actions. Application of these expressions to the six "cross reactions" (5)–(10) in Table I which all involve similarly charged reactants (−1 and −2) shows quite good agreement between the calculated and experimentally determined rate constants. This is particularly so when one considers the approximate values of certain E_0 values and the large differences in k_{11} and k_{22} and the large values for K_{12} which exist in some cases.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work (Grant GP-5671).

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Preparation and Reactions of Tetracarbonyl-μ-bis(difluorodithiophosphato)-dirhodium(I)

BY FREDERICK A. HARTMAN AND MAX LUSTIG

Received July 29, 1968

Several new rhodium compounds having the empirical formulas $Rh(CO)_2(S_2PF_2)$, $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$, $Rh(CO)[As(C_6H_5)_3](S_2PF_2)$, and $Rh(CO)[Sb(C_6H_5)_3](S_2PF_2)$ have been synthesized. The difluorodithiophosphate $PS_2F_2^-$ ligand[1,2] and its conjugate acid HPS_2F_2[1,3,4] are useful intermediates for the formation of compounds containing the $PS_2F_2^-$ group.[4,5] The chemistry of this ligand is, indeed, similar to that of the analogous dialkoxydithiophosphate ligands.[6]

Experimental Section

Materials.—Tetracarbonyl-μ-dichloro-dirhodium(I) was synthesized from $RhCl_3 \cdot 3H_2O$ (Alfa Inorganics, Inc.) and CO. The cesium salt of difluorodithiophosphate was prepared as described in the literature.[2] Triphenylphosphine, -arsine, and -stibine were obtained from commercial sources and used without further purification. Solvents were distilled from molecular sieves (Linde 5A) immediately before use.

Apparatus and General Procedure.—Infrared spectra of solid samples were measured on a Perkin-Elmer 521 spectrometer. The ^{19}F nmr spectra were obtained with a Varian Model V4310 spectrometer operating at 40 Mc using benzene as a solvent for the samples and fluorotrichloromethane as an internal standard. Solutions were placed in 5-mm o.d. tubes. Molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 301, in benzene solution.

Preparation of $[Rh(CO)_2(S_2PF_2)]_2$.—In a typical preparation, tetracarbonyl-μ-dichloro-dirhodium(I) (0.952 g, 2.45 mmol) dissolved in 100 ml of pentane was stirred with an excess af $CsPS_2F_2$ (1.34 g, 5.05 mmol). After 4 hr, the solvent was removed under reduced pressure (*ca.* 20 mm, between 0 and −10°). The residue was sublimed *in vacuo* onto a probe cooled to about −30°. The yield of the orange-red solid (mp 48°) was 0.640 g (44.6%). *Anal.* Calcd for $C_4F_4O_4P_2Rh_2S_4$: C, 8.22; F, 13.01; P, 10.62; mol wt, 584. Found: C, 8.20; F, 13.45; P, 9.2; mol wt, 590. The ^{19}F nmr spectrum showed a doublet ($J_{P-F} = 1312$ cps) at ϕ 3.4.

Preparation of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$.—Triphenylphosphine (0.314 g, 1.20 mmol) and $[Rh(CO)_2(S_2PF_2)]_2$, (0.350 g, 0.60 mmol) were weighed into a 50-ml flask. The flask was cooled to −196° and evacuated. Approximately 5 ml of benzene was distilled into the flask. Upon warming to room temperature, the solution changed from deep red to yellow and carbon monoxide was evolved. After 0.2 hr the solvent was removed and the residue was extracted with pentane until the extracts were colorless. The pentane solution was concentrated in a stream of nitrogen before cooling to 0°. Yellow crystals were collected and vacuum dried. The product weighed 0.510 g (81% of theory) and decomposed above 100°. *Anal.* Calcd for $C_{19}H_{15}F_2OP_2RhS_2$: C, 43.47; H, 2.87; mol wt, 526. Found: C, 43.50; H, 2.87; mol wt, 544. A doublet centered at ϕ 2.7 ($J_{P-F} = 1312$ cps) was observed in the nmr spectrum.

When a benzene solution of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$ was allowed to interact with excess triphenylphosphine, no further evolution of carbon monoxide was observed even when the solution was heated to 60° for several hours.

Reaction of $[Rh(CO)_2(S_2PF_2)]_2$ with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$.—Using a procedure similar to that described for the preparation of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$, both $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ react with the parent dicarbonyl. Carbon monoxide, detected by mass spectral analysis, was again evolved. Brownish red solids were obtained upon removal of benzene and subsequent recrystallization from CH_2Cl_2–C_5H_{12} mixtures. The outcome of these reactions appears to be the same when excess arsine or stibine is used. *Anal.* Calcd for $C_{19}H_{15}AsF_2OPRhS_2$: C, 40.02; H, 2.65; F, 6.66; P, 5.44; mol wt, 570. Found: C, 40.00; H, 2.66; F, 6.4; P, 4.9; mol wt, 700. Calcd for $C_{19}H_{15}F_2OPRhSbS_2$: C, 36.98; H, 2.45; F, 6.16; P, 5.02; Sb, 19.74; mol wt, 617. Found: C, 36.65; H, 2.50; F, 6.2; P, 4.8; Sb, 19.6; mol wt, 2100.

Results and Discussion

The reaction of tetracarbonyl-μ-dichloro-dirhodium(I) with $CsPS_2F_2$ yields a volatile, orange solid of empirical formula $Rh(CO)_2(S_2PF_2)$. The fluorine magnetic resonance spectrum of the complex consists of a doublet caused by phosphorus–fluorine coupling centered at ϕ 3.4 ($J_{P-F} = 1312$ cps). Additional splitting due to ^{103}Rh was not observed. The position of the signal and the magnitude of the PF spin-spin coupling are consistent with a chelate attachment of the difluorodithiophosphato group.[4,5] Molecular weight measurements indicate that the complex is dimeric in benzene solution.

Examination of the infrared spectrum (Table I) of the complex provides further insight into the structure of the new dicarbonyl. Absorptions associated with the P–S stretch are observed at 692 and 670 cm^{-1} in Nujol whereas the related absorptions of $CsPS_2F_2$ occur at 735 and 710 cm^{-1}. The shift of the P–S stretch to lower wave number values in the complex implies coordination of the PS_2F_2 entity to rhodium through equivalent sulfur atoms. The positions of the four absorptions in the metal carbonyl region are characteristic of terminal carbonyl ligands. Moreover, the spectral features in this region are similar to those of [Rh-

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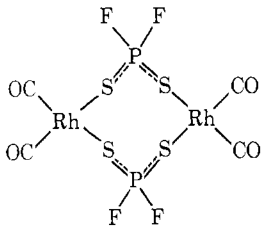
TABLE I

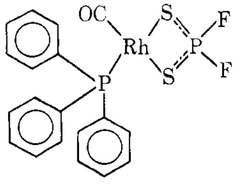
INFRARED DATA[a] (cm^{-1})

Complex	Metal–carbonyl str freq	P=S
$[Rh(CO)_2(S_2PF_2)]_2$	2088 s, 2075 ms, 2025 s, 1998 ms[b]	692 s, 670 sh
	2083 s, 2070 sh, 2020 s, 1992 mw	690 s, 670 sh
$[Rh(CO)_2(CH_3CO_2)]_2$	2083 vs, 2067 vs, 2027 vs, 1980 s	. . .
$Rh(CO)[P(C_6H_5)_3](S_2PF_2)$	1991 s	697 s, 689 s
$\{Rh(CO)[As(C_6H_5)_3](S_2PF_2)\}_n$[c]	2025 s, 2015 sh, 1996 s	702 s, 688 s
$\{Rh(CO)[Sb(C_6H_5)_3](S_2PF_2)\}_n$[c]	2027 s, 2010 s, 1995 sh	699 s, 685 s

[a] Nujol mulls unless noted otherwise. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] Pentane solution. [c] Chloroform solution.

$(CO)_2(CH_3CO_2)]_2$[7] which contains bridged acetate groups. The composite data suggest structure I for the parent difluorodithiophosphato complex.


I


II

The reaction of I with triphenylphosphine proceeds with the evolution of carbon monoxide and yields air-stable, yellow crystals. The physical and chemical properties of this material indicate the rupture of the bridged dithiophosphates and the rearrangement to a four-atom chelate as depicted in structure II. When I was allowed to react with triphenylarsine or -stibine, CO was again evolved and air-stable solids were obtained. Analytical data are in close agreement with complexes containing one carbonyl group, one triphenylarsine or -stibine, and one $PS_2F_2^-$ ligand per rhodium atom. Molecular weight determinations indicate that these materials are polymeric. However, the unexpectedly complex patterns in the metal–carbonyl region of the infrared spectra preclude acceptable structural assignments at this time.

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Derivatives of Dichlorohexaphenylphosphonitrile Tetramer

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Received August 9, 1968

During an investigation of the formation of polymers containing the phosphonitrile ring systems, dichlorohexaphenylphosphonitrile tetramer (Ia), mp 303–304°, was prepared by treating sodium azide with a mixture of diphenylchlorophosphine and phenyldichlorophosphine.[1] This communication describes the preparation of several amine derivatives and some interconversions among halogen, hydroxy, and amine ligands to give a series of tetrameric compounds with the general formula $(C_6H_5)_6X_2P_4N_4$ where X = Cl (Ia, Ib), OH (II), Br (III), $N(CH_3)_2$ (IV), and F (V).

Dihydroxyhexaphenylphosphonitrile tetramer (II) may be prepared by the hydrolysis of Ia in hot, aqueous pyridine.[1] Treatment of II with an excess of PCl_5 resulted in the regeneration of Ia in good yield

$$\mathrm{Ia} \underset{PCl_5\text{-}CHCl_3}{\overset{H_2O\text{-}py}{\rightleftharpoons}} \mathrm{II}$$

The reaction of II with $SOCl_2$, however, gave two isomeric forms of dichloro tetramer: Ia, mp 303–304°, in 67% yield, and a low-melting form (Ib), mp 194–195°, in 12% yield. This result is analogous to that found for diazidohexaphenyltetraphosphonitrile which has two isomers melting at 147.5–148 and 206–208°.[2] With the exception of the diazido and dichloro compounds, no other isomers of this cyclic tetramer have been isolated. Elucidation of the structure of these isomers awaits the attention of an X-ray crystallographer.

Hydrolysis of the low-melting isomer (Ib) in aqueous pyridine yielded the same product (II) that was obtained from hydrolysis of Ia, based upon comparison of infrared spectra.

The six amine derivatives shown in Table I were prepared by adding an excess of the appropriate amine to a chloroform suspension of Ia.

Dibromohexaphenylphosphonitrile tetramer (III) was prepared from II and phosphorus pentabromide; however, attempts to synthesize III by allowing thionyl bromide to react with II yielded no characterizable products.

The preparation of trimethyltrichlorophosphonitrile trimer, $(CH_3(Cl)PN)_3$, by treatment of trimethyltrisdimethylaminophosphonitrile trimer, $(CH_3((CH_3)_2N)PN)_3$, with anhydrous hydrogen chloride has been described.[3] In the present work, the cleavage of dimethylamino groups from phosphorus has been used to prepare Ia and III from hexaphenylbis(dimethylamino)phosphonitrile tetramer (IV) by reaction with an excess of the appropriate hydrogen halide

$$\mathrm{IV} \xrightarrow[CHCl_3]{\text{excess } HX} \mathrm{Ia \ or \ III} + (CH_3)_2NH \cdot HX$$

However, no identifiable products were isolated from the reaction of IV with hydrogen iodide, and none of the starting material was recovered.

Replacement of chlorine by fluorine in Ia was accomplished by use of cesium fluoride in refluxing acetonitrile. Other alkali metal fluorides in nitrobenzene as the solvent were employed in this substitution reaction, although the yield of the difluoro analog was considerably lower under these conditions.

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