7866 J. Am. Chem. Soc. 1993, 115, 7866–7867

Remarkable Reactivity of the Tetrathiotungstate Group in $[NBu_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$

Patricia A. Shapley* and Naijie Zhang

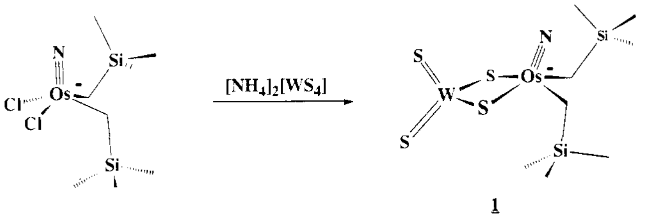
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Received November 12, 1992

The tetrathiomolybdate and tetrathiotungstate anions, MoS_4^{2-} and WS_4^{2-}, coordinate very well to transition metals, and a large number of inorganic complexes have been prepared.[1] Low oxidation state organometallic complexes containing tetrathiometallates and π-acceptor ligands have been synthesized.[2] Most of the research in this area has focused on the synthesis and structure of the complexes, and little is known of their reaction chemistry, but sulfur abstraction by phosphines and conversion of the coordinated tetramethylbutadiene ligand in $[(C_4Me_4)NiCl]_2$-WS_4 to free tetramethylthiophene[3] have been reported. We have prepared the first high oxidation state organometallic complex of tetrathiotungstate and have explored its reactivity.

A variety of oxyanions substitute for the chloride ligands in $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$. Nitridodialkylosmium(VI) complexes of carbonate, sulfate, perrhenate, and chromate have been prepared and characterized.[4] Tetrathiotungstate complexes can also be prepared by this route. The reaction of $[NBu^n_4]$-$[Os(N)(CH_2SiMe_3)_2Cl_2]$ with 1 equiv of $(NH_4)_2WS_4$ in acetonitrile or nitromethane at room temperature produces $[NBu^n_4]$-$[Os(N)(CH_2SiMe_3)_2(WS_4)]$ (Scheme I). The yellow product crystallizes from methylene chloride/hexane in 81% yield. The heterobimetallic complex **1** was characterized by elemental analysis and spectroscopic techniques.[5] The molecular structure of the molecule was determined by X-ray diffraction.[6]

Scheme I



Although both the osmium and the tungsten atoms are coordinately unsaturated, the osmium tetrathiotungstate complex does not react with CO, MeNC, pyridine, PPh_3, H_2O, O_2, S_8, or H_2. The addition of 10 equiv of the basic phosphine, PMe_3, to **1** in tetrahydrofuran gives a red solution containing trimethylphosphine sulfide and a mixture of metal–phosphine complexes (Scheme II). The $S{=}PMe_3$ is presumably formed by abstraction of sulfide from the tetrathiotungstate moiety, but we have been unable to isolate a desulfurized tungsten complex from the reaction mixture. Red crystals of the major product $[NBu^n_4][(PMe_3)_3$-$Os(CH_2SiMe_3)WS_4]$ (**2**) are obtained in 53% yield from toluene/hexane solution.[7] The complex is thermally stable but reactive to air. When 1 or 2 equiv of PMe_3 are added to **1** in dilute solution (CD_2Cl_2 or C_6D_6), NMR spectroscopy shows that $S{=}PMe_3$ is slowly produced along with metal–phosphine complexes but complex **2** is not formed.

Basic phosphines have been reported to reduce certain inorganic osmium nitrido complexes by reacting with the nitrido ligand[8] and to reduce some tetrathiometalate complexes by abstracting the sulfido ligands.[1] The reaction of $[NBu^n_4][Os(N)(CH_2$-$SiMe_3)_2(WS_4)]$ with PMe_3 is unique in that both types of reaction occur. When the nitride ligand reacts first, $[NBu^n_4][(PMe_3)_3$-$Os(CH_2SiMe_3)WS_4]$ is formed. This electron-rich osmium(II) tetrathiotungstate complex is much less reactive toward additional PMe_3 than is **1**. It should be noted that the nitrido ligands in other nitridoosmium(VI) alkyl complexes are not abstracted by phosphines. For example, the reaction between $[NBu_4]$-$[Os(N)(CH_2SiMe_3)_2Cl_2]$ and PMe_3 cleanly produces $Os(N)(CH_2$-$SiMe_3)_2Cl(PMe_3)_2$ and $[NBu_4]Cl$.[9]

Complex **1** does not react with ethylene or with electron-rich olefins but does react rapidly with tetracyanoethylene (TCNE) at room temperature (Scheme II). The addition of 1 equiv of TCNE to a CD_2Cl_2 solution of **1** immediately produces a purple solution containing a single organometallic product (**3**) and dicyanoacetylene.[10] The IR and ^1H NMR spectra of **3** show that the nitridoosmiumdialkyl moiety remains intact, but IR bands for the terminal sulfido ligands are replaced by bands associated with thiocyanate ligands.[11] The organometallic product completely decomposes in solution within 30 min at room temperature. Decomposition is accelerated by concentration of the solution. Our efforts to isolate the product in pure form have been unsuccessful. On the basis of the spectroscopic data, we propose that **3** is $[NBu^n_4][(NCS)_2WS_2Os(N)(CH_2SiMe_3)_2]$.

The reaction of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$ with TCNE is very unusual. Molybdenum sulfide complexes react with cyanide anion to give free or coordinated thiocyanate anion.[12]

---

(1) Müller, A.; Diemann, E.; Joetes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955.

(2) (a) Mizobe, Y.; Hosomizu, M.; Kawabata, J.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1226–1227. (b) Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 4667–4669. (c) Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 1710–1716. (d) Howard, K. E.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 297–299. (e) Adam, G. J. S.; Green, M. L. H. *J. Organomet. Chem.* **1981**, *208*, 299–308. (f) Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 400–401. (g) Rosenheim, L. D.; McDonald, J. W. *Inorg. Chem.* **1987**, *26*, 3414–3416.

(3) Howard, K. E.; Lockemeyer, J. R.; Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R.; Yang, X. *Inorg. Chem.* **1990**, *29*, 4385–4390.

(4) (a) Zhang, N.; Shapley, P. A. *Inorg. Chem.* **1988**, *27*, 976–977. (b) Zhang, N.; Mann, C.; Shapley, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 6591–6592.

(5) IR (KBr pellet, cm^{-1}): 1105 s ($\nu_{OS\equiv N}$); 499 vs, ($\nu_{W=S}$). UV–vis (CH_2Cl_2): $\lambda_{max} = 372$ nm, $\epsilon = 3012$. ^1H NMR (CD_2Cl_2, 300 MHz, 295K): δ 3.17 (d, $J = 10$ Hz, 2H, $OsCH^a$); 3.14 (m, 8H, NCH_2); 2.76 (d, 2 H, $J = 10$ Hz, $OsCH^b$); 1.62 (m, 8H, $NCH_2CH_2CH_2CH_3$); 1.45 (m, 8H, $NCH_2CH_2CH_2CH_3$); 1.02 (t, 12H, $NCH_2CH_2CH_2CH_3$); –0.02 (s, 18H, $OsCH_2SiCH_3$). $^{13}\{^1H\}$NMR (CD_2Cl_2, 50.3 MHz, 295 K): δ 59.40 (NCH_2); 24.34 ($NCH_2CH_2CH_2CH_3$); 20.17 ($NCH_2CH_2CH_2CH_3$); 13.84 ($NCH_2CH_2CH_2CH_3$); 6.88 ($OsCH_2$); 1.29 ($OsCH_2SiCH_3$). Anal. Calcd for $OsWN_2Si_2S_4H_{58}$: C, 30.89; H, 6.26; N, 3.00. Found: C, 30.90; H, 6.27; N, 2.99. MS (FAB): *m/z* $[Os(N)(CH_2SiMe_3)_2(WS_4)]^-$, 692 (100); $[NBu^n_4]^+$, 242 (100).

(6) Shapley, P. A.; Gebeyehu, Z.; Zhang, N.; Wilson, S. R. *Inorg. Chem.*, in press.

(7) ^1H NMR (d_8-THF, 300 MHz, 293 K): δ 3.44 (m, 8H, NCH_2); 2.11 (br s, 2H, $OsCH_2SiMe_3$); 1.55 (m, 16H, $NCH_2CH_2CH_2CH_3$); 1.15 (m, 12H, $NCH_2CH_2CH_2CH_3$); 1.05 (m, 27H, PMe_3); 0.64 (s, 9H, $OsCH_2SiMe_3$). $^{13}C\{^1H\}$ (d_8-THF, 75 MHz, 293 K): δ 59.99 (s, $NCH_2CH_2CH_2CH_3$); 25.27 (s, $NCH_2CH_2CH_2CH_3$); 21.72 (d, PMe_3); 20.80 (s, $NCH_2CH_2CH_2CH_3$); 15.1 (m, $OsCH_2SiMe_3$); 14.36 (s, $NCH_2CH_2CH_2CH_3$); 5.58 (s, $OsCH_2SiMe_3$). $^{31}P\{^1H\}$ (d_8-THF, 121 MHz, 293 K): δ –55.19 (t, $PMe_{3(ax)}$); –55.46 (d, $PMe_{3(eq)}$). IR (KBr, pellet, cm^{-1}): 1477 (s); 1298 (s), 1279 (s); 963 (s), 943 (vs); 854 (vs), 824 (s); 467 (vs), 431 (s) $\nu_{W=S}$. Anal. Calcd for $C_{29}H_{74}NOsP_3SiS_4W$: C, 32.85; H, 7.04; N, 1.32; P, 8.76; Si, 2.65; S, 12.10; W, 17.34. Found: C, 33.40; H, 7.12; N, 1.63; P, 8.04; Si, 2.39; S, 12.29; W, 17.13.

(8) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417–423.

(9) Marshman, R. W. Ph.D. Thesis, University of Illinois, 1990.

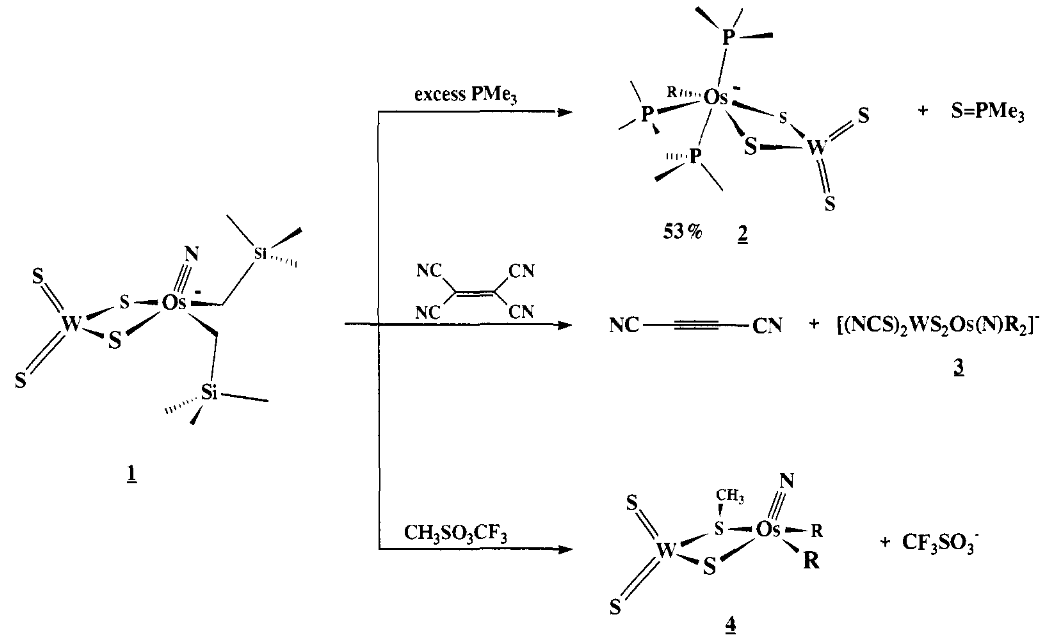
(10) ^1H NMR (CD_2Cl_2, 300 MHz, 293K): δ 3.16 (d, $J = 11$ Hz, 2H, $Os{-}CH^aH$); 3.06 (m, 8H, NCH_2); 2.59 (d, $J = 11$ Hz, 2H, $Os{-}CH^aH^b$); 1.56 (m, 8H, $NCH_2CH_2CH_2CH_3$); 1.41 (m, 8H, $NCH_2CH_2CH_2CH_3$); 1.01 (t, 12H, $NCH_2CH_2CH_2CH_3$); 0.54 (s, $OsCH_2SiMe_3$). MS (EI): *m/z* 76 (12.49), $CNC{\equiv}CCN$. IR (CH_2Cl_2 solution): 2249 (m), ($\nu_{C\equiv N}$); 2215 (m) ($\nu_{C\equiv C}$); 2145 (s) ($\nu_{SC\equiv N}$); 1098 (s) ($\nu_{Os\equiv N}$); 756 (vs), 750 (vs) (ν_{C-S}).

(11) Other S-bonded thiocyanate complexes have C–N and C–S stretching vibrations at similar energies in the IR spectrum. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York, 1970; pp 187–190.

(12) (a) Drew, M. G. B.; Mitchell, P. C. H.; Pygall, C. F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 784–785. (b) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72–73.

0002-7863/93/1515-7866$04.00/0

Scheme II



We are not aware of any previous example of cyanide abstraction from TCNE by a metal sulfide, but the reaction of ferrocene with TCNE gives a mixture of cyanoferrocene and tricyanovinylferrocene at 150 °C.[13] Metal complexes frequently react with TCNE to give charge-transfer complexes, and easily oxidized metal complexes, including the metallocenes and metallocene derivatives, form salts of the TCNE radical anion in polar soltuions.[14] Complex **1**, however, is not easily oxidized. The mechanism of cyanide abstraction from TCNE by **1** is under investigation.

The organic electrophiles $CH_3SO_3CF_3$, CH_3I, or Me_3OBF_4 alkylate one of the sulfur atoms of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2(WS_4)]$. The reaction between **1** and 1 equiv of $CH_3SO_3CF_3$ in methylene chloride produces $[NBu^n_4][SO_3CF_3]$ and a yellow, hexane-soluble oil, $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)(\mu\text{-}SCH_3)WS_2]$ (Scheme II).[15] The ^1H and ^{13}C NMR spectra of **4** show inequivalent alkyl groups, indicating that alkylation must occur at a bridging rather than a terminal sulfide. The osmium tetrathiotungstate complex can be protonated with $HBF_4 \cdot Et_2O$ to give a product that is very similar to $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)(\mu\text{-}SCH_3)WS_2]$ by ^1H NMR. The protonated material is thermally unstable.

The osmium(VI) tetrathiotungstate complex **1** is unusually reactive. The terminal nitrido ligand can be abstracted by PMe_3 to give an osmium(II) tetrathiotungstate complex. The terminal sulfido ligands also react with this basic phosphine to give $S{=}PMe_3$ and a mixture of metal–phosphine complexes. Upon reaction with tetracyanoethylene, the terminal sulfido ligands are converted to thiocyanate groups. The bridging sulfur atoms are electron rich and susceptible to electrophilic attack by organic electrophiles and protic acids.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (CHE 88-07707) in support of this work. Spectra were obtained on NMR instruments purchased through grants from the NIH and the NSF (NIH PHS 1532135, NIH 1531957, and NSF CHE 85-14500). P.A.S. gratefully acknowledges financial support from an Aldred P. Sloan Foundation Fellowship.

---

(13) Nefedov, V. A.; Bespalov, B. P.; Titov, V. V. *Zh. Org. Khim.* **1974**, *10*, 1553.

(14) Tumanov, A. A.; Zakharov, L. N.; Sennikov, P. G.; Egorochkin, A. N.; Razuvaev, G. A.; Smirnov, A. S.; Dodonov, V. A. *J. Organomet. Chem.* **1984**, *263*, 213–224.

(15) ^1H NMR (200 MHz, CD_2Cl_2, 293 K): δ 4.89 (s, SCH_3); 3.45, (d, $OsCH^aH^b$); 2.88, (d, $OsCH^aH^b$); 2.59, (d, $OsCH^cH^d$); 2.05, (d, $OsCH^cH^d$); 0.05, (s, $OsCH_2SiMe_3$); 0.04, (s, $OsCH_2SiMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 293 K): δ 35.88 (SCH_3); 10.88 ($OsCH_2$); 10.78 ($OsCH_2$); 0.90 ($OsCH_2SiMe_3$); 0.82 ($OsCH_2SiMe_3$). IR (CH_2Cl_2 solution): 1100 (s) ($\nu_{Os\equiv N}$); 468, 453 (s) ($\nu_{W=S}$).