar coupling constant for the platinum-methyl group *trans* acetone is also, as expected, greater (84.5 Hz at 233 K) than that for the methyl group *trans* solvent in either DMSO or methanol solution, indicating that the Pt-O(acetone) interaction is weaker.

Although caution should be exercised when interpreting entropy of activation data, the sizeable positive magnitudes of ΔS^\ddagger measured for the windscreen-wiper

fluxion point towards a transition state which is at least partially dissociated. However, even at fast rates of exchange, the $^4J\{\text{Pt-N=C-CH}_3\}$ scalar coupling is retained. The Pt-N(oximate) bond must therefore remain intact during the course of the rearrangement; this provides an insight into the mechanism of the fluxional process. Although the precise nature of the mechanism is not known, it is believed to involve cleavage of the Pt-O(oximate) bond, followed by a 45° rotation of the ligand about the Pt-N(oximate) bond and displacement of the solvent molecule (*vide supra*). A possible transition state structure for the rearrangement is depicted in Figure 8.

NMR Spectra of Complexes 2 and 3.- The hydrogen-1 NMR spectrum of $[\text{PtMe}_3(\text{ppdm})(3,5\text{-lut})]$ **2**, in CDCl_3 at 303 K showed three Pt-Me signals, with ^{195}Pt satellites, in a 1:1:1 intensity ratio. The assignment of these signals (Table 2) was based on the magnitudes of their $^2J_{\text{PtH}}$ scalar coupling constants.^{1,13-16} The signals at $\delta = 1.92$ (3 H) and 2.30 (6 H) were assigned to the oximate-methyl group ($^4J_{\text{PtH}} \approx 3.8$ Hz) and the two methyls of 3,5-lutidine, respectively. The overlapping signals due to the oximate-phenyl ring hydrogen nuclides and the *para*-hydrogen of the lutidine ring were not fully resolved; this frustrated the measurement of reliable chemical shift and coupling constant data. The signal at $\delta = 8.16$ was unambiguously assigned to the *ortho*-position hydrogen nuclides of the lutidine ring, on account of their measurable coupling to platinum-195; $^3J_{\text{PtH}} \approx 11.1$ Hz. Hydrogen-1 NMR data are reported in Table 5.

The ^1H NMR spectrum of **3** in CDCl_3 at 303 K displayed two Pt-Me signals (with ^{195}Pt satellites) in a 2:1 intensity ratio; the $^2J_{\text{PtH}}$ scalar couplings (69.1 and 70.9 Hz, respectively) indicate that all three methyl groups are *trans* N^{1,13-16} (*cf. trans* O scalar couplings of *ca.* 80 Hz; see Table 2). The bipyridyl ligand must therefore be co-ordinated to the metal moiety in a bidentate chelate fashion, with the oximate ligand bound only through the oximate N donor atom. The signal at $\delta = 1.77$ was assigned to the oximate methyl group, on the basis of its chemical shift (*vide supra*); however, no ^{195}Pt satellites were observed, indicating that the

magnitude of the long range (4J) Pt-H coupling is strongly dependant on the conformation of the oximate ligand. This is in accord with data previously reported for the complex $[\text{PtMe}_3(\text{bdm})(\text{bipy})]$ (bdm = butane-2,3-dione monoximate anion).¹ The α -hydrogens of the bipyridyl ring gave rise to a doublet, with ^{195}Pt satellites, at $\delta = 8.65$; $^3J_{\text{PtH}} \approx 11.9$ Hz. Overlap of the other aromatic signals prevented their unambiguous assignment. Hydrogen-1 NMR data for **3** are reported in Table 5.

Conclusion.

Analytical and NMR data for the complexes $[\text{PtMe}_3(\text{ppdm})(\text{H}_2\text{O})]$ **1**, $[\text{PtMe}_3(\text{ppdm})(\text{py})]$ **2** and $[\text{PtMe}_3(\text{ppdm})(\text{bipy})]$ **3**, are consistent with the complexes having the structures shown in Figure 2. The parent complex, **1**, dissolves in polar solvents to form a solvent co-ordinates species, which undergoes a "windscreen-wiper" fluxional rearrangement. The kinetics of the fluxional process are dominated by the strength of the Pt-E(solvent) (E = S or O) interaction, and appear to be essentially independent of the nature of monoximate ligand. The Authors are currently investigating the behaviour of related N/O and N/S chelate ligand complexes of trimethylplatinum(IV) in order to establish whether or not the windscreen-wiper fluxional rearrangement occurs more generally; the results of these investigations will be published shortly.

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Figure Legends.

- Figure 1.* The two possible configurations for the ionised ligand butane-2,3-dione monoxime.
- Figure 2.* Proposed structures for the complexes [PtMe₃(ppdm)(H₂O)] **1**, [PtMe₃(ppdm)(3,5-lut)] **2** and [PtMe₃(ppdm)(bipy)] **3**.
- Figure 3.* 400 MHz ¹H NMR spectrum of **1** in [D₆]DMSO at 298 K, showing the platinum-methyl region. See Table 2 for assignments.
- Figure 4.* The "windscreen-wiper" fluxional rearrangement of **1**, showing the

effects of the fluxional process on the platinum-methyls. The numbers refer to the three sites of the *fac*-oriented methyl groups, and the letters identify the chemical environments.

Figure 5. 400 MHz ^1H two-dimensional exchange NMR spectrum of **1** in $[\text{D}_6]\text{DMSO}$ at 323 K. Cross peaks are displayed between the platinum-methyls *trans* solvent and *trans* O(oximate). Further, weak cross peaks are displayed between the platinum satellites of each of the signals.

Figure 6. 400 MHz ^1H NMR spectrum of **1** in $[\text{D}_6]\text{acetone}$ at 243 K, showing the platinum-methyl region. The signals due to the major- and minor-isomers are labelled (*) and (·), respectively. Refer to Table 2 for the assignments.

Figure 7. The four solution-state species of the complex $[\text{PtMe}_3(\text{ppdm})(\text{H}_2\text{O})]$ in $[\text{D}_6]\text{acetone}$, and the six interconversion pathways between them. Note that $k_2=k_5$ and $k_1=k_6$, giving four independent rate processes.

Figure 8. A possible transition state structure for the "windscreen-wiper" fluxional rearrangement of **1**.