

tion that the insoluble pyridinium salt did not precipitate even when the solution was concentrated and cooled.

Roughly equal quantities of the three isomers of phenylpyridine were isolated from the filtrate of the reaction of **2** in pyridine, along with some benzenethiol. The same result was obtained for the platinum compound **1** except that the yield of phenylpyridines was much lower.

There are two important contrasts here. The first is the striking difference between the solution reactions of the platinum(II) and the palladium(II) complexes. With the former, primarily complex arylation occurs, the unstable partially phenylated $[\text{Pt}(\text{S}_2\text{C}_2\text{O}_2)(\text{S}_2\text{C}_2\text{O}_2\text{-C}_6\text{H}_5)(\text{py})_2]$ being an intermediate step in the total phenylation and subsequent loss of one dithiooxalate from the platinum. On the other hand, the palladium complex undergoes very little sulfur phenylation, but predominantly solvent phenylation occurs. It should be mentioned that when the bis(dithiooxalato)palladate(II) ion is refluxed in pyridine in the absence of the diphenyliodonium ion, no change occurs; the phenomena we observe are indeed the result of diphenyliodonium reactions.

A second contrast in this work is that between the solution and solid-state experiments. In solution there is little tendency toward thiophenol formation, which of course predominates in the solid reaction. We feel that what actually happens in the solid is first the phenylation of coordinated dithiooxalate followed by a further reaction of the coordinated phenyl ester at the higher temperature of the solid reaction, giving the observed products.

The Reaction Mechanism.—A radical mechanism is warranted for the methanol solution reaction by its thermal or photoinduction, for the solid-state reactions by the large difference in reaction rate between 140 and 146°, as well as similarity of product obtained from methanol, and for the pyridine solution reactions by the production of all three phenylpyridines.¹⁷

In refluxing pyridine the solvent phenylation is a radical process, and we have assumed that here attack on the complex anion is also radical in nature. In view of our other results this is not unlikely. The drastic difference in behavior between **1** and **2** in solution must reflect a difference in the attractive forces between the complex and the reactive iodonium species. Here the course of the ligand reaction shows a pronounced dependence on the nature of the metal ion. This is indeed surprising considering the otherwise close similarity of palladium(II) and platinum(II).

In the solid-state reaction the observed products are consistent with a radical mechanism. However, no kinetic study was attempted and the details of the mechanism are unknown. We wish to emphasize that this is one of the very few ligand reactions studied in which a radical mechanism, rather than a nucleophilic substitution, is the apparent course.

Acknowledgment.—Initiation of this work was assisted by a grant from the University of Connecticut Research Foundation and thereafter supported by the National Institutes of Health under Grant No. GM 14080. We also wish to thank Dr. S. J. Huang of this department for helpful discussions during the course of this work.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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Spectroscopic Studies of Alkyl Sulfoxide Complexes of Platinum(II) and Palladium(II)

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A number of sulfoxide complexes of platinum(II) and palladium(II) have been synthesized, and their infrared and proton magnetic resonance spectra indicate that sulfur is the donor atom. The Pt(II) complexes are of the type PtCl_2L_2 (L = sulfoxide) and far-ir data suggest all have *cis* configurations except the diisopropyl sulfoxide complex. The Pd(II) complexes PdCl_2L_2 are *trans* in the *solid* state but in solution most appear to revert to the halo-bridged binuclear structures $\text{Pd}_2\text{Cl}_4\text{L}_2$. The pmr spectra of the Pt(II) complexes have been analyzed, and the values of ¹⁹⁵Pt-H coupling constants have been rationalized in terms of preferred conformations about the C-S bonds. In suitable sulfoxides, *e.g.*, diethyl, it is clear that S coordination to Pt(II) or Pd(II) results in a significant increase in the degree of methylene proton inequivalence. Magnetic anisotropic effects in these d⁸ square-planar structures are suggested to be responsible.

Introduction

The isolation and characterization of metal complexes of dimethyl sulfoxide (DMSO) were reported²⁻⁴ some

years ago, and it was recognized² and later demonstrated by spectroscopic²⁻⁴ and X-ray studies^{3,5,6} that while DMSO generally associated with metal ions through its oxygen atom, sulfur donation was favored

(1) (a) To whom inquiries should be directed at the University of Queensland. (b) University of Queensland. (c) Indiana University.

(2) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(3) D. W. Meek, D. K. Straub, and R. S. Drago, *ibid.*, **82**, 8013 (1960).

(4) For a review of coordination complexes of sulfoxides see J. Gopalakrishnan and C. C. Patel, *J. Sci. Ind. Res. (India)*, **27**, 475 (1968).

(5) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Cryst.*, **23**, 581 (1967); M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *ibid.*, **23**, 788 (1967).

(6) D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Commun.*, 1080 (1967).

for some cations, such as Pt(II) and Pd(II). Other reports have described complexes of metal ions with sulfoxides in addition to DMSO, *e.g.* diphenyl sulfoxide, di-*n*-propyl sulfoxide, etc.⁴ A recent report suggested that both O and S coordination to Pd(II) may occur in the one complex, *e.g.*, Pd(DMSO)₄²⁺,⁷

Most studies have described O complexes, and well-characterized S complexes were known only for DMSO bound to Pt(II) and Pd(II).²⁻⁴ More recently an iridium(III)-sulfur complex⁸ and possibly a rhodium(II)-sulfur complex with DMSO⁹ have been reported, but, in general, information on such S complexes has been sparse. It appeared very worthwhile to extend the range of information on S complexes and in particular on their spectroscopic properties.

Experimental Section

Dibenzyl sulfoxide was supplied by the Aldrich Chemical Co. Diethyl and diisopropyl sulfoxides were prepared by the periodate oxidation of the corresponding sulfides. Methyl benzyl sulfoxide and methyl isopropyl sulfoxide were prepared by peroxide oxidation of the sulfides. The sulfides in turn were prepared by established procedures.¹⁰ All of the sulfoxides were stored over calcium chloride.

Complexes of the types PtCl₂L₂, PdCl₂L₂, and PdCl₂L, where L is sulfoxide, were prepared, and one typical procedure is given for each.

PtCl₂L₂.—A 0.4153-g (0.001-mol) sample of K₂PtCl₄ was dissolved in *ca.* 1 ml of water, with warming. To this was added *ca.* 0.3 g (excess) of diethyl sulfoxide. The reddish solution gradually became yellow, and the complex separated as long yellow needles, which were filtered off, washed with water, and dried *in vacuo*.

PdCl₂L₂.—A 0.3824-g (0.001-mol) sample of PdCl₂(C₆H₅CN)₂ was dissolved in *ca.* 5 ml of benzene with warming. To this was added 0.3 g (excess) of diethyl sulfoxide in 5 ml of benzene. Several milliliters of hexane was added, and after 2 days, large orange plates had crystallized. These were filtered off, washed with benzene, and dried in air.

With some sulfoxides, the dark red color of the palladium chloride-bis(benzonitrile) solution was discharged immediately on addition of the sulfoxide; separation of the yellowish complex began soon after, and was complete within *ca.* 2 hr.

PdCl₂L.—In the case of dibenzyl and diisopropyl sulfoxides, the complexes of this type, which are dark red-brown, separated when the procedure outlined above was followed. In all other cases the procedure was the same, but 0.0005 mol of sulfoxide in benzene was added to 0.001 mol of palladium chloride-bis(benzonitrile) in benzene.

Proton magnetic resonance spectra were obtained on CDCl₃ or CHCl₃ solutions with internal tetramethylsilane as standard, on Varian A-60 and HA-100 instruments. The 220-MHz spectra were recorded on a Varian HR-220. Infrared spectra were obtained on Nujol mulls or CHCl₃ solutions on a Perkin-Elmer 457 spectrophotometer.

Analyses were by the Australian Microanalytical Service, Melbourne, or by Mr. J. Kent of the University of Queensland.

Results and Discussion

Platinum(II) complexes of the type MCl₂L₂ (L = sulfoxide) and palladium(II) complexes of types MCl₂L₂ and MCl₂L were isolated, depending on conditions and sulfoxide type (*vide infra*). The complexes isolated,

(7) B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, **8**, 971 (1969).

(8) M. McPartlin and R. Mason, *Chem. Commun.*, 545 (1967).

(9) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

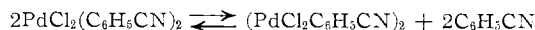
(10) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fildes, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

TABLE I

M	L	—% calcd—		—% found—		Mp, °C
		C	H	C	H	
MCl ₂ L ₂						
Pd	(CH ₃ CH ₂) ₂ SO	24.65	5.14	24.84	5.24	104–105
Pd	CH ₃ SOCH ₂ C ₆ H ₅	39.56	4.12	40.71	4.26	162
Pd	CH ₃ SOCH(CH ₃) ₂	24.65	5.14	25.69	4.82	130–132
Pt	(CH ₃ CH ₂) ₂ SO	20.08	4.18	20.52	4.21	112–114
Pt	CH ₃ SOCH ₂ C ₆ H ₅	33.44	3.48	33.73	3.58	141–143
Pt	(C ₆ H ₅ CH ₂) ₂ SO	46.28	3.85	45.89	3.93	142
Pt	CH ₃ SOCH(CH ₃) ₂	20.08	4.18	20.22	4.11	129–131
Pt	((CH ₃) ₂ CH) ₂ SO	26.96	5.24	27.23	5.43	142–143
MCl ₂ L						
Pd	DMSO	9.40	2.35	10.56	2.56	190
Pd	CH ₃ SOCH ₂ C ₆ H ₅	28.97	3.02	29.94	3.07	165
Pd	(C ₆ H ₅ CH ₂) ₂ SO	41.24	3.44	40.48	3.42	164–165
Pd	(C ₆ H ₅) ₂ SO	37.95	2.64	38.86	2.76	189–190
Pd	((CH ₃) ₂ CH) ₂ SO	23.15	4.50	23.36	4.73	170 dec
Pd	(CH ₃ CH ₂) ₂ SO	16.96	3.53	17.64	4.12	177

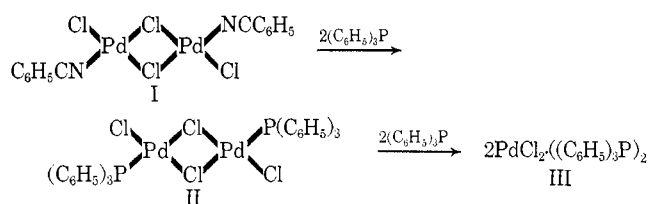
their melting or decomposition points, and analytical data are located in Table I. The bis-DMSO complexes of platinum(II) and palladium(II) dichlorides were known compounds.²

Synthesis of Complexes.—Details are located in the Experimental Section, but some general comments seem appropriate. The Pt(II) complexes were obtained readily by allowing K₂PtCl₄ to react with the sulfoxide, sometimes in an aqueous medium. This procedure led in every case to complexes of the type PtCl₂L₂, irrespective of the structure and basicity of the sulfoxides. Two types of Pd(II) complexes were characterized, but the route to each involved bis(benzonitrile)palladium(II) dichloride, (C₆H₅CN)₂-PdCl₂, as the source of soluble Pd(II). Some initial results, namely, the preparation of the dibenzyl sulfoxide complex, PdCl₂(C₆H₅CH₂)₂SO, instead of the anticipated bis-sulfoxide complex, even when excesses of sulfoxide were employed, prompted investigation of the Pd(II) species formed when (C₆H₅CN)₂-PdCl₂ was dissolved in benzene or chloroform. This nitrile complex, which is yellow and mononuclear *trans* in the solid,¹¹ produces deep red solutions in chloroform and benzene, a fact exciting no curiosity in the past. Solution ir spectra (CHCl₃) reveal two C–N stretching frequencies at 2230 and 2295 cm⁻¹, the former coincident with ν_{C≡N} for free benzonitrile. Intensity considerations indicated roughly equal concentrations of free and bound nitrile, after allowing for differences in intrinsic intensities of ν_{C≡N} under free and bound conditions. Molecular weight measurements confirmed that in solution disproportionation in the sense below was occurring, the position of equilibrium being heavily (if not exclusively) to the right.

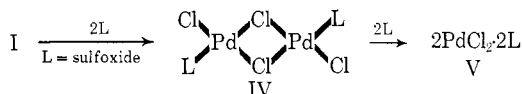


The only reasonable structure for (PdCl₂C₆H₅CN)₂ appears to be the chloro-bridged binuclear species I. Evaporation of the solvent (CHCl₃ or C₆H₆) resulted in eventual reversion to PdCl₂(C₆H₅CN)₂, due to the accumulation of C₆H₅CN.

(11) J. R. Holden and N. C. Baenziger, *Acta Cryst.*, **9**, 194 (1956).



Species I may be intercepted by treatment with the appropriate amount of triphenylphosphine to yield the known II,¹² while further addition of triphenylphosphine produces the known III.¹³ (It should be noted that the formation of II does not by itself prove the correctness of formulation I.) In the cases of sulfoxide addition, displacement of $\text{C}_6\text{H}_5\text{CN}$ seems first to yield IV, while further addition may yield V.

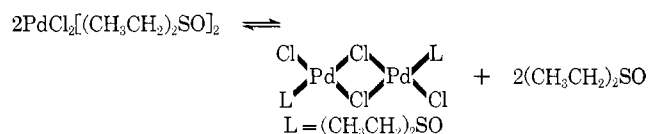


The IV \rightarrow V conversion involves cleavage of chloro bridges, and some sulfoxides, *e.g.*, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SO}$ and $((\text{CH}_3)_2\text{CH})_2\text{SO}$, are either too feebly basic or sterically prejudiced to effect the change. In some cases, *e.g.*, DMSO, exactly stoichiometric amounts of sulfoxide must be employed to isolate IV, since bridge cleavage occurs readily.

The MCl_2L_2 complexes are yellow-orange, while the MCl_2L variety ($\text{M} = \text{Pd}$) are deep red-brown, consistent with an extended chromophore as in IV. The former are generally soluble in typical organic and nmr solvents, but the latter are generally quite insoluble, so that solution properties could not be probed. All complexes reported here are quite stable.

Structures of the Complexes. (a) MCl_2L_2 Types. —Elemental analyses are consistent only with the empirical representation MCl_2L_2 ($\text{M} = \text{Pt}, \text{Pd}$; L = sulfoxide) for the solid yellow-orange complexes, and molecular weight data for $\text{PtCl}_2[(\text{CH}_3\text{CH}_2)_2\text{SO}]_2$ confirm its mononuclear character in solution (mol wt: calcd, 478; found, 495). There is no reasonable doubt that the other Pt(II) complexes are also mononuclear in solution.

Although almost certainly mononuclear in the solid (far-ir data), $\text{PdCl}_2[(\text{CH}_3\text{CH}_2)_2\text{SO}]_2$ is, with equal certainty, mostly binuclear in chloroform solution.



Solution ir spectra indicate essentially equal concentrations of free and bound sulfoxide (S-O stretching region) (Figure 1a) and molecular weight data also indicate the equilibrium to be heavily to the right. The same techniques suggest extensive (even complete) disproportionation for the methyl benzyl and

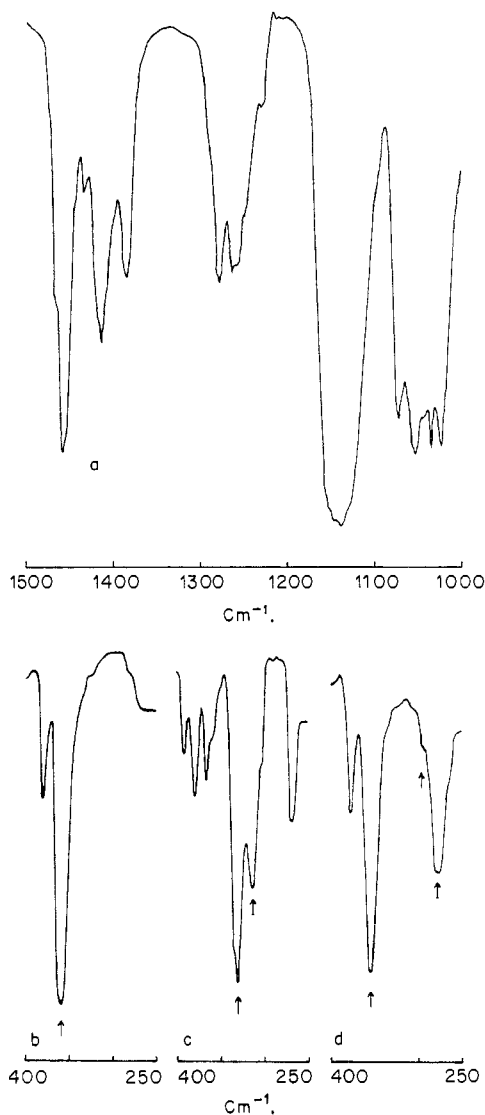


Figure 1.—(a) Infrared spectrum of $\text{PdCl}_2[(\text{CH}_3\text{CH}_2)_2\text{SO}]_2$ in CHCl_3 . The broad band at *ca.* 1040 cm^{-1} corresponds to free sulfoxide and that at *ca.* 1150 cm^{-1} to complexed sulfoxide. The comparable intensities of these bands is in line with reversion in solution to the binuclear structure. See text. (b) Far-ir spectrum of $\text{PdCl}_2(\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5)_2$; a single $\nu_{\text{Pd}-\text{Cl}}$ is indicated by the arrow, strongly suggesting a *trans* configuration. (c) Far-ir spectrum of $\text{PtCl}_2(\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5)_2$ (mull); two $\nu_{\text{Pt}-\text{Cl}}$ indicated support the *cis* structure. (d) Far-ir spectrum of $[\text{PdCl}_2(\text{CH}_3)_2\text{SO}]_2$ (mull), showing three regions for $\nu_{\text{Pd}-\text{Cl}}$, in line with the chloro-bridged binuclear structure.

methyl isopropyl sulfoxide complexes. Far-ir solution (CHCl_3) spectra show $\nu_{\text{M}-\text{Cl}}$, appropriate for bridged species, in the case of the methyl benzyl sulfoxide complex (*vide infra*). (We are deeply indebted to Dr. Glen Deacon and his associates at Monash University for their kindness in obtaining far-infrared solution spectra for us.)

The sharp pmr spectra for the Pt(II) complexes are consistent with diamagnetic species indicating little departure from planar structures, so that square-planar geometries seem appropriate. This is definitely the case for $\text{PdCl}_2(\text{DMSO})_2$ in the solid⁵ for which magnetic susceptibility measurements⁷ indicate essential diamagnetism. Questions remaining relate to the iden-

(12) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc., A*, 1897 (1967).

(13) H. Itatani and J. C. Bailor, Jr., *J. Am. Oil Chemists' Soc.*, **44**, 147 (1967).

TABLE II^a

Sulfoxide	ν_{S-O} (free)	ν_{S-O} (PtCl ₂ L ₂)	ν_{S-O} (PdCl ₂ L ₂)	ν_{S-O} (CH ₃) ₂ SnCl ₂ ·2L
DMSO	1055	1135, 1160	1116	945 ^d
(CH ₃ CH ₂) ₂ SO	1030	1125, 1140	1135	940
CH ₃ SOCH ₂ C ₆ H ₅	1035	1120, 1150, 1170	1110, 1152, 1162	945, 975
(C ₆ H ₅ CH ₂) ₂ SO	1030	1150	1120, 1130, 1177	985 ^b
CH ₃ SOCH(CH ₃) ₂	1020, 1040	1130, 1145	1105, 1130	930, 955 ^c
((CH ₃) ₂ CH ₂)SO	1035	1125

^a ν_{S-O} in cm⁻¹ for Nujol mulls. ^b In this case, the complex has the five-coordinate structure¹⁶ (CH₃)₂SnCl₂·L, but this does not alter the validity of the argument. ^c Refers to the complex (C₆H₅)₂SnCl₂·2L. ^d This complex is certainly O complexed.¹⁵

tivity of the donor atom (*i.e.*, S or O) and the configuration (*cis* or *trans*) in the square plane. Infrared spectra allow firm conclusions on both.

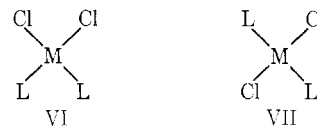
Ir Spectra of MCl₂L₂.—Although a thorough vibrational analysis has indicated that the band assigned commonly as ν_{S-O} in free DMSO derives about half of its potential energy from methyl rocking motions,¹⁴ investigations of a wide variety of sulfoxide complexes suggest strongly that the direction of change in energy of this band on coordination reflects the donor atom, *i.e.*, S or O.⁴ This has been confirmed directly by a number of actual X-ray determinations,^{5,6,8,15} and there is no exception to the generalization that an increase in ν_{S-O} indicates S coordination, and a decrease, O coordination. Thus $\Delta\nu_{S-O}$ (ν_{S-O} (ligand) - ν_{S-O} (complex)) if negative indicates S coordination, while if positive indicates O coordination.

Data pertaining to the S-O stretching region are located in Table II and information on the corresponding organotin complexes, all of which almost certainly are O complexed,^{15,16} is included for comparison.

From Table II, it is quite clear that $\Delta\nu_{S-O}$ is negative, strongly suggesting S coordination for all the Pd(II) and Pt(II) complexes. This has been established with certainty for PdCl₂(DMSO)₂.⁵ A feature of considerable interest is that in the spectra of the DMSO and (CH₃CH₂)₂SO complexes, the S-O band is "split" in the Pt(II) complex, but not perceptibly so for the corresponding Pd(II) complexes. For the other complexes the S-O region is more involved, and precise location of ν_{S-O} is not possible, since bands of similar energy appear. Deuterium substitution, as in PtCl₂(CH₃SOCD₂C₆H₅)₂, results in the disappearance of the bands at 1120 and 1170 cm⁻¹ (Table II), so that the 1150-cm⁻¹ band may be considered to derive most energy from S-O stretching. Rocking motions would be seriously affected (moving to lower frequencies) by deuterium substitution. However, $\Delta\nu_{S-O}$ is doubtlessly negative. The duality in the S-O stretching region of PtCl₂(DMSO)₂ has been taken to indicate a *cis* configuration,⁶ but assignments of configuration on the basis of splitting of bands due to coordinated groups such as -C≡N, >S=O, etc., must be uncertain, particularly when measurements have been made on solid samples.

Far-IR Spectra.—Our main purpose in examining this

region was to provide evidence for the *cis* or *trans* configurations of the square-planar structures, *i.e.*, VI or VII, where L = sulfoxide.



As required by symmetry, VI (C_{2v}) should yield two ν_{M-Cl} in the ir region while VII (D_{2h}) should possess one in the ir region. In addition, ν_{M-Cl} in VI should not in principle be constant but depend in some manner on the nature of the *trans* sulfoxides. On the other hand, in VII, we anticipated essential constancy of the band ν_{M-Cl} and lack of fluctuation would tend to confirm its assignment. In a wide range of square-planar complexes, PtCl₂L₂, Adams, *et al.*,¹⁷ have demonstrated the considerable dependence of ν_{M-Cl} on L in *cis* complexes but independence in the *trans* relatives. For the *cis* sulfoxide complexes, movements in ν_{M-Cl} could well be small.

However, there are other complications, the chief of which are identification of ν_{M-S} , which arises in the same region as ν_{M-Cl} ,⁷ and of various ligand skeletal, bending, and deformation modes. Fortunately, the M-Cl stretching motions are very strong absorbers, so that their intensity alone generally makes them readily distinguishable. Appreciable coupling of ν_{M-Cl} and ν_{M-S} may also occur and could be particularly serious in the *cis* complexes. For these reasons no detailed assignments will be attempted, except to locate what are probably ν_{M-Cl} .

The far-ir data (250–500 cm⁻¹) are located in Table III, and only the main frequencies are listed. In Figures 1b and 1c are the far-ir spectra (400–250 cm⁻¹) of the palladium- and platinum-methyl benzyl sulfoxide complexes.

The italic frequencies are the assignments for ν_{M-Cl} , and confidence in these can be derived from the observations, first, that they are invariably the strongest bands in the spectra and, second, that the frequencies fall nicely into the ranges generally agreed upon for ν_{M-Cl} , where M = Pt, Pd.^{18,19} On accepting these assignments, the conclusion follows that the Pt(II) compounds above are *cis* except for the diisopropyl sulfoxide complex, and the corresponding Pd(II) compounds are *trans*. The powder photographs of the

(14) W. D. Horrocks and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).
 (15) N. W. Isaacs, C. H. L. Kennard, and W. Kitching, *Chem. Commun.*, 802 (1968).

(16) W. Kitching, C. J. Moore, and D. Doddrell, *Australian J. Chem.*, **22**, 1149 (1969).

(17) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(18) D. M. Adams and P. J. Chandler, *ibid.*, **A**, 588 (1969).

(19) J. R. Allkins and P. J. Hendra, *ibid.*, **A**, 1325 (1967).

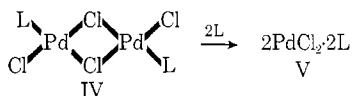
TABLE III
FAR-IR DATA (500–250 cm^{-1}) OF MCl_2L_2

Ligand	Metal	Principal freq., ^a cm^{-1}
DMSO	Pd	354 s, br, 415 s
DMSO	Pt	306 m, 330 s, 378 s, 428 s
$(\text{CH}_3\text{CH}_2)_2\text{SO}$	Pd	250 m, 344 m, 376 s, 409 s, 460 s
$(\text{CH}_3\text{CH}_2)_2\text{SO}$	Pt	270 m, 292 m, 329 s, 344 s, 420 s, 440 m, 469 m, 476 s
$(\text{CH}_3)(\text{CH}_3)_2\text{CHSO}$	Pd	289 m, 330 w, 374 s, 390 m, 451 s, 482 m
$(\text{CH}_3)(\text{CH}_3)_2\text{CHSO}$	Pt	300 m, sh, 320 s, 340 s, 380 m, 391 w, 451 s, 500 s
$\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_3^b$	Pd	360 s, 380 m, 427 s, 474 s
$\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_3$	Pt	268 m, 312 s, 331 s, 365 m, 379 m, 421 m, 440 s, 480 s
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SO}$	Pt	264 w, 308 s, 326 m, 350 m, 402 m, 411 m, 468 s, 478 s
$((\text{CH}_3)_2\text{CH})_2\text{SO}$	Pt	255 m, 291 m, s, 310 m, 352 s, 406 sh, 421 s, 440 m

^a Solid phase (Nujol mulls). Abbreviations: s, strong; br, broad; m, medium; sh, shoulder; w, weak. ^b In CHCl_3 solution bands are located at 303, 315, and 350 cm^{-1} , in line with the binuclear structure in solution. See text.

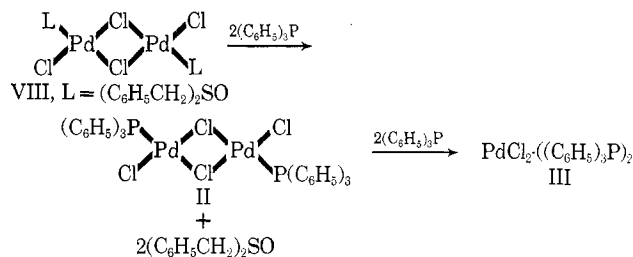
Pd(II) - and Pt(II) -DMSO complexes were also quite different. The variations in $\nu_{\text{M-Cl}}$ as a function of the sulfoxide are rather small (apart from the DMSO complexes), indicating little variation in metal-chlorine bond strengths. Utilizing the arguments of Adams and Chatt,¹⁷ it is possible to locate the above sulfoxides in the *trans*-effect series on the basis of the position of $\nu_{\text{Pt-Cl}}$ in the *cis* complexes, with the reservations mentioned in that report.¹⁷ Thus dibenzyl, diethyl, and methyl isopropyl sulfoxides are comparable to pyridine, while benzyl methyl and dimethyl sulfoxides exert a greater effect and lie close to dialkyl sulfides and selenides, but substantially removed from the stronger group V ligands. Steric effects, which are severe as judged by Dreiding models, probably account for the *trans* configuration of $\text{PtCl}_2[(\text{CH}_3)_2\text{CH}]_2\text{SO}$, but otherwise the predominating *cis* forms agree with thermodynamic considerations for Pt(II) complexes.

(b) MCl_2L Types.—Elemental analyses are consistent with the MCl_2L formulation (L = sulfoxide) and reactions of the complexes, chiefly reversions to the MCl_2L_2 types on treatment with L, and ir data strongly implicate binuclear structures (IV).



Chloro-bridged species, analogous to IV have been fully characterized previously¹² and actual X-ray structures have been determined.^{20,21} Bridge-splitting reactions were conducted in some detail on the dibenzyl sulfoxide complex with $(\text{C}_6\text{H}_5)_3\text{P}$ as indicated in the sequence below. Structures II and III are known compounds.¹²

The main point is that sulfoxide displacement to yield II appears to occur preferentially to bridge split-



ting, but disproportionation of initially formed unsymmetrical complexes ($\text{PdCl}_2\text{L}(\text{C}_6\text{H}_5)_3\text{P}$) to yield II and free sulfoxide cannot be discounted definitely. Treatment of VIII with excess dibenzyl sulfoxide or diisopropyl sulfoxide did not produce PdCl_2L_2 , but in other cases, e.g., DMSO, $\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5$, etc., binuclear compounds were readily converted to the mononuclear variety. The far-ir spectra are completely in accord with binuclear structures, and it is of interest to analyze our data in terms of data discussed^{12,18} for systems of the type $\text{M}_2\text{X}_4\text{L}_2$ (M = Pt, Pd; X = Cl, Br, I; L = neutral donor ligand). For a *trans* symmetrical chloride-bridged arrangement ($\text{Pd}_2\text{Cl}_4\text{L}_2$) theory predicts three regions of Pd-Cl stretching, one of which corresponds to $\nu_{\text{Pd-Cl}}$ (terminal) and two to $\nu_{\text{Pd-Cl}}$ (bridging). The range for the former is $340\text{--}366\text{ cm}^{-1}$ and the ranges for the latter are $308\text{--}294$ and $301\text{--}255\text{ cm}^{-1}$. Approximate descriptions of these modes have been given.¹² In Table IV are the principal absorptions of the bi-

TABLE IV
PRINCIPAL FAR-IR BANDS FOR $\text{Pd}_2\text{Cl}_4\text{L}_2$

L	Principal bands, ^a cm^{-1}
$(\text{C}_6\text{H}_5)_3\text{P}$	250 s, 295 m, s, 354 s
DMSO	280 s, 294 m, 355 s, 379 m, 429 m
$\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5$	280 s, 300 m, 345 s, 360 s
$(\text{C}_6\text{H}_5)_2\text{SO}$	285 s, 302 m, 353 s
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SO}$	280 s, 302 m, 324 m, 334 m, 357 m, 369 m
$((\text{CH}_3)_2\text{CH})_2\text{SO}$	280 s, 305 s, 369 s, 412 m, 440 m
$(\text{CH}_3\text{CH}_2)_2\text{SO}$	255 s, 280 s, 300 m, 320 m, 361 s

^a Abbreviations: s, strong; m, medium.

nuclear complexes in the far-ir spectra and other data (not tabulated) indicate all to be S bonded as expected since $\Delta\nu_{\text{S-O}}$ is negative. In Figure 1d is the far-ir spectrum of PdCl_2L where L = dimethyl sulfoxide.

The italic frequencies are considered to correspond to $\nu_{\text{Pd-Cl}}$; those in the 280-cm^{-1} region correspond to $\nu_{\text{Pd-Cl}}$ (*trans* sulfoxide), while the weaker band at ca. 300 cm^{-1} corresponding to $\nu_{\text{Pd-Cl}}$ (bridging) seems definite. In the 350-cm^{-1} region are $\nu_{\text{Pd-Cl}}$ (terminal), although in some cases two bands of comparable energy and intensity occur, and definite assignment is not possible, except that one is certainly the appropriate band. Besides agreements in frequencies, the relative intensities of the bands reported here (ca. 280, ca. 300, and ca. 350 cm^{-1} ; 10:3:8) correspond with values recently reported. Thus there appears little doubt of the assignments, and support is given to the all-*trans*-symmetrical form, as already written in the formulas (e.g., IV). The far-ir spectrum of $\text{PdCl}_2(\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5)_2$ (CHCl_3 solution) shows bands at 303, 315, and 350 cm^{-1} , in reasonable agreement with the relevant data

(20) J. N. Dempsey and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4984 (1955).

(21) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

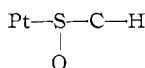
TABLE V
 PMR DATA FOR SULFOXIDES AND PtCl₂(sulfoxide)₂^a

Sulfoxide	Uncomplexed			Complexed					
	τ_{CH_3}	τ_{CH_2}	τ_{CH}	τ_{CH_3}	τ_{CH_2}	τ_{CH}	J_{CH_3}	J_{CH_2}	J_{CH}
DMSO	7.5	6.45	23
(CH ₃ CH ₂) ₂ SO	8.7	7.36	...	8.45	6.66	32	...
		7.25	...		6.16	...		7	...
CH ₃ SOCH ₂ C ₆ H ₅	7.68	6.15	...	6.86	5.55, 5.0	...	22.5	16	...
				6.72	5.30, 4.8	...	22.5	6	...
CH ₃ SOCH(CH ₃) ₂	8.9, 7.7	...	7.4	8.4, 6.66	...	5.86	23	...	6-7
(C ₆ H ₅ CH ₂) ₂ SO	...	6.13	5.30	26	...
					5.70	...		6	...
((CH ₃) ₂ CH) ₂ SO	9.28, 9.26	...	7.68	8.53	...	6.15	5-6
				8.37					

^a The spectra are discussed in the text. J values above are ¹⁹⁵Pt-¹H coupling constants. Geminal proton-proton couplings were observable were 13.5 Hz, while vicinal proton-proton couplings were 7.5 Hz. In some cases, the degree of inequivalence of methylene protons in the uncomplexed sulfoxides was unobservably small, but this depends on the solvent.

in Table IV for the bridged (PdCl₂CH₃SOCH₂C₆H₅)₂, considering possible solvent effects. The agreement is in harmony with other data strongly indicating binuclear solution structures (*vide infra*).

Proton Magnetic Resonance Spectra.—We recently reported pmr data for a number of oxygen-complexed sulfoxides,^{16,22} and it was clear that O complexation to tin or lead had little effect on sulfoxide resonance positions, and no M-¹H spin coupling (as in M-O-S-C-H) was visible. In certain cases, *e.g.*, diethyl sulfoxide, O complexation did, however, reduce the extent of methylene proton inequivalence.¹⁶ We envisaged a more interesting situation with S complexes, and we can now report that (a) S complexation of Pt(II) and Pd(II) has a substantial deshielding effect on α protons, (b) M-¹H spin coupling is clearly evident in



complexes,²³ and (c) methylene proton inequivalence is increased on S complexation.

Pt(II) Complexes. PtCl₂L₂.—Far-infrared spectra strongly indicate *cis* configurations (except for PtCl₂-[(CH₃)₂CH]₂SO)₂) and the pmr spectra are consistent with isomeric homogeneity in CDCl₃. The pmr spectra of these complexes are well resolved, and ¹⁹⁵Pt-¹H spin coupling (¹⁹⁵Pt, $I = 1/2$; 33.7% naturally abundant) results in the appearance of satellites about the main (66.3%) proton resonance. The separation of the satellites yields $J_{195\text{Pt}-1\text{H}}$ (Hz) and their presence indicates that any molecular reorganization *via* rupture of the platinum-sulfoxide linkage must be slow on the pmr time scale. In addition such satellites heavily implicate (although do not prove by themselves) donor action by sulfur. However, taken with the infrared data (*vide supra*), the chemical shift data of α protons in Pt(II)- and Pd(II)-complexed sulfoxides (Table IV), and the crystal structures of PdCl₂(DMSO)₂⁵ and Pd(NO₃)₂(DMSO)₂,⁶ the case for S complexation becomes almost irresistible. The spectral data are condensed in Table V and discussed below.

(22) V. G. K. Das and W. Kitching, *J. Organometal. Chem.* (Amsterdam), **10**, 59 (1967).

(23) W. Kitching and C. J. Moore, *Inorg. Nucl. Chem. Letters*, **4**, 691 (1968).

cis-PtCl₂(DMSO)₂.—This complex is sparingly soluble in most coordinating media and pyridine was reluctantly employed. Immediately on dissolution, major signals at τ 6.45 and 7.5 are observed, the former more intense but yielding to the τ 7.5 resonance with time. The latter resonance corresponds exactly with free DMSO in pyridine and there is no doubt that pyridine displacement of DMSO is occurring. The τ 6.45 resonance is flanked by ¹⁹⁵Pt satellites ($J = 23$ Hz) and this together with the downfield shift of *ca.* 1 ppm is indicative of S complexation.

cis-PtCl₂[(CH₃CH₂)₂SO]₂.—The methylene protons in free diethyl sulfoxide are inequivalent²⁴ and the spectrum has been analyzed by an iterative procedure.²⁴ Complexation to Pt(II) leads to increased complexity in the methylene region, since ¹⁹⁵Pt-¹H coupling occurs. The spectral features thus represent a superposition of an ABM₃ system (M₃ = CH₃) (66.3%) and an ABM₃X system (X = ¹⁹⁵Pt) (33.7%). Utilizing data from the spin-decoupled spectra, computed spectra were produced and an excellent fit of experimental and computed spectra was obtained (Figure 2) for the parameters located in Table V.

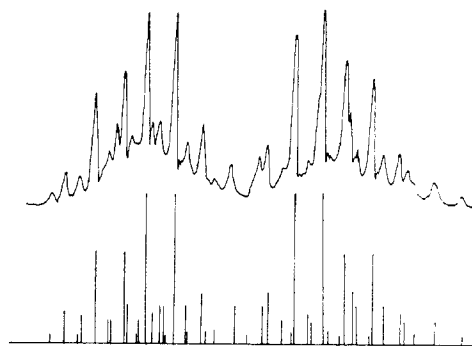


Figure 2.—Top: experimental 100-MHz spectrum of PtCl₂-[(CH₃CH₂)₂SO]₂ showing the complex methylene region of the spectrum. Bottom: computed spectrum, showing satisfactory simulation for the parameters located in Table V and discussed in the text.

cis-PtCl₂(CH₃SOCH₂C₆H₅)₂.—In addition to the magnetic inequivalence of the benzylic protons, an added

(24) (a) N. S. Ham, Abstracts, 6th Australian Spectroscopy Conference, Brisbane, Aug 1967; (b) private communication.

complication in this complex is the presence of two chiral centers, so that diastereoisomers (*dl* and *meso*) may coexist. This is certainly indicated, and analysis of the spectra (*i.e.*, the methylene region) is possible on the basis of almost equal populations of *dl* and *meso* forms. Two AB patterns and two AB regions of ABX systems can be distinguished and in Figure 3 is the experimental 100-MHz spectra with ^{195}Pt satellites indicated. The 220-MHz spectrum (Figure 4) confirms the $J_{^{195}\text{Pt}-^1\text{H}}$ values, and extraction of chemical shifts by inspection is possible. The dmr spectra (deuteron magnetic resonance) of $\text{CH}_3\text{SOCD}_2\text{C}_6\text{H}_5$ (D_2O , OD^\ominus catalyst with $\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5$) and the derived *cis*- PtCl_2 complex were obtained, with the intention of identifying $^{195}\text{Pt}-\text{D}$ coupling (which would be 1/6.5 of the corresponding $^{195}\text{Pt}-^1\text{H}$ coupling) but the spectrum of the complex is broad due to inequivalent deuterons and no ^{195}Pt coupling could be identified with certainty. However, a downfield shift of *ca.* 0.6 ppm in the D resonance is associated with complexation. $^{195}\text{Pt}-\text{CH}_3$ satellites are clearly visible about the equintense methyl signals which are due to the diastereoisomers (100-MHz proton spectrum (Figure 3)). The spectral parameters are located in Table V.

cis- $\text{PtCl}_2[\text{CH}_3\text{SOCH}(\text{CH}_3)_2]_2$.—Two chiral centers again lead to the possibility of the coexistence of *dl* and *meso* forms, but the pmr spectra are consistent with the presence of one, since a single CH_3-S resonance and a single methine resonance $-\text{CH}-\text{S}$ (decoupling of $-\text{CH}(\text{CH}_3)_2$) are observed. The isopropyl methyl groups are inequivalent and this is probably due to the proximity of the chiral sulfur center. The ^{195}Pt coupling to the methine proton is quite small ($> 6-7$ Hz).

cis- $\text{PtCl}_2[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SO}]_2$.—Although we obtained a small quantity in analytically pure form, subsequent attempts on a larger scale invariably produced mixtures, so that the pmr spectrum contains impurity signals. However, the downfield shift relative to free ligand and $^{195}\text{Pt}-^1\text{H}$ coupling identify the signals due to the complex. Analysis is possible on the basis of superposition of AB and ABX ($X = ^{195}\text{Pt}$ 33.7%) systems (Table V).¹

trans- $\text{PtCl}_2[(\text{CH}_3)_2\text{CHSO}]_2$.—Coupling between ^{195}Pt and $-\text{CH}$ is again quite small ($\sim 5-7$ Hz), and again the methyl groups are inequivalent, as they are in free diisopropyl sulfoxide. The extent of inequivalence is increased, and although other explanations (which may be considered for other of the complexes) such as ligand inequivalence or rotational problems (*e.g.*, about the Pt-S bond) may be advanced, a very likely reason is merely the intrinsic magnetic inequivalence, as found in the parent sulfoxide.

Pd(II) Complexes. *trans*- PdCl_2L_2 and *trans*- PdCl_4L_2 .—As already outlined, the solid *trans*- PdCl_2L_2 complexes on dissolution in chloroform yield the chloro-bridged binuclear species, and infrared and molecular weight data suggest essentially little persistence of the mononuclear form, so that free and bound sulfoxides coexist and rapid site exchange leads to somewhat broadened spectra. At -20° , this ligand exchange is

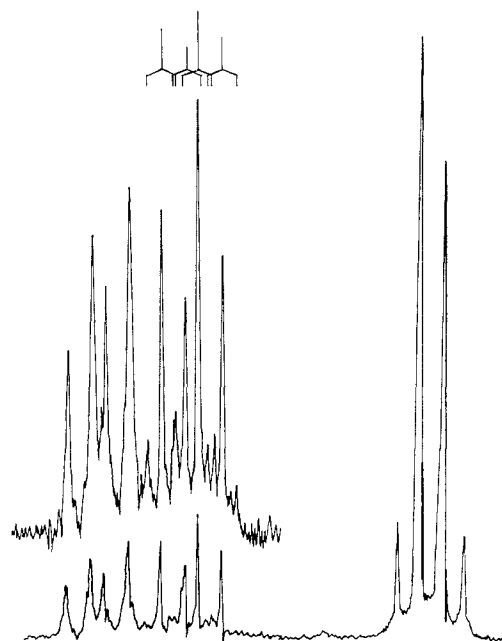


Figure 3.—The 100-MHz spectrum of $\text{PtCl}_2[\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5]_2$ showing methylene and methyl regions. Platinum-195 coupling is clearly visible to CH_3 and to the higher field components of the methylene patterns. Coupling to the lower field components appears as broadening about the bases of the signals.

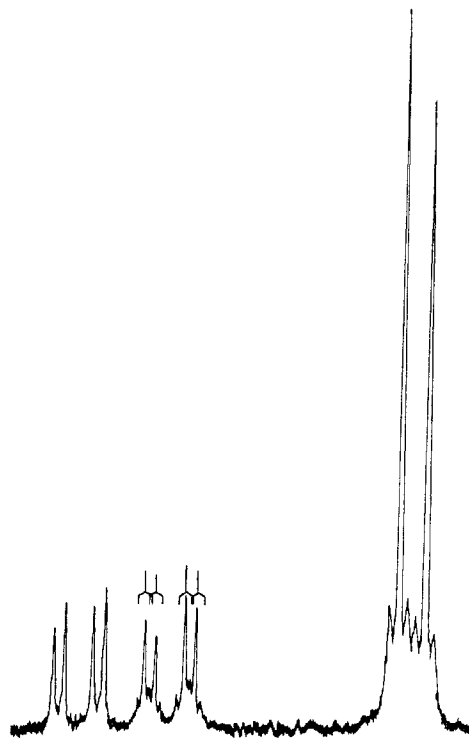


Figure 4.—The 220-MHz spectrum of $\text{PtCl}_2[\text{CH}_3\text{SOCH}_2\text{C}_6\text{H}_5]_2$ showing two CH_3 signals and two methylene AB patterns. Platinum-195 coupling is clearly visible. Coupling constants and chemical shifts are located in Table V and discussed in the text.

still quite rapid in the diethyl sulfoxide case. $\text{PdCl}_2(\text{DMSO})_2$ is too insoluble in other than pyridine (where rapid substitution reactions occur) to obtain a meaningful spectrum. In the cases of the diethyl, methyl benzyl, and methyl isopropyl sulfoxide complexes, only averaged positions for free and bound sulfoxides

could be ascertained. However, by using the known resonance values of the free sulfoxides, the calculated values for bound sulfoxide could be obtained and deshielding of α protons is a result of Pd(II) coordination to sulfur. An alternative device has allowed the observation of a well-resolved spectrum of Pd(II)-complexed diethyl sulfoxide. Addition of slightly less than the calculated amount of $(C_2H_5)_2SO$ to $PdCl_2 \cdot (C_6H_5CN)_2$ in chloroform produces a solution of the binuclear complex in the absence of free sulfoxide (IV, $L = (CH_3CH_2)_2SO$).

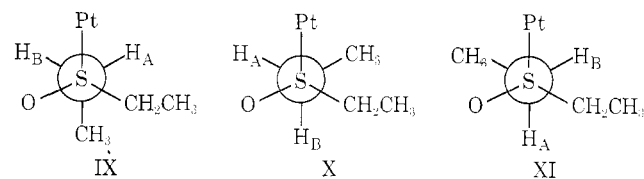
That displacement of C_6H_5CN and coordination of $(C_2H_5)_2SO$ were complete was confirmed by the essential absence of ν_{S-O} for free sulfoxide and $\nu_{C=N}$ for complexed nitrile. Utilizing the values τ_{CH_2} 6.27 and 6.85, $J_{AB} = 13.5$ Hz, and $J_{AM} = J_{BM} = 7.5$ Hz, an excellent reproduction of the methylene region was obtained. This pattern is very similar to that for the Pt(II) complex except that the X ($=^{195}Pt$) component of the spectrum is absent. As in the case of Pt(II), coordination to Pd(II) leads to an increase in the degree of methylene proton inequivalence.

The bridged complex $[PdCl_2((CH_3)_2CH)_2SO]_2$ is of sufficient solubility to obtain a well-resolved spectrum with the aid of the Varian computer of average transients (CAT). With site-exchange problems removed, resonance values for bound sulfoxide are straightforward, and the isopropyl methyl groups are more inequivalent than in the *cis*- $PtCl_2L_2$ complex. The relevant data are τ_{CH_3} 8.17 and 8.36 and τ_{CH} 6.29. The other bridged compounds are poorly soluble.

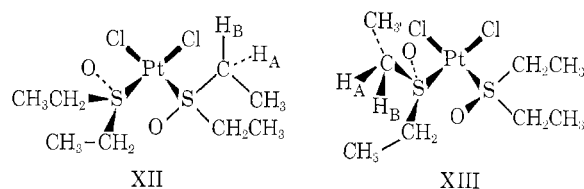
The chief features that emerge from the pmr data are (1) the presence and magnitudes of vicinal $^{195}Pt-^1H$ spin coupling, (2) the increase in methylene proton inequivalence on coordination, and (3) the deshielding effect on α protons resulting from coordination.

Vicinal $^{195}Pt-^1H$ Coupling.—The implications of the presence of ^{195}Pt satellites have been alluded to, and it is of interest that the magnitude of this vicinal coupling in sulfoxide complexes (e.g., in $PtCl_2(DMSO)_2$, $J = 23$ Hz) is substantially smaller than in the corresponding sulfide complexes²⁵ (e.g., $PtCl_2((CH_3)_2S)_2$, $J = 49.5$ Hz for *cis*). Although *a priori* prediction of $^{195}Pt-^1H$ coupling constants is difficult, the large difference cited is associated probably with the stronger σ $S \rightarrow Pt$ bond in the sulfide complexes, since the degree of s character in the π -bonding orbitals must surely be small. To consider differences in vicinal couplings in the one complex it is necessary to examine the preferred conformations for rotation about the C-S and Pt-S bonds. However, bonds involving metals are quite long²⁶ ($\sim 2-2.5$ Å), and although the metal atoms themselves are sterically large, the bond length could tend to minimize interactions with neighboring atoms or groups. Thus in the present cases, the steric requirement of Pt is not clear, but the enforced square-planar geometry might counter some of the favorable effects resulting from the long Pt-S bond.

cis- $PtCl_2[(CH_3CH_2)_2SO]_2$.—For rotation about the C-S bond the following forms need consideration, and relative sizes of groups suggest X to be disfavored



definitely. Dreiding models indicate that it is not possible for all $S-CH_2CH_3$ to be in conformation XI at once, but IX and XI appear the favored ones. As regards rotation about the Pt-S bonds, models indicate that ethyl-ethyl, ethyl-chloro, chloro-oxygen, and oxygen-oxygen interactions are minimized in conformations XII (relating to IX) and XIII (relating to XI).



Excellent simulation of the pmr spectrum of this complex was possible on the basis of a quite large coupling ($J \approx 32$ Hz) and a smaller coupling ($J \approx 6$ Hz) between ^{195}Pt and H_A and H_B . Furthermore, the proton coupled less strongly to Pt resonated at lower field. Analysis of conformations IX–XIII can account for both facts. Considering IX, Pt-H coupling would be anticipated to be similar since both H_A and H_B are *gauche* to Pt. Hence IX alone is incapable of explaining the substantial difference in J values. However in XI H_A being *trans* to Pt should be more strongly coupled, and thus H_A would be identified as the higher proton on this basis. Calculations by Buckingham and Stevens²⁷ on the screening anisotropy in square-planar Pt(II) complexes suggest that the location of methylene hydrogens relative to the square plane of the complex is an important factor in determining relative chemical shifts. Thus a proton further out of the plane was predicted to be more strongly deshielded. Considering XII (related to IX) it is clear that H_B is further removed from the plane than H_A . In XIII however (related to XI) both H_A and H_B occupy comparable positions relative to the plane. Thus H_B , predicted to have the smaller coupling to Pt, should also be at lower field as observed. The same approach has been applied to some dialkyl sulfide complexes of Pt(II) where it was considered that *gauche* coupling was less than *trans*.^{25,28}

Considerations of the above sort apply satisfactorily to the other complexes, and only a brief outline is presented.

cis- $PtCl_2(CH_3SOCH_2C_6H_5)_2$.—Vicinal $^{195}Pt-^1H$ couplings of 15 and >6 Hz to the inequivalent methylene

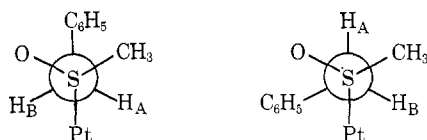
(25) P. C. Turley and P. Haake, *J. Am. Chem. Soc.*, **89**, 4617 (1967).

(26) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(27) A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 4583 (1964).

(28) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **89**, 4611 (1967).

protons in both *dl* and *meso* forms satisfactorily reproduced the spectra. Compared with the diethyl sulfoxide complex, a significant reduction in the larger coupling has occurred. Two reasons may be involved. First, the substituent effect of benzyl at sulfur compared with ethyl may hinder the coupling mechanism, or, second, conformations about the S-CH₂ bond with *gauche* hydrogens may be more favored. The former seems unlikely since J_{Pt-CH_3} in the DMSO and CH₃-SOCH₂C₆H₅ complexes are the same. Certainly, however, one conformation with *gauche* and *trans* hydrogens must be substantially populated to account for the observed difference. The conformations below appear favored, but the effective size of Pt makes their relative importance difficult to gauge. However H_A should

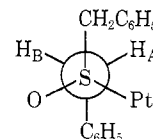


have the larger coupling and, considering rotation about the Pt-S as before, is also predicted to lie at higher field, as observed.

For *cis*-PtCl₂[CH₃SOCH(CH₃)₂]₂ and *trans*-PtCl₂-[((CH₃)₂CH)₂SO]₂ conformations with the methine proton *gauche* to Pt are definitely favored, in line with the very small coupling (\gtrsim 6-7 Hz). The preferred conformation about the Pt-S bond is one with one CH₃-CH further removed from the square plane than its geminal companion, thus accounting for the increased inequivalence compared with free sulfoxide.

In *cis*-PtCl₂[(C₆H₅CH₂)₂SO]₂, vicinal couplings of 27 and \gtrsim 5 Hz are observed, suggesting minor impor-

tance of that conformer with *gauche* hydrogens. Of the remainder, that shown would be predicted to be more heavily populated.



Although our data on the Pd(II) complexes are less extensive, similar lines of reasoning (both are d⁸ complexes) account for the increase in methylene proton inequivalence on complexation. The general deshielding effect on coordination is associated simply with the σ -bond component between sulfur and the metal. A practical consequence is the increased acidity of such α hydrogens, and this could be useful for exchange purposes when groups facilitating exchange (*e.g.*, phenyl as in C₆H₅CH₂-SOCH₂) are absent. Some work along these lines has been reported.²⁰

Acknowledgments.—The authors are grateful to the Department of Chemistry, Indiana University, for permitting this collaboration, and to Professor L. Montgomery for use of his dmr equipment. C. J. M. is grateful for the award of a Commonwealth postgraduate scholarship. This research was financed in part by grants (Grant No. ARGC-23) from the Australian Research Grants Committee, to whom we are grateful. Dr. N. S. Ham of CSIRO, Melbourne, Australia, has kindly provided us with data and views related to this work.

(20) D. A. Johnson, *Inorg. Nucl. Chem. Letters*, **5**, 225 (1969).

CONTRIBUTION FROM CENTRO CHIMICA E TECNOLOGIA COMPOSTI METALLORGANICI
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Formation of the Platinum-Olefin Bond Catalyzed by SnCl₃⁻

BY R. PIETROPAOLO,¹ G. DOLCETTI, M. GIUSTINIANI, AND U. BELLUCO

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The kinetics of the reactions between PtCl₄²⁻ and various olefins have been studied in aqueous solutions 1.9 M in NaCl and 0.1 M in HCl, at 25°, in the presence of SnCl₃⁻. The product is a π -olefinic complex of the Zeise's salt type. The rate law is a two-term expression of the type: $k_{\text{obsd}} = k'[\text{ol}] + k''[\text{SnCl}_3^-]^2$. The first term is interpreted as a bimolecular attack of the olefin on the PtCl₄²⁻ complex and the second depends also on [SnCl₃⁻]². As far as the first SnCl₃⁻-uncatalyzed term is concerned, the reactivity changes in the order: allyl NH₃⁺ > butyl NH₃⁺ > allyl SO₃⁻ > allyl alcohol > pentenyl NH₃⁺. The second SnCl₃⁻-catalyzed term is interpreted as an easier attack of the olefin on a species of the type Pt(SnCl₃)₂Cl₂²⁻, probably the *cis* isomer, formed in the rate-determining step. The accelerating effect of the group SnCl₃⁻ is related to its high *trans* effect.

Introduction

We have recently reported a study on the catalytic effect of the SnCl₃⁻ ion on the formation of the metal-olefin bond in the attack of ethylene on PtCl₄²⁻. The species which are catalytically active are the isomers

cis- and *trans*-Pt(SnCl₃)₂Cl₂²⁻, the *cis* isomer being more active than the *trans* one.² The research has been now extended to the reactions of PtCl₄²⁻ with a series of α -olefins such as CH₂=CHCH₂NH₃⁺, CH₂=CHCH₂-OH, CH₂=CHCH₂SO₃⁻, CH₂=CHCH₂CH₂NH₃⁺, and

(1) On leave from Messina University, Messina, Italy.

(2) R. Pietropaolo, M. Graziani, and U. Belluco, *Inorg. Chem.*, **8**, 1506 (1969).