Summary and Conclusions

The electrochemical response of $[Rh_2(dimen)_4]^{2+}$ has been studied by cyclic voltammetry, potential-step methods, and double-potential-step chronocoulometry. The appearance of the CV is dramatically influenced by relatively weak ionic aggregation of the $[Rh_2(dimen)_4]^{2+}$ species and the strong complexation of the 2e oxidized species $[Rh_2(dimen)_4]^{4+}$ formed at the electrode. The potential odd-electron intermediate ($[Rh_2(dimen)_4]^{3+}$) is quite unstable. It either is oxidized further at the electrode or undergoes rapid disproportionation. This behavior is in contrast with the behavior of $[Rh_2(bridge)_4]^{3+}$, which has previously been found to dimerize at the diffusion limit to form the stable $[Rh_2(bridge)_4]_2^{6+}$ ion.[4,5,8]

The observed differences in the behavior of the bridge and dimen systems are intriguing, because they must involve the interplay of several factors: differences in the Rh–Rh bond length of the $[Rh_2(L)_4]^{3+}$ complexes, the changes in stability caused by axial complexation, and steric restraints in the dimen system along the Rh–Rh bond axis which might preclude dimerization to the $[Rh_2(L)_4]_2^{6+}$ species. The observed propensity of the $[Rh_2(dimen)_4]^{2+}$ system to undergo net 2e jumps in oxidation state indicates that it may have importance in solar energy storage schemes. Studies designed to test the viability of this idea are currently in progress.

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Registry No. $[Rh_2(dimen)_4](PF_6)_2$, 72478-06-9; $[Rh_2(dimen)_4Cl_2](PF_6)_2$, 90269-63-9; $[Rh_2(dimen)_4]^{2+}$, 72478-05-8; $[Rh_2(dimen)_4Cl_2]^{2+}$, 90269-62-8; $[Rh_2(dimen)_4(ClO_4)_2]^{2+}$, 90269-64-0; $[Rh_2(dimen)_4]^{4+}$, 90269-65-1; $[Rh_2(dimen)_4(PF_6)_2]^{2+}$, 90269-66-2; Rh, 7440-16-6; Cl_2, 7782-50-5; benzyltriethylammonium chloride, 56-37-1.

Supplementary Material Available: A listing of Q_r ratios for double-potential-step chronocoulometry (1 page). Ordering information is given on any current masthead page.

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Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF^+ Salts and PtF_6

KARL O. CHRISTE,* WILLIAM W. WILSON, and RICHARD D. WILSON

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The usefulness of KrF^+ salts and PtF_6 as oxidative fluorinators for the syntheses of the coordinatively saturated complex fluoro cations NF_4^+, ClF_6^+, and BrF_6^+ was studied. The syntheses of NF_4SbF_6, NF_4AsF_6, NF_4BF_4, and $NF_4TiF_5{\cdot}nTiF_4$ from KrF_2–Lewis acid adducts and NF_3 were investigated under different reaction conditions. The fluorination of NF_3 by $KrF^+SbF_6^-$ in HF solution was found to proceed quantitatively at temperatures as low as −31 °C, indicating an ionic two-electron oxidation mechanism. An improved synthesis of $KrF^+MF_6^-$ (M = As, Sb), Raman data and solubilities in HF, and the existence of a $Kr_2F_3^+{\cdot}nKrF_2BF_4^-$ adduct in HF at −40 °C are reported. Attempts to fluorinate OF_2, CF_3NF_2, and ClF_4O^- with KrF^+ salts were unsuccessful. Whereas KrF^+ is capable of oxidizing NF_3, ClF_5, and BrF_5 to the corresponding complex fluoro cations, PtF_6 was shown to be capable of oxidizing only NF_3 and ClF_5. Since the yield and purity of the NF_4^+ fluoroplatinate salts obtained in this manner were low, NF_4PtF_6 was also prepared from NF_3, F_2, and PtF_6 at elevated temperature and pressure. General aspects of the formation mechanisms of coordinatively saturated complex fluoro cations are discussed briefly.

Introduction

The preparation of coordinatively saturated complex fluoro cations presents a great challenge to the synthetic chemist. The nonexistence of the corresponding parent molecules preempts the normally facile cation formation by a simple F^- abstraction from a parent molecule, and an F^+ addition to a lower fluoride is ruled out by the fact that fluorine is the most electronegative element and therefore F^+ cannot be generated by chemical means.[1] In view of these difficulties it is not surprising that at the present time only three coordinatively saturated fluoro cations, NF_4^+,[2,3] ClF_6^+,[4,5] and BrF_6^+,[6] are known to exist. In addition to their challenge to the synthetic chemist, the formation mechanism of these cations represents an intriguing and as yet unsolved puzzle.[7]

These problems were complicated by the facts that each of the three known coordinatively saturated fluoro cations had been prepared by a different method[2-6] and that these methods could not readily be transferred from one cation to another. The purpose of this study was to examine whether the synthesis of each coordinatively saturated fluoro cation is indeed limited to a specific method and whether these methods possess any commonalties.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless steel–Teflon FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. Metathetical reactions and solubility measurements were carried out in HF solution with use of an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.[8]

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an

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Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and Claassen filter[9] for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Materials. Literature methods were used for the preparation of PtF_6,[10] KrF_2,[11] CF_3NF_2,[12] ClF_3O,[13] ClF_5,[14] and FNO[15] and for the drying of HF.[16] Nitrogen trifluoride (Rocketdyne), F_2 (Air Products), OF_2 (Allied Chemical), BrF_5 and BF_3 (Matheson), and AsF_5, SbF_5, and TiF_4 (Ozark Mahoning) were commerically available. Their purity was checked by vibrational spectroscopy prior to use and, where necessary, improved by fractional condensation or distillation.

Preparation of $KrFSbF_6$. Antimony pentafluoride (21.7 mmol) was syringed in the drybox into a prepassivated Teflon FEP U-tube equipped with two stainless steel valves. The tube was connected to the vacuum line, and dry HF (5 mL of liquid) was distilled into the tube. The HF and SbF_5 were allowed to homogenize at ambient temperature, and a preweighed amount of KrF_2 (22.9 mmol) was transferred under a dynamic vacuum into the U-tube at −196 °C. The mixture was warmed toward room temperature until a slight effervescence was noted. At this point the tube was cooled again, and the warmup procedure was repeated. After a total of three warmup cycles, all volatile material was pumped off at −22 °C, leaving behind pure $KrFSbF_6$ (21.5 mmol = 99% yield based on SbF_5). $KrFAsF_6$ was prepared in an analogous manner, except the AsF_5 was loaded into the tube on the vacuum line.

Reaction of NF_3 with KrF_2 and AsF_5. A prepassivated (with ClF_3) 10-mL stainless steel Hoke cylinder equipped with a $^1/_8$ in. Whitey stainless steel valve was loaded on the vacuum line at −196 °C with KrF_2 (6.15 mmol), AsF_5 (3.07 mmol), and NF_3 (21.9 mmol). The cylinder was placed in a liquid-N_2–dry-ice slush bath and allowed to warm slowly to room temperature over a 30-h time period and then was kept in an oven at 53 °C for 4 days. The cylinder was cooled to −210 °C (N_2 slush bath, prepared by pumping on liquid N_2), and the volatile products were separated during warmup of the cylinder by fractional condensation through traps kept at −156 °C (nothing) and −210 °C (24.9 mmol of NF_3 and Kr). The white solid residue (827.6 mg = 2.97 mmol) was identified by infrared and Raman spectroscopy as pure NF_4AsF_6[17] (96.7% yield based on AsF_5).

Reaction of NF_3 with KrF_2 and BF_3. The reaction was carried out as described above for the corresponding AsF_5 system, except for a 40% reduction in the amount of starting materials used. The yield of solid NF_4BF_4 was 30.6% based on BF_3.

Reaction of Solid $KrFSbF_6$ with NF_3. $KrFSbF_6$ (2.42 mmol) was added in the drybox to a prepassivated Teflon PFA U-tube (59 mL volume) equipped with Teflon PFA valves. The tube was connected to the vacuum line, and NF_3 (2.43 mmol) was added at −196 °C. After 3 h at 22 °C, the volatile products were removed. Analyses of the volatile material and of the solid residue showed that 12.7% of the $KrFSbF_6$ had been converted to an NF_4^+ salt.

When the reaction was repeated with 2.32 mmol of $KrFSbF_6$ and 6.84 mmol of NF_3 at 30 °C for 3.5 h, the conversion of $KrFSbF_6$ to NF_4^+ salts was 43.8%. An additional treatment of the solid mixture of NF_4^+ salts and unreacted $KrFSbF_6$ with more NF_3 for 4 h at 30 °C resulted in little further conversion to NF_4^+ salts. Vibrational spectra of the white solid product showed the presence of the NF_4^+,[17] KrF^+,[18] SbF_6^-,[19] and $Sb_2F_{11}^-$[17] ions.

Table I. Oxidative Fluorination of NF_3 to NF_4SbF_6 by $KrFSbF_6$ in HF Solution

reacn temp, °C	$KrFSbF_6:NF_3$	reacn time, h	conversion of $KrFSbF_6$, %	products (composition, %)
25	1:1	3	100	$NF_4Sb_2F_{11}$ (91), NF_4SbF_6 (9)
−31	1:1	3	37	NF_4SbF_6 (37), $KrFSbF_6$ (63)
−31	large excess of NF_3, P_{NF_3} = 1000 mm	1	100	NF_4SbF_6 (100)
−45	1:1	3	23	NF_4SbF_6 (23), $KrFSbF_6$ (77)
−78	1:1	3	0	$KrFSbF_6$ (100)

Reactions of $KrFSbF_6$ with NF_3 in HF Solution. General Procedure. $KrFSbF_6$ (~3 mmol) was weighed in the drybox into a prepassivated 0.5 in. o.d. Teflon PFA U-tube (58 mL volume) equipped with two Teflon PFA valves. The tube was connected to the vacuum line, and anhydrous HF (~1.25 g) and NF_3 were added at −196 °C. The contents of the tube were warmed for a specified time period to the desired reaction temperature. The reaction was stopped by quickly pumping off the NF_3, followed by removal of the HF solvent. The material balances were obtained by separating the volatile products via fractional condensation through traps kept at −126 and −210 °C, by PVT measurements and infrared analysis of each fraction, and by the weight change of the solid phase and its Raman and infrared spectra, which were compared against those of mixtures of known composition. When stoichiometric amounts of $KrFSbF_6$ and NF_3 were used, the NF_3 was condensed into the U-tube and the valves were closed. When a large excess of NF_3 was used, the NF_3 pressure was kept constant at 1000 mm by the use of a large ballast volume and a pressure regulator. The results of these reactions are summarized in Table I.

Reaction of PtF_6 with NF_3 in HF. A prepassivated Teflon FEP U-trap (119 mL volume) was loaded at −196 °C with HF (5 mL liquid) and equimolar amounts (4.88 mmol each) of PtF_6, NF_3, and F_2. The contents of the trap were kept at 25 °C for 14 h. All volatile material was pumped off at 25 °C, leaving behind 828 mg of a dark red tacky solid, which based on its infrared spectrum was an NF_4^+ salt (1158 vs cm^{-1}, $\nu_3(F_2)$) of PtF_6^- and/or a fluoroplatinate polyanion (665 vs, 625 s, 560 vs cm^{-1}). Attempts were unsuccessful to purify the sample by extraction with anhydrous HF.

UV Photolysis of NF_3–PtF_6. A prepassivated 0.5 in. o.d. sapphire reactor[1] (26 mL volume) was loaded at −196 °C with PtF_6 (1.22 mmol) and NF_3 (1.31 mmol). The mixture was irradiated for 2 days at ambient temperature with a Hanovia Model 616A high-pressure quartz mercury vapor arc lamp. All volatile material was pumped off at 25 °C, leaving behind a red-brown solid (116 mg), which based on its infrared spectrum contained the NF_4^+ cation (2000 w cm^{-1}, $\nu_1 + \nu_3(F_2)$; 1218 mw cm^{-1}, $2\nu_4(A_1 + E + F_2)$; 1159 vs cm^{-1}, $\nu_3(F_2)$; 607 m cm^{-1}, $\nu_4(F_2)$)[17] and a fluoroplatinate polyanion (690 vs, 659 vs, 636 s, 535 vs, br cm^{-1}).

Synthesis of NF_4PtF_6. Into a prepassivated Monel cylinder (100 mL volume) were loaded PtF_6 (2.22 mmol), NF_3 (211.8 mmol), and F_2 (216.7 mmol) at −196 °C. The cylinder was heated to 125 °C for 7 days, followed by removal of all material volatile at 25 °C. The residue consisted of 802 mg of a dark red solid (weight calcd for 2.22 mmol of NF_4PtF_6 = 884 mg), which on the basis of its infrared and Raman spectra consisted mainly of NF_4PtF_6.[15,17,20] IR (cm^{-1}): NF_4^+, 2305 vw ($2\nu_3$), 1995 w ($\nu_1 + \nu_3$), 1758 vw ($\nu_3 + \nu_4$), 1452 w ($\nu_1 + \nu_4$), 1220 mw ($2\nu_4$), 1180 sh, 1158 vs, 1145 sh (ν_3), 1049 w ($\nu_2 + \nu_4$) 606 m (ν_4); PtF_6^-, 1320, 1300, 1280 w ($\nu_1 + \nu_3$), 1220 ($\nu_2 + \nu_3$), 675 sh, 650 vs, 625 sh (ν_3), 570 s, tr (ν_2). Raman (cm^{-1}): NF_4^+, 850 mw (ν_1); PtF_6^-, 641 vs (ν_1), 580 mw (ν_2), 239 m (ν_5), 194 w (ν_6).

Reaction of PtF_6 with ClF_5 in HF. A prepassivated 0.75 in. o.d. Teflon FEP ampule (49-mL volume) was loaded at −196 °C with PtF_6 (2.10 mmol), HF (2 mL liquid), and ClF_5 (4.20 mmol). The mixture was allowed to slowly warm to ambient temperature in an empty cold Dewar. After the ampule was kept for 2 days at ambient temperature, the brown PtF_6 color had disappeared. The volatile material was

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removed in vacuo at room temperature and separated by fractional condensation. It consisted of the HF solvent and ClF_5 (2.1 mmol). The orange-yellow solid residue (0.91 g) was shown by infrared and Raman spectroscopy to be an about equimolar mixture of ClF_4PtF_6 and ClF_6PtF_6[15] (weight calculated for a mixture of 1.05 mmol of ClF_4PtF_6 and 1.05 mmol of ClF_6PtF_6 = 0.923 g).

When the reaction was repeated under the same conditions, except for use of BrF_5 in place of ClF_5, no evidence for the formation of a stable BrF_6^+ salt was obtained.

Results

Syntheses and Some Properties of KrF_2–Lewis Acid Adducts. Although the synthesis of $KrF^+MF_6^-$ (M = As, Sb) salts is well-known,[6,18,21,22] the reported direct combination of KrF_2 with the Lewis acids can result in a spontaneous exothermic decomposition of KrF_2 accompanied by a bright flash and gas evolution.[18] In this study this problem was avoided by dissolving the Lewis acid in a large excess of anhydrous HF before adding a stoichiometric amount of KrF_2. This procedure resulted in an easily controllable, scalable, and quantitative synthesis of the desired KrF_2–Lewis acid adducts.

Since the Raman spectra of solid $KrF^+MF_6^-$ salts show many more bands than expected for an isolated diatomic cation and an octahedral anion,[18] we have recorded the Raman spectrum of $KrF^+SbF_6^-$ in HF solution at −5 °C. The total number of bands was reduced to four, as expected for a diatomic KrF^+ (610 cm^{-1}) and octahedral SbF_6^- ($\nu_1(A_{1g})$ = 656, $\nu_2(E_g)$ = 576, $\nu_5(F_{2g})$ = 278 cm^{-1}), thus confirming that the additional bands observed for solid $KrF^+SbF_6^-$[18] are indeed due to solid-state effects. The solubility of $KrF^+SbF_6^-$ in anhydrous HF at −31 °C was also measured as 43.9 mg/g of HF by the use of a previously described method.[16]

Since mixtures of KrF_2 and BF_3 in anhydrous HF are capable of oxidizing NF_3 to NF_4^+ (see below), it was interesting to establish whether BF_3 forms an adduct with KrF_2 under these conditions. Raman spectra of an equimolar mixture of KrF_2 and BF_3 in anhydrous HF at −40 °C showed bands (597 (10), 561 (2), 462 (7.5), 334 (1), 179 (1.7) cm^{-1}) characteristic for $Kr_2F_3^+{\cdot}xKrF_2$[18] and a weak band at 879 cm^{-1} due to $\nu_1(A_1)$ of BF_3.[23] The bands expected for BF_4^- were difficult to observe under the given conditions due to their low relative intensity and the low signal to noise ratio. Removal of volatile material under a dynamic vacuum at −78 °C resulted in a white solid residue which, on the basis of its Raman spectrum (461 cm^{-1}) at −110 °C, consisted of KrF_2.[24] These results clearly show that KrF_2 does not form a stable solid adduct with BF_3 at temperatures as low as −78 °C but that in HF solution, even at temperatures as high as −40 °C, ionization to $[Kr_2F_3^+{\cdot}xKrF_2][BF_4^-]$ occurs. The observation of free BF_3 is readily accounted for by the formation of krypton fluoride polycations, which leaves most of the BF_3 uncomplexed. Whether any free KrF_2 is also present in the HF solution is difficult to say because the KrF_2 band coincides with the 462-cm^{-1} band of $Kr_2F_3^+{\cdot}xKrF_2$.[18]

Fluorination Reactions with KrF^+ Salts. The oxidative fluorination of NF_3 to NF_4^+ by KrF^+ salts was first discovered[25] by Artyukhov and Khoroshev and independently rediscovered in our laboratory. In our study, mixtures of NF_3, KrF_2, and either AsF_5 or BF_3 in mole ratios of 7:2:1 were allowed to warm in stainless steel cylinders from −196 to +50 °C under autogenous pressures of about 75 atm. In 2 days NF_4AsF_6 and NF_4BF_4 had formed in 97 and 30% yield, respectively, based on the limiting reagents AsF_5 and BF_3, in agreement with the equations

$$NF_3 + KrF_2 + AsF_5 \rightarrow NF_4AsF_6 + Kr$$

$$NF_3 + KrF_2 + BF_3 \rightarrow NF_4BF_4 + Kr$$

In the Russian study the reactions were carried out at room temperature either with solid $KrF^+SbF_6^-$ and 1 atm of NF_3 or in HF solution with stoichiometric amounts of KrF_2, NF_3, and one of the Lewis acids SbF_5, NbF_5, PF_5, TiF_4, and BF_3 at total pressures of 3–4 atm and with reaction times of 1–3 h. On the basis of elemental analyses and vibrational spectra their products were assigned to NF_4^+ salts of SbF_6^-, NbF_6^-, PF_6^-, TiF_6^{2-}, and BF_4^-, respectively.[25] We have repeated some of these reactions in our laboratory because for $(NF_4)_2TiF_6$ and NF_4SbF_6 the reported vibrational spectra were those of polyanions,[17,19,26] and no yields and concentration or temperature dependences were given that would help to shed some light on the possible mechanism of these reactions.

Our results for the reaction of solid $KrFSbF_6$ with NF_3 showed that indeed the NF_4^+ cation is formed but that under the reported conditions[25] the reaction is incomplete and that the NF_4^+ salt is mainly $NF_4Sb_2F_{11}$ and not NF_4SbF_6.

When the reaction of KrF_2–SbF_5 mixtures or of preformed $KrFSbF_6$ with stoichiometric amounts of NF_3 was carried out, as previously reported,[25] in HF solution at ambient temperature, the reaction was complete in less than 3 h. However, contrary to the previously reported elemental analysis but in agreement with the listed vibrational spectra,[25] the solid product consisted mainly of $NF_4Sb_2F_{11}$ (~90%) and not NF_4SbF_6. The formation of mainly $NF_4Sb_2F_{11}$ suggests that under these conditions the oxidation of NF_3 by $KrFSbF_6$ is not quantitative and that some $KrFSbF_6$ decomposes to Kr, F_2, and SbF_5 with the latter combining with NF_4SbF_6 to form $NF_4Sb_2F_{11}$. By lowering the reaction temperature, we succeeded in completely suppressing the formation of $NF_4Sb_2F_{11}$, and NF_4SbF_6 was obtained as the only product, contaminated by large amounts of unreacted $KrFSbF_6$. However, a quantiative oxidation of NF_3 by $KrFSbF_6$ according to

$$NF_3 + KrFSbF_6 \rightarrow NF_4SbF_6 + Kr$$

was accomplished by the use of a sufficient excess of NF_3. Since the concentration of NF_3 in the HF solution is proportional to the NF_3 pressure above the solution,[27] the excess of NF_3 required for a complete reaction can be minimized by using a small ullage in the reactor. This results in a high NF_3 pressure and consequently in a high concentration of NF_3 in the HF solution. The results of a series of runs are summarized in Table I and demonstrate that, for example at −31 °C in HF solution at an NF_3 pressure of 1000 mm, NF_3 can quantitatively be oxidized by $KrFSbF_6$ to NF_4SbF_6 in less than 1 h.

In the absence of yield data in the previous report,[25] it was of interest to examine whether NF_4BF_4 can also be formed quantitatively under similar conditions. We found that an equimolar mixture of KrF_2, NF_3, and BF_3 in anhydrous HF, when allowed to warm slowly from −196 to +25 °C and kept at 25 °C for 3 h, resulted in only a 28.1% yield of pure NF_4BF_4. When the reaction was carried out at −78 °C for 3 h, the yield of NF_4BF_4 (7.1%) was, contrary to the NF_3–$KrFSbF_6$ system, still appreciable. Without the use of HF as a solvent and at ambient pressure, no detectable amounts of NF_4BF_4 were obtained after 3 h at 25 °C. However, as stated above, the use of a sevenfold excess of NF_3 at 45 atm pressure and gentle heating to 53 °C for 4 days resulted in a 31% yield of NF_4BF_4.

In view of the known tendency of TiF_4 to form polyanion salts with $(NF_4)_2TiF_6$[26] and the fact that the vibrational bands

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attributed in the Russian study[25] to TiF_6^{2-} resemble those of a polyanion,[26] we have also repeated the reaction of NF_3 with KrF_2 and TiF_4 in the same 2:2:1 mole ratio in HF solution at room temperature for 3 h. On the basis of the observed material balance, our solid product had the average composition $NF_4TiF_5{\cdot}2.25TiF_4$. The presence of only polytitanate anions and of no TiF_6^{2-} was confirmed by vibrational spectroscopy (strongest Raman bands at 795 and 755 cm^{-1}). On the basis of our above results for NF_4SbF_6, it appears safe to predict that the use of a large excess of NF_3 and particularly of an increase in the NF_3 pressure and concentration should also decrease the extent of polyanion formation in the NF_3–KrF_2–TiF_4 system.

Attempts to prepare the unknown $OF_3^+AsF_6^-$ and $OF_3^+SbF_6^-$ salts by the above methods (reaction of OF_2 with $KrFMF_6$ in either HF solution at temperatures as low as −31 °C or neat in a nickel cylinder under 25 atm of OF_2 pressure) produced no evidence for the existence of these salts.

We have also attempted to oxidatively fluorinate CF_3NF_2 with KrF^+ salts to $CF_3NF_3^+$ salts. A mixture of KrF_2, AsF_5, and CF_3NF_2 in a mole ratio of 1.86:1:5.62, when slowly warmed in a nickel reactor from −196 to +50 °C, produced NF_3 and CF_4 as the main products, with the excess of CF_3NF_2 being decomposed to give CF_4 and *cis*- and *trans*-N_2F_2. *cis*-N_2F_2 reacted with AsF_5 to form solid $N_2F^+AsF_6^-$.[28] Attempts to moderate this reaction by using preformed $KrFSbF_6$ and HF as a solvent resulted again in an oxidative fluorination of the C–N bond with CF_4, NF_3, and some *trans*-N_2F_2 as the main products. However, in this case the white solid product consisted mainly of $NF_4SbF_6{\cdot}xSbF_5$.

An attempt was also made to oxidize the ClF_4O^- anion[29,30] with preformed $KrFSbF_6$ in anhydrous HF solution at −78 °C. The reaction

$$KrFSbF_6 + CsClF_4O + HF \rightarrow CsSbF_6 + Kr + F_2 + ClF_2O^+HF_2^-$$

was observed. This result is not surprising since $CsClF_4O$ was shown to readily undergo solvolysis in HF

$$CsClF_4O + 2HF \rightarrow CsHF_2 + ClF_2O^+HF_2^-$$

and because the ClF_2O^+ cation is difficult to oxidize.[15] Reaction of solid $KrFSbF_6$ with $CsClF_4O$ and of liquid ClF_3O with KrF_2 also did not result in oxidation of the ClF_4O^- anion.

Fluorination Reactions with PtF_6. Since gaseous PtF_6 does not react with gaseous NF_3 at ambient temperature to any significant extent,[20] we have studied this reaction in HF solution without irradiation and in the gas phase under the influence of unfiltered UV irradiation. In both cases, the vibrational spectra of the solid reaction products demonstrated the formation of some NF_4^+ salts. The anions in these salts were not very well defined due to the simultaneous formation of PtF_5 and possibly lower platinum fluorides and their interaction with PtF_6^- to form polyanions. Attempts to purify the products by extraction with anhydrous HF were unsuccessful.

To obtain a better defined sample of an NF_4^+ fluoroplatinate salt for comparison, we have prepared NF_4PtF_6 by a known, but unpublished, method.[20] When a large excess of F_2 and NF_3 was used and the reaction was carried out at 125 °C under an autogenous pressure of about 140 atm, NF_4PtF_6 was obtained in high yield according to

$$2NF_3 + F_2 + 2PtF_6 \rightarrow 2NF_4PtF_6$$

The NF_4PtF_6 salt is a stable solid that shows spectra characteristic for tetrahedral NF_4^+ [17] and octahedral PtF_6^-.[15]

It was shown that the known oxidative fluorination of ClF_5 to ClF_6^+ with PtF_6[4,5,15] can also be carried out at room temperature in HF solution without requiring UV irradiation:

$$2ClF_5 + 2PtF_6 \xrightarrow[25\ °C]{HF} ClF_4^+PtF_6^- + ClF_6^+PtF_6^-$$

However, attempts to prepare $BrF_6^+PtF_6^-$ in an analogous manner from BrF_5 and PtF_6 were unsuccessful.

Discussion

Syntheses of Coordinatively Saturated Fluoro Cations. At present, only three coordinatively saturated fluoro cations, i.e. NF_4^+, ClF_6^+, and BrF_6^+, are known to exist. They can be prepared from the corresponding lower fluorides by one or more of the following three methods: (1) oxidation of KrF^+ salts; (2) oxidation by PtF_6; (3) oxidation by F_2 in the presence of a strong Lewis acid and an activation energy source.

One of the goals of this study was to examine the scope of these methods. A priori one would expect that the ease of preparing a given coordinatively saturated fluoro cation should increase with increasing oxidizing power of the fluorinating agent and with decreasing oxidation potential of the desired coordinatively saturated fluoro cation. Although the oxidation potentials of the three coordinatively saturated fluoro cations are unknown, a comparison with those of either the isoelectronic fluorides CF_4, SF_6, and SeF_6 or the corresponding oxo anions in the same oxidation states, i.e. NO_3^-, ClO_4^-, and BrO_4^-, suggests that the oxidation potentials should increase in the order $NF_4^+ < ClF_6^+ < BrF_6^+$. As far as the order of oxidizing power of KrF^+, PtF_6, and F_2–Lewis acid combinations is concerned, Sokolov et al. have shown that KrF^+ can oxidize PtF_6^- to PtF_6,[31] and both KrF^+ and PtF_6 are expected to be stronger oxidizers than mixtures of F_2 with Lewis acids. Therefore, the oxidizer strength should increase in the order F_2–Lewis acid < PtF_6 < KrF^+.

The results of this study are in accord with these predictions. Thus, KrF^+, the most powerful oxidizer, is capable of oxidizing all three substrates, NF_3, ClF_5, and BrF_5. The second strongest oxidizer, PtF_6, can still fluorinate NF_3 and ClF_5, whereas the weakest oxidizer, the Lewis acid–F_2 mixtures, can oxidize only NF_3. These results show that the preparative methods are transferable from one coordinatively saturated fluoro cation to another, provided that the oxidant is powerful enough to oxidize the substrate. Obviously, secondary effects such as the possibility of high activation energy barriers and competitive side reactions might also be important. For example, the activation energy sources used in the F_2–Lewis acid method can cause breakdown of ClF_5 and BrF_5 to F_2 and lower fluorides with the latter being continuously removed from the equilibrium by rapid complexing with the Lewis acid. For NF_3, such a side reaction is not effective, and the F_2–Lewis acid method is therefore well suited for the preparation of NF_4^+ salts.

Formation Mechanisms of Coordinatively Saturated Fluoro Cations. Previous reports[7] have been concerned almost exclusively with the formation and decomposition mechanisms of NF_4^+ salts, and several different mechanisms have been proposed. These include the heterolytic fission of fluorine[2,32] (mechanism I), the dissociation of NF_4AsF_6 to yield unstable

mechanism I

$$NF_3 + F^{\delta+}{-}F^{\delta-} + AsF_5 \xrightarrow{\Delta E} NF_4^+AsF_6$$

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NF_5[33] (mechanism II), the formation of an intermediate strongly oxidizing Lewis acid–F radical[34] (mechanism III), the formation of an intermediate NF_4 radical[7] (mechanism IV), and the absorption and ionization of NF_3 on a $KrF^+MF_6^-$ surface[25] (mechanism V).

mechanism II

$$NF_4AsF_6 \rightleftarrows [NF_5] + AsF_5$$
$$[NF_5] \leftarrow NF_3 + F_2$$

mechanism III

$$F_2 \rightleftarrows 2\dot{F}$$
$$\dot{F} + AsF_5 \rightleftarrows \dot{A}sF_6$$
$$\dot{A}sF_6 + NF_3 \rightleftarrows \dot{N}F_3^+AsF_6^-$$
$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

mechanism IV

$$F_2 \rightleftarrows 2\dot{F}$$
$$\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$$
$$\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$$
$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

mechanism V

$$NF_3 + KrF^+SbF_6^- \rightarrow (F_3N^{\delta+}\cdots F^{\delta-}\cdots Kr^{\delta+})^+SbF_6^- \rightarrow NF_4^+SbF_6^- + Kr$$

For the formation of NF_4^+ salts from NF_3, F_2, and Lewis acids, the importance of the F_2 dissociation step and of NF_3^+ formation has previously been experimentally confirmed,[34,35] thus rendering mechanisms III and IV most likely. Of these two mechanisms, mechanism IV has previously been preferred by us because the formation and decomposition of NF_4^+ salts were assumed to follow the same mechanism, and the decomposition of NF_4AsF_6 is suppressed more strongly by AsF_5 than by NF_3.[7] However, recent ab initio molecular orbital calculations[36] have provided evidence for $\dot{N}F_4$ being energetically unfavorable, and the formation and decomposition of NF_4^+ salts do not necessarily proceed by the same mechanism. These considerations prompted us to reconsider our previous preference.

The results of the present study confirm that NF_4^+ salts can be formed from NF_3 and F_2–Lewis acid mixtures, KrF^+ salts, or PtF_6. Furthermore, the fact that the reaction of KrF^+ with NF_3 not only proceeds quantitatively but also proceeds at temperatures (−31 to −45 °C) at which $KrF^+SbF_6^-$ is completely stable rules out a free-radical mechanism based on the decomposition of KrF_2 to Kr and F atoms and supports an ionic mechanism for the KrF^+–NF_3 reaction. In such an ionic mechanism, NF_3 is oxidized either to an intermediate NF_3^+ radical cation or directly to NF_4^+. In view of the quantitative yields of NF_4^+ salts and our failure to obtain evidence for an intermediate NF_3^+ radical cation in these KrF^+ reactions by ESR spectroscopy, the direct fluorination to NF_4^+ is preferred. One can easily envision an intermediate activated complex between the electrophilic KrF^+ cation and the, albeit weak, electron donor NF_3, which could readily decompose to NF_4^+ with Kr elimination.

For the reactions of NF_3 with F_2–Lewis acid mixtures the requirement for an activation energy source capable of dissociating F_2,[34] the ESR evidence for the intermediate formation of the NF_3^+ radical cation,[35] and the unlikely formation of an NF_4 radical[36] favor free-radical mechanism III. For the thermal decomposition of NF_4^+ salts which are derived from stable Lewis acids, mechanism II is preferred because it best explains the observed strong rate suppression by the Lewis acids.[7]

Even in the absence of experimental data it appears rather safe to propose for the PtF_6 oxidation reactions a one-electron transfer leading to $NF_3^+PtF_6^-$ as an intermediate, which is then further fluorinated by a second PtF_6 molecule to NF_4^+. Such a mechanism is in accord with the rather low yields of NF_4^+ salts obtained for the NF_3–PtF_6 system and has previously also been proposed for the ClF_5–PtF_6 system.[15]

Considering all the experimental evidence presently available for the formation mechanisms of coordinatively saturated complex fluoro cations, it appears that all reactions exhibit a certain commonality. The crucial step in all systems appears to be the reaction of a powerful one-electron (PtF_6 or Lewis acid–F) or two-electron (KrF^+) oxidizer with the substrate (NF_3, ClF_5, or BrF_5) resulting in an electron transfer from the substrate to the oxidant, with a simultaneous (in the case of KrF^+) or subsequent (in the case of PtF_6 and Lewis acid–F) fluorination of the intermediate radical cation (NF_3^+, ClF_5^+, BrF_5^+) to give the final product (NF_4^+, ClF_6^+, BrF_6^+). Thus, the mechanisms of the three presently known methods for the syntheses of NF_4^+ salts might be written

Lewis acid–F_2 system

$$F_2 \xrightarrow{\Delta E} 2\dot{F}$$
$$\dot{F} + AsF_5 \rightarrow \dot{A}sF_6$$
$$\dot{A}sF_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^-$$
$$\dot{N}F_3^+AsF_6^- + \dot{F} \text{ (or } \dot{A}sF_6) \rightarrow NF_4^+AsF_6^-$$

PtF_6 system

$$NF_3 + PtF_6 \rightarrow \dot{N}F_3^+PtF_6^-$$
$$\dot{N}F_3^+PtF_6^- + PtF_6 \rightarrow NF_4^+PtF_6^-\cdot PtF_5$$

KrF^+ system

$$NF_3 + KrF^+SbF_6^- \rightarrow [KrF\cdots NF_3]^+SbF_6^-$$
$$[KrF\cdots NF_3]^+SbF_6^- \rightarrow NF_4^+SbF_6^- + Kr$$

As can be seen from these equations, an ionic oxidant (KrF^+) results in an ionic mechanism and a radical oxidant ($\dot{L}AF$ or PtF_6) in a radical mechanism.

If in the Lewis acid–F_2 reactions the hard base NF_3 is replaced by a soft base, such as Xe, the reaction can proceed even in the absence of an activation energy source, as was demonstrated by Stein for the Xe–F_2–SbF_5 system.[37] Although XeF^+ is not a coordinatively saturated cation, this reaction is most interesting. Contrary to the NF_3–F_2–Lewis acid reactions, it probably proceeds as a two-electron oxidation reaction by F_2 and therefore might be considered as the only presently known example of an actual heterolytic fission of fluorine by a Lewis acid and a Lewis base:[32]

$$Xe\cdots F^{\delta+}-F^{\delta-}\cdots SbF_5 \rightarrow XeF^+SbF_6^-$$

The lower activation energy required for fluorinating Xe, compared to that for NF_3, is attributed mainly to its increased polarizability (i.e., it is a softer base) and to a lesser degree to the difference in their ionization potentials ($IP_{NF_3} = 13.0$ eV, $IP_{Xe} = 12.13$ eV), because the hard base O_2 has an even lower IP of 12.06 eV but does not react with fluorine and a

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Lewis acid in the absence of an activation energy source.

Conclusion. Although the present study has provided us with more insight into the formation reactions of coordinatively saturated complex fluoro cations, and particularly into those involving the use of KrF^+ salts as an oxidant, there is a definite need for more experimental and theoretical work in this field to further establish the mechanisms of these interesting reactions.

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Registry No. $KrFSbF_6$, 52708-44-8; SbF_5, 7783-70-2; NF_3, 7783-54-2; NF_4AsF_6, 16871-75-3; BF_3, 7637-07-2; NF_4BF_4, 15640-93-4; $NF_4Sb_2F_{11}$, 58702-89-9; PtF_6, 13693-05-5; NF_4PtF_6, 90025-87-9; ClF_5, 13637-63-3; F_2, 7782-41-4; ClF_4PtF_6, 38123-69-2; ClF_6PtF_6, 36609-91-3; BrF_5, 7789-30-2; AsF_5, 7784-36-3.

Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Reactions of Mono(disilylamino)phosphines with Carbon Tetrachloride[1]

RANDAL R. FORD, MARY A. GOODMAN, ROBERT H. NEILSON, AROOP K. ROY,
URSZULA G. WETTERMARK, and PATTY WISIAN-NEILSON*

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A series of mono(disilylamino)phosphines $(Me_3Si)_2NPRR'$ (R, R′ = Me, Et, *i*-Pr, *t*-Bu, CH_2SiMe_3, $CH_2CH{=}CH_2$, CH_2Ph, Ph, NMe_2, OMe, OCH_2CF_3) and two related phosphines, $\overline{Me_2SiCH_2CH_2Me_2SiN}P(t\text{-}Bu)CH_2SiMe_3$ and $(t\text{-}BuMe_2Si)_2NPMe_2$, were treated either with neat CCl_4 or with CCl_4 in CH_2Cl_2. The reactions proceeded with elimination of $CHCl_3$ and/or Me_3SiCCl_3 to form a variety of new *P*-chloro-*N*-silylphosphoranimines of general formula $Me_3SiN{=}P(Cl)R'R''$. The preferential course of the reaction was dependent on solvent polarity and on the electronic and steric influence of the substituents at nitrogen and phosphorus. Complete physical and spectroscopic (^1H, ^{13}C, and ^{31}P NMR) characterization data are given for the new phosphines and *P*-chloro-*N*-silylphosphoranimines.

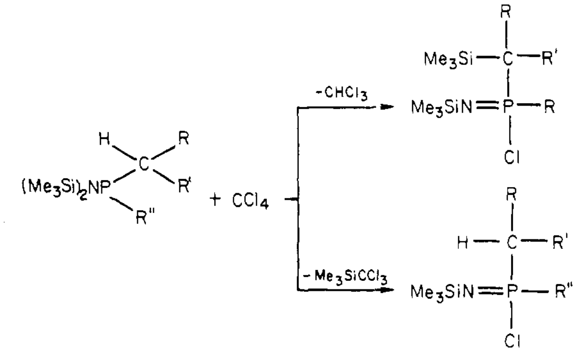
Introduction

Due to the reactivity of the silicon–nitrogen bond, the chemistry of (disilylamino)phosphines, i.e. $(Me_3Si)_2NPRR'$, often differs substantially from that of simple alkyl- or aryl-substituted phosphines.[2] As part of our continuing study of the reactivity of silicon–nitrogen–phosphorus compounds, we have investigated the oxidation reactions of a variety of bis(disilylamino)phosphines[3] and mono(disilylamino)phosphines with CCl_4.

The reaction of CCl_4 with tertiary phosphines that contain a CH proton α to phosphorus, but no disilylamino groups, produces $CHCl_3$ and phosphorus ylides.[4] This presumably occurs via initial formation of an ion-pair intermediate $[R_3PCl^+][CCl_3^-]$[5] with subsequent attack at the hydrogen by the CCl_3^- anion.

It was shown earlier that an alternate reaction pathway also becomes important when CCl_4 interacts with phosphines containing both an α-hydrogen and two disilylamino groups.[3] In addition to proton abstraction by the CCl_3^- anion, attack at a silicon–nitrogen bond may occur with elimination of Me_3SiCCl_3. The competition between these two pathways is influenced by the steric bulk of the substituents at phosphorus and by solvent polarity.

In this paper, we report the reactions of CCl_4 with mono(disilylamino)phosphines that contain α-hydrogens. As in the reactions of CCl_4 with bis(disilylamino)phosphines, both the silicon–nitrogen bond and the α-hydrogens are potentially reactive sites. Two different types of *N*-silylphosphoranimine products may, therefore, be produced from these reactions (eq 1).



(1)

Our primary objectives were (a) to compare the CCl_4 reaction products with those obtained from bis(disilylamino)phosphines or from tertiary phosphines with no disilylamino substituents, (b) to better understand the influence of steric and electronic differences of substituents at phosphorus, i.e. R, R′, and R″, and (c) to prepare various *P*-chloro-*N*-silylphosphoranimines, which are potential precursors to polyphosphazenes and to novel three-coordinate phosphorus compounds.

Results and Discussion

Phosphine Synthesis. The various bis(disilylamino)phosphines used in this study can be divided into four general categories: (1) simple dialkyl- or alkyl(phenyl)phosphines (**1** – **7**); (2) ((trimethylsilyl)methyl)phosphines (**8**–**14**); (3) phosphines with benzyl or allyl substituents (**15**–**18**); (4) systems with *N*-silyl groups other than Me_3Si (**19** and **20**).

Many of these phosphines were prepared as described previously by using the Wilburn procedure[6] or related methods.[7,8] Of the compounds reported here for the first time, phosphines **8** and **13** were prepared by the nucleophilic sub-

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