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Electrophilic Substitution Reactions of Metallabenzynes

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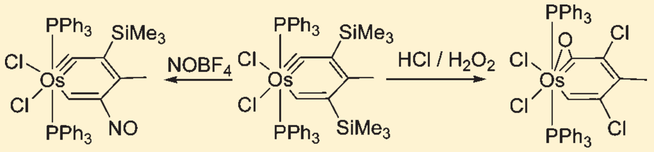


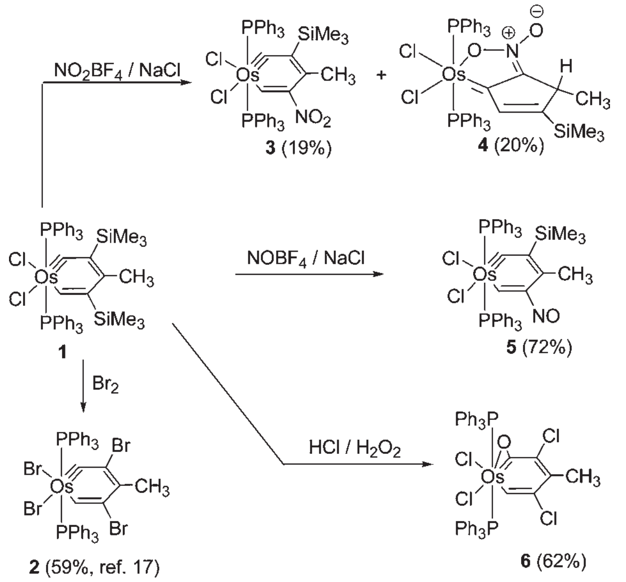
ABSTRACT: The electrophilic substitution reactions of metallabenzynes $Os(\equiv CC(R){=}C(CH_3)C(R){=}CH)Cl_2(PPh_3)_2$ ($R = SiMe_3$, H) were studied. These metallabenzynes react with electrophilic reagents, including Br_2, NO_2BF_4, $NOBF_4$, HCl/H_2O_2, and $AlCl_3/H_2O_2$ to afford the corresponding bromination, nitration, nitrosation, and chlorination products. The reactions usually occur at the C2 and C4 positions of the metallacycle. These observations support the notion that metallabenzynes exhibit aromatic properties.

■ INTRODUCTION

There has been much interest in the chemistry of transition-metal-containing metallaaromatics. The chemistry of transition-metal-containing metallabenzenes,[1] in particular, has attracted considerable recent attention. Previous investigations have led to the isolation and characterization of an impressive number of stable metallabenzenes, especially those of osmium,[2−4] iridium,[5−8] platinum,[9] ruthenium,[10,11] and rhenium.[12] The structural parameters as well as the NMR (^1H and ^{13}C) data associated with the metallabenzene ring suggest that metallabenzenes have aromatic character. The fact that metallabenzenes have chemical properties similar to those of benzene has also been confirmed experimentally through reactivity studies. For example, it has been demonstrated that metallabenzenes can undergo typical aromatic electrophilic substitution reactions[2b,5d] and nucleophilic aromatic substitution of hydrogens[2f] and can function as η^6 ligands to form half-sandwich, sandwich,[13] and triple-decker[14] complexes.

Compounds closely related to metallabenzenes are metallabenzynes,[15] which can be thought as being formed by replacement of a C atom or a CH group in benzene with an isolobal transition-metal fragment. In comparison with that of metallabenzenes, the chemistry of metallabenzynes is less developed. The first such compound was reported in 2001,[16] and several additional stable metallabenzynes have been successfully isolated more recently.[17,18] Unlike benzyne, which is thermally unstable, metallabenzynes can be isolated as thermally stable solids and can be conveniently characterized by NMR spectroscopy and X-ray diffraction. The X-ray diffraction study of known metallabenzynes shows that the six-membered metallacycle has a planar delocalized structure. The delocalized structural feature is similar to that of aromatic ring systems such as benzene and metallabenzenes. In this regard, it would be interesting to find out if metallabenzynes could also undergo typical reactions of aromatic compounds or benzynes.

Scheme 1



One of the typical chemical properties of aromatic compounds is that they can undergo electrophilic aromatic substitution reactions.[19] An interesting question is whether metallabenzynes could also undergo electrophilic aromatic substitution reactions. In this paper, we report our comprehensive study on the reactions of osmabenzynes $Os(\equiv CC(R){=}C(CH_3)C(R){=}CH)Cl_2(PPh_3)_2$ ($R = SiMe_3$, H) with various electrophiles, including NO_2BF_4, $NOBF_4$, HCl/H_2O_2, $AlCl_3/H_2O_2$, and Br_2. In the literature, only the reactions of the $SiMe_3$-containing osmabenzyne $Os(\equiv CC(SiMe_3){=}C(CH_3)C(SiMe_3){=}CH)Cl_2(PPh_3)_2$ with Br_2 and HBF_4 were briefly communicated by us.[17]

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Table 1. Crystallographic Details

	$3\cdot 2C_6H_6$	4	$5\cdot 0.5C_6H_{14}$	$6\cdot 1.5CH_2Cl_2$	$7\cdot 0.5C_6H_{14}$	$9\cdot 0.75CH_2Cl_2$
empirical formula	$C_{45}H_{43}Cl_2NO_2OsP_2Si\cdot 2C_6H_6$	$C_{45}H_{44}Cl_2NO_2OsP_2Si$	$C_{45}H_{43}Cl_2NOOsP_2Si\cdot 0.5C_6H_{14}$	$C_{42}H_{34}Cl_4OOsP_2\cdot 1.5CH_2Cl_2$	$C_{45}H_{43}Cl_3OsP_2Si.0.5C_6H_{14}$	$C_{42}H_{35}Cl_2NO_3OsP_2\cdot 0.75CH_2Cl_2$
formula wt	1137.15	981.94	1008.02	1076.02	1029.46	988.44
temp, K	253(2)	100(2)	100(2)	173(2)	100(2)	100(2)
radiation (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$I2$
a, Å	10.386(11)	12.0580(10)	10.1908(10)	21.2492(10)	10.0996(7))	26.730(5)
b, Å	18.76(2)	12.4671(10)	17.7202(18)	10.0490(5)	18.2847(12)	10.8726(18)
c, Å	27.36(3)	14.8212(12)	24.634	39.926(2)	23.7928(16)	26.972(5)
α, deg	90.00	83.779(2)	90	90.00	90.00	90
β, deg	99.125(18)	72.020(2)	95.5520(10)°	99.8030(10)	94.9460(10)	91.149(5)
γ, deg	90.00	75.575(2)	90	90.00	90.00	90
V, Å^3	5265(10)	2051.2(3)	4427.6(8)	8401.0(7)	4377	7837(2)
Z	4	2	4	8	4	8
d_{calcd}, g cm^{-3}	1.435	1.590	1.512	1.701	1.562	1.676
abs coeff, mm^{-1}	2.649	3.385	3.137	3.592	3.233	3.617
F(000)	2296	982	2028	4248	2068	3916
no. of rflns collected	36 763	11 155	27 899	28 935	33 907	14 803
no. of indep rflns	9155	7827	8602	7245	7584	8029
no. of data/restraints/params	9155/0/595	7827/29/505	8602/8/506	7245/0/492	7584/9/500	8029/16/971
goodness of fit on F^2	0.982	1.002	1.019	1.012	1.029	1.036
final R ($I > 2\sigma(I)$)	R1 = 0.0226, wR2 = 0.0480	R1 = 0.0613, wR2 = 0.0993	R1 = 0.0315, wR2 = 0.0621	R1 = 0.0268, wR2 = 0.0618	R1 = 0.0368, wR2 = 0.0591	R1 = 0.0496, wR2 = 0.1160
peak and hole, e Å^{-3}	0.910 and −0.365	1.444 and −1.420	0.818 and −0.436	0.870 and −0.861	0.928 and −1.087	2.805 and −2.718

RESULTS AND DISCUSSION

Reactions of $Os(\equiv CC(SiMe_3)=C(CH_3)C(SiMe_3)=CH)Cl_2(PPh_3)_2$ (1). We have previously reported that reaction of **1** with excess bromine affords the osmabenzyne $Os(\equiv CC(Br)=C(CH_3)C(Br)=CH)Cl_2(PPh_3)_2$ (**2**) as the predominant product (Scheme 1).[17] The reaction can be regarded as a rare example of an electrophilic substitution reaction of a metallabenzyne. The reactivity is unusual when compared with that of benzynes. The reactivities of benzynes are usually associated with the C≡C triple bond.[20] Thus, benzynes react with bromine to give 1,2-dibromobenzenes.[21] Formation of **2** from the reaction of **1** with Br_2 promoted us to study electrophilic substitution reactions of **1** with other electrophiles. The results are summarized in Scheme 1.

Nitration. Nitration is one of the typical electrophilic substitution reactions of aromatic organic compounds. Inspired by the success of the electrophilic substitution reaction of osmabenzene $Os[C_5H_4(SMe\text{-}1)]I(CO)(PPh_3)_2$ with $Cu(NO_3)_2/(CH_3CO)_2O$,[2b] we initially carried out the reaction of **1** with $Cu(NO_3)_2/(CH_3CO)_2O$. However, the reaction produced a complicated mixture, which could not be separated and identified. We then carried out the nitration reaction with the nitronium salt NO_2BF_4. Complexes **3** and **4** were isolated from the reaction of **1** with NO_2BF_4 (in 1:4.5 molar ratio) in the presence of NaCl in CH_2Cl_2 at −16 to −5 °C (Scheme 1). In the absence of NaCl, a complicated mixture was obtained, probably due to partial displacements of the chloride ligands. The reaction temperature appears also to be important for the success of the reaction. Higher temperature led to the production of a complicated mixture while the reaction did not proceed at a lower temperature.

Complex **3** was isolated as a yellow solid. It has been characterized by elemental analysis and multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction analysis. The crystallographic details are given in Table 1. Selected bond lengths and angles are given in Table 2.

The molecular structure of **3** is shown in Figure 1, which reveals that it is a metallabenzyne complex formed via replacing the $SiMe_3$ substituent at C4 in **1** by NO_2. The complex contains an essentially planar six-membered metallacycle, with the sum of the angles in the six-membered ring of 719.55°, which is very close to the ideal value of 720°. The Os−C1 bond length (1.788(3) Å) is slightly shorter than that of **1** (1.815(4) Å),[16] while the Os−C5 bond length (2.013(3) Å) is longer than the corresponding bond of **1** (1.939(5) Å). The bond distances of the remaining C−C bonds within the metallacycle (1.366(4)−1.440(4) Å) are within the range of typical aromatic C−C bond lengths. The bond distances of O(1)−N(1) and O(2)−N(1) are 1.215(3) and 1.242(3) Å, respectively, with an O(1)−N(1)−O(2) angle of 123.1(3)°.

The solid-state structure of **3** is supported by multinuclear NMR spectroscopy and elemental analysis. The ^1H NMR spectrum (in C_6D_6) showed a downfield singlet signal at 12.88 ppm, which can be assigned to the Os*CH* proton. The CH_3 proton signal was observed at 1.75 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **3** (in $CDCl_3$) displayed the signals of the two metal-bound carbon atoms at 297.5 ppm for the carbyne-like carbon (Os≡*C*) and at 216.4 ppm for the other carbon (Os*C*H). The ^{13}C signals for the remaining carbon atoms of the metallacycle (CCH_3, $OsCH=C(NO_2)$, and $Os\equiv CC(Si(CH_3)_3)$ were observed at 187.3, 171.6, and 116.2 ppm, respectively. The CH_3

Table 2. Selected Bond Lengths and Angles for 3 and 5

	3	5
	Bond Lengths (Å)	
Os(1)−P(1)	2.425(2)	2.4346(11)
Os(1)−P(2)	2.425(2)	2.4209(7)
Os(1)−Cl(1)	2.455(3)	2.4502(9)
Os(1)−Cl(2)	2.474(2)	2.4612(9)
Os(1)−C(1)	1.788(3)	1.770(4)
Os(1)−C(5)	2.013(3)	1.992(3)
C(1)−C(2)	1.375(4)	1.363(5)
C(2)−C(3)	1.410(4)	1.405(5)
C(3)−C(4)	1.440(4)	1.451(5)
C(4)−C(5)	1.366(4)	1.381(5)
	Bond Angles (deg)	
C(1)−Os(1)−C(5)	78.65(13)	79.12(5)
C(2)−C(1)−Os(1)	153.7(2)	154.7(3)
C(1)−C(2)−C(3)	111.6(3)	110.6(3)
C(2)−C(3)−C(4)	119.1(2)	120.8(3)
C(5)−C(4)−C(3)	127.4(2)	125.0(3)
C(4)−C(5)−Os(1)	129.1(2)	129.7(3)

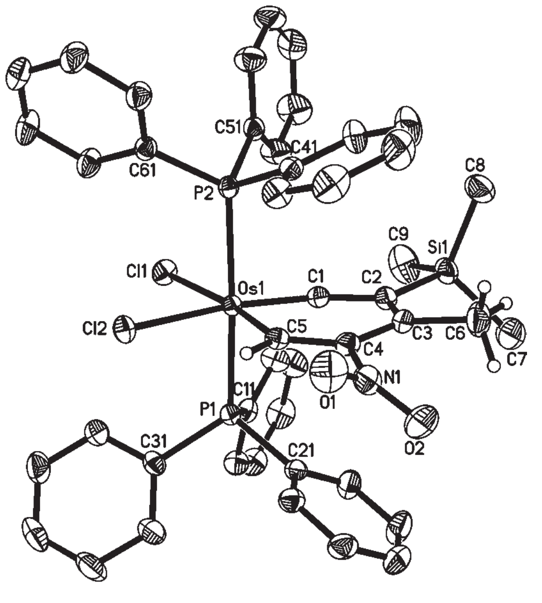


Figure 1. Molecular structure of 3. The hydrogen atoms of PPh_3 and $SiMe_3$ are omitted for clarity.

signal was observed as a singlet at 23.0 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum (in $CDCl_3$) showed a singlet at −0.8 ppm.

Complex 4 was isolated as an orange-red solid. The paramagnetic compound has been characterized by elemental analysis as well as single-crystal X-ray diffraction analysis. The molecular geometry is shown in Figure 2. The crystallographic details are given in Table 1. Selected bond lengths and angles are given in Table 3.

As shown in Figure 2, the osmium center of 4 is in a five-membered ring. The Os−C1 bond distance (1.957(8) Å) is within the range of Os−C(vinyl) bonds (1.897−2.195 Å)[22,23] and Os−C(carbene) bonds (1.837−2.045 Å for non Fisher Os carbene).[22,24] The C4−C5 bond length of 1.369(11) Å is in the range of typical C−C double bonds, while bond lengths of C(2)−C(3) (1.502(8) Å) and C(3)−C(4) (1.505(9) Å) are in the range of C−C single bonds. The bond length of C(1)−C(2) (1.395(10) Å) is shorter than typical C−C single bonds and longer than typical C−C double bonds, probably due to the delocalization involving C(1), C(2), and the NO_2 group. The C(2)−N(1) bond (1.304(9) Å) is appreciably shorter than the C−N bond in complex 3 (1.482(4) Å) and longer than the C═N bond

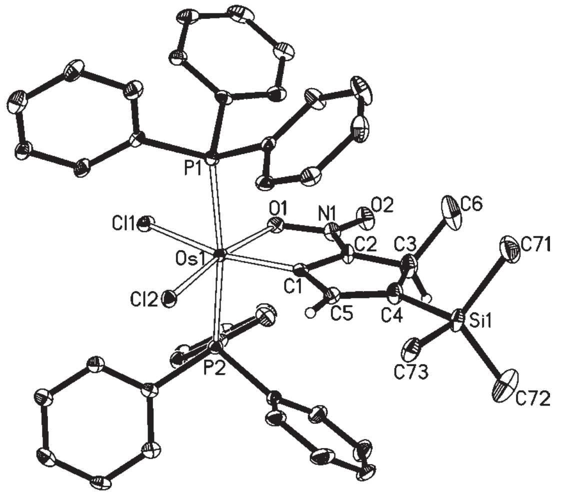
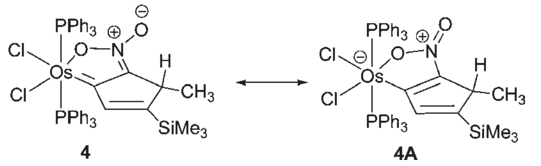


Figure 2. Molecular structure of paramagnetic complex 4. The hydrogen atoms of PPh_3, CH_3, and $SiMe_3$ are omitted for clarity.

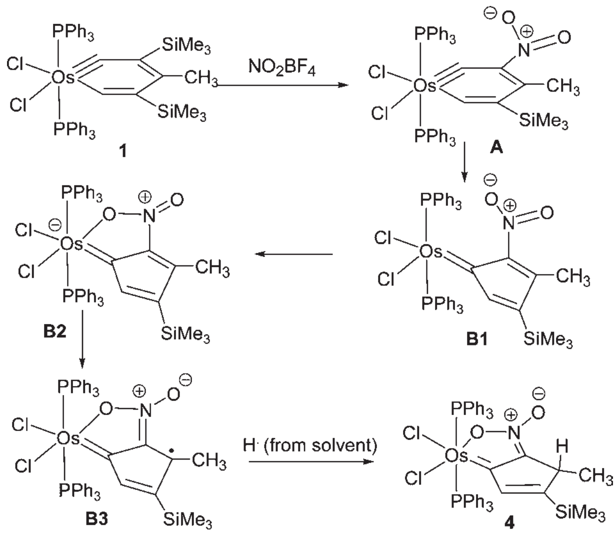
Table 3. Selected Bond Lengths and Angles for 4

Bond Distances (Å)			
Os(1)−P(1)	2.398(2)	Os(1)−P(2)	2.403(2)
Os(1)−Cl(1)	2.410(2)	Os(1)−Cl(2)	2.3233(19)
Os(1)−C(1)	1.957(8)	Os(1)−O(1)	2.095(5)
C(1)−C(2)	1.395(10)	C(1)−C(5)	1.463(10)
C(2)−N(1)	1.304(9)	C(2)−C(3)	1.502(9)
C(3)−C(4)	1.505(9)	C(3)−C(6)	1.540(9)
C(4)−C(5)	1.369(11)	N(1)−O(2)	1.253(7)
N(1)−O(1)	1.307(10)		
Bond Angles (deg)			
C(1)−Os(1)−O(1)	76.9(3)	C(2)−C(1)−Os(1)	114.6(5)
C(2)−C(1)−C(5)	105.5(7)	C(1)−C(2)−C(3)	109.5 (7)
C(2)−C(3)−C(4)	103.4(8)	C(4)−C(5)−C(1)	112.5(7)
C(5)−C(4)−C(3)	106.3(8)	C(5)−C(1)−Os(1)	139.9(6)
C(2)−C(3)−C(6)	117.7(12)	C(4)−C(3)−C(6)	118.7(12)
P(1)−Os(1)−P(2)	172.73(8)	C(1)−Os(1)−Cl(1)	161.4(2)
O(1)−Os(1)−Cl(1)	84.57(16)	P(1)−Os(1)−Cl(1)	87.58(7)
P(2)−Os(1)−Cl(1)	86.97(7)	C(1)−Os(1)−Cl(2)	92.8(2)
O(1)−Os(1)−Cl(2)	169.57(17)	P(1)−Os(1)−Cl(2)	87.58(7)
P(2)−Os(1)−Cl(2)	88.94(7)	C(1)−Os(1)−P(1)	92.8(2)
O(1)−Os(1)−P(1)	94.14(16)	C(1)−Os(1)−P(2)	93.9(2)
O(1)−Os(1)−P(2)	90.14(16)	Cl(2)−Os(1)−Cl(1)	105.75(7)
N(1)−C(2)−C(1)	118.5(8)	N(1)−C(2)−C(3)	131.0(8)
O(2)−N(1)−C(2)	127.0(8)	O(2)−N(1)−O(1)	118.1(6)
C(2)−N(1)−O(1)	114.9(7)	N(1)−O(1)−Os(1)	115.0(4)

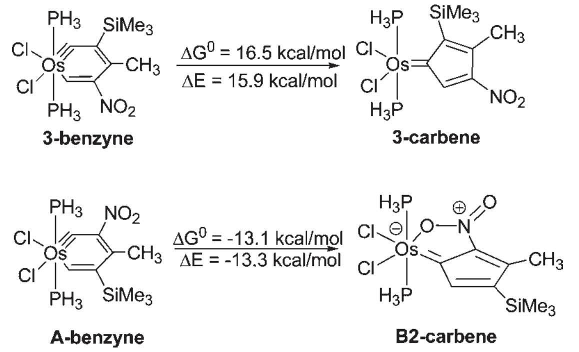
Chart 1



Scheme 2



Scheme 3



(1.283(2) Å) in PhN=C(C_6H_4-*m*-NO_2).[25] The O(1)−N(1) bond (1.307(10) Å) is appreciably longer than the O(2)−N(1) bond (1.253(7) Å). The structural parameters suggest that the metallacycle of **4** has a delocalized structure with contributions from resonance structures such as **4** and **4A**, with **4** being more important (Chart 1).

A plausible mechanism for the formation of the paramagnetic species **4** is shown in Scheme 2. Initially electrophilic substitution of NO_2^+ at the C2 position of the metallacycle of **1** would produce osmabenzyne **A**, which may undergo reductive elimination to give intermediate **B1** and then **B2**.[26] A biradical **B3** generated from **B1** could abstract a hydrogen atom from solvent to give the paramagnetic osmium complex **4**.

One may ask why osmabenzyne **A** would undergo rearrangement to afford the osmium carbene complex **4** while transformation of **3** to an osmium carbene complex was not observed. To gain insight into the difference between **A** and **3** in this rearrangement reaction, we have studied, by DFT calculations, the reductive elimination reactions of **3-benzyne** (a model complex of **3**) and **A-benzyne** (a model complex of **A**). Consistent with the experimental observation, the computational study suggests that **3-benzyne** is thermodynamically more stable than **3-carbene,** while **A-benzyne** is thermodynamically less stable than **B2-carbene** (Scheme 3). The additional coordination of the NO_2 group to the metal center via one of the two NO_2 oxygens apparently stabilizes **B2-carbene**.

In the proposed mechanism for the formation of **4**, we proposed that a biradical generated from osmabenzyne **A** is involved. The calculation indeed confirms that the biradical singlet **B3-carbene** is more stable than the diamagnetic **B2-carbene** by 12.3 kcal/mol (Figure 3), suggesting that a biradical can be readily generated from the intermediate **B2** proposed in Scheme 2.

Nitrosation. Electrophilic nitrosation reactions of arenes have been used previously to prepare nitrosoarenes.[27] It is known that the chemical reactivities of NO^+ and NO_2^+ toward aromatic donors are significantly different. The activity of NO^+ is estimated to be at least 10^{14} times lower than that of NO_2^+. Thus, direct nitration of arenes with nitronium salts generally occurs immediately upon mixing of reagents even at low temperature, whereas the corresponding nitrosation with nitrosonium salt is usually too slow to be detected, except for electron-rich arenes.[27] It is then of interest to find out if osmabenzynes can react with the relatively unreactive electrophile NO^+.

Treatment of **1** with $NOBF_4$ (1:4) and NaCl in CH_2Cl_2 at −20 to −5 °C for 3 h produced a brown solution, from which complex **5** was isolated as an orange solid in 72% yield (Scheme 1). As indicated by in situ NMR, the reaction also produced other minor unidentified products. The structure of **5** has been determined by an X-ray diffraction study. The crystallographic details are listed in Table 1. Selected bond lengths and angles are given in Table 2. A view of the molecular geometry of **5** is shown in Figure 4. As shown in Figure 4, **5** is a complex formed through replacing only the $SiMe_3$ group at C4 of **1** by an NO group. The structural features of the six-membered metallacycle are nearly identical with those of **3**.

The solid-state structure of **5** is supported by multinuclear NMR spectroscopy and elemental analysis. In particular, the Os*CH* proton signal was located at 12.11 ppm in the ^1H NMR spectrum (in $CDCl_3$). The CCH_3 proton signal was observed at 2.81 ppm. The $^{13}C\{^1H\}$ NMR spectrum (in $CDCl_3$) displayed the Os≡C signal at 297.0 ppm. The signal corresponding to OsCH appeared at 215.9 ppm. The ^{13}C signals of other carbons of the metallacycle were observed at 187.0 (CCH_3), 171.2 (CNO), and 115.8 ($CSi(CH_3)_3$) ppm. The CH_3 signal on the metallacycle appeared at 22.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **5** (in $CDCl_3$) displayed a singlet at −0.18 ppm.

Complex **5** can be regarded as a product resulting from nitrosation of **1** at the C4 position of the metallacycle. In the nitration reaction of **1**, we successfully isolated products resulting from reaction at both C2 and C4. We cannot exclude the possibility that a product resulting from nitrosation of **1** at the C2 position of the metallacycle was also produced, although we have failed to isolate or identify such a species. The fact that complex **5** can be isolated in 72% yield suggests that nitrosation at the C4 position is favored. The higher reactivity of C4 compared to that of C2 can be related to the difference in the π-electron density distribution

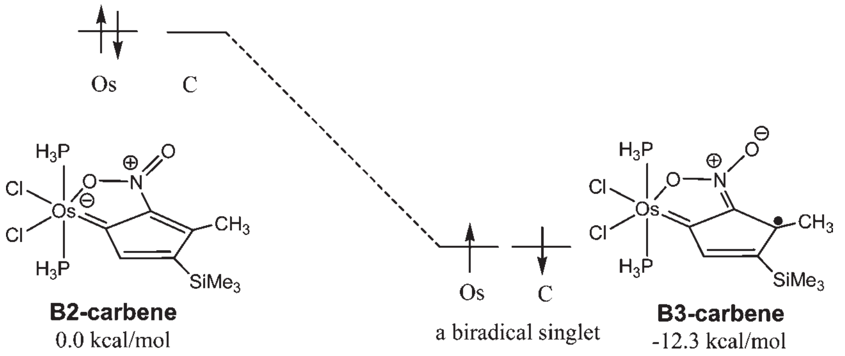


Figure 3. Relative electronic energies of the diamagnetic complex **B2-carbene** and its biradical singlet species **B3-carbene**.

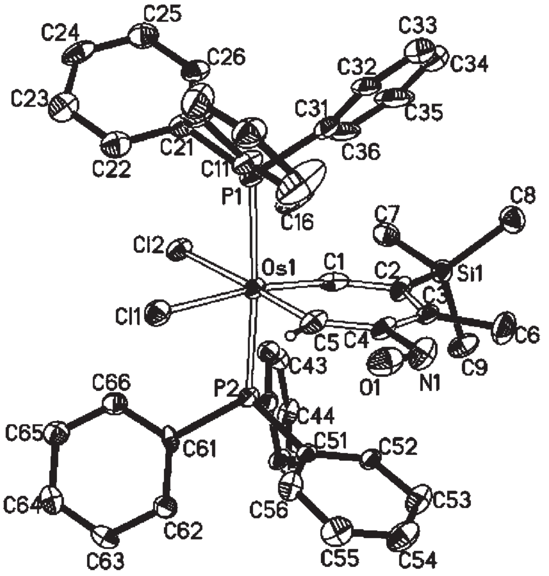


Figure 4. Molecular structure of **5**. The hydrogen atoms of PPh_3, CH_3, and $SiMe_3$ are omitted for clarity.

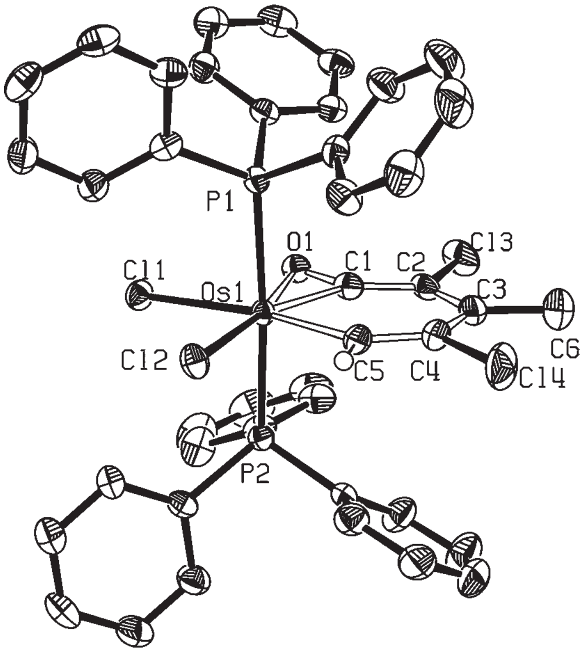


Figure 5. Molecular structure of complex **6**. The hydrogen atoms of PPh_3 and CH_3 are omitted for clarity.

in the HOMO of the metallacycle. DFT calculations suggest that in the HOMO of the complex $Os(\equiv CC(SiH_3)=C(CH_3)C(SiH_3)=CH)Cl_2(PH_3)_2$ (a model of **1**), the π-electron population on C2 is 0.20e and that on C4 is 0.24e. Thus, C4 is more nucleophilic and more reactive toward electrophiles. The difference in the nitration and nitrosation may be related to the different reactivities of the electrophiles (NO^+ and $NO_2{}^+$). One might expect that the less reactive electrophile NO^+ will react more selectively, at the more nucleophilic C4 position.

Chlorination. It is known that HCl/H_2O_2 can be used as a chlorination reagent for aromatic substrates.[28] Consequently, we investigated the reaction of osmabenzyne **1** with HCl/H_2O_2. Treatment of osmabenzyne **1** with excess HCl/H_2O_2 in dichloromethane at 0 °C produced a mixture of species, from which the chlorinated product **6** was isolated in 62% yield (Scheme 1). Complex **6** has been characterized by multinuclear NMR spectroscopy and elemental analysis. The solid-state structure has been confirmed by single-crystal X-ray diffraction.

As shown in Figure 5, complex **6** has two chlorides at the C2 and C4 positions of the metallacycle. Furthermore, an oxygen atom is attached at the C1 position and the C1−O unit is bonded to the osmium center in an η^2 fashion. The complex is closely related to the η^2-C(S)-containing osmabenzene $Os(C_5H_2(S\text{-}1))(CO)(PPh_3)_2$[2a] and the iridabenzene $[Ir(C_5H_4(S\text{-}1))(MeCN)(PPh_3)_2][CF_3SO_3]$.[5c] As expected, complex **6** also contains a nearly planar six-membered metallacycle. The Os−C1 bond length (1.956(3) Å) is slightly shorter than that of $Os[C_5H_4(SMe)](Cl)(CO)(PPh_3)_2$ (2.109(3) Å).[1c] The Os−C5 bond length (2.041(4) Å) is nearly identical with that of $Os[C_5H_4(SMe)](Cl)(CO)(PPh_3)_2$ (2.027(3) Å). The distances of the other C−C bonds of the metallacycle are in the range of 1.347(5)−1.411(6) Å which are between normal C−C single- and double-bond lengths and are close to the distances of the C−C bonds in benzene (1.390 Å).

The solid-state structure of complex **6** is supported by MS, multinuclear NMR spectroscopy, and elemental analysis. In particular, the FAB-MS displayed an ion peak at m/z 877.1 for $[M - Cl]^+$. The ^1H NMR spectrum (in CD_2Cl_2) showed a singlet signal at 12.62 ppm which can be assigned to the OsC*H* proton. The $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) displayed the signals of the two metal-bound carbon atoms at 203.6 ppm (OsC(O)) and 192.1 ppm (OsCH). The ^{13}C signals of the remaining

Scheme 4

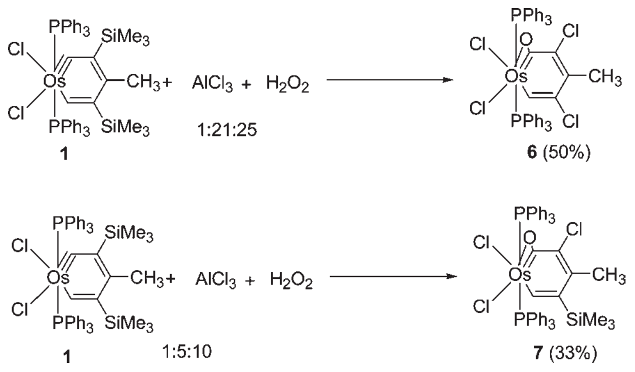


Table 4. Selected Bond Lengths and Angles for 6, 7, and 9

	6	7	9
	Bond Lengths (Å)		
Os(1)−P(1)	2.4273(9)	2.4155(13)	2.424(3)
Os(1)−P(2)	2.4207(9)	2.4126(14)	2.404(3)
Os(1)−Cl(1)	2.4437(9)	2.4422(12)	2.375(3)
Os(1)−Cl(2)	2.3808(8)	2.3894(14)	2.424(3)
Os(1)−C(1)	1.956(3)	1.937(6)	1.988(13)
Os(1)−C(5)	2.041(4)	2.044(4)	2.074(12)
Os(1)−O(1)	2.144(2)	2.131(3)	2.145(8)
O(1)−C(1)	1.234(4)	1.238(6)	1.251(15)
C(1)−C(2)	1.370(5)	1.371(7)	1.400 (17)
C(2)−C(3)	1.380(6)	1.390(7)	1.361(18)
C(3)−C(4)	1.411(6)	1.433(7)	1.418(18)
C(4)−C(5)	1.347(5)	1.371(6)	1.370(17)
	Bond Angles (deg)		
C(1)−Os(1)−C(5)	77.79(15	76.2(2)	76.3(5)
C(1)−Os(1)−O(1)	34.64(13)	35.03(16)	35.0(4)
C(5)−Os(1)−O(1)	112.42(13)	111.20(17)	111.2(4)
O(1)−C(1)−Os(1)	81.1(2)	81.1(4)	79.4(7)
C(1)−C(2)−C(3)	121.8(3)	119.6(5)	120.4(10)
C(2)−C(3)−C(4)	116.7(3)	119.2(5)	118.1(11)
O(1)−C(1)−C(2)	136.8(3)	134.0(6)	135.1(12)
C(2)−C(1)−Os(1)	142.1(3)	144.7(4)	145.5(12)
C(5)−C(4)−C(3)	127.2(4)	121.5(5)	127.8(11)
C(4)−C(5)−Os(1)	134.3(3)	137.8(4)	133.2(9)

carbon atoms of the metallacycle (*C*-CH$_3$, OsCH═CCl, Os═C-(O)CCl) were observed at 161.4 (CCH$_3$), 131.1 (OsCH═CCl), and 125.9 (Os═C(O)CCl) ppm. The CH$_3$ signal on the metallacycle was observed as a singlet at 22.9 ppm. The ^{31}P{^{1}H} NMR spectrum (in CD$_2$Cl$_2$) showed a singlet at −17.7 ppm.

Considering the fact that complex **1** readily undergoes bromination, nitration, and nitrosation reactions at the C2 and C4 positions of the metallacycle, it is likely that complex **6** may be formed by initial electrophilic substitution of **1** by chlorine followed by oxidation of C1 of the metallacycle, although the possibility of initial oxidation of C1 of the metallacycle followed by electrophilic substitution by chlorine could not be excluded. Experimentally, we have failed to get evidence for either of the processes. An example of oxidation of metallabenzenes has been previously reported. Oxidation of C*α* of the iridabenzene Ir(C$_5$H$_3$Me$_2$)(PMe$_3$)$_3$ with N$_2$O, followed by rearrangement, affords the iridacyclohexadienone complex IrH(C(O)CMeCH-CMeCH)(PMe$_3$)$_3$.[8c,d]

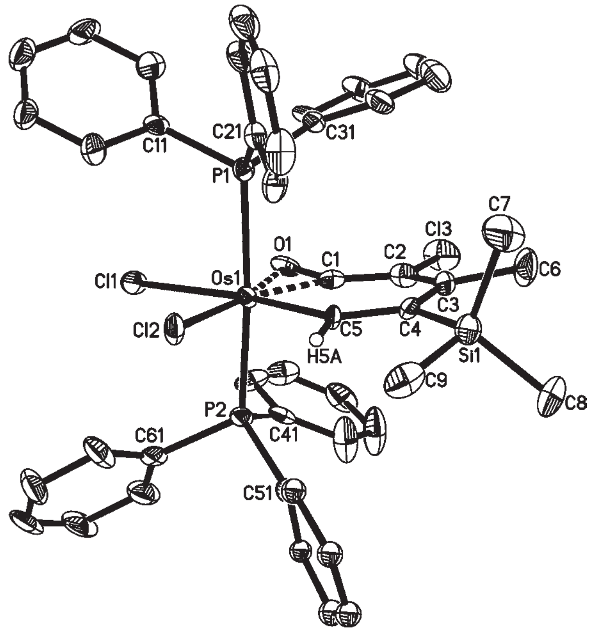
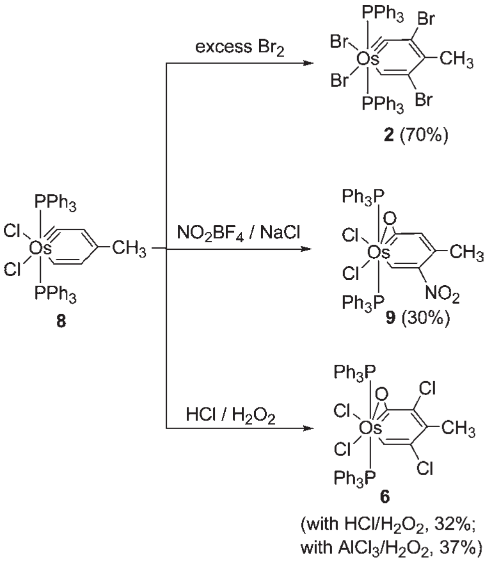


Figure 6. Molecular structure of complex 7. The hydrogen atoms of PPh$_3$, CH$_3$, and SiMe$_3$ are omitted for clarity.

Scheme 5



It has been reported that arenes could react with hydrogen peroxide in the presence of aluminum chloride to give a mixture of hydroxylated products (phenols) and chlorinated products (aryl chlorides).[29] We have therefore explored the possibility of hydroxylation of osmabenzyne **1** with hydrogen peroxide/aluminum chloride. However, the expected hydroxylated osmabenzynes could not be obtained from the reaction. The reaction was found to produce a mixture of species from which the chlorinated complexes **6** and **7** could be isolated (Scheme 4). The relative

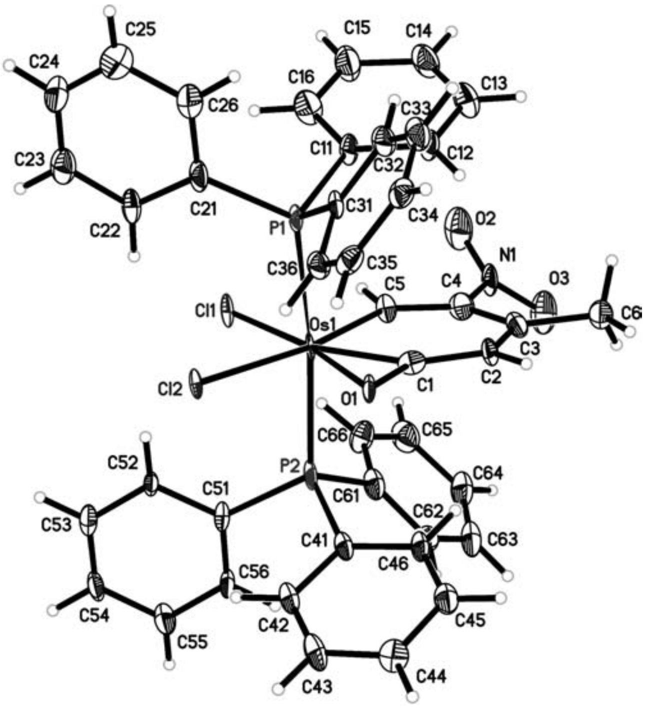


Figure 7. Molecular structure of **9**.

amounts of **6** and **7** can be controlled by the ratio of **1**, $AlCl_3$, and H_2O_2. Treatment of **1** with $AlCl_3$ and H_2O_2 (in a 1:21:25 molar ratio) in CH_2Cl_2 at −15 to 0 °C for 2 h afforded mainly **6** along with a trace amount of **7**. Complex **7** was produced as the major product when the molar ratio **1**:$AlCl_3$:H_2O_2 is 1:5:10.

The structure of **7** has been confirmed by single-crystal X-ray diffraction analysis and multinuclear NMR spectroscopy. The crystallographic details are given in Table 1, and selected bond distances and angles are given in Table 4. As shown in Figure 6, complex **7** is essentially the same as **6**, except that **7** has only one Cl atom at the C2 position of the metallacycle while **6** has two (one at C2 and the other one at C4). The solid-state structure of **7** is fully consistent with the solution NMR data.

Reactions of $Os(\equiv CCH{=}C(CH_3)CH{=}CH)Cl_2(PPh_3)_2$ (8). It is known that reactions of Ar-$SiMe_3$ with electrophiles usually lead to the cleavage of the C−$SiMe_3$ bond, implying that C−SiR_3 bonds are more reactive than C−H bonds toward electrophiles. In this respect, it would be interesting to study reactions of electrophiles with metallabenzynes without a $SiMe_3$ group. For this reason, we have studied the reaction of $Os(\equiv CCH{=}C(CH_3)CH{=}CH)Cl_2(PPh_3)_2$ (**8**) with electrophiles such as Br_2, NO_2BF_4, HCl/H_2O_2, and $AlCl_3$/H_2O_2. The results are summarized in Scheme 5.

Bromination. Treatment of osmabenzyne **8** with excess Br_2 produced the brominated product **2** as the major product. The same complex was produced from the reaction of **1** with Br_2.[16] As in the case of reaction involving **1**, excess bromine was essential for obtaining pure osmabenzyne **2**. A complicated mixture was produced, as indicated by the in situ NMR when a lesser amount of bromine was used, probably due to partial displacement of the H and Cl groups. For example, when **1** was allowed to react with 1 equiv of Br_2, the reaction produced a mixture of at least eight phosphorus-containing species, including some unreacted **1**. It is difficult to separate or fully separate or identify all these species.

Nitration. Complex **8** also undergoes a nitration reaction when treated with NO_2BF_4. After a mixture of **8** and NO_2BF_4 (in 1:4 molar ratio) and NaCl in CH_2Cl_2 was stirred at −16 to 5 °C for 2 h, a brown solution was obtained, from which the NO_2-containing osmabenzyne complex **9** could be isolated in 30% yield as an orange solid. The reaction also produced other unidentified species. Complex **9** is probably formed through a mononitrated osmabenzyne intermediate analogous to **3**, which was oxidized by excess NO_2^+. The oxygenated product of **3** was not observed, probably because the $SiMe_3$ group in **3** may help to prevent it from oxidation.

Complex **9** has been characterized by NMR spectroscopy and elemental analysis. In the ^1H NMR spectrum (in C_6D_6), the signals of the two protons of the metallacycle were observed at 13.67 (OsC*H*=) and 5.53 ppm (OsCH=C*H*). In the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2), the signals of the two metal-bound carbon atoms were observed at 205.2 (Os*C*(O)) and 203.3 (OsCH) ppm. The ^{13}C signals of the remaining carbon atoms of the metallacycle (*C*-CH_3, OsCH=CNO_2, Os=C(O)CH) were observed at 161.4, 129.8, and 92.5 ppm. The molecular structure of **9** has also been unambiguously confirmed by X-ray diffraction (Figure 7), despite difficulties due to absorption and desolvation of the crystal. As shown in Table 4, the structural features associated with the six-membered metallacycle are similar to those of **6** and **7**.

Chlorination. Reaction of **8** with HCl/H_2O_2 in CH_2Cl_2 at room temperature produced a brown solution, from which the chlorinated product **6** was isolated in about 32% yield. Treatment of **8** with $AlCl_3$ and H_2O_2 (in a 1:15:20 molar ratio) in CH_2Cl_2 at −15 to 0 °C also afforded **6**, which could be isolated in 37% yield.

■ CONCLUSION

In summary, we have investigated the electrophilic substitution reactions of two metallabenzynes, including nitration, nitrosation, chlorination, and bromination. The substitution reactions occurred at the C2 and C4 positions of the six-membered metallacycle. The regioselectivity of the electrophilic substitution reactions can be related to the π electron density distribution in the HOMO of the metallacycle. The observed reactivity of the metallabenzynes toward electrophiles demonstrates that metallabenzynes, like benzene and metallabenzenes, can undergo electrophilic substitution reactions and exhibit aromatic properties. Electrophilic substitution reactions of metallabenzynes reported in this work are unusual, especially when the reactivities of benzynes are considered. The reactivities of benzynes are usually associated with the C≡C triple bond, and electrophilic substitution reactions of benzynes, to our knowledge, have not been demonstrated. The formation of η^2-C(O)-containing osmabenzenes from the reactions of **1** or **8** with H_2O_2 or NO_2BF_4 represents a rare example of oxidation reactions of osmium carbyne complexes.

■ 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 materials $Os(\equiv CC(SiMe_3){=}C(Me)C(SiMe_3){=}CH)Cl_2(PPh_3)_2$ (**1**)[16] and $Os(\equiv CCH{=}C(Me){-}CHCH)$ $Cl_2(PPh_3)_2$ (**8**)[17] were prepared following the procedures described in the literature. Microanalyses were performed at M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz) or a Bruker ARX-400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

Compounds 3 and 4. An ice-cooled solution of **1** (0.300 g, 0.300 mmol) in CH_2Cl_2 (10 mL) was transferred to a suspension of NO_2BF_4 (0.178 g, 1.34 mmol) and NaCl (1.000 g, 17.11 mmol) in CH_2Cl_2 (60 mL) which was kept at −16 °C. The mixture was stirred for 2 h to give a brown suspension. The temperature was raised to −5 °C naturally. Ice-cooled water (60 mL) was added at −5 °C with vigorous stirring. Sodium hydrogen carbonate (0.140 g, 1.67 mmol) in water (10 mL) was added. After the above mixture was stirred for 2 min, the top aqueous layer was removed and the organic layer was further washed with 2 × 30 mL of water. The solvent of the organic layer was then removed under vacuum. The residue was dissolved in 3 mL of CH_2Cl_2 and loaded on a silica gel column. The column was eluted with benzene to give an orange-red solution, from which the paramagnetic compound **4** was obtained as an orange-red solid, after the solvent was removed completely under vacuum. Yield: 60 mg, 20%. Anal. Calcd for $C_{45}H_{42}Cl_2NO_2P_2SiOs$: C, 55.04; H, 4.52; N, 1.43. Found: C, 55.18; H, 4.66; N, 1.66. The column was further eluted with benzene to give a yellow solution, from which the compound $Os(\equiv CC(SiMe_3)=C(CH_3)C(NO_2)=CH)Cl_2(PPh_3)_2$ (**3**) was obtained as a yellow solid after the solvent was removed completely under vacuum. Yield: 56 mg, 19%. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −0.8 (s). ^{1}H NMR (300.13 MHz, C_6D_6): δ 0.00 (s, 9H, Si(CH_3)$_3$), 1.75 (s, 3H, CH_3), 7.05−7.46 (m, 30H, PPh_3), 12.88 (s, 1H, OsC*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 297.5 (t, *J*(PC) = 11.8 Hz, $Os\equiv C$), 216.4 (t, *J*(PC) = 5.8 Hz, OsCH), 187.3 (s, CCH_3), 171.6 (s, $OsCH=C(NO_2)$), 134.0 (t, *J*(PC) = 4.9 Hz, *m*-PPh_3), 130.6 (t, *J*(PC) = 27.8 Hz, *ipso*-PPh_3), 130.3 (s, *p*-PPh_3), 127.6 (t, *J*(PC) = 5.2 Hz, *o*-PPh_3), 116.2 (s, $Os\equiv CC(Si(CH_3)_3)$), 23.0 (s, CCH_3), 0.4 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{45}H_{43}Cl_2NO_2P_2SiOs\cdot 0.5CH_2Cl_2$: C, 52.75: H, 4.06: N, 1.42. Found: C, 53.12; H, 4.36; N, 1.38.

Compound 5. An ice-cooled solution of **1** (300 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was transferred to a suspension of $NOBF_4$ (139 mg, 1.19 mmol) and NaCl (600 mg, 10.3 mmol) in CH_2Cl_2 (20 mL) which was kept at −20 °C. The mixture was stirred for 3 h to give a brown suspension. The temperature was raised to −5 °C naturally. Ice-cooled water (20 mL) was added at 0 °C with vigorous stirring. The mixture was allowed to stand for 5 min. The top aqueous layer was then removed, and the organic layer was further washed with water (2 × 20 mL). The solvent of the organic layer was then removed under vacuum. The residue was dissolved in 1 mL of CH_2Cl_2, and diethyl ether (30 mL) was added slowly with stirring to give an orange precipitate, which was separated by filtration. The solid was washed with diethyl ether (3 × 10 mL) and hexane (3 × 10 mL) and then dried under vacuum. Yield: 287 mg, 72%. ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ −0.18 (s). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.33 (s, 9H, $Si(CH_3)_3$), 2.81 (s, 3H, C*H*$_3$), 7.21−7.70 (m, 30H, PPh_3), 12.11 (s, 1H, OsC*H*). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 297.0 (s, $Os\equiv C$), 215.9 (s, OsCH), 187.0 (s, CMe), 171.2 (s, C-NO), 134.5−127.0 (Ph), 115.8 (s, $Os\equiv CC(Si(CH_3)_3)$), 22.5 (s, CH_3), 0.0 (s, $Si(CH_3)_3$). Anal. Calcd for $C_{45}H_{43}Cl_2NOP_2SiOs$: C, 56.01; H, 4.49; N, 1.45. Found: C, 55.80; H, 4.40; N, 1.60.

Compound 6. *Method A.* To a solution of **1** (150 mg, 0.15 mol) in CH_2Cl_2 (10 mL) was added HCl (1.5 mL, 1 M in Et_2O, 1.5 mmol) and hydrogen peroxide (146 μL, 35% by weight, 1.5 mmol). The reaction mixture was stirred for 0.5 h at 0 °C to give a brown solution. This solution was washed with a K_2CO_3 solution (10 mL) and then brine (10 mL × 2). The organic layer was dried with anhydrous $MgSO_4$. The solvent was removed completely under vacuum. The residue was redissolved in 2 mL of CH_2Cl_2 and loaded on a silica gel column. The column was eluted with CH_2Cl_2/*n*-hexane (1:1) to give an orange solution, from which $Os(C(O)CCl=C(CH_3)CCl=CH)Cl_2(PPh_3)_2$ (**6**) was obtained as an orange solid, after the solvents were removed completely under vacuum. Yield: 87 mg, 62%.

Method B. To a suspension of **1** (0.280 g, 0.280 mmol) and aluminum chloride (0.800 g, 6.00 mmol) in CH_2Cl_2 (15 mL) cooled in an ice−salt bath was added hydrogen peroxide (0.6 mL, 35% by weight, 6.98 mmol). The reaction mixture was stirred for 1 h at −2 to 0 °C to give an orange solution. The solvent was removed completely under vacuum, and the resulting orange residue was extracted with benzene (5 mL) and filtered. The solvent of the extract was removed under vacuum, and the resulting residue was dissolved in CH_2Cl_2 (1 mL). Addition of hexane (15 mL) to the residue gave an orange precipitate which was collected by filtration, washed with hexane (2 × 3 mL), and dried under vacuum. The solid was redissolved in 1 mL of CH_2Cl_2, and the mixture was loaded on a silica gel column. The column was eluted with benzene to give an orange solution, from which $Os(C(O)CCl=C(CH_3)CCl=CH)Cl_2(PPh_3)_2$ (**6**) was obtained as an orange solid, after the solvent was removed completely under vacuum. Yield: 0.134 g, 50%.

Method C. To a solution of **8** (200 mg, 0.23 mol) in CH_2Cl_2 (10 mL) was added HCl (2.3 mL, 1 M in Et_2O, 2.3 mmol) and hydrogen peroxide (220 μL, 35% by weight, 2.2 mmol). The reaction mixture was stirred for 3 h at room temperature to give a brown solution. The solution was washed with K_2CO_3 solution (10 mL) and then brine (10 mL × 2). The organic layer was dried with anhydrous $MgSO_4$. The solvent was removed completely under vacuum. The residue was redissolved in 2 mL of CH_2Cl_2 and loaded on a silica gel column. The column was eluted with CH_2Cl_2/*n*-hexane (1:1) to give an orange solution, from which $Os(C(O)CCl=C(CH_3)CCl=CH)Cl_2(PPh_3)_2$ (**6**) was obtained as an orange solid, after the solvent was removed completely under vacuum. Yield: 70 mg, 32%.

Method D. To a suspension of **8** (172 mg, 0.20 mmol) and aluminum chloride (400 mg, 3 mmol) in CH_2Cl_2 (15 mL) (cooled to −15 °C) was added hydrogen peroxide (0.48 mL, 30% by weight, 4 mmol). The reaction mixture was stirred for 3 h at −15 °C. The temperature was raised to 0 °C naturally to give an orange solution. The solvent was removed completely under vacuum, and the resulting orange residue was extracted with benzene (2 × 8 mL) and then filtered. The filtrate was evaporated to dryness under vacuum. The resulting residue was dissolved in CH_2Cl_2 (1 mL), which was loaded on a silica gel column. The column was eluted with benzene to give an orange-red solution, from which compound **6** was obtained as an orange solid, after the solvent was removed completely under vacuum. Yield: 69.8 mg, 37%.

Characterization data of **6** are as follows. FAB-MS (NBA, *m*/*z*): 877.1 ($M^+ - Cl$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ −17.7 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 1.71 (s, 3H, C*H*$_3$), 7.27−7.47 (m, 30H, PPh_3), 12.62 (t, *J*(PH) = 1.4 Hz, 1H, OsC*H*). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 203.6 (t, *J*(PC) = 4.7 Hz, $Os=C$), 192.1 (t, *J*(PC) = 6.0 Hz, OsCH), 161.4 (s, CCH_3), 134.4 (t, *J*(PC) = 4.8 Hz, *m*-PPh_3), 131.1 (s, $OsCH=CCl$), 130.7 (s, *p*-PPh_3), 129.1 (t, *J*(PC) = 25.7 Hz, *ipso*-PPh_3), 128.0 (t, *J*(PC) = 4.9 Hz, *o*-PPh_3), 125.9 (s, $Os=C(O)CCl$), 22.9 (s, CH_3). Anal. Calcd for $C_{42}Cl_4H_{34}OP_2Os$: C, 53.76; H, 3.57. Found: C, 53.59; H, 3.61.

Compound 7. To a suspension of **1** (0.216 g, 0.20 mmol) and aluminum chloride (0.14 g, 1.0 mmol) in dichloromethane (15 mL) (cooled to −15 °C) was added hydrogen peroxide (0.24 mL, 30% by weight, 2 mmol). The reaction mixture was stirred for 2 h at −15 °C. The temperature was raised to 0 °C naturally to give an orange-brown solution. The solvent was removed completely under vacuum, and the resulting orange residue was extracted with benzene (10 mL) and filtered. The filtrate was dried under vacuum. The resulting residue was dissolved in dichloromethane (1 mL). The mixture was loaded on a silica gel column. The column was eluted with benzene and then dichloromethane to give an orange-yellow solution. The solvent was removed completely under vacuum to give an orange-yellow solid. Yield: 64 mg, 33%. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −16.9 (s). ^1H NMR (300.13 MHz, C_6D_6): δ 0.00 (s, 9H, Si(CH_3)$_3$), 1.84 (s, 3H, CH_3), 6.91−7.83 (m, 30H, PPh_3), 14.61 (s, br, 1H, Os*CH*). Anal. Calcd for $C_{45}Cl_3H_{43}OP_2SiOs \cdot 0.5CH_2Cl_2$: C, 52.84; H, 4.34. Found: C, 52.32; H, 4.21.

Compound 2. To a CH_2Cl_2 solution (1 mL) of **8** (100 mg, 0.100 mmol) in a Schlenk tube was added a solution of Br_2 (344 mg, 2.18 mmol) in CH_2Cl_2 (0.8 mL) with stirring. The reaction mixture was stirred at room temperature for 1 h to give a brown solution. The solvent and excess Br_2 were removed under vacuum. Addition of hexane (5 mL) to the residue produced a pale green solid which was collected by filtration, washed with diethyl ether (2 × 2 mL), and dried under vacuum to give a green powder. Yield: 90 mg, 70%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −4.1 (s). ^1H NMR (300.13 MHz, C_6D_6): δ 1.68 (s, 3H, CH_3), 7.23−7.25 (m, 18 H, PPh_3), 7.48−7.55 (m, 12 H, PPh_3), 12.22 (s, 1H, OsCH). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 289.0 (t, ^2J(PC) = 12.0 Hz, Os≡*C*), 199.6 (t, ^2J(PC) = 5.7 Hz, OsCH), 167.6 (s, CCH_3), 134.8−128.0 (m, PPh_3), 109.9 (s, OsCH═CBr), 107.5 (s, Os≡CCBr), 27.1 (s, CH_3). Anal. Calcd for $C_{42}H_{34}Br_4OsP_2$: C, 45.43; H, 3.09. Found: C, 45.53; H, 3.09.

Compound 9. An ice-cooled solution of **1** (300 mg, 0.35 mmol) in CH_2Cl_2 (10 mL) was transferred to a suspension of NO_2BF_4 (185 mg, 1.38 mmol) and NaCl (1.00 g, 17.11 mmol) in CH_2Cl_2 (60 mL) which was kept at −15 °C. The mixture was stirred for 2 h to give a brown suspension. The temperature was raised to −5 °C naturally. Ice-cooled water (20 mL) was added at −5 °C with vigorous stirring. Sodium hydrogen carbonate (140 mg, 1.67 mmol) in water (10 mL) was then added. After the above mixture was stirred for 2 min, the top aqueous layer was removed and the organic layer was further washed with water (2 × 30 mL). The solvent of the organic layer was then removed under vacuum. The residue was dissolved in 2 mL of CH_2Cl_2, and the mixture was loaded on a silica gel column. The column was eluted with benzene and then with dichloromethane to give an orange-red solution, from which compound **9** was obtained as an orange-red solid, after the solvent was removed completely under vacuum. Yield: 95 mg, 30%. $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ −18.20 (s). ^1H NMR (400.13 MHz, C_6D_6): δ 1.95 (s, 3H, CH_3), 5.53 (s, 1H), 7.50−7.27 (m, 30H, PPh_3), 13.67 (s, 1H, Os*CH*). $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ 205.2 (t, *J*(PC) = 5.2 Hz, Os*C*(O)), 203.3 (t, *J*(PC) = 6.9 Hz, OsCH), 161.4 (s, CCH_3), 147.4 (s, *p*-PPh_3), 133.4 4 (t, *J*(PC) = 4.5 Hz, *m*-PPh_3), 129.8 (s, Os═C(O)*C*(NO_2)), 128.1 1 (t, *J*(PC) = 25.0 Hz, *ipso*-PPh_3), 127.0 (t, *J*(PC) = 4.2 Hz, *o*-PPh_3), 92.5 (s, CH), 24.1 (s, CH_3). Anal. Calcd for $C_{42}H_{35}Cl_2NO_2P_2Os \cdot 0.2CH_2Cl_2$: C, 54.75; H, 3.85; N, 1.51. Found: C, 54.56; H, 4.25; N, 1.42.

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from a benzene solution layered with hexane for **3** and from CH_2Cl_2 solutions layered with hexane for **4**−**7** and **9**, respectively. All the crystals were mounted on glass fibers. The diffraction intensity data were collected with a Bruker CCD diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å). Lattice determination and data collection was carried out using SMART v. 5.625 software. Data reduction and absorption correction were performed using SAINT v. 6.26 and SADABS v 2.03, respectively. Structure solution and refinement for all four compounds were performed using either SHELXTL v. 6.10[30] or OLEX2[31] software packages. They were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless specified.

In general the structures refined acceptably well; however, for compound **9** the data quality was badly impacted by the effect of partial desolvation and absorption. The structure had large electron density peaks and difference holes of +4.85/ −3.88 e/Å^3 associated with the two Os centers of the asymmetric unit, at distances of approximately 0.9 Å. As a method of last resort, an empirical correction using the "DIFABS" procedure of Walker and Stuart was applied.[32] The resulting refinement afforded better discrepancy indices, lower residual peaks and holes near Os, and more physically sensible refinement of light atom thermal parameters. The suppression of the absorption peaks also helped reveal an additional partial CH_2Cl_2 solvate of crystallization. Despite the poorer quality of diffraction data, the molecular identity and geometry of compound **9** were still unambiguously revealed.

Computational Details. Molecular geometries of complexes were optimized without constraints via DFT calculations using the MPW-PW91 functional.[33] Frequency calculations at the same level of theory were also performed to identify the stationary points as minima (zero imaginary frequencies). The 6-31G Pople basis set[34] was used for C, O, N, and H atoms, while the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (Lanl2DZ)[35] were used to describe Os, P, Si, and Cl atoms. The polarization functions were added for Os (ζ(f) = 0.886), P (ζ(d) = 0.340), Si (ζ(d) = 0.284), and Cl (ζ(d) = 0.514) and C (ζ(d) = 0.600) atoms bonded to the metal center.[36]

Geometry optimization of the structure of the biradical singlet species **B3-carbene** was based on an open-shell singlet state wave function in which both the α spin density at the metal center and the β spin density at the methyl-substituted carbon are close to 1. The wave function obtained for the optimized structure was found to be slightly contaminated with triplet state wave functions, and the $\langle S^2\rangle$ values calculated are close to 1. In order to exclude the triplet state contribution, spin-projection corrections were applied to re-evaluate the spin-corrected singlet state total energy E_{singlet} according to the equation[37]

$$E_{\text{singlet}} = \frac{2E_{\text{OSS}} - E_{\text{triplet}}\langle S^2\rangle_{\text{OSS}}}{2 - \langle S^2\rangle_{\text{OSS}}}$$

where E_{OSS} and E_{triplet} are the total electronic energies of the open-shell singlet and triplet states, respectively, obtained from the UMPWPW91 calculations. $\langle S^2\rangle_{\text{OSS}}$ corresponds to the $\langle S^2\rangle$ value obtained from the UMPWPW91 calculations of the open-shell singlet state. All the DFT calculations were performed with the Gaussian 03 package.[38]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Text giving the complete ref 38, tables giving Cartesian coordinates and electronic energies for all the calculated structures, and CIF files giving X-ray crystallographic data for **3**−**7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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