in the zeolite framework due to the assumption of the equivalence of Si and Al ions and their environments,[16] and (3) the relatively small fraction of threefold axis scattering matter due to the zero-coordinate cation, make this determination the least definitive of the three, and worthy of further concern. However, the detailed agreement of the positional and thermal parameters of the zero-coordinate cation found here with those found in the previous two structures, coupled with newer results in dehydrated Tl_{12}-A,[17] affirms the present result and allows it to constitute a reconfirmation of the existence of zero coordination.

Conclusion

Zero-coordinate cations, as have been found in dehydrated K_{12}-A,[1] dehydrated $Rb_{11}Na_1$-A,[3,4] and now in dehydrated Cs_7K_5-A, occur when well-defined conditions involving the zeolite and the cations are satisfied. Briefly, zero coordination occurs when all of the coordination sites available to large cations in the zeolite framework are filled before all anionic charges of the framework are balanced. By difference, one cation per unit cell remains uncoordinated. This has been discussed earlier[3,4] in greater detail.

As a working definition, similar to the distance criterion used to decide whether a significant hydrogen bonding interaction exists, an ion is considered not coordinated to another ion if the distance between them exceeds the sum of their corresponding radii by more than 1.0 Å.[3] At least, the bond order is much less than one. On this basis, the ion at K(3) is termed zero coordinate, zero being the sum of integers, all zero, describing its bond orders to its nearest neighbors.[3] For this particular structure, the distance discrepancy, 1.75 Å, is substantially larger that the value of 1.0 Å used in the criterion.

It appears that zero-coordinate cations can be found in any dehydrated sample of $K_rRb_sCs_t$-A, where $r + s + t = 12$ for charge balance. As in $Rb_{11}Na$-A, zero coordination may persist when one or more smaller exchangeable cations are present per unit cell.

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Supplementary Material Available: Listings of the observed and calculated structure factors (supplementary table) (2 pages). Ordering information is given on any current masthead page.

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Asymmetric Synthesis. Interligand Chiral Recognition between Prochiral Olefins and a Chiral Sulfoxide Coordinated to Platinum(II)

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Abstract: A series of complexes of the type *cis*-[Pt((*S*)-TMSO)(olefin)Cl_2] where, TMSO is *p*-tolyl methyl sulfoxide, have been prepared and characterized. The object was to determine to what extent chiral sulfoxide ligands were capable of distinguishing the prochiral faces of coordinated olefins, and whether chiral sulfoxides might prove useful for metal assisted asymmetric synthesis. By a variety of techniques, the absolute configurations of the (coordinated) olefins were assigned, and the extent of chiral induction was determined quantitatively. The amount of chiral induction was found to be generally small. However, quite large discrimination was observed for the olefinic rotation barriers of the *R* and *S* olefin diastereomers; in all cases studied, the *S* olefin appeared to rotate much more quickly than the *R* olefin diastereomer. The reasons for this and other chiral effects are suggested and their significance to the design of metal complexes for asymmetric synthesis is discussed.

Transition metal complexes, because of their simplicity and ready susceptibility to subtle variation, provide attractive reagents for asymmetric syntheses of organic molecules.[1-3] Of particular note are the modified versions of Wilkinson's catalyst, for which very high optical yields for the catalytic hydrogenation of prochiral olefins have been reported.[4,5] Although symmetry dictates that any chiral reagent will distinguish between the enantiotopic groups or faces of a prochiral substrate,[6] the rational design of asymmetric systems which give high optical yields requires a fairly detailed understanding

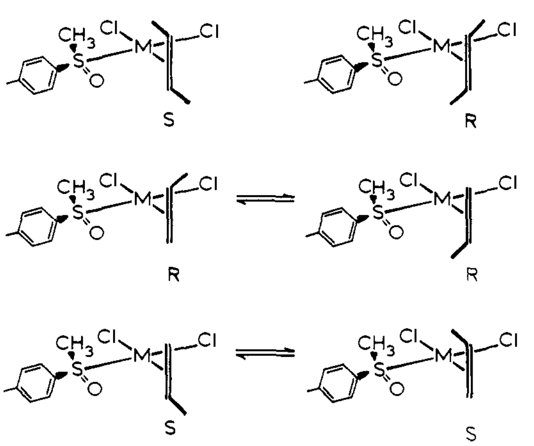


Figure 1. The various types of isomerism which may occur with the *cis*-[Pt((*S*)-TMSO)(olefin)Cl_2] complexes. The top diagrams show the *R* and *S* olefin diastereomers when the olefin is symmetrically trans-disubstituted. The lower sets of diagrams show, in addition to the diastereomers, the possible rotamers which may occur for a monosubstituted olefin. The absolute configuration of (free) (*R*)-TMSO is shown.

of the factors which are involved in the diastereotopic interaction.[7] This paper describes an investigation of some of the factors which may be involved in the diastereotopic discrimination of coordinated prochiral olefins. For this purpose we sought monoolefinic metal complexes which were conveniently stable and which were susceptible to variation of both the olefin and the other coordinated ligands. In a number of ways the monoolefin complexes of platinum(II) seemed to be the most promising for such a study, although even these are somewhat restrictive. It is known[8] that robust monoolefin complexes of platinum(II) are generally found only when the resultant species are either negatively charged or neutral and when the olefin is not coordinated trans to a ligand with a strong π-trans effect. In order to maximize the diastereotopic interaction between the chiral ligand and the coordinated prochiral olefin, it seemed desirable to have the two chiral centers coordinated cis to each other. Moreover, we might expect a more effective discrimination if the donor atom of the inducing ligand were a chiral center, and if each of its substituent groups were to exhibit distinctly different properties, either steric or electronic.

Practical matters restricted the chiral (inducing) ligand to an arsine, phosphine, or sulfoxide, unless extensive elaboration about other donor systems were contemplated. Of the three, the superficially studied platinum-olefin-sulfoxide complexes[9] seemed to present the most interesting species, particularly in view of the inertness of sulfoxides to racemization under a wide range of conditions.[10] Also, the quite large discriminations observed for the exchange of the benzylic protons of (*S*)-benzyl methyl sulfoxide[11] and for the addition of piperidine to (*R*)-*cis*-propenyl *p*-tolyl sulfoxide[12] suggested that the discriminatory power of coordinated sulfoxides might be quite large. Since, in general, sulfoxides coordinate via the sulfur atom to platinum(II)[13] and have a pronounced trans directing influence,[14] as do coordinated olefins, the conditions that the asymmetrically ligated atom be the donor atom and also that the chiral ligand and the prochiral olefin be coordinated cis to each other are met.

This paper describes the preparation and characterization of a series of *cis*-[Pt(sulfoxide)(olefin)Cl_2] complexes, where the sulfoxide is (*R*)-*p*-tolyl methyl sulfoxide ((*R*)-TMSO), and a study of the chiral discrimination provided by the sulfoxide ligand. The TMSO ligand was chosen because its sulfur methyl protons provide a convenient and sensitive probe for the determination of diastereomer ratios, as well as for other features of the system.

1. Stereochemistry

On coordination of a prochiral olefin to a platinum(II) center, the olefinic unit is chiral, and, in dilute noncoordinating solvents, the rate of racemization is slow at room temperature.[15] Thus, when the chiral (*R*)-TMSO ligand and a prochiral olefin, such as *trans*-2-butene, are coordinated to a metal atom, two diastereomers are formed (Figure 1). Although the *trans*-2-butene ligand can adopt only one distinct perpendicular orientation in each diastereomeric complex, a monosubstituted olefin, such as propene, can adopt two (Figure 1), as the vinylic substituent may point either at or away from the TMSO ligand. It is convenient for the present purpose to refer to these as *rotamers* in order to distinguish them from diastereomers. Rotamers can be interconverted by rotation about the olefin-metal bond axis without bond rupture, whereas diastereomers require the interchange of olefinic faces.

2. Preparations

A stirred, dilute aqueous hydrochloric acid solution containing $K_2[PtCl_4]$ and 1 equiv of (*R*)-TMSO under 1 atm of ethylene gradually deposits the corresponding off-white *cis*-[Pt(SO)(C_2H_4)Cl_2] complex in high yield. The conditions, however, are critical, for if the solution is not sufficiently dilute the insoluble [Pt(SO)$_2$$Cl_2$] complex is deposited, whereas if there is insufficient acid, platinum metal forms and if the acid concentration is too high, a very (water) soluble yellow material is formed which probably is the product of acid catalyzed reduction of the sulfoxide (oxygen abstraction) and the corresponding oxidation of platinum(II). The *cis*-[Pt(SO)(C_2H_4)Cl_2] complex is quite robust and provides a convenient starting material for the preparation of the substituted ethylene complexes, as olefin exchange occurs rapidly[16] in the presence of an excess of olefins which are not sterically hindering. Thus the propene, 1-butene, *cis*- and *trans*-2-butene, and isopropylethylene derivatives are formed by bubbling the appropriate olefin into a cooled acetone solution of the parent ethylene complex, while the styrene derivative results on dissolving the ethylene complex in the "neat" olefin. Less reactive, higher boiling olefins such as *trans*-3-hexene, *tert*-butylethylene, and *trans*-diisopropylethylene are most efficiently prepared by refluxing a CH_2Cl_2-acetone solution of the ethylene complex with the appropriate olefin in excess. The preparation of all these derivatives can be troublesome if the reactions are carried out in either alcohols or DMF or to a lesser extent in chlorinated solvents, particularly if the temperature is raised above about 50 °C, because of the production of a yellow side product, which we have not identified completely.[17] Moreover, crystallization is difficult with complexes which contain prochiral olefins, mainly because of the presence of two diastereomers. However, under appropriately controlled conditions, all of the diastereomeric complexes, except the propene and *trans*-2-butene derivatives, can be induced to transform into a single crystalline diastereomer. For the propene and *trans*-2-butene complexes, a 1:1 and a 3:2 ratio, respectively, of the two diastereomers were obtained as crystals under our conditions. These (second-order) asymmetric transformations, together with a regional rule, allowed us to determine the absolute configurations of the coordinated olefins; NMR was used to determine the diastereomer proportions quantitatively.

3. Characterization and Absolute Configurations

The *cis*-[Pt((*S*)-TMSO)(olefin)Cl_2][18] complexes are nonelectrolytes in both acetone and dichloromethane. In solutions of the latter, all the complexes exhibit a strong (stretching) vibration in the infrared at about 1150 cm^{-1}, which is consistent with sulfoxides coordinated to a metal via the sulfur atom.[13,19] The cis configuration and sulfur coordination of the TMSO ligand in the complexes *cis*-[Pt((*S*)-

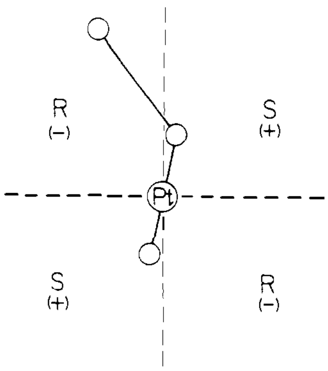


Figure 2. The quadrant rule used for the determination of the absolute configuration of the coordinated prochiral olefins. The horizontal dotted line represents the mean molecular plane of the complex and the sign of the contribution to the circular dichroism of the lowest energy d-d band of Pt(II) is shown; the *R* and *S* designations refer to the absolute configuration of the olefin. The sector occupancy of the styrene ligand is shown. Note that the Pt atom faces the observer.

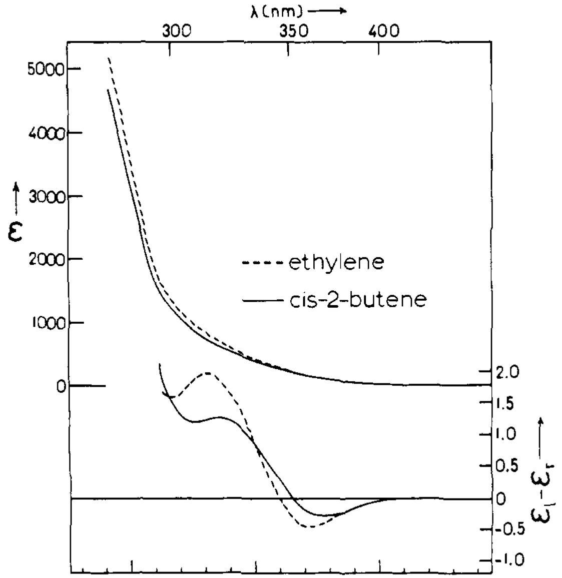


Figure 3. The absorption and circular dichroism of the ethylene and *cis*-2-butene complexes of *cis*-[Pt((*S*)-TMSO)(olefin)Cl$_2$], in chloroform solutions.

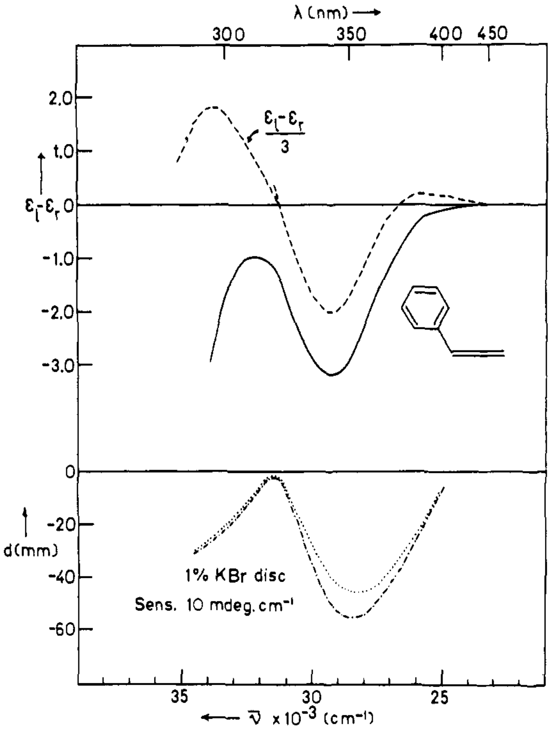


Figure 4. The circular dichroism of the *cis*-[Pt((*S*)-TMSO)((*R*)-styrene)Cl$_2$] complex. The lower two curves are solid state spectra referring to two crystalline modifications, white plates (···) and yellow blocks (- - -). The upper two curves are CHCl$_3$ solution spectra and refer to the initially dissolved (unequilibrated) complex (—) and the equilibrated complex (—).

TMSO)((*S*)-isopropylethylene)Cl$_2$] and *cis*-[((*R*)-styrene)-Cl$_2$] have been confirmed by absolute crystal structure determinations.[20]

A study[21] of an extensive series of platinum(II)-olefin complexes has suggested that the chirality of a coordinated prochiral olefin may be determined from the circular dichroism associated with the d-d transitions of the platinum chromophore. The rule states that for a prochiral olefin, oriented perpendicular to the mean molecular plane of the complex, an *R* configuration will generate negative circular dichroism in the lowest energy d-d band. Figure 2 shows this rule as a quadrant space demarcation together with the crystallographically determined occupancy of the styrene molecule in the *cis*-[Pt((*S*)-TMSO)((*R*)-styrene)Cl$_2$] complex.[20] The present complexes contain the chiral sulfoxide ligand as well as the chiral olefinic unit, both of which induce optical activity in the d-d transitions. This, however, does not appear to vitiate the rule.

Figure 3 shows the absorption and circular dichroism spectra of the *cis*-[Pt((*S*)-TMSO)(ethylene)Cl$_2$] and *cis*-[Pt((*S*)-TMSO)(*cis*-2-butene)Cl$_2$] complexes, for which the major source of dissymmetry is the chiral sulfoxide ligand. As expected, the two sets of spectra are nearly identical, each giving a minus-plus couplet under the featureless region of the d-d absorptions. Figure 4 shows the circular dichroism spectra of the *cis*-[Pt((*S*)-TMSO)((*R*)-styrene)Cl$_2$] complex. The two solid-state spectra refer to two different crystalline modifications, off-white plates and yellow blocks, the latter of which is the modification for which the structure was determined. Both the two solid state spectra and the (CHCl$_3$) solution spectrum obtained before (diastereomeric) equilibration give very similar differential absorptions. This we take as evidence of the diastereomeric identity of the solid and initially dissolved species, a matter which is confirmed (vide infra) by NMR. Moreover, the fact that the (crystallographically determined) (*R*)-styrene configuration gives negative circular dichroism for the lowest energy d-d transitions supports the applicability of the quadrant rule to these systems (Figure 2).[22]

The diastereomeric equilibrium, *cis*-[Pt((*S*)-TMSO)-((*R*)-olefin)Cl$_2$] $\rightleftharpoons$ *cis*-[Pt((*S*)-TMSO)((*S*)-olefin)Cl$_2$], is slow for all the complexes in the dilute (10^{-3} M) chloroform solutions used for the spectral measurements at 25 °C. The styrene complex, which is the most rapid, takes 6 days to reach equilibrium at 25 °C. Upon the addition of the common olefin, however, equilibration can be induced to occur rapidly, usually within 1 h. The equilibrium circular dichroism spectrum of the styrene complex, induced by the addition of a catalytic amount of styrene, is shown in Figure 4. The initial and equilibrium spectra of the 1-butene, isopropylethylene, propene, and *trans*-2-butene complexes are shown in Figure 5. The spectrum of the *tert*-butylethylene species (Figure 6) remained unchanged despite all attempts at equilibration.

An inspection of Figures 3, 4, 5, and 6 suggests that the preponderant olefinic configuration in both the solid and in chloroform solution is *R* for the styrene and *trans*-2-butene complexes, but is *S* for the 1-butene, isopropylethylene, and

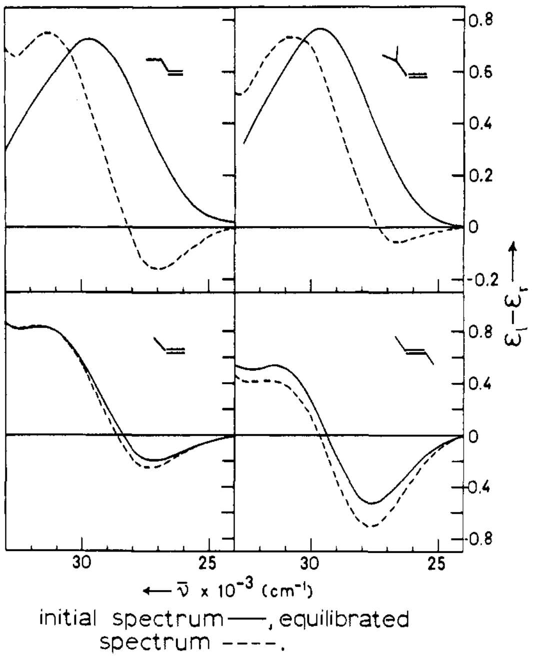


Figure 5. The circular dichroism spectra of the complexes *cis*-[Pt((*S*)-TMSO)(olefin)Cl_2], initially dissolved in $CHCl_3$ (—) and after equilibration (- - -). The olefin referred to is shown in the diagram.

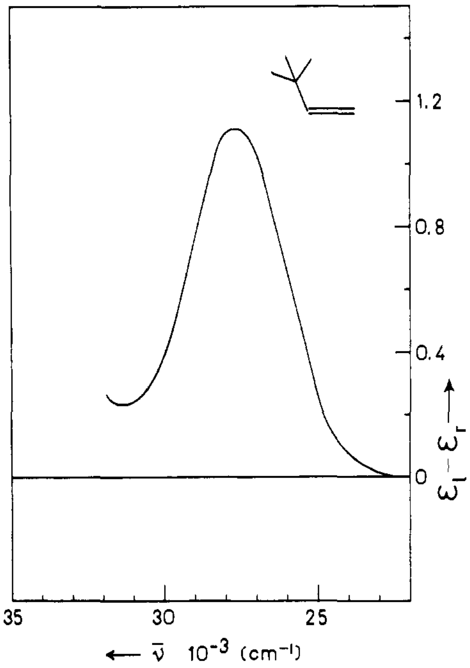


Figure 6. The circular dichroism spectrum of *cis*-[Pt((*S*)-TMSO)(*tert*-butylethylene)Cl_2] in $CHCl_3$ solution.

tert-butylethylene complexes. The propene complex, as we shall show, has a 1:1, *R*:*S* olefinic ratio in the solid, but equilibrates in solution to give a slight excess of the *R* olefin diastereomer. It is notable that its unequilibrated circular dichroism spectrum is nearly identical with that of the ethylene and *cis*-2-butene complexes (Figures 5 and 3), an expected result since the major source of dissymmetry in all three cases is the chiral sulfoxide ligand.

4. Diastereomer Proportions

In the concentrated chloroform solutions used for the NMR measurements (0.2–0.4 M), most of the complexes equilibrate rapidly and spontaneously at 25 °C. Because the velocity of this equilibration increases with increasing concentration, we assume that dimeric species are involved in the equilibration process.

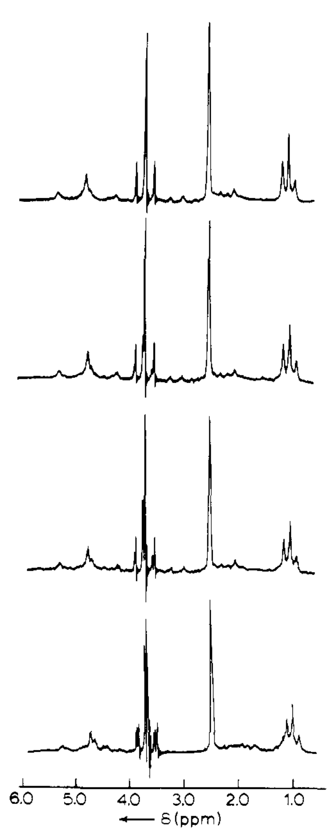


Figure 7. The NMR spectra of an equilibrating $CDCl_3$ solution of *cis*-[Pt((*S*)-TMSO)(1-butene)Cl_2] at 30 °C. The top spectrum refers to a freshly prepared solution and the lower spectra show the growth of the second diastereomer; the bottom spectrum was taken after 24 h.

If, however, the 0.2 M solutions are held at ~0 °C, the initial NMR spectra can be conveniently obtained. As an example of the equilibration, we show the NMR spectra of *cis*-[Pt((*S*)-TMSO)(1-butene)Cl_2] (0.2 M) in chloroform at 31 °C and the changes which occur over the 24 h required for equilibration (Figure 7). It is notable that the initial spectrum shows a single sharp methyl proton signal at δ 3.68 split by ^{195}Pt (J_{Pt} = 20.2 Hz) and a sharp *p*-tolyl methyl proton signal at δ 2.50, which shows no coupling to the ^{195}Pt nucleus. The olefinic protons (which are ^{195}Pt coupled) occur between δ 4.1 and 5.3. As diastereomeric equilibration proceeds, a new sulfur methyl proton signal develops at δ 3.72 (Figure 7). At 60 MHz, the *p*-tolyl methyl proton signal broadens, but is not resolved.

It is clear, therefore, that the crystalline 1-butene complex is a single diastereomer which, in solution, equilibrates to yield a diastereomeric mixture. That this is so was confirmed as follows. The NMR spectrum of a 0.2 M solution of the 1-butene complex in $CDCl_3$ at ~0 °C was run to observe the initial (NMR) spectrum; the solution was immediately diluted to 10^{-3} M (at which concentration the equilibration is slow) and the circular dichroism spectrum was measured. This spectrum and that observed by making up 10^{-3} M solution initially were identical. Moreover, when the NMR had indicated that equilibration had occurred, a constant circular dichroism spectrum was obtained. Thus the NMR gave the quantitative diastereomeric ratio, while the circular dichroism identified the chirality of the coordinated olefin.

In this way the diastereomeric ratios and the chiralities of the coordinated olefins were obtained for all of the complexes, except that the equilibration was achieved more expeditiously

Table I. Configurational Assignments of the *cis*-[Pt((*S*)-TMSO)(olefin)$\mathrm{Cl_2}$] Complexes

Olefin	Configuration of olefin in the crystal	Predominant diastereomer at equilibrium (%); 31 °C, $\mathrm{CDCl_3}$, 0.4 M
Propene	1:1, *R*:*S*	*R* (56)
1-Butene	*S*	*S* (55)
Isopropylethylene	*S*^{d}	*S* (66)
trans-2-Butene	3:2, *R*:*S*	*R* (66)
trans-3-Hexene	*a*	*R* (60)
trans-Diisopropylethylene	*a*	*R* (55)
Styrene	*R*	*R* (75)
tert-Butylethylene	*S*	*S* (100)^c
Ethyl vinyl ether	*b*	*R* (75)

[a] Not isolated as crystals. [b] Diastereomeric equilibration is "instantaneous" at all detectable concentrations. [c] May not be an equilibrium value, see text. [d] A recent absolute crystal structure determination of *cis*-[Pt((*S*)-TMSO)(isopropylethylene)$\mathrm{Cl_2}$] shows that this assignment is indeed correct; the isopropyl group points away from the sulfoxide. (N. C. Payne, private communication.)

by adding the common olefin. The results are collected in Table I together with those for the *trans*-3-hexene and *trans*-diisopropylethylene complexes, which were isolated as oils. The NMR spectra of these indicated that they were pure substances. The chirality of these coordinated olefins and the unstable ethyl vinyl ether complex was determined from the circular dichroism spectra on the plausible assumption (vide supra) that, for each compound, an equimolar mixture of the two diastereomers would give a circular dichroism spectrum similar to that observed for the 1:1 mixture of the propene complex. There is, however, a (NMR) complication with the monosubstituted olefins, namely, the possibility that each diastereomer could contain a pair of rotamers (Figure 1). In some cases this is so, but, as we show in the next section, the velocity of (rotameric) interconversion is rapid at 31 °C and an averaged NMR spectrum is obtained for each diastereomer. Even so, at 31 °C, depending on the chemical shifts, some of the signals are broadened. It is in order to obtain sharp signals that some of the NMR data shown in Table II refer to higher temperatures.

5. Fluxional Behavior

The ^{1}H NMR spectra of all the equilibrated complexes were measured at intervals between 50 and −60 °C, these being the practical limits determined by complex decomposition and solubility. The spectra of the ethylene, propene, 1-butene, and isopropylethylene complexes were found to be temperature dependent, in that changes characteristic of fluxional behavior were observed. In contrast, the NMR spectra of the styrene, *tert*-butylethylene, *cis*-2-butene, *trans*-2-butene, and *trans*-3-hexene complexes remained essentially constant over this range. We have established that the *trans*-2-butene and *trans*-3-hexene complexes, and probably also the *cis*-2-butene derivative, are not rotating on the ^{1}H NMR time scale at 50 °C. Equilibrated solutions of the *trans*-2-butene and *trans*-3-hexene complexes show somewhat complicated NMR patterns for the olefinic methyl proton resonances. An analysis of these shows clearly that in each diastereomer, the two olefinic methyl groups are in distinct chemical environments, and that the integrated intensities of the assigned signals correspond to the previously determined diastereomer ratios. Were these olefins rotating on the NMR time scale, the magnetic environments of the olefinic methyl groups would be rapidly averaged, giving rise to only one olefinic methyl resonance in the NMR spectrum of each diastereomeric complex (Figure 1). A summary of the NMR analysis is shown in Table II. The resolution of the olefinic methyl proton resonances for the *trans*-diisopropylethylene complex was insufficient for full analysis. However, in view of the bulk of the olefin and the static nature of the *trans*-2-butene and *trans*-3-hexene complexes, we think it reasonable to assume that the *trans*-diisopropylethylene complex is also static. The *cis*-2-butene species appears to contain two static rotamers; the olefinic methyl proton signals, which show, in addition to the normal coupling, diastereotopic splitting, occur as two sets of *unequal* intensities (~4:3), indicating that two locked rotamers exist for this

Table II. High Temperature Limit ^{1}H NMR Spectral Data of *cis*-[Pt((*S*)-TMSO)(olefin)$\mathrm{Cl_2}$] Complexes^a

Olefin	Temp, °C	$\delta_{\mathrm{SCH_3}}$, ppm, and olefinic configuration	$J_{\mathrm{Pt\,SCH_3}}$, Hz	$\delta_{\text{tolyl-CH}_3}$, ppm	$\delta_{\text{olefin-H}}$, ppm	$J_{\text{Pt-olefin-H}}$, Hz	$\delta_{\text{olefin-CH}_3}$, ppm	$^3J_{\mathrm{HCH_3}}$, Hz	$J_{\mathrm{PtCH_3}}$, Hz
Ethylene	31	3.70	20.4	2.49	4.64	64.2			
Propene	49	3.68 (*S*)	20.5	2.50	4.0–5.3		1.91	6.0	44.0
		3.72 (*R*)^b	20.8^b	2.48^b			1.80^{b,c}	7.0^b	*b,c*
1-Butene	48	3.68 (*S*)^b	20.2^b	2.50^b	4.1–5.3		1.03^b	7.4	0
		3.72 (*R*)	20.0	2.48			*c*	*c*	0
cis-2-Butene^f	31	3.787	20.7	2.49	4.0–5.9		1.91	6.5	41.0
		3.787	20.7	2.49			1.855^e	6.3^e	40.5^e
trans-2-Butene^f	31	3.70 (*S*)	21.0	2.49	4.8–6.3		1.832, 2.228	6.4, 6.0	45.0, 45.0
		3.77 (*R*)^b	20.0^b	2.46^b			1.576,^{b}	6.0,^{b}	45.0,^{b}
							2.020^b	6.0^b	45.0^b
Styrene^f	31	3.54 (*R*)^b	21.0^b	2.355^b	4.1–5.6				
		3.74 (*S*)	16.0	2.580					
tert-Butylethylene^f	31	3.68 (*S*)	21.0	2.51	4.2–5.6	011.07		0	
trans-3-Hexene^f	31	3.70 (*S*)	20.8	2.48^d	4.6–5.2		0.96, 1.00	7.0, 7.0	0
		3.76 (*R*)^b	20.0^b	2.46^d			0.89,^{b} 1.30^b	7.0,^{b} 7.0^b	0
Isopropylethylene	49	3.68 (*S*)^b	20.5^b	2.50^b	4.1–5.2		1.014	6.8	0
		3.72 (*R*)	20.0	2.48			0.981	6.7	0
trans-Diisopropylethylene	31	3.51 (*R*; *R*)	20.8	2.47	4.0–5.9				
		3.57 (*S*; *S*)	20.0	2.47					
Ethyl vinyl ether	31				*h*		1.447	7.0	0
							0.942^b	7.2^b	0

[a] 100 MHz, $\mathrm{CDCl_3}$ solvent, internal reference and lock $\mathrm{Me_4Si}$, complexes equilibrated at 31 °C. [b] More abundant diastereoisomer. [c] Resonance near coalescence. [d] Shoulder. [e] More abundant rotamer. [f] The spectrum is temperature independent. [g] Complex patterns. [h] Extensive overlap between S–$\mathrm{CH_3}$ and O–$\mathrm{CH_2}$ and olefinic protons.

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

Olefin	Temp, °C	$\Delta G^{\ddagger}$, kcal mol^{-1}	δ_{SCH_3}, ppm, and olefinic configuration	J_{PtSCH}, Hz	$\delta_{tolyl-CH_3}$, ppm	$\delta_{olefin-H}$, ppm	$\delta_{olefin-CH_3}$, ppm	$^3J_{HCH_3}$, Hz	J_{PtCH_3}, Hz
Ethylene	−30		3.72	20.5	2.49	3.1–5.4			
Propene	−18	14.6 ± 0.3	3.73 (*S*)	21.5	2.53 (*S*)	4.0–5.5	1.89 (*S*)	5.7	44.0
			3.74 (*R*)[b,c]	21.0[b]	2.50 (*R*)[b]		1.63 (*R*)[b,c]	6.2[b,c]	46.0[b,c]
			3.78 (*R*)[b]	20.0[b]			2.04 (*R*)[b]	6.2[b]	44.0[b]
1-Butene	−23	14.7 ± 0.3	3.71 (*S*)[b]	21.0[b]	2.53 (*S*)[b]	4.0–5.5	0.996 (*S*)[b]	7.0[b]	
			3.73 (*R*)[c]	20.0	2.50 (*R*)		0.855 (*R*)[c]	8.0[c]	
			3.78 (*R*)	20.0			1.320 (*R*)	7.4	
Isopropylethylene	−12	14.0 ± 0.3	3.70 (*S*)[b]	20.7[b]	2.49 (*S*)[b]	4.1–5.1	*d*	*d*	0
			3.74 (*R*)	~20.5	2.47 (*R*)		*d*	*d*	0
			3.76 (*R*)[c]	~20.5					

[a] 100 MHz, CDCl$_3$ solvent, internal reference and lock Me$_4$Si, complexes equilibrated at 25 °C. [b] More abundant diastereoisomer. [c] More abundant rotamer. [d] Extensive overlap. [e] Determined approximately from $\delta G^{\ddagger} = -RT \ln (\pi(\delta\nu)h/\sqrt{2}\,kT)$ using the S-CH$_3$ signals.

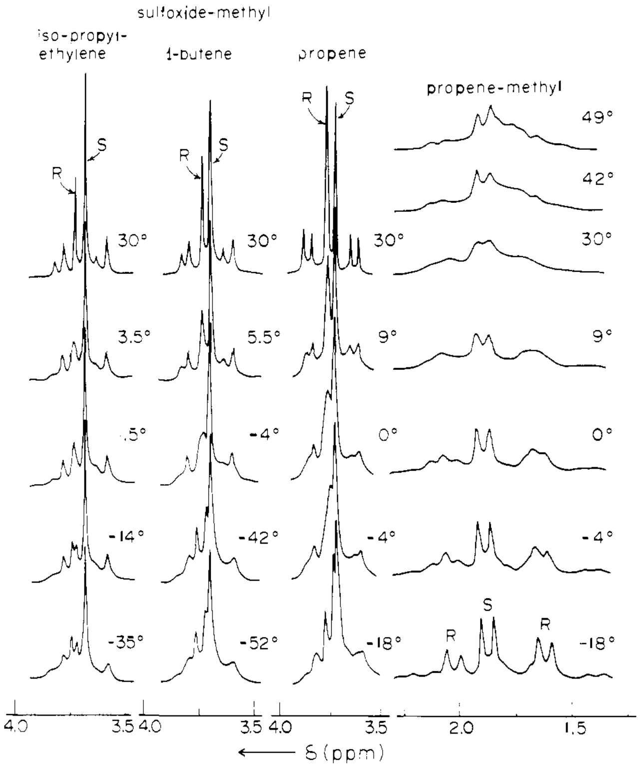


Figure 8. The NMR temperature profiles of selected regions of the spectra of the equilibrated complexes *cis*-[Pt((*S*)-TMSO)(olefin)Cl$_2$]. The various olefins studied and the regions of the spectra are shown.

complex (Table II). One perplexing feature of this system, however, is that, even at 100 MHz we were unable to observe the expected splitting of either the sulfur or *p*-tolyl methyl proton signals.[23] The temperature independence of the styrene species does not allow for a conclusion to be drawn about the fluxional nature of the olefin.

The propene, 1-butene, and isopropylethylene complexes show remarkable fluxional behavior which is qualitatively the same for each of the equilibrated complexes. In Figure 8, we show a series of variable temperature NMR spectra of *cis*-[Pt((*S*)-TMSO)(propene)Cl$_2$] in the sulfur methyl and olefin methyl proton regions, together with the NMR behavior of the sulfur methyl protons of the corresponding 1-butene and isopropylethylene complexes. It will be seen that, for each of the complexes, the two sharp sulfur methyl proton signals, observed at higher temperatures, retain their ^{195}Pt coupling as the temperature is lowered, and that, in all three cases, the downfield signal, representing the *R* diastereomer, first broadens, then collapses, and finally resolves itself into two sharp peaks of unequal intensity. These two peaks, we believe, represent the two rotameric possibilities of the *R* olefin diastereomers, olefinic rotation being slow on the NMR timescale. What is remarkable, however, is that, between 50 and −60 °C, the upfield sulfur methyl proton resonance, representing the *S* olefin diastereomer in each case, remains essentially unchanged. Moreover, the olefinic methyl proton signals for the propene and 1-butene complexes behave in an analogous way. We show the patterns observed for the simpler of the two, the propene species, in Figure 8. The sharp central olefinic methyl proton doublet, assigned to the *S* diastereomer, and which is clearly seen at −18 °C, retains its chemical shift and resolution up to 49 °C. The two wing doublets of unequal intensities, assigned to the two rotamers of the *R* olefin diastereomer,[24] undergo drastic changes as the temperature is raised. These resonances are not fully resolved at the highest temperature, 49 °C, we could achieve without decomposition, but it is clear that the central doublet, despite its overlap with the coalescing wing doublets, remains essentially unchanged over the temperature range, while the two wing doublets begin to merge at 49 °C at 100 MHz. Similar behavior is observed for the 1-butene complex, for which the olefinic methyl proton resonances corresponding to the *S* olefin diastereomer (Figure 7, top spectrum; δ 0.996; $^3J_{H-CH_3}$ = 7.0 Hz) remain unchanged, but those associated with the *R* olefin diastereomer change with temperature between −23 and 50 °C. The low temperature data are summarized in Table III. We have found that the olefinic methyl protons of the isopropylethylene compound are poorly resolved; two broad signals are observed at 30 °C which split into four as the temperature is lowered. No specific conclusion could be drawn, other than evidence of temperature dependence for these olefinic methyl proton signals. As expected, the ethylene complex was found to be fluxional. The approximate barriers to rotation for the complexes are listed in Table III.

The invariance of the NMR spectra of the *S* olefin diastereomers admits to a number of explanations of varying plausibility. The first is that both the sulfur methyl and olefin methyl proton resonances of the (*S*)-propene and (*S*)-1-butene rotamers, and the sulfur methyl proton resonances of the (*S*)-isopropylethylene rotamers, are nearly degenerate. Since this is not the case for any of the *R* olefin diastereomers, we consider this circumstance improbable. The second is that one stereomer of the *S* olefin diastereomer is strongly preferred thermodynamically over the other, so that whatever the chemical shifts of the two, the signal of the predominant rotamer is (detectably) insensitive to olefin rotation. Inspection of Figure 8 reveals that in all three cases, the two rotamers of the *R* olefin diastereomer occur in similar proportions and hence we find this explanation implausible. For the same reason we consider it unlikely that the *S* olefin complexes have only a single detectable rotamer populated, which is not rotating on the NMR time scale. The final explanation, which we prefer, is that the *S* olefin diastereomers have two rotamers of comparable stability, which rapidly interconvert on the NMR time scale between −60 and 50 °C. Our instrument did not permit us to go to significantly lower temperatures, and there are also practical problems with solubility. If, however, we were to suppose that collapse would occur for the sulfur methyl protons of the *S* olefin diastereomers at about −70 °C and that the two rotamers had a similar sulfur methyl proton chemical shift separation as is observed for the *R* olefin diastereomer (Figure 8), then we can calculate a free energy of activation of about 11 kcal $\mathrm{mol^{-1}}$ compared to about 15 kcal $\mathrm{mol^{-1}}$ for the rotational barrier of the *R* olefin diastereomers (Table III). A value of 11 kcal $\mathrm{mol^{-1}}$ is not abnormal for platinum olefin rotation, rotational barriers as low as 10 kcal $\mathrm{mol^{-1}}$ having been observed.[25]

6. Discussion

Table I shows that the discriminatory effect of the chiral sulfoxide ligand is not large provided we exclude the result for the *tert*-butylethylene system, which is probably not an equilibrium value. Nonetheless the results are revealing in a number of ways. First, although most of the olefins are induced to prefer an *R* configuration, at least two, the 1-butene and isopropylethylene species, prefer to adopt an *S* configuration. Moreover, those olefins which adopt the *S* configuration preferentially do so to about the same extent as those which prefer the *R* configuration. Second, increasing the length or bulk of the aliphatic side chain of the olefin has only a small effect on the discrimination and in some cases, for example propene vs. 1-butene, the sense of the discrimination is reversed. Finally, it might have been supposed that a disubstituted olefin would experience a stronger discrimination than an analogous monosubstituted olefin, because, in the former case, one olefinic substituent will always be directed to some extent at the chiral sulfoxide whereas, in the latter case, the substituent can point away from the chiral ligand (Figure 1). That this is not a significant factor can be seen in, for example, the cases of the isopropylethylene and *trans*-diisopropylethylene ligands.

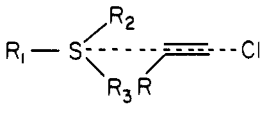
In order to rationalize some of these observations, it is important to distinguish between two types of interactions which occur between chiral molecules.[7] The first is the total interaction, which may be quite large; the second is that part of the total interaction which is discriminatory. The latter, which we call the diastereotopic interaction, may constitute only a few percent of the total interaction, but it is this interaction which leads to asymmetric discrimination. The total interaction between the sulfoxide and the olefin undoubtedly increases as the bulk of the olefinic side chains is increased, but as can be seen, the diastereotopic interaction is only marginally affected. Furthermore, the chiral sulfoxide molecule is capable of generating diastereotopic interactions which are opposite in sense for two closely related olefins, propene and 1-butene. This last observation suggests that the sulfoxide ligand is rotating and therefore is capable of presenting the olefin with a variety of rotameric conformations, some of which may induce an *R* configuration and others an *S* configuration of the olefin. The resultant sense of the induction would then depend on the population average of the various rotameric conformations. If the bulk of the olefinic substituent were to change the populations of these rotameric conformations, then the observation that the sense of discrimination may change could be understood. A similar argument could apply for a rotating olefinic ligand although, in these cases, the preferred rotamer population is likely to be that in which the orientation of the olefin is nearly perpendicular to the mean molecular plane.

This rotational effect is seen in the fluxional behavior of the two diastereomers of the propene, 1-butene, and isopropylethylene complexes (Figure 8), where, in each case, the *S* olefin diastereomer appears to rotate more quickly than the *R* diastereomer despite the differing thermodynamic preferences of the diastereomers (Table I). This effect must therefore be associated with the transition state of the rotational process, which is approximately reached when the olefin lies in the mean molecular plane of the complex. Before we discuss this, however, it is important to ascertain what is involved in the so-called rotation.

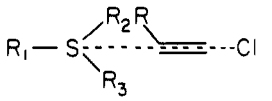
The present results show that ethylene and the three monosubstituted olefins are undergoing a fluxional exchange in their complexes, for which, observationally, the olefinic groups or atoms pointing at the (cis) chloro ligand are interchanged with those facing the sulfoxide ligand. The results also show that this does not occur with disubstituted olefins under similar conditions. This fluxional exchange can occur by either complete rotation about the olefin–platinum axis, or by an oscillatory motion, where one end of the olefin always passes the same cis group, but is unable to pass the other under the same conditions. (The notion that the olefinic faces are interchanging is excluded, for, if this were so, "instantaneous" diastereomeric equilibration would occur and we would not observe the synchronous slow development of the NMR and circular dichroism spectra.)

We propose that the ethylene ligand is undergoing complete rotation about the olefin-platinum axis, but that the propene, 1-butene, and isopropylethylene ligands undergo an oscillatory motion, in which the substituted end of the olefin passes the sulfoxide ligand, but cannot pass the (cis) chloro ligand under the same conditions. The evidence for this is as follows. The disubstituted olefins do not rotate because, as we assume, either a complete rotation or an oscillatory motion would require a substituent to pass the chloro ligand. That the cis halogen is generally more hindering to rotation than other cis ligands is suggested by the observations of Lewis[25] on the *cis*-$[\mathrm{Pt(L)(olefin)Cl_2}]$ complexes, where L is an aryl or alkyl arsine or phosphine. Lewis found that the olefin "rotational" barriers roughly paralleled the effective bulk of the nonhalide ligand; for example, whereas propene was observed to "rotate" in the triethylarsine and triethylphosphine complexes ($\Delta G^{\ddagger} = 12.0$ and 12.5 kcal $\mathrm{mol^{-1}}$, respectively), "rotation" was not observed in the complexes containing the triphenyl analogues ($\Delta G^{\ddagger} \geq$ 16 kcal $\mathrm{mol^{-1}}$). Moreover, for [Pt(acac)(propene)X] where X = Cl or Br, the "rotational" barrier actually decreases in going from the chloro to the bromo analogue ($\Delta G^{\ddagger}{}_{\mathrm{Cl}} = 13.3$, $\Delta G^{\ddagger}{}_{\mathrm{Br}} = 12.8$ kcal $\mathrm{mol^{-1}}$). Although the disubstituted olefins do rotate in the [Pt(acac)(olefin)X] system, the necessity, in these cases, for the substituted end of the olefin to pass the halogeno group increases the barrier to rotation, and, consistently, the bromo species has a higher barrier than the chloro complex (for *trans*-2-butene, $\Delta G^{\ddagger}{}_{\mathrm{Cl}} = 15.8$, $\Delta G^{\ddagger}{}_{\mathrm{Br}} = 16.1$ kcal $\mathrm{mol^{-1}}$). This conclusion that the substituted end of the olefin requires more energy to pass a halogeno ligand than the organic ligand is important in understanding the different rotational behavior of the *R* and *S* olefin diastereomers. If, in the present systems, the monosubstituted olefins were oscillating with the substituent passing the chloro ligand, we would not expect the large diastereotopic discrimination in the rotational behavior, because, in the transition state, the chiral end of the olefin would be distant from the chiral sulfoxide, and the major interaction would occur with the nonchiral chloro group.

Since the sulfoxide ligand is probably rotating, it is not possible to specify precisely how chiral discrimination of the olefins occurs in the transition state. However, the general principle is shown in Figure 9; the olefin is in its (approximate) transition state and the sulfoxide ligand is in an arbitrary ro-



S− olefin



R−olefin

Figure 9. The proposed structures of the *R* and *S* olefins in the ("rotational") transition state. The sulfoxide ligand is shown in a particular rotameric conformation so as to emphasize how the *R* and *S* olefins may be interactively discriminated in the transition state.

tameric conformation. It is readily seen that because the *R* groups on the sulfoxide are (necessarily) different, the interaction energies of the *R* and *S* olefins in their transition states are different. It is not difficult to discern that this will be so, to a greater or lesser extent, for any sulfoxide rotamer.

7. Experimental Section

The instruments used were a Roussel-Jouan Dichrographe, Varian T-60, and HA 100 NMR spectrometers, a Unicam SP 800A spectrophotometer, and a Perkin-Elmer Model 141 digital polarimeter.

(+)-(*R*)-*p*-Tolyl Methyl Sulfoxide. Methyl Grignard, prepared from magnesium (5.3 g) and methyl iodide (35 g) in dry ether (100 mL), was added dropwise to a well-stirred solution of (−)-*p*-tolyl-*l*-methyl sulfinate[26,27] (30 g) in dry ether (500 mL) at 0 °C. The resultant solution was stirred at room temperature for 30 min. It was then cooled and hydrolyzed with aqueous ammonium chloride solution (1 M, 150 mL). The ether layer was separated, back-extracted with ammonium hydroxide (1 M, 5 mL), dried ($MgSO_4$), and reduced to dryness. The residue was diluted with hexene (50 mL) and cooled (0 °C, 12 h), and the pale yellow needles which had separated from the menthol were collected and washed with hexene (6.4 g).

The aqueous phase of the reaction mixture was thoroughly extracted with ether (six 200-mL portions) to yield a further 5.0 g of product uncontaminated with menthol. The crude products were combined, taken up in hot cyclohexane (7 mL/g), and decolorized with charcoal. On cooling, the product deposited as lustrous white flakes: $[\alpha]_D = +143°$ (1% in acetone, lit.[28] $[\alpha]_D = +145.5°$) The above workup can be applied to any of the sulfoxides derived from (−)-*p*-tolyl-*l*-menthyl sulfinate, even those that are liquids, for, in these cases, the sulfoxide deposits as an oil from cold (−78 °C) hexane and the menthol can be removed by decantation. This is superior to the previous steam distillation methods.[28]

Anal. Calcd for $C_8H_{10}SO$: C, 62.3; H, 6.5; S, 20.8; O, 10.4. Found: C, 62.5; H, 6.6; S, 20.8; O, 10.5.

***cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2].** (*R*)-*p*-Tolyl methyl sulfoxide (1.85 g) dissolved in aqueous HCl (0.5 M, 150 mL) was added to a solution of $K_2[PtCl_4]$ (5.00 g) in aqueous HCl (0.5 M, 150 mL). The resulting solution was immediately placed in an atmosphere of ethylene and vigorously stirred. Within 1 h the product began to separate from the solution and, after 3 days, it was collected, washed with water, and then with ether (4.8 g). The product was taken up in hot acetone (50 mL) and was filtered to remove small amounts of platinum metal. Upon the slow addition of light petrol, long, colorless needles of the product separated: $(\epsilon_l - \epsilon_r)_{316\,nm} = +2.07$, $(\epsilon_l - \epsilon_r)_{360\,nm} = -0.44$ (10^{-3} M in $CHCl_3$).

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_2H_4)Cl_2]$: C, 26.8; H, 3.1; Cl, 15.9; S, 7.1; O, 3.6; Pt, 43.5. Found: C, 26.8; H, 3.2; Cl, 16.1; S, 7.1; O, 3.8; Pt, 43.2.

***cis*-[Pt((*S*)-TMSO)(propene)Cl_2].** Propene was bubbled through a solution of *cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2] (0.3 g) in acetone (12 mL) at 0 °C for 1.25 h. The cold solution was reduced to dryness under vacuum and the oily residue was dissolved in dichloromethane (1 mL) and then diluted with anhydrous ether (5 mL). Propene was slowly bubbled through the solution as light petrol (3.5 mL) was slowly added. The flask was stoppered and the solution was cooled (4 °C, 2 h), whereupon a colorless oil separated out. The solution was diluted with ether (5 mL) and light petrol (5 mL). On cooling (4 °C), the oil slowly converted to clumps of small white needles. These were collected and washed with petrol (0.22 g). The crude material was recrystallized from dichloromethane (1.5 mL) containing ether (1 mL) by the addition of light petrol (7 mL); seeding gave colorless needles. Subsequent preparations are facilitated by seeding the initial solution.

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_3H_6)Cl_2]$: C, 28.6; H, 3.5; S, 6.9; Cl, 15.4. Found: C, 28.6; H, 3.4; S, 7.0; Cl, 15.3.

***cis*-[Pt((*S*)-TMSO)(*cis*-2-butene)Cl_2].** *cis*-2-Butene was bubbled through a solution of *cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2] (0.50 g) in acetone (15 mL) at 25 °C for 25 min. The resultant pale yellow solution was taken to dryness under vacuum, and the crystalline residue was recrystallized from dichloromethane (2 mL) containing ether (2 mL) by the slow addition of light petrol (15 mL). After cooling, the small white needles were collected and washed with petrol (0.50 g). Recrystallization of the crude product from dichloromethane (3 mL) by the addition of ether (3 mL), followed by light petrol (25 mL), yielded pale yellow plates (0.38 g).

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_4H_8)Cl_2]$: C, 30.3; H, 3.8; S, 6.7; Cl, 14.9. Found: C, 29.9; H, 3.8; S, 6.5; Cl, 14.8.

***cis*-[Pt((*S*)-TMSO)(*trans*-2-butene)Cl_2].** *trans*-2-Butene was bubbled through a solution of *cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2] (0.50 g) in acetone (15 mL) at 0 °C for 0.75 h and then for a further 0.75 h as the temperature was allowed to rise 25 °C. The solution was reduced to dryness under vacuum, and the resultant pale yellow oil was dissolved in dichloromethane (2 mL). The solution was then diluted with ether (3.5 mL). Light petrol was added to the cloud point and, on cooling (4 °C, 1 h), a flocculent white material separated and was removed by filtration. The solution was again brought to the cloud point with petrol, saturated with olefin, and cooled (4 °C, 1 h). The oil which separated was induced to crystallize by scratching. The mixture was then diluted with more petrol (30 mL) and cooled (4 °C, 12 h) before the solid was collected (0.22 g). The crude product was dissolved in dichloromethane (1.5 mL) and diluted with ether (1 mL). Petrol was added to the cloud point and the solution was seeded. On cooling to 4 °C, the product slowly crystallized as clumps of white needles. (Use of seed crystals greatly aids crystallization at each stage of the isolation procedure and crystallization must be induced to occur as quickly as possible to avoid extensive decomposition.)

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_4H_8)Cl_2]$: C, 30.3; H, 3.8; S, 6.7; Cl, 14.9. Found: C, 30.2; H, 3.8; S, 7.2; Cl, 14.4.

***cis*-[Pt((*S*)-TMSO)(1-butene)Cl_2].** *cis*-[Pt((S)-TMSO)(C_2H_4)Cl_2] (0.5 g) was converted to the 1-butene complex by the method used for the *trans*-2-butene species. The complex formed as long, pale yellow needles (0.48 g). It was recrystallized from dichloromethane (2 mL) containing ether (2 mL) by the careful addition of petrol (25 mL).

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_4H_8)Cl_2]$: C, 30.3; H, 3.8; S, 6.7; Cl, 14.9. Found: C, 30.3; H, 3.7; S, 7.0; Cl, 15.0.

***cis*-[Pt((*S*)-TMSO)(styrene)Cl_2].** A suspension of *cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2] (1.50 g) in "neat" styrene (20 mL) was stirred at room temperature for 1 h. The orange solution was filtered and diluted with ether (7 mL), then petrol (20 mL) was added to cause precipitation of white flakes. The solution was maintained at 4 °C for 3 days, during which time the white crystals transformed into large lemon yellow blocks. These were collected and washed with ether in petrol (1:1) (1.60 g). The product was recrystallized from dichloromethane (7 mL) containing ether (3.5 mL) by the addition of petrol (20 mL) to give deep yellow crystals (1.32 g). The white and yellow crystals have the same molecular isomerism and constitution.

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_8H_8)Cl_2]$: C, 36.6; H, 3.4; S, 6.1; Cl, 13.6. For the white plates, found: C, 36.7; H, 3.5; S, 6.2; Cl, 13.6. For the yellow blocks, found: C, 36.7; H, 3.4; S, 6.3; Cl, 13.4.

***cis*-[Pt((*S*)-TMSO)(isopropylethylene)Cl_2].** 3-Methyl-1-butene was bubbled through a solution of *cis*-[Pt((*S*)-TMSO)(C_2H_4)Cl_2] (1.20 g) in acetone (30 mL) for 0.5 h, the solution allowed to stand for 1.5 h, and then reduced to dryness. The oily residue was dissolved in dichloromethane (2 mL), diluted with ether (4 mL), and petrol was added to the cloud point. The solution was cooled (4 °C, 12 h), then was filtered and again brought to the cloud point with petrol. An oil separated on cooling (4 °C, 2 days), which transformed to a solid on vigorous scratching. A further 7 mL of petrol was added and, after cooling (4 °C, 1 day), the solid was collected (1.08 g). Recrystallization from dichloromethane (8 mL) containing ether (8 mL) by the slow addition of petrol gave colorless plates.

Anal. Calcd for $[Pt(C_8H_{10}SO)(C_5H_{10})Cl_2]$: C, 31.8; H, 4.1; S, 6.5; Cl, 14.5. Found: C, 31.7; H, 4.1; S, 6.7; Cl, 14.4.

***cis*-[Pt((*S*)-TMSO)(*tert*-butylethylene)Cl$_2$].** To *cis*-[Pt((*S*)-TMSO)(C$_2$H$_4$)Cl$_2$] (1.0 g) dissolved in a 1:3 mixture of dichloromethane/acetone (8 mL) was added 3,3-dimethyl-1-butene (10 mL) and the solution was gently refluxed for 1 h. The yellow solution was filtered and diluted with ether (2 mL); hexane (70 mL) was added to cause rapid formation of long, pale yellow needles. The mixture was cooled for 1 h and the solid was collected (0.62 g). The product was twice recrystallized from dry, peroxide-free tetrahydrofuran (3 mL/g) by the slow addition of hexane and yielded long, off-white needles.

Anal. Calcd for [Pt(C$_8$H$_{10}$SO)(C$_6$H$_{12}$)Cl$_2$]: C, 33.3; H, 4.4; S, 6.4; Cl, 14.1. Found: C, 33.5; H, 4.5; S, 6.4; Cl, 14.3.

***cis*-[Pt((*S*)-TMSO)(ethyl vinyl ether)Cl$_2$].** Finely ground *cis*-[Pt((*S*)-TMSO)(C$_2$H$_4$)Cl$_2$] (0.5 g) was suspended in dry, peroxide-free tetrahydrofuran (10 mL) and then freshly distilled ethyl vinyl ether (2.5 mL) was added. The mixture was stirred at room temperature: vigorous effervescence occurred, the solution turned yellow, and the solid dissolved in 5 min. The resulting solution was warmed on a steam bath for 1 min and then was filtered. Pale yellow needles deposited after the addition of petrol (30 mL): after cooling (4 °C, 15 min) these were collected (0.45 g). The product was recrystallized from dichloromethane (3 mL) by the careful addition of hexane (17 mL). This compound is very unstable even in the solid state and the procedures above should be carried out with dispatch.

Anal. Calcd for [Pt(C$_8$H$_{10}$SO)(C$_2$H$_5$OC$_2$H$_3$)Cl$_2$]: C, 29.3; H, 3.7; Cl, 14.4; S, 6.5. Found: C, 29.1; H, 3.7; Cl, 14.6; S, 6.7.

cis-[Pt((*S*)-TMSO)(*trans*-3-hexene)Cl$_2$]. *cis*-[Pt((*S*)-TMSO)(C$_2$H$_4$)Cl$_2$] (0.15 g) was dissolved in a 1:3 mixture of dichloromethane/acetone (2 mL), then *trans*-3-hexene (0.3 mL) was added, and the solution was maintained at 60 °C for 2 h. The pale yellow solution was reduced to an oil under vacuum and the residue was treated thrice with chloroform and pumped, on each occasion, to remove the solvent and olefin. The resultant oil was taken up in 0.6 mL of CDCl$_3$ and the NMR was taken. Two drops of the free olefin were added and the solution was allowed to equilibrate at 30 °C for 15 h. The final spectrum differed from the original.

***cis*-[Pt((*S*)-TMSO)(*trans*-diisopropylethylene)Cl$_2$].** This complex was prepared in situ by the method described for the *trans*-3-hexene complex, except that the reaction mixture was maintained at 60 °C for 1 h, then equilibrated similarly.

Stability of the Complexes. All the above complexes are unstable even in the solid state at room temperature. Those containing highly substituted ethylenes are the least stable, but even the ethylene complex decomposes after a few weeks at room temperature. The life of the complex can be prolonged by storage at −5 °C.

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(6) The enantiotopic atoms, groups, or faces of a prochiral molecule in the free state are interchanged only by a plane of symmetry. A chiral molecule is devoid of secondary symmetry operations (planes, inversions, or alternating axes of symmetry): pure rotational elements can be present. Thus when the chiral molecule and the prochiral substrate are brought together, the total system cannot possess secondary elements of symmetry and hence the enantiotopic atoms, groups, or faces are no longer symmetry related, and hence are, in principle, different. See K. Mislow and K. Raban, *Top. Stereochem.*, **1**, 1 (1967), for nomenclature.

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(16) In the case of the *cis*-[Pt((*S*)-TMSO)(propene)Cl$_2$] complex, the two sharp S–CH$_3$ proton signals representing the nearly equally abundant olefin diastereomers (vide infra) are considerably broadened (at 60 MHz, 30 °C) when a CH$_2$Cl$_2$ solution of the complex is saturated with propene. This suggests that rapid diastereomer interconversion is occurring via a (rapid) exchange of the coordinated and free olefin. See R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

(17) The yellow side product does not appear to be the (expected) dimer [Pt$_2$(TMSO)$_2$Cl$_4$], at least not of the conventional kind, but rather, a redox product resulting from reaction between the sulfoxide and platinum. We found that on heating the ethylene (*R*)-TMSO complex in methanol containing HCl, a yellow product is formed which has no optical activity and no S–O stretch in the infrared. For an analogous reaction with Pd(II), see D. W. Meek, W. E. Hatfield, and R. S. Drago, *Inorg. Chem.*, **3**, 1637 (1964).

(18) The configuration of $(+)_{\mathrm{D}}$-*p*-tolyl methyl sulfoxide is *R* (U. de la Camp and H. Hope, *Acta Crystallogr. Sect. B*, **26**, 346 (1970)) in the free molecule, but is designated *S* upon coordination because the substituent of least priority in the free sulfoxide, the electron pair, is replaced by the substituent of highest priority, the metal atom. Stereochemical inversion does not occur.

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(23) Despite this, we are inclined to believe that two rotamers exist, because with the *cis*-[Pt(Me$_2$SO)(*cis*-2-butene)Cl$_2$] complex, the two rotamers are clearly seen in the olefinic methyl proton region, but the splitting of the sulfur methyl protons due to the two rotamers is a mere δ 0.004.

(24) The assignment is based on the fact that at −18 °C the *R* olefin diastereomer shows two sulfur methyl proton signals of unequal intensities. The exact relative intensities could not be obtained because of overlap (Figure 8), but the relative intensities of the sulfur methyl protons and those of the olefinic methyl protons which represent the two rotamers of the *R* olefin diastereomer are seen to be approximately correct.

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