

"Na⁺-free" wave is correct, then operationally the processes responsible for it are not all that different from those responsible for the Na⁺ ion paired wave.

Conclusions

1. In the presence of simple cations such as Na⁺, the binuclear Cu(II) 1,3,5-triketones and their diamine Schiff-base derivatives undergo reversible, sequential, two-electron reduction (in the range -0.5 to -0.65 V) in which the potentials for the transfer of the two electrons are nearly equal.

2. The only significant difference between the electrochemical results for Cu₂(BAA)₂ and Cu₂(PAA)₂ vs. those for Cu₂(BAA)₂en and Cu₂(PAA)₂en is a difference in the potential. The perturbation of the electroactive center by the diamine nitrogen donor atoms results in a more negative value of $E_{1/2}$ but does not cause E_1 and E_2 to separate. In this regard, the complexes behave as if they have one electroactive center that is sensitive to the average ligand environment rather than two.

3. Na⁺ ions form ion pairs with reduced complexes and in doing so significantly stabilize the Cu^I, Cu^I state as evidenced by the potential shift of about +0.3 V from that for the Na⁺-free system. In addition, the equivalence of E_1 and E_2 is dependent upon the Na⁺ concentration.

4. In the absence of simple cations such as Na⁺ (with Et₄NClO₄ as supporting electrolyte) a quasi-reversible, two-electron CV wave is observed in the range -0.8 to -1.0 V. This Na⁺-free species appears to have a potential separation, $E_2 - E_1$, of approximately -40 mV for the transfer of the two electrons. Addition of 1 equiv of Na⁺ causes the disappearance of this wave and the appearance of the -0.5 to -0.65 V wave.

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Registry No. Cu₂(PAA)₂en, 60116-99-6; Cu₂(PAA)₂, 84130-49-4; Cu₂(BAA)₂en, 56550-34-6; Cu₂(BAA)₂, 29745-70-8; Na, 7440-23-5; TEAP, 2567-83-1.

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Mechanism of Nucleophilic Displacement of the Bromide Ion by Thioethers in the Bromo(1,5-diamino-3-azapentane)platinum(II) Cation

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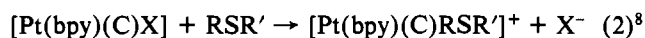
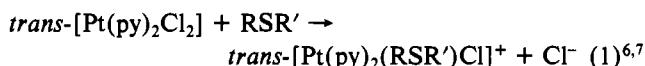
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The kinetics of the displacement of bromide from Pt(dien)Br⁺ (dien = 1,5-diamino-3-azapentane) by the thioethers (CH₃)₂S, (C₂H₅)₂(CH₃)S, (C₂H₅)₂S, (β-ClC₂H₄)(CH₃)S, (*i*-C₃H₇)₂S, (*n*-C₄H₉)₂S, (*sec*-C₄H₉)₂S, (CH₂)₄S, and thioxane have been studied in 95/5 vol % methanol/water solution at 25.0 °C. The second-order rate constants are insensitive to the changes in the inductive effect of the organic groups attached to the sulfur but decrease as their bulkiness is increased.

Introduction

Systematic studies of the way in which the nucleophilicities with respect to platinum(II) of a series of ligands with a constant donor atom depend upon the nature of the substituents have so far been confined to N donors (amines and heterocyclic nitrogen bases) and S donors (thioethers) reacting with neutral substrates.³ It has been possible, unambiguously, to separate electronic and steric effects in heterocyclic nitrogen bases by choosing the 4-position for the variation of the electronic effect and the 2- and 6-positions for the variation of the steric effect, and the conclusion from studies of this sort could be used to assess hindrance of less obvious molecules; i.e., it was shown that diethylamine had a steric hindrance similar to that of 2-methylpyridine.⁴ Early observations suggested significant retardation by steric hindrance and the absence of any marked inductive effects (as measured by the proton basicity of the amine) on the reactivity. Recently we have shown that this is not always true for substitutions at platinum(II) but depends upon the nature of the intimate mechanism.⁵

In the case of thioethers, the systematic studies involve the reaction of the neutral substrates⁶⁻⁸



(py = pyridine; bpy = 2,2'-bipyridyl; C and X are anionic ligands, X being the one which is displaced). In the reactions of the bpy complexes the plots of log k_2 against $-\sum\sigma^*$, where k_2 is the second-order rate constant for the entry of thioether and σ^* the Taft polar parameter for a substituent, are linear, with no significant deviations that might be ascribed to steric hindrance, while the reactions of *trans*-[Pt(py)₂Cl₂] with aliphatic thioethers show both effects.⁶ In the systematic study of Gaylor and Senoff⁷ the steric effect is held constant by using 4,4'-substituted diphenyl sulfides as nucleophiles. Here there is a marked dependence of nucleophilicity upon the inductive effect.

However, a study of the reaction between the palladium(II) substrate [Pd(dien)H₂O]²⁺ and thioethers in methanol/water has revealed the importance of steric effects and very little

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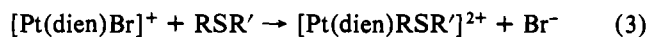
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influence of inductive effects,⁹ and in order to investigate how the observed behavior patterns depend upon the nature of the substrate, we intend to study a number of different platinum(II) substrates. This paper reports the kinetics of the reaction



Experimental Section

Materials. $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ was prepared according to the method of Mann¹⁰ by reacting dien (6.9 g; 66.9 mmol) with K_2PtCl_4 (13.86 g; 33.4 mmol) in water (200 cm³) acidified to pH 1 with HCl at 70 °C for 10 days under constant stirring. The reaction mixture was cooled and the product filtered off and dissolved in water. Excess LiBr was added, and pale yellow needles of the product separated. These were filtered off, washed with ice water, acetone, and ether, and dried under vacuum: yield 46.7% with respect to K_2PtCl_4 .

Anal. Calcd for $\text{C}_4\text{H}_{13}\text{N}_3\text{Br}_2\text{Pt}$: C, 10.59; H, 2.85; N, 9.2; Br, 34.9. Found: C, 10.8; H, 2.96; N, 9.3; Br, 35.3.

Complexes of the type $[\text{Pt}(\text{dien})\text{RSR}'](\text{ClO}_4)_2$ were obtained by stirring methanolic solutions of $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ with AgClO_4 in a 1/2 molar ratio and, after filtering off the precipitated AgBr, adding an equimolar amount of the desired thioether. The product was precipitated with ether as white crystals, which were filtered off, washed with ether, and dried.

Anal. $\text{RSR}' = (\text{CH}_3)_2\text{S}$: Calcd for $\text{C}_6\text{Cl}_2\text{H}_{19}\text{N}_3\text{O}_8\text{SPt}$: C, 12.9; H, 3.42; N, 7.51; Cl, 12.7; S, 5.73. Found: C, 12.9; H, 3.56; N, 7.44; Cl, 12.8; S, 5.88. $\text{RSR}' = (\text{ClCH}_2\text{CH}_2)(\text{CH}_3)\text{S}$: Calcd for $\text{C}_7\text{Cl}_3\text{H}_{20}\text{N}_3\text{O}_8\text{SPt}$: C, 13.9; H, 3.32; N, 6.92; Cl, 17.5; S, 5.28. Found: C, 13.8; H, 3.37; N, 6.90; Cl, 17.7; S, 5.26. $\text{RSR}' = (n\text{-C}_4\text{H}_9)_2\text{S}$: Calcd for $\text{C}_{12}\text{Cl}_2\text{H}_{31}\text{N}_3\text{O}_8\text{SPt}$: C, 22.4; H, 4.86; N, 6.53; Cl, 11.0; S, 4.89. Found: C, 22.3; H, 4.92; N, 6.51; Cl, 10.9; S, 4.89.

1,5-Diamino-3-azapentane (Aldrich) was an analytical grade reagent and was used without further purification. The thioethers (Aldrich) were purified by distillation at atmospheric or reduced pressure.

Kinetics. The reactions were started by mixing known prethermostated volumes of a nearly saturated solution of $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ in a 95/5 vol % methanol/water solvent system, which had been filtered and brought to the reaction temperature, and one of the appropriate thioether in the same solvent, in the thermostated cell of a Varian-Cary 219 or a Perkin-Elmer-Coleman 575 spectrophotometer, thermostated at 25.0 °C. The reactions were followed spectrophotometrically by scanning the spectra periodically in the range 260–340 nm and/or measuring the decreasing absorbance at 285 nm as a function of time. In all cases the concentration of the entering thioethers was at least 10 times greater of that of the substrate, in order to ensure pseudo-first-order conditions.

Results and Discussion

The spectrophotometric changes observed in the repetitive scanning of the spectra of the reaction mixture in the region 260–340 nm are characteristic of a single chemical change with well-maintained isobestic points throughout. The complexes $[\text{Pt}(\text{dien})\text{Br}]^+$ and $[\text{Pt}(\text{dien})(\text{RSR}')^{2+}$ (as measured for $\text{RSR}' = (\text{CH}_3)_2\text{S}$, $(\beta\text{-ClC}_2\text{H}_4)(\text{CH}_3)\text{S}$, and $(n\text{-C}_4\text{H}_9)_2\text{S}$) obey Beer's law in this solvent, and the initial and final spectra are virtually identical with those of authentic samples of $[\text{Pt}(\text{dien})\text{Br}]^+$ and $[\text{Pt}(\text{dien})(\text{RSR}')^{2+}$, respectively; therefore, we have no doubt that the measured kinetics refer to processes of type (3).

The change of the spectra with time follows first-order kinetics, and the plots of $\ln(A_t - A_\infty)$ vs. time (A_t and A_∞ being the absorbances of the reaction mixture at the wavelength chosen at time t and at the end of the reaction, respectively) are linear. The slopes of these plots (k_{obsd}) were determined by a weighted linear regression analysis of the data and are summarized in Table I. Plots of k_{obsd} vs. thioether concentration are linear, and the kinetics obey the two-term rate law $k_{\text{obsd}} = k_1 + k_2[\text{RSR}']$, which is usual for substitutions at planar tetracoordinate d^8 complexes. The slopes of these plots,

Table I. First-Order Rate Constants, k_{obsd} , for Reaction 3 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (95/5 vol %) at 25.0 °C

thioether	$[\text{RSR}']$, mol dm ⁻³	$10^4 k_{\text{obsd}}$, s ⁻¹
dimethyl sulfide	0.525	64.3 ± 0.5
	0.2625	31.5 ± 0.3
	0.105	13.2 ± 0.2
	0.0525	7.97 ± 0.03
	0.035	4.51 ± 0.02
ethyl methyl sulfide	0.501	50.8 ± 0.4
	0.3757	38.1 ± 0.5
	0.2505	24.0 ± 0.2
	0.0751	8.7 ± 0.2
	0.0376	3.74 ± 0.03
β -chloroethyl methyl sulfide	0.403	18.3 ± 0.5
	0.252	12.0 ± 0.2
	0.168	7.4 ± 0.1
	0.101	5.10 ± 0.04
	0.046	2.25 ± 0.01
diethyl sulfide	0.5091	32.3 ± 0.2
	0.4243	27.0 ± 0.2
	0.2121	13.06 ± 0.06
	0.0636	4.04 ± 0.02
	0.0427	2.64 ± 0.01
tetrahydrothiophene	0.4381	39.5 ± 0.5
	0.3286	30.55 ± 0.08
	0.2190	20.6 ± 0.1
	0.1314	12.87 ± 0.05
	0.0857	8.61 ± 0.09
diisopropyl sulfide	0.3238	0.994 ± 0.005
	0.2024	0.674 ± 0.003
	0.1349	0.486 ± 0.001
	0.0810	0.3276 ± 0.0007
	0.0530	0.238 ± 0.001
di- <i>n</i> -butyl sulfide	0.2424	10.2 ± 0.1
	0.1697	6.83 ± 0.01
	0.1131	4.70 ± 0.06
	0.0339	1.54 ± 0.01
	0.0170	0.760 ± 0.003
di- <i>sec</i> -butyl sulfide	0.3752	0.506 ± 0.004
	0.3449	0.469 ± 0.005
	0.2587	0.382 ± 0.004
	0.1724	0.270 ± 0.002
	0.1123	0.203 ± 0.001
1,4-thioxane	0.5403	29.7 ± 0.2
	0.3602	20.08 ± 0.07
	0.2494	14.85 ± 0.04
	0.1529	8.85 ± 0.01
	0.1147	7.039 ± 0.009
	0.0765	5.067 ± 0.005
	0.0529	3.756 ± 0.006

Table II. Second-Order Rate Constants, k_2 , for Reaction 3 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (95/5 vol %) at 25.0 °C

thioether	$-\Sigma\sigma^*$	$10^4 k_2$, M ⁻¹ s ⁻¹
dimethyl sulfide	0.00	120 ± 2
ethyl methyl sulfide	+0.10	100 ± 2
diethyl sulfide	+0.20	63.8 ± 0.5
β -chloroethyl methyl sulfide	-0.385	45 ± 1
diisopropyl sulfide	+0.38	2.73 ± 0.03
di- <i>n</i> -butyl sulfide	+0.26	40 ± 1
di- <i>sec</i> -butyl sulfide	+0.25	1.15 ± 0.06
tetrahydrothiophene	+0.18	87 ± 2
1,4-thioxane		53 ± 2

corresponding to the k_2 values, were obtained by a weighted linear regression analysis and are collected in Table II.

Apart from the reactions with the less reactive thioethers, the contribution from the solvolytic (k_1) pathway was always small and the error in the determination consequently very large. The reactions with diisopropyl sulfide and di-*sec*-butyl sulfide give $(11.0 \pm 1) \times 10^{-6}$ and $(7.5 \pm 0.6) \times 10^{-6}$ s⁻¹, respectively, but no other data exist for comparison in this

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solvent mixture. The value of k_1 for the bromo substrate in water at 25.0 °C is $1.32 \times 10^{-4} \text{ s}^{-1}$.¹¹ An increase of this magnitude on going from methanol to water is quite usual.

Attempts to extend the range of thioethers to include aryl substituents, e.g., the study of $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{S}$ and $(p\text{-CH}_3\text{C}_6\text{H}_4)(\text{CH}_3)\text{S}$ were unsuccessful because the first step was followed by a second change characterized by a very large increase in absorbance over the whole range of the spectrum studied. This interfered with the study of the first step even at early stages of the reaction. This effect is now being examined.

The bromo complex was chosen originally because of the very favorable absorbance changes accompanying the reaction, but there are no examples of kinetic studies of thioethers replacing coordinated bromide with which to compare these data. Nevertheless, the change of leaving group from Br to Cl does not greatly affect the reactivity patterns,³ and we feel justified in making comparison with systems where chloride is the leaving group. Table II also contains the values (where known) for $-\sum\sigma^*$, the sum of the Taft polar constants, which have been shown to be an acceptable measure of the relative reactivities of thioethers toward $[\text{Pt}(\text{bpy})(\text{C})\text{X}]$,⁸ where the inductive effects of R and R' control the rate.

The values of k_2 reported in Table II follow the sequence $(\text{CH}_3)_2\text{S} > (\text{CH}_2)_4\text{S} > (\text{C}_2\text{H}_5)(\text{CH}_3)\text{S} > (\text{C}_2\text{H}_5)_2\text{S} > \text{thioxane} > (\text{CH}_3)(\beta\text{-ClC}_2\text{H}_4)\text{S} > (n\text{-C}_4\text{H}_9)_2\text{S} > (i\text{-C}_3\text{H}_7)_2\text{S} > (sec\text{-C}_4\text{H}_9)_2\text{S}$, indicating that the inductive effects are negligible if not slightly negative and the 10^2 -fold change in reactivity is due almost entirely to steric effects.

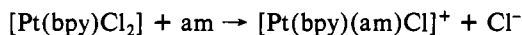
The difference in reactivity of dimethyl sulfide and tetrahydrothiophene could be used as a criterion for the relative contribution of electronic effects. The two ligands have much the same steric effects, but as the reactivity is enhanced by electron displacement toward the sulfur, the latter nucleophile would be more reactive. This has been found to be so in the reactions (1) and (2), but in the reaction with $[\text{Pt}(\text{dien})\text{Br}]^+$ (3) the effect is in the opposite direction. Other inversions of reactivity sequences have been reported,¹² as for example the negative slope of the plot of $\log k_2$ against the $\text{p}K_a$ of amH^+ for the reaction



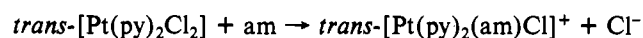
where L is a moderate to strong trans-effect ligand such as R_2S , $(\text{CH}_3)_2\text{SO}$, PR_3 , and $\text{P}(\text{OR})_3$, but it is very unlikely that the explanation offered for these systems applied in this case.

It is therefore clear that the general behavior of $[\text{Pt}(\text{dien})\text{Br}]^+$ with thioethers is totally opposite to that reported previously, particularly for the reactions of the type (2), but is very similar to that observed for $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$.

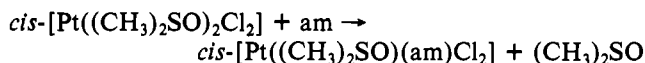
Such a duality of behavior for the entry of thioethers appears to be closely related to the recently observed analogous duality for the nucleophilicity of amines toward platinum(II) substrates.⁵ Amines were known to react with platinum(II) complexes in ligand displacement processes with a very small dependence (positive or negative) upon their proton basicity, as measured by the corresponding $\text{p}K_a$ values. For instance, in the reactions



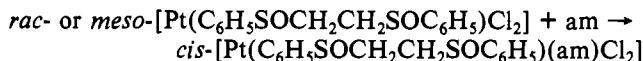
the dependence of the reactivity upon the basicity of the amines having the same extent of steric hindrance obeys the relationship $\log k_2 = A(\text{p}K_a) + \text{constant}$, but the value of A is only 0.06,⁴ while in the reactions



A is 0.05.³ However, in the reactions



and in the processes



corresponding to the opening of the chelate ring, in 1,2-dimethoxyethane at 25 °C the dependence of the reactivity upon proton basicity is quite important, the corresponding coefficients A being 0.41 and 0.58, respectively.^{5,13} In the cases of amines such a duality has been attributed to differences in the intimate mechanism. It is known³ that in these substitutions the formation of the new bond between platinum and the entering group is relatively well separated from the rupture of the bond between the metal and the leaving group so that the total process is asynchronous and two maxima separated by a minimum (corresponding to a transient 5-coordinated intermediate) are present in the reaction profile. The interpretation for the cases in which proton basicity of the entering amine strongly affects the reactivity was that the second maximum must be the rate-determining transition state. This conclusion, which appears to contradict the general supposition that, if the rate of entry of a nucleophile is sensitive to substituent effects (as measured by proton basicity, $-\sum\sigma^*$ or $-\sum\sigma\text{p}$), it must indicate that the rate-determining step is bond formation, has been justified by a proper consideration of the intimate mechanism. The donor capacity of the ligand is most important when the bond with the metal is broken, and a stationary-state treatment applied to the concentration of the 5-coordinate intermediate gives $k_2 = k_a k_d / (k_{-a} + k_d)$, where k_a is the rate constant associated with the initial bond formation and k_{-a} and k_d are the rate constants associated with the bond breaking leading to reagents and products, respectively. When bond making is rate limiting, i.e., $k_d \gg k_{-a}$, $k_2 \rightarrow k_a$, and only when bond breaking is rate limiting ($k_{-a} \gg k_d$, $k_2 \rightarrow k_a k_d / k_{-a}$), does the breaking of the bond with the entering group contribute to k_2 .

This duality is also found in the case of thioethers as nucleophiles, and we can apply the same kind of interpretation. In the present case, where the inductive effects of the groups attached to the sulfur atom and therefore their relative σ -donor abilities do not affect the rate constant, the bond between the platinum and the sulfur must be relatively weak in the rate-determining transition state, which must therefore correspond to the first maximum in the reaction profile. In the other systems, where k_2 does depend on the inductive effect, the bond-breaking maximum must rise with respect to that for bond making, as in reactions 1 and 2.

Although the nucleophilicity of thioethers toward $[\text{Pt}(\text{dien})\text{Br}]^+$ is insensitive to inductive effects, there is a significant retardation by steric hindrance. This is the first time that this has been demonstrated for thioethers entering a platinum(II) substrate. Diethyl sulfide is less reactive toward $\text{trans-}[\text{Pt}(\text{py})_2\text{Cl}_2]$ than dimethyl sulfide,⁶ but no discussion of steric effects was introduced and the studies of Gaylor and Senoff⁷ do not include variation of the steric hindrance. Such effects are absent in the reactions of $\text{Pt}(\text{bpy})(\text{C})\text{X}$ with thioethers.⁸ Since steric hindrance arises from the interaction between the entering group and the axial ligands in the trigonal-bipyramidal transition state (i.e., those that were cis to the leaving group in the substrate),³ any comparison must take account of the variation of these cis ligands. Although the

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reaction center is different, the $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+} + \text{RSR}'$ reaction provides the closest comparison.⁹ In spite of the difference in charge, leaving group, and reaction center and the very large resultant difference in reactivity (6 orders of magnitude), the relative rates in both systems are reasonably similar. Neither shows any sensitivity to inductive effects and the relative rate constants are in the order $(\text{CH}_3)_2\text{S}$ (85) > $(\text{C}_2\text{H}_5)_2\text{S}$ (33) > $(n\text{-C}_4\text{H}_9)_2\text{S}$ (18) > $(i\text{-C}_3\text{H}_7)_2\text{S}$ (2.5) > $(\text{sec-C}_4\text{H}_9)_2\text{S}$ (1.0) for the palladium system and $(\text{CH}_3)_2\text{S}$ (104) > $(\text{C}_2\text{H}_5)_2\text{S}$ (55) > $(n\text{-C}_4\text{H}_9)_2\text{S}$ (35) > $(i\text{-C}_3\text{H}_7)_2\text{S}$ (2.4) > $(\text{sec-C}_4\text{H}_9)_2\text{S}$ (1.0) for the platinum complex. Since the dimensions of Pd(II) and Pt(II) are essentially the same,¹⁴ this

suggests a close similarity of the intimate mechanism of the two processes.

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Registry No. Pt(dien)Br⁺, 15522-24-4; (CH₃)₂S, 75-18-3; (C₂H₅)(CH₃)S, 624-89-5; (C₂H₅)₂S, 352-93-2; (β-ClC₂H₄)(CH₃)S, 542-81-4; (i-C₃H₇)₂S, 625-80-9; (n-C₄H₉)₂S, 544-40-1; (sec-C₄H₉)₂S, 626-26-6; (CH₂)₄S, 110-01-0; thioxane, 505-29-3.

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Oxidation Reactions of Perfluoro(methanimine) and Related Compounds. Electrophilic Additions to CF₂=NF and Fluoride-Promoted Oxidation of Perhalo Imines and Nitriles by Cl₂ and Br₂

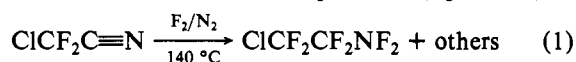
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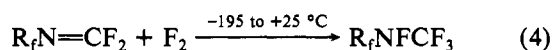
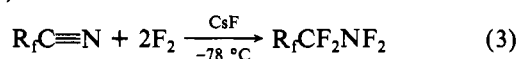
Reactions of CF₂=NF with S₂O₆F₂, BrOSO₂F, ClOSO₂F, CF₃OF, CF₃OCl, FOSO₂F, Cl₂, Br₂, and I₂ were carried out. The electrophilic halides and pseudohalide XOSO₂F (X = Cl, Br, OSO₂F) add in high yield to form FSO₂OCF₂NFX. The other reagents are unreactive under the same conditions, and only FOSO₂F resulted in a small yield of the addition product FSO₂OCF₂NF₂ on heating. The in situ formation of CF₃NF⁻ from CF₂=NF and MF (M = K, Cs) in the presence of Cl₂ and Br₂ results in the formation of CF₃NXF (X = Cl, Br). These reactions were extended with Br₂ to the imines CF₃CF=NF and C₂F₅CF=NF with similar results. With the nitriles CF₃CN and XCN (X = Cl, Br), reactions of Cl₂ in the presence of MF results in chlorofluorinations forming C₂F₅NCl₂, C₂F₅N=NC₂F₅, and CF₃NCl₂, respectively. With Br₂, bromofluorination is observed, forming CF₃CF=NBr, C₂F₅N=NC₂F₅, and CF₃N=NCF₃ as the respective products.

Introduction

The oxidation of fluorinated compounds containing carbon-nitrogen multiple bonds by halogens has been studied by many investigators. Earlier work on the direct fluorination of fluorocarbon nitriles, dinitriles, and other related compounds at higher temperatures led to a variety of interesting products, including in some cases products resulting from the simple addition of fluorine to the C-N multiple bonds (eq 1 and 2).²⁻⁴

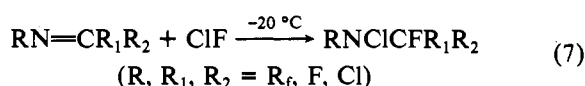
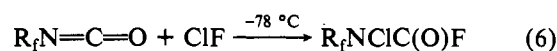
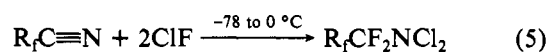


In general, these reactions are low yield and lead to many different products resulting from bond cleavage. Subsequently, it was shown that CsF catalyzed the low-temperature addition of fluorine to fluorocarbon nitriles⁵ and that certain fluorinated imines would add fluorine directly without apparent catalysis (eq 3 and 4).⁶

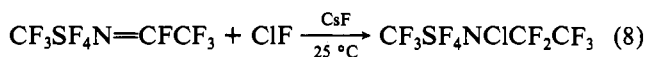


Chlorine monofluoride has also been shown to add readily to almost any fluorinated compound containing a carbon-

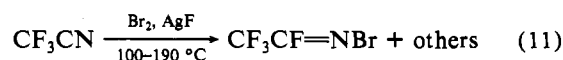
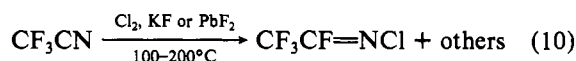
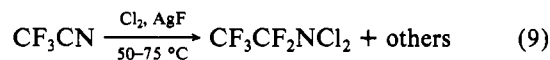
nitrogen double or triple bond.⁷⁻¹¹ Thus nitriles react at low temperatures to add 2 mol of ClF, and a variety of imines add ClF (eq 5-7). However, some reactions of ClF with imines



require a CsF catalyst (eq 8).¹² Similarly, certain per-



fluoroalkyl nitriles undergo low-yield chlorofluorination or bromofluorination on heating with metal fluorides (AgF, PbF₂, KF) and halogen (eq 9-11).¹³ Finally, ClOSO₂F has also been



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