6.38 and 7.15 (s, 1 H, H-6); M^+ 236.152 (calcd for $C_{13}H_{20}N_2O_2$, 236.152).

1,1′-Diacetyl-1,2,3,4,1′,2′,3′,4′-octahydro-5,6′-bipyridyl (22). Hystrine hydrochloride (**11**)[4] (125 mg) was refluxed for 1 hr with excess anhydrous sodium acetate and acetic anhydride, 10% KOH was added, and the mixture was extracted with dichloromethane to give **22** as a colorless oil (125 mg, 80%): ir (neat) 1640 cm^{-1}; nmr 1.8–2.2 (b, 8 H), 2.05 (s, 6 H, H-8,8′), 3.69 (t, 4 H, H-2,2′), 5.40 (t, 1 H, H-5′), 6.70 and 7.35 (s, 1 H, H-6); M^+ 248.152 (calcd for $C_{14}H_{20}N_2O_2$, 248.152).

Ammodendrine-*1′*-d_1 (1a). When **1** was slurried with D_2O and the mass spectrum taken, the best incorporation obtained in several attempts was 40% d_1, 60% d_0.

Ammodendrine-*8,8,8*-d_3 (1b). Isotripiperidine (**23**) was treated with acetyl-d_3 chloride as described for the preparation of **15** to give **1b** of 95% isotopic purity.

Ammodendrine-*2′*-d_1 (1c). *N*-Acetylhystrine (**12**)[4] (24 mg) was refluxed with excess sodium borodeuteride for 1 hr in EtOH. The solvent was removed *in vacuo*, 10% KOH was added, and the mixture was extracted with dichloromethane to give **1c** (95% d_1).

Ammodendrine-*2,2,6′,6′*-d_4 (1e). 4-Cyanobutyraldehyde diethyl acetal (**24a**)[21] was refluxed overnight with lithium aluminum deuteride in ether.[22] After careful addition of water, the mixture was filtered and extracted with 10% HCl. This solution, containing 1,2,3,4-tetrahydropyridine-*2,2*-d_2 (**25a**), was neutralized (K_2CO_3), extracted with ether, dried ($MgSO_4$), and evaporated to yield the labeled trimer. Refluxing with piperidine hydrochloride in acetone gave the labeled isotripiperidine. Acetylation and acid treatment as previously described led to **1e** (90% d_4, 10% d_3).

Ammodendrine-*3,3,5′,5′*-d_4 (1f). Calcium metal (2.5 g) was dissolved in heavy water (25 ml) and **24a** (2 g) was added. This was refluxed for 12 hr, cooled, filtered, extracted with ether, dried ($MgSO_4$), and evaporated to give 4-cyanobutyraldehyde-*4,4*-d_2 diethyl acetal (**24b**) (1.7 g, 80% d_2). This was converted to the labeled isotripiperidine and then to **1f** (60% d_4, 30% d_3, 10% d_2).

Ammodendrine-*3′,3′*-d_2 (1d). Ethyl 1,4,5,6-tetrahydronicotinate (**26**)[24] (500 mg) was refluxed under N_2 for 30 min in dilute deuteriophosphoric acid (from P_2O_5 (700 mg) and heavy water (30 ml))[19] After cooling and neutralization (K_2CO_3), the labeled isotripiperidine was extracted with ether and then converted by the standard method to **1d** (70% d_2, 20% d_1, 10% d_0).

Ammodendrine-*2,2,6,2′,6′,6′*-d_6 (1g). Glutarimide (**27**) (Aldrich Chem.) (4 g) was refluxed with lithium aluminum deuteride (1.7 g) for 3 days in tetrahydrofuran. After careful addition of water, the mixture was filtered and distilled to yield piperidine-*2,2,6,6*-d_4 (**28**). This was converted to the labeled isotripiperidine by known procedures.[25] Acetylation gave **1g** (90% d_6, 10% d_5).

***N′*-Methylammodendrine-*7′,7′,7′*-d_3 (9a).** Refluxing of **1** with excess methyl-d_3 iodide in acetone overnight, solution of the precipitated salt in 10% KOH, extraction with dichloromethane, drying ($MgSO_4$), and evaporation gave **9a** of 95% isotopic purity.

Labeled *N′*-Acetylammodendrines (13a–g). The labeled compounds were prepared by two methods. Method A involved acetic anhydride (or acetic-d_6 anhydride)–pyridine acetylation of the appropriately labeled ammodendrine. Method B involved heating the appropriately labeled isotripiperidine (described above) with excess acetic anhydride at 100° for 1 hr. The following list gives the method of preparation and deuterium incorporations for **13a–g**: **13a**, *N′*-acetylammodendrine-*2′*-d_1, method A, 95% d_1; **13b**, *N′*-acetylammodendrine-*8′,8′,8′*-d_3, method A, 90% d_3, 10% d_2; **13c**, *N′*-acetylammodendrine-*8,8,8,8′,8′,8′*-d_6, method A, 85% d_6, 10% d_5, 5% d_4; **13d**, *N′*-acetylammodendrine-*3′,3′*-d_2, method B, 70% d_2, 20% d_1, 10% d_0; **13e**, *N′*-acetylammodendrine-*3,3,5′,5′*-d_4, method B, 60% d_4, 30% d_3, 10% d_2; **13f**, *N′*-acetylammodendrine-*2,2,6′,6′*-d_4, method B, 90% d_4, 10% d_3; **13g**, *N′*-acetylammodendrine-*2,2,6,2′,6′,6′*-d_6, method B, 90% d_6, 10% d_5.

Oxaziridine–Silver Fluoborate Complexes. Site of Complexation by Carbon-13 Nuclear Magnetic Resonance and X-Ray Photoelectron Spectroscopy[1]

DeLanson R. Crist,* Guy J. Jordan, and Joseph A. Hashmall

Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. 20007. *Received January 2, 1974*

Abstract: Silver fluoborate complexes of a variety of oxaziridines, the first stable complexes of oxaziridines reported, were isolated and found to have the stoichiometry 2(oxaziridine)·$AgBF_4$. In methylene chloride, proton and ^{13}C nmr spectra of oxaziridines showed downfield shifts upon complexation. Comparison of these shifts with those for diethyl ether and triethylamine provides evidence for complexation at nitrogen. X-Ray photoelectron spectroscopy in the solid state also indicates complexation at nitrogen with considerable back-donation from Ag^+ to the oxaziridine, an interpretation supported by MINDO/2 calculations. Complexation with other salts, $AgClO_4$, $AgNO_3$, $LiClO_4$, and $CsClO_4$, is also discussed along with reactivity of the $AgBF_4$ complexes and their importance in mechanistic pathways.

Small ring charged heterocycles,[2] shown to be useful for their biological activity[3] as well as for synthetic intermediates[4] and polymerization catalysts,[5] and metal complexes of some small ring heterocycles[6] have attracted the interest of many researchers in recent years.

Oxaziridines, three-membered ring compounds containing oxygen and nitrogen atoms, are nonbasic compounds,[7] and although SCF–LCAO–MO calculations for protonation of oxaziridines suggest nitrogen to be the most favored position for protonation,[8] mechanisms for acid hydrolysis have been proposed with

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(2) D. R. Crist and N. J. Leonard, *Angew. Chem., Int. Ed. Engl.*, 8, 962 (1969).

(3) A. Loveless, "Genetic and Allied Effects of Alkylating Agents," The Pennsylvania University Press, University Park, Pa., 1966.

(4) N. J. Leonard, J. V. Paukstelis, and L. E. Bradley, *J. Org. Chem.*, 29, 3383 (1964).

(5) P. E. Fanta in "Heterocyclic Compounds with Three- and Four-Membered Rings," Vol. 19, Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 557.

(6) (a) R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. R. Thirtle, and H. Gilman, *J. Amer. Chem. Soc.*, 78, 6027 (1956); (b) T. B. Jackson and J. O. Edwards, *Inorg. Chem.*, 1, 398 (1962); (c) R. W. Kiser and T. W. Lapp, *ibid.*, 1, 401 (1962); (d) J. Scherzer, P. K. Phillips, L. B. Clapp, and J. O. Edwards, *ibid.*, 5, 847 (1966); (e) K. Krishnan and R. A. Plane, *ibid.*, 5, 852 (1966).

(7) E. Schmitz, *Advan. Heterocycl. Chem.*, 2, 90 (1963).

(8) C. Ghio and J. Tomasi, *Theor. Chim. Acta*, 30, 151 (1973).

Table I. Analysis of Solid Oxaziridine·$AgBF_4$ Complexes Based on 2D·$AgBF_4$ Stoichiometry

Oxaziridine donor, D	Mp, deg	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%Ag Calcd	%Ag Found	%D[c] Calcd	%D[c] Found
1	81–82	30.26	30.17	5.59	5.48	7.06	6.94	27.17	27.53[a]	50.96	50.45
2b	69–71	40.28	40.18	6.34	6.39	5.87	5.70	22.61	22.81[a]	59.20	59.87
2c	81–82	35.20	35.17	5.17	5.18	5.13	5.07	19.76	22.64[b]		

[a] Volhard titration. [b] Mohr titration. [c] By nmr integrations using dioxane as internal standard.

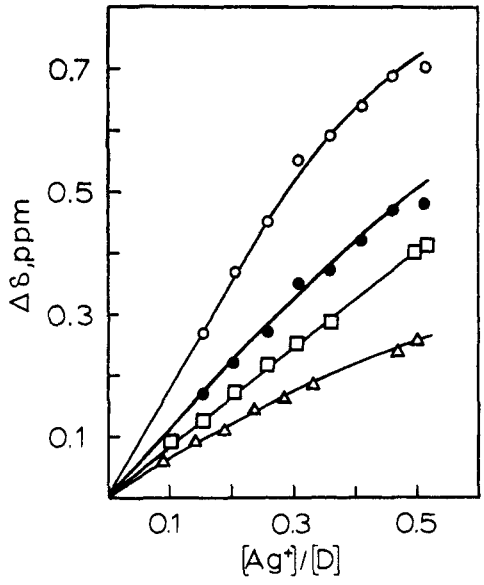


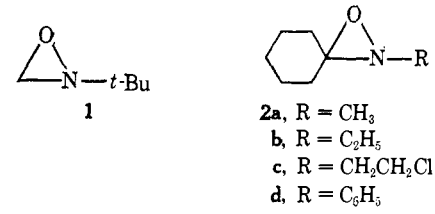
Figure 1. Dependence of α proton downfield shifts upon complexation on moles of $AgBF_4$ added per mole of donor: (△) diethyl ether; (□) triethylamine; (●) H_A of **1**; (○) H_B of **1**.

protonation at oxygen.[9] Some work has been done on Fe^{2+}- and Fe^{3+}-catalyzed reactions of oxaziridines, though mechanisms for these reactions are not clearly understood.[10]

Since there is evidence that suggests Ag^+ can bond to oxygen,[11] nitrogen,[12,13] and strained σ bonds,[14] and, since there is evidence suggesting that stabilities of Ag^+ complexes do not necessarily follow donor basicity,[13,15] we undertook a spectroscopic study to determine the most favored site of complexation in oxaziridine–Ag^+ complexes which were isolated in this laboratory. To our knowledge, these represent the first examples of stable oxaziridine–metal ion complexes. We now report the results of our characterization and study of $AgBF_4$ complexes with oxaziridines under nonnucleophilic conditions in methylene chloride and in the solid state. The possibility of complexation with Li^+, which could serve as a model for H^+, was also investigated.

Results

Isolation of Solid $AgBF_4$ Complexes. Various oxaziridine donors, **1**, **2a–d**, were treated in methylene chloride with $AgBF_4$ in a 2:1 mole ratio. On cooling with added ether, white crystals, which separated for **1**, **2b**, **2c**, and **2d**, were stable for several days at room temperature under nitrogen. The composition of the crystals was determined by microanalysis, titration for Ag^+, and nmr analysis of the donor. Results given in Table I show that solid complexes had the stoichiometry 2D·$AgBF_4$. Free oxaziridine could be recovered from its solid complex by repeated washings with distilled water.



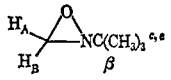
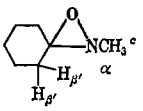
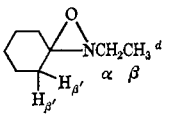
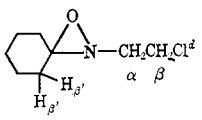
When **2d** was treated with $AgBF_4$, a crystalline product was obtained, but this was shown to be the $AgBF_4$ complex of *N*-phenylcaprolactam. The complex was prepared independently by pyrolysis of **2d** at 140° and then treatment of the product, *N*-phenylcaprolactam,[16] with $AgBF_4$. Silver ion is apparently an effective catalyst for this ring-expansion reaction.

Nmr of $AgBF_4$ Complexes in Methylene Chloride. In order to determine the extent of complexation of $AgBF_4$ with oxaziridines, a detailed study with 2-*tert*-butyloxaziridine, diethyl ether, and triethylamine was made, with the latter two donors serving as models for oxygen and nitrogen complexation sites, respectively. Various amounts of $AgBF_4$ added to a solution of donor caused downfield shifts in all protons, as shown for the α protons in Figure 1. Similar trends were observed for all β protons. The fact that there were no signals for free donor, even at low Ag^+:donor ratios, shows that there is rapid exchange of Ag^+ between donors. Data with mole ratios of $AgBF_4$ greater than 0.5 could not be obtained, since in all cases this represented nearly the solubility limit of $AgBF_4$, as also obtained for ketone–$AgBF_4$ solutions.[17] The slight, apparent curvature in Figure 1 for diethyl ether and oxaziridine **1** suggests[18] comparable formation constants for 3D·$AgBF_4$[11] and 2D·$AgBF_4$.

We consider that at a 0.5 mol ratio of $AgBF_4$, essentially all the donor is complexed for the following reasons: adding a small amount of free $AgBF_4$ to a 2% solution of 2(**1**)·$AgBF_4$ and 25% solutions of 2(**1**)·$AgBF_4$ (Figure 1) causes slight *upfield* shifts, the opposite effect one would predict assuming mass action on a partially dissociated complex, and, more significantly, the solubility limit of $AgBF_4$ in solutions containing *ca.* 25% donor (Figure 1 data) occurs at 0.5 mol ratio (a sol-

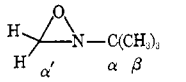
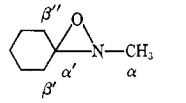
(9) A. R. Butler and B. C. Challis, *J. Chem. Soc. B*, 778 (1971).
(10) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).
(11) H. Meerwein, V. Hederich, and K. Wunderlick, *Arch. Pharm. (Weinheim)*, **291**, 541 (1958).
(12) C. Golumbic, *J. Amer. Chem. Soc.*, **74**, 5777 (1952).
(13) J. L. Pauley and H. H. Hau, *J. Phys. Chem.*, **70**, 3363 (1966).
(14) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).
(15) W. J. Peard and R. T. Pflaum, *J. Amer. Chem. Soc.*, **80**, 1593 (1958).
(16) H. Krimm, *Chem. Ber.*, **91**, 1057 (1958).
(17) D. R. Crist, Z.-H. Hsieh, G. J. Jordan, F. P. Schinco, and C. A. Maciorowski, *J. Amer. Chem. Soc.*, **96**, 4932 (1974).
(18) M. I. Foreman, J. Gorton, and R. Foster, *Trans. Faraday Soc.*, **66**, 2120 (1970).

Table II. Proton Shifts on Complexation with $AgBF_4$ in Methylene Chloride

Donor	Donor concn, mol/kg soln	Position	δ_{donor}[a]	$\delta_{complex}$[a]	$\Delta\delta$[b]
$(C_2H_5)_2NCH_2CH_3$[c]	2.36	α	2.46	2.86	0.40
α β		β	0.97	1.25	0.28
$C_2H_5OCH_2CH_3$[c]	2.57	α	3.42	3.68	0.26
α β		β	1.14	1.32	0.18
	2.36	H_A	3.76	4.27	0.51
		H_B	3.66	4.38	0.72
		β	1.05	1.25	0.20
	2.81	α	2.68	3.11	0.43
		β'	1.77	1.91	0.14
	~0.8	α	2.83, 2.86	3.12, 3.30	0.29, 0.44
		β	1.20	1.45	0.25
		β'	1.78	1.97	0.19
	~0.8	α	3.12, 3.28	3.40, 3.62	0.28, 0.34
		β	3.88	4.10	0.22
		β'	1.85	1.98	0.12

[a] Reported in ppm from internal TMS. [b] Downfield shift on complexation, relative to free donor. [c] Data taken on a Bruker HFX-90 at 90 MHz (26°) with an uncertainty of ±0.01 ppm. [d] Data taken on a Varian A-60 (36°) with an uncertainty of ±0.04 ppm. [e] H_A cis to the lone pair of nitrogen, H_B trans to the lone pair of nitrogen. Assignments based on the work of R. D. Boyd, R. Spratt, and D. M. Jerina, *J. Chem. Soc. C*, 2650 (1969).

Table III. Carbon-13 Shifts on Complexation with $AgBF_4$ in Methylene Chloride

Donor	Donor concn, mol/kg soln	Position	δ_{donor}[a]	$\delta_{complex}$[a]	$\Delta\delta$[b]
$(C_2H_5)_2NCH_2CH_3$	2.36	α	4.70	50.6	+3.6
α β		β	12.4	13.2	+0.8
$C_2H_5OCH_2CH_3$	2.57	α	66.2	68.3	+2.1
α β		β	15.5	16.0	+0.5
	2.36	α[c]	58.1	61.8	+3.7
		β	25.1	25.5	+0.4
		α'[c]	65.5	69.3	+3.8
	2.81	α	40.7	44.1	+3.4
		α'	84.3	87.9	+3.6
		β'[d]	36.5	38.7	+2.2
		β''[d]	27.6	27.0	−0.6

[a] In ppm from internal TMS. Data taken on a Bruker HFX-90 at 22.63 MHz (26°) with an uncertainty of ±0.1 ppm. [b] Shifts on complexation, relative to free donor. [c] Assignments of α carbons were made based on an off-resonance experiment. [d] A tentative assignment of β' cis to the nitrogen lone pair and β'' trans to the lone pair was made by analogy to work done on oximes by G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972).

ubility *ca.* 380 times that in pure CH_2Cl_2) requiring near quantitative formation of a 2:1 complex.[19] Throughout this paper we will consider nmr chemical shifts obtained at a 0.5 mol ratio as characteristic of the pure complex. Small errors resulting from this assumption will not affect the general conclusions.

(19) J. Solodar and J. P. Petrovich, *Inorg. Chem.*, **10**, 395 (1971), have shown similar, near quantitative formation of cyclohexene·$AgBF_4$ complex in CH_2Cl_2 by an alternate method in solutions which, however, would not be suitable for obtaining ^{13}C nmr spectra.

Proton shifts for all complexes are given in Table II, where it can be seen that complexation causes a downfield shift for all protons. Natural abundance ^{13}C shifts for complexes with two oxaziridines and the model compounds are given in Table III. To our knowledge, these represent the first ^{13}C data reported for Ag^+ complexes with ethers or simple amines.[20] To determine the effect of BF_4^-, the proton spectrum of **1** was taken in the presence of tetrabutylammonium fluoborate (see Table IV). Since no changes in chemical shifts occurred, $\Delta\delta$ values observed with $AgBF_4$ are due to a specific interaction with Ag^+.

Table IV. Effect of Various Salts on Proton Chemical Shifts of 2-*tert*-Butyloxaziridine[a]

Added salt	Mole ratio, [salt]/[donor]	H_A δ_{obsd}	H_A $\Delta\delta$	H_B δ_{obsd}	H_B $\Delta\delta$	H_{CH_3} δ_{obsd}	H_{CH_3} $\Delta\delta$
None	0.0	3.76		3.68		1.04	
$AgBF_4$	0.50	4.18	0.42	4.37	0.69	1.24	0.20
$AgClO_4$	0.50	4.13	0.37	4.35	0.67	1.23	0.19
$AgNO_3$	*ca.* 0.15[b]	3.91	0.15	3.91	0.23	1.11	0.07
Bu_4NBF_4	0.1	3.77	0.01	3.68	0.0	1.04	0.0

[a] In ppm from internal TMS. Data taken on a Bruker HFX-90 at 90 MHz (26°) with an uncertainty of ±0.01 ppm. Donor concentration was 0.79 mol/kg soln. [b] Solution saturated with salt.

Complexation of Other Metal Salts in Methylene Chloride. As indicated in Table IV, similar trends were observed for the interaction of $AgClO_4$ with **1**. The downfield shifts observed for the interaction of $AgNO_3$ with **1** were similar to those observed for $AgBF_4$

(20) J. P. C. M. van Dongen and C. D. M. Beverwijk, *J. Organometal. Chem.*, **51**, C36 (1973), have reported some ^{13}C chemical shifts of some hetero-substituted alkenes with Ag^+; however, their data represent interaction of Ag^+ with the alkene double bond as well as with the heteroatom.

and $AgClO_4$ but proportional to its solubility. Apparently, complexation with Ag^+ by **1** was not sufficient to offset the favorable crystal forces of $AgNO_3$. In Table V, ^{13}C chemical shift changes for **1** in the presence of

Table V. Effects of Various Salts on ^{13}C Chemical Shifts of 2-*tert*-Butyloxaziridine[a]

Added salt	Mole ratio, [salt]/[donor]	C_α δ_{obsd}	C_α $\Delta\delta$	C_β δ_{obsd}	C_β $\Delta\delta$	$C_{\alpha'}$ δ_{obsd}	$C_{\alpha'}$ $\Delta\delta$
None	0.0	58.1		25.1		65.5	
$AgBF_4$	0.50	68.8	3.7	25.5	0.4	69.3	3.8
$LiClO_4$	<0.05[b]	57.9	−0.2	25.0	−0.1	65.5	0.0
$CsClO_4$	<0.01[b]	57.8	−0.3	24.9	−0.2	65.4	−0.1

[a] In ppm from internal TMS with the notation of Table III. Data taken on a Bruker HFX-90 at 22.63 MHz (26°) with an uncertainty of ±0.1 ppm. Donor concentration was 2.36 mol/kg soln. [b] Solution saturated with salt.

$CsClO_4$ and $LiClO_4$ are reported. For these salts, small *upfield* shifts were observed, though the extent of complexation was very slight.

X-Ray Photoelectron Spectroscopy (XPES). The X-ray photoelectron spectra of **2b** and its solid $AgBF_4$ complex were taken. The nitrogen 1s peak in the oxaziridine occurred at a binding energy of 399.5 eV while the equivalent ionization in the complex was 398.9 eV. For both the parent compound and its silver complex, the oxygen 1s binding energies were 531.6 eV.

Discussion

Site of Complexation in Oxaziridines. For complexes with silver salts, the similar trends in $\Delta\delta$ for $AgBF_4$ and $AgClO_4$ with no effect for tetrabutylammonium fluoborate show that Ag^+ bonds to oxaziridines. Although there are three sites of complexation, ^{13}C shifts in Table III indicate clearly that nitrogen is the most favored donor site in methylene chloride. On complexing, the ring carbon of **1** shifted downfield by 3.8 ppm, the same as the α carbon in triethylamine (3.6 ppm). This $\Delta\delta$ is substantially larger than that of 2.1 ppm for the α carbon of the diethyl ether complex. Even more conclusive is the shift noted for the α carbon of the *tert*-butyl group in **1** which is also 3.7 ppm and rules out bonding to oxygen.

Proton data in Table II are consistent with this conclusion but do not provide as clear a distinction between nitrogen *vs.* oxygen sites. This is probably due to the fact that protons on the ring of **1** are fixed with respect to the nitrogen lone pair, while the α protons in triethylamine and diethyl ether are free to rotate, and hence an averaging of various conformations is observed.

In the solid state, the fact that XPES shows a shift of 0.6 eV for the nitrogen 1s binding energy, together with lack of any measurable shift in the oxygen 1s ionizations, supports the conclusion that the nitrogen atom is the site of complexation. Interestingly, the nitrogen is shifted to *lower* binding energy on complexation, indicating an increase in electron density on the nitrogen. This must be explained by back-donation of the filled silver d orbitals into the lowest unoccupied oxaziridine orbitals.[21] This explanation is supported by MINDO/2[22] calculations on 2-methyloxaziridine using a geometry derived from that of *cis*-2-isopropyl-3-(4-nitrophenyl)oxaziridine[23] with optimization of C–H bond lengths according to the method of Hashmall and Raynor.[24] The highest occupied molecular orbital resulting from this calculation has a population of approximately one at the nitrogen and about one-half on the oxygen. This orbital can best be described as a Walsh type[25] N–O bond. The lowest unoccupied molecular orbital has potential populations of about one-half on the nitrogen and 0.3 to 0.4 on the adjacent carbons. There is only a very small contribution of the oxygen atomic orbitals to this molecular orbital. These orbitals are both of satisfactory geometry for interaction with metal orbitals on an atom complexing at the nitrogen. Electron donation from the oxaziridine to the silver atom would remove electron density mainly from the nitrogen and oxygen atoms, while back-donation would transfer density to the nitrogen and carbons. The lack of measurable shift in the oxygen together with the apparent increase in electron density on nitrogen indicate that the dominant factor is back-donation from silver to nitrogen.

On the basis of these XPES results, a tentative interpretation of ^{13}C downfield shifts on complexation is that deshielding by electron withdrawal, as in the case of $2Et_3N \cdot AgBF_4$, determines the direction of the change in chemical shift. This is somewhat analogous to alkene $\cdot AgBF_4$ complexes,[26] in which α carbons are also deshielded despite back-donation of electrons to olefinic carbon atoms.

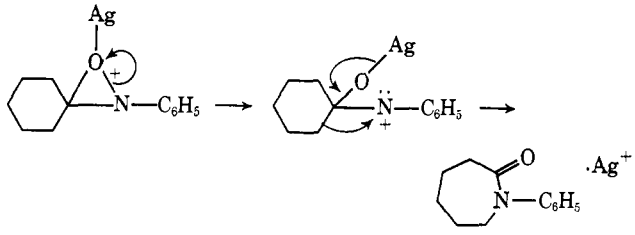
Complexation at nitrogen is not unexpected on the basis of calculations for the site of protonation.[8] Also, if the effect of the three-membered ring is not taken into consideration, nitrogen has a greater affinity for Ag^+ than does oxygen as shown by a stability constant which is 7.6 times greater for *p*-(*N*,*N*-dimethyl)benzenesulfonate ion[27] than for *p*-methoxybenzenesulfonate.[28] Finally, the oxygen–Ag^+ bond is longer, and therefore weaker, than a nitrogen–Ag^+ bond as shown by X-ray structures of 3(dioxane)$\cdot AgClO_4$[29] and 2(pyridine)$\cdot AgNO_3$,[30] with oxygen–Ag^+ and nitrogen–Ag^+ bond lengths of 2.46 and 2.16 Å, respectively.[31]

For $CsClO_4$ and $LiClO_4$, possible sites of complexation could not be determined due to low solubility. However, the data in Table V suggest an interaction

(21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, p 730.
(22) N. Bodor, M. J. S. Dewar, A. Harget, and F. Haselback, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).
(23) J. F. Cannon, J. Daly, J. V. Silverton, D. R. Boyd, and D. M. Jerina, *J. Chem. Soc., Perkin Trans. 2*, 1137 (1972).
(24) J. A. Hashmall and S. Raynor, *J. Chem. Phys.*, **58**, 5464 (1973).
(25) A. D. Walsh, *Nature (London)*, **159**, 167, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).
(26) R. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 743 (1970).
(27) S. Ahrland, J. Chatt, N. R. Davis, and A. A. Williams, *J. Chem. Soc.*, 276 (1958).
(28) S. Ahrland, J. Chatt, N. R. Davis, and A. A. Williams, *J. Chem. Soc.*, 264 (1958); the authors point out that Ag^+ may be coordinated to an oxygen of the SO_3^- group in this case.
(29) R. J. Prosen and K. N. Trueblood, *Acta Crystallogr.*, **9**, 741 (1956).
(30) S. Menchetti, G. Rossi, and V. Tazzoli, *Rend. Ist. Lomb. Sci. Lett., A*, **104**, 309 (1970); *Chem. Abstr.*, **74**, 80763s (1971).
(31) It should be noted that in 3(dioxane)$\cdot AgClO_4$ six oxygen atoms are coordinated to Ag^+ while in 2(pyridine)$\cdot AgNO_3$, only two nitrogen atoms are coordinated to Ag^+.

with **1**. It is interesting to note that in both cases the slight *upfield* shifts of 0.1 to 0.3 ppm are in the same direction as those reported for α carbons on protonation of amines.[32]

Reactivity of Complexes. Although we have shown that complexation is clearly favored at nitrogen in terms of thermodynamic equilibria, small concentrations of Ag^+–oxygen complexes may be the reactive species in certain Ag^+-catalyzed reactions and oxidations. Three reactions, observed in the present study and which may be of this type, are the instantaneous oxidations of styrene oxide and diethylaminomethyl methyl ether and the rearrangement of the *N*-phenyloxaziridine **2d**. In the formation of *N*-phenylcaprolactam, complexation on oxygen followed by ring opening could lead to a stabilized nitrenium ion[33] and rearrangement. For this case and perhaps proton-



catalyzed reactions as well, complexation on oxygen may be kinetically significant, with complexation on nitrogen occurring as an important side equilibrium.

Experimental Section

General. Proton nmr were measured on a Varian A-60 (60 MHz) and a Bruker HFX-90 (90 MHz) spectrometer with internal TMS as a standard. Completely decoupled ^{13}C nmr spectra were taken on a Bruker HFX-90 at 22.63 MHz with internal TMS as a standard in a 10-mm coaxial sample tube containing hexafluorobenzene for external field locking on ^{19}F. All ^{13}C spectra, except that of **2a**, were recorded in a single scan. For **2a** and its complex, 4–6 scans were accumulated on a Varian C-1024 time-averaging computer. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer. Analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

The X-ray photoelectron spectra were measured on a Varian IEE-15 spectrometer using Mg Kα radiation. Samples were placed on graphite sample holders and the spectra run at liquid nitrogen temperature with a resolution of *ca.* 1.2 eV fwhm, and the maxima were measured with a precision of ±0.2 eV. For each sample, the carbon 1s peak from the graphite was measured and was more intense by at least an order of magnitude than the nitrogen or oxygen peaks. The positions of the nitrogen and oxygen peaks reported are shifted so that the carbon peak falls at 284.0-eV binding energy.

Materials. Diethyl ether and triethylamine were distilled and dried over sodium; the oxaziridines and spectroquality CH_2Cl_2 were dried over molecular sieves (Baker 4A and 5A, respectively) prior to use. Preparation of all silver-containing samples was done in a drybox with a nitrogen atmosphere.

Anhydrous $AgBF_4$ was obtained from Alfa Inorganics and was used without further purification.[34] The $AgNO_3$, $AgClO_4$, $LiClO_4$, and Bu_4NBF_4 were commercially available. The $CsClO_4$ was prepared by the reaction of $AgClO_4$ and CsCl and dried under vacuum.

2-*tert*-Butyloxaziridine (**1**) was prepared by the method of Emmons[10] giving a 28% yield, bp 52–54° (75 mm) [lit.[10] 52–54° (75 mm)].

2-Methyl-1-oxa-2-azaspiro[2.5]octane (**2a**) was prepared by the method of Pews.[35] To 16 g (0.14 mol) of *N*-cyclohexylidenemethylamine, prepared by the method of Campbell, *et al.*,[36] in 24% yield with bp 63–64° (25 mm), in 100 ml of CH_2Cl_2 was added 25 g of *m*-chloroperoxybenzoic acid (0.15 mol) in 100 ml of CH_2Cl_2. The reaction mixture was washed with 2 × 100 ml of 5% Na_2SO_3 and 3 × 100 ml of 5% Na_2CO_3 and then dried over Na_2CO_3. Distillation of the reaction mixture gave 5 g (27%) of product, bp 41–43° (1 mm) [lit.[37] 76° (1 mm)].

2-Ethyl-1-oxa-2-azaspiro[2.5]octane (**2b**) was prepared in 37% yield from *N*-cyclohexylidenemethylamine[36] as described above, bp 54–55° (5 mm) [lit.[38] 76° (14 mm)].

2-Phenyl-1-oxa-2-azaspiro[2.5]octane (**2d**) was prepared in 19% yield from *N*-cyclohexylidenephenylamine[16] as described above: mp 74° [lit.[16] 75°]; nmr (60 MHz, CH_2Cl_2, TMS) δ 1.3–1.7 (6 H, m), 1.7–1.9 (4 H, m), 1.0–1.5 (5 H, m).

2-(2-Chloroethyl)-1-oxa-2-azaspiro[2.5]octane (**2c**) was prepared in 29% yield from *N*-cyclohexylidene-(2-chloroethyl)amine, bp 51° (0.04 mm), as described above, bp 55° (0.07 mm).

$AgBF_4$ Complexes of Oxaziridines. The general method of preparing solid complexes can be illustrated for 2-*tert*-butyloxaziridine. To 5.3 g of $AgBF_4$ (27 mmol) was added 5 g (50 mmol) of the oxaziridine in 20 ml of CH_2Cl_2. The mixture was filtered to remove insoluble matter, diethyl ether was added to the cloudpoint, and the temperature was lowered to −20°. After *ca.* 2 days crystals began to appear and after *ca.* 1 week 8.3 g (42%) of crystals was collected. Analytical and physical data for all solid complexes obtained in this way are given in Table I.

Reaction of $AgBF_4$ with 2-Phenyl-1-oxa-2-azaspiro[2.5]octane (2d). To 0.35 g (1.8 mmol) of $AgBF_4$ was added 0.68 g of **2d** (3.6 mmol) in 20 ml of CH_2Cl_2. The mixture was filtered, ether was added to the cloudpoint, and the mixture was cooled to −20°. After 3 days, crystals began to appear and were collected after 2 weeks: mp 105–106°; ir (KBr) 1650 cm^{-1}; nmr (60 MHz, CH_2Cl_2, TMS) δ 1.8–2.1 (6 H, m), 2.7–2.9 (2 H, m), 3.8–4.0 (2 H, m), 7.2–7.8 (5 H, m). The crystals were analyzed by a Volhard titration for Ag^+ and an nmr analysis with internal *tert*-butyl alcohol for *N*-phenylcaprolactam.

Anal. Calcd for $2(C_{12}H_{15}NO)\cdot AgBF_4$: Ag, 18.8; $C_{12}H_{15}NO$, 66.0. Found: Ag, 19.1; $C_{12}H_{15}NO$, 62.9.

The product as described above was synthesized by an alternate route. Oxaziridine **2d** (1 g) was refluxed in xylene for 18 hr, the xylene removed by distillation, and hexane added to the remaining oil. On cooling, 0.8 g of *N*-phenylcaprolactam[16] (80%) crystallized from solution: mp 73–75° [lit.[7] 75°]; ir (KBr) 1665 cm^{-1}; nmr (60 MHz, CH_2Cl_2, TMS) δ 1.7–1.9 (6 H, m), 2.5–2.8 (2 H, m), 3.6–3.9 (2 H, m), 7.2–7.5 (5 H, m). To 0.05 g (0.3 mmol) of $AgBF_4$ was added 0.1 g (0.5 mmol) of *N*-phenylcaprolactam in 10 ml of CH_2Cl_2 and ether was added to the cloudpoint. After *ca.* 1 day at −20° crystals began to form and were collected after *ca.* 1 week, giving mp 105–106° and spectral properties identical with those of the compound isolated from reaction of $AgBF_4$ with **2d**. It should be noted that **2d** stored in CH_2Cl_2–ether at −20° was stable for several months.

Reaction of Diethylaminomethyl Methyl Ether with $AgBF_4$. To 3.7 g of $AgBF_4$ (19 mmol) was added, dropwise, a solution of 25 ml of CH_2Cl_2 containing 2.2 g (19 mmol) of diethylaminomethyl methyl ether which had been prepared in 51% yield by the method of Stewart and Bradley,[39] bp 115–116° [lit.[39] 114–120°]. A silver mirror was formed immediately along with a heavy dark oil. No attempt was made to isolate products.

Reaction of Styrene Oxide with $AgBF_4$. To 2.6 g (13 mmol) of $AgBF_4$ was added 3.2 g (26 mmol) of styrene oxide in 100 ml of CH_2Cl_2. Heat was evolved on mixing and a heavy oil along with a silver mirror was formed. No attempt was made to isolate products.

Recovery of 2-*tert*-Butyloxaziridine from Its $AgBF_4$ Complex.

(32) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York, N. Y., 1972, p 52.

(33) P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

(34) A portion of $AgBF_4$ was purified as described by K. Heyns and H. Paulsen, *Angew. Chem.*, **72**, 349 (1960). The purified $AgBF_4$ gave the same $\Delta\delta$ as unpurified $AgBF_4$.

(35) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).

(36) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, **66**, 82 (1944).

(37) E. Schmitz, R. Ohme, and D. Murawski, *Chem. Ber.*, **98**, 2516 (1965).

(38) L. Horner and E. Jurgens, *Chem. Ber.*, **90**, 2184 (1957).

(39) T. D. Stewart and W. E. Bradley, *J. Amer. Chem. Soc.*, **54**, 4176 (1932).

A 3-g sample of the solid complex was dissolved in 250 ml of CH_2Cl_2 and the silver salt was extracted with 4 × 100-ml portions of distilled water. The organic layer was dried with $MgSO_4$ and CH_2Cl_2 removed by evaporation. The remaining liquid, 0.8 g (53%), had identical spectral properties with those of **1**.

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Complexes of Silver Fluoborate with Simple Aliphatic and Aromatic Ketones. The Carbonyl Group as an n *vs.* π Donor Based on Carbon-13 Nuclear Magnetic Resonance Spectroscopy[1]

DeLanson R. Crist,* Zon-Hong Hsieh, Guy J. Jordan, Frank P. Schinco, and Carol A. Maciorowski

Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. 20007. *Received January 2, 1974*

Abstract: Cyclohexanone and acetophenones were found to form complexes with $AgBF_4$ in methylene chloride as shown by enhanced solubility of the silver salt, infrared shifts of carbonyl bands to lower frequencies, and downfield nmr shifts of α protons. Downfield ^{13}C shifts of $COCH_2$ carbons upon complexation were very similar for both aliphatic and aromatic systems, indicating that the site of complexation is the carbonyl group in both cases. The carbonyl group appears to act as an n donor toward silver ion, since upon complexation the downfield ^{13}C shifts of the carbonyl carbon compared favorably with those for the α carbons of known n donors such as diethyl ether and amines and were in the opposite direction from those for known π donors such as cyclohexene, toluene, and styrene. The nature of this silver–oxygen bond, considered to be rather weak, was best elucidated by spectroscopic studies under nonhydroxylic conditions such as employed in the present work.

It is well known that silver ion forms stable complexes with unsaturated alkenes and aromatic systems as π donors.[2] Enhanced solubility in the presence of silver salts has been accepted as due to formation of complexes, which have been characterized by ir,[3] Raman,[3a,4] uv,[4,5] and proton[3b,6] and ^{13}C nmr[7] methods. The nature of bonding, described in terms of σ bonding to Ag^+ with back-bonding from d orbitals to the ligand,[8] has recently been investigated by extended Hückel methods,[9] and spectroscopic results have been explained theoretically by perturbation[4] and CNDO–MO calculations.[10] Silver salts also complex with n donors such as amines[11] and, less strongly, ethers.[12]

Much less is known about Ag^+ interactions with carbonyl compounds, though a solid complex with acetone has been isolated.[12b] In some reported cases, the bonding site is probably another functional group, as in amides,[13] urea,[14] or olefinic ketones.[15] Formation constants in aqueous media have been reported for acetone[16] and acetophenone,[17] but perhaps due to the low concentrations, these complexes were not characterized further. In a proton nmr study of cyclohexene·$AgBF_4$ in organic solvents, the use of acetone-d_6 precluded observation of ketone·Ag^+ interactions.[6b]

We now report the first spectroscopic data on complexes of $AgBF_4$ with representative aliphatic and aromatic ketones which can be formed in stoichiometric amounts in methylene chloride. Since the carbonyl group contains the electronic features of both π and n donors, model systems were also investigated in order to determine the site of complexation.

(1) Research supported in part by a National Science Foundation Traineeship grant to one of us (G. J. J.).

(2) C. D. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 215 (1970).

(3) (a) H. J. Taufen, M. J. Murray, and F. F. Cleveland, *J. Amer. Chem. Soc.*, **63**, 3500 (1941); (b) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965), and references therein; (c) H. W. Quinn and D. N. Glew, *ibid.*, **40**, 1103 (1962).

(4) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Jap.*, **37**, 249 (1964).

(5) J. N. Murrel and S. Carter, *J. Chem. Soc., London*, 6185 (1964).

(6) (a) J. C. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962); (b) J. Solodar and J. P. Petrovich, *Inorg. Chem.*, 10, 395 (1971).

(7) (a) C. D. M. Beverwijk and J. P. C. M. van Dongen, *Tetrahedron Lett.*, 4291 (1972); (b) K. R. Aris, V. Aris, and J. M. Brown, *J. Organometal. Chem.*, **42**, C67 (1972); (c) P. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 743 (1970); (d) J. P. C. M. van Dongen, *J. Organometal. Chem.*, **51**, C36 (1973).

(8) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

(9) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

(10) S. Sakaki, *Theor. Chim. Acta*, **30**, 159 (1973).

(11) (a) See, for example, C. Golumbic, *J. Amer. Chem. Soc.*, **74**, 5777 (1952); (b) J. L. Pauley and H. H. Hau, *J. Phys. Chem.*, 70, 3363 (1966).

(12) (a) A. E. Comyns and H. J. Lucas, *J. Amer. Chem. Soc.*, **76**, 1019 (1954); (b) H. Meerwein, V. Hederich, and K. Wunderlick, *Arch. Pharm. (Weinheim)*, **291**, 541 (1958); (c) S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc., London*, 264, 276 (1958).

(13) (a) S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965); (b) M. A. Klochko and G. F. Gubskaya, *Zh. Neorg. Khim.*, **5**, 2491 (1960).

(14) K. S. Sulaimankulov, Z. F. Alieva, O. V. Agashkin, and Y. A. Kushnikov, *Khim. Kompleks. Soedin. Redk. Soputstv. Elem.*, 157 (1970); *Chem. Abstr.*, **77**, 26970*f* (1972).

(15) (a) D. Gray, R. A. Wies, and W. D. Closson, *Tetrahedron Lett.*, 5639 (1968); (b) A. C. Cope and D. J. Marshall, *J. Amer. Chem. Soc.*, **75**, 3208 (1953).

(16) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **60**, 836 (1938).

(17) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **72**, 3113 (1950).