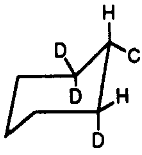
At 24 °C, in toluene as solvent, about 140 mol of $C_6H_{11}Cl$ was produced per mole of platinum in 120 h. Under the same conditions, in the absence of the platinum complex, cyclohexene and HCl gave no significant reaction. Similar results were obtained by using $Pt_2Cl_4(CO)_2$ or *cis*-$PtCl_2(CO)_2$ as catalyst precursors. In order to ascertain the stereochemistry of the reaction, cyclohexene-1,3,3-d_3 was hydrochlorinated in the presence of *cis*-$PtCl_2(CO)_2$. This reaction was run with a stoichiometric amount of the platinum complex in order to increase the rate and thus minimize deuterium scrambling over long times. At room temperature, all the olefin had substantially reacted; the solution contained the products shown in eq 4. It is worth noting that these results again differ considerably from those obtained in glacial acetic acid as solvent[20b,c] in the hydrochlorination of the same deuterated substrate, the main difference being that no anti product 3 was observed in the platinum-catalyzed reaction. The prevailing formation of the syn adduct suggests that addition of the HCl components occurs on the same side of the carbon–carbon double bond coordinated to platinum. Platinum-catalyzed hydrochlorination was also verified with 1-decene, *cis*-2-decene, *trans*-2-decene, *trans*-5-decene, styrene, and norbornene. In all cases, an increase of the reaction rate was observed with platinum(II): the increase was high (cyclohexene, 1-decene) or moderate (propylene, *cis*-2-decene, *trans*-2-decene, styrene, norbornene). For example, styrene and norbornene (Tables V and VI) undergo HCl addition without $PtCl_2(CO)_2$, but the reaction is promoted by the metal complex. In the case of nonsymmetrical olefins, such as propylene, 1-decene, and styrene, the product of hydrochlorination arising from the chlorine addition to the less-substituted carbon atom (Markovnikov rule) was found, namely, 2-chloropropane, 2-chlorodecane and 1-(chlorophenyl)ethane, respectively, as if protonation of the unsaturated carbon atom, leading to the more stable carbocation, were the primary attack.



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In conclusion, this paper has shown that soluble platinum(II) carbonyl derivatives are able to promote the hydrochlorination of several olefins. The reaction is regioselective in the case of terminal olefins giving the Markovnikov product. While the addition of HBr or HI to olefins are well known to occur at room temperature, HCl usually requires higher temperatures[35] or the presence of a catalyst, generally a Lewis acid, such as $AlCl_3$ or $FeCl_3$.[36,37]

Acknowledgment. The authors wish to thank the NATO Collaborative Research Grants Programme for an award (Grant No. 0052/89), the Consiglio Nazionale delle Richerche (C.N.R., Roma), Progetto Finalizzato di Chimica Fine II and the Natural Sciences and Engineering Research Council of Canada for support of this research.

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Synthesis and Reactivity of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$, the First Cyclopentadienyl–Nitrido Transition-Metal Complex

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The first cyclopentadienyl–nitrido complexes of a transition metal were prepared by the reactions between $[NBu^n_4][Os(N)Cl_2(CH_2SiMe_3)_2]$ and either NaC_5H_5 or LiC_5Me_5. The complexes $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and $(\eta^5\text{-}C_5Me_5)Os(N)(CH_2SiMe_3)_2$ were characterized by spectroscopic techniques and elemental analysis. They are soluble in organic solvents, volatile, and stable to air and water. The nitrogen atom in $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ is a "soft" Lewis base. It binds reversibly to BF_3 in solution, forming a 1:1 adduct. With silver(I) salts, a 2:1 adduct is formed. The silver-bridged complex $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$ was isolated in good yield from the reaction between $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and $AgBF_4$ and was structurally characterized. Crystal data for $Os_2AgSi_4F_4N_2C_{26}BH_{54}$ are $a = 15.348$ (3) Å, $b = 18.272$ (3) Å, $c = 14.114$ (2) Å, $\beta = 91.76$ (1)°, $V = 3956$ (2) Å^3, $\rho = 1.817$ g/cm^3, $\mu = 70.56$ cm^{-1}, space group = $P2_1/c$ ($C^5{}_{2h}$), and $Z = 4$. Final agreement factors are $R = 0.065$ and $R_w = 0.078$. The nitrido complex is displaced from silver by PPh_3 but not by $Me_2NCH_2CH_2NMe_2$. Alkylation of the nitrogen atom in $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and $CH_3OSO_2CF_3$ produced an alkylimido complex, $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2][OSO_2CF_3]$.

Introduction

Cyclopentadienylmetal compounds are known for all of the transition metals. The ligand is versatile and can coordinate through one carbon atom to form a simple σ bond to the metal, through three carbon atoms to form an allyl-type metal complex (η^3 coordination), or with all five carbon atoms (η^5 coordination). The σ-donor and π-acceptor abilities of the ligand stabilize transition-metal complexes in low oxidation states. Complexes containing both carbonyl and cyclopentadienyl ligands have been studied for many years.[1]

The cyclopentadienyl ligand is also compatible with metals in higher oxidation states. Many cyclopentadienyl

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransitionmetal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.7 (see also references therein).

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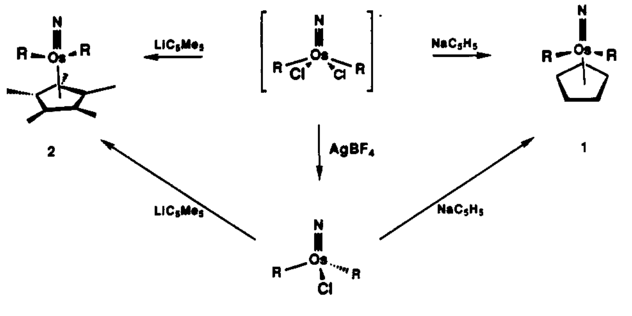
Scheme I



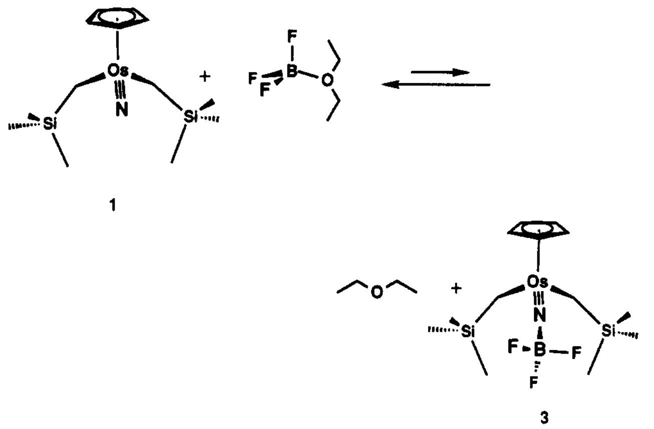
R = CH$_2$SiMe$_3$

compounds containing oxo[2-4] and imido[5,6] ligands have recently been prepared. However, no examples of cyclopentadienyl compounds containing nitrido ligands have previously been reported. The terminal nitrido ligand (N^{3-}) is isoelectronic with oxo (O^{2-}) and imido (NR^{2-}) ligands. It is similar to oxo and imido groups in its bonding to transition metals,[7] but differences have been observed in the reactivity of a series of oxo, imido, and nitrido complexes.[8] We present here the synthesis, characterization, and reaction chemistry of complexes of osmium(VI) that have both cyclopentadienyl and terminal nitrido ligands.

Results and Discussion

Synthesis of (η^5-C$_5$H$_5$)Os(N)(CH$_2$SiMe$_3$)$_2$ and (η^5-C$_5$Me$_5$)Os(N)(CH$_2$SiMe$_3$)$_2$. We have previously shown that the chloride ligands in the osmium complexes [NBu$^n_4$][Os(N)Cl$_2$R$_2$] (R = Me, CH$_2$SiMe$_3$) can be replaced by a variety of other monodentate and bidentate ligands.[9] Although the complexes [NBu$^n_4$][Os(N)X$_2$R$_2$] are coordinatively unsaturated, they do not bind donor molecules strongly in the sixth coordination position due to steric strain and the strong trans labilizing effect of the nitrido group. The anionic cyclopentadienyl group should also substitute for a chloride at the osmium center to form, initially, a σ cyclopentadienyl complex, [NBu$^n_4$][Os(N)Cl(η^1-C$_5$H$_5$)R$_2$].

Scheme II



The reaction between sodium cyclopentadienide and [NBu$^n_4$][Os(N)Cl$_2$(CH$_2$SiMe$_3$)$_2$] in diglyme is slow, requiring 5 h at 80 °C. Both chloride ligands are displaced and a η^5-cyclopentadienyl complex of osmium, (η^5-C$_5$H$_5$)Os(N)(CH$_2$SiMe$_3$)$_2$ (1), is produced. The osmium cyclopentadienyl complex can be isolated as a yellow crystalline solid in 34% yield after purification by chromatography on silica gel. It can also be readily purified by sublimation. Complex 1 is very soluble in hydrocarbon solvents and has a low melting point, 48–49 °C. The reaction between [NBu$^n_4$][Os(N)Cl$_2$(CH$_2$SiMe$_3$)$_2$] and lithium pentamethylcyclopentadienide in tetrahydrofuran produces the analogous osmium pentamethylcyclopentadienyl complex (η^5-C$_5$Me$_5$)Os(N)(CH$_2$SiMe$_3$)$_2$ (2) in 8% yield after 10 h at 80 °C.

Both cyclopentadienyl complexes can be prepared in higher yield starting from Os(N)Cl(CH$_2$SiMe$_3$)$_2$. The reaction between AgBF$_4$ and [NBu$^n_4$][Os(N)Cl$_2$(CH$_2$SiMe$_3$)$_2$] in diethyl ether cleanly produces Os(N)Cl(CH$_2$SiMe$_3$)$_2$ and AgCl. This neutral, four-coordinate complex of osmium(VI) can be isolated as a yellow crystalline compound from concentrated hexane solution, but it is very sensitive toward air and water. Solutions of Os(N)Cl(CH$_2$SiMe$_3$)$_2$ in diethyl ether, prepared in situ, react with sodium cyclopentadienide at room temperature to give 1 in 80% isolated yield. The pentamethylcyclopentadienyl complex, 2, is produced in 35% isolated yield by reaction of Os(N)Cl(CH$_2$SiMe$_3$)$_2$ and LiC$_5$Me$_5$ in tetrahydrofuran.

The cyclopentadienyl complexes are coordinatively saturated, 18-electron complexes. Complex 1 does not react with carbon monoxide, ethylene, trimethylphosphine, or triphenylphosphine. Both complexes 1 and 2 are thermally stable and stable to air and water.

The cyclopentadienyl complexes 1 and 2 were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy and by elemental analysis. A single resonance was observed for the cyclopentadienyl group in the ^{1}H and ^{13}C NMR spectra of 1, and there was no broadening of the cyclopentadienyl resonances down to −80 °C. The ^{1}H NMR of 1 showed a singlet at δ 5.63 for the equivalent cyclopentadienyl protons, two doublets at δ 2.08 and 0.85 for the diastereotopic methylene protons on the (trimethylsilyl)methyl ligands, and a singlet at δ 0.16 corresponding to the equivalent trimethylsilyl groups of the alkyl ligands. The same pattern was seen in the spectrum of 2, with the pentamethylcyclopentadienyl protons at δ 1.47, the methylene protons at δ 0.99 and 0.86, and the trimethylsilyl protons at δ 0.47. The α-carbon atoms of the (trimethylsilyl)methyl ligands showed an unusual upfield shift in the ^{13}C spectra

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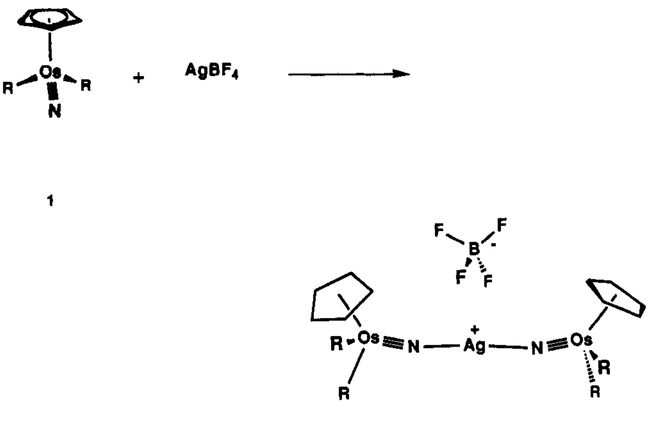
Scheme III



4

of these complexes. They resonated at −25 ppm in the ^{13}C NMR spectrum of 1 and at −14.6 ppm in the spectrum of 2. In other osmium(VI) complexes, the resonances for the α-carbon of (trimethylsilyl)methyl groups range from +5 to +50 ppm.

The infrared spectra show bands associated with the (trimethylsilyl)methyl and cyclopentadienyl ligands. A band at 1086 cm^{-1} in the spectrum of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ is assigned to the osmium–nitrogen stretching vibration. This was verified by isotopic labeling since this band shifts to 1050 cm^{-1} in $(\eta^5\text{-}C_5H_5)Os(^{15}N)(CH_2SiMe_3)_2$. The osmium–nitrogen stretching vibration was found at lower energy, 1076 cm^{-1}, in the more electron-rich pentamethylcyclopentadienyl complex, $(\eta^5\text{-}C_5Me_5)Os(N)(CH_2SiMe_3)_2$.

Formation of an Adduct between $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and Boron Trifluoride. The nitrogen atom of a terminal nitrido complexes has a nonbonding electron pair and should behave as a Lewis base. The nitrido-osmium complexes, $[NBu^n_4][Os(N)R_4]$,[10] and the nitrido-rhenium complex $Re(N)Cl_2(PEt_2Ph)_2$[11] have been shown to bind boron trifluoride and other Lewis acids at the nitrido nitrogen atom.

The addition of $BF_3{\cdot}OEt_2$ to methylene chloride solutions of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ results in the formation of a 1:1 adduct, $(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2(NBF_3)$ (3). The adduct cannot be isolated. There is a rapid exchange between 1 and 3 at room temperature in solution, and we see only averaged signals in the NMR spectra. At −80 °C exchange is slow and we observe separate resonances for both complexes by ^1H and ^{13}C NMR spectroscopy. Diethyl ether coordinates more strongly to boron trifluoride than does the nitridoosmium complex. The equilibrium favors 1 and $BF_3{\cdot}OEt_2$ with K_{eq} between 5×10^{-3} and 3×10^{-2} over the temperature range +25 to −80 °C. When 1 and $BF_3{\cdot}OEt_2$ are combined in an equimolar ratio (approximately 3.5×10^{-2} M initial concentration of each), we calculate a 93:7 ratio of 1 to 3 in solution on the basis of the chemical shift of the α protons in the ^1H NMR spectrum.

Silver(I) also coordinates to the nitrido group in 1. The addition of silver tetrafluoroborate to a methylene chloride solution of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ causes a rapid color change from yellow to orange. Removal of solvent in vacuo followed by crystallization of the crude product from toluene/hexane gives dark red prismatic crystals of $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$ (4) in good yield.

Table I. Bond Lengths (Å) in 4 (Labels Shown in Figure 1)

bond	Os1	Os2	bond	Os1	Os2
Os–N	1.60 (1)	1.61 (2)	Ag–N	2.15 (1)	2.12 (2)
Os–C_a	2.13 (2)	2.11 (2)	Os–C_b	2.13 (2)	2.16 (2)
C_a–Si_a	1.85 (2)	1.87 (2)	C_b–Si_b	1.88 (2)	1.86 (2)
Si_a–C_{1a}	1.88 (2)	1.90 (3)	Si_b–C_{1b}	1.89 (3)	1.86 (2)
Si_a–C_{2a}	1.85 (2)	1.88 (3)	Si_b–C_{2b}	1.87 (3)	1.89 (2)
SI_a–C_{3a}	1.83 (3)	1.84 (3)	Si_b–C_{3b}	1.85 (2)	1.84 (2)
C_1–C_2	1.39 (4)	1.42 (3)	C_2–C_3	1.41 (3)	1.41 (3)
C_3–C_4	1.41 (4)	1.41 (3)	C_4–C_5	1.38 (4)	1.42 (3)
C_5–C_1	1.47 (4)	1.38 (3)	Os–C_1	2.26 (3)	2.30 (2)
Os–C_2	2.18 (3)	2.22 (3)	Os–C_3	2.28 (2)	2.25 (2)
Os–C_4	2.47 (2)	2.43 (2)	Os–C_5	2.45 (3)	2.45 (2)
B–F_1	1.40 (3)		B–F_2	1.29 (3)	
B–F_3	1.40 (4)		B–F_4	1.35 (4)	
Os–(η^5-C_5H_5)	2.00 (3)	2.01 (3)			

Table II. Selected Bond Angles (deg) in 4 (Labels Shown in Figure 1)

angle	Os1	Os2	angle	Os1	Os2
N–Os–C_a	98.4 (8)	97.4 (8)	N1–Os–C_b	97.9 (8)	102.5 (7)
Ag–N–Os	166.7 (10)	163 (1)	N–Ag–N	175.8 (6)	
C_a–Os–C_b	87 (1)	84.6 (7)			
Os–C_a–Si	117 (1)	120.6 (9)	Os–C_b–Si	115 (1)	115.4 (9)
C_1–C_2–C_3	110 (3)	103 (2)	C_2–C_3–C_4	108 (2)	112 (2)
C_3–C_4–C_5	108 (2)	107 (2)	C_4–C_5–C_1	110 (2)	110 (2)
C_5–C_1–C_2	104 (2)	109 (2)	Cp–Os–N	141 (1)	139.4 (10)
Cp–Os–C_a	111 (1)	111 (1)	Cp–Os–C_b	109.2 (9)	108.7 (9)

The IR, ^1H NMR, and ^{13}C NMR spectra of the silver-bridged complex show marked similarities to those of the monometallic osmium complex, 1. Along with bands in the infrared spectrum due to the cyclopentadienyl and (trimethylsilyl)methyl ligands, there is a strong osmium–nitrogen stretching vibration at 1086 cm^{-1}. The frequency of the Os≡N stretching band is unchanged by coordination of the nitrogen atom to silver. The ^1H and ^{13}C NMR spectra of 4 are very similar to those of 1 except that the methylene carbon and the methylene proton resonance lines of the (trimethylsilyl)methyl groups are shifted slightly downfield. This may imply a slight decrease in electron density on the osmium center due to coordination of silver to the nitride.

The nitrido complex 1 binds more strongly to the "soft" Lewis acid Ag^+ than to the "harder" Lewis acid BF_3. We see no evidence for dissociation of silver from nitrogen in methylene chloride solution by NMR analysis. Amines, such as tetramethylethylenediamine, do not react with $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$. Triphenylphosphine reacts rapidly, forming $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ and $[Ag(PPh_3)_2][BF_4]$.

Molecular Structure of $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2(N)]_2Ag\}\{BF_4\}$. The structure of 4 was determined by single-crystal X-ray diffraction. The compound was found to be a dimer of the formula $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$. Bond lengths are given in Table I, while selected bond angles are given in Table II. Atom labels are shown in Figure 1.

The molecule consists of two $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ units connected by the nitrogen to a silver atom. Within the $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ unit is a distortion from the normal "piano stool" geometry of $(\eta^5\text{-}C_5H_5)W(O)(CH_2SiMe_3)_2$.[3] The angle between the center of the cyclopentadienyl ring, osmium, and the nitrogen atom is significantly greater (ca. 140°) than the Cp–Os–C angles (109, 111°). The structure of $(\eta^5\text{-}C_5Me_5)Re(O)(CH_2SiMe_3)(Me)$ also shows this distortion.[4,6]

There is a distinct ring slippage of the cyclopentadienyl ligand in 4. The cyclopentadienyl carbon–osmium bond lengths trans to the osmium–nitrogen bond are signifi-

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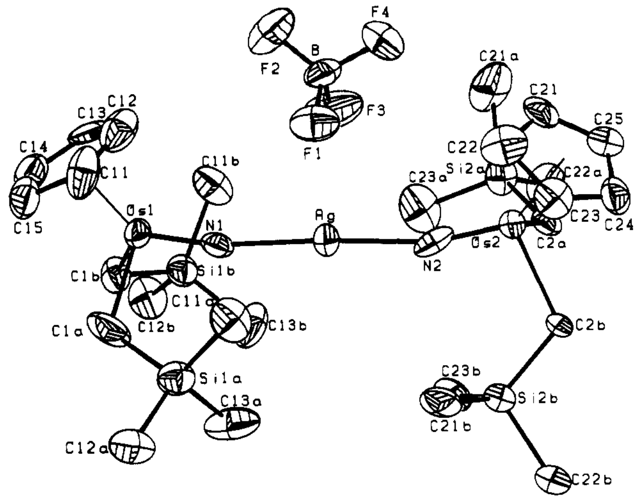
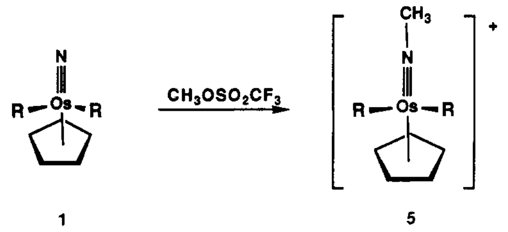


Figure 1. ORTEP diagram of 4.

Scheme IV



cantly longer (range, 2.47 (2)–2.43 (2) Å) than the others (range, 2.30 (2)–2.18 (3) Å). Cyclopentadienyl carbon–carbon bond distances also appear distorted, ranging from 1.38 (4) to 1.47 (4) Å in one ring and 1.38 (3) to 1.50 (3) Å in the other. The distortion results from the the strong trans effect of the nitrido ligands. A similar distortion has been observed previously in certain cyclopentadienyl complexes with oxo, imido, and μ-dinitrogen ligands.[4,6,12]

The osmium–nitrogen bond distances in this compound are short and correspond to triple bonds. The lengths 1.60 (1) and 1.61 (2) Å are considerably shorter than the length of 1.686 Å seen in the d^2 organometallic osmium imido complex $Os(NMe)(CH_2SiMe_3)_4$[13] and even shorter than the lengths 1.62 (1)–1.63 (1) Å found in organometallic osmium nitrido complexes.[13,14] The metal–nitrogen bonds are also shorter than in any of the known cyclopentdienyl imido complexes.

The two nitrogen atoms coordinate the Ag(I) cation in a nearly linear fashion. The N–Ag–N angle is 175.8 (6)°. The BF_4^- counterion is located very close to the silver cation. The Os-N-Ag angles (166.7 and 163°) are slightly smaller than the Re-N-Au angle (173.8°) in $Re(NAuCl)Cl_2(PMe_3Ph)_3$.[15]

Formation of $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][CF_3SO_3]$. Complex 1 reacts slowly with methyl trifluoromethanesulfonate to produce the cationic methylimido complex $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][CF_3SO_3]$ (5). The rate is first order in 1 and $CH_3OSO_2CF_3$ as is expected for an S_N2 reaction. The product is a dark orange, nonvolatile solid that was characterized y ^1H and ^{13}C NMR spectroscopy and by elemental analysis. The ^1H NMR spectrum shows a pattern of resonances similar to those of complexes 1–4 with the addition of a singlet for the methylimido protons at δ 2.8. The resonances of the α-carbon and α-hydrogen atoms of the alkyl groups are shifted downfield with respect to those of complexes 1–4. This indicates that some electron density is removed from the complex when the nitrogen atom uses its nonbonding electron pair to coordinate to a Lewis base, but more electron density is lost when the electron pair is used to form a σ bond to carbon.

The imido complex is thermally unstable. It decomposes at room temperature slowly in the solid state, more rapidly in solution. The products have not yet been identified.

Conclusion

Cyclopentadienyl and pentamethylcyclopentadienyl complexes of osmium(VI) have been prepared. The cyclopentadienyl ligands in $(\eta^5\text{-}C_5Me_5)Os(N)(CH_2SiMe_3)_2$ and $(\eta^5\text{-}C_5Me_5)Os(N)(CH_2SiMe_3)_2$ occupy three coordination sites, making the metal center six-coordinate with a valence electron count of 18. Because of this, the metal is unreactive toward donor molecules.

The nitrogen atom of the terminal nitride ligand in 1 has a nonbonding electron pair and behaves as a soft Lewis base. It forms a donor bond to the polarizable silver(I) cation. The osmium–nitrogen interaction is probably not dramatically changed upon coordination of silver. There is no change in the energy of the Os–N stretching vibration in the IR spectrum, and the X-ray crystal structure of 4 shows osmium–nitrogen triple bonds. The distortion of the cyclopentadienyl groups in 4 can be attributed to the strong trans effect of the nitrido ligand. The nitride complex is displaced by triphenylphosphine but not by the less polarizable amines. The nitrogen atom in 1 coordinates to boron trifluoride less strongly than does diethyl ether.

The nitrogen atom in 1 can also be alkylated with organic electrophiles. The cationic methylimido complex $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][CF_3SO_3]$ has been isolated and characterized. This species is much less stable than the parent nitrido complex, and an investigation of its reaction chemistry is underway.

Experimental Section

All reactions were done under a 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 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. The compounds $[NBu^n{}_4][Os(N)Cl_2(CH_2SiMe_3)_2]$,[10] NaC_5H_5,[16] and $LiC_5(CH_3)_5$[17] were prepared according to literature methods.

NMR spectra were recorded on one of the following spectrometers: GE GN-500 GE GN-300NB, GE QE300, and Varian XL-200 FT NMR. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer with 4-cm^{-1} resolution. Electronic spectra were recorded on an HP 8452 Diode Array UV/VIS spectrophotometer. Mass spectra were recorded on a Finnigan MAT CH-5 (EI) or 731 (FI, FD) instrument. All analyses were performed by the University of Illinois microanalytical service.

Synthesis of $(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2$ (1). Method 1. To a 100-mL flask equipped with a nitrogen inlet and reflux condenser was added $[NBu^n{}_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.250 g,

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0.36 mmol), NaC_5H_5 (0.160 g, 1.81 mmol), and 50 mL of diglyme. The solution was heated to 80 °C for 5 h and then allowed to cool to room temperature. Solvent was slowly removed in vacuo. The product was extracted with pentane, and the solution was filtered and flash-chromatographed on a silica gel column.[18] Analytically pure product (0.055 g, 34%) was obtained as a yellow oil after evaporation of the pentane solution. Yellow solid was obtained by sublimation at 25 °C, 10^{-4} Torr.

Method 2. To a solution of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.100 g, 0.14 mmol) in 30 mL of CH_2Cl_2 was added $AgBF_4$ (0.056 g, 0.28 mmol). The solution became cloudy and changed from orange-red to yellow. After stirring for 1 h, it was filtered through Celite. Solvent was removed in vacuo from the filtrate, and the residual yellow oil was extracted with hexane. The extract was filtered and concentrated. The hexane-soluble material was dissolved in 25 mL of diethyl ether. NaC_5H_5 (0.013 g, 0.14 mmol) was added, and the mixture was stirred for 14 h. The solution was concentrated, cooled to −30 °C, and filtered through Celite. Solvent was removed in vacuo to give the crude product as a yellow oil. Crystals of 1 were obtained (0.051 g, 0.114 mmol, 80%) from concentrated pentane solution. IR (KBr pellet, cm^{-1}): 2948 (m), 2923 (m), 2854 (s), 1462 (w), 1406 (w), 1253 (m), 1240 (m), 1086 (s, ν_{OsN}), 1025 (m), 988 (m). ^1H NMR (C_6D_6, 500 MHz, 18 °C): δ 4.91 (s, 5 H, $C_5\mathbf{H}_5$), 1.92 (d, J = 12.4 Hz, 2 H, $OsCH^a\mathbf{H}^bSi$), 0.92 (d, J = 12.3 Hz, 2 H, $OsC\mathbf{H}^aH^bSi$), 0.40 (s, 18 H, $Si(C\mathbf{H}_3)_3$). ^1H NMR ($CDCl_3$, 500.1 MHz, 18 °C): δ 5.63 (s, $C_5\mathbf{H}_5$), 2.05 (d, 2 H, $OsC\mathbf{H}^aH^bSi$), 0.88 (d, 2 H, $OsCH^a\mathbf{H}^bSi$), 0.14 (s, $Si(C\mathbf{H}_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.75 MHz, 19 °C): δ 93.5 (C_5H_5), 1.1 ($Si(CH_3)_3$), −25.3 ($OsCH_2Si$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.75 MHz, 18 °C): δ 93.8, 0.9, −25.1. ^{13}C NMR (CD_2Cl_2, 125.7 MHz): δ 93.7 (d, J = 180 Hz, C_5H_5), 1.3 (q, J = 115 Hz), −25.1 (t, J = 118 Hz). The DEPT pulse sequence and HETCOR pulse sequence (carbon data followed by proton data) were used to assign ^{13}C resonances. Anal. Calcd for $C_{13}H_{27}NOSi_2$: C, 35.19; H, 6.13; N, 3.16. Found: C, 35.31; H, 6.19; N, 3.11.

Synthesis of $(\eta^5\text{-}C_5H_5)Os(^{15}N)(CH_2SiMe_3)_2$. Prepared as above in 36% yield from $[NBu^n_4][Os(^{15}N)(CH_2SiMe_3)_2Cl_2]$ and NaC_5H_5. IR (KBr pellet, cm^{-1}): 2947 (m), 2920 (vw), 2879 (m), 1464 (vw), 1407 (w), 1253 (w), 1239 (m), 1050 (m, ν_{OsN}), 1026 (w), 988 (m).

Synthesis of $(\eta^5\text{-}C_5Me_5)Os(N)(CH_2SiMe_3)_2$ (2). Method 1. To a 100-mL flask equipped with a nitrogen inlet and reflux condensor was added $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.050 g, 0.072 mmol), LiC_5Me_5 (0.051 g, 0.36 mmol), and 20 mL of THF. The reaction mixture was heated to reflux for 10 h and then cooled to room temperature. Solvent was removed in vacuo and the residue extracted with pentane. After purification by flash chromatography on silica gel, 2 was obtained in 8% yield (3 mg).

Method 2. To a solution of $[NBu^n_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ (0.065 mg, 0.09 mmol) in 25 mL of CH_2Cl_2 was added $AgBF_4$ (0.037 g, 0.19 mmol). The solution became cloudy and changed from orange-red to yellow. After stirring for 1 h, it was filtered through Celite. Solvent was removed in vacuo and the filtrate, and the residual yellow oil was extracted with hexane. The extract was filtered and concentrated. The hexane-soluble material was dissolved in 30 mL of THF. LiC_5Me_5 (0.020 g, 0.14 mmol) was added, and the mixture was stirred for 20 h. The solution was filtered through Celite, and the THF was removed in vacuo. The yellow-brown residue was extracted with pentane, the extract was filtered, and the pentane was removed in vacuo. Yellow crystals of 2 (0.017 g, 0.033 mmol, 35%) were obtained by sublimation at 75 °C and approximately 10^{-4} Torr. IR (KBr pellet, cm^{-1}): 2949 (m), 2860 (m), 1458 (w), 1383 (w), 1240 (m), 1099 (sh), 1076 (s), 1042 (vw), 1032 (m), 858 (s), 830 (s). ^1H NMR (200 MHz, C_6D_6, 17.1 °C: δ 1.47 (s, 15 H, $C_5(C\mathbf{H}_3)_5$), 0.99 (d, J = 11.6 Hz, 2 H, $OsC\mathbf{H}^aH^bSi$), 0.86 (d, J = 11.7 Hz, 2 H, $OsCH^a\mathbf{H}^bSi$), 0.47 (s, 18 H, $Si(C\mathbf{H}_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 18 °C): δ 101.8 (C_5Me_5), 11.1 ($C_5(CH_3)_5$), 1.7 ($Si(CH_3)_3$), −14.6 ($OsCH_2Si$). MS (EI), 70 eV: M^+ m/z 515, 513.

Reaction of 1 with $BF_3 \cdot OEt_2$. A solution of 1 (0.010 g, 0.023 mmol) in 0.65 mL of $CDCl_3$ was added to a 5-mm NMR tube. ^1H NMR spectra were obtained after the addition of each equivalent of $BF_3 \cdot OEt_2$. Observed NMR shifts are shown in Table III.

Table III. 300-MHz ^1H NMR Data for 1 and $BF_3 \cdot OEt_2$

amt of $BF_3 \cdot OEt_2$ added, equiv	$(\eta^5\text{-}C_5H_5)$	CH_a		CH_b		CH_3
0	5.632	2.068	2.027	0.872	0.831	0.134
0.25	5.638	2.090	2.050	0.913	0.872	0.135
0.50	5.641	2.103	2.062	0.938	0.897	0.136
0.75	5.641	2.103	2.062	0.939	0.898	0.136
1.0	5.643	2.111	2.070	0.955	0.914	0.136
1.5	5.647	2.126	2.085	0.982	0.941	0.137
2.0	5.649	2.137	2.096	1.003	0.962	0.137
3.0	5.654	2.158	2.117	1.042	1.001	0.137
4.0	5.657	2.175	2.134	1.072	1.031	0.136
6.0	5.664	2.205	2.164	1.127	1.086	0.135
8.0	5.669	2.228	2.187	1.166	1.124	0.133

Spectra were obtained at 300 MHz, 17 °C. The labels CH_a and CH_b refer to the downfield and upfield methylene protons of the (trimethylsilyl)methyl ligand. CH_3 refers to the methyl protons of that ligand.

A solution of 1 (0.008 g, 0.018 mmol) and $BF_3 \cdot OEt_2$ (13.6 μL, 0.082 mmol) in CD_2Cl_2 (0.7 mL) was added to a 5-mm NMR tube. The composition of the species in solution was studied by ^1H and ^{13}C NMR spectroscopy from +19.1 to −80 °C. At the low-temperature limit, resonances for both 1 and $(\eta^5\text{-}C_5H_5)Os(NBF_3)(CH_2SiMe_3)_2$ (3) were seen. $(\eta^5\text{-}C_5H_5)Os(NBF_3)(CH_2SiMe_3)_2$: ^1H NMR (500.01 MHz, CD_2Cl_2, −80 °C) δ 5.81 (s, $C_5\mathbf{H}_5$), 2.73 (d, J = 12.5 Hz, $OsC\mathbf{H}^aH^bSi$), 2.02 (d, J = 12.5 Hz, $OsCH^a\mathbf{H}^bSi$), 0.09 (s, $Si(C\mathbf{H}_3)_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, −80 °C), δ 93.9 (C_5H_5), −0.1 ($Si(CH_3)_3$), −11.4 ($OsCH_2Si$).

Synthesis of $\{[(\eta^5\text{-}C_5H_5)Os(\mu\text{-}N)(CH_2SiMe_3)_2]_2Ag\}\{BF_4\}$ (4). To a solution of 1 (0.040 g, 0.092 mmol) in 20 mL of CH_2Cl_2 was added solid $AgBF_4$ (0.036 g, 0.18 mmol). The mixture was stirred for 3 h. Solvent was removed in vacuo, and the residue was dissolved in toluene and filtered. The product (0.032 g, 66% yield) was obtained as red crystals from toluene/hexane at −30 °C. IR (KBr pellet, cm^{-1}): 2948 (m), 2879 (m), 1408 (m), 1242 (s), 1113 (s), 1086 (s), 1048 (m), 1006 (m), 849 (vs), 829 (vs), 802 (m), 720 (m), 680 (m). ^1H NMR (300 MHz, $CDCl_3$, 17 °C): δ 5.76 (s, 5 H, C_5H_5), 2.38 (d, J = 12.5 Hz, 2 H, $OsC\mathbf{H}^aH^bSi$), 1.40 (d, J = 12.4 Hz, 2 H, $OsCH^a\mathbf{H}^bSi$), 0.12 (s, 18 H, $Si(C\mathbf{H}_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 17 °C): δ 94.6 (C_5H_5), 1.3 ($Si(CH_3)_3$), −18.9 ($OsCH_2$). Anal. Calcd for $AgBN_2Os_2Si_4F_4C_{26}H_{54}$: C, 28.86; H, 5.03; N, 2.59. Found: C, 29.09; H, 5.03; N, 2.55.

Reaction of 4 with PPh_3. Compound 4 was generated in situ by adding 4 equiv of $AgBF_4$ (0.033 g, 0.17 mmol) to a CH_2Cl_2 solution of 1 (0.018 g, 0.0042 mmol). The solution was filtered to remove any unreacted $AgBF_4$. PPh_3 (43 mg, 0.164 mmol) was added. The color changed from orange to yellow. After 20 min, solvent was removed in vacuo. A ^1H NMR spectrum of the residue showed *1* and $[Ag(PPh_3)_2][BF_4]$.

Reaction of 4 with TMEDA. The reaction was performed as above. TMEDA (5 μL) was added to a CH_2Cl_2 solution of 1. After 1 h, solvent was removed in vacuo. A ^1H NMR spectrum of the residue showed only 4.

Collection and Reduction of X-ray Data for 4. The red, opaque, prismatic crystal used for data collection was cut from a larger crystal. The crystals were air stable, and no special precautions were taken. The crystal was mounted by using epoxy to a thin glass fiber with the (041) scattering planes roughly normal to the spindle axes. Minor crystal movement was a problem throughout data collection. The first crystal selected move before completion of the first shell, so a second was selected and centered. The second crystal, of smaller volume than the first, moved during the collection of the second shell, but full intensity was recovered through recentering. The compound may react slowly with epoxy. No other problems were encountered in collecting these data, and there was no change in the appearance of the sample during the experiment. Unit cell parameters were obtained from a least-squares fit to the automatically centered settings for 15 reflections in the range 9.4° ≤ 2θ ≤ 19.6°. Data were collected on a Syntex $P2_1$ four-circle diffractometer equipped with Crystal Logic automation using Mo Kα radiation. The space group was unambiguously determiend from systematic absences. Cell parameters and other crystallographic information are given in Table IV along

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Table IV. Crystal and Experimental Data

formula	$Os_2AgSi_4F_4N_2C_{26}BH_{64}$
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	15.348 (3)
b, Å	18.272 (3)
c, Å	14.114 (2)
β, deg	91.76 (1)
V, Å^3	3956 (2)
Z	4
dens (calc), g/cm^3	1.817
dimens, mm	0.2 × 0.4 × 0.5
μ, cm^{-1}	70.56
transm factor range	0.265–0.052 (numerical)
2θ limit, deg (octants)	46° (+h,+k,+l)
no. of intensities (unique, R_i)	6089 (4575, 0.081)
no. of intensities > $2.58\sigma(I)$	3692
R	0.065
R_w (for $w = 1/\sigma^2(F_o) + pF_o^2$)	0.078 (p = 0.03)
max dens in ΔF map, e/Å^3	2.58

with additional details concerning the collection of the data.

Solution and Refinement of the Structure. The structure was solved by direct methods (SHELXS-86);[19] correct positions for the osmium and silver atoms were deduced from an E map. Subsequent least squares-difference Fourier calculation revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for nonhydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. The highest peaks in the final difference map were in the vicinity of the heavy-metal positions. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors.

Synthesis of $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2][OSO_2CF_3]$ (5). A solution of 1 (10 mg, 0.023 mmol) in $CDCl_3$ (0.65 mL) was placed in a 5-mm NMR tube along with $MeOSO_2CF_3$ (26 μL, 0.23 mmol). The reaction was monitored by ^{1}H NMR spectroscopy. After 10 h, the reaction mixture was filtered and solvent and unreacted starting materials were removed in vacuo. The residue consisted of 9 mg (64%) of analytically pure 4. ^{1}H NMR (500 MHz, CD_2Cl_2, 18 °C): δ 6.06 (s, C_5H_5), 3.05 (d, J = 12.9 Hz, $OsCH^aH^b$), 2.78 (s, NCH_3), 2.49 (d, J = 12.9, $OsCH^aH^b$), 0.19 (s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 18 °C): δ 96.2 (C_5H_5), 61.5 (NCH_3), 1.5 ($Si(CH_3)_3$), −6.3 ($OsCH_2$). Anal. Calcd for $C_{15}H_{30}F_3NO_3OsSSi_2$: C, 29.64; H, 4.97; N, 2.30. Found: C, 29.85; H, 4.79; N, 2.37.

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Supplementary Material Available: For $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$, tables of atomic coordinates, thermal parameters, and selected distances and angles (5 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Rearrangement of Acetylide and Vinylidene Ligands on the Coordination Spheres of Cluster Complexes. Reaction of the Trinuclear Acetylide Cluster $CpWOs_2(CO)_8(C{\equiv}CPh)$ with Mononuclear Metal Hydride Complexes $LW(CO)_3H$ (L = Cp, Cp*)

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Reaction of $CpWOs_2(CO)_8(C{\equiv}CPh)$ with 1.2 equiv of Me_3NO in a mixture of dichloromethane–acetonitrile at room temperature followed by in situ reaction with hydride complexes $LW(CO)_3H$, L = Cp and Cp*, in refluxing toluene produced the acetylide cluster complexes $CpLW_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2a**, L = Cp; **2b**, L = Cp*) and vinylidene cluster complexes $CpLW_2Os_2(CO)_9(CCHPh)$ (**3a**, L = Cp; **3b**, L = Cp*). Heating of the acetylide or vinylidene complex in refluxing toluene induced a reversible rearrangement, giving a mixture of both isomeric complexes. The structures of complexes **2b** and **3b** have been determined by single-crystal X-ray diffraction. Crystal data for **2b**: space group $P2_1/c$; a = 34.301 (6), b = 12.319 (4), c = 24.718 (6) Å; β = 103.38 (2)°; Z = 12; final R_F = 0.092, R_w = 0.101 for 8771 reflections with $I > 2\sigma(I)$. Crystal data for **3b**: space group $P4_2/n$; a = 25.486 (6), c = 9.747 (4) Å; Z = 8; final R_F = 0.034, R_w = 0.030 for 3724 reflections with $I > 2\sigma(I)$.

Introduction

The C_2 hydrocarbons hold a key position in the development of organometallic chemistry.[1] Much research has been focused on the synthesis of complexes containing the so-called C_2 hydrocarbon ligands such as acetylene, ethylene, vinyl, vinylidene, or acetylide.[2] The synthesis

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