Inorg. Chem. **1994**, *33*, 498–502

Synthesis of Nitridoosmium(VI) Phosphine Complexes

Patricia A. Shapley,* Robert M. Marshman, Jeanine M. Shusta, Zewdu Gebeyehu, and Scott R. Wilson

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received September 14, 1993[⊗]

Organoosmium(VI) complexes of PMe_3, PPh_3, and $Ph_2PCH_2CH_2PPh_2$ (dppe) have been prepared and characterized. Unlike inorganic complexes of nitridoosmium(VI), the alkyl complexes are not reduced by basic phosphines. The reactions of $[NBu_4][Os(N)(CH_2SiMe_3)_4]$ with HBF_4 in the presence of either PMe_3 or PPh_3 produces $Os(N)(CH_2SiMe_3)_3(PR_3)$. The addition of either PMe_3 or dppe to $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ produces $Os(N)(CH_2SiMe_3)_2L_2Cl$ (L = PMe_3, $^1/_2$ dppe). Abstraction of the chloride ligand in $Os(N)(CH_2SiMe_3)_2L_2Cl$ with $[Ag(NCMe)_4][BF_4]$ gives $[Os(N)(CH_2SiMe_3)_2L_2(NCMe)][BF_4]$. In the absence of acetonitrile, $[Os(N)(CH_2SiMe_3)_2L_2][BF_4]$ forms. The molecular structure of $[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)][BF_4]$ was determined by X-ray diffraction. Crystals are monoclinic in space group $P2_1/a$ with $a = 17.544(7)$ Å, $b = 12.269(5)$ Å, $c = 20.666(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 104.76(3)°$, $Z = 4$, $R = 0.036$, and $R_w = 0.038$.

Introduction

Trialkyl- and triarylphosphines are among the most important ligands for transition metals. They form complexes with all of the transition metals and bind to metals in a wide range of oxidation states.[1] These ligands can greatly modify the electronic and steric properties of the metal center. The ligand cone angle and the electron-donor ability of the phosphine have been shown to affect substitution reactions at the metal center.[2]

Although some high-oxidation-state oxo, sulfido, and nitrido complexes are stable to tertiary phosphines, many others are reduced by these molecules.[3] A common reaction between metal–oxo complexes and phosphines gives reduced metal species and phosphine oxides.[4] Similarly, sulfido complexes can react with phosphines to produce phosphine sulfides and a reduced metal complex. Trialkyl- or triarylphosphines add to the nitrogen atom in certain metal–nitrido complexes, reducing the metal center by two electrons and forming a phosphoraniminato ligand. For example, the rhenium(VII) nitrido complexes $Re(N)Cl_4$ and $Re(N)(SPh)_4$ react with PPh_3 at the nitrido ligand to give the rhenium(V) phosphoraniminato complexes $Re(NPPh_3)Cl_4(PPh_3)$ and $Re(NPPh_3)(SPh)_4$ while the more electron-rich rhenium(V) nitrido complexes $Re(N)Cl_2(PR_3)_2$ are not reduced by phosphines.[5,6]

Inorganic nitrido complexes of osmium(VI) and ruthenium(VI) are reduced by triphenylphosphine, but we have found that the nitrido ligand in certain organometallic nitridoosmium(VI) complexes are stable to triphenylphosphine and even to the more basic trialkylphosphines. In this paper, we report the reactions of nitridoalkylosmium(VI) complexes with triphenylphosphine, trimethylphosphine, and 1,2-bis(diphenylphosphino)ethane (dppe).

Results

Synthesis of $Os(N)(CH_2SiMe_3)_2ClL_2$ (L = PMe_3, $^1/_2$ dppe). The addition of excess trimethylphosphine to a methylene chloride solution of $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ causes the color to change from dark orange to yellow. The product, *trans*-$Os(N)(CH_2SiMe_3)_2Cl(PMe_3)_2$ (**1**), can be isolated in 60–70% yield as yellow crystals by removing the reaction solvent under vacuum, extracting the residue with hexane, and cooling the hexane solution. Conductivity studies on **1** show it to be the neutral molecule $Os(N)(CH_2SiMe_3)_2Cl(PMe_3)_2$, rather than an ionic complex, $[Os(N)(CH_2SiMe_3)_2(PMe_3)_2][Cl]$, in polar organic solvents.

The product was characterized by IR and NMR spectroscopy and by elemental analysis. The infrared spectrum shows bands due to trimethylphosphine and (trimethylsilyl)methyl ligands and a band at 1094 cm^{-1} for the osmium–nitrogen stretching vibration. In the ^{1}H NMR spectrum of **1** are resonances for the six equivalent methyl groups of the PMe_3 ligands, for the four equivalent methylene protons of the (trimethylsilyl)methyl ligands, and for the six equivalent methyl groups of the (trimethylsilyl)methyl ligands. The equivalent methylene protons of the (trimethylsilyl)methyl groups are coupled to two equivalent phosphorus atoms. The triplet for these protons collapses into a singlet in the phosphorus-decoupled spectrum. The $^{31}P\{^1H\}$ NMR spectrum includes a single peak at −35 ppm for the phosphorus atoms of the PMe_3 ligands.

A bis(diphenylphosphino)ethane complex, $Os(N)(CH_2SiMe_3)_2(dppe)Cl$ (**2**), is prepared similarly from $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and dppe or from the chloride-bridged dimer $[Os(N)(CH_2SiMe_3)_2Cl]_2$ and dppe in dichloromethane solution. The dppe complex must have a *cis* arrangement of alkyl ligands due to the presence of the chelating diphosphine ligand. The ^{1}H NMR of **2** is consistent with this structure and shows that the two methylene protons on each equivalent alkyl are diastereotopic. The ^{31}P NMR spectrum of **2** has a single resonance for the equivalent phosphorus atoms of the *cis*-chelated dppe ligand at 29.8 ppm.

Another neutral triphenylphosphine complex, *cis*-$Os(N)(CH_2SiMe_3)_2Cl(PPh_3)$ (**3**), is formed by the reaction between $[Os(N)(CH_2SiMe_3)_2Cl]_2$ and PPh_3. Even with excess triphenylphosphine, only one phosphine coordinates to the metal center. The ^{31}P NMR spectrum shows only one type of phosphorus, and the ^{1}H NMR shows that there are two kinds of alkyl groups in the molecule, one *cis* and one *trans* to the phosphine. The reaction between $[Os(N)(CH_2SiMe_3)_2Cl]_2$ and dppe produces the 6-coordinate complex $Os(N)(CH_2SiMe_3)_2(dppe)Cl$ (**2**).

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1994.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Section 3.3.

(2) (a) Wilson, M. R.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 2044–2050. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole; Monterey, CA, 1985; Chapter 4.

(3) Nugent, W. A.; Meyer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience, New York, 1988; Chapter 6.3.

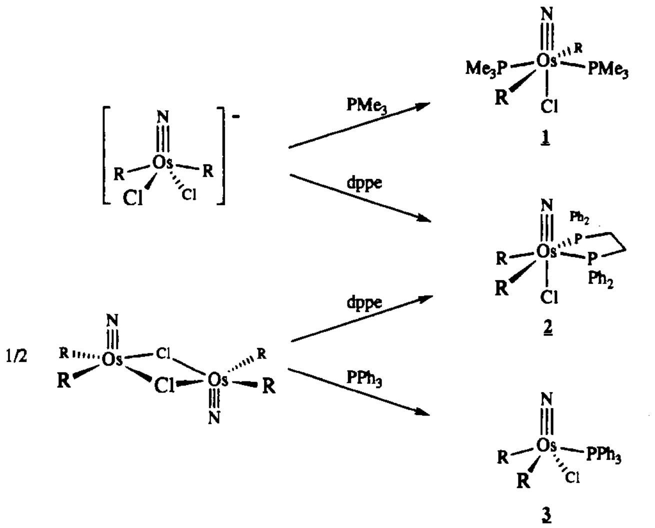
(4) For example see: (a) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671–4679. (b) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 200–202. (c) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183–221.

(5) (a) Dilworth, J.; Neaves, B.; Hutchinson, J.; Zubieta, J. *Inorg. Chim. Acta* **1982**, *65*, L223–L224. (b) Dehnicke, K.; Prinz, H.; Kafitz, W.; Kujanek, R. *Liebigs Ann. Chem.* **1981**, 20–27.

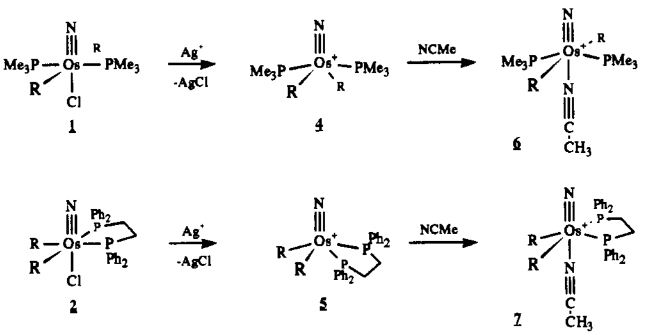
(6) Yam, V. W. W.; Tam, K. K.; Cheng, M. C.; Peng, S. M.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 1717–23.

0020-1669/94/1333-0498$04.50/0

Scheme 1



Scheme 2



Synthesis of $[Os(N)(CH_2SiMe_3)_2L_2][BF_4]$ and $[Os(N)(CH_2SiMe_3)_2(NCMe)L_2][BF_4]$ (L= PMe_3, $^1/_2$ dppe). The addition of $AgBF_4$ to methylene chloride solutions of **1** or of **2** results in the immediate precipitation of 1 equiv of AgCl and the formation of cationic complexes *trans*-$[Os(N)(CH_2SiMe_3)_2(PMe_3)_2][BF_4]$ (**4**), and *cis*-$[Os(N)(CH_2SiMe_3)_2(dppe)][BF_4]$ (**5**). In each case, analytically pure crystals are obtained by removing the solvent from the reaction mixture under vacuum, extracting the residue with toluene, and cooling the toluene solution. The cationic phosphine complexes decompose rapidly in air. Conductivity studies confirm that **4** is a salt in polar organic solvents.

The cationic phosphine complexes **4** and **5** react with small quantities of acetonitrile to give the 6-coordinate complexes *trans*-$[Os(N)(CH_2SiMe_3)_2(PMe_3)_2(NCMe)][BF_4]$ (**6**) and *cis*-$[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)][BF_4]$ (**7**), respectively. Complex **7** is quite stable and does not lose the acetonitrile ligand even under high vacuum. The reaction between $[Ag(NCMe)_4][BF_4]$ and **2** produces only **7**. The more electron-rich trimethylphosphine complex, **6**, readily dissociates its acetonitrile ligand and has been characterized only by ^1H NMR and IR spectroscopy.

The signal for the equivalently coordinated phosphorus atoms in the ^{31}P NMR spectrum of each of the cationic complexes **4**, **5**, and **7** shifts upfield by 17–18 ppm from the neutral complexes **1** and **2**. The IR spectra of complexes **4**–**7** include strong bands due to the phosphine ligands, the alkyl groups, and the BF_4 counterion. Complexes **6** and **7** have bands at 2294 and 2268 cm^{-1} for the C–N stretch of the coordinated acetonitrile.

Molecular Structure of $[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)][BF_4]$. The osmium center in **7** is in a distorted octahedral environment. The nitride ligand and the nitrogen atom of the coordinated acetonitrile are *trans* to one another with an angle of nearly 180°. The osmium–nitrido bond distance of 1.638(5) Å is similar to the Os–N distances in the 6-coordinate 2-pyridinethiolato complex $[Os(N)(CH_2SiMe_3)_2(2\text{-}SNC_5H_4)]_2$, 1.62(1) and 1.64(1) Å.[7] The osmium–nitrogen bond in the 5-coordinate alkyl nitrido complexes varies between 1.617(6) and 1.631(8) Å.[8] The presence of the acetonitrile ligand increases the osmium–nitride bond distance very slightly.

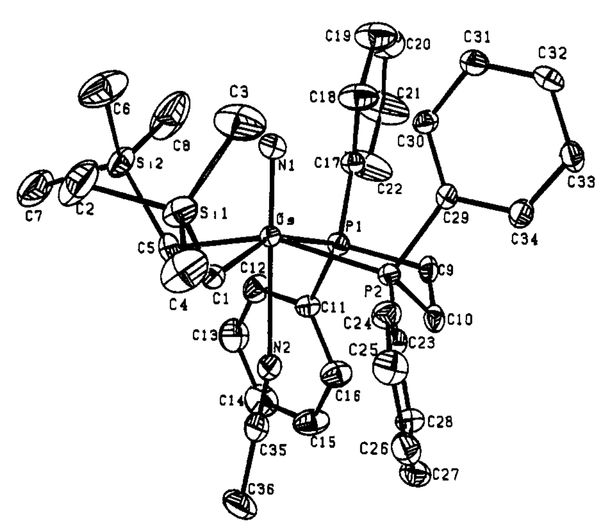


Figure 1. ORTEP diagram of $[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)]\cdot[BF_4]\cdot{}^1/_2C_4H_{10}O$.

Table 1. Selected Bond Distances and Angles

			Distances, Å				
Os–P1	2.455(2)	Os–P2	2.451(2)	Os–N1	1.638(5)		
Os–Cl	2.147(6)	Os–C5	2.142(6)	Os–N2	2.399(6)		
N2–C35	1.119(10)	C35–C36	1.47(1)	P1–C9	1.841(7)		
P2–C10	1.823(7)	C9–C10	1.522(10)				
			Angles, deg				
P1–Os–P2	81.67(6)	P1–Os–N1	98.9(2)	P1–Os–Cl	157.4(2)		
P1–Os–C5	92.7(2)	P1–Os–N2	79.3(1)	N1–Os–Cl	103.4(3)		
N1–Os–C5	100.5(3)	N1–Os–N2	178.2(2)	Cl–Os–C5	86.9(3)		
C5–Os–N2	79.7(2)	Os–N2–C35	168.2(6)	N2–C35–C36	178.8(9)		

The bond between osmium and the nitrogen of coordinated acetonitrile at 2.399(6) Å is relatively long. Other ruthenium and osmium acetonitrile complexes have metal–nitrogen distances between 2.04 and 2.14 Å.[9]

The coordination geometry is distorted from octahedral with the equatorial ligands bent toward the acetonitrile ligand. The angles between the nitrido atom and the four equatorial ligands is approximately 100°, while the angle between the acetonitrile nitrogen and these ligands is approximately 78°. In 5-coordinate alkylnitridoosmium(VI) complexes, the angles between the nitrido atom and the equatorial ligands averages 106°.[8]

Synthesis of $Os(N)(CH_2SiMe_3)_3(PR_3)$ (R = Me, Ph). Two neutral, 5-coordinate phosphoros complexes, $Os(N)(CH_2SiMe_3)_3(PMe_3)$, (**8**), and $Os(N)(CH_2SiMe_3)_3(PPh_3)$ (**9**), were prepared by the reaction of $[Y][Os(N)(CH_2SiMe_3)_4]$ (Y= PPh_4, NBu_4) with trimethylphosphonium tetrafluoroborate and triphenylphosphonium tetrafluoroborate, respectively, in methylene chloride. The reaction with triphenylphosphonium tetrafluoroborate is instantaneous with an immediate color change from yellow to orange, while that with the trimethylphosphonium tetrafluoroborate occurs more slowly. These complexes are isolated as analytically pure yellow or orange crystals in 80–90% yield from concentrated hexane solutions.

Both complexes have been characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, infrared and mass spectroscopy, and ele-

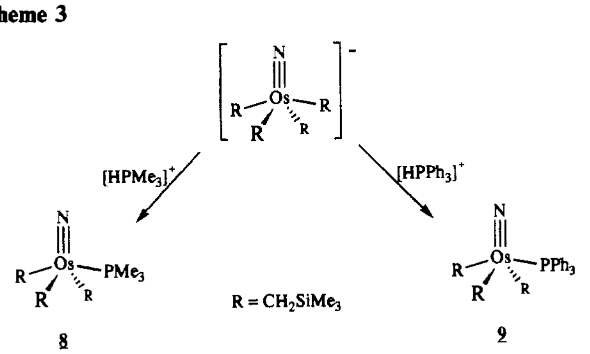
---

[7] Zhang, N.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1988**, *7*, 1126–1131.

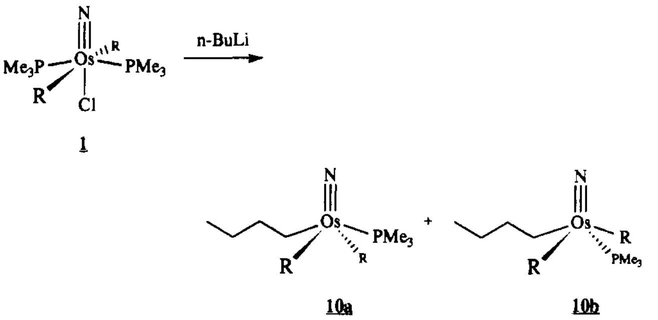
[8] (a) Shapley, P. A.; Gebeyehu, Z.; Zhang, N.; Wilson, S. R. *Inorg. Chem.*, in press. (b) Shapley, P. A.; Own, Z. Y.; Huffman, J. C. *Organometallics* **1986**, *5*, 1269–1271.

[9] (a) Das, B. K.; Chakravarty, A. R. *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **1992**, *31A*, 408–411. (b) Cox, D. N.; Small, R. W. H.; Roulet, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2013–2018. (c) Robinson, P. D.; Ali, I. A.; Hinckley, C. C. *Acta Crystallogr.* **1991**, *C47*, 1397–1401.

Scheme 3



Scheme 4



mental analysis. In the ^{1}H NMR spectra of complexes **8** and **9**, the equivalent methylene protons of the trimethylsilylmethyl group *trans* to the phosphine are coupled to phosphorus to give a doublet. The diastereotopic methylene protons of the *cis* (trimethylsilyl)-methyl groups show both proton and phosphorus couplings. The ^{31}P NMR spectra of both **8** and **9** show a singlet for the phosphorus of the trimethylphosphine and triphenylphosphine ligands at -12.92 and 30.7 ppm, respectively. The singlet assigned to the phosphorus of the triphenylphosphine ligand in **9** is quite broad.

Reactions with Bases. The cationic alkyl complexes **4** and **5** act as Lewis acids in their reactions with trace amounts of acetonitrile but neither functions as a source of protons. There is no reaction between these complexes and NaH, DBU, *n*-BuLi, or $Ph_3P{=}CH_2$. Complex **1** is alkylated by *n*-butyllithium to form two isomeric butyl complexes, *cis* and *trans* isomers of $Os(N)(CH_2SiMe_3)_2(CH_2CH_2CH_2CH_3)(PMe_3)$ (**10a,b**), isolated together as a yellow oil.

Discussion

Griffith and co-workers first reported the nucleophilic attack of tertiary phosphines on metal nitrides to form phosphoraniminato ligands. They showed that the osmium(VI) complexes $[NBu_4][Os(N)Cl_4]$ and $Os(N)Cl_3L_2$ (L = $AsPh_3$, $SbPh_3$, $AsEt_3$, $^1/_2$ bpy, PEt_3, PPh_3, PPh_2Et, $PPhEt_2$, PPh_2Me, $PPhMe_2$) reacted with PPh_3 or more basic phosphines to generate osmium(IV) complexes with the coordinated $[R_3PN]^-$ ligand.[10] A related terpyridyl complex of osmium(VI), $[Os(N)Cl_2(tpy)][PF_6]$, also forms an osmium(IV) phosphoraniminato complex upon reaction with triphenylphosphine.[11] Similar reactions occur with nitrido complexes of Mo(VI),[12] Mo(V),[13] and Re(VII).[5]

We have shown that organometallic nitridoosmium(VI) complexes $[NBu_4][Os(N)R_4]$ and $(\eta^5\text{-}C_5H_5)Os(N)R_2$ (R = CH_2SiMe_3) do not react with triaryl- or trialkylphosphines.[14,15] It is interesting that, when X is Cl, $[NBu_4][Os(N)X_4]$ is reduced by triphenylphosphine but, when X is an alkyl group, the complex is stable to PPh_3 and to the more basic PMe_3. One difference between these two complexes is that, for $[NBu_4][Os(N)Cl_4]$, the chloride ligands are labile and one, two, or three of these may be substituted by donor ligands. With that in mind, we treated $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with phosphines. The chloride ligands in this complex are quite labile and can be replaced by oxy anions,[16] sulfur donors,[7] and pyridine.[17]

The dialkyl dichloro complex $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ does react with PMe_3 and with dppe, but the metal center is not reduced in these reactions. Instead, stable, 6-coordinate phosphine complexes, **1** and **2**, are formed. These do not react with additional phosphine. Triphenylphosphine is not sufficiently nucleophilic to displace chloride from $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$. A PPh_3 complex, **3**, can be obtained by addition to $[Os(N)(CH_2SiMe_3)_2Cl]_2$. The chloride-bridged dimer is in equilibrium with a coordinatively unsaturated and very reactive monomer, $Os(N)(CH_2SiMe_3)_2Cl$. Complex **3** does not react with additional PPh_3.

The differences in reactivity between $[NBu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and $[NBu_4][Os(N)Cl_4]$ and between $Os(N)Cl(CH_2SiMe_3)_2L'_2$ (L′ = PMe_3, $^1/_2$ dppe) and $Os(N)Cl_3L_2$ are difficult to understand. If we examine the Os–N stretching vibrations in the IR spectra as a measure of the strength of the metal–nitride interaction, we see no correlation with reactivity of the nitride ligand toward phosphines. For $[NBu_4][Os(N)Cl_4]$, the Os–N stretching vibration is 1122 cm^{-1}. This is identical to the energy of the Os–N stretch in $[NBu_4][cis\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$. The Os–N stretching vibrations in both $[NBu_4][trans\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$ and $[NBu_4][Os(N)(CH_2SiMe_3)_4]$ are approximately 1105 cm^{-1}. The metal–nitride stretching vibrations in $Os(N)Cl_3L_2$ (L = PPh_xEt_{x-3}) range from 1058 to 1070 cm^{-1}, and the comparable stretching vibrations in $Os(N)Cl(CH_2SiMe_3)_2L'_2$ (L′ = PMe_3, 1/2 dppe) are 1094 and 1097 cm^{-1}.

Chloride abstraction from **1** and **2** yields the cationic phosphine complexes **4** and **5**, respectively. Spectroscopic studies are consistent with a distorted square pyramidal structure for these two complexes. The nitrido ligand is axial. The alkyl groups are *trans* to one another in **4** and *cis* in the dppe complex, **5**. Both complexes bind acetonitrile in the sixth coordination position, *trans* to the nitride. Probably because the basic PMe_3 ligands donate more electron density to the osmium center than does dppe, complex **6** binds MeCN much more weakly than **7**. Although $[BF_4][Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)]$ does not lose acetonitrile in solution or under vacuum in the solid state, the X-ray crystal structure shows that the nitrile ligand–metal interaction is weaker than in other osmium and ruthenium acetonitrile complexes. The structure is very similar to that of 5-coordinate nitridoosmium(VI) complexes, with a pronounced distortion of the equatorial ligands away from the axial nitride.

The nitridoosmium anion $[Os(N)(CH_2SiMe_3)_4]^-$ reacts readily with 1 equiv of acid to cleave a carbon–osmium bond.[18] The reaction of $[HPPh_3][BF_4]$ or $[HPMe_3][BF_4]$ with the anion initially forms the reactive 4-coordinate complex $Os(N)(CH_2SiMe_3)_3$, which is trapped by the phosphine to form $Os(N)(CH_2SiMe_3)_3(PR_3)$. A similar reaction occurs between $[Os(N)(CH_2SiMe_3)_4]^-$ and pyridinium tetrafluoroborate.[17] The ^{1}H NMR spectra of the trialkyl complexes $Os(N)(CH_2SiMe_3)_3L$ demonstrate the trend in basicity of the ligands, L. The resonances assigned to the methylene protons of the (trimethylsilyl)methyl group *trans* to L shift upfield in the order $Os(N)(CH_2SiMe_3)_3(NC_5H_5)$ (δ 2.45) < $Os(N)(CH_2SiMe_3)_3(PPh_3)$ (δ 2.34) < $Os(N)(CH_2SiMe_3)_3(PMe_3)$ (δ 2.25).

---

(10) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1975**, 417–423.

(11) Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835–2836.

(12) (a) Schmidt, I.; Kynast, U. H. J.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39B*, 1248–1251. (b) Gibson, V. C.; Williams, D. N.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1989**, 1863–1864.

(13) Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, 13–18.

(14) Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493–7496.

(15) Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671–1676.

(16) Zhang, N.; Shapley, P. A. *Inorg.Chem.* **1988**, *27*, 976–977.

(17) Shusta, J. M. Ph.D. Thesis, University of Illinois, 1993.

(18) Marshman, R. W.; Shapley, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 8369–8378.

Conclusion

The alkyl ligands in organometallic nitridoosmium(VI) complexes stabilize the high oxidation state of the metal. The nitridoosmium(VI) complexes $[\mathrm{NBu_4}][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$, $[\mathrm{Os(N)(CH_2SiMe_3)_2Cl}]_2$, and $\mathrm{Os(N)(CH_2SiMe_3)_3}$ react with tertiary phosphines to form stable phosphine complexes. Phosphoraniminato complexes are not formed in these reactions and there is no reduction of the metal. The neutral phosphine complexes $\mathrm{Os(N)(CH_2SiMe_3)_2(PMe_3)_2Cl}$, $\mathrm{Os(N)(CH_2SiMe_3)_2(dppe)Cl}$, $\mathrm{Os(N)(CH_2SiMe_3)_2(PPh_3)Cl}$, $\mathrm{Os(N)(CH_2SiMe_3)_3(PMe_3)}$, and $\mathrm{Os(N)(CH_2SiMe_3)_3(PPh_3)}$ are thermally stable and do not react with excess phosphine. Cationic phosphine complexes are formed by the abstraction of the chloride ligands in $\mathrm{Os(N)(CH_2SiMe_3)_2(PMe_3)_2Cl}$ and $\mathrm{Os(N)(CH_2SiMe_3)_2(dppe)Cl}$.

Experimental Section

All reactions were conducted under a nitrogen atmosphere using standard air-sensitive techniques on a Schlenk line or in a Vacuum Atmospheres drybox. All solvents were of reagent grade. Anhydrous diethyl ether, tetrahydrofuran, and hexane were distilled from sodium/benzophenone, toluene was distilled from sodium, and methylene chloride and acetonitrile were distilled from calcium hydride under dinitrogen. The corresponding deuterated solvents were also dried in the same manner and were stored over activated sieves. Silver tetrafluoroborate was recrystallized from acetonitrile/hexane. Dialkylmagnesium reagents were prepared from the Grignard reagents according to literature procedures.[19] $\mathrm{K_2Os(O)_2(OH)_4}$,[20] $[\mathrm{Y}][\mathrm{Os(N)Cl_4}]$,[21] $[\mathrm{N}(n\text{-}\mathrm{Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$ and $[\mathrm{Y}][\mathrm{Os(N)(CH_2SiMe_3)_4}]$ ($\mathrm{Y = N}(n\text{-}\mathrm{Bu})_4, \mathrm{PPh_4}$)[14] 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 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 $\mathrm{H_3PO_4}$. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. Microanalyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Conductivity measurements were made using a BAS-100 electrochemical analyzer. Mass spectra were recorded on a Finnigan MAT CH-5 (EI) or 731 (FI, FD).

Synthesis of $[\mathrm{Os(N)(CH_2SiMe_3)_2Cl}]_2$. To a solution of $[\mathrm{N}(n\text{-}\mathrm{Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$ (0.100 g, 0.144 mmol) in 25 mL of $\mathrm{CH_2Cl_2}$ was added $[\mathrm{Ag(NCMe)_4}][\mathrm{BF_4}]$ (0.052 g, 0.144 mmol). A white solid precipitated from solution, and the color of the reaction mixture changed from orange-red to yellow-green and then to yellow-orange. The solution was stirred for 1 h and then filtered through Celite. The filtrate was concentrated to approximately 1 mL, 30 mL of hexane was added, and the mixture was filtered. The solution was concentrated and cooled to –30 °C, giving microcrystals of the product. It was recrystallized from concentrated $\mathrm{CH_2Cl_2}$, giving 0.049 g (82%) of red-orange crystals consisting of two isomers of $[\mathrm{Os(N)(CH_2SiMe_3)_2Cl}]_2$. IR (KBr pellet, cm^{-1}): 2956–2856 (m, ν_{CH}), 1411 (w, δ_{CH}), 1367 (w, δ_{CH}), 1244 (s, δ_{SiC}), 1128 (m, ν_{OsN}, major isomer), 1122 (m, ν_{OsN}, minor isomer), 1017 m, 850 (s, ν_{SiC}), 834 (s, ν_{SiC}), 774 w, 750 w, 717 w, 686 w. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 18 °C): δ 3.99 (d, J = 9.8 Hz, 2 H, $\mathrm{OsC}H^{\mathrm{a}}\mathrm{H^b}$, major isomer), 3.87 (d, J = 9.5 Hz, 2 H, $\mathrm{OsC}H^{\mathrm{a}}\mathrm{H^b}$, minor isomer), 2.70 (d, J = 9.8 Hz, 2 H, $\mathrm{OsCH^a}H^{\mathrm{b}}$, major isomer), 2.35 (d, J = 9.5 Hz, 2 H, $\mathrm{OsCH^a}H^{\mathrm{b}}$, minor isomer), 0.06 (s, 18 H, $\mathrm{SiCH_3}$, minor isomer), 0.09 (s, 18 H, $\mathrm{SiCH_3}$, major isomer). ^{13}C{^{1}H} (100.6 MHz, $\mathrm{CD_2Cl_2}$, 18 °C): δ 14.58 ($\mathrm{OsCH_2}$, major isomer), 13.96 ($\mathrm{OsCH_2}$, minor isomer), 0.12 ($\mathrm{SiCH_3}$, major isomer), 0.00 ($\mathrm{SiCH_3}$, minor isomer). Anal. Calcd for $\mathrm{OsC_8H_{22}NSi_2Cl}$: C, 23.2; H, 5.36; N, 3.38; Cl, 8.56. Found: C, 23.17; H, 5.44; N, 3.25; Cl, 8.51.

Synthesis of $\mathrm{Os(N)Cl(CH_2SiMe_3)_2(PMe_3)_2}$ (1). Three equivalents of $\mathrm{PMe_3}$ (90 μL) was added by syringe to a solution of $[\mathrm{NBu_4}][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$ (200 mg, 0.29 mmol) in 30 mL of methylene chloride. The solution was stirred for 6 h. During this time, the color of the solution changed from orange to yellow. Solvent was removed under vacuum and the residue extracted with toluene. After filtration, the toluene was removed under vacuum. The product was crystallized from toluene/hexane. Yellow tabular crystals (111 mg, 0.20 mmol, 68%) were collected. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, 17 °C): δ 2.11 (t, J = 7.4 Hz, 4 H, $\mathrm{CH_2Si}$), 1.36 (t, J = 4.6 Hz, 18 H, $\mathrm{PCH_3}$), 0.33 (s, 18 H, $\mathrm{SiCH_3}$). ^{1}H{^{31}P} NMR (500 MHz, $\mathrm{C_6D_6}$, 19 °C): δ 2.11 (s), 1.36 (s), 0.33 (s). ^{13}C{^{1}H} NMR (125.8 MHz, $\mathrm{C_6D_6}$, 17 °C): δ 14.45 (t, J = 19 Hz, $\mathrm{PCH_3}$), 2.910 (s, $\mathrm{SiCH_3}$), –1.175 (t, J = 5 Hz, $\mathrm{CH_2Si}$). ^{31}P{^{1}H} NMR (131 MHz, $\mathrm{CDCl_3}$, 18 °C): δ -33.8 (s). IR (KBr pellet, cm^{-1}): 2999–2887 (m, ν_{CH}), 1434 (m, δ_{CH}), 1286 (m, δ_{CH}), 1236 (s, δ_{SiC}), 1094.1 (s, ν_{OsN}), 978 (m), 954 (s, ν_{PC}), 851 (s, ν_{SiC}), 829 (s, ν_{SiC}), 768 (m), 741 (m), 676 (m). Anal. Calcd for $\mathrm{C_{14}H_{40}ClNOsP_2Si_2}$: C, 29.70; H, 7.12; N, 2.47; Cl, 6.27. Found: C, 29.69; H, 7.15; N, 2.47; Cl, 6.26.

Synthesis of $\mathrm{Os(N)(CH_2SiMe_3)_2Cl(dppe)}$ (2). $[\mathrm{NBu_4}][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$ (0.30 g, 0.43 mmol) and dppe (0.20 g, 0.5 mmol) were dissolved in 30 mL of $\mathrm{CH_2Cl_2}$. The mixture was stirred at room temperature, the color changed from orange to yellow, and a white solid formed. The mixture was filtered and the filtrate concentrated under vacuum. Hexane was added, and the solution was cooled to –30 °C. Compound **2**, a yellow microcrystalline solid, was collected by filtration and dried under vacuum (0.325 g, 0.40 mmol, 92.93%).

A solution of dppe (0.078 g, 0.195 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$ was added dropwise to a stirred solution of $[\mathrm{Os(N)(CH_2SiMe_3)_2Cl}]_2$ (0.081 g, 0.098 mmol) in 20 mL of $\mathrm{CH_2Cl_2}$ at room temperature. The color immediately changed to yellow-green. The solution was concentrated under vacuum, hexane was added, and the solution was cooled to –30 °C. Yellow crystals of **2** (0.084 g, 0.10 mmol, 53%) were isolated. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 19 °C): δ 7.78 (m, 4 H, Ph), 7.66 (m, 4 H, Ph), 7.48 (m, 8 H, Ph), 7.36 (m, 4 H, Ph), 3.40 (m, 2 H, $\mathrm{SiC}H^{\mathrm{a}}\mathrm{H^b}$), 2.23 (m, 2 H, $\mathrm{SiCH^a}H^{\mathrm{b}}$), 2.05 (m, 2 H, $\mathrm{PC}H^{\mathrm{c}}\mathrm{H^d}$), 1.90 (m, 2 H, $\mathrm{PCH^c}H^{\mathrm{d}}$), 0.07 (s, 18 H, $\mathrm{SiCH_3}$). ^{31}P {^{1}H} NMR (161.9 Hz, $\mathrm{CDCl_3}$, 20.0 °C): δ 29.8 (s). IR (KBr pellet, cm^{-1}): 3050–2867 (m, ν_{CH}), 1480, 1428 (s, δ_{CH}), 1232 (s, δ_{SiC}), 1097 (s, ν_{OsN}), 1088 (s), 845 (s, ν_{SiC}), 821 (s, ν_{SiC}), 724 (s), 691 (m). Mass spectrum (FD, m/z): 778 ($\mathrm{M^+ - Cl^-}$); 399 ($\mathrm{dppeH^+}$). Anal. Calcd for $\mathrm{OsNClSi_2P_2C_{34}H_{46}}$: C, 50.26; H, 5.71; N, 1.72. Found: C, 49.03; H, 5.66; N, 1.68.

Synthesis of $\mathrm{Os(N)(CH_2SiMe_3)_2Cl(PPh_3)}$ (3). Approximately 10 mg (0.012 mmol) of $[\mathrm{Os(N)Cl(CH_2SiMe_3)_2}]_2$ was added to an NMR tube under $\mathrm{N_2}$ along with 0.75 mL of $\mathrm{CDCl_3}$ and 10 mg (0.038 mmol) of $\mathrm{PPh_3}$. The color changed from yellow-brown to light yellow, and the solution remained homogeneous. The product was characterized by NMR spectroscopy. ^{1}H ($\mathrm{CDCl_3}$, 300 MHz, 20 °C): δ 7.7–7.3 (m, 41 H, $\mathrm{PPh_3}$), 3.3 (dd, J = 8.8 Hz, 3.5 Hz, 1 H, $\mathrm{C}H^{\mathrm{a}}\mathrm{H^bSi}$), 2.85 (dd, J = 10.6 Hz, 3.5 Hz, 1 H, $\mathrm{CH^c}H^{\mathrm{d}}\mathrm{Si}$), 1.92 (dd, J = 10.6 Hz, 1.8 Hz, 1 H, $\mathrm{C}H^{\mathrm{c}}\mathrm{H^dSi}$), 1.89 (dd, 8.8 Hz, 2.6 Hz, 1 H, $\mathrm{CH^a}H^{\mathrm{b}}\mathrm{Si}$), 0.10 (s, 9 H, $\mathrm{SiMe_3}$), –0.10 (s, 9H, $\mathrm{SiMe_3}$). ^{31}P{^{1}H} ($\mathrm{CDCl_3}$, 121 MHz, 20 °C): δ 32.9 ($\mathrm{OsPPh_3}$), –4.7 (free $\mathrm{PPh_3}$).

Synthesis of $[\mathrm{Os(N)(CH_2SiMe_3)_2(PMe_3)_2}][\mathrm{BF_4}]$ (4). A solution of **1** (0.019 g, 0.034 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$ was combined with $\mathrm{AgBF_4}$ (0.016 g, 0.082 mmol), and the mixture was magnetically stirred for 20 min. It was filtered and solvent was removed from the filtrate under vacuum. The yellow solid residue was crystallized from toluene/hexane at –30 °C. Orange prismatic crystals of **4** (0.012 g, 0.019 mmol, 57%) were collected and dried under vacuum. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$, 19 °C): δ 2.01 (t, J = 8.7 Hz, 4 H, $\mathrm{SiCH_2}$), 1.30 (t, J = 4.7 Hz, 18 H, $\mathrm{PCH_3}$), 0.21 (s, 18 H, $\mathrm{SiCH_3}$). ^{1}H{^{31}P} NMR (500 MHz, $\mathrm{C_6D_6}$, 19 °C): δ 2.00 (s), 1.30 (s), 0.21 (s). ^{13}C{^{1}H} NMR (125.8 MHz, $\mathrm{CDCl_3}$, 19 °C): δ 14.9 (t, J = 18.9 Hz, $\mathrm{P}C\mathrm{H_3}$), 8.4 (t, J = 4.3, $\mathrm{SiCH_2}$), 2.9 (s, $\mathrm{SiCH_3}$). ^{31}P NMR (125 MHz, $\mathrm{CDCl_3}$, 17 °C): δ –15.7. IR (KBr pellet, cm^{-1}): 3009–2892 (m, ν_{CH}), 1427 (m, δ_{CH}), 1413 (s, δ_{CH}), 1290 (m, δ_{CH}), 1248 (m, δ_{SiC}), 1079 (s, br, ν_{BF}), 957 (s, ν_{PC}), 849 (s, ν_{SiC}), 833 (s, ν_{SiC}). Anal. Calcd for $\mathrm{C_{14}H_{40}BF_4NOsP_2}$: C, 27.23; H, 6.53; N, 2.27. Found: C, 27.52; H, 6.31; N, 2.29.

Conductivity Studies of 1 and 4. A solution of the compound of interest (5–30 mg) in acetonitrile (6 mL) was prepared and placed into an electrochemical cell. A platinum working electrode, gold pseudoreference, electrode and platinum auxiliary electrode were used. The cell was connected as for a cyclic voltammetry experiment. IR compensation was used to measure the internal resistance of the cell. The measurement was taken at several different rest potentials and three different concentrations for each compound. Experimentally it was found that the rest potential had little effect (<5%) on the resistance, so average values of the resistance were used. Relative molar conductivities were calculated from the resistance. The conductivities of three well-characterized osmium complexes and complexes **1** and **4** were determined: $[\mathrm{PPh_4}]_2[\mathrm{OsCl_6}]$ (99.6 $\Omega^{-1}\cdot\mathrm{cm^3}\cdot\mathrm{mol^{-1}}$), $[\mathrm{NBu_4}][\mathrm{OsNCl_4}]$ (45.5 $\Omega^{-1}\cdot\mathrm{cm^3}\cdot\mathrm{mol^{-1}}$), and $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Os(N)(CH_2SiMe_3)_2}$ (4.6 $\Omega^{-1}\cdot\mathrm{cm^3}\cdot\mathrm{mol^{-1}}$), **1** (2.46 $\Omega^{-1}\cdot\mathrm{cm^3}\cdot\mathrm{mol^{-1}}$), **4** (37.4 $\Omega^{-1}\cdot\mathrm{cm^3}\cdot\mathrm{mol^{-1}}$).

---

(19) Lindsell, W. E. In *Comprehensive Organometallic Chemsitry*; Wilkinson, G., Stone, F. G. A., Abel, W., Eds.; Pergamon: Oxford, U.K., 1983; Vol. 1, p 198.

(20) Lott, K. A. K.; Symons, M. C. R. *J. Chem. Soc.* **1960**, 973–313.

(21) Griffith, W. P.; Pawson, D.; *J. Chem. Soc., Dalton Trans.* **1973**, 1315–20.

Synthesis of [Os(N)(CH_2SiMe_3)$_2$(dppe)][BF_4] (5). $AgBF_4$ (0.078 g, 0.4 mmol) was added to a solution of **2** (0.325 g, 0.40 mmol) in 20 mL of CH_2Cl_2. The mixture was magnetically stirred for 30 min and then filtered. The filtrate was concentrated under vacuum. Hexane was added, and the solution was cooled to –30 °C. Yellow crystals of **5** (0.265 g, 0.31 mmol, 77%) were collected and dried under vacuum. ^{1}H NMR (300 MHz, C_6H_6, 19 °C): δ 7.6–6.8 (m, 20 H, Ph), 3.2 (m, 2 H, CH_2), 2.9 (m, 2 H, CH_2), 2.7 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 0.1 (s, 18 H, $SiCH_3$). ^{31}P{^{1}H} NMR (161.9 Hz, $CDCl_3$, 20.0 °C): δ 48.2 (s). IR (KBr pellet, cm^{-1}): 3057–2881 (m, ν_{CH}), 1480 (s, δ_{CH}), 1428 (s, δ_{CH}), 1245 (m, δ_{SiC}), 1089 (s, br, ν_{BF}), 919 (s, ν_{PC}), 841 (s, ν_{SiC}), 745 (s), 691 (m). Anal. Calcd for $OsNSi_2P_2C_{34}H_{46}BF_4$: C, 47.27; H, 5.37; N, 1.62. Found: C, 47.11; H, 5.23; N, 1.54.

Synthesis of [Os(N)(CH_2SiMe_3)$_2$(dppe)(NCMe)][BF_4] (7). $AgBF_4$ was crystallized from $CH_3CN/(C_2H_5)_2O$. The resulting crystalline solid contained coordinated acetonitrile. Excess Ag(I) ([Ag(NCMe)$_4$][BF_4], 0.024 g) was added to a solution of **2** (0.050 g, 0.062 mmol) in 15 mL of CH_2Cl_2. The mixture was magnetically stirred for 1 h and then filtered. The filtrate was concentrated under vacuum, hexane was added, and the solution was cooled to –30 °C. Light yellow crystals of **7** (0.035 g, 66%) were collected and dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$, 19 °C): δ 8.0–7.6 (m, 20 H, Ph), 3.55 (m, 2 H, CH_2), 2.95 (m, 2 H, CH_2), 2.5 (m, 4 H, CH_2), 2.1 (s, 3 H, $NCCH_3$), 0.05 (s, 18 H, $SiCH_3$). ^{31}P{^{1}H} NMR (161.9 Hz, $CDCl_3$, 20.0 °C): δ 48 (s). IR (KBr pellet, cm^{-1}): 3057–2861 (m, ν_{CH}), 2294 (m, ν_{CN}), 2268 (m, ν_{CN}), 1480 (s, δ_{CH}), 1434 (s, δ_{CH}), 1239 (m, δ_{SiC}), 1062 (s, br, ν_{BF}), 841 (s, ν_{SiC}), 743 (s), 697 (m). Anal. Calcd for $OsN2Si_2P_2C_{36}H_{49}BF_4$: C, 47.78; H, 5.46; N, 3.1. Found: C, 48.25; H, 5.66; N, 2.79.

Crystallization and Reduction of X-ray Diffraction Data. Transparent, tabular yellow crystals of **7** suitable for X-ray crystallographic analysis were grown by slow cooling of a CH_2Cl_2/hexane solution under dinitrogen. The data crystal had well-developed faces and uniformly extinguished plane-polarized light. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber and then cooled to –75 °C with the ($\bar{1}00$) scattering planes roughly normal to the spindle axis on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochromator (λ(Mo Kα) = 0.710 73 Å). The data crystal was bound by the {001}, {010}, and {100} forms. Distances from the crystal center to these facial boundaries were 0.06, 0.16, and 0.20 mm, respectively. Data were collected at –75 °C and corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods (SHELXS-86);[22] the correct osmium position was deduced from a vector map, and partial structure expansion gave positions for silicon and phosphorus atoms. Subsequent least-squares refinements and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms. Cation hydrogen atoms were included as fixed contributors in "idealized" positions. The anion and solvate molecules were disordered; solvate hydrogen atoms were not included in structure factor calculations. Owing to extreme correlations between disordered positions, the anion was refined as an "idealized" rigid group and solvate molecule bond lengths and angles were constrained preceding each least-squares refinement cycle. In the final cycle of least squares, common isotropic thermal parameters were refined for hydrogen, boron, and fluorine atoms, independent isotropic thermal coefficients were refined for the solvate atoms, and all remaining atoms were refined with anisotropic thermal coefficients. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peak in the final difference Fourier map was in the vicinity of the disordered anion. A final analysis of the variance between observed and calculated structure factors showed a slight dependence on sin(θ).

Synthesis of Os(N)(CH_2SiMe_3)$_3$(PMe_3) (8). Yellow crystals of [N(*n*-Bu)$_4$][NOs(CH_2SiMe_3)$_4$] (0.025 g, 0.031 mmol) were dissolved in 10 mL of CH_2Cl_2. One equivalent of [$HPMe_3$][BF_4] (0.005 g, 0.031 mmol) was added with stirring. After 1 h, solvent was removed under vacuum, the residue was extracted with hexane, the exract was filtered, and the filtrate was cooled to –30 °C. Yellow crystals of **8** (0.015 g, 0.028 mmol, 89%) were collected by filtration and dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$, 18 °C): δ 2.25 (d, *J* = 5.5 Hz, 2 H, $SiCH_2$), 1.60 (dd, *J* = 14.6, 9.4 Hz, 2 H, $SiCH^aH^b$), 1.59 (d, *J* = 9.9 Hz, 9 H, PCH_3), 1.30 (dd, *J* = 5.2, 9.5 Hz, 2 H, $SiCH^aH^b$), 0.13 (s, 18 H, $SiCH_3$), –0.17 (s, 9 H, $SiCH_3$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 21.0 °C): δ 14.5 (d, *J* = 33.6 Hz, PCH_3), 11.1 (d, *J* = 34.3 Hz, $SiCH_2$), 8.48 (d, *J* = 3.1 Hz, $SiCH_2$), 3.58 (s, $SiCH_3$), 1.73 (s, $SiCH_3$). ^{31}P{^{1}H} NMR (161.9 Hz, $CDCl_3$, 21.1 °C): δ –12.92 (s). IR (KBr pellet, cm^{-1}): 2950–2860 (s, ν_{CH}), 1425 (m, δ_{CH}), 1396 (w, δ_{CH}), 1253 (s, δ_{SiC}), 1242 (s, δ_{SiC}), 1109 (s, ν_{OsN}), 963 (s, ν_{PC}), 851 (s, ν_{SiC}), 830 (s, ν_{SiC}). Mass spectrum (FD, *m/z*): 543 (M$^+$). Anal. Calcd for $OsNPSi_3C_{15}H_{42}$: C, 33.24; H, 7.81; N, 2.58; P, 5.72. Found: C, 33.49; H, 7.79; N, 2.52; P, 5.37.

Table 2. Crystal Data Collection and Refinement Parameters

compound	7
formula	[$C_{36}H_{49}N_2Si_2P_2Os$][BF_4]·$^1/_2C_4H_{10}O$
fw	941.98
space group	*P*2$_1$/*a* (No. 14)
a, Å	17.544(7)
b, Å	12.269(5)
c, Å	20.666(4)
$\alpha = \gamma$, deg	90
β, deg	104.76(3)
formulas/unit cell (*Z*)	4
density calcd (ρ), g/cm^3	1.454
temp, °C	–75
radiation	Mo Kα (graphite crystal monochromator)
λ, Å	Kα_1 = 0./709 30, Kα_2 = 0.713 59, Kα = 0.710 73
abs coeff (μ), cm^{-1}	31.38
$R = \sum\lVert F_o - F_c\rVert \sum\lvert F_o\rvert$	0.036
$R_w = (\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2)^{1/2}$	0.038

Synthesis of Os(N)(CH_2SiMe_3)$_3$(PPh_3) (9). The preparation was above with [$HPPh_3$][BF_4] (11 mg, 0.031 mmol). Orange-yellow microcrystals of **9** (0.018 g, 0.025 mmol, 80%) were collected and were dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$, 18 °C): δ 7.62 (m, Ph), 7.43 (m, Ph), 2.34 (d, *J* = 3.1 Hz, 2 H, $SiCH_2$), 2.31 (dd, *J* = 14.2, 9.9 Hz, 2 H, $SiCH^aH^b$), 1.20 (dd, *J* = 5.2, 9.5 Hz, 2H, $SiCH^aH^b$), –0.10 (s, 9 H, $SiCH_3$), –0.13 (s, 18 H, $SiCH_3$). ^{13}C{^{1}H} NMR (100.6 Hz, $CDCl_3$, 20.1 °C): δ 134.5 (d, *J* = 10.7 Hz, $P(C_6H_5)_3$), 131.0 (d, *J* = 2.3 Hz, $P(C_6H_5)_3$), 129.3 (d, *J* = 48.1 Hz, $P(C_6H_5)_3$), 128.8 (d, *J* = 9.9 Hz, $P(C_6H_5)_3$), 10.1 (d, *J* = 42.0 Hz, $SiCH_2$), 9.74 (br s, $SiCH_2$), 3.05 (s, $SiCH_3$), 2.27 (s, $SiCH_3$). ^{31}P{^{1}H} NMR (161.9 Hz, $CDCl_3$, 20.0 °C): δ 30.72 (s). IR (KBr pellet, cm^{-1}): 3080–2894 (s, ν_{CH}), 1436 (s, δ_{CH}), 1256 (s, δ_{SiC}), 1242 (s, δ_{SiC}), 1114 (s, ν_{OsN}), 848 (s, ν_{SiC}), 830 (s, ν_{SiC}), 743 (s, phenyl δ_{CH}), 719 (s, phenyl δ_{CH}), 693 (s, phenyl δ_{CH}), 680 (m, phenyl δ_{CH}). Mass spectrum (FD, *m/z*): 729 (M$^+$), 467 (M$^+$ – PPh_3), 262 (PPh_3). Anal. Calcd for $OsNPSi_3C_{30}H_{48}$: C, 49.49; H, 6.64; N, 1.92; P, 4.25. Found: C, 49.78; H, 6.74; N, 1.86; P, 4.52.

Reaction of 1 with LiBu. A toluene solution of **1** (10 mg, 0.018 mmol) was prepared and cooled to 0 °C. One equivalent of *n*-butyllithium (10 μL of a 1.6 M solution in hexane) was added. Upon addition of the LiBu, the solution turned red orange. The color persisted for 30–60 s before dissipating. The remaining solution was pale yellow. After 30 min of stirring, the solvent was removed under vacuum, leaving a pale yellow oil. Extraction with hexane gave a yellow solution. The product was extracted with hexane and isolated by taking the sample to dryness. Major product (77% based on integration): ^{1}H NMR (300 MHz, C_6D_6, 19 °C) δ 3.14 (m, 2 H, $OsCH_2CH_2CH_2CH_3$), 1.75–1.4 (m, $OsCH_2CH_2CH_2CH_3$), 1.103 (t, *J* = 7.2 Hz, 4 H, $SiCH_2$), 0.841 (d, *J* = 9.74 Hz, 9 H, PMe_3), 0.421(s, 18 H, $SiCH_3$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 19 °C) δ 36.3 (s, $CH_2CH_2CH_2CH_3$), 30.0 (s, $CH_2CH_2CH_2CH_3$), 28.7 (d, *J* = 4.6 Hz, $OsCH_2CH_2$–), 14.5 ($CH_2CH_2CH_2CH_3$), 13.9 (d, *J* = 31.5 Hz, PCH_3), 10.5 (d, *J* = 2.8 Hz, $OsCH_2Si$), 2.5 (s, $SiCH_3$); ^{31}P NMR (131 MHz, C_6D_6, 19 °C) δ –21.6; mass spectrum (EI, *m/z*): 513.1 (M$^+$), 455 (M$^+$ – C_4H_{10}). The isotope pattern of the observed mass spectrum was identical to that of the calculated spectrum.

Acknowledgment. We gratefully acknowledge financial support in the form of grants from the National Science Foundation (CHE 90-14374 and CHE 93-08450). Spectra were obtained on NMR instruments purchased through grants from the NIH and the NSF (NIH PHS 1532135, NIH 1531957, and NSF CHE 85-14500). P.A.S. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Fellowship.

Supplementary Material Available: For [Os(N)(CH_2SiMe_3)$_2$(dppe)(NCMe)][BF_4]·$^1/_2C_4H_{10}O$, tables of additional crystal data collection and refinement parameters, atomic coordinates, thermal parameters, and selected distances and angles (10 pages). Ordering information is given on any current masthead page.

---

[22] Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., and Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189.