Table VII. Analytical Data and Proton Magnetic Resonance of Methylpalladium Complexes *trans*-Pd$L_2X(CH_3)$

L	X	Mp (dec), °C	Analysis, % C Calcd	C Found	H Calcd	H Found	X Calcd	X Found	Chem shift (τ, ppm)[b] of *Pd*-CH_3 in $CDCl_3$
PPh_3	I	147–154	57.50	57.65	4.30	4.41	16.42	17.01	9.92 (t, $J_{P-H} = 6$ Hz)
$PPh_2(CH_3)$	I	140–142	49.99	50.04	4.51	4.73	19.56	19.36	9.90 (t, $J_{P-H} = 6$ Hz)
$PPh(CH_3)_2$	I	126–128	38.92	39.19	4.80	4.97	24.19	24.02	9.77 (t, $J_{P-H} = 6.5$ Hz)
$P(CH_3)_3$	I	138	20.99	21.25	5.29	5.34	31.68	31.08	9.46 (t, $J_{P-H} = 6.5$ Hz)
$P(n\text{-}C_4H_9)_3$[a]	I								9.60 (t, $J_{P-H} = 6$ Hz)
$PPh_2(C_6H_{11})$	I	155–160	56.61	56.35	5.78	6.01	16.17	15.92	9.67 (t, $J_{P-H} = 5.5$ Hz)
$PPh(CH_3)_2$	Br	130–132	42.75	42.39	5.28	5.11	16.73	17.27	9.86 (t, $J_{P-H} = 6$ Hz)
$P(OPh)_3$	I	104–107	51.15	51.38	3.83	3.79	14.60	14.92	9.33 (t, $J_{P-H} = 4.5$ Hz)
$P(OC_2H_5)_3$	I	64–65	26.89	26.99	5.73	5.78	21.86	21.60	9.13 (t, $J_{P-H} = 5$ Hz)

[a] Oily product. [b] Abbreviation: t, triplet.

trans-Pd$[PPh_2(CH_3)]_2I_2$ (1.0 g, 1.3 mmol) in methylene chloride (10 ml) was added cyclohexyl isocyanide (0.44 g, 4 mmol) in benzene (4 ml) at 25°; the mixture was then stirred for 20 min. Evaporation of the solvent and crystallization of the residue from methylene chloride–hexane gave $[Pd\{PPh_2(CH_3)\}_2(CNC_6H_{11})_2I]I$ (1.16 g, 92%).

Anal. Calcd for $C_{40}H_{48}N_2I_2P_2Pd$: C, 49.07; H, 4.98; N, 2.86. Found: C, 49.07; H, 5.07; N, 2.52. The infrared spectrum (KBr) shows a strong band at 2195 cm^{-1} due to the terminal isocyanide group. The proton nmr spectrum in $CDCl_3$ consists of three broad peaks at τ 8.2–9.2 (20 H), 6.3–6.8 (2 H), and 2.0–2.6 (30 H) and a singlet at τ 7.24 (6 H). The molar conductivity in nitrobenzene is 15.2 ohm^{-1} cm^{-1} at 25°. This is in agreement with those of the uni-univalent electrolyte of palladium.[22]

(b) By using analogous procedures, $[Pd(PPh_3)_2I(CNC_6H_{11})_2]I$ (1.8 g, 91%; mp 119–122° dec) was obtained from treatment of $Pd(PPh_3)_2I_2$ (1.6 g, 1.8 mmol) with cyclohexyl isocyanide (0.45 g, 4.1 mmol) in methylene chloride (30 ml).

Anal. Calcd for $C_{50}H_{52}N_2I_2P_2Pd$: C, 54.44; H, 4.76; N, 2.54; I, 23.01. Found: C, 54.06; H, 4.77; N, 2.31; I, 23.84. The infrared spectrum (KBr) shows a strong band 2195 cm^{-1} ($\nu_{N\equiv C}$). The proton nmr spectrum in $CDCl_3$ consists of three peaks at τ 8.3–9.2 (20 H), 6.3–6.7 (2 H), and 2.1–2.7 (30 H).

Oxidative Reaction of *trans*-Iodobis(diphenylmethylphosphine)(1-cyclohexyliminomethyl)palladium with Hydrogen Peroxide. To a solution of *trans*-Pd$[PPh_2(CH_3)]_2I[C(CH_3)=NC_6H_{11}]$ (1.0 g, 1.30 mmol) in benzene (20 ml) was added H_2O_2 (0.5%, 10 ml). After 1 hr, the brown organic layer was separated and dried over anhydrous sodium sulfate. The solution was chromatographed on silica gel, eluting with benzene–acetone (20:1). The first layer gave *N*-cyclohexylacetamide (0.12 g, 65%) and the second one gave diphenylmethylphosphine oxide (0.65 g, 89%).

Registry No. *trans*-Pd$(PPh_3)_2I[C(CH_3)=NC_6H_{11}]$, 42582-33-2; *trans*-Pd$[PPh(CH_3)_2]I[C(CH_3)=NC_6H_{11}]$, 42582-34-3; *trans*-Pd$[P(n\text{-}C_4H_9)_3]_2I[C(CH_3)=NC_6H_{11}]$, 42582-35-4; *trans*-Pd$[PPh_2(C_6H_{11})]_2I[C(CH_3)=NC_6H_{11}]$, 42582-36-5; *trans*-Pd$[PPh(CH_3)_2]_2I[C(C_6H_5)=NC_6H_{11}]$, 42582-37-6; *trans*-Pd$[PPh_2(CH_3)]_2I[C(o\text{-}C_6H_4CH_3)=NC_6H_{11}]$, 42582-52-5; *trans*-Pd$[PPh_2(CH_3)]_2I[C(CH_3)=NC_6H_5]$, 42582-51-4; *trans*-Pd$[PPh(CH_3)_2]_2I[C(CH_3)=NC_6H_5]$, 42582-50-3; *trans*-Pd$[PPh(CH_3)_2]_2I[C(CH_3)=NC(CH_3)_3]$, 42582-49-0; *trans*-Pd$[PPh(CH_3)_2]_2I[C(CH_3)=NCH_2Ph]$, 42582-47-8; *trans*-Pd$[P(CH_3)_3]_2I[C(CH_3)=NC(CH_3)_3]$, 42582-46-7; *trans*-Pd$[PPh(CH_3)_2]_2Br[C(CH_3)=NC_6H_{11}]$, 42582-45-6; $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NC_6H_{11}\}]_2$, 29186-97-8; $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NC(CH_3)_3\}]_2$, 42735-36-4; *trans*-Pd$(PPh_3)_2I[(C=NC_6H_{11})_2(CH_3)]$, 29190-51-0; *trans*-Pd$[PPh_2(CH_3)]_2I[(C=NC_6H_{11})_2(CH_3)]$, 29186-98-9; *trans*-Pd$[PPh(CH_3)_2]_2I[(C=NC_6H_{11})_2(CH_3)]$, 42582-43-4; *trans*-Pd$[P(CH_3)_3]_2I[(C=NC_6H_{11})_2(CH_3)]$, 42582-42-3; *trans*-Pd$[P(n\text{-}C_4H_9)_3]_2I[(C=NC_6H_{11})_2(CH_3)]$, 42582-41-2; Pd$[PPh_2(CH_3)]I[(C=NC_6H_{11})_3(CH_3)]$, 42735-35-3; *trans*-Pd$(PPh_3)_2I(CH_3)$, 18115-58-7; *trans*-Pd$[PPh_2(CH_3)]_2I(CH_3)$, 42582-53-6; *trans*-Pd$[PPh(CH_3)_2]_2I(CH_3)$, 42582-38-7; *trans*-Pd$[P(CH_3)_3]_2I(CH_3)$, 42582-39-8; *trans*-Pd$[P(n\text{-}C_4H_9)_3]_2I(CH_3)$, 42582-40-1; *trans*-Pd$[PPh_2(C_6H_{11})]_2I(CH_3)$, 42744-99-0; *trans*-Pd$[PPh(CH_3)_2]_2Br(CH_3)$, 42745-00-6; *trans*-Pd$[P(OPh)_3]_2I(CH_3)$, 42745-01-7; *trans*-Pd$[P(OC_2H_5)_3]_2I(CH_3)$, 42719-81-3; *trans*-Pd$[PPh(CH_3)_2]_2I(C_6H_5)$, 42745-02-8; *trans*-Pd$[PPh_2(CH_3)]_2I(o\text{-}C_6H_4CH_3)$, 42745-03-9; $[Pd\{PPh_2(CH_3)\}_2(CNC_6H_{11})_2I]I$, 42745-04-0; $[Pd(PPh_3)_2I(CNC_6H_{11})_2]I$, 42745-05-1; cyclohexyl isocyanide, 931-53-3; *trans*-Pd$[PPh_2(CH_3)]_2I_2$, 25332-94-9; H_2O_2, 7722-84-1.

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The Ylide-Metal Complex. Preparations and Structures of Palladium(II) and Platinum(II) Halide Complexes with a Stable Sulfur Ylide

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Platinum(II) and palladium(II) halide complexes with a stable sulfur ylide, $PtX_2(R_2S)(Sy)$ and $PdX_2(Sy)_2$ [X = Cl, Br, I; R = CH_3, C_2H_5; Sy = $CH_3(C_6H_5)SCHC(O)C_6H_4Cl\text{-}p$], have been prepared. The ν(C=O) band of the complexes occurs at higher frequencies than the original one of the ylide, and spin–spin coupling between the ylide methine proton and the ^{195}Pt nucleus is observed. These facts indicate the formation of the ylide carbon–metal bond in the complexes. The configurations of the complexes are elucidated on the basis of ir and pmr spectra. The trans influence of this ylide is concluded to be more or less larger than that of dimethyl or diethyl sulfide on the basis of measurements of ν(Pt–Cl) and the spin–spin coupling constants between the methyl protons of the coordinating dimethyl sulfide and the ^{195}Pt nucleus.

Introduction

Generally, ylides which have an electronic structure $>C^{-}-X^{+}$ (X = heteroatoms)[1] are expected to interact with various Lewis acids through the nucleophilic carbon atom having lone-pair electrons. Recently many studies have been reported concerning the reactions of various ylides with boron,[2-4]

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Table I. Melting Point, Elemental Analysis, Molecular Weight, and Conductivity Data of the Ylide Complexes

Complex	Mp, °C	% C		% H		Mol wt[a]		Molar conductance,[b] ohm^{-1} cm^2 mol^{-1}
		Calcd	Found	Calcd	Found	Calcd	Found	
$PdCl_2(Sy)_2$	173 dec	49.30	48.54	3.59	3.55			
$PdBr_2(Sy)_2$	177 dec	43.95	43.70	3.20	3.34			
$PdI_2(Sy)_2$	148.5–149 dec	39.43	38.68	2.87	2.86			
$PtCl_2[(CH_3)_2S](Sy)\cdot 0.5CH_2Cl_2$[c]	144–145 dec	32.47	32.50	3.11	3.25	647	612	3.3
$PtBr_2[(CH_3)_2S](Sy)\cdot 0.5CH_2Cl_2$[c]	140–142 dec	28.54	28.80	2.74	2.76	736	650	13
$PtI_2[(CH_3)_2S](Sy)\cdot 0.5CH_2Cl_2$[c]	121–123 dec	25.32	25.80	2.43	2.50	830	727	9.1
$PtCl_2[(C_2H_5)_2S](Sy)$	152–153 dec	36.05	36.29	3.66	3.63	633	612	3.3
$PtBr_2[(C_2H_5)_2S](Sy)$	157–158 dec	31.61	31.61	3.21	3.07	722	659	8.0
$PtI_2[(C_2H_5)_2S](Sy)$	125–129 dec	27.97	28.18	2.84	2.85	816	750	2.4

[a] In chloroform. [b] Concentrations of (1-4) × 10^{-4} *M* in acetonitrile. [c] The existence of 0.5 mol of dichloromethane was confirmed by pmr spectra.

aluminum,[4,5] mercury,[6,7] silicon,[4,6,8] germanium,[4,6] and tin compounds.[4,6,8,9] However, there have been few reports of reactions of ylides with transition metals,[10-12] and studies of metal complexes containing coordinating ylides have been also very rare to date.[13,14] Lately, several stable sulfur ylides have been synthesized and characterized.[15] Among these, methylphenylsulfonium phenacylides are very stable in air. Although the *p*-chlorophenacyl derivative (Sy) is a weak base whose conjugated acid, $CH_3(C_6H_5)SCH_2C(O)C_6H_4Cl\text{-}p^+\text{-}BF_4^-$, has a small pK_a value of 6.44,[16] one may expect the formation of complexes between some suitable metal halides and Sy.

This paper will report the isolation of several stable platinum(II) and palladium(II) halide complexes with the ylide (Sy) and will discuss their configurations from ir and pmr spectra.

Experimental Section

Preparation of Methylphenylsulfonium *p*-Chlorophenacylide (Sy). According to the literature,[17] to a suspension of methylphenyl-*p*-chlorophenacylsulfonium bromide $[CH_3(C_6H_5)SCH_2C(O)C_6H_4Cl\text{-}p]^+Br^-$ (15.0 g) in ethanol (60 ml) on an ice bath, triethylamine (8.5 g) was added dropwise under vigorous stirring. The reaction mixture was stirred under the same conditions for 3 hr, diluted with water (250 ml), and extracted with chloroform repeatedly. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The resulting crude products were recrystallized from benzene to give light yellow crystals (4.5 g, yield 39%), mp 131–131.5° (lit.[18] mp 131–132°).

Preparation of Dichloro(dimethyl sulfide)(methylphenylsulfonium *p*-chlorophenacylide)platinum(II). A 10-ml dichloromethane solution of Sy (0.50 g, 1.8 mmol) was added to a 5-ml dichloromethane solution of *cis*-dichlorobis(dimethyl sulfide)platinum(II) (0.30 g, 0.77 mmol), and the reaction mixture was stirred for about 4 hr. Addition of petroleum ether to the solution gave greenish yellow crystals, which were filtered off and dried *in vacuo* (0.12 g, yield 24%). A reaction of Sy with *trans*-dichlorobis(dimethyl sulfide)platinum(II) yields also the same product. These were crystallized with 0.5 mol of dichloromethane, which was not removed on heating under reduced pressure.

Other platinum(II) complexes, dibromo- and diiodo(dimethyl sulfide)(methylphenylsulfonium *p*-chlorophenacylide)platinum(II) and dichloro-, dibromo- and diiodo(diethyl sulfide)(methylphenylsulfonium *p*-chlorophenacylide)platinum(II) were prepared in the same way.

Preparation of Dichlorobis(methylphenylsulfonium *p*-chlorophenacylide)palladium(II). A 10-ml dichloromethane solution of Sy (0.88 g, 3.2 mmol) was added to a 10-ml dichloromethane solution of *trans*-dichlorobis(dimethyl sulfide)palladium(II) (0.40 g, 1.3 mmol). The reaction mixture was stirred for about 4 hr. Addition of petroleum ether to the mixture gave yellow crystals, which were filtered off and dried *in vacuo* (0.58 g, yield 60%).

Other palladium(II) complexes, dibromo- and diiodobis(methylphenylsulfonium *p*-chlorophenacylide)palladium(II) were similarly prepared.

The melting points and analytical data of the complexes are summarized in Table I.

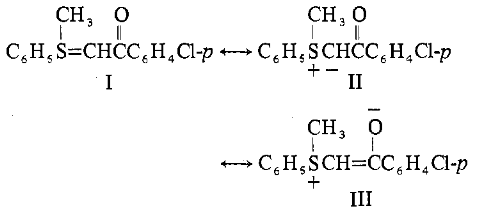
Physical Measurements. Ir spectra were recorded in Nujol mulls on Hitachi 225 (4000–400 cm^{-1}) and Hitachi EPI-L (700–200 cm^{-1}) spectrophotometers and in solid paraffin of low melting point on a Hitachi FIS-3 vacuum spectrophotometer (400–30 cm^{-1}).

Pmr spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer operating at 100 MHz against tetramethylsilane as the internal standard at room temperature.

Molecular weights were determined in chloroform using a Hitachi Perkin-Elmer 115 vapor pressure osmometer. Conductivity measurements were carried out in acetonitrile solution using a Yokogawa universal bridge BV-Z-13A. The molecular weights and conductivities of the ylide complexes are also listed in Table I.

Results and Discussion

Coordination of the Ylide to Metal. The sulfur ylide (Sy) used here is described by the canonical structures[17] I–III, and the carbonyl stretching band of this compound observed



$$\underset{\text{I}}{C_6H_5\overset{CH_3}{\overset{|}{S}}{=}CH\overset{O}{\overset{\|}{C}}C_6H_4Cl\text{-}p} \longleftrightarrow \underset{\text{II}}{C_6H_5\underset{+}{\overset{CH_3}{\overset{|}{S}}}\underset{-}{C}H\overset{O}{\overset{\|}{C}}C_6H_4Cl\text{-}p} \longleftrightarrow \underset{\text{III}}{C_6H_5\underset{+}{\overset{CH_3}{\overset{|}{S}}}CH{=}\overset{\bar{O}}{\overset{|}{C}}C_6H_4Cl\text{-}p}$$

at 1578 cm^{-1} suggests an important contribution of III, in which lone-pair electrons on the ylide carbon are considerably delocalized. The ylide has two coordination sites toward metal halides; coordination through the carbonyl oxygen would cause a low-frequency shift of $\nu(C{=}O)$ owing to an increasing contribution of III, and coordination through the nucleophilic methine carbon would lead to a high-frequency

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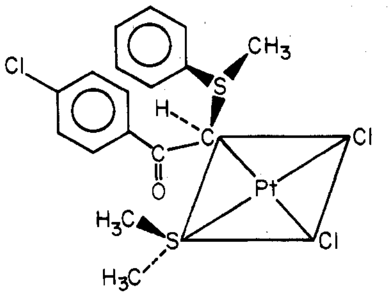
shift because of increasing contribution of II. As is shown in Table II, the ν(C=O) band of the complexes is observed at higher frequencies than that of the original ylide. Therefore, the coordination to metal halide through the methine carbon of Sy is concluded. In addition, the methylphenyl-*p*-chlorophenacylsulfonium cation, which is perfectly protonated on the methine carbon, exhibits the ν(C=O) at 1677 cm^{-1}.[19] So the higher frequency shift of ν(C=O) seems to reveal the larger coordinating strength of the methine carbon to Lewis acids. Thus the metal-ylide bond of platinum(II) complexes would be stronger than that of palladium(II) complexes.

Platinum(II) Ylide Complexes. A pmr spectrum of $PtCl_2[(CH_3)_2S](Sy)$ in deuteriochloroform is shown in Figure 1, which indicates two S–CH_3 signals of coordinated dimethyl sulfide with equal intensity. Measurements of molecular weight and electric conductivity indicate that this compound is essentially monomeric and a nonelectrolyte in solution. Therefore, the appearance of two S–CH_3 signals may be due to hindered rotation around the platinum-sulfur bond, which may result from a steric repulsion by the close-neighboring bulky coordinating ylide in the complex with a cis structure around the platinum atom, as is depicted in A. Each of two S–CH_3 signals has satellites due to the spin-spin coupling with the ^{195}Pt nucleus. The coupling constants [$J(^{195}Pt\text{-}S\text{-}CH_3)$ = 54.5, 52.4 Hz] are larger than that of *trans*-$PtCl_2[(CH_3)_2S]_2$ (40.7 Hz) and rather close to that of *cis*-$PtCl_2[(CH_3)_2S]_2$ (50.9 Hz). This suggests an increasing s character in the platinum-sulfur bond in $PtCl_2[(CH_3)_2S](Sy)$ compared with the case of the bis(dimethyl sulfide) complex and also supports a cis configuration around the platinum of the present complex in solution. In the ir spectrum of this complex, two ν(Pt–Cl) bands are observed at 322 and 288 cm^{-1} in the solid state, suggesting that there is essentially no difference between the configurations in the solid state and in solution.



A

On the other hand, $PtI_2[(CH_3)_2S](Sy)$ has a single S-CH_3 signal of the coordinating dimethyl sulfide in the pmr spectrum, which is consistent with free rotation around the platinum-sulfur bond. The $J(^{195}Pt\text{-}S\text{-}CH_3)$ value (34.9 Hz) is much smaller than that of *trans*-$PtI_2[(CH_3)_2S]_2$ (45.4 Hz). These facts indicate that this complex has a trans configuration, and the Sy could loosen the metal-sulfur bond in the trans position. Correspondingly, only one ν(Pt-I) band appears at 164 cm^{-1} in the ir spectrum of this compound in the solid state.

Table II. Ir Data of the Ylide Complexes in Nujol Mull (cm^{-1})

Complex	ν(C=O)	ν(M-X)
Sy	1578	
$PdCl_2(Sy)_2$	1633	338, 331
$PdBr_2(Sy)_2$	1629	245
$PdI_2(Sy)_2$	1628	148
$PtCl_2[(CH_3)_2S](Sy)$	1638	322, 288
$PtBr_2[(CH_3)_2S](Sy)$	1641	217, 193
$PtI_2[(CH_3)_2S](Sy)$	1634	164
$PtCl_2[(C_2H_5)_2S](Sy)$	1643	321, 299
$PtBr_2[(C_2H_5)_2S](Sy)$	1642	219, 203
$PtI_2[(C_2H_5)_2S](Sy)$	1652	146

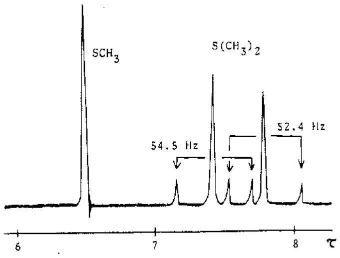


Figure 1. Pmr spectrum of *cis*-$PtCl_2[(CH_3)_2S](Sy)$ in $CDCl_3$ at 23°.

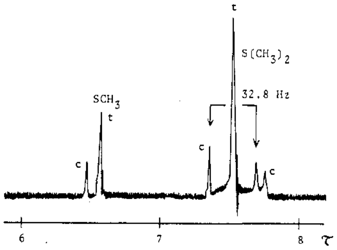


Figure 2. Pmr spectrum of *cis*- and *trans*-$PtBr_2[(CH_3)_2S](Sy)$ in $CDCl_3$ at 23°: t, trans isomer; c, cis isomer.

In a pmr spectrum of $PtBr_2[(CH_3)_2S](Sy)$, two kinds of S–CH_3 signals of the coordinating ylide are observed, as is shown in Figure 2. This would suggest the coexistence of a cis and a trans isomer in solution. The $J(^{195}Pt\text{-}S\text{-}CH_3)$ value (32.8 Hz) of the major isomer is smaller than that of *trans*-$PtBr_2[(CH_3)_2S]_2$ (41.8 Hz) and the relative magnitude of these values is analogous with the case of the corresponding diiodide complex. Thus the major isomer is assumed to have a trans configuration. The minor signal of S-CH_3 of the coordinating ylide is assigned as the cis isomer, and one signal of the coordinating dimethyl sulfide of the cis isomer appears at the same position as the lower field satellites of dimethyl sulfide CH_3 signal of the trans isomer (Figure 2). In the solid state this complex shows only two ν(Pt-Br) bands at 217 and 193 cm^{-1}. In the case of $PtBr_2[(CH_3)_2S](Sy)$ prepared in chloroform solution the pmr spectrum indicates that the major isomer is a cis form.

It can be seen from the above considerations that the configuration of the ylide-platinum(II) complexes depends on the nature of halide ions attached to the platinum(II). The present result is consistent with a tendency of increasing equilibrium portions of trans isomers in the order of X = Cl < Br < I in $PtX_2[(C_2H_5)_3P]_2$.[20]

The ylide proton signals shift in these dimethyl sulfide complexes to a lower field upon complex formation because of the inductive effect of metal ions, and this is particularly the case of the methine proton (see Table III). Unfortunately, no spin-spin coupling between the methine proton and the ^{195}Pt nucleus has been observed because of poor solubility of the complexes.

As is shown in Figure 3, $PtCl_2[(C_2H_5)_2S](Sy)$ in deuteriochloroform exhibits two kinds of signals (CH_3- and -CH_2-)

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(19) This is the value of bis(methylphenyl-*p*-chlorophenacylsulfonium)tetrachlorocadmium(II), which was prepared from refluxing Sy and cadmium(II) dichloride in an aqueous solution of diluted hydrochloric acid, mp > 240°. *Anal.* Calcd for $C_{30}H_{26}Cl_6O_2S_2Cd$: C, 44.61; H, 3.24. Found: C, 44.29; H, 3.55.

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Table III. Pmr Data of the Ylide Complexes in Chloroform-d_1 at 23°

	Chem shifts, τ, ppm				Coupling constants, Hz	
Complex	Ylide S–CH_3	Ylide C–H	$S(CH_3)_2$	$S(CH_2\text{–}CH_3)_2$	$J(^{195}Pt\text{–}CH\text{–})$	$J(^{195}Pt\text{–}S\text{–}CH_3)$
Sy	6.79	5.45				
cis-$PtCl_2[(CH_3)_2S](Sy)$	6.49	3.19	7.41, 7.79			54.5, 52.4
cis-$PtBr_2[(CH_3)_2S](Sy)$	6.49	*a*	7.37, 7.77			*a*
trans-$PtBr_2[(CH_3)_2S](Sy)$	6.59	3.14	7.53			32.8
trans-$PtI_2[(CH_3)_2S](Sy)$	6.61	*a*	7.41			34.9
cis-$PtCl_2[(C_2H_5)_2S](Sy)$	6.47	3.15		8.52, 9.18	124.7	
cis-$PtBr_2[(C_2H_5)_2S](Sy)$	6.48	2.99		8.54, 9.20	126.1	
trans-$PtI_2[(C_2H_5)_2S](Sy)$	6.61	2.65		8.75	118.8	

[a] Not seen.

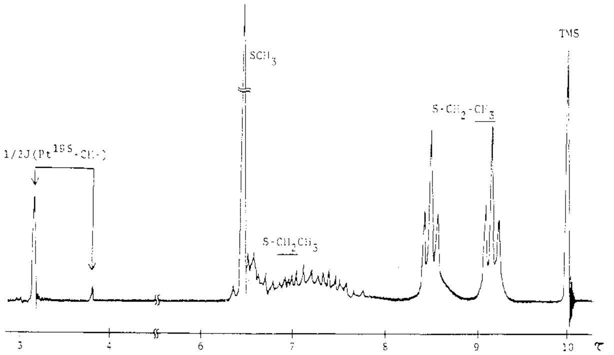

Figure 3. Pmr spectrum of *cis*-$PtCl_2[(C_2H_5)_2S](Sy)$ at 23°.

of coordinating diethyl sulfide with equal intensities, respectively. A similar spectrum is also observed in $PtBr_2[(C_2H_5)_2S](Sy)$, whereas in $PtI_2[(C_2H_5)_2S](Sy)$ there appears one kind of ethyl signal. Therefore, both the $PtCl_2$ and $PtBr_2$ complexes are in a cis configuration, while the PtI_2 complex is in a trans one in solution. Ir spectra of these complexes in the solid state indicate that they have the same structures as in solution (Table II). The coupling constants $J(^{195}Pt\text{–}CH\text{–})$ between the ylide methine proton and the ^{195}Pt nucleus were determined to be 124.7, 126.1, and 118.8 Hz for the dichloro, dibromo, and diiodo complexes, respectively, which confirm the existence of a direct platinum–carbon bond. These values are compared with that (123 Hz) of $K[Pt(acac)_3]$[21] which has also a direct platinum–carbon bond.

Palladium(II) Ylide Complexes. $PdX_2(Sy)_2$ (X = Cl, Br, I) are almost insoluble in common organic solvents and measurements of pmr spectra have not been successful. In the solid-state ir spectra, the $PdCl_2$ complex exhibits two ν(Pd–Cl) bands at 338 and 331 cm^{-1}, and both the $PdBr_2$ and PdI_2 complexes show a single ν(Pd–X) band at 245 and 148 cm^{-1}, respectively. The former will therefore take a cis configuration and the latter two a trans configuration around the palladium atom.

Affinity and Trans Influence of Sy toward Pd(II) and Pt(II). As was described above, the dimethyl sulfide molecules of $PdX_2[(CH_3)_2S]_2$ (X = Cl, Br, I) can easily be substituted by the ylide, forming stable complexes of $PdX_2(Sy)_2$, while in the corresponding platinum complexes only one molecule of the dialkyl sulfide is replaced by the ylide to give $PtX_2(R_2S)(Sy)$ (X = Cl, Br, I; R = CH_3, C_2H_5). On the basis of the $J(^{195}Pt\text{–}S\text{–}CH_3)$ value, it is also confirmed that the s character of the platinum-sulfur bond trans to Sy in *trans*-$PtX_2[(CH_3)_2S](Sy)$ is smaller than that in *trans*-$PtX_2[(CH_3)_2S]_2$. In addition, the average value of two ν(Pt–Cl) frequencies of *cis*-$PtCl_2(R_2S)(Sy)$ is lower than that of *cis*-$PtCl_2(R_2S)_2$ (R = CH_3, C_2H_5).[22,23] In view of these results, the affinity of Sy toward Pd(II) and Pt(II) and the trans influence of this ligand are concluded to be somewhat larger than those of dimethyl and diethyl sulfide.

Registry No. $PdCl_2(Sy)_2$, 42885-81-4; $PdBr_2(Sy)_2$, 42885-82-5; $PdI_2(Sy)_2$, 42885-83-6; *cis*-$PtCl_2[(CH_3)_2S](Sy)$, 42885-84-7; *cis*-$PtBr_2[(CH_3)_2S](Sy)$, 42885-85-8; *trans*-$PtI_2[(CH_3)_2S](Sy)$, 42949-45-1; *cis*-$PtCl_2[(C_2H_5)_2S](Sy)$, 42885-86-9; *cis*-$PtBr_2[(C_2H_5)_2S](Sy)$, 42885-87-0; *trans*-$PtI_2[(C_2H_5)_2S](Sy)$, 42885-88-1; *trans*-$PtBr_2[(CH_3)_2S](Sy)$, 42885-89-2; *cis*-dichlorobis(dimethyl sulfide)platinum(II), 17836-09-8; *trans*-dichlorobis(dimethyl sulfide)platinum(II), 17457-51-1; *trans*-dichlorobis(dimethyl sulfide)palladium(II), 18534-70-8; bis(methylphenyl-*p*-chlorophenacylsulfonium)tetrachlorocadmium(II), 42885-80-3.

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