

preferred for the spirometallooxaziridine.

Reaction of either **3** or the corresponding dioxo complex with either *N*-methylhydroxylamine or benzohydroxamic acid so far has not yielded pure metallooxaziridine complexes.^{1,3}

The metallooxaziridines do behave as "nitrenoids". This is suggested by thermal decomposition of **4** to azobenzene and by the formation of a mixture of 2-(*N*-phenyl)iminocyclohexanone and azobenzene when **4** is treated with cyclohexanone in chlorobenzene at 80 °C. The scope and mechanism of the reaction of metallooxaziridines of the type **4** containing ligands more labile than HMPT or spirometallooxaziridine **9** with ketones, esters, and nitriles is under investigation and will be reported in the future.

Acknowledgment. We thank Mr. G. E. Babbitt for measurement of ¹³C NMR spectra.

References and Notes

- S. E. Jacobson, R. Tang, and F. Mares, presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978; *J. Chem. Soc., Chem. Commun.*, in press.
- The best catalysts proved to be peroxo complexes stabilized by picolinato and pyridine-2,6-dicarboxylato ligands. The X-ray single-crystal structures of these complexes were determined.¹
- Formation of oxoperoxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) from dioxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) and H₂O₂ is fast at room temperature.
- When we obtained indications of the existence of *N*-methyl metallooxaziridines in solution, Sharpless reported his findings on the preparation of *N*-phenyl-substituted metallooxaziridines stabilized by *N,N*-dialkyl dithiocarbamate and by *N*-(salicylidine)-2-hydroxyaniline ligands (19th Industrial Symposium, Stanford, Calif., Jan 1978).
- Dioxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) can be prepared by a reaction of oxoperoxo(pyridine-2,6-dicarboxylato)(HMPT)molybdenum(VI) with suitable reducing agents. Thus peroxo complex **3** (2.1 g, 6.44 mmol) was reacted with *N*-methylhydroxylamine (0.47 g, 10 mmol) in acetonitrile (80 mL) at 25 °C overnight. Small amounts of a white precipitate was removed by filtration. The filtrate was concentrated under vacuum at 25 °C to about one third of its volume. About the same amount of ether was added to the concentrate and the mixture was placed in the freezer. On the next day, orange crystals (1.28 g, 62%) were collected: IR (Nujol mull) 913, 937 (Mo=O); 1710 cm⁻¹ (C=O). Anal. Calcd for C₁₃H₂₁MoN₄O₇P: C, 33.06; H, 4.49; Mo, 20.31; N, 11.86; P, 6.56. Found: C, 33.14; H, 4.52; Mo, 20.55; N, 11.91; P, 6.44. Complexation of pyridine rings to high valent group 6 metals exhibits a large (5–7 ppm) and characteristic chemical shift for C(4).²
- IR spectra were taken in Nujol mulls and fluorocarbon mulls.
- Complexation of pyridine type ligands results in strong ¹³C NMR shifts, often in opposite directions, depending on the type of bonding between the metal and the ligand.
- Crystal data and refinement results: orthorhombic; *a* = 13.165 (8), *b* = 13.898 (6); *c* = 12.555 (8) Å; space group *P*2₁2₁2₁; *z* = 4; *R*₁ = 0.097, *R*₂ = 0.096; 1333 observed reflections. No hydrogens were located. The complete structure will be published later.
- The N–O bond distances of nitrosobenzene η² bound to Pd(0) (1.35 Å) or to Fe(0) (1.40 Å) are significantly shorter than in **4**: M. Calligaris, T. Yoshida, and S. Otsuka, *Inorg. Chim. Acta*, **11**, L15 (1974); M. J. Barrow and O. S. Mills, *J. Chem. Soc. A*, 864 (1971). This fact may suggest π bonding in the Pd and Fe complexes in contrast to a typical σ bonding in the Mo and W metallooxaziridines described in this report. Notice that the O–O distance in peroxo complexes is practically insensitive to the type of metal (*d⁰ → d¹⁰*) involved: M. Laing, *J. Chem. Soc., Chem. Commun.*, 660 (1975); P. J.-M. Le Carpentier, R. Schlupp, and R. Weiss, *Acta Crystallog. Sect. B*, **28**, 1278 (1972); P. J.-M. Le Carpentier, A. Mitschler, and R. Weiss, *ibid.*, **28** (1972); ref 2.
- International Tables for X-ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1968, p 270.
- The aquo ligand in **3** can be readily displaced by compounds such as ketones. The ketone complexes were isolated and characterized by elemental analyses, ¹H NMR, and ¹³C NMR. The easy displacement of H₂O by ketones may be the reason why complex **1** is an active catalyst for oxidation of cyclic ketones to lactones by H₂O₂. When the aquo ligand in **3** is displaced by less labile ligands such as HMPT, the catalytic activity of **1** is drastically decreased: S. E. Jacobson and F. Mares, unpublished results.
- Structures of the corresponding Mo and W peroxo complexes are also equivalent.²
- Benzohydroxamic acid displaces pyridine-2,6-dicarboxylato ligand in **3** as well as in the corresponding dioxo complex. As a result only Mo(O)₂(PhC(O)NHO)₂ is isolated in high yields. This fact has been demonstrated by elemental analysis and by comparison of IR spectra with that of an authentic sample prepared from benzohydroxamic acid and Mo(O)₂(acac)₂.

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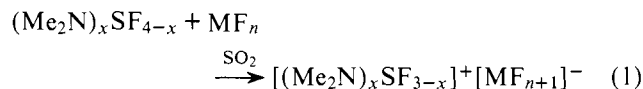
Received July 18, 1978

Amino-Substituted Sulfonium Salts. Synthesis and Stereochemistry

Sir:

Amino-substituted sulfonium cations, [(R₂N)_xSF_{3-x}]⁺ (*x* = 1, 2, 3), are isoelectronic with aminophosphines and, consequently, their stereochemistry, reactivity, and ligand behavior are of significant potential interest.¹

We find that the syntheses of the [Me₂NSF₂]⁺ (**1**) and [(Me₂N)₂SF]⁺ (**2**) cations can be accomplished in high yields by treatment of the appropriate fluorosulfurane with a fluoride ion acceptor such as BF₃, PF₅, or AsF₅ in SO₂ solutions at -60 to -65 °C:



This is a similar approach to that used² for the synthesis of [SF₃]⁺[BF₄]⁻. However, since the fluorosulfurane, (Me₂N)₃SF, is unknown it was necessary to develop a novel synthesis for the completely amino-substituted cation, [(Me₂N)₃S]⁺ (**3**). After several unsuccessful attempts to prepare the latter by treating **1** or **2** with dimethylamide anion, we discovered that the reaction of SF₄ with B(NMe₂)₃ affords high yields of **3** as its tetrafluoroborate salt:



Typically, an equimolar mixture of SF₄ and (Me₂N)₃B in SO₂ solution is allowed to warm slowly from -196 to +10 °C. Removal of the SO₂ and trace quantities of volatiles in vacuo produces white, solid [(Me₂N)₃S]⁺[BF₄]⁻, mp 110 °C dec.³ The reaction of SF₄ and (Me₂N)₃B can be followed by NMR spectroscopy. Immediately after warming to -60 °C, ¹H peaks corresponding to **1** (triplet,⁴ δ 3.18, *J*_{FSNCH} = 7.5 Hz), **2** (doublet, δ 2.95, *J*_{FSNCH} = 7.0 Hz), and **3** (singlet, δ 2.55) and (Me₂N)₃B are clearly discernible. The resonances corresponding to **1**, **2**, and (Me₂N)₃B decrease with time and that of **3** increases until, after 20 min at ambient temperature, all that remains is the singlet resonance of **3**. ¹⁹F spectra⁵ taken in the early stages of the reaction confirm the presence of SF₃⁺ (singlet, -19 ppm), **1** (septet, -16.0 ppm, *J*_{FSNCH} = 7.5 Hz), and **2** (multiplet, +15.6 ppm, *J*_{FSNCH} = 7.0 Hz) and, in addition, exhibit four poorly resolved "quartet" resonances which we attribute to BF₄⁻ (143.5 ppm, *J*_{11BF} = 2 Hz), [Me₂NBF₃]⁻ (153 ppm, *J*_{11BF} = 20 Hz), [(Me₂N)₂BF₂]⁻ (155 ppm, *J*_{11BF} = 18 Hz), and [(Me₂N)₃BF]⁻ (156 ppm, *J*_{11BF} = 17 Hz).⁶ As time elapses the resonance due to BF₄⁻ grows at the expense of the other three. To accommodate the foregoing observations we postulate that the initial step in the reaction is F⁻ abstraction by (Me₂N)₃B to form [(Me₂N)₃BF]⁻ and SF₃⁺, the latter undergoing F⁻/Me₂N⁻ exchange with either (Me₂N)₃B or [(Me₂N)_xBF_{4-x}]⁻. In support of this postulate we find that (a) the AsF₆⁻ salts of SF₃⁺, **1**, and **2** undergo rapid reaction with (Me₂N)₃B to afford **3**, and (b) the sulfurane (Me₂N)₂SF₂ does not react with (Me₂N)₃B in this temperature range.

The stereochemistry of aminosulfonium cations has been investigated by dynamic NMR spectroscopy. For example, below -30 °C the ¹H spectrum of **1** consists of two overlapping triplets which we attribute to two Me environments (Me_a, δ 3.06, *J*_{FSNCH_a} = 9.5 Hz; Me_b, δ 2.98, *J*_{FSNCH_b} = 5.5 Hz).⁷ This deduction is confirmed by the presence of two singlets in the ¹³C spectrum (Me_a, 41.2, and Me_b, 36.7 ppm).^{5,7} Under the same conditions the ¹⁹F spectrum comprises a 16-line spectrum which is due to the coupling of the two Me groups to two equivalent F ligands. Taken collectively, the low-temperature NMR data establish structure **4** for **1**, and thereby demonstrate that aminosulfonium cations and aminophosphines are isosteric.⁸ Upon warming to -15 °C the ¹H spec-

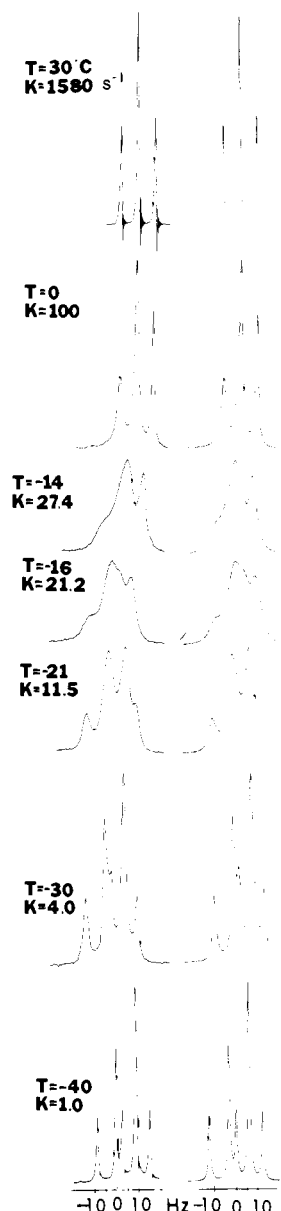
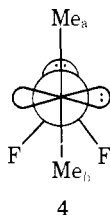


Figure 1. Experimental (left) and computer-simulated ^1H NMR spectra of $[\text{Me}_2\text{NSF}_2]^+$ (**1**). The experimental spectra were obtained in SO_2 solution.



trum collapses and emerges as a triplet, while the ^{13}C and ^{19}F spectra become a singlet (39.3 ppm) and a septet (-16.0 ppm, $J_{\text{HCNSF}} = 7.5$ Hz), respectively. These spectral changes are attributed to rotation around the N-S bond becoming rapid on the NMR time scale. Computer line-shape analyses of the ^1H dynamic NMR spectra indicate that the barrier to N-S rotation in **1** is 14.7 kcal/mol. This result implies that the N-S torsional barriers in aminosulfonium cations are significantly larger than the N-P barriers of the corresponding aminophosphines.⁹ Thus, aminosulfonium salts might find use as models for aminophosphine stereochemistry in cases where, because of low N-P torsional barriers, considerable doubt persists regarding the ground-state geometry.

The coordination chemistry of aminosulfonium cations is under active investigation and will be reported in subsequent publications.

Acknowledgments. The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612) for financial support. Gratitude is also expressed to the Jet Propulsion Laboratory, Pasadena, Calif., for the loan of the Varian A 56/60 NMR spectrometer.

References and Notes

- (1) For very interesting related work on the synthesis and ligand behavior of phosphinium cations, see, for example, S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, **11**, 2534 (1972); M. G. Thomas, C. W. Schultz, and R. W. Parry, *ibid.*, **16**, 994 (1977); R. W. Light and R. T. Paine, *J. Am. Chem. Soc.*, **100**, 2230 (1978); and R. G. Montemayer, D. T. Sauer, S. Fleming, D. W. Bennett, M. G. Thomas, and R. W. Parry, *ibid.*, **100**, 2231 (1978).
- (2) (a) N. Bartlett and P. L. Robinson, *Chem. Ind. (London)*, 1351 (1956); (b) N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 3417 (1961); (c) F. Seel and O. Detmer, *Angew. Chem.*, **70**, 163 (1958); (d) F. Seel and O. Detmer, *Z. Anorg. Allg. Chem.*, **301**, 113 (1959).
- (3) Satisfactory elemental analyses and vibrational spectra were obtained for $[(\text{Me}_2\text{N})_3\text{S}]^+[\text{BF}_4]^-$.
- (4) In some experiments the ^1H resonance of **1** appeared as a singlet, presumably due to intermolecular exchange by F^- . The dynamic NMR spectroscopic experiments described below were conducted under carefully controlled conditions on very pure **1**.
- (5) ^{19}F chemical shifts in parts per million relative to external CCl_3F ; ^{13}C chemical shifts in parts per million relative to external Me_4Si .
- (6) The ^{19}F chemical shift and ^{11}B - ^{19}F constant of BF_4^- have been shown to be markedly dependent on concentration and on the nature of the cation and solvent. See R. Haque and L. W. Reeves, *J. Phys. Chem.*, **70**, 2753 (1966), and references therein. Presumably, the same is true for the "mixed" anions, $[(\text{Me}_2\text{N})_x\text{BF}_{4-x}]^-$.
- (7) In aminophosphines the Me protons cis to the phosphorus lone pair (Me_a) appear at lower field than those which are trans to the phosphorus lone pair (Me_b), and, furthermore, the Me_a protons are more strongly coupled to phosphorus than the Me_b protons: A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.*, **92**, 1085 (1970). Subsequently, the ^{13}C chemical shifts of Me_a and Me_b were found to be in the order $\text{Me}_a > \text{Me}_b$; M.-P. Simonnin, R.-M. Lequan, and F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, 1204 (1972).
- (8) The isoelectronic aminophosphine, Me_2NPF_2 , has been shown to possess structure **4** by low-temperature X-ray crystallography: E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).
- (9) The N-P torsional barrier of the isoelectronic species, Me_2NPF_2 , is too small to be measured by dynamic NMR. For aminophosphines with more bulky substituents the N-P torsional barriers fall typically in the range of 8–10 kcal/mol. See A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.*, **92**, 5206 (1970), and references therein. The N-P torsional barrier of Me_2NPF_2 has been estimated to be 2.8 kcal/mol by the CNDO/2 method: M.-C. Bach, C. Brian, F. Crasnier, J.-F. Labarre, C. Leibovici, and A. Dargelos, *J. Mol. Struct.*, **17**, 23 (1973).

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Received May 15, 1978

Solvolytic of Cyclooctatetraenyl Trifluoromethanesulfonate¹

Sir:

Cyclic vinyl trifluoromethanesulfonates (triflates) and nonafluoro-*n*-butanesulfonates (nonaflates) solvolyze in suitable solvents² with formation of cyclic vinyl cations. The rate of solvolysis of the reaction, and with that the tendency of the cyclic vinyl cations to exist as intermediates, depends on the size of the ring. With the exception of 1-cyclobutenyl nonaflate, which stands out in the cyclic series because of its high solvolysis rate,³ a steady rise in the rate of solvolysis going from the slowly reacting 1-cyclohexenyl triflate up to the 1-cyclononyl triflate was observed owing to the increasingly easy formation of a stable linear vinyl cation.²

Additional stabilization of cyclic vinyl cations can be achieved by conjugated double bonds in the ring system, when the size of the ring allows orthogonality of the double bonds for a good overlap of the vacant p orbital of the vinyl cation