A η^2-triflate (OTf) intermediate in the solution dynamics of PtMe₃(OTf)·TMEDA: the 'windscreen-wiper process' revisited ‡

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The reaction of tetrameric $[PtMe_3(OTf)]_4$ (OTf = triflate = $CF_3SO_3^-$) with TMEDA (N,N,N',N'-tetramethylethylene-diamine) gave the monomeric compound $PtMe_3(OTf)\cdot TMEDA$ in quantitative yield. The non-planar TMEDA ligand contains two different sorts of methyl groups in $PtMe_3(OTf)\cdot TMEDA$, and thus offers a second and independent set of NMR parameters in addition to the commonly used signals of the Me_3Pt unit. The additional information derived from these NMR data provides detailed insight into the mechanistic picture of chelating phenomena at Pt^{IV}. At low temperature the twisting of the ethylene bridge of the TMEDA ligand can be observed; at room temperature an intramolecular two-step ligand exchange takes place. Evidence for an equilibrium involving a TMEDA chelate as well as a η^2-O_3SCF_3 chelate has been found. Dependent on the applied temperature, two types of ligand exchange motions can be distinguished by dynamic NMR spectroscopy because of their different activation parameters. These motions have been identified as the two essential steps in the so-called 'windscreen-wiper process' that has been invoked for exchange phenomena in Me_3Pt complexes previously. Moreover, the data indicate the crucial role of a η^2-triflate in this process in $PtMe_3(OTf)\cdot TMEDA$.

Introduction

Dimeric and monomeric trimethylplatinum(IV) complexes have been a subject of dynamic NMR investigations for more than two decades.[1–5] The majority of the complexes involve chelating ligands like disulfides,[1] aminocarboxylates,[2] oximes[3] or tridentate nitrogen donors.[4] When a neutral chelating ligand is used the anion is normally a halide which does not participate in solution dynamics at normal temperatures.[1]

Recently, we reported the selective deaggregation of tetrameric $[PtMe_3(OTf)]_4$ **1** by various bases of differing strength.[6] When TMEDA is used the monomeric $PtMe_3(OTf)\cdot TMEDA$ **2** can be obtained. The non-rigid structural behaviour of this complex in solution is correlated to the elongation of the Pt–O (232 pm) and the Pt–N (224 pm) bonds that is found in the crystal structure.[6] This weakened co-ordination was confirmed by dynamic NMR studies of the trimethylplatinum moiety *and* the TMEDA ligand. TMEDA turned out to be an especially suitable ligand for this purpose because of its chemically non-equivalent methyl signals in the complex. A precise knowledge of the dynamic behaviour of base adducts of $PtMe_3(OTf)$ is not only of mechanistic interest but is also important for synthetic use of adducts with enantiomerically pure nitrogen bases such as $(-)$-sparteine or (S)-1-methyl(piperidinomethyl)pyrrolidine as chiral Lewis acids.[7] We were interested to learn whether the chelating ligand stays at the metal center in solution, as this would be the basic requirement for efficient chiral induction.

Experimental

General procedures

All reactions were performed using standard Schlenk tech-niques under an atmosphere of dry, oxygen-free argon. Solvents were distilled from appropriate drying agents prior to use (sodium for toluene and sodium/potassium alloy for diethyl ether and hexane). Microanalytical data were obtained at the Routineanalytik des Fachbereich Chemie, Marburg. Proton, ^2H, ^{13}C, ^{17}O and ^{195}Pt NMR spectra were recorded on a Bruker AMX 500 spectrometer and referenced to $SiMe_4$ ($^1H, ^{13}C$), D_2O (^{17}O) and in terms of the frequency ratio $\varXi$ (^{195}Pt) according to ref. 8. The IR spectra were measured on a Bruker IFS 88 spectrometer with Nujol mulls and caesium iodide plates, mass spectra on a Varian CH7 spectrometer, EI, 70 eV.

The compound $[PtMe_3I]_4$ was prepared by a literature method.[9] All other starting materials were purchased commercially and dried prior to use: silver triflate (Merck-Schuchardt), TMEDA (Aldrich), PMDTA (N,N,N',N'',N''-pentamethyldiethylenetriamine) (Fluka), CD_3I, CD_2Cl_2, C_6D_6, chlorobenzene-d_5 and n-BuLi, 1.6 M in hexane (all Aldrich).

Preparations

$[PtMe_3(OTf)]_4$ 1. The tetrameric triflate was prepared according to a literature procedure,[10] but toluene was used as a solvent.

$PtMe_3(OTf)\cdot TMEDA$ 2. To a stirred off-white suspension of 1.0 g (0.65 mmol) compound **1** in 5 ml hexane, 0.39 ml (0.65 mmol) of TMEDA was added slowly at room temperature. A shiny white precipitate formed immediately. The suspension was stirred for 30 min then the hexane was removed *in vacuo*. The monomeric **2** was obtained in quantitative yield. NMR (CD_2Cl_2, -40 °C): ^1H, δ 0.79 [3 H, s, $^2J(^1H,^{195}Pt) = 82.9$, CH_3Pt], 1.01 [6 H, s, $^2J(^1H,^{195}Pt) = 67.2$, CH_3Pt], 2.41 [6 H, s, $^3J(^1H,^{195}Pt) = 17.5$, $N(CH_3)_2$], 2.68 [6 H, s, $^3J(^1H,^{195}Pt) = 8.2$ Hz, $N(CH_3)_2$], 2.62 (2 H, br, CH_2N) and 2.86 (2 H, br, CH_2N); ^{195}Pt, δ 2456; ^{17}O (chlorobenzene-d_5, 298 K, 415000 scans), δ 158 (2 O, s, S=O), 67 (1 O, s, Pt–O–S). IR (Nujol mull, $\tilde{v}_{max}/cm^{-1}$): 1304vs, 1214vs, 1164s, 1021vs, 961s, 803s, 770m, 635vs, 513s and 486m (Found: C, 23.40; H, 5.37; N, 5.28. $C_{10}H_{25}F_3N_2O_3PtS$ requires C, 23.76; H, 4.95; N, 5.54%).

TMEDA-d_3. 19.7 ml (31.5 mmol) of a 1.6 M solution of n-BuLi in hexane were added to a solution of 4.0 ml (31.5

Table 1 Structural data and activation parameters of several TMEDA complexes

Complex	d(M–N)/pm	N–M–N/°	d(N$\cdots$N)/pm	$\Delta G^{\ddagger}$ (twist)/kJ mol^{-1}
2 PtMe$_3$(OTf)·TMEDA	224.3	82.6	296.1	38.3
[Li(HMDS)·TMEDA]$_2$·LiCl [17,19]	223.5	83.8	298.7	37.3
Li(NC$_8$H$_6$)·TMEDA [15]	219.5	84.9	296.5	39.4
Li[C$_3$H$_3$(SiMe$_3$)$_2$]·TMEDA [16]	208.0	89.6	293.1	32.3 ($\Delta H^{\ddagger}$)
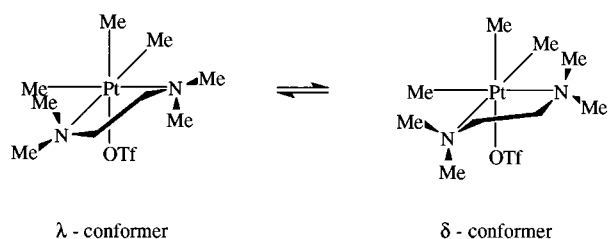
Fig. 1 Enantiomeric conformers of compound **2** (TMEDA twist motion, temperature range 175–213 K).

Fig. 2 Methyl and methylene signals of the TMEDA ligand at $T = 183$ K: (a) methylene signals, (b) methyl groups directed to triflate, (c) methyl groups directed to MePt.

mmol) of trimethylethylenediamine (TriMEDA) in 15 ml of diethyl ether at −78 °C. The resulting reaction mixture was stirred for 30 min at −78 °C and then 4.58 g (32 mmol) of CD$_3$I in 10 ml of diethyl ether were added dropwise. With stirring the mixture was allowed to warm up to room temperature and a white voluminous precipitate of LiI·TMEDA-d$_3$ was formed. The precipitate was filtered off and dried *in vacuo*. A large excess of PMDTA (25 ml) was added to the dry LiI·TMEDA-d$_3$, the suspension was heated to 160 °C and the volatiles were distilled fractionally. The compound TMEDA-d$_3$ was obtained as the fraction at bp 122 °C. Yield: 2.49 g (66%). NMR: ^{1}H(CDCl$_3$), δ 1.98 (9 H, s, NCH$_3$, 2.12 (4 H, s, CH$_2$N); ^{2}H(C$_6$H$_6$), δ 2.12 (3 D, s, NCD$_3$); ^{13}C(CDCl$_3$), δ 44.6 (sept, NCD$_3$), 45.6 (s, NCH$_3$) and 57.4 (s, CH$_2$N). Mass spectrum: m/z 119 (M$^+$, 6%).

Line shape analysis

The line shapes of the variable temperature ^{1}H NMR spectra were analysed with the dynamic NMR simulation program WIN-DYNA.[11] Errors are quoted as defined by Binsch and Kessler.[12]

Results and discussion

The compound PtMe$_3$(OTf)·TMEDA **2** was prepared by de-aggregation of [PtMe$_3$(OTf)]$_4$ in quantitative yield. It is a white hygroscopic powder which can be recrystallized from hexane–CH$_2$Cl$_2$ 1:1 to afford single crystals.[13] Solutions of **2** were handled under conditions of light exclusion in order to prevent precipitation of platinum black. Compound **2** was characterized by NMR and IR spectroscopy and by elemental analysis (see Experimental section). It is soluble in CH$_2$Cl$_2$ and in aromatic hydrocarbons allowing dynamic NMR measurements in CD$_2$Cl$_2$ and in deuteriated aromatics.

Twist motion of the TMEDA ethylene bridge in PtMe$_3$(OTf)·TMEDA

The dynamic behaviour of many TMEDA complexes has continually been a subject of investigation, especially in lithium chemistry.[14] For the three mono TMEDA adducts of *N*-lithio-indole,[15] 1,3-bis(trimethylsilyl)allyllithium[16] and Li(HMDS)[17] (HMDS = hexamethyldisilazanide) Eyring activation parameters for the ethylene twist of the TMEDA ligand could be determined. In the case of PtMe$_3$(OTf)·TMEDA **2** the twist of the ethylene bridge leads to an interconversion of the enantiomeric λ- and δ-conformers of this essentially achiral complex (Fig. 1).[18] At temperatures low enough to freeze out the 'windscreen-wiper process' occurring at room temperature (see
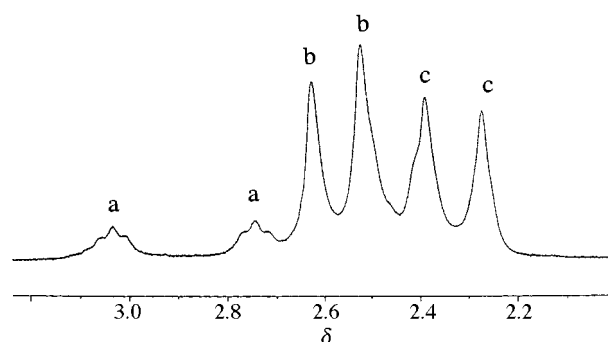
below) this conversion could be observed by dynamic NMR spectroscopy in CD$_2$Cl$_2$. The ^{1}H NMR resonances of the methyl groups *trans* to the TMEDA ligand and of the TMEDA methyl groups in the temperature range from 175 to 213 K were measured. At very low temperature the methyl groups become inequivalent because of the non-identical conformational arrangement at the two nitrogen atoms (Fig. 2). Coalescence is observed at 193 K, at which temperature the twist motion of the ethylene bridge equilibrates both local environments. Eyring activation parameters were determined by line shape analysis of the signals of the two methyl groups *trans* to TMEDA in the temperature range from 183 to 208 K:[11,12] $\Delta H^{\ddagger} = 42.0 \pm 2.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 12.5 \pm 11.3$ J K^{-1} mol^{-1} and $\Delta G^{\ddagger}_{298} = 38.3 \pm 1.2$ kJ mol^{-1}. The $\Delta G^{\ddagger}$ value found for the TMEDA twist in **2** is identical within the standard deviation with the free activation energies found for this motion in Li(HMDS)·TMEDA ($\Delta G^{\ddagger} = 37.3$ kJ mol^{-1})[14] and in the corresponding *N*-lithioindole adduct ($\Delta G^{\ddagger} = 39.4$ kJ mol^{-1}).[15] While the similarity of the $\Delta G^{\ddagger}$ values is surprising, given the different nature of platinum and lithium, comparison of the structural data of the *N*-lithioindole adduct,[15] [Li(HMDS)·TMEDA]$_2$·LiCl[19] and **2** provides a rational explanation (Table 1). Despite the various co-ordination numbers and binding characteristics in these three compounds, the metal–nitrogen distance, the bite angle of the TMEDA, and the nitrogen–nitrogen distance in the ligand remain almost constant. Hence, there is no substantial difference in the geometry or the strain of the ethylene bridge which might have an influence on the free activation energy of the twist motion. The non-variation of the nitrogen–nitrogen distance ($d = 290 \pm 10$ pm) in such chelates of vicinal diamines has been observed previously but has only been discussed for alkali metal complexes.[20] In the 1,3-bis-(trimethylsilyl)allyllithium adduct,[16] however, the metal–nitrogen distance (Table 1) and the activation energy ($\Delta H^{\ddagger} = 32.3$ kJ mol^{-1}) are remarkably different. To examine whether there is a dependence of the activation barrier of the TMEDA twist on the metal–nitrogen distance the $\Delta G^{\ddagger}$ values of TMEDA complexes with long metal–nitrogen bonds like NaCp·TMEDA[21] [d(Na–N) = 262.3 pm] or SnCp$_2$·TMEDA[22] [d(Sn–N) = 288 pm] must be measured.

Internal 'windscreen-wiper process' of PtMe$_3$(OTf)·TMEDA in CD$_2$Cl$_2$

In contrast to the trimethylplatinum halide complexes bearing a

Table 2 Rate constants and population ratios for the chelate equilibrium and the 'windscreen-wiper process'

T/K	$k(\text{TMEDA})^a/\text{s}^{-1}$	$k(\text{Me}_3\text{Pt})^a/\text{s}^{-1}$	Population ratio $trans$ N : $trans$ O[b]
253	0	4[c]	0.63 : 0.37
263	4[c]	12[c]	0.60 : 0.40
273	18	27	0.56 : 0.44
283	50	40	0.59 : 0.41
293	148	75	0.67 : 0.33
300	305	200	0.67 : 0.33
308	920	410	0.67 : 0.33
313	1420	720	0.67 : 0.33
318	2200	1100	0.67 : 0.33

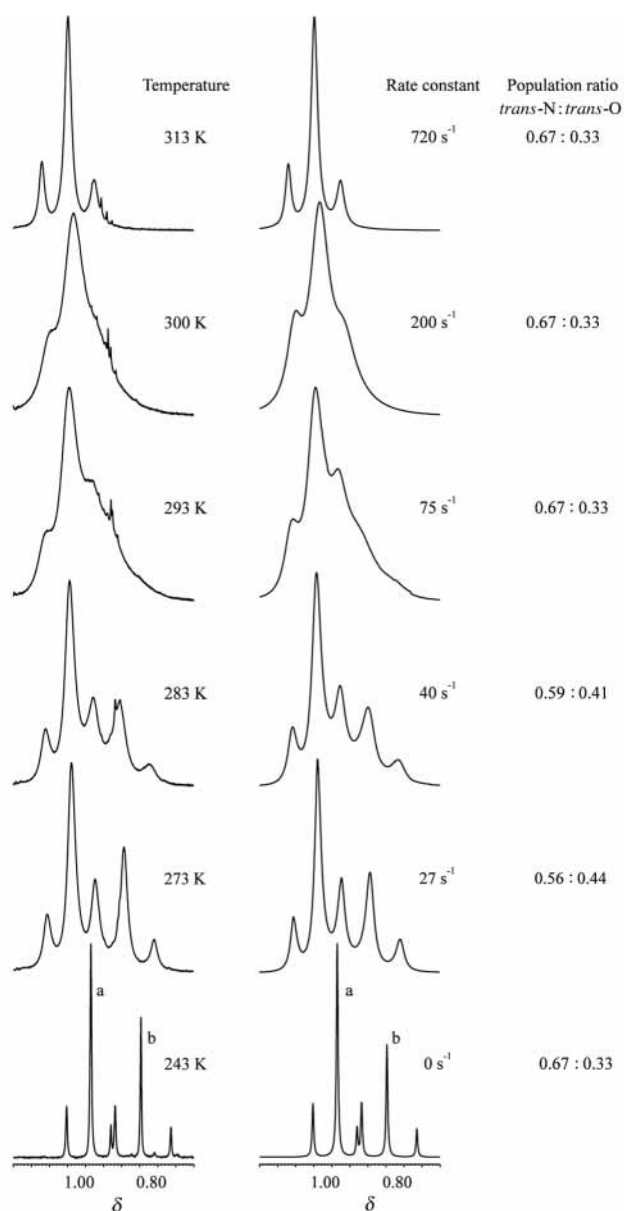[a] Accuracy: ±10%. [b] Accuracy ± 4%. [c] Accuracy: ±2 s^{-1}.

Fig. 3 Experimental (left) and simulated (right) ^{1}H DNMR spectra of the Me$_3$Pt unit of compound **2**: (a) methyl groups *trans* to N, (b) methyl groups *trans* to O.

Fig. 4 Experimental (left) and simulated (right) ^{1}H DNMR spectra of the TMEDA ligand in compound **2**: (a) methyl groups directed to the triflate ligand, (b) methyl groups directed to MePt (the stereochemical assignment was done by a NOESY experiment), (c) methylene groups, not simulated.

bidentate ligand in which the halide does not participate in fluxional phenomena, the monomer PtMe$_3$(OTf)·TMEDA **2** can be compared to the well known anionic species [PtMe$_3$-(AA)$_2$]$^-$ (AA = aminocarboxylate).[2] Both complexes have two bidentate ligands and there is competition between the donor atoms of the ligands for the six co-ordination sites of the
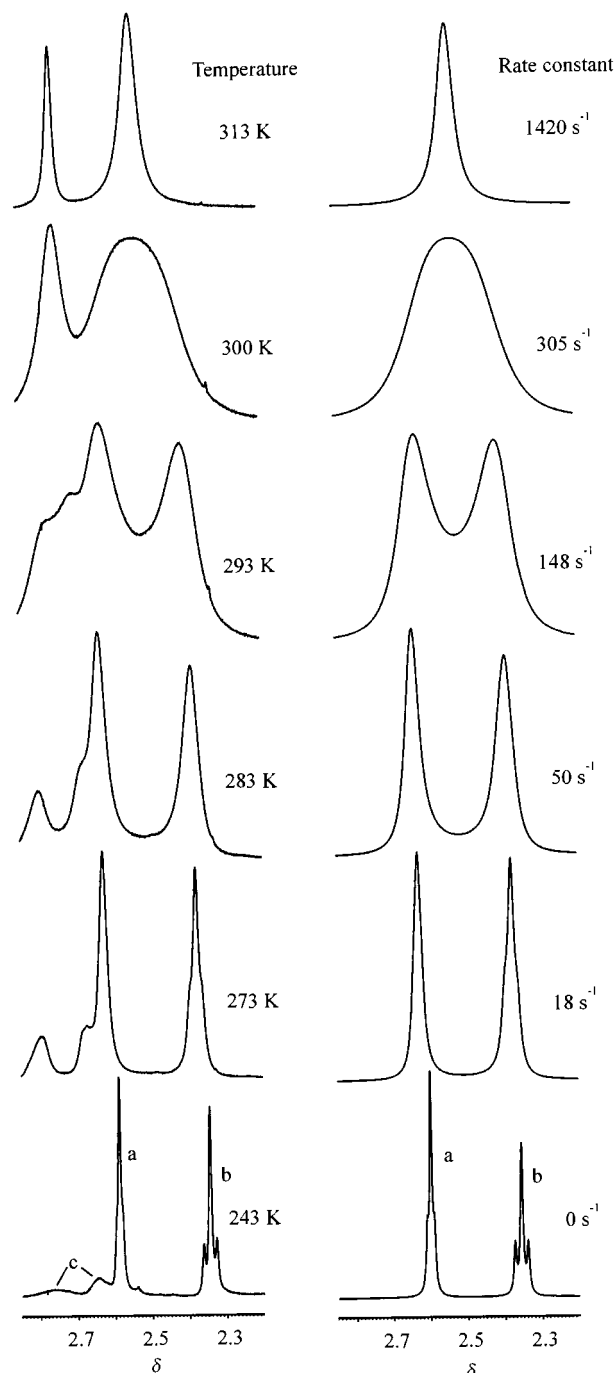
octahedra. Although triflates are known to be weakly co-ordinating ligands, in **2** the triflate moiety is able to compete successfully with the nitrogen donor TMEDA. Selected ^{1}H NMR spectra of **2** in CD$_2$Cl$_2$ in the temperature range from 243 to 313 K are depicted in Figs. 3 and 4.

Line shape analyses for the methyl signals of TMEDA and of the Me$_3$Pt unit have been carried out. Rate constants and population ratios are given in Table 2. Whereas the Eyring plot for the TMEDA methyl signals shows the same gradient in the whole temperature range (253–318 K), that plot for the dynamics of the trimethylplatinum group clearly indicates a two step mechanism (Fig. 5). The presence of a two step mechanism is also supported by the relative values of the rate constants for the Me$_3$Pt unit and the TMEDA methyl signals (Table 2). Up to
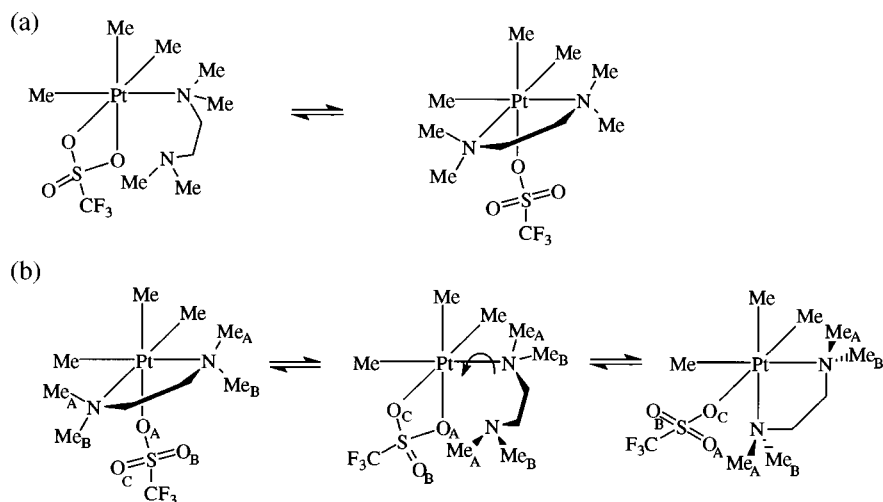
Scheme 1 (a) TMEDA/triflate chelate equilibrium in compound **2** (temperature range 253–283 K), (b) 'windscreen-wiper process' (temperature range 283–318 K).
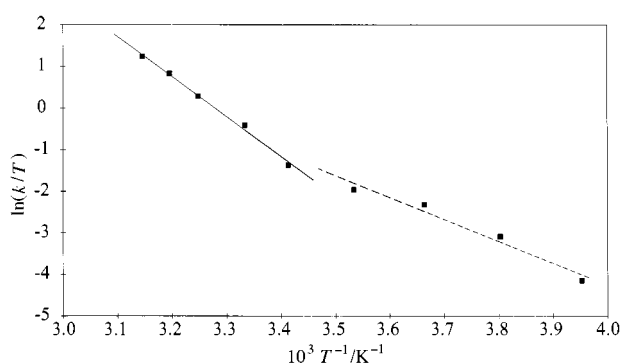

Fig. 5 Eyring plot for the dynamic behaviour of the methyl groups of Me$_3$Pt in the range of 243–313 K. (– – –) Chelate equilibrium, (——) 'windscreen-wiper process'.

273 K the exchange rate for the Me$_3$Pt moiety exceeds the rate for the TMEDA methyl groups. Then, at temperatures higher than 300 K, k(TMEDA): k(Me$_3$Pt) is close to the 2:1 ratio expected for 'windscreen-wiper' mechanism (see below). Additionally, in the temperature range 253–283 K the simulations of the ^{1}H NMR spectra of Me$_3$Pt strictly require a variation of the population of methyl groups *trans* to nitrogen and *trans* to oxygen from 0.67:0.33 to a minimum ratio of 0.56:0.44 (see SUP 57531 for 0.67:0.33 ratio). This can be explained by the presence of an equilibrium between a TMEDA chelate and a triflate chelate [Scheme 1(a)]. The temperature dependence of the population ratio (Table 2) also agrees well with the formation of an intermediate with a lower activation barrier. In the temperature range from 253 to 273 K the η^2-triflate intermediate is accumulated. At temperatures higher than that the 'windscreen-wiper process' quickly consumes the intermediate and the population ratio goes back to 2:1. The rate determining step in the chelate equilibrium[23] is the cleavage of one Pt–N bond and our experimental value of $\Delta H^\ddagger$ (44.0 ± 5.8 kJ mol^{-1}) for this step is in good agreement with the calculated value of $\Delta H^\ddagger$ (49.4 kJ mol^{-1}) for the cleavage of one metal–nitrogen bond in LiH·H$_2$NCH$_2$CH$_2$NH$_2$.[16]

Strikingly, the chelate equilibrium gives rise to an exchange of platinum bound methyl groups but no appropriate exchange is seen for the TMEDA methyl groups. This leads to the conclusion that the opening and re-co-ordination process of the TMEDA chelate takes place without an accompanying inversion–rotation at the nitrogen atoms.

At temperatures higher than 283 K a different intramolecular motion is observed [Scheme 1(b)] which has been called the 'windscreen-wiper process' for a similar molecule,[5] and which

was proposed for aminocarboxylate complexes of Me$_3$Pt many years ago.[2] In the case of **2** the η^1-TMEDA ligand does not re-co-ordinate to the same site but to the neighbouring one which has been left by the triflate. This can be regarded as a rotation around the platinum–nitrogen bond after the opening of the η^2-TMEDA chelate. The 'windscreen-wiper process' formally interchanges the two sorts of methyl groups in the TMEDA ligand. The methyl groups on the same side as the triflate ligand (Me$_B$) migrate to the side of the third methyl group on the platinum centre (Me$_A$) and *vice versa* [Scheme 1(b)]. For the 'windscreen-wiper process' we found $\Delta H^\ddagger = 78.0 \pm 3.2$ kJ mol^{-1}, $\Delta S^\ddagger = 63.9 \pm 11.5$ J K^{-1} mol^{-1} and $\Delta G_{298}^\ddagger = 59.0 \pm 0.4$ kJ mol^{-1} in the analysis of the TMEDA CH$_3$ signals and $\Delta H^\ddagger = 79.5 \pm 5.4$ kJ mol^{-1}, $\Delta S^\ddagger = 63.5 \pm 16.8$ J K^{-1} mol^{-1} and $\Delta G_{298}^\ddagger = 60.6 \pm 0.4$ kJ mol^{-1} in the analysis of the PtMe$_3$ resonances. The fact that these data are almost identical supports the idea that the interconversion of the TMEDA methyl groups is caused *only* by the 'windscreen-wiper process'. Further evidence comes from the rate constants in the regime of fast exchange. From 308 K on k(TMEDA) is close to double k(Me$_3$Pt) (Table 2), which is expected for the 'windscreen-wiper process' because a complete scrambling of all three methyl groups on Me$_3$Pt requires twice as many exchange events than the complete interconversion of the TMEDA methyl groups. Moreover, the 2:1 ratio of the rate constants also implies that there is still no inversion–rotation at the TMEDA nitrogen atoms even under these relatively drastic conditions; an inversion–rotation motion at the N atoms would lead to a statistical re-co-ordination of the free nitrogen atom with respect to Me$_A$ and Me$_B$. This motion would lower the ratio of the rate constants to k(TMEDA): k(Me$_3$Pt) = 1.5:1. Rotation around the N–Pt bond seems to be favoured over rotation around the N–C bond in this particular case.

Potential TMEDA dissociation

As discussed above, one of the nitrogen atoms of the diamine ligand leaves the platinum centre in the intramolecular exchange processes. In order to confirm that the TMEDA does not completely dissociate, we investigated whether the complexed TMEDA is in equilibrium with free TMEDA in solution. If so, the addition of free TMEDA-d$_3$ to a solution of **2** would have to lead to a considerable amount of **2**-d$_3$ and free undeuteriated TMEDA. The ^{2}H NMR measurements of (a) **2**-d$_3$, (b) TMEDA-d$_3$ and (c) **2** (1 equivalent) + TMEDA-d$_3$ (1 equivalent) in C$_6$H$_6$ clearly indicated that no complexed TMEDA-d$_3$ can be found in case (c). There is no dissociation of TMEDA from **2** leading to the "free" ligand.
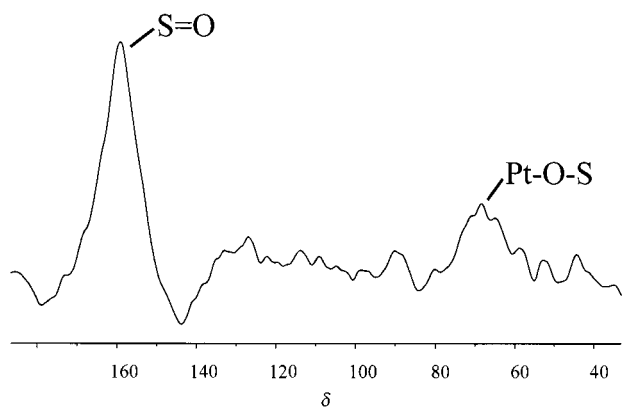
Fig. 6 Natural abundance ^{17}O NMR spectrum at 298 K in chlorobenzene-d$_5$.

Natural abundance ^{17}O NMR measurement

Analogous to the dissociation of the diamine, dissociation of the triflate is also conceivable. To elucidate whether there is triflate dissociation or a fast mono site exchange with the triflate hopping from one oxygen to another we recorded a natural abundance ^{17}O NMR spectrum (Fig. 6) at 298 K. Two resonances with a 2:1 integral ratio are observed at δ 158 (S=O) and 67 (Pt–O–S), which confirms that the triflate is co-ordinated as a monodentate ligand and that there is no tendency to a *fast* mono site exchange or to dissociation, which would equilibrate all oxygen atoms. Owing to the large frequency difference of the two ^{17}O signals (which is very much larger than the frequency differences of the ^1H NMR signals) the 'windscreen-wiper process' occurring at this temperature cannot be observed. Nor can we rule out a *slow* mono site exchange of the triflate ligand. A natural abundance ^{17}O NMR spectrum run at 330 K did not show any exchange broadening compared to the spectrum taken at 298 K. Attempts to measure the ^{17}O NMR spectrum of **2** at 393 K lead to decomposition of the compound.

Conclusion

We have found evidence for a relatively stable η^2-triflate[24] in solution which can compete successfully even with a chelating diamine for a co-ordination site of a platinum(IV) centre. Very recently, Werner *et al.*[25] showed the existence of η^2-triflate ligands in the solid state in the *absence* of a competing ligand. The η^2-triflate is of crucial importance in the intramolecular 'windscreen-wiper process' in PtMe$_3$(OTf)·TMEDA. For the equilibrium of PtMe$_3$(OTf)·TMEDA we confirmed not only that the 'windscreen-wiper process' operates, but also that chelate opening and rotation (Pt–N bond)/re-co-ordination are two separate and clearly detectable steps in the process. Finally, we showed that neither the triflate nor the TMEDA ligand completely dissociates from the Me$_3$Pt moiety in a non-co-ordinating solvent such as dichloromethane. The absence of diamine dissociation is essential for a future use of PtMe$_3$-(OTf)·(−)-sparteine for example as an effective chiral Lewis acid in stereoselective organic synthesis.

The activation barrier of the TMEDA twist motion in the transition metal complex PtMe$_3$(OTf)·TMEDA was found to be identical with the barriers in TMEDA complexes of several lithium compounds for *geometrical* reasons.

Acknowledgements

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Paper 8/09811E