moieties in $[Ni(TAAB)(CH_3CN)_2][I_3]_2$, compared with interactions found in I_8^{2-}, were examined to shed some light on factors influencing polyiodide formation. I–I distances in I(4)–I(5)–I(6) of 2.974 (6) and 2.963 (5) Å indicate a symmetrical I_3^-; however, the corresponding distances in I(1)–I(2)–I(3) are slightly asymmetric at 3.016 (6) and 2.924 (5) Å, probably due to either intermolecular interactions or packing effects. The closest approaches of the triiodides with macrocycle and acetonitrile carbons range from 3.69 (7) to 3.98 (7) Å and are considerably longer than even the weak associations of I_8^{2-} with macrocyclic benzo groups in $[Pd(TAAB)][I_8]$ (3.52 Å).[1] The triiodide asymmetry thus is more probably due to packing effects. The two I_3^- units do not appear to be related in any discernible fashion, their closest approach being 4.216 (7) Å (I(6) to I(4)″; I(4)″ is related to I(4) by a unit cell translation along the *a* axis). Iodine–benzo group or iodine–acetonitrile interactions do not appear to be systematic or related to the interactions observed in $[Pd(TAAB)][I_8]$, therefore. The presence of axial coordination may thus be sufficient to disrupt the packing of the cations to the extent that required stabilizing influence of iodine–benzo group interactions necessary for higher chain polyiodide formation is prevented.

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Registry No. $[Ni(TAAB)(CH_3CN)_2][I_3]_2$, 85479-99-8; $[Ni(TAAB)][I_8]$, 85480-00-8; $[Ni(TAAB)][BF_4]_2$, 14220-76-9.

Supplementary Material Available: Tables of observed and calculated structure factors and thermal parameters (15 pages). Ordering information is given on any current masthead page.

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Mechanism of Reductive Elimination of 1,1,1-Trifluoroethane from *cis*-Hydrido(2,2,2-trifluoroethyl)bis(triphenylphosphine)platinum(II)

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The mechanism of 1,1 reductive elimination processes involving formation of hydrogen–hydrogen,[1] hydrogen–carbon,[2-4] and carbon–carbon[5,6] species from transition-metal complexes is a subject of current interest.

In particular, *cis*-hydridoalkylplatinum(II)–tertiary phosphine complexes are rather unstable toward alkane elimination[3,7a,8] unless the alkyl group bears electron-withdrawing stabilizing substituents.[9-11]

In our search for structure–reactivity correlations for organoplatinum derivatives with electronegative metal-bonded (sp^3) carbon groups, we were led to investigate the ability of fluoroalkyls to stabilize Pt(II) metal complexes containing the hydride ligand. We found that the complex *cis*-$PtH(CH_2CF_3)(PPh_3)_2$ (**1**) is easily isolated from the reaction of the cationic $Pt(CH_2CF_3)(PPh_3)_2(solvent)^+$ with $NaBH_4$ in ethanol at 0 °C.

Since **1** appeared to undergo slow thermal reductive elimination of CH_3CF_3 at room or slightly above room temperature in contrast with the highly unstable hydrido–methyl analogue[3] (eq 1), we thought it worthwhile to undertake a kinetic investigation of this elimination reaction, the results of which will be reported in a sequel.

$$cis\text{-}PtH(CH_2CF_3)(PPh_3)_2 \rightarrow \text{“}Pt(PPh_3)_2\text{”} + CH_3CF_3 \qquad (1)$$

Experimental Section

General Procedures, Apparatus, and Materials. All reactions were carried out under dry nitrogen or argon atmosphere. The solvents benzene, toluene, tetrahydrofuran, and diethyl ether were distilled under nitrogen from sodium and degassed before use by a series of freeze–pump–thaw cycles. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification.

IR spectra were recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 597 spectrophotometer calibrated against polystyrene film. ^1H NMR spectra were registered on Varian FT-80 A and Bruker WH-360 instruments in CD_2Cl_2 (99%); all the chemical shifts are reported from tetramethylsilane by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. ^{19}F NMR spectra (CD_2Cl_2) were run on a Varian FT-80 A spectrometer with $CFCl_3$ as internal reference. $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) were recorded on the above instruments with H_3PO_4 (85%) or PEt_3 as external reference. In the case where PEt_3 was used as external reference, the chemical shifts are reported from H_3PO_4 (85%) with use of the conversion $\delta(H_3PO_4) = \delta(PEt_3) - 19.7$ ppm (at 30 °C). In all the spectra, negative chemical shifts are *upfield* from the reference used. The correctness of the NMR data analyses was checked by spectral simulation.

UV spectra were recorded with a Varian Cary 219 C spectrophotometer equipped with an F3-C Haake circulating-fluid cryothermostat.

Melting points were taken on a hot plate apparatus and are uncorrected. Elemental analyses were performed by the Institute of Organic Chemistry of the University of Padua. 2-Iodo-1,1,1-trifluoroethane and $NaBD_4$ were used as purchased from EGA-Chemie, Steinheim, FRG.

cis-$PtI(CH_2CF_3)(PPh_3)_2$ was prepared according to a literature procedure.[12]

Preparation of the Complexes. *cis*-$PtH(CH_2CF_3)(PPh_3)_2$ (1). A solution of *cis*-$PtI(CH_2CF_3)(PPh_3)_2$ (1.86 g, 2.0 mmol) in CH_2Cl_2 (100 mL) was treated with a solution of $AgBF_4$ (0.39 g, 2.0 mmol) in MeOH (3 mL) and stirred at room temperature for 2 h. AgI was filtered off and the volume of the filtrate reduced to ca. 20 mL. Dropwise addition of Et_2O gave a white precipitate of the cationic solvato complex, which was filtered and dried under vacuum. This was dissolved in absolute EtOH (150 mL) and cooled in an ice–water bath. A solution of $NaBH_4$ (0.08 g, 2.11 mmol) in EtOH (50 mL) was added dropwise in a period of 1 h. The pale cream solid that precipitated from the alcoholic solution was filtered. Recrystallization from CH_2Cl_2/MeOH by evaporation under reduced pressure gave **1** as a white product (1.0 g, 62% yield), mp 109–111 °C dec with effervescence. Anal. Calcd for $C_{38}H_{33}F_3P_2Pt$: C, 56.78; H, 4.14. Found: C, 56.66; H, 4.22.

^1H NMR: $\delta(H) = -4.79$ (doublet of double quartets ($^1J_{PtH} = 1113$, $^2J_{PH(trans)} = 194$, $^2J_{PH(cis)} = 21.3$, $^3J_{FH} = 4.5$ Hz), $\delta(CH_2) = 1.66$

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($^3J_{PH(trans)} = {}^3J_{PH(cis)} = 8.1$, $^3J_{FH} = 16.3$, $^2J_{PtH} = 87.2$ Hz; signal appears as a 1:2:4:6:6:6:4:2:1 multiplet due to accidental equality of $^3J_{PH(trans)} = {}^3J_{PH(cis)} \cong {}^1/_2({}^3J_{FH})$). ^{19}F NMR: $\delta(CF_3) = -52.3$ (doublet of quartets; $^3J_{PtF} = 226$, $^3J_{FH} = 16$, $^4J_{FH} = 4.5$, $^4J_{PF(trans)} = 14.9$ Hz; the similarity of $^3J_{FH}$ with $^4J_{PF(trans)}$ gives rise to a quartet instead of a theoretical doublet of triplets). $^{31}P\{^1H\}$ NMR: δ(P(trans to CH_2CF_3)) = 22.4 (quintet since $^2J_{PP} \cong {}^4J_{PF(trans)}$; $^1J_{PtP} = 2352$, $^2J_{PP} = 14.7$, $^4J_{PF(trans)} = 14.9$ Hz), δ(P(cis to CH_2CF_3)) = 26.9 (doublet; $^1J_{PtP} = 1868$, $^2J_{PP} = 14.7$ Hz). IR (cm^{-1}): ν(PtH) = 2107 (medium, Nujol mull); ν(PtH) = 2105 (medium, CH_2Cl_2 solution).

***cis*-PtD(CH_2CF_3)(PPh_3)$_2$.** To a solution of *cis*-PtI(CH_2CF_3)(PPh_3)$_2$ (0.93 g, 1.0 mmol) in CH_2Cl_2 (50 mL) was added 1 mL of a 1 M solution of $AgBF_4$ in acetone and the mixture stirred at room temperature for 1 h. The white AgI was filtered off and the solution concentrated under reduced pressure. Dropwise addition of Et_2O (50 mL) gave a white precipitate, which was filtered and dried under vacuum. It was then dissolved in degassed EtOD (30 mL) and treated at 0 °C with a solution of $NaBD_4$ (0.05 g, 1.19 mmol) in EtOD (20 mL) in a period of 1 h. A white precipitate formed, which was filtered and recrystallized from CH_2Cl_2/Et_2O to give *cis*-PtD(CH_2CF_3)(PPh_3)$_2$ (0.42 g, 52% yield).

^{1}H NMR: $\delta(CH_2) = 1.68$ (signal appears as a 1:2:4:6:6:6:4:2:1 multiplet due to accidental equality of $^3J_{PH(trans)} = {}^3J_{PH(cis)} \cong {}^1/_2({}^3J_{FH})$; $^3J_{FH} = 16.3$, $^3J_{PH(trans)} = {}^3J_{PH(cis)} = 8.1$, $^2J_{PtH} = 87.2$ Hz). ^{19}F NMR: $\delta(CF_3) = -52.1$ (signal appears as a quartet due to almost equality of $^3J_{FH}$ and $^4J_{PF(trans)}$; $^3J_{FH} = 16$, $^4J_{PF(trans)} = 15.1$, $^3J_{PtF} = 226$ Hz). $^{31}P\{^1H\}$: δ(P(trans CH_2CF_3)) = 24.2 (signal appears as a quintet due to virtual equality of $^2J_{PP}$ and $^4J_{PF(trans)}$; $^2J_{PP} = 14.7$, $^4J_{PF(trans)} = 15.1$, $^1J_{PtP} = 2355$ Hz), δ(P(cis to CH_2CF_3)) = 28.7 (signal appears as a six-line multiplet; $^2J_{PD} = 29.6$, $^2J_{PP} = 14.7$, $^1J_{PtP} = 1851$ Hz). IR (cm^{-1}): ν(PtD) = 1512 (medium, Nujol mull).

Kinetics. In a typical experiment followed by IR spectroscopy, a solution of **1** (ca. 0.25 g) in the chosen solvent (ca. 5 mL) in a septum-capped Schlenk tube under argon was placed in a thermostated bath. At timed intervals, aliquot portions were withdrawn by syringe and transferred into a matched (path length 0.5 mm) NaCl solution cell. The IR spectrum was then quickly scanned in the range 2200–2000 cm^{-1} to monitor the progressive disappearance of the Pt–H stretching absorption.

When the kinetics were followed by UV spectroscopy, the runs were started by quickly dissolving the substrate in the previously thermostated reaction medium in a 1-cm quartz cell placed in the cell compartment of the spectrophotometer. The complex concentration was on the order of 10^{-4} M. The temperature was maintained constant within ±0.05 °C by means of a circulating-water thermostat. Spectral changes with time were recorded in the region 360–300 nm. Absorbance readings were taken for 6–7 half-lives at 340 nm, where the difference in absorbance between the starting reactant and the product was the highest. The treatment of experimental data and the determination of rate constants were carried out as described previously.[13]

The same experimental procedure was adopted in the presence of excess of diphenylacetylene or triphenylphosphine. In these cases, however, the reference cell contained a solution of ligand at the same concentration as the sample cell.

Identification of Products. The formation of 1,1,1-trifluoroethane as the only organic product of the reductive elimination of eq 1 was confirmed by ^{19}F and ^{1}H NMR spectroscopy of a reaction mixture in a deuterated solvent. ^{19}F NMR (C_6D_6): $\delta(CF_3) = -60.6$ (quartet; $^3J_{FH} = 13.1$ Hz). ^{19}F NMR (CD_2Cl_2): $\delta(CF_3) = -61.1$ (quartet; $^3J_{FH} = 13.1$ Hz). ^{1}H NMR (C_6D_6): $\delta(CH_3) = 1.09$ (quartet; $^3J_{FH} = 13.1$ Hz).[14]

The reaction was accompanied by a progressive change in solution color from colorless to orange-red, due to the formation of platinum(0)–triphenylphosphine clusters (see Results and Discussion). When the reaction was carried out in the presence of excess diphenylacetylene, the solution turned yellow due to the presence of Pt(PPh_3)$_2$(PhC≡CPh). The latter was identified by comparison of its IR spectrum with that of an authentic sample independently prepared.[15] 2-Deuterio-1,1,1-trifluoroethane resulting from the reductive elimination from the parent Pt–D complex was detected by its ^{19}F NMR spectrum in CD_2Cl_2: $\delta(CF_3) = -60.9$ ($^3J_{FH} = 13.0$, $^3J_{FD} = 1.8$ Hz). The CF_3 signal appears as a triplet by coupling with the CH_2 protons, and each line of the triplet is further split into a 1:1:1 three-line pattern due to coupling with deuterium.

Statistical Data Reduction and Handling. All statistical and graphical analyses of kinetic data were performed by P.U. with a comprehensive software package implemented on a Tektronix 4052 graphic system (64 kbytes RAM) equipped with a Tektronix 4662 digital plotter and an Anadex DP-9500 fast printer. The package was in part derived from the Tektronix Plot 50 statistical software and locally tailored to suit the needs of the system under study. Detailed information is available from this author upon request.

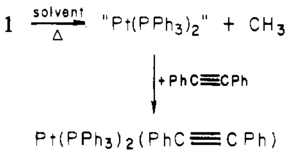
Results and Discussion

The reaction sequence leading to *cis*-PtH(CH_2CF_3)(PPh_3)$_2$ is summarized in eq 2. Abstraction of iodide from the starting

$$\begin{aligned} &cis\text{–PtI}(CH_2CF_3)(PPh_3)_2 + Ag^+ \xrightarrow[-AgI]{solv} \\ &\qquad \text{Pt(solv)}(CH_2CF_3)(PPh_3)_2^+ \xrightarrow[0\ °C]{NaBH_4,\ EtOH} \\ &\qquad\qquad cis\text{–PtH}(CH_2CF_3)(PPh_3)_2 \quad (2) \\ &\qquad\qquad\qquad \mathbf{1} \end{aligned}$$

substrate with an equimolar amount of $AgBF_4$ in CH_2Cl_2/MeOH allows the isolation of the stable cationic intermediate, which upon treatment at 0 °C with a slight excess of $NaBH_4$ in EtOH is converted into the insoluble final hydrido derivative. This is a white solid indefinitely stable in the air, which can be stored without decomposition in a refrigerator for prolonged periods of time. Its cis configuration was fully established by IR and NMR spectroscopy (see Experimental Section).

When dissolved in benzene or toluene, **1** slowly decomposes with formation of CH_3CF_3 (identified by ^{1}H and ^{19}F NMR spectroscopy) and of a still unidentified Pt(0)–triphenylphosphine cluster, which imparts an orange-red color to the solution.[5,7] This thermal decomposition does not apparently produce platinum metal, in contrast with the behavior of the methyl counterpart, *cis*-PtH(Me)(PPh_3)$_2$.[3] In the presence of excess diphenylacetylene which acts as trapping agent for the bona fide primary intermediate product of reductive elimination, "Pt(PPh_3)$_2$", the stable Pt(0) complex Pt(PPh_3)$_2$(PhC≡CPh) ensues along with the fluorinated hydrocarbon (see eq 3).



(3)

2

solvent = benzene, toluene, THF
temperature = 25–50 °C

The kinetics of reductive elimination of CH_3CF_3 from **1** could be easily studied by monitoring either the disappearance of the Pt–H stretching vibration or the increase in absorbance of solutions of **1** in the range 360–300 nm. In the latter case, an isosbestic point is developed at ca. 293 nm, which is destroyed in the later portion of the reaction when no PhC≡CPh is added, apparently owing to the slow decomposition of "Pt(PPh_3)$_2$". When excess PhC≡CPh is present, the corresponding isosbestic point is maintained throughout the reaction, thanks to the stabilization properties of this ligand toward Pt(0)–PPh_3 species.

The presence of **1** and either "Pt(PPh_3)$_2$" or **2** as the only UV-absorbing species in the system as long as the isosbestic point is maintained was unequivocally confirmed by computer abstract factor analysis of absorbance data.[16]

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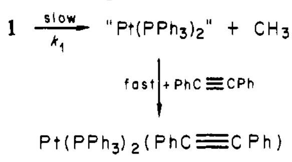
Table I. Rate Constants for the Reaction *cis*-$PtH(CH_2CF_3)(PPh_3)_2 \rightarrow$ "$Pt(PPh_3)_2$" + CH_3CF_3

solvent	temp, °C	10^4k_1, s^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[a] eu	log A[b]
benzene	25	0.59 ± 0.008	24.6 ± 0.6	4.9 ± 2	14 ± 2
	30	1.22 ± 0.006			
	35	2.34 ± 0.02			
	40	4.67 ± 0.05			
	45	8.71 ± 0.06			
toluene	25	0.58 ± 0.02	25.4 ± 1	7.8 ± 3	16 ± 2
	30	1.27 ± 0.02			
	35	2.63 ± 0.04			
	40	5.16 ± 0.03			
	45	9.68 ± 0.1			
tetrahydrofuran	30	0.78 ± 0.006	23.9 ± 2	2 ± 3	13 ± 2
	35	1.55 ± 0.01			
	40	3.02 ± 0.03			
	45	5.42 ± 0.1			
	50	9.10 ± 0.2			

[a] From an Eyring-Polanyi plot. [b] Preexponential factor from an Arrhenius plot.

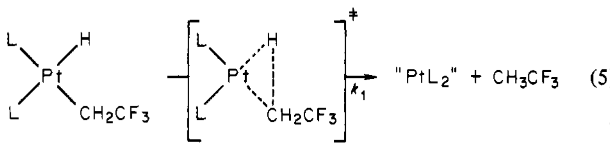
Reductive elimination from **1** follows strictly first-order kinetics, according to eq 4.



(4)

Rate data from UV measurements along with activation parameters are listed in Table I for reactions in benzene, toluene, and THF (uncertainties quoted are standard errors of estimate from computer fits[13] corrected for the degrees of freedom at 95% confidence levels). The corresponding Eyring plots are shown in Figure 1. The results from the infrared-monitoring technique based on the ν(Pt–H) decay (see Experimental Section) were virtually the same.

These findings are in agreement with a mechanism involving primary *concerted unimolecular reductive elimination* with rupture of both Pt–H and Pt–C bonds during the rate-determining step with concomitant C–H bond formation:



(5)

The rates of reductive elimination are unaffected by the presence of excess $PhC{\equiv}CPh$ (10–100-fold), as expected from the role of this ligand in trapping the labile PtL_2 intermediate in a fast association step subsequent to the activation process. The rates are also insensitive to the presence of excess PPh_3: thus, the k_1 values in benzene at 40 °C at PPh_3 concentrations of 0, 5×10^{-3}, and 1×10^{-2} M are 4.67×10^{-4}, 4.71×10^{-4}, and 4.70×10^{-4} s^{-1}, respectively.

This also rules out any contribution to the mechanism from possible triphenylphosphine displacement routes in the primary slow stage. Such a dissociative pathway, however, is a common feature of some reductive eliminations.[6b]

The high activation enthalpies observed in all the solvents examined are consistent with a dissociative process, as are the positive activation entropies. The latter however are not very high, probably because the increasing degrees of freedom in the activation process are somewhat counterbalanced by restriction of conformational freedom in the three-membered transition state, which apparently requires some "freezing" of the ligands.

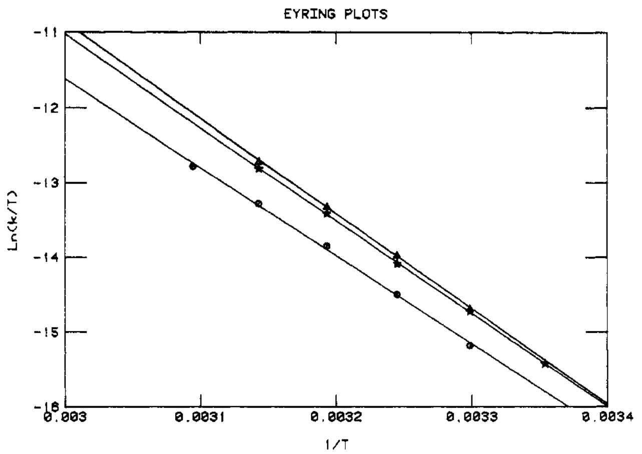


Figure 1. Plots of ln (k/T) vs. $1/T$ for reaction 1 in benzene (stars), toluene (triangles), and tetrahydrofuran (circles). Straight lines are least-squares best fits to the Eyring–Polanyi equation.

Highly negative $\Delta S^{\ddagger}$ values were indeed observed for the reductive elimination of biaryls from *cis*-$PtAr_2L_2$,[5] where the effect of constraint in the mutual orientation of the aryl groups required by interaction of p_π aryl orbitals is much more pronounced than in our case, wherein only σ orbitals are involved.

As can be seen from Table I, the rates in benzene and toluene are very close, due to an almost exact compensation between enthalpic and entropic factors. The reaction in THF is slower, essentially due to a less positive activation entropy (see also Figure 1). We also found that the reaction is slowed in dichloromethane, indicating that increasing solvent polarity makes the activation process less favorable.

Comparison of the rates of reductive elimination of **1** and of the corresponding deuteride *cis*-$PtD(CH_2CF_3)(PPh_3)_2$ gave an appreciable normal primary isotopic effect ($k_H/k_D = 2.2$ at 40 °C in benzene), in agreement with the rate-determining step involving Pt–H bond breaking. As is known,[17] the major portion of the kinetic isotopic effect arises from contributions to the activation energy from changes in zero-point energy differences occurring in the activated complex formation. Since the zero-point energy difference between Pt–H and Pt–D is ca. 0.9 kcal/mol (if only the stretching vibration is considered), complete loss of a Pt–H vibration at 40 °C would result in a k_H/k_D ratio of ca. 4.0. The observed value of 2.2 indicates that loosening of the Pt–H bond in the rate-determining step is accompanied by formation of a new C–H bond, so that there is some energy gain compensation, since the zero-point energy for C–H is greater than that of Pt–H by ca. 1 kcal/mol. A similar explanation has been offered to account for even lower values of k_H/k_D[18] and is consistent with the indicated formation of a three-center transition state in eq 5 involving both breaking of the Pt–H bond and making of the C–H bond.

The independence of the rate of reductive elimination from added free ligand seems to be a general feature when hydrido–alkyl substrates are involved. Thus, elimination of CH_4 from $OsH(CH_3)(CO)_4$[2] or from *cis*-$PtH(CH_3)(PPh_3)_2$[3] was unaffected by the presence of free ligand (tertiary phosphine or diphenylacetylene). This would indicate that ligand dissociation is not a prerequisite for reductive elimination in these systems since the expected role of an added free ligand would be to interfere as a nucleophile with the dissociation of the coordinated ligands. In contrast, it has been shown that

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tertiary phosphines affect in diverse ways the reductive elimination of alkanes from transition-metal dialkyl complexes.[5,6a,c]

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Platinum(II) Complexes of Tridentate Bis(2-aminoethyl)methylamine

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In the course of preparing the trans-spanned platinum(II) complex [Pt(*sym*-medien·HCl)$(NH_3)_2$]Cl_2,[1] the iodo iodide [Pt (*sym*-medien)I]I was prepared by the method of Watt and Cude.[2]

By the methylation of iodo(diethylenetriamine)platinum(II) iodide, [Pt(dien)I]I, Watt and Cude obtained what they believed to be symmetrical product [Pt(medien)I]I. They attributed this rather surprising result to the secondary trans effect in the I–Pt–N–H chain. Their identification of the product was based on the fact that their product was different from the analogous compound prepared from a commercial sample of the diamine that was said to be the unsymmetrical isomer.

Our results do not agree with those of Watt and Cude in regard to the position of the methyl group in the triamine ligand. The discrepancies are important because the position at which methylation occurred in the complex is the crux of their discussion concerning the secondary trans effect in platinum(II) complexes.

We have synthesized the symmetrical isomer of [Pt(medien)X]X by using the triamine of which the structure had been fully determined by the method of synthesis, as well as NMR and IR spectra.

Experimental Section

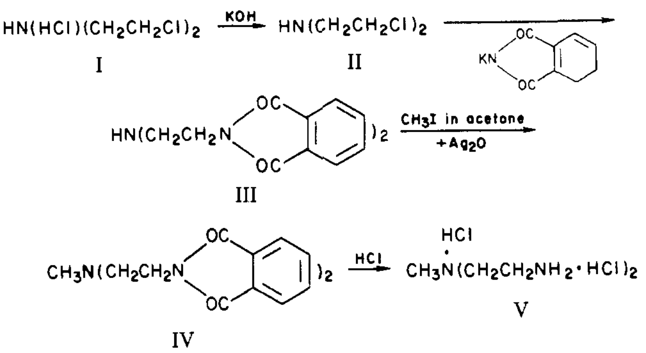
Symmetrical *N*-methyldiethylenetriamine was synthesized by the phthalamide synthesis as described by Mann (Scheme I).[3] Anal. Calcd for $C_5H_{18}N_3Cl_3$ (V): C, 26.65; H, 8.00; N, 18.50; Cl, 46.95. Found: C, 26.46; H, 8.05; N, 18.25; Cl, 46.62.

[Pt(*sym*-medien)I]I. Symmetrical *N*-methyldiethylenetriamine trihydrochloride (medien·3HCl) was converted to the free amine by treatment with Ag_2O, and the amine was made to react with $PtI_2{\cdot}H_2O$ to form [Pt(medien)I]I according to the method of Watt and Cude.[2] Anal. Calcd for $C_5H_{15}N_3I_2Pt$: C, 10.70; H, 2.66; N, 7.44; I, 44.60; Pt, 34.50. Found: C, 10.63; H, 2.71; N, 7.49; I, 44.72; Pt, 34.35.

Results and Discussion

The formation of $CH_3N(CH_2CH_2NH_2)_2$ through the phthalimide synthesis shows that methylation occurs exclusively on the central nitrogen atom of the triamine. This is confirmed by the NMR spectrum, which was compared with that of 1,4,7-trimethyldiethylenetriamine, in which the peaks of the methyl groups are easily identified by their relative intensities. The chemical shift values of the methyl group in the *N*-methyldiethylenetriamine synthesized in this way agree very well with that of the central methyl group of 1,4,7-trimethyldiethylenetriamine. Also, the IR spectrum of our *N*-methyldiethylenetriamine trihydrochloride shows an absorption band of medium intensity at 1990 cm^{-1}, which is attributed to the stretching vibration of the N–H bond in the tertiary amine.[4] No peak was found in the 2700-cm^{-1} region, where the absorption due to the N–H stretching vibration of a secondary ammonium ion would be expected.[4]

Scheme I



Platinum Complexes of *N*-Methyldiethylenetriamine. Watt and Cude[2] reported that one of the nitrogen atoms in [Pt(dien)I]I is methylated by methyl iodide in liquid ammonia at −70 °C in the presence of potassium amide. From the NMR spectrum of the product and a comparison of its IR spectrum with that of supposed unsymmetrical [Pt(medien)I]I, but without comparison with that of the isomer containing symmetrical medien, they concluded that the product was [Pt(*sym*-medien)I]I, in other words that the methylation occurred on the central nitrogen atom of the ligand, *trans to the coordinated iodine atom.*

Watt and Cude obtained their medien from K & K Laboratories, Inc., and used it without further purification. We also obtained a sample of medien from K & K Laboratories; the NMR data indicate that it is a mixture of the two isomers in the ratio of *sym* to *unsym* of 1.24 to 1.0, although it is labeled "*N′*-medien". On the basis of the greater reactivity of the primary amine groups as compared with that of the secondary amine, it is possible that only the symmetrical medien reacts with PtI_2 in spite of the presence of the unsymmetrical isomer in the mixture. This suggestion is supported by the fact that our attempts to prepare [Pt(*unsym*-medien)I]I by the same method that we used to make [Pt(*sym*-medien)I]I were unsuccessful.

Secondary Trans Effect. The data on the secondary trans effect which Watt and Cude[2] give and which led to their conclusions must be reconsidered; although they tried to determine on which nitrogen atom the methylation occurred, they unfortunately had the wrong triamine for comparison. The results of the present investigation indicate that the methyl group was on a terminal nitrogen atom rather than on the central one. This is what would be expected, for the terminal primary nitrogen atoms are more reactive than the secondary ones, and in this case, they offer four reaction sites instead of one. Moreover, in the free ligand, methylation occurs on the primary amine.[5]

We must conclude that in Watt and Cude's experiment methylation occurred on the nitrogen atom cis to the iodo group and that the trans effect is not strong enough to provoke the change in the relative reactivities of N–H bonds of coordinated dien.

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