to dryness and the residue was extracted with 10–20 ml of ethanol. After evaporation of the ethanol, the solid that remained was checked by infrared spectroscopy for the presence of perchlorate. If any absorption for the anion was present in the spectrum, the solid was dissolved in 5–10 ml of water and passed over an anion-exchange column (Dowex 1-X8, 100–200 mesh, Cl⁻ form). The eluent was evaporated to dryness and the solid collected. All products, regardless of origin, were dried in vacuo over P_4O_{10}.

Supplementary Material Available: Table of analytical data and NMR spectra of N-alkylated complexes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. K. Barefield and M. T. Mocella, Abstracts, 165th National Meeting of American Chemical Society, Dallas, Tex., April 1973, No. INOR 139; *J. Am. Chem. Soc.* 97, 4238 (1975).

(2) G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 11, 1145 (1972); L. L. Rusnak and R. B. Jordan, *ibid.*, 10, 2686 (1971).

(3) E. K. Barefield and F. Wagner, *Inorg. Chem.*, 2, 2435 (1973).

(4) (a) R. Buxtorf, W. Steinmann, and T. A. Kaden, *Chimia*, 28, 19 (1974); (b) R. Buxtorf and T. A. Kaden, *Helv. Chim. Acta*, 57, 1035 (1974);

(c) L. Hertli and T. A. Kaden, *ibid.*, 57, 1328 (1974).

(5) M. J. D'Aniello, Jr., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, 97, 192 (1975).

(6) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 4 1102 (1965); B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(7) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, 91, 4092 (1969).

(8) L. G. Warner and D. H. Busch, "Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, Jr.", Plenum Press, New York, N.Y., 1969, p 1.

(9) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 92, 2151 (1970).

(10) L. F. Lindoy, *Coord. Chem. Rev.*, 4, 41 (1969).

(11) G. W. Watt and P. W. Alexander, *Inorg. Chem.*, 7, 537 (1968).

(12) A preliminary account of part of this work has appeared: F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H.-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, 96, 2625 (1974).

(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 32.

(14) G. W. Watt and D. H. Carter, *Inorg. Chem.*, 7, 2451 (1968).

(15) C. P. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, 89, 1730 (1967).

(16) E. L. Blinn and D. H. Busch, *Inorg. Chem.*, 7, 820 (1968).

(17) Complexes 20, 21, and 22 were prepared by the same procedure utilized for [Ni(cyclam)]²⁺ using the appropriate tetramine. See E. K. Barefield, *Inorg. Chem.*, 11, 2273 (1972), and E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Synth.*, in press, for the cyclam procedure. A publication describing the preparations and properties of these complexes and others prepared by glyoxal condensation methods has been submitted.

(18) D. K. Cabbiness, Ph.D. Thesis, Purdue University, 1970. 2.3.2-tet is 1,4,8,11-tetraazaundecane.

(19) F. Hinz, Ph.D. Thesis, Purdue University, 1973.

(20) M. T. Mocella, Ph.D. Thesis, University of Illinois, 1974.

(21) C. R. Sperati, Ph.D. Thesis, The Ohio State University, 1971.

(22) E. M. Arnett, *Acc. Chem. Res.*, 6, 404 (1973).

(23) W. H. Perkin, *J. Chem. Soc.*, 5 (1888).

(24) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(25) (a) W. H. Elfring, Jr., Ph.D. Thesis, University of Washington, 1972; S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 9 1131 (1970); (b) J. G. Martin and S. C. Cummings, *ibid.*, 12, 1477 (1973).

(26) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 84, 866 (1962); 87, 1345 (1965).

(27) Potassium hydroxide pellets were pulverized in a Waring blender. Caution should be exercised when handling this material as the dust is very irritating to the eyes and nose. Material thus prepared could be kept in a tightly sealed bottle for long periods of time.

(28) TSP is sodium 3-trimethylsilylpropionate-2,2,3,3-d₄.

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The Ylide–Metal Complex. Preparations and Structures of Palladium(II) and Platinum(II) Halide Complexes with Some Phenacylides

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Platinum(II) halide complexes of some phenacylides, p-CH3C5H4N⁺–CHC(O)C6H5 (=Ny), CH3(C6H5)2P⁺–CHC(O)C6H5 (=Py), (C6H5)3As⁺–CHC(O)C6H5 (=Ay), and (CH3)2S⁺–CHC(O)C6H5 (=Sy), were synthesized and their configurations elucidated on the basis of infrared and ¹H NMR spectra. The coupling constant between the ¹⁹⁵Pt nucleus and the ylide methine proton, ²J(Pt–CH), in trans-PtCl2LY (L = PPhMe2, PMe3; Y = Ny, Py, Ay, Sy) increases with increasing basicity of the ylide: Ny > Ay > Sy > Py. In trans-PtX2(PPhMe2)Y (X = Cl, Br, I; Y = Ny, Py, Sy), the ²J(Pt–CH) value also increases in the order of Cl < Br < I and at the same time the ν(Pt–C) band moves to high frequencies. This result is interpreted in terms of the interaction of the positively charged ylide heteroatom with halogen. Palladium(II) ylide complexes PdCl2LY (L = PPhMe2, PMe3; Y = Py, Ay, Sy) were also prepared and their structures are discussed.

Introduction

Ylide molecules differ from other organic ligands in that ylides coordinate to metal ions as a *neutral* ligand to form a σ bond between the ylide carbon and the metal atom. This was shown by means of x-ray analyses of some ylide-metal complexes, in which the configuration of the ylide carbon is tetrahedral rather than planar.[1-3] The copper,[4] silver,[4] gold,[5] nickel,[6,7] and thallium[8] compounds of ylides are known to be thermally stable and the stability has been ascribed to the role of the onium center of the ylide.[7-9] Previously we reported several stable palladium(II) and platinum(II) ylide com-

plexes.[10] We attempted to perform more systematic studies on the configurations of metal–ylide complexes and the interactions between metal ions and some phenacylides.

This paper reports the preparative, infrared, and ¹H NMR studies of palladium(II) and platinum(II) halide complexes with some stable phenacylides as in

$$\overset{+}{Z}-CHCC_6H_5$$
$$\overset{\|}{O}$$
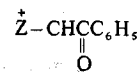
$$Z = p\text{-}CH_3C_5H_4N \text{ (Ny)}, \; CH_3(C_6H_5)_2P \text{ (Py)},$$
$$(C_6H_5)_3As \text{ (Ay)}, \; (CH_3)_2S \text{ (Sy)}$$

Table I. Melting Points, Elemental Analyses, and Molecular Weights of the Ylide Complexes

Complex	Mp, °C	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	Mol wtᵃ Calcd	Mol wtᵃ Found
trans-PtCl₂(PPhMe₂)(Ny)	>165 dec	42.94	42.82	3.93	4.19	2.27	2.30	615	590
trans-PtBr₂(PPhMe₂)(Ny)·½CH₂Cl₂ᵇ	>112 dec	36.19	36.52	3.37	3.46	1.88	2.05		
trans-PtI₂(PPhMe₂)(Ny)·½CH₂Cl₂ᵇ	>97 dec	32.14	32.55	3.00	2.77	1.67	1.83		
trans-PtCl₂(PMe₃)(Ny)	179-182 dec	36.90	36.85	4.01	4.05	2.53	2.48	553	535
cis-PdCl₂(PPhMe₂)(Ay)	169-173 dec	55.20	55.17	4.36	4.39			740	693
PdCl₂(PMe₃)(Ay)ᶜ	171-173 dec	51.39	51.30	4.46	4.14			678	663
trans-PtCl₂(PPhMe₂)(Ay)	183-184 dec	49.29	49.43	3.89	4.02			829	863
trans-PtCl₂(PMe₃)(Ay)	169-171 dec	45.45	45.27	3.95	3.76			766	739
cis-PdCl₂(PPhMe₂)(Sy)	176-177 dec	43.61	43.32	4.68	4.79				
cis-PdCl₂(PMe₃)(Sy)	191-194 dec	36.01	35.99	4.88	4.88				
trans-PtCl₂(PPhMe₂)(Sy)	>165.5 dec	36.99	36.95	3.97	4.02				
cis-PtCl₂(PPhMe₂)(Sy)·CHCl₃ᵇ	179-183 dec	32.43	32.82	3.44	3.23				
trans-PtBr₂(PPhMe₂)(Sy)	>155 dec	32.11	32.05	3.44	3.30				
cis-PtBr₂(PPhMe₂)(Sy)·CHCl₃ᵇ	172.5-175 dec	28.79	28.95	3.05	3.18				
trans-PtI₂(PPhMe₂)(Sy)	151-153 dec	28.18	27.98	3.02	2.99			763	745
cis-PtI₂(PPhMe₂)(Sy)	150-153 dec	28.18	27.85	3.02	3.11				
trans-PtCl₂(PMe₃)(Sy)·½C₆H₆ᵇ	108-112	34.23	34.29	4.31	4.69				
trans-PdCl₂(PPhMe₂)(Py)	170-173.5 dec	54.96	54.42	4.77	4.78			634	603
trans-PdCl₂(PMe₃)(Py)·⅓C₆H₆ᵇ	107-110 dec	52.24	52.14	5.06	4.67				
trans-PtCl₂(PPhMe₂)(Py)	>178 dec	48.21	47.75	4.19	4.15			723	758
trans-PtBr₂(PPhMe₂)(Py)	>175 dec	42.93	42.88	3.73	3.59				
trans-PtI₂(PPhMe₂)(Py)	131-133 dec	38.47	38.38	3.34	3.27			905	863
trans-PtCl₂(PMe₃)(Py)·⅓C₆H₆ᵇ	137-138	45.49	45.74	4.41	4.26				

ᵃ In chloroform at 37°. ᵇ The existence of solvents was confirmed by ¹H NMR spectra. ᶜ It is not obvious whether this complex is cis or trans.

Experimental Section

Materials. *p*-Methylpyridinium phenacylide (Ny),[11] methyldiphenylphosphonium phenacylide (Py),[12] and dimethylsulfonium phenacylide (Sy)[13] were prepared according to the literature. Triphenylarsonium phenacylide (Ay) was synthesized in the same way as Py.

All manipulations for preparing the ylide complexes were carried out in air.

Preparation of Dihalogenodimethylphenylphosphine(dimethylsulfonium phenacylide)platinum(II), PtX₂(PPhMe₂)(Sy) (X = Cl, Br, I), and Related Compounds. A 10-ml dichloromethane solution of Sy (0.094 g, 0.52 mmol) was added to a 5-ml dichloromethane solution of di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum(II)[14] (0.20 g, 0.25 mmol), and the mixture was stirred for 3.5 hr. The addition of petroleum ether to the solution gave a small amount of white crystals of *cis*-PtCl₂(PPhMe₂)(Sy), which was separated by filtration and dried in vacuo. The trans isomer was obtained as yellow crystals (0.18 g, yield 62%) by further additions of petroleum ether to the filtrate. The dibromo and diiodo complexes were synthesized in the same way. The former was mainly obtained as a trans isomer (yellow), whereas the latter was predominantly a cis one (yellow).

The recrystallizations of the *trans*-dichloride and -dibromide from chloroform gave the corresponding cis complex containing one molecule of chloroform.

Other platinum(II) complexes, PtX₂LY (X = Cl, L = PPhMe₂, Y = Ny, Py, Ay; X = Br, I, L = PPhMe₂, Y = Ny, Py; X = Cl, L = PMe₃, Y = Ny, Py, Ay, Sy) were prepared in dichloromethane or 1,2-dichloroethane in the similar way. PtCl₂(PMe₃)Y (Y = Py, Sy) were purified from a benzene–diethyl ether mixture, and the remaining complexes from dichloromethane or 1,2-dichloroethane–petroleum ether.

Preparation of Dichlorodimethylphenylphosphine(dimethylsulfonium phenacylide)palladium(II), PdCl₂(PPhMe₂)(Sy), and Related Compounds. A 10-ml dichloromethane solution of Sy (0.12 g, 0.67 mmol) was dropped into a 5-ml dichloromethane solution of di-μ-chloro-dichlorobis(dimethylphenylphosphine)dipalladium(II) (0.20 g, 0.32 mmol). The solution changed in color from orange to yellow. After the reaction mixture had been stirred for 1 hr, petroleum ether was added to the solution to give light yellow crystals (0.17 g, yield 54%).

Other palladium(II) complexes, PdCl₂LY (L = PPhMe₂, Y = Py, Ay; L = PMe₃, Y = Py, Ay, Sy) were isolated in the same way, but only PdCl₂(PMe₃)(Py) was obtained from benzene–diethyl ether.

The melting points and analytical data for the ylide complexes prepared are summarized in Table I.

Physical Measurements. Infrared (4000-200 cm⁻¹), ¹H NMR

Table II. Ir Data of the Ylide Complexes (cm⁻¹)

Complex	ν(C=O) Nujol mull	ν(M–C) Nujol mull	ν(M–X) Nujol mull (dichloromethane)
Ny	1499		
trans-PtCl₂(PPhMe₂)(Ny)	1645	525	331 (332)
trans-PtBr₂(PPhMe₂)(Ny)	1644	528	243
trans-PtI₂(PPhMe₂)(Ny)	1647	524	
trans-PtCl₂(PMe₃)(Ny)	1643	527	335 (334)
Ay	1508		
cis-PdCl₂(PPhMe₂)(Ay)	1633	a	a
PdCl₂(PMe₃)(Ay)	1627	a	a
trans-PtCl₂(PPhMe₂)(Ay)	1629	a	339 (338)
trans-PtCl₂(PMe₃)(Ay)	1637	a	330 (330)
Sy	1508		
cis-PdCl₂(PPhMe₂)(Sy)	1631	517	296, 265 (350ᵇ)
cis-PdCl₂(PMe₃)(Sy)	1633	523	268, 245 (351, 270, 246)
trans-PtCl₂(PPhMe₂)(Sy)	1633	516	337 (337)
cis-PtCl₂(PPhMe₂)(Sy)	1636	544	312, 280
trans-PtBr₂(PPhMe₂)(Sy)	1632	513	243
cis-PtBr₂(PPhMe₂)(Sy)	1636	535	
trans-PtI₂(PPhMe₂)(Sy)	1633	520	
cis-PtI₂(PPhMe₂)(Sy)	1627	519	
trans-PtCl₂(PMe₃)(Sy)	1623	510	338 (337)
Py	1499		
trans-PdCl₂(PPhMe₂)(Py)	1607	a	345 (346)
trans-PdCl₂(PMe₃)(Py)	1621	510	348 (347)
trans-PtCl₂(PPhMe₂)(Py)	1622	517	334 (337)
trans-PtBr₂(PPhMe₂)(Py)	1632	517	245
trans-PtI₂(PPhMe₂)(Py)	1636	524	
trans-PtCl₂(PMe₃)(Py)	1633	525	338 (336)

ᵃ Obscured by the ligand bands. ᵇ Other bands were not observed due to its low solubility.

spectra,[10] and molecular weights[15] were measured as described elsewhere. The complexes are essentially monomeric in chloroform as shown in Table I.

Results and Discussion

The carbonyl stretching band of the ylide complexes was observed at higher frequencies than those of the original ylides as found in Table II. This indicates increasing double-bond

Table III. ¹H NMR Data of the Ylide Complexes at 23°

Complex	Solvent[b]	Chem shifts, δ, ppm					Coupling constants, Hz[a]			
		Ylide CH	Ylide CH₃	Ylide o-H[c]	Ny α-H[d]	P–CH₃	²J(¹⁹⁵Pt–CH)	³J(³¹P–M–CH)	²J-(³¹P–CH₃)	³J(¹⁹⁵Pt–P–CH₃)
Ny	A	6.64	2.35	7.80	9.47					
trans-PtCl₂(PPhMe₂)(Ny)	A	6.88	2.53	8.44	8.84	1.64, 1.62	91	12	11	23
trans-PtBr₂(PPhMe₂)(Ny)	A	7.13	2.52	8.43	8.90	1.76	96	13	11	25
trans-PtI₂(PPhMe₂)(Ny)	A	7.57	2.53	8.38	8.99	2.06	100	11	10	27
trans-PtCl₂(PMe₃)(Ny)	A	6.82	2.56	8.48	8.86	1.39	90	12	11	22
Ay	A	4.70		7.97						
trans-PdCl₂(PPhMe₂)(Ay)	A	5.71		8.43		1.67, 1.61		12	11	
trans-PdCl₂(PMe₃)(Ay)	A	5.63		8.40		1.35		12	12	
trans-PtCl₂(PPhMe₂)(Ay)	A	6.05		8.43		1.71, 1.64	85	10	10	26
trans-PtCl₂(PMe₃)(Ay)	A	5.97		8.40		1.39	82	11	11	25
Sy	A	4.32	2.96	7.79						
	B	4.40	2.81	7.69						
trans-PdCl₂(PPhMe₂)(Sy)	B	5.08	3.00, 2.71	8.27		1.59		13	12	
cis-PdCl₂(PPhMe₂)(Sy)	B	5.72	3.12, 2.80	8.06		1.74		0[e]	12	
trans-PdCl₂(PMe₃)(Sy)	B	4.95	3.04, 2.69	8.29		1.32		12	12	
cis-PdCl₂(PMe₃)(Sy)	B	5.69	3.12, 2.83	8.29		1.39		0[e]	12	
trans-PtCl₂(PPhMe₂)(Sy)	A	5.33	3.02, 2.76	8.36		1.69, 1.67	85	11	11	24
cis-PtCl₂(PPhMe₂)(Sy)	B	5.98	3.04, 2.77	8.05		1.80, 1.73	134[e]	0[e]	12	37
trans-PtBr₂(PPhMe₂)(Sy)	A	5.63	3.00, 2.73	8.38		1.82, 1.80	90	11	11	24
cis-PtBr₂(PPhMe₂)(Sy)	B	f	3.07, 2.81	8.07		1.86	f	f	11	37
trans-PtI₂(PPhMe₂)(Sy)	A	6.22	3.00, 2.74	8.36		2.12	94	10	11	28
cis-PtI₂(PPhMe₂)(Sy)	B	f	2.96, 2.80	8.01		2.00	f	f	11	39
trans-PtCl₂(PMe₃)(Sy)	A	5.24	3.05, 2.77	8.41		1.44	84	11	11	25
Py	A	4.24	2.43	7.89						
trans-PdCl₂(PPhMe₂)(Py)	A	5.14	2.82	8.38		1.65, 1.62		g	11	
trans-PdCl₂(PMe₃)(Py)	A	5.01	2.85	8.35		1.34		g	12	
trans-PtCl₂(PPhMe₂)(Py)	A	5.36	2.78	8.38		1.68, 1.65	79	g	11	26
trans-PtBr₂(PPhMe₂)(Py)	A	5.71	2.80	8.39		1.82, 1.79	84	g	10	26
trans-PtI₂(PPhMe₂)(Py)	A	6.33	2.85	8.36		2.12, 2.09	91	g	11	27
trans-PtCl₂(PMe₃)(Py)	A	5.25	2.81	8.34		1.39	77	g	11	26

[a] Uncertainty ±1 Hz. [b] A = chloroform-d_1; B = dimethyl-d_6 sulfoxide. [c] Ortho protons of the phenyl group. [d] α protons of the pyridine ring. [e] Not accurate because of broad signals. [f] Obscured by the phenyl signals. [g] Not determined due to the couplings between the ylide methine proton and two ³¹P nuclei.

character of the carbon–oxygen bond of the ylides upon coordination of the ylide carbon to the metal ions, as previously mentioned.[10,16] The existence of the ylide carbon–metal bond is also suggested by the observation of the spin–spin coupling between the ylide methine proton and the ¹⁹⁵Pt nucleus, as shown in Table III. The formation of the ylide carbon–metal bond leads to a downfield shift of the ortho phenacyl phenyl protons (Table III), which may be due to the increased anisotropy of the carbonyl group.[17] The ylide methine signal also shifted to a lower magnetic field owing to the inductive effect of the metal ions upon complexation.

It was previously pointed out that the α protons of the pyridine ring of the free Ny were markedly deshielded for the formation of the hydrogen bond with the carbonyl oxygen, giving a six-membered ring.[18] This α-proton signal shifts to a higher magnetic field upon complexation. This may be due to the change of the hybridization of the ylide carbon orbitals from sp² to sp³ and the reduction of negative charges on the

carbonyl oxygen upon formation of the ylide carbon–metal bond.

The Palladium(II)–Ylide Complexes. The PdCl₂L(Sy) complexes (L = PPhMe₂, PMe₃) exhibited two ν(Pd–Cl) bands in the solid state (Table II), which suggests a cis configuration around the palladium atom. In dichloromethane, however, an additional band was observed at 350 or 351 cm⁻¹ when L = PPhMe₂ or PMe₃, indicating the appearance of a trans isomer. The coexistence of the cis and trans isomers in solution is also confirmed by the ¹H NMR spectra; the Sy complexes in dimethyl-d_6 sulfoxide displayed two doublets of S–CH₃ and a singlet and a doublet of methine signals (Table III). The higher field pair of S–CH₃ signals and the doublet signals of methine proton may be assigned to the trans isomer, because (i) the Sy in the trans isomer is subjected to a strong trans influence of the phosphorus ligand, which may result in a weaker palladium–carbon bond than the cis one and (ii) the spin–spin coupling between the ylide methine proton and ³¹P

nucleus is expected to occur in the trans isomer rather than in the cis isomer (Table III). Integrated intensity of the S-CH3 signals revealed that the ratio of the cis to trans isomer was about 2.8:1 and 4.5:1 for the PPhMe2 and PMe3 complexes, respectively. The fact that PdCl2(PMe3)(Sy) has a larger portion of the cis isomer would be mainly attributed to a smaller steric repulsion between Sy and PMe3.

The ^1H NMR spectra of PdCl2L(Ay) (L = PPhMe2, PMe3) in chloroform-d_1 indicated the existence of only one isomer, and the ^3J(P-Pd-CH) values were both 12 (±1) Hz. This value is almost identical with those of *trans*-PdCl2L(Sy), suggesting a trans arrangement of the complexes in solution, although the configuration in the solid state has not been determined because the ν(Pd-Cl) is obscured by the absorptions of Ay. In the synthetic process of PdCl2-(PPhMe2)(Ay), the addition of a large amount of petroleum ether to a solution containing di-μ-chloro-dichlorobis(dimethylphenylphosphine)dipalladium(II) and Ay gave a mixture of a yellow powder and orange crystals. They exhibited the ν(C=O) band at 1633 and 1621 cm^{-1} in the solid state, respectively. The former frequency, however, moved down to 1623 cm^{-1} in dichloromethane. In addition, the ^1H NMR spectra of both products in chloroform-d_1 were quite similar to that of the trans isomer described above. In view of these results, the yellow compound would be a cis isomer which easily isomerizes to a trans isomer in solution, and the orange crystals would be a trans isomer.

PdCl2L(Py) (L = PPhMe2, PMe3) exhibited only one ν(Pd-Cl) band both in the solid state and in solution, suggesting a trans configuration around the palladium atom.

The Platinum(II)-Ylide Complexes. The solid-state spectra of PtX2LY (X = Cl, L = PPhMe2, Y = Ny, Ay, Py; X = Cl, L = PMe3, Y = Ny, Ay, Sy, Py; X = Br, L = PPhMe2, Y = Ny, Py) show only one ν(Pt-X) band around 335 cm^{-1} for the dichlorides, or 245 cm^{-1} for the dibromides, indicating a trans configuration around the platinum. The ^3J(P-Pt-CH) values (11 ± 1 Hz) of these complexes suggest a trans structure in solution. The diiodide complexes PtI2(PPhMe2)Y (Y = Ny, Py) in solution are also assigned to a trans arrangement on the basis of the ^3J(P-Pt-CH) and ^3J(Pt-P-CH3) values, which are almost identical with those of the corresponding dichloride and dibromide complexes (Table III). In view of the fact that the configurations of the dichlorides and dibromides in solution are identical with those in the solid state, respectively, the diiodide complexes may be assumed to have a trans configuration in the solid state, too.

Two isomers of PtX2(PPhMe2)(Sy) (X = Cl, Br, I) were separately isolated; the major product is a trans isomer and the minor one a cis isomer when X = Cl or Br, as revealed from infrared spectra. The diiodo complex was predominantly a cis form. The cis-dichloride and -dibromide and the *trans*-diiodide are stable to isomerization in solution. On the other hand, the *trans*-dichloro complex quickly underwent an isomerization to a cis form and the *trans*-dibromide slowly did so when dissolved in chloroform. The cis-diiodide partly isomerized in dimethyl-d_6 sulfoxide, as detected by means of ^1H NMR spectra. These observations may be related to the fact that the ν(Pt-C) of the dichloride and dibromide complexes is lower in the trans isomers than in the cis isomers, while both isomers of the diiodide complexes, whose melting points are very close, display nearly the same ν(Pt-C) frequencies (Table II).

The average frequency (296 cm^{-1}) of two ν(Pt-Cl) bands of cis-PtCl2(PPhMe2)(Sy) is lower than that (304 cm^{-1}) of cis-PtCl2(PPhMe2)2,[19] indicating a larger trans influence of Sy than of PPhMe2.

The pK_a values of the conjugated acids of Ny, Ay, Sy, and Py were reported to be 10.5, 8.25, 7.68, and 6.51, respec-

tively.[18,20] The ^2J(Pt-CH) value of the platinum-ylide complexes with the same configuration approximately increases in this order of the pK_a value (see Table III). It should be noted that the ^2J(Pt-CH) values obtained in the present trans complexes (77-100 Hz), though they are smaller than the ^2J(Pt-CH) value of *trans*-PtCl2(CH3CH2C-HN+C5H5)-(C5H5N) (115 Hz),[21] are somewhat larger than the ^2J(Pt-CH3) of cis-PtMe2(PPhMe2)2 (67 Hz)[22] and [PtMe-(PPhMe2)3]+ (57 Hz),[23] which have the same phosphorus ligand in the trans position as *trans*-PtX2(PPhMe2)Y (X = Cl, Br, I; Y = Ny, Sy, Py). Thus, the ylide complexes may involve a larger s character in the platinum-carbon bond than the methylplatinum compounds. This is also shown from the assumption that a positively charged, electronegative heteroatom causes an increase in the s character in the Pt-C bond as a result of the rehybridization of the ylide carbon.[24]

Influence of Ligands Cis or Trans to the Ylides. A substitution of PMe3 for the PPhMe2 trans to an ylide caused a reduction in the ^2J(Pt-CH). This is explained by the weakening of the ylide carbon-metal bond in the PMe3 complexes, which resulted from the larger trans influence of PMe3 (pK_a = 8.65) than of PPhMe2 (pK_a = 6.50).[25]

The ν(Pt-C) frequency of cis-PtX2(PPhMe2)(Sy) (X = Cl, Br, I) decreases on going from Cl to I. This result is consistent with the order of the trans influence of the halide ions. On the other hand, *trans*-PtX2(PPhMe2)Y (X = Cl, Br, I; Y = Ny, Sy, Py) showed an opposite trend; the ν(Pt-C) frequency of the diiodide complex is equal to or higher than that of the corresponding dichloride. In addition, the ^2J(Pt-CH) value increases in the order of Cl < Br < I. These are not explained in terms of the cis labile property of halide ions, i.e., I > Br > Cl, estimated from the spin-spin coupling constant between the ^{31}P and ^{195}Pt nuclei in a variety of platinum(II) complexes.[26,27] In view of a significant role of the onium center to stabilize ylide-metal complexes, as mentioned in the introductory section, the phenomena conflicting with the cis influence of halide ions may be interpreted as follows; the electronic polarizability of the halogens augments on passing from Cl to I, and therefore the electronic interaction (A) of
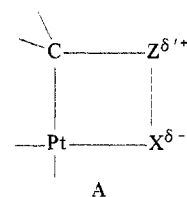
A
(Z = a heteroatom group)

the halide ion with a heteroatom involving positive charges increases in the same order. This interaction polarizes the platinum-halogen bond to decrease the s character, resulting in enrichment of the electron density in the 6s valence orbital at the platinum atom. A similar electronic polarization may occur in the ylide carbon-heteroatom bond. These interactions recall an intermediate of the Wittig reaction. The synergetic polarization of this kind would cause a high-frequency shift of the ν(Pt-C) and an increase of the ^2J(Pt-CH) value in the diiodo complexes (see Tables II and III). An increase of the ^3J(Pt-P-CH3) value is also seen on going from Cl to I. It is therefore suggested that the increment of ^2J(Pt-CH) and ν(Pt-C) is mainly due to the polarization of the metal-halogen bond, because that of the ylide carbon-heteroatom bond would strengthen the platinum-ylide carbon bond to weaken the platinum-phosphorus bond, resulting in a decrease of the ^3J(Pt-P-CH3) value.

trans-PdCl2(PMe3)(Ay), 57396-12-0; *trans*-PtCl2(PPhMe2)(Ay), 57396-13-1; *trans*-PtCl2(PMe3)(Ay), 57396-14-2; *trans*-PdCl2-(PPhMe2)(Sy), 57396-15-3; *cis*-PdCl2(PPhMe2)(Sy), 57456-88-9; *trans*-PdCl2(PMe3)(Sy), 57396-16-4; *cis*-PdCl2(PMe3)(Sy), 57456-89-0; *trans*-PtCl2(PPhMe2)(Sy), 57396-17-5; *cis*-PtCl2-(PPhMe2)(Sy), 57456-90-3; *trans*-PtBr2(PPhMe2)(Sy), 57396-18-6; *cis*-PtBr2(PPhMe2)(Sy), 57456-91-4; *trans*-PtI2(PPhMe2)(Sy), 57396-19-7; *cis*-PtI2(PPhMe2)(Sy), 57456-92-5; *trans*-PtCl2-(PMe3)(Sy), 57396-20-0; *trans*-PdCl2(PPhMe2)(Py), 57396-21-1; *trans*-PdCl2(PMe3)(Py), 57396-22-2; *trans*-PtCl2(PPhMe2)(Py), 57396-23-3; *trans*-PtBr2(PPhMe2)(Py), 57396-24-4; *trans*-PtI2-(PPhMe2)(Py), 57396-25-5; *trans*-PtCl2(PMe3)(Py), 57396-26-6; Ny, 25357-50-0; Ay, 24904-06-1; Sy, 5633-34-1; Py (charged form), 57395-87-6; di-μ-chloro-dichlorobis(dimethylphenylphosphine)di-platinum(II), 15699-79-3; di-μ-chloro-dichlorobis(dimethylphenyl-phosphine)dipalladium(II), 15699-80-6; Py (uncharged form), 57395-88-7.

References and Notes

(1) M. Keeton, R. Mason, and D. R. Russell, *J. Organomet. Chem.*, **33**, 259 (1971).
(2) F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E. G. Hoffmann, G. Schroth, K. Seevogel, and W. Stempfle, *Isr. J. Chem.*, **10**, 293 (1972).
(3) P. Bravo, G. Fronza, C. Ticozzi, and G. Gaudiano, *J. Organomet. Chem.*, **74**, 143 (1974).
(4) H. Schmidbaur, J. Adlkofer, and W. Buchner, *Angew. Chem.*, **85**, 448 (1973); H. Schmidbaur, J. Adlkofer, and M. Heimann, *Chem. Ber.*, **107**, 3697 (1974).
(5) H. Schmidbaur and R. Franke, *Angew. Chem.*, **85**, 449 (1973).
(6) H. H. Karsch and H. Schmidbaur, *Angew. Chem.*, **85**, 910 (1973); H. H. Karsch and H. Schmidbaur, *Chem. Ber.*, **107**, 3684 (1974).
(7) H. H. Karsch, H.-F. Klein, and H. Schmidbaur, *Chem. Ber.*, **107**, 93 (1974).
(8) H. Schmidbaur and H.-J. Füller, *Chem. Ber.*, **107**, 3674 (1974).
(9) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975).
(10) H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, **13**, 443 (1974).
(11) F. Krohnke, *Chem. Ber.*, **68**, 1177 (1935).
(12) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).
(13) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).
(14) F. R. Hartley and G. W. Searle, *Inorg. Chem.*, **12**, 1949 (1973).
(15) H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, **14**, 253 (1975).
(16) Y. Oosawa, T. Miyamoto, T. Saito, and Y. Sasaki, *Chem. Lett.*, 33 (1975).
(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 88.
(18) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **35**, 3144 (1970).
(19) D. G. Cooper and J. Powell, *J. Am. Chem. Soc.*, **95**, 1102 (1973).
(20) A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).
(21) R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organomet. Chem.*, **33**, 247 (1971).
(22) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).
(23) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970).
(24) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).
(25) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).
(26) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(27) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); G. Socrates, *J. Inorg. Nucl. Chem.*, **31**, 1667 (1969); F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc. A*, 2087 (1970); F. H. Allen and S. N. Sze, *ibid.*, 2054 (1971).

Magnetic Properties of α-Di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridinecopper(II)] Perchlorate, α-[Cu(DMAEP)OH]2(ClO4)2

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The magnetic susceptibility and electron paramagnetic resonance spectra of α-di-μ-hydroxo-bis[2-(2-dimethylamino-ethyl)pyridinecopper(II)] perchlorate are reported. The susceptibility data are characteristic of exchange-coupled copper(II) pairs with a small interpair interaction. The pairwise interaction results in a singlet ground state for the pair with a very low-lying triplet excited state. A crossover of the triplet and singlet energy levels is produced with an applied field of ∼50 kG. The magnetic parameters derived are $J = -2.35 \pm 0.2$ cm^{-1}, $J' \simeq -0.1$ cm^{-1}, $g = 2.08 \pm 0.02$, and $D \approx 0.4$ cm^{-1}. The results are discussed in terms of the molecular structure of the complex and compared to structurally similar systems.

The preparation and characterization of a number of di-hydroxo-bridged copper(II) complexes which belong to the general class [Cu(L)OH]2X2·nH2O have been reported.[1-4] Here L has been a variety of chelating amines and X⁻ has been several counterions such as ClO4⁻, Br⁻, 1/2 SO4²⁻, etc. The magnetic properties of this series are characteristic of exchange-coupled copper(II) ions. For these systems, the singlet–triplet (S–T) splitting energy, which results from the isotropic exchange interaction, ranges from large positive values (triplet ground states) to very large negative values (singlet ground states). Studies on this series have yielded much useful information in our continuing efforts to correlate the structural and magnetic properties of magnetically condensed systems. The structural properties vary only slightly throughout the series while the magnetic properties vary greatly. Our investigation of several members of the series has revealed[2-4] a striking correlation between the S–T splitting 2*J* and the Cu–O–Cu bridge angle φ.

Recently, Uhlig and co-workers reported[5] the preparation of complexes formed with copper(II) and N-substituted 2-(2-aminoethyl)pyridine which, on the basis of the spectral and high-temperature magnetic data, should belong to this series.

Of particular interest is the reaction of copper(II) perchlorate and 2-(2-dimethylaminoethyl)pyridine (DMAEP). Recent structural investigations[3,6] have revealed the existence of two forms of complex. The monoclinic β form does belong to the structural class and obeys the near-linear 2*J* vs. φ relationship. The triclinic α form, however, does not belong to this structural class since the copper(II) ions are bridged by the perchlorato anions as well as the hydroxo groups.

We report here the magnetic properties of the α form of the DMAEP complex which indicate that the exchange interaction is greatly affected by this structural change. The magnetic properties of α-DMAEP are of special interest since an "S–T crossover" is produced by large applied magnetic fields, a phenomenon which has received very little attention in previous reports of exchange-coupled systems.

Experimental Section

Preparation. The addition of 2-(2-dimethylaminoethyl)pyridine to an equimolar quantity of copper(II) perchlorate hexahydrate in a minimum volume of an alcohol–ether solution yields a blue precipitate having the stoichiometry Cu(DMAEP)OHClO4. Magnetic measurements (vide supra) indicate that this precipitate is a mixture of the α and β forms of the complex. Crystal growth from an absolute