product formation, i.e., the $(CH_3)SiClF_3^-$ anion could not be formed in this fashion. A C_{2v} structure was found to be preferred for the $(CH_3)SiF_4^-$ anion, while no structural information could be extracted for the $(CH_3)_2SiF_3^-$ anion.

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Registry No. $(CH_3)SiF_4^-$, 44244-53-3; $(CH_3)_2SiF_3^-$, 51108-60-2; $(CH_3)SiF_3$, 373-74-0; $(CH_3)_2SiF_2$, 353-66-2; CsF, 13400-13-0.

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Autocatalysis: Yet Another Mechanism for Spontaneous Cis–Trans Isomerization of Square-Planar Platinum(II) Complexes

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A detailed knowledge of the mechanisms and factors influencing cis–trans isomerization of square-planar and octahedral complexes is of vital importance in homogeneous catalysis since critical steps such as oxidative addition, reductive elimination, and insertion are mostly stereospecific reactions.[1] In by far the majority of cases the latter two steps proceed only if the relevant molecules are in the cis position.[1] Thus, groups which are mutually trans to each other would have to rearrange before they can undergo insertion or reductive elimination.

Octahedral complexes isomerize by a mechanism usually containing a trigonal bipyramid–octahedral equilibrium.[2] In contrast, square-planar systems isomerize via quite a number of different mechanisms. Some of these reactions may be catalyzed by ligands such as phosphines, arsines, stibines, and amines through either a consecutive displacement or a pseudorotation mechanism, depending on the polarity of the solvent and the softness of the coordinated ligands.[3]

The uncatalyzed cis–trans isomerization of $PtRXL_2$ systems (R = alkyl, aryl, substituted aryl; X = halide; L = phosphine) was proposed to proceed through a three-coordinate intermediate, but this intermediate was later shown to be a four-coordinate solvated species.[4] The actual isomerization step is still not clear. On the other hand the spontaneous

$$cis\text{-}PtX_2L_2 \rightleftarrows trans\text{-}PtX_2L_2 \qquad (1)$$

(X = halide, L = phosphine) isomerization rate was found to increase as the polarity and thus the coordinating ability of the solvent decreases.[3] Since noncoordinating solvents cannot form solvated intermediates or act as catalysts in a consecutive displacement or pseudorotation mechanism, it appeared to us that yet another mechanism was operative in this system. We have now investigated reaction 1 (X = I; L = PMe_2Ph, PEt_3; solvent = dimethylformamide, dimethyl sulfoxide, acetonitrile, benzene, toluene) kinetically and have found evidence for an autocatalytic mechanism.

Experimental Section

Complexes and Reagents. *cis*- and *trans*-PtI_2L_2[3] (L = PEt_3, PMe_2Ph) and $[(cod)Ir(phen)]ClO_4$[5] (cod = 1,5-cyclooctadiene, phen = phenanthroline) were prepared according to literature methods. All reagents and solvents were of AR grade.

Table I. Product and Absorption Maxima (nm) for Substrate and Product for the Cis-Trans Isomerization of PtI_2L_2 in Different Solvents

	L	
	PEt_3	PMe_2Ph
DMF product	two consecutive reactions	20% trans–80% cis eq[b]
λ_{max}(substrate)	cis 355; trans 335, 284	cis 353; trans 331, 288
λ_{max}(product)		352
λ_{diff}[a]	290	290
benzene product	100% trans	100% trans
λ_{max}(substrate)	cis 261; trans 337, 285	cis ...; trans 332, 292
λ_{max}(product)	337, 285	332, 292
λ_{diff}	290	300
toluene product	100% trans	100% trans
λ_{max}(substrate)	cis ...; trans 335	cis 363; trans 331, 292
λ_{max}(product)	335	331, 292
λ_{diff}	300	300
CH_3CN product	90% trans–10% cis eq	10% trans–90% cis eq
λ_{max}(substrate)	cis 352; trans 334, 283	cis 352; trans 332, 288
λ_{max}(product)	334, 280	348
λ_{diff}	284	290
Me_2SO product	80% trans–20% cis eq	20% trans–80% cis eq
λ_{max}(substrate)	cis 352; trans 334, 284	cis 351; trans 331, 288
λ_{max}(product)	340, 283	350, 287
λ_{diff}	284	290

[a] Wavelength of maximum difference in absorbance between substrate and product. [b] eq = equilibrium.

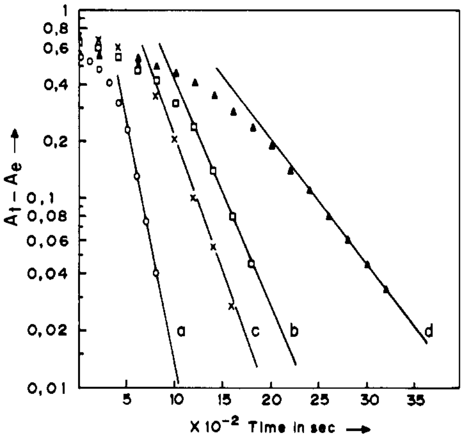

Figure 1. log ($A_t - A_e$) vs. time for reaction 1 (*trans*-$PtI_2(PMe_2Ph)_2$ substrate) in DMF at 50 °C: (a) under an N_2 atmosphere, k_{obsd} = 5.78 × 10^{-3} s^{-1}; (b) under an O_2 atmosphere, k_{obsd} = 2.89 × 10^{-3} s^{-1}; (c) under an O_2 atmosphere and in the presence of 2.1 × 10^{-4} M $n\text{-}Bu_4NI$, k_{obsd} = 3.61 × 10^{-3} s^{-1}; (d) under an N_2 atmosphere and in the presence of 0.2 × 10^{-4} M $[(cod)Ir(phen)]^+$, k_{obsd} = 1.31 × 10^{-3} s^{-1}.

Kinetics. $(cod)Ir(phen)^+$ is dioxygen sensitive, and reactions involving this complex were always executed under nitrogen atmosphere.

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Table II. Effect of [Complex], $[(cod)Ir(phen)]^+$, $[I^-]$, and Atmosphere (atm) on the Observed Rate Constants for the Cis–Trans Isomerization of $PtI_2(PMe_2Ph)_2$ at 50 °C in DMF

substrate isomer	atm	10^{-4}[complex], M	$10^{-4}[(cod)Ir(phen)]^+$, M	$10^{-4}[I^-]$, M	$10^{-3}k_{obsd}$, s^{-1} [a]
trans	O_2	1.1	0	0	2.98
		1.2	0	0	4.13
		2.5	0	0	2.98
		2.8	0	0	4.13
		3.4	0	0	2.89
	N_2	0.35	0	0	5.78
		0.5	0	0	5.25
		2.2	0	0	6.93
		2.5	0	0	5.78
		3.5	0	0	5.25
		5.06	0	0	6.03
		5.13	0	0	5.78
		2.2	0.2	0	1.31[b]
		2.4	1.0	0	0.24[b]
	O_2	2.6	0	2.1	3.61[c]
cis	O_2	1.0	0	0	3.40
		2.5	0	0	3.21
		4.8	0	0	2.89
	N_2	0.75	0	0	3.61
		1.5	0	0	4.44
		1.8	0	0	4.44
		4.5	0	0	5.77
		0.75	0.25	0	1.44[b]
		2.7	0.2	0	1.60[b]
		2.5	0.8	0	0.43[b]
		4.5	0	4.3	5.78[c]
		4.2	0	18	6.30[c]
		1.2	0	27	5.78[c]

[a] Calculated from the linear part of the plots in Figure 1. [b] Induction period lengthens. [c] No effect on induction period.

Dioxygen-free solutions were obtained by bubbling nitrogen through the solvent for approximately 2 h, and reaction solutions were prepared in a glovebag under a nitrogen atmosphere. The kinetics were followed on a Cary 15 spectrophotometer at the wavelengths shown in Table I as λ_{diff}.

Results and Discussion

Table I shows the end products and Uv–vis data for equilibrium 1 (X = I; L = PMe_2Ph, PEt_3) in different solvents. The typical semilog plots in Figure 1 illustrate the influence of O_2 and N_2 atmospheres, n-Bu_4NI, and $[(cod)Ir(phen)]ClO_4$ on reaction 1. k_{obsd} values, determined from the linear parts of the curves (Figure 1), are listed in Tables II and III.

The plots in Figure 1 exhibit induction periods typical of autocatalysis, which can be depicted by the parallel reactions 2 and 3, where the relative rate will determine the length of the induction period.

$$A \rightleftarrows B + C \tag{2}$$

$$A + C \rightleftarrows D + C \tag{3}$$

As mentioned earlier, it was previously found that the cis–trans isomerization reaction 1 are catalyzed[3] by phosphine (L = PMe_2Ph, PEt_3; X = Cl, Br, I) and by iodide (L = PMe_2Ph, PEt_3; X = I). Dissociation of iodide or phosphine from PtI_2L_2 could therefore give rise to reactions 2 and 3 (A = *cis*- or *trans*-PtI_2L_2, C = I^- or L, D = *trans*- or *cis*-PtI_2L_2) and consequently an induction period.

From Figure 1 and Tables II and III it is clear that addition of n-Bu_4NI to the reaction solution has no effect on either the reaction rate or the induction period, ruling out autocatalysis by iodide ions. On addition of catalytic amounts of PEt_3 or PMe_2Ph which are known to catalyze reaction 1 (L = PEt_3 or PMe_2Ph, respectively) no induction period was observed.[3] Furthermore, addition of more or less stoichiometric amounts of $[(cod)Ir(phen)]ClO_4$ retards the reaction and lengthens the induction period. Since $[(cod)Ir(phen)]ClO_4$ binds phosphine strongly,[5] it acts as a phosphine "scavenger". The above data support phosphine dissociation from PtI_2L_2 followed by phosphine catalysis as the most viable mechanism for spontaneous cis–trans isomerization of PtX_2L_2.

Table III. Effect of $[(cod)Ir(phen)]^+$,[a] $[I^-]$,[b] and Solvent on the Observed Rate Constants[c] for the Cis–Trans PtI_2L_3 Isomerization under an N_2 Atmosphere

solvent	L	substrate isomer	temp, °C	added species	$10^{-3}k_{obsd}$, s^{-1}
Me_2SO	PMe_2Ph	cis	50		10.0
				$[(cod)Ir(phen)]^+$	0.92[e]
				I^-	11.8[f]
		trans	50		8.41
				$[(cod)Ir(phen)]^+$	1.65[e]
				I^-	9.12[f]
	PEt_3	cis	50		very slow
		trans	50		very slow
CH_3CN	PMe_2Ph	trans	50		6.66
				$[(cod)Ir(phen)]^+$	1.11[e]
				I^-	9.12[f]
		cis	50		OD change too small
	PEt_3	cis	50		very slow
		trans	50		very slow
benzene	PEt_3	cis	36		1.44[d]
	PMe_2Ph	cis	30		fast[d]
toluene	PEt_3	cis	36		0.72[d]
	PMe_2Ph	cis	30		5.78[d]

[a] Less than stoichiometric amounts. [b] More than stoichiometric amounts. [c] Calculated from the linear part of the plots in Figure 1. [d] The cis complexes were dissolved in a few drops of CH_2Cl_2 before solvent was added. n-Bu_4NI is insoluble in these solvents while $[(cod)Ir(phen)]ClO_4$ is insoluble in benzene. [e] Induction period lengthens. [f] No effect on the induction period.

Phosphine dissociation from PtI_2L_2 may be achieved in a number of ways.

(i) PtI_2L_2 Dissociation to a Three-Coordinate Species (Eq 4). First, this three-coordinate trigonal intermediate will most

$$PtI_2L_2 \rightleftarrows PtI_2L + L \rightleftarrows PtI_2L_2 \tag{4}$$

probably be very reactive and would be expected to pick up free phosphine rapidly to form the product. Since reaction scheme 4 entails two consecutive reactions, an induction period will not materialize. Second, three-coordinate Pt(II) and Pd(II) species have so far not been detected. Such an intermediate ($PtRL_2$) has been postulated for the spontaneous cis–trans isomerization of $PtRXL_2$, but, as was mentioned earlier, this was later found to be the solvent species $PtX(MeOH)L_2$.[4]

(ii) Substitution of Phosphine by Solvent. If this were the mechanistic pathway, then no induction period or reaction would be expected in the noncoordinating solvents benzene and toluene, which is not the case.

(iii) Dimer Formation. It was recently found that prolonged photolysis of a cis–trans mixture of $PdCl_2(P\text{-}n\text{-}Pr_3)_2$ yielded high concentrations of the dimer $Pd_2Cl_4(P\text{-}n\text{-}Pr_3)_2$ and P-n-Pr_3.[6] It is therefore feasible that both *cis*- and *trans*-PtI_2L_2 could form a dimeric (or even polymeric) species in the same manner, but in low concentrations since a NMR study of equilibrium 1 did not reveal any dimer (or polymer) species.[3]

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Attempts to isolate the dimer were unsuccessful.

The most probable mechanism for the spontaneous cis–trans isomerization of PtX_2L_2 therefore seems to be

$$2\,cis\text{- or }trans\text{-PtX}_2\text{L}_2 \rightleftarrows \text{Pt}_2\text{X}_4\text{L}_2 + 2\text{L} \qquad (5)$$

$$cis\text{- or }trans\text{-PtX}_2\text{L}_2 + \text{L} \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} trans\text{- or }cis\text{-PtX}_2\text{L}_2 + \text{L} \qquad (6)$$

Reaction 6 may proceed via either pseudorotation or consecutive displacement.[3] The observed reaction rate for the isomerization step (reaction 6) is thus a function of [L].[3] The induction period can be attributed to phosphine generation via reaction 5 and will exist until [L] reaches a stage where reaction 6 becomes much faster than reaction 5. Since phosphine acts as a catalyst, reaction 6 will be a pseudo-first-order reaction, and this explains why the semilog curves in Figure 1 become linear.

The rate law for reaction 6[3] (solvent = DMF, Me_2SO, CH_3CN) (see eq 7) predicts that the k_{obsd} values found for

$$k_{obsd} = (k_i + k_{-i})[\text{L}] \qquad (7)$$

the cis and trans substrates should be identical and that the rate should be first order in [complex]. From Tables II and III it can be seen that these k_{obsd} values are in fact comparable and independent of [complex]. For the solvents benzene and toluene $k_{-i} = 0$. Unfortunately [L] is not known, and the k_i values are thus not obtainable. The fact that reaction 6 is slower under an O_2 atmosphere can be attributed to free-phosphine oxygenation.

From the study of the photolysis of the cis–trans mixture of $PdCl_2(P\text{-}n\text{-}Pr_3)_2$,[6] it was not clear whether the isomerization results from the cis or trans isomer. Our present study requires that both isomers dimerize and that the cis isomer dimerizes faster than the trans isomer since the induction period for the trans substrate is longer. On the assumption that a two-step associative dimerization mechanism is operative, it can be shown that the trans dimer will be the product for both the cis and trans substrates.

The rate of the isomerization step (reaction 6) decreases with the polarity of the solvent (benzene > toluene > CH_3CN ~ Me_2SO > DMF) not only because this reaction is faster in nonpolar solvents but also most probably due to enhanced dimer formation and thus phosphine generation in nonpolar solvents, as is the case in the Ir(I)[7] and Rh(I)[8] systems.

Reaction 1 (X = I, L = PEt_3) in methanol exhibits no induction period.[3] This can be explained by the relative high polarity of the solvent preventing dimer formation.

Registry No. *cis*-$PtI_2(PEt_3)_2$, 35084-99-2; *trans*-$PtI_2(PEt_3)_2$, 15636-79-0; *cis*-$PtI_2(PMe_2Ph)_2$, 41119-52-2; *trans*-$PtI_2(PMe_2Ph)_2$, 41119-53-3; $[(cod)Ir(phen)]^+$, 48195-12-6.

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Synthesis and Characterization of Ni(II), Pd(II), and Pt(II) Complexes of $M'OS_3^{2-}$ (M' = Mo, W) and the Mixed-Ligand Compounds $[M(M'S_4)(S_2CNEt_2)]^-$

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A number of studies on the complexes formed by $M'X_4^{2-}$ ions (M' = Mo, W; X = O, S, Se, or a mixture of them) with first-row transition-metal ions have been published in the last few years.[1-3] As these materials involve three or four transition elements bound to each other through sulfur bridges, they have become interesting to groups studying metal–metal bonding and the effects of bridging ligands on such interactions, especially those between different transition metals.

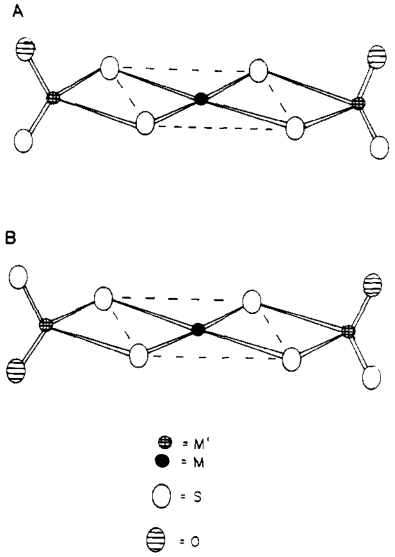

Figure 1. Possible structures of $M(M'OS_3)_2^{2-}$ complexes: A, cis isomer; B, trans isomer.

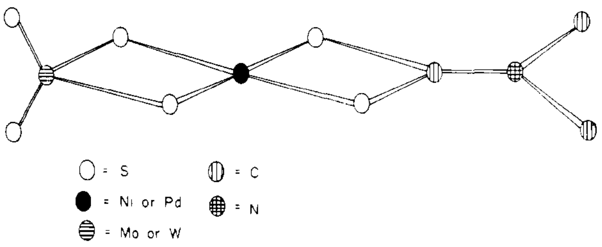

Figure 2. Proposed structure of $[M(S_2CNEt_2)(M'S_4)]^-$ complexes, where M = Ni or Pd and M' = Mo or W. Ethyl groups are represented by single carbon atoms.

We have previously reported a study of the Ni(II), Pd(II), and Pt(II) complexes of MoS_4^{2-} and WS_4^{2-}[4,5] and shown that their electrochemical behavior corresponds to sequential reduction localized at the central d^8 M(II) metal, with little influence on the part of the $M'S_4^{2-}$ ligands. Here we report the synthesis and characterization of the monooxo analogues of these species $M(M'OS_3)_2^{2-}$ and the mixed-ligand complexes $[M(M'S_4)(S_2CNEt_2)]^-$. The electrochemical properties of these materials will be discussed in a subsequent paper.[6]

Results and Discussion

I. Synthesis and Characterization of $M(M'OS_3)_2^{2-}$ Complexes. As earlier work had shown[4,5] a mixed CH_3CN–H_2O solvent system to be beneficial in the preparation of d^8 metal complexes of $M'S_4^{2-}$, we used this route to prepare the Ni(II) and Pd(II) complexes of the $M'OS_3^{2-}$ ions, as shown in eq 1.

$$\text{M(II)} + 2\text{M}'\text{OS}_3^{2-} \rightarrow \text{M(M}'\text{OS}_3)_2^{2-} \qquad (1)$$

The dianionic products were isolated as tetraalkylammonium

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