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Synthesis of π-(Arylsilane)chromium Tricarbonyl Complexes and Their High-Pressure Reaction with Hydrogen Chloride[1]

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Arylsilanes of the type $C_6H_5SiMe_xCl_y$ ($x + y = 3$) reacted at the reflux temperature of the arylsilane in an argon atmosphere to form π complexes containing the $Cr(CO)_3$ grouping. The complexes were characterized by their thermal stability and reactions with water and oxygen, as well as by NMR, mass, and infrared spectra. Pressures up to 4000 atm increased the rate of cleavage of the phenylsilicon linkage by HCl for the complexes as well as for the uncoordinated arylsilane ligands. The phenyl–silicon linkage of the ligand cleaved at lower temperatures and pressures when the ligand was attached to the $Cr(CO)_3$ moiety. The conditions required for cleavage became more rigorous as chloro groups replaced methyl groups for the complexes as well as for the ligand even at elevated pressures.

This study further demonstrates[2-5] that certain reactions which are thermodynamically permitted but which are slow at moderate temperatures and normal pressures will have measurable yields at the same temperature when the pressure is increased in excess of 1000 atm. This article reports the effect of pressures up to 4000 atm on the reactivity of anhydrous HCl with the silicon–phenyl linkage of $C_6H_5SiMe_xCl_y$ ($x + y = 3$) both as a pure substance and as a complex coordinated to the $Cr(CO)_3$ grouping. The pressure increase enhances the cleavage reaction for the uncoordinated ligand

$$PhSiCl_3 + HCl \rightarrow PhH + SiCl_4$$

as well as for the ligand coordinated to the $Cr(CO)_3$ grouping. Also, coordination of the ligand in itself is sufficient to reduce the physical conditions needed to cleave the phenyl–silicon bond.

The work of Nicholls and Whiting[6] with arenechromium tricarbonyl complexes developed the ground work for numerous studies describing the effect of coordination of aromatic ligands with the $Cr(CO)_3$ moiety. However, $PhSiMe_3Cr(CO)_3$,[7] *p*-$(Me_3Si)_2C_6H_4(CO)_3$,[8] *p*-$Me_3SiC_6H_4RCr(CO)_3$ (R = NMe$_2$ or Me),[9] and novel compounds of general formula $(PhRSiCH_2XCH_2)Cr(CO)_3$ (R = Ph, X = CH$_2$; R = Me, X = SiMe$_2$)[10] are the only arylsilane complexes which have been fully described.

Discussion

Properties of the Complexes. The π complexes $PhSiCl_3Cr(CO)_3$, $PhSiMeCl_2Cr(CO)_3$, $PhSiMe_2ClCr(CO)_3$, and $PhSiMe_3Cr(CO)_3$ were synthesized, using argon as an inert atmosphere, from $Cr(CO)_6$ and the corresponding arylsilane at their respective reflux temperatures using excess arylsilane as the only solvent,[11] e.g.

$$PhSiCl_3 + Cr(CO)_6 \rightarrow PhSiCl_3Cr(CO)_3 + 3CO$$
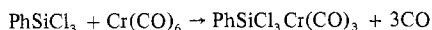
The complexes decompose slightly at 150 °C when heated at 10^{-4} Torr for 16 h. The decomposition products are $Cr(CO)_6$, ligand, CO, and chromium. When heated to 300 °C for 24 h the complexes completely decompose to the same products plus small amounts of intractable black solid.

The complexes react with air. With pure oxygen at 0 °C the complexes undergo a violent reaction. The products include CO_2, H_2O, Cr_2O_3, very small amounts of unreacted ligand, and traces of benzene. When the ligand contains chlorine, major amounts of HCl also form.

Reactions with water at 25 °C (1 atm) are normal for the cleavage of a silicon–chlorine bond. The mass spectrum of the final mixture indicated none of the original complex remained. The silicon–methyl linkages are unaffected by H_2O. For the chloro complexes, mass and infrared spectral measurements indicated that substances form which contain Si–O–Si linkages and $Cr(CO)_3$ groups.

The NMR spectra of the complexes exhibit a small upfield shift of the methyl protons and an upfield shift of 2.1–2.5 ppm for the protons on the ring as compared to the uncomplexed arylsilane. This upfield shift has been explained by an appropriate blend of electron density withdrawal from the ring, the magnetic anisotropy of the chromium tricarbonyl moiety, and the quenching of the ring current.[12]

The infrared spectra of the complexes were recorded in cyclohexane, in carbon disulfide, and as potassium bromide pellets.[1] The carbonyl stretching bands shift about 2–5 cm^{-1} in CS_2 and 20–40 cm^{-1} in KBr toward lower energy as compared to the bands as recorded in cyclohexane. Davidson and Riley[13] reported that in dilute cyclohexane solutions the E modes of the C–O stretching frequencies of several chromium tricarbonyls, including $(C_6H_5CH_3)Cr(CO)_3$, were split when a side chain destroyed the C_{3v} symmetry. Splitting of the E mode was observed only for $PhSiMeCl_2Cr(CO)_3$ and $PhSiMe_2ClCr(CO)_3$.

The mass spectra were similar to the previously reported fragmentation patterns of other chromium tricarbonyl complexes.[14-16] The spectra[1] exhibit many low-intensity peaks which indicate a successive loss of CO groups to give fragments for $[ArCr(CO)_n]^+$. Fragments where $n = 2$ are extremely weak and are noted only at higher inlet pressures for $PhSiCl_3Cr(CO)$. Also, at higher inlet pressures, lower intensity peaks could be detected and assigned to ions of the type $[(Ar \text{ minus } R)Cr(CO)_n]$ ($n = 3, 2, 1, 0$; R = Me or Cl). In the spectra of both ligand and complex, the fragmentation pattern from successive removal of groups from the silicon atom is present, although the relative intensities of corresponding ions are significantly altered upon complex formation.

Reaction with HCl

Table I summarizes the reactions of the silicon–carbon linkage with HCl. The heterolytic fission of the silicon–phenyl linkage by hydrogen halides has been considered to be an electrophilic substitution involving a σ complex[17-19]

(1)
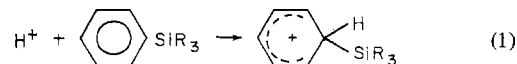
The catalytic action of $AlCl_3$ on the reaction supports this mechanism, but no evidence exists which clearly eliminates the possibility of a four-centered transition state
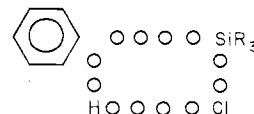
The relative ease with which $PhSiMe_3$ and $PhSiMe_2Cl$ react with hydrogen chloride as compared to $PhSiMeCl_2$ and $PhSiCl_3$ is supported by a comparison of group electronegativity values. Group electronegativity values for the C_6H_5

Table I. High-Pressure Reactions with HCl[a]

Substance	Temp, °C	% yield		
		5 atm[b]	1000 atm	4000 atm
PhSiMe₃	22	99 [5]		
PhSiMe₃Cr(CO)₃	22	100 [10]		
PhSiMe₂Cl	22	69 [2]		
PhSiMe₂ClCr(CO)₃	22	97 [4]		
PhSiMeCl₂	22	0 [10]	0 [8]	6 [5]
	50	0 [12]	2 [4]	50 [3]
	100	0 [3]	5 [10]	57 [9]
PhSiMeCl₂Cr(CO)₃	22	0 [30]		2 [31]
	50	0 [20]	0 [31]	75 [27]
	100	19 [7]	33 [54]	100 [4]
PhSiCl₃	120			0 [4]
	150		0 [4]	18 [8]
	220	0 [5]	0 [8]	17 [2]
PhSiCl₃Cr(CO)₃	50			0 [13]
	100		2 [37]	25 [12]
	150	0 [21]	0 [41]	29 [21]

[a] Yield based on recovered silicon tetrachloride or (methyl)-chlorosilane. All reactions were for 16 h. The values in brackets indicate the moles of HCl per mole of reactant. [b] Autogenous pressure.
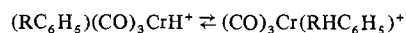
and $C_6H_5Cr(CO)_3$ moieties calculated by Gubin and Khandarova[20] when combined with group electronegativity values for the SiMe₃, SiMe₂Cl, SiMeCl₂, and SiCl₃ groupings calculated according to Huheey[21] support the observed reactivity order. For the uncomplexed arene the SiMe₃ and SiMe₂Cl groupings should donate electrons to the ring and the other groups should be electron withdrawing. All of the silicon groupings are predicted to be electron donating when the phenyl ring is coordinated to the chromium tricarbonyl moiety. Indeed, all of the complexed phenylsilanes react at less rigorous conditions than the free ligands.

Anderson and Brown[22] suggested the ν_{CO} E/A₁ intensity ratio measures the importance of the π-acceptor character of arenes in $ArCr(CO)_3$ systems. The measured intensity ratios for the complexes of PhSiCl₃, PhSiMeCl₂, PhSiMe₂Cl, and PhSiMe₃ were 1.16, 1.30, 1.61, and 1.62 which means the PhSiCl₃ complex is the best π acceptor. This ordering also matches the SiR₃ group electronegativity order and the ordering for the most positive silicon atom. The observed average carbonyl stretching frequency, $(A_1 + 2E)/3$, also follows the group electronegativity ordering. The increase in ν_{CO} as the electronegativity of an attached grouping increases can be rationalized by a decrease in $(d \rightarrow p)\pi$ bonding between chromium and the carbonyl groups.

A detailed NMR study[23] has shown the $Cr(CO)_3$ moiety removes electron density from the σ system of the ring with little or no change in the π-electron density. The complexed ring should therefore be positive with respect to the free ligand and the reaction with HCl should be hindered when a positive charge forms in the transition state. An alternate mechanism which does not initially require the phenyl ring to accept a proton would arise if the H^+ attacked the chromium[23]

$$(RC_6H_5)(CO)_3Cr + H^+ \rightleftharpoons (RC_6H_5)(CO)_3CrH^+$$
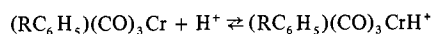
The proton could then shift to the ring

$$(RC_6H_5)(CO)_3CrH^+ \rightleftharpoons (CO)_3Cr(RHC_6H_5)^+$$

Thermochemical calculations based on bond energies or enthalpies and free energies of formation indicate the cleavage reactions have favorable equilibrium constants at 25 °C (1 atm).[24-28] However, no reaction is observed. At relatively low pressures the equilibrium constant for the reaction

$$HCl(g) + C_6H_5SiCl_3 (l) \rightarrow C_6H_6 (l) + SiCl_4 (l)$$
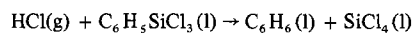
would be expected to increase with pressure since there is an obvious volume reduction. However at pressures in excess of

1000 atm the rate of change in the Gibbs free energy of formation for the individual reactants and products would be nearly the same since their compressibilities would be similar. The greatest change in Gibbs free energy would occur for HCl (and for the reaction) within the first 1000-atm pressure increase during the compression of the gaseous hydrogen chloride. This change, however, would be at most about 5 kcal at 25 °C. The lack of reaction at 1000 atm when compared to the 4000-atm experiments (Table I) implies that a change in free energy is not the major function of the pressure change.

The preservation of the well-established cleavage order PhSiMe₃ > PhSiMe₂Cl > PhSiMeCl₂ > PhSiCl₃ at high pressures stresses the importance of electronic effects in this reaction since the steric effect of replacing a methyl group by a chlorine atom would be expected to be less dominant at 4000 atm than at 1 atm.[17,18] If the cleavage reaction would have taken place at 1000 atm or lower pressures, rather than at 4000 atm, for PhSiMeCl₂ and PhSiCl₃ the postulation of a four-centered transition state would have gained support since the relative change in volume for the system in going from 1 to 1000 atm would have been much greater than the relative volume change for the 1000–4000-atm pressure increase.[29]

We believe the major role of pressure in the cleavage reactions is to increase the rate of reaction. This rate increase can be related to the increased concentration of reactants or to the increased formation of an active species. Such a species could be the hydrogen cation formed by the autoionization of dense hydrogen chloride fluid. This reaction in itself would be pressure favored since the developing ionic charges would be solvated by the hydrogen chloride causing a volume reduction for the system (and most likely for the activated state of the autoionization).

The postulated ionic mechanisms for the cleavage reaction would also be favored by the formation of very dense hydrogen chloride. This fluid would solvate the ionic intermediate in the reaction causing a volume reduction which would increase the rate of cleavage.

The yields of the reactions of the complexes with HCl were based on the recovery of silicon tetrachloride or (methyl)-chlorosilane since in the higher temperature experiments not all of the chlorine or chromium could be accounted for in the volatile products. The solid residue has been shown to contain a mixture of chromium(II) chloride and chromium(III) chloride by x-ray powder pattern measurements.[1] In a related study[1] the CrCl₃:CrCl₂ ratio was found to be a function of pressure and temperature when HCl and $Cr(CO)_6$ were combined. At 350 °C (4000 atm) CrCl₃ was the only observed chromium chloride and at 200 °C (20 atm) only CrCl₂ was formed. At intermediate conditions mixtures were present.

Experimental Section

A borosilicate glass vacuum system with Teflon stopcocks (Fischer & Porter Co., Warminster, Pa.) was employed to purify and analyze volatile materials. Reactions at less than 50 atm were performed in heavy-walled borosilicate glass reactors.[30]

High pressures were generated using a nitrogen gas pressure booster (High Pressure Equipment Co., Erie, Pa.) attached to a high pressure–high temperature hydrothermal research unit (Model HR-1B-4, Tem-Pres Research, State College, Pa.). Ampules made from 3-mm diameter thin-walled gold tubing contained the samples which were placed in a high-pressure reactor. At the end of a reaction period the reactor was cooled to −196 °C before release of the pressure. The ampule was then placed into an opening device attached to the vacuum line. After warming of the system to room temperature, all condensable materials on the surface of the gold tubing were pumped away. The volatile substances were transferred directly into the vacuum line. Solid material was recovered in a glovebag under an N₂ or Ar atmosphere. All products were identified and confirmed by two or more techniques including infrared spectroscopy, mass spectroscopy, vapor pressure measurements, melting point determinations, or elemental analysis. Authentic samples of volatile

molecular materials were used for identification of reaction products.[31]

Instrumentation. Infrared absorption spectra were obtained in the 4000–300-cm⁻¹ region using a Beckman Model IR-12 double-beam grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. Infrared spectra of the complexes were recorded as 0.015 M cyclohexane solutions. The instrument was calibrated using polystyrene. The mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7E mass spectrometer with an ionizing potential of 3600 V and a pressure between 10^{-6} and 5×10^{-5} Torr as measured by the unit's gauge. Mass spectra are reported as a percentage of the total ion intensity. Nuclear magnetic resonance spectra were measured on a Varian Associates T-60 spectrometer at 60 MHz at 37 °C in sealed glass tubes. The NMR spectra were recorded as 5% by weight CCl₄ solutions using cyclohexane as an internal standard. All chemical shifts were adjusted to the tetramethylsilane scale by adding 1.42 ppm. Powder x-ray spectra were obtained using a Norelco water-cooled diffraction unit with a copper target (λ(CuKα) 1.542 Å) and a nickel filter (0.000 75 in.) operated at 40-kV accelerating potential and 20-mA accelerating current.

Reagents. All reagents were commercial materials. Phenyltrichlorosilane (Union Carbide), C₆H₅Si(CH₃)₂Cl (Pierce), C₆H₅-Si(CH₃)₂Cl₂ (Dow Corning), and C₆H₅Si(CH₃)₃ (Marshallton Research Laboratory) were fractionally distilled prior to use. Chromium hexacarbonyl (Strem) and hydrogen chloride (Matheson) were used as obtained.

Synthesis of PhSiCl₃Cr(CO)₃. In a nitrogen-filled glovebag, phenyltrichlorosilane (39.72 g, 188.0 mmol) and Cr(CO)₆ (6.080 g, 27.63 mmol) were placed in a 50-ml round-bottom flask. The flask was attached to a Strohmeier jacketed reflux condenser[32] and the contents were heated in an argon atmosphere until the Cr(CO)₆ was completely consumed (approximately 16 h). The yellow-brown solution was cooled to room temperature. The excess PhSiCl₃ was removed at 50 °C (0.01 Torr). The remaining yellow solid was sublimed three times at 90 °C (0.01 Torr) using liquid nitrogen in the cold finger of a vacuum sublimer. The sublimate consisted of yellow PhSiCl₃Cr(CO)₃ (6.79 g, 19.55 mmol; 70.8% yield; mp 107–109 °C). Anal. Calcd for C₉H₅Cl₄CrO₃Si: C, 31.10; H, 1.45; Cl, 30.69. Found: C, 31.27; H, 1.27; Cl, 30.38. Ir: ν(CO) 1999, 1939 cm⁻¹. Mass spectrum, m/e (T): 346 (0.64), 246 (3.51), 262 (2.72), 105 (1.01), 87 (2.27), 77 (3.56), 65 (3.50), 63 (9.54), 54 (2.68), 53 (11.27), 52 (27.08), 51 (2.61), 50 (4.85). NMR: complex multiplet δ 4.66–5.52.

Synthesis of PhSiMeCl₂Cr(CO)₃. The above procedure was used to combine phenylmethyldichlorosilane (35.59 g, 186.2 mmol) and Cr(CO)₆ (5.690 g, 25.86 mmol) to form yellow PhSiMeCl₂Cr(CO)₃ (6.390 g, 19.53 mmol; 75.5% yield; mp 78–80 °C). Anal. Calcd for C₁₀H₈Cl₂CrO₃Si: C, 36.71; H, 2.46; Cl, 21.67. Found: C, 36.88; H, 2.60; Cl, 21.42. Ir: ν(CO) 1992, 1933, 1925 cm⁻¹. Mass spectrum, m/e (T): 326 (0.65), 244 (3.94), 243 (1.47), 242 (6.14), 155 (2.47), 105 (4.20), 63 (3.55), 53 (7.47), 52 (20.50), 50 (2.86). NMR: δ 1.06, complex multiplet δ 4.97–5.63.

Synthesis of PhSiMe₂ClCr(CO)₃. The same procedure was utilized for the reaction of phenyldimethylchlorosilane (37.55 g, 220.0 mmol) and Cr(CO)₆ (8.489 g, 38.57 mmol) forming yellow PhSiMe₂ClCr(CO)₃ (9.393 g, 30.62 mmol; 79.4% yield; mp 74–75 °C). Anal. Calcd for C₁₁H₁₁ClCrO₃Si: C, 43.07; H, 3.61; Cl, 11.56. Found: C, 42.87; H, 3.50; Cl, 11.70. Ir: ν(CO) 1986, 1927, 1919 cm⁻¹. Mass spectrum, m/e (T): 306 (2.20), 271 (1.46), 224 (5.41), 223 (3.77), 222 (17.04), 155 (1.81), 136 (2.20), 135 (14.15), 105 (1.75), 53 (2.21), 52 (14.42), 50 (1.09). NMR: δ 0.70, complex multiplet δ 4.97–5.59.

Synthesis of PhSiMe₃Cr(CO)₃. Following the same procedure, PhSiMe₃ (20.16 g, 134.2 mmol) and Cr(CO)₆ (4.153 g, 18.88 mmol) formed yellow PhSiMe₃Cr(CO)₃ (4.921 g, 17.19 mmol; 91.0% yield; mp 72–73 °C, lit.[6] mp 72–73 °C). Ir: ν(CO) 1982, 1915 cm⁻¹. Mass spectrum, m/e (T): 286 (0.45), 230 (1.22), 204 (2.02), 203 (5.85), 202 (21.39), 135 (6.08), 105 (1.11), 53 (3.47), 52 (27.21), 50 (1.59), 43 (1.66). NMR: δ 0.30, complex multiplet δ 4.95–5.42.

Reactions with HCl at Autogenous Pressures. In a nitrogen-filled glovebag, PhSiMe₃Cr(CO)₃ (175.4 mg, 0.6126 mmol) was placed into a 25-ml glass pressure reactor. The vessel was evacuated and an excess of HCl (232.4 mg, 6.368 mmol) was condensed into the reactor. The stopcock was closed and the mixture was allowed to warm to and stand at 22 °C (~5 atm) for 16 h. The vessel was then opened and the material which volatilized at room temperature was transferred into the vacuum system. This volatile material was passed through

a trap cooled to –78 °C (dry ice/acetone mixture) into a –196 °C trap. The former contained Me₃SiCl (66.6 mg, 0.613 mmol; 100% recovery) and the latter unreacted HCl. The yellow-green solid residue in the reactor after sublimation yielded yellow PhHCr(CO)₃ (128 mg, 0.598 mmol) and a small amount of residual green solid. A similar procedure was followed with the other complexes and the free ligands.

High-Pressure Reactions with HCl. In a drybag PhSiMeCl₂Cr-(CO)₃ (316 mg, 0.966 mmol) was placed in a gold tube and then anhydrous HCl (127 mg, 3.50 mmol) was condensed into the tube under vacuum. The tube was sealed and held at 100 °C (4000 atm) for 16 h. The ampule was opened into the vacuum system. There was a small amount of noncondensable gas, shown by mass spectral measurements to be CO and H₂. All other volatile material was passed through traps cooled to 0 °C (ice/H₂O), –45 °C, and –78 °C with the excess HCl stopping in a –196 °C trap. The first trap contained Cr(CO)₆ (94.0 mg, 0.427 mmol). The second held benzene (77.0 mg, 0.986 mmol), and the third, MeSiCl₃ (147 mg, 0.983 mmol). The gold tube contained a small amount of solid shown by powder x-ray spectra to be a mixture of CrCl₃ and CrCl₂.[33] An identical procedure was followed with PhSiCl₃, PhSiCl₃Cr(CO)₃, and PhSiMeCl₂.

Thermal Decomposition. Under an argon atmosphere, PhSiCl₃Cr(CO)₃ (48.0 mg, 0.138 mmol) was placed in a glass pressure reactor. The reactor was evacuated and sealed. After the vessel was heated at 150 °C for 16 h, it was cooled to –196 °C. A manometer reading indicated only a very small amount of noncondensable gas was present. After warming of the system to room temperature, Cr(CO)₆ (1.0 mg, 0.05 mmol) and a trace of PhSiCl₃ were the only volatile materials. There was only a trace of decomposition in the complex after 1 h at 150 °C. Identical experiments with PhSiMeCl₂Cr(CO)₃, PhSiMe₂ClCr(CO)₃, and PhSiMe₃Cr(CO)₃ produced analogous results in which decomposition varied along the series but was always 5% or less. Decomposition increased considerably as the temperature was increased. All samples were completely decomposed at 300 °C within 24 h.

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Chromium(II)-Catalyzed Aquation of the Fluoroisothiocyanatotetraaquochromium(III) Ion[1]

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The kinetics of the chromium(II)-catalyzed aquation of the fluoroisothiocyanatotetraaquochromium(III) ion have been investigated. The reaction proceeds to about 80% completion forming predominantly fluoropentaaquochromium(III) ion. An unusual rate law for Cr(III)–Cr(II) reactions of the form $d(\ln [Cr(NCS)F^+])/dt = a[Cr^{2+}]/(1 + b[Cr^{2+}])$ has been observed in the temperature range 15–35 °C and $\sum[ClO_4^-] = 1.0$ M, where $a = 5.38$ (± 0.04) $\times 10^{-2}$ M^{-1} s^{-1} and $b = 1.9 \pm 0.3$ M^{-1} at 25 °C. The rate law has been interpreted in terms of a mechanism involving the equilibrium formation of an unproductive intermediate $FCr(NCS)Cr^{3+}$ followed by a fluoride ion bridged, rate-determining reaction between $Cr(NCS)F^+$ and Cr^{2+}. Alternate mechanisms are also discussed.

Introduction

The chemistry of disubstituted tetraaquochromium(III) ions has been rather well documented in the literature for those species involving identically substituted groups, i.e., $Cr(H_2O)_4X_2^{2+}$.[2] By contrast, however, progress in the study of the chemistry for mixed disubstituted species, $CrXY^{n+}$, has been limited due largely to difficulties in their preparation. Taube[3] prepared the first such complex in noting the effect of added pyrophosphate ion on the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction. A chromium(III) complex containing both chloride and pyrophosphate ions was isolated. Earley and Gorbitz[4] repeated this work and formulated its composition as $Cr(H_2O)_n(P_2O_7H_2)Cl$, where $n \leq 4$. Subsequently, Manning and Jarnagin[5] reported that in the presence of chloride ion the $Co(NH_3)_5FumH^{2+}$–Cr^{2+} reaction yielded a substantial fraction of a complex containing both fumarate and chloride ions. More recently, Brown and Pennington[6] reported the preparation, aquation, and linkage isomerization of $Cr(H_2O)_4(SCN)(NCS)^+$, and Pennington[7] reported some general strategies for the preparation of mixed-ligand complexes. Vanderheiden and King[8] have since isolated a complex, $Cr(DMSO)I^{2+}$, from aqueous dimethyl sulfoxide and separated the geometric isomers by ion-exchange chromatography. Finally, Schilt and Schaap[9] reported that the anation of $CrCN^{2+}$ by thiocyanate ion produces $Cr(NCS)(CN)^+$.

In addition to the above direct observations of mixed disubstituted tetraaquochromium(III) ions there have been numerous studies in which such species have been postulated as reaction intermediates. Thus the spontaneous[10,11] and chromium(II)-catalyzed[12,13] aquations, as well as the formation reactions,[14] of monosubstituted pentaaquochromium(III) ions exhibit kinetic terms (inverse first order in hydrogen ion) which are interpreted in terms of $Cr(OH)X^+$ species. Ardon[15] observed the formation of ~15% $CrCl^{2+}$ or $CrBr^{2+}$ among the products of aquation of CrI^{2+} in HCl or HBr media, assuming that the replacement occurs only by the acid-dependent path. Whereas Ardon interpreted his results in terms of an S_N1 mechanism, Moore, Basolo, and Pearson[16] suggested that the substitution products arose from intermediates of the type $CrIX^+$. Carey, Jones, and Swaddle[17]

extended Ardon's observations to the $CrBr^{2+}$ and $CrONO_2^{2+}$ complexes. Their results, taken together with the results of Haim and Sutin[18] for $CrSCN^{2+}$, rule out the sole operation of an S_N1 (or dissociative) mechanism for the aquation/anation reactions since the yields of $CrCl^{2+}$ vary with the substituent on chromium(III). Moreover they noted a rough linear free energy relationship of slope >0.9 for a plot of log k_{-1} vs. log Q (where k_{-1} and Q are the rate constant for the inverse acid path and the concentration quotient) for the aquations of CrX^{2+}, a result implying a dissociative interchange mechanism for aquations of $Cr(OH)X^+$ species. The observed slope is markedly greater than the value of 0.56 observed by Swaddle and Guastalla[19] for the acid-independent path, where an associative interchange mechanism is postulated. Pennington and Haim[13] also postulated the formation of $CrIX^+$ species in the chromium(II)-catalyzed substitutions of iodide ion in CrI^{2+} by fluoride, chloride, and bromide ions.

Anet and Leblanc[20] and Kochi and Buchanan[21] have postulated the formation of several benzylchromium(III) intermediates of the type $Cr(Bzl)X^+$. More recently, Matts and Moore[22] postulated the formation of some mixed-ligand O-bonded nitrito complexes in the nitrogen(IV)-catalyzed aquations of aquochromium(III) species. Similarly Carlyle and King[23] examined the sulfur(IV)-catalyzed aquations of a variety of chromium(III) complexes but they, like Matts and Moore,[22] were unable to detect the analogous labile intermediates. Scott, Weeks, Bracken, and King[24] postulated the existence of $Cr(DMSO)I^{2+}$ in a study of the aquation of CrI^{2+} in aqueous dimethyl sulfoxide, and the complex was subsequently isolated.[8] In the present work we wish to report our results on the preparation and chromium(II)-catalyzed aquation of the $Cr(NCS)F^+$ ion.

Experimental Section

Materials. Chromium(II) perchlorate solutions were prepared, stored, and analyzed as described previously.[12] Solutions of the air-sensitive material were transfered by means of hypodermic syringe techniques.

Sodium perchlorate solutions were prepared by neutralization of standard perchloric acid solutions with anhydrous sodium carbonate. Solutions of sodium thiocyanate were prepared from the reagent grade