Table I. Rate Constants for Reactions of Intermediate with VO^{2+} ($[H^+] = 1.00$ M, $\mu = 1.00$ M, $T = 23.5$ °C)

10^3-$[VO^{2+}]_0$, M	10^4-$[MnO_4^-]_0$, M	Reaction II		Reaction II	
		k^2_{obsd}, s^{-1}	k_2, $M^{-1}\ s^{-1}$	k^3_{obsd}, s^{-1}	k_3, $M^{-2}\ s^{-1}$
20.2	1.48	0.66	32.4	0.180	441
	1.97	0.74	36.7	0.164	402
	1.97[a]	0.70	34.6	0.171	419
	1.97[b]	0.68	33.7	0.156	382
	2.95	0.60	29.5	0.146	359
	3.93	0.73	36.0	0.156	382
40.3	1.48	1.41	35.2	0.587	361
	1.97	1.22	30.2	0.524	323
	2.95	1.39	34.4	0.627	386
	3.93	1.27	31.2	0.559	344
			Av 33.4 ± 2.3		Av 380 ± 33

[a] $[VO_2^+]_0 = 0.20 \times 10^{-3}$ M. [b] $[VO_2^+]_0 = 1.00 \times 10^{-3}$ M.

postulated to proceed by means of an intermediate containing Mn(III), it is believed that the intermediate observed in the present study contains Mn(V). Under the reaction conditions of this study, the reaction of VO^{2+} with Mn(III) would take place much more rapidly with a complex H^+ dependency[4] and Mn(III) has an absorption maximum at 460 nm, with an extinction coefficient of 187 $M^{-1}\ cm^{-1}$.[5] Intermediates believed to contain Mn(V) were observed in the MnO_4^- oxidations of cinnamic acid[6] and crotonic acid[7] and these species absorbed at 410–415 nm. Thus, it appears that the Mn(VI) product formed by the initial reduction of MnO_4^- by VO^{2+} must react rapidly with additional VO^{2+} to yield the Mn(V)-containing intermediate. (ESR experiments might be helpful in indicating the presence of Mn(V)). It was proposed by Sutter et al., in the study of the $HClO_4$ decomposition of MnO_4^{2-}, that $H_2MnO_4^-$ may be formed.[8] It is possible that a rapid reaction of the type $HMnO_4^- + VO^{2+} + H_2O \rightarrow H_3MnO_4 + VO_2^+$ may occur; this process is similar to the reaction believed to occur in the oxidation of VO^{2+} by $HCrO_4^-$.[9]

The disappearance of the intermediate occurs by two distinct processes. The faster process (reaction II) is first order in $[VO^{2+}]$ and is independent of $[H^+]$. If the intermediate is written as Mn(V), this reaction sequence appears to be

$$\mathrm{Mn(V)} + VO^{2+} \xrightarrow{k_2} \mathrm{Mn(IV)} \xrightarrow{2VO^{2+}} \text{products}$$

Although, it is difficult to speculate on the types of Mn(IV) and Mn(V) species present since so little is known about them in acidic solutions,[10] the Mn(V) species in reaction II is most likely $H_2MnO_4^-$ and the Mn(IV) is probably $H_2MnO_4^{2-}$. This latter species has been postulated as being present in acidic Mn(IV) solutions.[11] The reduction of $H_2MnO_4^-$ to $H_2MnO_4^{2-}$ would require no change in coordination number and would be independent of H^+ concentration.

The slower reaction of the Mn(V) intermediate with VO^{2+} (reaction III) is more complex with a second-order dependence on VO^{2+} and takes place by both a hydrogen ion independent and an inverse H^+ dependent pathway. A mechanism for reaction III can be written as

$$\begin{array}{ll} HMn^{V} + 2VO^{2+} \rightarrow HMn^{III} + 2VO_2^+ & k_{30} \\ HMn^{V} \rightleftharpoons H^+ + Mn^{V} & K_{3H} \\ Mn^{V} + 2VO^{2+} \rightarrow Mn^{III} + 2VO_2^+ & k'_{3H} \\ Mn^{III} + VO^{2+} \rightarrow Mn^{II} + VO_2^+ & \text{fast} \end{array}$$

The inverse hydrogen ion dependence appears to implicate $H_2MnO_4^-$ as the Mn(V) species in this step. The value of $K_a(OMn(OH)_3)$ can be approximated as 10^{-2} M in keeping with the rule of Pauling[15] and k'_{3H} would be $1.5 \times 10^4\ M^{-2}\ s^{-1}$.

Other reaction schemes are also possible depending upon the nature of the initial Mn(V) species and upon whether or not the reaction proceeds by a single two-electron step or by two one-electron-transfer steps with the formation of a transient Mn(IV) species. The final reduction of Mn(III) would be expected to be rapid.[4]

Table II. Hydrogen Ion Dependency of the Rates of Reactions II and III (λ 410 nm, $[VO^{2+}]_0 = 20.2 \times 10^{-3}$ M, $[MnO_4^-]_0 = 3.93 \times 10^{-4}$ M, $\mu = 1.00$ M, $T = 23.5$ °C)

$[H^+]$, M	k^2_{obsd}, s^{-1}	k_2, $M^{-1}\ s^{-1}$	k^3_{obsd}, s^{-1}	k_3, $M^{-1}\ s^{-1}$
0.10	0.66	32.5	0.693	1686
0.20	0.52	25.6	0.390	965
0.40	0.71	35.2	0.255	625
0.50	0.66	32.5	0.213	521
0.60	0.61	30.4	0.166	408
0.80	0.65	32.5	0.171	419
1.00	0.73	36.0	0.156	382
		Av 32.1 ± 3.2		

Although the oxidation potentials for the Mn(III)/Mn(IV) and Mn(IV)/Mn(V) couples have not been measured in acidic media, Rosseinsky and Nicol have estimated the potential of the $Mn(III)/MnO^{2+}$ couple as −1.53 V and that of the MnO^{2+}/MnO_4^{3-} system as −3.66 V.[12] This latter value is probably too negative, since MnO_4^{3-} would readily oxidize water, so the potential of this system is probably closer to the value of −0.9 V found for the MnO^{2+}/MnO_4^{3-} couple in basic solution.[7] It would appear that both MnO_4^{3-} and MnO^{2+} are capable of oxidizing VO^{2+} if these potentials are nearly correct. The starting Mn(V) species could be $H_2MnO_4^-$ or H_3MnO_4 and the final Mn(III) species are Mn^{3+} and $MnOH^{2+}$. A change in coordination number from 4 to 6 must occur which partially explains the slowness of this reaction. The rate-determining step in most chromium(VI) oxidations is believed to be due to a change in coordination number from 4 to 6 ($HCrO_4^-$ to Cr^{3+}).[13,14]

Registry No. VO^{2+}, 18252-79-4; MnO_4^-, 14333-13-2; Mn(V), 20574-97-4.

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Preparation and Fluxional Properties of *cis*-Dichloro(sulfoxide)(olefin)platinum(II) Complexes

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During the course of an investigation of the interaction of chiral sulfoxide ligands with prochiral olefins coordinated to platinum(II), we had occasion to develop a direct, efficient

Table I. High-Temperature-Limit ^{1}H NMR Spectral Data of the *cis*-[Pt(DMSO)(olefin)Cl$_2$] Complexes[a]

Olefin	Temp, °C	δ_{S-CH_3}, ppm	J_{Pt-SCH_3}, Hz	$\delta_{olefin-H}$, ppm	$J_{Pt-olefin-H}$, Hz	$\delta_{olefin-CH_3}$, ppm	$^3J_{H-CH_3}$, Hz	J_{Pt-CH_3}, Hz
Ethylene	31	3.545	20.2	4.66	61.0			
Propene	50	3.53	21.0	4.1-5.1		2.066	6.2	45.7
		3.61	21.1					
1-Butene	40	3.53	20	4.04-5.05		1.29	8.6	
		3.59	20					
cis-2-Butene[d]	31	3.553[b]	21.8	4.1-5.1		1.95[b]	5.4	
		3.547	21.8			1.95	3.3	
trans-2-Butene[d]	31	3.48	20.5	4.9-6.0		1.98[c]	6.0	42.0
		3.66	19.9			2.03[c]	6.0	44.0

[a] At 100 MHz; CDCl$_3$ solvent; internal reference and lock TMS. [b] More abundant stereoisomer; relative abundance 3:1. [c] $^4J_{H-CH_3} \simeq$ 0.6 Hz. [d] The NMR spectrum is independent of temperature.

Table II. Low-Temperature-Limit ^{1}H NMR Spectral Data of the *cis*-[Pt(DMSO)(olefin)Cl$_2$] Complexes[a]

Olefin	Temp, °C	$\Delta G^\ddagger$,[d] kcal mol^{-1}	δ_{S-CH_3}, ppm	J_{Pt-SCH_3}, Hz	$\delta_{olefin-CH_3}$, ppm	$^3J_{H-CH_3}$, Hz	J_{Pt-CH_3}, Hz	$\delta_{olefin-H}$, ppm
Ethylene	−47		3.60	20.5				4.61; 4.68
Propene	−58	14.6 ± 0.3	3.50 3.61[b]	20.4 20.0[b]	2.07[b]	7.0[b]	45.5[b]	
			3.64[b] 3.68	20.0[b] 20.0	2.155	6.7	48.0	
1-Butene	−15	14.9 ± 0.3	3.49 3.60[c]	20.0 21.0[c]	1.32[c]	7.3		
			3.60[c] 3.65	20.0[c] 20.0	1.29	7.0		

[a] At 100 MHz; CDCl$_3$ solution; internal reference and lock TMS. [b] Most abundant stereoisomer; relative abundance ~2:1. [c] Most abundant stereoisomer; relative abundance ~3:1. [d] Determined approximately from $\Delta G^\ddagger = -RT \ln \pi(\Delta\nu)h/2^{1/2}kT$ using the S–CH$_3$ proton signals.

method of preparing *cis*-[Pt(sulfoxide)(olefin)Cl$_2$] complexes. This note describes this method which we believe is general, provided the sulfoxide is not excessively bulky and is soluble in water solution to the extent of about 10^{-2} M. The advantage of the method is that it obviates the necessity of isolating the sometimes elusive [Pt(sulfoxide)Cl$_3$]$^-$ ion.[1] We have found the method efficient for the *p*-tolyl methyl sulfoxide and dimethyl sulfoxide (DMSO) ligands but not for the bulky and water-insoluble *p*-tolyl isopropyl sulfoxide and *p*-tolyl *tert*-butyl sulfoxide ligands. We describe here the preparations of some DMSO complexes and the fluxional behavior of the coordinated olefins.

1. Preparations

A stirred dilute aqueous hydrochloric acid solution containing K$_2$[PtCl$_4$] and 1 equiv of DMSO under an atmosphere of ethylene gradually deposits the *cis*-[Pt(DMSO)(C$_2$H$_4$)Cl$_2$] complex in high yield and purity. High dilution inhibits the competitive formation of the very insoluble [Pt(DMSO)$_2$Cl$_2$] species,[2,3] but the acid concentration is critical, for excess acid leads to a slow (Pt-catalyzed) reduction of the sulfoxide and too little acid causes the deposition of platinum metal. The ethylene is rapidly replaced[4] by higher olefins in this complex and the derivatives containing propene, *cis*-2-butene, *trans*-2-butene, and 1-butene were readily isolated. All of these complexes are quite robust, they are nonelectrolytes in dichloromethane and acetone, and all show in CH$_2$Cl$_2$ solution an infrared S–O stretching frequency at around 1150 cm^{-1}, characteristic of S-bonded sulfoxides.[2,5] The cis configuration is assigned on the basis of the strong (thermodynamic) influence of the sulfoxide and olefin ligands.[1] This configuration was confirmed crystallographically for the styrene–platinum(II) derivative of an analogous sulfoxide.[6]

2. Fluxional Behavior

The (proton) NMR data for these complexes are summarized in Table I for the high-temperature limit, while those for the low-temperature limit are given in Table II. The reason for this differentiation is that some of the complexes were found to be fluxional.[7] Thus the ethylene complex shows a single sharp olefinic proton signal and a single sharp methyl proton resonance for the DMSO, both resonances having accompanying satellites due to ^{195}Pt coupling. As the temperature is lowered, the coupling is retained, but the olefin proton signal collapses and at about −47 °C gives two new resonances which are broadened by internal coupling (Table II). The methyl proton signals are invariant with temperature. The propene and 1-butene complexes are also fluxional but their behavior is more interesting. These two olefins are prochiral and hence, upon coordination, the two DMSO methyl groups are no longer equivalent, for they are diastereotopic. Moreover, two stereoisomers may exist depending on whether the vinylic substituent points at or away from the (cis) DMSO ligand (Figure 1). These two stereoisomers can be interchanged by partial or complete rotation about the olefin–platinum bond. Figure 2 shows the NMR profile of the propene complex as the temperature is varied. At high temperatures both the sulfur and olefinic methyl protons show a doublet with accompanying ^{195}Pt satellites. As the temperature is lowered, these signals individually collapse and then sharpen at −20 °C to generate, in each set of signals, a pair of doublets of unequal intensities. These, we believe, represent the two stereoisomers which are unequally populated. The 1-butene complex shows similar behavior. The approximate barriers ($\Delta G^\ddagger$) to rotation (or oscillation) for this and the propene complex are given in Table II. There appears nothing unusual about these values.[8]

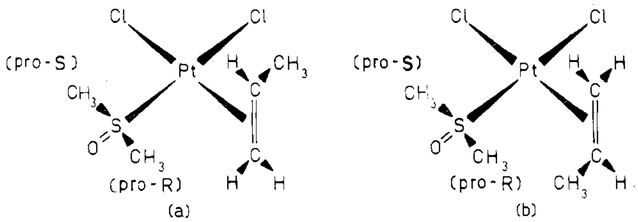

Figure 1. Structures of the two stereoisomers of *cis*-[Pt(DMSO)(*R*-C$_3$H$_6$)Cl$_2$].

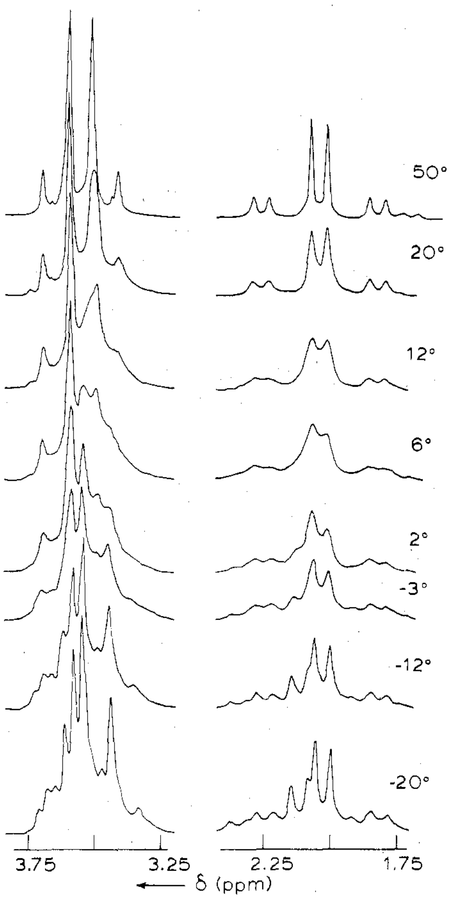

Figure 2. Temperature-variation profile of the proton NMR signals of *cis*-[Pt(DMSO)(C_3H_6)Cl_2] in $CDCl_3$. The downfield sets of resonances correspond to the DMSO protons; those to higher fields refer to the olefinic methyl protons.

Neither the *cis*-2-butene nor the *trans*-2-butene complex is fluxional below 50 °C. The *trans*-2-butene complex, in addition to the diastereotopically split methyl proton signals, shows two olefinic methyl proton doublets of equal intensity indicating that the vinylic methyl groups are experiencing different environments. Were the olefin rotating, the methyl proton chemical shifts would be averaged. The *cis*-2-butene ligand is not prochiral but can have two isomeric forms of the same kind as described for the propene system. Two sulfur methyl proton signals as well as two olefinic methyl proton doublets are observed. The corresponding signals are of unequal intensity and we ascribe them to the two isomers which, because these signals persist up to 50 °C, are not interconverting on an NMR time scale below this temperature.

3. Experimental Section

The variable-temperature spectra were carried out using a Varian HA 100 spectrometer. $CDCl_3$ was the solvent and TMS the reference.

***cis*-[Pt(DMSO)(C_2H_4)Cl_2].** Dimethyl sulfoxide (0.850 g) in 0.1 N HCl (50 ml) was added to a solution of $K_2[PtCl_4]$ (4.150 g) in 0.1 N HCl (75 ml). The resulting solution was immediately placed under an atmosphere of ethylene and vigorously stirred. A pale gray solid began to deposit within 1 h, and after 2 days, the product was collected and was washed with water and then with ether (2.80 g). The solid was taken up in a small volume of boiling acetone and then was filtered under gravity to remove small amounts of platinum metal. The slow addition of hexane to the warm solution afforded white needles of the pure complex (2.5 g).

Anal. Calcd for [Pt(C_2H_6SO)(C_2H_4)Cl_2]: C, 12.9; H, 2.7; S, 8.6; Cl, 19.1. Found: C, 13.0; H, 2.7; S, 8.8; Cl, 18.9.

***cis*-[Pt(DMSO)(C_3H_6)Cl_2].** Propene was bubbled through a solution of *cis*-[Pt(DMSO)(C_2H_4)Cl_2] (0.40 g) in acetone (16 ml) for 1 h. The solution was reduced to dryness under vacuum, and the oily residue was dissolved in CH_2Cl_2 (1.5 ml) containing ether (1 ml); then 30–60 °C petroleum ether (15 ml) was added very slowly to precipitate very pale yellow crystals. The collected product was washed with petroleum ether. The product (0.38 g) was recrystallized from CH_2Cl_2 (2 ml) containing ether (2 ml) by the slow addition of 30–60 °C petroleum ether (0.36 g).

Anal. Calcd for [Pt(C_2H_6SO)(C_3H_6)Cl_2]: C, 15.5; H, 3.1; S, 8.3; Cl, 18.4. Found: C, 15.9; H, 3.2; S, 8.1; Cl, 18.4.

***cis*-[Pt(DMSO)(*cis*-2-C_4H_8)Cl_2].** *cis*-2-Butene was bubbled through a solution of *cis*-[Pt(DMSO)(C_2H_4)Cl_2] (0.50 g) in acetone (11 ml) for 3 h. The solution was reduced to dryness and the crystalline residue was dissolved in CH_2Cl_2 (3 ml); then ether (2 ml) was added and precipitation was begun by the careful addition of 30–60 °C petroleum ether (10 ml). After cooling (4 °C; 15 h), the pale yellow needles were collected and were washed with petroleum ether. Recrystallization from CH_2Cl_2 (4 ml) containing ether (3 ml) by the careful addition of 30–60 °C petroleum ether (35 ml) afforded shiny, off-white flakes (0.22 g).

Anal. Calcd for [Pt(C_2H_6SO)(C_4H_8)Cl_2]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 17.7; H, 3.6; S, 8.2; Cl, 18.1.

***cis*-[Pt(DMSO)(*trans*-2-C_4H_8)Cl_2].** This complex was prepared by the method described for the *cis*-2-butene complex. Following the removal of the solvent, the crystalline residue was precipitated from CH_2Cl_2 (1 ml) followed by the successive slow addition of ether (2 ml) and 30–60 °C petroleum ether (5 ml). The product was recrystallized from CH_2Cl_2 (2 ml) containing ether (2 ml) by the slow addition of 30–60 °C petroleum ether (10 ml) (0.32 g).

Anal. Calcd for [Pt(C_2H_6SO)(C_4H_8)Cl_2]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 18.2; H, 3.4; S, 8.2; Cl, 17.9.

***cis*-[Pt(DMSO)(1-C_4H_8)Cl_2].** This complex was prepared by the method described for the *cis*-2-butene compound.

Anal. Calcd for [Pt(C_2H_6SO)(C_4H_8)Cl_2]: C, 18.0; H, 3.5; S, 8.0; Cl, 17.8. Found: C, 18.2; H, 3.5; S, 7.9; Cl, 17.8.

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Registry No. *cis*-[Pt(DMSO)(ethylene)Cl_2], 31902-28-0; *cis*-[Pt(DMSO)(propene)Cl_2], 39832-16-1; *cis*-[Pt(DMSO)(1-butene)Cl_2], 39722-88-8; *cis*-[Pt(DMSO)(*cis*-2-butene)Cl_2], 61128-89-0; *cis*-[Pt(DMSO)(*trans*-2-butene)Cl_2], 61176-42-9; $K_2[PtCl_4]$, 10025-99-7.

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Transition Metal Photoassisted Valence Isomerization of Norbornadiene. An Attractive Energy-Storage Reaction

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Olefins undergo a variety of facile thermal and photochemical reactions in the presence of transition metal complexes. Examples of such metal-assisted processes include cis–trans isomerization, hydrogen shifts, hydrogenation, and dimerization.[1] During an investigation into the role of transition metal compounds in the photoassisted reactions of strained olefins, we have observed that norbornadiene (NBD) undergoes efficient valence isomerization to quadricyclene (Q) in the presence of catalytic amounts of cuprous chloride (reaction 1).[2] The surprising absence of significant competing