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Solvolysis of Platinum Complexes with Substituted Ethylenediamines in Dimethyl Sulfoxide

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The solvolysis of platinum complexes with substituted ethylenediamines, $[PtCl_2(L)]$ (L = 1,4-diazabutane (dab) (**1**), 2-Me-dab (**2**), 2,3-Me_2-dab (**3**), 2,3-[μ-$(CH_2)_4$]-dab (**4**), 1,4-Me_2-dab (**5**), 1,4-$(i\text{-Pr})_2$-dab (**6**), and 1,4-$(t\text{-Bu})_2$-dab (**7**)), in DMSO has been investigated by ^{195}Pt NMR and UV–vis spectroscopy. A chloride ion is displaced by DMSO in all cases with the exception of **7**. The rate of chloride substitution in compounds **1–6** decreases with increasing number and bulk of substituents in the ligand chain; the effect is more marked when the substituents are on the coordinated nitrogen atoms rather than on the adjacent carbon atoms. In the case of compounds **3–6** having a disubstituted dab ligand, the rate of solvolysis is greater when both substituents are on one side of the coordination plane (cis configuration) than on opposite sides (trans configuration). In the solvato species, the configuration at nitrogen is not as stable as it was in the dichloro complexes because of the trans-labilizing effect of the DMSO ligand. Complex **7**, unlike all the others, reacts with DMSO, displacing one end of the diamine rather than a chloride ion. At room temperature, the monodentate diamine undergoes a fast head-to-tail rearrangement that makes the *t*-Bu groups equivalent on the NMR time scale ($\Delta G^* = 52$ kJ mol^{-1}). The different behavior of complexes **6** and **7** (containing respectively *i*-Pr and *t*-Bu substituents) is a consequence of the steric interaction, between the nitrogen substituents and the Cl ligands, which is far greater in the case of *t*-Bu than it is in the case of *i*-Pr.

Introduction

cis-Diamminedichloroplatinum(II) (cisplatin) is one of the most powerful anticancer drugs available at present.[1] With a second platinum drug [diammine(1,1-cyclobutanedicarboxylato)platinum(II), carboplatin] now on the market and several other second generation analogues in clinical trials,[2] the interest in the chemistry of platinum coordination compounds can be expected to persist or even grow in the near future.

Because of its good solvent properties, dimethyl sulfoxide (DMSO) has been extensively used in biological experiments, particularly when high concentrations of complex were required. The well-known affinity of platinum(II) for sulfur compounds[3] did not discourage the use of this solvent, and more recently a kinetic study on the solvolysis of *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ in DMSO has given a general warning.[4]

We are currently investigating the effect of the steric configuration of platinum-bonded diamines upon the chemistry and biochemistry of their corresponding complexes and have found that diastereoisomeric complexes also have different rates of solvolysis in DMSO.[5] This prompted us to perform a more detailed kinetic study, which is presented hereafter.

Results and Discussion

The complexes examined had the general formula $[PtCl_2(L)]$ (L = 1,4-diazabutane (dab) (**1**), 2-Me-dab (**2**), 2,3-Me_2-dab (**3**), 2,3-[μ-$(CH_2)_4$]-dab (**4**), 1,4-Me_2-dab (**5**), 1,4-$(i\text{-Pr})_2$-dab (**6**), and 1,4-$(t\text{-Bu})_2$-dab (**7**)). The carbon and nitrogen atoms of 1,4-diazabutane (dab) bearing alkyl substituents are chiral centers and give rise to the formation of different stereoisomers. In the case of substituents on the carbon atoms, the different isomers of the ligand can be separated prior to their coordination to platinum.[5] However, in the case of alkyl substituents at the nitrogen atoms, since a stable chirality arises only upon coordination to the metal, the separation of the different isomers must be performed on the complexed species.[6,7]

Symmetrically substituted diamines will give rise to the formation of two geometrical isomers depending upon the relative position of the substituents with respect to the coordination plane: the cis isomer, if both substituents are on the same side of the coordination plane; the trans isomer, if the two substituents are on opposite sides.

Table I. ^{195}Pt NMR Data (δ, Downfield from $[PtCl_6]^{2-}$) for Complexes of Platinum with 1,4-$(i\text{-Pr})_2$-dab[a]

compd	δ
cis-[$PtCl_2$\{1,4-$(i\text{-Pr})_2$-dab\}]	−2300
trans-[$PtCl_2$\{1,4-$(i\text{-Pr})_2$-dab\}]	−2340
cis-[PtCl\{1,4-$(i\text{-Pr})_2$-dab\}(DMSO)]Cl	−3150
trans-[PtCl\{1,4-$(i\text{-Pr})_2$-dab\}(DMSO)]Cl	−3180

[a] Solvent DMSO-d_6; for conditions see the Experimental Section. Cis and trans refer to the relative position of the diamine substituents with respect to the coordination plane.

Identification of the Solvolytic Products. Compounds **1–6** dissolved in DMSO undergo a solvolytic reaction in which one chlorine ligand is displaced by a DMSO molecule.[8] The reaction products were identified by comparison with authenticated samples

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(6) Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Manotti-Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chem.* **1988**, *27*, 2422–2431 and references therein.
(7) The inversion of configuration is fast in free amines in which a lone pair of electrons is present on nitrogen but rather difficult in complexed amines in which the lone pair is engaged in bonding with the metal. In the latter case, inversion of configuration can still occur, but it requires a predissociation of either a N–H or a N–metal bond. In the complexes of the type here examined, the N–H bond dissociation takes place only under basic conditions (Buckingam, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5227–5232) and the N–Pt bond is stable (there are however some reported examples, dealing usually with cationic complexes, in which the N–Pt bond can dissociate under acidic conditions: Carter, M. G.; Beattie, J. K. *Inorg. Chem.* **1967**, *9*, 1233. Natile, G.; Albertin, G.; Bordignon, E.; Orio, A. A. *J. Chem. Soc., Dalton Trans.* **1976**, 626–631). The same arguments apply to the process of proton exchange on the nitrogen atoms.
(8) Under dilute conditions, there is also the possibility that the second chloride ion is substituted by DMSO. This latter process, when it occurs, is much slower than the former one and only causes a less accurate determination of the rate constant for the first solvolysis.

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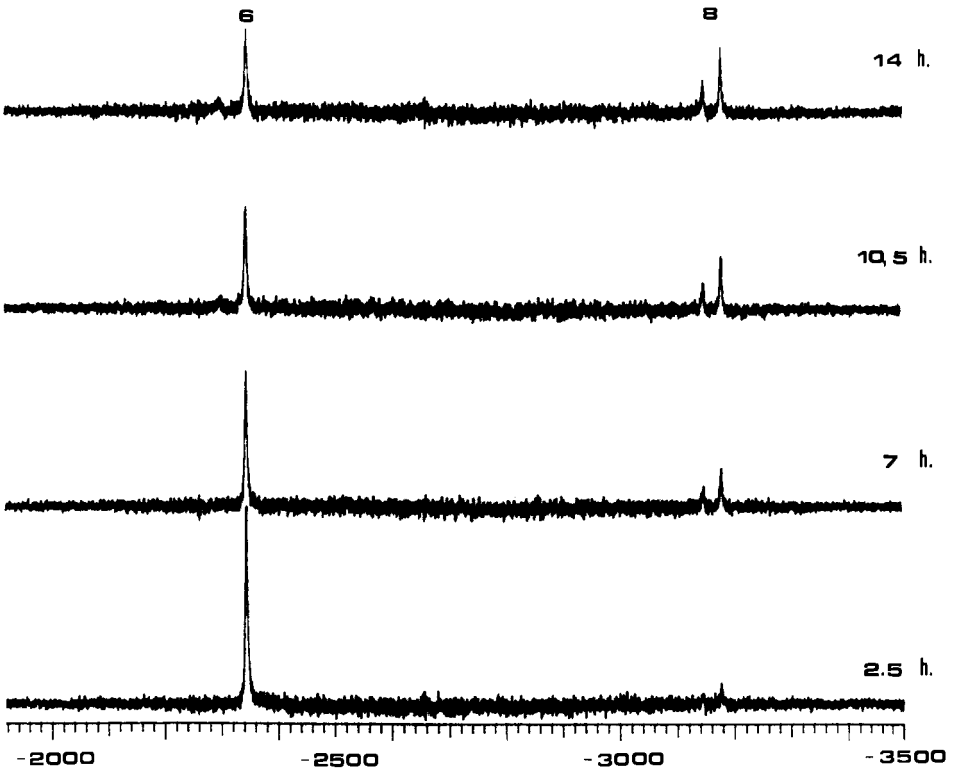

Figure 1. ^{195}Pt NMR spectra of a solution of **6** in DMSO taken at 22 °C and at different time intervals (2.5, 7, 10.5, and 14 h). Starting with a pure isomer (trans) of the dichloro complex (**6**), we obtained an equilibrated mixture of the two isomers of the solvato species (**8**) right from the beginning.

Table II. Proton Chemical Shift (δ, Downfield from $SiMe_4$; 20 °C) for the DMSO-containing Compounds *cis*- and *trans*-[PtCl{1,4-(*i*-Pr)$_2$-dab}(DMSO)]ClO_4 (**8**)[a]

		δ				
compd	solv	N-H[d]	N-CH_2[e]	C-H[d]	C-Me[d]	DMSO[d]
cis-**8**	*b*	6.58 [66]	2.91 m {2}	3.61 h[f] (6.5)	1.35 d (6.5)	3.35 [22]
		5.98 [68]	2.89 m {1}	3.59 h (6.5)	1.27 d (6.5)	3.32 [22]
			2.62 m {1}		1.22 d (6.5)	
					1.08 d (6.5)	
	c	7.10 [66]	2.86 m {4}	3.66 m	1.33[g]	3.45
		6.57 [68]		3.51 m	1.14[g]	3.43
trans-**8**	*b*	*h*	2.66 m {2}	3.74 h (6.8)	1.36 d (6.8)	3.38
			2.86 m {2}	3.62 h (6.8)	1.28 d (6.8)	3.31
					1.12 d (6.8)	
					1.06 d (6.8)	
	c	6.90	2.66 m {4}	3.86 m	1.44 d (6.8)	3.48
		6.80		3.79 m	1.34 d (6.8)	3.41
					1.16 d (6.8)	
					1.15 d (6.8)	

[a] Cis and trans refer to the relative positions of the diamine substituents with respect to the coordination plane. [b] D_2O. [c] DMSO-d_6. [d] Values of J(H-H) (in parentheses) and J(Pt-H) (in brackets) in Hz are given when assignable. [e] Integral values are given in braces. [f] h stands for heptet. [g] Signals related to two overlapping doublets. [h] Not assignable.

of [PtCl(DMSO)(L)]Cl obtained by reaction of L with [$PtCl_2$-(DMSO)$_2$]. [PtCl(DMSO)(L)]Cl is the first product of this reaction; however, if it is not removed from the solution, it undergoes a further transformation in which the ionic chloride reenters the coordination sphere of platinum, displacing the second molecule of DMSO and giving the neutral species [$PtCl_2$(L)].

Compound **7** also reacts with DMSO, but in this case, the addition of a solvent molecule is not followed by a chloride ion dissociation (see further on in the discussion).

In the case of compounds **5** and **6**, the question arises if the nitrogen atoms keep their original configuration in the solvato species as well. A change of configuration could, in fact, take place either during the substitution reaction (the rate of nitrogen inversion has been shown to be rather fast in five-coordinate species of the type hypothesized as the transition state in the substitution process) or in the solvato species if the DMSO ligand weakens the trans Pt-N bond to such an extent that it can dissociate and the nitrogen inverts configuration while it remains close to platinum.[6,9]

To answer this question, an experiment was performed in which compound **6** was dissolved in DMSO and ^{195}Pt NMR spectra were run at different time intervals (Figure 1, Table I). Starting with a pure isomer of the dichloro complex (either cis or trans) gave the resulting solvato species always as a mixture of two isomers, the ratio of which was the same right from the beginning. The same mixture of isomers was detected by proton NMR (Table II) when a pure crystalline sample of solvato species with trans configuration of the ligand was dissolved in D_2O and set aside at 20 °C for ca. 1 h. Therefore, we conclude that the rate of nitrogen inversion is faster in the solvato species than it is in the dichloro complex so that starting with a pure isomer of the latter gives an equilibrated mixture of the cis and trans isomers of the former.

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Table III. k_{obs} (s^{-1})[a] and $t_{1/2}$ (Values in Brackets in min) for the Substitution of a Chloride ion by a DMSO Molecule in Compounds **1–6** and for the Displacement of One End of the Diamine by DMSO in Compound **7** at 30 °C

compd	k_{obs} [$t_{1/2}$]
cis-$[PtCl_2(NH_3)_2]$[b]	9.33 (4) × 10^{-5} [124]
$[PtCl_2(dab)]$ (**1**)	1.53 (1) × 10^{-4} [75]
$[PtCl_2(2\text{-Me-dab})]$ (**2**)	1.30 (2) × 10^{-4} [88]

compd	k_{obs} [$t_{1/2}$] cis[c]	k_{obs} [$t_{1/2}$] trans[c]
$[PtCl_2(2,3\text{-Me}_2\text{-dab})]$ (**3**)	1.39 (8) × 10^{-4} [83]	9.3 (5) × 10^{-5} [124]
$[PtCl_2[2,3\text{-}[\mu\text{-}(CH_2)_4]\text{-dab}]]$ (**4**)	1.06 (1) × 10^{-4} [109]	9.1 (5) × 10^{-5} [127]
$[PtCl_2(1,4\text{-Me}_2\text{-dab})]$ (**5**)	0.92 (1) × 10^{-4} [126]	7.7 (1) × 10^{-5} [150]
$[PtCl_2[1,4\text{-}(i\text{-Pr})_2\text{-dab}]]$ (**6**)	0.47 (1) × 10^{-4} [246]	3.0 (2) × 10^{-5} [385]
$[PtCl_2[1,4\text{-}(t\text{-Bu})_2\text{-dab}]]$ (**7**)	1.76 (3) × 10^{-4} [66]	7.8 (5) × 10^{-5} [148]

[a] The number in parentheses refers to the error in the last digit. [b] Literature data. [c] Cis and trans refer to the relative position of the diamine substituents with respect to the coordination plane.

In the case of compound **7**, the spectral changes in DMSO solution were different from those observed in the other compounds of the series and also the rate of the transformation was different from that expected (Table III). Conductivity measurements in DMSO solution also showed that during the transformation no ionic species were produced.

An experiment was performed in which *cis*-**7** and DMSO (molar ratio 1:1) were allowed to react in $CDCl_3$ and the solution was monitored by proton NMR (Figure 2). A new species, showing a single resonance for *t*-Bu and a sharp, ^{195}Pt-coupled resonance for DMSO, was formed.[10] Under the above conditions, an equilibrium ratio of 1:1.2, between the starting material and the newly formed product, was attained. Increasing the DMSO concentration caused the equilibrium to shift toward the DMSO-containing species. However, the transformation was not complete even when pure DMSO was used as solvent (ca. 70% transformation in a 2 × 10^{-2} M solution of the complex). Lowering the temperature caused the *t*-Bu resonance of the DMSO-containing product first to broaden and then to split into two resonances 0.36 ppm apart.[11] These results are in accord with the formation of an addition product between **7** and DMSO. In the absence of a chloride ion dissociation, the most likely alternative is the displacement of one end of the diamine. Hence, the single resonance for the *t*-Bu protons observed at room temperature is indicative of a fast head-to-tail rearrangement of the singly bonded diamine, which is frozen out as the temperature is lowered. The estimated ΔG^* of activation for this process is 52 kJ mol^{-1}.[12] Another possibility would be the formation of a five-coordinate species of platinum(II) containing two chloride ions, one DMSO, and a chelating 1,4-$(t\text{-Bu})_2$-dab ligand. This possibility, however, is rather unlikely for several reasons: (a) The ligand would undergo a dynamic process that makes the *t*-Bu groups equivalent at room temperature and different below −20 °C while the two methyl groups of DMSO remain equivalent. Such a process is rather difficult to envisage for a five-coordinate species of this sort. (b) The formation of a simple addition product between **7** and DMSO would be expected to be a faster process than observed. (c) There is no reason why the formation of such an addition product would not be observed in the case of **6** as this contains *i*-Pr groups, which, being smaller than *t*-Bu, could be better accommodated in a sterically crowded five-coordinate complex.

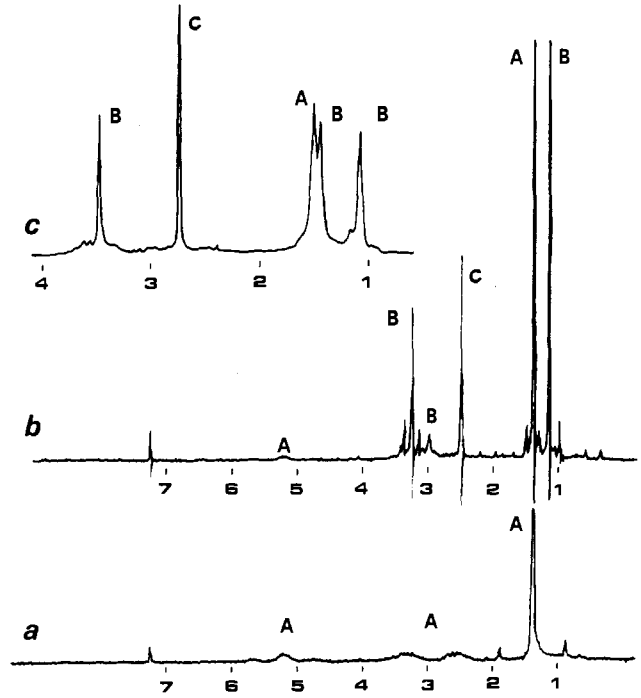

Figure 2. ^{1}H NMR spectra of compound **7** in $CDCl_3$ (a) and after the addition of DMSO (molar ratio 1:1) at +37 °C (b) and at −70 °C (c). A, B, and C mark the resonances of **7**, of its DMSO addition product, and of free DMSO, respectively.

We cannot conclude this section without giving a plausible explanation of the different behavior of **6** and **7**, i.e. why in one case DMSO displaces a chloride ion and in the other case it displaces one end of a chelate diamine. In a recent study, concerning the stereochemistry of coordinated N,N′-disubstituted ethylenediamines in complexes of this type,[6] it has been shown that the nitrogen ligand conforms itself to minimize the steric hindrance within the coordination sphere of the metal; therefore, the N-substituents are rotated in such a way as to direct the least bulky group toward the cis chlorine atoms. In the case of **6** the *i*-Pr groups can direct the less hindering tertiary hydrogen atom toward the cis chlorine ligands so that the steric interactions inside the coordination sphere of platinum are quite small. On the other hand, in the case of **7**, a bulkier Me group has taken the place of the tertiary hydrogen and therefore there is no way to avoid a significant steric interaction between the nitrogen substituents and the cis chlorine ligands.[6] Therefore, while in **6** a bigger DMSO ligand can still take the place of a chlorine ligand, this is no longer possible with **7**, which prefers to dissociate one end of the diamine so releasing the steric hindrance inside the coordination sphere and, in the meantime, providing a free place for accommodating an incoming DMSO ligand.

Kinetics of Solvolysis in DMSO. The solvolysis of *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ in DMSO has already been studied by ^{195}Pt and UV–vis absorption spectroscopy.[4,13] In the case of the cis isomer, the kinetic data, for a short reaction time, conform to a first-order rate equation and are in accord with the substitution of one chloride ion by a DMSO molecule. For longer reaction times (3–24 h), five additional species are formed (^{195}Pt NMR): the trans solvato species, two species (cis and trans isomers) in which the DMSO has displaced an amine instead of a chlorine ligand, and finally two more species containing three ammonia molecules and either a chlorine or a DMSO ligand. The solvolysis of *trans*-$[PtCl_2(NH_3)_2]$ in DMSO proceeds more rapidly (ca. 8 times) than that of the cis isomer, and apparently it only produces the monosolvato species.

The solvolysis of $[PtCl_2(dab)]$ has also been studied. The rate is ca. 2 times greater than that observed in *cis*-$[PtCl_2(NH_3)_2]$ and

(10) ^{1}H NMR (20 °C, δ): 1.21 (*t*-Bu), 3.04 (N–CH_2), 3.28 [*J*(PtH)20 Hz, DMSO].

(11) ^{1}H NMR, (−70 °C, δ): 1.08, 1.44 (*t*-Bu), 3.28, 2.95 (N–CH_2), 3.40 (DMSO).

(12) A change of the chelate bonding mode of a dinitrogen ligand to an unidentate mode has been observed in other platinum complexes containing in the coordination sphere a weak chelator and/or a trans ligand with a strong labilizing effect (Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618–2624. van der Poel, H.; van Koten, G.; Grove, D. M.; Pregosin, P. S.; Ostoja Starzewski, K. *Helv. Chim. Acta* **1981**, *64*, 1174. van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145–1151. Maresca, L.; Natile, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1140–1142).

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the monosolvato species is the only product formed (the two nitrogens are bound to be cis and the chelate effect makes the displacement of one end difficult).

The introduction of alkyl substituents in the chain of 1,4-diazabutane has the effect of lowering the rate of solvolysis (Table III). The retardation effect increases with increasing number of alkyl substituents on the chain (compounds **2** and **3**) and is more marked if the substituents are on the donor nitrogen atoms than if they are on the adjacent carbon atoms (compounds **3** and **5**). Moreover, further increasing the bulkiness of the substituents decreases the rate of solvolysis (compounds **5** and **6**). These observations are in accordance with a retardation effect due to a destabilization of the five-coordinate transition state, the sterical demand of which increases with increases in the number of substituents, their bulkiness, and their proximity to the metal atom.

It is also meaningful to compare the rate of solvolysis of different diastereoisomers. We have examined complexes having the amine substituents either in the cis or in the trans position with respect to the chelate ring and have found that the rate of solvolysis is always greater in the case of a cis configuration. Again the effect is more marked when the substituents are on the coordinating nitrogen atoms than when they are on the adjacent carbon atoms. A mechanistic explanation for such an effect is that in the cis isomer the two substituents, being both on one side of the coordination plane, leave the other side completely free to the attack by an incoming nucleophile. Moreover, in the five-coordinate transition state, the same substituents both point toward the leaving chloride, so favoring its dissociation. Although the observed differences are not great, they are significant and can be expected to be much greater in the case of a substitution reaction carried on by a nucleophile bigger than DMSO such as a nucleobase inserted in a polynucleotidic chain. In the latter case, the chirality of the complex (the trans isomers have two enantiomeric configurations) can also play an important role that is not shown in the reaction with the achiral DMSO.

The rate of solvolysis of compound **7** does not conform to the general trend. The steric hindrance of the N-substituents increases steadily from **5** to **7**; however, the rate of solvolysis decreases from **5** to **6** but increases from **6** to **7**. Conductivity and NMR data have shown that in the case of **7** the coordination of a DMSO molecule to platinum is not accompanied by release of a chloride ion (as in all other complexes examined) but by dissociation of one end of the diamine, which becomes singly bonded to platinum. The release of steric crowding inside the coordination sphere of platinum, consequent to dissociation of one bulky end of the diamine, could possibly contribute to the greater rate of solvolysis observed in **7**. In order to ascertain if also in the case of **7** an associative mechanism is operative, we have carried on a temperture dependence study and calculated the activation parameters [$\Delta H^* = 67$ (3) and 79 (4) kJ mol^{-1}; $\Delta S^* = -96$ (4) and -63 (5) J K^{-1} mol^{-1} for the cis and trans isomers, respectively]. Both parameters are in accord with an associative activation mode.[9] They also indicate that the greater reactivity of the cis isomer (having both substituents on one side of the coordination plane) is mainly due to a smaller enthalpy of activation in accord with a more favorable bond formation between the substrate and the incoming nucleophile.

Materials and Methods

Starting Materials. Commercial reagent grade chemicals were used without further purification. 1,4-Diazabutane (dab), 2-Me-dab, 2,3-[μ-$(CH_2)_4$]-dab, and 1,4-Me_2-dab were purchased from Aldrich; 1,4-(i-Pr)$_2$-dab and 1,4-(t-Bu)$_2$-dab were purchased from ICN pharmaceuticals. 2,3-Me_2-dab was prepared from dimethylglyoxime (Merck) by reduction with Raney nickel.[14]

The separation of meso (R,S) and racemic ($R,R + S,S$) forms was performed in the case of 2,3-[μ-$(CH_2)_4$]-dab by complexation of the commercial product to nickel(II) chloride and fractional crystallization of the corresponding complexes from methanol;[15] in the case of 2,3-Me_2-dab, separation was achieved by fractional crystallization of the hydrochlorides from methanol.[14]

Zeise's salt, K[Pt(η^2-C_2H_4)Cl_3], was prepared according to the method of Cramer et al. from potassium tetrachloroplatinate(II) and ethylene gas.[16]

[$PtCl_2(DMSO)_2$] was prepared by the method of Kukushkin et al.[17] and used as a starting material for the preparation of the ionic species [PtCl(DMSO)(R_n-dab)]Cl according to the method of Romeo et al.[18]

Preparation of Complexes. The complexes [$PtCl_2$(L)] (L = 1,4-diazabutane (dab) (**1**), 2-Me-dab (**2**), 2,3-Me_2-dab (**3**), 2,3-[μ-$(CH_2)_4$]-dab (**4**)) were prepared by thermal decomposition of the ionic species [PtCl(DMSO)(L)]Cl as already described.[5]

[$PtCl_2${1,4-(i-Pr)$_2$-dab}] (**6**) was prepared by a similar procedure, and the two isomers (with cis and trans configuration of the ligand) were separated by taking advantage of their different solubilities in DMF (dimethylformamide).[6]

The cis and trans isomers of [$PtCl_2${1,4-(t-Bu)$_2$-dab}] (**7**) were prepared separately by decomposition of the ionic species [PtCl(DMSO)-{1,4-(t-Bu)$_2$-dab}]Cl and of the five-coordinate complex [Pt(η^2-C_2H_4)-Cl_2{1,4-(i-Bu)$_2$-dab}], respectively.[6]

The cis isomer of [$PtCl_2$(1,4-Me_2-dab)], *cis*-**5**, was prepared by a two-step reaction: (a) preparation of [μ-(1,4-Me_2-dab){Pt(C_2H_4)Cl_2}$_2$]; (b) decomposition of the amine-bridged species in the presence of a stoichiometric amount of free amine.

(a) Zeise's salt (420 mg, 1 mmol) was dissolved in methanol (10 cm^3) and cooled to -10 °C. Addition of 1,4-Me_2-dab (44 mg, 0.5 mmol, in 2 cm^3 of methanol) caused an immediate precipitation of a yellow solid, which was filtered, washed twice with cold methanol, and dried in the air; yield 70%. Anal. Calcd for $C_8H_{20}Cl_4N_2Pt_2$: C, 14.2; H, 3.0; Cl, 21.0; N, 4.1. Found: C, 13.9; H, 2.8; Cl, 20.8; N, 4.0. ^{1}H NMR (CD_2Cl_2, δ): 2.81 [d, J(HH) = 6 Hz, J(PtH) = 33 Hz, N-CH_3], 3.43 and 4.41 [m, N-CH_2], 4.69 [J(PtH) = 60 Hz, C_2H_4], 5.76 [J(PtH) = 74 Hz, NH].

(b) The amine-bridged compound (140 mg in 10 cm^3 of CH_2Cl_2) was treated with free amine (1,4-Me_2-dab, 15 mg, 0.17 mmol, in 1 cm^3 of CH_2Cl_2) and the resulting solution left overnight at room temperature. The yellow-green microcrystalline precipitate which was formed was filtered, washed with 5 cm^3 of CH_2Cl_2 and then with diethyl ether, and dried in the air; yield 70%. Anal. Calcd for $C_4H_{12}Cl_2N_2Pt$: C, 13.6; H, 3.4; Cl, 20.0; N, 7.9. Found: C, 14.0; H, 3.4; Cl, 19.8; N, 8.0. ^{1}H NMR (CD_2Cl_2, δ): 2.75 [d, J(HH) = 6 Hz, J(PtH) = 41 Hz, N-CH_3], 2.42 and 3.34 [m, N-CH_2], 5.76 [J(PtH) = 76 Hz, NH].

The trans isomer of [$PtCl_2$(1,4-Me_2-dab)], *trans*-**5**, was prepared by reaction of K_2[$PtCl_4$] with amine (molar ratio 1:1) in water at 70 °C as already reported.[19] Cooling the reaction solution to room temperature caused pale yellow crystals to precipitate out. These were collected, washed with water, and dried; yield 80%. The trans configuration was assigned on the basis of the IR and NMR data.[20] Anal. Calcd for $C_4H_{12}Cl_2N_2Pt$: C, 13.6; H, 3.4; Cl, 20.0; N, 7.9. Found: C, 13.6; H, 3.3; Cl, 19.7; N, 8.0. ^{1}H NMR (DMSO-d_6, δ): 2.47 [d, J(HH) = 6 Hz, J(PtH) = 42 Hz, N-CH_3], 2.17 and 2.72 [m, N-CH_2], 6.20 [J(PtH) = 66 Hz, NH].

[PtCl(DMSO){1,4-(i-Pr)$_2$-dab}]ClO_4 (**8**) was prepared from [PtCl-(DMSO){1,4-(i-Pr)$_2$-dab}]Cl (200 mg) and $LiClO_4$ (2 g) dissolved in methanol (40 cm^3). The resulting solution was concentrated to one-fifth of its initial volume, filtered, and left in the refrigerator for 1 week. The white crystalline product formed was separated, washed with 2 cm^3 of cold methanol and then with diethyl ether, and dried in the air; yield 60%. Anal. Calcd for $C_{10}H_{26}Cl_2N_2O_5SPt$: C, 21.7; H, 4.7; Cl, 12.8; N, 5.1. Found: C, 21.5; H, 4.7; Cl, 12.5; N, 4.9. The configuration of the ligand was determined to be trans.[21]

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(20) The IR spectra showed very characteristic N–H stretching bands either in the cis or in the trans species. In the trans isomers only one N–H stretching mode was observed, and this occurred at 3128, 3125, and 3155 cm^{-1} for **5**, **6**, and **7**, respectively. In the cis isomers, two N–H stretching modes were observed at 3162, 3197; 3140, 3180; and 3155, 3210 cm^{-1} for **5**, **6**, and **7**, respectively. The NMR multiplets related to the N–CH_2 protons were always more separated in the cis isomer than they were in the trans species.

Kinetic Measurements. Rate data were obtained spectrophotometrically by measuring changes of absorbance with time. The complex was dissolved directly in a thermostated cell containing DMSO and the change of absorbance monitored as a function of time. First-order rate constants were calculated from plots of ln $(A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least 6 half-lives, respectively. These plots were linear for at least 4 half-lives. The least-squares method was used to fit the experimental data (Table III). A temperature-dependence study was performed in the case of **7**. The rate of solvolysis was measured at 30 (Table III), 25 [1.11 (3) × 10^{-4} and 5.0 (4) × 10^{-5} s^{-1} for the cis and trans isomers, respectively], and 50 °C [9.5 (3) × 10^{-4} and 5.8 (4) × 10^{-4} s^{-1} for the cis and trans isomers, respectively]. The enthalpy and entropy of activation were evaluated from an Eyring plot of ln $k_{obs.}$ against $1/T$ [$\Delta H^* = 67$ (3) and 79 (4) kJ mol^{-1} and $\Delta S^* = -96$ (4) and −63 (5) J K^{-1} mol^{-1} for the cis and trans isomers, respectively].

Physical Measurements. IR spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets; spectra in the range 400–200 cm^{-1} were recorded as polythene pellets on Perkin-Elmer 283 and FT1600 spectrophotometers. ^1H NMR spectra were obtained with Varian XL 200 and VXR 300 spectrometers. ^1H-decoupled ^{195}Pt NMR spectra were recorded on the VXR 300 instrument operating at 64.332 MHz and using a sweep width of 100 kHz, a pulse width of 20 μs, and an acquisition time of 0.096 s; the chemical shift values, referred to $Na_2[PtCl_6]$ used as external standard, are uncorrected for the solvent. UV–vis spectra were recorded on a Varian 2002 double-beam spectrophotometer.

Calculation of ΔG^*. The free energy of activation was calculated by using the expression $\Delta G^*_{T_c} = -RT \ln [\pi(\Delta\nu)h/2^{1/2}kT]$, where $\Delta\nu$ represents the chemical shift difference ($\Delta\delta$ in Hz) of the coalescing peaks in the absence of exchange, T represents the coalescence temperature, and R, k, and h have their normal thermodynamic significances.[22]

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Registry No. **1**, 14096-51-6; **2**, 33727-98-9; **3**, 92283-43-7; *cis*-**4**, 61848-70-2; *trans*-**4**, 38780-40-4; **5**, 16786-98-4; **6**, 123807-65-8; **7**, 103601-36-1; **8**, 123751-05-3; DMSO, 67-68-5; Pt, 7440-06-4.

(21) The ^1H NMR spectrum taken soon after dissolution of the crystalline compound in D_2O showed only one set of signals; when the solution was left standing for 1 h at room temperature, a new, less intense, set of signals appeared. This indicates that in the crystalline solid the ligand has only one configuration and this is probably trans (only one N–H stretching mode was observed in the IR at 3220 cm^{-1}).

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Examination of the Reactivity of Bis(trifluoromethyl)tellurium: Oxidative Trifluoromethylations and Ligand Exchanges with Group 5A and 6A (15 and 16) Elements and Their Halides

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Bis(trifluoromethyl)tellurium reacts with I_2, S_8, Se, P_4, and As at 220 °C to afford CF_3I, $(CF_3)_2S$, $(CF_3)_2Se$, $(CF_3)_3P$, and $(CF_3)_3As$, which are separated in 97, 92, 92, 70, and 46% yields, respectively. The interaction of $(CF_3)_2Te$ with Sb at 170 °C results in very small amounts of $(CF_3)_3Sb$, ca. 3%, but no (trifluoromethyl)germanes were observed when $(CF_3)_2Te$ was exposed to Ge at 170 °C. At 170 °C the reactions of $(CF_3)_2Te$ with $SeBr_4$, PI_3, and AsI_3 generate $(CF_3)_2Se$, $(CF_3)_3P$, and $(CF_3)_3As$, which can be isolated in 98, 65, and 88% yields, respectively. The reaction of SCl_2 with $(CF_3)_2Te$ at 170 °C, however, is less productive, presumably because there are several alternative pathways that are competitive with the reaction channel that leads to $(CF_3)_2S$. At 170 °C SbI_3 and $(CF_3)_2Te$ form trace amounts (ca. 0.2%) of $(CF_3)_3Sb$, but in the temperature range 120–170 °C, the reaction of GeI_4 with $(CF_3)_2Te$ gave no evidence for the formation of (trifluoromethyl)germanes.

Introduction

For 40 years trifluoromethyl iodide has been by far the most widely utilized reagent in the field of perfluoroalkyl organometallic chemistry. The synthesis and reactivity of this compound were initially examined by Emeleus and his students, who found that CF_3I oxidatively trifluoromethylated elemental P, As, Sb, S, Se, and amalgamated Hg.[1-6] Subsequently, CF_3I was demonstrated to be reactive in ligand exchange reactions with, e.g., the trimethyl derivatives of the main group 5 elements, generating, for example, $CF_3P(CH_3)_2$[7] and $CF_3Bi(CH_3)_2$.[8]

Others, most notably Stone, investigated the reactions between CF_3I and low-valent transition-metal complexes. They found that while CF_3I is not as strong an oxidizing agent as elemental iodine, many trifluoromethyl derivatives, like $CF_3Fe(CO)_4I$ or $CF_3Ni(PPh_3)_2I$, could be formed by the oxidation of appropriate substrates with trifluoromethyl iodide.[9] Ligand interchanges between the iodine center and transition-metal species, for example, platinum(II) dimethyl complexes,[10] have also been demonstrated.[11]

Trifluoromethyl iodide has also been employed as a reagent in organic chemistry but to a much more modest extent. Here, the majority of the reported reactions have been designed to result in the addition of CF_3 and iodine across alkene or alkyne bonds. Typically, the reaction conditions that were employed have been

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