Comparative Reactivity of Isoelectronic Nitrido, Methylimido, and Oxo Complexes of Osmium(VI)

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Abstract: The structures, physical properties, and reaction chemistry of isoelectronic alkyl complexes of osmium(VI) are compared. The three, five-coordinate alkyl complexes [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$], Os(NMe)(CH$_2$SiMe$_3$)$_4$, and Os(O)(CH$_2$SiMe$_3$)$_4$ have been characterized by single-crystal X-ray diffraction, NMR, IR, UV–visible spectroscopy, and by electrochemical techniques. All have a square-pyramidal structure in the solid state, with the imido and oxo complexes having a slight distortion toward trigonal bipyramidal. The terminal heteroatom ligand is triply bonded to the metal in each compound, but the extent of π donation to the metal decreases in the order Os≡N > Os≡NMe > Os≡O. The nitrido complex, [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$], does not react with carbon monoxide, while both Os(NMe)(CH$_2$SiMe$_3$)$_4$ and Os(O)(CH$_2$SiMe$_3$)$_4$ are reductively carbonylated under CO pressure to produce Os(CO)$_5$, (Me$_3$SiCH$_2$)$_2$CO, and either MeNCO or CO$_2$. The methylimido complex is much more reactive than the oxo complex, and the acyl species Os(NMe)(C(O)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)$_3$ and Os(NMe)(C(O)-CH$_2$SiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_2$ are produced with 1 and 2 equiv of carbon monoxide, respectively. An insertion product, Os-(NMe){C(NCMe$_3$)CH$_2$SiMe$_3$}(CH$_2$SiMe$_3$)$_3$, is formed in the reaction between Os(NMe)(CH$_2$SiMe$_3$)$_4$ and *tert*-butylisonitrile. The order of reactivity toward electrophilic attack is [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$] > Os(NMe)(CH$_2$SiMe$_3$)$_4$ ≫ Os(O)-(CH$_2$SiMe$_3$)$_4$. The nitrido complex forms 1:1 adducts with Lewis acids, alkylates at nitrogen upon reaction with organic electrophiles, and reacts with mineral acids by cleavage of one or two of the metal–carbon bonds. Electrophilic cleavage of one metal–carbon bond occurs more slowly with the methylimido complex upon reaction with HBF$_4$ or HCl. The oxo complex is stable toward electrophiles. The observed differences in reactivity can be ascribed to subtle changes in the bonding between the metal and the terminal heteroatom ligand and to the formation of a structural isomer of the methylimido complex.

Introduction

The study of oxo, imido, and nitrido complexes of transition metals has greatly expanded due to their role in oxidation, ammoxidation, and nitrogen fixation reactions as well as the interest in these as electronic materials.[1] One would expect the properties of oxo, imido, and nitrido ligands to be similar since they are isoelectronic π-donors. Direct comparisons are difficult, however, since there are few cases where isostructural and isoelectronic metal complexes containing these π-donor ligands have been prepared. The structures of transition-metal complexes containing multiply bonded ligands were recently compiled by Nugent and Mayer.[2]

The reactions of certain nitrido, imido, and oxo complexes with π-acceptor molecules have been studied. Carbon monoxide induced the reductive carbonylation of OsO$_4$ to Os$_3$(CO)$_{12}$, Re$_2$O$_7$ to Re$_2$(CO)$_{10}$, and (η^5-C$_5$Me$_5$)Re(O)Cl$_2$ to (η^5-C$_5$Me$_5$)Re-(CO$_2$)Cl$_2$.[3] The reaction of carbon monoxide with (μ-O)$_2$-(Cp*ReO)(Cp*Re(OReO$_3$)$_2$) produced a bridged oxo dimer, (μ-O)(Cp*Re(CO)$_2$),[4] and it has been reported that CO will react with ReO(PMe$_3$)(CH$_2$SiMe$_3$)$_3$ to form the acyl complex ReO-(PMe$_3$)(C(O)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)$_2$.[5] Carbon monoxide adducts have been formed by reaction of metal–oxo and imido complexes with CO.[6] Transition-metal alkylidene and alkylidyne complexes which also contain oxo or imido ligands have been shown to catalyze the metathesis of olefins and acetylenes.[7] The

addition of acetylenes, olefins, and carbon monoxide to alkylimido and oxo complexes has been reported.[8]

In general, transition-metal complexes with multiple, terminal, heteroatom ligands (oxo, imido or nitrido) react readily with acids and other electrophiles, while complexes containing only one of these ligands are usually resistant to electrophilic attack at the heteroatom. The nitrido ligands in transition-metal nitrido complexes are seldom nucleophilic enough to react with electrophiles.[9] However, the nitrogen atom in the electron-rich molybdenum-nitrido complex, Mo(N)(S$_2$CNR$_2$)$_3$, can be protonated by acids or alkylated by [Me$_3$O][BF$_4$],[10] and the nitrogen atom in *trans*-[Mo(N)X(dppe)$_2$] can also be protonated.[11] The nitrogen atom of the rhenium nitrides, ReNY$_2$(PEt$_2$Ph)$_3$, where Y = Cl, Br, acts as a Lewis base, forming adducts with the boron trihalides and gold complexes.[12] Coordination of Lewis acids to the oxo group in a tungsten–oxo complex has been observed spectroscopically.[13] Protonation of alkylimido ligands[7,14] and of oxo ligands[15] in certain complexes has been observed. Addition of electrophiles to the metal center in electron-rich complexes has been reported.[16]

On the basis of previous reports in the literature, it is difficult to ascertain the relative reactivities of oxo, nitrido, and alkylimido complexes toward electrophiles. The oxo groups in the osmium-(VIII) complex, [Os(N)O$_3$]$^-$, are more readily protonated than the nitride upon reaction which HCl.[17] Preferential protonation

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Table I. Comparison of Physical Data (R = CH$_2$SiMe$_3$)[23]

	[NBu$_4$][Os(N)R$_4$]	Os(NCH$_3$)R$_4$	Os(O)R$_4$
IR ν_{Os-Y}	1110 cm^{-1}	1281, 1019 cm^{-1}	1054 cm^{-1}
^{1}H NMR Os–CH_2	2.01 ppm	3.50 ppm	3.87 ppm
^{13}C NMR Os–CH$_2$	10.85 ppm	42.59 ppm	38.64 ppm
$E_{1/2}$ Os(VI)/Os(VII)	0.64 V	0.90 V	1.20 V
UV–visible	232 nm	232 nm	229 nm
	331, 374, 434	325, 376, 465	386, 476, 500

at the nitrido ligand has been proposed in the synthesis of Mo-(NH)(O)Cl$_2$(PEtPh$_2$)$_2$.[18] Imido ligands have been reported to be more reactive or less reactive than oxo ligands in different oxo-imido–metal complexes. Oxo, imido, and nitrido have not previously been directly compared, either in the same complex or in isostructural complexes.

Alkyl complexes of osmium(VI) and ruthenium(VI) have been synthesized and characterized in this laboratory. In this paper we compare the physical and chemical properties of a series of isoelectronic osmium(VI) alkyl complexes which contain terminal nitrido, alkylimido, or oxo ligands. Reactions of [Os(N)-(CH$_2$SiMe$_3$)$_4$]$^-$, Os(NCH$_3$)(CH$_2$SiMe$_3$)$_4$, Os(N)(CH$_2$SiMe$_3$)$_4$, and related molecules with electrophiles and certain nucleophiles are reported.

Results

Syntheses of [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$], Os(NMe)-(CH$_2$SiMe$_3$)$_4$, and Os(O)(CH$_2$SiMe$_3$)$_4$. We have reported the preparation of the nitrido complex, [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$], 1, in high yield from bis(trimethylsilylmethyl)magnesium and either [NBu$^n_4$][Os(N)(OSiMe$_3$)$_4$] or [NBu$^n_4$][Os(N)Cl$_4$].[19] Methylation of [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$] with methyl trifluoromethanesulfonate produced Os(NMe)(CH$_2$SiMe$_3$)$_4$, 2, in quantitative yield.[20] The oxo complex Os(O)(CH$_2$SiMe$_3$)$_4$, 3, was prepared by us in 50% yield from [PPh$_4$]$_2$[Os(O)$_2$Cl$_4$] and (trimethylsilylmethyl)magnesium reagents.[21] This compound was previously reported by Wilkinson and co-workers.[22] All are thermally stable, yellow or orange crystalline solids and are soluble in organic solvents.

Spectroscopic Properties. Each of the tetrakis(trimethylsilylmethyl)osmium(VI) complexes has been characterized by IR, UV–visible, ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and elemental analysis. The electrochemistry of the three complexes was examined by cyclic voltammetry, Osteryoung square wave voltammetry, and bulk electrolysis. The spectroscopic and electrochemical data are summarized in Table I.

Since the alkyl ligands are the same for compounds 1-3, a comparison of the bands in each IR spectrum allows bands associated with the multiply bonded heteroatom ligand to be readily assigned. The relatively high energy of these bands as compared to other transition-metal–nitrido, –alkylimido, and –oxo complexes indicates the presence of an osmium–heteroatom triple bond in each complex. The osmium–nitrogen stretching vibration of 1 was confirmed by isotopic labeling. The strong, sharp band at 1110 cm^{-1} in 1 shifted to 1073 cm^{-1} in the ^{15}N labeled compound, [NBu$^n_4$][Os(^{15}N)(CH$_2$SiMe$_3$)$_4$]. The osmium–nitrogen stretching vibration in the alkyl complex, [NBu$^n_4$][Os(N)(CH$_2$SiMe$_3$)$_4$], can be directly compared with that band in [NBu$^n_4$][Os(N)Cl$_4$] (ν_{Os-N} = 1125 cm^{-1}),[24] [NBu$^n_4$][Os(N)(OSiMe$_3$)$_4$] (ν_{Os-N} = 1118 cm^{-1}),[19]

or [NBu$_4$][Os(^{15}N)(OCH$_3$)$_4$] (ν_{Os-N} = 1111 cm^{-1}).[25] All reported transition-metal–nitrido complexes have a metal–nitrogen stretching vibration in the range of 948–1125 cm^{-1}.[26] We assign a broad band of medium intensity at 1281 cm^{-1} and a weak, broad band at 1019 cm^{-1} in the IR spectrum of 2 to the osmium–nitrogen–carbon vibrations of the osmium–methylimide moiety. Both of these bands shift to lower energy in the isotopically labeled compounds: Os(N^{13}CH$_3$)(CH$_2$SiMe$_3$)$_4$, Os(^{15}NCH$_3$)-(CH$_2$SiMe$_3$)$_4$, and Os(^{15}N^{13}CH$_3$)(CH$_2$SiMe$_3$)$_4$. Osborne Trogler have proposed that the IR band commonly observed for metal imides between 1300 and 1100 cm^{-1} is actually due to an N–C vibration of the imide ligand and that the metal–nitrogen stretch is at lower energy.[27] The osmium–oxo band was assigned by comparison of the IR spectrum of 2 and 3. The spectrum of the oxo complex is essentially identical with that of the methylimido complex except for the presence of a broad band of medium intensity at 1054 cm^{-1} and the absence of the bands associated with the N–CH$_3$ unit. The energy of the osmium–oxo stretching vibration indicates that there is a strong bond between these two atoms. Other terminal, monooxo complexes of osmium have been reported to have the metal–oxo stretching vibration in the range of 960–1040 cm^{-1}.[26]

The four trimethylsilylmethyl groups are equivalent at room temperature by ^{1}H and ^{13}C NMR spectroscopy. The α carbon resonances are widely separated in the three complexes, with this resonance in the nitrido complex being over 30 ppm downfield of the methylene carbon resonance of the methylimido complex. Since the chemical shift is sensitive to electron density at the carbon atom, Os≡NCH$_3$ and Os≡O must act as much stronger electron-withdrawing groups than does [Os≡N]$^-$ toward the methylene carbon. The chemical shifts of the methylene proton resonances in the ^{1}H NMR spectra are consistent with this since the methylene protons of 2 and 3 are significantly downfield those of 1.

Below –70 °C, two sets of trimethylsilylmethyl resonances in a 1:1 ratio are observed in the ^{1}H NMR spectra of both 2 and 3. The alkyl resonances of the nitrido complex, 1, begin to broaden at –80 °C. The Gibbs free energy of activation for the fluxional processes in Os(O)(CH$_2$SiMe$_3$)$_4$ and Os(NMe)(CH$_2$SiMe$_3$)$_4$ were found to be the same within experimental error, 9.6 ± 0.2 and 9.5 ± 0.2 kcal/mol, respectively. This indicates that the orientation of the alkyl ligands in these complexes at low temperature in solution is somewhat different from that in the solid-state structures, with the trimethylsilyl groups alternatively pointing up (toward the heteroatom ligand) and down (away from the heteroatom ligand). Rotation around the Os–CH$_2$ bonds of the bulky trimethylsilyl ligands is rapid at room temperature.

Electrochemical studies show that all three of these osmium(VI) complexes can be quasi-reversibly oxidized in methylene chloride with 0.1 M [NBu$_4$][BF$_4$] at a Pt electrode, but none show reversible reduction waves. Potentials were measured versus a Ag/AgCl reference. The oxidation waves of all three complexes are one-electron oxidations as shown by coulometry and bulk electrolysis. The relative potentials for the Os(VI)/Os(VII) couples in 1, 2, and 3 are consistent with information from the NMR chemical shifts. The anionic nitrido–osmium tetraalkyl complex is significantly more electron rich and easier to oxidize

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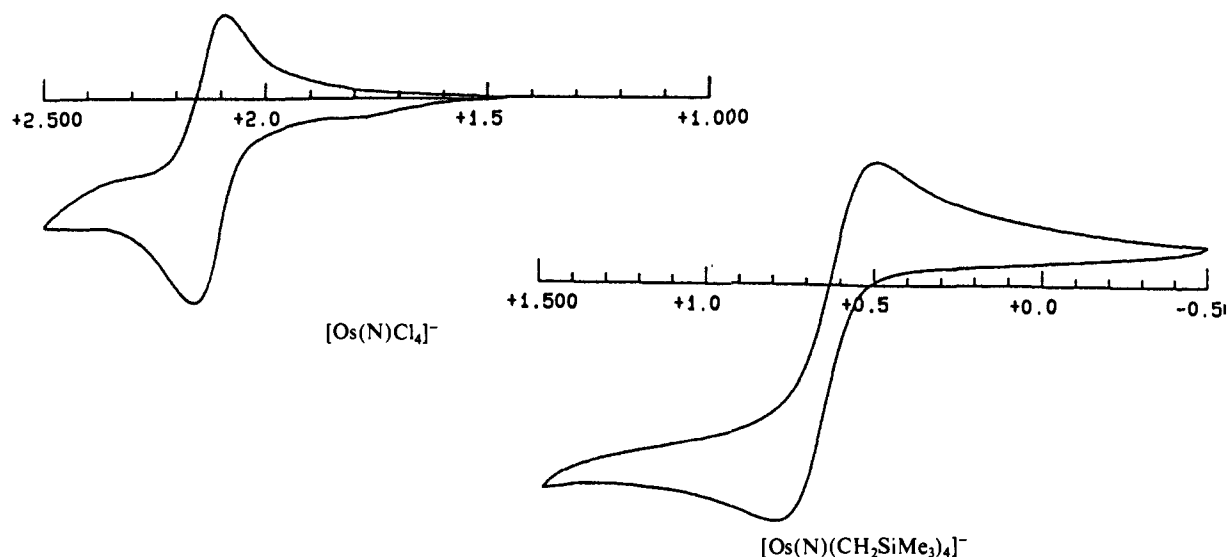(26) Nugent, W. A.; Mayer, J. M. Metal-Ligand Multiple Bonds; John Wiley & Sons: New York, 1988; Chapter 4.

Nitrido, Methylimido, and Oxo Complexes of Os(VI)

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Figure 1. Cyclic voltammograms for $[Os(N)(CH_2SiMe_3)_4]^-$ and $[Os(N)Cl_4]^-$.

Table II. Comparison of Structural Data $(R = CH_2SiMe_3)^a$

	$[NBu_4][Os(N)R_4]$	$Os(NCH_3)R_4$	$Os(O)R_4$
Os–Y distance, Å	1.631 (8)	1.686 (5)	1.692 (6)
av Os–C distance	2.130 (2.144–2.115)	2.104 (2.132–2.069)	2.078 (2.099–2.057)
av Y–Os–C angle	107.7° (108.8–107.0)	110.1° (122.8–103.78)	110.8° (114.0–107.7)
av C–Os–C angle	84.7° (86.2–83.6)	83.9° (85.9–81.9)	82.9° (84.9–80.4)

^{a} Range of averaged values in parentheses.

than either the oxo or methylimido complexes of osmium. Changing ligands on the osmium(VI) center changes the electron density of the metal and its oxidation potential. This can be seen in the series of complexes $[NBu^n_4][Os(N)Cl_{4-n}(CH_2SiMe_3)_n]$ ($n = 0, 2, 4$) where the oxidation potential of the metal decreases significantly with the substitution of electron-withdrawing chloride ligands for electron-donating alkyl groups. The oxidation potentials decrease from 2.12 V for $[NBu^n_4][Os(N)Cl_4]$ to 1.05 V for *trans*-$[NBu^n_4][Os(N)Cl_2(CH_2SiMe_3)_2]$ to 0.64 V for $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$. The cyclic voltammograms for $[NBu^n_4][Os(N)Cl_4]$ and **1** in 0.1 M $[NBu^n_4][BF_4]$ in CH_2Cl_2 are shown in Figure 1.

An intense charge-transfer absorption band centered at approximately 230 nm is present for compounds **1–3** in the UV–visible spectra. The yellow to orange color of these complexes is due to a tailing of these bands into the visible region. Three very weak bands ($\epsilon = 10–25$) in the spectrum of each complex may be due to d → d transitions. The absorption and emission spectra of $[Os(N)Cl_4]^-$ were examined by Gray and by Mabbs.[28,29] The nitridoosmium tetrachloride anion has a similar UV–visible spectrum in solution to compounds **1–3**, with an intense band in the UV and three weak bands at 390, 441, and 493 nm.

Molecular Structure. The molecular structures of $[NBu_4]$-$[Os(N)(CH_2SiMe_3)_4]$, $Os(NMe)(CH_2SiMe_3)_4$, and $Os(O)$-$(CH_2SiMe_3)_4$ have been reported in preliminary communications.[20,21] A comparison of the significant bond distances and angles is shown in Table II. As can be seen in Figure 2, the structures of these three complexes are quite similar. Minor differences exist in the metal–heteroatom bond distances and in certain bond angles.

In all three complexes, there is a strong interaction between the osmium and the heteroatom. The osmium–nitrogen distance in **1** is longer than it is in $[Os(N)Cl_4]^-$ (1.604 Å)[30] but is shorter

than the corresponding distance in $[Os(O)_3(N)]^-$ (1.676 Å)[31] where competition for metal π-symmetry orbitals decreases the bond order. The metal–nitrogen distance in **2** is shorter than the osmium–imide distance in the oxo–imido complexes of osmium.[32] The difference of 0.055 Å in the Os–N distance between **1** and **2** is within the range observed for other nitrido and alkylimido complexes.[9] The osmium–oxygen distance of 1.692 (6) Å in **3** is longer than it is in all other five-coordinate, monooxo complexes of osmium but shorter than it is in six-coordinate complexes, where a ligand trans to the oxide weakens the bonding.[33] It is also shorter than it is in any of the structurally characterized dioxo-osmium complexes, where competition for metal orbitals weakens the metal–oxo π-bonding.[34] It is interesting to note that the osmium–oxo distance is somewhat longer than the osmium–imido distance even though the van der Waals radius of oxygen is less than the radius of nitrogen. This indicates that there is more triple bond character to the osmium–nitrogen bond of **2** than to the osmium–oxygen bond of **3**. An unexpectedly small difference in rhenium–nitrogen and rhenium–oxygen distances in the complexes $(C_5H_5)Re(NCMe_3)Cl_2$ (1.709 Å) and $(C_5H_5)Re(O)Cl_2$ (1.700 Å) was also attributed to greater degree of π-bonding in the imido complex.[35]

In all structurally characterized five-coordinate complexes of osmium(VI), the metal atom is above the plane of the square base, increasing the axial ligand–metal–basal ligand angle and decreasing the angles between the basal ligands from 90°. In the crystal structure determination of $[Os(N)Cl_4]^-$, the N–Os–Cl angles were found to be 104.5° and the Cl–Os–Cl angles were 86.4°.[30] The average Y–Os–C (where Y = N^-, NMe, O) angles

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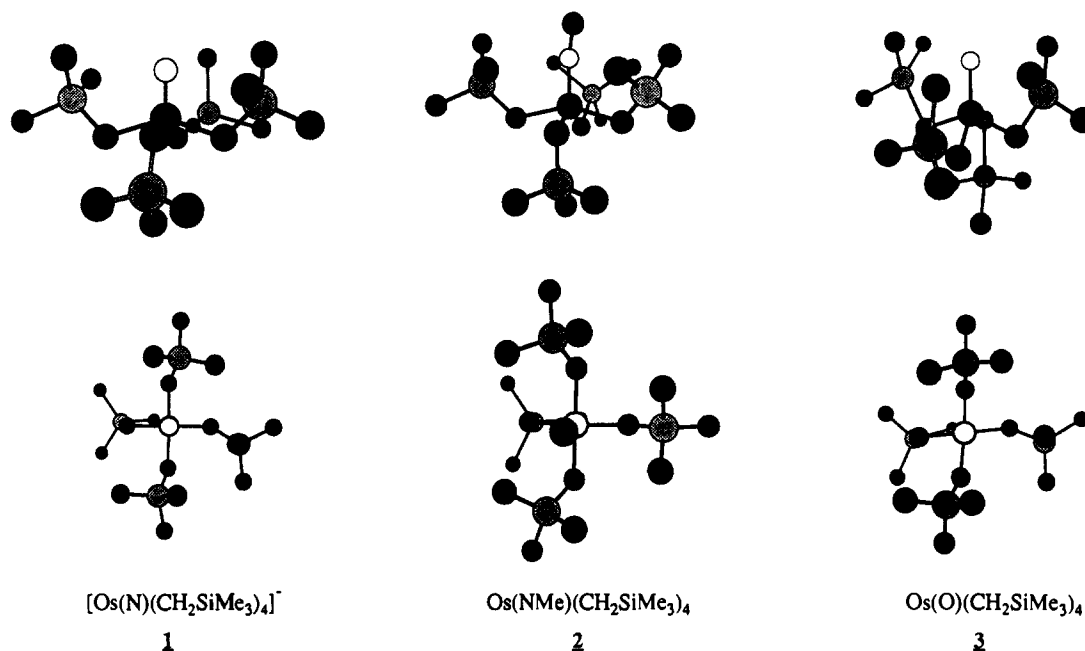(30) Phillips, F. L.; Skapski, A. C. *J. Cryst. Mol. Struct.* **1975**, *5*, 83–92.

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[Os(N)(CH₂SiMe₃)₄]⁻   Os(NMe)(CH₂SiMe₃)₄   Os(O)(CH₂SiMe₃)₄

1   **2**   **3**

Figure 2. Structures of complexes 1-3.

in the three tetrakis(trimethylsilylmethyl)osmium(VI) complexes range from 107.7 (4)° to 110.8 (4)°. The nitrido complex shows the least distortion of the three. The nitrogen–osmium–carbon angle varies from 107.0 (4)° to 108.8 (4)°. There is a greater range of N–Os–C angles in **2** with one of these, 122.8 (3)°, being much greater than the other three angles, 108.8 (3), 105.0 (3), and 103.8 (3)°. The large angle is due, at least in part, to a steric interaction between the methyl group of the imido ligand and one of the trimethylsilylmethyl groups. The methyl group of the methylimide points toward the alkyl group with the greatest N–Os–C angle. There are two larger O–Os–C angles in **3**, 114.0 (3) and 113.5 (4)°, and two shorter angles, 107.7 (3) and 108.0 (3)°. This cannot be explained by steric factors. There is a similar distortion in the d² rhenium–oxo complex, Re(O)(PMe₃)-(CH₂SiMe₃)₃.[36] In the solid-state structures of all three complexes, three of the trimethylsilyl groups point toward the axial heteroatom ligand, while the remaining one points away from this ligand. It should be noted that all three of these molecules are fluxional in solution, and the alkyl groups in each complex are equivalent at room temperature. The geometry of all three molecules can best be described as distorted square-pyramidal. The distortion is more significant in the methylimido– and oxo–osmium complexes, and their structures are intermediate between trigonal-bipyramidal geometry with equatorial heteroatom ligand and square-pyramidal geometry with axial heteroatom ligand.

Reactions with Carbon Monoxide. Although the nitridoosmium alkyl complexes are coordinatively unsaturated, they do not react with carbon monoxide either to form carbonyl complexes or with insertion into the metal–carbon bond to form metal–acyl complexes. Treatment of a toluene solution of [NBuⁿ₄][Os(N)-(CH₂SiMe₃)₄] with 1000 psig CO at 100 °C for seven days resulted in no observable reaction. The starting material was recovered in quantitative yield. We initially assumed that the steric bulk of the complex prevented reaction, but the less hindered methyl complex, [NBuⁿ₄][Os(N)Me₄], is also stable to carbon monoxide under these conditions.

The oxo complex, Os(O)(CH₂SiMe₃)₄, reacts with carbon monoxide under conditions of elevated pressure and temperature. The reaction proceeds only with at least 20 psig pressure of carbon monoxide and a temperature of at least 85 °C. The main products of the reaction are Os(CO)₅, CO₂, and (Me₃SiCH₂)₂CO. Typically, reactions were done by heating a hexane solution of **3** in a medium pressure reaction vessel at 108 °C under a pressure of

500 psig of carbon monoxide. The osmium carbonyl was characterized by comparison of the IR spectrum with that of an authentic sample. The ketone was separated by distillation and characterized by NMR, IR, and mass spectroscopy. Slow formation of Os(¹³CO)₅, Os₃(¹³CO)₁₂, ¹³CO₂, and (Me₃SiCH₂)₂¹³CO was observed by ¹³C NMR spectroscopy when a sealed NMR tube containing **3**, C₆D₆, and ¹³CO was heated to 85 °C.

The methylimido complexes, Os(NMe)(CH₂SiMe₃)₄ and Os-(NMe)Me₄, are much more reactive than the nitrido or oxo complexes with carbon monoxide. The trimethylsilyl complex, **2**, reacts with 1 equiv of CO or ¹³CO at -20 °C to form a single product, **4**. The IR spectrum of the product has one carbonyl band at 1636 cm⁻¹. The ¹³C NMR spectrum of **4** shows three types of trimethylsilylmethyl groups in a ratio of 1:1:2 as well as a carbonyl carbon. With labeled carbon monoxide, the carbonyl carbon retains the label, and one of the trimethylsilylmethyl groups shows ¹³C coupling to the α carbon. The methylene protons on the two equivalent trimethylsilylmethyl groups are diastereotopic in the ¹H NMR. On the basis of this spectroscopic data, the product can be formulated as a monoacyl complex, Os(NMe)-(COCH₂SiMe₃)(CH₂SiMe₃)₃. The data are insufficient to differentiate between two possible geometries: square-pyramidal with an axial methylimide or trigonal-bipyramidal with an equatorial methylimide.

Treatment of **4** with additional carbon monoxide produces another acyl complex, **5**. The ¹H and ¹³C NMR spectra show that there are two inequivalent acyl groups and two equivalent alkyl ligands in this product. Again, the α protons of the equivalent alkyl ligands are diastereotopic. Only a trigonal-bipyramidal geometry for Os(NMe)(COCH₂SiMe₃)₂(CH₂SiMe₃)₂ is consistent with this data. Attempted isolation, however, has always resulted in some decomposition to the ketone, (Me₃SiCH₂)₂C=O, and unidentified polynuclear osmium complexes which has prevented accurate elemental analysis. The parent ions of both **4** and **5** are present in the low energy electron impact mass spectra, however. The methyl complex, Os(NMe)Me₄, reacts more rapidly with carbon monoxide than does **2**, and mixtures of Os(NMe)Me₃{C-(O)Me} and Os(NMe)Me₂{C(O)Me}₂ are always produced upon reaction with CO even when a deficiency of the gas is used. Thermal decomposition of any of the acyl complexes, Os-(NMe)R₄₋ₓ{C(O)R}ₓ (R = Me, CH₂SiMe₃; x = 1, 2), in the absence of CO produces only 1 equiv of ketone per metal. No methyl isocyanate has been detected.
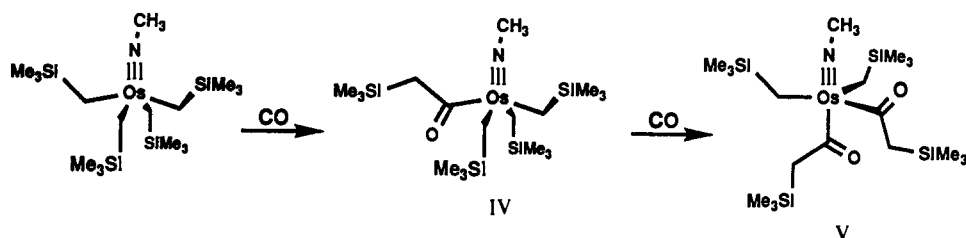
The same conditions used for the reaction of the oxo complex, **3**, with CO also result in the reductive carbonylation of the methylimido complex, **2**. The principle products are osmium car-

(36) Cai, S.; Hoffman, S. M.; Lappas, D.; Woo, H.; Huffman, J. C. *Organometallics* **1987**, *6*, 2273-8.
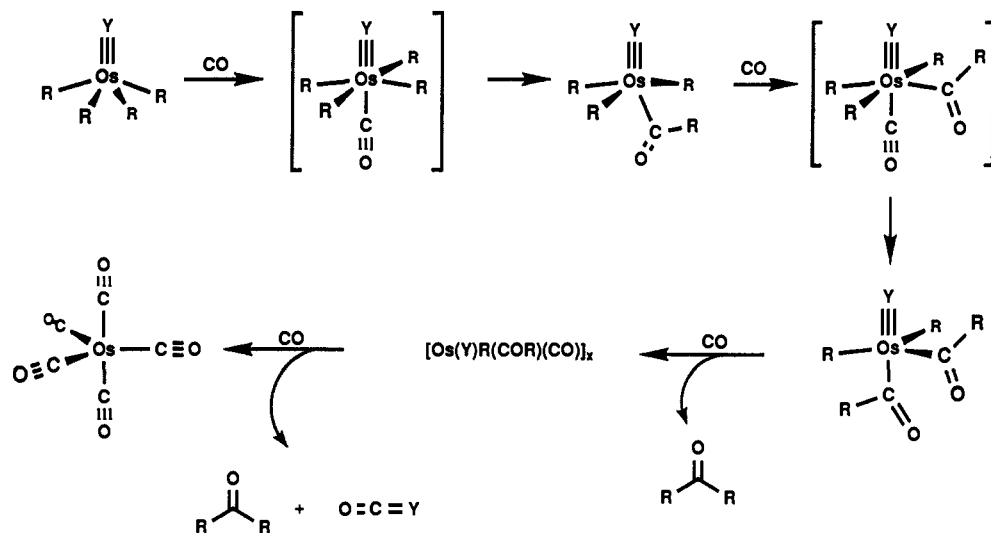
Scheme I. Syntheses of Oxo, Imido, and Nitrido Complexes
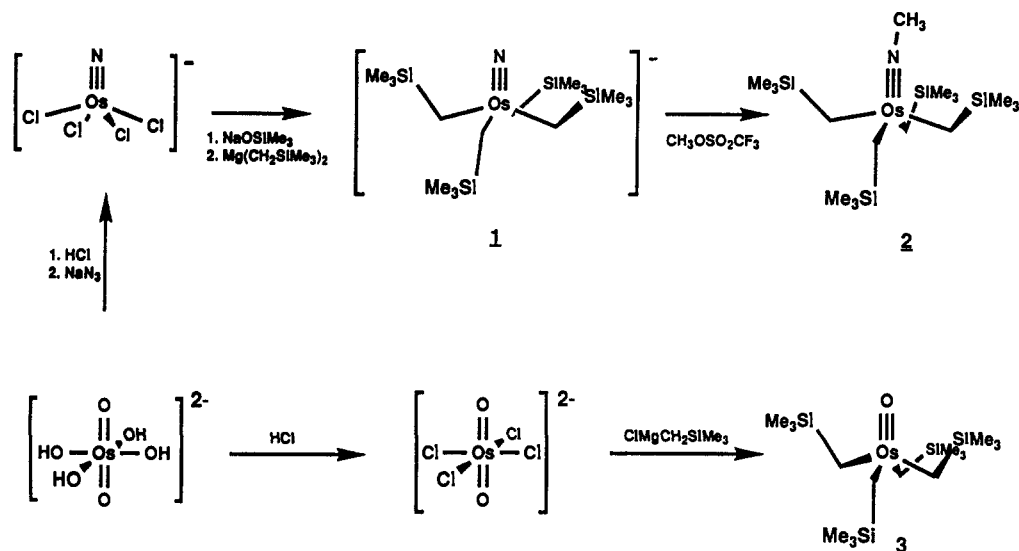
Scheme II. Formation of Osmium–Acyl Complexes

**Scheme III.** Reactions of CO with Os(Y)R4 where Y = O, NR'

bonyl, Os(CO)₅, the ketone, (Me₃SiCH₂)₂CO, and MeNCO. The methyl isocyanate polymerizes under reaction conditions and cannot be isolated. The addition of water to the reaction mixture results in the in situ hydrolysis of methyl isocyanate to carbon dioxide and methylamine. With ¹³CO, labeled carbon dioxide was observed in the ¹³C NMR spectrum of the reaction mixture. Bridging arylimido ligands in polynuclear metal complexes have been reported to react with carbon monoxide to give the corresponding aryl isocyanate and a terminal imido complex was shown to react with CO to give an isocyanate complex.[37,8b]

The reactions of both **2** and **3** with carbon monoxide probably proceed by the same pathway (Scheme III). Carbon monoxide initially coordinates to the osmium center. An alkyl group migration to the CO forms an acyl complex. Additional CO can then coordinate and a bis acyl complex can form. Reductive elimination reactions in the presence of CO produce the organic products and Os(CO)₅. With the methylimide complexes, the rate of alkyl migration to coordinated CO is more rapid than the rate of reductive elimination, and the intermediate acyl complexes can be observed.

Reactions with Other Nucleophiles. None of the osmium complexes **1–3** react at room temperature with phosphorus or nitrogen bases such as PPh₃, PMe₃, pyridine, or MeCN. Only the methylimido complex, **2**, reacts with isonitriles. The reaction between Os(NMe)(CH₂SiMe₃)₄ and excess BuᵗNC produces only the monoinsertion product, Os(NMe)(CH₂SiMe₃)₃{C(NBuᵗ)-

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Scheme IV. Reaction of Os(NMe)(CH₂SiMe₃)₄ with CNCMe₃
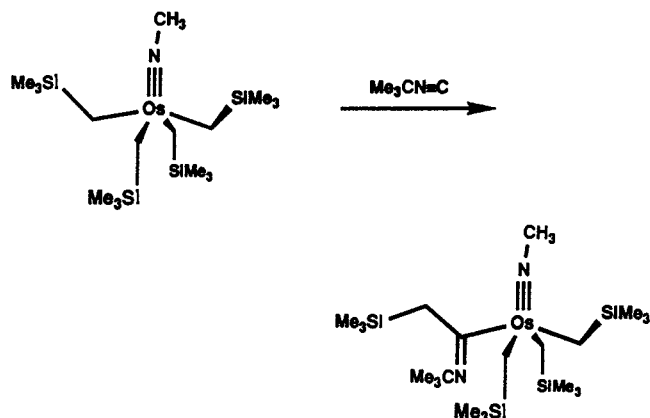
CH₂SiMe₃). This compound was isolated and characterized spectroscopically and by elemental analysis. Steric factors are clearly important in the reactions of the imido–osmium complexes with CO and isonitriles. The bulk of the *tert*-butyl group probably prevents more than one *tert*-butylisonitrile from adding to the complex.

Reactions with Electrophiles. We have previously reported that the anionic tetraalkylnitrido complexes of osmium(VI)[19] and ruthenium(VI)[38] react cleanly with HCl(g). The reaction between [NBuⁿ₄][Os(N)(CH₂SiMe₃)₄] and 2 equiv of HCl(g) occurs rapidly at 0 °C to produce 2 equiv of tetramethylsilane and the *cis*-dialkyldichloro complex [NBuⁿ₄][*cis*-Os(N)(CH₂SiMe₃)₂Cl₂] in 80% yield after recrystallization. The remaining material consists of a mixture of the trialkyl and the monoalkyl complexes, [NBuⁿ₄][Os(N)(CH₂SiMe₃)₃Cl] and [NBuⁿ₄][Os(N)-(CH₂SiMe₃)Cl₃]. By changing the quantity of added hydrogen chloride and the temperature of the reaction, the production of any of these alkyl chloride complexes can be maximized. We have not observed hydrido or imido intermediates in these reactions by IR, ¹H NMR, or ¹⁵N NMR spectroscopy. Acids of noncoordinated conjugate bases, such as HBF₄, react with [NBuⁿ₄]-[Os(N)(CH₂SiMe₃)₄] to form the neutral trialkyl complex Os-(N)(CH₂SiMe₃)₃. Carboxylic acids, being weaker, reacted only very slowly at elevated temperatures to form the corresponding alkyl carboxylate complexes, [NBuⁿ₄][*cis*-Os(N)(CH₂SiMe₃)₂-(O₂CR)₂].

A variety of organic electrophiles and Lewis acids react with [NBuⁿ₄][Os(N)(CH₂SiMe₃)₄] at the nitride. Alkylimido complexes, Os(NR)(CH₂SiMe₃)₄ where R = CH₃, C₂H₅, or SiMe₃, are formed by the alkylation of [NBuⁿ₄][Os(N)(CH₂SiMe₃)₄] with alkyl halides, alkyl trifluoromethanesulfonates, or from trialkyloxonium salts.[20] Alkylations with 3-chloro-1-propene and benzoic acid chloride produce Os(NCHCH=CH₂)(CH₂SiMe₃)₄ and Os(NC(O)Ph)(CH₂SiMe₃)₄, respectively.[39] A kinetic investigation of the reaction between [NBuⁿ₄][Os(N)(CH₂SiMe₃)₄] and methyl iodide showed a first-order dependence on both the concentration of the osmium complex and the alkyl halide.[40] The Lewis acids BF₃ and AlMe₃ form 1:1 complexes with [NBuⁿ₄][Os(N)(CH₂SiMe₃)₄]. Although none of these have been structurally characterized, the consistent reduction of the Os–N stretch in the IR spectrum leads us to believe that the nitride is the basic site in this molecule.

The methylimido complex, Os(NMe)(CH₂SiMe₃)₄, reacts with protic acids more slowly than the nitrido complex. Upon reaction with HCl at 25 °C, one of the metal–alkyl bonds is cleaved to produce tetramethylsilane and Os(NMe)(CH₂SiMe₃)₃Cl. The product is much less stable than the tetraalkyl–imido complex and decomposes slowly in solution. The reaction of Os(NMe)-(CH₂SiMe₃)₄ with HBF₄ products TMS and a very unstable organometallic product. There is no reaction between 2 and the

organic electrophiles CH₃I, CH₃OSO₂CF₃, or [(CH₃)₃O][BF₄], nor do Lewis acids, such as BF₃·(CH₃)₂O, add to the imido complex.

The oxo complex, Os(O)(CH₂SiMe₃)₄, is remarkably stable toward electrophilic attack. There is no reaction between this complex in toluene solution with excess HCl(g) or HBF₄ at room temperature. The complex is even stable to 12 N aqueous HCl. There is no reaction between Os(O)(CH₂SiMe₃)₄ and CH₃I, CH₃OSO₂CF₃, [(CH₃)₃O][BF₃·(C₂H₅)₂O.

Discussion

Bonding in Os(Y)(CH₂SiMe₃)₄, Y = N⁻, NMe, O. The bonding in five-coordinate complexes containing either an oxo or a nitrido ligand has been described by using extended Hückel calculations,[41] ab initio calculations,[42] and a simple valence bond picture.[43] The bonding in 1 should be analogous to that in [Ru(N)Cl₄]⁻.[41,28] The electron pair in each of these d² metal complexes would be in the nonbonding d$_{xy}$ orbital. The d$_{xz}$ and d$_{yz}$ orbitals are equivalent in these distorted square-pyramidal molecules and are used for π-bonding to the nitride. The increase in the nitrogen–metal-ligand angle from 90° was attributed to a mixing of the p$_x$ and p$_y$ orbitals with the d$_{xz}$ and d$_{yz}$ orbitals which would increase the π-symmetry overlap with the nitrogen p$_x$ and p$_y$ orbitals. Molecular orbitals composed mainly of the metal d$_{z^2}$ and d$_{x^2-y^2}$ orbitals are higher in energy and are antibonding with respect to the ligand–metal σ-bonds. In a square-pyramidal geometry, the nitrido ligand in 1 as well as the isoelectronic oxo and methylimido ligands in 2 and 3 should be bonded to the osmium through triple bonds.

The structural changes in going from 1 to 2 to 3 are consistent with a progressive weakening of one π-bond in the order [Os–N]⁻ > Os–NMe > Os–O. The latter two complexes show a distortion toward trigonal-bipyramidal geometry. Decreasing one of the C–Os–C$_{trans}$ angles, that is, distorting toward a trigonal bipyramid, removes the degeneracy of the d$_{xz}$ and d$_{yz}$ orbitals. This allows one Y–Os π-bond to be stronger than the other. The nitrido complex must have two equivalent π-bonds and a N–Os bond order of three, while the imido and oxo complexes can have MeN–Os and O–Os bond orders between two and three.

Reactivity. Although nitrido, alkylimido, and oxo groups are isoelectronic and are usually considered to be very similar ligands, we see pronounced differences in the reaction chemistry of the three complexes which differ only in the nature of the terminal heteroatom ligand. The order of reactivity toward nucleophiles is 2 > 3 ≫ 1, while the order of reactivity toward electrophiles is 1 > 2 ≫ 3. These differences can be explained by subtle changes in the bonding between osmium and either nitrogen or oxygen in these complexes.

Simple adducts could not be isolated with complexes 1–3 and any donor molecule. This is probably due to a combination of steric problems, since these are very crowded molecules with four bulky alkyl groups, and the trans labilizing effect of the nitrido, alkylimido, and oxo ligands.

With π-acid ligands, such as CO and isonitriles, we must consider both the metal's ability to bind to the donor and the ability of the metal center to π-bond (back-bonding interaction). In the nitrido complex, there is no orbital available for the Os–CO π-bond since the π-symmetry orbitals are used to form the Os–N triple bond. The situation with 2 and 3 would be only slightly better since these complexes have at least a partial triple bond between osmium and the imido or oxo ligand.

The differences in reactivity with CO of the three isoelectronic osmium complexes can be related to the relative strength of the metal–heteroatom bond. Carbon monoxide coordinates most strongly to electron-rich, low-valent metal centers since filled, π-symmetry metal orbitals are required for metal-to-ligand back bonding. A π-acid ligand like carbon monoxide would not be expected to bind strongly to an osmium(VI) center. In the nitrido

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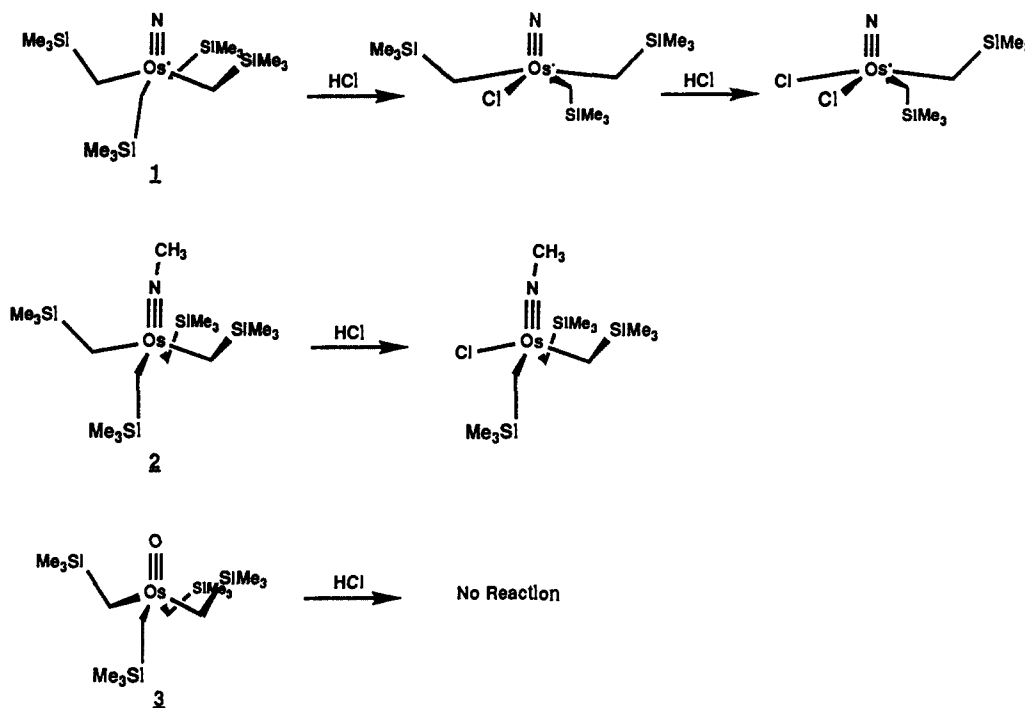
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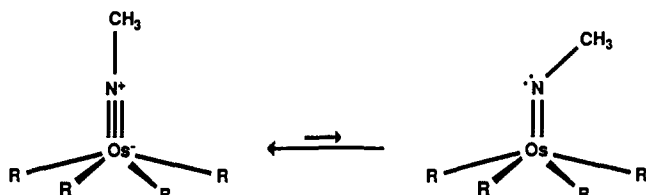
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Scheme V. Reaction of Os(Y)(CH$_2$SiMe$_3$)$_4$ with HCl

1

2

3

Scheme VI. Equilibrium between Linear and Bent Imido Complexes

complex, 1, the π-symmetry orbitals on the metal are used to form the triple bond with the nitride and are not available for back-bonding to CO. Both oxo and alkylimido ligands can formally bond to a metal through either a double bond or a triple bond. The reduced order of the Os–O and Os–NMe bonds relative to Os–N should permit some Os–CO backbonding in 2 and 3 but not in 1. Compounds 2 and 3 should have approximately the same reactivity toward CO.

The increased reactivity of the imido complex over the oxo species could be explained by the presence of a small concentration of a bent imido isomer in equilibrium with the linear imido complex. The isomer with a bent imido ligand would have only a double bond between osmium and nitrogen. The imido–nitrogen atom would have a nonbonding electron pair, and the osmium center would have an orbital of appropriate symmetry available for M–CO back bonding. Isomerization of nitrosyl ligands from the linear to bent configuration,[44] isomerization of allyl ligands from η^3 to η^1 coordination,[45] and isomerization of pentadienyl[46] and cyclopentadienyl[47] ligands from η^5 to η^3 or η^1 coordination have previously been proposed to explain associative reactions in coordinatively saturated transition-metal complexes.

The differences in reactivity of complexes 1–3 with electrophiles can best be explained by an initial attack on the heteroatom ligand. There is electron density on both the metal and the heteroatom ligand in each of the complexes 1–3, but it is unlikely that the metal center is the site of electrophilic attack. The osmium center is d^2 in all of these complexes with the lone pair in the d$_{xy}$ orbital.

Although the anionic nitrido complex is clearly more electron rich than either the methylimide or the oxide, there is very little difference in the electron density at the metal in compounds 2 and 3 as shown by electrochemistry and by the chemical shifts of the methylene resonances in the NMR spectra.

In [Os(N)(CH$_2$SiMe$_3$)$_4$], there is a lone pair on the nitrogen atom which is available for reaction with electrophiles. The terminal heteroatom ligands in 2 or 3 should not be as susceptible to electrophilic attack. With a bond order between 2 and 3, there should be a partial positive charge on the ligating atom. The oxo group, but not the imido, would have a lone pair of electrons, but the basicity of this electronegative center should be low. In order to explain the reactivity of Os(NMe)(CH$_2$SiMe$_3$)$_4$ with protons, we must again postulate a change in the bonding mode. Isomerization from the linear mode to the bent mode transfers a bonding electron pair to the nitrogen and should make that atom reactive toward mineral acids. Steric interactions probably prevent reaction of the imido nitrogen with other Lewis acids and alkylating agents.

Conclusions

A study of the physical properties and comparative reaction chemistry of three osmium complexes which differ only in the nature of a single heteroatom ligand provides information on the intrinsic effect of nitrido, alkylimido, and oxo ligands on a metal center. The nitrogen atom in the nitrido complex donates strongly to the metal center with the formation of a strong triple bond but still retains enough electron density to be subject to attack by electrophiles. The osmium–ligand bond distance and bond strength decreases in the order Os–N > Os–NMe > Os–O. The oxo and methylimido ligands are very similar in the extent to which they donate electron density to the osmium center. The rather dramatic difference in reaction chemistry between Os(NMe)R$_4$ and Os(O)R$_4$ may be due to an isomerization of the methylimido ligand in Os(NMe)R$_4$ from a linear to a bent structure. Although a bent imido isomer of Os(NMe)(CH$_2$SiMe$_3$)$_4$ has not yet been observed, such a change in the bonding between the metal and the methylimido ligand would greatly change the reactivity of the complex toward electrophiles and nucleophiles.

Experimental Section

All reactions were done under nitrogen atmosphere by using standard air-sensitive techniques with a Schlenk line or in a Vacuum Atmospheres glovebox unless otherwise stated. Anhydrous ether, tetrahydrofuran and hexane were distilled from sodium/benzophenone. Methylene chloride

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and acetonitrile were distilled from calcium hydride. Toluene was distilled from sodium. Deuterated benzene and deuterated chloroform were distilled from calcium hydride and sealed in ampules before use. Tetra-*n*-butylammonium tetrafluoroborate was recrystallized twice from methylene chloride/ether. The complexes $K_2[OsO_2(OH)_4]$,[48] $[NBu^n_4][Os(N)Cl_4]$,[24] $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$,[19] $[NBu^n_4][Os(N)(OSiMe_3)_4]$,[19] $[NBu^n_4][Os(N)(CH_2SiMe_3)_2]$,[19] $[NBu^n_4][Os(N)Me_4]$,[19] and $[PPh_4]_2[Os(O)_2Cl_4]$[21] were prepared according to literature methods.

NMR spectra were recorded on one of the following instruments: GE GN-500, GE GN-300NB, GE QE300, or Varian XL-200 FT NMR spectrometer. IR spectra were recorded on either a Perkin-Elmer 1600 series FTIR or a IBM IR/32 FTIR spectrophotometer with 4-cm⁻¹ resolution. UV and visible spectra were recorded on a Perkin-Elmer Lambda 3 UV–vis spectrophotometer. Mass spectra were recorded on a Finnigan MAT CH-5 (EI) or 731 (FI, FD). All analyses were performed by the University of Illinois microanalytical service.

Electrochemical measurements were made with a BAS 100 Electrochemical Analyzer. All electrochemistry was done in a Vacuum Atmospheres drybox. Measurements were taken on approximately 0.01 M solutions of the compound of interest by using $[NBu_4][BF_4]$ as the supporting electrolyte. Platinum disk microelectrode and a platinum wire were used as the working and auxiliary electrodes, respectively. Solutions of 0.1 M $[NBu_4][BF_4]$ in either methylene chloride or acetonitrile were prepared from freshly distilled solvent. Potentials are reported vs Ag/AgCl.

Preparation of $Os(O)(CH_2SiMe_3)_4$. A solution of $(PPh_4)_2[OsO_2Cl_4]$ (50 mg, 0.048 mmol) in 30 mL of dichloromethane was prepared. Four equivalents of (trimethylsilylmethyl)magnesium chloride (0.192 mmol, 0.192 mL of a 1.0 M solution in ether) were added by syringe. Upon addition, the blue solution turned orange. Solvent was removed in vacuo. The residue was redissolved in 1 mL of dichloromethane and filtered to removed any undissolved material. Column chromatography on silica gel eluted with hexane gave an orange solution. Removal of solvent in vacuo followed by crystallization at −30 °C from hexane yielded 13.4 mg (50.3%) of orange crystalline solid. Product could be sublimed at 2 × 10⁻⁵ Torr, 75 °C: IR (KBr pellet, cm⁻¹) 2953 m, 2898 w, 1416 w, 1384 w, 1256 w, 1248 s, 1054 m (ν_{OsO}), 1019 m, 942 w, 853 vs, 840 vs, 757 m, 695 m, 672 m (CH_2SiMe_3); ¹H NMR (300 MHz, $CDCl_3$, 18 °C) δ 3.739 (s, 2 H, $OsCH_2$), 0.078 (s, 9 H, $Si(CH_3)_3$); ¹H NMR (300 MHz, C_6D_6, 19 °C) δ 3.870 (s, 2 H, $OsCH_2$), 0.192 (s, 9 H, $Si(CH_3)_3$); ¹³C{¹H} NMR (75.4 MHz, C_6D_6, 19 °C) δ 38.64 ($OsCH_2$), 1.67 ($Si(CH_3)_3$). MS (EI, 70 eV) M⁺ 556, M⁺ − CH_3 541, M⁺ − CH_2SiMe_3 469. Anal. Calcd for $C_{12}H_{44}OOsSi_4$: C, 34.62; H, 7.98. Found: C, 34.84; H, 7.76.

Preparation of $Os(NMe)(CH_2SiMe_3)_4$. A solution of $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$ (62 mg, 0.078 mmol) in methylene chloride was prepared. Two equivalents of methyltrifluoromethane sulfonate (17.8 μL, 0.156 mmol) was added by syringe. The solution was stirred for 15 min and then concentrated to 0.5 mL. Hexane was added, and the resulting white precipitate was removed by filtration. Solvent was removed in vacuo leaving an orange brown residue. This residue was redissolved in hexane and filtered. The solvent was then removed in vacuo. Orange brown crystals were obtained by the slow evaporation of a hexane solution at −30 °C: yield 0.029g, 66%; IR (KBr pellet, cm⁻¹) 2952 m, 2895 m, 2853 m, 1407 m, 1367 w, 1281 m (ν_{OsNC}), 1256 w, 1245 s, 1019 w (ν_{OsNC}). 962 w, 935 w, 846 s, 836 s, 827 s, 767 w, 756 w, 746 m, 711 m, 678 m; ¹H NMR (300 MHz, C_6D_6, 18 °C) δ 3.495 (s, 8 H, $OsCH_2$), 1.589 (s, 3 H, NCH_3), 0.173 (s, 36 H, $Si(CH_3)_3$); ¹H NMR (300 MHz, CD_2Cl_2, 18 °C) δ 3.302 (s, 8 H, $OsCH_2$), 2.159 (s, 3 H, NCH_3), 0.042 (s, 36 H, $Si(CH_3)_3$); ¹³C{¹H} NMR (50 MHz, C_6D_6, 24 °C) δ 46.18 ($OsNCH_3$), 42.59 ($OsCH_2Si$), 3.18 ($Si(CH_3)_3$). Anal. Calcd for $C_{17}H_{47}NOsSi_4$: C, 35.90; H, 8.30; N, 2.50. Found: C, 35.88; H, 8.16; N, 2.43.

$Os(N^{13}CH_3)(CH_2SiMe_3)_4$ was prepared as above except that C-13 labeled methyl iodide was used instead of methyl trifluoromethanesulfonate, and the reaction time was increased to 91 h: ¹H NMR (C_6D_6, 500 MHz, 19 °C) δ 3.49 (s, $OsCH_2Si$), 1.59 (d, J = 142 Hz, $N^{13}CH_3$), 0.17 (s, $SiMe_3$); ¹³C{¹H} NMR (CD_2Cl_2, 75.6 MHz, 17 °C) δ 46.9, 42.5, 3.0; IR (KBr pellet, cm⁻¹) 2951 m, 2895 m, 2853 m, 1406 m, 1366 w, 1357 vw, 1269 w (ν_{OsNC}), 1255 w, 1245 s, 1030 w, 1005 w (ν_{OsNC}), 992 vw, 961 w, 935 w, 846 s, 836 s, 827 s, 768 w, 756 w, 746 w, 711 m, 678 m, 619 vw, 607 vw, 582 vw, 542 vw, 533 vw, 503 vw, 466 vw, 454 vw; ¹H NMR (C_6D_6, 500 MHz, 19 °C) δ 3.49 (s, $OsCH_2Si$), 1.59 (d, J_{CH} = 142.3, NCH_3), 0.173 (s, $Si(CH_3)_3$).

$Os(^{15}NCH_3)(CH_2SiMe_3)_4$ was prepared as above from $[NBu^n_4][Os(^{15}N)(CH_2SiMe_3)_4]$ and methyltrifluoromethane sulfonate: ¹H NMR (C_6D_6, 200 MHz, 21 °C) δ 3.49 (s, $OsCH_2Si$), 1.60 (d, J = 2.6 Hz, $^{15}NCH_3$), 0.17 (s, $SiMe_3$); IR (KBr pellet, cm⁻¹) 2952 m, 2895 m, 2853

m, 1406 m, 1366 w, 1357 vw, 1284 vw, 1255 w, 1250 sh (ν_{OsNC}), 1245 s, 1031 w, 991 br w (ν_{OsNC}), 961 w, 934 w, 846 s, 836 s, 827 s, 768 w, 756 w, 746 w, 711 m, 678 m, 620 vw, 608 vw, 542 vw, 532 vw, 504 w, 460 vw.

$Os(^{15}N^{13}CH_3)(CH_2SiMe_3)_4$ was prepared as above from $[NBu^n_4][Os(^{15}N)(CH_2SiMe_3)_4]$ and C-13 labeled methyl iodide: ¹H NMR (C_6D_6, 500 MHz, 19 °C) δ 3.49 (s, $OsCH_2Si$), 1.59 (dd, J = 142.3, 2.6, $^{15}N^{13}CH_3$), 0.172 (s, $SiMe_3$); IR (KBr pellet, cm⁻¹) 2951 m, 2895 m, 2853 m, 1406 m, 1366 w, 1357 vw, 1285 vw, 1256 w, 1244 s, 1235 sh (ν_{OsNC}), 1173 vw, 1166 vw, 1158 vw, 1030 w, 995 br w (ν_{OsNC}), 962 w, 936 w, 846 s, 836 s, 827 s, 767 w, 756 w, 746 w, 711 m, 678 m, 639 vw, 620 vw, 608 vw, 585 vw, 543 vw, 532 vw, 503 vw, 465 vw, 454 vw.

Preparation of $Os(NMe)Me_4$. A solution of $[NBu^n_4][Os(N)Me_4]$ (12 mg, 0.024 mmol) in methylene chloride (1 mL) was prepared. Two equivalents of methyltrifluoromethane sulfonate (5 μL, 0.05 mmol) were added by syringe. After stirring for 15 min hexane (5 mL) was added resulting in the precipitation of a white solid. After filtration the product was isolated as follows: The solvent was removed in vacuo. The residue was dissolved in 2 mL of hexane, filtrated, and taken to dryness. The product could be recrystallized by allowing a concentrated hexane solution to evaporated at −30 °C. The product, $Os(NMe)Me_4$, is volatile so care must be taken to minimize the time the compound remains under vacuum: ¹H NMR (500 MHz, C_6D_6, 20 °C) δ 2.97 (s, 12 H, $OsCH_3$), 1.44 (s, 3 H, $OsNCH_3$); ¹³C{¹H} NMR (50 MHz, C_6D_6, 24 °C) δ 43.08 ($OsNCH_3$), 25.81 ($OsCH_3$). Anal. Calcd for $C_5H_{15}NOs$: C, 21.49; H, 5.41; N, 5.01. Found: C, 21.86; H, 5.15; N, 5.01.

$Os(N^{13}CH_3)Me_4$ was prepared as above except that C-13 labeled methyl iodide was used instead of methyl trifluoromethanesulfonate, and the reaction time was increased to 3 days: ¹H NMR (500 MHz, C_6D_6, 20 °C) δ 2.969 (s, 12 H, $OsCH_3$), 1.441 (d, J = 142 Hz, 3 H, $OsNCH_3$).

VT NMR Studies of $Os(O)(CH_2SiMe_3)_4$, $Os(NMe)(CH_2SiMe_3)_4$, and $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$. Proton NMR studies were conducted in either toluene-d_8 or methylene chloride-d_2 from −90 °C to 20 °C. In a typical experiment $Os(O)(CH_2SiMe_3)_4$ (5 mg, 0.009 mmol) was dissolved in deuterated solvent (0.6 mL). The sample was cooled to the desired temperature and then allowed to equilibrate for 10 min before the spectrum was taken. Spectra were stored on floppy disk for later analysis. Line widths were calculated by using a linefit routine available in the CHARM and GEN software programs (GE Instruments). ΔG^* values were calculated from the following formula: $\Delta G^* = 0.00457 T_c (9.97 + \log (B) BC[(F(T_c,\Delta\delta))]$ (kcal/mol) where T_c is the observed coalescence temperature and $\Delta\delta$ is the peak separation in hertz at the slow-exchange limit.[49] For $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$ the slow exchange limit was not observed. However significant broadening of both methyl and methylene resonances of the trimethylsilylmethyl ligand was observed at −80 °C.

Reaction of $Os(O)(CH_2SiMe_3)_4$ with CO. A solution of $Os(O)(CH_2SiMe_3)_4$ (20 mg, 0.036 mmol) in hexane (25 mL) was prepared and loaded into a medium pressure apparatus. The apparatus was brought outside of the glovebox, flushed three times with carbon monoxide, and then pressurized to 820 psig. The solution was heated at 108 °C for 12 h. After cooling the apparatus to room temperature and depressurizing, a pale yellow solution remained. Volatile compounds were removed by fractional vacuum distillation. A small amount of material (~2 mg) was left in the flask. An IR spectrum of this material (KBr pellet, cm⁻¹) showed the following bands: 2030 vs, 2125 m, 1974 w, 1951 s (ν_{CO}), 2963 m, 2922 m, 2853 m, 1407 m, 1262 s, 1096 s, 1023 m, 840 m, 803 s. The remaining osmium-containing material was identified as $Os(CO)_5$ by comparison of the IR spectrum in solution with hexane with literature values.[50] This product is thermodynamically unstable and is slowly converted to $Os_3(CO)_{12}$.[51] The organic product was identified as $(Me_3SiCH_2)_2CO$ by NMR spectroscopy (see the following experiment).

Reaction of $Os(O)(CH_2SiMe_3)_4$ with ^{13}CO. A sample of $Os(O)(CH_2SiMe_3)_4$ (6 mg, 0.011 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. Excess 13-C labeled carbon monoxide (1.5 mL, 0.067 mmol) was injected by syringe, and the NMR tube flame was sealed. After an initial spectrum was taken, the sample was allowed to stand for 20 h. The sample was heated at 73 °C for 2 h, at 85 °C for 2 days, at 110 °C for 10 days, and finally at 135 °C for 10 days. NMR spectra were taken periodically: ¹³C{¹H} NMR (125.8 MHz, C_6D_6, 18 °C) δ $(Me_3SiCH_2)_2^{13}CO$ 205.06 (CO); $^{13}CO_2$, 124.7;[52] $Os(^{13}CO)_5$,

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179.6;[44] $Os_3(^{13}CO)_{12}$, 177.5, 169.5.[53]

Reaction of $Os(NCH_3)(CH_2SiMe_3)_4$ with CO. A solution of Os-$(NMe)(CH_2SiMe_3)_4$ (15 mg, 0.026 mmol) in deuterated chloroform was prepared and placed in a 10-mm NMR tube. After an initial spectrum was taken, 1.18 mL of carbon monoxide (0.052 mmol) was injected. The solution turned from orange to yellow. Spectra were taken periodically until the reaction was complete. The NMR tube was then removed from the probe, placed in a dry ice/ethanol bath, and freeze–pump–thaw degassed with nitrogen. The sample was stored at –30 °C. Samples for EI MS were prepared as follows: A small amount of solution was removed by microliter syringe and carefully injected into a metal crucible contained in a reactivial which was sealed with a septum. Solvent was slowly removed in vacuo until the sample was dry. This process was repeated several times until a sufficient amount of material for analysis was deposited in the crucible: IR (C_6D_6 solution, cm^{-1}) 1636 (ν_{CO}); ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.51 (s, 2 H, OsCH_2), 3.10 (s, 2 H, OsC(O)CH_2), 2.70 (d, J = 11.1 Hz, 2 H, *cis*-OsCHHSi), 2.27 (d, J = 11.1 Hz, 2 H, *cis*-OsCHHSi), 2.06 (s, 3 H, OsNCH_3), 0.274 (s, 9 H, Si(CH_3)$_3$). 0.184 (s, 18 H, *cis*-CH$_2$Si(CH_3)$_3$), 0.161 (s, 9 H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, CD$_2$Cl$_2$, –40 °C) 50.105 (OsNCH_3), 48.661 (d, 2 H, OsC(O)CH_2), 40.900 (OsCH_2), 26.484 (*cis*-OsCH_2Si), 1.675 (*cis*-CH$_2$Si(CH_3)$_3$), 1.571 (CH$_2$Si(CH_3)$_3$), –0.412 (CH$_2$Si(CH_3)$_3$); MS (EI, 70 eV) M$^+$ ($C_{18}H_{47}NOOsSi_4$) 597, M$^+$ – CH$_3$ 582, M$^+$ – CH$_2$Si-(CH$_3$)$_3$ 511.

Reaction of $Os(NCH_3)(COCH_2SiMe_3)(CH_2SiMe_3)_3$ with CO. Four experiments were done to identify the products of the reaction.

(a) A solution of $Os(NCH_3)(CH_2SiMe_3)_4$ (5 mg, 0.009 mmol) in C_6D_6 was prepared and placed in an NMR tube. $Os(NCH_3)$-$(COCH_2SiMe_3)(CH_2SiMe_3)_3$ was generated in situ by injecting carbon monoxide (0.40 mL) by syringe. Once the monoacyl compound was formed, additional carbon monoxide (1.58 mL, 0.071 mmol) was injected. Spectra were taken periodically until the reaction was complete (2 h). (Me$_3$SiCH$_2$)$_2$CO: IR (C_6D_6 solution, cm^{-1}) 1666 (ν_{CO}); ^{1}H NMR (500 MHz, C_6D_6 solution, 19 °C) δ 1.96 (s, 4 H, C(O)CH_2), 0.042 (s, 18 H, Si(CH_3)$_3$); Os(NCH$_3$)(COCH$_2$SiMe$_3$)$_2$(CH$_3$SiMe$_3$): IR (C_6D_6 solution, cm^{-1}) 1722, 1605 (ν_{CO}); ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.19 (s, 2 H, OsC(O)CH_2), 2.88 (s, 3 H, OsNCH_3), 2.40 (s, 2 H, OsC(O)CH_2), 2.01 (d, J = 11.7, 2 H, *cis*-OsCHH), 1.87 (d, J = 11.7, 2 H, *cis*-OsCHH), 0.202 (s, 9 H, Si(CH_3)$_3$), 0.182 (s, 18 H, *cis*-CH$_2$Si(CH_3)$_3$), 0.134 (s, 9 H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, CD$_2$Cl$_2$, 19 °C) δ 58.28 (OsNCH_3), 48.06 (OsC(O)CH_2), 43.10 (OsC(O)CH_2), 14.19 (*cis*-OsCH_2Si), 1.97 (*cis*-CH$_2$Si(CH_3)$_3$), –0.09 (CH$_2$Si(CH_3)$_3$), –0.18 (CH$_2$Si(CH_3)$_3$): MS (FI) M$^+$ 625.

(b) A solution of $Os(NMe)(CH_2SiMe_3)_4$ (11 mg, 0.019 mmol) in hexane (4 mL) was prepared. Excess carbon monoxide (2.16 mL, 0.096 mmol) was injected by syringe. The solution was stirred for 2 days. The product was analyzed by GC-MS: MS (EI) M$^+$ 202.1, M$^+$ – CH$_3$ 187, 163, 147, 131, M$^+$ – SiMe$_3$ 129, M$^+$ – CH$_2$SiMe$_3$ 115, 99, Me$_3$Si$^+$ 73, 66, Me$_2$SiH$^+$ 59, MeSiH$_2^+$ 45.

(c) $Os(NMe)(CH_2SiMe_3)_4$ (13 mg, 0.023 mmol) was dissolved in 15 mL of hexane and placed in a medium pressure apparatus. The apparatus was removed from the glovebox and placed under 60 psig of carbon monoxide. The solution was heated at 107 °C for 19 h. After heating the bomb was allowed to cool. The product was separated by fractional vacuum distillation: IR (hexane solution, cm^{-1}) 2036 ms, 1993 s.

(d) A solution of $Os(NMe)(CH_2SiMe_3)_4$ in deuterated benzene (0.6 mL) was prepared and placed in a valved NMR tube. An initial spectrum was taken, and then the sample was freeze–pump–thaw degassed and placed under ^{13}CO. NMR spectra were taken periodically to monitor product formation. The product, CH$_3$NCO, was analyzed as the hydrolysis product. CO$_2$: ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 19 °C) δ 124.8 ppm. All attempts to isolate the isocyanate directly failed due to either the rapid reaction with water or to polymerization at elevated temperatures.[54]

Reaction of $Os(NMe)(CH_2SiMe_3)_4$ with ^{13}CO. A solution of Os-$(NCH_3)(CH_2SiMe_3)_4$ (0.005 g, 0.009 mol) in 0.6 mL of C_6D_6 was prepared and placed in an NMR tube. An initial spectrum was taken and then excess C-13 labeled carbon monoxide (1.00 mL, 0.044 mmol) was injected by syringe. The sample was returned to the probe, and NMR spectra were taken periodically to monitor product formation. By NMR the monoacyl, bis-acyl, and ketone compounds were observed. Os-$(NCH_3)(^{13}C(O)CH_2SiMe_3)(CH_2SiMe_3)_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.505 (s, 2 H, OsCH_2), 3.102 (d, J_{CH} = 6.4, OsC(O)CH_2Si), 2.710 (d, J = 11.1, 2 H, OsCHH), 2.278 (d, J = 11.1, 2 H, OsCHH), 2.069 (s, OsNCH_3), 0.270 (s, 9 H, Si(CH_3)$_3$), 0.182 (s, 18 H, *cis*-

CH$_2$Si(CH_3)$_3$), 0.160 (s, 9 H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 19 °C) δ 241.3 (s, Os^{13}C(O)CH$_2$). Os(NCH$_3$)(^{13}C(O)-CH$_2$SiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_2$: ^{1}H NMR (500 MHz, C_6D_6, °C) 3.184 (d, J = 6.7, 2 H, ^{13}C(O)CH_2Si), 2.877 (s, 3 H, OsNCH_3), 2.395 (d, J = 6.3, 2 H, ^{13}C(O)CH_2Si), 2.021 (d, J = 11.7, 2 H, OsCHH), 1.877 (d, J = 11.7, 2 H, OsCHH), 0.203 (s, 9 H, Si(CH_3)$_3$), 0.180 (s, 18 H, *cis*-CH$_2$Si(CH_3)$_3$), 0.135 (s, 9 H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 19 °C) δ 244.66 (Os^{13}C(O)CH$_2$), 234.13 (s, Os^{13}C(O)CH$_2$). (CH$_3$)$_3$SiCH$_2$)2^{13}CO: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 1.963 (d, J = 5.8, ^{13}C(O)CH_2), 0.043 (s); ^{13}C{^{1}H} NMR (124.8 MHz, C_6D_6, 19 °C) δ 205.10 (s, CH$_2$$^{13}C$(O)CH$_2$), 39.25 (d, J_{CC} = 36.2, ^{13}C(O)CH$_2$Si), –1.13 (Si(CH_3)$_3$).

Reaction of $Os(N^{13}CH_3)(CH_2SiMe_3)_4$ with CO. A solution of Os-$(N^{13}CH_3)(CH_2SiMe_3)_4$ (11 mg, 0.019 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. Carbon monoxide (1.6 mL, 0.071 mmol) was injected, and spectra were taken periodically to monitor the reaction. Os(N^{13}CH$_3$)(C(O)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.504 (s, 2 H, OsCH_2), 3.101 (s, 2 H, OsC(O)-CH_2), 2.70 (d, J = 11.0 Hz, 2 H, OsCHH), 2.27 (d, J = 11.0 Hz, 2 H, OsCHH), 2.062 (d, J = 141.1 Hz, 3 H, OsNCH_3), 0.271 (s, 9 H, Si-(CH_3)$_3$), 0.182 (s, 18 H, Si(CH_3)$_3$), 0.160 (s, 9 H, Si(CH_3)$_3$). Os-$(N^{13}CH_3)(C(O)CH_2SiMe_3)_2(CH_2SiMe_3)_2$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) 3.185 (s, 2 H, OsC(O)CH_2), 2.876 (d, J = 139.8 Hz, 3 H, OsNCH_3), 2.40 (s, 2 H, OsC(O)CH_2), 2.01 (d, J = 11.8 Hz, 2 H, OsCHH), 1.87 (d, J = 11.8, 2H, OsCHH), 0.202 (s, 9 H, Si(CH_3)$_3$), 0.181 (s, 18 H, Si(CH_3)$_3$), 0.135 (s, 9 H, Si(CH_3)$_3$).

Reaction of $Os(NMe)Me_4$ with Excess CO. A solution of Os-$(NMe)Me_4$ (6 mg, 0.022 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. Excess carbon monoxide (1.5 mL, 0.067 mmol) was injected by syringe. Proton NMR were taken at approximately 1-min intervals. Three products were observed. Os(NMe)(C(O)Me)-Me$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.021 (s, 3 H, OsCH_3), 2.680 (s, 3 H, OsC(O)CH_3), 2.430 (s, 6 H, OsCH_3), 1.780 (s, 3 H, OsNCH_3). Os(NMe)(C(O)Me)$_2$Me$_2$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 2.657 (s, 3 H, OsNCH_3), 2.641 (s, 3 H, OsC(O)CH_3), 2.116 (s, 3 H, OsC-(O)CH_3), 1.931 (s, 6 H, OsCH_3). CH$_3$C(O)CH$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 1.532(s). The assignment of the acetone peak was verified by injecting small amounts of acetone (2 × 0.1 μL) into the sample.

Reaction of $Os(NMe)Me_4$ with ^{13}CO. A solution of Os(NMe)Me$_4$ (6 mg, 0.022 mmol) in C_6D_6 was prepared and placed in an NMR tube. Excess C-13 labeled carbon monoxide (1.0 mL, 0.045 mmol) was injected by syringe. Proton NMR were taken at approximately 1-min intervals. Os(NMe)(C(O)Me)Me$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.02 (s, 3 H, OsCH_3), δ 2.68 (d, J = 5 Hz, 3 H, OsC(O)CH_3), 2.43 (s, 6 H, OsCH_3), 1.78 (s, 3 H, OsNCH_3). Os(NMe)(C(O)Me)$_2$Me$_2$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 2.66 (s, 3 H, OsNCH_3), 2.65 (d, J = 4.9 Hz, 3 H, OsC(O)CH_3), 2.12 (d, J = 5.7 Hz, 3 H, OsC(O)CH_3), 1.93 (s, 6 H, OsCH_3). CH$_3$C(O)CH$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 1.53 (d, J = 5.8 Hz).

Reaction of $Os(N^{13}CH_3)Me_4$ with CO. A solution of Os(N^{13}CH$_3$)Me$_4$ (7 mg, 0.025 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. Excess carbon monoxide (1.0 mL, 0.045 mmol) was injected by syringe. Proton NMR were taken at approximately 1-min intervals. Os(NMe)(C(O)Me)Me$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 3.021 (s, 3 H, OsCH_3), 2.680 (s, 3 H, OsC(O)CH_3), 2.430 (s, 6 H, OsCH_3), 1.769 (d, J = 141.7 Hz, 3 H, OsNCH_3). Os(NMe)(C(O)Me)$_2$Me$_2$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 2.66 (d, J = 140.4, 3 H, OsNCH_3), 2.641 (s, 3 H, OsC(O)CH_3), 2.116 (s, 3 H, OsC(O)CH_3), 1.931 (s, 6 H, OsCH_3). CH$_3$C(O)CH$_3$: ^{1}H NMR (500 MHz, C_6D_6, 19 °C) δ 1.532 (s).

$Os(NMe)(C(NCMe_3))(CH_2SiMe_3))(CH_2SiMe_3)_3$. A solution of Os-$(NMe)(CH_2SiMe_3)_4$ (19 mg, 0.034 mmol) in toluene (5 mL) was prepared. One and one quarter equivalents of *tert*-butyl isocyanide (3.0 μL, 0.026 mmol) was added by syringe. After stirring for 15 min, the solvent was removed in vacuo. The yellow orange residue was redissolved in hexane and filtered. After filtration the product was isolated from solution by removing the solvent in vacuo, redissolving the residue in 2 mL of hexane, filtrating, and again removing the solvent in vacuo. Yellow crystalline solid was obtained by sublimation (2 × 10^{-5} Torr, 22 °C): yield 11 mg (50%). IR (KBr pellet, cm^{-1}) 2970 w sh, 2944 m, 2899 w, 2866 w, 1719 m (ν_{CN}), 1364 w, 1306 m (ν_{OsNC}), 1251 m, 1239 m, 1201 w, 1170 w, 1126 w, 1050 w, 1015 w, 975 w, 960 vw, 848 s, 825 s, 763 w, 724 w, 674 m; ^{1}H NMR (500 MHz, C_6D_6, 18 °C) δ 3.106 (s, 2 H, OsCH$_2$Si), 2.724 (s, 2 H, OsCH_2Si), 2.329 (d, J = 12.8, 2 H, *cis*-CHHSi), 1.982 (s, 3 H, NCH_3), 1.505 (d, J = 12.8, 2 H, *cis*-CHHSi), 0.968 (s, 9 H, C(CH_3)$_3$), 0.482 (s, 9 H, Si(CH_3)$_3$), 0.260 (s, 18 H, *cis*-CH$_2$Si(CH_3)$_3$), 0.206 (s, 9 H, Si(CH_3)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 18 °C) δ 178.65 (OsC(NBu)CH$_2$Si), 57.09 (NCH_3), 56.77 (NCMe$_3$), 30.88 (C(CH_3)$_3$), 27.84 (C(NBu)CH_2Si), 12.47 (*cis*-

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CH_2SiMe_3), 7.88 (CH_2Si), 4.60 ($Si(CH_3)_3$), 3.77 (cis-$CH_2Si(CH_3)_3$), –0.03 ($Si(CH_3)_3$). MS (EI, 70 eV) M^+ – CH_3 637, M^+ – CH_2SiMe_3 565, M^+ – $C(CMe_3)CH_2SiMe_3$ 482; MS (EI, eV) M^+ – CH_2SiMe_3 565, (M^+ – $C(NCMe_3)CH_2SiMe_3$) 482, ($C(NCMe_3)(CH_2SiMe_3)_2)^+$ 257, ($C(NCMe_3)CH_2SiMe_3)^+$ 170, ($NCH(CH_2SiMe_3)^+$/114. Anal. Calcd for $C_{21}H_{56}N_2OsSi_4$: C. 40.58; H, 8.67; N, 4.30. Found: C, 38.26; H, 7.94; N, 4.06.

Reaction of $Os(NCH_3)(CH_2SiMe_3)_4$ with HCl. A solution of Os-($NMe)(CH_2SiMe_3)_4$ (4 mg, 0.007 mmol) in C_6D_6 (0.6 mL) was prepared and placed in a NMR tube. One equivalent of HCl gas (0.17 mL, 0.007 mmol) was injected. Proton NMR spectra were taken periodically as reaction proceeded. By NMR 1 equiv of $SiMe_4$ was observed for every equivalent of $Os(NMe)(CH_2SiMe_3)_3Cl$ produced. $Os(NMe)$-($CH_2SiMe_3)_3Cl$: ^1H NMR (200 MHz, C_6D_6, 16.5 °C) δ 4.527 (d, J = 5.6, 2 H, cis-$OsCH_2$), 4.489 (s, 2 H, $OsCH_2$), 4.178 (d, J = 5.6, 2 H, cis-$OsCH_2$), 1.260 (s, 3 H, $OsNCH_3$) 0.175 (s, 18 H, cis-$Si(CH_3)_3$), 0.045 (s, 9 H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 20.0 °C) δ 52.10 (cis-$OsCH_2$), 50.96 ($OsNCH_3$), 28.31 ($OsCH_2$), 2.96 (CH_2Si-($CH_3)_3$), 2.37 (cis-$CH_2Si(CH_3)_3$). $SiMe_4$: ^1H NMR (200 MHz, C_6D_6,

16.5 °C) δ –0.010 (s). The assignment of the $SiMe_4$ peak was verified by injecting small amounts of $SiMe_4$ into the sample.

Reaction of $Os(O)(CH_2SiMe_3)_4$ with Electrophiles, General Procedure. A solution of $Os(O)(CH_2SiMe_3)_4$ (11 mg, 0.020 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. One equivalent of reactant was added, and an NMR was taken. The sample was allowed to sit for 4–5 h and then heated at 70 °C for 2–3 h, and the NMR study was repeated. Alternately a larger amount of electrophile would be added, and the above procedure was repeated. The following electrophiles were tested: $BF_3 \cdot O(CH_3)_2$, $CH_3OSO_2CF_3$, $(CH_3)_3SiOSO_2CF_3$, $HCl(g)$, $[(CH_3)_3O][BF_4]$, and CH_3I.

Living Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized Norbornadienes by Mo(CH-*t*-Bu)(N-2,6-C₆H₃-*i*-Pr₂)(O-*t*-Bu)₂

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Abstract: Benzonorbornadiene (1), 2,3-dicarbomethoxynorbornadiene (2), and 2,3-bis(trifluoromethyl)norbornadiene (5) can be polymerized by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)₂ (Mo(CH-*t*-Bu)) in a well-behaved living manner to give essentially monodisperse homopolymers. Poly-2 and (especially) poly-5 are highly trans and are believed to be tactic. The rate of polymerization of 2 is approximately 30 times faster than that of 5 at room temperature, a factor of approximately 10 of which can be ascribed to the lower reactivity of 5 relative to 2, and the remainder to the lower reactivity of living poly-5 relative to living poly-2. 7-Isopropylidene-2,3-dicarbomethoxynorbornadiene is not polymerized at all by Mo(CH-*t*-Bu), although it does react with Mo(CH-*t*-Bu) to give an isolable "first insertion product" (4) about 500 times more slowly than 2 reacts with Mo(CH-*t*-Bu). An X-ray structure of 4 shows it to be a pseudo-tetrahedral species containing a syn alkylidene ligand (substituent pointing toward the imido nitrogen atom), one face of which is blocked by the isopropylidene group and the other face of which is blocked by a carbomethoxy group. (Crystal data for 4 are a = 13.64 (1) Å, b = 17.414 (5) Å, c = 17.64 (1) Å, V = 4130 (5) Å³, β = 99.84 (6)°, space group = P2₁/n, Z = 4, M_r = 735.85, ρ = 1.183 g/cm³, μ = 3.48 cm⁻¹, R_1 = 0.047, and R_2 = 0.064.) 5 reacts with W(CH-*t*-Bu) to give an isolable square-pyramidal metallacycle at a rate that is second order overall and for which Δ$S^\ddagger$ = –40 eu. (Crystal data for 6 are a = 12.268 (8) Å, b = 18.436 (3) Å, c = 16.08 (1) Å, β = 94.63 (3)°, V = 3624 (5) Å³, space group = P2₁/n, Z = 4, M_r = 803.62, ρ = 1.473 g/cm³, μ = 33.12 cm⁻¹, R_1 = 0.067, and R_2 = 0.074.) The imido group is in an apical position in this metallacycle with the *tert*-butyl group in the WC₃ ring pointing toward the imido nitrogen atom and the monomer away from it (a trans metallacyclic ring). This metallacycle rearranges to give the "first insertion product" in a first-order manner for which Δ$S^\ddagger$ = –3 eu.

Introduction

Complexes of the type M(CHR)(NAr)(O-*t*-Bu)₂ (M = W[1] or Mo;[2] NAr = N-2,6-C₆H₃-*i*-Pr₂) are relatively inactive for metathesis of ordinary internal olefins, but will effect living ring-opening metathesis polymerization (living ROMP[3]) of mono- and polycyclic olefins.[4] Both Mo and W initiators (and related more active species containing more electron-withdrawing alkoxide ligands[1]) are now available via relatively direct high yield syntheses of versatile precursors of the type M(CHR)(NAr)(triflate)₂(dme)

(R = CMe₃ or CMe₂Ph; M = W[1b] or Mo[2b]). *tert*-Butoxide initiators that contain molybdenum are potentially the most in-

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