

Osmabenzenes from the Reactions of a Dicationic Osmabenzynes Complex

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Abstract: Treatment of the osmabenzynes $\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2$ (**1**) with 2,2'-bipyridine (bipy) and thallium triflate (TlOTf) produces the thermally stable dicationic osmabenzynes $[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2](\text{OTf})_2$ (**2**). The dicationic osmabenzynes **2** reacts with ROH ($\text{R} = \text{H}, \text{Me}$) to give osmabenzene complexes $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$, in which the metallabenzene ring deviates significantly from planarity. In contrast, reaction of the dicationic complex **2** with NaBH_4 produces a cyclopentadienyl complex, presumably through the osmabenzene intermediate $[\text{Os}(\equiv\text{CHC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$. The higher thermal stability of $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ relative to $[\text{Os}(\equiv\text{CHC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ can be related to the stabilization effect of the OR groups on the metallacycle. A theoretical study shows that conversion of the dicationic osmabenzynes complex $[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2](\text{OTf})_2$ to a carbene complex by reductive elimination is thermodynamically unfavorable. The theoretical study also suggests that the nonplanarity of the osmabenzenes $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ is mainly due to electronic reasons.

Introduction

Transition metal-containing metallabenzenes¹ are an interesting class of compounds, because they can display properties of both organic and organometallic compounds. These species were first predicted theoretically in 1979.² The first stable transition metal-containing metallabenzenes were reported in 1982 by Roper et al.³ Since then, the chemistry of transition metal-containing metallabenzenes has attracted considerable attention both experimentally⁴ and theoretically,⁵ especially in recent years. Previous study has led to the isolation and characterization of an impressive number of stable metallabenzenes, especially those of osmium,^{3,4a,6–8} iridium,^{4b,d–f,9–14} platinum,¹⁵ and

ruthenium.^{4c} Very rich chemical properties of metallabenzenes have also been demonstrated. For example, metallabenzenes were found to undergo electrophilic substitution⁶ and [4+2] cycloaddition^{13,16} reactions and to form coordination complexes with transition metals.^{13,17}

Compounds closely related to metallabenzenes are metallabenzynes.^{18,19} At first sight, one may expect that metallabenzynes may, like benzyne,²⁰ be thermally unstable due to the presence of ring strain. However, several stable metallabenzynes have been successfully isolated.^{21–24} Metallabenzynes are also interesting because they may show properties similar to those

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of metallabenzenes, benzenes, and benzyne. Indeed, electrophilic substitution reactions of metallabenzenes have been recently reported.²²

While stable metallabenzenes and metallabenzynes are known, and benzene and benzyne derivatives can be transformed into each other chemically, similar transformations have not been demonstrated with metallabenzenes and metallabenzynes. Interconversion of metallabenzenes and metallabenzynes can provide a route to generate metallabenzynes from metallabenzenes, or metallabenzenes from metallabenzynes. An attractive feature of the transformation is that it could give metallabenzynes and metallabenzenes with the same metal fragment, which are virtually unknown at present.

It is now well established that metallabenzenes can thermally rearrange to cyclopentadienyl (Cp) complexes.^{4d,10b,25,26} The rearrangements have been elegantly demonstrated with isolated metallabenzene complexes^{4d,10b} and spectroscopically character-

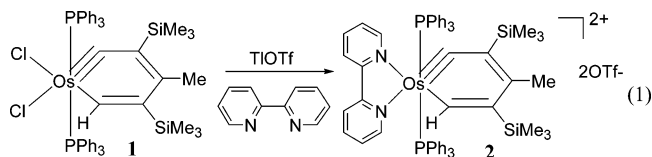
ized metallabenzenes.²⁵ The thermodynamics and the kinetic of the transformation are critically dependent on the metal fragment and the substituents on the metallacycle. In principle, metallabenzynes could also undergo similar transformations to give carbene complexes. In this regard, generation of metallabenzynes and metallabenzenes with the same metal fragment is interesting, because it provides the opportunity to compare the relative thermal stability of metallabenzenes and metallabenzynes without complication from the effect of the metal fragment.

In this work, we have prepared a thermally stable dicationic osmabenzynes complex and investigated its conversion to osmabenzenes by nucleophilic addition to the carbyne carbon. We indeed found that the nucleophilic addition reactions lead to the formation of metallabenzene species, which may be thermally stable at ambient temperature or rearrange to a cyclopentadienyl complex, depending on the nucleophiles. To better understand the chemistry, a computational study was carried out to compare the thermodynamics and kinetics of the conversion of osmabenzenes to carbene complexes and the conversion of osmabenzenes to cyclopentadienyl complexes.

Results and Discussions

Preparation of a Dicationic Osmabenzynes. We have previously shown that the osmabenzynes $\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2$ (**1**),²¹ like organic aromatic compounds and metallabenzenes, can undergo electrophilic substitution reactions at the 3,5-positions of the metallacycle.^{22,23} A theoretical study indicates that the regiochemistry is controlled by the highest occupied molecular orbital (HOMO).^{22,27} The study also suggests that the lowest unoccupied molecular orbital (LUMO) of the metallacycle is mainly made of a d orbital of the metal and p orbitals of the carbyne carbon and carbons at the 4,6-positions of the metallacycle.²⁷ Thus, it is expected that nucleophiles will attack the carbyne carbon and carbons at the 4,6-positions of the metallacycle. Since attack on the carbyne carbon can relieve the ring strain, we expect that reactions of osmabenzenes with nucleophiles are more likely to give osmabenzenes by nucleophilic attack on the carbyne carbon of osmabenzenes.

To test this possibility, we initially studied the reactivity of **1** with NaBH_4 . However, complex **1** is not electrophilic enough to react with NaBH_4 in tetrahydrofuran (THF) at room temperature. To increase the electrophilicity of the metallacycle, we have prepared the dicationic osmabenzynes **2** by replacement of the chloride ligands in **1** with 2,2'-bipyridine (bipy). The transformation is accomplished by treatment of **1** with bipy in the presence of thallium triflate (TiOTf ; eq 1).



Complex **2** was isolated as a purple solid. Its structure has been confirmed by X-ray diffraction. The molecular structure is shown in Figure 1, and selected bond distances and angles

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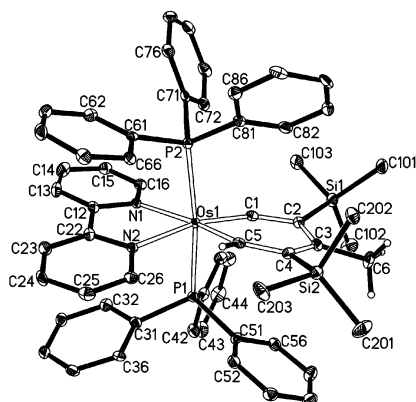


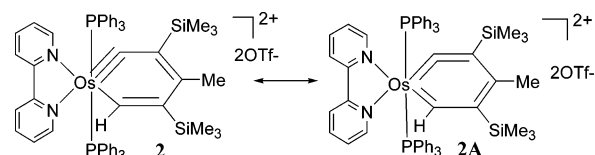
Figure 1. X-ray structure of complex **2**. Counteranion and some of the hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Osmabenzynes **2** and Osmabenzenes **3** and **5**

	compound		
	2	3	5
Os1–C1	1.780(3)	1.921(4)	1.958(5)
C1–C2	1.370(5)	1.464(4)	1.436(7)
C2–C3	1.419(5)	1.362(6)	1.390(7)
C3–C4	1.436(5)	1.472(6)	1.461(7)
C4–C5	1.379(5)	1.383(5)	1.343(7)
Os1–C5	2.015(3)	2.010(4)	2.008(5)
Os1–P1	2.4156(9)	2.3704(9)	2.3795(15)
Os1–P2	2.4403(9)	2.3988(9)	2.4056(14)
Os1–N1	2.173(3)	2.142(3)	2.177(4)
Os1–N2	2.208(3)	2.190(3)	2.181(4)
Os1–C1–C2	153.8(3)	123.0(3)	123.7(4)
C1–C2–C3	111.1(3)	124.9(4)	124.1(5)
C2–C3–C4	122.2(3)	122.9(4)	123.6(5)
C3–C4–C5	120.0(3)	117.2(4)	117.4(5)
C4–C5–Os1	134.7(3)	132.5(3)	134.3(4)
C1–Os1–C5	76.32(14)	85.53(15)	85.0(2)
C1–Os1–P1	87.98(11)	91.42(11)	91.44(17)
C1–Os1–P2	97.57(11)	89.57(11)	88.30(17)
C1–Os1–N1	120.29(13)	105.13(14)	106.09(19)
C1–Os1–N2	163.56(13)	177.26(12)	175.6(2)
C5–Os1–P1	96.46(10)	89.08(10)	87.31(16)
C5–Os1–P2	89.26(10)	95.04(10)	96.93(16)
C5–Os1–N1	163.01(12)	168.95(13)	168.2(2)
C5–Os1–N2	89.12(12)	94.18(13)	94.12(19)
P1–Os1–P2	172.85(3)	175.83(3)	175.72(5)
P1–Os1–N1	88.19(7)	87.76(8)	88.28(12)
P1–Os1–N2	86.10(7)	91.30(7)	92.80(12)
P2–Os1–N1	85.12(7)	88.07(8)	87.69(12)
P2–Os1–N2	89.71(7)	87.74(7)	87.55(12)
N1–Os1–N2	74.86(11)	75.32(11)	75.15(16)

are given in Table 1. As shown in Figure 1, the complex contains an essentially coplanar six-membered metallacycle. The maximum deviation from the least-squares plane through Os1 and C1–C5 is 0.086 Å for C3, and the sum of angles in the six-membered ring is 718.1°, which is very close to the ideal value of 720°. The Os–C1–C2 angle of 153.8(3)° is significantly smaller than that expected for either a carbyne or a vinylidene complex, owing to the constraint of the six-membered ring. The metallacycle has a delocalized structure, as reflected by the observation that the C1–C2 distance (1.370(5) Å) is comparable to that of C4–C5 (1.379(5) Å) and that the C2–C3 distance (1.419(5) Å) is similar to that of C3–C4 (1.436(5) Å). The Os–C1 bond length of 1.780(3) Å is at the high end of those observed for typical Os≡C bond distances (1.694–1.792 Å)^{28,29} and is slightly shorter than those found for typical Os=C bonds

in osmium vinylidene complexes (1.786–1.892 Å).^{28,30} The Os–C5 bond length of 2.015(3) Å is within the range of Os–C(vinyl) bonds (1.897–2.195 Å)^{28,31} and is at the high end of those reported for Os–CH(carbene) bonds (1.831–2.050 Å).^{28,32} Overall, the structural feature associated with the metallacycle of **2** is very similar to that of **1**,²¹ although the Os–C1 bond (1.780(3) Å) is slightly shorter and the Os–C5 bond (2.015(3) Å) is slightly longer than the corresponding bonds (1.815(4) and 1.939(5) Å, respectively) in **1**. The structural data indicate that the metallacycle of **2** has a delocalized structure with contributions from the resonance structures **2** and **2A**, with **2** being more important.

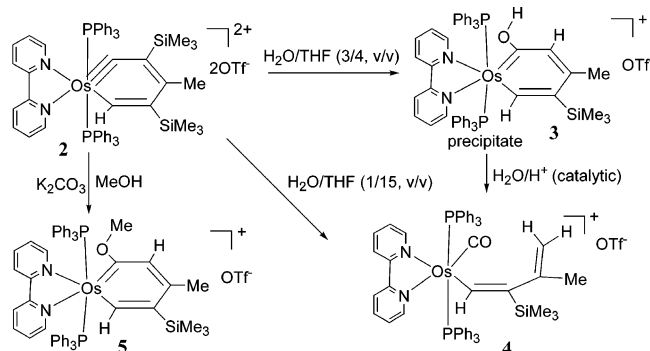


The solid-state structure of **2** is fully supported by NMR spectroscopy. In particular, the ¹H NMR (in CDCl₃) spectrum showed the OsCH signal at 13.45 ppm, and the ¹³C{¹H} NMR spectrum showed the five ring carbon signals at 316.4 (OsC), 216.3 (OsCH), 118.7 (Os≡CCSiMe₃), 145.6 (CSiMe₃), and 198.4 (CMe) ppm.

Reactions of Complex 2 with H₂O. Solid sample of complex **2** can be stored in an inert atmosphere for at least one week without appreciable decomposition, indicating that it is thermally stable at ambient temperature. However, it is very electrophilic and readily reacts with nucleophiles. Even water can function as a nucleophile to react with **2**. The products of the reaction of **2** with H₂O depend on the reaction conditions, especially the amount of water present and the reaction time. When a solution of **2** in THF/water (4:3, v/v) was stirred at room temperature for 2 h, the osmabenzene complex **3** was formed and precipitated out from the reaction mixture as a brownish-red solid (Scheme 1). The poor solubility of **3** in the solvent mixture helps the isolation of **3**. When a solution of **2** in a mixed solvent of THF/water (15:1, v/v) was stirred at room temperature, the reaction initially produced complex **3** along with unreacted **2** and a small amount of the vinyl complex **4**, and eventually all complexes **2** and **3** were completely consumed to produce a mixture of species with complex **4** as the dominant

- (28) Based on a search of the Cambridge Structural Database, CSD version 5.26 (November 2004).
- (29) More recent examples. (a) Os(≡CC₆H₄CHMe₂)H₂(N(SiMe₂CH₂PrBu₂)) (1.746(3) Å): Lee, J. H.; Pink, M.; Caulton, K. G. *Organometallics* **2006**, *25*, 802. (b) [OsH(≡CCH=CPh₂)(H₂O)₂(PPr₃)₂][BF₄]₂ (1.733(6) Å): Bolano, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Onate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184. (c) Os(≡CCH₃)Cl₂(PPh₃)₂ (1.724(5) Å): Wen, T. B.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Eur. J. Inorg. Chem.* **2004**, 2837.
- (30) A recent example, CpOsCl(=C=CHPh)(PPr₃)(C(CH₃)=CH₂) (1.817(5) Å): Baya, M.; Buil, M. L.; Esteruelas, M. A.; Onate, E. *Organometallics* **2005**, *24*, 2030.
- (31) Recent examples. (a) [Os(OTf)(NC₅H₄CH=CH)(NC₅H₄CH=CH₂)(PPr₃)]-OTf (1.995(2) Å): Esteruelas, M. A.; Fernandez-Alvarez, F. J.; Olivan, M.; Onate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (b) CpOs(CH=CHCOMe)(PPr₃) (1.989(4) Å): Esteruelas, M. A.; Hernandez, Y. A.; Lopez, A. M.; Olivan, M.; Onate, E. *Organometallics* **2005**, *24*, 5989. (c) Os(SnPh₂Cl)(NC₅H₄CH=CH)(H₂)(PPr₃)₂ (2.068(4) Å): Eguillor, B.; Esteruelas, M. A.; Olivan, M.; Onate, E. *Organometallics* **2005**, *24*, 1428. (d) OsCl(CH=CH(*p*-tolyl)(CO)(PPh₃))₂ (2.105(7) Å): Xia, H.; Wen, T. B.; Hu, Q. Y.; Wang, X.; Chen, X.; Shek, L. Y.; Williams, I. D.; Wong, K. S.; Wong, G. K. L.; Jia, G. *Organometallics* **2005**, *24*, 562.
- (32) A recent example, CpOsCl(=CHPh)(PPr₃)(C(CH₃)=CH₂) (1.895(5) Å): Esteruelas, M. A.; Gonzalez, A. I.; Lopez, A. M.; Onate, E. *Organometallics* **2004**, *23*, 4858.

Scheme 1



product (Scheme 1). Complex **4** could be isolated as a yellow solid in 41% yield after a solution of complex **2** in THF/water (15:1, v/v) was stirred at room temperature for 2 days. In the mixed solvent of $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$, complex **2** is also reactive toward water to give **3** and **4**, although the reaction is slow and usually produced a mixture of species.

Complex **3** can be stored in the solid form under an inert atmosphere for at least one week without appreciable decomposition. The structure of **3** can be readily deduced on the basis of the NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR (in CD_2Cl_2) spectrum showed a singlet at 2.5 ppm. The ^1H NMR spectrum showed the OsCH signal at 13.80 ppm, the CH signal at 5.41 ppm, and the OH signal at 9.15 ppm. The ^{13}C NMR spectrum showed the five carbon signals of the metallacycle at 252.3 (OsC(OH)), 223.6 (OsCH), 164.1 (CCH_3), 141.5 (CSiMe_3), and 119.7 (OsC(OH)CH) ppm. Complex **3** is structurally related to Roper's osmabenzene complex $[\text{Os}(\text{C}(\text{SH})\text{CH}=\text{CHCH}=\text{CH})\text{-(CO)}_2(\text{PPh}_3)_2]^+$.³ Complex **3** can be regarded as a metallaphenol. The iridaphenols $[\text{Ir}(\text{C}(\text{OH})\text{C}(\text{Me})=\text{CHC}(\text{Me})=\text{CH})(\text{X})\text{-(PMe}_3)_3]\text{OTf}$ ($\text{X} = \text{OTf}, \text{CF}_3\text{CO}_2$) reported by Blecke et al. are the rare stable metallaphenols reported previously.¹² We noted that metallaphenoxides of Ru, Fe, and Re and metallaphenanthrene oxides of Ru and Re have been proposed or detected spectroscopically at low temperature.^{25,26c,f,g}

The structure of **3** has been confirmed by X-ray diffraction. The molecular structure is shown in Figure 2, and selected bond distances and angles are given in Table 1. The X-ray diffraction study confirms that the complex contains a six-membered metallacycle with an OH group attached to one of the α -carbons. Several osmabenzenes have been previously characterized structurally.^{3,4a,6–8} In these reported examples, the osmabenzene ring usually has a planar or nearly planar structure. However, the metallacycle of complex **3** deviates significantly from planarity, as reflected by the sum of angles in the six-membered ring of 706.03° , which is significant smaller than the ideal value of 720° . The mean deviation from the least-squares plane through the C1–C5 chain is 0.0771 \AA . The Os is out of the plane of the metallacyclic carbon atoms by 0.68 \AA . The OH at C1 and H at C5 are also out of the plane. Although not common, a few nonplanar metallabenzene are known. For example, in iridabenzene supported by a Tp ligand, the iridium metal is bent by $0.50\text{--}0.76 \text{ \AA}$ out of the plane of the metallacyclic carbon atoms,^{4b,f,11} in the ruthenabenzene $[\text{Ru}(\text{C}(\text{H})\text{C}(\text{PPh}_3)=\text{CHC}(\text{PPh}_3)=\text{CH})(\text{bipy})\text{Cl}(\text{PPh}_3)]\text{Cl}_2$, the ruthenium center lies $-0.6722(56) \text{ \AA}$ out of the plane of the ring carbon atoms.^{4c} The conformation of the metallacycle of **3** is somewhat similar to

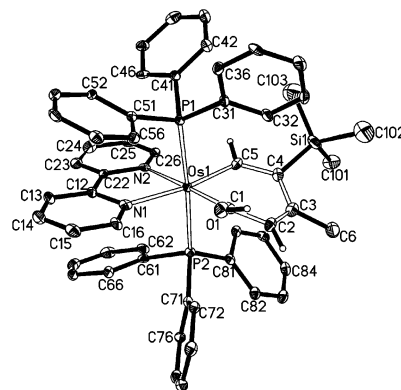


Figure 2. X-ray structure of complex **3**. Counteranion and some of the hydrogen atoms are omitted for clarity.

some of the transition states calculated for the conversion of metallabenzene to cyclopentadienyl complexes.^{5b}

The electron delocalization in the metallacycle of **3** is poor, as reflected by the marked short–long C–C distance alternations. The C1–C2 ($1.464(5) \text{ \AA}$) and C3–C4 ($1.472(6) \text{ \AA}$) bonds are appreciably longer than the C2–C3 ($1.362(6) \text{ \AA}$) and C4–C5 ($1.383(5) \text{ \AA}$) bonds. The Os–C1 bond ($1.921(4) \text{ \AA}$) is also shorter than the Os–C5 bond ($2.010(4) \text{ \AA}$). The shorter Os–C(OH) bond compared with Os–CH is probably not surprising, as a similar trend has been observed in Blecke's iridaphenol $[\text{Ir}(\text{C}(\text{OH})\text{C}(\text{Me})=\text{CHC}(\text{Me})=\text{CH})(\text{OTf})(\text{PMe}_3)_3]\text{OTf}$ ($1.916(16)$ and $2.031(16) \text{ \AA}$, respectively).¹² In osmabenzene $\text{Os}(\text{C}(\text{SMe})\text{CH}=\text{CHCX}=\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{NO}_2, \text{Br}$), in which I is trans to CH and CO is trans to C(SMe), the Os–C(SMe) bond is also slightly shorter than Os–CH.⁶

The structure of **4** can be readily assigned on the basis of the spectroscopic and analytical data. In particular, the ^1H NMR (in CD_2Cl_2) spectrum showed the ^1H signals of $\text{OsCH}=\text{C}(\text{SiMe}_3)\text{CMe}=\text{CH}_2$ at ca. 8.43 (OsCH), -0.03 (SiMe_3), 1.68 (Me), 4.36, and 4.44 ($=\text{CH}_2$) ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed the carbon signals of the vinyl ligand $\text{OsCH}=\text{C}(\text{SiMe}_3)\text{CMe}=\text{CH}_2$ at 146.9 (OsCH), 154.9 (C(Me)), 151.8 (C(SiMe_3)), 112.2 (CH_2), 25.0 (CH_3), and 0.3 (SiMe_3) ppm and the CO signal at 188.6 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a singlet at -1.7 ppm. The structure has been confirmed by an X-ray diffraction study. A view of the complex cation is shown in Figure 3.

In the reaction of **2** with water, complex **3** can be formed either by first nucleophilic attack of water on the carbyne carbon of **2**, followed by desilylation, or by first desilylation of **2**, followed by nucleophilic attack of water on the carbyne carbon of a desilylated osmabenzynes intermediate. We have no experimental evidence to differentiate the two possibilities. Desilylation of **2** by water is not unusual, as there are many reports on the cleavage of the Si–C bond by water to give C–H bonds, especially in the reactions of L_nM with $\text{HC}\equiv\text{CSiMe}_3$ to give vinylidene complexes $\text{L}_n\text{M}(\text{C}=\text{CH}_2)$.³³ As will be discussed below, the fact that only the SiMe_3 adjacent to the carbyne carbon is preferentially desilylated can be related to the higher nucleophilicity of the Si-bound carbon.

(33) See, for example: (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (b) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romero, A.; Rossi, R. *Organometallics* **1996**, *15*, 3804. (c) Kawata, Y.; Sato, M. *Organometallics* **1997**, *16*, 1093. (d) Werner, H.; Lass, R. W.; Gevert, L. O.; Wolf, J. *Organometallics* **1997**, *16*, 4077. (e) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951.

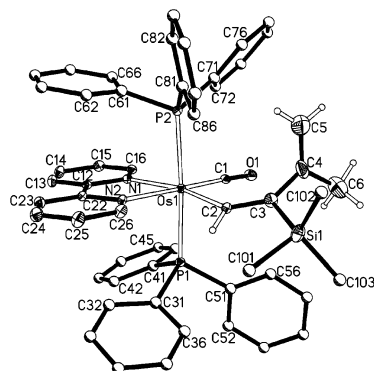
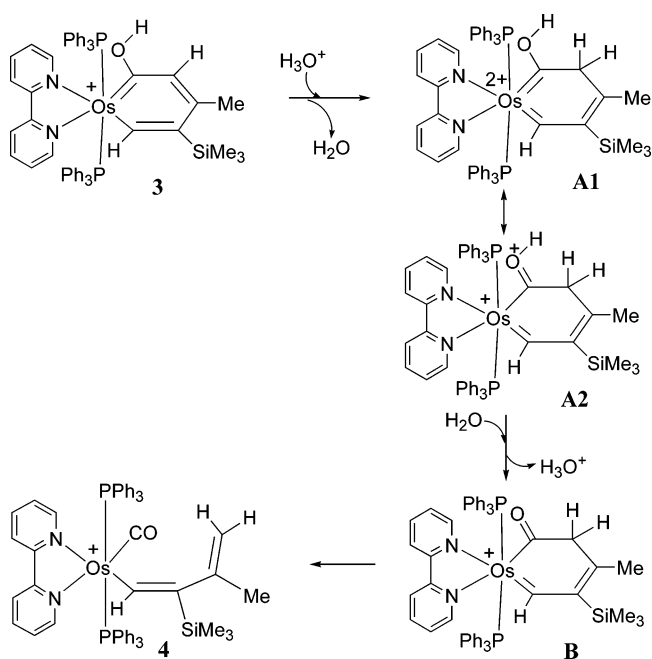


Figure 3. X-ray structure of complex **4**. Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–C(1) 1.851(6), Os(1)–C(2) 2.093(5), Os(1)–P(1) 2.3804(14), Os(1)–P(2) 2.4112(14), Os(1)–N(1) 2.149(5), Os(1)–N(2) 2.170(4), C(1)–O(1) 1.152(7), C(2)–C(3) 1.353(8), C(3)–C(4) 1.491(10), C(4)–C(5) 1.308(5), C(4)–C(6) 1.478(13), O(1)–C(1)–Os(1) 176.3(5), Os(1)–C(2)–C(3) 140.6(5), C(2)–C(3)–C(4) 124.2(6), C(3)–C(4)–C(5) 121.1(9), C(3)–C(4)–C(6) 121.8(8), C(5)–C(4)–C(6) 116.8(9).

As mentioned previously, nucleophilic attack at the carbyne carbon of osmabenzynes is expected if we assume that the reaction is frontier orbital (LUMO here) controlled. The reactivity is similar to that of Fischer carbynes, which can be nucleophilically attacked at the carbyne carbon to give carbene complexes.³⁴ For osmium carbyne complexes, nucleophilic addition reactions with methanol and water have been reported, for example, in the reactions of $\text{CpOs}(\text{CPh})(\text{L})$ ($\text{L} = \text{P}(\text{iPr})_3$, $\text{P}(\text{iPr}_2\text{CH}=\text{CH}_2)$) with MeOH to give $\text{CpOsH}(\text{C}(\text{OMe})\text{Ph})(\text{L})$,³⁵ the reaction of $[\text{Os}(\text{CPh})(\text{NH}_3)_5]^{3+}$ with MeOH to give $[\text{Os}(\text{C}(\text{OMe})\text{Ph})(\text{NH}_3)_5]^{2+}$,³⁶ and the reaction of $[\text{Os}(\text{CPh})\text{I}(\text{CO})(\text{PPh}_3)_2]^+$ with H_2O to give $\text{OsPhCl}(\text{CO})_2(\text{PPh}_3)_2$.³⁷ Reactions of vinylidene complexes $\text{L}_n\text{M}=\text{C}=\text{CHR}$ with methanol usually give carbene complexes $\text{L}_n\text{M}=\text{C}(\text{OMe})\text{CH}_2\text{R}$.³⁸ In this sense, in the reaction of **2** with H_2O , complex **2** shows more carbyne than vinylidene character.

The formation of **4** from the reaction of **2** with water presumably proceeds through complex **3**. In fact, it can be demonstrated that the isolated complex **3** can also be converted to complex **4**. Conversion of complex **3** to **4** seems to be promoted by acid/ H_2O . Transformation of the isolated complex **3** to **4** is very slow in drying solvents. In a mixed solvent of THF/ H_2O , the conversion of **3** to **4** was observed, but the reaction was not completed even after 5 days. When a solution of the isolated complex **3** in CD_2Cl_2 was treated with water in the presence of purposely added HBF_4 , the reaction was completed after 12 h to give **4** as the dominant product. Indeed, in the reaction of **2** with water, HOTf can be generated in situ during the formation of **3**, which may catalyze the transformation of **3** to **4**. On the basis of the above observations, a plausible mechanism for the formation of **4** from **3** is proposed in Scheme 2. Protonation of **3** at C2 may give intermediate **A**, which can be deprotonated with H_2O to give the ketone form **B**. The

Scheme 2



isomerization of **3** to the ketone form **B** can be related to the interconversion of enols and ketones, which is well known in organic chemistry and can be catalyzed by both acids and bases.³⁹ A six-electron retro-electrocyclization reaction of **B** would give complex **4**. Six-electron electrocyclicization of hexatrienes and retro-electrocyclization of cyclohexadienes are well-known reactions.⁴⁰ We noted that 16e acyl complexes L_nMCOR usually undergo de-insertion reactions to give 18e complexes $\text{L}_n\text{MR}(\text{CO})$.⁴¹ In our case, complex **4**, formed via retro-electrocyclization from **B**, is an 18e complex, while a normal CO de-insertion of **B** would give a 20e metallacycle, and therefore is very unlikely.

Reaction of Complex 2 with Methanol. Complex **2** is also reactive toward methanol. In the presence of K_2CO_3 , complex **2** in dichloromethane readily reacted with MeOH (Scheme 1) to give the osmabenzene **5**. In the absence of K_2CO_3 , formation of complex **5** also occurred, although the reaction is much slower and also produced other uncharacterized products. Like the reaction with water, one of the SiMe_3 groups in **2** is also changed to H in the reaction with MeOH. Complex **5** can be formed either by first nucleophilic addition of OMe^- to the carbyne carbon of **2**, followed by desilylation, or by first desilylation of **2**, followed by nucleophilic addition of OMe^- to the carbyne carbon of a desilylated osmabenzynes intermediate.

Complex **5** is isolated as a brownish-red solid. The structure of **5** has been confirmed by X-ray diffraction (Figure 4). The structural features of the metallacycle of **5** are similar to those of osmabenzene **3** in that the metallacycle ring also deviates significantly from planarity. The sum of angles in the six-membered ring of **5** is 708.1° . The mean deviation from the least-squares plane through the C1–C5 chain is 0.0669 \AA . The Os is out of the plane of the metallacyclic carbon atoms by

(34) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, 95, 2281.

(35) (a) Esteruelas, M. A.; Gonzalez, A. I.; Lopez, A. M.; Onate, E. *Organometallics* **2003**, 22, 414. (b) Reference 32.

(36) Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, 32, 371.

(37) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, 25, 121.

(38) For reviews on vinylidene complexes, see, for example: (a) Bruce, M. I. *Chem. Rev.* **1991**, 91, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, 22, 59. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, 193–195, 977. (d) Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2006**, 45, 2176.

(39) Loudon, G. M. *Organic Chemistry*, 2nd ed.; Benjamin/Cummings Publishing Co. Inc.: 1984; Chapter 22, p 919.

(40) Ansari, F. L.; Oureshi, R.; Qureshi, M. L. *Electrocyclic Reactions, From Fundamental to Research*; Wiley-VCH: Weinheim, 1999.

(41) Crabtree, R. H. *Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-VCH: Weinheim, 2005.

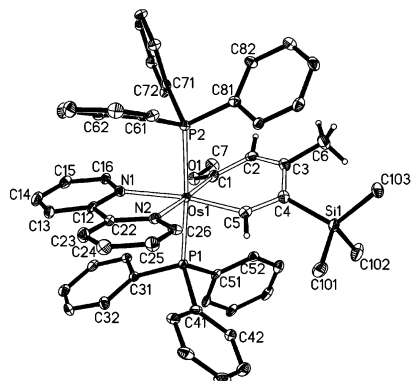
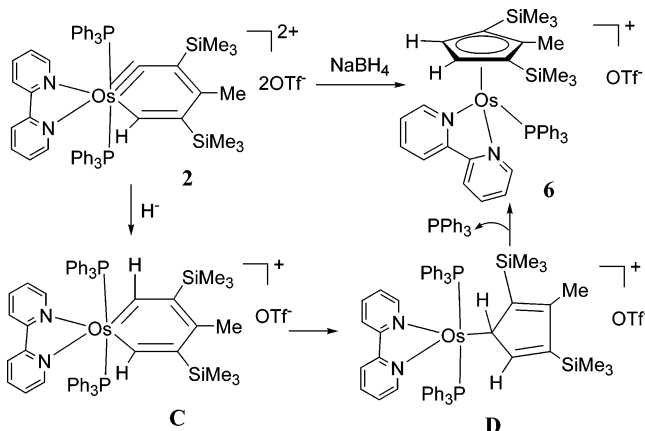


Figure 4. X-ray structure of complex **5**. Counteranion and some of the hydrogen atoms are omitted for clarity.

Scheme 3



0.64 Å. The OMe at C1 and H at C5 are also out of the plane. Consistent with the solid-state structure, the ^1H NMR (in CDCl_3) spectrum showed the OsCH signal at 14.20 ppm, the CH signal at 5.25 ppm, and the OMe signal at 3.47 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed the five carbon signals of the metallacycle at 251.8 (OsC(OMe)), 227.5 (OsCH), 121.8 (OsC(OMe)-CH), 165.0 (CCH_3), and 141.0 (CSiMe_3) ppm. Roper and Wright et al. have previously isolated the related osmabenzene complexes $[\text{Os}(\text{C}(\text{SMe})\text{CH}=\text{CHCH}=\text{CH})(\text{CO})_2(\text{PPh}_3)_2]^+$ and $\text{Os}(\text{C}(\text{SMe})\text{CH}=\text{CHCX}=\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{NO}_2, \text{Br}$).^{3,6} Another related complex, $\text{Ru}(\text{C}(\text{OEt})\text{CPh}=\text{CHCH}=\text{CPh})(\text{Cp})(\text{CO})$, has been detected spectroscopically at low temperature by Jones et al.²⁵ Unlike complex **5**, complexes $\text{Os}(\text{C}(\text{SMe})\text{CH}=\text{CHCX}=\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{NO}_2, \text{Br}$) have a planar metallacycle.⁶

Reaction of Complex 2 with NaBH_4 . Treatment of **2** with NaBH_4 in THF produced the cyclopentadienyl complex **6** (Scheme 3), rather than the expected metallabenzene. The structure of **6** has also been confirmed by X-ray diffraction. The X-ray structure (Figure 5) clearly shows that the complex is a cyclopentadienyl complex with one bipy and one PPh_3 ligand. The solution NMR spectroscopic data are consistent with the solid-state structure. In particular, the ^1H NMR spectrum showed a characteristic Cp proton signal at 4.47 ppm, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed the three Cp carbon signals at 109.8 ($\text{C}(\text{Me})$), 80.9 (CH), and 76.0 (CSiMe_3) ppm.

Mechanistically, complex **6** can be formed by initial attack of the carbyne carbon of the osmabenzynes **2** by H^- to give intermediate **C**, although we have failed to observe the intermediate. Intermediate **C** can undergo a reductive elimination

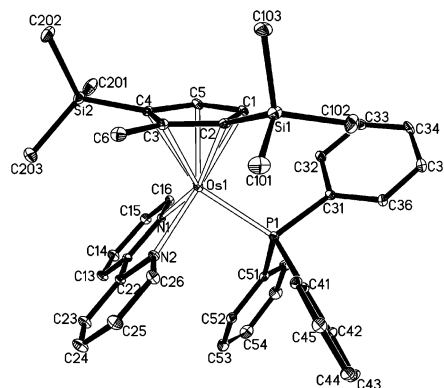


Figure 5. X-ray structure of the complex **6**. Counteranion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–P(1) 2.3218(12), Os(1)–N(1) 2.078(3), Os(1)–N(2) 2.088(3), Os(1)–C(1) 2.181(4), Os(1)–C(2) 2.261(3), Os(1)–C(3) 2.235(4), Os(1)–C(4) 2.236(4), Os(1)–C(5) 2.152(4), C(1)–C(2) 1.460(5), C(2)–C(3) 1.445(6), C(3)–C(4) 1.438(5), C(4)–C(5) 1.426(5), C(1)–C(5) 1.405(6), C(3)–C(6) 1.500(5), N(1)–Os(1)–P(1) 88.91(8), N(2)–Os(1)–P(1) 94.61(9), N(1)–Os(1)–N(2) 75.74(11).

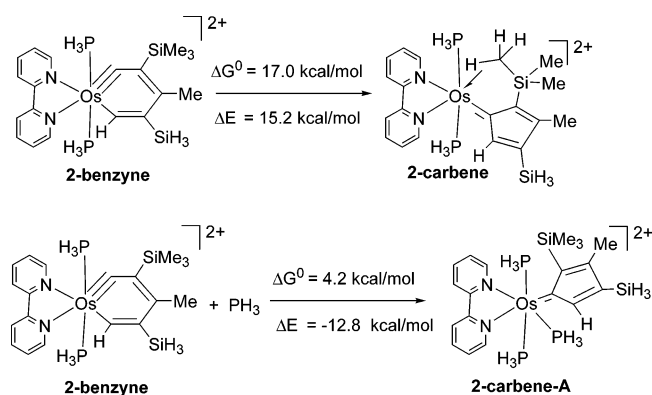
reaction to give the η^1 -cyclopentadienyl complex **D**, which then rearranges to give **6**. Formation of Cp complexes via metallabenzenes has been previously proposed²⁶ and confirmed by reactions of isolated metallabenzene complexes^{4d,10b} and spectroscopically characterized metallabenzenes.²⁵ The easy formation of the Cp complex **6** from intermediate **C** is somewhat unexpected, because the related complexes **3** and **5** can be isolated and were found to be thermally stable at ambient temperature.

Ready conversion of metallabenzene **C** to Cp complex **6** is interesting, especially in view of the fact that osmabenzynes **2**, although it has ring strain, does not undergo reductive elimination to give a carbene complex under similar conditions. Intuitively, the difference can be related to the fact that **C** can evolve to the 18e Cp complex **6**, but a similar reductive elimination reaction of **2** would lead to a 16e osmium carbene complex. A better understanding of the interesting observation comes from a computational study (see below).

Density Functional Theory (DFT) Calculations. Several questions arise from the experimental data. (i) It is noted that metallabenzene **C** readily rearranges to Cp complex **6**, but osmabenzenes **3** and **5**, and even osmabenzynes **2**, which has ring strain, are stable at ambient temperature. It is not obvious whether the difference is kinetic or thermodynamic in origin. (ii) The metallacycles of osmabenzenes **3** and **5** deviate significantly from planarity. However, the closely related osmabenzenes $\text{Os}(\text{C}(\text{SMe})\text{CH}=\text{CHC}(\text{X})=\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{NO}_2, \text{Br}$) adopt a nearly planar structure.⁶ One may ask what causes the nonplanarity in our complexes. (iii) In the reactions of **2** with H_2O and MeOH , one of the SiMe_3 groups in **2** is selectively removed. It is not clear why the SiMe_3 adjacent to the carbyne carbon is preferentially desilylated. To address these problems, DFT calculations were carried out. In consideration of the computational cost, unless otherwise stated, PH_3 and SiH_3 were used to model PPh_3 and SiMe_3 , respectively, in our calculations.

The osmabenzynes $[\text{Os}(\text{C}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})\text{-(bipy)}(\text{PPh}_3)_2](\text{OTf})_2$ (**2**) is structurally closely related to the osmabenzene intermediate $[\text{Os}(\text{C}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2](\text{OTf})_2$ (**C**). **C** is thermally unstable and

Scheme 4



rearranges to cyclopentadienyl complex **6** through a formal reductive elimination reaction. In principle, metallabenzene **2** could also undergo a similar transformation to give a carbene complex containing a five-membered ring. However, such transformation was not observed for **2**. To gain insight into why the reaction did not proceed, we have studied, by DFT calculations, the reductive elimination reaction of **2-benzynes**, a model complex of **2**. The reductive elimination product, **2-carbene**, is an 18e complex with a C–H agostic interaction (Scheme 4). In the model complexes, we replace only one SiMe_3 with SiH_3 and retain one SiMe_3 group in order to avoid the unexpected interaction between an H–Si bond and the metal center in **2-carbene**. ΔG° , the relative Gibbs free energy at $T = 298$ K, and ΔE , the relative electronic energy of the reaction, given in Scheme 4, show that **2-benzynes** is thermodynamically much more stable than **2-carbene**, consistent with the experimental observation that metallabenzynes **2** does not undergo reductive elimination to give a carbene complex. The higher stability of metallabenzynes **2-benzynes** versus carbene **2-carbene** is likely a result of the former having a high degree of conjugation,²⁷ while the latter has very limited conjugation.

Reactions of osmium carbyne complexes $\text{L}_n\text{Os}(\equiv\text{CR})(\text{R}')$ with a two-electron donor ligand L' are known to give carbene complexes $\text{L}_n\text{L}'\text{Os}(\equiv\text{CRR}')$.^{29a,b,42} Thus, one may think that an additional ligand is able to stabilize the reductive elimination product. Therefore, we also calculated the energetics associated with the reaction of **2-benzynes** + $\text{PH}_3 \rightarrow$ **2-carbene-A** (Scheme 4). Indeed, the additional ligand stabilizes the carbene complex significantly. The reaction (electronic) energy becomes -12.8 kcal/mol. However, when the entropy effect is considered, the reaction has a reaction free energy of 4.2 kcal/mol, indicating that the reaction is still thermodynamically unfavorable. We expect that when more realistic phosphine ligands (PPh_3) were employed in the calculations, the reaction (electronic) energy should be much less negative and, therefore, the reaction free energy much more positive. These theoretical calculations indicate that conversion of metallabenzynes to carbene complexes is, in general, thermodynamically unfavorable.

As discussed above, the metallabenzene intermediate **C** easily rearranges to the Cp complex **6**, while the metallabenzene complexes **3** and **5** do not. Figure 6 shows the energetics calculated for the conversion of **C-benzene**, a model complex of **C**, to **6-Cp**, a model complex of **6**, and the conversion of

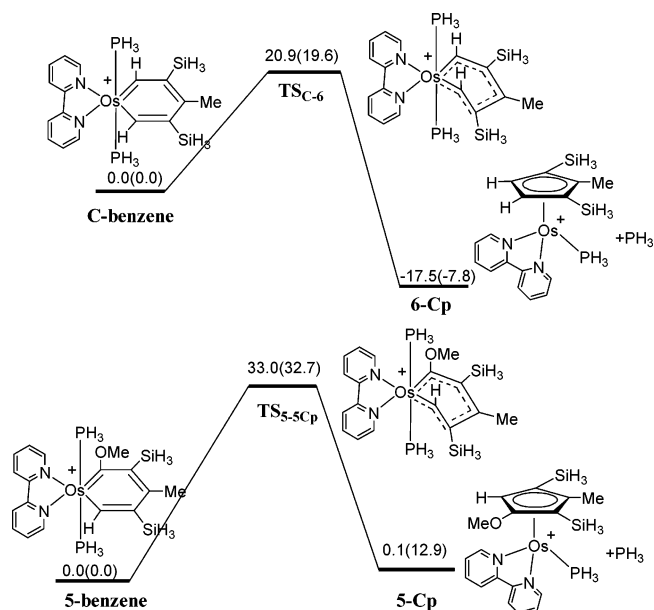


Figure 6. Energy profiles for the conversion of metallabenzynes to Cp complexes. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

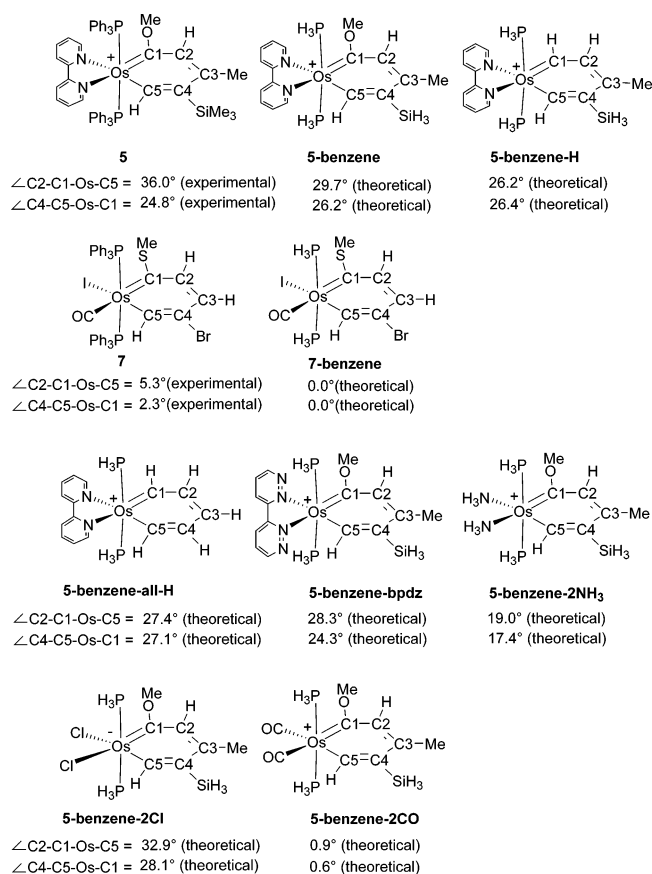
5-benzene, a model complex of **5**, to a Cp complex **5-Cp**. We did not calculate the energetics for the conversion of **3** because we expect that the results should be similar to those calculated for **5**. Interestingly, the results of calculations show that both of the conversions are one-step processes and do not occur via an η^1 -Cp intermediate species such as **D** shown in Scheme 3. Consistent with the experimental observations, the conversion of **C-benzene** to **6-Cp** is exothermic and has a relatively small barrier, while the conversion of **5-benzene** to **5-Cp** is slightly endogonic and has a significantly high barrier. The finding that the conversion of the metallabenzene complex **C-benzene** to **6-Cp** is thermodynamically favorable is not unusual, as it has been found that 18e Cp complexes generally have higher thermodynamic stability when compared with the corresponding metallabenzene complexes.^{5b}

The finding that the conversion of **5-benzene** to **5-Cp** is slightly endogonic is unexpected. This unexpected result has the following important implication: one might be able to synthesize metallabenzynes from Cp complexes if the substituents on the Cp ring and metal fragments were finely tuned. A plausible explanation is given below to explain the unexpected result. The OMe substituent is highly electron-donating and is able to stabilize the metallabenzene structure **C-benzene** because **C-benzene** is expected to have Fischer carbene character and can be stabilized significantly by an electron-donating substituent at the carbene carbon. In addition, the electron-donating OMe substituent on the Cp ligand may also destabilize the Cp complex **5-Cp** because Cp is not a large ring and strong electron-donating substituents, such as OMe or OH, could make the ring too electron-rich to be very stable. To support the plausible explanation, we replaced the OMe substituent in **5-benzene** with H to give the model complex **5-benzene-H** and calculated the reaction energy for the corresponding benzene-to-Cp conversion for **5-benzene-H**. The energetics is similar to that we found for the conversion of **C-benzene** to **6-Cp** shown in Figure 6.

The nonplanarity of the metallabenzene complexes **3** and **5** was reasonably reproduced by our calculations on the model

(42) See, for example: Spaivak, C. J.; Caulton, K. G. *Organometallics* **1998**, *17*, 5260.

Scheme 5



complex **5-benzene** (see the dihedral angles given in Scheme 5). We also calculated the structure of **7-benzene**, a model of Roper's Br-containing osmabenzene **7**. The calculated geometry of **7-benzene** also reproduces well the planarity found in Roper's osmabenzene (see also Scheme 5). Initially, we thought that the OMe or silyl substituent might play a role in the nonplanarity. However, the relevant dihedral angles calculated for **5-benzene-H** and **5-benzene-all-H** (Scheme 5) do not differ much from those calculated for **5-benzene**, suggesting that the OMe and silyl substituents do not play a major role. We also suspected that the repulsive interactions derived from the close contact of C1-OMe and C5-H with their respective nearest C-H bonds in the bipyridine ligand were responsible for the nonplanarity. The nonplanarity remains in the model complex **5-benzene-bpdz**, indicating that the suspicion is not well founded.

Further calculations on **5-benzene-2NH₃**, **5-benzene-2Cl**, and **5-benzene-2CO** (Scheme 5) allow us to see that strong π -acceptor ligands (CO) promote planarity while weak π -acceptor (bipy), π -neutral (NH₃), or π -donor (Cl⁻) ligands give a nonplanar geometry. The results can be explained by considering the four occupied π molecular orbitals, shown in Figure 7, that are characteristics for any given planar osmabenzene. Among the four occupied π orbitals, three have bonding interactions between the metal center and the metal-bonded ring carbon atoms and one, which is the HOMO, has an antibonding interaction between the metal center and the metal-bonded ring carbon atoms. In the π -conjugation system of metallabenzene complexes, two metal d orbitals (d_{xz} and d_{yz} ; see Figure 7 for the Cartesian coordinates), instead of one, participate in the π -bonding interactions, making the HOMO different from that

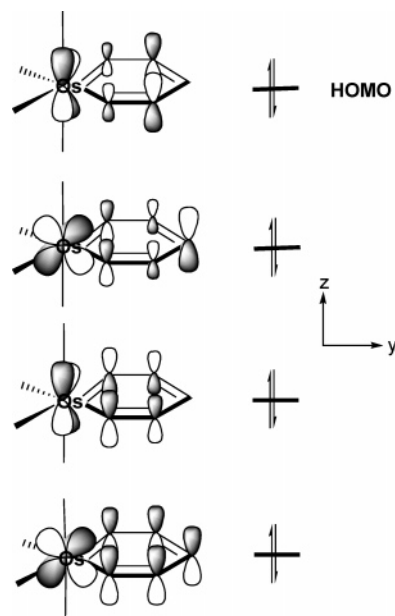
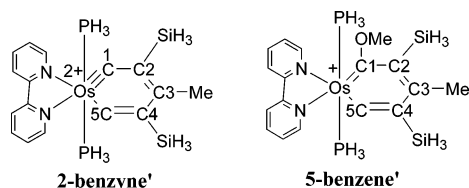


Figure 7. Schematic illustration of the four occupied π -molecular orbitals for osmabenzenes.

found in benzene. A planar geometry should maximize the metal-carbon π -bonding interaction derived from the three bonding orbitals as well as the metal-carbon π -antibonding interaction derived from the HOMO. The π -interactions are reduced in a nonplanar geometry. In theory, the three versus one pattern in the occupied π molecular orbitals should ensure planarity. However, the occupied π orbital that has an antibonding interaction between the metal center and the metal-bonded ring carbon atoms is the HOMO and is expected to have a greater impact than other π orbitals on the structure. Therefore, in certain cases that have a proper combination of ligands and a metal center, such as the osmabenzenes we studied here, the antibonding effect of the HOMO can lead to a nonplanar geometry. The calculation results suggest that strong π -acceptor ligands are able to alleviate the antibonding interaction in the HOMO, giving a planar geometry. Ligands with weak π -acceptor, π -neutral, or π -donor ligands are not able to alleviate the antibonding interaction in the HOMO. Therefore, a nonplanar geometry minimizes the antibonding π -interaction. We are now expanding our calculations in order to better understand how the two opposite forces (three versus one) balance each other and affect the nonplanarity in other related systems.

In the reactions of **2** with H₂O or MeOH, the SiMe₃ group at the carbon next to the carbyne carbon in **2** is removed. As mentioned above, there are two possible pathways, i.e., either first nucleophilic attack on the carbyne carbon of **2**, followed by desilylation, or first desilylation of **2**, followed by nucleophilic attack on the carbyne carbon of a desilylated osmabenzynes intermediate. Experimentally, it is hard to differentiate the two pathways. Desilylation could be initiated by electrophilic attack on the metallacycle by H⁺ or by nucleophilic attack on the silicon centers by water or MeOH. The former process is related to the π electron densities on the carbon centers of the metallacycle, while the latter process is related to the partial atomic charges of the silicon centers in the silyl substituents on the metallacycle. We therefore calculated the partial atomic charges on the Si centers and the π electron densities on the carbon centers of the metallacycles in **2-benzynes**, a model

Scheme 6



complex of **2**, and **5-benzene'**, a model complex of an intermediate formed by nucleophilic attack of **2** (Scheme 6).

The process involving first desilylation of **2**, followed by nucleophilic attack of water on the carbyne carbon of a desilylated osmabenzynes intermediate, is not supported by calculations. The regiochemistry observed for desilylation cannot be explained by the charge distribution on the two silicon centers of **2-benzynes'** (Scheme 6). The partial atomic charges, which were calculated on the basis of the natural bond orbital analysis, associated with the two silicon centers in **2-benzynes'** are almost indistinguishable. The partial atomic charge on the Si center of the silyl substituent at C2 is +0.999, while the partial atomic charge on the Si center of the silyl substituent at C4 is +0.994. When the three occupied π_{\perp} molecular orbitals, which represent the π system of the ring (π_{\perp} stands for π orbitals perpendicular to the six-membered ring of each complex), were considered, we found that the C2 and C4 centers of **2-benzynes'** have 0.55 and 0.60 π electrons, respectively. Electrophilic desilylation based on the π electron density distribution of **2-benzynes'** would give a regiochemistry opposite to what we observed.

The process involving nucleophilic attack on the carbyne carbon of **2**, followed by desilylation, gains support from our calculations. While the partial atomic charges on the Si centers of the silyl substituents at C2 and C4 (+0.960 versus +0.992) in **5-benzene'** are not correlated with the observed regiochemistry of desilylation, we found that the C2 and C4 centers of **5-benzene'** have 0.66 and 0.54 π electrons, respectively. These results show that, after the nucleophilic addition of OMe^- to the carbyne carbon of **2-benzynes'**, the π electron density on C2 becomes higher than that on C4. The π electron density distributions of **5-benzene'** correlate well with the regiochemistry when we assume that desilylation is an electrophilic substitution process.

Conclusion. The thermally stable dicationic osmabenzynes $[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2](\text{OTf})_2$ (**2**) was obtained by treatment of $\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2$ (**1**) with 2,2'-bipyridine and TiOTf . The osmabenzynes complex **2** can be converted to osmabenzenes by nucleophilic addition at its carbyne carbon. The thermal stability of the osmabenzenes generated from the reactions is dependent on the nucleophiles. Thus, **2** reacts with water or methanol to give osmabenzene complexes $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ ($\text{R} = \text{H}, \text{Me}$), but it reacts with NaBH_4 to produce a cyclopentadienyl complex, presumably through the osmabenzene intermediate $[\text{Os}(\equiv\text{CHC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$. Ready conversion of the intermediate to a Cp complex is interesting, especially in view of the fact that osmabenzynes **2**, although it has ring strain, does not undergo reductive elimination to give a carbene complex under similar conditions. A computational study shows that the higher thermal stability of the dicationic osmabenzynes is mainly of thermodynamic origin.

The higher thermal stability of $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ relative to $[\text{Os}(\equiv\text{CHC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ can be related to the stabilization effect of the OR groups on the metallacycle. Unlike reported osmabenzenes, the new osmabenzene complexes deviate significantly from planarity. A theoretical study suggests that the nonplanarity of the osmabenzenes $[\text{Os}(\equiv\text{C}(\text{OR})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ is mainly of electronic origin. Deviation from a planar structure can help to reduce the antibonding π interaction between the metal center and the metal-bonded ring carbon atoms in the HOMO of the metallacycle.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, CHCl_3). The starting material $\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2$ (**1**)²¹ was prepared following the procedure described in the literature. Microanalyses were performed at M-H-W Laboratories (Phoenix, AZ). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 .

$[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2](\text{OTf})_2$ (**2**). A mixture of **1** (0.32 g, 0.32 mmol), 2,2'-bipyridine (0.10 g, 0.63 mmol), and thallium triflate (0.34 g, 0.96 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 18 h to give a brownish-purple solution along with a white precipitate. The volume of the reaction mixture was reduced to ca. 5 mL. The mixture was filtered through Celite to remove the insoluble white solid (TiCl and excess TiOTf). The filtrate was concentrated to ca. 2 mL, and diethyl ether (30 mL) was added slowly with stirring to give a brownish-purple precipitate, which was collected by filtration, washed with diethyl ether (10 mL), and dried under vacuum. THF (5 mL) was added to the crude product to give a suspension, which was stirred for 5 min. The mixture was then allowed to stand for ca. 2 min to afford a purple solid and a brown solution, which were separated by filtration. The solid was collected, washed with diethyl ether (5 mL), and dried under vacuum (0.33 g). The filtrate was also collected and concentrated to ca. 1 mL to produce additional purple solid, which was collected by filtration, washed with diethyl ether (2 mL), and dried under vacuum (0.06 g). Total yield: 0.39 g, 88%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 8.4 (s). ^1H NMR (300.13 MHz, CDCl_3): δ 0.20 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.61 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 2.37 (s, 3 H, CH_3), 6.88–6.95 (m, 12 H, *o*- PPh_3), 7.27–7.32 (t, $J(\text{HH}) = 7.5$ Hz, 12 H, *m*- PPh_3), 7.41 (t, $J(\text{HH}) = 7.3$ Hz, 6 H, *p*- PPh_3), 7.75 (t, $J(\text{HH}) = 6.6$ Hz, 1 H, bipy), 7.85 (d, $J(\text{HH}) = 7.9$ Hz, 1 H, bipy), 7.98–8.09 (m, 3 H, bipy), 8.17 (d, $J(\text{HH}) = 8.0$ Hz, 1 H, bipy), 9.21 (d, $J(\text{HH}) = 5.7$ Hz, 1 H, bipy), 9.23 (d, $J(\text{HH}) = 5.7$ Hz, 1 H, bipy), 13.45 (s, 1 H, OsCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 316.4 (t, $J(\text{PC}) = 8.7$ Hz, $\text{Os}=\text{C}$), 216.3 (t (unresolved), $J(\text{PC}) \approx 4.9$ Hz, $\text{OsCH}=\text{C}$), 198.4 (s, $\text{C}-\text{CH}_3$), 156.4 (s, CH of bipy), 156.1 (s, quaternary C of bipy), 155.3 (s, quaternary C of bipy), 148.9 (s, CH of bipy), 145.6 (s, $\text{OsCH}=\text{C}(\text{SiMe}_3)$), 142.8 (s, CH of bipy), 142.3 (s, CH of bipy), 133.6 (t, $J(\text{PC}) = 4.7$ Hz, *o*- PPh_3), 132.8 (s, *p*- PPh_3), 130.4 (s, CH of bipy), 129.9 (t, $J(\text{PC}) = 4.7$ Hz, *m*- PPh_3), 127.9 (s, CH of bipy), 127.0 (s, CH of bipy), 126.7 (s, CH of bipy), 126.1 (t, $J(\text{PC}) = 27.6$ Hz, *ipso*- PPh_3), 118.7 (s, $\text{Os}=\text{CC}(\text{SiMe}_3)$), 28.9 (s, CH_3), 1.8 (s, SiMe_3), 1.5 (s, SiMe_3). ($^{13}\text{C}\{^1\text{H}\}$ assignment has been confirmed by DEPT-135, $^1\text{H}-^{13}\text{C}$ COSY, and $^1\text{H}-^{13}\text{C}$ COLOC experiments.) Anal. Calcd for $\text{C}_{60}\text{H}_{60}\text{N}_2\text{F}_6\text{O}_6\text{OsP}_2\text{S}_2\text{Si}_2$: C, 51.79; H, 4.35; N, 2.01. Found: C, 51.59; H, 4.55; N, 1.93.

$[\text{Os}(\equiv\text{C}(\text{OH})\text{CH}=\text{C}(\text{Me})\text{C}(\text{SiMe}_3)=\text{CH})(\text{bipy})(\text{PPh}_3)_2]\text{OTf}$ (**3**). To a suspension of **2** (0.10 g, 0.072 mmol) in water (4 mL) was added

THF (3 mL) with stirring. The reactant was dissolved immediately to give a clear, brownish-purple solution. The reaction mixture was stirred for 2 h to give a brownish-red precipitate. The solid was collected by filtration, washed with diethyl ether (2×5 mL), and dried under vacuum. Yield: 78 mg (91%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ 2.5 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 0.16 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.58 (s, 3 H, CH_3), 5.41 (s, 1 H, $\text{OsC}(\text{OH})\text{CH}$), 6.69–6.75 (m, 12 H, *o*-PPh₃), 7.04 (t, $J(\text{HH}) = 7.6$ Hz, 12 H, *m*-PPh₃), 7.21 (t, $J(\text{HH}) = 7.3$ Hz, 6 H, *p*-PPh₃), 7.23–7.30 (m, 2 H, bipy), 7.49–7.56 (m, 2 H, bipy), 7.76 (d, $J(\text{HH}) = 8.0$ Hz, 1 H, bipy), 7.84 (t, $J(\text{HH}) = 7.7$ Hz, 1 H, bipy), 8.71 (d, $J(\text{HH}) = 5.3$ Hz, 1 H, bipy), 9.15 (s, 1 H, $\text{OsC}(\text{OH})$), 9.81 (d, $J(\text{HH}) = 5.3$ Hz, 1 H, bipy), 13.80 (t (unresolved), $J(\text{PH}) \approx 3.9$ Hz, 1 H, OsCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): δ 252.3 (t, $J(\text{PC}) = 11.0$ Hz, $\text{Os}=\text{C}(\text{OH})$), 223.6 (t, $J(\text{PC}) = 9.4$ Hz, OsCH), 164.1 (s, $\text{C}-\text{CH}_3$), 158.5 (s, quaternary C of bipy), 156.5 (s, CH of bipy), 156.4 (s, quaternary C of bipy), 149.3 (s, CH of bipy), 141.5 (s, $\text{OsCH}=\text{C}(\text{SiMe}_3)$), 138.5 (s, CH of bipy), 137.0 (s, CH of bipy), 134.1 (t, $J(\text{PC}) = 4.9$ Hz, *o*-PPh₃), 131.6 (t, $J(\text{PC}) = 23.2$ Hz, *ipso*-PPh₃), 130.1 (s, *p*-PPh₃), 128.3 (t, $J(\text{PC}) = 4.4$ Hz, *m*-PPh₃), 127.3 (s, CH of bipy), 127.2 (s, CH of bipy), 124.2 (s, CH of bipy), 123.6 (s, CH of bipy), 119.7 (s, $\text{OsC}(\text{OH})\text{CH}$), 27.2 (s, CH_3), 2.1 (s, SiMe_3). Anal. Calcd for $\text{C}_{56}\text{H}_{53}\text{N}_2\text{F}_3\text{O}_4\text{OsP}_2\text{SSi}$: C, 56.65; H, 4.50; N, 2.36. Found: C, 56.13; H, 4.63; N, 2.38.

[Os(CH=C(SiMe₃)C(Me)=CH₂)(CO)(bipy)(PPh₃)₂OTf (4). To a suspension of **2** (0.16 g, 1.15 mmol) in THF (15 mL) was added H₂O (1 mL) with stirring. The reactant was dissolved immediately to give a clear, brownish-purple solution. The reaction mixture was stirred at room temperature for 2 days to give a reddish-brown solution. The solvent was reduced to one-third under reduced pressure. CH_2Cl_2 (15 mL) and degassed water (5 mL) were added to the solution. The mixture was stirred for 1 min and then allowed to stand for 5 min. The aqueous layer (top layer), of which the pH value was found to be 1–2, was removed via cannulation. The organic layer was again washed with water (5 mL) and collected by cannulation. The solvent was evaporated to dryness under vacuum. The residue was dissolved in THF (10 mL), and the solution was concentrated to ca. 1 mL. Addition of benzene (10 mL) with stirring produced an orange solid, which was collected by filtration, washed with diethyl ether (2×5 mL), and dried under vacuum. The solid was then redissolved in CH_2Cl_2 (5 mL). The resulting solution was concentrated to ca. 0.5 mL. Diethyl ether (15 mL) was added to the residue to give a yellow solid, which was collected by filtration, washed with diethyl ether (2×5 mL), and dried under vacuum. Yield: 56 mg, 41%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ -1.7 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ -0.03 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.68 (s, 3 H, CH_3), 4.36 (d (unresolved), $J(\text{HH}) \approx 2.0$ Hz, 1 H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 4.44 (d (unresolved), $J(\text{HH}) \approx 2.0$ Hz, 1 H, $\text{C}(\text{CH}_3)=\text{CH}_2$), 6.96 (t, $J(\text{HH}) = 6.7$ Hz, 1 H, bipy), 7.01–7.16 (m, 12 H, *o*-PPh₃), 7.13 (t, $J(\text{HH}) = 7.7$ Hz, 12 H, *m*-PPh₃), 7.25–7.32 (m, 7 H, *p*-PPh₃ and 1 CH of bipyridine (confirmed by a $^1\text{H}-^1\text{H}$ COSY experiment)), 7.49 (t, $J(\text{HH}) = 7.5$ Hz, 1 H, bipy), 7.66 (d, $J(\text{HH}) = 8.1$ Hz, 1 H, bipy), 8.04–8.11 (m, 2 H, bipy), 8.42–8.45 (m, 2 H, $\text{OsCH}=\text{C}(\text{SiMe}_3)$ and 1 CH of bipyridine, confirmed by $^1\text{H}-^{13}\text{C}$ COSY), 8.62 (d, $J(\text{HH}) = 5.3$ Hz, 1 H, bipy). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, CD_2Cl_2): δ 188.6 (t, $J(\text{PC}) = 9.1$ Hz, $\text{Os}(\text{CO})$), 158.9 (s, quaternary C of bipy), 157.8 (s, quaternary C of bipy), 154.9 (s, $-\text{C}(\text{CH}_3)=\text{CH}_2$), 153.4 (s, CH of bipy), 151.8 (s, $\text{OsCH}=\text{C}(\text{SiMe}_3)$), 149.4 (s, CH of bipy), 146.9 (t, $J(\text{PC}) = 9.0$ Hz, $\text{OsCH}=\text{C}(\text{SiMe}_3)$), 140.9 (s, CH of bipy), 137.9 (s, CH of bipy), 134.4 (t, $J(\text{PC}) = 5.0$ Hz, *o*-PPh₃), 131.2 (s, *p*-PPh₃), 130.0 (t, $J(\text{PC}) = 24.3$ Hz, *ipso*-PPh₃), 128.9 (t, $J(\text{PC}) = 4.8$ Hz, *m*-PPh₃), 128.2 (s, CH of bipy), 127.6 (s, CH of bipy), 126.0 (s, CH of bipy), 125.2 (s, CH of bipy), 112.2 (s, $-\text{C}(\text{CH}_3)=\text{CH}_2$), 25.0 (s, CH_3), 0.3 (s, SiMe_3). Anal. Calcd for $\text{C}_{56}\text{H}_{53}\text{N}_2\text{F}_3\text{O}_4\text{OsP}_2\text{SSi}$: C, 56.65; H, 4.50; N, 2.36. Found: C, 56.98; H, 4.09; N, 2.11.

[Os(=C(OMe)CH=C(Me)C(SiMe₃)=CH)(bipy)(PPh₃)₂OTf (5). To a mixture of **2** (0.12 g, 0.086 mmol) and K_2CO_3 (0.12 g, 0.87 mmol) were added CH_2Cl_2 (8 mL) and MeOH (2 mL). The reaction mixture

was stirred at room temperature for 24 h and then filtered through Celite to give a brownish-red filtrate. The solvent was evaporated to dryness under vacuum, and the residue was extracted with CH_2Cl_2 (4 mL). The mixture was filtered through Celite to remove the insoluble solid (K_2CO_3). The extractant was concentrated to ca. 0.5 mL, and diethyl ether (10 mL) was added slowly with stirring to afford a brownish-red solid, which was collected by filtration, washed with diethyl ether (2×5 mL), and dried under vacuum. Yield: 65 mg, 63%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 1.7 (s). ^1H NMR (300.13 MHz, CDCl_3): δ 0.16 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.55 (s, 3 H, $\text{C}-\text{CH}_3$), 3.47 (s, 3 H, OCH_3), 5.25 (s, 1 H, $\text{Os}=\text{C}(\text{OMe})\text{CH}$), 6.57–6.63 (m, 12 H, *o*-PPh₃), 7.01 (t, $J(\text{HH}) = 7.4$ Hz, 12 H, *m*-PPh₃), 7.19 (t, $J(\text{HH}) = 7.2$ Hz, 6 H, *p*-PPh₃), 7.22–7.35 (m, 2 H, bipy), 7.63 (t, $J(\text{HH}) = 7.8$ Hz, 1 H, bipy), 7.90 (d, $J(\text{HH}) = 7.8$ Hz, 1 H, bipy), 8.05 (t, $J(\text{HH}) = 7.8$ Hz, 1 H, bipy), 8.27 (d, $J(\text{HH}) = 8.1$ Hz, 1 H, bipy), 8.70 (d, $J(\text{HH}) = 5.1$ Hz, 1 H, bipy), 9.43 (d, $J(\text{HH}) = 5.4$ Hz, 1 H, bipy), 14.20 (t, $J(\text{PH}) = 3.6$ Hz, 1 H, OsCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 251.8 (t, $J(\text{PC}) = 9.2$ Hz, $\text{Os}=\text{C}(\text{OMe})$), 227.5 (t, $J(\text{PC}) = 8.1$ Hz, OsCH), 165.0 (s, $\text{C}-\text{CH}_3$), 158.3 (s, quaternary C of bipy), 156.4 (s, quaternary C of bipy), 155.2 (s, CH of bipy), 148.7 (s, CH of bipy), 141.0 (s, $\text{OsCH}=\text{C}(\text{SiMe}_3)$), 139.2 (s, CH of bipy), 137.7 (s, CH of bipy), 133.7 (t, $J(\text{PC}) = 4.9$ Hz, *o*-PPh₃), 131.6 (t, $J(\text{PC}) = 23.0$ Hz, *ipso*-PPh₃), 130.1 (s, *p*-PPh₃), 128.2 (t, $J(\text{PC}) = 4.5$ Hz, *m*-PPh₃), 127.1 (s, CH of bipy), 126.9 (s, CH of bipy), 125.6 (s, CH of bipy), 124.8 (s, CH of bipy), 121.8 (s, $\text{Os}=\text{C}(\text{OMe})\text{CH}$), 58.6 (s, OCH_3), 27.9 (s, $\text{C}-\text{CH}_3$), 2.2 (s, SiMe_3). Anal. Calcd for $\text{C}_{57}\text{H}_{55}\text{N}_2\text{F}_3\text{O}_4\text{OsP}_2\text{SSi}$: C, 56.99; H, 4.61; N, 2.33. Found: C, 56.68; H, 4.48; N, 2.31.

[Os($\eta^5\text{-C}_5\text{H}_2\text{Me}(\text{SiMe}_3)_2$)(bipy)(PPh₃)₂OTf (6). A mixture of **2** (0.32 g, 0.23 mmol) and sodium borohydride (0.33 g, 8.6 mmol) in THF (10 mL) was stirred for 4 h to give a brown solution with some white precipitate. The mixture was filtered to remove the white precipitate. The filtrate was evaporated to dryness under vacuum, and the resulting residue was redissolved in CH_2Cl_2 (2 mL). Addition of diethyl ether (30 mL) to the solution gave a reddish brown precipitate, which was collected by filtration, washed with hexane (2×2 mL), and dried under vacuum. Yield: 0.18 g, 57%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 13.8 (s). ^1H NMR (300.13 MHz, CDCl_3): δ 0.11 (s, 18 H, $\text{Si}(\text{CH}_3)_3$), 1.77 (s, 3 H, CH_3), 4.63 (s, 2 H, CH), 7.13 (t, $J(\text{HH}) = 8.1$ Hz, 6 H, *o*-PPh₃), 7.30 (t, $J(\text{HH}) = 6.6$ Hz, 2 H, bipy), 7.43 (t, $J(\text{HH}) = 8.4$ Hz, 6 H, *m*-PPh₃), 7.51 (t, $J(\text{HH}) = 7.2$ Hz, 3 H, *p*-PPh₃), 7.93 (t, $J(\text{HH}) = 7.5$ Hz, 2 H, bipy), 8.40 (d, $J(\text{HH}) = 8.1$ Hz, 2 H, bipy), 9.35 (d, $J(\text{HH}) = 5.7$ Hz, 2 H, bipy). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 158.7 (s, quaternary C of bipy), 156.6 (s, CH of bipy), 136.6 (s, CH of bipy), 133.7 (d, $J(\text{PC}) = 10.6$ Hz, *o*-PPh₃), 131.0 (d, $J(\text{PC}) = 50.2$ Hz, *ipso*-PPh₃), 131.0 (s, *p*-PPh₃), 129.0 (d, $J(\text{PC}) = 10.1$ Hz, *m*-PPh₃), 127.0 (s, CH of bipy), 124.7 (s, CH of bipy), 109.8 (d, $J(\text{PC}) = 5.0$ Hz, $\text{C}(\text{CH}_3)$), 80.9 (s, CH), 76.0 (d, $J(\text{PC}) = 3.8$ Hz, $\text{C}(\text{SiMe}_3)$), 14.0 (s, $\text{C}(\text{CH}_3)$), 0.4 (s, SiMe_3). Anal. Calcd for $\text{C}_{41}\text{F}_3\text{H}_{46}\text{O}_3\text{N}_2\text{PSSi}_2\text{Os}$: C, 50.18; H, 4.73; N, 2.85. Found: C, 50.01; H, 4.65; N, 2.75.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 solutions layered with hexane for **2**, **3**, **5**, and **6** and from CH_2Cl_2 solution layered with benzene and hexane for **4**. Selected crystals of **2**–**6** were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on a Bruker Apex CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Multiscan absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL (Version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. The OH group at the C1 of the metallabenzene **3** was hydrogen-bonded to the solvent water molecule, and the solvent water molecule was hydrogen-bonded to one of the O atoms of the OTf anion. The OTf counteranion in **3** was disordered over two sites, which were refined with common

Table 2. Crystal Data and Structure Refinement for 2–6

	compound				
	2	3	4	5	6
empirical formula	C ₆₀ H ₆₀ F ₆ N ₂ O ₆ Os-P ₂ S ₂ Si ₂	C ₅₆ H ₅₅ F ₃ N ₂ O ₅ Os-P ₂ SSi	C ₆₂ H ₆₁ F ₃ N ₂ O ₅ Os-P ₂ SSi	C ₅₇ H ₅₅ F ₃ N ₂ O ₄ Os-P ₂ SSi	C ₄₂ H ₄₈ Cl ₂ F ₃ N ₂ O ₃ Os-PSSi ₂
formula weight	1391.54	1205.31	1283.42	1201.32	1066.13
temperature, K	100(2)	173(2)	173(2)	100(2)	298(2)
radiation (Mo K α), Å	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	21.5222(11)	13.857(3)	16.294(3)	13.7519(7)	10.7215(11)
<i>b</i> , Å	22.0572(11)	19.181(4)	20.435(4)	19.6084(11)	11.4672(11)
<i>c</i> , Å	12.4107(6)	19.294(4)	18.652(4)	19.1742(11)	20.273(2)
α , °	90	90	90	90	104.072(2)
β , °	98.1510(10)	97.087(3)	109.188(4)	97.3640(10)	101.455(2)
γ , °	90	90	90	90	95.036(2)
<i>V</i> , Å ³	5832.1(5)	5089.1(17)	5866(2)	5127.7(5)	2345.1(4)
<i>Z</i>	4	4	4	4	2
<i>d</i> _{calcd} , g cm ^{−3}	1.585	1.573	1.453	1.556	1.510
abs coeff, mm ^{−1}	2.426	2.696	2.344	2.674	3.012
<i>F</i> (000)	2808	2432	2600	2424	1068
crystal size, mm	0.20 × 0.20 × 0.12	0.14 × 0.10 × 0.06	0.24 × 0.16 × 0.10	0.15 × 0.12 × 0.10	0.18 × 0.15 × 0.13
θ range, °	1.90–27.50	1.71–25.50	1.44–25.00	1.49–25.50	2.00–25.00
reflns collected	35 203	30 361	30 563	26 797	15 084
indep reflns	13 278 (<i>R</i> _{int} = 0.0468)	9455 (<i>R</i> _{int} = 0.1063)	10 302 (<i>R</i> _{int} = 0.0349)	9521 (<i>R</i> _{int} = 0.0675)	8025 (<i>R</i> _{int} = 0.0555)
obsd reflns (<i>I</i> > 2 σ (<i>I</i>))	10 960	5971	8406	6997	5734
data/restraints/params	13 278/0/730	9455/41/629	10 302/31/652	9521/0/640	8025/0/514
goodness-of-fit on <i>F</i> ²	1.005	0.993	1.072	0.949	0.993
final <i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0378, <i>wR</i> ₂ = 0.0751	<i>R</i> ₁ = 0.0564, <i>wR</i> ₂ = 0.1218	<i>R</i> ₁ = 0.0415, <i>wR</i> ₂ = 0.1179	<i>R</i> ₁ = 0.0427, <i>wR</i> ₂ = 0.0786	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.0678
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.0787	<i>R</i> ₁ = 0.1082, <i>wR</i> ₂ = 0.1322	<i>R</i> ₁ = 0.0534, <i>wR</i> ₂ = 0.1231	<i>R</i> ₁ = 0.0695, <i>wR</i> ₂ = 0.0845	<i>R</i> ₁ = 0.0756, <i>wR</i> ₂ = 0.0726
peak and hole, e Å ^{−3}	1.366 and −0.600	2.469 and −2.351	1.528 and −0.706	1.313 and −0.649	1.371 and −0.799

variable isotropic thermal parameters using suitable restraints. The benzene solvent molecule in **4** was disordered over two sites; each site was treated as a rigid body and refined with common variable isotropic thermal parameters. The solvent water molecule in **4** was also disordered over two sites, which were refined isotropically without addition of hydrogen atoms. Further details on crystal data, data collection, and refinements are summarized in Table 2.

Computational Study. All structures were optimized at the mPW1K level of density functional theory.⁴³ Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima or transition states. In the DFT calculations, the effective core potentials (ECPs) of Stuttgart/Dresden (SDD)⁴⁴ were used to describe Os, I, Cl, Br, S, Si, and P atoms, while the standard 6-31g basis set was used for C, O, N, and H. Polarization functions were added for Os ($\zeta_f = 0.707$), I ($\zeta_d = 0.266$), Cl ($\zeta_d = 0.514$), P ($\zeta_d = 0.340$), and Si ($\zeta_d = 0.262$).^{5b,45} Calculations of intrinsic reaction coordinates⁴⁶ were

also performed on transition states to confirm that such structures are indeed connecting two minima. All the calculations were performed with the Gaussian 03 software package.⁴⁷

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Supporting Information Available: Complete ref 47; tables giving Cartesian coordinates and electronic energies for all the calculated structures (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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