

Synthesis of a Series of Nitridoosmium(VI) Alkyl Complexes

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Abstract: $[\text{NOsCl}_4][\text{NBu}_4]$ and $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ are useful starting materials for the synthesis of a series of nitridoosmium(6+) alkyl complexes. $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ can be prepared from $[\text{NOsCl}_4][\text{NBu}_4]$ by reaction with $\text{Na}(\text{OSiMe}_3)$. Alkylation with MgR_2 , AlR_3 , or XMgR gives very high yields of yellow, crystalline products $[\text{NOsR}_x\text{Cl}_{4-x}][\text{NBu}_4]$ ($\text{R} = \text{CH}_2\text{SiMe}_3$, $x = 2, 4$; $\text{R} = \text{CH}_2\text{CMe}_3$, CH_2Ph , and Me , $x = 4$) or NOsR_3L_2 ($\text{R} = \text{Me}$, $\text{L} = \text{THF}$ or $1/2\text{TMEDA}$). $\text{NOsCl}_3(\text{TMEDA})$ is formed by treatment of $[\text{NOsCl}_4][\text{NBu}_4]$ with TMEDA, but this is not alkylated cleanly. Only the trans isomer of $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$ is formed by the partial alkylation of $[\text{NOsCl}_4][\text{NBu}_4]$, but the cis isomer is the exclusive product of the reaction of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ with 2 equiv of $\text{HCl}(\text{g})$.

Reactions of high oxidation state, early transition-metal alkyl complexes have provided mechanistic information on catalytic Ziegler-Natta polymerization of olefins and olefin metathesis.¹ High oxidation state group 8B metal complexes are also active in catalysis of certain hydrocarbon transformations. Sharpless has proposed an osmium(VIII) alkyl complex to be an intermediate in the oxidation of olefins by OsO_4 ,² and such an intermediate may have been observed spectroscopically.³ No d^0 osmium alkyl complexes have yet been isolated, so the factors that influence the very specific decomposition of this key intermediate remain unexplored.

Prior to this work, there was only one reported organoosmium(VI) complex. Wilkinson et al. prepared oxotetrakis(trimethylsilylmethyl)osmium(VI) in low yield by the interaction of the dialkylmagnesium with osmium tetroxide at low temperature.⁴ The alkyl complex, once formed, was thermally stable.

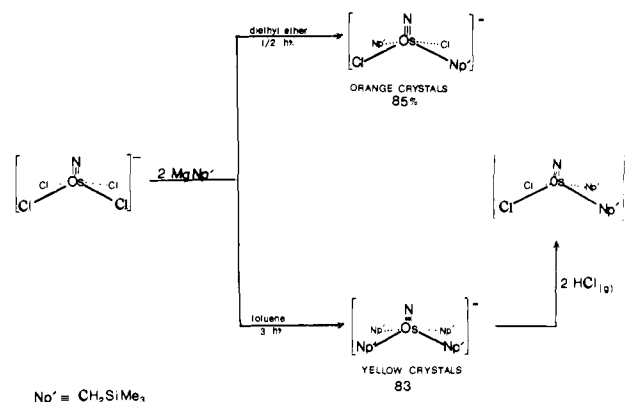
We set out to prepare a series of osmium(VI) alkyl complexes in order to study the reaction chemistry of these complexes and to oxidize them to prepare the corresponding alkylosmium(VIII) complexes.

Since the desired product would be in the +6 oxidation state, it seemed desirable to start with an osmium(VI) halide and alkylate the metal in controlled fashion. Griffith and Pauson described the synthesis of an especially convenient starting material, $[\text{NOsCl}_4][\text{NBu}_4]$.⁵ This compound can be prepared in 95% yield from osmium tetroxide. It is air stable and soluble in polar organic solvents. We have used this nitridoosmium(VI) complex to prepare a series of nitridoosmium(VI) alkyl complexes in very high yield. The ready availability of these compounds will allow the reaction chemistry of high oxidation state organoosmium compounds to be thoroughly studied.

Results and Discussion

Direct Alkylation of $[\text{NOsCl}_4][\text{NBu}_4]$. $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ reacts with a suspension of $[\text{NOsCl}_4][\text{NBu}_4]$ in toluene. As the pink osmium salt disappears, the solution becomes yellow. Yellow needles of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ can be crystallized from

Scheme I



the solution in excellent yield (usually 85%). None of this compound is formed when the reaction is carried out in tetrahydrofuran (THF) solution.

The ^1H NMR spectrum of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ shows all four alkyl ligands to be equivalent, which is consistent with a square-based pyramidal geometry. An X-ray crystal structure determination has shown that $[\text{NOsCl}_4][\text{AsPh}_4]$ has this geometry.⁶

An intermediate, partially alkylated compound, *trans*- $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$, can be isolated when the reaction is carried out in diethyl ether, and the reaction time is reduced from 3 to 0.5 h. Yield of this compound is also excellent, 83% after recrystallization. A singlet is seen in the ^1H NMR spectrum at 3.01 ppm for the equivalent methylene protons. Traces of the cis dialkyl complex can be observed in the NMR spectrum (0–5%). The inequivalent methylene protons are found as doublets at 3.92 and 3.41 ppm. Presumably, “ $\text{NOsCl}_3(\text{CH}_2\text{SiMe}_3)^-$ ” is the initial product. Either the greater *trans*-labilizing effect of an alkyl group over a chloride⁷ or stabilization due to a less sterically demanding transition state causes the chloride *trans* to the first alkyl ligand to be preferentially replaced.

The cis isomer can be specifically prepared by reacting $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ with 2 equiv of $\text{HCl}(\text{g})$ in toluene. Two equivalents of tetramethylsilane are also produced. If $\text{NOsCl}(\text{CH}_2\text{SiMe}_3)_3$ is formed initially, the alkyl group *trans* to another alkyl would have a greater partial negative charge than an alkyl *trans* to the electronegative chloride. Electrophilic attack by H^+ on the most electron-rich alkyl would give the observed product (Scheme I and Figure 1).

In a similar reaction, a suspension of $[\text{NOsCl}_4][\text{NBu}_4]$ in toluene reacts with $\text{Mg}(\text{CH}_2\text{Ph})_2$ at room temperature to produce an osmium-benzyl complex, $[\text{NOs}(\text{CH}_2\text{Ph})_4][\text{NBu}_4]$. Yellow

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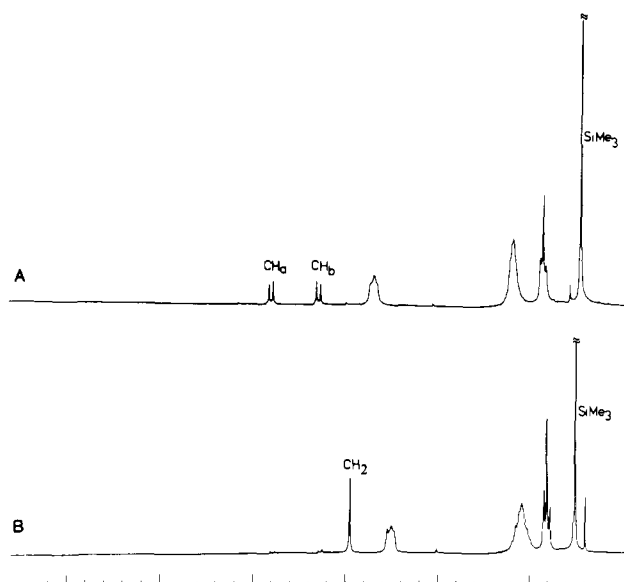


Figure 1. 200-MHz ^1H NMR spectra in C_2D_6 : (A) *cis*- $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$; (B) *trans*- $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$.

crystals of the product can be obtained in 44% yield by cooling and concentrating the toluene solution. Once formed, the crystals are no longer soluble in toluene or benzene.

The remaining osmium-containing material is a rather insoluble brown oil. This material has not yet been identified but has a very broad ^1H NMR spectrum and probably contains reduced osmium compounds. Electron transfer can compete with alkylation when using main-group alkyls to replace halide for alkyls on transition-metal compounds.^{4,8}

Alkylation of $[\text{NOsCl}_4][\text{NBu}_4]$ with $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ -dioxane produces the tetraepentylnitridoosmium(VI) anion in poor yield, 19% after recrystallization. Alkylations with $\text{Li}(\text{CH}_2\text{CMe}_3)$, AlMe_3 , AlEt_3 , ZnMe_2 , and $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ give very poor yields of the corresponding alkyl complexes $[\text{NOsR}_4][\text{NBu}_4]$.

Alkylation of $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$. Replacement of alkoxide ligands on transition metals with MgR_2 frequently proceeds more cleanly than replacement of chloride ligands. Because of problems we encountered in the direct alkylation of NOsCl_4^- with certain alkylating agents, we decided to prepare an osmium alkoxide complex as a more general precursor to osmium(VI) alkyl complexes.

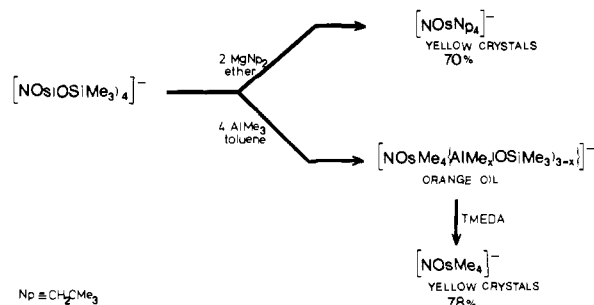
Many group 8 transition-metal alkoxides are unstable, however, decomposing by transfer of a hydride from the β atom to the metal. This leads to reduction of the metal and formation of an aldehyde or ketone. Use of the trimethylsiloxy ligand eliminates this decomposition mode.

Four equivalents of sodium siloxide, prepared by the hydrolysis of Me_3SiCl followed by treatment with sodium metal, react with a tetrahydrofuran solution of $[\text{NOsCl}_4][\text{NBu}_4]$ to form $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ in up to 90% yield. The siloxy complex is quite soluble in ethers and aromatic hydrocarbons but can be crystallized from toluene/pentane solutions at low temperature.

$[\text{NOs}(\text{CH}_2\text{CMe}_3)_4][\text{NBu}_4]$ can be obtained by reaction of $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ with $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ -dioxane at low temperature in diethyl ether. The reaction mixture is homogeneous and yellow-brown. Yellow crystals of the product are formed in 70% yield from concentrated ether solutions or from toluene/pentane solutions. The complexes $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ and $[\text{NOs}(\text{CH}_2\text{Ph})_4][\text{NBu}_4]$ can be prepared under the same conditions from $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ and the appropriate dialkylmagnesium reagent. Yields of recrystallized products are 70–80%.

$[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ is alkylated by 4 equiv of trimethylaluminum in toluene. The product, an orange oil, appears

Scheme II



to be an alkylaluminum adduct of the nitridotetramethyl-osmium(VI) anion. When a large excess of AlMe_3 is used in the reaction, an orange, crystalline product can be isolated. From its ^1H NMR spectrum, this material appears to be $[\text{NOsMe}_4\text{AlMe}_2][\text{NBu}_4]$ along with a small amount of $[\text{NOsMe}_4][\text{NBu}_4]$. The structure of the trimethylaluminum adduct is not known. AlMe_3 , a Lewis acid, could coordinate to the nitrido group, or it could bind to the osmium complex through a bridging methyl group.⁹ The nitridotetramethyl-osmium(VI) anion $[\text{NOsMe}_4][\text{NBu}_4]$ is cleanly formed by adding tetramethylethylenediamine (TMEDA) or tetrahydrofuran to the aluminum adduct. The product crystallizes from toluene/pentane solution as yellow needles in 78% overall yield (from $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$) (Scheme II).

Reactions of $[\text{NOsR}_x\text{Cl}_{4-x}][\text{NBu}_4]$. All of the complexes $[\text{NOsR}_x\text{Cl}_{4-x}][\text{NBu}_4]$ ($\text{R} = \text{Me}$, CH_2Ph , and CH_2CMe_3 , $x = 4$; $\text{R} = \text{CH}_2\text{SiMe}_3$, $x = 2, 4$) are yellow or orange crystalline solids. As solids, they are stable in air but solutions are air sensitive. In the absence of air, the alkyl compounds can be heated to over 100 $^\circ\text{C}$ without decomposition.

Even though these compounds are coordinatively unsaturated, they are remarkably unreactive. $[\text{NOs}(\text{CH}_2\text{CMe}_3)_4][\text{NBu}_4]$, for example, does not react with $\text{CO}(\text{g})$ or $\text{H}_2(\text{g})$ at 30–40 psi pressure. Neither does it react with the phosphines PMe_3 , PBu_3 , or PPh_3 . The phosphine reactions were run in sealed NMR tubes. No change was observed spectroscopically even after several days at 90 $^\circ\text{C}$. It should be noted that $[\text{NOsCl}_4][\text{NBu}_4]$ does react with phosphines to give phosphine imidato complexes of osmium(IV), $[\text{Os}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$.¹⁰

Alkyl ligands on the metal must make the metal more electron rich, lessening the amount of π electron donation from the nitrido group to osmium and so making the nitride less susceptible to nucleophilic attack. This correlates with changes in the IR spectrum upon alkylation. The osmium–nitrogen stretching mode decreases from 1125 cm^{-1} in NOsCl_4^- to approximately 1100 cm^{-1} in the spectra of the alkylated complexes.

$[\text{NOsCl}_4][\text{NBu}_4]$ has been reported to form $\text{NOsCl}_3(\text{bpy})$ upon reaction with bipyridine.¹⁰ We prepared an analogous TMEDA complex by the addition of tetramethylethylenediamine to solutions of $[\text{NOsCl}_4][\text{NBu}_4]$ in tetrahydrofuran or acetonitrile. This violet, crystalline TMEDA adduct is composed of two isomers of $\text{NOsCl}_3(\text{TMEDA})$, meridional and facial, in a ratio of 2.7:1. The Os–N stretching mode in the IR spectrum is reduced to 1080 cm^{-1} upon coordination of the sixth ligand trans to the nitride. The dialkyl complex $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$ does not react with TMEDA.

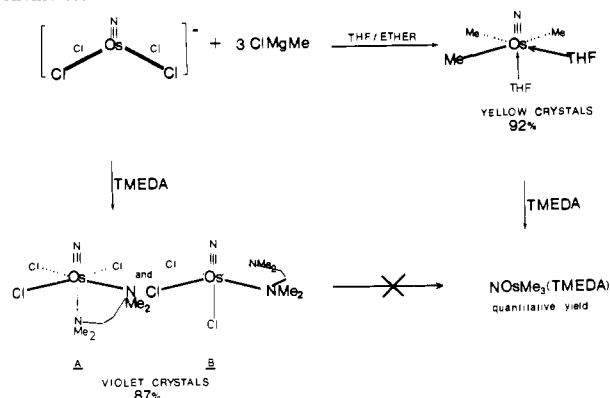
$\text{NOsMe}_3(\text{THF})_2$. When 3 equiv of methyl Grignard reagent are added to a tetrahydrofuran solution of $[\text{NOsCl}_4][\text{NBu}_4]$ at low temperature, a white precipitate forms (which is probably $[\text{MgCl}_3][\text{NBu}_4]$ and MgCl_2). Yellow $\text{NOsMe}_3(\text{THF})_2$ can be crystallized from the supernatant in nearly quantitative yield. The three methyl groups are equivalent in the ^1H NMR spectrum. This probably results from a fluxional process involving loss of

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Scheme III



coordinated tetrahydrofuran since the complexed THF is observed to exchange rapidly with free THF in solution (Scheme III).

The neutral nitridotrimethylsmium complex is quite stable in coordinating solvents but decomposes rapidly in toluene or benzene in the absence of excess tetrahydrofuran.

Coordinated tetrahydrofuran can be replaced by other donor molecules. Upon addition of tetramethylethylenediamine to a solution of $\text{NOsMe}_3(\text{THF})_2$, $\text{NOsMe}_3(\text{TMEDA})$ crystallizes out in quantitative yield. The bidentate amine ligand is not labile.

Conclusions

A series of five-coordinate and six-coordinate nitridoosmium(VI) alkyl complexes has been prepared in excellent yield. All of these complexes are yellow or orange crystalline solids, and all are thermally stable in the absence of air. These complexes have been characterized by elemental analysis, IR spectra, and ^1H (and in some cases ^{13}C) NMR spectra. The metal-carbon bonds in $[\text{NOsR}_4][\text{NBu}_4]$ can be cleaved by acid but not by $\text{H}_2(\text{g})$. Donor molecules, such as carbon monoxide and trialkylphosphines, do not add to the 16-electron complexes $[\text{NOsR}_4][\text{NBu}_4]$. $\text{NOsMe}_3(\text{THF})_2$ is much more reactive since the coordinated tetrahydrofuran ligands are readily lost, leaving a 14-electron species, NOsMe_3 .

Additional reactions of NOsR_3L_2 and chemical and electrochemical oxidations of $[\text{NOsR}_x\text{Cl}_{4-x}][\text{NBu}_4]$ are currently being investigated.

Experimental Section

All operations, except where otherwise specified, were performed under dinitrogen either by Schlenk techniques or in a Vacuum Atmospheres drybox. A procedure published by Griffith was used to prepare $[\text{NOsCl}_4][\text{NBu}_4]$.⁵

Pentane, diethyl ether, tetrahydrofuran, toluene, and benzene were distilled from sodium benzophenone ketyl under dinitrogen. Reagent grade acetonitrile and chloroform were distilled from calcium hydride. Deuterated NMR solvents were used without further purification. Pyridine and tetramethylethylenediamine (TMEDA) were distilled under dinitrogen and stored over 4-Å molecular sieves. All other solvents and reagents were purchased reagent grade and used without further purification.

NMR data are listed in parts per million downfield from Me_4Si . NMR spectra were recorded on a Bruker WP80 FT NMR spectrometer or on a Bruker WP-200SY FT NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 521 infrared spectrophotometer.

Preparation of NaOSiMe_3 . To a flame-dried, 500-mL, two-necked flask equipped with stir bar, N_2 inlet, and addition funnel was added 10.86 g (100 mmol) of Me_3SiCl in 100 mL of diethyl ether. The solution was cooled to 0 °C under dinitrogen. A solution of water (1.8 g, 100 mmol) and pyridine (7.91 g, 100 mmol) in 150 mL of diethyl ether was added to the Me_3SiCl solution, dropwise, with magnetic stirring. Pyridinium chloride precipitated. The mixture was warmed to room temperature and filtered. Sodium (2.09 g, 91 mmol) was added to the filtrate. After being stirred for 12 h, the mixture was filtered. Solvent was removed in vacuo. The residue was crystallized from ether/pentane at -30 °C: yield 6.28 g (56%) white, crystalline solid; ^1H NMR (C_6D_6 , 80 MHz) 0.5 ppm (s).

Preparation of $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$. $[\text{NOsCl}_4][\text{NBu}_4]$ (0.31 g, 0.527 mmol) was dissolved in 5 mL of thf and the solution filtered into a 25-mL flask equipped with magnetic stirrer. NaOSiMe_3 (0.24 g, 2.10

mmol) was dissolved in a few milliliters ether and added to the thf solution with stirring. The color of the solution changed from purple to rose. The volume was doubled with pentane. The solution was filtered and the filtrate cooled. Rose colored crystals (0.36 g, 85%) were collected by filtration: ^1H NMR (C_6D_6 , 200 MHz, 297 K) 0.65 ppm (s, 9 H, SiMe_3), 2.36 (m, 2 H, NCH_2), 1.0 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.83 (t, 3 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); IR (Nujol mull) $\nu_{\text{Os-N}}$ 1120 cm^{-1} . Anal. Calcd for $\text{OsN}_2\text{O}_4\text{Si}_4\text{C}_{28}\text{H}_{72}$: C, 41.85; H, 9.03; N, 3.49. Found: C, 41.28; H, 8.96; N, 3.51.

Preparation of $\text{NOsCl}_3(\text{TMEDA})$. $[\text{NOsCl}_4][\text{NBr}_4]$ (0.588 g, 1 mmol) was dissolved in 5 mL of acetonitrile. Excess TMEDA (0.50 ml) was added. The color of the solution changed immediately from purple to violet. The volume of the solution was doubled with diethyl ether. Cooling resulted in the formation of violet crystals, 0.43 g. The product was recrystallized from THF/ether: yield 0.374 g, (87%); IR (Nujol mull) $\nu_{\text{Os-N}}$ 1080 cm^{-1} ; ^1H NMR (CD_3CN , 200 MHz, 297 K) meridional isomer, 3.639 (s, 3 H, NMe), 3.638 (s, 3 H, NMe), 3.062 (s, 3 H, NMe), 3.060 (s, 3 H, NMe), 3.681 ppm (q, 4 H, NH_2), facial isomer, 3.732 (s, 6 H, NMe), 2.240 (s, 6 H, NMe), 3.309 ppm (m, 2 H, NH_2). Anal. Calcd for $\text{OsN}_3\text{Cl}_3\text{C}_6\text{H}_{16}$: C, 16.89; H, 3.78; N, 9.89. Found: C, 16.02; H, 3.40; N, 8.96.

Preparation of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2][\text{NBu}_4]$. $[\text{NOsCl}_4][\text{NBr}_4]$ (0.050 g, 0.085 mmol) was added to a 100-mL flask along with 30 mL of diethyl ether and a stir bar. A solution of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (0.050 g, 0.18 mmol) in 5 mL of diethyl ether was added to the stirred suspension of $[\text{NOsCl}_4]^-$ all at once. After 30 min at room temperature, no starting material remained. The orange solution was filtered. Pentane was added, and the solution was cooled to -30 °C. Orange crystals of $[\text{NOsCl}_2(\text{CH}_2\text{SiMe}_3)_2][\text{NBu}_4]$ (0.050 g, 85%) were collected by filtration: mp 85 °C dec; IR (KBr) $\nu_{\text{Os-N}}$ 1105 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz, 297 K) 3.01 (s, 2 H, H_2Si), 2.63 (m, 4 H, NCH_2), 1.22 (m, 8 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.93 (t, 6 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.60 ppm (s, 9 H, SiMe_3). Anal. Calcd for $\text{OsN}_2\text{Cl}_2\text{Si}_2\text{C}_{24}\text{H}_{58}$: C, 41.66; H, 8.35; N, 4.01. Found: C, 41.34; H, 8.37; N, 4.09.

Preparation of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$. $[\text{NOsCl}_4][\text{NBr}_4]$ (0.050 g, 0.085 mmol) was suspended in 30 mL of toluene in a 100-mL flask with a magnetic stir bar. Solid $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (0.050 g, 0.18 mmol) was added all at once. The mixture was stirred for 3 h at 25 °C and then filtered. Heptane was added to the golden yellow filtrate. After the solution was cooled to -30 °C, 0.056 g (83%) of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ was collected as yellow crystals: mp 120 °C dec; IR (Nujol mull) $\nu_{\text{Os-N}}$ 1100 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz, 297 K) 2.25 (m, 2 H, NH_2), 2.01 (s, 2 H, CH_2Si), 1.00 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.88 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.73 (t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.56 ppm (s, 9 H, SiMe_3); ^{13}C NMR (C_6D_6) 58.55 (t, NCH_2), 23.78 (t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.71 (t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.62 (q, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 10.85 (t, CH_2Si), 3.92 ppm (q, SiMe_3). Anal. Calcd for $\text{OsN}_2\text{Si}_4\text{C}_{32}\text{H}_{80}$: C, 48.31; H, 10.14; N, 3.52. Found: C, 48.29; H, 10.23; N, 3.61.

Reaction of $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ with HCl. $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ (0.020 g, 0.025 mmol) was dissolved in 10 mL of toluene containing 7.3 μL of heptane (0.050 mmol) as an internal standard. The solution was cooled to -78 °C, and, with magnetic stirring, 5 mL of $\text{HCl}(\text{g})$ (0.22 mmol) was added to syringe. The mixture was warmed to 0 °C and stirred for 1 h, during which time the color of the solution changed from yellow to orange. GC analysis of the solution showed 0.050 mmol of tetramethylsilane was formed.

In a separate reaction, $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_4][\text{NBu}_4]$ (0.050 g, 0.063 mmol) was reacted with 7 mL of $\text{HCl}(\text{g})$ (0.285 mmol) at 25 °C in 40 mL of toluene. After being stirred for 3 h, the solution was concentrated to a volume of 10 mL and cooled to -10 °C. Orange needles (0.035 g, 0.050 mmol, 80%) of *cis*- $[\text{NOs}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2][\text{NBu}_4]$ were collected by filtration and dried in vacuo: IR (KBr) $\nu_{\text{Os-N}}$ 1105 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz, 297 K) 3.92 (d, 1 H, $\text{CH}_4\text{H}_5\text{SiMe}_3$), 3.41 (d, 1 H, $\text{CH}_4\text{H}_5\text{SiMe}_3$), 2.60 (m, 4 H, NCH_2), 1.12 (m, 8 H, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 0.82 ppm (t, 6 H, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

Preparation of $[\text{NOs}(\text{CH}_2\text{Ph})_4][\text{NBu}_4]$. To a suspension of $[\text{NOsCl}_4][\text{NBu}_4]$ (0.050 g, 0.0855 mmol) in 100 mL of toluene was added solid $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (0.070 g, 0.340 mmol). The mixture was stirred for 30 min, during which time the toluene solution became yellow. The mixture was filtered. Pentane was added to the filtrate, and it was cooled to -30 °C. Yellow crystals of $[\text{NOs}(\text{CH}_2\text{C}_6\text{H}_5)_4][\text{NBu}_4]$ (0.029 g, 42%) were obtained: mp 88 °C dec; IR (KBr) $\nu_{\text{Os-N}}$ 1100 cm^{-1} ; ^1H NMR (CD_3CN , 200 MHz, 297 K) 6.98 (m, 5 H, C_6H_5), 3.43 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 3.06 (m, 2 H, $\text{NCH}_2\text{C}_6\text{H}_5$), 3.06 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.93 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.95 ppm (t, 3 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Anal. Calcd for $\text{OsN}_2\text{C}_{44}\text{H}_{64}$: C, 65.15; H, 7.95; N, 3.45. Found: C, 65.00; H, 7.92; N, 3.21.

Preparation of $[\text{NOs}(\text{CH}_2\text{CMe}_3)_4][\text{NBu}_4]$. $[\text{NOs}(\text{SiMe}_3)_4][\text{NBu}_4]$ (0.075 g, 0.093 mmol) was dissolved in 10 mL of diethyl ether. The

solution was cooled to -78°C with magnetic stirring, and a solution of $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ -dioxane (0.048 g, 0.190 mmol) in 5 mL of ether was added slowly. The color of the solution changed from pink to yellow-brown. It was slowly warmed to room temperature and filtered and solvent removed from the filtrate in vacuo. The residue was recrystallized from toluene/pentane at 30°C : yield 0.047 g (69%) yellow crystals; IR (Nujol mull) $\nu_{\text{Os-N}}$ 1110 cm^{-1} ; ^1H NMR (C_6H_6 , 200 MHz, 297 K) 3.456 (s, 2 H, CH_2CMe_3), 2.389 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.637 (s, 9 H, CMe_3), 0.977 (m), 0.779 ppm (m, 7 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (C_6D_6) 58.45 (t, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 53.359 (t, $J_{\text{CH}} = 116\text{ Hz}$, CH_2CMe_3), 35.0 (s, CH_2CMe_3), 34.846 (q, $J_{\text{CH}} = 123\text{ Hz}$, CMe_3), 23.777 (t, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 19.663 (t, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.590 (q, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

Preparation of $[\text{NOsMe}_4][\text{NBu}_4]$. $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ (0.564 g, 0.702 mmol) was dissolved in 20 mL of toluene. A toluene solution of AlMe_3 (2.40 mmol) was added slowly with magnetic stirring at 25°C . The color of the solution changed from pink to yellow-brown, and a brown oil precipitated. Solvent was removed in vacuo, and the residual oil was extracted with several portions of diethyl ether. The yellow extract was filtered through diatomaceous earth. Pentane was added and the solution cooled to -30°C . Yellow crystals were collected by filtration: yield of $[\text{NOsMe}_4][\text{NBu}_4]$ 0.246 g (69%); IR (Nujol mull) $\nu_{\text{Os-N}}$ 1105 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz, 297 K) 2.62 (m, 2 H, NCH_3), 2.085 (s, 3 H, OsCH_3), 1.18 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89 ppm (t, 3 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (C_6D_6) 58.82 (NCH_2), 24.16 (OsMe), 24.13 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.02 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.84 ppm ($\text{N}(\text{CH}_2)_3\text{CH}_3$). Anal. Calcd for $\text{OsN}_2\text{C}_{20}\text{H}_{49}$: C, 47.40; H, 9.55; N, 5.53. Found: C, 47.21; H, 9.55; N, 5.46.

Preparation of $[\text{NOsMe}_2\text{AlMe}_3][\text{NBu}_4]$. $[\text{NOs}(\text{OSiMe}_3)_4][\text{NBu}_4]$ (0.339 g, 0.452 mmol) was dissolved in 15 mL of toluene. The solution was cooled to -78°C . With magnetic stirring, a toluene solution of AlMe_3 (5.0 mmol in 10 mL) was added dropwise. The solution was slowly warmed to 25°C . Solvent and excess AlMe_3 were removed in vacuo. The residue was crystallized from ether/pentane solution at -30°C . Orange crystals of $[\text{NOsMe}_2\text{AlMe}_3][\text{NBu}_4]$ (0.225 g, 86%) were obtained: ^1H NMR (C_6D_6 , 200 MHz, 298 K) 2.85 (br s, NCH_2 and OsCH_3 , 17 H), 2.35 (br s, 3 H, CH_3), 1.6 (m, 16 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.40 (m, 12 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), -0.05 ppm (br s, 9 H, AlMe_3).

Preparation of $[\text{NOsMe}_4][\text{NBu}_4]$ from $[\text{NOsMe}_2\text{AlMe}_3][\text{NBu}_4]$. In a vial, $[\text{NOsMe}_2\text{AlMe}_3][\text{NBu}_4]$ (0.10 g, 0.17 mmol) was dissolved in 3 mL of toluene. Excess TMEDA (0.5 mL) was added. The color of the solution immediately changed from orange to yellow. Yellow needles formed on standing. Additional yellow crystals were obtained by doubling the volume with pentane and cooling the mixture to -30°C . Yield of pure $[\text{NOsMe}_4][\text{NBu}_4]$ was 0.075 g (87%).

Preparation of $\text{NOsMe}_3(\text{THF})_2$. $[\text{NOsCl}_4][\text{NBu}_4]$ (1.70 g, 3.04 mmol) was dissolved in 75 mL of THF in a 200-mL flask equipped with a stir bar, dropping funnel, and N_2 (g) inlet. The solution was cooled to -78°C , and MeMgI (15.4 mmol) in 30 mL of ether was added slowly by means of the addition funnel. White precipitate formed, and the color of the solution changed from purple to yellow. The mixture was warmed to room temperature and filtered. Solvent was removed from the filtrate under vacuum. The residue was crystallized from toluene/pentane solution at -30°C : yield, 1.10 g (92%) yellow solid; IR (Nujol mull) $\nu_{\text{Os-N}}$ 1025 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz, 297 K) 3.55 (m, 2 H, THF), 2.167 (s, 3 H, OsMe), 1.36 ppm (m, 2 H, THF). Anal. Calcd for $\text{OsNO}_2\text{C}_{11}\text{H}_{25}$: C, 33.57; H, 6.40; N, 3.56. Found: C, 33.01; H, 6.75; N, 3.38.

Preparation of $\text{NOsMe}_3(\text{TMEDA})$. $\text{NOsMe}_3(\text{THF})_2$ (0.040 g, 0.10 mmol) was dissolved in 0.5 mL of acetonitrile. TMEDA (0.20 mL, 0.15 mmol) was added by microliter syringe. Yellow crystals formed on standing. Approximately 1.5 mL of diethyl ether was added, and the mixture was cooled. The solution was decanted, and the yellow crystals were washed with diethyl ether and dried under vacuum: yield 0.036 g (98%); IR (KBr) 1110 cm^{-1} ; ^1H NMR (CD_3CN , 200 MHz, 297 K) 2.12 (s, 6 H, NMe), 2.09 (s, 6 H, NMe), 1.94 (s, 3 H, OsMe), 1.88 (s, 6 H, OsMe), 1.74 (s), 1.69 (s), 2.2 (m), 1.8 (m, NH_2). Anal. Calcd for $\text{OsN}_3\text{C}_9\text{H}_{25}$: C, 29.57; H, 6.89; N, 11.49. Found: C, 30.94; H, 7.18; N, 10.61.

Procedure for Thermal Decomposition Reactions of $[\text{NOsR}_4][\text{NBu}_4]$. A sample of $[\text{NOsR}_4][\text{NBu}_4]$ (10 mg) was added to a thick-walled NMR tube. The NMR tube was connected, through an adaptor, to the vacuum line. An appropriate NMR solvent, C_6D_6 or $\text{CD}_3\text{C}_6\text{D}_5$, was condensed into the tube, and the tube was sealed with a flame under vacuum. An initial NMR spectrum was obtained. The tube was heated in an oil bath to 90°C . NMR spectra were obtained periodically.

Reaction of $[\text{NOsR}_4][\text{NBu}_4]$ with PMe_3 , PBr_3 , or TMEDA. The same procedure was followed as for the thermal decomposition reactions, except that a known quantity of ligand (PMe_3 , PBr_3 , or TMEDA) was condensed in along with the NMR solvent.

Reaction of $[\text{NOsR}_4][\text{NBu}_4]$ with CO and H_2 . To a moderate pressure glass reaction vessel was added 20 mg of $[\text{NOsR}_4][\text{NBu}_4]$, a stir bar, and 5 mL of toluene. The vessel was pressurized to 30–40 psi with either CO or H_2 . The solution was magnetically stirred for 2 days. Solution was analyzed by gas chromatography. NMR spectra were obtained of the osmium-containing products.

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Reactions of Polyfluoroalkyl Fluorosulfates with Nucleophiles: An Unusual Substitution at the Sulfur–Fluorine Bond

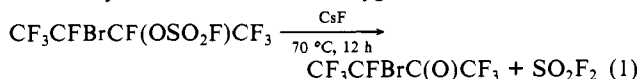
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Abstract: Polyfluoroalkyl fluorosulfates $\text{R}_f\text{OSO}_2\text{F}$ [$\text{R}_f = \text{CF}_3\text{CH}_2$ and $(\text{CF}_3)_2\text{CH}$] react with amines and alcohols or alkoxides to yield new polyfluoroalkyl sulfamates and dialkyl sulfate esters, respectively. Unlike both perfluoroalkyl fluorosulfates and alkyl fluorosulfates, the sulfur–oxygen bond in these polyfluoroalkyl fluorosulfates remains intact in the presence of hard nucleophiles. With methanethiol, however, nucleophilic attack occurs primarily at the α -carbon of $\text{CF}_3\text{CH}_2\text{OSO}_2\text{F}$ to give methyl 2,2,2-trifluoroethyl sulfide.

In the past, the reaction chemistry of fluorosulfate esters has been limited to the formation of ketones and acyl derivatives due

to the easy scission of the sulfur–oxygen bond, e.g.,² eq 1. Nucleophiles, such as F^- , predictably attack the hard sulfur(VI) atom,



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