

Heteroatom-Substituted Carbene Complexes of High-Valent Tungsten: $\text{Tp}'\text{W}(\text{O})\text{X}(\text{=C}(\text{R})\text{OSiR}_3)$ Derivatives

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Reaction of $\text{Tp}'\text{W}(\text{O})(\text{I})(\text{CO})$ (**1**; $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$) with MeLi followed by trapping of the resultant anion by ClSiPh_2Me leads to the formation of a single isomer of the tungsten(VI) heteroatom-substituted carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(\text{=C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**5a**). The connectivity of complex **5a** was confirmed by X-ray crystallography and spectral data. The acyl intermediate in the reaction, $[\text{Tp}'\text{W}(\text{O})(\text{I})(\text{C}(\text{O})\text{Me})][\text{Li}]$ (**6**), was observed by spectroscopic techniques. Trapping of the acyl intermediate **6** with H^+ yields the neutral hydroxy carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(\text{=C}(\text{Me})\text{OH})$ (**5c**). Reaction of complex **1** with PhLi generates the anionic phenyl–acyl complex $[\text{Tp}'\text{W}(\text{O})(\text{I})(\text{C}(\text{O})\text{Ph})][\text{Li}]$ (**8**), which may be trapped with ClSiPh_2Me , yielding the phenyl carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(\text{=C}(\text{Ph})\text{OSiPh}_2\text{Me})$ (**7**). Carbene complex **5a** reacts with AgSO_3CF_3 to form silver iodide and a coordinated triflate complex, $\text{Tp}'\text{W}(\text{O})(\text{OSO}_2\text{CF}_3)(\text{=C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**9**). In contrast to the acyl product formed with MeLi and **1**, combining LiCuMe_2 with **1** leads to the replacement of iodide by a methyl group to form $\text{Tp}'\text{W}(\text{O})(\text{Me})(\text{CO})$ (**2**). Protonation of this methyl tungsten complex (**2**) in CH_2Cl_2 in the presence of acetonitrile yields methane and the cationic nitrile adduct $[\text{Tp}'\text{W}(\text{O})(\text{CO})(\text{NCMe})]^+$ (**3**), while protonation of **2** in *neat* acetonitrile produces a cationic hydroxy carbene complex, $[\text{Tp}'\text{W}(\text{O})(\text{NCMe})(\text{=C}(\text{Me})\text{OH})]^+$ (**4**).

Introduction

Transition-metal carbene complexes are now the preferred reagents for a variety of organic transformations, including olefin metathesis,¹ ring-closing metathesis,² ring-opening metathesis polymerization,³ and asymmetric synthesis.⁴ Metal carbene intermediates have been postulated and implicated in many catalytic processes.⁵ Indeed, the study of transition-metal carbene complexes epitomizes the successful development of organometallic chemistry applications for organic syntheses over the past 40 years.

Metal carbene complexes are traditionally classified as either Fischer-type or Schrock-type. Fischer-type carbene complexes are typically low-valent transition-

metal complexes that contain ancillary π -acceptor ligands bound to the metal center, the sp^2 carbene carbon is electrophilic, and often one or more π -donor substituents (e.g. OMe, NMe_2) are directly bound to the carbene carbon. In contrast, Schrock-type carbene complexes are typically high-valent metal complexes containing ancillary π -donor ligands bound to the metal center and the sp^2 carbene carbon, with only carbon and hydrogen substituents, is nucleophilic.

Fischer-type carbene complexes are associated with electrophilic reactivity at C_α , and Schrock-type carbenes bring to mind nucleophilic carbene reactivity, but these reactivity patterns are not inviolate. Abundant examples of carbene complexes that resist these simple categorizations exist. A rhenium carbene complex that behaves as both an electrophile and a nucleophile⁶ provides a recent example of a single complex that displays both Fischer and Schrock reactivity patterns. $\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_2\text{CH}_2\text{CMe}_3$ reacts with PMe_3 to give the zwitterionic complex $\text{Cp}(\text{CO})_2\text{ReCH}(\text{PMe}_3)\text{CH}_2\text{CH}_2\text{CMe}_3$, and it also undergoes stereospecific addition of HCl to give the chloroalkyl complex $\text{Cp}(\text{CO})_2\text{ClReCH}_2\text{CH}_2\text{CH}_2\text{CMe}_3$.⁶

Tris(pyrazolyl)borate ligands⁷ have been used to firmly anchor three coordination sites of reactive complexes. Alkylidene complexes of W and Mo containing

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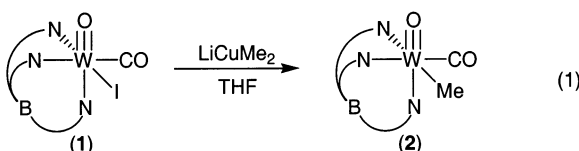
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the Tp ligand are resistant to air and moisture.⁸ Even the reactive family of Grubbs catalysts, Ru(=C(R)H)(PR₃)₂(Cl)₂, has been modified by introduction of the Tp ligand into the ruthenium coordination sphere to render a more easily manipulated complex.⁹

Despite the plethora of carbene complexes that have been synthesized, and although examples of low-oxidation-state carbene complexes containing no heteroatoms are common,¹⁰ a surprising gap exists in the area of high-oxidation-state carbene complexes containing heteroatom substituents.¹¹ This paper addresses the deficiency of complexes that can be viewed as having d⁰ metal configurations with a CR(OR')²⁻ ligand in the coordination sphere. The synthesis and characterization of neutral and cationic high-oxidation-state tungsten carbene complexes with the Tp' ligand (Tp' = hydrido-tris(3,5-dimethylpyrazolyl)borate) in the coordination sphere and heteroatom substituents on the carbene carbon bound to the metal are described here.

Results and Discussion

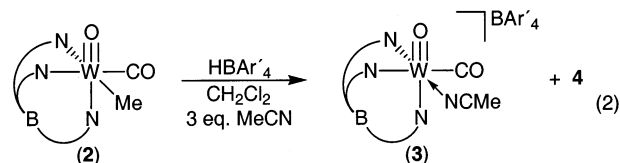
Addition of 1.5 equiv of LiCuMe₂ to a purple THF solution of Tp'W(O)(CO)(I) (**1**) results in formation of a dark brown solution. Monitoring the reaction by IR spectroscopy shows the disappearance of the CO stretch for **1** at 1975 cm⁻¹ and the appearance of a terminal CO stretch at 1945 cm⁻¹. Isolation and characterization of the reaction product indicated that the new complex is the methyl tungsten complex Tp'W(O)(CO)(Me) (**2**) (eq 1). The ¹H NMR spectrum of **2** shows unique



resonances for each CH and CH₃ site of the Tp' ligand, indicating that the complex has C₁ symmetry. More informative is a singlet at 2.07 ppm (3H) in the ¹H spectrum, possessing coupling to tungsten of 8.0 Hz (¹⁸³W, 14%, I = 1/2), and a methyl signal at 8.9 ppm with ¹J_{WC} = 103 Hz in the ¹³C NMR spectrum; these signals are indicative of a tungsten-bound methyl group. Complexes with cis-ligated oxo and carbonyl ligands are rare due to the π-donor/π-acid conflict between the O²⁻ and CO ligands,¹² and incorporation of an adjacent alkyl group, here a methyl, sets the stage for additional organometallic transformations.

Attempts to create an open coordination site at the metal center via protonation of the W–Me fragment were carried out using HBAR'₄·2OEt₂ (BAR'₄ = tetrakis-

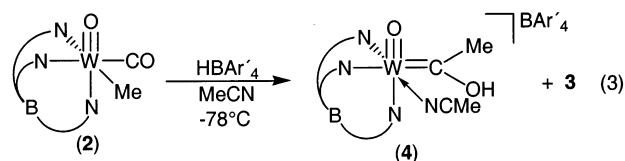
[3,5-bis(trifluoromethyl)phenyl]borate). Protonation of **2** in CH₂Cl₂ in the presence of a small amount of acetonitrile produced a dark purple solution containing the target tungsten(IV) complex, [Tp'W(O)(CO)(NCMe)]-[BAR'₄] (**3**) (eq 2). This complex is the result of formal



protonation of the methyl group to release methane and subsequent trapping of the cationic metal fragment by acetonitrile.

The ¹H NMR spectrum of the reaction mixture revealed two chiral metal products in a 6:1 ratio, with the major species being complex **3**. The ¹H NMR spectrum for complex **3** displays unique resonances for each of the methyl and methine units of the Tp' ligand, and the methyl of the coordinated nitrile resonates at 3.08 ppm. The IR spectrum displays a terminal CO absorption at 2023 cm⁻¹ for the product, an increase from the stretching frequency of reagent **2** at 1945 cm⁻¹, consistent with the formation of a cationic species.

Protonation of **2** in neat acetonitrile generates species **4** as the major product. On the basis of extensive spectral data complex **4** is postulated to be the cationic hydroxy carbene complex [Tp'W(O)(NCMe)(=C(OH)Me)]-[BAR'₄] (**4**) (eq 3).



Complex **4** could result from protonation of the carbonyl oxygen and methyl migration to CO, followed by acetonitrile trapping of the unsaturated metal intermediate. The ¹H NMR spectrum of **4** has a total of eight methyl signals. The downfield methyl signal at 4.67 ppm, showing coupling to tungsten of 4.4 Hz, is assigned to the carbene methyl group. The hydroxy proton is observed as a broad singlet at 8.7 ppm, while the Tp' and acetonitrile methyl groups fall between 2 and 3 ppm. The carbene carbon is found at 313.6 ppm with ¹J_{WC} = 170 Hz in the ¹³C NMR spectrum. The methyl group carbons for the carbene and coordinated nitrile are observed at 40.7 and 4.9 ppm, respectively. The data obtained for **4** are similar to data obtained for other hydroxy carbene complexes.¹³ Although the cationic hydroxy carbene complex **4** could not be isolated cleanly, these results suggested that heteroatom carbene complexes of tungsten(VI) should be accessible in this Tp' system.

In an effort to synthesize an isolable electron-rich tungsten(VI) carbene complex, the classic Fischer car-

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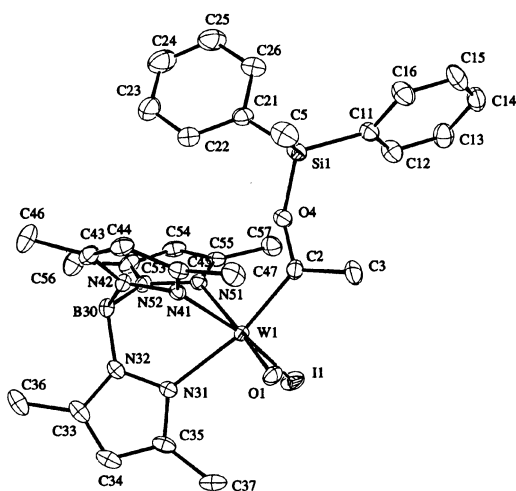
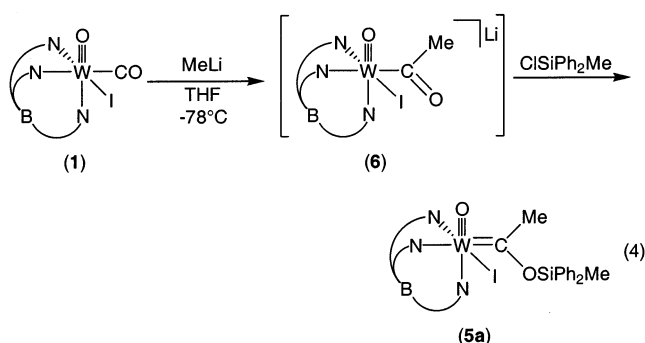


Figure 1. ORTEP diagram of $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**5a**). Ellipsoids are drawn with 50% probability.

Carbene synthetic methodology was utilized.¹⁴ Sequential reaction of **1** with MeLi and then with ClSiPh_2Me results in the formation of a single isomer (vide infra) of the carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**5a**) (eq 4). The carbene methyl group appears at 5.05



ppm ($^3J_{\text{WH}} = 4.5$ Hz) in the ^1H NMR spectrum and 44.1 ppm in the ^{13}C NMR spectrum, data reminiscent of chemical shift values observed for hydroxy carbene complex **4**. The carbene carbon ^{13}C resonance itself appears far downfield at 321.0 ppm for **5a**, again mirroring **4**.

Recrystallization of **5a** from CH_2Cl_2 /hexanes provided crystals suitable for X-ray analysis. Crystallographic data collection parameters are given in Table 4. Single-crystal X-ray crystallography of **5a** reveals a "trans" configuration with respect to the $\text{W}-\text{C}-\text{O}-\text{Si}$ linkage in the isolated carbene complex (Figure 1). Note that no isomerization of complex **5a** to form other isomers is observed by NMR. If, however, ClSiMe_3 is used as the trapping silane, four isomers of the resulting carbene $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OSiMe}_3)$ (**5b**) are observed (Figure 2). These four isomers interconvert slowly in solution at room temperature, thus resulting in conversion to the two thermodynamically favored isomers over a period of days. Isolation of crystalline **5b** was never achieved, perhaps due to the multiple isomers present in solution.

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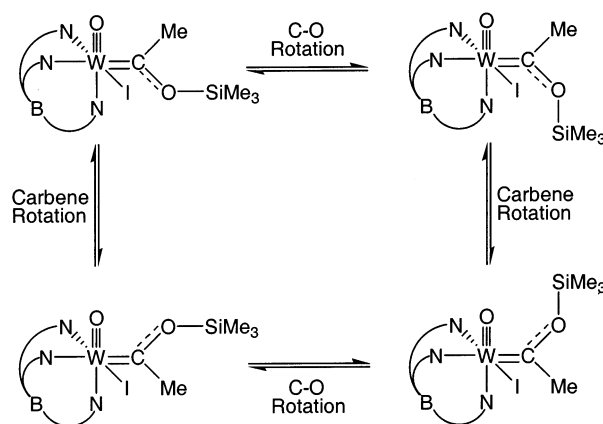


Figure 2. Isomers of $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OSiMe}_3)$.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **5a**

W1–C2	1.997(4)	W1–N31	2.254(3)
W1–N41	2.151(3)	W1–N51	2.339(3)
C2–C3	1.519(6)	C2–O4	1.351(5)
W1–O1	1.6987(24)	W1–I1	2.7848(3)
C3–C2–O4	112.8(3)	W1–C2–O4	123.0(3)
W1–C2–C3	124.2(3)	C2–O4–Si1	137.5(3)
O1–W1–C2–C3 ^a	16.6(3)		

^a Torsion angle.

The tungsten–carbon distance to the carbene ligand in **5a** (1.997 Å; Table 1) is similar to previously reported high-oxidation-state tungsten alkylidene $\text{W}=\text{C}$ bond lengths (1.949 Å, $\text{Tp}'\text{W}(\text{O})(\text{Cl})(=\text{C}(\text{H})\text{CMe}_3)$;⁸ 2.006 Å, $\text{W}(\text{O})(\text{PMe}_3)_2(\text{Cl})_2(=\text{C}(\text{H})\text{Me}_3)$ ¹⁵). The $\text{C}(2)-\text{O}(4)$ bond length of 1.351 Å is similar to that reported for $\text{Re}(\text{V})$ complexes (1.35 Å, $(\text{THF})_2(\text{OR})_2(\text{C}-t\text{Bu})\text{Re}=\text{CHOEt}$ ^{11a}). This C–O bond length, slightly longer than is observed in typical octahedral Fischer-type carbene complexes, is consistent with decreased $\text{C}=\text{O}$ π bonding in **5a** relative to classic Fischer-type carbene complexes. Bond angles at the carbene carbon are all close to 120°, as expected for sp^2 hybridization. The orientation of the carbene plane in complex **5a** is approximately parallel to the $\text{W}=\text{O}$ bond: an angle of 16.6° is observed for the carbene plane ($\text{C}(3)-\text{C}(2)-\text{O}(4)$) relative to the $\text{W}=\text{O}$ bond. This slight twist probably reflects steric interactions between the Tp' methyl groups and the carbene substituents. The parallel orientation of the carbene plane and the $\text{W}=\text{O}$ moiety is optimal for utilization of all three $d\pi$ orbitals of octahedral parentage in constructive metal–ligand π bonds.¹⁶ Also, one of the two phenyl rings of the silyl group is situated between two of the pyrazolyl rings in the Tp' ligand. Similar π -interaction phenomena are common in Tp' complexes.¹⁷

As in classic Fischer syntheses, the carbene complex presumably results from initial nucleophilic attack of the organometallic methyl reagent at the carbonyl

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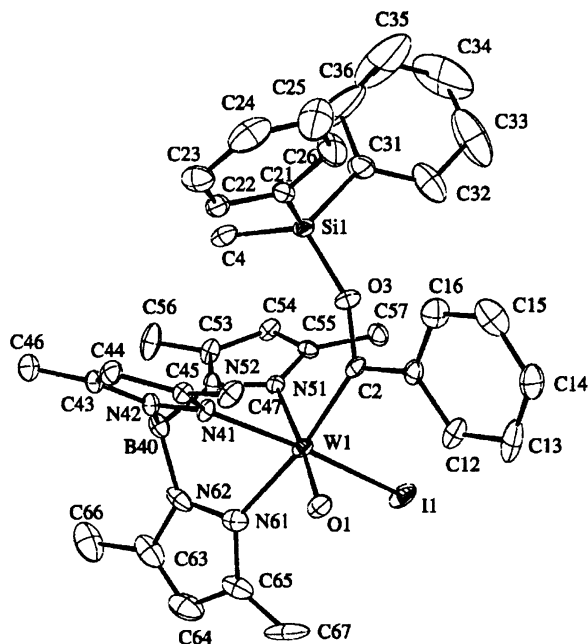
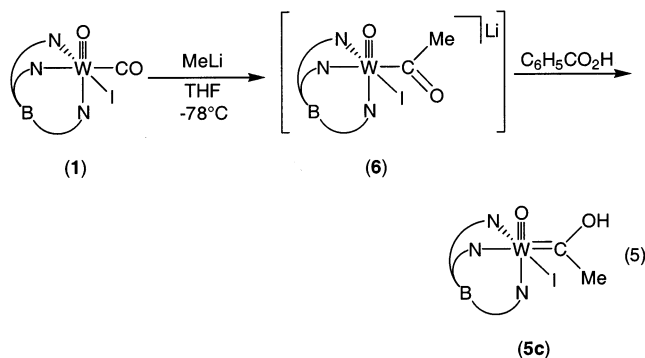


Figure 3. ORTEP diagram of $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Ph})\text{OSiPh}_2\text{Me})$ (**7**). Ellipsoids are drawn with 50% probability.

carbon of **1**, followed by trapping at oxygen with the chlorosilane. Spectral characterization of the putative anionic acyl intermediate was pursued. Addition of MeLi to a -78°C THF- d_8 solution of **1** in an NMR tube results in immediate formation of a royal blue solution of the anionic acyl complex $[\text{Tp}'\text{W}(\text{O})(\text{I})(\text{C}(\text{O})\text{Me})][\text{Li}]$ (**6**) (eq 4). Characterization by NMR at low temperatures shows unique signals for the Tp' ligand bound to a chiral metal center. A ^1H signal at 3.59 ppm is integrated for three protons and is assigned to an acyl methyl group. The ^{13}C NMR spectrum shows the acyl methyl carbon signal at 54.3 ppm and the acyl $\text{C}=\text{O}$ carbon at 308.3 ppm. This downfield ^{13}C chemical shift mimics the carbon shifts observed for carbene carbons, and it may indicate association of the $[\text{Li}^+]$ counterion with the carbonyl oxygen to give "carbeneoid" character to the acyl moiety. The anionic acyl complex has proven elusive; warming the solution results in decomposition.

As an alternative to silyl trapping reagents, benzoic acid has been used as a proton source to trap acyl complex **6**. Addition of a THF solution of benzoic acid to a cold THF solution of anionic complex **6** forms the corresponding neutral hydroxy carbene $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OH})$ (**5c**) (eq 5). Unique signals are observed



for the three Tp' ligand pyrazole rings, and the hydroxy proton resonates at 7.70 ppm in the ^1H spectrum. The

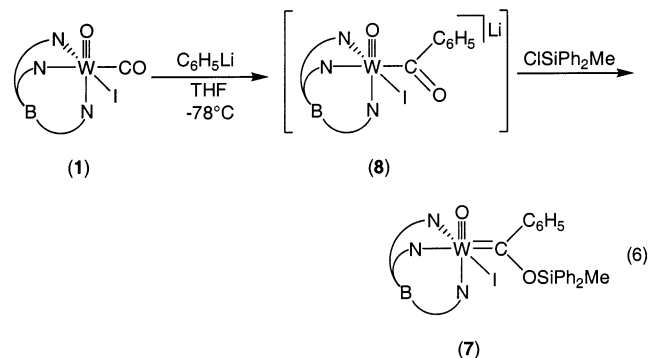
Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **7**

W1–C2	2.016(7)	W1–N61	2.238(6)
W1–N41	2.143(5)	W1–N51	2.300(5)
C2–C11	1.490(9)	C2–O3	1.376(8)
W1–O1	1.705(5)	W1–I1	2.7942(5)
C11–C2–O3	110.0(6)	W1–C2–O3	125.5(5)
W1–C2–C11	124.5(4)	C2–O3–Si1	148.5(5)
O1–W1–C2–C1 ^a			20.6(5)

^a Torsion angle.

carbene methyl signal appears at 4.83 ppm ($^2J_{\text{WH}} = 5$ Hz) in the ^1H spectrum and at 39.6 ppm in the ^{13}C spectrum. The carbene carbon resonates at 312.2 ppm in the ^{13}C spectrum. Only a single isomer of complex **5c** is initially observed, but in solution slow isomerization to form a second isomer is observed. The small size of the hydroxy proton relative to the bulky silyl substituents in **5a** and **5b** surely offers little steric encumbrance in any isomer. An IR stretch for the hydroxy moiety is observed at 3466 cm^{-1} , and after exchange with D_2O a new infrared band for O–D is observed at 2474 cm^{-1} .

Sequential reaction of **1** with PhLi and then ClSiPh_2Me results in a single isomer of the phenyl carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Ph})\text{OSiPh}_2\text{Me})$ (**7**) (eq 6). Com-



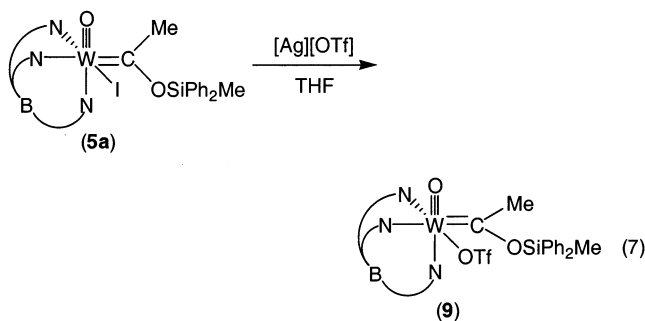
plex **7** displays unique resonances for the Tp' ligand and an upfield resonance at 0.09 ppm for the silyl methyl group. Resonances for the carbene phenyl group are intermingled with the silyl phenyl resonances between 6.9 and 7.6 ppm. The carbene carbon resonates at 318.1 ppm in the ^{13}C spectrum.

Crystals of complex **7** were grown from $\text{CH}_2\text{Cl}_2/\text{hexanes}$, and an X-ray crystal structure was obtained (Figure 3). In the $\text{W}-\text{C}-\text{O}-\text{Si}$ linkage in complex **7** the $\text{C}(2)-\text{O}(3)$ bond length has increased to 1.376 Å (1.351 Å in **5a**) and the $\text{W}(1)-\text{C}(2)$ and $\text{O}(3)-\text{Si}(1)$ bonds are orthogonal to one another. This configuration indicates that in complex **7** there exists very little, if any, double-bond character between $\text{C}(2)$ and $\text{O}(3)$. The $\text{W}=\text{C}$ bond distance of 2.016 Å (Table 2) is only slightly elongated from that found for complex **5a**. A torsion angle of 20.6° was found for the carbene plane ($\text{C}(11)-\text{C}(2)-\text{O}(3)$) relative to the $\text{W}=\text{O}$ bond, and the carbene phenyl ring is twisted approximately 25° relative to the carbene plane. As in **5a** the $\text{W}-\text{N}$ distances to the tridentate Tp' ligand reflect the increasing trans influence of I (2.14 Å), $=\text{C}(\text{OR})'$ (2.24 Å), and $=\text{O}$ (2.30 Å).

Observation of the anionic phenyl–acyl complex $[\text{Tp}'\text{W}(\text{O})(\text{I})(\text{C}(\text{O})\text{Ph})][\text{Li}]$ (**8**) was carried out by low-

temperature NMR. Complex **8** shows unique signals for a Tp' ligand bound to a chiral metal center and multiplets for the phenyl ring between 7.0 and 8.1 ppm. The acyl C=O carbon resonates at 309.0 ppm, similar to the chemical shift seen for the anionic methyl-acyl complex and also to the shifts for the isolated carbene complexes. Only one isomer of complex **8** was observed. Isolation of the anionic phenyl-acyl complex has not been accomplished.

Replacement of the iodide in the iodo-carbonyl reagent complex **1** by simple substitution with other ligands has proven difficult. Even replacement of the iodide with $[\text{CH}_3^-]$ using LiCuMe_2 reagents (vide supra) is plagued by low yields; other reagents such as silver salts have been completely ineffective. In contrast, iodide substitution in carbene complex **5a** with a silver salt proceeds in high yields. Replacement of the iodide ligand in carbene complex **5a** is facile with the use of $\text{Ag}[\text{SO}_3\text{CF}_3]$ as a source of both an iodide trap (Ag^+) and a weakly coordinating ligand (OTf^-). Addition of a slight excess of $\text{Ag}[\text{SO}_3\text{CF}_3]$ to a red THF solution of **5a** at room temperature leads to an immediate color change to form a light orange solution with concomitant formation of a dark precipitate, presumably AgI . Filtration through Celite followed by solvent removal yields $\text{Tp}'\text{W}(\text{O})(\text{OTf})(=\text{C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**9**) as a light orange powder (eq 7). Proton NMR characterization of this complex



shows a carbene methyl signal at 5.36 ppm with $^3J_{\text{WH}} = 5.6$ Hz, a silicon-bound methyl signal at 0.62 ppm with $^2J_{\text{SiH}} = 6.6$ Hz, and phenyl multiplets between 7.10 and 7.40 ppm. The carbene carbon appears at 317.2 ppm with $^1J_{\text{WC}} = 190$ Hz in the ^{13}C NMR spectrum. The trifluoromethyl carbon appears as a quartet at 119.4 ppm ($^1J_{\text{CF}} = 318$ Hz), while the carbene methyl carbon appears at 44.0 ppm.

A crystal structure of complex **9** was obtained (Figure 4). Both the $\text{W}=\text{C}$ bond length (1.994 Å, Table 3) and the torsion angle of the carbene plane with the $\text{W}=\text{O}$ vector (15.8°) are approximately the same as in the corresponding iodo complex **5a**. The $\text{W}-\text{N}$ bond distance trans to the triflate ligand, 2.134 Å, is slightly shorter than the corresponding bond trans to the iodide in **5a** (2.151 Å), consistent with the triflate ligand being a weaker trans influence ligand in complex **9** than is the iodide in complex **5a**.

Preliminary investigations into the reactivity of the carbene moieties in these complexes reveal that under mild conditions these complexes do not react with simple olefins. In solution, iodo-carbene complexes **5a-c** and **7** react readily with oxygen to form the tungsten(VI) complex $\text{Tp}'\text{W}(\text{O})_2\text{I}$.

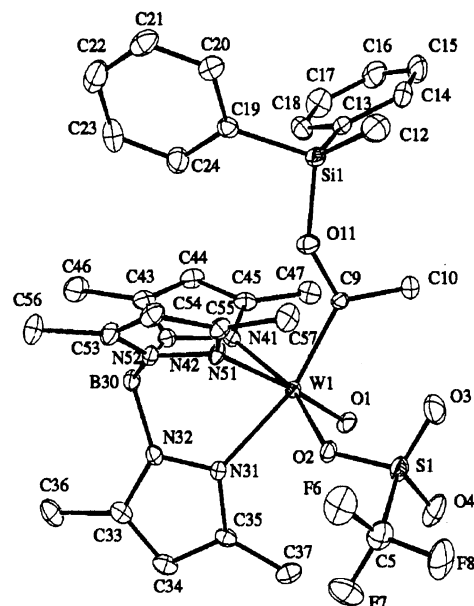


Figure 4. ORTEP diagram of $\text{Tp}'\text{W}(\text{O})(\text{OTf})(=\text{C}(\text{Me})\text{OSiPh}_2\text{Me})$. Ellipsoids are drawn with 50% probability.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **9**

W1–C9	1.994(5)	W1–N31	2.219(5)
W1–N41	2.134(5)	W1–N51	2.308(4)
C9–C10	1.505(9)	C9–O11	1.357(6)
W1–O1	1.715(4)	W1–O2	2.128(4)
C10–C9–O11	114.2(5)	W1–C9–O11	120.2(4)
W1–C9–C10	125.6(4)	C9–O11–Si1	140.3(4)
O1–W1–C9–C10 ^a			15.8(6)

^a Torsion angle.

Conclusion

Reaction of $\text{Tp}'\text{W}(\text{O})(\text{I})(\text{CO})$ (**1**) with MeLi generates the anionic acyl complex $[\text{Tp}'\text{W}(\text{O})(\text{I})(\text{C}(\text{O})\text{Me})][\text{Li}]$ (**6**). Trapping of the reactive acyl complex with chlorosilane reagents yields the corresponding neutral carbene complexes. Trapping of **6** with H^+ forms the neutral hydroxy carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Me})\text{OH})$ (**5c**). Reaction of **5a** with $\text{Ag}[\text{SO}_3\text{CF}_3]$ produces the coordinated triflate carbene complex $\text{Tp}'\text{W}(\text{O})(\text{OSO}_2\text{CF}_3)(=\text{C}(\text{Me})\text{OSiPh}_2\text{Me})$ (**9**). The sequential reaction of **1** with PhLi and then ClSiPh_2Me generates the neutral phenyl-substituted carbene complex $\text{Tp}'\text{W}(\text{O})(\text{I})(=\text{C}(\text{Ph})\text{OSiPh}_2\text{Me})$ (**7**). Protonation of the methyl tungsten complex $\text{Tp}'\text{W}(\text{O})(\text{Me})(\text{CO})$ (**2**) in acetonitrile gives the cationic hydroxy carbene complex $[\text{Tp}'\text{W}(\text{O})(\text{NCMe})(=\text{C}(\text{Me})\text{OH})^+]$ (**4**).

These high-oxidation-state heteroatom-substituted carbene complexes of tungsten exhibit spectral properties and solid-state structures that are congruent with expectations based on the properties of related carbene complexes.

Experimental Section

Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Hexanes, methylene chloride, and pentane were purified by passage through an activated alumina column under a dry argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under a dry nitrogen atmosphere. Deuterated solvents were dried using CaH_2 or sodium benzophenone ketyl

Table 4. Crystallographic Data Collection Parameters

	5a	7	9
formula	C ₃₀ H ₃₈ BN ₆ O ₂ SiW	C ₃₅ H ₄₀ BN ₆ O ₂ SiW	C ₃₁ H ₃₅ BN ₆ O ₅ F ₃ SSiW
mol wt	864.31	926.38	883.45
cryst syst	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1
<i>a</i> , Å	9.8529(3)	10.3471(4)	11.7903(5)
<i>b</i> , Å	16.8079(5)	15.2400(5)	12.2128(5)
<i>c</i> , Å	20.9057(7)	23.1784(8)	14.1367(1)
α, deg	90	90	85.157(1)
β, deg	101.736(1)	90	86.691(1)
γ, deg	90	90	61.821(1)
<i>V</i> , Å ³	3389.75(18)	3655.00(22)	1787.54(13)
<i>Z</i>	4	4	2
calcd density, Mg/m ³	1.694	1.684	1.641
<i>F</i> (000)	1685.08	1813.15	877.85
cryst dimens, mm	0.35 × 0.20 × 0.20	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.05
temp, °C	−100	−100	−100
2θ range, deg	5–60	5–60	5–60
μ, mm ^{−1}	4.39	4.08	3.39
scan mode	<i>ω</i>	<i>ω</i>	<i>ω</i>
total no. of rflns	49 245	61 838	20 699
total no. of unique rflns	9899	10 688	8518
no. of rflns with <i>I</i> > 2.5σ(<i>I</i>)	8367	9461	7164
<i>R</i> _F , %	0.033	0.047	0.045
<i>R</i> _{wF} , %	0.043	0.056	0.049
GOF	1.6306	2.3708	1.5810

and deoxygenated using standard freeze–pump–thaw techniques. Diphenylmethylchlorosilane was dried over CaH₂ and deoxygenated using standard freeze–pump–thaw techniques. CuI was obtained and used directly as received from Aldrich Chemical Co. Methyl lithium was obtained and used directly as received from ACROS Organics. The acid of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, (H(Et₂O)₂BAR'₄), was prepared according to literature methods.¹⁸ Tp'W(O)(CO)(I) was prepared by a modified literature preparation.¹⁹ Organolithium reagents were titrated using 1,3-diphenylacetone *p*-tosylhydrazide to determine actual reagent concentrations.²⁰

¹H NMR, ¹³C NMR, and two-dimensional NMR spectra were recorded on Bruker AMX300, DRX400, AMX400, and Avance500 spectrometers. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 FT-IR spectrometer. Chemical analyses were performed by Atlantic Microlabs of Norcross, GA.

Tp'W(O)(I)(CO) (1). Complex **1** was prepared using a modified literature preparation method. Tetrahydrofuran was used as the reaction solvent in place of toluene. Yield: 5.54 g (72%). Spectroscopic and analytical data for **1** have been reported.¹⁹

Tp'W(O)(Me)(CO) (2). In a 500 mL round-bottomed flask, Tp'W(O)(I)(CO) (**1**; 0.514 g, 7.9 mmol) was dissolved in ca. 70 mL of THF. To this dark purple solution was added 50 mL of a freshly prepared THF solution of LiCuMe₂ (1.5 equiv) via cannula. A dark brown solution resulted. The solution was stirred for 2 h at room temperature before the THF was removed to afford a dark brown oily solid, which was redissolved in CH₂Cl₂ and filtered through Celite to remove insoluble species. Using a mixture of CH₂Cl₂ and hexanes as the eluant, a dark yellow fraction was collected from a Florisil column. Solvent removal yielded the product as a dark yellow solid. Yield: 0.066 g (16%). IR (KBr): ν_{CO} 1934 cm^{−1}, ν_{WO} 956 cm^{−1}. ¹H NMR (CD₂Cl₂): δ 6.50, 6.27, 5.90 (Tp'CH), 2.93, 2.83, 2.82, 2.72, 2.52, 2.47 (Tp'CH₃), 2.07 (²J_{WH} = 8.0 Hz, W–CH₃). ¹³C NMR (CD₂Cl₂): δ 153.2, 151.7, 151.3, 147.0, 145.9, 145.2 (Tp'CCH₃), 108.7, 107.3, 107.1 (Tp'CH), 16.8, 15.3, 15.2, 12.8,

12.8, 12.4 (Tp'CH₃), 8.9 (¹J_{WC} = 102 Hz, W–CH₃). Anal. Calcd for C₁₇H₂₅BN₆O₂W: C, 37.81; H, 4.67; N, 15.57. Found: C, 37.87; H, 4.70; N, 15.43.

General Procedure for the Synthesis of LiCuMe₂. To a 200 mL round-bottom flask was added CuI (0.50 g, 2.63 mmol). The flask was wrapped with aluminum foil and cooled to −78 °C. Approximately 50 mL of THF was added to give a gray suspension. To this gray suspension was added MeLi (1.4 M in Et₂O, 3.8 mL, 5.30 mmol) to give a colorless solution. If a yellow solid is obtained, the flask is allowed to warm slightly to promote dissolution of the solid and then cooled again to −78 °C. Note: the LiCuMe₂ must be clear and colorless before using. If a yellow color is obtained, addition of more MeLi may be required.

[Tp'W(O)(NCMe)(CO)][BAR'₄] (3). A 250 mL round-bottom flask was charged with the solids **2** (0.250 g, 0.463 mmol) and HBAR'₄·2OEt₂ (0.47 g, 0.463 mmol) and a stir bar. A mixture of CH₂Cl₂ (30 mL) and MeCN (75 μL, 1.40 mmol) was prepared in a second 100 mL round-bottom flask. The solvent mixture was cannula-transferred to the first flask while being stirred vigorously at room temperature. The dark purple solution which resulted was stirred for 30 min before the solvent was removed in vacuo. Recrystallization of the resulting oil from CH₂Cl₂ and hexanes afforded product **3** as a purple powder. Yield: 0.537 g (82%). IR (CH₂Cl₂): ν_{CO} 2023 cm^{−1}. ¹H NMR (CD₂Cl₂): δ 7.71 (8H, *o*-Ar'), 7.56 (4H, *p*-Ar'), 6.24, 6.28, 5.82 (Tp'CH), 3.09 (W–NCCCH₃), 2.63, 2.52, 2.49, 2.47, 2.28, 2.20 (Tp'CH₃). Anal. Calcd for C₅₀H₃₇B₂F₆N₇O₂W: C, 42.02; H, 2.61; N, 6.86. Found: C, 42.13; H, 2.70; N, 6.95.

[Tp'W[=C(OH)(Me)](O)(NCMe)][BAR'₄] (4). To a 100 mL round-bottom flask charged with solids **2** (0.080 g, 0.148 mmol) and HBAR'₄·2OEt₂ (0.150 g, 0.148 mmol) was added 50 mL of CH₃CN at −78 °C with stirring. Immediate formation of a dark orange solution was observed. Following an additional 30 min of stirring at room temperature, the solvent was removed in vacuo to yield a dark orange oil. The oil was taken up in CD₂-Cl₂ for spectroscopic characterization. ¹H NMR (CD₂Cl₂): δ 8.70 (bs, OH), 7.85 (8H, *o*-Ar'), 7.62 (4H, *p*-Ar'), 6.17, 6.07, 5.97 (Tp'CH), 4.80 (³J_{WH} = 4.4 Hz, W=C(OH)CH₃), 2.84, 2.67, 2.52, 2.41, 2.38, 2.34, 2.14 (Tp'CH₃ and W–NCCCH₃). ¹³C NMR (CD₂-Cl₂): δ 313.6 (¹J_{WC} = 170 Hz, W=C), 162.2 (q, ¹J_{BC} = 50 Hz, *ipso* of BAR'₄), 153.8, 153.2, 152.3, 150.2, 149.3, 147.7 (Tp'CCH₃), 135.3 (*o*-C of BAR'₄), 129.4 (q, ²J_{CF} = 25 Hz, *m*-C of BAR'₄), 125.1 (q, ¹J_{CF} = 270 Hz, CF₃), 117.9 (*p*-C of BAR'₄), 109.7, 108.9, 108.6

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(Tp'CH), 40.71 (W=C(OH)CH₃), 16.4, 15.2, 14.6, 13.0, 12.9, 12.2 (Tp'CH₃), 4.9 (W-NCCH₃).

Tp'W(O)(I)(C(Me)OSiPh₂Me) (5a). In a 200 mL round-bottomed flask, **1** (0.258 g, 0.396 mmol) was dissolved in ca. 30 mL of THF. The solution was cooled to -78 °C. To this solution was added 1 equiv of MeLi (0.247 mL, 1.6 M). The solution underwent an immediate color change from purple to a deep blue. After the mixture was stirred for 15 min, ClSiPh₂Me (0.082 mL, 0.395 mmol) was added to the solution. A slow color change to red occurred over 10 min. The solution was slowly warmed to room temperature, and the THF solvent was removed to yield an oily red solid. The solid was redissolved in a mixture of CH₂Cl₂ and hexanes (1:10) and cannula-filtered to remove insoluble species. The solvents were removed to yield a red powder (0.266 g, 78%). Crystals suitable for structure elucidation were grown by slow evaporation from a CH₂Cl₂-hexanes mixture (1:10). ¹H NMR (CD₂Cl₂): δ 7.36 (m), 7.21 (m), 7.07 (m) (-OSiPh₂Me), 5.98, 5.98, 5.49 (Tp'CH), 5.05 (³J_{WH} = 4.5 Hz, W-C(CH₃)OSiPh₂Me), 2.84, 2.54, 2.41, 2.40, 2.11, 1.99 (Tp'CH₃), 0.63 (²J_{SiH} = 6.6 Hz, -OSiPh₂Me). ¹³C NMR (CD₂Cl₂): δ 321.0 (W=C), 154.6, 153.8, 153.0, 147.0, 145.9, 144.7 (Tp'CCH₃), 136.3, 135.6, 134.6, 134.3, 130.4, 130.2, 128.1, 127.9 (-OSiPh₂Me), 108.4, 108.1, 108.0 (Tp'CH), 20.1, 17.4, 17.2, 13.1, 13.0, 12.6 (Tp'CH₃), -1.0 (-OSiPh₂Me). Anal. Calcd for C₃₀H₃₈BN₆O₂WSiI: C, 41.69; H, 4.43; N, 9.72. Found: C, 41.39; H, 4.64; N, 9.75.

Tp'W(O)(I)(C(Me)OSiMe₃) (5b). A procedure analogous to that used for **5a** was utilized with ClSiMe₃ in place of ClSiPh₂Me. Complex **5b** was obtained as a pink powder (yield 34%). ¹H NMR (CD₂Cl₂; major isomer): δ 6.04, 5.97, 5.75 (Tp'CH), 5.02 (³J_{WH} = 4.8 Hz, W-C(CH₃)OSiMe₃), 2.84, 2.45, 2.42, 2.38, 2.33, 2.31 (Tp'CH₃), 0.08 (²J_{SiH} = 6.8 Hz, -OSiMe₃).

Tp'W(O)(I)(C(Me)OH) (5c). In a 100 mL round-bottomed flask, **1** (0.315 g, 0.483 mmol) was dissolved in ca. 25 mL of THF. The solution was cooled to -78 °C. To this solution was added 1.1 equiv of MeLi (0.326 mL, 1.6 M). The solution undergoes an immediate color change from purple to a deep blue. After this mixture was stirred for 15 min, a THF solution containing 1.1 equiv of C₆H₅CO₂H (0.068 g, 0.555 mmol) was cannulated into the tungsten solution. A slow color change to a red-purple solution occurred over 10 min. The solution was slowly warmed to room temperature, and the THF solvent was removed to yield an oily purple solid. The solid was redissolved in a mixture of CH₂Cl₂ and hexanes (1:10) and cannula-filtered to remove insoluble species. The solvents were removed to yield a purple powder (0.236 g, 73%). IR (KBr): ν_{OH} 3466 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.70 (-OH), 6.08, 6.03, 5.86 (Tp'CH), 4.84 (³J_{WH} = 4.5 Hz, W=C(CH₃)OH), 2.87, 2.46, 2.42, 2.40, 2.36, 2.34 (Tp'CH₃). ¹³C NMR (CD₂Cl₂): δ 312.2 (W=C), 155.0, 154.1, 153.4, 147.7, 147.0, 146.3 (Tp'CCH₃), 109.2, 108.3, 108.1 (Tp'CH), 39.6 (W=C(CH₃)OH), 18.7, 17.6, 16.8, 14.1, 13.0, 12.5 (Tp'CH₃). Anal. Calcd for C₁₇H₂₆BN₆O₂WI: C, 30.57; H, 3.92; N, 12.58. Found: C, 30.75; H, 3.87; N, 12.30.

[Tp'W(O)(I)(C(O)Me)][Li] (6). In an NMR tube, **1** (0.070 g, 0.11 mmol) was dissolved in 1.0 mL of THF-*d*₆. The solution was shaken to dissolve the solid and cooled to -78 °C. To this solution was added 1 equiv of MeLi (0.067 mL, 1.6 M in Et₂O). The solution underwent an immediate color change from purple to royal blue. Complex **6** has not been isolated. ¹H NMR (THF-*d*₆): δ 6.05, 5.94, 5.58 (Tp'CH), 3.59 (W-C(O)CH₃), 3.07, 2.54, 2.47, 2.46, 2.30, 2.30 (Tp'CH₃). ¹³C NMR (THF-*d*₆): δ 308.3 (W-C(O)CH₃), 153.5, 152.8, 152.8, 145.8, 143.9, 142.2 (Tp'CCH₃), 107.2, 107.0, 106.8 (Tp'CH), 54.3 (W-CCH₃), 18.8, 17.8, 17.7, 12.9, 12.9, 12.5 (Tp'CH₃).

Tp'W(O)(I)(C(Ph)OSiPh₂Me) (7). In a 200 mL round-bottomed flask, **1** (0.104 g, 0.154 mmol) was dissolved in ca. 30 mL of THF. The solution was stirred and cooled to -78 °C. To this solution was added 1 equiv of PhLi (0.10 mL, 1.66 M).

The solution undergoes an immediate color change from purple to olive green. After the mixture was stirred for 15 min, ClSiPh₂Me (0.04 mL, 0.170 mmol) was added to the solution. The solution was slowly warmed to room temperature. While it was warmed, the solution underwent a slow color change to red-brown. The solvent was removed to yield an oily red-brown solid. The solid was redissolved in a mixture of CH₂Cl₂ and pentane (1:10) and cannula-filtered to a new flask to remove any insoluble species. The solvents were removed to yield a red-brown powder (0.077 g, 54%). ¹H NMR (CD₂Cl₂): δ 7.3 (m) (-OSiPh₂Me and W=C(C₆H₅)OSiPh₂Me), 6.00, 5.88, 5.61 (Tp'CH), 2.85, 2.51, 2.42, 2.42, 2.18, 2.03 (Tp'CH₃), 0.08 (²J_{SiH} = 6.9 Hz, -OSiPh₂Me). ¹³C NMR (CD₂Cl₂): δ 318.1 (W=C), 155.2, 154.5, 153.1, 147.9, 147.3, 146.0, 145.3, 137.0, 136.5, 134.9, 134.4, 131.5, 130.3, 130.0, 129.4, 128.1, 128.0, 127.0 (Tp'CCH₃ and 3 Ph), 108.8, 108.4, 108.4 (Tp'CH), 20.7, 18.3, 17.6, 13.4, 13.3, 12.8 (Tp'CH₃), -2.6 (-OSiPh₂Me). Anal. Calcd for C₃₅H₄₀BN₆O₂WSiI: C, 46.10; H, 4.71; N, 8.72. Found: C, 45.76; H, 4.73; N, 8.44.

[Tp'W(O)(I)(C(O)Ph)][Li] (8). In an NMR tube, **1** (0.070 g, 0.11 mmol) was dissolved in 0.60 mL of THF-*d*₆. The solution was shaken to dissolve the solid and cooled to -78 °C. To this solution was added 1 equiv of PhLi (53.7 μL, 1.6 M). The solution underwent an immediate color change from purple to olive green. The anionic phenyl-acyl complex has not been isolated. ¹H NMR (THF-*d*₆): δ 8.13 (d), 7.28 (t), 6.98 (t) (C₆H₅), 5.92, 5.90, 5.59 (Tp'CH), 3.09, 2.47, 2.44, 2.29, 2.24, 2.04 (Tp'CH₃). ¹³C NMR (THF-*d*₆): δ 309.0 (C(O)Ph), 153.6, 152.5, 152.4, 145.8, 143.2, 142.1 (Tp'CCH₃), 156.5, 143.5, 141.3 (-C(O)Ph), 107.0, 106.6, 106.6 (Tp'CH), 18.5, 17.6, 17.1, 12.6, 12.5, 12.0 (Tp'CH₃).

Tp'W(O)(OSO₂CF₃)(=C(Me)OSiPh₂Me) (9). In a dry Schlenk flask, **5a** (0.116 g, 0.134 mmol) was dissolved in 20 mL of THF. AgSO₃CF₃ was weighed out under an inert atmosphere, placed in a dry Schlenk flask, and stirred in 10 mL of THF. The red-purple solution of **5a** was cannulated into the [Ag][OTf] solution. The solution color changed to orange, and concomitant precipitation of a white solid occurred. The solution was stirred for 15 min and then filtered through a plug of Celite to remove insoluble materials. Solvent was removed under vacuum to yield an oily orange solid. The solid was redissolved in a minimum amount of CH₂Cl₂ and mixed with excess hexanes. Removal of the solvent yielded an orange powder. The powder was washed with 3 × 5 mL of dry pentane to yield clean material (0.100 g, 84%). Crystals suitable for structure elucidation were grown from slow diffusion of pentane into a CH₂Cl₂ solution of the complex. ¹H NMR (CD₂Cl₂): δ 7.3 (m, Si-(C₆H₅)₂), 6.06, 5.94, 5.52 (Tp'CH), 5.37 (³J_{WH} = 4.8 Hz, W=C(CH₃)OSiCH₃(C₆H₅)₂), 2.58, 2.58, 2.38, 2.37, 2.00, 1.97 (Tp'CH₃), 0.63 (²J_{SiH} = 6.6 Hz, SiCH₃(C₆H₅)₂). ¹³C NMR (CD₂Cl₂): δ 317.2 (¹J_{WC} = 191 Hz, W=C), 154.0, 153.9, 152.6, 148.3, 146.2, 145.8 (Tp'CCH₃), 136.3, 135.5, 134.3, 130.5, 130.3, 128.2, 128.0 (-OSiPh₂Me), 119.4 (q, ¹J_{CF} = 318 Hz, OSO₂CF₃), 108.4, 108.2, 107.8 (Tp'CH), 44.0 (W=C(CH₃)-OSiCH₃(C₆H₅)₂), 17.0, 14.9, 13.6, 13.3, 12.9, 12.4 (Tp'CH₃), -1.1 (OSi(C₆H₅)₂CH₃). Anal. Calcd for C₃₁H₃₈BN₆O₅WSiF₃S: C, 42.00; H, 4.32; N, 9.48. Found: C, 41.34; H, 4.49; N, 9.45.

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Supporting Information Available: Complete crystallographic data for **5a**, **7**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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