Proton Magnetic Resonance Spectra of Platinum(II) Complexes. II. *cis*- and *trans*-Bis(dialkyl sulfide)dichloroplatinum(II) Complexes. Mechanism of Inversion at Sulfur and Vicinal Platinum–Proton Couplings[1,2]

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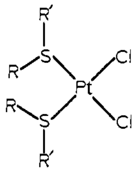
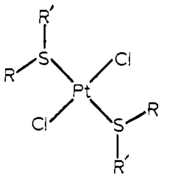
Abstract: The proton magnetic resonance spectra of several platinum–sulfide complexes have been studied at various temperatures. The rates of inversion at pyramidal sulfur are reported for *cis*- and *trans*-[$(R_2S)_2PtCl_2$] complexes with three different sulfide ligands. *trans* complexes invert considerably more rapidly than *cis* complexes. Inversion at sulfur in these complexes is about 10^{18} times faster than inversion at sulfur in sulfoxides. The data are consistent with a mechanism for inversion in which the sulfur retains a distorted tetrahedral configuration and the platinum atom forms σ bonds alternately with the two sulfur lone pairs. The ratio of platinum–proton coupling constants (Pt–S–C–H) is fairly constant: $J_{trans}/J_{cis} = 0.82$. The sensitivity of the coupling interaction to the nature of the *trans* ligand is discussed.

In the preceding paper we have reported studies of the nmr spectra of **1**.[3] The methylene region was proven to be an AB (66%) + ABX (34%) system, sensitive to solvent and temperature as well as sulfur inversion. This paper describes observations by nmr on a series of *cis* and *trans* platinum(II) complexes (**1**–**8**). The results enable us to propose a mechanism for inversion at sulfur, and we discuss some factors affecting platinum–proton couplings.



1, R = R′ = $C_6H_5CH_2$
3, R = R′ = CH_3CH_2
5, R = CH_3; R′ = $C_6H_5CH_2$
7, R = R′ = CH_3



2, R = R′ = $C_6H_5CH_2$
4, R = R′ = CH_3CH_2
6, R = CH_3; R′ = $C_6H_5CH_2$
8, R = R′ = CH_3

Experimental Section

Nmr Spectra. The nmr spectra were recorded with two Varian A-60's, one of which was equipped with a variable-temperature probe, and a Varian HR-60 equipped with a temperature probe and a frequency-sweep unit. Spectra were calibrated by the sideband technique[4] using Hewlett-Packard 200AB or 200CD wide-range oscillators and a Hewlett-Packard 5233L frequency counter. Tetramethylsilane (TMS) was used as the internal standard. Rates of inversion and activation parameters were determined as previously described.[3]

Preparation of ***cis*-** **and** ***trans*-Bis(dimethyl sulfide)dichloroplatinum(II).** An attempt to prepare pure *cis* complex as described by Cox[5] resulted in a *cis* (83%) and *trans* (17%) isomeric mixture as determined by their nmr spectra (see Results section).

Preparation of ***trans*-Bis(diethyl sulfide)dichloroplatinum(II).** Kauffman's method was used,[6] mp 104–105° (lit.[6] 107°).

Anal. Calcd for $C_8H_{20}Cl_2PtS_2$: Pt, 43.72. Found: Pt, 43.21. One Pt–Cl stretching vibration was found at 342 cm^{-1} in the far-infrared spectrum as expected for a *trans* complex.[7]

Preparation of ***cis*-Bis(diethyl sulfide)dichloroplatinum(II).** Kauffman's method was used,[6] mp 104–105° (lit.[6] 107°).

Anal. Calcd for $C_8H_{20}Cl_2PtS_2$: Pt, 43.72; C, 21.52; H, 4.52. Found: Pt, 43.68; C, 21.73; H, 4.69.

Two Pt–Cl bands at 314 and 330 cm^{-1} were found in the far-infrared as expected for a *cis* complex.[7]

Preparation of ***cis*-Bis(methyl benzyl sulfide)dichloroplatinum(II).** A mixture of K_2PtCl_4 (2 g, 0.005 mole) dissolved in 25 ml of water and methyl benzyl sulfide (2.07 g, 0.015 mole) in 10 ml of methanol was shaken for 12 hr. Yellow crystals were filtered off and recrystallized from hot aqueous ethanol to give fine yellow needles, mp 157–159°.

Anal. Calcd for $C_{16}H_{20}Cl_2PtS_2$: Pt, 36.00; C, 35.45; H, 3.72. Found: Pt, 35.95; C, 35.60; H, 3.86.

Two Pt–Cl bands at 324 and 318 cm^{-1} were found in the far-infrared.

Results

Bis(dibenzyl sulfide)dichloroplatinum(II) Complexes. The detailed study of the *cis* complex is in the previous paper.[3] Above 25° a 1:4:1 set of signals appears in the $CDCl_3$ solution of the *cis* complex which is assigned to the *trans* isomer on the basis of chemical shift and coupling constant.[8] When the solution is cooled, these signals disappear indicating a reversible, temperature-dependent isomerization. Since at 27° the 1:4:1 signal from **2** shows no magnetic nonequivalence as observed for **1**,[3] a limit can be set on the rate of inversion at sulfur in **2** (Table I).

Bis(diethyl sulfide)dichloroplatinum(II) Complexes. Figures 1–3 record the nmr spectra of the methylene

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[1] Dedicated to the late Dr. A. J. R. Bourn.

[2] Research supported by Grant GP-3726 from the National Science Foundation, by Grant AM-6870 from the U. S. Public Health Service, by a grant from the Faculty Research Committee of U.C.L.A., and by an Alfred P. Sloan Research Fellowship to P. H. A preliminary report of this work has appeared: P. Haake and P. C. Turley, *Inorg. Nucl. Chem. Letters*, **2**, 173 (1966).

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Table I. Activation Parameters for Inversion in Platinum–Sulfur Compounds

Compound[a]	T_c, °K[b]	k_T, sec^{-1} [c]	Log A, sec^{-1} [d]	E_a, kcal/mole[d]	ΔF^*, kcal/mole[e]	ΔH^*, kcal/mole	ΔS^*, eu
cis-$[(C_6H_5CH_2)_2S]_2PtCl_2$ (**1**)	307.5	10.3	13.8[f]	18.0[f]	16.6[f]	17.4	3
trans-$[(C_6H_5CH_2)_2S]_2PtCl_2$ (**2**)	<300	>10^2			<15		
cis-$[(C_2H_5)_2S]_2PtCl_2$ (**3**)	333	64.7			16.8		
trans-$[(C_2H_5)_2S]_2PtCl_2$ (**4**)	274	36.4			13.9		
cis-$(CH_3SCH_2C_6H_5)_2PtCl_2$ (**5**)	309	11.6	14.8[g]	19.2[g]	16.5	18.6	7
trans-$(CH_3SCH_2C_6H_5)_2PtCl_2$ (**6**)	<223	>50			<12		

[a] Solvent was $CDCl_3$ except for **5** where it was CH_2Cl_2. [b] Coalescence temperature = T_c. [c] Rate of inversion at coalescence temperature = k_T. [d] Arrhenius parameters for $k = Ae^{-E_a/RT}$. [e] Estimated probable error is ±0.3 kcal/mole. [f] Standard deviations: σ_{E_a} = 0.5 kcal/mole; $\sigma_{\log A}$ = 0.3. [g] Standard deviations: σ_{E_a} = 1.1 kcal/mole; $\sigma_{\log A}$ = 0.8.

protons of **3** and **4** at various temperatures. The lack of symmetry in the resonance below the coalescence temperatures indicates there are two different platinum proton coupling constants in each complex. In **4**, coalescence of the center and most intense portion of the ABM_3 system (J_{Pt} = 0) occurs at +1 ± 5° (Figure 2b); in **3**, coalescence of the center multiplet to an A_2M_3 system occurs at +60 ± 5° (Figure 3b).

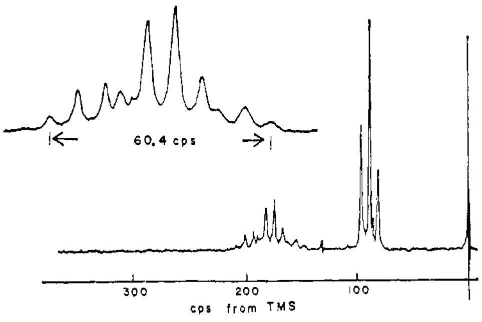

Figure 1. Nmr spectrum of *trans*-bis(diethyl sulfide)dichloroplatinum(II) in $CDCl_3$ at normal probe temperatures (about 30°); upper trace is an enlargement of the methylene region.

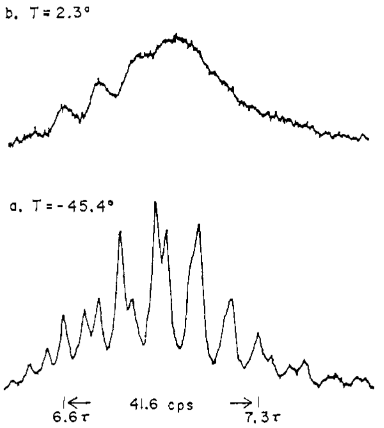

Figure 2. Temperature dependence of methylene resonance in *trans*-bis(diethyl sulfide)dichloroplatinum(II).

The low-temperature nmr spectra of **3** and **4** are too complex to permit complete analyses, but four quartets can be extracted from the center of the methylene signals; from their relative spacings they can be assigned as the AB part of an ABM_3 system. This enabled determination of $\Delta\nu_{AB}$ which was found to be temperature dependent (Figure 4). This linear relationship

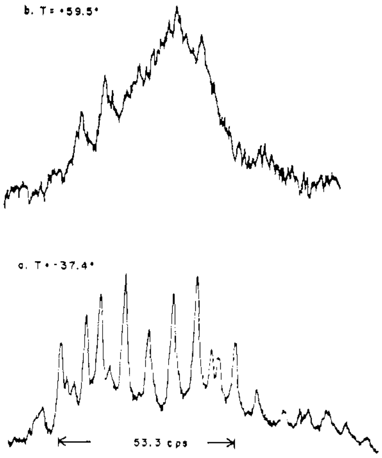

Figure 3. Methylene region in nmr of *cis*-$[(Et_2S)_2PtCl_2]$.

($\Delta\nu$ *vs.* T) observed in the absence of exchange permits the true chemical shift, $\Delta\nu$, to be obtained at the coalescence temperature. For **4**, the least-squares line observed over the temperature range −50 to −15° is

$$\Delta\nu = -0.073T + 16.44 \qquad (1)$$
$$\sigma_{\text{slope}} = 0.003 \quad \sigma_{\text{intercept}} = 0.09$$

For **3**, the least-squares line observed over the temperature range −50 to +20° is

$$\Delta\nu = -0.025T + 30.68 \qquad (2)$$
$$\sigma_{\text{slope}} = 0.004 \quad \sigma_{\text{intercept}} = 0.09$$

The rate constants and free energies of activation for sulfur inversion at the coalescence temperature are listed in Table I.

***cis*-Bis(methyl benzyl sulfide)dichloroplatinum(II).** The methylene region of the nmr spectrum of **5** is not resolved enough for analysis. However, the methyl region is quite suitable for rate determinations (Figure 5). The two 1:4:1 triplets, Figure 5a, are assigned to the *meso* and *dl* isomers which arise from the two asymmetric sulfur atoms in the complex. The peak separa-

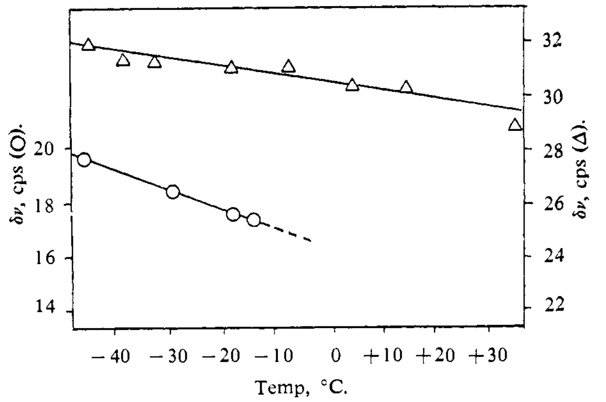

Figure 4. The dependence of chemical shift on temperature in *cis*-bis(diethyl sulfide)dichloroplatinum(II) (Δ) and *trans*-bis(diethyl sulfide)dichloroplatinum(II) (O).

tion between the *cis* methyl signals of **5** is linearly dependent upon temperature in the range −90 to 0° in methylene chloride, and the least-squares relationship is

$$\Delta\nu = -0.050T + 8.35 \qquad (3)$$

$$\sigma_{\text{slope}} = 0.001 \quad \sigma_{\text{intercept}} = 0.06$$

Since the two methyl sites appear equally populated, rate equations[9] used previously[3] are applicable. Rate determinations above the coalescence temperature were complicated by the appearance of a new 1:4:1 triplet which was assigned to *trans*-bis(methyl benzyl sulfide)-dichloroplatinum(II) (**6**) and enabled determination of $J_{\text{Pt-S-C-H}}$ in the *trans* isomer. The rate constants and activation parameters are given in Table I. A plot of log *k vs.* 1/*T* is shown in Figure 6.

Bis(dimethyl sulfide)dichloroplatinum(II) Complexes. The nmr spectrum of our preparation of $[(CH_3)_2S]_2PtCl_2$ consisted of two 1:4:1 triplets in the methyl region. The high-field resonances (17% of spectrum) are centered at −149 cps from TMS with $J_{\text{Pt-S-C-H}}$ = 41.0 cps. The low-field set (83% of spectrum) is centered at −156 cps with $J_{\text{Pt-S-C-H}}$ = 49.5 cps. On the basis of Pt–H couplings, the latter set is assigned to the *cis* isomer.[8]

Platinum–Proton Coupling Constants. Above the coalescence temperatures it was possible to determine vicinal platinum–proton coupling constants for compounds **1–8**. These couplings and the *cis–trans* ratios are shown in Table II.

Table II. Vicinal Platinum–Proton Coupling Constants in *cis*- and *trans*-Bis(dialkyl sulfide)dichloroplatinum(II) Complexes

Sulfide ligand	$J_{\text{Pt-S-C-H}}$[a] cis	trans	J_{trans}/J_{cis}
$(C_6H_5\mathit{CH_2})_2S$[b,c]	43.0	37.0	0.86
$(CH_3\mathit{CH_2})_2S$[b,d]	46.4	37.2	0.80
$\mathit{CH_3}SCH_2C_6H_5$	49.7	41.6	0.84
$(CH_3)_2S$	49.5	41.0	0.83

[a] Estimated uncertainty in coupling constants is ±0.5 cps. [b] Coupling constants were measured above the coalescence temperature. Coupling constants given for italic hydrogens. [c] $J_{\text{H-C-H}} = -13.0$ cps. [d] $J_{\text{H-C-C-H}} = 7.4$ cps for both isomers; $J_{\text{H-C-H}} = -12.0$ and -11.6 cps for *cis* and *trans* isomers, respectively.

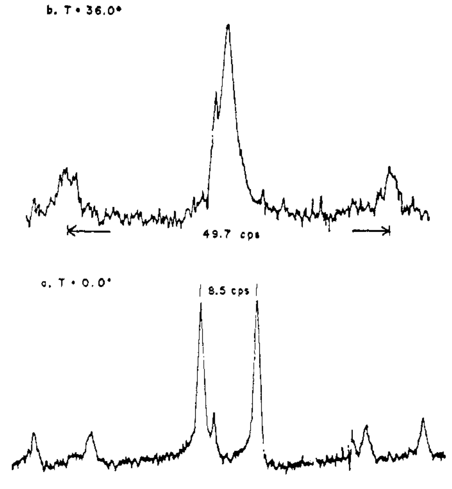

Figure 5. Temperature dependence of methyl region in nmr spectrum of *cis*-$[(MeSCH_2C_6H_5)_2PtCl_2]$. Solvent is CH_2Cl_2.

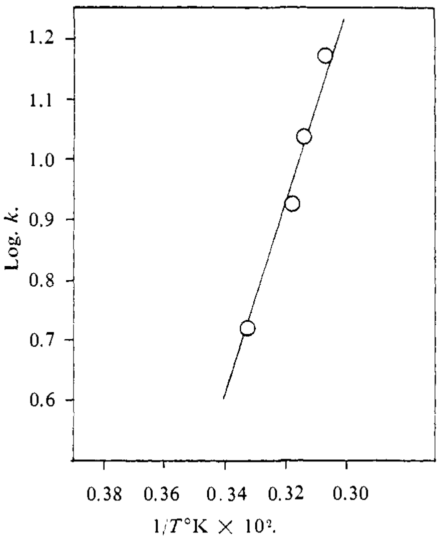

Figure 6. Arrhenius plot for sulfur inversion in *cis*-bis(methyl benzyl sulfide)dichloroplatinum(II).

Two vicinal Pt–H couplings are known below the coalescence temperature. In the *cis* dibenzyl sulfide complex (**1**), $J_{\text{Pt-S-C-H}_A}$ = 55.7 cps and $J_{\text{Pt-S-C-H}_B}$ = 29.3 cps.[3] In the *cis* methyl benzyl sulfide complexes (*dl* and *meso*), $J_{\text{Pt-S-C-H}_3}$ = 49.7 cps for both diastereoisomers.

Discussion

The Inversion Process. The AB nature of the benzylic protons in the pmr spectrum of **1** and the spectral observations of other platinum–sulfide complexes studied are consistent with a nonplanar sulfur configuration.[3] These data supplement some solid-state analyses where the sulfur atom was found to be pyramidal in metal complexes.[10] The facile inversion process is a departure from the behavior of the other tricoordinated sulfur compounds.

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(9) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(10) (a) C.-I. Branden, *Arkiv Kemi*, **22**, 83 (1964); (b) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Am. Chem. Soc.*, **87**, 5251 (1965).

Table III. Rates of Inversion in Tricoordinated Sulfur Compounds

Compound	Temp, °C	k, sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu	Rel rate[a] at 25°
CH_3SO-*p*-$C_6H_4CH_3$[a]	250	6.7×10^{-5}	43	+3	1
$C_6H_5CH_2SO$-*p*-$C_6H_4CH_3$[a,b]	145	7.3×10^{-5}	43	+24	$10^{4.5}$
$CH_3CH_2S^+(CH_3)C(CH_3)_3$[c]	50	4×10^{-4}	25[d]		10^{13}
cis-$[(C_6H_5CH_2)_2S]_2PtCl_2$[e]	25	10	17.4	+3	10^{18}
cis-$[(CH_3CH_2)_2S]_2PtCl_2$[e]	60	65	18[d]		10^{18}
trans-$[(CH_3CH_2)_2S]_2PtCl_2$[e]	1	36	15[d]		10^{20}

[a] In xylene or acetone, ref 12c. [b] Evidence found for a homolytic dissociation–recombination mechanism. [c] In ethanol, ref 16. [d] Calculated from rate constants assuming $\Delta S^* = 3$ eu as in the two cases where ΔS^* has been measured. [e] This work; see Table I.

Sulfoxides invert at measurable rates with hydrogen chloride catalysis;[11] however, the mechanism involves a bimolecular chemical reaction where the intermediate is a sulfur dihalide compound with a plane of symmetry and therefore incapable of optical activity.[11b] In the absence of catalysis, vigorous thermal[12] and photolytic[13] conditions are required for inversion. Except in special cases, thermal inversion of sulfoxides appears to proceed through a pyramidal inversion mechanism.[12c] Benzyl *p*-tolyl sulfoxide is a special case where homolytic dissociation of benzyl radicals appears to be involved in inversion at 135–155°.[12c]

Sulfonium salts are another type of tricoordinated sulfur compound which do not invert readily.[14] Kincaid and Henriques[15] calculated an activation energy of 100 kcal/mole for inversion of a sulfonium sulfur through a planar transition state. However, recent measurements indicate that inversion in *t*-butylethylmethylsulfonium ion proceeds at 50° with a first-order rate constant $> 10^{-4}$ sec^{-1}.[16] Although activation parameters were not evaluated, ΔH^* must be lower than the theoretical estimates.

The rate constants and activation parameters which have been measured for inversion at pyramidal sulfur are summarized in Table III. The relative rates show that inversion in the sulfide complexes we have studied is immensely faster than in sulfoxides and 10^5–10^7 times faster than in sulfonium salts.

At least three mechanisms for sulfur inversion must be considered: tunneling, inversion through a trigonal planar state, and a dissociation–recombination pathway. A dissociation–recombination pathway for the inversion process in platinum–sulfide complexes is impossible since we observe no loss of Pt–S–C–H coupling above the coalescence temperature.[3]

The height of the potential barrier to inversion in these complexes is not known, so it is difficult to predict the contribution from tunneling. However, related considerations indicate that the contribution from tunneling should not be large relative to the total height of the barrier.[15,17]

Considerations of Inversion through a Trigonal Planar State. Nitrogen inversion has been studied in aliphatic amine compounds;[18,19] the process involves passage through a trigonal planar state (the contribution to inversion from tunneling has not been determined). There appear to be at least five factors influencing the energy required for nitrogen inversion: (1) mass of the atoms directly bonded to nitrogen (for tetramethylaziridine, $E_a = 11.5$ kcal/mole, and for 1-deuteriotetramethylaziridine, $E_a = 14.7$ kcal/mole;[18c] (2) steric effects (large substituents close to nitrogen should increase the inversion rate since steric interactions are decreased in a planar state);[19] (3) electron repulsion (when the atom bonded to nitrogen contains an electron lone pair, *e.g.*, oxygen, electron repulsion will be greater in the planar state, decreasing the inversion rate);[19c] (4) inductive effects (an electronegative substituent will increase the s character of the unshared pair on nitrogen, decreasing the inversion rate);[19c] (5) conjugative effects (double bond character of the type $N^+{=}X^-$ increases nitrogen inversion since π-orbital overlap is most effective in a planar system).[19d,e] Since there is $O \rightarrow S$ π bonding in sulfoxides,[20] they should be a reasonable model for the compounds we have studied where there is $Pt \rightarrow S$ π bonding.[3] Therefore, the important comparisons from Table III concern sulfoxides and *cis* and *trans* sulfide complexes.

None of the effects mentioned above appear capable of explaining the 10^{18}–10^{20} rate differences between sulfoxides and sulfide complexes with inversion through a planar state. In fact, a large effect would probably be the mass effect which would predict a slower rate of inversion of the sulfide complexes compared to sulfoxides. We therefore must reject the three mechanisms suggested above for inversion of the sulfide complexes although they have been suggested for sulfoxides;[12]

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(11) (a) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **86**, 2935 (1964); (b) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964); (c) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965).

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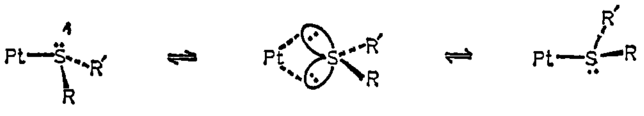
a benzyl sulfoxide appears to invert by a dissociative mechanism and most sulfoxides appear to invert *via* a planar state.

Inversion through a Partially Dissociated State. The multiple bonding possibilities available in platinum(II) complexes lead us to suggest an inversion mechanism in which sulfur retains its distorted tetrahedral configuration and some bonding to platinum persists through the inversion process. This process is depicted below.



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The configuration **9**, midway in the inversion process, could be an intermediate or a transition state, but a reasonable hypothesis is that there is bonding to both sulfur unshared pairs so that the platinum atom has a distorted pentacoordinate configuration in **9**.[21] The inversion process then is really an internal displacement of one sulfide pair by another sulfide pair in a rearrangement mechanism similar to that suggested for displacement on platinum(II).[22] This proposal is consistent with the retention of Pt–S–C–H coupling above the coalescence temperature, since bond weakening and bond strengthening are involved but there is never opportunity for dissociation of the sulfide ligand.

In **9**, R, R′, Pt, and S are coplanar, but the important difference between this proposal and the suggested mechanism of inversion at nitrogen and at sulfoxide sulfur is that the configuration of sulfur is tetrahedral, not trigonal, in **9**.[23] Also, this proposal would mean there is an internal displacement at platinum rather than true inversion at sulfur in these complexes.

Platinum–Proton Coupling Constants. The average ratio of J_{trans}/J_{cis} is 0.83 (Table II). Three explanations are possible based on coupling through σ bonds, π bonds, and space. Coupling through space is rare.[24] The amount of s character in the π bonds must be small. Therefore, the most reasonable explanation for this ratio is the increased strength of the σ Pt–S bonds in the *cis* isomers due to increased $Pt \rightarrow S$ π bonding which makes the *cis* sulfurs better ligands than the *trans* sulfurs.[8,25]

Acknowledgment. We are particularly indebted to the late Dr. A. J. R. Bourn and to Professor F. A. L. Anet for valuable discussions and help with the instrumentation.

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Olefin Coordination Compounds of Rhodium. V. The Relative Stabilities and Rates of Exchange of Olefin Complexes of Rhodium(I)

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Abstract: The stabilities of a number of olefin complexes of rhodium(I) have been compared. Alkyl substituents on olefin carbons destabilize rhodium(I) complexes much more than the corresponding silver compounds. Conversely, coordination is enhanced by electronegative substituents, and this is attributed to a stronger π or back-bond. Since C_2F_4 (which coordinates very strongly) displaces ethylene from rhodium(I) much more slowly than do propene or butenes (which coordinate weakly), it is inferred that formation of a π bond plays a minor role in the development of the transition state for nucleophilic olefin exchange.

The bond uniting olefins and transition metals is currently described[1] as comprising (1) a σ bond formed by overlap of the filled π orbital of the olefin with an empty σ-type orbital of the metal atom and (2) a π-type "back-bond" from overlap of a filled, metal d_{xy} or other $d\pi$–$p\pi$ hybrid orbital with the antibonding π orbital of the olefin. It is expected that the strength of both the σ bond and π "back-bond" are affected by olefin structure. For example, an electronegative olefin substituent, by reducing the electron density of the olefin, would weaken the σ bond and strengthen the π bond. Depending upon the relative contributions of each, the

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[1] M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).