

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

## Sulfur Ligand Complexes. IX.<sup>1</sup> Reactions of Metal Xanthates and Their Derivatives. The Formation of Bisphosphine-Dithiocarbonate and -Trithiocarbonate Complexes of Palladium(II) and Platinum(II)

BY J. P. FACKLER, JR., AND WILLIAM C. SEIDEL

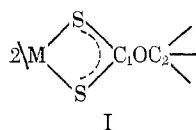
Received November 17, 1968

Metal xanthates react with primary and secondary amines to form dithiocarbamates. With cobalt(III) benzylxanthate, for example, the reaction with excess piperidine in tetrahydrofuran leads to ~95% conversion to the cobalt(III) dithiocarbamate complex. The formation of the monodithiocarbamate species using *n*-propylamine has been shown to follow second-order kinetics. Phosphines generally form adducts with dithiolates of the nickel triad elements. However, excess phosphine may produce ligand-substitution products. Quantitative formation of the bisphosphine-dithiocarbonate complexes occurs when excess methyldiphenylphosphine reacts with the benzylxanthates of palladium or platinum. These dithiocarbonates were compared with the bisphosphine-trithiocarbonate complexes of the same metal ions as prepared by direct ligand substitution on the anionic bistrithiocarbonates. Characterization reactions of the bisphosphine-dithiocarbonate species are described.

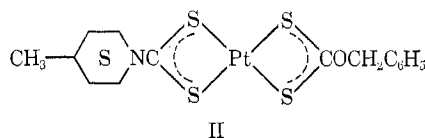
### Introduction

For over 150 years,<sup>2</sup> the reaction of carbon disulfide with metal alkoxides in the presence of alcohols has been known to produce xanthates (I). Certain heavy-metal complexes of these O-alkyldithiocarbonates have received substantial study,<sup>2b</sup> primarily because of their commercial importance; however, little definitive reaction chemistry has been reported.

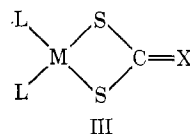
The structures of many metal xanthates are well established. For example, nickel(II) ethylxanthate is known to contain a planar NiS<sub>4</sub> unit<sup>3</sup> with chelating ligands bonding to the metal ion through sulfur atoms. Since the palladium(II) and platinum(II) complexes Pd(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and Pt(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> are isomorphous with the nickel(II) species,<sup>4</sup> it is likely that these complexes are also nearly isostructural with the nickel(II) complex I.



As indicated previously,<sup>5,6</sup> xanthate complexes of nickel(II), palladium(II), and platinum(II) react with nucleophiles such as pyridine (nickel) and phosphines (palladium and platinum) to expand the coordination number of the metal atom. In addition, other reactions also occur.<sup>7</sup> By rupture of the C<sub>2</sub>-O (I) bond, some metal xanthates decompose<sup>8</sup> to produce olefins. Presumably this occurs with the intermediacy of a complex



Attempts to characterize the bisphosphine-dithiocarbonate and -trithiocarbonate species (III) have led us to explore alkylation and other reactions of these complexes. As a result, some interesting new sulfide and disulfide coupling reactions have appeared, including one which presumably involves the intermediacy of a metal carbonyl.



(1) Part VII: M. J. Weeks and J. P. Fackler, Jr., *Inorg. Chem.*, **7**, 2548 (1968). Part VIII: J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2784 (1968).

(2) (a) W. C. Zeise, *Rec. Mem. Acad. Roy. Sci. Copenhagen*, **1**, 1 (1815); (b) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962.

(3) M. Franzini, *Z. Krist.*, **118**, 393 (1963).

(4) G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, **27**, 898 (1965).

(5) D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, **6**, 2047 (1967).

(6) J. P. Fackler, Jr., W. C. Seidel, and J. A. Fetchin, *J. Am. Chem. Soc.*, **90**, 2707 (1968).

(7) J. P. Fackler, Jr., D. Coucouvanis, W. C. Seidel, R. C. Masek, and W. Holloway, *Chem. Commun.*, 924 (1967).

(8) J. P. Fackler, Jr., W. C. Seidel, and M. Myron, to be submitted for publication.

TABLE I  
 ANALYSIS OF COMPLEXES

Compound	Calcd				Found				Mp, °C	Color
	% C	% H	% S	Mol wt	% C	% H	% S	Mol wt		
$((C_6H_5)_2PCH_2)_2PtS_2CO$	47.15	3.78	9.30	688	47.29	4.02	9.16	720 <sup>e</sup>	220-222 <sup>g</sup>	White
$((C_6H_5)_2PCH_2)_2PdS_2CO$	54.14	4.34	10.7	599	52.93	4.19	6.47 <sup>f</sup>	620 <sup>e</sup>	164-166 <sup>g</sup>	Yellow
$((C_6H_5)_3P)PtS_2CO \cdot CHCl_3^b$	49.1	3.3	...	931	49.14	3.30	...	...	274-276 <sup>g</sup>	White
$((C_6H_5)_2PCH_2)_2PtS_2CS$	46.06	3.69	13.66	704	45.99	3.78	11.62 <sup>f</sup>	...	170 <sup>g</sup>	Yellow
$((C_6H_5)_2PCH_2)_2PdS_2CS$	52.75	4.23	...	...	52.42	4.31	...	...	230-231 <sup>g</sup>	Yellow
$((C_6H_5)_2PCH_2)_2Pd(S_2COC_2H_5)_2$	41.58	4.19	...	...	41.50	4.09	...	...	135 <sup>g</sup>	Yellow
$((C_6H_5)_3P)_2Cu(S_2COC_2H_5)$	66.04	4.93	9.04	...	65.88	5.05	8.30	...	182-186 <sup>g</sup>	Brown
									98-100	White
									175 <sup>g</sup>	White

<sup>a</sup> Uncorrected. <sup>b</sup>  $CHCl_3$  present by mass spectral analysis. <sup>c</sup> Color change. <sup>d</sup> Spectrophotometric titration with  $I_2$  in  $CHCl_3$ ; formula weight calculated assuming the stoichiometry  $I_2 + Pt(S_2CO)((C_6H_5)_2PCH_2)_2 \rightarrow$  products. <sup>e</sup> Vapor pressure osmometer in  $CHCl_3$  at 37°; concentration  $\sim 2 \times 10^{-2} M$ . <sup>f</sup> Sulfur analysis generally nonreproducible. <sup>g</sup> With decomposition.

### Experimental Section

All commercially available chemicals were used as received, unless otherwise indicated. Methylphenylphosphine was prepared from chlorodiphenylphosphine and methyl Grignard. Metal xanthates were prepared by standard procedures<sup>4</sup> from the potassium salts.

Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All melting points are uncorrected (Table I).

**Physical Measurements.**—Infrared spectra were obtained as Nujol mulls with a Beckman IR-8 recording spectrophotometer, frequency-calibrated with polystyrene. A Varian A-60 nmr spectrometer and a Varian M-66 mass spectrometer were used for nmr and mass spectral measurements, respectively.

Solution molecular weights were performed using a Mechrolab vapor-phase osmometer calibrated with benzil. A Debye-Scherrer camera utilizing nickel-filtered copper radiation was used to observe the X-ray powder patterns of the  $L_2MS_2CO$  complexes, where  $M = Pd$  and  $Pt$ , which were found to be identical by visual comparison of the films.

**Preparation of Alkylxanthates.**—The potassium salt (in excess) of the appropriate xanthic acid was allowed to react with alkyl halide in absolute alcohol. After alkali halide precipitation appeared complete, water and ether were added and the ether layer was removed. The ether was dried with anhydrous  $Na_2SO_4$  and evaporated. These alkylxanthates were not further purified.

**Preparations. Dithiocarbonatobis(methylphenylphosphine)platinum(II).**—To a solution of 1.0 g of  $Pt(S_2COCH_2C_6H_5)_2$  (1.78 mmol) in  $CHCl_3$ , 0.7 ml of methylphenylphosphine (3.75 mmol) was added. After 30 min 100 ml of *n*-pentane was added with stirring. The white precipitate which formed was filtered by gravity and air dried. The crude product was recrystallized from  $CHCl_3$  and  $C_2H_5OH$  to give white crystals in yields greater than 90%.

**Dithiocarbonatobis(methylphenylphosphine)palladium(II).**—This yellow crystalline complex was prepared from  $Pd(S_2COCH_2C_6H_5)_2$  in a manner analogous to the preparation of the platinum(II) derivative.

**Trithiocarbonatobis(methylphenylphosphine)platinum(II).**—To a solution<sup>12</sup> of 1.0 g of  $((C_6H_5)_2PCH_2C_6H_5)_2Pt(CS_3)_2$  dissolved in 40 ml of DMF, 3 ml of  $(C_6H_5)_2PCH_2$  (large excess) was added. The solution was heated to 70°, and after 0.5 hr, 100 ml of water and 100 ml of  $CHCl_3$  were added with cooling. This mixture was shaken and the yellow  $CHCl_3$  layer separated. This  $CHCl_3$  solution was washed with water, dried with anhydrous  $Na_2SO_4$ , and evaporated to dryness in a hood, leaving a yellow oil. This oil was washed with ether, leaving a yellow, ether-insoluble material which was recrystallized from  $CHCl_3-C_2H_5OH$  to yield bright yellow needles, which became black at approximately 170° (Table I).

**Trithiocarbonatobis(methylphenylphosphine)palladium(II).**—This complex was prepared from  $((C_6H_5)_2PCH_2C_6H_5)_2Pd(CS_3)_2$

in a manner analogous to the preparation of the platinum complex above.

**Bis(*o*-ethylthiocarbonato)(methylphenylphosphine)palladium(II).**—To a solution of 1.0 g of  $Pd(S_2COC_2H_5)_2$  (2.9 mmol) in 50 ml of  $CHCl_3$ , 1.55 ml of methylphenylphosphine (5.8 mmol) was added with stirring. After 0.5 hr pentane was added until the red solution turned cloudy. After standing 24 hr at  $-5^\circ$ , large, yellow-brown needles formed. The crude product was recrystallized from  $CHCl_3$ -pentane.

Nmr:  $CH_2CH_3$ ,  $\tau$  8.61,  $J = 7$  (triplet),  $\tau$  5.42,  $J = 7$  (quartet);  $CH_3$ ,  $\tau$  7.83,  $J = 11$  (doublet); phenyl,  $\tau$  2.50, complex (multiplet).

**Dithiocarbonatobis(triphenylphosphine)platinum(II).**— $Pt(S_2COCH_2C_6H_5)_2$ , 0.86 g (0.33 mmol), and 0.220 g of triphenylphosphine (0.82 mmol) were mixed together and dissolved in 10 ml of  $CHCl_3$ . After 30 min a precipitate formed; 30 ml of *n*-pentane was added and the white precipitate was filtered by gravity and washed with ether. The product was recrystallized from  $CHCl_3-C_2H_5OH$  to yield white, multifaceted crystals. The compound thus prepared contains 1 mol of  $CHCl_3$  per mole of complex.

**Tris(*N*-pentamethylenedithiocarbamate)cobalt(III) from  $Co(S_2COCH_2C_6H_5)_3$ .**—To  $Co(S_2COCH_2C_6H_5)_3$ , 1.0 g, dissolved in 10 ml of tetrahydrofuran, 2.0 g of piperidine was added (14:1 mole ratio of amine to xanthate). After approximately 20 min, 50 ml of pentane was added and the solid product was removed by filtration. This product is dark green while an independently prepared recrystallized piperidine-dithiocarbamate complex of cobalt(III) was light green. The yield of crude dry piperidine-dithiocarbamate complex was 1.0 g, representing a nearly quantitative conversion of the xanthate to the dithiocarbamate.

The ir spectra of the two products were identical except for two small bands which appeared at 700 and 725  $cm^{-1}$  in the crude substitution product. A comparison of the nmr of the two products showed approximately 95% conversion of the xanthate to the dithiocarbamate.

**O-Ethylthiocarbonato[bis(triphenylphosphine)]copper(I).**—A concentrated solution of potassium ethylxanthate in acetonitrile was slowly added to a concentrated solution of copper(II) bromide in acetonitrile. The dark red solution color slowly disappeared as the xanthate solution was added and a yellow precipitate formed. When the last trace of red disappeared from the solution, the precipitate, a mixture of copper(I) ethylxanthate and copper(I) bromide, was filtered off and air dried. To a solution of 1.2 g of  $(C_6H_5)_3P$  in 100 ml of  $CHCl_3$ , 1.0 g of the above mixture was added. After stirring for 1 hr the solution was filtered to remove  $CuBr$  and the filtrate was evaporated almost to dryness. After 200 ml of ether was added, the product was removed by filtration. The crude product was recrystallized as white platelets from  $CHCl_3$ -ether.

**O-Benzylthiocarbonatobis(triphenylphosphine)copper(I).**—This white crystalline material was prepared in a manner analo-

gous to the  $((C_6H_5)_3P)_2Cu(S_2COC_2H_5)$  preparation starting with potassium benzylxanthate. There appears to be 1 mol of chloroform per mol of complex in the product, mp  $\sim 120^\circ$  dec.

*Anal.* Calcd for  $C_{48}H_{38}Cl_3OP_2S_2Cu$ : C, 62.79; H, 4.41. Found: C, 61.80; H, 4.48.

**Diethyldithiocarbamatobis(triphenylphosphine)copper(I).**—

This complex was prepared according to the method of Raynor.<sup>9a</sup>

**Bis(methyldiphenylphosphine)-O-ethylthiophosphatopalladium(II).**—Bis(O,O'-diethyldithiophosphato)palladium(II), prepared according to the method of Jørgensen,<sup>9b</sup> 0.31 g, was dissolved in 10 ml of  $CHCl_3$  and 0.27 g of methyldiphenylphosphine was added. This solution was placed in a stoppered vial and heated at  $55^\circ$  for 2 hr. The product was precipitated from the  $CHCl_3$  solution upon the addition of ether, filtered, air dried, and recrystallized from  $CHCl_3$ -hexane as yellow plates, dec pt  $>150^\circ$ .

*Anal.* Calcd for  $C_{28}H_{31}P_3O_2S_2Pd$ : C, 50.70; H, 4.68. Found: C, 49.93; H, 4.57.

Nmr:  $\tau$  2.52 (multiplet) (20);  $\tau$  6.00 (multiplet) (2);  $\tau$  8.24 (triplet) (6);  $\tau$  8.72 (triplet) (3).

**Bis(benzyltrithiocarbonato)di- $\mu$ -benzylthio-dinickel(III),  $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ .**—To a solution of 6.1 g of benzyl mercaptan in 100 ml of tetrahydrofuran (dried over Linde Molecular Sieves No 5A), sodium hydride was added until hydrogen evolution ceased. Carbon disulfide was added in sufficient quantity, 1.5 ml, to produce approximately equal quantities of mercaptide and xanthate. The solution was added to an  $NiCl_2 \cdot 6H_2O$  solution, 6.0 g in 400 ml of water. The brown precipitate which formed was removed by filtration, washed with methanol, and air dried. Fine brown needles were formed on crystallization from  $CHCl_3$  after filtration, addition of methanol, and cooling to  $\sim 0$ , mp  $215-216^\circ$ .<sup>10</sup>

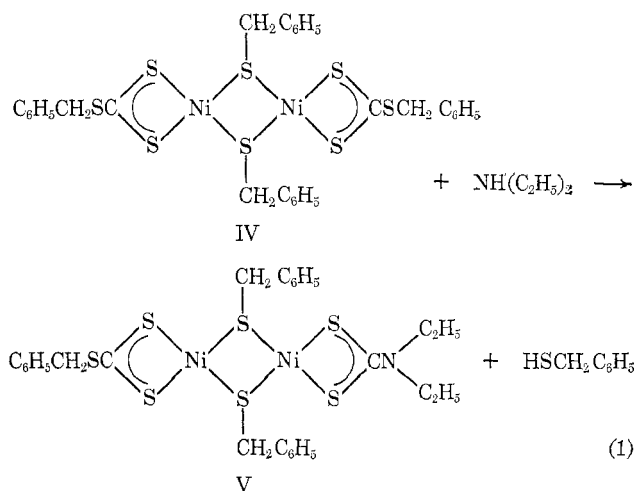
**Bis(diethyldithiocarbamato)di- $\mu$ -benzylthio-dinickel(II),  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$ .**—In 60 ml of  $CHCl_3$ , 0.4 g of  $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$  and 1.0 ml of diethylamine were added with stirring. After 1 hr the mixture was added to 400 ml of petroleum ether (boiling range  $30-60^\circ$ ) and the green precipitate produced was removed by filtration. It was crystallized from chloroform-methanol, mp  $222-223^\circ$ .

*Anal.* Calcd for  $C_{24}H_{34}N_2S_6Ni_2$ : C 43.6; H, 5.1; mol wt, 660. Found: C, 43.2; H, 4.9; mol wt (osmometrically in  $CHCl_3$ ), 635.

The complex shows a strong ir band attributed to a CN stretch at  $1520\text{ cm}^{-1}$  and nmr absorbances at  $\tau$  3.18 (multiplet) (5),  $\tau$  6.45 (quartet) (4),  $\tau$  7.50 (singlet) (2), and  $\tau$  8.75 (triplet) (6), consistent with the chemical formulation given.

**Attempted Isolation of Benzyltrithiocarbonato(N,N-diethyldithiocarbamato)di- $\mu$ -benzylthio-dinickel(II),  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)(S_2CSCH_2C_6H_5)_2$ .**—By treating  $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ , IV, with a 0.5 molar quantity of amine (based on the dimer), an attempt was made to produce the mixed-ligand dimer, V, according to reaction 1. Addition of the amine to IV in 5 ml of  $CHCl_3$  gave a solution which when spotted on a thin layer chromatography sheet (Eastman, silica gel) eluted as three distinct spots with a  $CHCl_3$ -petroleum ether mixture. The retention time of the slowest moving spot was identical with that of  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$ , while the fastest moving spot had a retention time identical with that of IV. The middle spot presumably contained the desired material V.

By eluting the entire solution on a silica gel column, three distinct components appeared to be separated. However, analysis of the middle component by thin layer chromatography showed it to contain the other two components also. A mixture of IV with  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$  in  $CHCl_3$  also develops the same three spots, suggesting that an equilibrium is established among IV, V, and  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$  at a rate sufficiently slow to allow chromatographic separation of the com-



ponents, yet too rapid to enable isolation and crystallization of the pure mixed-ligand component V.

**Reactions of  $L_2PtS_2CO$ .**—The reactions of  $L_2PtS_2CO$  ( $L = (C_6H_5)_2PCH_3$ ) with the reagents given in Figure 1 were carried out in an nmr tube in  $CHCl_3$  or  $CDCl_3$  at  $55^\circ$  until no changes occurred in the spectrum (2-24 hr). The products were identified by comparison with authentic samples using three procedures. (1) The nmr spectra of the samples were compared *in situ* with spectra of authentic samples in  $CHCl_3$ . (2) Contents of the nmr tube were evaporated to an oil. The oil was extracted with ether and the ether was evaporated to leave an organic liquid or solid which was then identified. (3) The solid residues remaining from ether extraction of the oil in procedure 2 were analyzed without further purification. Materials were identified as follows: benzyl disulfide (procedures 1 and 2; glpc 20% GE SF-96 on Chromosorb W at  $200^\circ$ ); methyl sulfide (procedure 1); benzyl benzylxanthate (procedure 1); ethyl ethylxanthate (procedures 1 and 2; mass spectrum); benzyl ethylxanthate (procedure 1); *cis*- $((C_6H_5)_2PCH_3)_2PtBr_2$  (procedures 1 and 3; infrared spectrum); 1,3-dihydroisothionaphthene (procedure 2; mass spectrum); carbon monoxide (procedure 1; infrared spectrum; also present by glpc).

**Reaction of  $L_2PtS_2CO$  with Benzyl Bromide.**—To 15 ml of  $CHCl_3$  (Matheson "spectral quality") was added 0.2 ml of benzyl bromide and 0.30 g of  $L_2PtS_2CO$  in a sealed flask. The mixture was allowed to react at  $55^\circ$  until infrared analysis showed the reaction to be complete. During the reaction the two infrared bands at  $\sim 1650\text{ cm}^{-1}$  decreased in intensity and a new band appeared at  $\sim 2040\text{ cm}^{-1}$ . After 8 hr the bands at  $1650\text{ cm}^{-1}$  had completely disappeared. The band at  $2040\text{ cm}^{-1}$  was removed by bubbling nitrogen through the solution. Quantitative glpc measurement of the vapors from the alkylation reaction on a 6-ft Linde 5A Molecular Sieve column using methane as a marker showed the presence of a species having the same retention time as carbon monoxide.

The above reaction mixture was transferred to a glass pressure vessel and placed under 100 psi pressure of CO for 3 days. A sample of the solution was removed and examined each day by infrared analysis. No band at  $2040\text{ cm}^{-1}$  was observed, even after 3 days.

**Spectrophotometric Study of the Reaction of 4-Methylpiperidine with Platinum Benzylxanthate.**—Platinum benzylxanthate was recrystallized from peroxide-free tetrahydrofuran with hexane. The amine was distilled from sodium. Benzene was shaken with  $H_2SO_4$  (concentrated), refluxed over sodium, and distilled. Solutions were prepared in a drybox to exclude water and oxygen. The near-ultraviolet spectrum of  $Pt(S_2COCH_2C_6H_5)_2$  in benzene was recorded as a function of added 4-methylpiperidine and is presented in Figure 2.

**Kinetics of the Reaction of *n*-Propylamine with Tris(O-benzylthiocarbamato)cobalt(III).**—It was possible to determine the rate of formation of the monosubstituted derivative in chloroform-*d*, by integration of the various nmr signals for the meth-

(9) (a) J. B. Raynor, *J. Chem. Soc.*, 997 (1966); (b) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(10) D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967, erroneously reported the complex to have a melting point of  $115-116^\circ$ .

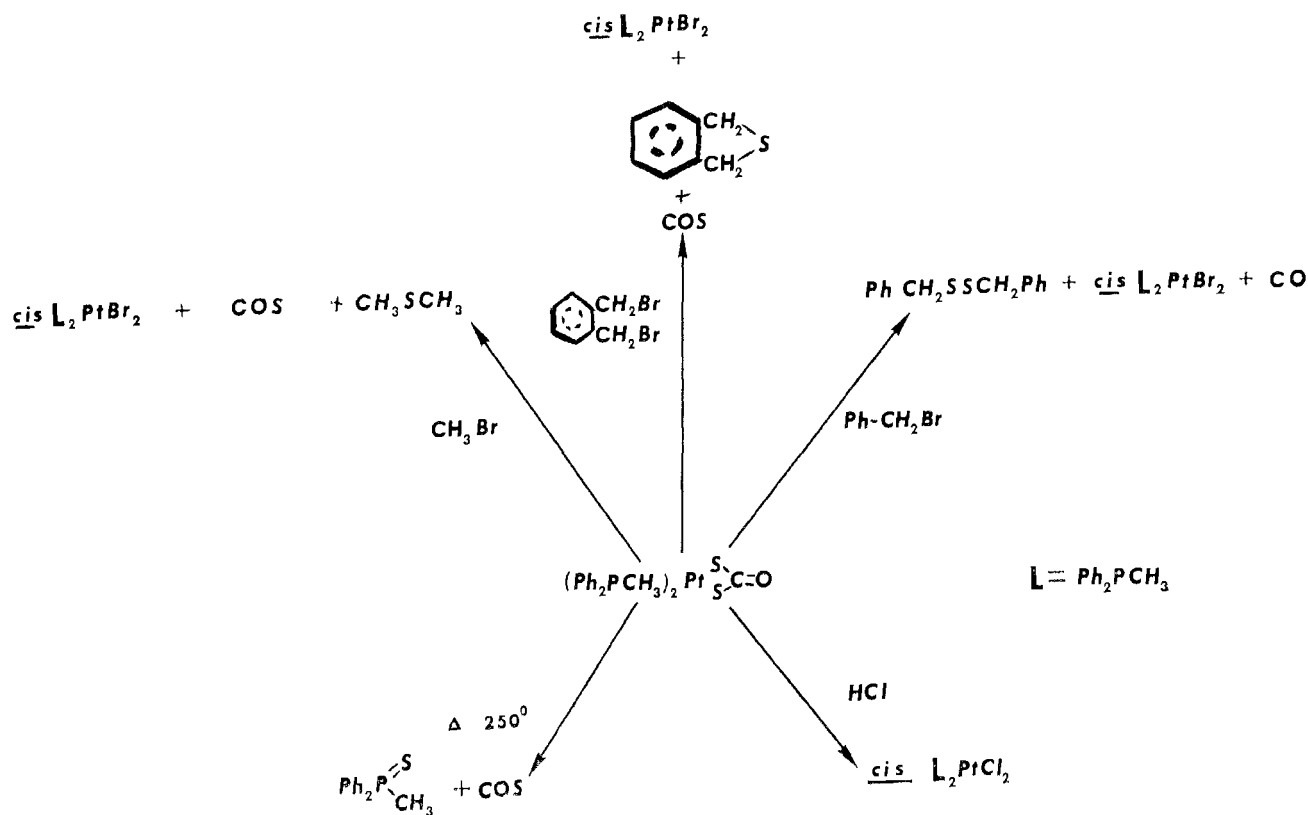
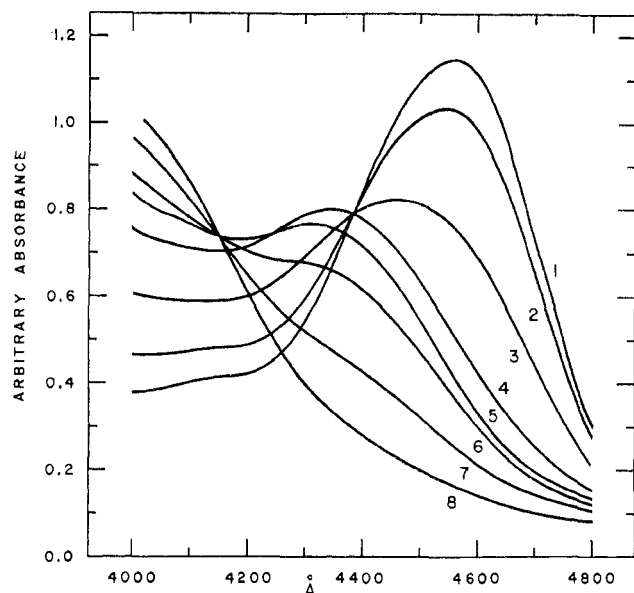
Figure 1.—Reactions of  $L_2MS_2CO$ .

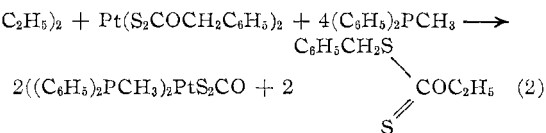
Figure 2.—The near-ultraviolet spectrum of  $\text{Pt}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$  in benzene with added increments of 4-methylpiperidine. Ratio of amine to metal: 1, 0; 2, 0.2; 3, 0.6; 4, 1.0; 5, 1.4; 6, 1.6; 7, 2.0; 8, 2.4.

ylene groups in the  $\text{Co}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_3$ , the  $\text{Co}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2(\text{S}_2\text{CNH}(n\text{-C}_3\text{H}_7))$ , and the benzyl alcohol produced. Since the quantity of each product changed slightly, but perceptibly, during integration of the signals at the concentrations needed to observe good spectra, the precision of the data was poorer than normally obtained by conventional techniques and will not be recorded here. Second-order plots were obtained over the first 15 min of reaction time at the  $\sim 0.1\text{--}0.2\text{ M}$  concentrations employed.

## Results

$\text{Pt}(\text{S}_2\text{COC}_2\text{H}_5)_2$  reacts with equivalent amounts of methyl-diphenylphosphine in either  $\text{CS}_2$  or  $\text{CHCl}_3$  to form a 1:1 adduct. In  $\text{CS}_2$ , additional phosphine seems to have no effect, but in  $\text{CHCl}_3$ ,  $L_2\text{PtS}_2\text{CO}$  is formed in nearly quantitative yield, the organic product being S,O-diethyl xanthate. With  $\text{Pd}(\text{S}_2\text{COC}_2\text{H}_5)_2$ , however, adduct formation occurs but no further reaction takes place in either of the above solvents. A crystalline 1:1 adduct has been isolated from a chloroform-pentane solution. The benzylxanthates of both palladium(II) and platinum(II)<sup>11</sup> readily react with 2 equiv of phosphine to produce the  $L_2MS_2CO$  product. The reaction of bis(O,O'-diethyldithiophosphato)palladium(II) with 2 equiv of L leads to the formation of the formally analogous complex bis(methyl-diphenylphosphine)-O-ethyldithiophosphatopalladium(II).

When equimolar quantities of ethyl- and benzylxanthates of platinum(II) were allowed to react with 2 equiv of phosphine in chloroform, the S-benzyl-O-ethyl xanthate appeared to be the major organic product, reaction 2. Under the same reaction con-



(11)  $\text{Ni}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$  reacts with 2 equiv of phosphine to form S,O-dibenzyl xanthate but the inorganic product was not purified or identified.

ditions, a chloroform solution of S-benzyl-O-benzyl xanthate and S-ethyl-O-ethyl xanthate containing  $L_2PtS_2CO$  does not exhibit alkyl group exchange.

The anionic dithiolates,<sup>12</sup>  $M(S_2CS)_2^{2-}$ , where M is Pt(II) or Pd(II), react readily with  $(C_6H_5)_2PCH_3$  to form  $L_2PtS_2CS$  species in dimethylformamide. This product shows an nmr spectrum nearly identical with that of the dithiocarbonate derivative (Figure 3).

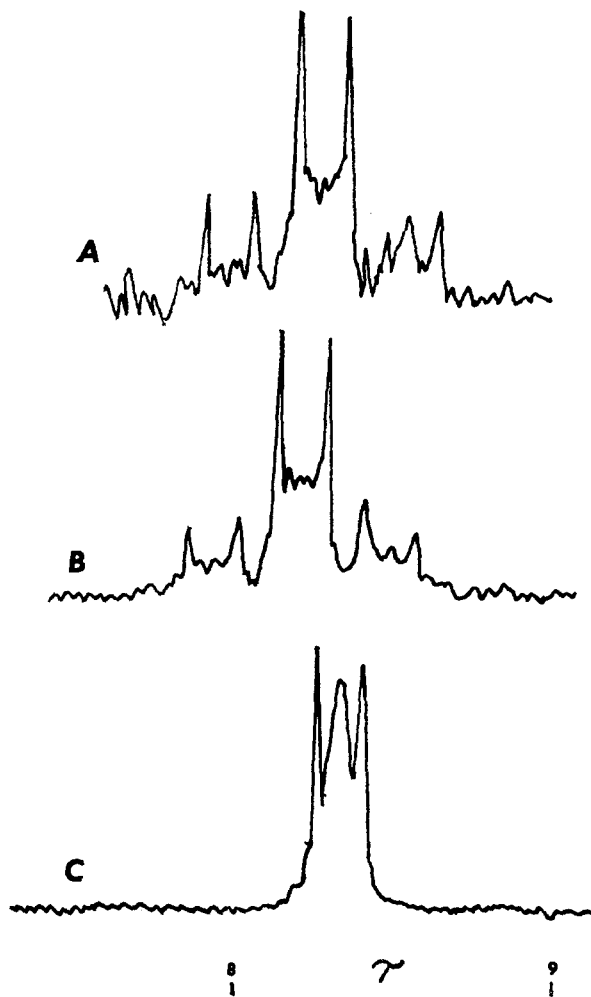


Figure 3.—Methyl proton magnetic resonance spectra of (A)  $L_2PtS_2CS$ , (B)  $L_2PtS_2CO$ , and (C)  $L_2PdS_2CO$  in chloroform-*d*.

The infrared spectra for the two complexes are also very similar (Figure 4) except in the  $C=O$  region<sup>13</sup> ( $1650-1700\text{ cm}^{-1}$ ) where  $L_2PtS_2CO$  absorbs and the  $C=S$  region ( $900-1100\text{ cm}^{-1}$ ) where  $L_2PtS_2CS$  has a band. The carbonyl band in the dithiocarbonate complex is doubled with  $\sim 80\text{ cm}^{-1}$  separating the two components. The CS frequency in  $L_2PtS_2CS$  is  $\sim 30\text{ cm}^{-1}$  higher than the same band in the bis(trithiocarbonato)platinum(II) anion.

Alkylation of  $L_2PtS_2CO$  with methyl bromide, benzyl bromide, or  $\alpha,\alpha'$ -dibromoxylene produces<sup>14</sup>

(12) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1956.

(14) Dimethyl sulfate alkylation leads to products which were not identified except to note that neither  $CH_3SCH_3$  nor  $(CH_3S)_2$  was produced.

sulfide or disulfide organic products with no nmr evidence for  $RSC(O)SR$  or  $RSC(S)OR$ . A glpc investigation of the gaseous products from the benzyl bromide reaction with  $L_2PtS_2CO$  showed that only 1–2% of the carbon monoxide expected is liberated by the solution. The infrared spectrum of the solution gives a sharp CO stretch at  $2040\text{ cm}^{-1}$  which is many times more intense than the CO band in chloroform saturated with carbon monoxide (in CO-saturated  $CHCl_3$ , this band appears at  $2145\text{ cm}^{-1}$ ). Nitrogen or argon purging removes the carbon monoxide, as does evaporation of the solutions.

Attempts to introduce large quantities of carbon monoxide back into a  $CHCl_3$  solution containing the products of alkylation of  $L_2PtS_2CO$  were unsuccessful with pressures of CO up to  $\sim 100$  psi. On pressure release, only a small quantity of CO remained in the sample, as detected by its ir spectrum.

The platinum and palladium dithiocarbonates also react with  $HCl(g)$ ,  $Cl_2(g)$ ,  $I_2$ , and  $CH_3I$ . Only the geometry of the  $L_2M$  portion of the molecule was determined using nmr. With the halogens, the oxidation product does not appear to contain CO. With  $L_2PtS_2CO$ , iodine in chloroform produces an oxidation product which gives an nmr spectrum typical of a *cis*- $L_2Pt$  geometry.<sup>15</sup> This slowly rearranges to a *trans*- $L_2Pt$  species.

The reaction of 4-methylpiperidine with  $Pt(S_2CO-CH_2C_6H_5)_2$  in benzene shows spectral changes indicative of the formation of a 1:1 product with an isosbestic point (Figure 2) at  $4380\text{ \AA}$ . Additional base produces a new isosbestic point at  $4155\text{ \AA}$ . The near-ultraviolet spectrum of an independently prepared sample of the platinum dithiocarbamate is virtually identical with the spectrum of the final reaction product.

The reaction of *n*-propylamine with  $Co(S_2COCH_2C_6H_5)_3$ , followed by nmr in chloroform-*d*, showed second-order kinetics over the first 20 min. Eyring activation theory<sup>16</sup> leads to the kinetic parameters listed in Table II.

The dimer  $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$  also undergoes reaction with secondary amines such as  $HN(C_2H_5)_2$  to produce the analogous dithiocarbamate dimer. However, some ligand exchange occurs since mixtures of  $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$  and  $Ni_2(SCH_2C_6H_5)_2(S_2CN(C_2H_5)_2)_2$  in  $CHCl_3$  indicate the presence of a third component using thin layer chromatography. This same component also is produced by allowing the xanthate dimer to react with less than stoichiometric amounts of amine. However, it was not isolated.

## Discussion

As we indicated in a recent communication,<sup>7</sup> complexes of *gem*-disulfide ligands undergo a wide variety of interesting chemical reactions. In addition to olefin formation by pyrolysis (reaction 3) which will

(15) J. P. Fackler, Jr., J. Fetchin, J. Mayhew, W. C. Seidel, T. Swift, and M. Weeks, *J. Am. Chem. Soc.*, **91**, 1941 (1969).

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 101.

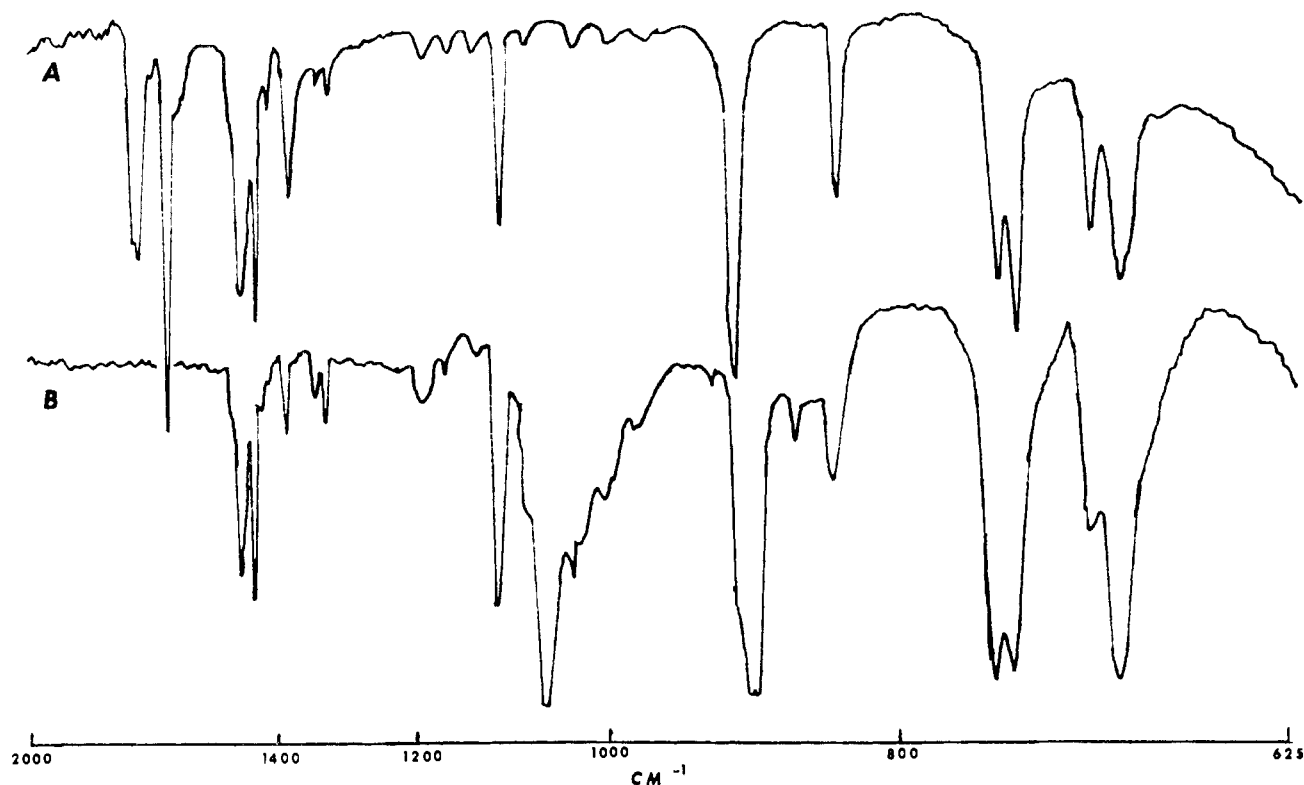
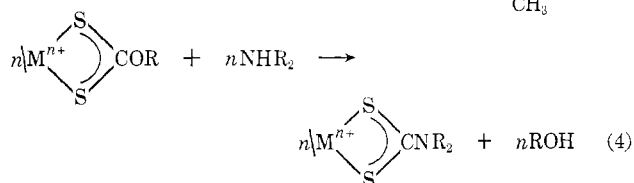
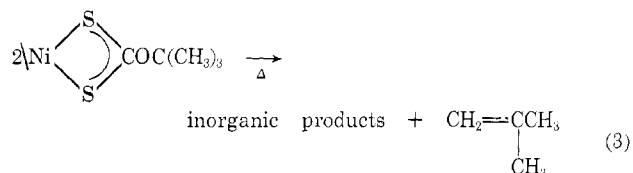
Figure 4.—Infrared spectra for Nujol mulls of (A)  $L_2PtS_2CO$  and (B)  $L_2PtS_2CS$ .

TABLE II  
REACTION OF COBALT (III) BENZYLXANTHATE  
WITH *n*-PROPYLAMINE IN CHLOROFORM-*d*

Temp, °C	$k, M^{-1} \text{ min}^{-1}$
6.0	0.162
12	0.175
17.5	0.20
23.5	0.19
28	0.29

$\Delta H^\ddagger \approx 4.5 \pm 2.0 \text{ kcal/mol}$      $\Delta S^\ddagger \approx -50 \pm 20 \text{ eu}$

form the subject of a future communication, metal xanthates readily undergo ligand nucleophilic substitution with amines to form dithiocarbamates (reaction 4). In the case of the nickel(II), palladium-

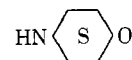


(II), and platinum(II) complexes the nucleophile may attack the complex initially either at the metal or on the ligand. In the case of the coordinately saturated cobalt(III) complex, attack directly on the metal atom is less likely. The resultant product in each of these reactions is dependent on the particular nucleophile

used as well as the metal ion. With phosphines the chemistry is significantly different from the chemistry observed with amines.

Alkali metal xanthates have long been known to react in the presence of alcohol with primary nitrogenous bases. The initial product, the dithiocarbamate anion, reacts further to form thiourea in the presence of sufficient amine.<sup>17</sup> The transition metal xanthates studied in this paper also undergo nucleophilic substitution with primary or secondary amines. The reaction stops with the dithiocarbamate, however, presumably because the metal ion is coordinated to both sulfur atoms of the ligand. Since these reactions occur in nonpolar or only weakly polar organic solvents, the influence of the solvent can be minimized.

The reaction of morpholine<sup>7</sup>



with  $\text{Ni}(\text{S}_2\text{CNH}_2)_2$  to produce ammonia and the dithiocarbamate derivative of morpholine was the first ligand reaction we observed with 1,1-dithiolates in which nucleophilic substitution had occurred. Since alkoxy groups are known to be good leaving groups in nucleophilic organic reactions,<sup>18</sup> it occurred to us that metal xanthates should behave in a similar manner. Indeed, essentially quantitative conversion of xanthates, formed from primary alcohols, can be achieved by reaction with amines. Reaction with xanthates of secondary and

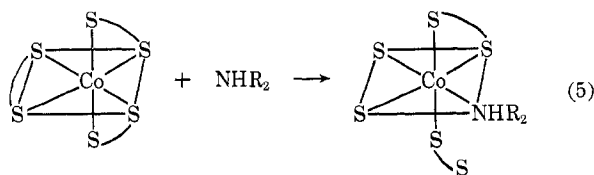
(17) P. A. Aravindakshan, A. Bhramaramba, G. V. Nair, and C. N. V. Nambury, *Indian J. Chem.*, **1**, 395 (1963).

(18) D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 364.

tertiary alcohols is somewhat more complicated owing to the presence of side reactions (*vide infra*). Since the benzyloxy group is a particularly good leaving group, we chose to examine the reaction of  $\text{Pt}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$  with 4-methylpiperidine in some detail. By following the reaction spectrophotometrically (Figure 2), it has been possible to show conclusively that reaction occurs first to form the mixed-ligand species, II, and in the presence of excess amine the bis-dithiocarbamate derivative.

It is significant that a mixed xanthate-dithiocarbamate complex is essentially the only species detected spectrophotometrically in the "carbamation" reaction (reaction 4) at a 1:1 ratio of complex to amine. This indicates that a dithiocarbamate ligand deactivates remaining xanthate ligands relative to their activity in the starting material. This result is consistent<sup>19</sup> with the evidence presented elsewhere<sup>5,6</sup> that the electron density at the metal atom in bis dithiocarbamates is greater than in bis xanthates. (The xanthate complexes of nickel(II) form base adducts with nitrogenous bases such as pyridine much more readily than do the dithiocarbamate complexes.<sup>6</sup>) No such deactivation is expected if dissociation of the xanthate complex occurs prior to reaction with the nitrogenous base. Electron-donating ligands coordinated to the metal atom also appear to reduce the electrophilicity of the xanthate  $\text{C}_1$  carbon atom in mixed-ligand complexes. With  $\text{L}_2\text{Cu}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$ , for example, no nucleophilic substitution occurs even with the excellent nucleophiles piperidine or morpholine. However, steric effects have not been sorted out.

While it is very difficult to prove the absence of chelate ring opening in the reaction of metal xanthates with amines, the reaction of methylpiperidine with  $\text{Pt}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$  and the reaction of *n*-propylamine with  $\text{Co}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_3$  are unlikely to involve metal-sulfur atom bond breaking simply because Pt(II)-S and Co(III)-S bonds are kinetically inert.<sup>20</sup> Also we have observed no evidence for amine-substitution products, reaction 5, as might be expected if metal-sulfur atom bond breaking were significant.

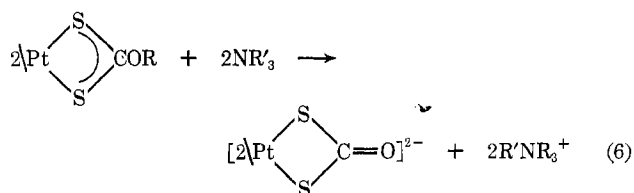


The reaction of  $\text{Co}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_3$  with *n*-propylamine in chloroform-*d* follows the kinetic order expected for a nucleophilic attack by the base on the ligand. If predissociation of a Co-S bond were important, the reaction might be expected to follow first-order kinetics, as commonly found for octahedral substitution in cobalt(III) complexes. Furthermore, the large

negative entropy of activation for the reaction is comparable with that of organic nucleophilic reactions involving direct attack on an aromatic ring.<sup>21</sup> The cobalt data, like the platinum(II) data, suggest a stepwise displacement by the amine of the alkoxy groups on the complex. Attempts are in progress to isolate and characterize mixed-ligand complexes indicated to be present by these studies.

Since mercaptide groups also are good leaving groups for nucleophilic substitution, the reaction observed between  $\text{Ni}_2(\text{SCH}_2\text{C}_6\text{H}_5)_2(\text{S}_2\text{CSC}_6\text{H}_5)_2$  and diethylamine was not surprising. The dithiocarbamate product obtained in this manner,  $\text{Ni}_2(\text{SCH}_2\text{C}_6\text{H}_5)_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ , also can be prepared by mixing the sodium mercaptide with  $\text{Na}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$  in water and then adding aqueous nickel(II) chloride.

In addition to the above nucleophilic substitution of the amine at the ligand  $\text{C}_1$  carbon atom site, other reactions may occur between metal xanthates and amines. For example, quinuclidine reacts with  $\text{Pt}(\text{S}_2\text{COCH}_2\text{C}_6\text{H}_5)_2$  to form a solution which contains the quaternized amine as indicated by its nmr spectrum. We suspect that the formation of an anionic dithiocarbamate complex occurs also, reaction 6, although we have not obtained direct proof for this.



Metal xanthates formed from tertiary alcohols are very unstable to  $\text{C}_2\text{-O}$  cleavage,<sup>8</sup> reaction 3. While the potassium salt of the xanthate formed from *t*-butyl alcohol and carbon disulfide has been isolated as a crystalline material which slowly decomposes over a period of weeks, an aqueous solution of this species will decompose to form olefins when various heavy-metal ions are added. With nickel(II) xanthates formed from secondary alcohols, pyrolysis at temperatures near  $150^\circ$  forms, among other things, some olefinic products. Alkyl xanthates have been known for some time to produce olefins in the Chugeav pyrolysis.<sup>22</sup> (Metal dithiophosphates apparently undergo a similar type of cleavage reaction upon pyrolysis at temperatures in excess of  $100^\circ$ .<sup>23</sup>) Thus processes which break the  $\text{C}_2\text{-O}$  bond may participate significantly in reactions of certain metal xanthates under various conditions.

Alkyl xanthates of the nickel triad react with certain aromatic phosphines first to form adducts and then products which require a  $\text{C}_2\text{-O}$  bond cleavage. Since the nickel system is complicated by the paramagnetic character of the adduct and the apparent instability of the dithiocarbamate product, no definitive results have been obtained. However, with the palladium(II) and platinum(II) xanthates, the reaction with phosphines

(19) Presumably metal atoms (or other ligands in a mixed ligand complex) which can effectively influence the electron density at the xanthate  $\text{C}_1$  carbon atom will influence the rate of nucleophilic substitution at this site.

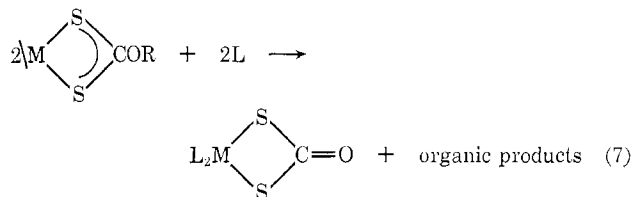
(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

(21) J. Bunnett, *Quart. Rev.* (London), **12**, 1 (1968).

(22) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

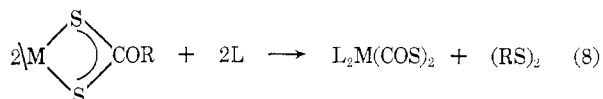
(23) J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, **32**, 647 (1967).

has been successfully characterized and the products identified. With both palladium(II) and platinum(II) xanthates, 1:1 adducts are the initial products.<sup>5,6</sup> Then, depending on the solvent, the particular phosphine, and the xanthate, the reaction may proceed to form a (phosphine)<sub>2</sub>MS<sub>2</sub>CO derivative and the S-alkyl xanthate. However, excess phosphine above the 1:1 mole ratio was required for the elimination reaction to occur, reaction 7, in all cases in which it was observed.



In the reaction, the ethyl group appears to be eliminated less readily than the benzyl group and the platinum(II) complex undergoes the reaction somewhat more readily than does the palladium(II) species. Carbon disulfide appears to inhibit the reaction relative to the solvent chloroform. Both the greater solvation of the phosphine by carbon disulfide compared with chloroform and the weakly polar character of the latter solvent may contribute to this solvent effect. The relative ability of the ethyl and benzyl groups to undergo cleavage at the C<sub>2</sub>-O bond is consistent with the greater stability of the benzylcarbonium ion.<sup>24</sup>

Characterization of the L<sub>2</sub>MS<sub>2</sub>CO species required the identification of the organic component formed by reaction of the phosphine with the metal xanthate. Elemental analysis of the inorganic component was insufficient to distinguish between the formation of L<sub>2</sub>M(COS)<sub>2</sub>, by a possible reductive elimination of an alkyl disulfide, reaction 8, or the dithiocarbonate



species. The presence of the benzyl disulfide as a minor product in the reaction of Pt(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> with methyldiphenylphosphine complicated this study. It appears, however, that this disulfide is formed by decomposition of the alkylation product S-benzyl-O-benzyl xanthate.<sup>25</sup> With the ethyl xanthate, it was possible to identify the principal organic component as S-ethyl-O-ethyl xanthate by means of nuclear magnetic resonance and mass spectrometry.

The final proof for the composition of the L<sub>2</sub>MS<sub>2</sub>CO species, III, X = O, was obtained by comparing it with L<sub>2</sub>MS<sub>2</sub>CS obtained by reaction of the well-characterized M(S<sub>2</sub>CS)<sub>2</sub><sup>2-</sup> complex<sup>12</sup> with the phosphine. Trithiocarbonate complexes of both palladium(II) and platinum(II) undergo substitution at the metal with phosphines to replace one of the CS<sub>3</sub><sup>2-</sup> ligands. A neutral complex results, reaction 9, which undoubtedly



(24) D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 275.

(25) G. Bulner and F. G. Mann, *J. Chem. Soc.*, 666 (1945).

edly has the planar structure presented by III, X = S. The nmr spectrum for methyl groups in L<sub>2</sub>MS<sub>2</sub>CS indicates a *cis* arrangement of the phosphine ligands (Figure 3), but the phosphorus-phosphorus coupling constant is not zero as usually is found in the case of *cis*-phosphine complexes of platinum(II) and palladium(II). In fact, with the palladium derivative<sup>26,27</sup> such significant P-P coupling occurs that the pattern for the protons is indicative of substantial "virtual coupling." However, the coupling is not nearly as large as is found in characterized<sup>27</sup> *trans*-phosphine complexes. The non-zero *J*<sub>P-P</sub> in these *cis* derivatives must be caused by the four-membered chelate ring and its influence on the LML bonding.<sup>26</sup>

The physical properties of the L<sub>2</sub>MS<sub>2</sub>CO and L<sub>2</sub>MS<sub>2</sub>CS complexes are very similar. As described earlier, their infrared spectra are identical except in the C=O and C=S stretching regions and the proton nmr spectra are nearly indistinguishable. The carbonate complex recently isolated by Nyman, *et al.*,<sup>28</sup> L<sub>2</sub>PtO<sub>2</sub>CO, may also have a similar structure.

It is interesting to note that dithiocarbonate complexes generally cannot be obtained directly from the ligand since it is unstable to disproportionation. At present the xanthate reaction is the only suitable way to obtain such species.

While detailed studies of the mechanism for the formation of the dithiocarbonate complexes from the xanthates have not been explored, it appears reasonable that nucleophilic attack by a sulfur atom of one xanthate complex on the C<sub>2</sub> carbon of another molecule constitutes an important step in the reaction. Using equal mixtures of ethyl and benzyl xanthates, it was possible to show that the major organic component (under conditions which do not produce alkyl exchange of the alkyl xanthates themselves) is the S-benzyl-O-ethyl xanthate. Thus nucleophilic attack by the sulfur of the ethyl xanthate on the benzyl group of another molecule appears to be kinetically favored over attack by a benzyl xanthate ligand on the ethyl group of another molecule. The absence of large quantities of S,O-dibenzyl xanthate and S,O-diethyl xanthate tends to eliminate intramolecular alkyl migration as the principal pathway for the reaction to occur. Why phosphines promote this reaction is not at present understood. They may increase the nucleophilicity of sulfur atoms on the complex or simply stabilize the dithiocarbonate product.

Metal dithiophosphate complexes undergo reactions similar in many respects to those of the xanthates.

(26) In the case of *trans*-C<sub>6</sub>H<sub>5</sub>P(CH<sub>3</sub>)<sub>2</sub>PtX<sub>2</sub>, *J*<sub>P-P</sub> has been estimated (W. MacFarlane, *J. Chem. Soc., A*, 1922 (1967)) to be ~90 cps while the analogous *trans* palladium complex displays a narrow, well-defined 1:2:1 triplet in which<sup>27</sup> *J*<sub>P-P</sub> is probably ~500-800 cps. In view of the small S-Ni-S angle (~77°) found in Ni(S<sub>2</sub>CS)<sub>2</sub><sup>2-</sup> (J. S. McKechnie, S. L. Miesel, and I. C. Paul, *Chem. Commun.*, 152 (1967)), it is reasonable to believe that the LML angle in L<sub>2</sub>Pd will be larger than 90°. Thus a residual P-P coupling in *cis*-L<sub>2</sub>PdS<sub>2</sub>CX sufficient to cause the methyl proton spectrum to be intermediate between examples for pure *cis* and *trans* palladium(II) complexes is not entirely unexpected. With the L<sub>2</sub>PtS<sub>2</sub>CX species this "virtual coupling" is much less apparent.

(27) A. Pidcock, *Chem. Commun.*, 92 (1968), and references therein.

(28) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc., A*, 561 (1968).



For example, thermal decomposition of metal dithiophosphates formed from ligands produced by allowing secondary alcohols to react with  $P_2S_5$  leads to substantial olefin formation.<sup>28</sup> Phosphines also apparently promote a carbon-oxygen bond cleavage since nearly quantitative yields of  $L_2PdS_2P(O)OC_2H_5$  are obtained when the palladium diethyldithiophosphate is treated with methyldiphenylphosphine in chloroform.

The nucleophilicity of the sulfur atoms in the 1:1 dithiolate complexes is shown by the reactions, Figure 1, we have observed between  $L_2PtS_2CO$  and various alkylating agents. Benzyl bromide reacts readily with the dithiocarbonate complex to produce benzyl disulfide and the *cis*- $L_2PtBr_2$  complex. Carbon monoxide must be produced in this reaction, but it is not present in the isolated products which are obtained in essentially quantitative yield. An infrared spectrum of the reaction mixture shows that the carbon monoxide remains in the chloroform solution in considerable excess of its normal solubility. It can be removed by bubbling nitrogen or argon through the solution and

also by evaporation of the solvent. The frequency of this CO band,  $\bar{\nu}$  2040  $cm^{-1}$ , indicates that the carbon monoxide is associated with the metal. While a *cis*- $L_2PtCOBr^+$  species might be expected as a reaction product, the CO frequency appears to be too low by comparison with the known  $\bar{\nu}_{CO}$  values of  $\sim 2100$   $cm^{-1}$  in *trans*-(phosphine) $_2Pt(CO)X^+$  species.<sup>29</sup> However, *cis*-(phosphine) $_2Pt(CO)X^+$  species have not been reported so no direct comparison can be made. The ease with which CO is removed and the irreversibility of its removal are still puzzling. Also a detailed explanation of why a disulfide is formed with benzyl bromide while sulfides are produced, along with COS, when some other alkylating agents are used, Figure 1, is not available at present.

**Acknowledgment.**—The donors of the Petroleum Research Fund as administered by the American Chemical Society are gratefully acknowledged for partial support of this work, along with the National Science Foundation (Grant GP-7889).

(29) M. J. Church and M. J. Mays, *J. Chem. Soc., A*, 3074 (1968).

CONTRIBUTION NO. 2376 FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

## The Stepwise Aquation of the 1,6-Dibromo-2-aquo-3-ammineethylenediaminechromium(III) Cation to the Tetraaquoethylenediaminechromium(III) Cation<sup>1</sup>

BY THEODORE J. WILLIAMS AND CLIFFORD S. GARNER

Received February 10, 1969

The kinetics of the successive aquation steps of green  $Cr(en)(NH_3)(OH_2)Br_2^+$  to  $Cr(en)(OH_2)_4^{3+}$  have been investigated by spectrophotometry and also by  $Br^-$  release for the first two aquation steps. The first step produces magenta  $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ , and was studied in 0.1–2 *F*  $HClO_4$  ( $\mu = 0.3$ –2 *M*,  $NaClO_4$ ) from 20 to 35°. At 25° the first-order rate constant is  $k_1 = 4.1 \times 10^{-4}$   $sec^{-1}$  (0.1–0.3 *F*  $HClO_4$ ;  $\mu = 0.3$  *M*,  $NaClO_4$ ),  $E_a = 20.7 \pm 0.3$   $kcal\ mol^{-1}$ , and  $\log PZ(sec^{-1}) = 11.81 \pm 0.23$ . Aquation of the monobromo product appears to give a single pink isomer of  $Cr(en)(NH_3)(OH_2)_3^{3+}$ . In 0.15–1 *F*  $HClO_4$  ( $\mu = 1$  *M*,  $NaClO_4$ ) at 34–53° the observed hydrolysis rate constant  $k_{2,obsd}$  has the form  $k_{2,obsd} = k_2 + (k_2'/[H^+])$ , where  $k_2$  is the first-order rate constant for aquation of magenta  $Cr(en)(NH_3)(OH_2)_2Br^{2+}$  and  $k_2'$  has been interpreted as  $k_{2h}K_a$ , where  $k_{2h}$  is the first-order rate constant for aquation of  $Cr(en)(NH_3)(OH_2)(OH)Br^+$  and  $K_a$  is the first acid dissociation constant of magenta  $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ . At 25°  $k_2 = 4 \times 10^{-5}$   $sec^{-1}$  (by extrapolation),  $E_a = 23.2 \pm 0.1$   $kcal\ mol^{-1}$ , and  $\log PZ(sec^{-1}) = 11.57 \pm 0.09$ . At 34° and  $\mu = 1$  *M*,  $k_{2h} \approx 0.01$   $sec^{-1}$ . Aquation of pink  $Cr(en)(NH_3)(OH_2)_3^{3+}$  to  $Cr(en)(OH_2)_4^{3+}$  was studied in 0.15–3 *F*  $HClO_4$  from 45 to 60° and was found to be first order. In 0.15–1 *F*  $HClO_4$  ( $\mu = 1.0$  *M*),  $k_3 = 5.7 \times 10^{-5}$   $sec^{-1}$  at 52.50° (ca.  $1 \times 10^{-5}$   $sec^{-1}$  at 25° by extrapolation),  $E_a = 27.5 \pm 0.3$   $kcal\ mol^{-1}$ , and  $\log PZ(sec^{-1}) = 14.08 \pm 0.17$ . There is no evidence for Cr–N bond rupture involving the ethylenediamine ligand in any of these reactions. The kinetic results confirm the *trans*-dibromo and *trans*-bromoaquo configurations spectrophotometrically assigned earlier to green  $Cr(en)(NH_3)(OH_2)Br_2^+$  and magenta  $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ .

### Introduction

The aquation kinetics of the green isomer of dibromo-aquoammineethylenediaminechromium(III) cation,  $Cr(en)(NH_3)(OH_2)Br_2^+$ , and its successive aquation products is interesting for a number of reasons. As mem-

bers of a series of halomonoethylenediaminechromium(III) cationic complexes, this dibromo complex and its monobromo daughter provide data for comparison with their analogs. These comparisons can be used to support the earlier tentative isomeric assignments made for the dibromo and monobromo complexes. Other comparisons demonstrate the effect on the loss of a ligand through aquation due to a change in other ligands of the coordination sphere. A comparison of the aqua-

(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 170, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P170-1 to the AEC. (b) Abbreviations used: en, ethylenediamine; dien, diethylenetriamine.