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Molecular Structure and Absolute Configuration of *cis*-Dichloro((*S*)-methyl *p*-tolyl sulfoxide)(3-methyl-1-butene)platinum(II)

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The molecular structure and absolute configuration of *cis*-dichloro((*S*)-methyl *p*-tolyl sulfoxide)(3-methyl-1-butene)platinum(II), $PtCl_2[CH_3(O)S(C_6H_4CH_3)][(CH_3)_2CHCH{=}CH_2]$, have been determined by standard Patterson and Fourier techniques using x-ray data collected by counter methods. The molecule crystallizes in the monoclinic space group $P2_1$ with $Z = 2$. The unit cell dimensions are $a = 10.556$ (2) Å, $b = 10.488$ (2) Å, $c = 7.941$ (2) Å, and $\beta = 107.72$ (1)°. The structure has been refined by full-matrix least-squares techniques on F, using 2820 unique reflections for which $F^2 > 2\sigma(F^2)$, to a final agreement factor of 0.0377. The complex exhibits a square-planar coordination geometry with the double bond of the coordinated olefin ligand tilted from the perpendicular by 5.7 (6)°. The absolute configuration at the asymmetric carbon atom of the olefin was determined by the Bijvoet method to be *S*.

Introduction

In the first paper of this series[1] we described the structure of a complex which exhibited a strong asymmetric bias for the coordination of one enantiotopic face of the prochiral olefin styrene. The preferred configuration of the coordinated olefin ligand and the arrangement of the *p*-tolyl group on the asymmetric sulfoxide ligand positioned the two phenyl rings in such a way that an attractive interaction between them could occur. In attributing the preferential formation of one diastereomer to this interligand attraction, we felt it necessary to examine the molecular structure of a similar complex which contained an olefin ligand for which an attractive interaction of comparable magnitude was unlikely. This would involve replacing the aryl olefinic substituent with an alkyl group. The 3-methyl-1-butene complex had been found to exist preferentially as one diastereomer in a ratio of 2:1 at equilibrium.[2] On the basis of circular dichroism spectra the complex was postulated to contain the olefin with the *S* absolute configuration. Suitable crystals were eventually obtained and we report here the results of the single-crystal x-ray structural analysis of *cis*-dichloro((*S*)-methyl *p*-tolyl sulfoxide)(3-methyl-1-butene)platinum(II).

Experimental Section

The crystals of *cis*-dichloro((*S*)-methyl *p*-tolyl sulfoxide)(3-methyl-1-butene)platinum(II), $PtCl_2[CH_3(O)S(C_6H_4CH_3)]$-$[(CH_3)_2CHCH{=}CH_2]$, kindly provided by H. Boucher and B. Bosnich, appeared as translucent, white, triangular blocks. Preliminary Weissenberg and precession photography showed the crystals to be monoclinic with Laue symmetry $2/m$. The systematic absences observed, $0k0$ for k odd, and the requirement of an acentric space group for an optically active molecule determined the space group to be $P2_1$, C_2^2, No. 4.[3]

The crystal chosen for data collection was of approximate dimensions 0.23 × 0.20 × 0.10 mm. It was carefully measured on a microscope fitted with a filar eyepiece before application of an absorption correction. The crystal had seven faces, {100}, (110), ($\bar{1}\bar{1}0$), (011), ($01\bar{1}$), and ($0\bar{1}0$), which were identified by optical goniometry. The crystal was mounted on a Picker FACS-1 computer-controlled diffractometer in a random orientation with [010] approximately 28° from coincidence with the ϕ axis. Cell constants and an orientation matrix were obtained from a least-squares refinement of 18 intense, carefully centered reflections with $20 < 2\theta < 50°$. Prefiltered Cu radiation was used, λ 1.540 56 Å, at an ambient temperature of 20 °C. The crystal data are summarized in Table I.

Table I. Crystal Data

$C_{13}H_{20}Cl_2OPtS$	Fw 490.36
$a = 10.556$ (2) Å	Space group $P2_1$
$b = 10.488$ (2) Å	$Z = 2$
$c = 7.941$ (2) Å	Density (obsd)^a = 1.950 (2) g cm^{-3}
$\beta = 107.72$ (1)°	Density (calcd) = 1.944 g cm^{-3}
Cell vol 837.51 Å^3	$\mu = 187.4$ cm^{-1} for Cu Kα_1

^{a} By neutral buoyancy in hexane and 1,2-dibromotetrafluoroethane.

Table II. Experimental Conditions for Data Collection

Radiation: Cu Kα, Ni foil (0.018 mm) prefilter
Takeoff angle: 2.3° (90% of maximum Bragg intensity)
Aperture: 4 × 4 mm, 31 cm from crystal
Data collected: $\pm h, \pm k, l$, for $0 < 2\theta < 130°$
Scan: θ–2θ at 2° min^{-1}, with α_1–α_2 dispersion correction
Scan range: 1.2° symmetric for $2\theta < 70°$, 0.8° below α_1 to 0.6° above α_2 for $70 < 2\theta < 130°$
Background: 10 s stationary crystal, stationary counter measured at limits of scan for $2\theta < 110°$ and 20 s for $2\theta > 110°$
Standards: Six recorded every 175 observations, 020, $\bar{1}00$, $0\bar{2}0$, 100, 001, and $\bar{1}02$

The conditions used for data collection are given in Table II. The measurement of standard reflections over the course of data collection and an examination of ω scans for several intense, low-angle reflections before and after data collection showed no significant degradation of crystal quality had occurred. The standard reflections showed an average increase of 0.46% with the largest change being 3.8%.

The intensity data were processed as previously described.[4] The value of p, the "ignorance factor", was chosen to be 0.02 from an examination of both the variations in the standard reflections[5] and the final weighting scheme. An absorption correction was applied to all 3088 data with $F^2 > 0$.[6] The maximum and minimum transmission coefficients were 0.838 and 0.661, respectively, a variation of 26.8%. There were 211 pairs of symmetry-equivalent reflections, for the planes $hk0$ and $\bar{h}k0$. These were averaged to give a weighted agreement factor of 6.0% based on F^2 before the absorption correction.

Table III. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	−0.07305 (3)	0.3000	0.18430 (4)	391 (2)	365 (2)	321 (2)	−23 (3)	122 (1)	−13 (3)
Cl(1)	0.1091 (3)	0.4296 (3)	0.2094 (4)	497 (14)	557 (16)	612 (17)	−154 (12)	117 (13)	7 (14)
Cl(2)	0.0026 (3)	0.2658 (3)	0.4861 (4)	681 (16)	852 (31)	333 (12)	−122 (14)	59 (12)	16 (12)
S	−0.2388 (2)	0.1629 (2)	0.1660 (3)	479 (13)	419 (12)	342 (12)	−68 (10)	186 (11)	−21 (10)
O	−0.3328 (8)	0.1428 (8)	−0.0106 (10)	620 (46)	735 (53)	318 (37)	−190 (41)	155 (35)	−90 (36)
C(1)	−0.1027 (10)	0.2810 (14)	−0.0979 (12)	654 (57)	510 (95)	302 (43)	−109 (61)	184 (42)	−2 (51)
C(2)	−0.1880 (10)	0.3807 (10)	−0.0744 (15)	489 (57)	403 (56)	439 (59)	−25 (45)	95 (49)	40 (46)
C(3)	−0.1724 (13)	0.5227 (11)	−0.095 (2)	652 (72)	420 (60)	754 (87)	−21 (55)	135 (68)	190 (61)
C(4)	−0.236 (2)	0.5969 (14)	0.023 (3)	1276 (144)	523 (82)	1190 (148)	245 (87)	407 (122)	−83 (89)
C(5)	−0.244 (2)	0.551 (2)	−0.292 (2)	974 (115)	928 (119)	888 (120)	−74 (92)	−5 (98)	482 (98)
C(6)	−0.1668 (13)	0.0146 (10)	0.248 (2)	747 (77)	315 (51)	810 (91)	86 (51)	485 (73)	96 (54)
C(7)	−0.5866 (11)	0.308 (3)	0.614 (2)	602 (60)	1148 (116)	687 (73)	91 (115)	322 (57)	−312 (139)
C(11)	−0.3322 (9)	0.2063 (10)	0.3083 (13)	369 (48)	482 (55)	320 (49)	−28 (41)	187 (41)	−3 (42)
C(12)	−0.4323 (10)	0.293 (2)	0.2421 (14)	609 (54)	641 (69)	498 (53)	146 (92)	233 (46)	185 (102)
C(13)	−0.5135 (11)	0.3292 (12)	0.343 (2)	516 (57)	697 (127)	703 (81)	190 (59)	188 (57)	34 (64)
C(14)	−0.4972 (10)	0.2736 (11)	0.5059 (14)	425 (46)	566 (96)	437 (53)	7 (46)	156 (42)	−120 (49)
C(15)	−0.3957 (11)	0.1877 (12)	0.5685 (14)	528 (62)	740 (79)	312 (53)	27 (55)	189 (48)	2 (52)
C(16)	−0.3126 (10)	0.1526 (12)	0.4704 (14)	480 (56)	639 (69)	333 (54)	103 (51)	123 (46)	67 (50)

[a] The thermal parameters have been multiplied by 10^4. $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits.

This value reduced to 3.6% after correction. The structure solution and preliminary refinement employed the 1553 data with $k > 0$ and $F^2 > 3\sigma(F^2)$.

Structure Solution and Refinement

The positional parameters for the Pt atom were determined from a three-dimensional Patterson synthesis. A series of least-squares refinements and difference-Fourier synthesis calculations revealed the positions of the remaining 17 nonhydrogen atoms. From the results of a single-crystal x-ray structural study on a similar complex[1] we knew the absolute configuration of the sulfoxide ligand to be *S* and this enabled the choice of the correct hand for the model from the beginning. Refinement of atomic parameters was carried out by full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure factor amplitudes. The weighting factor w is given by $w = 4F_o^2/(\sigma^2(F_o^2))$.

The neutral-atom scattering factors for the Pt, S, Cl, O, and C atoms were those of Cromer and Waber[7] while those for the H atoms were taken from Stewart, Davidson, and Simpson.[8] The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were those of Cromer and Liberman[9] and were included in the calculations for the Pt, S, and Cl atoms.

One cycle of full-matrix least-squares refinement on the molecule, with the phenyl ring constrained as a rigid group (D_{6h} symmetry, C–C = 1.392 Å) with individual atomic isotropic temperature factors, and varying the positional and anisotropic thermal parameters for the nongroup atoms resulted in values of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.0493$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2} = 0.0611$. Using the 2980 absorption-corrected data with $F^2 > 3\sigma(F^2)$, two cycles of refinement varying the positional and anisotropic thermal parameters for all nonhydrogen atoms gave R_1 and R_2 values of 0.0393 and 0.0487, respectively. Of the 20 H atoms in the molecule all were located in regions of positive electron density by a difference Fourier synthesis. The locations determined for the nonolefinic H atoms compared favorably to idealized positions computed assuming appropriate sp^3 and sp^2 coordination geometries at the C atoms and C–H bond lengths of 0.95 Å. The H atoms were assigned isotropic thermal parameters 1.0 Å^2 greater than those of the atoms to which they are bonded. Rather than constrain the olefinic H atoms to an artifical model it was decided to refine their positional coordinates keeping the isotropic thermal parameters constant. Two cycles of refinement on this model gave acceptable geometries for the two H atoms on C(1), but H1C(2) refined to a position 1.42 Å distant from C(2). Accordingly it was decided to fix the H atoms for the final cycles with H1C(2) moved to a position 0.95 Å from C(2). The model was refined using all data for which $F^2 > 2\sigma(F^2)$. One cycle of full-matrix least-squares refinement, using 3031 data to refine 162 variables, served to converge the model with final agreement factors for R_1 and R_2 of 0.0377 and 0.0449, respectively. In the final cycle the largest parameter shift was 0.95 of its estimated standard deviation and was associated with the β_{33} of the Pt atom. The error in an observation of unit weight was 2.6 electrons. A statistical analysis of R_2 in terms of $|F_o|$, diffractometer setting angles χ and ϕ, and $\lambda^{-1}\sin\theta$ showed no unusual trends. A difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance. The highest peak, located 1.73 Å from the Pt atom (fractional coordinates −0.16, 0.30, 0.34), has an electron density of 1.1 (3) e Å^{-3}. An examination of F_o and F_c showed no evidence for secondary extinction. Structure factors calculated for those reflections with $F^2 < 2\sigma(F^2)$ showed only four reflections for which $F_o - F_c$ exceeded 3σ. Final positional and thermal parameters for the non-H atoms are given in Table III; those for the H atoms are in Table IV. Structure amplitudes are presented in Table V,[10] as $10F_o$ vs. $10F_c$ in electrons.

Table IV. Derived Hydrogen Atom Positional (×10^4) and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
H1C(1)	−170	3181	−812	4.80
H2C(1)	−1299	1795	−1477	4.80
H1C(2)	−2713	3452	−764	4.35
H1C(12)	−4456	3291	1294	5.19
H1C(13)	−5794	3924	3007	5.72
H1C(15)	−3835	1502	6811	4.77
H1C(16)	−2510	932	5412	4.56
H1C(3)	−810	5428	−656	5.61
H1C(4)	−2069	6829	285	8.15
H2C(4)	−3296	5930	−256	8.15
H3C(4)	−2089	5604	1375	8.15
H1C(5)	−2452	6407	−3105	8.41
H2C(5)	−1907	5136	−3610	8.41
H3C(5)	−3282	5164	−3276	8.41
H1C(6)	−2343	−499	2131	5.32
H2C(6)	−985	−45	1968	5.32
H3C(6)	−1328	178	3713	5.32
H1C(7)	−5828	3970	6350	7.07
H2C(7)	−6755	2836	5522	7.07
H3C(7)	−5583	2638	7243	7.07

[a] H atoms are numbered according to the atom to which they are bonded; thus H1C(1) is bonded to C(1), etc.

To confirm that the correct choices for the absolute configurations of the asymmetric sites were made, we compared F_o and F_c for all reflections with calculated Bijvoet differences exceeding 5%. The agreement factor for this comparison $R_{Bij} = \sum|F_o - F_c|/\sum F_o = 0.0453$ is quite good. A comparison of $F_c(hkl)$ and $F_c(h\bar{k}l)$ values for reflections exhibiting Bijvoet differences in excess of 20% based on the final model is presented in Table VI. The R factor ratio test[11] was also applied after refining the chosen model and its enantiomer under identical conditions. For a refinement using 171 variables and 2980 data, agreement factors R_2 of 0.0453 and 0.0661 were obtained for the two structures. This indicates the first model is preferred at a significance level of greater than 99.5%.

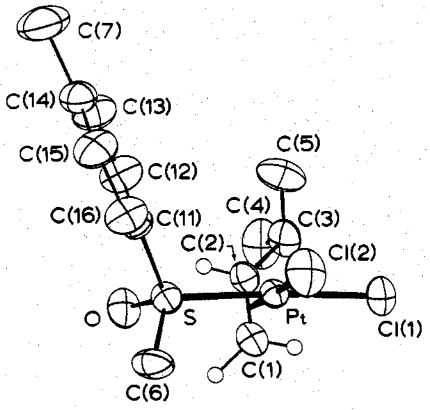


Figure 1. Perspective view of the complex, showing the atom-numbering scheme. The H atoms included on the olefin ligand have been reduced in size to achieve clarity.

Structure Description

A perspective view of a single molecule showing the atom-numbering scheme is presented in Figure 1. A stereoview of the molecule including H atoms is shown in Figure 2. Selected interatomic distances and angles are given in Table VII. A diagram of a unit cell content is presented in Figure 3 and illustrates apparently normal packing with no unusual interactions between molecules in the crystal. The closest intermolecular contact is 2.34 Å between H1C(15) and the O atom of the molecule related by a unit cell translation along z. The shortest Pt–Pt and Pt–Cl intermolecular distances are 6.418 (1) and 7.266 (3) Å, respectively.

The inner coordination sphere of the Pt atom is of square-planar geometry with the double bond of the olefin ligand approximately perpendicular to the square plane. The angle between the Pt–Cl(1)–Cl(2) plane and the olefinic bond is 84.3 (6)°. This twisting of the olefin away from the perpendicular is a commonly encountered phenomenon.[1,12] The olefin C atoms are displaced by 0.681 and −0.744 Å from the mean coordination plane of the Pt atom, Table VIII. The Pt–C distances to the olefin are Pt–C(1) = 2.175 (9) and Pt–C(2) = 2.211 (11) Å. The C–C double-bond distance of 1.43 (2) Å is within the range commonly seen for coordinated double bonds.[15,16]

Table VI. Determination of Absolute Configuration

hkl	$F_c(hkl)$	Obsd relationship	$F_c(h\bar{k}l)$
$\bar{4}40$	3.42	<	6.29
440	3.42	>	6.29
021	19.25	>	11.14
$\bar{8}\bar{9}2$	5.35	<	7.01
$\bar{5}\bar{3}6$	8.43	>	6.10
$\bar{1}\bar{3}2$	23.77	<	30.35
$\bar{4}74$	6.84	>	8.72
661	3.17	<	4.03
$\bar{9}17$	8.70	>	6.35
$\bar{4}\bar{3}4$	15.31	>	11.64
$\bar{3}80$	5.54	<	6.84
$\bar{9}83$	5.16	>	3.97
$2\bar{6}5$	7.70	>	5.94
$9\bar{1}1$	6.95	<	5.37
$\bar{1}58$	6.36	<	7.76
$\bar{6}56$	7.55	<	9.19

The initial refinement of the olefinic H atoms allowed an estimate of the bend-back angle α, defined as the angle between the normals of the planes of the substituents.[16] The value determined was 154 (8)°, with the error estimated from the last cycle of refinement in which the H atom parameters were varied. This angle compares favorably to values reported for a number of other structures.[16]

The Cl–Pt–Cl angle of 89.20 (11)° and the Pt–Cl distances of 2.313 (3) and 2.312 (3) Å, to Cl(1) and Cl(2), respectively, represent a normal geometry for square-planar Pt complexes containing cis Cl ligands opposite weak trans-influence ligands.[13] The Pt–S distance of 2.235 (3) Å is somewhat shorter than observed in the styrene complex but both values are consistent with the range of Pt–S and Pd–S distances observed in other structures.[14] The S–C(sp^2) and S–C(sp^3) distances of 1.771 (9) and 1.766 (11) Å, respectively, are similar to values normally observed for coordinated sulfoxide ligands, as is the S–O distance of 1.466 (7) Å.[1,14]

The absolute configuration of the sulfoxide ligand is S, as expected from the structural results of the styrene complex, which contains the same ligand. The asymmetric C atom of

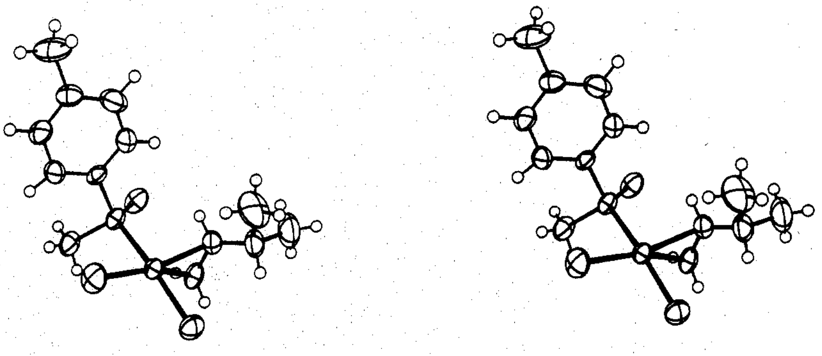


Figure 2. Stereoview of the molecule. Atoms other than H are represented by 50% probability thermal ellipsoids.

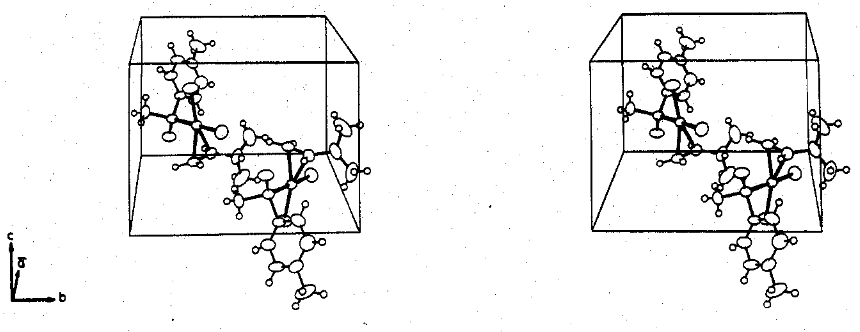


Figure 3. Stereoview of the unit cell contents.

Table VII. Selected Interatomic Bond Distances (Å) and Angles (deg)

	Distances		
Pt-Cl(1)	2.313 (3)	C(7)-C(14)	1.50 (1)
	2.326 (3)[a]	C(1)-C(2)	1.43 (2)
Pt-Cl(2)	2.312 (3)	C(2)-C(3)	1.51 (1)
	2.330 (3)[a]	C(3)-C(4)	1.52 (2)
Pt-S	2.235 (3)	C(3)-C(5)	1.54 (2)
Pt-C(1)	2.175 (9)		
Pt-C(2)	2.211 (11)	C(1)-H1C(1)	0.956 (11)[b]
S-O	1.466 (7)	C(1)-H2C(1)	1.42 (14)
S-C(6)	1.766 (11)		
S-C(11)	1.771 (9)		
	Angles		
Cl(1)-Pt-Cl(2)	89.20 (11)	C(1)-C(2)-C(3)	128 (1)
S-Pt-Cl(2)	89.09 (10)	C(2)-C(3)-C(4)	111 (1)
C(1)-Pt-Cl(1)	89.9 (3)	C(2)-C(3)-C(5)	105 (1)
C(2)-Pt-Cl(1)	93.5 (3)	H1C(1)-C(1)-H2C(1)	124
Pt-S-O	116.3 (3)	H1C(1)-C(1)-C(2)-C(3)	23 (1)[c]
Pt-S-C(6)	107.6 (4)	H2C(1)-C(1)-C(2)-H1C(2)	16 (1)
Pt-S-C(11)	111.7 (3)		

[a] Distance corrected for Cl "riding" on Pt.[6] [b] Errors estimated from last cycle in which H atoms were refined. [c] A positive angle indicates a clockwise rotation of atom 1 about the atom 2–atom 3 bond to superimpose its image on atom 4.

Table VIII. Weighted Least-Squares Planes and Displacements (Å) of Atoms Therefrom[a]

Plane 1: $5.53x + 7.76y + 1.93z - 0.363 = 0$			
C(11)	−0.003 (10)	C(14)	−0.011 (10)
C(12)	−0.011 (19)	C(15)	0.005 (12)
C(13)	0.016 (13)	C(16)	0.003 (12)
Plane 2: $6.58x - 8.07y - 2.56z + 3.37 = 0$			
Pt	−0.0003 (2)	S	0.063 (3)
Cl(1)	0.087 (3)	C(1)	0.681
Cl(2)	−0.000 (3)	C(2)	−0.744

[a] Displacements without esd's refer to atoms not included in the calculation of the plane.

the olefin is also in the *S* absolute configuration, in contrast to the *R* absolute configuration observed for that in the styrene complex.

A comparison of the conformations of the sulfoxide ligand and the $PtCl_2$ segments of the molecule for the structures of the complexes with the two olefin ligands was carried out by probability plot analysis.[18,19] The resulting plot for interatomic distances less than 4.65 Å is shown in Figure 4 and indicates two distinct groups of points. Those falling along the line through the origin with unit slope are associated with the internal distances of the sulfoxide ligand and indicate no systematic differences between the two structures. The other group of points (which do not lie on a line through the origin) are associated with the interatomic distances about the Pt atom and indicate that these distances in the two structures are not systematically related and the differences are not the result of random error. These differences graphically illustrate the change in the nature of the olefin and its stereochemical arrangement with respect to the other ligands on the Pt atom.

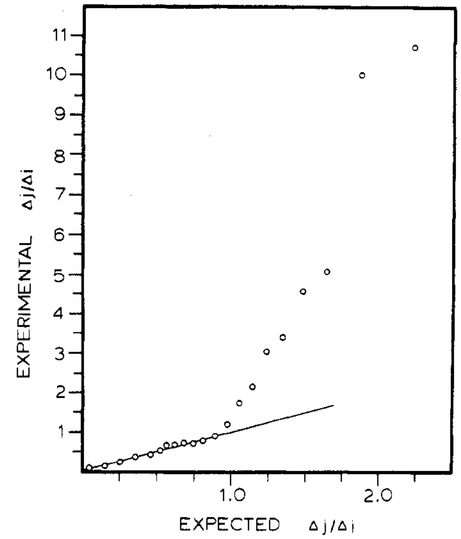
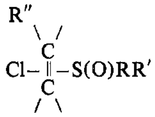


Figure 4. Half-normal probability plot of selected interatomic distances for *cis*-dichloro((*S*)-methyl *p*-tolyl sulfoxide)((*R*)-styrene)platinum(II) and *cis*-dichloro((*S*)-methyl *p*-tolyl sulfoxide)(3-(*S*)-methyl-1-butene)platinum(II).

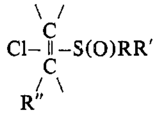
Discussion

When a prochiral olefin, namely, one which is dissymmetrically substituted at one or both carbon atoms, coordinates to a metal atom, it may do so through either of two enantiotopic faces resulting in either *R* or *S* absolute configurations at the substituted carbon atoms.[17] If the metal atom is already part of an asymmetric complex, discrimination between the two enantiotopic faces is possible to an extent dependent on the degree of interaction between an asymmetric site in the complex and the dissymmetric olefin. This interaction may result from electronic and steric effects which may or may not be complementary. In the case of the styrene derivative,[1] any repulsive steric interactions were apparently strongly outweighted by the attractive electronic interactions between the two phenyl rings, with the result that there was a 3:1 diastereomeric excess at equilibrium for the complex with the olefin in the *R* absolute configuration. In the present case the lack of such an attractive electronic influence presumably leaves the repulsive steric components of the interaction to dictate the stereochemical arrangement of the isopropyl group and the coordinated sulfoxide ligand.

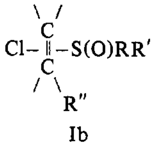
The positioning of the olefin with respect to the sulfoxide may occur in several ways:



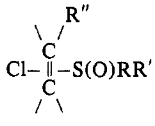
Ia



IIa



Ib



IIb

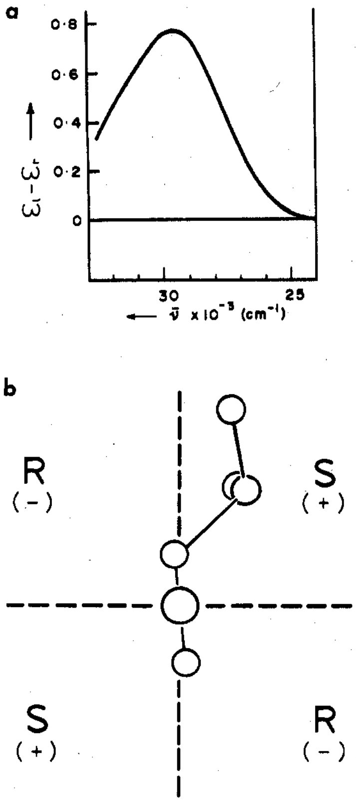


Figure 5. (a) Circular dichroism spectrum of the complex. (b) Projection of the Pt–olefin geometry with respect to the quadrant rule for coordinated olefin ligands.

Ia and IIa result from coordination of the two enantiotopic faces of the olefin to the Pt atom. Ib and IIb are isomers generated from Ia and IIa, respectively, by rotation about the metal–olefin bond. The difference in energy between structures Ia and IIa is presumably low (as indicated by a study of molecular models), since the olefin substituent is remote from the asymmetric sulfoxide ligand.

However, the energies of Ib and IIb can be very different depending on the nature and extent of the interactions between the sulfoxide ligand and the substituent on the olefin. If there are strong interactions in either Ib or IIb, there will be a net bias for an *S* or *R* form of the olefin in the final complex. For the complex with the 3-methyl-1-butene ligand the configuration in the solid state is Ia with the *S* form of the olefin being preferred 2:1 at equilibrium in solution. This is a lesser discrimination than that observed for the styrene complex.

A comparison of the geometries of the coordinated olefins in the two structures shows different degrees of tilting of the olefinic bond from the coordination plane normal. Since the barrier to rotation about the metal–olefin bond is accepted to be very low,[12] it is presumably steric considerations which determine the magnitude of the twist which minimizes the nonbonded interactions.

Another difference noted for the two olefins is that one, the styrene, has "slid" out of the coordination square plane. The substituted C atom of the styrene olefin is 0.817 Å above the mean coordination plane, with the other C atom 0.499 Å below this plane. For the 3-methyl-1-butene olefin the two C atoms are almost equidistant above and below the Pt–Cl–Cl plane (see Table VIII). It has been suggested[16] that this phenomenon is associated with both steric and electronic factors but as yet this has not been systematically investigated nor are we aware of any complete theoretical studies in this area.

The orientation of the sulfoxide ligand in this structure is quite similar to that in the styrene complex, with the exception that, presumably due to steric requirements, the phenyl ring has rotated through approximately 90° in order to present the least interaction with the substituent on the olefin.

The circular dichroism spectrum of the 3-methyl-1-butene complex has been measured[2] and is reproduced in Figure 5a. The band at ~29 400 cm^{-1} is positive in sign and on the basis of the quadrant rule[1,2] (depicted in Figure 5b) would indicate the presence of the *S* absolute configuration for the coordinated olefin. This prediction is confirmed by the x-ray structural analysis.

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Registry No. $PtCl_2[CH_3(O)S(C_6H_4CH_3)][(CH_3)_2CHCH{=}CH_2]$, 62708-14-9; $PtCl_2[CH_3(O)S(C_6H_4CH_3)][PhCH{=}CH_2]$, 59821-93-1.

Supplementary Material Available: Table V, a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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