as well as the failure to observe electrochemical oxidation, consistently suggest that inner-sphere coordination is necessary for reduction. Therefore, in accepting Kreevoy's proposed mechanism for the proton, we conclude that the mechanisms for reduction are different for proton and metal ions. Further work in this area is underway in an attempt to elucidate the exact nature of the metal ion reactions and their mechanisms.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to thank Mr. Robert Carter of Kansas University for his assistance with the Raman studies and Mr. Robert Wade of Ventron Corp. for generously donating samples of $NaBH_3CN$ and $NaBD_3CN$.

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Metal Complexes of the Difluorodithiophosphate Ligand

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Difluorodithiophosphato, $F_2PS_2^-$, derivatives of monovalent Cu, Ag, and Au, divalent Mn, Fe, Co, Ni, Pd, Pt, Zn, Cd, and Hg, and trivalent Cr, Co, and Rh have been isolated and characterized. Many of these transition metal complexes are extremely volatile as exemplified by the Co(II) derivative which has a vapor pressure of 20 mm at 95°. In contrast, the silver and copper(I) derivatives are nonvolatile and may have polymeric structures. All the difluorodithiophosphato complexes are susceptible to hydrolysis, but the rates vary widely from low in chromium(III) and nickel(II) to high in many of the bis derivatives. Chemically, the bis derivatives are the most reactive set and complex with donor molecules such as water, acetonitrile, phosphines, and anions. In this manner $R_3PPd(S_2PF_2)_2$, $R_3AsPd(S_2PF_2)_2$, $(R_3P)_2Pd(S_2PF_2)_2$, and $Pd(S_2PF_2)_3^-$ have been isolated. These palladium complexes are believed to have square-planar form. Nitric oxide reacts with the bis derivatives of iron and cobalt to give the unusual nitrosyls $(ON)_2MS_2PF_2$.

Introduction

Through reactions of tetraphosphorus decasulfide a series of novel anions of the type $X_2PS_2^-$ was prepared.[1,2] Of primary interest to us has been the transition metal derivative chemistry of these anions, and there is a preliminary account of the $F_2PS_2^-$ system.[3] Later, several difluorodithiophosphatometal carbonyls, *e.g.*, $[Rh(CO)_2(S_2PF_2)]_2$, were reported.[4] Herein are reported the details of our transition metal studies with the difluorodithiophosphate anion.

Results and Discussion

Synthesis.—Complexes of the more electropositive metals were prepared by simply stirring the anhydrous acid HS_2PF_2 with finely divided metal. In this manner, the tris derivative of chromium, the mono derivative of copper, and the bis derivatives of manganese, iron, cobalt, nickel, zinc, and cadmium were obtained. Chloride displacement from the chlorides of palladium(II), platinum(II), rhodium(III), and triphenylphosphinegold(I) with HS_2PF_2 yielded the respective crystalline complexes with the metals in unaltered valence states. The silver derivative was prepared by neutralization of silver oxide with the acid. The cobalt(III) and iron(III) complexes were obtained by the oxidation of the divalent derivatives with air or $(F_2PS_2)_2$.[2] The latter reagent was employed to oxidize mercury to $Hg(S_2PF_2)_2$.

Spectral Data.—Spectral data are presented here in general outline to facilitate later discussions of structure for the difluorodithiophosphato complexes. Fluorine nmr spectra were obtained for diamagnetic and the paramagnetic $Cr(S_2PF_2)_3$ and $Co(S_2PF_2)_2$ complexes. Spectra of the paramagnetic species consisted of broad structureless resonances. Diamagnetic species generally produced simple sharp doublets arising from P–F coupling on the order of 1200–1300 Hz. Fine structure in the spectrum of $Co(S_2PF_2)_3$ (Figure 1) apparently reflects $^{59}Co-^{19}F$ coupling. Platinum–fluorine coupling is apparent in the spectrum of $Pt(S_2PF_2)_2$. This and the spectrum of $Pd(S_2PF_2)_2$ contain additional structure arising from long-range phosphorus or fluorine coupling. The magnitudes of P–F coupling constants for derivatives of $F_2PS_2^-$ were sensitive to the environment of the group, and most of the values were clustered around one of three numbers. The lowest value encountered was 1158 Hz for the anion as a tetraalkylammonium salt. Coordination of the group through one or both of the sulfur atoms resulted in an increase of the coupling constant. Several compounds of reasonably certain structure such as $C_2H_5SP(S)F_2$ and HS_2PF_2[1,2] have coupling constants in the neighborhood of 1200 Hz. In addition several species of unknown structure such as complexes of the copper and zinc triads have coupling

(1) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **89**, 1272 (1967).
(2) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *Inorg. Chem.*, in press.
(3) F. N. Tebbe, H. W. Roesky, W. C. Rode, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 3578 (1968).
(4) F. A. Hartman and M. Lustig, *Inorg. Chem.* **7**, 2669 (1968).

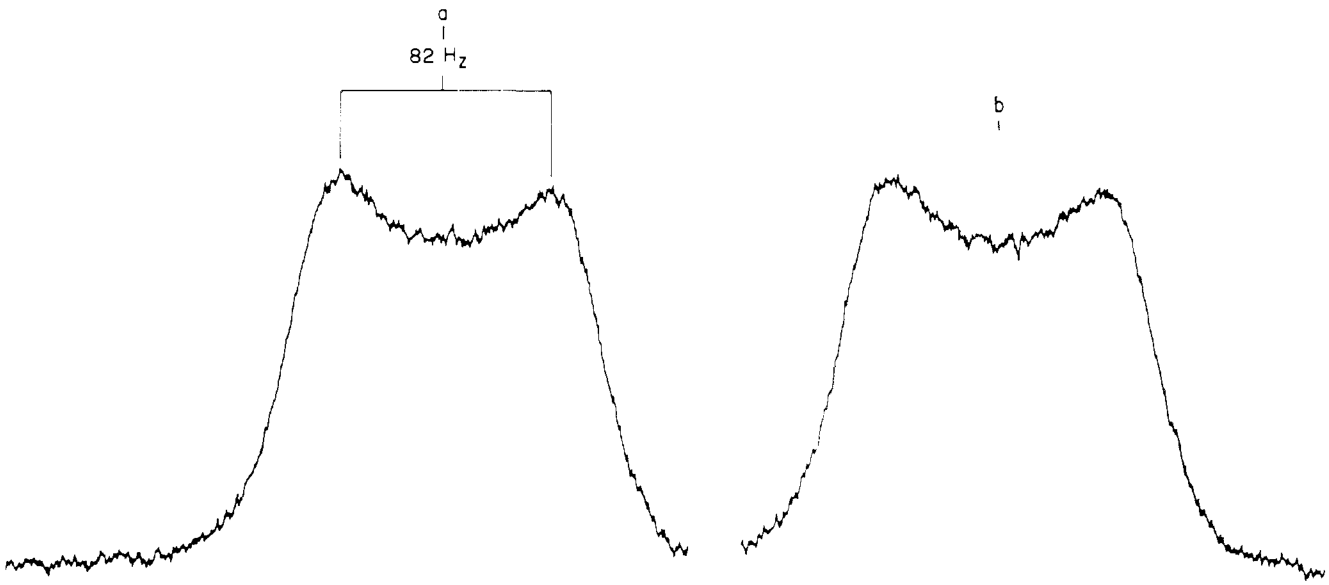


Figure 1.—Fluorine-19 nmr spectrum of $Co(S_2PF_2)_3$: ab separation, J_{PF} = 1315 Hz.

constants close to this value. Constants for the diamagnetic metal complexes which with high probability contain bidentate difluorodithiophosphate groups were significantly larger.[5,6] Values for $Co(S_2PF_2)_3$, $Ni(S_2PF_2)_2$, $Pd(S_2PF_2)_2$, and $Pt(S_2PF_2)_2$ ranged from 1315 to 1343 Hz. Chemical shifts compared with $CFCl_3$ ranged from 4 to 12 ppm for $Co(S_2PF_2)_3$ and $Cd(S_2PF_2)_2$, respectively. These values may be compared with 2 and 16 ppm for, respectively, $(n\text{-}C_3H_7)_4N^+S_2PF_2^-$ and the anhydrous acid HS_2PF_2.

The positions of the infrared vibrations in the P–F stretching region varied from 900 to 770 cm^{-1} and in some cases spectra in this region provide structural information. The chelated structures of tris(difluorodithiophosphato)chromium(III), -cobalt(III), and -rhodium(III) and bis complexes of Ni(II), Pd(II), and Pt(II) showed a single or two closely spaced lines at approximately 900 cm^{-1}. For comparison, the P–F stretching frequencies for $F_2PS_2^-$ as a tetraalkylammonium salt consisted of two well-defined lines positioned at 804 and 774 cm^{-1}.

Mass spectra were fairly consistent among the compounds studied. Except for $Cr(S_2PF_2)_3$, the parent ion was most abundant. Loss of one F_2PS_2 or PF_2 group was the most facile fragmentation process for both bis- and tris-chelated complexes. Other metal-containing fragments present in high concentration were MS_2^+ and MS^+.

Properties of $M(S_2PF_2)_3$.—The tris derivatives of chromium(III), cobalt(III), and rhodium(III) are volatile, and mass spectral analyses showed them to be monomeric in the gas phase. The relatively high vapor pressures of these tris complexes point to relatively low lattice energies in the solid state; the chromium derivative has a vapor pressure of about 2 mm at 95°. All three complexes are soluble in nonpolar organic solvents such as heptane and benzene.

The cobalt and rhodium derivatives are diamagnetic. In solution, the chromium compound is monomeric and the magnetic moment is 3.8 BM, consistent with an octahedral formulation. The electronic spectrum is also consonant with an octahedral structure. Jørgensen[7] has estimated for the chromium derivative a value for the interelectronic repulsion B of 445 cm^{-1} and $\beta_{35} = 0.484$. This would indicate less nephelauxetic character than in $R_2PS_2^-$ (R = alkyl) ligands as would be expected from simple electronegativity considerations.

These complexes are among the least reactive of the group prepared in this study. However, all hydrolyze on exposure to the atmosphere. The rate of hydrolysis is lowest, as expected, for the d^3 chromium derivative and highest for the cobalt. The cobalt derivative is slowly attacked by nitric oxide with displacement of one difluorodithiophosphate ligand to give $(ON)_2CoS_2PF_2$ and $(F_2PS_2)_2$ (*vide infra*).

Crystalline $Fe(S_2PF_2)_3$ was prepared from $Fe(S_2PF_2)_2$ and $(F_2PS_2)_2$ but complete separation from the iron(II) derivative was not achieved. No chemical or physical properties were established for this tris complex.

Properties of $M(S_2PF_2)_2$.—Bis(difluorodithiophosphato)cobalt(II), -nickel(II), -palladium(II), and -platinum(II) are very soluble in solvents such as hexane and benzene in which they appeared to be monomeric.[8] All these compounds can be sublimed at room temperature. The most volatile are $Co(S_2PF_2)_2$ and $Ni(S_2PF_2)_2$ which have vapor pressures at 95° of approxi-

(5) An apparent exception to this generalization is provided by $[(C_6H_5)_3P]_2N^+Cr(CO)_4S_2PF_2^-$ [6] which was presumed[6] to have a chelated difluorodithiophosphato group. The ^{19}F nmr data were J_{PF} = 1196 Hz (δ 12.3). We prepared a different anion by the reaction: $HS_2PF_2 + (C_2H_5)_4N^+Cr(CO)_5Cl^- \rightarrow HCl + (C_2H_5)_4N^+Cr(CO)_5S_2PF_2^-$ (quantitative in HCl and no CO or $Cr(CO)_6$ was formed). This new anion has a J_{PF} of 1190 Hz (δ 11.9) and a CO ir stretching pattern virtually identical with that reported for the $Cr(CO)_4S_2PF_2^-$ ion.

(6) J. K. Ruff and M. Lustig, *Inorg. Chem.* **7**, 2171 (1968).

(7) C. K. Jørgensen, *Inorg. Chim. Acta*, **2**, 65 (1968).

(8) Difficulties[3] associated with molecular weight determinations on compounds reactive with water or oxygen necessarily make conclusions based solely on these data of a qualified nature.

mately 20 and 14 mm, respectively. The gaseous nickel complex is monomeric as determined by vapor density measurements.

The nickel, palladium, and platinum derivatives are diamagnetic in solution, consistent with a square-planar polytopal[9] formulation. This diamagnetism for the nickel complex prevails also for the solid and liquid states. Hence weak intermolecular interactions to give a quasi-octahedral form are not operative here. The cobalt species appears to be high-spin tetrahedral. Magnetic susceptibilities obtained for $Co(S_2PF_2)_2$ in solvents such as heptane and 1,2-dichloroethane by Gouy methods were 5.1 BM as compared to the reported ranges of 4.2–4.9 and 4.7–5.9 BM for tetrahedral and octahedral high-spin derivatives, respectively.[10] The moments obtained by the nmr reference shift method consistently fell in the range of 5.9–6.2 BM for the same solvents. The reason for the discrepancy between the values from Gouy and nmr techniques has not as yet been established. No esr spectra signals were detected for $Co(S_2PF_2)_2$ in dichloromethane or in $Zn(S_2PF_2)_2$ or $Ni(S_2PF_2)_2$ matrices between room and liquid helium temperatures.

In contrast to the above complexes, the volatility of manganese(II) and iron(II) derivatives is considerably reduced, and the former is not soluble in hexane. In solution, the manganese and iron compounds appeared monomeric by osmometry,[8] and the solution susceptibility moments of the manganese and iron complexes are 5.9 and 5.2 BM, respectively. The value for the iron compound is not inconsistent with a tetrahedral form.[11]

The lower volatility of the manganese and iron derivatives might be ascribed to greater ionic character in the metal–sulfur bonding, and, in fact, the manganese derivative does not show the strong charge-transfer bands which are so pronounced in the chromium, cobalt, and nickel difluorodithiophosphates. However, there is a reasonable possibility that association in the solid state occurs to reduce the vapor pressure of the manganese and iron derivatives. It is presumed that even in the solid state the ligand functions as a bidentate moiety although the possibility of bridging functionality cannot be ruled out. The manganese derivative in solution is pale yellow, not inconsistent with a tetrahedral formulation. In the solid state it has a slight pink cast strongly suggestive of an octahedral environment for the manganese. Increase in coordination number for the metal ion cannot be achieved by simply invoking bridging functionality of the ligand but might result from stacking such as shown in Figure 2. In any case, only X-ray studies will resolve this point.

The zinc(II), cadmium(II), and mercury(II) complexes are volatile but much less so than the transition group analogs. These compounds were sublimable under vacuum at temperatures of 110–150°. The mercury derivative appears to be the most volatile of the group. The zinc complex is not soluble in nondonor solvents, and it as well as its congeners is colorless. We suggest that zinc and cadmium form less covalent chelates with the difluorodithiophosphate anion and that possibly there is association in the solid state analogous to that outlined for manganese. Acetonitrile solutions of the bis derivatives of this triad displayed simple doublet (J_{PF} = ~1200 Hz) ^{19}F resonances. These doublets shifted downfield on temperature decrease (~1 ppm at −50°) but there was no detectable change in J_{PF} nor were there any satellites indicative of Cd– or Hg–F coupling. Free $F_2PS_2^-$ ion is not present in significant concentrations in these solutions; however, stronger donor molecules than acetonitrile displace the ion. After addition of dimethyl sulfoxide or water to acetonitrile solutions of $Zn(S_2PF_2)_2$ and $Cd(S_2PF_2)_2$, the ^{19}F spectrum was that of the uncoordinated ion as judged by the J_{PF} and δ values. Absence of metal–fluorine coupling in the ^{19}F spectrum of acetonitrile solutions of $Cd(S_2PF_2)_2$ and $Hg(S_2PF_2)_2$ suggests rapid ligand exchange even at −50°.

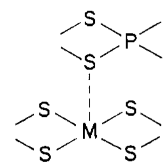


Figure 2.—Possible mode of polymerization of $M(S_2PF_2)_2$ groups through sulfur bridging.

The bis derivatives for the most part are the most reactive of the group described here. The difluorodithiophosphate ligand is readily displaced by a wide range of other donor ligands and its leaving-group character determines much of the chemistry of these complexes. Ligand loss through hydrolysis, as well as oxidation for manganese(II), iron(II), and cobalt(II), occurs on exposure to the atmosphere. Water added to the green tetrahedral cobalt chelates to give a blue sublimable solid which dissociated in attempted isolation; the nickel chelate behaved similarly. Alkyl- and arylphosphines readily reacted with the bis chelates of manganese, iron, cobalt, and nickel to give relatively intractable products.

A clean reaction with ligand displacement occurred between $Co(S_2PF_2)_2$ and nitric oxide. The reaction took place with substitution of one thiophosphate ligand by two nitrosyl groups

$$2Co(S_2PF_2)_2 + 2NO \longrightarrow (ON)_2CoS_2PF_2 + Co(S_2PF_2)_3 \quad (1)$$

$$2Co(S_2PF_2)_3 + 4NO \longrightarrow 2(ON)_2CoS_2PF_2 + (F_2PS_2)_2 \quad (2)$$

The process represented by the sum of (1) and (2) is quantitative. Reaction 1 is at least an order of magnitude faster than (2) and may occur in two steps with generation of $F_2PS_2\cdot$ or $(F_2PS_2)_2$ to react subsequently with $Co(S_2PF_2)_2$. The reaction

$$2Co(S_2PF_2)_2 + (F_2PS_2)_2 \longrightarrow 2Co(S_2PF_2)_3 \quad (3)$$

is, however, so fast that a stepwise sequence for (1) would not be easily detected. Nitric oxide and Fe-

(9) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).
(10) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 188, 191 (1964).
(11) B. N. Figgis and J. Lewis, *ibid.*, **6**, 178 (1964).

Table I

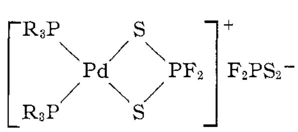
Ir and Nmr Spectra of $Pd(S_2PF_2)_2$ Derivatives

Derivative[a]	Ir, P–F str freq, cm^{-1}			Nmr,[b] P–F coupling constants, Hz		
L^-			804, 774			1158
PdL_2	899, 890 sh			1316		
$[(C_6H_5)_3P]_2PdL_2$	899, 884		804, 774	1284[c]		1157[c]
$(C_6H_5)_3PPdL_2$	902, 881	860, 824		1303[c]	1213[c]	
$(C_6H_5)_3AsPdL_2$	902, 881	860, 825		1311	1213	
PdL_3^-	898, 888	854, 830		1313 (1)[d]	1209 (2)	

[a] L = F_2PS_2. [b] Limiting, low-temperature data. [c] Nmr data for the more soluble $(p\text{-}CH_3C_6H_4)_3P$ analog. [d] Relative intensity.

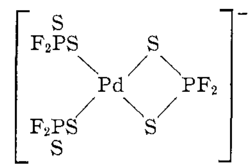
$(S_2PF_2)_2$ yielded $(ON)_2FeS_2PF_2$. In this case the oxidized form of the metal, $Fe(S_2PF_2)_3$, was not isolated. In contrast, iron(II) or cobalt(II) dithiocarbamate complexes add one molecule of nitric oxide with retention of sulfur coordination.[12,13] Mass spectral data indicate both $(ON)_2CoS_2PF_2$ and $(ON)_2FeS_2PF_2$ are monomeric in the gas phase.

The palladium complex $Pd(S_2PF_2)_2$ reacted in a stepwise manner with up to 2 mol of triphenyl- or tri-*p*-tolylphosphine. The infrared spectrum of $[(C_6H_5)_3P]_2Pd(S_2PF_2)_2$ had P–F absorptions at 900 and at 804 and 776 cm^{-1}. The positions of the latter two lines are characteristic of uncoordinated $F_2PS_2^-$ anion, and the former line closely resembles in position and appearance the spectrum of chelated difluorodithiophosphate ligand in $Pd(S_2PF_2)_2$. The ^{19}F nmr of the analogous bis-tri-*p*-tolylphosphine complex at $-121°$ consisted of two sets of doublets, one with a chemical shift and coupling constant similar to $F_2PS_2^-$ and the other with a larger coupling constant (J = 1284 Hz), approaching that of the chelated groups in $Pd(S_2PF_2)_2$ (J = 1316 Hz). These data suggest the structure

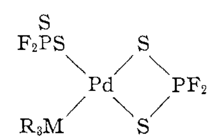


Consistent with an ionic formulation, dichloromethane solutions of $[(C_6H_5)_3P]_2Pd(S_2PF_2)_2$ were strongly conducting. The two difluorodithiophosphate groups appeared equivalent in the ^{19}F spectrum at room temperature reflecting rapid exchange of coordinated ligand with free ligand ($k > 10^3$ sec^{-1} mol^{-1}).

Adducts of 1:1 stoichiometry were obtained from $Pd(S_2PF_2)_2$ and donor molecules or ions, *e.g.*, $Pd(S_2PF_2)_2 \cdot PR_3$, $Pd(S_2PF_2)_2 \cdot As(C_6H_5)_3$, and $Pd(S_2PF_2)_3^-$. Relevant infrared and low-temperature ^{19}F nmr data are summarized in Table I. In the P–F infrared stretching region, the adducts as well as the parent $Pd(S_2PF_2)_2$ have a doublet at $\sim$900 cm^{-1}. In addition the adducts but not the parent chelate have a doublet at $\sim$845 cm^{-1}. The anionic complex $Pd(S_2PF_2)_3^-$ has a ^{19}F spectrum at $-64°$ which consists of a doublet of intensity 1 with J_{PF} = 1313 Hz and a doublet of intensity 2 with J_{PF} = 1209 Hz. An octahedral or D_{3h} trigonal prismatic structure is ruled out with these data. A C_{2v} trigonal prismatic structure is not rigorously ruled out, but it may be noted that six-coordination for palladium(II) is rare. Five-coordinate forms are not wholly consistent with the infrared and nmr data. We propose that a square-planar configuration is retained in the anion



The P–F coupling constant of the doublet of relative intensity 1 matches that of the groups in $Pd(S_2PF_2)_2$ (Table I) and this resonance may be assigned to the fluorine atoms in the chelated group. The coupling constant of the doublet of intensity 2 is significantly smaller and may reflect singly coordinated ligands. Because of similarities in infrared and nmr properties between $Pd(S_2PF_2)_3^-$ and the mono-triarylphosphine or -arsine adducts of $Pd(S_2PF_2)_2$, we are led to propose the structure (M = phosphorus or arsenic)



for the 1:1 phosphine or arsine adducts.

Properties of MS_2PF_2.—The copper and silver complexes are nonvolatile, insoluble in nondonor solvents, and apparently highly associated in the crystalline state. The association could be similar to that formulated above for the manganese derivative, but the probability of bridging difluorodithiophosphate groups must be seriously entertained for these derivatives. These complexes are soluble in donor solvents, *e.g.*, acetonitrile, and are strongly solvated in these solutions. The solvent is, however, not tightly bound since the copper derivative may be recrystallized from acetonitrile and solvent may be completely removed under vacuum. The silver complex behaves similarly. Triphenylphosphine reacts with the copper species to give $[(C_6H_5)_3P]_2CuS_2PF_2$ which is relatively stable in air. Interestingly, copper(I) difluorodithiophosphate is sparingly soluble in $(F_2PS_2)_2$ although no esr signal characteristic of a copper(II) complex or intermediate was detected.

The ^{19}F nmr spectrum of AgS_2PF_2 in acetonitrile consisted of a simple P–F doublet, and there was no spectral change from room temperature to $-40°$

(12) M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967).

(13) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

except a downfield shift in δ of 0.3 ppm. It would appear that substantial quantities of free ion are not present; however, there probably is rapid metal–ligand exchange since Ag–F coupling could not be detected.

Experimental Section

Preparative Procedures.—Anhydrous difluorodithiophosphoric acid was prepared by the previously described procedure.[2] The metal complexes were prepared and handled under nitrogen or vacuum. A drybox operating at oxygen and water levels of about 5 ppm was used for most manipulations. Solvents were dried over molecular sieves or activated alumina. In cases where the metal complexes could be suitably isolated by sublimation, reactions were carried out in a flask fixed to the bottom of a sublimation apparatus. The cold finger chilled to 0° served as a reflux condenser. Sublimations and other operations performed under vacuum were carried out at approximately 0.1 μ pressure.

Elemental analyses and solution molecular weight determinations were made by the Schwarzkopf Microanalytical Laboratories. Infrared spectra in the range 4000–670 cm^{-1} were obtained with a Perkin-Elmer 137 instrument or, for the chromium carbonyl and palladium complexes, a Perkin-Elmer 621 instrument. Unless otherwise stated, samples were examined as Nujol mulls. Fluorine nmr spectra were obtained with Varian A-56-60, HR-60, or HA-100 instruments. Chemical shifts (δ, ppm) are reported with reference to internal $CFCl_3$. Phosphorus nmr spectra were obtained with a Varian HA-100 instrument. Chemical shifts are referenced to external 85% phosphoric acid.

$Cr(S_2PF_2)_3$.—A mixture of 1.9 g (0.037 g-atom, particle size 10 μ) of chromium metal and 5.0 g (0.037 mol) of HS_2PF_2 was heated with stirring at 90° for 40 min. The product, a deep purple solid, was sublimed at 100° to a cold finger at 0°. The yield was 4.3 g (77%), mp 50.5–52°. Resublimation at 40° yielded a sample of mp 53.0–53.5°. *Anal.* Calcd for $CrF_6P_3S_6$: Cr, 11.5; F, 25.3; P, 20.6; S, 42.6; mol wt 451. Found: Cr, 11.5; F, 25.5; P, 19.8; S, 42.0; mol wt (mass spectrum) 451. Uv-visible maxima (CH_2Cl_2): 277 (ϵ 20,400), 314 (10,200), 525 (227), 693 mμ (359); ir spectrum: 894 (P–F stretch), 708, 700 cm^{-1} (sh).

The compound is readily soluble in saturated hydrocarbons and a variety of other nondonor solvents. It decomposes slowly (weeks) in air in solution. As a gas in the absence of air it was stable at 260° for 24 hr.

Reaction of $(C_2H_5)_4NCr(CO)_5Cl$ with HS_2PF_2.—Equimolar quantities of $(C_2H_5)_4NCr(CO)_5Cl$ and HS_2PF_2 were mixed in dichloromethane solution. Mass spectral analyses of the gases present over the solution showed hydrogen chloride was formed. No carbon monoxide was detected. In a separate experiment 0.312 g (2.33 mmol) of HS_2PF_2 was condensed into an evacuated flask, chilled with liquid nitrogen, containing 0.831 g (2.32 mmol) of $(C_2H_5)_4NCr(CO)_5Cl$ and 10 ml of dichloromethane. The mixture was stirred for 5 min at room temperature. Volatiles, removed under vacuum in a closed system, contained 2.26 mmol (97%) of hydrogen chloride (determined as silver chloride). *Anal.* Calcd for AgCl: Ag, 75.3; Cl, 24.7. Found: Ag, 74.5; Cl, 25.4. No noncondensable gas or $Cr(CO)_6$ was present. Infrared and nmr spectra were determined on freshly prepared dichloromethane solutions. Infrared bands in the carbonyl stretching frequency region were at 2062 (w), 1976 (m), 1930 (vs), 1882 cm^{-1} (s). The ^{19}F nmr spectrum calibrated with an external sample of $CFCl_3$ consisted of a doublet δ 11.9 and J_{PF} = 1190 Hz.

The compound was yellow and crystalline when freshly prepared. On standing overnight under vacuum at room temperature the color changed from yellow to brown. The compound also decomposed in dichloromethane solution in the dark. Elemental analyses were not attempted because of the thermal instability of the compound.

$Mn(S_2PF_2)_2$.—Difluorodithiophosphoric acid, 15 g (0.11 mol), was added to a suspension of manganese metal, 15 g (0.27 g-atom, 200 mesh), in 25 ml of toluene. After the initial exothermic reaction subsided, the stirred mixture was heated at 100° for 1 hr. When larger quantities of reactants were employed, the materials were combined at −80° and allowed to warm slowly to reaction temperature. Toluene was removed under vacuum and the pale pink product sublimed at 120–140° to a surface at 20°. The yield was 15 g (85%), mp 158–160° dec. Two further sublimations produced a sample of mp 168–170° dec. *Anal.* Calcd for $F_4MnP_2S_4$: F, 23.7; Mn, 17.1; P, 19.3; S, 39.9; mol wt 321. Found: F, 24.0; Mn, 17.0; P, 19.6; S, 39.4; mol wt (0.034 *M* in 1,2-dichloroethane) 325. Ir spectrum: 918, 905, 888, 874 (P–F stretch), 720, 698, 684 cm^{-1}.

$Mn(S_2PF_2)_2$ is essentially insoluble in saturated hydrocarbons and has limited solubility in aromatic hydrocarbons and some chlorinated hydrocarbons such as 1,2-dichlorobenzene, chloroform, and carbon tetrachloride. A saturated solution of $Mn(S_2PF_2)_2$ in 1,2-dichloroethane at room temperature is approximately 0.05 *M* in complex. It is relatively inert to dry air in the solid state but in solution reacts readily and irreversibly with oxygen.

$Fe(S_2PF_2)_2$.—Difluorodithiophosphoric acid, 48 g (0.36 mol), was added to a suspension of 25 g (0.45 g-atom) of iron powder in 30 ml of toluene at −80°. The mixture was stirred and warmed slowly to the reflux temperature. After 1 hr hydrogen evolution was complete and solvent was removed under vacuum. The crude product (35 g, 60%), a tan solid (mp 77–84°), was sublimed at 80–100°. The product was resublimed, crystallized from hexane, and again sublimed (mp 90–91°). *Anal.* Calcd for $F_4FeP_2S_4$: F, 23.6; Fe, 17.3; P, 19.2; S, 39.8; mol wt 322. Found: F, 23.6; Fe, 17.3; P, 19.2; S, 39.9; mol wt (0.1 *M* in toluene) 343. Ir spectrum: 920 (sh), 888 (P–F stretch), 715, 700, 683 cm^{-1}.

$(ON)_2FeS_2PF_2$.—Nitric oxide was bubbled into a stirred solution of 10.0 g (0.031 mol) of $Fe(S_2PF_2)_2$ in 70 ml of hexane. Absorption of nitric oxide was rapid and noticeably exothermic for about 15 min. Slow absorption at room temperature continued for about 5 hr. After removal of solvent a portion of the reaction product was extracted into 50 ml of *n*-heptane at the reflux temperature. When this solution was chilled to −5°, 1.32 g of a rust red solid, mp 68–69°, was deposited, which after sublimation (40°) under vacuum melted at 69–70°. *Anal.* Calcd for $F_2FeN_2O_2PS_2$: F, 15.3; Fe, 22.4; N, 11.3; P, 12.4; S, 25.8; mol wt 249. Found: F, 15.0; Fe, 22.7; N, 11.4; P, 12.4; S, 25.5; mol wt (mass spectrum) 249. Ir spectrum: 1850, 1790, 1740 (N–O stretch), 890 (P–F stretch), 718 cm^{-1}; ir spectrum (KBr): 1830, 1770, 1720 cm^{-1}; ir spectrum (CCl_4): 1830, 1760 cm^{-1}.

$Co(S_2PF_2)_2$.—Difluorodithiophosphoric acid, 38 g (0.28 mol), was added to 23 g (0.39 g-atom) of cobalt powder at −80°. The mixture was stirred and warmed slowly to 100°. After 1.5 hr hydrogen evolution was complete. The crude product (31 g, 67%), a green solid, mp 41–44°, was purified by sublimation, recrystallization from hexane, and resublimation at room temperature (mp 44–44.5°). *Anal.* Calcd for $CoF_4P_2S_4$: Co, 18.1; F, 23.4; P, 19.1; S, 39.4; mol wt 325. Found: Co, 17.5; F, 23.0; P, 19.2; S, 39.4; mol wt (mass spectrum) 325. Ir spectrum: 888 (P–F stretch), 697 cm^{-1}.

$Co(S_2PF_2)_3$.—Bis(difluorodithiophosphato)cobalt(II), 10 g (0.031 mol), and HS_2PF_2, 4.1 g (0.031 mol), were combined with 50 ml of toluene in a flask equipped with a condenser cooled to −80°, a stirring bar, and an air inlet. Approximately 2.6 l. of air dried by passage over phosphorus pentoxide was passed through the solution over a period of 50 min. Toluene was removed and the products were sublimed at 60° under vacuum to a 0° probe. Approximately 8 g of crude material was collected. After two recrystallizations from *n*-hexane (8 g of material/20 ml of solvent) followed by sublimation, the brown product melted at 33–34°. Resublimation yielded a product (1.9 g) of mp 34°. *Anal.* Calcd for $CoF_6P_3S_6$: Co, 12.9; F, 24.9; P, 20.3; S, 42.0. Found: Co, 12.9; F, 25.0; P, 20.2; S, 41.6. Ir spectrum: 900, 892 (sh) (P–F stretch), 700 (sh), 684 cm^{-1}; ^{19}F nmr spectrum (toluene): δ 3.9 (complex d, J_{PF} = 1315 Hz).

In an alternative procedure a mixture of 10 g (0.031 mol) of $Co(S_2PF_2)_2$ and 5.0 g (0.019 mol) of $(F_2PS_2)_2$[2] was heated at 40° for 10 min. Hexane, 10 ml, was added and the solution was chilled to −35°. The brown crystalline product was collected by filtration and sublimed to yield 6.6 g of material, mp 32°. A second crop, 4 g, mp 30–32°, was obtained from the solution. The infrared and the complex, characteristic ^{19}F nmr spectra for this and the compound prepared by air oxidation of $Co(S_2PF_2)_2$ were identical.

$(ON)_2CoS_2PF_2$.—To a stirred solution of 0.729 g (2.24 mmol) of $Co(S_2PF_2)_2$ in *n*-heptane at −50° was added 2.22 mmol of nitric oxide (purified by passage under vacuum through a U tube at −120°). Absorption of nitric oxide was complete in 6 min. The rate of absorption was limited by the rate of diffusion of gas into the vessel. At room temperature the ^{19}F nmr spectrum of the product mixture was comprised of only two sets of doublets assignable to $Co(S_2PF_2)_3$ and $(ON)_2CoS_2PF_2$. Overlap of the resonances of these compounds precluded estimation of the relative quantities. On a larger scale and at higher temperature the reaction was carried out in the absence of solvent using 20.0 g (0.0616 mol) of $Co(S_2PF_2)_2$ and 0.062 mol of nitric oxide. In the early stages of reaction the temperature was moderated by surrounding the vessel with an ice bath. After the initial vigorous reaction was complete, the mixture was warmed to room temperature and stirred until absorption of nitric oxide was complete. No nonvolatile material was present and 20.6 g (94%) of the mixture was isolated. Nmr spectra of this mixture and the solution described above were equivalent. The mixture, distilled using a 12-in. spinning-band column, yielded 5.4 g of material, bp 64° (12 mm), identified as $(ON)_2CoS_2PF_2$, as described below, by the boiling point and ir and nmr spectra, and 10.2 g of material, bp 70–76° (6 mm), identified as $Co(S_2PF_2)_3$ from the characteristic nmr spectrum and elemental analyses. Found, after recrystallization and sublimation: Co, 12.8; F, 23.9; P, 19.5; S, 41.3.

Using nitric oxide with the cobalt(II) complex in a 2:1 ratio, nitric oxide (7.30 mmol) at an initial pressure of 107 mm was placed in a vessel containing 1.66 g (3.62 mmol) of $Co(S_2PF_2)_3$ at 40°. Absorption of nitric oxide was half complete (p = 53 mm) in 1 hr and 84% complete in 3 hr. At 17 hr 0.12 mmol of nitric oxide was recovered corresponding to 99% completion of a reaction requiring the cobalt(III) complex and nitric oxide in a 1:2 mole ratio. Additional nitric oxide was supplied at a pressure of 200 mm. No significant further absorption occurred over 5 hr. The products were identified by the ^{19}F nmr spectrum as $(ON)_2CoS_2PF_2$ and $(F_2PS_2)_2$ in a 1.00:1.01 mole ratio. Thus, to carry the reaction of $Co(S_2PF_2)_2$ with nitric oxide to completion relatively long reaction times are required. In a preparative-scale experiment, nitric oxide was passed slowly into a nitrogen-flushed vessel chilled to 0° containing 20 g of $Co(S_2PF_2)_2$. After the initial vigorous reaction (~15 min), the mixture was warmed to room temperature and excess nitric oxide passed for 3 hr over the stirred melt. Mercury, 7 g, was added and the mixture was stirred at 100° for 1 hr. The product, bp 64° (12 mm), was distilled from excess mercury and $Hg(S_2PF_2)_2$ using a 12-in. spinning-band column and finally was redistilled (boiling point unchanged) from 1 drop of mercury. Recovery of purified product was 13.1 g (84%). The brown compound, isolated as a liquid, solidified on prolonged standing at or below room temperature (mp 65–66°). *Anal.* Calcd for $CoF_2N_2O_2PS_2$: Co, 23.4; F, 15.1; N, 11.1; P, 12.3; S, 25.4; mol wt 252. Found: Co, 23.5; F, 15.0; N, 11.0; P, 12.6; S, 25.6; mol wt (mass spectrum) 252. Ir spectrum: 1797, 1869 (N–O stretch), 890, 865 (sh) (P–F stretch), 707 cm^{-1}; ^{19}F nmr spectrum (neat): δ 3.9 (d, J_{PF} = 1300 Hz).

The complex consensed from the vapor as a brown mobile liquid which solidified on prolonged standing at room temperature. The infrared spectrum of the nitrosyl region of the compound was essentially the same in Nujol, 1,2-dichloroethane, and potassium bromide media.

$Rh(S_2PF_2)_3$.—Commercial rhodium trichloride, 5.0 g, heated at 85° for 6 hr with 10 g of HS_2PF_2 yielded 2.0 g of a sublimable reddish orange solid, mp 54°. Sixty-two per cent of the acid was recovered. An additional 1.2 g of rhodium complex was obtained after treatment of the nonvolatile residue with 10 g of HS_2PF_2 and 0.5 ml of water at 85° for 7 hr. *Anal.* Calcd for $F_6P_3RhS_6$: F, 22.7; P, 18.5; Rh, 20.5; S, 38.3; mol wt 502. Found: F, 22.7; P, 18.2; Rh, 20.2; S, 38.4; mol wt (mass spectrum) 502. Ir spectrum: 895, 885 (sh) (P–F stretch), 690 (sh), 680 cm^{-1}.

$Ni(S_2PF_2)_2$.—A mixture of nickel powder (15 g, 0.26 g-atom) and HS_2PF_2 (67 g, 0.50 mol), combined at −80°, was stirred and warmed slowly to 100°. After 45 min at this temperature, the dark green product was isolated by sublimation at 50° to a 0° surface. The yield was 56 g (69%), mp 42–44°. A portion of this sample twice sublimed at room temperature melted at 43–44°. *Anal.* Calcd for $F_4NiP_2S_4$: F, 23.4; Ni, 18.1; P, 19.1; S, 39.5; mol wt 325. Found: F, 23.0; Ni, 18.5; P, 18.6; S, 39.0; mol wt (mass spectrum) 325 and (at 160°, by the gas density technique) 329. Ir spectrum: 900, 860 (sh) (P–F stretch), 700 cm^{-1}; ^{19}F nmr spectrum (hexane): δ 8.2 (d, J_{PF} = 1326 Hz).

Nickel(II) difluorodithiophosphate is unreactive at room temperature with dry air in the solid state or in solution. It is stable for 2 hr at 260° in the gas phase but is unstable as a liquid at this temperature.

$Pd(S_2PF_2)_2$.—$PdCl_2$, 20 g (0.11 mol), and 30.5 g (0.23 mol) of HS_2PF_2 were combined at −80°. The mixture was stirred as the temperature was increased *slowly* to 60°. Hydrogen chloride evolution was complete after 1.5 hr at this temperature and the orange solid was sublimed at 100° to a 0° probe. The product, 40 g (97%), mp 54–57°, was twice recrystallized from hexane solution (0.5 g of complex/ml of hexane) at −30° and resublimed at room temperature. The melting point was 56.5–57°. *Anal.* Calcd for $F_4P_2PdS_4$: F, 20.4; P, 16.6; Pd, 28.6; S, 34.4; mol wt 373. Found: F, 20.5; P, 16.0; Pd, 28.6; S, 34.2; mol wt (0.11 *M* in 1,2-dichloroethane) 384. Ir spectrum: 899, 890 (sh) (P–F stretch), 720 (w), 685 cm^{-1}; ^{19}F nmr spectrum (CH_2Cl_2): δ 4.7 (complex d, J_{PF} = 1316 Hz); ^{31}P nmr spectrum (CH_2Cl_2): δ −94.6 (complex t, J_{PF} = 1315 Hz).

After exposure to air for 18 hr the melting point (55–57°) and composition (Found: S, 32.0) of the complex were significantly altered. The nmr spectrum of a sample in acetonitrile–water solution indicated the presence of $F_2PS_2^-$ and F_2POS^-.[14] A small sample heated at 250° in the liquid phase under nitrogen was recovered after 20 min unchanged (mp 56–57°).

$(C_6H_5)_3PPd(S_2PF_2)_2$.—A solution of 7.0 g (0.027 mol) of triphenylphosphine in 150 ml of toluene was added during 1 hr to a solution of 10 g (0.027 mol) of $Pd(S_2PF_2)_2$ dissolved in an equal volume of toluene. Solvent was removed under vacuum. No uncomplexed $Pd(S_2PF_2)_2$ sublimable at 100° (0.1 μ) was present. The solid was recrystallized from 100 ml of a 50:50 mixture of toluene and hexane to yield 8 g of orange crystalline product in the first crop. After a second recrystallization the melting point was 141–142°. *Anal.* Calcd for $C_{18}H_{15}F_4P_3PdS_4$: C, 34.1; H, 2.4; F, 12.0; P, 14.6; Pd, 16.8; S, 20.2. Found: C, 34.4; H, 2.6; F, 12.0; P, 14.4; Pd, 16.9; S, 20.3. Ir spectrum: 902 (s), 881 (m), 860 (s), 824 cm^{-1} (m) (P–F stretch); ^{19}F nmr spectrum (toluene, room temperature): δ 9.7 (d, J_{PF} = 1252 Hz); ^{31}P nmr spectrum (room temperature, 0.5 *M* in CH_2Cl_2): δ −98.0 (J_{PF} = 1254 Hz, S_2PF_2), −32.2 (broad s, coordinated $(C_6H_5)_3P$).

$(p\text{-}CH_3C_6H_4)_3PPd(S_2PF_2)_2$.—The mono-tri-*p*-tolylphosphine adduct of $Pd(S_2PF_2)_2$ was prepared using the procedure described for the triphenylphosphine analog. To purify the complex, a 9-g sample was dissolved in 170 ml of toluene, hexane was added until the solution became cloudy, and the mixture was chilled to 0°. The resulting orange crystalline product (5 g recovered from the first crop), dried under vacuum at room temperature, melted at 189–190° dec. *Anal.* Calcd for $C_{21}H_{21}F_4P_3PdS_4$: C, 37.3; H, 3.1; F, 11.2; P, 13.7; Pd, 15.7; S, 19.0. Found: C, 37.4; H, 3.4; F, 10.8; P, 13.6; Pd, 16.0; S, 18.8. Ir spectrum:

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892 (s), 879 (s, sh), 870 (s), 863 (s), 859 (m, sh), 842 cm^{-1} (m) (P–F stretch, absorptions near 800 cm^{-1} were masked by (p-$CH_3C_6H_4)_3P$ absorptions); ^{19}F nmr spectrum (dichloromethane–toluene, room temperature): δ 10.2 (d, J_{PF} = 1257 Hz).

$(C_6H_5)_3$**AsPd**$(S_2PF_2)_2$.—A solution of triphenylarsine (4.1 g, 0.013 mol) in 20 ml of toluene was added over a 20-min period to a solution of $Pd(S_2PF_2)_2$ (5.0 g, 0.013 mol). Solvent was removed under vacuum and the orange product was recrystallized from a toluene–hexane solution to a melting point of 122–123°. *Anal.* Calcd for $C_{18}H_{15}AsF_4P_2PdS_4$: C, 31.9; H, 2.2; As, 11.0; F, 11.2; P, 9.1; Pd, 15.7; S, 18.9. Found: C, 31.8; H, 2.1; As, 10.5; F, 10.9; P, 9.0; Pd, 15.4; S, 18.8. Ir spectrum: 902 (s), 881 (m), 860 (s), 837 (w), 825 cm^{-1} (m) (P–F stretch); ^{19}F nmr spectrum (dichloromethane–toluene, room temperature): δ 9.0 (d, J_{PF} = 1260 Hz).

$(n\text{-}C_3H_7)_4$**NPd**$(S_2PF_2)_3$.—A solution of 4.2 g (0.013 mol) of $(n\text{-}C_3H_7)_4NS_2PF_2$ in 8 ml of dichloromethane was added to a solution of 5 g (0.013 mol) of $Pd(S_2PF_2)_2$ in 8 ml of dichloromethane. The resulting solution, chilled to −30°, deposited 7.9 g (85%) of reddish orange, crystalline product. The product once again crystallized from dichloromethane and dried at room temperature under vacuum melted at 67–69°. *Anal.* Calcd for $C_{12}H_{28}F_6NP_3PdS_6$: C, 20.8; H, 4.1; F, 16.5; N, 2.0; P, 13.4; Pd, 15.4; S, 27.8. Found: C, 20.8; H, 4.3; F, 16.1; N, 2.0; P, 13.3; Pd, 15.3; S, 27.7. Ir spectrum: 898 (s), 888 (s), 854 (s), 830 cm^{-1} (s) (P–F stretch); ^{19}F nmr spectrum (CH_2Cl_2, room temperature): δ 8.5 (d, broad peaks, $J_{PF} \cong 1240$ Hz). Solutions of $(n\text{-}C_3H_7)_4NPd(S_2PF_2)_3$ decomposed slowly at room temperature.

$[(C_6H_5)_3P]_2$**Pd**$(S_2PF_2)_2$.—A solution of 7.0 g (0.027 mol) of triphenylphosphine in 25 ml of toluene was added to a solution of 5.0 g (0.013 mol) of $Pd(S_2PF_2)_2$ in 15 ml of toluene. The product separated from solution as an oil which on standing crystallized to a yellow solid. This solid was twice washed with 10-ml portions of toluene and dried under vacuum at room temperature. The yield was 11 g (93%), mp 161° dec. The material, recrystallized from a dichloromethane–hexane solution, consisted of bright yellow crystals, mp 160–161° dec. *Anal.* Calcd for $C_{36}H_{30}F_4P_4PdS_4$: C, 48.2; H, 3.4; F, 8.5; P, 13.8; Pd, 11.9; S, 14.3. Found: C, 47.6; H, 3.3; F, 8.8; P, 13.8; Pd, 11.6; S, 14.3. Ir spectrum: 899 (s), 884 (m), 804 (m), 774 cm^{-1} (w) (P–F stretch). $[(C_6H_5)_3P]_2Pd(S_2PF_2)_2$ was soluble in dichloromethane to give strongly conducting solutions. The compound decomposed slowly on exposure to air.

$[(p\text{-}CH_3C_6H_4)_3P]_2$**Pd**$(S_2PF_2)_2$.—A solution of 8.0 g (0.026 mol) of $(p\text{-}CH_3C_6H_4)_3P$ in 75 ml of toluene was added to 5.0 g (0.013 mol) of $Pd(S_2PF_2)_2$ in 15 ml of toluene. After about 5 min yellow solids precipitated. The mixture was stirred an additional 2 hr and 9.2 g (71%) of yellow-orange product was collected. Crystalline material was obtained by slow evaporation at room temperature of solvent from a solution of 6 g of product in a mixture of 40 ml of dichloromethane and 150 ml of toluene. Purified product, dried at room temperature under vacuum, melted at 172° dec. *Anal.* Calcd for $C_{42}H_{42}F_4P_4PdS_4$: C, 51.4; H, 4.3; F, 7.7; P, 12.6; Pd, 10.8; S, 13.1. Found: C, 51.5; H, 4.7; F, 7.5; P, 12.4; Pd, 10.5; S, 13.4. Ir spectrum: 890 (s), 870 cm^{-1} (m) (P–F stretch; absorptions near 800 cm^{-1} were masked by $(p\text{-}CH_3C_6H_4)_3P$ absorptions); ^{19}F nmr spectrum (dichloromethane–toluene, room temperature): δ 7.5 (d, J_{PF} = 1226 Hz). The compound decomposed slowly on exposure to air.

Pt$(S_2PF_2)_2$.—A mixture of $PtCl_2$, 5.0 g (0.019 mol), and HS_2PF_2, 5.0 g (0.037 mol), in 20 ml of toluene was heated at the reflux temperature for 3.7 hr. Solvent and unreacted acid were removed under vacuum and collected at −80°. The complex was isolated by sublimation to a 0° probe at 80°. Recovered toluene and acid were added to the nonvolatile residue and the mixture was heated for an additional 2.5 hr. The combined fractions of complex were resublimed to yield 4.8 g (53%) of yellow complex, mp 52–54°. It was recrystallized from hexane (2 ml/g) at −5° and resublimed at room temperature (mp 53–54°). *Anal.* Calcd for $F_4P_2PtS_4$: F, 16.5; P, 13.4; Pt, 42.3; S, 27.8; mol wt 461. Found: F, 16.4; P, 13.4; Pt, 42.1; S, 27.7; mol wt (mass spectrum) 461. Ir spectrum: 888 (P–F stretch), 847 (w), 720 (w), 687 cm^{-1}; ^{19}F nmr spectrum (n-heptane): δ 3.1 (complex d, J_{PF} = 1343 Hz); δ 3.1 (complex doublet of doublets, J_{PF} = 1343 Hz, J_{PtF} = 41.5 Hz).

Cu(S_2PF_2).—A suspension of copper powder, 10 g (0.16 g-atom), in 40 ml of toluene was stirred with 11 g (0.082 mol) of HS_2PF_2 at 70° for 21 hr. The reaction was slow and excess copper was useful. The product, insoluble in toluene, was collected, dissolved in acetonitrile, and filtered. After removal of solvent under vacuum 3.1 g (19%) of an off-white powdery solid was recovered (mp >400° dec). Yields may be increased by lengthening the reaction time. The solid was dissolved in 25 ml of acetonitrile, and ether, about 225 ml, was added until the solution became cloudy. The compound as an acetonitrile complex crystallized from solution at −25°. The crystals were dried under vacuum, initially at room temperature and finally at 50°. *Anal.* Calcd for CuF_2PS_2: Cu, 32.3; F, 19.3; P, 15.8; S, 32.6. Found: Cu, 32.5; F, 18.9; P, 15.8; S, 33.1. Ir spectrum: 905, 887 cm^{-1} (P–F stretch); ^{19}F nmr spectrum (CH_3CN): δ 10.9 (d, J_{PF} = 1189 Hz).

The copper(I) complex was also formed by reaction of HS_2PF_2 with copper(II) chloride. To a suspension of 5.0 g (0.037 mol) of anhydrous copper(II) chloride in 30 ml of toluene was added 5.9 g (0.044 mol) of HS_2PF_2. The mixture was stirred at 100° for 30 min. Insoluble materials were collected, washed with absolute ethanol to remove unreacted copper(II) chloride, and further purified by precipitation from a mixture of acetonitrile and methanol. *Anal.* Found: Cu, 31.7; F, 19.0; P, 15.4; S, 32.3. The appearance, thermal behavior (mp >400°), and infrared spectrum were characteristic of the Cu(I) complex. In addition, no electron spin resonance was detected from the compound in acetonitrile solution in accordance with the copper(I) formulation.

The complex CuS_2PF_2 may be handled for short periods in air in the solid state but was largely decomposed on standing in air over a period of months.

$[(C_6H_5)_3P]_2$**CuS**$_2$**PF**$_2$.—Triphenylphosphine, 4.4 g (0.017 mol), in a solution of 40 ml of toluene was added to a suspension of 1.96 g (0.010 mol) of CuS_2PF_2 in 20 ml of toluene. The mixture was stirred, brought to the boiling point, filtered hot, and allowed to cool to room temperature. White crystals precipitated from solution and were collected and dried at 50° under vacuum. The yield was 5.7 g (93%). After two recrystallizations from toluene the material melted at 200–202° dec. *Anal.* Calcd for $C_{36}H_{30}CuF_2P_3S_2$: C, 60.0; H, 4.2; Cu, 8.8; F, 5.3; P, 12.9; S, 8.9. Found: C, 62.2; H, 4.7; Cu, 8.4; F, 5.3; P, 12.0; S, 8.9. Ir spectrum (850–680 cm^{-1}): 839, 818 cm^{-1} (P–F stretch); ^{19}F nmr spectrum (toluene, 60°): δ 3.3 (d, J_{PF} = 1214 Hz). This complex is stable in air in the solid for extended periods (months).

AgS$_2$**PF**$_2$.—A solution of 5.0 g (0.037 mol) of HS_2PF_2 in 25 ml of toluene was added dropwise at room temperature to a stirred suspension of 4.0 g (0.017 mol) of silver oxide in 50 ml of toluene. The mixture was stirred and heated at 100° for 30 min. The resulting solid was collected, dissolved in anhydrous acetonitrile, and filtered. The product, isolated after removal of solvent under vacuum, was a white solid, 6.2 g (76%), mp 145°. Recrystallization was accomplished by addition of 45 ml of acetone to a solution of the product in 30 ml of acetonitrile and chilling the mixture to −20°. The product after three such recrystallizations followed by removal of solvent under vacuum at room temperature melted at 149–151°. *Anal.* Calcd for AgF_2PS_2: Ag, 44.8; F, 15.8; P, 12.9; S, 26.6. Found: Ag, 44.7; F, 15.6; P, 12.7; S, 26.2. Ir spectrum: 896 (sh), 884, 866, 840 (sh) (P–F stretch), 678 cm^{-1}; ^{19}F nmr spectrum (CH_3CN): δ 11.3 (d, J_{PF} = 1202 Hz); powder X-ray (Cu Kα, Ni filter), 10 highest d-spacing values (d (Å), relative intensity): 10.98, 10; 9.97, 50; 9.06, 100 (broad); 7.96, 20; 7.83, 5; 6.42, 30; 5.83, 40; 5.58, 5; 5.37, 70; 4.96, 30.

Silver difluorodithiophosphate is not volatile under vacuum at temperatures to its melting point and is soluble only in donor solvents such as acetonitrile. The solid is stable in dry air, but addition of water to the compound in solution produced black solid and, by the ^{19}F nmr spectrum, F_2POS^-.

$(C_6H_5)_3PAuS_2PF_2$.—A suspension of 8 g of $(C_6H_5)_3PAuCl$ in 25 ml of benzene was mixed with an equivalent amount of HS_2PF_2. Evolution of hydrogen chloride was complete within about 5 min. The product was obtained in a state of high purity on removal of solvent. A solution of the product in 30 ml of toluene was treated with *n*-hexane until it became cloudy. Crystals formed when the mixture was chilled to 0°. The product, dried under vacuum at 70°, melted at 98°. *Anal.* Calcd for $C_{18}H_{15}AuF_2P_2S_2$: C, 36.5; H, 2.6; Au, 33.3; F, 6.4; P, 10.5; S, 10.8; mol wt 592. Found: C, 36.9; H, 2.7; Au, 33.2; F, 6.2; P, 10.2; S, 10.9; mol wt (cryoscopic in benzene) 580. Ir spectrum: 851, 826 (P–F stretch), 710 cm^{-1} (P–S stretch); ^{19}F nmr spectrum (CCl_4): δ 8.3 (d, J_{PF} = 1193 Hz); ^{31}P nmr spectrum (CCl_4): δ −100.3 (t, S_2PF_2, J_{FP} = 1288 Hz), δ −37.8 (s, $(C_6H_5)_3P$).

The compound is very soluble in aromatic solvents, carbon disulfide, and dichloromethane. It is stable to light and air for periods of at least several days.

$Zn(S_2PF_2)_2$.—Zinc powder, 4 g (0.06 g-atom), 8.0 g of HS_2PF_2 (0.060 mol), and 20 ml of toluene were combined and heated with stirring at 100° for 1 hr. After removal of solvent under vacuum, the white solid product was twice sublimed at 150° under vacuum to a probe at 0°. The yield was 7.4 g (75%), mp 156–158°. *Anal.* Calcd for $F_4P_2S_4Zn$: F, 22.9; P, 18.7; S, 38.7; Zn, 19.7. Found: F, 22.2; P, 18.5; S, 38.4; Zn, 20.2. Ir spectrum: 898 (sh), 888 (P–F stretch), 716 (sh), 672 cm^{-1}; ^{19}F nmr spectrum (CH_3CN, room temperature): δ 8.5 (d, J_{PF} = 1180 Hz). The zinc complex is hygroscopic.

$Cd(S_2PF_2)_2$.—A mixture of cadmium powder, 6 g (0.05 mol), HS_2PF_2, 10 g (0.075 mol), and 20 ml of toluene was stirred at 100° for 2 hr. Solvent was removed under vacuum and the white solid product sublimed at 100–150°. The yield was 10.4 g (73%), mp 161–164° dec. This material was recrystallized from 1,2-dichloroethane (solubility ~2 g/100 ml of solvent at the boiling point) and resublimed (mp 173–175° dec). *Anal.* Calcd for $CdF_4P_2S_4$: Cd, 29.7; F, 20.1; P, 16.4; S, 33.9. Found: Cd, 29.3; F, 20.2; P, 16.2; S, 33.7. Ir spectrum: 890 (sh), 874 (P–F stretch), 717 (sh), 675 cm^{-1}; ^{19}F nmr spectrum (CH_3CN, room temperature): δ 11.5 (d, J_{PF} = 1183 Hz). The cadmium complex was not hygroscopic or otherwise reactive with air over a period of at least 3 days.

$Hg(S_2PF_2)_2$.—Mercury, 4.0 g (0.020 g-atom), was heated with 6.0 g (0.023 mol) of $(F_2PS_2)_2$ at 85° for approximately 3 hr. The white product, 6.4 g (69%), was sublimed at 110°. After resublimation the melting point was 163–164° dec. *Anal.* Calcd for $F_4HgP_2S_4$: Hg, 43.0; P, 13.3; S, 27.5; mol wt (for the ^{198}Hg isotope) 463.7952. Found: Hg, 41.4; P, 13.2; S, 26.0; mol wt (mass spectrum) 463.7961. Ir spectrum: 889 (sh), 876 (P–F stretch), 720 cm^{-1}; ^{19}F nmr spectrum (toluene): δ 14.3 (d, J_{PF} = 1210 Hz). Yellow solids and, by the nmr spectrum, $F_2PS_2^-$ and F_2POS^- were formed on addition of water to an acetonitrile solution of the complex.

Mass Spectra.—Mass spectra were obtained with a Consolidated Electrodynamics Corp. 21-103C instrument operated with 10.5-μA anode current, 70-eV ionizing current, and source temperature of 250°. Spectra of the nitrosyl and mercury complexes were obtained with a CEC-21-110B instrument with source temperature of 70°.

Mass spectra of the five most abundant metal-containing ions were as follows, for the indicated complex and metal isotope: $^{58}Ni(S_2PF_2)_2$: $Ni(S_2PF_2)_2^+$, 100; $NiS_2PF_2^+$, 66; NiS_2^+, 62; $S_2NiS_2PF_2^+$, 54; NiS^+, 19. $^{59}Co(S_2PF_2)_2$: $Co(S_2PF_2)_2^+$, 100; $CoS_2PF_2^+$, 77; $S_2CoS_2PF_2^+$, 65; CoS_2^+, 36; CoS^+, 24. $^{195}Pt(S_2PF_2)_2$: $Pt(S_2PF_2)_2^+$, 100; $S_2PtS_2PF_2^+$, 40; PtS_2^+, 29; $PtSP^+$, 28; PtS^+, 20. $^{52}Cr(S_2PF_2)_3$: $Cr(S_2PF_2)_2^+$, 100; $Cr(S_2PF_2)_3^+$, 36; $S_2CrPF_3^+$, 29; $CrS_2PF_2^+$, 28; CrS_2^+, 16. $^{103}Rh(S_2PF_2)_3$: $Rh(S_2PF_2)_3^+$, 100; $Rh(S_2PF_2)_2^+$, 93; RhS_2^+, 57; $S_2RhS_2PF_2^+$, 50; $RhS_2PF_2^+$, 30.

Solution Molecular Weights.—Molecular weights were obtained with a Mechrolab vapor pressure osmometer operating under a purified nitrogen atmosphere. Standardizations were made with azobenzene. Samples were transferred in a drybox. Solvents were added and solutions withdrawn through a rubber septum in the weighing bottle.

Molecular weights for the indicated concentrations (gram formula weights per liter) were as follows for $Cr(S_2PF_2)_3$: calcd, 451; found, 462 (0.0650, toluene). Comparable results were obtained to a concentration of 0.01 and with 1,2-dichloroethane (0.017–0.074) and *n*-heptane (0.018–0.071) solutions. Molecular weights for $Mn(S_2PF_2)_2$: calcd, 321; found, 325 (0.0340, 1,2-dichloroethane). Comparable results were obtained to a concentration of 0.009. Molecular weights for $Fe(S_2PF_2)_2$: calcd, 322; found, 343 (0.1065, toluene). Comparable results were obtained to a concentration of 0.03. Molecular weights for $Co(S_2PF_2)_2$: calcd, 325; found, 352 (0.0890, toluene). Comparable results were obtained to a concentration of 0.02 and with 1,2-dichloroethane (0.03–0.1) and *n*-heptane (0.02–0.04) solutions. Molecular weights for $Ni(S_2PF_2)_2$: calcd, 325; found, 367 (0.0575 in toluene). Comparable results were obtained to a concentration of 0.04 and with 1,2-dichloroethane (0.02–0.08) and *n*-heptane (0.02–0.09) solutions. Molecular weights for $Pd(S_2PF_2)_2$: calcd, 373; found, 396 (0.0256, toluene). Comparable results were obtained to a concentration of 0.01 and with 1,2-dichloroethane (0.02–0.1) and *n*-heptane (0.03–0.08) solutions.

Magnetic Data.—Magnetic susceptibilities were determined for the complexes in solution by Gouy[15] or Evans[16] nmr reference shift techniques. Solvents were purged with nitrogen, passed through a nitrogen-flushed column containing Woelm neutral activated alumina, and passed into a drybox (~5 ppm of oxygen and water) where they were exposed to equilibrate residual oxygen with the purified atmosphere. Solvents for nmr studies contained 5% by volume of tetramethylsilane (TMS). Reference solutions were contained either in a sealed capillary placed within the nmr tube or in the space between concentric tubes. Spectra were obtained with Varian HR-60 and HA-100 instruments. Data for paramagnetic substances from nmr measurements are collected in Table II. Within the limits of this technique the following compounds (L = $S_2PF_2^-$) were shown to be diamagnetic: $(NO)_2CoL$ in toluene; CoL_3, NiL_2, and PdL_2 in *n*-heptane; CuL and AgL in acetonitrile. The nickel compound was examined at a concentration of 0.4 *M*, and as a melt at 55°.

Gouy measurements were made on solutions of the cobalt(II) complex. Pyrex tubes (10-mm o.d. × 22 cm) separated into two chambers of equal dimension by a flat glass septum were loaded in one chamber with solution and sealed under vacuum at both ends. The field was supplied by a Varian V4004 4-in. electromagnet. Forces were measured with a seven significant figure balance of 80-g capacity. Tube calibrations were made with aqueous nickel chloride solutions (3–12% by weight $NiCl_2$) or distilled water. Results are presented in Table III.

Susceptibilites of $Co(S_2PF_2)_2$ (0.01571 g/ml at 306°K) in dichloromethane–TMS solution were measured by the Evans method as a function of temperature between 306 and 233°K. Corrected values of $10^6\chi_{mass}$ (temperature, °K; μ_{eff}, BM) were: 44.49 (306; 5.95); 46.62 (291; 5.94); 49.31 (272; 5.91); 54.66 (250; 5.96); 57.87 (233; 5.92). A Curie–Weiss plot of these values described a straight line within the limits of experimental error. Data obtained below 233–196°, were erratic, perhaps because of the increased breadth of the resonance signals at lower temperatures. Extrapolation of 306–233° data to zero reciprocal susceptibility provided a Weiss constant, θ, of approximately −12°.

Temperature-Dependent ^{19}F nmr Spectra.—Samples were examined at 56.4 MHz. Where determinations at a second field strength were required, a 94.1-MHz instrument was used. Difluorodichloromethane was used as an internal reference for spectra of the palladium derivatives. Chemical shift values are reported with reference to $CFCl_3$ using the relationship $\delta_{CF_2Cl_2}$ =

(15) See B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y. 1960, Chapter 6.

(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE II

MAGNETIC DATA FOR DIFLUORODITHIOPHOSPHATE COMPLEXES FROM NMR REFERENCE SHIFT MEASUREMENTS AT 303°K

Solute	Solvent	[Solute], g/ml	$10^6\chi_{mass}$[a]	μ_{eff}, BM
$Cr(S_2PF_2)_3$	*n*-Heptane	0.04939	12.72	3.7
$Cr(S_2PF_2)_3$	1,2-Dichloroethane	0.04217	13.22	3.8
$Cr(S_2PF_2)_3$	Dichloromethane	0.1877	13.04	3.8
$Mn(S_2PF_2)_2$	1,2-Dichloroethane	0.00840	45.19	5.9
$Fe(S_2PF_2)_2$	*n*-Heptane	0.01541	32.05	5.0
$Fe(S_2PF_2)_2$	1,2-Dichloroethane	0.03098	34.13	5.2
$Fe(S_2PF_2)_2$	Dichloromethane	0.03232	34.78	5.2
$Co(S_2PF_2)_2$	*n*-Heptane	0.03115	49.13	6.2
$Co(S_2PF_2)_2$	1,2-Dichloroethane	0.01628	47.62	6.1
$Co(S_2PF_2)_2$	1,2-Dichloroethane	0.03257	46.62	6.1
$Co(S_2PF_2)_2$	Dichloromethane	0.02428	47.66	6.1
$Co(S_2PF_2)_2$	Dichloromethane	0.03221	46.99	6.1
$Co(S_2PF_2)_2$	,Dichloromethane	0.1246	44.20	5.9

[a] Diamagnetic corrections for the metal, ligand, and 1,2-dichloroethane were estimated with Pascal's constants: P. W. Selwood "Magnetochemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1956, pp 78, 92. Corrections for *n*-heptane and dichloromethane were from the literature: R. C. Weast, Ed., "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p E-103.

TABLE III

MAGNETIC DATA FROM GOUY MEASUREMENTS OF $Co(S_2PF_2)_2$ IN SOLUTION AT 296°K

Solvent	Wt % solute	$10^6\chi_{mass}$[a] ($NiCl_2$ calib)	$10^6\chi_{mass}$[a] (water calib)	μ_{eff}, BM ($NiCl_2$ calib)	μ_{eff}, BM (water calib)
n-Heptane	9.2159	33.538	...	5.08	...
n-Heptane	16.851	33.481	...	5.08	...
1,2-Dichloroethane	4.0736	...	34.028	...	5.12
1,2-Dichloroethane	4.4658	33.400	33.855	5.08	5.11
1,2-Dichloroethane	18.157	33.005	33.989	5.04	5.12

[a] Corrected for diamagnetic contributions from solvent, ligand, and metal.

6.5 ($CFCl_3$ = 0) at temperatures below −40° and $\delta_{CF_2Cl_2}$ = 6.9 above −40°. Room-temperature data are recorded with the preparative procedures for the compounds.

A dichloromethane solution of $[(p\text{-}CH_3C_6H_4)_3P]_2Pd(S_2PF_2)_2$, 0.31 g/ml, was examined between 26 and −121°. The single doublet present at 26° was relatively sharp. The coalescence temperature was −104 to −108°. Measurements on the two sets of doublets present below −108° were made at −121°: δ 3.7 (sharp d, 1, J_{PF} = 1157 Hz), 11.3 (broad d, 1, J_{PF} = 1284 Hz). For reference, data at −121° for $(n\text{-}C_3H_7)_4N^+F_2PS_2^-$ in dichloromethane–fluorotrichloromethane solution were δ 2.4 (sharp d, J_{PF} = 1158 Hz).

A dichloromethane solution of $(n\text{-}C_3H_7)_4NPd(S_2PF_2)_3$, 0.22 g/ml, was examined between 31 and −125°. The broad doublet present at 31° broadened further as the temperature was lowered to −40°. The coalescence temperature was between −40 and −44°. Measurements on the two sets of doublets present below −44° were made at −64°: δ 7.6 (sharp d, 1, J_{PF} = 1313 Hz), 10.9 (sharp d, 2, J_{PF} = 1209 Hz). At −90° the peaks of intensity 2 were further split with a field-independent coupling of 5 Hz.

A dichloromethane (60% by volume)–toluene (40%) solution of $(p\text{-}CH_3C_6H_4)_3PPd(S_2PF_2)_2$, 0.22 g/ml, was examined between 28 and −120°. The coalescence temperature was between −103 and −106°. Measurements on the two sets of doublets were made at −120°: δ 10.0 (sharp d, 1, J_{PF} = 1303 Hz), 11.9 (sharp d, 1, J_{PF} = 1213 Hz). Spectra at 94.1 MHz allowed the four peaks to be properly matched.

A dichloromethane (70% by volume)–toluene (30%) solution of $(C_6H_5)_3AsPd(S_2PF_2)_2$, 0.22 g/ml, was examined between 31 and −116°. The coalescence temperature was between −93 and −96°. Measurements were made at −116°: δ 7.9 (sharp d, 1, J_{PF} = 1311 Hz), 11.1 (sharp d, 1, J_{PF} = 1213 Hz). Matching of peaks was achieved by comparison of spectra at 94.1 MHz.

Phosphorus–fluorine coupling constants were invariant between room temperature and the indicated temperature for $Zn(S_2PF_2)_2$ (CH_3CN solution, −50°), $Cd(S_2PF_2)_2$ (CH_3CN, −50°), $Hg(S_2PF_2)_2$ (CH_3CN, −50°), AgS_2PF_2 (CH_3CN, −40°), and $(C_6H_5)_3PAuS_2PF_2$ (CH_2Cl_2–$C_6H_5CH_3$, −118°). Chemical shift variations were less than 2.5 ppm.

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