DIBAL-H (3.8 mmol, 2.5 mL of a 1.5 M solution in toluene) was added dropwise at 0 °C. The first half of the addition produced a transient blue color. After addition was complete, the reaction mixture was a pale yellow solution. Workup as before gave a crude product mixture that showed an 80:20 ratio of 3a/8 to 7 by $^1$H NMR. The crystalline 7 was isolated in 0.16 g (17%) yield. The 3a/8 mixture was isolated in 0.71 g (77%) yield.

**DIBAL-H Addition to 3a/8.** DIBAL-H (1.5 mmol, 1.0 mL of a 1.5 M solution in toluene) was added dropwise to a solution of 3a (0.31 g, 1.0 mmol) in 10 mL of dry THF cooled to 0 °C under an argon atmosphere. After addition was complete, the reaction mixture was stirred 1.0 h at 0 °C and the reaction was quenched by the dropwise addition of 0.5 mL of 99% MeOD. The tellurapyran was recovered by the standard workup. Both $^1$H NMR and FDMS analyses of the recovered 3a showed no incorporation of deuterium.

**Electrochemical Reduction of Tellurapyrylium Salt 5a.** Tellurapyrylium salt 5a (6.9 mg, 0.015 mmol) was dissolved in 25 mL of a 0.2 M solution of tetra-*n*-butylammonium fluoroborate in dichloromethane to give a 6.1 × 10$^{-4}$ M solution in 5a. After the passage of 1.54 C between 0.0 and −0.5 V (vs SCE), the electrolysis was complete with 1.04 F/mol being passed. The CV of the electrolyzed solution showed complete consumption of starting material in a negative scan between 0.0 and −1.5 V (vs SCE). The positive scan showed $E_p^a$ = 0.63 V (vs SCE) for 7 while the negative scan following oxidation showed 5a with $E_p^c$ = −0.34 V (vs SCE). The absorption spectrum of the electrolyzed solution was indicative of a 2.8 × 10$^{-4}$ M solution of 7 assuming an extinction coefficient of 3130 at 440 nm.

**Electrochemical Oxidation of the Dimer 7.** The dimer 7 (12.8 mg, 0.0210 mmol) was dissolved in 25 mL of a 0.2 M solution of tetra-*n*-butylammonium fluoroborate to give an 8.4 × 10$^{-4}$ M solution in the dimer. Electrolysis between 0.0 and +0.90 V (vs SCE) resulted in the passage of 5.281 C of current (2.6 F/mol). The oxidized solution was examined by absorption spectroscopy

and showed a 1.5 × 10$^{-3}$ M solution of 5a assuming an extinction coefficient of 8400 at 345 nm. The CV of the oxidized solution showed complete consumption of starting material in a positive scan between 0.0 and +1.5 V (vs SCE) while the negative scan showed $E_p^c$ = −0.34 V (vs SCE) for 5a.

The oxidized solution was reduced between 0.0 and −0.40 V (vs SCE) resulting in the passage of 4.747 C (90% reversibility) which corresponds to 1.2 F/mol for the reduction of 5a if one assumes complete consumption of the dimer in the initial oxidation. Both the absorption spectrum and CV of the reduced solution were consistent with dimer 7 at 7.5 × 10$^{-4}$ M concentration.

**DIBAL-H Reduction of Thiapyranone 16.** Thiapyranone 16 (0.66 g, 2.0 mmol) in 10 mL of dry THF under an argon atmosphere was cooled to 0 °C. DIBAL-H (6.0 mmol, 4.0 mL of a 1.5 M solution in toluene) was added dropwise via syringe. After addition was complete, the reaction mixture was stirred 0.5 h at 0 °C and was then poured into 100 mL of moist ether. The organic solution was washed with cold, 10% HCl (4 × 25 mL), was dried over sodium sulfate, and was concentrated. Chromatography on silica gel eluted with dichloromethane gave 0.49 g (78%) of the carbinol as an oil: $^1$H NMR (CDCl$_3$) δ 7.30 (m, 5 H, aromatics), 6.22 (s, 1 H), 5.49 (t, 1 H, J = 5.4 Hz), 5.33 (s, 1 H), 2.51 (dd, 1 H, J = 6.2, 13.9 Hz), 2.32 (dd, 1 H, J = 6.2, 13.9 Hz), 1.43 (s, 9 H), 1.22 (s, 9 H); IR (film, NaCl) 3420 (s, br), 2960, 1363, 1015, 731, 700 cm$^{-1}$; FDMS, $m^+/e$ 316 (C$_{20}$H$_{28}$OS).

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# Organometallic Complexes of Osmium with Sulfur-Containing Ligands: Synthesis of *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(SCH$_2$CH$_2$S)]$^-$ and *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(SCN)$_2$]$^-$ and the Synthesis and X-ray Crystal Structure of *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(2-S-NC$_5$H$_4$)]$_2$

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New mononuclear complexes of osmium with sulfur-containing ligands have been prepared. The reaction of [N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] with 1,2-ethanedithiol and triethylamine produces the osmium dithiolate complex [N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(SCH$_2$CH$_2$S)]. Substitution of the halide on [N-*n*-Bu$_4$][Os(N)-(CH$_2$SiMe$_3$)$_2$Cl$_2$] by potassium thiocyanate gives an equilibrium mixture of two isomers of *cis*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(SCN)$_2$]. In the major isomer, both of the thiocyanate groups are bonded to osmium through nitrogen, while in the minor isomer osmium has one thiocyanato and one isothiocyanato ligand. 2-Pyridinethiol displaces both halides in [N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] in the presence of triethylamine to form two isomers of a neutral dimer in which the 2-pyridinethiolato ligands chelate and bridge the two metal centers. The crystal structure of one isomer of [Os(N)(CH$_2$SiMe$_3$)$_2$(SC$_5$H$_4$N)]$_2$ was determined by single-crystal X-ray diffraction: $a$ = 14.388 (4) Å, $b$ = 16.209 (4) Å, $c$ = 10.760 (4) Å, $\beta$ = 91.64 (3)°, $\gamma$ = 66.38 (2)°, $V$ = 2170 (2) Å$^3$, $Z$ = 2, $\alpha$ = 108.25 (2)°, $\rho_{calcd}$ = 1.496 g/cm$^3$, triclinic space group $P\bar{1}$.

## Introduction

Our interest in the influence of other ligands at the metal center on the reactivity of the nitride has led us to prepare a variety of organometallic nitrido complexes of osmium and ruthenium. The substitution of strongly σ-donating alkyl ligands for the more electron-withdrawing chlorides in the complexes [M(N)Cl$_4$]$^-$ dramatically alters the re-

activity of the nitride. Griffith found that [Os(N)Cl$_4$]$^-$ reacts with tertiary phosphines at nitrogen, with reduction of the metal, to form the phosphine imidato complexes Os(NPR$_3$)Cl$_3$(PR$_3$)$_2$.[1] The alkyl complexes, on the other hand, react with Lewis acids at nitrogen to form adducts

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(1) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* 1975, 417.

Scheme I



Scheme II
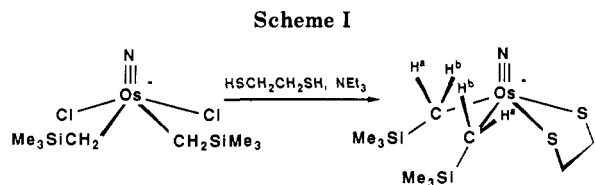


and react with a variety of organic electrophiles, such as alkyl halides, to form imido complexes $[Os(NR')R_4]^-$.[2] Mixed complexes $[Os(N)Cl_2R_2]^-$ do not react with either phosphines or alkyl halides.

Thiolate ligands, with the polarizable sulfur atom, ought to form electron-rich osmium complexes. $\pi$-Donation from sulfur to osmium may effect the multiple bonding between the metal and nitrogen and change the reactivity of the nitride.

Osmium clusters containing simple thiolate ligands have been prepared, but few mononuclear complexes are known.[3] Those that have been well-characterized include $Os(SC_{10}H_{13})_4(MeCN)$ and $mer$-$Os(PMe_2Ph)_3(N_2)Cl(SC_6F_5)$ and complexes of 2-pyridinethiolate in which both metal–sulfur and metal–nitrogen bonds can be formed.[4,5] Dithioether complexes of osmium(IV) and one thioether complex of osmium(III) have been reported.[6] An epi-thioosmabenzene complex was also prepared.[7] Several osmium dithiocarbamate complexes have also been prepared.[8] The paucity of osmium complexes having sulfur donors in surprising in view of the theory that second- and third-row metals, being more polarizable, ought to readily form bonds to easily polarizable sulfur ligands.[9]

Substitution of the halides in $[M(N)R_2X_2]^-$ (M = Ru, Os; R = Me, $CH_2SiMe_3$; X = Cl, Br) for other anionic ligands provides a route to a wide variety of organometallic complexes. Osmium(IV) and ruthenium(VI) complexes containing chelating oxygen ligands, $[Os(N)-(CH_2SiMe_3)_2(OYO)]^-$ (Y = CO, SO$_2$, CrO$_2$), have recently been prepared by the reaction of silver salts of carbonate, sulfate, and chromate anions with $[Os(N)-$
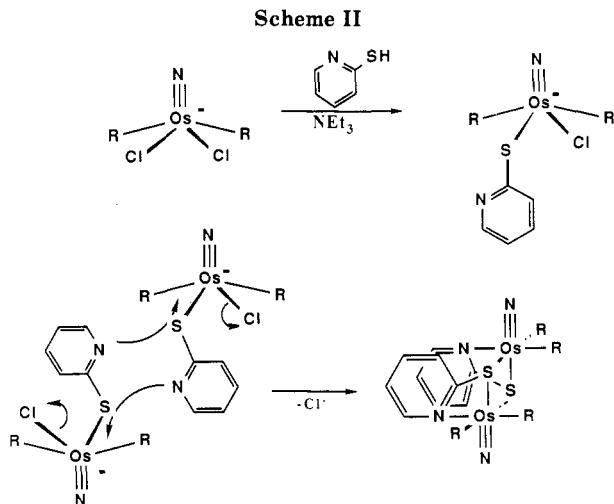
$(CH_2SiMe_3)_2Cl_2]^-$.[10] We now report the synthesis of new complexes of osmium-containing sulfur donor ligands by the substitution of chlorides in $[N$-$n$-$Bu_4][Os(N)-(CH_2SiMe_3)_2Cl_2]$.

## Results and Discussion

**Synthesis of an Ethanedithiolato Complex of Osmium.** Both the cis and trans isomers of $[N$-$n$-$Bu_4][Os-(N)(CH_2SiMe_3)_2Cl_2]$ react with 1,2-ethanedithiol in the presence of an amine to give the chelating dithiolato complex $[N$-$n$-$Bu_4][Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$ (see Scheme I). The yellow, crystalline product can be obtained in essentially quantitative yield. The dithiolato complex is stable to air and water and is also quite thermally stable. No decomposition occurs in refluxing toluene.

The complex was characterized by spectroscopy and elemental analysis. In the $^1H$ NMR spectrum of the product dithiolate complex, we observe a pair of doublets for the diastereotopic methylene protons. We have seen similar spectra for other cis-disubstituted complexes.[10,11] The ethanedithiolate proton resonances form an AA'BB' pattern. The nitrogen–osmium stretching vibration in the IR spectrum is a strong band at 1091 cm$^{-1}$.

It is interesting that under the same reaction conditions which result in the formation of the dithiolate complex, $[N$-$n$-$Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and ethylene glycol do not react to produce the analogous glycolate species. The starting material is recovered quantitatively from the reaction mixture. Even reaction with the sodium salt of the glycol under more vigorous conditions gives only a very small yield of $[N$-$n$-$Bu_4][Os(N)(CH_2SiMe_3)_2(OCH_2CH_2O)]$. Rhenium(V) complexes of both 1,2-ethanedithiolate and ethylene glycolate have been prepared from $(C_5Me_5)Re-(O)Cl_2$.[12]

A related nitridoruthenium(VI) complex with 1,2-benzenedithiolate ligands, $[Ru(N)(S_2C_6H_4)_2]^-$, was recently reported.[13]

**Reaction of $[N$-$n$-$Bu_4][Os(N)(CH_2SiMe_3)_2-(SCH_2CH_2S)]$ with Methyl Iodide.** In the osmium dithiolato complex, alkylation at the nitrido nitrogen or one of the thiolato sulfur atoms could occur in reactions with alkyl halides. We know from previous work that the ni-

(2) Shapley, P. A.; Own, Z.-Y. Huffman, J. C. *Organometallics* 1986, *5*, 1269.

(3) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. Cryst. Struct. Commun.* 1980, *b36*, 703. (b) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* 1979, *101*, 5862. (c) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* 1979, *101*, 1306. (d) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* 1981, *103*, 546. (e) Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Uden, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1983, *C39*, 1203. (f) Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Uden, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1983, *C39*, 1200. (g) Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Uden, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1983, *C39*, 1197. (h) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* 1981, *215*, C33. (i) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* 1982, *1*, 235.

(4) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* 1983, *105*, 3362. Cruz-Garritz, D.; Torrens, H.; Leal, J.; Richards, R. L. *Transition Met. Chem.* 1983, *8*, 127.

(5) Mura, P.; Olby, B. G.; Robinson, S. D. *J. Chem. Soc., Dalton Trans* 1985, 2101.

(6) (a) Gulliver, D. J.; Levason, W.; Smith, K. G.; Selwood, M. J. *J. Chem. Soc., Dalton Trans.* 1980, 1872. (b) Aires, B. E.; Fergusson, J. E.; Howarth, D. T.; Miller, J. M. *J. Chem. Soc. A* 1971, 1144.

(7) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* 1982, 811.

(8) (a) Dix, A. H.; Diesveld, J. W.; Van Der Linden, J. G. M. *Inorg. Chim. Acta* 1977, *24*, L51. (b) Given, K. W.; Wheeler, S. H.; Jick, B. S.; Mahen, L. J.; Pignolet, L. H. *Inorg. Chem.* 1979, *18*, 1261. (c) Given, K. W.; Pignolet, L. H. *Inorg. Chem.* 1977, *16*, 2982. (d) Cole-Hamilton, D. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* 1976, 2396. (e) Critcholow, P. B.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* 1975, 1367. (f) Preti, C.; Tosi, G.; Zannini, P. *Z. Anorg. Allg. Chem.* 1980, *469*, 234.

(9) Pearson, R. G., Ed. *Hard and Soft Acids and Bases*; Dowden, Hutchenson, and Ross: Stroudsburg, PA, 1973.

(10) Shapley, P. A.; Zhang, N., submitted for publication in *Inorg. Chem.*

(11) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* 1984, *106*, 7493.

(12) Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H.-J. *Angew. Chem.* 1987, *99*, 462.

(13) Sellmann, D.; Binker, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1987, *42B*, 341-7, Ger.
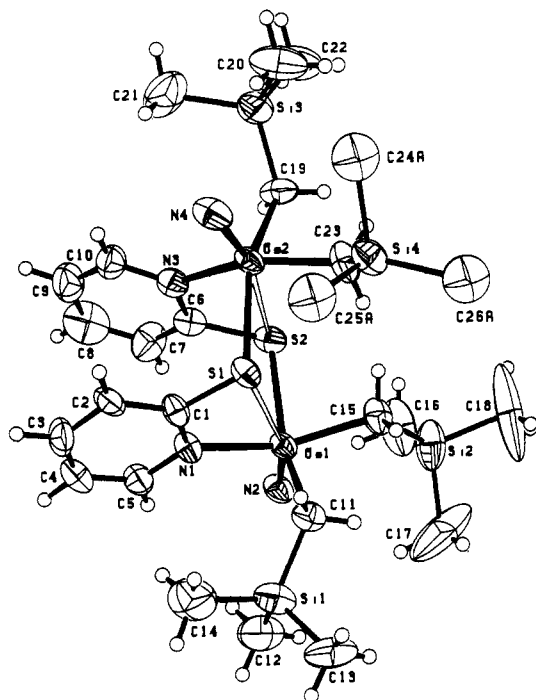
**Figure 1.** ORTEP diagram of *cis*-[Os(N)(CH₂SiMe₃)₂(pyridine-2-thiolate)]₂.

tridotetraalkylosmium(VI) anions react with alkyl halides, R′X, to form alkylimido complexes, Os(NR′)R₄.[2] Nucleophilic substitution reactions on alkyl halides by divalent sulfur is quite common.[14]

We observe only alkylation of sulfur in the reaction of methyl iodide with the nitridoosmium dithiolate complex. Addition of 1 equiv of methyl iodide to a solution of [N-*n*-Bu₄][Os(N)(CH₂SiMe₃)₂(SCH₂CH₂S)] in C₆D₆ causes an immediate reaction, with precipitation of tetra-*n*-butylammonium iodide. One organometallic product is formed, which retains a band characteristic of an osmium–nitrogen triple-bond stretching vibration at 1100 cm⁻¹. The two alkyl groups are inequivalent by ¹H NMR. These data are consistent with the formulation of the product as Os-(N)(CH₂SiMe₃)₂(SCH₂CH₂SMe).

**Synthesis of a Pyridine-2-thiolate Complex of Osmium.** A number of pyridine-2-thiolate complexes of osmium and ruthenium have been prepared.[5,15] The pyridine-2-thiolato ligand can be monodentate, with a metal–sulfur bond, it can chelate to one metal, or it can bridge two or three metal centers. We expected the reaction of [N-*n*-Bu₄][Os(N)(CH₂SiMe₃)₂Cl₂] with excess pyridine-2-thiol in the presence of base would produce either a bis (pyridine-2-thiolate) complex, [N-*n*-Bu₄][Os-(N)(CH₂SiMe₃)₂(SC₅H₄N)₂], analogous to the 1,2-ethanedithiolato complex, or a neutral chelate complex, Os-(N)(CH₂SiMe₃)₂(SC₅H₄N). Instead, the product of this reaction was found to be a dimer, [Os(N)(CH₂SiMe₃)₂-(SC₅H₄N)]₂ (see Scheme II).

By NMR, we have found that two isomers are formed in the reaction in a ratio of approximately 3:2. We see eight doublets in the methylene region of the ¹H NMR

(14) Modena, G.; Paradisi, C.; Scorrano, G. In *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: New York, 1985; pp 568–595.

(15) (a) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 1750. (b) Rosete, R. O.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1618. (c) Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc. A* **1972**, 635. (d) Constable, E. C.; Lewis, J. *J. Organomet. Chem.* **1983**, *254*, 105. (e) Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1982**, *233*, C55.

**Table I. Selected Bond Distances and Angles**

| | osmium 1 | | osmium 2 |
|---|---|---|---|
| | | Distances, Å | |
| Os1–N2 | 1.62 (1) | Os2–N4 | 1.64 (1) |
| Os1–N1 | 2.108 (10) | Os2–N3 | 2.12 (1) |
| Os1–S1 | 2.965 (4) | Os2–S2 | 2.972 (4) |
| Os1–C11 | 2.11 (2) | Os2–C19 | 2.13 (2) |
| Os1–C15 | 2.08 (1) | Os2–C23 | 2.08 (2) |
| Os1–S2 | 2.396 (4) | Os2–S1 | 2.404 (4) |
| | | Angles, deg | |
| N2–Os1–C11 | 101.2 (6) | N4–Os2–C19 | 102.6 (6) |
| N2–Os1–C15 | 105.6 (6) | N4–Os2–C23 | 101.3 (6) |
| N2–Os1–N1 | 102.0 (5) | N4–Os2–N3 | 102.5 (5) |
| N2–Os1–S2 | 104.8 (4) | N4–Os2–S1 | 106.0 (5) |
| N2–Os1–S1 | 160.6 (4) | N4–Os2–S2 | 161.5 (4) |
| C11–Os1–C15 | 86.1 (6) | C19–Os2–C23 | 88.2 (6) |
| C15–Os1–S2 | 81.7 (4) | C23–Os2–S1 | 83.6 (5) |
| S2–Os1–N1 | 90.5 (3) | S1–Os2–N3 | 89.8 (3) |
| N1–Os1–C11 | 89.5 (5) | N3–Os2–C19 | 86.7 (5) |
| S2–Os1–C11 | 153.4 (4) | S1–Os2–C19 | 151.3 (4) |
| N1–Os1–C15 | 152.4 (5) | N3–Os2–C23 | 156.2 (6) |
| S1–Os1–S2 | 76.7 (1) | S1–Os2–S2 | 76.4 (1) |
| S1–Os1–N1 | 58.6 (3) | S2–Os2–N3 | 59.0 (3) |
| S1–Os1–C11 | 80.7 (4) | S2–Os2–C19 | 77.4 (4) |
| S1–Os1–C15 | 93.8 (4) | S2–Os2–C23 | 97.2 (5) |

**Table II. Fractional Atomic Parameters for [Os(N)(CH₂SiMe₃)₂(SNC₅H₄)]₂**

| | x/a | y/b | z/c |
|---|---|---|---|
| Os1 | 0.20133 (4) | 0.48797 (4) | 0.16127 (5) |
| Os2 | 0.36967 (4) | 0.21365 (4) | 0.18538 (5) |
| S1 | 0.4036 (3) | 0.3244 (3) | 0.1092 (3) |
| S2 | 0.1638 (3) | 0.3674 (3) | 0.2038 (4) |
| Si1 | 0.2921 (4) | 0.6224 (4) | 0.0438 (6) |
| Si2 | 0.0932 (4) | 0.6372 (5) | 0.4689 (5) |
| Si3 | 0.3105 (4) | 0.0613 (4) | 0.2966 (5) |
| Si4 | 0.5471 (4) | 0.2611 (4) | 0.3874 (5) |
| N1 | 0.2648 (7) | 0.3964 (8) | -0.0319 (10) |
| N2 | 0.0932 (9) | 0.5621 (9) | 0.136 (1) |
| N3 | 0.2732 (9) | 0.1990 (9) | 0.035 (1) |
| N4 | 0.4711 (9) | 0.1123 (10) | 0.132 (1) |
| C1 | 0.352 (1) | 0.324 (1) | -0.041 (1) |
| C2 | 0.402 (1) | 0.251 (1) | -0.165 (1) |
| C3 | 0.355 (1) | 0.264 (1) | -0.275 (1) |
| C4 | 0.266 (1) | 0.340 (1) | -0.265 (1) |
| C5 | 0.221 (1) | 0.404 (1) | -0.146 (1) |
| C6 | 0.182 (1) | 0.278 (1) | 0.054 (1) |
| C7 | 0.112 (1) | 0.283 (1) | -0.035 (2) |
| C8 | 0.135 (2) | 0.205 (2) | -0.150 (2) |
| C9 | 0.228 (2) | 0.125 (2) | -0.166 (2) |
| C10 | 0.299 (1) | 0.121 (1) | -0.074 (1) |
| C11 | 0.296 (1) | 0.559 (1) | 0.158 (1) |
| C12 | 0.176 (2) | 0.685 (2) | 0.005 (3) |
| C13 | 0.345 (2) | 0.708 (2) | 0.114 (2) |
| C14 | 0.363 (2) | 0.538 (2) | -0.120 (2) |
| C15 | 0.204 (1) | 0.530 (1) | 0.364 (1) |
| C16 | -0.035 (1) | 0.628 (2) | 0.437 (2) |
| C17 | 0.084 (3) | 0.747 (2) | 0.435 (4) |
| C18 | 0.099 (2) | 0.663 (3) | 0.644 (2) |
| C19 | 0.277 (1) | 0.182 (1) | 0.297 (2) |
| C20 | 0.446 (2) | 0.005 (2) | 0.349 (3) |
| C21 | 0.325 (2) | -0.028 (2) | 0.129 (2) |
| C22 | 0.218 (2) | 0.059 (2) | 0.415 (3) |
| C23 | 0.412 (1) | 0.281 (1) | 0.362 (1) |
| C24A | 0.602 (3) | 0.134 (3) | 0.410 (4) |
| C25A | 0.632 (3) | 0.240 (3) | 0.246 (4) |
| C26A | 0.564 (3) | 0.352 (3) | 0.546 (4) |
| C24B | 0.603 (6) | 0.170 (5) | 0.484 (7) |
| C25B | 0.563 (5) | 0.395 (5) | 0.442 (6) |
| C26B | 0.623 (5) | 0.166 (5) | 0.212 (7) |

spectrum for the four inequivalent methylene protons in each of two molecules and four singlets for the inequivalent trimethylsilyl groups. These two compounds have the same solubility but crystallize in slightly different forms

Scheme III

$[Os(N)(CH_2SiMe_3)_2Cl_2]^-$

|
| 2 KSCN
↓

Me₃Si–C(CH₂SiMe₃)...Os(N)...NCS / NCS    +    Me₃Si–C(CH₂SiMe₃)...Os(N)...NCS / SCN

and so can be separated manually. Elemental analyses of the two complexes are identical, and IR spectra are very similar. Solutions of either isomer in $C_6D_6$ equilibrate to a mixture of the two isomers in several hours at room temperature.

**X-ray Crystal Structure of *cis*-[Os(N)-(CH₂SiMe₃)₂(pyridine-2-thiolate)]₂.** The structure of one isomer of $[Os(N)(CH_2SiMe_3)_2(pyridine-2-thiolate)]_2$ was determined by single-crystal X-ray diffraction. Selected bond lengths and angles are shown in Table I and atomic parameters in Table II. The complex is a dimer with each pyridine-2-thiolate unit chelating through sulfur and nitrogen to one metal center and bridging both metals through sulfur. The alkyl groups are in a cis configuration about the metal. The axial (trans to the nitride) osmium–sulfur bond is significantly longer than the equatorial (cis to the nitride) osmium–sulfur bond, so the principle interaction of the pyridine-2-thiolate unit is to bridge the two metals.

The osmium centers are six-coordinate but are distorted from an octahedral structure. In fact, the structure of this complex can be compared with the known five-coordinate nitridoosmium complexes. A square-pyramidal geometry, with the alkyl groups bent down below the plane of the metal is seen in the structures of $[AsPh_4][Os(N)Cl_4]^{16}$ and $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]^2$. The average nitrogen–osmium–ligand angle in $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$ (107.4°) and in $[AsPh_4][Os(N)Cl_4]$ (104.5°) can be compared with the average nitrogen–osmium–equatorial ligand angle of 103.4° in this pyridinethiolato complex.

The average osmium–nitrogen distance in this complex is the same as the distance found in $[N-n-Bu_4][Os(N)-(CH_2SiMe_3)_4]$, 1.631 Å, which is longer than this to the difference in the length of the Os–N bonds in $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$ and $[AsPh_4][Os(N)Cl_4]$, of 1.631 and 1.604 Å, respectively. The average metal–carbon bond distance in $[Os(N)(CH_2SiMe_3)_4]^-$ is 2.13 Å.

**Synthesis of Osmium Thiocyanate Complexes.** The thiocyanate anion is an ambidentate ligand that can coordinate to a transition metal through either the sulfur or the nitrogen atom.[17] There are well-characterized examples of osmium–thiocyanate and osmium–isothiocyanate complexes.[18]

Reaction of $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with 2 equiv of potassium thiocyanate produces a mixture of two isomers of $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_2(SCN)_2]$ in a ratio of 2:1 (see Scheme III). The products are thermally stable and stable to air and water.

We have identified the major isomer as being a molecule with two N-bonded thiocyanate ligands arranged in a cis configuration at the metal center. The proton NMR

spectrum shows two types of methylene protons as in the dithiolate complex above. The IR spectrum shows C–N and C–S stretching vibrations at 2073 and 833 cm⁻¹, respectively. Other N-bonded thiocyanate complexes have been found to have C–S stretching vibrations in the range of 780–860 cm⁻¹, while this vibration in S-bonded thiocyanate complexes is found in the range 690–720 cm⁻¹.[19]

The minor isomer has four inequivalent methylene protons in its ¹H NMR spectrum which is consistent with a molecule containing one S-bonded thiocyanate and one N-bonded thiocyanate ligand. A band at 2133 cm⁻¹ in the IR spectrum can be assigned to the C–N stretch of the S-bonded thiocyanate. For metals which coordinate to either the sulfur or nitrogen end of the thiocyanate ligand, the C–N stretch of S-bonded thiocyanate ligand is at somewhat higher energy than the N-bonded isomer. Two bands of medium to weak intensity at 719 and 850 cm⁻¹ fall in the expected range for the C–S stretch of an S-bonded thiocyanate and an N-bonded thiocyanate, respectively.

**The Effect of Sulfur Ligands on Osmium–Nitrogen Bonding.** Information on the strength of the osmium–nitrogen triple bond can be obtained from IR spectra since a decrease in the energy the osmium–nitrogen stretching vibration corresponds to an increase in the metal–nitrogen distance. The $\nu_{Os-N}$ of 1091 cm⁻¹ for the ethanedithiolato complex, $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$, is much lower than the corresponding band in $[Os(N)Cl_4]^-$ (1123 cm⁻¹) and lower than the $\nu_{Os-N}$ in $[Os(N)-(CH_2SiMe_3)_4]^-$ or $[Os(N)(CH_2SiMe_3)_2]^-$ (1105 cm⁻¹). For the pyridine-2-thiolate dimer $[Os(N)(CH_2SiMe_3)_2-(SC_5H_5N)]_2$, both the osmium–nitrogen stretching vibration and the average metal–nitrogen distance are the same as in $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_4]$. It appears from these data that the thiolate ligands are highly electron-donating.

In the ethanedithiolate complex, it is the nucleophilic thiolate sulfur atom rather than the nitride which engages in nucleophilic attack on methyl iodide. This reactivity demonstrates that a lone pair of electrons on sulfur is more available than the lone pair on the nitrido nitrogen atom. Since π-donation from thiolate to osmium would necessarily reduce π-donation from the nitride, making sulfur more electron-poor and nitrogen more electron-rich, the reactivity at sulfur allows us to conclude that the degree of π-donation from sulfur to osmium is small.

**Conclusion**

Osmium(VI) complexes with 1,2-ethanedithiolato, pyridine-2-thiolato, and thiocyanato ligands can be prepared in good yield by substitution of halide in the dihalide complex $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$. These complexes are thermally stable and stable to air and water. Analysis of IR spectra shows that in the major isomer of $[N-n-Bu_4][Os(N)(CH_2SiMe_3)_2(SCN)_2]$ both thiocyanate groups are bonded to osmium through nitrogen, while the minor isomer contains both S-bonded and N-bonded thiocyanate groups. The 1,2-ethanedithiolate and pyridine-2-thiolate ligands are strongly electron-donating to the osmium center. The pyridine-2-thiolate group acts as both a bridging and chelating ligand in $[Os(N)-(CH_2SiMe_3)_2(pyridine-2-thiolate)]_2$.

**Experimental Section**

All operations were carried out under nitrogen either in a Vacuum Atmosphere drybox or on a Schlenk line. Toluene, diethyl ether, hexane, benzene, and tetrahydrofuran were distilled

(16) Phillips, F. L.; Skapski, A. C. *J. Cryst. Mol. Struct.* **1975**, *5*, 83.

(17) (a) Burmeister, J. L.; Basolo, F. *J. Am. Chem. Soc.* **1963**, 1700. (b) Burmeister, J. L.; Basolo, F. *Inorg. Chem.* **1964**, 1587.

(18) (a) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *215*, C33. (b) Clark, G. R.; Edmonds, N. R.; Pauptit, R. A.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Organomet. Chem.* **1983**, *244*, C57.

(19) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1970; pp 187–190.

from sodium/benzophenone under nitrogen. Methylene chloirde and acetonitrile were distilled from CaH$_2$. Sodium trimethylsiloxide was prepared by hydrolysis of chlorotrimethylsilane. Triethylamine, pyridine-2-thiol, and 1,2-dithioethane were distilled under nitrogen prior to use. Mg(CH$_2$SiMe$_3$)Cl and KSCN were purchased from Aldrich and used without further purification. Mg(CH$_2$SiMe$_3$)$_2$ was prepared from Mg(CH$_2$SiMe$_3$)Cl and dioxane.[20] [OsNCl$_4$][NBu$_4$] was prepared according to Griffith.[21] The *trans*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] was prepared as previously described.[21] IR spectra were obtained on an IBM IR/32 spectrometer. NMR spectra were obtained on Varian XL200, General Electric QE300, or General Electric GN500 FT NMR spectrometers. Chemical shifts are reported in parts per million downfield from TMS for $^1$H and $^{13}$C NMR spectra.

**Preparation of *cis*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$-(SCH$_2$CH$_2$S)].** To a stirred solution of 0.06 g (0.086 mmol) of *trans*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] in 30 mL of THF was added 0.5 mL of Et$_3$N and 8.0 μL (0.086 mmol) of ethanedithiol. After the mixture was stirred for 12 h, the solvent was removed from the reaction mixture under vacuum and the residue was crystallized from hexane/CH$_2$Cl$_2$ at –30 °C. Yellow crystals of *cis*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(SCH$_2$CH$_2$S)] were collected: yield 0.065 g (98.3%); IR (KBr pellet, cm$^{-1}$) 1091 (s, Os–N); $^1$H NMR (C$_6$D$_6$, 300 MHz, 295 K) δ 3.01 (ddd, 4 H, S*CH$_2$CH$_2$*S), 2.68 (m, 8 H, N*CH$_2$*), 2.56 (d, 2 H, OsC*H*$^a$), 2.33 (d, 2 H, OsC*H*$^b$), 1.18 (m, 16 H, NCH$_2$*CH$_2$CH$_2$*CH$_3$), 0.86 (t, 12 H, NCH$_2$CH$_2$CH$_2$*CH$_3$*), 0.49 (s, 18 H, OsCH$_2$SiC*H$_3$*); $^{13}$C{$^1$H<<brb NMR (C$_6$D$_6$, 50.3 MHz, 295 K) δ 58.58 (N*C*H$_2$), 42.29 (S*C*H$_2$), 24.03 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.06 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.01 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 3.57 (OsCH$_2$Si*C*H$_3$), 2.76 (OsCH$_2$Si*C*H$_3$). Anal. Calcd for OsN$_2$Si$_2$S$_2$C$_{26}$H$_{62}$: C, 43.77; H, 8.69; N, 3.93. Found: C, 43.97; H, 8.73; N, 3.97.

**Preparation of *cis*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(SCN)$_2$] and *cis*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$(SCN)(NCS)].** Potassium thiocyanate, KSCN (20 mg, 0.17 mmol), was suspended in 30 mL of CH$_2$Cl$_2$. A solution of *trans*-[N-*n*-Bu$_4$][Os(N)-(CH$_2$SiMe$_3$)$_2$Cl$_2$] (30 mg, 0.043 mmol) was added dropwise to the solution with stirring. After the solution was stirred 2 h at room temperature, the color of solution had changed from orange to yellow. The mixture was stirred overnight. Solvent was removed under vacuum. The residue was crystallized from the CH$_2$Cl$_2$/hexane at –30 °C. Yellow crystals (26 mg, 82%) were obtained: IR (KBr pellet, cm$^{-1}$) 1121 (s, Os–N), 2133 (s, C–N), 2073 (vs, C–N), 850 (m, C–S), 833 (s, C–S), 719 (w, C–S); $^1$H NMR (CD$_2$Cl$_2$, 200 MHz, 295 K) δ 3.20 (m, NCH$_2$*CH$_2$CH$_2$*CH$_3$), 1.66 (m, NCH$_2$*CH$_2$CH$_2$*CH$_3$), 1.46 (m, NCH$_2$CH$_2$C*H$_2$*CH$_3$), 1.01 (t, NCH$_2$CH$_2$CH$_2$*CH$_3$*). *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(NCS)$_2$]$^-$: δ 2.79 (d, *J* = 10.1 Hz, OsC*H*$^a$), 2.09 (d, *J* = 10.1 Hz, OsC*H*$^b$), 0.009 (s, SiMe$_3$). *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(SCN)(NCS)]$^-$: δ 2.82 (d, *J* = 9.4 Hz, OsC*H*$^a$), 2.32 (d, *J* = 9.4 Hz, OsC*H*$^b$), 2.08 (d, *J* = 9.4 Hz, OsC*H*$^c$), 2.04 (d, *J* = 9.4 Hz, OsC*H*$^d$), –0.008 (s, SiMe$_3$). $^{13}$C{H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 295 K): δ 59.34 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 24.3 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.1 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (NC*H$_2$*CH$_2$CH$_2$CH$_3$), 8.5 (Os*C*H$_2$), 8.0 (Os*C*H$_2$), 5.5 (Os*C*H$_2$), 1.2, SiMe$_3$), 0.6 (SiMe$_3$), 0.5 (SiMe$_3$). Anal. Calcd for OsSi$_2$S$_2$N$_4$C$_{26}$H$_{58}$: C, 42.38; H, 7.88; N, 7.61. Found: C, 41.70; H, 7.75; N, 7.55.

**Preparation of *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$(pyridine-2-thiolate)]$_2$.** To a solution of 0.016 g (0.145 mmol) pyridine-2-thiol dissolved in 40 mL of THF was added 0.5 mL of Et$_3$N. The solution of *trans*-[N-*n*-Bu$_4$][Os(N)(CH$_2$SiMe$_3$)$_2$Cl$_2$] (0.10 g 0.145 mmol, in 5 mL of THF) was added dropwise at room temperature. After the mixture was stirred for 12 h, white solid Et$_3$NHCl was removed by filtration. The solvent was removed from the filtrate under vacuum, and the residue was crystallized from hexane/CH$_2$Cl$_2$ at –30 °C. Yellow crystals of dimer [Os(N)-(CH$_2$SiMe$_3$)$_2$(2-SC$_4$N)] were collected; yield 0.048 g, 67.8%; IR (KBr pellet, cm$^{-1}$) 1107 (s). $^1$H NMR (C$_6$D$_6$, 200 MHz, 293 K): major isomer, δ 7.61 (m, 1 H, *o*-C$_5$H$_4$N), 5.81–6.59 (m, 3 H, C$_5$H$_4$N), 3.59 (d, 1 H, OsC*H*$^a$), 2.85 (d, 1 H, OsC*H*$^b$), 2.39 (d, 1 H, OsC*H*$^c$), 2.10 (d, 1 H, OsC*H*$^d$), 0.40 (s, 9 H, OsCH$_2$Si(C*H$_3$*)$_3$), 0.19 (s, 9 H, OsCH$_2$Si(C*H$_3$*)$_3$); minor isomer, δ 7.68 (m, 1 H, *o*-C$_5$H$_4$N), 5.81–6.59 (m, 3 H, C$_5$H$_4$N), 3.12 (d, 1 H, OsC*H*$^a$), 2.91 (d, 1 H, OsC*H*$^b$), 2.07 (d, 1 H, OsC*H*$^c$), 1.96 (d, 1 H, OsC*H*$^d$), 0.47 (s, 9 H, OsCH$_2$Si-

### Table III. Crystal and Data Statistics

| | |
|---|---|
| chem formula | Os$_2$S$_2$Si$_4$N$_4$C$_{26}$H$_{52}$ |
| space group | P$\bar{1}$ |
| *a*, Å | 14.388 (4) |
| *b*, Å | 16.209 (4) |
| *c*, Å | 10.760 (4) |
| α, deg | 108.25 (2) |
| β, deg | 91.64 (3) |
| γ, deg | 66.38 (2) |
| *V*, Å$^3$ | 2170 (2) |
| *Z* | 2 |
| *d*(calcd), g/cm$^3$ | 1.496 |
| temp °C | 27 |
| radiatn | Mo Kα (graphite monochromator) |
| | Kα$_1$, 0.709 30, Kα$_2$, Kᾱ, 710 73 Å |
| abs coeff (μ), cm$^{-1}$ | 60.75 |
| transmissn factors, range | 0.407–0.062 (numerical correction) |
| scan rate, deg/min | variable from 3 to 16 |
| scan range, deg ω | 1.50 (1.00 + 0.35 tan θ) |
| bkgd ratio | 0.33 |
| 2θ limit, deg (octants) | 48 (+*h*,±*k*,±*l*) |
| reflctns (unique, consistency) | 7231 (6802, $R_i$ = 0.017) |
| reflctions with *I* > 2.58σ(*l*) | 5001 |
| *R* | 0.056 |
| *R*$_w$ | 0.078 |
| *p* | 0.030 |

(CH$_3$)$_3$), 0.18 (s, 9 H, OsCH$_2$Si(CH$_3$)$_3$). Anal. Calcd for OsSN$_2$Si$_2$C$_{12}$H$_{26}$: C, 31.94; H, 5.32; N, 5.73. Found: C, 32.02; H, 5.25; N, 5.38.

**Structure Determination of *cis*-[Os(N)(CH$_2$SiMe$_3$)$_2$-(pyridine-2-thiolate)]$_2$.** A transparent, orange, tabular crystal, grown from methylene chloride/hexane solution of dimensions 0.2 × 0.6 × 0.6 mm was used. The crystal was approximately bound by the following forms: {110}, {100}, and <<lrb001}. Distances from the crystal center to these inversion related faces were 0.07, 0.31, and 0.32 mm, respectively. The sample was mounted by using epoxy inside a 1.0-mm thin-walled, tapered glass capillary with the (3, –1, 2) scattering planes roughly normal to the spindle axis. A Enraf-Nonius CAD4 automated κ-axis diffractometer with graphite crystal monochromator was used. The crystal was triclinic, space group P$\bar{1}$, and there were two molecules per unit cell.[22] The structure was solved by Patterson methods (SHELXS-86); correct positions for two osmium atoms were deduced from a Patterson map.[23,24] A weighted difference Fourier synthesis gave positions for 19 additional non-hydrogen atoms and subsequent least-squares difference Fourier calculations revealed positions for the remaining non-hydrogen atoms. The methyl carbon positions on all four silicon atoms were probably disordered; however, owing to high correlation coefficients, only the positions for groups "A" and "B" on Si4 were sufficiently distinct to converge with six independent partially occupied carbon atom positions (the relative site occupancy factor for group "A" converged to 0.63 (2)). The remaining methyl carbon atoms converged with large anisotropic thermal coefficients, particularly atoms C16, C17, and C18, which resulted in artificially short Si–C bond lengths. Hydrogen atoms, except for methyl hydrogens on C24 through C26, were included as fixed contributors in "idealized" positions. In the final cycle of least squares, group isotropic thermal parameters were varied for methyl carbon atoms C24 through C26 and hydrogen atoms, the remaining non-hydrogen atoms were refined with anisotropic thermal coefficients, and an empircal isotropic extinction parameter converged to 5.0 (8) × 10$^{-8}$. Successful convergence was indicated by the maximum shift/error for the last cycle. The range of residual electron density in the final-difference Fourier map was broad; the highest peaks were in vicinity of the osmium atoms. A final analysis of variance between observed and calculated structure factors showed a slight

(20) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(21) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.

(22) Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 25 reflections.
(23) Sheldrick, G. M., Kruger, C., Goddard, R., Eds. SHELX-86 In *Crystallographic Computing 3*; Oxford University: Oxford, 1985; pp 175–189.
(24) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 61–66, 99–101, 149–150.

dependence on sin θ. The final agreement factors were R = 0.056 and $R_w$ = 0.078.

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# Tellurapyrylium Dyes. 2. The Electron-Donating Properties of the Chalcogen Atoms to the Chalcogenapyrylium Nuclei and Their Radical Dications, Neutral Radicals, and Anions

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Several series of chalcogenapyrylium dyes were prepared and were examined by absorption spectroscopy and cyclic voltammetry. Substitution of the heavier chalcogens for oxygen in each series gave sequential bathochromic shifts in the absorption maxima in the order O < S < Se < Te, gave less positive oxidation potentials in the order O < S < Se < Te, and gave less negative reduction potentials in the order O < S < Se < Te (with the pyrylium nucleus having the most negative reduction potential and the tellurapyrylium nucleus, the least negative). The redox data suggest that π-donation from the heteroatom to the carbon π-framework is important in determining the stability of the various states. The chalcogenapyranyl radicals can be oxidized to the Hückel aromatic chalcogenapyranyl anion. The oxidation of the radicals is increasingly positive in the order O < S < Se < Te while reduction of the radicals is increasingly negative in the order Te < Se < S < O. The decreased aromaticity and antiaromaticity as the size of the chalcogen increases would be expected with the larger available orbitals leading to less effective π-bonding. The structure of **6d**, as determined by single-crystal X-ray crystallography, also illustrates the differences in π-bonding between the pyrylium nucleus and the tellurapyrylium nucleus. The molecule, 4-[2,6-diphenyl-4*H*-pyran-4-ylidene)methyl]-2,6-diphenyltellurapyrylium fluoroborate, crystallizes in monoclinic space group 2₁C with Z = 4, a = 13.877 (2) Å, b = 11.344 (4) Å, c = 19.600 (2) Å, and β = 106.654 (11)°. In **6d**, single bonds are shorter and double bonds are longer in the pyrylium ring relative to the tellurapyrylium ring. MNDO calculations were performed on model pyrylium and thiapyrylium systems. Ionization potentials from the calculations as predicted by Koopmans' theorem do not track the experiment oxidation potentials as determined by cyclic voltammetry; theory predicts raising the magnitude of oxidation via a lowering of the HOMO energy level upon substitution of sulfur for oxygen. Both theory and experiment agree on the influence of the heteroatom with respect to electron affinities and reduction potentials. In each case, substitution of sulfur for oxygen is predicted to lower the LUMO energy level. The use of ΔSCF values for heats of formation of the completely optimized species involved (the parent chalcogenapyrylium nucleus, the radical dication, the neutral radical, and the anion) as determined by MNDO and/or AM1 calculations for the pyrylium and thiapyrylium species do track the trends observed in values of $E^{o\prime}$ by cyclic voltammetry. This suggests that values of $E^{o\prime}$ for oxidation and reduction parallel the adiabatic gas-phase ionization potentials and electron affinities, respectively. MNDO determined HOMO – LUMO gaps for model pyrylium and thiapyrylium dyes give a linear correlation with the energies of the experimental absorption maxima for 2,6-diphenyl- and 2,6-di-*tert*-butyl-substituted pyrylium and thiapyrylium derivatives. The magnitude of the heteroatom effect on oxidation and reduction potentials can be predicted by the magnitude of the coefficients at the heteroatom positions in the HOMO and LUMO of the model systems.

## Introduction

The relative σ- and π-electron-donating behavior of chalcogens (oxygen, sulfur, selenium, and tellurium) and the heteroatom effect on stabilizing adjacent carbon ion and carbon radical centers have been areas of interest.[1-5]

In particular, the chalcogen atom effect on the oxidation potentials of neutral chalcogen-containing donors such as the tetrachalcogenafulvalenes,[2] 5,6:11,12-bis(dichalcogeno)tetracenes,[3] and the (chalcogenapyranyl)-chalcogenapyrans[4] have been well-studied. In cyclic

(1) (a) Saeva, F. D.; Olin, G. R. *J. Am. Chem. Soc.* 1980, *102*, 299. (b) Boutique, J. P.; Verbist, J. J.; Fripiat, J. G.; Delhalle, J. *J. Chem. Soc., Perkin Trans. 2* 1984, 240. (c) Pau, J. K.; Ruggera, M. B.; Kim, J. K.; Caserio, M. C. *Ibid.* 1978, *100*, 4242 and references cited therein.
(2) (a) Wudl, F.; Aharon-Shalom, *J. Am. Chem. Soc.* 1982, *104*, 1154. (b) Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T.; Cowan, D. *J. Chem. Soc., Chem. Commun.* 1982, 336. (c) McCullough, R. D.; Kok, G. B.; Lerstrup, K. A.; Cowan, D. O. *J. Am. Chem. Soc.* 1987, *109*, 4115.
(3) Jones, M. T.; Jansen, S.; Acampora, L. A.; Sandman, D. J. *J. Phys. (Les Ulis, Fr.)* 1983, *44*, C3–1159.

(4) (a) Perlstein, J. H. *Angew. Chem., (Les Ulis, Fr.) Int. Ed. Engl.* 1977, *16*, 519. (b) Perlstein, J. H.; Van Allan, J. A.; Isett, L. C.; Reynolds, G. A. *Ann. N. Y. Acad. Sci.* 1978, *313*, 61. (c) Detty, M. R.; Hassett, J. W.; Murray, B. J.; Reynolds, G. A. *Tetrahedron* 1985, *41*, 4853. (d) Sandman, D. J.; Holmes, T. J.; Warner, D. E. *J. Org. Chem.* 1979, *44*, 880. (e) Chasseau, D.; Gaultier, J.; Hauw, C.; Fugnitto, R.; Gionis, V.; Strzelecka, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1980, *B38*, 1629.
(5) Bock, H.; Brähler, G.; Dauplaise, D.; Meinwald, J. *Chem. Ber.* 1981, *114*, 2622.