spectra of the di-μ-sulfido complexes (see Figure 3b), the excitation profile of the 935-cm^{-1} band indicates that the electronic absorption involving the Mo=O bonding is at wavelengths shorter than 470 nm. By contrast, the profile for the 417-cm^{-1} band (Figure 4a) exhibits no clear maximum in the range studied. The electronic absorption in this range has no maximum but only weak tailing. The scattered intensity data around 500 nm may indicate presence of a vibrational fine structure. Clearly further detailed study is needed to clarify these points.

The MO calculation of Brown et al.[17] on the di-μ-sulfido complex indicated extensive mixing of the individual ligand atomic orbitals at the lowest vacant MO which is responsible for the absorption occurring at the visible region. The CD spectra of various oligopeptide complexes involving di-μ-sulfido bridges always show extrema in the 400–450-nm range.[18] Contribution of chirality at the cysteine residue to the electronic absorption is apparent.

Two strong Raman lines were observed for the di-μ-sulfido molybdenum(V) complex of glutathione (GSH), $[Mo_2O_2S_2(\gamma\text{-Glu-cys-Gly})_2]^{2-}$,[19] at 950 and 425 cm^{-1}. A weak peak at 295 cm^{-1} and the 425-cm^{-1} peak were intensified by irradiation at 457.9 nm. The former peak may be due to the Mo–S_b or Mo–SC stretching. An indication of incorporation of di-μ-sulfido-bis(oxomolybdenum) ion into cys-containing proteins such as papain (M_r 23 400)[20] is readily obtainable by the Raman spectrum. Thus, our preliminary results show weak peaks at 930 and 420 cm^{-1} for this macromolecular Mo(V) complex.

The observation of a highly enhanced Raman line assigned to the di-μ-sulfido bridge helps to detect or identify its presence in metalloenzymes or metalloproteins. The frequency dependence could also give clues to the coordination environment at the metal and strengths of the participating bonds.

Registry No. $MoO_2(cysOMe)_2$, 29683-37-2; $MoO_2(cysOEt)_2$, 22775-78-6; $MoO_2(cysO\text{-}i\text{-}Pr)_2$, 76832-60-5; $MoO_2(cysOBzl)_2$, 76832-61-6; $MoO_2(S_2CNMe_2)_2$, 39248-36-7; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; $MoO_2(acac)_2$, 21884-95-7; $Na_2[Mo_2O_2(\mu\text{-}O)_2(cys)_2]$, 23331-32-0; $Na_2[Mo_2O_2(\mu\text{-}S)_2(cys)_2]$, 29683-41-8; $Mo_2O_2(\mu\text{-}O)_2(his)_2$, 26658-23-1; Na_2MoO_4, 7631-95-0.

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(19) The $[Mo_2O_2(\mu\text{-}S)_2(GSH)_2]^{2-}$ ion was synthesized by the addition of glutathione to a solution of $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ at pH 7. Isolation of the complex as a sodium salt was carried out by the addition of methanol to the aqueous solution.

(20) Papain and the $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ ion were mixed in water at pH 6.5. The metal complex was purified by dialysis. The binding site of the $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ ion should be located in a pocket having one each of thiolato and imidazole ligands (Ueyama, N.; Nakamura, A., unpublished results). Formation of this complex was also supported by the CD spectrum in water.

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Matrix Isolation Investigation of the Methylfluorosilicate Anions

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The Lewis acid or acceptor properties of inorganic fluorides such as BF_3, SiF_4, and PF_5 are well-known, including thorough ion cyclotron resonance and mass spectral studies of the fluoride affinities of these species.[1–3] The product anions such as SiF_5^-, have also been well characterized in condensed-phase studies.[4] More recently, attention has been directed toward the effects of alkyl substitution on the Lewis acid; studies have shown that the fluoride affinity drops off dramatically as the number of methyl groups increases for the fluoromethylsilanes.[1] Only one of the possible product anions, $(CH_3)SiF_4^-$, has been observed in solution,[5,6] and characterized by ^1H and ^{19}F NMR. The SiF_5^- anion has also been characterized in argon matrices after formation through the salt/molecule technique, in which CsF is reacted with SiF_4 to form the $Cs^+SiF_5^-$ ion pair.[7] Since the fluoride ion is known to catalyze a number of organosilicon reactions[8,9] and gas-phase studies indicate at least some stability for alkylfluorosilicate anions,[1–2] a similar study was conducted to attempt to isolate and characterize these anions in inert-gas matrices.

Experimental Section

All of the experiments conducted in this study were performed on a conventional matrix isolation apparatus which has been described previously.[10] CsF (Alfa) and CsCl (Fisher) were the salts employed in this study, and both were vaporized from a stainless-steel Knudsen cell at roughly 500 °C. $(CH_3)SiF_3$, $(CH_3)_2SiF_2$, and $(CH_3)_3SiF$ were purchased from PCR, Inc., and used after purification through a freeze–thaw cycle under vacuum. Argon was used as the matrix gas in all experiments and was used without further purification. Matrix samples were deposited for 20–24 h before final scans; both survey and high resolution scans were recorded on a Beckman IR-12 infrared spectrophotometer.

Results

Before salt/molecule reactions were undertaken with the fluoromethylsilanes, blank experiments were conducted at representative dilutions with each of the silane compounds; the recorded spectra agreed well with literature spectra.[11,12] When CsF was vaporized and codeposited with a sample of $Ar/(CH_3)SiF_3 = 1000$, four new bands were observed in the spectrum, which could not be attributed to parent species, at 742, 825, 837, and 862 cm^{-1}. When the concentration was increased to 400/1, the same set of bands appeared, with increased intensity, and a weaker band was observed near 450 cm^{-1}. These experiments were repeated several times, using different CsF levels, and the five bands appeared consistently and maintained a constant relative intensity.

CsF was codeposited with samples of $Ar/(CH_3)_2SiF_2$ in several experiments, with concentrations ranging from 1000/1 to 250/1. A number of medium-to-weak bands were detected in each experiment, reproducibly at 674, 695, and 868 cm^{-1}, along with bands which appeared as shoulders on parent bands at 787 and 834 cm^{-1}. The spectra of the reaction products of CsF with $(CH_3)SiF_3$ and $(CH_3)_2SiF_2$ are shown in the traces of Figure 1. CsF was also codeposited with samples of $Ar/(CH_3)_3SiF$ in several experiments, and in each case, weak bands were detected at 749 (sh), 986, and 1248 cm^{-1}. Even in the most concentrated experiments, $M/R = 200$, these bands had at most an optical density of 0.05.

For a test of the effect of chlorine atom substitution, CsCl was codeposited with a sample of $Ar/(CH_3)SiF_3 = 400$, and no bands were detected in the spectrum which could be attributed to a reaction product. Likewise, when CsF was reacted with a sample of $Ar/(CH_3)SiCl_3 = 400$ in one experi-

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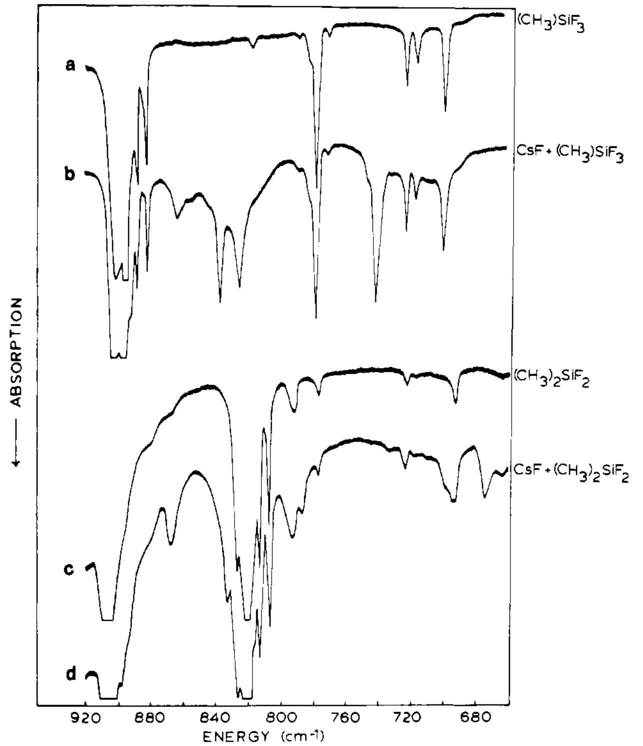

Figure 1. Infrared spectra of the reaction product of CsF with $(CH_3)SiF_3$ and $(CH_3)_2SiF_2$ in traces b and d compared to the infrared spectra of the parent silanes in traces a and c, all in argon matrices.

ment, no product bands were detected in the spectrum.

Discussion

Salt/molecule reactions of CsF with a variety of Lewis acids have led to ion pair formation through fluoride ion transfer.[13-15] Similar product ion formation might be anticipated in the present study, if the Lewis acid character of the appropriate methylfluorosilane is sufficiently great. From Figure 1, it is clear that a distinct reaction product was formed through the reaction of CsF with $(CH_3)SiF_3$ and, in view of past results, may be assigned to the $(CH_3)SiF_4^-$ anion ion paired with Cs^+. The reaction of CsF with $(CH_3)_2SiF_2$ gave rise to a reproducible set of product bands as well, although with much less intensity, while the reaction of CsF with $(CH_3)_3SiF$ did not give rise to any distinct product bands. Several weak bands were observed as shoulders on parent bands of the silane precursor, and the "product" in this latter experiment can probably best be represented as a $(CH_3)_3SiF$ molecule perturbed by an adjacent CsF molecule. Thus, when the silane contained a single methyl group, a distinct product was formed, while, when two methyl groups were present, a distinct product was formed but with much lower yield, and when the silane contained three methyl groups, no distinct reaction product was formed. The Lewis acid character, then, decreases as the number of methyl groups increases, which is in good agreement with gas-phase ICR studies. Beauchamp[1] found a decrease of about 6 kcal/mol in fluoride ion affinity going from SiF_4 to $(CH_3)SiF_3$ and a similar 6 kcal/mol decrease from $(CH_3)SiF_3$ to $(CH_3)_2SiF_2$. Significantly, he found a dramatic decrease in fluoride ion affinity when $(CH_3)_3SiF$ was studied; in fact, he was unable to form the $(CH_3)_3SiF_2^-$ anion, although Dillard[2] has reported gas-phase formation of this ion. Similarly, Muetterties[6] followed the analogous solution-phase reactions through NMR and reported formation of salts of $(CH_3)SiF_4^-$ but was unable to form salts of $(CH_3)_2SiF_3^-$. Matrix formation in the present study through the salt/molecule technique gives a similar ordering of stabilities of these anions. The formation of pentacoordinate silicon species is usually rationalized[1,16,17] through the involvement of d orbitals on the silicon center, and the above results demonstrate that relatively electronegative substituents on the silicon are needed to contract the otherwise diffuse d orbitals.

Chlorine substitution was investigated as well to test the electronegativity requirements further. When CsCl was reacted with the most acidic methylfluorosilane, $(CH_3)SiF_3$, no distinct reaction product was observed. While this may indicate some limitation of the salt/molecule technique, it certainly demonstrates the considerable difference in chemistry between the chloride and fluoride anions. When CsF was reacted with $(CH_3)SiCl_3$, no distinct product was observed, substantiating the difference between Cl^- and F^-.

Only for the product anion $(CH_3)SiF_4^-$ were the spectral features sufficiently distinct to make some structural determination. Four bands were observed between 700 and 900 cm^{-1}, in a region assignable to Si–F stretching motions, while a less intense band was observed near 450 cm^{-1}, in the Si–F deformation region. The four upper bands are close to the bands which Muetterties et al.[6] tentatively assigned to Si–F stretching modes of the $(CH_3)SiF_4^-$ anion in solution with large organic cations. Hence, the bands at 742, 825, 837, and 862 cm^{-1} can be assigned to four Si–F stretching modes in the product anion. The observation of four Si–F stretches indicates a symmetry of the anion of C_{2v} or lower,[18] the most likely form of which is a trigonal bipyramid with the methyl group in an equatorial position. It should be noted that this product anion is isoelectronic with $(CH_3)PF_4$, which has been determined to be C_{2v} with an equatorial methyl group through electron diffraction[19] and NMR.[20] The analogy to the phosphorus compound extends further—solution ^{19}F NMR studies show four equivalent fluorine atoms,[6,20] as a consequence of Berry pseudorotation,[21] except at very low temperatures. Hence, the C_{2v} structure, with the methyl group equatorial in a trigonal-bipyramidal arrangement about the silicon is the probable structure for the $(CH_3)SiF_4^-$ anion. Less can be said about the structure of the $(CH_3)_2SiF_3^-$ anion, which was formed through the reaction of CsF with $(CH_3)_2SiF_2$. Although product bands were observed and the band at 868 cm^{-1} can very likely be assigned to a Si–F stretching mode, the bands were sufficiently weak that a definitive structural assignment is not feasible. If the remaining weak bands are all assigned to Si–F stretching modes (and they are in the right region for such an assignment), then more than one isomeric form of the product anion must be present, as a single form of the $(CH_3)_2SiF_3^-$ anion should show three Si–F stretches. However, several of these bands appeared as shoulders on parent silane bands and may alternatively be assigned to perturbed parent species, rather than the distinct reaction product $(CH_3)_2SiF_3^-$.

Conclusions

The matrix reaction of CsF with methylfluorosilanes has led to the formation of the $(CH_3)SiF_4^-$ and $(CH_3)_2SiF_3^-$ anions, while formation of distinct anions containing more than two methyl groups was not possible, in agreement with gas-phase studies. Studies of chlorine atom substitution show that addition of even one chlorine atom in the reactants prevents

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product formation, i.e., the $(CH_3)SiClF_3^-$ anion could not be formed in this fashion. A C_{2v} structure was found to be preferred for the $(CH_3)SiF_4^-$ anion, while no structural information could be extracted for the $(CH_3)_2SiF_3^-$ anion.

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Registry No. $(CH_3)SiF_4^-$, 44244-53-3; $(CH_3)_2SiF_3^-$, 51108-60-2; $(CH_3)SiF_3$, 373-74-0; $(CH_3)_2SiF_2$, 353-66-2; CsF, 13400-13-0.

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Autocatalysis: Yet Another Mechanism for Spontaneous Cis–Trans Isomerization of Square-Planar Platinum(II) Complexes

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A detailed knowledge of the mechanisms and factors influencing cis–trans isomerization of square-planar and octahedral complexes is of vital importance in homogeneous catalysis since critical steps such as oxidative addition, reductive elimination, and insertion are mostly stereospecific reactions.[1] In by far the majority of cases the latter two steps proceed only if the relevant molecules are in the cis position.[1] Thus, groups which are mutually trans to each other would have to rearrange before they can undergo insertion or reductive elimination.

Octahedral complexes isomerize by a mechanism usually containing a trigonal bipyramid–octahedral equilibrium.[2] In contrast, square-planar systems isomerize via quite a number of different mechanisms. Some of these reactions may be catalyzed by ligands such as phosphines, arsines, stibines, and amines through either a consecutive displacement or a pseudorotation mechanism, depending on the polarity of the solvent and the softness of the coordinated ligands.[3]

The uncatalyzed cis–trans isomerization of $PtRXL_2$ systems (R = alkyl, aryl, substituted aryl; X = halide; L = phosphine) was proposed to proceed through a three-coordinate intermediate, but this intermediate was later shown to be a four-coordinate solvated species.[4] The actual isomerization step is still not clear. On the other hand the spontaneous

$$cis\text{-}PtX_2L_2 \rightleftarrows trans\text{-}PtX_2L_2 \qquad (1)$$

(X = halide, L = phosphine) isomerization rate was found to increase as the polarity and thus the coordinating ability of the solvent decreases.[3] Since noncoordinating solvents cannot form solvated intermediates or act as catalysts in a consecutive displacement or pseudorotation mechanism, it appeared to us that yet another mechanism was operative in this system. We have now investigated reaction 1 (X = I; L = PMe_2Ph, PEt_3; solvent = dimethylformamide, dimethyl sulfoxide, acetonitrile, benzene, toluene) kinetically and have found evidence for an autocatalytic mechanism.

Experimental Section

Complexes and Reagents. *cis*- and *trans*-PtI_2L_2[3] (L = PEt_3, PMe_2Ph) and $[(cod)Ir(phen)]ClO_4$[5] (cod = 1,5-cyclooctadiene, phen = phenanthroline) were prepared according to literature methods. All reagents and solvents were of AR grade.

Table I. Product and Absorption Maxima (nm) for Substrate and Product for the Cis–Trans Isomerization of PtI_2L_2 in Different Solvents

	L	
	PEt_3	PMe_2Ph
DMF product	two consecutive reactions	20% trans–80% cis eq[b]
λ_{max}(substrate)	cis 355; trans 335, 284	cis 353; trans 331, 288
λ_{max}(product)		352
λ_{diff}[a]	290	290
benzene product	100% trans	100% trans
λ_{max}(substrate)	cis 261; trans 337, 285	cis ...; trans 332, 292
λ_{max}(product)	337, 285	332, 292
λ_{diff}	290	300
toluene product	100% trans	100% trans
λ_{max}(substrate)	cis ...; trans 335	cis 363; trans 331, 292
λ_{max}(product)	335	331, 292
λ_{diff}	300	300
CH_3CN product	90% trans–10% cis eq	10% trans–90% cis eq
λ_{max}(substrate)	cis 352; trans 334, 283	cis 352; trans 332, 288
λ_{max}(product)	334, 280	348
λ_{diff}	284	290
Me_2SO product	80% trans–20% cis eq	20% trans–80% cis eq
λ_{max}(substrate)	cis 352; trans 334, 284	cis 351; trans 331, 288
λ_{max}(product)	340, 283	350, 287
λ_{diff}	284	290

[a] Wavelength of maximum difference in absorbance between substrate and product. [b] eq = equilibrium.

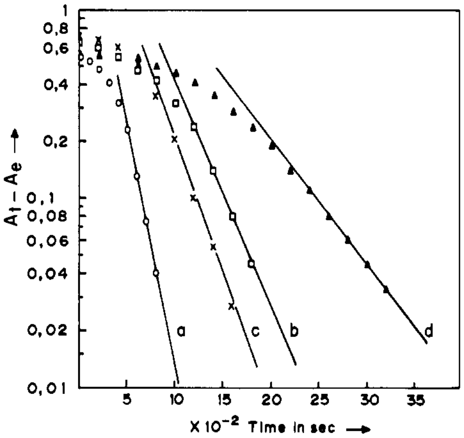

Figure 1. log $(A_t - A_e)$ vs. time for reaction 1 (*trans*-$PtI_2(PMe_2Ph)_2$ substrate) in DMF at 50 °C: (a) under an N_2 atmosphere, $k_{obsd} = 5.78 \times 10^{-3}\ s^{-1}$; (b) under an O_2 atmosphere, $k_{obsd} = 2.89 \times 10^{-3}\ s^{-1}$; (c) under an O_2 atmosphere and in the presence of 2.1×10^{-4} M $n\text{-}Bu_4NI$, $k_{obsd} = 3.61 \times 10^{-3}\ s^{-1}$; (d) under an N_2 atmosphere and in the presence of 0.2×10^{-4} M $[(cod)Ir(phen)]^+$, $k_{obsd} = 1.31 \times 10^{-3}\ s^{-1}$.

Kinetics. $(cod)Ir(phen)^+$ is dioxygen sensitive, and reactions involving this complex were always executed under nitrogen atmosphere.

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