value observed for **2** is, in fact, typical of aminoboranes in which only one nitrogen is oriented properly for π-bonding to boron[13] {e.g., [bis(trimethylsilyl)amino]boranes, Figure 2B}. The ΔG^{*} values indicate a substantial degree of (p–p)π interaction in the B–NMe_2 bond(s) and show that the ground-state configurations of **2** and **4** in solution are probably the same as the structure that is adopted in the solid state of **4**. The B–NMe_2 rotational barrier of **4** is significantly lower than that of **2**, indicative of a lowering of the B–N π bond order due to competition of two nitrogen electron pairs for the empty p orbital of boron.[13]

More detailed studies of the preparative chemistry, molecular structures, and thermal condensation reactions of the *N*-boryl derivatives of the 1,3,2-diazaboracycloalkane ring systems are currently in progress.

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Supplementary Material Available: Tables of atomic positional parameters and U_{eq} values, hydrogen atom positions and isotropic U values, anisotropic thermal parameters, interatomic distances, and valence angles (4 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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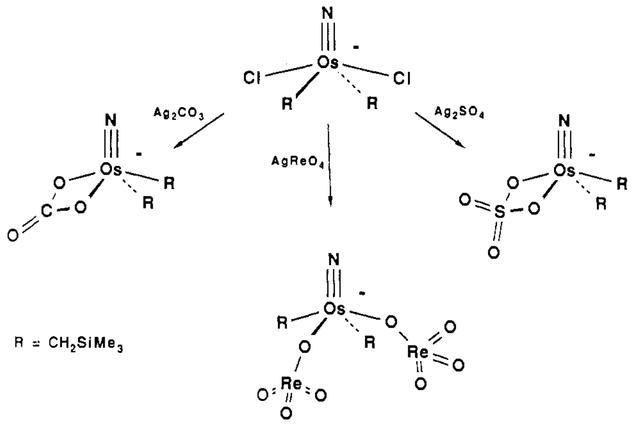
Halide Substitution Reactions of *trans*-$[Os(N)(CH_2SiMe_3)_2Cl_2]^-$. Synthesis of Carbonate, Sulfate, and Perrhenate Complexes of Osmium(VI)

Sir:

Complexes of ruthenium and osmium(VI) have been studied recently as oxidation reagents or catalysts.[1-3] Certain transition-metal oxyanions, MnO_4^-, for example, are strong oxidants toward both organic and inorganic molecules.[4] Coordination of oxyanions to coordinatively unsaturated osmium(VI) or ruthenium(VI) centers could lead to the development of new, bimetallic oxidation catalysts. Transition-metal complexes of the sulfate, carbonate, and perrhenate oxyanions are well-known in inorganic chemistry. Coordination compounds containing monodentate, bidentate, and tridentate sulfate and carbonate groups have been characterized.[5] An osmium cluster complex containing a tridentate sulfate ligand has been reported.[6] Although organometallic complexes of these ligands are rare, (pentamethylcyclopentadienyl)rhenium(V) complexes with bidentate sulfate and carbonate, $(C_5Me_5)Re(O)(CO_3)$ and $(C_5Me_5)Re(O)(SO_4)$, have recently been reported.[7] A copper complex of perrhenate and several rhenium complexes of perrhenate have been prepared and structurally characterized.[8-11]

Scheme I



Tetra-*n*-butylammonium or tetraphenylphosphonium salts of the coordinatively unsaturated nitridooxmium(VI) and nitridoruthenium(VI) dialkyl dichloride complexes, $[M(N)R_2Cl_2]^-$ (M = Ru, Os; R = Me, CH_2SiMe_3), have been prepared by reaction of $[M(N)R_4]^-$ with HCl.[12,13] Substitution of the halides in $[M(N)R_2Cl_2]^-$ for other anionic ligands provides a route to a wide variety of high-oxidation-state organometallic complexes. The preparation of osmium(IV) complexes containing sulfur donor ligands has recently been reported.[14] Thiols, such as 1,2-ethanedithiol, readily displace halides at osmium to form thiolato complexes in which the thiolato ligands are strong σ donors to the metal. Surprisingly, the oxygen analogue, ethylene glycol, does not react under the same conditions.

We were interested in the preparation of nitridoosmium dialkyl complexes with oxygen-containing ligands for two reasons. We wanted to see how they affect the electron density at the metal center and the π-bonding interaction between the nitrogen and the osmium or ruthenium centers. We were also interested in organometallic osmium and ruthenium complexes with oxygen-containing ligands in connection with our goal of preparing high-oxidation-state heterobimetallic oxidation catalysts. There should be similarities in the structures of the complexes and properties of the M–O bond between osmium complexes of the tetrahedral sulfate and chromate dianions and between complexes of the tetrahedral perrhenate and permanganate monoanions. Sulfate and perrhenate are much less oxidizing than chromate and permanganate, so complexes of these should be more stable and easier to study.

The reaction of *trans*-$[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with silver sulfate in methylene chloride produced *cis*-$[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2(SO_4)]$ (**1**) and precipitates of silver chloride. In a typical preparation, a solution of *trans*-$[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.090 g, 0.13 mmol) in 5mL of CH_2Cl_2 was added dropwise at room temperature to a suspension of Ag_2SO_4 (0.08 g, 0.26 mmol) in 50 mL of CH_2Cl_2. After the mixture was stirred for 12 h in the light (fluorescent lamp), AgCl was removed by filtration. The solvent was removed from the filtrate under vacuum, and the residue was crystallized from hexane/diethyl ether at −30 °C. Yellow crystals of **1** (0.089 g, 97%) were collected.[15] A similar reaction between *trans*-$[N\text{-}n\text{-}Bu_4][Os(N)\text{-}$

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(15) IR (KBr pellet, cm^{-1}): Os≡N obscured; 1119 vs, br (S=O). ^1H NMR (C_6D_6, 200 MHz, 293 K): δ 3.62 (d, 1 H, $OsCH^a$), 2.83 (m, 4 H, NCH_2), 2.42 (d, 1 H, $OsCH^b$), 1.30 (m, 8 H, $NCH_2CH_2CH_2CH_3$), 0.96 (t, 6 H, $NCH_2CH_2CH_2CH_3$), 0.41 (s, 9 H, $OsCH_2Si(CH_3)_3$. $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz, 295 K): δ 58.5 (NCH_2), 23.9 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$), 8.7 ($OsCH_2Si(CH_3)_3$), 0.6 ($OsCH_2Si(CH_3)_3$). Anal. Calcd for $OsSN_2Si_2O_4C_{24}H_{58}$: C, 40.19; H, 8.09; N, 3.90. Found: C, 40.38; H, 8.04; N, 3.70. MS: anion, *m/z* 476, 18%; cation, *m/z* 242, 100%.

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$(CH_2SiMe_3)_2Cl_2]$ and silver carbonate in methylene chloride produced *cis*-[N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_2(CO_3)$] (**2**). The crude product was crystallized from hexane/CH_2Cl_2 at −30 °C. Yellow crystals of **2** were collected in 82% yield.[16] Lower yields of these products were obtained when K_2SO_4 and K_2CO_3 were used in place of the silver salts.

The osmium perrhenate complex *cis*-[N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_2(ReO_4)_2$] (**3**) was prepared similarly from *trans*-[N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_2Cl_2$] and $AgReO_4$. In a typical preparation, a solution of *trans*-[N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_2Cl_2$] (0.05 g, 0.072 mmol) in 10 mL of THF was added dropwise at −78 °C to a suspension of $AgReO_4$ (0.050 g, 0.14 mmol) in 50 mL of THF. The solution was warmed to room temperature with stirring and was stirred overnight. The reaction was illuminated by a fluorescent lamp during this time. Solvent was removed under vacuum, and the residue was crystallized from hexane/CH_2Cl_2 at −30 °C. Red crystals of **3** (0.070 g, 82%) were collected.[17] One other osmium perrhenate complex was recently reported.[18]

The sulfate, carbonate, and perrhenate complexes of osmium are all thermally stable and stable to air and water. Similar sulfate and perrhenate complexes of ruthenium(VI) have been prepared from [PPh_4][$Ru(N)Me_2Cl_2$] and [N-*n*-Bu_4][$Ru(N)(CH_2SiMe_3)_2Cl_2$].[19]

All five-coordinate nitridoosmium(VI) complexes that have been structurally characterized have a square-pyramidal structure with apical nitrido group.[20,21] Spectroscopic data for complexes **1–3** are similar to those of other five-coordinate nitridoosmium(VI) alkyl complexes.[12,14] The NMR spectra of the diamagnetic complexes $[Os(N)(CH_2SiMe_3)_2Y]^-$ ($Y = SO_4, CO_3$) indicate a cis configuration of the alkyl groups. The alkyl groups are equivalent in the ^{13}C NMR spectra. In the ^1H NMR spectra, we observe a pair of doublets for the diastereotopic methylene protons in each complex. The ^1H–^1H coupling of the methylene protons cannot be resolved in $[Os(N)(CH_2SiMe_3)_2(ReO_4)_2]^-$. Broadening of these resonances may be due to unresolved coupling with the rhenium nuclei.

The energy of the osmium–nitrido stretching vibration in the IR spectrum is a good indication of the σ-donor ability of the other ligands at the osmium center. Strong σ-donor ligands, such as alkyls, make the metal center more electron rich and weaken the osmium–nitrogen triple bond. We have found the following ordering of the ν_{Os-N} band:[22]

$$\begin{aligned}&[Os(N)Cl_4]^-\ (1127\ cm^{-1}) > [Os(N)Ph_4]^-\ (1123\ cm^{-1}) >\\ &\quad [Os(N)(OSiMe_3)_4]^-\ (1118\ cm^{-1}) >\\ &\quad\quad [Os(N)L_2(CH_2SiMe_3)_2]^-,\ L =\\ &\quad\quad\quad CH_2SiMe_3,\ OSiMe_3,\ Cl\ (\sim 1107\ cm^{-1})\end{aligned}$$

Unlike that in the other complexes $[Os(N)L_2(CH_2SiMe_3)_2]^-$, the osmium–nitrogen stretch in **1–3** is at high energy (1119–1125 cm^{-1}), indicating that the sulfate, carbonate, and perrhenate groups are quite electron withdrawing. We see only one intense, broad band for each of the oxyanion ligands in **1–3**. Other bands may be obscured under bands associated with the alkyl groups on the metal and in the counterion.[23]

In conclusion, silver salts of a variety of oxyanions displace chloride from [N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_2Cl_2$] to form stable complexes. Work is now under way in our laboratory on the synthesis of organometallic osmium and ruthenium complexes of other transition-metal oxyanions.

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(16) IR (KBr pellet, cm^{-1}): 1120 s ($Os{\equiv}N$), 1703 vs, br ($C{=}O$). ^1H NMR (C_6D_6, 200 MHz, 294 K): δ 3.45 (d, 1 H, $OsC\mathit{H}^a$), 2.81 (m, 4 H, $NC\mathit{H}_2$), 2.19 (d, 1 H, $OsC\mathit{H}^b$), 1.28 (m, 8 H, $NCH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.93 (t, 6 H, $NCH_2CH_2CH_2C\mathit{H}_3$), 0.49 (s, 9 H, $OsCH_2Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz, 293 K): δ 196.3 ($\mathit{C}{=}O$), 59.1 ($N\mathit{C}H_2$), 24.5 ($NCH_2\mathit{C}H_2CH_2CH_3$), 20.5 ($NCH_2CH_2\mathit{C}H_2CH_3$), 14.5 ($NCH_2CH_2CH_2\mathit{C}H_3$), 2.9 ($Os\mathit{C}H_2Si(CH_3)_3$, 1.5 ($OsCH_2Si(\mathit{C}H_3)_3$). Anal. Calcd for $OsN_2Si_2O_3C_{25}H_{58}$: C, 44.07; H, 8.52; N, 4.11. Found: C, 43.68; H, 8.41; N, 4.11.

(17) IR (KBr pellet, Cm^{-1}): 1125 s ($Os{\equiv}N$), 914 vs, br ($Re{=}O$). ^1H NMR (CD_2Cl_2, 200 MHz, 293 K): δ 4.09 (s, 2 H, $OsC\mathit{H}^aH^bSiMe_3$), 3.12 (m, 8 H, $NC\mathit{H}_2$), 2.49 (s, 2 H, $OsCH^a\mathit{H}^bSiMe_3$), 1.62 (m, 8 H, $NCH_2C\mathit{H}_2CH_2CH_2CH_3$), 1.41 (m, 8 H, $NCH_2CH_2C\mathit{H}_2CH_3$), 1.01 (t, 12 H, $NCH_2CH_2CH_2C\mathit{H}_3$), 0.04 (s, 18 H, $OsCH_2Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.3 MHz, 294 K): δ 59.25 ($N\mathit{C}H_2$), 24.16 ($NCH_2\mathit{C}H_2CH_2CH_3$), 20.08 ($NCH_2CH_2\mathit{C}H_2CH_3$), 13.74 ($NCH_2CH_2CH_2\mathit{C}H_3$), 0.12 ($OsCH_2Si(\mathit{C}H_3)_3$). Anal. Calcd for $OsReN_2Si_2O_4C_{24}H_{58}$: C, 25.69; H, 5.17; N, 2.49; Os, 17.01. Found: C, 25.76; H, 5.29; N, 2.48; Os, 17.50. MS: $[Os(N)(CH_2SiMe_3)_2(ReO_4)_2]^-$, *m/z* 878, 8%; [N-*n*-$Bu_4$], *m/z* 242, 100%.

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