single bond.[23] There is no simple relationship between bond length and bond strength. Nevertheless, the rough correlation in Table II gives confidence to these data since each of the compounds was studied by different groups using different techniques. A recent theoretical study of Mo_2H_6 predicts a value for the Mo-Mo triple-bond strength of 68 kcal/mol,[24] in surprising agreement with our work. Additional thermochemical investigations on these and related complexes are in progress, and it is hoped that this work will provide a basis for practical and theoretical understanding of the chemistry of this important class of compounds.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-8314497) is gratefully acknowledged.

Registry No. $[Mo(CO)_2C_5H_5]_2$, 56200-27-2; $[Mo(CO)_2C_5(CH_3)_5]_2$, 12132-04-6; $[Mo(CO)_2C_9H_7]_2$, 98540-88-6; CO, 630-08-0; $HC\equiv CH$, 74-86-2; $PhC\equiv CH$, 536-74-3.

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(23) (a) A recent estimate for the loss of translational and rotational entropy in uptake of 1 mol of CO(g) is 36 eu.[23b] Thus there is a net unfavorable entropy change associated with reaction 2 of roughly 72 eu, which results in a $T\Delta S$ term of 21.5 kcal/mol opposing addition of CO to the triple-bonded dimer. For CO addition to occur at all the enthalpy of reaction 2 must be at least −21.5 kcal/mol to offset the entropy term. Considering the maximum gain in energy by addition of two terminal CO ligands to be 80 kcal/mol implies that a loss of metal-metal bond energy of more than 58.5 kcal/mol would lead to a net unfavorable free energy for addition of CO. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J. B.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics*, **1981**, *1*, 1166.

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(26) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Convenient Synthetic Route to Coordination and Organometallic Compounds of Alkanenitronate $[O_2N{=}CRR']^-$ Anions[1]

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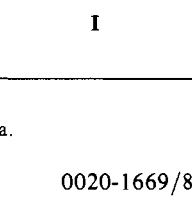
Nitronate anions (I) represent a potentially useful class of bidentate ligands whose coordination chemistry has been little studied. Numerous studies exist on the coordination chemistry of related nitrito and nitrato ligands—anions that exhibit N-bonded, monodentate O-bonded, chelating O-bonded, and bridging coordination modes.[2] Related to both of these ions are the alkanenitronato ligand, derived conveniently via base deprotonation of the corresponding nitroalkane.



I

The importance of aliphatic nitro compounds in the interconversion of organic functional groups has long been appreciated,[3] and recent attention has focused increasingly on the chemistry of mono- and dianions derived from such nitro compounds.[4] Our interest in such molecular fragments centers on (i) the potential for modification of reactivity of such anions via prior coordination and (ii) the possibility of diastereofacial selectivity in subsequent inter- and intramolecular reactions at the alkanenitronate moiety.

Recent reports demonstrate clearly the ability of alkanenitronate anions to bind in a symmetrically chelating fashion: synthetic approaches to such coordination complexes have required (i) the reactions of arylcopper(I) complexes, in the presence of phosphine base, with nitroalkanes (with concomitant loss of arene) to afford Cu(I)-nitronate species[5] and (ii) reaction of the nitronate anion, generated via sodium hydroxide deprotonation, in aqueous solutions of Ni(II) to yield a bis(nitronato)nickel(II) species.[6] We sought a more direct and potentially more generally applicable route to such compounds. Our approach involves the reaction, under nonaqueous conditions, of the appropriate nitroalkane anion with a metal halide. The alkanenitronate reagent employed may be a conveniently weighable free-flowing solid, or the anion may be generated in situ and reacted subsequently with the metal halide without prior isolation.

We report herein the preparation and characterization of a series of new $Cp_2Zr(X)(O_2N{=}CRR')$ ($X = Cl^-$ or alkyl, R, R′ = H or Me) complexes and the homoleptic, eight-coordinate $Zr[O_2N{=}C(CH_3)_2]_4$. In addition, one of these Cp_2ZrL_3 systems has been characterized via X-ray crystallography to substantiate the mode of coordination.

Experimental Section

All procedures were performed under nitrogen in Schlenk-type glassware with normal bench-top Schlenk techniques.[7] Manipulations involving O_2- and/or H_2O-sensitive solids were accomplished conveniently in an Ar-filled glovebox (Vacuum Atmospheres). Argon and nitrogen were purified by passage through a supported MnO oxygen removal column[8] and a Linde 4-Å molecular sieve column. Cp_2ZrCl_2 (Aldrich) was used as received while $ZrCl_4$ (Alfa) was sublimed prior to use and stored in the glovebox. Nitroethane and nitropropane (Aldrich) were refluxed over and distilled from phosphorus pentoxide under a nitrogen atmosphere and stored over molecular sieves under a nitrogen atmo-

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[†] University of Idaho.

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(1) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 8-13, 1985; Abstract No. 383. A more systematic name for an alkanenitronate would be as a derivative of an *N*-hydroxy imine *N*-oxide.

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sphere. Toluene, tetrahydrofuran, and pentane were refluxed over and distilled from Na/benzophenone immediately prior to use and transferred via cannula. Dichloromethane was refluxed over and distilled from phosphorus pentoxide immediately prior to use and transferred via cannula.

All infrared spectra were obtained on a Digilab Qualimatic FT-IR. Mass spectra were recorded on a VG 7070 mass spectrometer operating in the EI mode. Both ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Multiplicities of ^{13}C resonances were determined with off-resonance decoupling techniques. Chemical shifts are reported relative to internal $Si(CH_3)_4$. Elemental analyses were performed in-house.[9] Electrochemical studies were carried out with an IBM EC/225 voltammetric analyzer and IBM 7424 MT X-44 recorder.

Preparation of $Cp_2Zr(Cl)(O_2N{=}CMe_2)$ (1). To a stirred suspension of Cp_2ZrCl_2 (10 mmol) in 50 mL of THF was added powdered $LiO_2N{=}CMe_2$[10] (10 mmol, soluble in THF) over 0.5 h at 0 °C via a solids addition tube. The mixture was allowed to warm to room temperature and stirred for an additional 1 h. The solution, pale yellow in coloration, was then evaporated to dryness in vacuo. The residue was dissolved in ca. 50 mL of CH_2Cl_2 and filtered through Celite supported on a medium-porosity frit, followed by washing with an additional 30 mL of CH_2Cl_2. The solution was evaporated in vacuo to ca. 30 mL, pentane (15 mL) was added, and the solution was cooled to −78 °C to effect crystallization. The off-white microcrystals were recrystallized from 2:1 CH_2Cl_2/pentane solution: yield 87%; dec pt 126 °C.

Preparation of $Cp_2Zr(Cl)[O_2N{=}C(H)Me]$ (2). To a THF solution (−78 °C) containing 10 mmol of $CH_3CH_2NO_2$ was added 6.45 mL of an *n*-BuLi solution (1.55 M, 10 mmol). The solution was stirred for an additional 15 min followed by addition of solid Cp_2ZrCl_2 via a solids addition tube. The mixture was allowed to warm slowly (0.5 h) to room temperature and stirred for an additional 1 h. Following removal of solvent in vacuo purification was effected in a manner identical with that used for 1: yield 81%; dec pt 103 °C.

Preparation of $Cp_2Zr(CH_2CMe_2Ph)(O_2N{=}CMe_2)$ (3). To a solution of 2.0 mmol of $Cp_2Zr(Cl)(CH_2CMe_2Ph)$[11] in 15 mL of THF was added 2.0 mmol of powdered $LiO_2N{=}CMe_2$ via a solids addition tube. The mixture was stirred at room temperature for 2 h. After evaporation of solvent in vacuo the residue was dissolved in ca. 25 mL of toluene and filtered through a fine-porosity frit. Upon cooling (−78 °C), white needles separated from the solution and were isolated by cold filtration on a coarse-porosity frit: yield 81%; dec pt 91 °C.

Preparation of $Zr[O_2N{=}CMe_2]_4$ (4). To a solution of 20.0 mmol $LiO_2N{=}CME_2$ in ca. 50 mL THF was added 5.0 mmol $ZrCl_4$. Copious amounts of white crystalline solid separated from solution almost immediately. The mixture was stirred for an additional 1 h at room temperature followed by removal of solvent in vacuo. Dissolution of the solid in ca. 40 mL CH_2Cl_2 followed by filtration through a fine-porosity frit yielded a pale yellow solution. Addition of 20 mL of pentane and cooling slowly (~10 °C/h) to −78 °C resulted in formation of a white crystalline solid. A second recrystallization from 2:1 CH_2Cl_2/pentane provides analytically pure 4: yield 93%; dec pt 223 °C.

X-ray Data and Structure Determination. Diffraction data were measured with a Syntex $P2_1$ diffractometer equipped with a locally (U.C., Davis) modified low-temperature device. All calculations were performed with the Nicolet SHELXTL system, running on a Data General Eclipse S/230 computer.

Crystal data: formula $C_{13}H_{16}ClNO_2Zr$, $M_r = 337.5$; crystal selected from a sample recrystallized by pentane vapor diffraction into a saturated dichloromethane solution; rectangular prism of dimensions 0.60 × 0.70 × 0.75 mm obtained by cutting from a larger block; monoclinic space group $P2_1/c$; cell dimensions at 140 °K, $a = 7.864$ (2) Å, $b = 13.196$ (3) Å $c = 12.850$ (4) Å, $\beta = 93.91$ (2)°; Mo K, $\lambda = 0.71069$ Å, graphite monochromator, μ(Mo Kα) = 10.1 cm^{-1}; $d_{calcd} = 1.72$ Mg m^{-3}; 1° ω scan at 58.6° min^{-1},[12] background offset ±1°, scan/background time ratio = 1, max $2\theta = 55°$; 3052 unique reflections measured, 3006 with $I > \sigma(I)$ used in refinement of 171 parameters, empirical absorption correction[13] applied; anisotropic thermal motion for C, Cl, N, and O, slack constraint (sd = 0.002 Å) applied to ring C–C distances, H atoms riding on C in idealized geometry (H–C = 1.00 Å); final $R = 0.026$, $R_w = 0.033$, weights = $1/_{\sigma}{}^2(F)$.

Table I. C=N Absorptions (cm^{-1}) for Compounds 1–4[a]

compound	ν(C=N)
$Cp_2Zr(Cl)[O_2N{=}C(CH_3)_2]$ (1)	1646
$Cp_2Zr(Cl)[O_2N{=}C(H)CH_3]$ (2)	1638
$Cp_2Zr[CH_2C(CH_3)_2C_6H_5][O_2N{=}C(CH_3)_2]$ (3)	1643
$Zr[O_2N{=}C(CH_3)_2]_4$ (4)	1651

[a] KBr pellet.

Table II. Atom Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3) for 1

atom	x	y	z	U,[a] Å^2
Zr	560 (1)	964 (1)	2508 (1)	12 (1)
Cl	84 (1)	2172 (1)	982 (1)	21 (1)
C(1)	3343 (3)	−7 (2)	2576 (2)	20 (1)
C(2)	3218 (2)	480 (2)	1599 (1)	21 (1)
C(3)	1835 (2)	45 (2)	1002 (2)	23 (1)
C(4)	1116 (3)	−709 (2)	1609 (2)	26 (1)
C(5)	2013 (3)	−724 (2)	2598 (2)	23 (1)
C(6)	−1867 (3)	1313 (2)	3670 (2)	23 (1)
C(7)	−2487 (3)	1547 (1)	2647 (2)	21 (1)
C(8)	−2531 (3)	637 (1)	2065 (2)	19 (1)
C(9)	−2018 (3)	−161 (1)	2743 (1)	20 (1)
C(10)	−1546 (3)	261 (2)	3727 (2)	24 (1)
O(1)	2024 (2)	2338 (1)	3003 (1)	17 (1)
O(2)	1787 (2)	1095 (1)	4119 (1)	18 (1)
N	2630 (2)	1936 (1)	3913 (1)	16 (1)
C(11)	3893 (3)	2304 (2)	4498 (2)	17 (1)
C(12)	4452 (3)	1755 (2)	5478 (2)	24 (1)
C(13)	4720 (3)	3257 (2)	4165 (2)	21 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

The general synthetic approach to coordination and/or organometallic complexes of alkanenitronate anions, as described herein, is particularly appealing for systems not amenable to aqueous reaction conditions. In addition, it is a more direct route that does not require protonolysis of M–C or M–H bonds.[5,14] The alkanenitronate anion, generated via alkyllithium deprotonation of the corresponding nitroalkane, reacts directly and cleanly with metal halides under very mild conditions (eq 1). Even when the

$$M{-}Cl + Li[O_2N{=}CRR'] \xrightarrow{THF} M\langle O_2 \rangle N{=}C(R)R' + LiCl \qquad (1)$$

Zr(IV) ligation sphere contains the sterically demanding neophyl substituent (i.e., 3), the nitronate is able to add and, on the basis of the IR data, bind in a symmetrically chelating fashion. As isolation of the lithium nitronate is not required, the procedure is a "one-pot" synthetic approach utilizing metal halides, many of which are commercially available.

The infrared spectra of compounds 1–4, obtained as KBr pellets, reveal a particularly diagnostic absorption (ν(C=N)) in the 1630–1650-cm^{-1} region (Table I). The relative constancy of this absorption suggests a similar mode of coordination for all four complexes and implies considerable carbon–nitrogen double-bond character.[15] In comparison to alkali-metal salts of these same anions,[16] the values observed are interpretable as the result of tighter coordination of the nitronate oxygens with a metal center of high charge density (and oxophilicity) as well as greater covalency in the Zr–O bonds. The ν_s(NO), ν_a(NO), and δ(ONO) frequencies could not be assigned unambiguously due to the large number of bands observed in those regions of the spectrum.

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(9) All new compounds (1–4) gave satisfactory elemental analyses.

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(11) Prepared in a manner analogous to $Cp_2Zr(Cl)(CH_2SiMe_3)$; see: Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445.

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Table III. Selected Bond Distances (Å) and Angles (deg) for $(\eta\text{-}C_5H_5)_2Zr(Cl)[O_2N{=}C(CH_3)_2]$ (**1**)[a]

Zr–Cl	2.536 (1)	Zr–O(1)–N	94.2 (1)
Zr–O(1)	2.218 (2)	Zr–O(2)–N	94.0 (1)
Zr–O(2)	2.230 (2)	O(1)–N–O(2)	110.6 (2)
O(1)–N	1.341 (2)	O(1)–Zr–O(2)	59.1 (1)[b]
O(2)–N	1.330 (2)	Cl–Zr–O(1)	75.8 (1)
N–C(11)	1.298 (3)	Cl–Zr–O(2)	134.5 (1)
C(11)–C(12)	1.493 (3)	O(1)–N–C(11)	124.7 (2)
C(11)–C(13)	1.493 (3)	O(2)–N–C(11)	124.7 (2)
Zr–cent-Cp_a	2.232 (2)[c]	N–C(11)–C(12)	118.5 (2)
Zr–cent-Cp_b	2.229 (2)[c]	N–C(11)–C(13)	118.7 (2)
		C(12)–C(11)–C(13)	122.8 (2)
		cent-Cp_a–Zr–cent-Cp_b	127.5 (3)[c]

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The ligand "bite". [c] cent-Cp_a and cent-Cp_b refer to the centroids of the cyclopentadienyl rings C(1)–C(5) and C(6)–C(10), respectively.

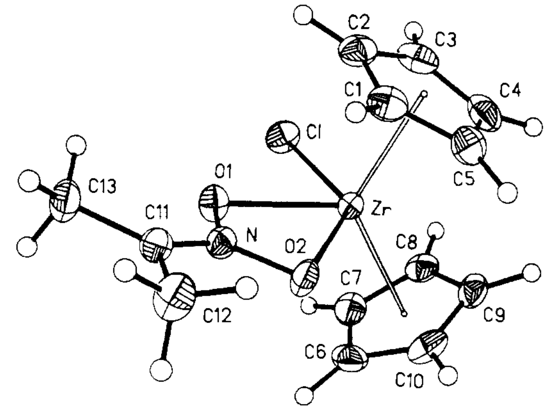


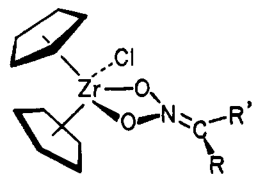
Figure 1. Thermal ellipsoid plot of the structure of $(\eta\text{-}C_5H_5)_2Zr(Cl)[O_2N{=}C(CH_3)_2]$ (**1**), showing the atomic numbering scheme. Ellipsoids are drawn to contain 70% of the distribution.

The ^1H and ^{13}C NMR spectral data[17] are consistent with the formulations given, and the ^{13}C assignments are supported by off-resonance decoupling experiments. The nitronate carbons are shifted considerably downfield relative to the parent nitroalkanes,[18] as expected for conversion of an sp^3 carbon to an sp^2 carbon.[19]

Electrochemical studies of **1** evidence the strong π-donor character of the alkanenitronate ligand. Whereas Cp_2ZrCl_2 shows a reversible cathodic wave at −1.8 V (Pt disk, Ag/Ag^+),[20] 10^{-2} M solutions (THF, Pt button, TBAP as supporting electrolyte) of **1** are electrochemically "silent" at potentials <−2.9 V.

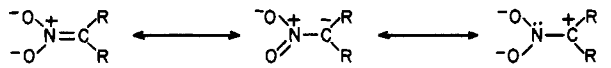
X-ray Structure of $(C_5H_5)_2Zr(Cl)(O_2N{=}CMe_2)$ (1). In order to establish unambiguously the mode of coordination of the nitronate moiety in these compounds, we have determined the structure of the 2-propanenitronate derivative by X-ray diffraction. The atomic coordinates and thermal parameters are presented in Table II. The principal intramolecular distances and angles are presented in Table III. A perspective view of the molecule showing the atom-numbering scheme is displayed in Figure 1.

Molecules of $(\eta\text{-}C_5H_5)_2Zr(Cl)[O_2N{=}C(CH_3)_2]$ have a bent metallocene geometry **5**, with the five-coordinate Zr atom attached to a Cl atom, a bidentate 2-propanenitronato-*O,O′* ligand, and two symmetrically bound $\eta\text{-}C_5H_5$ ligands. Eighteen-electron Cp_2ML_3 complexes are relatively uncommon for group 4 transition metals,[21] and examples of five-coordinate Zr(IV) are similarly rare.[22] The atoms Zr, Cl, O(1), and O(2) are coplanar to within ±0.07 Å. The mean Zr–C distance is 2.532 (2) Å (range 2.496–2.547 Å), with Zr–ring centers 2.232 (2) and 2.229 (2) Å, and the angle Cp–Zr–Cp = 127.5°. The Zr–Cl bond, 2.536 (1) Å; is substantially longer than that observed for Cp_2ZrCl_2, 2.441 (5) Å,[23] and is likely due to the crowding of the three relatively large donor atoms in the quasi mirror plane. This is evidenced by the facts that (i) the Cl···O(1) distance (2.93 Å) is 0.37 Å less than the sum of the van der Waals radii,[24] and (ii) the Cl–Zr–O(2) angle (134.5°) is ~37° larger than the Cl–Zr–Cl angle (97.15°) in Cp_2ZrCl_2.[21] The Zr–O(1) and Zr–O(2) bonds are effectively equivalent at 2.218 (2) and 2.230 (2) Å, respectively.



5

When the alkanenitronate ligand is attached to an electropositive metal center such as Zr(IV), resonance structure **6a** appears to be most reasonable, while structure **6b** and **6c** best represent the uncoordinated anion, as reflected in the chemical reactivity of nitronate anions.[4b,c] Bond lengths and angles within the 2-propanenitronate ligand, as well as spectral properties discussed above, correlate best with resonance structure **6a** also. The N–O(1) and N–O(2) bonds are 1.341 (2) and 1.330 (2) Å, respectively, only slightly shorter than a N–O single bond (N—O, 1.40 Å; N=O, 1.21 Å).[25] The carbon-nitrogen bond, at 1.298 (3) Å, is very much double bond in character (C—N, 1.47 Å; C=N, 1.27 Å),[25] and angles about C(11) are indicative of sp^2 carbon. The ligand "bite" is very similar to that observed in analogous $Cp_2Zr(Cl)$(dithiocarbamate) complexes.[26] The ligand structure in **1** is very similar to that observed in the homoleptic eight-coordinate $Zr[O_2N{=}C(CH_3)_2]_4$.[27]



6a 6b 6c

The methods described herein provide convenient, general synthetic access to organometallic and coordination compounds of alkanenitronate anions. Such coordination, as observed with Zr(IV), may well result in alteration of the predominant mode(s) of reactivity of such organic fragments relative to that of their uncoordinated counterparts. Studies of the chemistry of coordinated nitroalkane anions will be the subject of future publications.

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(17) Data for **1**: ^1H NMR (CD_2Cl_2) δ 6.22 (s, 10 H, Cp), 1.96 (s, 6 H, Me); $^{13}C\{^1H\}$ NMR δ 123.74 (C=N), 114.64 (Cp), 16.30 (Me); MS (EI), *m/e* 345, $[M]^+$. Data for **2**: ^1H NMR (CD_2Cl_2) δ 6.27 (s, 10 H, Cp), 1.91 (d, *J* = 6.35 Hz, 3 H, =CHMe), 6.10 (q, *J* = 6.35Hz, 1 H, =CHMe); $^{13}C\{^1H\}$ NMR δ 114.54 (Cp), 112.85 (C=N), 10.73 (Me); MS (EI), *m/e* 331, $[M]^+$. Data for **3**: ^1H NMR (CD_2Cl_2) δ 7.1–7.7 (m, 5 H, Ph), 5.88 (s, 10 H, Cp), 1.88 (s, 6 H, $=CMe_2$), 1.41 (s, 6 H, CMe_2Ph), 1.20 (s, 2 H, Zr—CH_2); $^{13}C\{^1H\}$ NMR δ 155.5, 127.97, 126.24, 124.87 (Ph), 120.76 (C=N), 110.99 (Cp), 64.15 (Zr—CH_2), 43.59 (quaternary C), 34.83 (CMe_2Ph), 16.24 ($=CMe_2$); MS (EI), *m/e* 443, $[M]^+$. Data for **4**: ^1H NMR (CD_2Cl_2) δ 2.01 (s, Me); $^{13}C\{^1H\}$ δ 126.48 (C=N), 16.54 ($=CMe_2$); MS (EI) *m/e* 444, $[M]^+$.

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Supplementary Material Available: Listings of final positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of final observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Convenient Synthesis of Thiazyl Hexafluoroarsenate(V), $[SN]^+[AsF_6]^-$, and Small Quantities of Thiazyl Fluoride, NSF

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The simplest, stable sulfur–nitrogen species is the cation $[SN]^+$. This has been known to have considerable potential as a building block in the synthesis of a wide range of sulfur–nitrogen-containing compounds.[2-4] $[SN]^+[MF_6]^-$ (M = As, Sb) were first prepared by the reaction of NSF and MF_5 according to eq 1.[5] It has also

$$NSF + MF_5 \rightarrow [SN]^+[MF_6]^- \qquad M = As, Sb \qquad (1)$$

been prepared as one of the products of thermal decomposition of $[S_3N_2F_2]^+[AsF_6]^-$[6] and the reaction of excess AsF_5 and $S_3N_3F_3$. $[SN]^+[SbCl_6]^-$ has also been prepared from a gas-phase reaction of $SbCl_5$ and NSCl.[7] None of these reactions give a high-yield synthesis of an $[SN]^+$-containing salt from an easily obtained starting material. Recently Herberhold and Haummaier published the preparation of a solution of $[SN]^+[PF_6]^-$ in nitromethane by a reaction of $S_3N_3Cl_3$ and $AgPF_6$.[8] The solution of $[SN]^+[PF_6]^-$ was used in situ and not isolated. This source of $[SN]^+$ has utility as a synthetic reagent but its potential would be expanded if a salt was readily prepared as a pure solid, but we were unable to separate the related $[SN]^+[AsF_6]^-$ from nitromethane. We report below a convenient, simple synthesis of solid, pure $[SN]^+[AsF_6]^-$ in approximately 75% yield by the reaction of $S_3N_3Cl_3$ and an excess of $AgAsF_6$ in sulfur dioxide solvent according to eq 2. Full details are reported below.

$$3AgAsF_6 + S_3N_3Cl_3 \xrightarrow{SO_2} 3AgCl\downarrow + 3[SN]^+[AsF_6]^- \quad (2)$$

Mews has reported the reaction of $[SN]^+[AsF_6]^-$ and S_8 leading to $[S_2N]^+[AsF_6]^-$.[9] We previously reported a convenient high-yield synthesis of $[S_2N]^+[AsF_6]^-$ and have shown its chemistry to be extensive and diverse.[10,11] The $[S_2N]^+$ cation was first made as the $SbCl_6^-$ salt in unspecified yield.[12] The $AlCl_4^-$ salt has also been reported in unspecified yield.[13] In order to compare our previously reported synthesis of $[S_2N]^+[AsF_6]^-$ with that reported by Mews, we repeated the reaction and found that it proceeded in about 50% recovered yield of highly crystalline product according to eq 3. Full details are reported below.

$$8[SN]^+[AsF_6]^- + S_8 \xrightarrow{SO_2} 8[S_2N]^+[AsF_6]^- \qquad (3)$$

The reactive gas thiazyl fluoride, NSF, is a versatile starting material and of central importance in the field of sulfur–nitrogen–fluorine chemistry.[14,15] The most important synthetic routes to it are summarized in ref 14. However, these methods suffer either from the formation of mixtures or from lengthy and expensive preparation of starting materials.[14]

We report below a convenient, small-scale method for the synthesis of NSF in good yield according to eq 4. We also describe an unoptimized, scaled-up preparation that demonstrates the potential of this method as a route to gram quantities of NSF.

$$[SN]^+[AsF_6]^- + CsF \xrightarrow{\Delta} NSF + CsAsF_6 \qquad (4)$$

Experimental Section

General Considerations. Except where stated, apparatus and chemicals have been previously described.[16-19] $AgAsF_6$ was prepared in quantitative yield by the reaction of powdered silver metal and a slight excess of arsenic pentafluoride ($AgAsF_6$ is also commercially available from Pfaltz and Bauer, Inc.) in sulfur dioxide solution by the addition of aliquots of AsF_5 to the silver in SO_2 at −196 °C and slow warming of the mixture to room temperature before the addition of the next aliquot. $S_3N_3Cl_3$ was prepared according to ref 20. Metal apparatus was prefluorinated with fluorine and SF_4 until minimal OSF_2 was detected (IR) in the SF_4. Solids were manipulated in a Vacuum Atmospheres drybox (Type 493), under dry nitrogen.

Preparation of $[SN]^+[AsF_6]^-$. In a typical reaction, a large excess of $AgAsF_6$ (6.94 g, 23.48 mmol), relative to eq 1, and $S_3N_3Cl_3$ (0.865 g, 3.45 mmol) were loaded into a Pyrex, two-bulbed (ca. 25-cm³) vessel incorporating a coarse-glass frit and a J. Young Teflon-in-glass valve. Sulfur dioxide (5.218 g, 81.53 mmol) was condensed onto this mixture at −196 °C. At room temperature a reaction occurred, giving a white solid and an opaque, greenish brown solution. After 20 h of stirring the solution was clear yellow over a white solid. The soluble products were washed through the frit into the second bulb, and the white insoluble solid was washed several times with solvent. The volatile products were slowly (approximately 3 h) condensed into a Pyrex U-tube fitted with two Teflon-stemmed Roto-flo valves, held at −196 °C in a closed system. A hard yellow solid and a fine white powder remained on the sides of the vessel that had contained the soluble and insoluble products. The vessel was broken open in the drybox and the soluble material (5.684 g), ground to a fine powder and loaded into a sublimation vessel through a side arm. The sublimation vessel was a Pyrex tube (40-cm length, 3-cm o.d.) fitted with a 1 cm o.d. side arm approximately 5 cm from the top of the tube and a J. Young Teflon-in-glass valve and made with a constriction (diameter 1.5 cm) 10 cm from the bottom of the tube. The end of the side arm was temporarily covered with Teflon tape in the drybox and then quickly sealed off and the vessel evacuated (10^{-3} torr). The valve and a short section of the glass tubing connecting it to the sublimation vessel was sealed off and removed. The side arm was sealed off, the vessel evacuated (10^{-3} Torr), and the valve sealed off and removed. The lower half of the sublimation tube was then heated to 120 °C. After 3 days a substantial amount of $[SN]^+[AsF_6]^-$ had sublimed onto the walls of the sublimation tube as a white film studded with large white crystals. The tube was scored at the constriction and broken open in the drybox. The unsublimed residue that remained consisted of unreacted $AgAsF_6$ and some of the slightly soluble AgCl originally precipitated from the

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