Thus, k_{12} and K_{12} in the Marcus cross relationship (eq 26) refer to k_{2et} and K_{2et} in eq 31. Values of k_{2et} and K_{2et} can be calculated from k_2 and K_2 by dividing these numbers by K_{ip}, which is defined by

$$2S_2O_3^{2-} \rightleftarrows S_2O_3^{2-},S_2O_3^{2-} \quad K_{ip} \qquad (32)$$

In such a treatment the self-exchange rate constants k_{11} and k_{22} are defined for the following reactions:

$$S_2O_3^{2-},S_2O_3^{2-} + {}^*S_4O_6^{3-} \rightarrow S_4O_6^{3-} + {}^*S_2O_3^{2-},{}^*S_2O_3^{2-} \quad k_{11} \qquad (33)$$

$$\mathrm{Os(III)} + {}^*\mathrm{Os(II)} \rightarrow \mathrm{Os(II)} + {}^*\mathrm{Os(III)} \quad k_{22} \qquad (34)$$

Values for k_{11} for this sort of reaction have never been measured directly, and they have only been estimated in the cases of $I_2^-/2I^-$ and $(SCN)_2^-/2SCN^-$ couples.[50,55] The approach used here is to calculate k_{11} by use of the Marcus cross relationship and see whether the result is reasonable.

A value for K_{ip} is required for these calculations. According to Hemmes, the Fuoss equation should be applicable to formation of ion pairs from two like-charged ions.[56] This equation yields a value of 7.06×10^{-4} M^{-1} for K_{ip} at zero ionic strength, and when corrected to 0.1 M ionic strength, K_{ip} is 6.70×10^{-3} M^{-1}. For the work-term calculations the charge and radius of the ion pair $S_2O_3^{2-},S_2O_3^{2-}$ were assumed to be −4 and 6.6 Å, respectively. Similarly $S_4O_6^{3-}$ was assumed to have a radius of 6.6 Å. Calculated values of k_{11} are presented in Table VIII. In view of the significant uncertainty in some of the values of k_2, the scatter in k_{11} is not unacceptable.

The average value of k_{11} calculated for the $S_4O_6^{3-}/2S_2O_3^{2-}$ system is 39 M^{-1} s^{-1}, which may be compared with the value of 3×10^4 M^{-1} s^{-1} that was calculated for the $I_2^-/2I^-$ system.[55] Further interpretation of these numbers is unwarranted because the S–S force constant in $S_4O_6^{3-}$ is unknown.

Conclusions. Oxidation of $S_2O_3^{2-}$ by Os(III) has parallel paths: one with rate-limiting formation of $S_2O_3^-$ and Os(II) and the other with concerted electron transfer and S–S bond formation to yield $S_4O_6^{3-}$ and Os(II). Subsequent steps lead to $S_4O_6^{2-}$. The first path has diffusion apart of the products rather than electron transfer as the rate-limiting step, and this leads to an estimate of $E° = 1.30$ V for the $S_2O_3^-/S_2O_3^{2-}$ redox couple. In the second path electron transfer is rate limiting, which affords an unusual opportunity to apply the Marcus cross relationship to reactions having concerted bond formation.

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Registry No. $S_2O_3^{2-}$, 14383-50-7; $[Os(phen)_3]^{3+}$, 47837-53-6; $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, 84259-30-3; $[Os(5,6\text{-}Me_2phen)_3]^{3+}$, 136174-22-6; $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, 70101-70-1; $[Os(phen)_3]Cl_2$, 73466-62-3; $[Os(5,6\text{-}Me_2phen)_3]Cl_2$, 136174-23-7; $[Os(5\text{-}Cl\text{-}phen)_3]Cl_2$, 136174-24-8; $[Os(4,7\text{-}Me_2phen)_3]Cl_2$, 136174-25-9.

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A New Reaction Pathway for the Geometrical Isomerization of Monoalkyl Complexes of Platinum(II): Kinetic Behavior of *cis*-[Pt(PEt₃)₂(neopentyl)Cl]

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The title complex converts spontaneously into its trans isomer in protic and in some polar aprotic solvents. The process can be easily followed by ^1H and ^{31}P NMR spectroscopy and, in transparent solvents, by conventional spectrophotometric techniques. In 2-propanol there are two reaction pathways. The first is controlled by solvolysis and implies the formation of and the rapid cis-to-trans conversion of a cationic $[Pt(PEt_3)_2(neopentyl)(S)]^+$ (S = 2-propanol) intermediate. At 298.16 K, $k_i = 11.7 \times 10^{-3}$ s^{-1}, $\Delta H^* = 60.7 \pm 0.7$ kJ mol^{-1}, and $\Delta S^* = -78 \pm 3$ J mol^{-1} K^{-1}. By addition of chloride ion, at $[Cl^-] > 0.1$ M, the solvolysis is blocked and a new pathway becomes important with $k_i = 0.76 \times 10^{-3}$ s^{-1} at 298.16 K, $\Delta H^* = 100 \pm 2$ kJ mol^{-1}, and $\Delta S^* = +31 \pm 7$ J mol^{-1} K^{-1}. In dichloromethane at 298.16 K, $k_i = 0.82 \times 10^{-4}$ s^{-1}, $\Delta H^* = 108 \pm 3$ kJ mol^{-1} and $\Delta S^* = +32 \pm 9$ J mol^{-1} K^{-1}. The reaction is thought to proceed through the dissociative loss of a phosphine ligand, presumably that in the trans position to the alkyl group, and the conversion of the uncharged $[Pt(PEt_3)(neopentyl)Cl]$ 14-electron intermediate. The rate of isomerization is strongly accelerated by the presence in solution of very small amounts of the complex *cis*-$[PtMe_2(Me_2SO)_2]$, and it is shown that its catalytic efficiency depends on the extent of formation of a coordinatively unsaturated 14-electron $[PtMe_2(Me_2SO)]$ species. A mechanism for the catalyzed pathway is proposed.

Introduction

There is great chemical interest in understanding the way in which square-planar complexes of d^8 transition metals undergo geometrical isomerization. Indeed, the course of many reactions of these species, such as nucleophilic substitution, electron transfer, oxidative addition, reductive elimination, thermal decomposition, interaction with molecules of biological interest, and so on, is dictated by the geometry in the square-planar configuration.[1-4] Despite the fundamental importance of geometrical isomerization in the chemistry of d^8 metal ion compounds, very few mechanistic studies have been devoted to date to this subject.[5]

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During the last few years, we have studied in great detail the cis-to-trans isomerization of complexes of the type [$PtL_2(R)X$] (L = phosphine; R = phenyl or substituted aryl groups; X = halide ions) that, in nonpolar solvents, is promoted by the presence of catalytic amounts of free ligand or by photochemical activation[6] while, in protic solvents, it takes place "spontaneously". The pathways through which the conversion proceeds are obviously different in the three cases, but our attention was drawn particularly toward the "spontaneous" process, since the main features of the reaction mechanism involve dissociative loss of the coordinated halide group and the interconversion of two geometrically distinct 3-coordinate T-shaped cationic intermediates.[7] Such unsaturated 14-electron species, whose configurational stability has been supported by MO calculations,[8-10] offer a favorable low-energy reaction route not only for the geometrical conversion but also for a number of other fundamental processes, such as an alternative to the intermediacy of 4- and 5-coordinate species. Dissociative pathways in platinum(II) chemistry and the role of three coordinate intermediates have been recently reviewed.[11]

We have recently extended our studies to the reactions of some monoalkyl *cis*-[$Pt(PEt_3)_2(R)Cl$] (R = CH_3, C_2H_5, C_2D_5, *n*-C_3H_7, *n*-C_4H_9, $CH_2Si(CH_3)_3$) complexes whose rates and activation parameters have been measured in 2-propanol.[12] The ethyl, *n*-propyl, and *n*-butyl derivatives, in addition to spontaneous isomerization, undergo β-hydride elimination through a concurrent pathway, yielding *trans*-[$Pt(PEt_3)_2(H)Cl$] and olefins. The isomerization mechanism was assumed to be the same as that proposed in the case of the related aryl complexes. An incipient interaction of the β-hydrogens of the alkyl groups with the metal, in the transition state leading to the first platinum cation intermediate, accounts for the much higher reactivity (at least 3 orders of magnitude) of the complexes in which R = C_2H_5, *n*-C_3H_7, and *n*-C_4H_9 with respect to that of complexes containing alkyl groups with no β-hydrogens (CH_3 or $CH_2Si(CH_3)_3$). In this context we considered it worthwhile to extend these studies to the kinetic behavior of the complex *cis*-[$Pt(PEt_3)_2(CH_2C(CH_3)_3)Cl$] containing a neopentyl group that does not possess β-hydrogens. During this study we found that this complex exhibits a new reaction pathway for isomerization in aprotic solvents, involving the dissociative loss of a phosphine ligand as the rate-determining step. The complex *cis*-[$PtMe_2(Me_2SO)_2$] catalyzes the isomerization, and it is shown that its catalytic efficiency depends on the extent of formation of a coordinatively unsaturated 14-electron [$PtR_2(Me_2SO)$] species. A mechanism for the catalyzed pathway is proposed.

Experimental Section

***cis*-Dineopentyl(1,5-cyclooctadiene)platinum(II) (3)** and ***cis*-dineopentylbis(triethylphosphine)platinum(II) (4)** were prepared by following essentially the same procedure described in the literature.[13] The spectroscopic properties of the compounds obtained (IR stretching frequencies and ^1H and ^{31}P resonances) were exactly the same as those reported in the literature reference. The elemental analysis was consistent with the theoretical formulas.

The synthesis of ***cis*-chloroneopentylbis(triethylphosphine)platinum(II) (1)** by protonolysis from **4** required a strict control either of the amount of acid added (HCl) or of the reaction time, in order to avoid the preferential formation of unwanted side products such as the trans isomer of **1** and *cis*- and *trans*-[$Pt(PEt_3)_2Cl_2$]. Thus, *cis*-[$Pt(PEt_3)_2$(neopentyl)$_2$] (0.57 g, 1 mmol) in degassed dry diethyl ether was treated with 10 times a stoichiometric quantity of dry HCl in diethyl ether (23 mL, 0.44 M) at room temperature with magnetic stirring. The addition of acid was completed in less than 1 min, and the course of the reaction was monitored spectrophotometrically, following by means of a rapid scanning spectrophotometer the spectral changes of various samples taken up from the reaction vessel at various times. When the identity of successive spectra (after 10–15 min) indicated the end of the reaction, solid $NaHCO_3$ was added to the reaction mixture with vigorous stirring in order to neutralize the excess of unreacted HCl. The organic layer was transferred by using a Teflon cannula to a 250-mL round-bottomed flask in a rotatory evaporator where most of the solvent was evaporated. After a further spectrophotometric control, 15 mL of *n*-hexane was added to the ethereal solution, and the residual diethyl ether was removed under vacuum. Crystallization at −20 °C gave 0.06 g of a white compound identified as unreacted material. Successive evaporation to 3 mL and crystallization gave 0.24 g of *cis*-[$Pt(PEt_3)_2$(neopentyl)Cl]: mp 75–76 °C; ^{31}P NMR (C_6D_6, H_3PO_4 external reference) δ +13.99 ($^1J(PtP)$ = 1422 Hz, $^2J(PP)$ = 13.7 Hz), +4.09 ($^1J(PtP)$ = 4427 Hz); ^1H NMR (CD_2Cl_2, TMS internal reference) δ 1.055 ($-C(CH_3)_3$). Anal. Calcd for $C_{17}H_{41}ClP_2Pt$: C, 37.95; H, 7.68. Found: C, 38.02; H, 7.57.

***trans*-Chloroneopentylbis(triethylphosphine)platinum(II) (2).** A 0.1-g sample of the corresponding cis isomer **1** was dissolved in 10 mL of methanol and the solution was left to stand for 30 min. The residue obtained after evaporation of the solvent was crystallized from petroleum ether (40–60) to give 0.085 g of *trans*-[$Pt(PEt_3)_2$(neopentyl)Cl]: mp 46–47 °C; ^{31}P NMR (C_6D_6, H_3PO_4 external reference) δ +11.1 (t, 1:4:1, $^1J(PtP)$ = 3011 Hz); ^1H NMR (CD_2Cl_2, TMS internal reference) δ 1.040 ($-C(CH_3)_3$). Anal. Calcd for $C_{17}H_{41}ClP_2Pt$: C, 37.95; H, 7.68. Found: C, 37.86; H, 7.82. The same compound was prepared by metathetical exchange from *trans*-[$Pt(PEt_3)_2$(neopentyl)Br] (**5**). The stoichiometric amount of $AgNO_3$ (0.17 g) was added to a solution of **5** (0.58 g, 1 mmol) in an acetone–water (5:1) mixture (10 mL). After 30 min of magnetic stirring, AgBr was filtered off, LiCl (1.1 mmol) was added, and the residue obtained after evaporation of the solvent was crystallized from petroleum ether (40–60).

***trans*-Bromoneopentylbis(triethylphosphine)platinum(II) (5).** To a stirred suspension of *cis*-[$Pt(PEt_3)_2Cl_2$] (2 g, 4 mmol) in 25 mL of dry benzene at 0 °C was added slowly 8 mL (6.24 mmol) of an ethereal solution (0.52 N) of neopentylmagnesium bromide. The reaction mixture was stirred for 60 min and then carefully hydrolyzed with a cold aqueous solution of NH_4Cl. The dried organic layer was evaporated under vacuum to give an oil that solidified on cooling. Crystallization from methanol gave *trans*-[$Pt(PEt_3)_2$(neopentyl)Br] (1.5 g, 2.57 mmol): mp 68–69 °C; ^{31}P NMR (C_6D_6, H_3PO_4 external reference) δ +8.82 (t, 1:4:1, $^1J(PtP)$ = 2995 Hz); ^1H NMR ($CDCl_3$, TMS internal reference) δ 1.30 ($-C(CH_3)_3$). Anal. Calcd for $C_{17}H_{41}BrP_2Pt$: C, 35.06; H, 7.10. Found: C, 35.15; H, 7.42.

***cis*-Dimethylbis(dimethyl sulfoxide)platinum(II) (6)** was prepared by reacting *cis*-[$Pt(Me_2SO)_2Cl_2$] with $SnMe_4$ in dimethyl sulfoxide, following essentially the procedure described by Eaborn et al.[14] The compound has been characterized through elemental analysis, UV, IR, and ^1H NMR spectra: ^1H NMR ($CDCl_3$, TMS as internal reference) δ 0.60 (t, 1:4:1, 6 H, $^2J(PtH)$ = 80 Hz, $PtCH_3$), 3.10 (t, 1:4:1, 12 H, $^3J(PtH)$ = 13 Hz, $S-CH_3$); IR (CH_2Cl_2)ν(S=O) 1105, 1014 cm^{-1}.

Infrared spectra were taken on a Perkin-Elmer Model FT 1720 X instrument; ^1H NMR spectra were recorded at 400 MHz on a Bruker WH 400 spectrometer. Chemical shifts are reported in parts per million downfield from Me_4Si. ^{31}P NMR spectra were recorded on a Bruker WP 80 SY instrument, and the chemical shifts, in parts per million, are relative to external phosphoric acid. Microanalysis were performed by Bernhardt Microanalytishes Laboratorium.

All reactions involving organometallic compounds were carried out under prepurified nitrogen or welding-grade argon by using standard techniques for handling air-sensitive compounds. Ethereal solvents were dried by distillation from disodium benzophenone dianion. Grignard reagents were titrated by using the procedure of Eastham.[15] Methylene chloride for use in kinetic runs was distilled from barium oxide under nitrogen and then redistilled through a 60-cm platinum spinning band column, collecting the center cut for use. Anhydrous methanol was obtained by distillation of the reagent grade solvent over $Mg(OCH_3)_2$.

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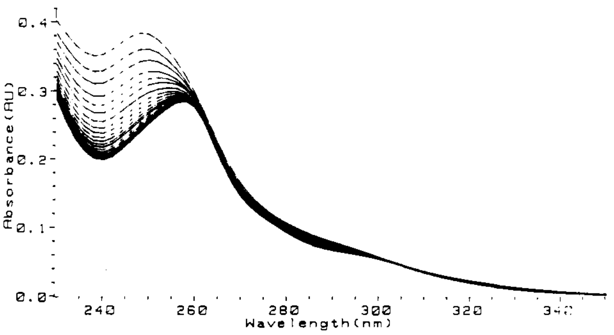

Figure 1. Spectral changes for the cis-to-trans isomerization of [Pt(PEt$_3$)$_2$(neopentyl)Cl] in 2-propanol at 298.16 K. Scanning time: 15 s.

2-Propanol was dried over magnesium ribbon and fractionally distilled in a 180-cm Dufton column. LiClO$_4$ "anhydrous" (99.8%) was purchased from K & K Fine and Rare Chemicals. Other compounds were the best available commercial materials and were used without further purification.

Kinetics. Isomerization reactions were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times in the range 300–220 nm or at a fixed wavelength, where the difference of absorbance was largest. The reactions were carried out in a silica cell in the thermostated cell compartment of a Cary 219 or a Perkin-Elmer Lambda 5 spectrophotometer with a temperature accuracy of ±0.02 °C. Isomerization was started by adding a weighed amount of a finely powdered sample of the cis complex to a prethermostated volume of solvent and shaking the solution rapidly. The kinetics of nucleophilic substitution on **1** with Br$^-$ and SCN$^-$ were followed on a rapid-scanning Hewlett-Packard Mod 8452 A spectrophotometer, following the procedure described above. The starting solid complex was rapidly added to a prethermostated standardized solution of the nucleophile. All the reactions obeyed a first-order rate law until well over 90% conversion and the rate constants k_{obsd} (s^{-1}) were obtained either graphically or from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)[\exp(-k_{\mathrm{obsd}}t)]$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 = absorbance after mixing of reagents, A_∞ = absorbance at completion of reaction). Activation parameters were derived from a linear least-square analysis of ln (k/T) vs T^{-1} data.

Results

Cleavage of the first Pt–C σ bond by HCl in *cis*-[Pt(PEt$_3$)$_2$(neopentyl)$_2$] gives the monoalkyl *cis*-[Pt(PEt$_3$)$_2$(neopentyl)Cl] complex. The synthesis is not as straightforward as it could appear, and when it is carried out by mixing dialkyl and acid in a 1:1 ratio, the yield of the resulting monoalkyl compound is very poor. The reason for this is that, under these circumstances, the electrophilic attack by the proton on the sterically hindered neopentyl group is relatively slow and other reactions become competitive, e.g. the cis–trans isomerization of the compound formed or the removal of the second neopentyl group with formation of *cis*- and *trans*-[Pt(PEt$_3$)$_2$Cl$_2$]. The use of an excess of acid (see Experimental Section) allows for a selective cleavage of the first alkyl group, and the shortening of the reaction time helps to increase the yield of the product. Crystallization is also a critical step, since the presence of traces of water provokes isomerization. The cis compound is easily converted to its trans isomer in protic solvents.

Satisfactory indications of the stereochemistry of the two monoalkyl isomers came from their IR and ^{31}P NMR spectra. The cis complex (**1**) shows two ^{31}P resonances (C$_6$D$_6$, H$_3$PO$_4$ external reference) at δ +13.99 (^1J(PtP$_A$) = 1422 Hz, ^2J(P$_A$P$_B$) = 13.7 Hz) and +4.09 (^1J(PtP$_B$) = 4427 Hz). The low coupling constant (^1J(PtP$_A$) is typical of a phosphorus atom trans to carbon in platinum complexes,[16] while the value of ^1J(PtP$_B$) of 4427 Hz is consistent with the presence of a weak trans donor ligand such as Cl$^-$. The trans complex shows only one phosphorus resonance (C$_6$D$_6$, H$_3$PO$_4$ external reference) as a 1:4:1 triplet at δ +11.1 (^1J(PtP) = 3011 Hz). Thus, isomerization in dichloromethane can be easily monitored at room temperature by ^{31}P NMR, through the decrease in the signals associated with **1** and the parallel and matching increase in the signal of the corresponding trans complex **2**. There is no evidence for the buildup in solution of any other intermediate species. This was confirmed by abstract factor analysis of the spectral changes in the UV region[17] (Figure 1), which is consistent with a smooth conversion of the cis compound into its trans isomer. The kinetics were followed by repetitive scanning of the spectrum in the UV region since the spectrophotometric technique offers the advantage over ^{31}P NMR, among others, of requiring far less complex for any run.

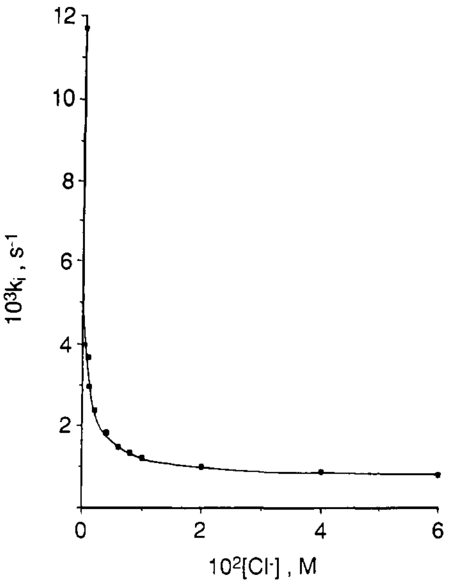

Figure 2. Effect of adding chloride ion on the rate of the cis-to-trans isomerization of [Pt(PEt$_3$)$_2$(neopentyl)Cl] in 2-propanol at 298.16 K.

Table I. Temperature Dependence of the Rate Constants for Uncatalyzed Cis-to-Trans Isomerization of [Pt(PEt$_3$)$_2$(neopentyl)Cl] in 2-Propanol[a] and in 2-Propanol Containing 0.1 M LiCl[b]

T, K	10^3k_i,[a] s^{-1}	10^3k_i,[b] s^{-1}
288.16	4.65	0.150
293.16	7.45	0.357
298.16	11.7	0.760
303.16	17.3	1.53
308.16	26.0	2.71
313.06		4.97
317.96		8.60

[a] $\Delta H^\ddagger$ = 60.7 ± 0.7 kJ mol^{-1}; $\Delta S^\ddagger$ = −78 ± 3 J mol^{-1} K^{-1}. [b] $\Delta H^\ddagger$ = 100 ± 2 kJ mol^{-1}; $\Delta S^\ddagger$ = +31 ± 7 J mol^{-1} K^{-1}.

(a) Isomerization in 2-Propanol. The plot in Figure 2 shows that addition of chloride ion in solution decreases the rate of isomerization of **1** in 2-propanol. It is possible to see that there is a curvilinear dependence of the rate on [Cl$^-$], which levels off to a limiting value at a chloride concentration greater than 0.1 M. This pattern of behavior is different from that usually found in similar systems, where a linear dependence of k^{-1} on [Cl$^-$] is observed and small amounts of halide are sufficient to stop the process completely. Thus, the complex isomerizes in 2-propanol through two concurrent pathways, one dependent on [Cl$^-$] and the other independent of chloride concentration. The nature of the reaction under saturation conditions was carefully controlled, to check that the process we were dealing with was still the cis-to-trans isomerization of **1**. Indeed, similar monoalkyl complexes containing alkyl groups with β-hydrogens (C$_2$H$_5$, *n*-C$_3$H$_7$, *n*-C$_4$H$_9$), when their geometrical isomerization is blocked by an excess of free halide, undergo a concurrent β-hydride elimination, yielding *trans*-[Pt(PEt$_3$)$_2$(H)Cl] and olefins.[12] The only product

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Table II. Rate Constants for the Substitution Reactions *cis*-$[PtPEt_3)_2(neopentyl)Cl] + Y^- \rightarrow$ *cis*-$[PtPEt_3)_2(neopentyl)Y] + Cl^-$ in 2-Propanol[a]

	[Y], M	10^3k_{obsd}, s^{-1}		[Y], M	10^3k_{obsd}, s^{-1}
Y = Br[a]	0.000	21.2[c]	Y = SCN[a]	0.000	21.2[c]
	0.001	19.2		0.001	20.9
	0.002	21.1		0.002	21.1
	0.004	20.8		0.004	21.1
	0.006	19.3		0.006	21.4
	0.008	18.9		0.008	21.2
	0.010	18.9		0.010	20.8

Y = SCN[b]

T, K	298.16	293.16	298.16	303.16	308.16
10^3k_1, s^{-1}	9.01	13.9	21.1	31.8	47.2

$\Delta H^* = 58.5 \pm 0.4$ kJ mol^{-1}; $\Delta S^* = -80 \pm 1$ J mol^{-1} K^{-1}

[a] At 298.16 K, $\mu = 0.02$ M ($LiClO_4$). [b] [SCN] = 0.01 M; $\mu = 0.02$ M ($LiClO_4$). [c] Rates of cis-to-trans isomerization at $\mu = 0.02$ M ($LiClO_4$).

Table III. Temperature Dependence of the Rate Constants for Uncatalyzed Cis-to-Trans Isomerization of $[Pt(PEt_3)_2(neopentyl)Cl]$ in Dichloromethane

T, K	10^5k_i, s^{-1}	*T*, K	10^5k_i, s^{-1}
288.86	2.09	308.16	37.3
293.16	3.89	313.56	61.1
298.16	8.23	318.56	150

$\Delta H^* = 108 \pm 3$ kJ mol^{-1}; $\Delta S^* = +32 \pm 9$ J mol^{-1} K^{-1}

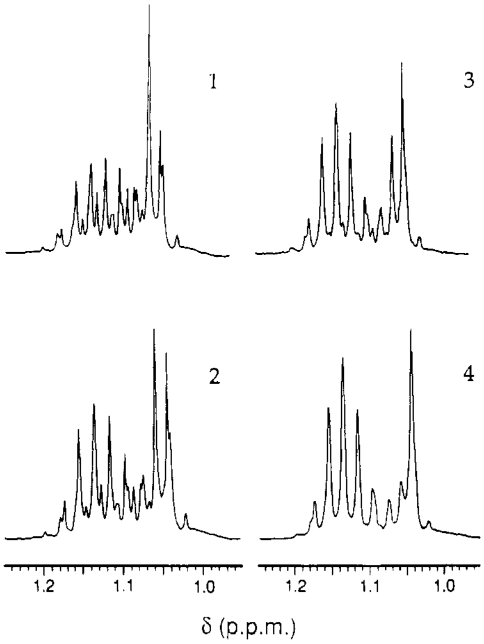


Figure 3. ^1H NMR spectra for the uncatalyzed cis-to-trans isomerization of $[Pt(PEt_3)_2(neopentyl)Cl]$ in CD_2Cl_2 at 293 K: (1) t = 10 min; (2) t = 150 min; (3) t = 300 min; (4) t = 600 min.

isolated from the reaction mixture was **2**, and there was no evidence of the presence of volatile products.

When the dependence of the rate of isomerization on $[Cl^-]$ was studied at constant ionic strength ($LiClO_4$), the decrease in rate was less pronounced than that shown in Figure 2 and the saturation conditions were reached at higher $[Cl^-]$, since the presence of an inert salt has an accelerating effect on the rate of isomerization and the value of the rate constant obtained is a compromise between opposing effects.

The values of the pseudo-first-order rate constants k_i (s^{-1}) for the cis-to-trans isomerization of **1** in 2-propanol and in 2-propanol containing excess of free chloride ion are set forth in Table I together with the associated activation parameters.

(b) Nucleophilic Substitution in 2-Propanol. The rates of the reactions

$$cis\text{-}[Pt(PEt_3)_2(neop)Cl] + Y^- \rightarrow cis\text{-}[Pt(PEt_3)_2(neop)Y] + Cl^- \quad (1)$$

$$Y^- = Br^- \text{ and } SCN^-$$

were studied in 2-propanol, in order to compare the rate of solvolysis with that of isomerization. The ionic strength was maintained constant at $\mu = 0.02$ M ($LiClO_4$).

The reactions with the two reagents showed different characteristics. When LiBr was used as a nucleophile, the removal of the coordinated chloride was followed by isomerization of the product *cis*-$[Pt(PEt_3)_2(neop)Br]$ into its trans isomer. It was possible to separate the values of the rate constants of the two consecutive processes by using either the method of the initial rate or a nonlinear regression analysis of the rate data with the expression

$$A_t = A''_\infty + (A_0 - A''_\infty)e^{-k_1t} + (A'_\infty - A''_\infty)(k_1/(k_2 - k_1))(e^{-k_1t} - e^{-k_2t})$$

with A_0 (absorbance at $t = 0$), A'_∞ (absorbance at the end of the first reaction), A''_∞ (absorbance at the end of the second reaction), k_1 (rate constant of the first process), and k_2 (rate constant of the second process) as the parameters to be optimized. The reaction of nucleophilic substitution (I° process) did not show any dependence on $[Br^-]$, within the range of concentrations examined, while the rate of the subsequent isomerization is clearly decreased, as found before for the corresponding chloride complex.

In the reactions with SCN^-, it was possible to avoid any uncertainty linked to the separation of rate constants of two consecutive processes since, in this case, the only reaction observed was the nucleophilic substitution to yield *cis*-$[Pt(PEt_3)_2(neop)SCN]$, the subsequent isomerization process being very much slower. The values of the pseudo-first-order rate constants k_{obsd} (s^{-1}) for the nucleophilic substitution of **1** in 2-propanol are listed in Table II. The process follows the well-known two terms rate law

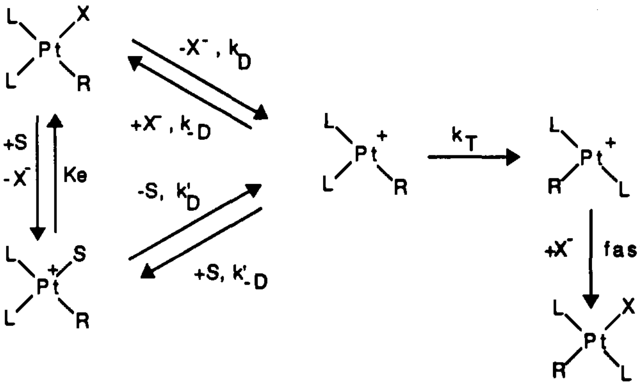
$$k_{obsd} = k_1 + k_2[Y] \quad (Y = Br^- \text{ or } SCN^-) \quad (2)$$

where the second-order rate constant k_2 (M^{-1} s^{-1}), which refers to the direct attack of the reagent on the square-planar substrate, does not make any significant contribution to the rate. A similar behavior has been already observed for organometallic compounds of this type.[7] The value of the rate constant for the solvolysis k_1, which represents the rate at which the solvent removes the chloride ion from the coordination sphere of the metal, is obtained as a statistical mean of the values in Table II. The activation parameters $\Delta H^* = 58.5 \pm 0.4$ kJ mol^{-1} and $\Delta S^* = -80 \pm 1$ J mol^{-1} K^{-1} were obtained from a study of the temperature dependence of the rate of solvolysis using thiocyanate as the entering nucleophile.

(c) Isomerization in Dichloromethane. The fact that isomerization of **1** proceeds in 2-propanol through a reaction pathway that is not affected by the presence in solution of large amounts of chloride ions suggested the possibility of the occurrence of the process even in aprotic solvents. Isomerization of **1** takes place easily in dichloromethane. The data for the temperature effect on the rate of this reaction are collected in Table III, and the derived activation parameters are $\Delta H^* = 108 \pm 3$ kJ mol^{-1} and $\Delta S^* = +32 \pm 9$ J mol^{-1} K^{-1}.

(d) Catalytic Effect of *cis*-$[PtMe_2(Me_2SO)_2]$ on Isomerization. When very small amounts of *cis*-$[PtMe_2(Me_2SO)_2]$ (**6**) are added in dichloromethane solutions containing *cis*-$[Pt(PEt_3)_2(neopentyl)Cl]$ (even in a ratio of 1:10) the conversion of the latter compound into its trans form is immediate, as demonstrated by the ^{31}P and ^1H NMR, IR, and electronic spectra. The catalytic species does not undergo any change during the course of the process. Indeed, it is possible to see by IR spectroscopy that the intensities and the positions of some characteristic peaks of a pure sample of **6** (at 1105 and 1014 cm^{-1}, respectively) remain unchanged upon addition of **1** in solution and after its conversion to the trans form **2**. This is revealed also by ^1H NMR experiments through the observation of the catalyst peaks at δ 0.70 (t, 1:4:1,

Scheme I



6 H, ^2J(PtH) = 78 Hz, PtCH_3) and at δ 3.17 (t, 1:4:1, 12 H, ^3J(PtH) = 13 Hz, S-CH_3).

However, the rate of the catalyzed process can be followed unambiguously by ^{1}H NMR spectroscopy only in the presence of a sufficient excess of added free dimethyl sulfoxide, which serves to slow down the velocity. The conversion can be monitored by the changes of the methyl peaks of **1** at various times as shown in Figure 3. The methyl resonances of the catalyst (see above) and that of the free sulfoxide come at higher and lower fields of the range shown, with intensities and positions that remain constant throughout the process. Once again, the proper kinetic study of the catalyzed isomerization has been carried out by conventional spectrophotometry, taking advantage of the transparency of the dichloromethane solvent in the region of the spectral changes. All reactions obeyed a first-order rate law, and the rate constants (Table SII) were independent of the concentration of the starting complex.

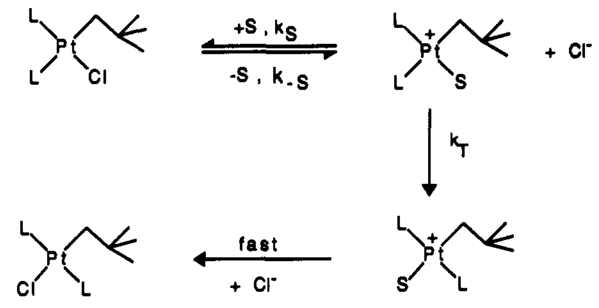
Discussion

(a) Uncatalyzed Isomerization. An essential feature of the mechanism of "spontaneous" isomerization of complexes of the type *cis*-[PtL$_2$(R)Cl] (R = alkyl or aryl) in protic solvents is the breaking of the Pt-Cl bond and the formation of a "cis-like" 3-coordinate intermediate [PtL$_2$(R)]$^+$ that interconverts into its trans analogue. The final attack of chloride ion on the latter species completes the process. This mechanism has been studied in great detail, and it has been shown that the interconversion of T-shaped 14-electron species is a key step in many fundamental organometallic reactions.[7-11] The mechanism of isomerization in protic solvents, in its more extended form, involves a solvolytic equilibrium between [PtL$_2$(R)Cl] and [PtL$_2$(R)S]$^+$ and the possibility for both species of forming a common T-shaped 3-coordinate intermediate whose fate depends on the efficiency with which it is intercepted by the reentry of either the halide ion (via k_{-D}) or the solvent molecule (via k'_{-D}) in competition with its conversion to the "*trans*-like" counterpart (k_T path) (see Scheme I). The rate expression derived for such a reaction scheme is

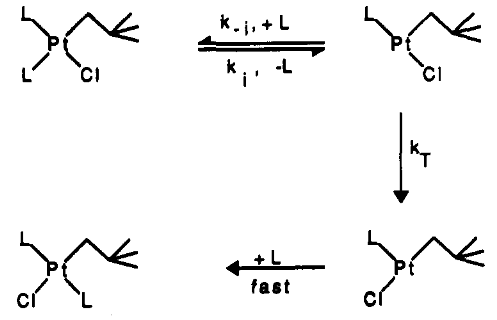
$$k_i = \frac{k_D[X^-] + k'_D Ke}{1 + (k'_{-D}/k_T)[S] + (k_{-D}/k_T)[X^-]}\,\frac{1}{Ke + [X^-]} \qquad (3)$$

A preequilibrium treatment such as that in Scheme I requires that solvolysis of *cis*-[PtL$_2$(R)X] is fast and reversible and isomerization of the solvento complex *cis*-[PtL$_2$(R)(S)]$^+$ (given by the rate term $k'_D/1 + (k'_{-D}/k_T)[S]$) is relatively slow ($k_S$ and $k_{-S} \gg k'_D/(1 + (k'_{-D}/k_T)[S])$; $Ke = k_S/k_{-S}$, where k_S and k_{-S} are the rates of solvolysis and anation, respectively). When the rates of solvolysis and anation are much slower than the rate of isomerization of the solvento complex (k_S and $k_{-S} \ll k'_D/(1 + (k'_{-D}/k_T)[S])$, the solvolytic path (via k_S) becomes the preferred route to the isomerization, the rates of isomerization and of solvolysis exhibit identical values, and both reactions assume the features of an associative process. Steric hindrance on the substrate is likely to favor such conditions since both the rates of bimolecular attack (k_S and k_{-S}) are decreased and the rate of conversion of the solvento intermediate ($k'_D/(1 + (k'_{-D}/k_T)[S])$) is accelerated.

Scheme II



Scheme III



Under these circumstances the isomerization is described by a simpler reaction scheme, Scheme II, which assumes as the rate-determining step the bimolecular attack of the solvent and the formation of a cationic solvento intermediate *cis*-[Pt(PEt$_3$)$_2$(neopentyl)(S)]$^+$, followed by its fast conversion into the trans analogue, which eventually takes up Cl$^-$ to yield *trans*-[Pt(PEt$_3$)$_2$(neopentyl)(Cl]. The rate law is given by the expression

$$k_i = \frac{k_S k_T}{k_T + k_{-S}[Cl^-]} \qquad (4)$$

which reduces to $k_i = k_S$ when $k_{-S}[Cl^-] \ll k_T$. Accordingly isomerization and solvolysis of *cis*-[Pt(PEt$_3$)$_2$(neopentyl)Cl] proceed at the same rate[18] and with very close values of activation parameters. The low value of the enthalpy of activation $\Delta H^\ddagger$ = 60.7 ± 0.7 kJ mol^{-1} and the largely negative entropy of activation $\Delta S^\ddagger$ = −78 ± 3 J mol^{-1} K^{-1} are indicative of an associative mode of activation.

A similar pattern of behavior is exhibited by another overcrowded complex, *cis*-[Pt(PEt$_3$)$_2$(mesityl)Br]. In this case, we were able to show[12] that the solvento complex *cis*-[Pt(PEt$_3$)$_2$(mesityl)(MeOH)]$^+$ isomerizes dissociatively at a much higher rate (k_i = 288 × 10^{-4} s^{-1}, at 303.16 K) than that with which it is formed by MeOH attack on the corresponding bromide complex (k_S = 1.9 × 10^{-4} s^{-1}, at 303.16 K), fitting the condition $k_S \ll k'_D/1 + (k'_{-D}/k_T)[S]$. We tried to prepare "in situ" *cis*-[Pt(PEt$_3$)$_2$(neopentyl)(S)]$^+$ (S = 2-propanol) by fast protonolysis of the dialkyl *cis*-[Pt(PEt$_3$)$_2$(neopentyl)$_2$] in 2-propanol with H$^+$BF$_4^-$, but the only product observed was always the trans-solvento derivative. This is a further indication of the rapidity of conversion of the cis-solvento intermediate. Summing up, Scheme I is a general reaction scheme that accounts for either associative or dissociative isomerization. Isomerization of mesityl and neopentyl halides exhibits associative characteristics in protic solvents mainly because of the low rate of bimolecular solvolysis and the comparatively fast isomerization of the solvento species *cis*-[PtL$_2$RS]$^+$. According to previous findings,[12] there is not much doubt that this latter process occurs dissociatively through the pathway shown

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[18] The values of the rates of isomerization in the neat solvent and of solvolysis at μ = 0.02 M (LiClO$_4$) are 0.0117 s^{-1} and 0.0211 s^{-1} respectively, at 298.16 K. The slight difference is accounted for by the accelerating effect of the inert salt added to adjust the ionic strength in the second process.

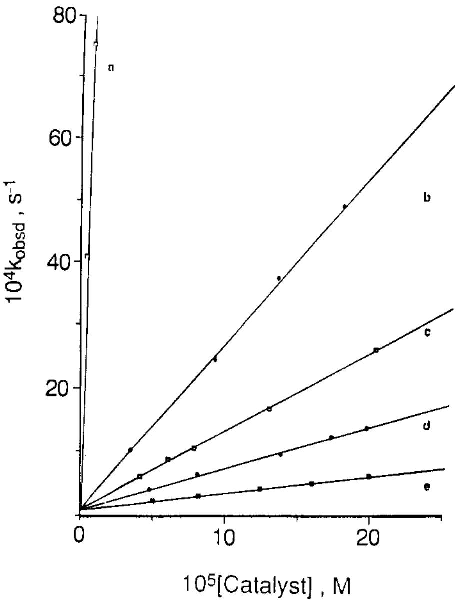


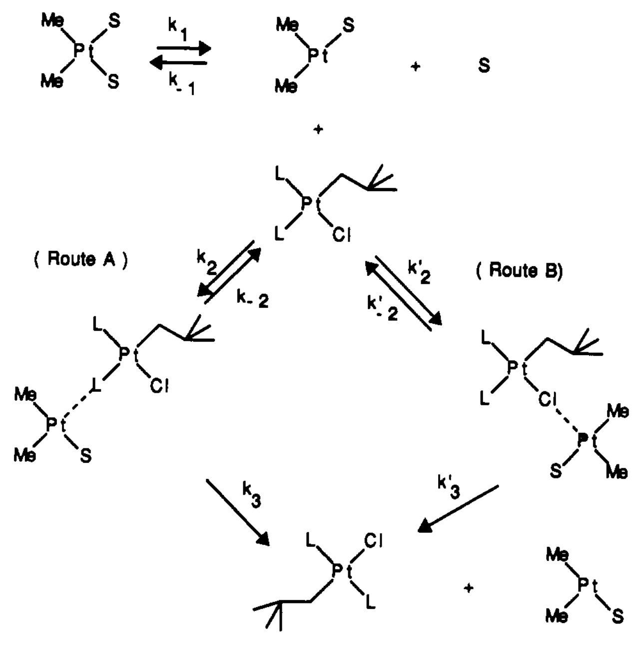
Figure 4. Catalytic effect of *cis*-[$PtMe_2(Me_2SO)_2$] on the rates of the cis-to-trans isomerization of [$Pt(PEt_3)_2$(neopentyl)Cl], in the presence of increasing amounts of added dimethyl sulfoxide (a → e) in CH_2Cl_2 at 298.16 K. [Complex] = 0.001 M. 10^3[Me_2SO], M: (a) 0.015; (b) 0.503; (c) 1.07; (d) 2.14; (e) 5.00.

in Scheme I (via k'_D) or more simply depicted in Scheme II (k_T).

As shown in Figure 2, the solvolytic pathway for isomerization suffers mass-law retardation by chloride ion, and when [Cl^-] is sufficiently high, an alternative isomerization pathway takes place. The most likely mechanism involves the dissociative loss of the phosphine in the trans position to the alkyl group and the geometrical conversion of an uncharged T-shaped 14-electron 3-coordinate intermediate, as shown in Scheme III. The dissociative mode of activation is supported by the high value of the enthalpy of activation, $\Delta H^* = 100 \pm 2$ kJ mol^{-1}, and the positive value of entropy of activation, $\Delta S^* = +31 \pm 7$ J mol^{-1} K^{-1}, which are in sharp contrast with the values obtained for the concurrent associative solvolytic pathway.

It is most likely that the same dissociative mechanism is operative in the aprotic dichloromethane solvent, where the activation parameters found for isomerization are $\Delta H^* = 108 \pm 3$ kJ mol^{-1} and $\Delta S^* = +32 \pm 9$ J mol^{-1} K^{-1}. The differences of rates observed on changing solvent seem to stem entirely from the difference in the values of the enthalpy of activation. The dissociative loss of phosphine from an organometallic platinum(II) compound is not surprising and has been frequently assumed as a key step in many fundamental organometallic processes,[9,19] even though is the first time that it is evidenced in the isomerization of [$PtL_2(R)X$] complexes, as an alternative to the halide loss and the intermediacy of a cationic [$PtL_2(R)$]$^+$ intermediate. This can be due to a specific trans effect of the neopentyl group that is known to behave, in many cases, in a different way with respect to other alkyls, as for example the strictly similar (trimethylsilyl)methyl group. Thus, dineopentylbis(phosphine)platinum(II) complexes have been reported to undergo intramolecular aliphatic γ-C–H activation and transfer, generating 3,3-dimethylmetallacyclobutanes.[20] While a relative inertness of strictly similar silaalkyl systems was expected, the thermolytic rearrangement of *cis*-[$Pt(CH_2SiMe_3)_2L_2$] complexes, in contrast to their neopentylplatinum analogues, did not yield metallacycles, but resulted in quantitative rearrangement to a novel *cis*-[$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$] species.[21]

Scheme IV



(b) Catalyzed Isomerization. The electronic and ^1H NMR evidence clearly indicates that, in the presence of the catalyst *cis*-[$PtMe_2(Me_2SO)_2$], the changes that are observed and kinetically analyzed correspond to the conversion of **1** to **2**. The isomerization is seen as a single process, and there was no indication of the presence of significant concentrations of any intermediate species. The detailed kinetic study was carried out in dichloromethane solution and followed spectrophotometrically. This enabled the concentration of the reagents to be drastically reduced, and the kinetics were generally studied by using a large excess of complex with respect to the catalyst. In all cases, even when equimolar solutions of complex and of catalyst were reacted, the kinetics obeyed a first-order rate law.

The dependence of the rate on the concentration of catalyst, at various concentrations of added Me_2SO, is described by a family of straight lines with a finite intercept, independent of [Me_2SO], and slopes inversely proportional to [Me_2SO] (Figure 4). The form of the rate law that can be derived is

$$k_{obs} = a + b[C]/[S] \qquad (5)$$

where C is *cis*-[$PtMe_2(Me_2SO)_2$] and S is Me_2SO. The marked retardation of the catalytic effect by excess [Me_2SO] certainly indicates that the reaction occurs after dissociation of Me_2SO from *cis*-[$PtMe_2(Me_2SO)_2$]. This is not unexpected since we showed before[22] that dissociation of S in *cis*-[PtR_2S_2] (R = Ph or Me; S = sulfoxides or thioethers) is the dominant pathway in the ligand exchange reaction or nucleophilic substitution with a variety of entering groups in nonpolar solvents. Here too, dissociation of the starting complex is a prerequisite to the occurrence of the catalytic pathway. The catalytic species is indeed the coordinatively unsaturated T-shaped [PtR_2S] species, whose role is to assist the removal of either PEt_3 or Cl^- from the coordination sphere of *cis*-[$Pt(PEt_3)_2$(neopentyl)Cl].

The most likely mechanism is shown in Scheme IV, and it involves a preliminary dissociation of the bis(sulfoxide) square-

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planar complex to yield a coordinatively unsaturated 14-electron $[PtMe_2(Me_2SO)]$ species as a reaction intermediate. This strong electrophilic species is able to interact with the alkyl complex either by accepting a phosphine ligand released by the substrate (route A) or by interaction with a lone pair of the coordinated chloride (route B). In route A, the release of the phosphine yields the uncharged "cis-like" 14-electron 3-coordinate [PtL(R)Cl] intermediate. This latter easily interconverts into its "trans-like" analogue that eventually undergoes the reentry of L to yield *trans*-$[PtL_2(R)Cl]$, with a sequence of reaction steps like those described in Scheme III. Electrophilic removal of chloride and interconversion of a cationic $[PtL_2R]^+$ intermediate (route B) leads to the same final trans product. This is in agreement with the low energy barrier found for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt$,[8] Me_3Au,[9] or $Et_2(PEt_3)Pt$.[10] The mechanism leads to the rate expression

$$k_{\text{obsd}} = \frac{k_1}{k_{-1}}\left[\frac{k_2k_3}{k_{-2}+k_3} + \frac{k'_2k'_3}{k'_{-2}+k'_{-3}}\right]\left[\frac{\mathrm{C}}{\mathrm{S}}\right] \qquad (6)$$

which is consistent with rate law 5, a part from the constant term *a* (the value of the intercept in Figure 4), which represents the contribution of the uncatalyzed pathway to the overall process.

This mechanism is reminiscent of that proposed by Scott and Puddephatt[23] in the study of the methyl for chloro exchange reaction in $CDCl_3$ solution between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ to yield *trans*-$[Pt(SMe_2)_2MeCl]$ that occurs after preliminary dissociation of the dimethyl sulfide from the dialkyl compound to form a coordinatively unsaturated "cis-like" $[PtMe_2(SMe_2)]$ intermediate. This was borne out by the mass law retardation produced in the rate of exchange by addition of free SMe_2 in solution. A key step of the process is thought to be the attack of the electron-deficient $[PtMe_2(SMe_2)]$ species to either the chloride or the thioether groups bonded to $[PtCl_2(SMe_2)_2]$ to yield a μ-chloro- or μ-SMe_2-bridged adduct. Thus two reaction pathways for the breakdown of the adduct are feasible followed by fast readdition of thioether.

At this stage we are unable to establish whether both pathways in Scheme IV for uncatalyzed isomerization are operative or to infer which is the favored one. Perhaps a detailed investigation of catalyzed isomerization of similar substrates, where the halides or the σ-donor power of the group in trans to the phosphine is alternatively changed, could shed some light on the problem. However, we think that the most significant aspect of this work is the clear demonstration that an electron-deficient 3-coordinate species is acting as a catalyst of isomerization. This adds a new example to the growing list of reactions of d^8 transition-metal complexes in which such 14-electron species are implicated as key intermediates.[11] The use of *cis*-$[PtR_2S_2]$ complexes as precursors of potential catalysts in other processes, where the removal of a phosphine from the coordination sphere of a metal is a critical step, is being investigated.

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Supplementary Material Available: Tables SI and SII, giving primary kinetic data (2 pages). Ordering information is given on any current masthead page.

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Spectroscopy and Electrochemistry of U(IV)/U(III) in Basic Aluminum Chloride–1-Ethyl-3-methylimidazolium Chloride

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The redox chemistry of UCl_4 has been investigated in the solvent $AlCl_3$–1-ethyl-3-methylimidazolium chloride ($AlCl_3$–EMIC), a room-temperature ionic liquid. In basic solutions (<50 mol % $AlCl_3$) the reduction of U(IV) to U(III) on glassy carbon electrodes is reversible. Visible/near-IR spectroscopic data and potentiometric measurements for U(IV)/U(III) as a function of the basic composition of $AlCl_3$–EMIC indicate U(IV) and U(III) are both hexachloro anions. Diffusion coefficients were measured for the U(IV) and U(III) complexes by two methods. The values are comparable to those of transition-metal hexachloro anionic complexes in the same solvent, supporting the assignment of $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$.

Introduction

Mixtures of aluminum chloride and certain organic chlorides (1-butylpyridinium chloride (BPC) and 1-ethyl-3-methylimidazolium chloride (EMIC)) produce room-temperature ionic liquids which exhibit widely varying Lewis acid–base properties depending on their composition.[1] Ionic liquids containing greater than 50 mol % $AlCl_3$ are considered "acidic" because they contain the strongly Lewis acidic species $Al_2Cl_7^-$, whereas those that contain less than 50 mol % $AlCl_3$ are denoted as "basic" because they contain free chloride ion.

Basic $AlCl_3$–BPC and $AlCl_3$–EMIC have been used extensively to study the electrochemistry and spectroscopy of transition-metal,[2] lanthanide,[3] and actinide[4] chloride complexes. These ionic liquids do not undergo solvolysis reactions that are common in aqueous solutions, and they form chloride complexes more readily than in molecular solvents such as acetonitrile or methyl alcohol. The electrochemistry of U(IV) was examined in basic $AlCl_3$–BPC,

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