concentrations, yields as high as 90% of the desired products can be obtained. Sulfoxides such as phenyl sulfoxide which do not have a methyl or methylene carbon adjacent to the sulfur fail to give the expected derivatives under the reaction conditions described in this paper. Acetyl chloride has also been used as the acylating agent, but its reaction with sulfoxides is exothermic enough to create a potential hazard and therefore it is less desirable than acetic anhydride.

Since earlier workers[4,5] did not report the proton magnetic resonance spectra of the dimethyl sulfide derivatives of $B_{12}H_{12}{}^{2-}$, we were interested in seeing how the methyl protons compare with the corresponding protons in derivatives of $B_{10}H_{10}{}^{2-}$. The first thing which should be noted is the fact that despite the intervening positively charged sulfur the charge density of the adjacent boron appears to influence the chemical shift of the methyl protons. The effect shows up in two ways. Thus the conversion of the singly charged $B_{12}H_{11}S(CH_3)_2{}^-$ to the neutral $B_{12}H_{10}[S(CH_3)_2]_2$ shifts the position of the proton resonance from τ 7.79 to 7.53. At the same time these protons appear to resemble the corresponding protons in the equatorially substituted $B_{10}H_{10}{}^{2-}$ (τ 7.63 in 2-$B_{10}H_9S(CH_3)_2{}^-$) more than they do those in the apically substituted isomers[3] (τ 6.92 in 1-$B_{10}H_9S(CH_3)_2{}^-$). This fact is consistent with the charge distribution calculations which assign a value of −0.17 to each of the 12 equivalent borons in $B_{12}H_{12}{}^{2-}$ and −0.17 and −0.33, respectively, to the equatorial and apical borons in the $B_{10}H_{10}{}^{2-}$ ion.[8] In view of our results, it is surprising that the conversion of 1-$B_{10}H_9S(CH_3)_2{}^-$ to 1,10-$B_{10}H_8[S(CH_3)_2]_2$ only shifts the position of the apical methyl-proton peaks from τ 6.92 to 6.95. The equatorially substituted derivatives exhibit a similar insensitivity to the total ionic charge.[3]

Experimental Section

Instruments and Reagents. The infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer; the proton nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer at 60 Mc. The following compounds were obtained: $Na_2B_{12}H_{12}\cdot 2H_2O$, Du Pont Chemical Co.; methyl sulfoxide, *n*D 1.4790, lot 2171, Aldrich Chemical Co.; *n*-propyl sulfoxide, *n*D 1.4633, lot 080607, Aldrich Chemical Co.; acetic anhydride, lot 702789, Fisher Chemical Co.; tetramethylammonium hydroxide, supplied as 10% aqueous solution, Eastman Organic Chemicals.

$B_{12}H_{11}S(CH_3)_2{}^-$. To a 25-ml portion of acetic anhydride, 50% vol in methyl sulfoxide, was added 1.077 g of $Na_2B_{12}H_{12}\cdot 2H_2O$. After the clear solution was maintained at 50° for 27 hr, it was poured into 450 ml of 2-propanol and stirred for 10 min; then 15 ml of aqueous tetramethylammonium hydroxide was added dropwise with continued stirring. The white precipitate which formed was filtered and dried *in vacuo*. The filtrate was saved for later recovery of the disubstituted product. The precipitate was recrystallized twice from 150-ml portions of water. The dried product weighed 0.791 g (62%): mp 192–194.5° (cor); nmr (DMSO-d_6) τ 7.79 (s, 1, $[CH_3]_2S$) and 7.12 ppm (s, 2, $[CH_3]_4N^+$); the principal ir bands (KBr wafer) are at 3015, 2490, 1475, 1415, 1325, 1175, 1065, 1040, 990, 965, 950, 835, 825, and 710 cm^{-1}. *Anal.* Calcd for $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$: C, 26.01; H, 10.55; N, 5.06; B, 46.82. Found: C, 26.05; H, 10.48; N, 5.07; B, 46.62.

$B_{12}H_{10}[S(CH_3)_2]_2$. The filtrate from the precipitation described above was flash evaporated to 50 ml and stirred into 250 ml of water. The white precipitate which appeared was removed by filtration, dried *in vacuo*, and twice recrystallized from 20-ml portions of 95% ethanol. The dried crystals weighed 0.146 g (12%): mp 220.5–234.5° dec; nmr (DMSO-d_6) τ 7.53 ppm (s, 1, $[CH_3]_2S$); tlc (silica gel eluted with 1,2-dichloroethane) two isomers reducing $PdCl_2$ to black metal were distinguished; the principal ir bands (KBr wafer) are at 3015, 2500, 1425, 1325, 1025, 990, 960, 850, 800, and 720 cm^{-1}. *Anal.* Calcd for $B_{12}H_{10}[S(CH_3)_2]_2$: C, 18.19; H, 8.40; B, 49.12; S, 24.28. Found: C, 18.21; H, 8.53; B, 49.35; S, 23.88.

In another experiment a 0.7545-g sample of $Na_2B_{12}H_{12}\cdot 2H_2O$ was dissolved in a solution consisting of 10 ml of acetic anhydride in 20 ml of methyl sulfoxide and the reaction mixture was allowed to stand at room temperature for 3 weeks when it was poured into 250 ml of 2-propanol and stirred for 15 min. Addition of 20 ml of aqueous tetramethylammonium hydroxide to the 2-propanol solution precipitated $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$, which was removed by filtration, recrystallized from water, and dried. It weighed 0.0875 g (9.4%). The filtrate was mixed with 500 ml of water and the resulting precipitate after two recrystallizations from 95% ethanol and drying weighed 0.7947 g. This represents a yield of 89% of $B_{12}H_{10}[S(CH_3)_2]_2$.

$B_{12}H_{11}S(CH_2CH_2CH_3)_2{}^-$. A 1.35-g portion of *n*-propyl sulfoxide was diluted to 10 ml with acetic anhydride. To this was added 1.17 g of $Na_2B_{12}H_{12}\cdot 2H_2O$. After 5 min of stirring and crushing, the solids had completely dissolved and the homogeneous reaction mixture was left standing for 13 hr at 25°. It was then quenched by dilution to 50 ml with 2-propanol and placed in a freezer overnight. The mixture was filtered cold, the small amount of solid residue discarded, and the filtrate was treated with 6 ml of aqueous tetramethylammonium hydroxide. The precipitate which appeared at this point was removed by filtration and washed with two 30-ml portions of 2-propanol and then dried *in vacuo*. The white crystals were recrystallized from 120 ml of water. Their dry weight was 1.59 g (91.5%): mp 266–266.5°; nmr (DMSO-d_6) τ 9.02 (τ 3, $[CH_3CH_2CH_2]_2S$, 8.23 (m, 2, $[CH_3CH_2CH_2]_2S$), 7.10 (t, 3, $[CH_3CH_2CH_2]_2S$), and 6.86 ppm (s, 6, $[CH_3]_4N^+$); the principal ir bands (KBr wafer) are at 3010, 2950, 2920, 2860, 2500, 1480, 1450, 1410, 1280, 1060, 1035, 265, 945, 820, and 710 cm^{-1}. *Anal.* Calcd for $(CH_3)_4NB_{12}H_{11}S(C_3H_7)_2$: C, 36.04; H, 11.19; N, 4.30; S, 9.60; B, 38.92; equiv wt, 333 g. Found: C, 35.88; H, 11.17; N, 4.47; S, 9.47; B, 38.74; equiv wt, 328 g.

Registry No. $(CH_3)_4NB_{12}H_{11}S(CH_3)_2$, 37291-09-1; $Na_2B_{12}H_{12}\cdot 2H_2O$, 12448-20-3; $B_{12}H_{10}[S(CH_3)_2]_2$, 37291-10-4; $(CH_3)_4NB_{12}H_{11}S(C_3H_7)_2$, 37291-13-7; *n*-propyl sulfoxide, 4253-91-2; acetic anhydride, 108-24-7; methyl sulfoxide, 67-68-5.

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Mechanism of Photosubstitution in Rhodium(III) Chloroammines

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Received November 30, 1972

Previous photochemical investigations of d^6 systems have focused mainly on the ammine complexes of cobalt(III) which, although undergoing facile photoredox decomposition upon charge transfer to metal (CTTM) excitation, show little photoreactivity in the wavelength region of the first d–d transition.[1-3] The situation is quantitatively different with rhodium(III) amines. The d–d bands are very photoactive, in some cases more so than the CTTM ones.[4-8] In addition,

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Table I. Direct Photolysis Results for Several Rhodium(III)–Ammine Complexes

Compd	Wavelength irradiated, nm	Product yields[a]			Predominant product
		ϕ_{Cl^-}	ϕ_{NH_3}	ϕ_{H^+}	
$Rh(NH_3)_5Cl^{2+}$	358	0.13 ± 0.01[b]			$Rh(NH_3)_5OH_2{}^{3+}$
trans-$Rh(NH_3)_4Cl_2{}^+$	407	0.13 ± 0.02	$<2 \times 10^{-3}$		*trans*-$Rh(NH_3)_4(OH_2)Cl^{2+}$
	407	0.14 ± 0.01[c]			
	358[d]	0.17			
trans-$Rh(en)_2Cl_2{}^+$ [e]	407	0.057 ± 0.002		$<3 \times 10^{-3}$	*trans*-$Rh(en)_2(OH_2)Cl^{2+}$
	407	0.054[c]			
trans-$Rh(cyclam)Cl_2{}^+$ [e]	407	0.011 ± 0.001		$<10^{-4}$	*trans*-$Rh(cyclam)(OH_2)Cl^{2+}$

[a] Where quoted, error limits represent mean deviations for two or more runs. [b] Kelly and Endicott[5] reported $\phi_{Cl^-} = 0.16$ and $\phi_{NH_3} < 10^{-3}$ at 350 nm; Moggi[4] gave $\phi_{Cl^-} = 0.14$ at 365 nm. [c] Solution deaerated by purging with helium gas. [d] Wavelength of the minimum between the two ligand field bands. [e] en = ethylenediamine; cyclam = 1,4,8,11-tetraazacyclotetradecane.

luminescence, seldom seen from cobalt(III) ammines,[9] has been observed for several rhodium(III) ammines at low temperature.[10-12] We report here a photochemical study of several rhodium(III)-chloroammine complexes, the results of which allow inference as to the mechanism of reaction following ligand field or d–d excitation.

Experimental Section

The compounds, listed in Table I, were prepared by literature methods[13,14] and characterized both by spectroscopy and by elemental analysis. Solutions were in the range 2×10^{-3} to 3×10^{-3} *M* in complex and were acidified to pH 3.0 with nitric acid. Irradiations were at room temperature (26 ± 2°) and in the wavelength region of the first ligand field band (${}^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h symmetry) and were made with the use of a PEK lamp and suitable interference and blocking filters. Light intensities were measured by ferrioxalate actinometry.[15] Released chloride ion was determined by titration with mercuric nitrate using diphenylcarbazone as the indicator.[16] Free ammonia was found colorimetrically as indophenol.[17] Upper limits to the quantum yields for proton uptake, ϕ_{H^+}, were estimated from the lack of any noticeable pH change following irradiation. Product stereochemistry was assigned from the observed spectral changes.

Results and Discussion

The photochemical results are summarized in Table I. Chloride aquation is the predominant reaction in all cases, there being no indication of any lasting decoordination of an ammine function. The products are the corresponding *trans*-aquochloro species; in all cases, clean isosbestic points are maintained to more than 25% reaction, allowing a clear identification of the product and also indicating that no significant secondary photolysis occurs. Photoanation is not important; ϕ_{Cl^-} is unchanged in 0.1 *M* Cl^- and decreases at most by 10% in 1 *M* Cl^-, in the cases of *trans*-$Rh(NH_3)_4Cl_2{}^+$ and *trans*-$Rh(cyclam)Cl_2{}^+$.

The results contrast with those for the analogous chromium(III) complexes. While only chloride aquation is observed (as predicted by established rules[18]), the products are *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [19] and *cis*-$Cr(en)_2(OH_2)Cl^{2+}$,[20] formed in the high and relatively uniform respective yields of 0.37 and 0.32. Imposition of stereorigidity by using the belt ligand cyclam prevents isomerization and drops ϕ_{Cl^-} to about 3×10^{-4}, suggesting that a concerted process is preferred.[21] In the case of the Rh(III) series, however, ϕ_{Cl^-} drops in small and relatively uniform stages (0.13, 0.056, 0.011), and, moreover, the photoproduct is the *trans*-aquochloro complex in *all* cases. It thus seems clear that the mechanism of the excited-state reaction differs between the two families of complexes.

It appears that the photochemistry of rhodium(III) ammines originates from the lowest triplet state[5] (note, however, the lack of any oxygen effect on ϕ_{Cl^-}) which in D_{4h} symmetry is ${}^3E_g$. The change in electron density relative to the ground state should strongly labilize the ligands lying along the *z* direction (predicted by ligand field theory to be primarily the Cl-Cl axis[22]), while the continued occupancy of the remaining orbitals should act to stabilize the basic tetragonal symmetry of the molecule. It thus seems reasonable on ligand field grounds that the "thexi" (thermally equilibrated excited[23]) state reacts by direct dissociation of a chloride ligand.

Our experimental findings support such a mechanism[24] in that increasing the degree of chelation or ring stricture in the plane perpendicular to the labilized axis has no major effect (relative to chromium(III) ammines) on ϕ_{Cl^-} and in that the isomeric configuration is retained during the photoreaction. It can be argued that ϕ_{Cl^-} should be entirely independent of the nature of the belt ligands in the case of a direct dissociative process; however, there may well be some participation of the incoming water ligand and this could be hindered by increasing ring stricture. Alternatively, the decrease in ϕ_{Cl^-} in the Rh(III) series may result from changes in the efficiency of formation of the thexi state or in the rate of its radiationless deactivation.

Registry No. $Rh(NH_3)_5Cl^{2+}$, 15379-09-6; *trans*-$Rh(NH_3)_4Cl_2{}^+$, 38781-29-2; *trans*-$Rh(en)_2Cl_2{}^+$, 18539-17-8; *trans*-$Rh(cyclam)Cl_2{}^+$, 38781-23-6; $Rh(NH_3)_5OH_2{}^{3+}$, 15337-79-8; *trans*-$Rh(NH_3)_4(OH_2)Cl^{2+}$, 38781-25-8; *trans*-$Rh(en)_2(OH_2)Cl^{2+}$, 15337-41-4; *trans*-$Rh(cyclam)(OH_2)Cl^{2+}$, 38781-26-9.

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Acknowledgment. These investigations were supported in part by Grant GP-27984X between the National Science Foundation and the University of Southern California.

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Fluorophosphine Ligands. IX. Reactions of Difluorophosphine with Alcohols

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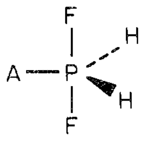
Received December 19, 1972

The controlled interaction of alcohols and primary or secondary amines with halophosphines is known to proceed in accordance with the general equation

$$PR_yX_{3-y} + AH \rightarrow HX + PR_yX_{2-y}A$$

where AH equals amine or alcohol, X equals halogen, and R signifies any other group.[2] Removal of HX through interactions with a suitable base will drive the reaction to completion. Yields are generally good with few side products. One of the most logical mechanisms for this process involves a pentacoordinate phosphorus intermediate.[3] The pentacoordinate complexes of general compositions $HF_2P{\cdot}HOR$ and $HF_2P{\cdot}HSR$ have now been isolated at low temperatures. The adducts have been unequivocally characterized as five-coordinate species by spectroscopic techniques. The data support the expected trigonal-bipyramidal structure with the fluorines in the apical positions



where A is OR or SR

Although several alkoxyfluorophosphoranes have been isolated,[4-6] the adducts reported herein are the first reported cases of a dihydridoalkoxyfluorophosphorane.[7,8]

Experimental Section

Materials and General Techniques. The F_2PH was prepared by literature methods.[9] Thioethanol was obtained from Eastman Organic Chemicals and used without purification. High-vacuum techniques were used throughout. Infrared spectra were recorded on a Beckman IR-20 using a gas cell with KBr windows. Nmr spectra for ^{19}F and ^1H were recorded on a Varian HR 56/60 spectrometer operating at 56 Hz for ^{19}F and 60 Hz for ^1H at $-60°$. Chemical shifts for fluorine are referred to $CFCl_3$ by tube interchange; for protons tetramethylsilane was used as an internal standard. Spectra for ^{31}P were obtained on a Varian HA-100 spectrometer operating at 40.4 Hz at $-60°$. Chemical shifts are referred to H_3PO_4 as external standard (tube interchange).

Synthesis of H_2F_2POR. Equimolar samples of HPF_2 and ROH ($R = CH_3, C_2H_5$) were condensed at $-196°$ into a 75-cm^3 reaction bulb. The mixture was allowed to warm slowly to 0°. The sample was condensed rapidly into an nmr tube at $-196°$ after which the tube was sealed. Decomposition in the gaseous state at room temperature occurred in less than 1 min. For this reason temperatures were held below 0°.

Nmr and Ir Spectra for $F_2H_2POCH_3$. The ^{19}F spectrum consists of a doublet (δ 40 ppm, $J_{FP} = 713$ Hz) each member of which is split into a triplet ($J_{FPH} = 104$ Hz). The ^{31}P spectrum is a triplet (δ 39.8 ppm, $J_{PH} = 805$ Hz) each member of which is split into a triplet ($J_{PF} = 704$ Hz). No further splitting was observed. The proton spectrum is a doublet (δ_{HP} -6.6 ppm, $J_{HP} = 813$ Hz) each member of which is split into a triplet ($J_{HPF} = 103$ Hz). The methyl protons appeared as a doublet (δ_{H_3C} -3.4 ppm, $J_{HCOP} = 11$ Hz). Infrared spectra in the P–H stretching region showed (gas phase) ν_s 2450 cm^{-1} and ν_{as} 2530 cm^{-1}. The data confirm the structure written.

Nmr and Ir Spectra for $F_2H_2POC_2H_5$. The ^{19}F spectrum is a doublet (δ_F 38.5 ppm, $J_{FP} = 711$ Hz) with each member split into a triplet ($J_{FPH} = 102$ Hz). The ^{31}P spectrum is a triplet (δ_P 38.2 ppm, $J_{PH} = 811$ Hz) with each member split into a triplet ($J_{PF} = 703$ Hz). The ^1H spectrum is a doublet (δ_{HP} -6.8 ppm, $J_{HP} = 804$ Hz) with each member split first into a triplet ($J_{HPF} = 102$ Hz). The methyl protons appear as a triplet (δ_{H_3C} -1.2 ppm, $J_{HCCH} = 11$ Hz) and the methylene protons appear as a quintet (δ_{H_2C} -3.9 ppm, $J_{HCCH} = 11$, $J_{HCOP} = 11$ Hz). Infrared spectra in the P–H stretching region show (gas phase) ν_s 2450 cm^{-1} and ν_{as} 2530 cm^{-1}.

Synthesis of $C_2H_5SPF_2H_2$. Equimolar samples of C_2H_5SH and PF_2H were condensed at $-196°$ into a 75-cm^3 reaction vessel. On warming to 0°, a reaction occurred, but it was accompanied by extensive product decomposition. The impure product was held at $-78°$ while the PH_3 and PF_3 were pumped off. The purified sample was then warmed to 0° and condensed into an nmr tube. A nonvolatile oil remained in the reaction vessel.

Nmr and Ir Spectra for $C_2H_5SPF_2H_2$. The ^{19}F pattern was identical in form with that observed for PF_2H_2OR (δ_F 28.9 ppm, $J_{FP} = 824$ Hz, $J_{FPH} = 109$ Hz); the ^{31}P pattern was a quintet resulting from the overlap of two triplets of triplets (δ_P 13.5 ppm, $J_{PH} = 840$ Hz, $J_{PF} = 840$ Hz). The infrared P–H stretching frequencies in the gas phase appear as ν_s 2475 cm^{-1} and ν_{as} 2540 cm^{-1}.

Results and Discussion

The nmr data at low temperature ($-60°$) support the expected trigonal-bipyramidal structure with the two fluorine atoms in the axial position. The PF coupling constant for $PF_2H_2OCH_3$ ($J_{PF} = 713$ Hz) and the comparatively low fluorine chemical shift (δ 40 ppm) are characteristic of axial fluorine atoms in difluorophosphoranes.[10] Further proof for the axial assignments is seen when comparing $CH_3OPF_2H_2$ with $C_6H_5PF_3OR$.[11] In $C_6H_5PF_3OR$ the axial fluorine appears as a doublet at 41 ppm ($CFCl_3$) with a J_{PF} of 830 Hz. The equatorial fluorine in $C_6H_5PF_3OR$ appears at 66 ppm ($CFCl_3$) with a J_{PF} of 975 Hz. The fluorine atoms in $H_2PF_2OCH_3$ appear at 40 ppm and show a J_{PF} of 713 Hz. Thus at the lowest temperature of the instrument the nmr offers direct evidence for the axial assignments for the fluorine and suggest no pseudorotation. At higher temperatures a broadening of the peaks occurs suggesting an exchange process (pseudorotation, dissociation of the adduct, etc.).

Registry No. $H_2F_2POCH_3$, 39023-06-8; $H_2F_2POC_2H_5$, 39023-07-9; $C_2H_5SPF_2H_2$, 39023-08-0.

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