The First Imido Complex of Osmium(VI), $[CpOs(NH)(CH_2SiMe_3)_2][SO_3CF_3]$

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Summary: Protonation of $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$ with either HBF_4 or CF_3SO_3H at low temperature produces a thermally unstable imido complex, $[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)_2][X]$ ($X = BF_4$, SO_3CF_3). The imido complex is a strong acid and readily deprotonates. A similar reaction between the nitridoosmium complex and $[AuPPh_3][BF_4]$ forms a gold adduct, $[Os(\eta^5\text{-}C_5H_5)(NAuPPh_3)(CH_2SiMe_3)_2][BF_4]$. Each of the two complexes has a three-legged piano stool molecular structure, but the Os−N distance in the imido ligand is longer than that in the gold adduct. Lewis bases displace (triphenylphosphine)gold from the osmium nitrido group.

The imido (NH) and oxo (M═O) groups are isoelectronic, but terminal transition metal complexes of NH are much less common and more reactive than complexes of the oxo ligand. Most imido complexes are substituted with alkyl or aryl groups.[1] Chatt and Dilworth reported the first terminal imido complexes, $Mo(NH)X_2(dppe)_2$, in 1975.[2] Terminal imido complexes of vanadium, molybdenum, tungsten, and rhenium have been characterized since that time.[3]

Transition metal imido complexes are important due to the potential role of that ligand in dinitrogen reduction and nitrogen transfer reactions.[4] A recent theoretical study suggested that high-valent Os(NH) complexes should be more reactive than the oxo analogues with alkenes.[5] While there are many stable oxo complexes of osmium(VI) and ruthenium(VI), the only imido complexes of these metals are in a lower oxidation state.[6] Meyer and co-workers prepared $Os(Tp)(NH)Cl_2$ and $Os(bpy)(NH)Cl_3$ by reduction followed by protonation of osmium(VI) nitrido complexes.[7]

Many nitridoosmium(VI) complexes have been prepared, and the reactivity of the nitrido group in these molecules depends greatly on the ancillary ligands. Electron-rich osmium(VI) nitrido complexes react with electrophilic alkylating agents to produce alkylimido complexes.[8] Electron-poor nitridoosmium complexes react with nucleophiles such as phosphines, amines, arylboranes, and phenylmagnesium compounds at the nitrogen.[9] Osmium nitrides and imides also react with unsaturated organic molecules, including cyclohexadienes.[10] Here we report the reactions between $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$ and three types of electrophiles: $CF_3S(O)_2OSiMe_3$, $CF_3S(O)_2OH$ or HBF_4, and $[AuPPh_3][BF_4]$.

Results and Discussion

The complex $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$, **1**, contains a weakly nucleophilic nitrido group. It reacts with excess $CH_3OSO_2CF_3$ in 3−5 h to give $[Os(\eta^5\text{-}C_5H_5)(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$.[11] The reaction between **1** and excess $Me_3SiOSO_2CF_3$ is slow. Because the product is not thermally stable, we have not been able to isolate a (trimethylsilyl)imido product and have characterized it only by NMR spectroscopy. While silylimido complexes are well known for the early transition metals, silylimido complexes of the later transition elements are much less stable than alkylimido analogues.[12]

When the mixture of **1** and excess $Me_3SiOSO_2CF_3$ in concentrated hexane is exposed to humid air and then cooled to −20 °C, $[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)_2][SO_3CF_3]$, **2a**, crystallizes in 15% yield (Scheme 1). Protonation of $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$ with HSO_3CF_3 or HBF_4 in hexane at low temperature gives **2a** or $[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)][BF_4]$, **2b**, in approximately 20% yield. The weaker acid pyridinium tetrafluoroborate does not react with **1**.

The imido group in $[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)_2]^+$ is acidic. The addition of either $KOCMe_3$ or pyridine to

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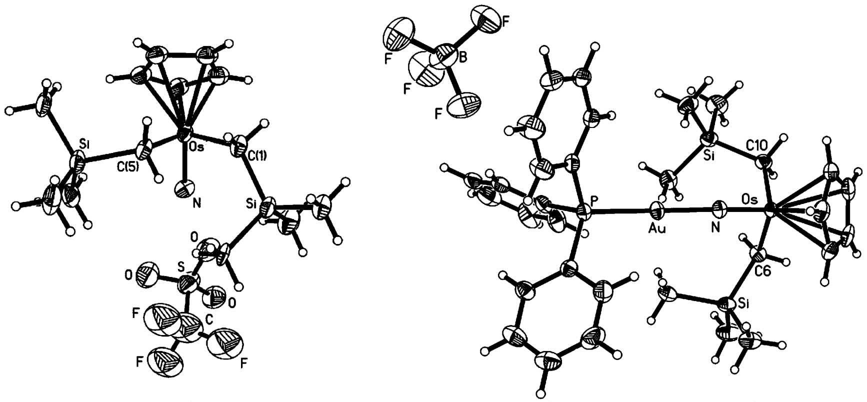
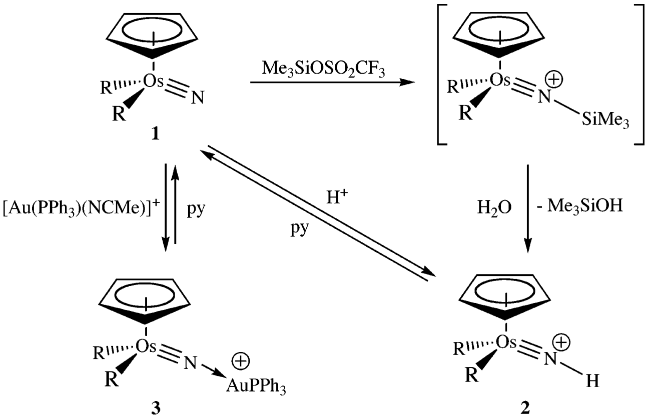


2a: Os-N, 1.75 (3) Å; Os-Cp$_{cent}$, 1.89 (7) Å; Os-C(1), 2.034 (17) Å; Os-C(5), 2.07 (3) Å; Cp$_{cent}$-Os-N, 144.0 deg.

3: Os-N, 1.68 (4) Å; Os-Cp$_{cent}$, 1.97 (3) Å; Os-C(6), 2.13(2) Å; Os-C(10), 2.12 (4) Å; N-Au, 2.01 (4) Å; Cp$_{cent}$-Os-N, 139.7 deg.; Os-N-Au, 176.6 deg.

Figure 1. Molecular structures of [Os(η^5-C_5H_5)(NH)(CH_2SiMe_3)$_2$][SO_3CF_3] and [Os(η^5-C_5H_5)(NAuPPh$_3$)(CH_2SiMe_3)$_2$][BF_4] with selected bond distances and angles.

Scheme 1



samples of **2b** in $CDCl_3$ generates **1** quantitatively by ^1H NMR spectroscopy. The IR spectra of the imido complexes **2** have an N−H stretching vibration at 3125 cm^{-1}, and the acidic imido proton appears downfield at 9.15 ppm in the ^1H NMR spectra. Proton transfer between the imido group and an osmium−carbon bond may be the principle decomposition mode of the imido-alkyl complex. Both salts of **2** produce $SiMe_4$ and insoluble, osmium-containing products within 30 min at room temperature.

The gold(I) cation $[(Ph_3P)Au]^+$ can act as a mimic of H^+ in transition metal complexes, and because its greater steric bulk slows some decomposition reactions, gold adducts can be more thermally stable than protonated complexes.[13] A gold adduct, [Os(η^5-C_5H_5)(NAuPPh$_3$)(CH_2SiMe_3)$_2$][BF_4], **3**, results from the reaction between Os(η^5-C_5H_5)(N)(CH_2SiMe_3)$_2$ and [Au(PPh$_3$)(NCMe)][BF_4]. The osmium-nitrido unit acts as a relatively weak ligand for gold(I). Treatment of **3** in $CDCl_3$ solution with Lewis bases (L = PPh_3, TMEDA, or pyridine) gives Au(PPh$_3$)L and Os(η^5-C_5H_5)(N)(CH_2SiMe_3)$_2$ within 10 min by ^1H NMR spectroscopy.

Single-crystal X-ray diffraction studies of **2a** and **3** show that these complexes each have a similar three-legged piano stool geometry at osmium.[14] The bond distances and angles of the Os(η^5-C_5H_5)(N)(CH_2SiMe_3)$_2$ unit are very similar in the molecular structures of **2a**, **3**, and the silver(I)-bridged dimer [{Os(η^5-C_5H_5)(CH_2SiMe_3)$_2$(N)}$_2$Ag][BF_4].[11] The Os−N bond distances for the complexes are 1.75(3) Å for **2a** and 1.68(4) Å for **3**. We could not locate the N−H proton of **2a** due to a twinning disorder in the crystal. The Os^V−N distance in the tris-pyrazolylborate complex Os(Tp)(NH)Cl_2 is very similar to that of **2a** at 1.749(7) Å.[7] The nitrido group of **1** is moderately basic and reacts with strong protic acids as well as Lewis acids. The nitride displaces acetonitrile from $[Au(PPh_3)]^+$ and is displaced by pyridine. In terms of relative Lewis basicity, pyridine > CpOsR$_2$(N) > CH_3CN. The structural data show that protonation of the nitride has a greater effect on the Os≡N bond than does the addition of Ag^+ or Au^+ to that atom.

The tris-pyrazolylborate and cyclopentadienyl ligands form similar complexes with transition metals, but the Cp ligand can act as a π donor, while the Tp is primarily a σ donor. The complexes Os(Tp)(N)X_2 (X = Cl, Br, OCOCF$_3$)[15] and Os(Cp)(N)R_2 have the same oxidation state, electron count, and arrangement of ligands. The complex Os(Tp)(N)Cl_2, like related tris-pyrazoylmethane and bipyridyl complexes, can be protonated only after one-electron reduction of the metal. The reaction between Os(Tp)(N)X_2 and the Lewis acid BPh_3 does not produce simple adducts but instead gives reduced borylanilido complexes. These and Os(VI) or Ru(VI) salen complexes typically react with nucleophiles rather

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(14) (a) Crystallographic data collection details for **2a**: $C_{14}H_{28}F_3NO_3OsSSi_2$, fw = 593.81, orange crystals, crystal size 0.28 × 0.22 × 0.03 mm^3, monoclinic ($P2_1/n$), a = 10.963(3) Å, b = 10.605(3) Å, c = 22.625(7) Å, α = 90°, β = 96.433(5)°, γ = 90°, V = 2613.8(14) Å^3, Z = 4, T = 193(2) K, final R1(2σ) = 0.0985, wR2 = 0.2436. All of the crystals examined were twinned. The best available crystal showed one dominant orientation (roughly 80%) with at least six partially overlapping domains. Monoclinic Laue symmetry was imposed on all calculations. (b) Crystallographic data collection details for **3**: $C_{31}H_{42}AuBF_4NOsPSi_2$, fw = 989.78, orange crystals, crystal size 0.30 × 0.22 × 0.06 mm^3, triclinic ($P\bar{1}$), a = 10.623(3) Å, b = 12.484(3) Å, c = 15.080(4) Å, α = 104.166(4)°, β = 106.647(4)°, γ = 98.880(4)°, V = 1802.9(8) Å^3, Z = 2, T = 193(2) K, final R(2σ) = 0.0258, final wR2 = 0.0579.

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than electrophiles at the nitrido group.[16] Because of the π-donor cyclopentadienyl group and the σ-donor alkyl ligands, the nitrido ligand in $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$ reacts directly with electrophiles without prior reduction of the metal.

Experimental Section

All manipulations were conducted under N_2 except where noted. Hexane and THF were distilled from Na/Ph_2CO. Ampules of THF-d_8 and $CDCl_3$ were purchased from Aldrich or Cambridge Isotope Laboratories and dried by chromatography on a short column of dried alumina. NMR spectra were recorded on Varian-Oxford U400 spectrometers. The complex $Os(\eta^5\text{-}C_5H_5)(N)(CH_2SiMe_3)_2$, **1**, was prepared from $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and NaC_5H_5.[17]

Reaction of 1 with $Me_3SiOSO_2CF_3$. To a solution of **1** (0.077 g, 0.174 mmol) in 12 mL of hexane at −78 °C was added $Me_3SiOSO_2CF_3$ (0.038 g, 0.170 mmol). After 2 days at −78 °C, the solution warmed to −23 °C and a solid precipitated. The solution was decanted, and the solid (0.007 g) was dried under vacuum. ^1H NMR (400 MHz, $CDCl_3$, δ): 5.90 (s, 5H, C_5H_5), 2.41 (d, $J = 14.4$ Hz, 2H, $OsCH^aH^bSi$), 2.24 (d, $J = 14.6$ Hz, 2H, $OsCH^aH^bSi$), 0.24 (s, 9H, $NSi(CH_3)_3$), 0.14 (s, 18H, $CH_2Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 93.2 (s, C_5H_5), 26.5 (s, CH_2Si), 2.4 (s, $CH_2Si(CH_3)_3$), 2.2 (s, $NSi(CH_3)_3$).

$[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)_2][SO_3CF_3]$, 2a. Two equivalents of $Me_3SiOSO_2CF_3$ (0.075 g, 0.62 mL) were combined with **1** (0.075 g, 0.17 mmol) in approximately 1 mL of hexane. After 1.5 h at 25 °C, the solution was exposed to air, then cooled to −20 °C. After several weeks, orange crystals (0.015 g, 0.025 mmol, 15%) formed in the solution. These were collected and used for the molecular structure determination.

$[Os(\eta^5\text{-}C_5H_5)(NH)(CH_2SiMe_3)_2][BF_4]$, 2b. One equivalent of $HBF_4\cdot OMe_2$ (0.007 g, 0.005 mmol) was added to **1** (0.022 g, 0.0050 mmol) in 6 mL of hexane. The solution was stored at −20 °C for 2 days. Small orange crystals (0.006 g, 0.011 mmol, 20% yield) were isolated and dried under vacuum and stored at −20 °C. ^1H NMR (400 MHz, $CDCl_3$, δ): 9.15, (br, 1 H, NH); 6.03 (s, 5 H, C_5H_5), 3.01 (d, $J = 12$ Hz, 2 H, $OsCH^aH^bSi$), 2.47 (d, $J = 12$ Hz, 2H, $OsCH^aH^bSi$), 0.19 (s, 18 H, $Si(CH_3)_3$). IR (KBr pellet, cm^{-1}): 3125 (m, ν_{NH}), 3085 (w, ν_{CH}), 2955 (s, ν_{CH}), 2898 (m, ν_{CH}), 1299 (w), 1251 (m), 1125 (sh), 1083 (s), 1055 (s, BF_4), 836 (s), 787 (s). ESIMS *m/z*: 516.2 ($M^+ - CH_4$). Anal. Calcd for $OsNBSi_2F_4C_{13}H_{28}$: C, 29.37; H, 5.31; N, 2.63. Found: C, 29.25; H, 5.01; N, 2.43.

X-ray Crystal Structure Determination of $[CpOs(NH)(CH_2SiMe_3)_2][OSO_2CF_3]$, 2a. All of the crystals examined were twinned. The best available crystal showed one dominant orientation (roughly 80%) with at least six partially overlapping domains. Owing to the close proximity of these overlapping domains and the likelihood of additional pseudosymmetric twinning, minor domains were very difficult to orient. Monoclinic Laue symmetry was imposed on all calculations. Four frame series were filtered for statistical outliers, then corrected for absorption by integration using SHELXTL/XPREP before using SAINT/SADABS to sort, merge, and scale the combined data.[18] A series of identical frames was collected twice during the experiment to monitor decay. No decay correction was applied. Systematic conditions suggested the unambiguous space group. Structure was solved by direct methods.[19] The proposed model shows the host molecule symmetrically disordered about a pseudomirror normal to the *b*-axis. The anion was modeled with an asymmetric disorder about this pseudomirror. Chemically equivalent bond lengths and angles were restrained to be equal with an effective standard deviation of 0.01 Å. Rigid bond restraints were imposed on all displacement parameters, and a common set of displacement parameters was refined for the two disordered Os positions. The amido H atom failed to surface in late difference Fourier maps and was not included in structure factor calculations. Remaining H atoms were included as riding idealized contributors. Methyl H atom *U*'s were assigned as 1.5 times adjacent methyl C atom U_{eq}. Remaining H atom *U*'s were assigned as 1.2 times U_{eq} of adjacent non-H atoms. The space group choice was supported by successful convergence of the full-matrix least-squares refinement on F^2. The highest peaks in the final difference Fourier map were in the vicinity of the disordered Os atoms; the final map had no other significant features.

$[Os(\eta^5\text{-}C_5H_5)\{NAu(PPh_3)\}(CH_2SiMe_3)_2][BF_4]$, 3. One equivalent of $[Ag(NCCH_3)_4][BF_4]$ (0.015 g, 0.043 mmol) was added to a 2 mL of a THF solution of $(PPh_3)AuCl$ (0.021 g, 0.043 mmol). A precipitate of AgCl formed immediately. After 1 min, the solution was filtered through Celite into a vial containing solid **1** (0.020 g, 0.043 mmol). Hexane was added and the solution cooled to −20 °C. Orange crystals of **4** were collected (0.025 g, 0.025 mmol, 59%). ^1H NMR (400 MHz, THF-d_8, δ): 7.55 (m, 15 H, $P(C_6H_5)_3$), 5.89 (s, 5 H, C_5H_5), 2.42 (br, 2 H, $OsCH^aH^bSi$), 1.28 (br, 2 H, $OsCH^aH^bSi$), 0.20 (s, 18 H, $Si(CH_3)_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.60−7.41 (m, 15 H, PPh_3), 5.92 (s, 5 H, C_5H_5), 2.65 (d, $J = 12.4$ Hz, 2 H, $OsCH^aH^bSi$), 1.81 (d, $J = 12.4$ Hz, 2 H, $OsCH^aH^bSi$), 0.23 (s, 18 H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 135.37 (d, $J = 13.8$ Hz, PPh_3), 133.39 (d, $J = 2.4$ Hz, PPh_3), 130.58 (d, $J = 12.4$ Hz, PPh_3), 96.08 (s, C_5H_5), 1.62 (s, $Si(CH_3)_3$), 0.88 (s, CH_2Si). ^{31}P NMR (162 MHz, THF-d_8, δ): 35.79 ($NAuPPh_3$). IR (KBr pellet, cm^{-1}): 3089 (w, ν_{CH}), 2947 (s, ν_{CH}), 2920 (m, ν_{CH}), 1479 (m), 1464 (w, δ_{CH}), 1438 (s), 1406 (m), 1297 (w), 1252 (sh, δ_{OsNAu}), 1238 (s, δ_{SiC}), 1102 (s), 1086 (s, ν_{B-F}), 1060 (br), 998 (w), 832 (sh), 802 (s), 769 (w), 748 (s). Anal. Calcd for $AuC_{31}H_{42}NOsPSi_2$: C, 37.62; H, 4.28; N, 1.41. Found: C, 37.48; H, 3.95; N, 1.21.

X-ray Crystal Structure Determination of 3. Crystals were grown from THF/hexane. Five frame series were filtered for statistical outliers then corrected for absorption by integration using SHELXTL/XPREP before using SAINT/SADABS to sort, merge, and scale the combined data. A series of identical frames were collected twice during the experiment to monitor decay. No decay correction was applied. Systematic conditions suggested the ambiguous space group. Structure was solved by direct methods. Anion was disordered over two positions. The two disordered anion positions were restrained to have tetrahedral geometry with an effective standard deviation of 0.01 Å. Disordered positions were further restrained to have similar displacement parameters (esd 0.01). Methyl H atom positions, $R{-}CH_3$, were optimized by rotation about R−C bonds with idealized C−H, R- -H, and H- -H distances. Remaining H atoms were included as riding idealized contributors. H atom U's were assigned as 1.2 times U_{eq} of adjacent non-H atoms. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2. The highest peaks in the final difference Fourier map were in the vicinity of atoms Os1 and Au1; the final map had no other significant features.

Reaction of $[CpOs(NAuPPh_3)(CH_2SiMe_3)_2][BF_4]$ and Lewis Bases. For each reaction, a solution of $[CpOs(NAuPPh_3)(CH_2SiMe_3)_2][BF_4]$ (0.016 g, 0.022 mmol) in 0.5 mL of dry THF-d_8 was added to an NMR tube. One equivalent of PPh_3, TMEDA, or pyridine was added. The orange solution immediately turned yellow in each case. The ^1H and ^{31}P NMR spectra obtained after 10 min showed complete conversion of **3** to **1**.

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Supporting Information Available: Crystallographic files in CIF format for **2a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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