CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Metal Complexes of Substituted Dithiophosphinic Acids. IV. Complexes of Divalent Nickel, Palladium, and Platinum

BY R. G. CAVELL,* W. BYERS, E. D. DAY, AND P. M. WATKINS

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The infrared, electronic (visible and ultraviolet), and mass spectra of the planar dithiophosphinato complexes, M[S_2PX_2]$_2$ (M = Ni, Pd, Pt; X = CH_3, C_6H_5, OC_2H_5, F, and CF_3, except in the case of this latter substituent the M = Pt complex), are examined in the context of the electronic effects of the substituents and their relationship to the analogous pseudotetrahedral complexes of Mn, Fe, Co, Zn, Cd, and Hg. The novel complex formulated as $Pt_2S_6P_4(CF_3)_8$ representing a "sulfur deficient" dimer is described. All the normal complexes are diamagnetic and monomeric in solution. The substituents which represent a range of inductive and π-bonding possibilities fall in the spectrochemical order $OC_2H_5 \sim F > CH_3 \sim C_6H_5 \sim CF_3$. A correlation has been found between the metal–sulfur stretching frequencies in the infrared and the first electronic transition, and this correlation has been compared with previous correlations of M–S bond lengths with ligand field strength. The Ni[$S_2P(CH_3)_2$]$_2$ complex shows two reduction waves and one oxidation wave in the polarogram obtained from an acetonitrile solution.

Introduction

The chemical and structural properties of planar complexes containing the MS_4 chromophore have recently been reviewed.[1-5] Although much is known, a satisfactory theoretical description of the bonding in these planar 1,1-dithioacid complex systems has yet to be developed which is consistent with all the experimental data now available. In continuation of our investigations[6-9] of the chemical and electronic properties of the various coordination geometries obtainable within the dithiophosphinic acid system using substituents of varying electronic effects, we report herein preparations and further studies of the planar, diamagnetic complexes M[S_2PX_2]$_2$ (M = Ni, Pd, and Pt; X = CH_3, C_6H_5, OC_2H_5, F, and CF_3), some of which have been initially reported elsewhere. Molecular and crystal structures[1] of the nickel dithiophosphinates, Ni[S_2PX_2]$_2$, where X = CH_3[10a] C_2H_5,[10b] C_6H_5,[11] OC_2H_5,[1] and OCH_3,[10c] verify the planar geometry of the MS_4 moiety; however, no Pt or Pd structure has yet been reported. Electronic spectral data have been discussed in detail only for the Ni, X = C_6H_5 and OC_2H_5, complexes[11-14] and the Pd and Pt, X = OC_2H_5[12] and C_6H_5,[15] complexes although band positions have been reported for the X = C_6H_5,[11] C_2H_5[16,17] and OCH_3, OC_2H_5, OC_2H_4Cl, C_6H_{11}, $OCH(CH_3)C_6F_5$,[18] and unsymmetrically substituted X = F, X′ = CH_3 or C_2H_5[19] complexes of Ni(II).

Experimental Section

Volatile air-sensitive compounds, particularly those containing F and CF_3 substituents, were handled in a conventional vacuum system greased with Apiezon N stopcock grease or in the grease-free apparatus described below. Transfers to weighing containers and other manipulations were carried out in drybags under nitrogen. Air-stable systems were handled with typical bench-top techniques.

Infrared spectra were recorded over the range 4000–250 cm^{-1} using a Perkin-Elmer 457 instrument on Nujol mulls of the solids contained between CsBr plates or as solutions in 0.5-mm CsBr solution cells. Ultraviolet and visible spectra were measured with a Cary 14 spectrometer, and the reflectance spectra were obtained on the same instrument equipped with the Cary 1411 diffuse reflectance attachment operating in Type II mode. The room-temperature diamagnetism of the compounds was determined by the Faraday technique.[6] Mass spectra were obtained by means of the direct probe sample insertion system of the AEI MS9 mass spectrometer operating at 70 eV. Fluorine nmr spectra were obtained on ~5% solutions in CCl_3F or CH_2Cl_2 by means of a Varian A56/60A instrument. Analytical data are collected in Table I.

Preparation of Compounds.—Syntheses of acids or acid salts have been described elsewhere.[6,20,21]

M[$S_2P(CH_3)_2$]$_2$ and M[$S_2P(C_6H_5)_2$]$_2$.—Concentrated aqueous solutions of the metal salts ($NiCl_2 \cdot 6H_2O$, $(NH_4)_2PdCl_4$, K_2PtCl_4) were mixed with aqueous solutions of the ligand salts ($NaS_2P(CH_3)_2 \cdot 2H_2O$ or $NH_4S_2P(C_6H_5)_2$) followed by extraction with and crystallization from dichloromethane. Recrystallization could be effected from a 1:1 (by volume) dichloromethane–2-propanol mixture by reducing the volume by half and setting flask and solution aside to cool undisturbed. Dilute aqueous solutions of starting salts of Pd and especially Pt were particularly susceptible to precipitation of a brown material (presumably the metal sulfide) and the readily detectable evolution of H_2S gas. The Pt complex was purified by fractional sublimation up a vertically mounted evacuated glass tube surrounded by a copper jacket heated at the bottom to 250° in a bath of Wood's metal.

M[$S_2P(OC_2H_5)_2$]$_2$.—The Ni and Pd complexes were prepared by adding the metal salt ($NiCl_2 \cdot 6H_2O$ or $(NH_4)_2PdCl_4$) to

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TABLE I

ANALYTICAL DATA[a]

				Color			
X	M	% C	% H	Solid	CH_2Cl_2 soln	Mol wt (osmometrically)	Mol wt (mass spec) (^{58}Ni, ^{106}Pd, ^{195}Pt)
CH_3	Ni	15.68 (15.55)	4.17 (3.91)	Deep purple	Deep blue	304[b] (309)	308 (308)
	Pd	13.65 (13.47)	3.44 (3.39)	Red-orange	Red-orange	385[b] (357)	356 (356)
	Pt	10.82 (10.79)	2.95 (2.72)	Orange-yellow	Yellow	522[b] (445)	445 (445)
C_6H_5	Ni	51.77 (51.72)	3.82 (3.62)	Purple	Yellow-green	558[b] (557)	556 (556)
	Pd	47.53 (47.65)	3.43 (3.33)	Red-orange	Red-orange	623[b] (605)	604 (604)
	Pt	41.44 (41.55)	3.09 (2.91)	Orange	Yellow	674[b] (694)	693 (693)
OC_2H_5	Ni	22.44 (22.39)	4.57 (4.70)	Purple	Purple-pink	407[c] (429)	426 (426)
	Pd	20.31 (20.15)	4.19 (4.23)	Orange	Orange-yellow	431[c] (477)	476 (476)
	Pt	16.66 (16.99)	3.63 (3.56)	Yellow	Yellow	513[c] (566)	565 (565)
F	Ni			Dark green (black)	Pink	329[d] (325)	323.7641 (323.7659)
	Pd			Red-orange	Red-orange	384[d] (373)	372.7333 (372.7326)
	Pt			Orange-yellow	Yellow	(461)	460.7935 (460.7942)
		% CF_3[e]	% S				
CF_3	Ni	26.1 (26.2)	24.88 (24.42)	Blue-green	Yellow-green	507[c] (520)	523.7523 (523.7519)
	Pd	24.0 (24.1)	22.39 (22.39)	Brick-red	Red-orange	633[c] (572)	571.7190 (571.7198)
	Pt[f]	21.3 (21.9)	15.31 (15.28)	Yellow	Yellow	>1000[c] (1258)	1257.6160 (1257.6181)

[a] Values in parentheses calculated according to formulation as $M[S_2PX_2]_2$. [b] Dibromomethane solution. [c] Carbon tetrachloride solution. [d] Taken from ref 10. [e] Calculated from HCF_3 evolved on base hydrolysis of compound, assuming 1 mol of HCF_3 evolved per mole of P present. [f] Values in parentheses calculated according to formulation as $Pt_2S_6P_4(CF_3)_8$.

an ethanol solution of the acid.[18] The Pt complex could only be made by reaction of $NaS_2P(OC_2H_5)_2$ with Pt salts in concentrated aqueous solutions followed by extraction into CH_2Cl_2. The complexes were recrystallized by boiling a solution in 1:1 (by volume) dichloromethane–2-propanol mixture to half-volume and setting aside to cool. The crystals were washed with cold 2-propanol and dried under vacuum.

$M[S_2PF_2]_2$.—These compounds were prepared essentially as described elsewhere[22] from F_2PS_2H acid[20] except that milligram quantities of starting materials were used and solvents omitted in the "grease-free" vacuum apparatus represented schematically in Figure 1. The advantages of this simple design are more efficient collection and separation of the products, and fractional sublimation within the apparatus is possible. Materials may be passed back and fourth between the large reaction volume and cold finger through the intermediate U-trap cooled in slush baths of the desired temperature. When the solid complexes had been isolated in the cold finger and the other volatile reaction materials distilled from the apparatus, the whole unit was removed to a nitrogen-filled drybag where the cold finger was cut off and the product manipulated as desired. The $Pt[S_2PF_2]_2$ complex was prepared by the direct reaction between K_2PtCl_4 or $PtCl_2$ and HS_2PF_2; the Pd complex was prepared from $PdCl_2$ and the Ni compound from Ni metal.

$M[S_2P(CF_3)_2]_2$.—(a) **Nickel(II) bistrifluoromethyldithiophosphinate** was prepared by refluxing $HS_2P(CF_3)_2$[21] with Ni metal at room temperature in an evacuated sublimer (fitted with a cold water probe) for 24 hr. Volatile products were removed under vacuum and identified as excess acid, $(CF_3)_2PSH$, H_2S, and hydrogen. The blue-green solid product $Ni[S_2P(CF_3)_2]_2$ was sublimed at 60° to the cold water probe and subsequently fractionally resublimed to obtain the pure product. The ^{19}F nmr spectrum in CH_2Cl_2 showed a doublet (J_{PF} = 109 Hz, ϕ = 59.6 ppm *vs.* CCl_3F).

(b) **Palladium(II) bistrifluoromethyldithiophosphinate** was prepared as described above from $PdCl_2$ and $HS_2P(CF_3)_2$. The reaction was rapid giving HCl and $Pd[S_2P(CF_3)_2]_2$ at room temperature within 30 min. The ^{19}F nmr in CCl_4 solution showed a simple doublet (J_{PF} = 108 Hz, ϕ = 71.5 ppm *vs.* $CFCl_3$).

The "Sulfur-Deficient" Dimer of Pt(II).—The reaction between $PtCl_2$ and $HS_2P(CF_3)_2$ in the same apparatus as described above was slow, several days refluxing at room temperature being required to give a yellow solid product; HCl, $(CF_3)_2P(S)Cl$, and H_2S as volatile products were collected in cold traps on the vacuum line. Not all of the $PtCl_2$ taken was consumed. The desired yellow product was separated by sublimation at 70° to the cold water probe. A quantity of yellow colored involatile material which remained with the $PtCl_2$ was not further investigated. The resublimed yellow solid was found by mass spectral and chemical analysis to be $Pt_2S_6P_4(CF_3)_8$. Both K_2PtCl_4 and $Pt(NH_3)_2Cl_2$ reacted very slowly with the acid to give the same solid product, but $Pt(NH_3)_4Cl_2$ did not react. The ^{19}F nmr spectrum on a saturated solution in CH_2Cl_2 containing $CFCl_3$ as an internal standard gave the spectrum illustrated in Figure 6.

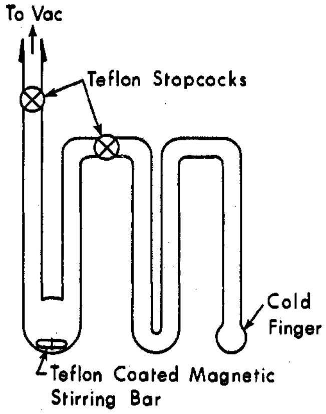

Figure 1.—Grease-free apparatus for the preparation of volatile solid complexes.

Results and Discussion

Mass Spectra.—The mass spectral data with the exception of the X = OC_2H_5 complexes are summarized in Tables II and III. In all cases, the parent monomer ions were the most intense. In general the fragments containing the metal atom were readily identifiable by their characteristic isotopic patterns. Since the behavior of the Pd, Pt, X = OC_2H_5 complexes in the mass spectrometer is similar to that of $Ni[S_2P(OC_2H_5)_2]_2$ which has been thoroughly analyzed,[18] these spectra are omitted from Tables II and III. The fragmentation patterns observed for the Ni(II) compounds are very similar to those of the polymeric, tetrahedrally coordinated Co(II) analogs for all X;[9] however, the spectra of the Ni, Pd, and Pt complexes differ markedly from those of the Zn, Cd, and Hg compounds.[9]

The mass spectrum of $Pt_2S_6P_4(CF_3)_8$ (Table IV) is very much dominated by the parent molecule ion of the formula given and the "monomeric" unit of exactly half the above formula. All other ions are very weak and do not contribute greatly to the total ionization. The mass spectrum thus provides strong evidence in

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TABLE II

MASS SPECTRAL DATA (m/e VALUES) FOR PLANAR $M[S_2PX_2]_2$ COMPLEXES[a]

Assignment[b]	X = CH_3			X = C_6H_5			X = F			X = CF_3	
	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd
$MS_4P_2X_4$	308 (100)	356 (100)	445 (100)	556 (100)	604 (100)	693 (100)	324 (100)	372 (100)	461 (100)	524 (100)	572 (100)
$MS_4P_2X_3$	293 (4)	341 (11)	430 (10)			616 (0)	305 (0)	353 (1)	442 (1)	455 (3)	
$MS_4P_2X_2F$										405 (6)	453 (16)
MS_4PX_2			384 (9)				255 (29)	303 (2)	392 (33)	355 (22)	403 (0)
MS_4PX							236 (8)		373 (5)	286 (3)	
MS_4					234 (4)		186 (3)	284 (10)	323 (9)	186 (5)	
$MS_3P_2X_4$	276 (1)	324 (1)		524 (7)	572 (3)	661 (1)				492 (0)	540 (0)
$MS_3P_2X_3$	261 (3)	309 (3)	398 (4)	447 (0)	495 (8)	584 (5)				423 (6)	471 (6)
$MS_3P_2X_2F$										373 (3)	421 (6)
MS_3P_2X				293 (22)							333 (1)
MS_3P_2F											
MS_3PX_3				416 (12)							
MS_3PX_2	215 (3)					476 (1)	223 (3)	271 (0)	360 (3)	323 (9)	371 (1)
MS_3PF										204 (12)	
MS_3P			322 (4)							185 (11)	233 (5)
MS_3			291 (6)				154 (5)	202 (3)	291 (6)	154 (3)	
$MS_2P_2X_4$	244 (34)	292 (36)	381 (25)	492 (7)	540 (27)	629 (23)		308 (1)		460 (1)	508 (1)
$MS_2P_2X_3$	229 (26)	277 (28)	366 (29)	415 (8)	463 (4)	552 (6)			378 (1)		
MS_2PX_3	198 (1)		335 (5)	384 (18)							
MS_2PX_2	183 (20)	231 (26)	320 (8)	307 (3)	355 (3)		191 (36)	239 (32)	328 (13)	291 (25)	339 (36)
MS_2PXF										241 (5)	289 (10)
MS_2PX	168 (6)	216 (2)		230 (5)		367 (3)		220 (0)	309 (3)	222 (5)	270 (1)
MS_2PF										172 (16)	220 (6)
MS_2P						290 (1)				153 (21)	201 (24)
MS_2	122 (3)						122 (20)	170 (18)	259 (12)	122 (26)	170 (33)
MSP_2X_3	197 (0)	245 (1)	334 (4)		431 (23)	520 (12)					
MSP_2X_2F										309 (0)	357 (0)
MSP_2X		215 (2)	304 (4)	229 (12)	277 (1)						
MSP_2F										171 (3)	219 (5)
$MSPX_3$	166 (4)			352 (32)	400 (16)						
$MSPX_2$	151 (6)	199 (39)	288 (4)	275 (2)	323 (24)	159 (6)		207 (8)	296 (7)	259 (1)	307 (11)
$MSPXF$											257 (10)
$MSPX$	136 (3)	184 (7)		198 (18)						190 (2)	
$MSPF_2$										159 (4)	207 (9)
$MSPF$										140 (13)	188 (3)
MSP		169 (26)	258 (7)		169 (66)	258 (7)				121 (31)	169 (90)
MS		138 (1)	227 (1)				90 (7)	138 (4)	227 (6)	90 (10)	138 (4)
MP_2X	135 (1)	183 (7)	272 (1)	197 (3)	245 (6)	334 (8)					
MP_2							120 (7)				
MPX_3					368 (8)						
MPX_2				243 (11)	291 (24)			175 (8)	264 (3)		
MPF_2											175 (9)
MPF										108 (7)	
MP										89 (1)	137 (6)
M		106 (3)	195 (0)	58 (10)	106 (1)		58 (11)	106 (9)		58 (23)	106 (14)
Source temp (°C)	150	200	200	270	260	260	60	80	25	50	80

[a] Peaks listed all contain the metal isotopic pattern. The intensities, in parentheses following the m/e values, are obtained from the component of the major isotopic species (^{58}Ni, ^{106}Pd, ^{195}Pt). Spectra were scaled such that parent ion intensity is set at 100 and peaks are included only if at least one entry in a row has an intensity >4 on this intensity scale. [b] For the assignments, fragmentation of the substituent X was allowed only for X = CF_3 so that assignment formulas ending with an F apply only to CF_3-substituted compounds. Owing to the P = CF mass ambiguity, arbitrary assignments are made in some cases.

TABLE III

METASTABLE AND MULTIPLY CHARGED IONS INDICATED IN MASS SPECTRA OF PLANAR $M[S_2PX_2]_2$ COMPLEXES[a]

X	Ni	Pd	Pt
CH_3	215.0 = 244 → 229 (214.9)	326.6 = 356 → 341 (326.6)	415.0 = 455 → 430 (415.5)
	193.3 = 308 → 244 (193.3)	262.5 = 292 → 277 (262.8)	352.0 = 381 → 366 (357.6)
		239.3 = 356 → 292 (239.5)	343.0 = 430 → 384 (342.9)
			326.5 = 445 → 381 (326.2)
			222.5 = 445^{2+}
			190.5 = 381^{2+}
C_6H_5	~436 = 556 → 492 (435.4)	483.0 = 604 → 540 (482.8)	571.0 = 693 → 629 (571.0)
	265.0 = 556 → 384 (265.2)	345 = 540 → 431 (344.0)	430.0 = 629 → 520 (429.9)
			346.5 = 693^{2+}
			314.5 = 629^{2+}
F		217.0 = 372 → 284 (216.8)	230.5 = 461^{2+}

[a] Numbers in parentheses are the *m/e* values for the metastable peaks calculated as d^2/p where the metastable peaks result from the transition p → d.

TABLE IV

MASS SPECTRAL DATA FOR $Pt_2S_6P_4(CF_3)_8$[a]

Peaks with Pt_2 isotopic pattern[b]			Peaks with Pt isotopic pattern[c]		
Assignment	*m/e*	Intensity	Assignment	*m/e*	Intensity
$Pt_2S_6P_4X_8$	1258	100	$PtS_4P_2X_4$	661	13
$Pt_2S_6P_4X_7CF_2$	1239	7	$PtS_3P_2X_4$	629	65
$Pt_2S_6P_4X_7$	1189	22	$PtS_3P_2X_3$	560	6
$Pt_2S_5P_4X_7$	1157	6	$PtS_4P_2X_2F$	542	2
$Pt_2S_6P_3X_6$	1089	8	$PtS_2P_2X_2F_3$	516	6
$Pt_2S_5P_3X_6$	1057	10	$PtS_3P_2X_2F$	510	9
$Pt_2S_5P_3X_5F$	1007	5	$PtS_2P_2X_2F$	478	16
$Pt_2S_5P_3X_4$	919	6	PtS_3PX_2	460	3
$Pt_2S_5P_2X_4$	888	7	$PtSP_2X_2F$	446	3
$Pt_2S_4P_3X_4$	887	7	PtS_2PX_2	428	5
$Pt_2S_4P_3X_2$	749	5	$PtSPX_2$	396	3
$Pt_2S_2P_2X_3$	723	7	PtS_2PXF	378	1
$Pt_2S_4P_2X_2$	718	6	PtS_3P_2F	372	3
$Pt_2S_2P_2X_2F$	673	5	$PtSP_2X$	358	1
$Pt_2S_2P_2X$	585	8	PtS_3P_2	353	2
$Pt_2S_4P_2$	580	6	$PtSPXF$	346	3
$Pt_2S_3P_2F$	567	5	PtS_2P_2F	340	10
Pt_2SP_2X	553	7	PtS_4	323	3
$Pt_2S_3P_2$	548	10	$PtPXF$	314	2
$Pt_2S_2P_2F$	535	7	$PtSP_2F$	308	7
$Pt_2S_2P_2$	516	6	PtS_2P	290	3
Pt_2S_2P	485	5	$PtSPF$	277	1

Metastable peaks[d]

498.5 = 629 → 560 (calcd 498.6)
408 = 560 → 478 (calcd 408.0)
383 = 478 → 428 (calcd 383.2)
314.5 = 1258 → 629 (calcd 314.5)

[a] Spectrum obtained with source temperature at 85°. Spectrum is scaled such that parent ion intensity = 100. X = CF_3. [b] Only peaks with Pt_2 isotopic patterns of intensity >4% of the parent ion peak intensity are included. [c] All discernible peaks with simple Pt isotopic pattern are included. [d] Calculated metastable peaks determined as in footnote of Table III.

support of the formulation of this compound as a sulfur-deficient dimer.

Infrared Spectra.—The infrared spectra of the planar complexes (presented in Table V) are very similar due to the predominance of intraligand vibrations in the range 4000–250 cm^{-1}. The general similarity of the infrared spectra for a given X within a column of the periodic table provides general support for the isostructural formulation of the compounds. In further support, the X-ray powder patterns of the Pd and Pt (X = CH_3) complexes are nearly superimposable and very similar to that of the nickel compound[10a] of known structure. Small differences with respect to shapes and splitting of known patterns of ir bands allow distinction between the spectra of these planar complexes and those of the pseudotetrahedrally coordinated metal ion complexes.[9] It is also notable that no P–O stretching frequencies were observed (except with X = OC_2H_5, of course), indicating little substitution of O for S such as that found in $Co[S_2P(CH_3)_2]_2$.[9] A sample of $Ni[S_2P(CH_3)_2]_2$, which had been kept in air for about 1 year, did however yield a very small amount of $(CH_3)_2P(S)OP(S)(CH_3)_2$ upon sublimation under vacuum, suggesting that oxygen substitution in the ligands can occur upon exposure to air, but the reaction rates must be extremely slow.

Electronic Spectra.—The reflectance spectra of the solids are similar to the spectra of dichloromethane solutions (except for the hypsochromic shifts noted previously[11]), which is strong evidence for the retention of the planar geometry in solution. The crystal packing, where known,[10,11] and the solution molecular weight determinations reinforce the contention that the absorbing species in solution are indeed monomers in contrast with the cobalt compounds, where the degree of polymerization in solution is in some cases an unresolved problem.[9] Solutions of the complexes were observed to obey the Beer–Lambert law within experimental error over the concentration range 10^{-2}–10^{-4} *M*. The spectra are collected in Table VI and, as representative illustrations, the spectra of the Ni, Pd, and Pt fluoro complexes are shown in Figure 2. All of the nickel and platinum complexes (with the exception of the platinum sulfur-deficient dimer $Pt_2S_6P_4(CF_3)_8$ illustrated in Figure 3) and the Pd (X = CH_3, C_6H_5, and CF_3) complexes show almost perfectly symmetric Gaussian band shapes for the first (lowest energy) visible band in keeping with single-crystal spectral results[13] on $Ni(S_2PX_2)_2$ (X = OC_2H_5 and C_6H_5), which also did not show any components under the envelope of this band. Thus the entire Ni system is represented by the spectrum illustrated for $Ni(S_2PF_2)_2$ in Figure 2, and the illustrated $Pt(S_2PF_2)_2$ spectrum in Figure 2 represents the following systems: M = Pt; X = F, CH_3, C_6H_5, OC_2H_5; and M = Pd; X = CF_3, CH_3, C_3H_5. The low-energy asymmetry shown in the spectrum of $Pd(S_2PF_2)_2$ also occurs in the spectrum of $Pd[S_2P(OC_2H_5)_2]_2$ and is found unchanged in all samples of these compounds obtained from different preparations, indicating that the band shape is real, although the previously published spectrum of $Pd[S_2P(OC_2H_5)_2]_2$ did not reveal this feature.[12] The observed similarity of spectral behavior of the F and OC_2H_5 complexes is consistent with the observed similarity of behavior exhibited by this pair of ligands in all complexes so far investigated.[6-9] It is somewhat disconcerting that similar splittings were not observed with X = CH_3, C_6H_5,

TABLE V: INFRARED SPECTRA OF PLANAR $M[S_2PX_2]_2$ COMPLEXES[a]

X															
CH_3			C_6H_5			OC_2H_5			F			CF_3			Assignment
Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt[b]	
1412 m	1412 m	1411 w	1433 s	1432 s	1431 s										
1394 m	1394 m	1395 w													δ_{CH_3}
1381 m	1382 m														
			1304 w	1303 w	1302 w	1277 w	1277 w	1278 w							
1291 w	1291 w	1291 w													
1279 m	1279 m	1279 m													
												1303 w	1302 w	1302 w	
														1294 wsh	
												1202 s	1204 s	1222 s	
														1210 ssh	
												1182 s	1184 s	1187 s	ν_{C-F}
												1172 s	1174 w	1171 s	
													1145 m	1140 s	
			1178 w	1178 w	1178 w										
			1157 w	1156 w	1156 w	1158 m	1157 m	1156 m							
			1103 s	1102 s	1101 s	1101 m	1101 w	1101 w							
			1095 m	1095 s	1095 s										
			1063 w	1063 w	1061 w							1078 m			
			1022 w	1022 s	1022 s										
						1044 ssh	1049 ssh	1047 s							
						1000 s	1010 s	1008 s							ν_{P-O}
			994 m	994 m	993 m	963 s	967 s	966 s							
940 s	940 s	941 s													
934 s	935 ssh	936 s													
900 m	898 m	897 m													
890 m	888 m	887 m													
									895 s	895 s	897 s				ν_{P-F}
									855 wsh	864 wsh	886 ssh				
848 m	847 m	846 m										884 m	885 m	892 m	
844 m						817 ssh	814 s	813 s							
837 w						805 s	800 ssh	799 ssh				756 m	756 w	756 w	
736 w	735 w	732 s	746 s	746 w	741 s	782 msh	777 msh	778 msh	722 w	722 w	720 m	722 w	721 m	722 w	ν_{P-S}
			716 msh	716 msh	714 msh	723 wsh	721 msh	722 msh							
			710 s	708 s	704 s										
												697 wsh	684 wsh		
			687 msh	687 s	683 s				688 s	688 s	688 s	685 s	671 m	676 m	
			685 s			640 s			670 wsh	670 wsh	670 wsh	632 ssh	628 msh	622 ssh	
			625 m	621 m	616 m		625 s	623 s				626 s	620 s	614 s	
			609 m	603 m	598 m							608 msh	602 wsh	608 msh	
586 s	576 s	568 s	576 s	573 s	565 s	546 m	534 m	530 m	561 m	561 m	557 m	537 msh	538 m	538 m	ν_{P-S}
513 s	506 s	502 s										534 m	534 msh	490 m	
			488 m	487 m	483 m							474 s	473 m	473 m	
			465 w	465 w	463 wsh										
			454 w	453 w	455 w				432 wsh	432 wsh	421 wsh	422 w	418 w		
					450 wsh	394 w	396 w	400 w	404 s	403 s	402 s	378 ssh		380 m	
			360 wsh	356 m	362 m						368 w	373 s	372 s		
347 s			339 m	320 ssh		354 s	354 w	350 w	349 m	350 m	345 m	337 s	327 m	326 w	
	309 s	308 m		308 s		332 wsh	311 s		312 s	311 s	304 wsh	332 ssh	303 s	306 w	ν_{M-S}
283 m	283 m	300 s		305 msh	299 m	326 w	305 msh	302 s	299 msh	299 m	300 m	284 wsh		282 wsh	
271 m	268 m	267 m						290 wsh				278 w	279 w	271 w	

[a] Spectra in the range 1450–250 cm^{-1} obtained from Nujol mulls. Band maxima positions in cm^{-1}. Abbreviations: ν = stretching mode, δ = deformation mode; s = strong, m = medium, w = weak, sh = shoulder. [b] $Pt_2S_6P_4(CF_3)_8$.

TABLE VI

ELECTRONIC SPECTRA OF PLANAR $M[S_2PX_2]_2$ COMPLEXES[a,b]

	X				
	CH_3 $10^{-3}\nu$ (10^4f)	C_6H_5 $10^{-3}\nu$ (10^4f)	OC_2H_5 $10^{-3}\nu$ (10^4f)	F $10^{-3}\nu$ (10^4f)	CF_3 $10^{-3}\nu$ (10^4f)
Ni	13.77 (8.22)	13.58 (11.1)	14.54 (8.42)	14.08 (7.72)	12.65 (5.65)
	17.90 (12.6)	17.75 (15.8)	19.10 (13.5)	18.91 (9.12)	17.33 (3.25)
					21.2 (13) sh
	~25.6 (130) sh	24.9 (190) sh	25.9 (132) sh	25.49 (59.8) sh	24.3 (25) sh
	30.18 (3280)	29.75 (4270)	31.27 (4580)	32.00 (2360)	30.55 (2130)
	~34.1 (210) ?	~32.8 (390) ?	35.6 (1010) sh	36.4 (610) sh	~34.8 (120) ?
	39.5 (200) i	37.1 (1410)	40 (?)	40.0 (470) sh	39.3 (100) sh
	43.2 (~4000)	43.6 (?)	43.2 (4000)	?	43.6 (~500)
Pd			21.28 (33.1)	19.7 (5.4) sh	
	20.48 (43.5)	20.02 (62.3)	23.2 (3.3) sh	22.31 (33.7)	20.20 (37.5)
	28.1 (380) sh	27.4 (580) sh	29.3 (450) sh	29.0 (250) sh	27.4 (270) sh
	32.82 (4610)	32.00 (5690)	33.90 (4160)	34.49 (4020)	32.87 (4570)
	~36.4 (550) ?	36.2 (2600) sh	38.7 (1100) sh	39.2 (1130) sh	37.3 (580) sh
	?	43.6 (510) sh	~44.4 (604) ?	45.8 (1700)	44.8 (880)
Pt	~19.8 (1.7) ?	~19.6 (2.3) ?	~20.6 (0.71)	~20.3 (1)	25.0 (150) sh
	22.93 (21.2)	22.43 (34.3)	23.86 (16.0)	23.16 (13.3)	29.2 (480) sh
	~31.4 (54) ?	~28.7 (140) ?	~31.0 (280) ?	29.7 (80) sh	31.6 (150) sh
	33.9 (220) sh	33.0 (550) sh	35.4 (490) sh	35.10 (254)	34.8 (?) sh
	37.8 (1500) sh	36.8 (2800) sh	39.3 (835) sh	40.6 (2700)	39.1 (?)
	42.11 (5000)	43.34 (5000)	42.5 (5000)	46.0 (?)	41.2 (?)

[a] In CH_2Cl_2 solution. [b] Positions of band maxima, in units of 1000 cm^{-1}, are followed by the oscillator strengths (f) × 10^4 in parentheses, where $f = 4.60 \times 10^{-9}\epsilon_{max}\Delta\nu_{1/2}$. Abbreviations are: sh = band is observed as shoulder; i = band detected as minor inflection only; ? = no shoulder nor inflection observed, but further band required to account for total intensity, assuming Gaussian form for both sides of peaks.

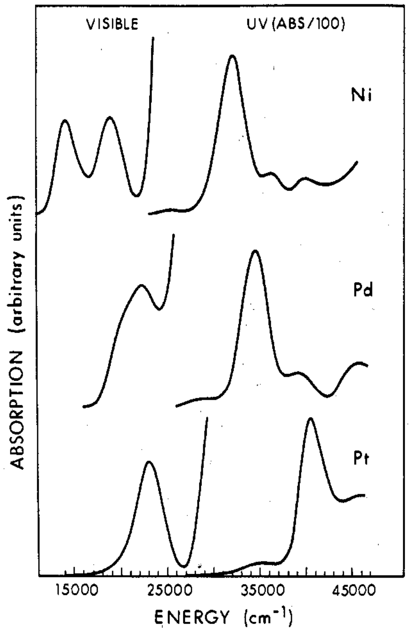

Figure 2.—Visible and ultraviolet spectra of $M[S_2PF_2]_2$ complexes of Ni, Pd, and Pt in CH_2Cl_2 solution. The spectra were determined on approximately 5×10^{-3} M solutions. The absorption scales are similar to each other but are not identical. In all cases the uv absorption scale is $^1/_{100}$th that of the visible scale.

or CF_3 complexes of Pd. None of the four Pt compounds nor the remaining three Pd complexes with spectra similar to the $Pt(S_2PF_2)_2$ spectrum in Figure 2 provide any concrete evidence (*i.e.*, inflections in the envelope) to support the extraction of a band from the low-energy side of the lowest visible band as suggested by the inflections on the low-energy band of the Pd (X = F, OC_2H_5) complexes; however the tailing properties of this band in the platinum compounds would allow for such a component. Recent MCD studies[14] of $Ni[S_2P(OC_2H_5)_2]_2$ and $Ni[S_2CN(C_2H_5)_2]_2$ complexes suggested that the first excited state of both of the

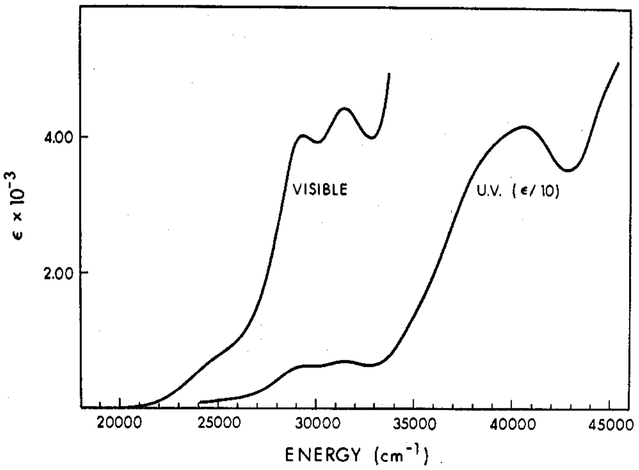

Figure 3.—Electronic absorption spectrum of $Pt_2S_6P_4(CF_3)_8$ in CH_2Cl_2 solution. The ultraviolet absorption scale is one-tenth that of the visible.

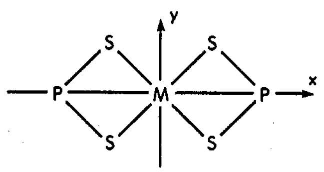

Figure 4.—Coordinate system used for the square-planar complexes.

compounds is degenerate; thus the order of levels suggested[14] is $d_{z^2} < d_{x^2-y^2} < d_{xz}, d_{yz} < d_{xy}$ after conversion to the coordinate system illustrated in Figure 4. The ligand field analysis[23] using the same coordinate system suggests the order $d_{z^2} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{xy}$; that is, $d_{x^2-y^2}$ and the d_{xz}, d_{yz} pair should be interchanged. It should also be noted that the highest actual symmetry possible in this system of planar dithiophosphinates is D_{2h} in which the d_{xz} and d_{yz} orbitals trans-

[23] H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965).

form as the B_{2g} and B_{3g} irreducible representations, respectively, thus formally removing their D_{4h} degeneracy. If, however, the "effective" coordination ends at the sulfur atoms, as has been suggested,[24] the symmetry of the "effective" ligand field experienced by the central metal atom would be nearly D_{4h}. Studies of single crystal polarized spectra of $Ni[S_2P(C_6H_5)_2]_2$ and $Ni[S_2P(OC_2H_5)_2]_2$ unfortunately have not provided conclusive assignments for the electronic spectra and present interpretations are at variance with the MCD results.[14] Studies of single crystal polarized spectra at variable temperature and additional MCD studies on this system (and in particular on the $Pd(S_2PX_2)_2$ complexes) may ultimately resolve this problem.

Even without firm spectral assignments, it is still possible to arrange the ligands in a spectrochemical order of the substituent X based on the position of the first visible band. The order obtained, $OC_2H_5 > F > CH_3 > C_6H_5 \sim CF_3$, is in agreement with that found elsewhere[6-9] for the same series of ligands in different geometrical situations. Again, the π-bonding capability of the lone pairs of the substituent appears to dominate the possible inductive effects; for example, CF_3 substituents produce a weaker ligand field effect than F.[6-9]

Polarographic Results.—Previous polarographic investigations of $Ni[S_2P(OC_2H_5)_2]_2$ in ethanol showed a single irreversible reduction wave with a half-wave potential of -0.552 V *vs.* sce using 0.2 *M* $NaClO_4$ as a supporting electrolyte.[25] Investigations of the redox behavior of $Ni[S_2P(CH_3)_2]_2$ at a rotating platinum electrode in acetonitrile solution reveal a single oxidation wave at $+1.8$ V and two reduction waves at -0.5 and -0.8 V *vs.* the Ag|$AgNO_3$, 0.1 *M* couple also in acetonitrile. It has been reported that acetonitrile has very little effect on the visible spectrum of $Ni[S_2P(OC_2H_5)_2]_2$[26] and hence is assumed to be only weakly coordinating, perturbing the energy levels of the complex only slightly. Ethanol is known to have a profound effect on the visible spectrum of $Co[S_2PX_2]_2$ complexes[9,27] but appears to have little effect on the spectrum of $Ni[S_2P(OC_2H_5)_2]_2$, whereas water seems to affect only the intensity of the bands,[12] indicating an "all-or-nothing" ligand substitution. Isolation and characterization of a reduced or oxidized form of the complexes should provide valuable information on the ground state and perhaps aid in the resolution of the excited-state geometry problem.[28] Work is proceeding along these lines.

Vibrational and Electronic Spectral Correlations.—An interesting correlation between Ni–S distances in planar complexes and the ligand field strengths (taken from the energy of the first electronic transition) has been recently reported.[11] It seemed reasonable to assume that variable M–S distances should be reflected in the M–S stretching frequencies of planar $M[S_2PX_2]_2$ complexes, with due concern for the changing mass effect with X. Recently similar studies have been reported for planar N-coordinated copper compounds in which nearly straight-line correlations were found between the square of the metal–ligand stretching frequency (ν^2_{M-N}) and the first d–d band ($\nu_{1\,el}$) in the electronic spectrum.[29] We have investigated the possibility of such a correlation in the present system. The molecular environment was standardized by comparing vibrational and electronic spectra obtained in dichloromethane solution which presents a window in the infrared spectrum between 300 and 450 cm^{-1} in which M–S vibrations[30] are observed. The available bond length and frequency data are presented in Table VII. The mass effect of the substituent cannot be estimated in a simple way so that a simple plot of ν^2_{M-S} *vs.* $\nu_{1\,el}$ (Figure 5) might not be expected to yield a straight line. This unsophisticated approach yields a surprisingly good linear correlation for the $Ni[S_2PX_2]_2$ compounds, indicating that the substituent mass effect is not predominant. The small spread in the vibrational frequencies observed for ν_{M-S} in the Pd and Pt cases makes such an analysis less meaningful when the uncertainty associated with these frequencies is at least ± 1 cm^{-1}. However, the infrared spectrochemical order observed for the nickel compounds predicts that the Ni–S bond lengths should occur in the order (by X) $OC_2H_5 < F < CH_3 < C_6H_5 < CF_3$, where the average Ni–S bond length order observed[10,11] is found to be $OC_2H_5 < CH_3 < C_6H_5$. It is recognized that the spread between the bond lengths is nearly within their standard deviations; nevertheless, the order is considered significant.

TABLE VII
LIGAND FIELD METAL–SULFUR VIBRATIONAL FREQUENCY CORRELATION[a]

M	X	ν_{M-S} (cm^{-1})[b]	ν (10^3 cm^{-1})	Average M–S bond length (Å)[c]
Ni	CH_3	346 (347)	13.77	2.238
	C_6H_5	339 (339)	13.58	2.236 (7)
	OC_2H_5	353 (354)	14.53	2.233 (4)
	F	348 (349)	14.08	
	CF_3	334 (337)	12.75	
Pd	CH_3	307 (309)	20.48	
	C_6H_5	306 (308)	20.02	
	OC_2H_5	309 (311)	21.28 23.2	
	F	309 (311)	19.7 22.31	
	CF_3	300 (303)	20.20	
Pt	CH_3	299 (300)	22.93	
	C_6H_5	295 (299)	22.43	
	OC_2H_5	304 (302)	23.86	
	F	298 (300)	23.16	
	CF_3	...	...	

[a] Spectra obtained from CH_2Cl_2 solutions. [b] Bands observed in "window" of CH_2Cl_2 spectrum, 300–450 cm^{-1}; values in parentheses are band positions observed in Nujol mulls. [c] Bond lengths taken from ref 10a, 11, and 10c, respectively.

The "Sulfur-Deficient Dimer" of Platinum, $Pt_2S_6P_4(CF_3)_8$.—The reaction of $PtCl_2$ or K_2PtCl_4 with $(CF_3)_2PS_2H$ did not yield the monomeric complex $Pt[S_2P(CF_3)_2]_2$, but rather a dinuclear species of empirical formula $Pt_2S_6P_4(CF_3)_8$. Dimers of the expected type are well known for pseudotetrahedrally coordinated metal complexes of dithiophosphinates,[1,4,9] but this "dimer," deficient by two sulfur atoms per molecule, is a most unexpected variation. From a knowledge of the products of the reaction between

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[24] C. K. Jørgensen, *Mol. Phys.*, **5**, 485 (1962).

[25] P. S. Shetty and Q. Fernando, *J. Inorg. Nucl. Chem.*, **28**, 2873 (1966).

[26] C. K. Jørgensen, *Acta Chem. Scand.*, **17**, 533 (1963).

[27] C. K. Jørgensen, *ibid.*, **16**, 2017 (1962).

[28] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. Hare, *Inorg. Chem.*, **4**, 514 (1965).

[29] A. P. B. Lever and E. Mantovani, *ibid.*, **10**, 817 (1971).

[30] D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1299 (1968).

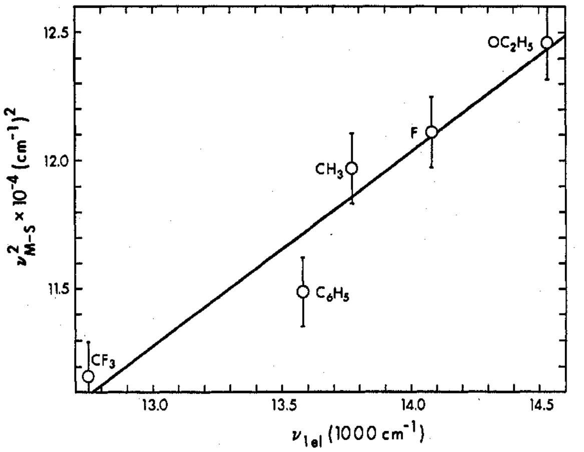

Figure 5.—A plot of the square of the metal–sulfur infrared stretching frequency ($\nu_{\text{M-S}}$) *vs.* the energy of the first electronic absorption band ($\nu_{1\ \text{el}}$) for the square-planar Ni[S_2PX_2]$_2$ complexes. The vertical error lines represent an uncertainty of ±2 cm^{-1} in $\nu_{\text{M-S}}$.

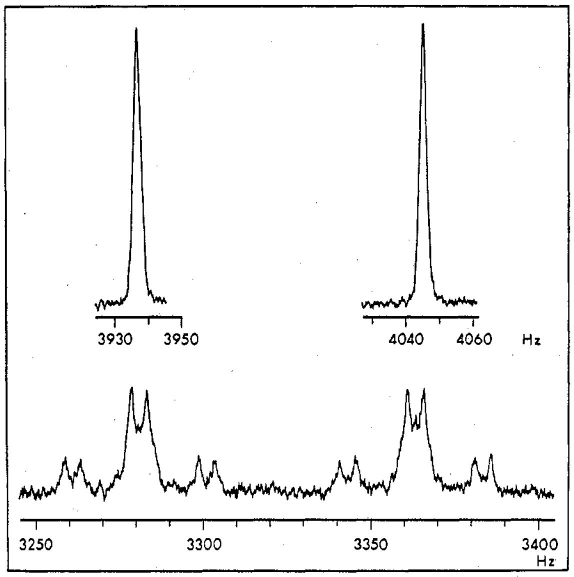

Figure 6—The ^{19}F nmr spectrum of $Pt_2S_6P_4(CF_3)_8$ obtained at 56.4 MHz on a saturated solution of the compound in CH_2Cl_2 containing ~5% $CFCl_3$. The line positions are given in cycles to high field of the $CFCl_3$ reference.

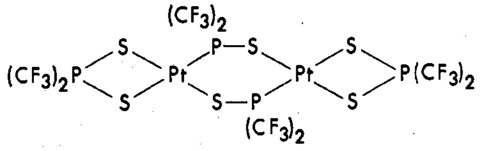

Figure 7.—The proposed structure of $Pt_2S_6P_4(CF_3)_8$.

$PtCl_2$ and $(CF_3)_2P(S)SH$, eq 1 may be written. How-

$$2PtCl_2 + 6(CF_3)_2P(S)SH \longrightarrow Pt_2S_6P_4(CF_3)_8 + 2(CF_3)_2P(S)Cl + 2H_2S + 2HCl + 2S \quad (1)$$

ever, the reaction is slow and quantitative results have not been obtained. The compound has been characterized by chemical and mass spectral analysis, with the parent ion molecule and S_8^+ ions showing strongly in mass spectra of the sublimable solid reaction products. Solution molecular weight studies were hampered by the large molecular weight and limited solubility in suitable solvents but indicated that the dinuclear species does not dissociate in halocarbon solvents. The mass spectrum has a prominent ion which has been identified as $PtS_3P_2(CF_3)_4^+$ by mass measurement in addition to the parent ion indicating that the dimer structure may be symmetrical such that it can readily split in half. The infrared spectrum differs markedly from that of the other complexes of $(CF_3)_2PS_2^-$ discussed here and the electronic spectrum as shown in Figure 3 is also markedly dissimilar to those of the "normal" platinum complexes illustrated in Figure 2. The ^{19}F nmr spectrum (Figure 6) may be explained on the basis of a bridged dimer structure (Figure 7). The simple doublet (ϕ = 71 ppm *vs.* CCl_3F, $^2J_{PF}$ = 109 Hz) has similar parameters to those assigned to normal bidentate $(CF_3)_2PS_2^-$ ligand units on Pd and Ni (*vide supra*), Zn, Cd, and Hg.[9] The other group which can be approximately described as a doublet of doublets of "triplets" (Figure 6) at ϕ = 59 ppm (*vs.* CCl_3F) possesses equal total intensity to the first and is assigned to the bridging $(CF_3)_2P$ structural unit in the complex. The major doublet separation of 79 Hz is assigned to phosphorus–CF_3 coupling, $^2J_{PF}$, the lower value being typical of a "trivalent" $(CF_3)_2P$ unit[31] or a $(CF_3)_2P$ unit coordinated to metals[32] rather than a normal $(CF_3)_2PS_2^-$ ligand which has $^2J_{PF}$ values of approximately 110 Hz.[9,21a,c] This difference is certainly reasonable for the different electronic environment of the phosphorus atoms which we suggest are part of the bridges. The "triplet" actually possesses an intensity distribution more in keeping with a doublet splitting created by 30% natural abundance of the ^{195}Pt (I = $^1/_2$) isotope. Since the four-bond Pt–F coupling ($^4J_{PtF}$) is not observed in the normal bidentate ligand part of the spectrum (*vide supra*) whereas $^3J_{PtF}$ = 41.5 Hz in Pt[S_2PF_2]$_2$, we suggest that the appearance of the 40-Hz doublet is due to the enhanced spin coupling interaction between Pt and F provided by the *three* bond separation between these nuclei in the Pt–P$(CF_3)_2$-(S–) bridge (Figure 7); hence the 40-Hz doublet is assigned to $^3J_{PtF}$. The further spacing of 5 Hz can be assigned to coupling of the distant phosphorus across the bridge ($^5J_{PF}$), but on close examination each component of the ϕ = 59 ppm region appears to consist of two outer strong lines with another line in between (all of which are fairly broad) which is reminiscent of $X_6AA'X'_6$ ("deceptively simple") spectra observed elsewhere.[33] There do not appear to be any coupling interactions between "bridging" and "nonbridging" ligand groups. Unfortunately, the compound was not sufficiently soluble in toluene or CH_2Cl_2 to enable the ^{31}P nmr spectrum to be obtained, for this would have provided additional support for direct Pt–P bonds. An X-ray single-crystal study is presently under way.[34] Preliminary results show that the molecule contains two platinum atoms and the unit cell contains eight molecules; however, unusual difficulties in obtaining good crystals have delayed solution of the structure.[34]

Several attempts to prepare the missing member of the present series of compounds, namely Pt[$S_2P(CF_3)_2$]$_2$, have been made. A reaction of K_2PtCl_4 with molten

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[31] K. J. Packer, *J. Chem. Soc.*, 960 (1963).

[32] R. C. Dobbie, *J. Chem. Soc. A*, 230 (1971).

[33] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); R. G. Cavell and A. A. Pinkerton, unpublished observations.

[34] R. M. Tuggle and M. J. Bennett, personal communication.

$[(CH_3)_3NH][S_2P(CF_3)_2]$ (70°) produced a red solution from which traces of elemental sulfur sublimed (100° (10^{-4} Torr)), but no sublimable platinum complex was isolated. The mass spectrum (source temperature at 100°) of the red material showed an intense peak due to $PtS_4P_2(CF_3)_4$ and a barely detectable peak corresponding to $Pt_2S_6P_4(CF_3)_8$. The presence of peaks for the sulfur-deficient dimer is consistent with the formation of elemental sulfur. While K_2PtCl_4 is not soluble in dichloromethane, the product of the salt reaction is extractable into dichloromethane producing deep red solutions. The low volatility of this red material suggests the presence of a salt possibly analogous to $[(n\text{-}C_3H_7)_4N][Pd(S_2PF_2)_3]$.[22] Preliminary attempts to reduce Pt(IV) compounds with $(CF_3)_2P(S)SH$ have been unsuccessful. There seems to be no convincing reason why $Pt[S_2P(CF_3)_2]_2$ should not exist, and attempts to obtain it are continuing.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT BUFFALO,
BUFFALO, NEW YORK 14214

Infrared Intensities of the Carbonyl Stretching Vibrations in Cyclopentadienyliron Dicarbonyl Derivatives

BY DONALD J. DARENSBOURG

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The integrated infrared intensities of the ν_{CO} stretching vibrations have been determined for a series of iron complexes of the types $(C_5H_5)Fe(CO)_2X$ (where X = Cl, I, CN, $SnCl_3$, or $C(O)CH_3$) and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ in chloroform solution. Dipole moment derivatives for the carbonyl stretching modes have been calculated assuming that the A′ and A″ vibrational modes each exhibit a characteristic MCO group moment derivative. Variations in these derivatives as a function of the angle (θ) between MCO groupings in the series of complexes have also been considered in detail. In all cases the dipole moment derivatives for the symmetric stretching motion were found to be substantially smaller than that of the corresponding derivatives for the asymmetric stretching motion. It is concluded on the basis of these results that the cyclopentadienyl ligand is primarily acting as a donor grouping in the complexes studied.

Introduction

The bonding in cyclopentadienyl(transition metal) carbonyls is a subject of active discussion by both theoretical and experimental chemists, and there are still several unanswered questions. The relative importance of the donor and acceptor bonding properties of the cyclopentadienyl ion is one of these unresolved issues. Semiempirical calculations on ferrocene have led to conflicting reports on the charge distribution in this molecule.[1-3] Recently, photoelectron spectroscopy measurements on several π-cyclopentadienylmetal complexes have indicated the ring carbons of the cyclopentadienyl residues to be slightly positively charged.[4] In order to aid in these discussions, as well as for their intrinsic value, the absolute infrared intensities of the carbonyl stretching vibrations in substituted cyclopentadienyliron carbonyl compounds have been measured in chloroform solution. Integrated intensity measurements of the infrared CO stretching vibrations in transition metal carbonyl compounds have given additional information on the electronic character of the CO groupings.[5-17] Specifically, the integrated infrared intensities of the CO stretching vibrations have been shown to be highly dependent on the extent of π bonding between the metal and CO.[11,14]

The compounds examined in this study were $(C_5H_5)Fe(CO)_2X$ (where X = Cl, I, CN, $SnCl_3$, or $C(O)CH_3$) and $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$. The experimental data were examined to find correlations between changes in the infrared intensities of the two CO stretching modes in these compounds and the nature of the affixed ligands $C_5H_5^-$ and X.

Experimental Section

Preparation of Compounds.—Cyclopentadienyliron dicarbonyl dimer (mp 194° dec) was obtained from Strem Chemicals, Inc. All reactions were performed under a dry nitrogen atmosphere. $(C_5H_5)Fe(CO)_2Cl$,[18] $(C_5H_5)Fe(CO)_2I$,[19] $(C_5H_5)Fe$-

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