Reactivity of the Imido Group in $[CpOs(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$

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The imido ligand in $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ reacts with basic and nucleophilic molecules. Triphenylphosphine, pyridine, and water act as bases and deprotonate the methylimido ligand forming the first osmium(IV) methyleneamido complex, $(\eta^5\text{-}C_5H_5)Os(N{=}CH_2)(CH_2SiMe_3)_2$. The reaction is reversible, and treatment of $(\eta^5\text{-}C_5H_5)Os(N{=}CH_2)(CH_2SiMe_3)_2$ with HBF_4 produces $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][BF_4]$. Triphenylphosphine also abstracts the imido ligand to form $MeN{=}PPh_3$. The imido complex reacts with ethylene to produce an olefin complex, $[(\eta^5\text{-}C_5H_5)Os(NHCH_2)(CH_2CH_2)_2][SO_3CF_3]$. Under pressures of ethylene, products resulting from imide transfer to the olefin are obtained.

Introduction

Transition metal imido complexes are important species in inorganic chemistry.[1] They have been proposed as intermediates in certain nitrogen fixation[2] and industrial ammoxidation[3] processes. One of the major focuses in the study of metal imido complexes today is to demonstrate their ability to transfer the nitrogen moiety to unsaturated substrates.

Transition metal alkylimido complexes containing a variety of ancillary ligands, including some organometallic alkylimido complexes, are known.[4−7] Complexes containing a cyclopentadienyl ligand are known for zirconium, vanadium, niobium tantalum, rhenium, and iridium.[8−11] We previously reported the synthesis and characterization of (alkylimido)osmium alkyl complexes, $Os(NR')R_4$,[12] and have also prepared the analogous ruthenium species.[13] Other known osmium alkylimido and arylimido complexes include the oxo−imido complexes $OsO_x(NR)_{4-x}$,[14] a homoleptic imido complex $Os(NR)_3$ and derivatives of this complex,[15] a porphyrin complex,[16] and a low-valent arene complex.[17]

We have synthesized $(\eta^5\text{-}C_5R_5)Os(N)(CH_2SiMe_3)_2$ (R = H, Me) by the reactions of $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ or $[Os(N)(CH_2SiMe_3)_2Cl]_2$ and NaC_5H_5 or LiC_5Me_5.[18] The methyl complexes, $(\eta^5\text{-}C_5R_5)Os(N)(CH_3)_2$ (R = H, Me), were prepared similarly.[19] The osmium centers in these coordinatively saturated nitrido complexes are relatively unreactive, but the nitrido ligands act as a weak Lewis base, coordinating reversibly to the Lewis acids Ag^+ and BF_3. The nitrido ligand is alkylated by organic electrophiles. The reaction of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ with methyl trifluoromethanesulfonate results in the formation of a cationic methylimido complex, $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$, **1** (Scheme 1).

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(1) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123−175.

(2) (a) Henderson, R. A.; Lee, G. J.; Pickett, C. J. *Adv. Inorg. Radiochem.* **1983**, *27*, 197. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1977**, *78*, 589−625. (c) Thorneley, R. N. F.; Lowe, D. J. In *Metals in Biology*; Spiro, T., Ed.; Wiley: New York, 1984; Chapter 7. (d) Postgate, J. R. *The Fundamentals of Nitrogen Fixation*; Cambridge University Press: Cambridge, U.K., 1982. (e) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249. (f) *Molybdenum and Molybdenum-Containing Enzymes*; Coughlin, M., Ed.; Pergamon: New York, 1980. (g) *A Treatise on Dinitrogen Fixation*; Hardy, R. W. F., Bottomley, F., Eds.; Wiley-Interscience: New York, 1979.

(3) (a) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1125−1127. (b) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1994**, *86*, 267−85.

(4) Su, F. M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261−1277.

(5) (a) Sundermeyer, J.; Weber, K.; Werner, H.; Mahr, N.; Bringmann, G.; Schupp, O. *J. Organomet. Chem.* **1993**, *444*, C37−C40. (b) Hursthouse, M. B.; Motevalli, M.; Sullivan, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Comm.* **1986**, 1398−1399. (c) Takacs, J.; Herrmann, W. A. *Polyhedron* **1993**, *12*, 2371−2375. (d) Lai, R.; Piasco, V.; Belin, C.; Ros, C.; Feneau-Dupont, J.; Declercq, J. P. *Polyhedron* **1993**, *12*, 2513−2517.

(6) De With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493−1496.

(7) (a) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771−2773. (b) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560−4571. (c) Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148−1160.

(8) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am.Chem. Soc.* **1988**, *110*, 8731−8733. (b) Preuss, F.; Becker, H.; Wieland, T. Z. *Naturforsch* **1990**, *45b*, 191−18. (c) Buijink, J. F.; Teuben, J. K.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922−2924. (d) Poole, A. D.; Williams, D. N.; Kenwright, A. M.; Gibson, V. C.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A. *Organometallics* **1993**, *12*, 2549−2555. (e) Chernega, A. N.; Green, M. L. H.; Suarez, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3031−3034. (f) Gibson, V. C.; Poole, A. D.; Siemeling, U.; Williams, D. N.; Clegg, W.; Hockless, D. C. R. *J. Organomet. Chem.* **1993**, *462*, C12−C14. (g) Baldwin, T. C.; Huber, S. R.; Bruck, M. A.; Wigley, D. E. *Inorg. Chem.* **1993**, *32*, 5682−5686. (h) Glueck, D. S.; Hollander, F. J.; Bergmann, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719−2721.

(9) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489−496.

(10) Walsh P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723.

(11) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651−2660.

(12) Shapley, P. A.; Own, Z. Y.; Huffman, J. C. *Organometallics* **1986**, *5*, 1269−1271.

(13) Schwab, J. J. Ph.D. Thesis, University of Illinois, 1993.

(14) (a) Milas, N. A.; Iliopulos, M. I. *J. Am. Chem. Soc.* **1959**, *81*, 6089. (b) Herranz, E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2544−2548.

(15) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642−1643.

(16) Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614−16.

(17) (a) Michelman, R. I.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1993**, *12*, 2741−51. (b) Michelman, R. I.; Ball, G. E.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1994**, *13*, 869−881.

(18) Marshman, R. W.; Shusta, J. M.; Willson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671−1676.

(19) Shusta, J. Ph.D Thesis, University of Illinois, 1992.

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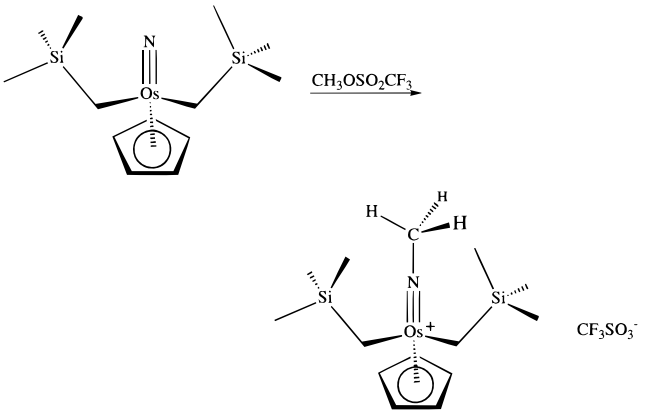
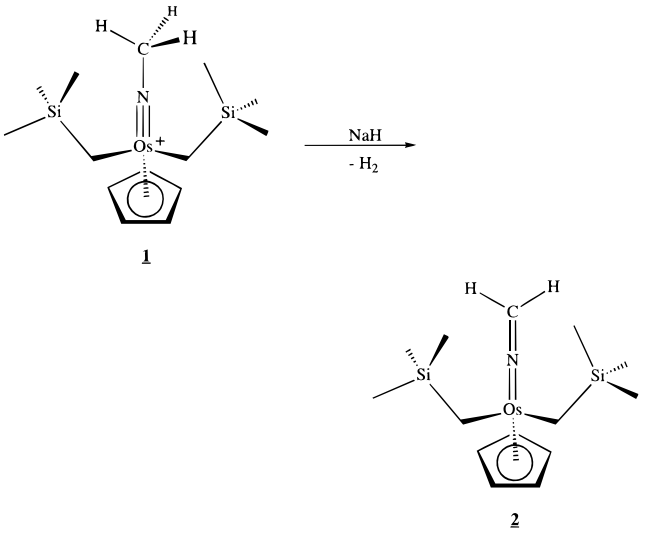
Scheme 1



Scheme 2



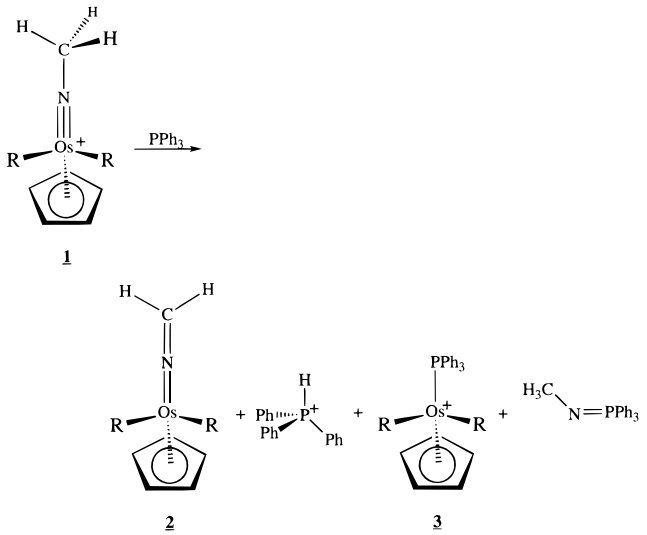
The methylimido ligand in **1** is quite reactive, and it can be transferred to certain unsaturated organic molecules. In this paper we report some of the reaction chemistry of this complex with nucleophiles.

Results

Complex **1** can be obtained in only moderate yields by the alkylation of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ with $CH_3SO_3CF_3$ because the alkylation reaction is slow at room temperature and the product is thermally unstable. It decomposes slowly in solution to produce an insoluble solid and organic products derived from the alkyl ligands: $Me_3SiCH_2CH_2SiMe_3$ and $SiMe_4$. Complex **1** does not react with carbon monoxide at 500 psi, 25 °C, but does react with other Lewis bases.

Deprotonation of $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2][SO_3CF_3]$. The methylimido complex, **1**, is acidic. The addition of 1 equiv of NaH to a THF solution of **1** results in an immediate reaction. The color changes from orange to purple and hydrogen gas bubbles from the solution. After purification of the crude product by column chromatography or by crystallization from hexane, we obtain $(\eta^5\text{-}C_5H_5)Os(N{=}CH_2)(CH_2SiMe_3)_2$, **2**, in 94% yield (Scheme 2). Complex **1** also reacts with pyridine to give **2**. Even water is able to slowly deprotonate the methylimido group in **1**. The ^{15}N-labeled complex $(\eta^5\text{-}C_5H_5)Os(^{15}N{=}CH_2)(CH_2SiMe_3)_2$ results from the deprotonation of $[(\eta^5\text{-}C_5H_5)Os(^{15}NMe)(CH_2SiMe_3)_2][SO_3CF_3]$.

Scheme 3



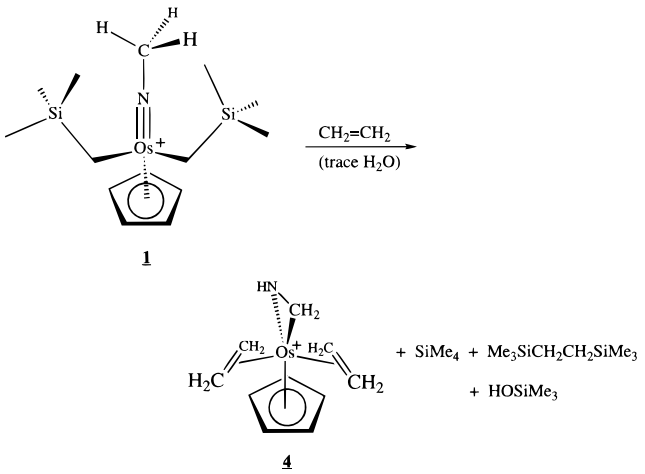
Complex **2** was characterized by elemental analysis and spectroscopic methods. It is a diamagnetic osmium(IV) complex. The ^1H NMR spectrum of **2** includes resonances for the cyclopentadienyl protons and methylene and methyl protons of the (trimethylsily)methyl ligands and a singlet for the protons of the methyleneamido ligand at −0.56 ppm. In the labeled complex, $(\eta^5\text{-}C_5H_5)Os(^{15}N{=}CH_2)(CH_2SiMe_3)_2$, the resonance at −0.56 ppm is split into a doublet with a coupling constant of 3.1 Hz by the ^{15}N nucleus. The proton-decoupled ^{13}C NMR spectrum of **2** shows a singlet at δ 128.95 for the carbon of the methyleneamido group along with resonances for the carbons of the equivalent alkyl ligands and the carbons of the cyclopentadienyl group. The infrared spectrum of **2** includes a band at 1606 cm^{-1} for the $N{=}CH_2$ stretch.

The methyleneamido ligand is reprotonated at carbon by strong acids. Tetrafluoroboric acid converts **2** to the tetrafluoroborate salt of **1**. Neither pyridinium tetrafluoroborate nor triphenylphosphonium tetrafluoroborate reacted rapidly with **2**. After several days, both $[Hpy][BF_4]$ and $[HPPh_3][BF_4]$ caused some decomposition of **2**, producing $SiMe_4$ by protonolysis of the alkyl ligands. Complex **2** does not react with ethylene or with PPh_3.

Reaction of 1 with PPh_3. Triphenylphosphine reacts with **1** as both a base and as a nucleophile. The reaction of **1** with 2 equiv of triphenylphosphine gives nearly equal amounts of **2** and $[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2(PPh_3)][SO_3CF_3]$, **3**, by ^1H NMR, along with $[HPPh_3][SO_3CF_3]$ and $MeN{=}PPh_3$ (Scheme 3). An intermediate species, which we presume to be $[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2(MeN{=}PPh_3)][SO_3CF_3]$, can be observed in solution but has not been isolated. In the ^{31}P NMR spectrum, the signals for the intermediate (19.3 ppm) and for PPh_3 (−4.9 ppm) decrease as the signals for free $MeN{=}PPh_3$ (15.7 ppm) and **3** (53.7 ppm) increase. When $[(\eta^5\text{-}C_5H_5)Os(^{15}NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ is treated with PPh_3, the labeled nitrogen is found in $Me^{15}N{=}PPh_3$. We also observe $[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2(Me^{15}N{=}PPh_3)][SO_3CF_3]$ in solution. The resonances associated with these compounds in the proton-decoupled ^{31}P NMR spectrum are split into doublets due to $^{31}P-^{15}N$ coupling.

Complex **2** can be isolated in 49% yield from the reaction mixture. Complex **3** is more sensitive than is

Scheme 4



1 **4**

2, and it reacts with $[HPPh_3]^+$ formed in the reaction to give Me_4Si and insoluble osmium-containing products. It also reacts with additional PPh_3. The isolated yields of **3** are low. The organic products from this reaction were identified by comparison of their ^1H, ^{13}C, and ^{31}P NMR spectra with those of authentic samples.

The ^1H NMR spectrum of **3** shows a singlet at δ −0.16 for the methyl protons of the (trimethylsilyl)methyl ligands, a singlet at δ 4.94 for the equivalent cyclopentadienyl protons and multiplets in the aromatic region for the phenyl protons. The methylene protons of the alkyl ligands appear as a pair of doublet of doublets at δ 3.85 and 1.95 due to both H−H and P−H coupling. The ^{13}C NMR spectrum gives a doublet at δ 83.21 with $J_{PC} = 2.2$ Hz assigned to the cyclopentadienyl carbons, a doublet at δ 3.09 with a $J_{PC} = 3.1$ Hz assigned to the methylene carbons of the (trimethylsilyl)methyl ligands, and a singlet at δ 0.02 for the methyl carbons of the (trimethylsilyl)methyl ligands.

Reaction of 1 with Ethylene. The methylimido complex reacts with ethylene to give a single product. The reaction of **1** in methylene chloride solution with an excess of ethylene at approximately 1 atm, 25 °C, produces a π-bonded imine complex $[(\eta^5\text{-}C_5H_5)Os(\eta^2\text{-}HN{=}CH_2)(\eta^2\text{-}C_2H_4)_2][SO_3CF_3]$, **4** (Scheme 4). The organic products of the reaction are derived from the (trimethylsilyl)methyl ligands and include $Me_3SiCH_2CH_2SiMe_3$, $SiMe_4$, and small quantities of Me_3SiOH and $Me_3SiOSiMe_3$. The trimethylsilanol and hexamethyldisiloxane probably result from trace quantities of water in the ethylene. The ^{15}N-labeled complex, $[(\eta^5\text{-}C_5H_5)Os(\eta^2\text{-}H^{15}N{=}CH_2)(\eta^2\text{-}CH_2{=}CH_2)_2][SO_3CF_3]$, is prepared from $[(\eta^5\text{-}C_5H_5)Os(^{15}NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ and ethylene. Analytically pure crystals of **4** are obtained by rapid crystallization in THF/hexane solutions at −30 °C. Complex **4** is unstable in coordinating solvents and decomposes slowly in THF or acetonitrile solution with loss of ethylene. Trace amounts of **4** are also formed in the hydrolysis of **1** in the absence of ethylene.

The ^1H NMR spectrum of **4** shows resonances for the imine and ethylene ligands. The nonequivalent methylene protons of the methyleneimino ligand are found at δ 7.59 and at δ 7.95, and a broad singlet at δ 12.15 is assigned to the proton on the quadripolar ^{14}N nucleus. The multiplet at δ 7.59 is assigned to the methylene proton *trans* to N−H (J = 20.2, 12.9 Hz) while the multiplet at δ 7.95 is due to the methylene proton *cis* to N−H (J = 12.9, 12.9 Hz). In ^{15}N-labeled **4**, the N−H resonance is coupled to the adjacent ^{15}N atom (J_{NH} = 76.0 Hz) and to the nonequivalent methylene protons of the methyleneimino ligand (J = 20.2, 12.9 Hz). Symmetric multiplets at δ 3.18 and 3.02 having an AA′BB′ second-order splitting pattern are assigned to the protons of the η^2-bonded olefin, and the singlet at δ 5.39 is assigned to the equivalent cyclopentadienyl protons. The AA′BB′ pattern was simulated using the ITRCAL program in order to obtain the accurate coupling constants and chemical shift data for the nonequivalent olefin protons.

The protons of the cyclopentadienyl ligand, the methyleneimino ligand, and the ethylene ligands relax at quite different rates ($T1$). An optimal delay time of 25 s gave accurate integrations for each multiplet in the ^1H NMR spectrum of **4**. The COSY spectrum obtained of **4** showed correlations among the resonances at δ 7.95, 7.59, and 12.15, and between the resonances at δ 3.18 and 3.02. Three resonances are observed in the ^{13}C NMR spectrum of **4** for the methylene carbon of imine ligand, for the equivalent carbons of the two ethylene ligands, and for the equivalent cyclopentadienyl carbons. The HETCOR and APT spectra verified the heteronuclear correlations and carbon types.

The IR spectrum of **4** includes a NH stretching absorption at 3155 cm^{-1} and bands for the aromatic and olefinic C−H stretching vibrations. An intense absorption at 1382 cm^{-1} may be assigned to a C−N stretching vibration.

^1H NMR spectroscopy shows that **4** slowly converts to an isomeric complex, **4′**. The multiplets due to the methyleneimino ligand and the two olefin ligands shift downfield slightly, while the coupling constants and splitting patterns remain the same.

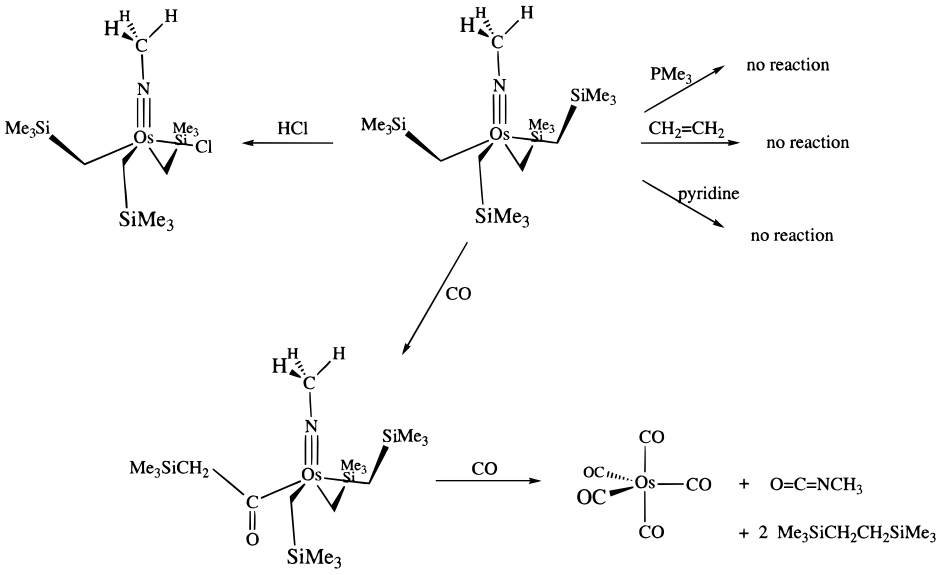
Complex **1** reacts with ethylene at higher pressure to give products in which the methylimido group was transferred to the olefin. After a solution of **1** was stirred at 760 psi, 41 °C, for 4 days, volatile organic products derived from the (trimethylsilyl)methyl ligands and ethylene, a nonvolatile polymeric mixture derived from *N*-methylaziridine, and an insoluble osmium-containing material were produced. When ^{15}N-labeled **1** was treated with ethylene under these conditions, essentially all of the ^{15}N label was in the nonvolatile fraction. The volatile organic products were distilled and analyzed by GCMS. This mixture contained propenyl(trimethyl)silane, tetramethysilane, butene, and small amounts of hexamethyldisiloxane and octamethyltrisiloxane. No *N*-methylaziridine was detected in the volatile organic products.

A pure sample of *N*-methylaziridine was exposed to the reaction conditions above. The ^1H NMR spectrum, UV−visible spectrum, and mass spectrum of the polymeric product mixture from *N*-methylaziridine/ethylene were identical to that of the soluble, non-volatile fraction from **1**/ethylene.

Discussion

Comparison of the Reactivity of 1 with That of $Os(NCH_3)(CH_2SiMe_3)_4$. A series of osmium(VI) alkylimido complexes $Os(NR)R'_4$ (R = CH_3, CH_2CH_3, $SiMe_3$, $CH_2CH{=}CH_2$; R′ = CH_3, CH_2Ph, CH_2SiMe_3, $CH_2CH{=}CH_2$) were prepared previously in this labora-

Scheme 5



tory.[12,20] The reaction chemistry of $Os(NCH_3)(CH_2SiMe_3)_4$, **5**, has been thoroughly studied and can be compared with that of **1**.[21] The reaction chemistry of the two methylimido complexes is very different (Scheme 5). Unlike **1**, **5** is not deprotonated by pyridine or phosphines. We seen no evidence for the formation of methyleneamido complexes in the reactions of **5** with bases. The methylimido group in **5** is not transferred to either phosphines or to olefins. We have seen no reaction between **5** and PPh_3, the more basic PMe_3, or C_2H_4. Carbon monoxide does react with **5** in a stepwise fashion. Strong acids protonate the alkyl ligands in both **1** and **5**, leading to decomposition of the complexes.

The greatly enhanced reactivity of the methylimido group in **1** over **5** can be explained as a result of π competition. Complex **5** has only a single π-donor ligand. The nitrogen p orbitals can form two strong π-bonds with the d_{xz} and d_{yz} orbitals on the metal. The η^5-cyclopentadienyl ligand and the methylimido ligand in **1** each require one σ symmetry metal orbital and two π symmetry orbitals on osmium for bonding, and the ligands are competing with each other for the metal π-symmetry orbitals. This can lead to structural distortions or increased reactivity of the π-bonded ligands.[22] There is a distinct ring slippage of the cyclopentadienyl ligand in the silver(I) adduct $\{(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)(N)\}_2AgBF_4$.[18] A similar distortion has been observed previously in certain cyclopentadienyl complexes with oxo, imido, and μ-dinitrogen ligands.[9,23] Reactions leading to loss of the methylimido ligand or a modification of the ligand to reduce π-bonding should be favorable for **1**. These are observed. Deprotonation converts the triply-bonded imido to a doubly-bonded amido ligand. The reaction with ethylene under mild conditions results in the conversion of the imido to an imine ligand. Reactions with PPh_3 or ethylene (high pressure) result in the complete loss of the imido group.

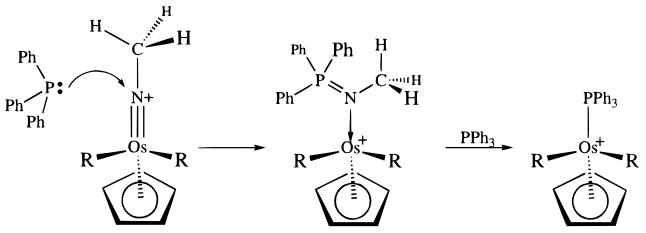
Acidity of the Methylimido Group in 1. Complex **1** is a surprisingly strong carbon acid, deprotonated by even weak bases. Enhanced acidity has been observed for the β-hydrogen atoms of alkylimido groups in some other transition metal imido complexes, and this acidity may be explained by the electron-accepting character of the imido nitrogen atom. Chatt has demonstrated that the rhenium complexes $Re(NCH_2R)Cl_2L_2$ (R = H, CH_3, CH_2CH_3; L = PPh_3, $PMePh_2$, $PEtPh_2$) are deprotonated with pyridine to give the (alkylideneamido)-rhenium(III) complexes $Re(N{=}CHR)Cl_2L_2(NC_5H_5)$.[24] The tungsten hydridotris(3,5-dimethylpyrazolyl)borate complexes $[Tp'(CO)_2W(NCH_2R)][PF_6]$ (R = Pr, Ph) are also deprotonated by NEt_3 to form $Tp'(CO)_2W(N{=}CHR)$.[25]

The methyleneamido ligand in **2** is probably bonded linearly to the osmium center, forming a double bond. The methylene protons are equivalent at room temperature and remain equivalent in the low temperature ^1H NMR spectra. There is a moderately strong C−N double bond as shown by the C−N stretching vibration at 1606 cm^{-1} in the IR spectrum. The N=C stretching vibrations of the reported alkylideneamido complexes occur in the range 1325−1725 cm^{-1}.[25,26] Many inorganic osmium(IV) complexes are paramagnetic, but **2**, with its high-field ligands, is a diamagnetic species.

Transfer of the Methylimido Group in 1 to PPh_3. Certain transition metal imido complexes have an electrophilic character and react with phosphines at the imido nitrogen. McElwee-White has shown that $(CO)_5W{=}NPh$ reacts with PPh_3 to form $(CO)_5W(PhNPPh_3)$ and, upon addition of carbon monoxide to the metal,

(20) Zhang, N. Ph.D. Thesis, University of Illinois, 1991.
(21) Marshman, R. W.; Shapley, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 8369−8378.
(22) Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3287−3294.
(23) (a) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331−4338. (b) Churchill, M. R.; Li, Y. J. *J. Organomet. Chem.* **1986**, *301*, 49−59. (c) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434−1443.
(24) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435−2443.
(25) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851−1864.
(26) (a) Farmery, K.; Kilner, M.; Midcalf, C. *J. Chem. Soc. A* **1970**, 2279−2285. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443−450. (c) Erker, G.; Fromberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68−69.

Scheme 6



1 3

$PhN{=}PPh_3$.[27] A hydrazido tungsten complex behaves similarly.[28] Other imido complexes have been shown to react with trialkyl- or triarylphosphines to form the free phosphinimines and the reduced metal complexes.[15,29]

The methyleneamido complex **2** cannot be an intermediate in the formation of **3** and $Ph_3P{=}NMe$ because **2** does not react with PPh_3 or with $[HPPh_3]^+$. Nucleophilic attack of PPh_3 on the imido nitrogen of **1** forms a phosphinimine complex, $(\eta^5\text{-}C_5H_5)Os(MeNPPh_3)(CH_2\text{-}SiMe_3)_2$. The phosphinimine complex is unstable and loses $MeN{=}PPh_3$ in the presence of excess phosphine to give **3**.

Synthesis and Structure of 4. Data from the NMR spectra of **4** allow us to propose a structure for this molecule. The carbon atoms of the two coordinated ethylene ligands are equivalent in the ^{13}C NMR spectrum. ^1H NMR shows two sets of ethylene protons in a AA′BB′ spin system. This has been observed in other ethylene complexes.[30] For example, the iridium(I) ethylene complexes $(\eta^5\text{-}C_5H_5)Ir(CH_2{=}CH_2)L$ and $(\eta^5\text{-}C_9H_7)\text{-}Ir(CH_2{=}CH_2)L$, where $L = C_2H_4$, CO, show an AA′BB′ spin system in the ^1H NMR spectrum for the ethylene ligand with coupling constants and chemical shifts similar to those of **4**.[31] To explain the equivalence of the carbon atoms, the ethylene ligands must be freely rotating about the osmium−ethylene axis. If the imino ligand lies in the plane which bisects the olefin ligands, rotation of each ethylene ligand would cause H^A to rotate into the position of $H^{A'}$ and H^B into $H^{B'}$ (Figure 1). Even in this symmetrical structure, the nitrogen-bound hydrogen would be pointed toward one of the two coordinated olefins making them inequivalent. Note that the methylene protons of the imine are inequivalent and show separate *cis* and *trans* coupling constants to this proton. However, the chemical shift differences of the resonances in these inequivalent ethylene ligands is much smaller than we can detect even in the ^1H NMR spectrum obtained on a 500 MHz instrument.

Complexes containing coordinated simple monodentate imines have been isolated.[32] For example, the synthesis of the methyleneimino complex $(\eta^5\text{-}C_5Me_5)\text{-}Ta(MeN{=}CH_2)Me_2$ was reported by Bercaw.[11] The C−N stretching vibration in the IR spectrum of **4** shows that the imine ligand has more single-bond than double-bond character. This has been observed in other reported imine complexes. The osmium−imine ligand is best represented as a heterometallacyclopropane. The kinetic product of the reaction may be the sterically favorable isomer with the methylene *trans* to the cyclopentadiene ligand. Later transition metals usually form stronger bonds with carbon atoms than with nitrogen or oxygen atoms. The sterically favored kinetic product should isomerize because having the methylene ligand *trans* to the cyclopentadienyl ligand should be thermodynamically less favorable than having the nitrogen ligand in this position (Scheme 7).

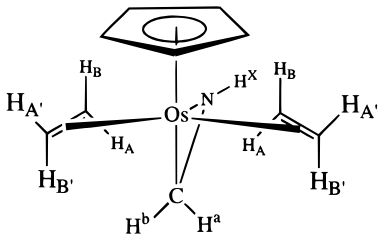
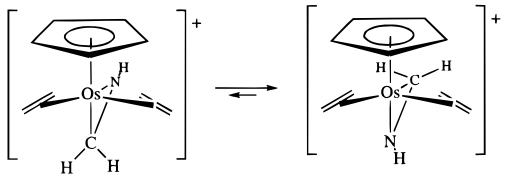


Figure 1. Proposed structure of **4**.

Scheme 7



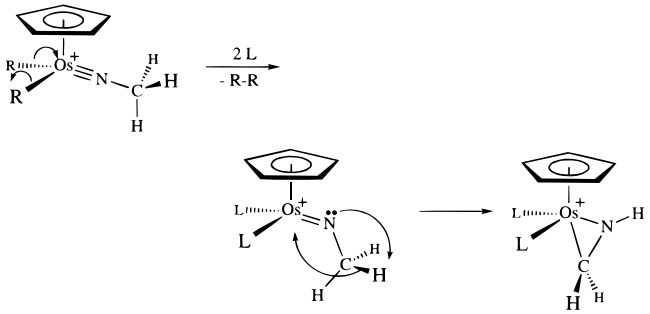
4 4'

Reductive elimination of the alkyl ligands precedes isomerization of the methylimido ligand in the formation of **4** from **1**. Complex **2** is protonated at carbon, not at nitrogen, by strong acids, and **2** does not react with ethylene. Reductive elimination of the alkyl ligands from **1** occurs slowly in solution, even in the absence of ethylene. Ethylene accelerates this process and allows us to trap the reduced metal complex. The strong π-donor imido ligand in the d^4 complex $[CpL_2Os{\equiv}NCH_3][SO_3CF_3]$ would be destabilized and should rapidly isomerize (Scheme 8).

Complex **4** is also produced in small quantities by the reaction of **1** with degassed water. The tetramethylsilane is produced by protonation of one of the (trimethylsilyl)methyl ligands, while the hexamethyldisiloxane is formed by the hydrolysis of a Si−C bond in this ligand. Hydrolysis of the (trimethylsilyl)methyl ligand may also produce a transient methylene species that

(27) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007−8009.
(28) Arntdsen, B. A.; Sleiman, H. F.; McElwee-White, L. *Organometallics* **1993**, *12*, 2440−2444.
(29) (a) Dobbs, D. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 3836−3837. (b) Huang, J.-S.; Che, C.-M.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1992**, 161−163. (c) Fourquet, J. L; Leblanc, M.; Saravanamuthu, A.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1991**, *30* , 3241−3243. (d) Harlan, E. W.; Holm, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 186−193. (e) Elliot, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191−2192. (f) Moubaraki, B.; Murray, K. S.; Nichols, P. J.; Thomson, S.; West, B. O. *Polyhedron* **1994**, *13*, 485−495.
(30) Eppley, D. F.; Wolczanski, P. T.; Van Duyne, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *5*, 584−585.
(31) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357−361.
(32) (a) Adams, R. D.; Chen, G. *Organometallics* **1992**, *11*, 3510−3511. (b) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661−2664. (c) Adcock, P. A.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 6494−6495. (d) Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161−6164 and references therein. (e) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336−2343. (f) Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161−6164 (g) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 7979−7980. (h) Chiu K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088−2097. (i) Takahashi, Yl.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525−528.

Scheme 8



reacts bimolecularly to yield ethylene (eqs 1−3). Schrock has reported evidence for the intermolecular coupling of methylene ligands in $Cp_2Ta(=CH_2)(CH_3)$ to give an ethylene complex.[33]

$$[CpOs(NCH_3)(CH_2SiMe_3)_2]^+ + H_2O \rightarrow Me_3SiOH + Me_3SiOH + Me_4Si + [(CH_2)CpOs(NCH_3)]^+ \quad (1)$$

$$2[(CH_2)CpOs(NCH_3)]^+ \rightarrow CH_2{=}CH_2 + 2[CpOs(NCH_3)]^+ \quad (2)$$

$$2CH_2{=}CH_2 + [CpOs(NCH_3)]^+ \rightarrow [CpOs(NCH_3)(CH_2{=}CH_2)_2]^+ \quad (3)$$

Formation of Polyaziridine. Certain transition metal imido complexes react with alkenes to give metallacyclic products. The reactions of $Cp_2Zr{=}NBu^t$ with ethylene and with norbornene produced azametallacyclobutanes by reversible, 2 + 2 cycloadditions. The metallacycle derived from norbornene was isolated.[10] Similarly, the (imido)vanadium complex $V(NSiMe_3)_2(NHSiMe_3)(OEt_2)$ reacted reversibly with ethylene and propylene to produce azametallacyclobutanes. These were not isolated because they isomerized to vinyl complexes, $V(NSiMe_3)(NHSiMe_3)_2(CH{=}CHR)$, at room temperature.[6] In neither system was the imido unit transferred to the olefin to give organic products. Poly(imido)osmium complexes, such as $Os(NCMe_3)_3(O)$, combine with olefins by 3 + 2 cycloaddition reactions to give isolable diazametallacyclopentanes.[34] Reduction gives the corresponding diaminoalkanes.

A 2 + 2 cycloaddition of ethylene to **1** would give $[CpR_2Os\overline{CH2CH_2NCH_3}][SO_3CF_3]$. Reductive elimination from this complex would produce *N*-methylaziridine and a coordinatively unsaturated osmium(IV) species, $[CpOsR_2][SO_3CF_3]$, but these products cannot survive the reaction conditions. While there are, as yet, no examples of the formation of aziridines from transition metal imido complexes and olefins,[35] the reverse of this reaction has been demonstrated.[36]

Conclusion

The nitrido complexes $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_4]$ are methylated by methyl trifluoromethanesulfonate giving the corresponding imido species, **1** and **5**, respectively. The reactivity of **1** is much greater than **5**. The increased reactivity may be attributed to the presence of two π-donor ligands in the former complex. Complex **1** is thermally unstable, and the alkyl ligands are lost by reductive elimination or electrophilic attack. Unlike **5**, **1** reacts with phosphines, olefins, acetylenes, pyridine, and water.

Higher acidity of the methylimido group in **1** leads to facile deprotonation reactions. Triphenylphosphine, pyridine, and water act as bases and deprotonate the imido ligand forming the first osmium(IV) methyleneamido complex, **2**. This complex has been completely characterized, and the data compare well with other transition metal alkylideneamido species reported in the literature. The complex is stable and can be reprotonated with strong acids to give **1**.

In the reaction of **1** with water, hexamethyldisiloxane, and small amounts of a bis(olefin)(imino)osmium complex, **4**, are also formed. Reductive elimination reactions of **1** in the presence of ethylene lead to the formation of a reduced imine complex, **4**, in good yield. Spectroscopic data for this complex correlate well with those reported in the literature for both alkylideneimino and ethylene complexes. Complex **2** does not react with olefins under the same conditions, and this complex cannot be an intermediate in the formation of **4** from **1**.

The reaction of **1** with triphenylphosphine or with ethylene leads to imido group transfer, forming a phosphinimine or polymers of methylaziridine, respectively. In the PPh_3 reaction, an osmium phosphine product has been isolated and characterized. No organometallic product has so far been isolated in imido transfer to ethylene.

Experimental Section

All reactions were conducted under N_2 using standard air-sensitive techniques. Anhydrous diethyl ether, THF, and hexane were distilled from Na/benzophenone, while toluene was distilled from Na. Methylene chloride and acetonitrile were distilled from CaH_2. The corresponding deuterated solvents were dried in the same manner and were stored over 4 Å molecular sieves. $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][BF_4]$, $[(\eta^5\text{-}C_5H_5)Os(^{15}NCH_3)(CH_2SiMe_3)_2][BF_4]$,[18] $[HPPh_3][BF_4]$, $MeN{=}PPh_3$, $[MeN(H)PPh_3]Br$,[37] and *N*-methylaziridine[38] were prepared according to literature procedures.

NMR spectra were recorded at 200 MHz on a Varian XL-200 NMR spectrometer, at 300 MHz on a General Electric QE-300 NMR spectrometer, at 360 MHz on a GE/Nicolet NT-360

(33) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389−2399.

(34) (a) Chong. A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420−3426. (b) Schofield, M. H.; Kee, T. P; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H., Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595−3604.

(35) Stoichiometric transfer of a derivatized nitride has been demonstrated: Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073−2074. There are examples of metal catalyzed aziridination of olefins with RN_3, RNIPh, and related reagents, but (imido)metal complexes have not been observed in these systems. (a) Kahn, A. A.; Kwart, H. *J. Am. Chem. Soc.* **1967**, *89*, 1951−1953. (b) Mansuy, D.; Mayh, J.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commum.* **1984**, 1161−1163. (c) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744−6746. (d) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326−5327.

(36) Atagi, L. M.; Over, D. E.; McAlister, D. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 870−874.

(37) Zimmer, H.; Singh, G. *J. Org. Chem.* **1963**, *28*, 483−486.

(38) (a) Stogryn, E. L.; Brois, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 605−609. (b) Elderfield, R. C.; Hageman, H. A. *J. Org. Chem.* **1949**, *14*, 605−615.

NMR spectrometer, at 400 MHz on a General Electric 400 NMR spectrometer, and at 500 MHz on a General Electric GN-500 NMR spectrometer. ^{31}P NMR spectra were referenced to external H_3PO_4. ^{1}H NMR second-order splitting patterns were simulated using ITRCAL program on a NIC1280 computer. Electronic spectra were recorded on an HP 8452 diode array UV/vis spectrometer. Gas chromatography was performed on a Hewlett Packard 5790 Series gas chromatograph. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR Spectrometer. GCMS were obtained on a VG 70-VSE instrument with EI/CI ion source. Elemental analyses were performed at the University of Illinois School of Chemical Sciences Microanalytical Laboratory.

Preparation of 1. The yellow crystals of (η^5-C_5H_5)-Os(N)(CH_2SiMe_3)$_2$ (0.045 g, 0.10 mmol) were dissolved in 1 mL of CH_2Cl_2 in small vial along with a small stirring bar. A 10 equiv amount of $MeOSO_2CF_3$ (0.16 mL, 1.45 mmol) was then added via syringe. The reaction mixture was stirred for 3 h at room temperature, and the yellow-orange solution turned darker orange-brown in color. The reaction mixture was then cooled to −30 °C and stored at that temperature for 2 d. The solution was filtered, and the solvent was removed under vacuum. The resulting orange-brown oil was washed several times with hexane. The product was crystallized from CH_2Cl_2 at −30 °C giving orange crystals of [CpOs(NCH_3)(CH_2SiMe_3)$_2$][SO_3CF_3] (0.056 g, 90% yield). IR (KBr pellet, cm^{-1}): 3107 (m, Cp ν_{CH}), 2956 (m, ν_{CH}), 2896 (m, ν_{CH}), 1439 (m, δ_{CH}), 1420 m, 1278 sh, 1252 (s), 1226 m, 1161 (s, ν_{SO}), 1033 (ν_{SO}), 850 (s, ν_{SiC}), 833 (s, ν_{SiC}), 639 (s, Cp δ_{CC}). ^{1}H NMR (500 MHz, CD_2Cl_2, 18 °C; δ): 6.06 (s, 5 H, C_5H_5); 3.05 (d, J = 12.9 Hz, 2 H, OsC*H*^{a}H^b); 2.78 (s, 3 H, $OsNCH_3$); 2.49 (d, J = 12.9 Hz, 2 H, OsCH^a*H*^{b}); 0.19 (s, 18 H, $SiCH_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 18 °C; δ): 96.2 (OsC_5H_5); 61.5 ($OsNCH_3$); 1.5 ($SiCH_3$); −6.3 ($OsCH_2$). UV/visible spectrum (CH_2Cl_2, 1.1 × 10^{-4} M, nm (ϵ, M^{-1} cm^{-1}): 232 (10 100), 276 (6119), 368 (sh).

Preparation of ^{15}N-1. This was prepared as above from (η^5-C_5H_5)Os(^{15}N)(CH_2SiMe_3)$_2$ and excess $MeOSO_2CF_3$. IR (KBr pellet, cm^{-1}): 3107 (m, Cp ν_{CH}), 2956 (m, ν_{CH}), 2896 (m, ν_{CH}), 1439 (m, δ_{CH}), 1420 m, 1278 sh, 1252 (s), 1226 m, 1161 (s, ν_{SO}), 1050 m, 1033 (ν_{SO}), 850 (s, ν_{SiC}), 833 (s, ν_{SiC}), 639 (s, Cp δ_{CC}). ^{1}H NMR (200 MHz, $CDCl_3$, 18 °C; δ): 6.09 (s, 5 H, OsC_5H_5); 3.00 (d, J = 12.9 Hz, 2 H, OsC*H*^{a}H^b); 2.82 (d, 4.4 Hz, 3 H, Os^{15}NCH_3); 2.46 (d, J = 12.9 Hz, 2 H, OsCH^a*H*^{b}); 0.19 (s, 18 H, Si(CH_3).

Preparation of 2. NaH (0.10 g, 4.1 mmol) was added to a stirred solution of **1** (0.020 g, 0.033 mmol) in 5 mL of THF. The brown solution changed to deep purple within 30 s. The mixture was filtered, solvent was removed from the filtrate under vacuum, and the residue was dissolved in hexane and purified by column chromatography using silylated silica gel/hexane. The purple band was collected, and solvent was removed under vacuum to give (η^5-C_5H_5)Os(NCH_2)(CH_2SiMe_3)$_2$ in 94% yield (0.0142 g, 0.031 mmol) as a purple oil. Anal. Calcd for $C_{14}H_{29}NOsSi_2$: C, 36.73; H, 6.39; N, 3.06. Found: C, 36.97; H, 6.52; N, 3.2. ^{1}H NMR (300 MHz, CD_2Cl_2, 19 °C; δ): 5.35 (s, 5 H, C_5H_5), 2.51 (d, J = 12.9 Hz, 2 H, OsC*H*^{a}H^b), 2.00 (d, J = 12.6 Hz, 2H, OsCH^a*H*^{b}), −0.07 (s, 18 H, $SiCH_3$), −0.57 (s, 2 H, NCH_2). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 18 °C; δ): 128.9 (NCH_2), 88.3 (C_5H_5), 2.4 ($SiCH_3$), −19.5 ($OsCH_2$). ^{13}C NMR assignments were confirmed by APT and HETCOR pulse sequences. IR (CH_2Cl_2 solution, cm^{-1}): 3011 (w, Cp ν_{CH}), 2956 (s, ν_{CH}), 2928 (s, ν_{CH}), 2896 (m, ν_{CH}), 1606 (m, ν_{NC}), 1464 (w, δ_{CH}), 1378 (w, δ_{CH}), 1240 (m, δ_{SiC}), 853 (s, ν_{SiC}), 828 (s, ν_{SiC}). UV−visible spectrum (CH_2Cl_2, nm (ϵ)): 232 (17 546), 260 (12 542), 368 (380). Mass spectrum (EI, 70 eV, *m*/*z*): 459, 457 (M^+)

Reaction of 1 with PPh_3. A solution of PPh_3 (0.048 g, 0.18 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **1** (0.055 g, 0.09 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 24 h, after which time the brown solution was filtered. The solvent was removed under vacuum, and the brown-yellow residue was extracted with ether. The purple ether extract was filtered, and solvent was removed from the filtrate. The residue was dissolved in hexane, the solution was filtered, and solvent was removed from the filtrate under vacuum. The residue was dissolved in a small amount of hexane and the solution was cooled to −30 °C to give purple crystals of **2** (0.020 g, 0.044 mmol, 49%).

The ether insoluble material from the reaction of **1** with PPh_3 was dissolved in CH_2Cl_2. Diethyl ether was added, and the solution was cooled to −30 °C. Brown crystals of **3** were collected by filtration and dried under vacuum (0.015 g, 0.019 mmol, 21%). ^{1}H NMR (300 MHz, CD_2Cl_2, 18 °C; δ): 7.30 (m, 15 H, PPh), 4.94 (s, 5 H, C_5H_5), 3.85 (dd, J_{HH} = 15 Hz, J_{PH} = 10 Hz, 2 H, OsC*H*^{a}H^b), 1.95 (dd, J_{HH} = 15 Hz, J_{PH} = 31 Hz, 2 H, OsCH^a*H*^{b}), −0.16 (s, 18 H, $SiCH_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 18 °C; δ): 137.5 (d, J_{PC} = 14 Hz, PPh), 134.0 (d, J_{PC} = 24 Hz, PPh), 128.9 (d, J_{PC} = 23 Hz, PPh), 128.8 (d, J_{PC} = 21 Hz, PPh), 83.21 (d, J_{PC} = 2.2 Hz, C_5H_5), 3.09 (d, J_{PC} = 3.1 Hz, $OsCH_2$), 0.02 ($SiCH_3$). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 18 °C; δ): 53.65 ($OsPPh_3$).

PPh_3 (0.033 g, 0.125 mmol) and **1** (0.011 g, 0.018 mmol) were dissolved in 0.7 mL of CD_2Cl_2 in a 5 mm NMR tube. ^{13}C and ^{31}P NMR spectra showed resonances for unreacted PPh_3 (^{31}P NMR, −4.91 ppm), **2**, **3**, [$HPPh_3$][SO_3CF_3] (^{31}P NMR, −0.15 ppm), and $MeN{=}PPh_3$ (^{31}P NMR, 15.76 ppm; ^{13}C NMR, 180.8 ppm (d, J = 24.7 Hz, NMe)).

Preparation of (η^5-C_5H_5)Os(^{15}N=CH_2)(CH_2SiMe_3)$_2$ (^{15}N-2). This was prepared as above, by the reaction of [(η^5-C_5H_5)Os(^{15}NCH_3)(CH_2SiMe_3)$_2$][SO_3CF_3] with PPh_3 in CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, 18 °C; δ): 5.30 (s, 5 H, C_5H_5), 2.44 (d, J = 12.8 Hz, 2 H, OsC*H*^{a}H^b), 2.00 (d, J = 12.8 Hz, 2 H, OsCH^a*H*^{b}), −0.09 (s, 18 H, $SiCH_3$), −0.60 (d, J = 3.1 Hz, 2 H, Os^{15}N=CH_2);

Reaction of 1 with H_2O. Complex **1** (0.011 g, 0.018 mmol) was dissolved in 0.75 mL of CD_2Cl_2 in a 5 mm NMR tube along with 4 μL (0.2 mmol) of degassed water. The reaction was monitored by ^{1}H NMR spectroscopy. Complex **2** was observed in the spectrum within 10 min. The starting material was completely consumed in 2 h, giving **2** (δ 5.35, 2.51, 2.00, −0.07, −0.56), $SiMe_4$ (δ 0.0), Me_3SiOH (δ 0.12), and a brown solid. After 24 h, **2** was completely degraded. There was solid deposited on the sides of the NMR tube, and the ^{1}H NMR showed $SiMe_4$, Me_3SiOH, $Me_3SiOSiMe_3$, and a small amount of [(η^5-C_5H_5)Os($NHCH_2$)(η^2-C_2H_4)$_2$][SO_3CF_3], **4** (vide infra). GCMS of the reaction mixture confirmed the presence of $SiMe_4$, Me_3SiOH, and $Me_3SiOSiMe_3$.

Reaction of 1 with Pyridine. Complex **1** (0.011 g, 0.018 mmol) was dissolved in 0.75 mL of CD_2Cl_2 in a 5 mm NMR tube along with 2 μL (0.024 mmol) of pyridine. The reaction was monitored by ^{1}H NMR spectroscopy. The starting material was completely consumed in 2.5 h, giving **2** (δ 5.35, 2.51, 2.00, −0.07, −0.56) and small quantities of $SiMe_4$ (δ 0.0), $Me_3SiCH_2CH_2SiMe_3$ (δ −0.03), and a brown solid. After 40 h, **2** was completely degraded and the reaction mixture consisted of pyridine, $SiMe_4$, soluble and insoluble osmium-containing products, and a small amount of $Me_3SiCH_2CH_2SiMe_3$. GCMS of the reaction mixture confirmed the presence of $SiMe_4$ and $Me_3SiCH_2CH_2SiMe_3$.

Protonation of (η^5-C_5H_5)Os(N=CH_2)(CH_2SiMe_3)$_2$ with HBF_4. Complex **2** (8.6 mg, 0.019 mmol) was dissolved in CD_2Cl_2, and the purple solution was added to a 5 mm NMR tube. HBF_4 (50 μL of a 0.164 M solution in methylene chloride, 0.008 mmol) was added via syringe to the purple solution. The solution immediately became orange in color. A ^{1}H NMR spectrum was obtained after addition which showed a 1:1 mixture of **1** and **2**.

Synthesis of [(η^5-C_5H_5)Os($HNCH_2$)(C_2H_4)$_2$][SO_3CF_3], 4. Complex **1** (0.028 g, 0.046 mmol) was dissolved in 0.75 mL of CD_2Cl_2. Excess ethylene (15 mL) was added slowly via syringe over a period of 30 min. The reaction was monitored by ^{1}H NMR spectroscopy. After 4 days, **1** was completely converted to **4**. The solution was filtered, and the solvent was removed from the orange-brown filtrate. The residue was extracted

with hexane, and by diethyl ether, and then dried for 1 h under vacuum to give **4** as a brown oil. Analytically pure crystals of **4** were obtained from thf/hexane solutions at −30 °C (0.016 g, 70%). Anal. Calcd for $OsC_{11}H_{16}NO_3SF_3{\cdot}OC_4H_8$: C, 32.08; H, 4.31; N, 2.49. Found: C, 31.75; H, 4.49; N, 2.55. IR (CH_2Cl_2 solution, cm^{-1}): 3155 (m, ν_{NH}), 3112 and 3067 (m, ν_{CH}), 2959 (m, ν_{CH}), 2930 (m, ν_{CH}), 1382 (s, ν_{NC}), 1166 (s, ν_{SO}), 1029 (s, ν_{SO}), 639 (s, δ_{CC}). ^{1}H NMR (500 MHz, CD_2Cl_2, 18 °C; δ): 12.15 (s, 1 H, HN), 7.95 (dd, J = 12.9 Hz, J = 12.9 Hz, 1 H, NCH^aH^b), 7.59 (dd, J = 12.9 Hz, J = 20.2 Hz, 1 H, NCH^aH^b), 5.39 (s, 5 H, C_5H_5), 3.18 (m, J = 12.0 Hz, J = 9.0 Hz, J = −0.70 Hz, 4 H, $CH^aH^b{=}CH^{b'}CH^{a'}$), 3.02 (m, J = 12.0 Hz, J = 9.0 Hz, J = −0.70 Hz, 4 H, $CH^aH^b{=}CH^{b'}CH^{a'}$). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 18 °C; δ): 172.42 (NCH_2), 84.64 (C_5H_5), 43.62 ($CH_2{=}CH_2$). ^{13}C NMR assignments were confirmed by APT and COSY pulse sequences.

Solutions of **4** in CD_2Cl_2 slowly isomerized. ^{1}H NMR (400 MHz, CD_2Cl_2, 18 °C; δ): 12.69 (s, 1 H, HN), 8.16 (dd, J = 13.0 Hz, J = 13.0 Hz, 1 H, NCH^aH^b), 7.70 (dd, J = 13.0 Hz, J = 20.3 Hz, 1 H, $N{=}CH^aH^b$), 5.61 (s, 5 H, C_5H_5), 3.48 (m, J = 12.0 Hz, J = 9.0 Hz, J = −0.70 Hz, 4 H, $CH^aH^b{=}CH^{b'}CH^{a'}$), 3.14 (m, J = 12.0 Hz, J = 9.0 Hz, J = −0.70 Hz, 4 H, $CH^aH^b{=}CH^{b'}CH^{a'}$).

Synthesis of $[(\eta^5\text{-}C_5H_5)Os(^{15}NHCH_2)(C_2H_4)_2][SO_3CF_3]$ (^{15}N-4). This is the same as described above for **4** using $[(\eta^5\text{-}C_5H_5)Os(^{15}NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ and excess ethylene. ^{1}H NMR (500 MHz, CD_2Cl_2, 18 °C; δ): 12.41 (ddd, J_{Nx} = 76.0 Hz, J_{xa} = 12.9 Hz, J_{xb} = 20.2 Hz, 1 H, $H^{x15}N{=}CH^aH^b$), 7.96 (td, J_{Na} = 3.2 Hz, J_{ab} = 12.9 Hz, J_{ax} = 12.9 Hz, 1 H, *syn*-$H^{x15}N{=}CH^aH^b$), 7.56 (dd, J_{ba} = 12.9 Hz, J_{bx} = 20.2 Hz, 1 H, *anti*-$H^{x15}N{=}CH^aH^b$), 5.35 (s, 5 H, C_5H_5), 3.15 (m, $J_{AA'}$ = 12.0 Hz, $J_{AB'}$ = 9.0 Hz, J_{AB} = −0.70 Hz, 4 H, $CH^AH^B{=}CH^{B'}CH^{A'}$), 3.02 (m, $J_{BB'}$ = 12.0 Hz, $J_{A'B}$ = 9.0 Hz, $J_{A'B'}$ = −0.70 Hz, 4 H, $CH^AH^B{=}CH^{B'}CH^{A'}$). ^{13}C {^{1}H} NMR (125.8 MHz, CD_2Cl_2, 18 °C; δ): 172.42 ($HN{=}CH_2$), 84.64 (C_5H_5), 43.62 ($CH_2{=}CH_2$).

Reaction of 1 with Ethylene under Pressure. Complex **1** (0.055 g, 0.090 mmol) was dissolved in 3 mL of CD_2Cl_2, and the solution was added to a medium-pressure reaction vessel under N_2. The vessel was pressurized with 760 psi $CH_2{=}CH_2$ at 41 °C and stirred for 4 days. After cooling of the sample to −78 °C, the ethylene was released. The vessel was warmed to 22 °C. Solvent and volatile products were removed under vacuum. The residue was extracted with CD_2Cl_2 and filtered. ^{1}H NMR (400 MHz, $CDCl_3$, 18 °C; δ): 7.84 (m); 7.56 (m); 2.91 (q, J = 7.1 Hz); 1.42 (pentet, J = 7.1 Hz); 1.27 (m); 0.84 (t, J = 7.3 Hz). Mass spectrum (EI, 70 eV, m/z): 213, 170, 141, 123, 109, 97, 83, 77 ($C_6H_5^+$), 69, 57 ($CH_2MeNCH_2^+$), 42 ($CH_2NCH_2^+$).

Reaction of *N*-Methylaziridine with Ethylene. *N*-Methylaziridine (0.006 g, 0.1 mmol) was dissolved in 3 mL of CD_2Cl_2, and the solution was added to a medium-pressure reaction vessel under nitrogen. The vessel was pressurized with 1200 psi of ethylene at 31 °C and stirred for 4 days. After cooling of the sample to −78 °C, the ethylene was released. The vessel was warmed to 22 °C. Solvent and volatile products were removed by vacuum distillation. The residue was extracted with CD_2Cl_2 and filtered into an NMR tube. ^{1}H NMR (400 MHz, $CDCl_3$, 18 °C; δ): 7.84 (m); 7.56 (m); 2.91 (q, J = 7.1 Hz); 1.42 (pentet, J = 7.1 Hz); 1.27 (m); 0.84 (t, J = 7.3 Hz). Mass spectrum (EI, 70 eV, m/z): 213, 170, 141, 123, 109, 97, 83, 77 ($C_6H_5^+$), 69, 57 ($CH_2MeNCH_2^+$), 42 ($CH_2NCH_2^+$).

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