4480 *Organometallics* **2009,** *28,* 4480–4490
DOI: 10.1021/om900307p

ORGANOMETALLICS
Article

Toward Alkane Functionalization Effected with Cp*W(NO)(alkyl)(η^3-allyl) Complexes

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Received April 22, 2009

Cp*W(NO)(*n*-alkyl)(η^3-allyl) complexes result from the selective activations of the terminal C−H bonds of alkanes. Consequently, the reactions of prototypical members of this family of complexes with a range of electrophiles and nucleophiles have been explored with a view to developing methods for functionalizing the newly formed alkyl ligands. The two principal complexes investigated in this regard have been Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (**1**) and Cp*W(NO)($CH_2C_6H_5$)(η^3-$CH_2CHCHMe$) (**2**). It has been found that treatment of **1** and **2** with the oxidant I_2 at −60 °C produces Cp*W(NO)I_2 and terminally functionalized ICH_2SiMe_3 and $ICH_2C_6H_5$, respectively. Oxidation of **1** by H_2O_2 also results in the loss of the allyl ligand and production of the known oxo peroxo complex Cp*W(O)(η^2-O_2)(CH_2SiMe_3). Treatment of **1** and **2** with electrophiles affords the products resulting from addition of the electrophile to the electron-rich terminus of the $\sigma-\pi$ distorted allyl ligands in the reactants. Thus, reagents of the type E-X (E = triphenylcarbenium, H, catecholborane; X = Cl, BF_4) liberate $CH_3CH{=}CHCH_2E$ and form the organometallic products Cp*W(NO)(X)(CH_2SiMe_3) and Cp*W(NO)(X)($CH_2C_6H_5$), respectively. Exposure of the tungsten alkyl allyl complexes to isocyanide reagents leads to the formation of complexes bearing β,γ-unsaturated η^2-iminoacyl ligands that apparently arise from the migratory insertion of isocyanide into the tungsten−allyl linkages. For instance, reaction of **1** with 2,6-xylylisocyanide produces Cp*W(NO)(CH_2SiMe_3)(η^2-$CH_3CHCHCH_2C{=}NC_6H_3Me_2$) (**4a**). Interestingly, gentle heating or chromatography of **4a** causes isomerization of the olefin and conversion to the conjugated product Cp*W(NO)(CH_2SiMe_3)(η^2-$CH_3CH_2CHCHC{=}NC_6H_3Me_2$) (**4b**). A similar reaction of **2** with 2,6-xylylisocyanide affords both unconjugated and conjugated isocyanide insertion products, while treatment of **2** with *n*-butylisocyanide produces primarily the conjugated product. Finally, exposure of these tungsten alkyl allyl complexes to 1000 psi of CO gas generally results in the desired migratory insertion of the CO into the metal−alkyl linkages to form acyl compounds. Hence, **1** is first converted into Cp*W(NO)(C(O)CH_2SiMe_3)(η^3-$CH_2CHCHMe$), which then subsequently transforms into isolable Cp*W(NO)(C(O)CH_3)(η^3-$CH_2CHCHMe$) (**7**). Interestingly, **2** does not react with CO under these experimental conditions. Nevertheless, the generality of this mode of reactivity is established by the fact that similar treatment of four other Cp*(W)(NO)(CH_2CMe_3)(η^3-allyl) complexes with CO gas at elevated pressures does afford the corresponding acyl products (**8**−**11**). All new organometallic complexes have been characterized by conventional spectroscopic and analytical methods, and the solid-state molecular structures of several compounds have been established by X-ray crystallographic analyses.

Introduction

The selective activation and subsequent functionalization of hydrocarbon C−H bonds by transition-metal complexes continues to be a topic of current interest for synthetic chemists.[1−3] C−H bond activation by metal complexes frequently involves cleavage of the C−H bond and formation of a new metal−carbon bond, with the corresponding hydrogen becoming involved in a direct metal−hydride interaction or being stored elsewhere in the metal's coordination sphere.[2,3] Systems that activate the sp^3 C−H bonds of alkanes remain relatively rare, and those that can combine

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 Published on Web 06/23/2009

alkane activation with subsequent functionalization of the alkyl ligand are even more unique.[3] In this connection three systems that both activate and functionalize alkane C−H bonds merit special mention since they employ relatively mild reaction conditions and produce functionalized molecules in good yields. These functionalizations involve the selective oxidation of alkanes in aqueous solution by soluble Pt(II) and Pt(IV) salts first described by Shilov and co-workers,[3i] the catalytic conversion of methane to methyl bisulfate mediated by ligated Pt(II) complexes reported by Periana and co-workers,[4] and the catalytic, regioselective functionalization of alkanes using transition-metal boryl complexes developed by Hartwig and co-workers.[5]

One of our recent contributions to this area involved the synthesis and characterization of several Cp*W(NO)(alkyl)(η^3-allyl) complexes[6] and the discovery that one of them, namely, Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$), effects single C−H activations at the terminal positions of *n*-alkanes such as heptane, pentane, ethane, and methane at room temperature.[7] This nitrosyl complex displays remarkable selectivity for primary over secondary positions, and the Cp*W(NO)(*n*-alkyl)(η^3-$CH_2CHCHMe$) products resulting from the C−H activation processes are isolable at room temperature.

To exploit more fully these unique C−H activations, we set out to develop the conditions for effecting these activations and subsequent functionalizations of the resulting alkyl ligands in a catalytic manner. As a first step, we therefore decided to investigate the reactions of the various Cp*W(NO)(alkyl)(η^3-$CH_2CHCHMe$) product complexes with a range of electrophiles and nucleophiles to discover those reagents that react preferentially with the alkyl ligands. However, we quickly encountered a practical limitation. On a preparative scale, Cp*W(NO)(R)(η^3-allyl) [R = alkyl] complexes are prepared via sequential metatheses reactions of Cp*W(NO)Cl_2 with $MgR_2 \cdot x$(dioxane) and Mg(allyl)$_2 \cdot x$-(dioxane) reagents.[6] Unfortunately, preparation of the R = *n*-alkyl members of this family of complexes by this route is not possible since the intermediate *n*-alkyl chloro complexes are thermally unstable and readily decompose, probably by β-hydrogen elimination. Since the desired Cp*W(NO)(*n*-alkyl)(η^3-allyl) reagents cannot be conveniently synthesized on a large scale, we have instead employed two other complexes that can be readily prepared by the metathesis route, namely, Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (**1**) and Cp*W(NO)($CH_2C_6H_5$)(η^3-$CH_2CHCHMe$) (**2**), as prototypical reactants during our studies. Subsequently, the reactivity studies resulting in the desired functionalization of the alkyl ligands were extended to encompass other members of this family of complexes to establish the generality of these transformations. To the best of our knowledge such a study of the comparative reactivity of alkyl and allyl ligands at the same metal center has not been undertaken previously.

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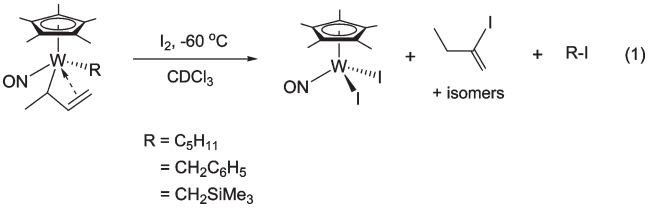
Results and Discussion

Syntheses of Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (1) and Cp*W(NO)($CH_2C_6H_5$)(η^3-$CH_2CHCHMe$) (2). The 18e complexes **1** and **2** were first prepared by the C−H activation of tetramethylsilane and toluene, respectively, by Cp*W(NO)(η^2-CH_2=CHCH=CH_2).[7] However, they are most conveniently obtained on a preparative scale in good yields by metathesis reactions originating with Cp*W(NO)Cl_2.[6] Both **1** and **2** exhibit diagnostic ^{1}H NMR signals in C_6D_6 indicative of their possessing piano-stool molecular geometries in solution with the allyl ligands being in endo conformations pointing away from the bulky Cp* rings and displaying significant $\sigma-\pi$ distortions.[6] X-ray crystallographic analyses of both compounds have confirmed these inferences. Complex **2** exhibits just the syn isomer in the solid state, and its NMR data are consistent with this structure being maintained in solutions.[7] Complex **1**, on the other hand, exists as a 2:1 mixture of geometrical isomers in solution and in the solid state.[6] Its major isomer has the methyl group of the 1-methylallyl ligand in the syn orientation, pointing toward the less bulky NO ligand, while the minor isomer has it in the same orientation but pointing toward the much larger CH_2SiMe_3 fragment.[6]

The ^{1}H NMR spectrum of **1** in C_6D_6 reveals a pair of doublets at −0.62 and −0.09 ppm due to the diastereotopic methylene protons of CH_2SiMe_3. Similarly, complex **2** displays resonances at 1.95 and 2.82 ppm, which can be attributed to the $CH_2C_6H_5$ protons. Both complexes also exhibit a multiplet at approximately 5 ppm attributable to the meso proton of the allyl ligand. These spectral features are particularly useful for monitoring the progress of reactions involving **1** and **2**.

Reactions of 1 and 2 with Oxidizing Agents. The reactivity of molecular iodine with complexes **1** and **2** is identical to that exhibited by related *n*-alkyl tungsten complexes and is summarized in eq 1. As briefly noted previously,[7] both the alkyl and allyl ligands are liberated from the tungsten's coordination sphere with the Cp*W(NO) fragment being recoverable as the diiodide.



Compound **1** is also relatively stable toward oxygen and moisture in the crystalline state. However, reaction of **1** with aqueous hydrogen peroxide cleanly produces the known oxo peroxo complex Cp*W(O)(η^2-O_2)(CH_2SiMe_3),[8] readily identifiable by its diagnostic ^{1}H NMR resonances. A plausible mechanism for the formation of the tungsten oxo peroxo complex is presented in Scheme 1.

Precedent for the oxidatively induced intramolecular insertion of NO into a tungsten−carbon bond depicted in Scheme 1 is provided by the reaction summarized in eq 2. Thus, we have recently discovered that treatment of Cp*W(NO)(CH_2SiMe_3)$_2$ with 1 equiv of cumene

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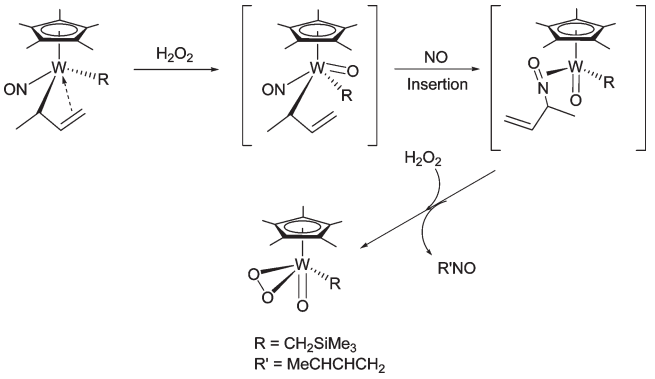
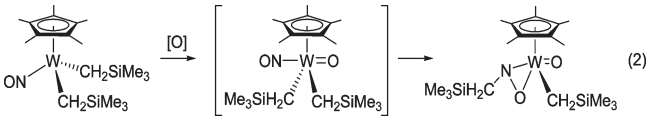
Scheme 1



hydroperoxide produces Cp*W(O)(CH_2SiMe_3)(η^2-O=NCH_2SiMe_3).[9]



The hydroperoxide evidently delivers a single oxygen atom to form initially an oxo species, which then undergoes migratory insertion of the nitrosyl ligand into the W−C bond. We believe that a similar mechanism is operative during the conversion summarized in Scheme 1 with the NO insertion first occurring into the metal−allyl linkage and subsequent oxidation then producing the final oxo-peroxo complex. Particularly intriguing in this regard is the fact that it is the allyl, and not the alkyl, group that migrates with such selectivity. The released nitrosoalkene depicted in Scheme 1 has not been detected by ^{1}H NMR spectroscopy, and it is probably unstable under the reaction conditions employed.[10] In any event, the use of hydrogen peroxide results in preferential functionalization of the allyl over the alkyl ligand.

Reactions of 1 and 2 with Electrophilic Reagents. Nucleophilic attack on η^3-allyl ligands in group 6 half-sandwich compounds of this type is a common mode of reactivity and usually occurs trans to the better π-accepting NO ligand.[11] It might therefore have been expected that electrophiles would preferentially attack the alkyl ligands of the Cp*W(NO)(alkyl)(η^3-allyl) reactants. However, every electrophilic reagent with which complexes **1** and **2** have been treated to obtain an isolable product attacks the allyl ligands. No functionalization of the alkyl ligands has been detected under these experimental conditions.

Hence, treatment of **1** with HCl in MeCN-d_3 affords ink blue Cp*W(NO)(CH_2SiMe_3)Cl[6] and probably 2-butene, the direct result of electrophilic addition of H^+ to the allyl ligand. The analogous reaction of **1** with pyridinium chloride affords the same products. Finally, reaction of **1** with *B*-chlorocatecholborane produces Cp*W(NO)(CH_2SiMe_3)Cl and a borane-functionalized alkene, characterized by

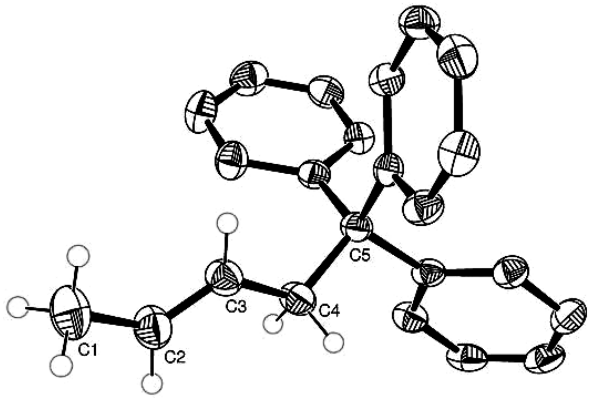
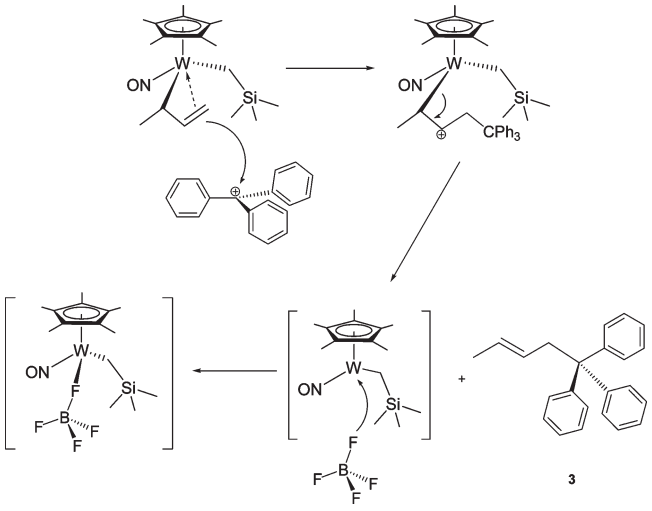
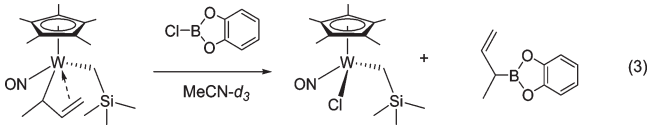


Figure 1. Solid-state molecular structure of **3** with 50% probability thermal ellipsoids. Selected interatomic distances (Å): C(1)−C(2) = 1.492(2), C(2)−C(3) = 1.310(2), C(3)−C(4) = 1.502(2).

Scheme 2



multiplets at 1.30, 2.47, 5.07, and 6.10 ppm in the ^{1}H NMR spectrum of the final reaction mixture, which indicate that it is principally the isomer shown in eq 3.



Treatment of **1** with triphenylcarbenium tetrafluoroborate affords a crystalline white solid following extraction of the final reaction mixture with pentane and subsequent chromatography. An X-ray crystallographic analysis of the crystalline material has confirmed it to be $H_3CCHCHCH_2C(C_6H_5)_3$ (**3**) (Figure 1). The interatomic distance of 1.310(2) Å between C2 and C3 is indicative of a carbon−carbon double bond, and the trans orientation of the substituents is evident from the solid-state molecular structure. The organometallic product of the reaction possesses an intact CH_2SiMe_3 ligand, with the resonances attributable to the diastereotopic protons appearing at −1.15 and 0.01 ppm. In addition, singlets at 0.36 and 1.63 ppm correspond to $SiMe_3$ and C_5Me_5 fragments, respectively. While the identity of this product remains to be confirmed, a complex of the type Cp*W(NO)(CH_2SiMe_3)(η^1-BF_4) can be postulated on the

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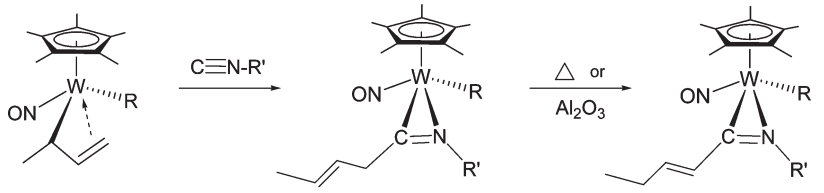
Scheme 3



A **B**

R = CH_2SiMe_3, R' = 2,6-$Me_2C_6H_3$ (**4a, 4b**)
R = $CH_2C_6H_5$, R' = 2,6-$Me_2C_6H_3$ (**5a, 5b**)
R = $CH_2C_6H_5$, R' = C_4H_9 (**6b**)

basis of our previous work with iron nitrosyl complexes.[12] Similar treatment of **2** with triphenylcarbenium tetrafluoroborate also affords **3** and an organometallic species bearing C_5Me_5 and $CH_2C_6H_5$ ligands, characterized by ^{1}H NMR resonances at 1.63 (C_5Me_5), 1.70 ($CH_2C_6H_5$), and 2.90 ($CH_2C_6H_5$) ppm. Clearly, the steric bulk of the alkyl ligands in **1** and **2** does not influence the site of electrophilic attack.

On the basis of the current experimental evidence a plausible mechanism can be proposed for the formation of compound **3** (Scheme 2). As noted before, the electronic asymmetry extant at the metal center causes a $\sigma-\pi$ distortion of the allyl ligand. This feature results in the accumulation of electron density on the terminal position of the allyl ligand trans to the nitrosyl group, thereby creating a site for electrophilic attack.

Electrophilic addition of the triphenylcarbenium ion to the terminal position of the allyl ligand leads to the formation of a new carbon−carbon bond and places the positive charge formerly residing on the triphenyl fragment onto the meso position of the 1-methylallyl ligand. This 16*e* species may then undergo cleavage of the remaining W−C σ-bond and rearrange to produce compound **3** and the postulated 16*e* complex Cp*W(NO)(CH_2SiMe_3)(η^1-BF_4). No coordination of the C=C bond of compound **3** to the tungsten center occurs probably because of steric interactions between the bulky CPh_3 and CH_2SiMe_3/$CH_2C_6H_5$ fragments.

The mechanism proposed in Scheme 2 can also be applied to the reactions of complexes **1** and **2** with other electrophiles, including H^+ and *B*-chlorocatecholborane. In all cases, electrophilic addition occurs at the allyl ligand, the resulting olefin apparently does not coordinate to the metal center, and a new, electronically unsaturated metal complex is formed.

Reactions of 1 and 2 with Isocyanides: Synthesis of η^2-Iminoacyl Complexes. Treatment of the tungsten alkyl allyl complexes with isocyanide reagents leads to the formation of compounds bearing β,γ-unsaturated η^2-iminoacyl ligands arising from migratory insertion of isocyanide into the tungsten−allyl linkages. Gentle warming of these product complexes or their chromatography on alumina results in isomerization of the newly formed ligands to afford compounds containing conjugated α,β-unsaturated η^2-iminoacyl ligands (Scheme 3).

Thus, reaction of **1** with 2,6-xylylisocyanide produces Cp*W(NO)(CH_2SiMe_3)(η^2-$CH_3CHCHCH_2C$=$NC_6H_3Me_2$) (**4a**), whose $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 displays a distinctive resonance at 214.8 ppm due to the iminoacyl carbon. An X-ray crystallographic analysis has been performed on a single crystal of **4a**, and its solid-state molecular structure is shown in Figure 2. The crystal of complex **4a** exhibited some disorder at the terminal positions of the allyl ligand because of their rotational mobility, and so only one of the two rotational isomers is shown in this figure. Chromatography of a solution of **4a** on alumina and subsequent cooling of the eluate leads to the isolation of the isomeric Cp*W(NO)(CH_2SiMe_3)(η^2-CH_3CH_2CHCHC=$NC_6H_3Me_2$) (**4b**). $^{13}C\{^1H\}$ NMR spectroscopy of **4b** reveals that the resonance attributable to the iminoacyl carbon remains at 214.8 ppm, but the peak due to the CH_2 unit of the former allyl ligand has shifted from 37.4 to 27.1 ppm. A single-crystal X-ray crystallographic analysis of **4b** has confirmed it to be the conjugated isomer of **4a** (Figure 3).

The η^2-binding mode of the iminoacyl fragment of **4a** is clearly established by its intramolecular metrical parameters (Figure 2). The W1−C14, W1−C5, and W1−N2 bond lengths in **4a** are indicative of single σ-bonds.[13] The C5−N2 interatomic distance of 1.257(10) Å indicates a carbon−nitrogen bond order similar to that extant in free imines.[14] Consequently, the bonding of the iminoacyl ligand to the tungsten center in **4a** is best described as consisting of a W−C σ-bond and a W←N dative interaction that provides a total of three electrons necessary for the Cp*W(NO)(alkyl) fragment to achieve an 18e configuration while leaving the C−N multiple bond unperturbed. The solid-state molecular structure of **4b** (Figure 3) displays similar metrical parameters. The conjugation of the alkene and imine functionalities is also evident in the intramolecular metrical parameters of **4a** and **4b**.

In a similar fashion, reaction of 2,6-xylylisocyanide with complex **2** affords the unconjugated insertion product Cp*W(NO)($CH_2C_6H_5$)(η^2-$CH_3CHCHCH_2C$=$NC_6H_3Me_2$) (**5a**) as the major component of a mixture also containing Cp*W(NO)($CH_2C_6H_5$)(η^2-CH_3CH_2CHCHC=$NC_6H_3Me_2$) (**5b**). Complex **5a** may be separated from the mixture by fractional recrystallization and fully characterized. Chromatography of the mixture on alumina leads to isomerization of **5a** to **5b**, which can then be recrystallized and fully characterized. Treatment of **2** with *n*-butylisocyanide leads immediately to the formation of a 3:2 mixture of the conjugated insertion product Cp*W(NO)($CH_2C_6H_5$)(η^2-CH_3CH_2CHCHC=NC_4H_9) (**6b**)

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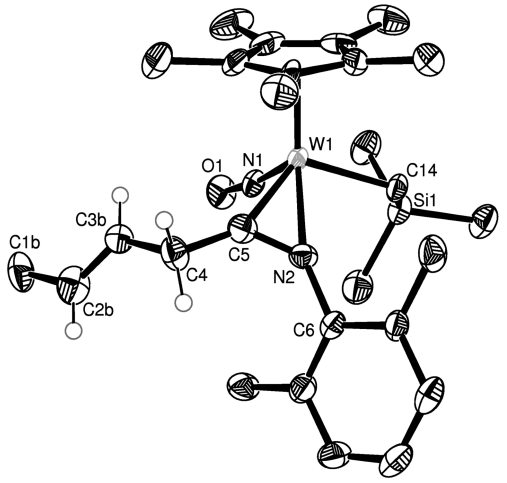


Figure 2. Solid-state molecular structure of **4a** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(5) = 2.072(8), W(1)−N(2) = 2.156(6), W(1)−C(14) = 2.197(7), C(1b)−C(2b) = 1.51(3), C(2b)−C(3b) = 1.29(2), C(3b)−C(4) = 1.55(2), C(4)−C(5) = 1.470(11), C(5)−N(2) = 1.257(10), W(1)−N(1)−O(1) = 172.3(6).

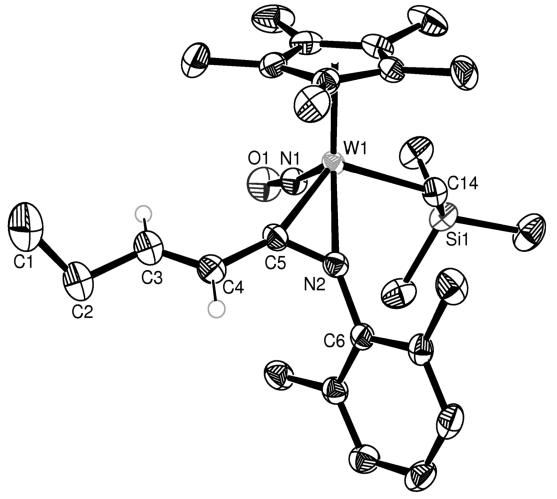


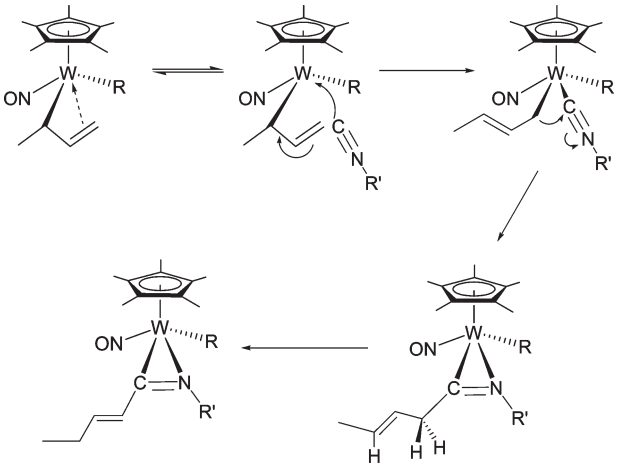
Figure 3. Solid-state molecular structure of **4b** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(5) = 2.0873(19), W(1)−C(14) = 2.211(2), W(1)−N(2) = 2.1315(16), C(1)−C(2) = 1.482(5), C(2)−C(3) = 1.483(4), C(3)−C(4) = 1.319(4), C(4)−C(5) = 1.439(3), C(5)−N(2) = 1.260(2), W(1)−N(1)−O(1) = 170.73(17).

with the unconjugated isomer (**6a**), as judged by ^{1}H NMR spectroscopy. Complex **6a** cannot be characterized since attempts to separate it from the reaction mixture by chromatography result in its isomerization to **6b**. Attempts to fractionally recrystallize **6a** from the crude reaction mixture have also been unsuccessful. Regrettably, reaction of **1** with *n*-butylisocyanide does not provide a tractable product.

A reasonable mechanism may be proposed to account for the reactions of these alkyl allyl complexes with isocyanides. The demonstrated affinity of the allyl ligand in these tungsten complexes for electrophilic reagents (vide supra) suggests that a coordination−insertion mechanism of the type presented in Scheme 4 is probably operative.

Precedent for the allyl ligand undergoing an $\eta^3 \rightarrow \eta^1$ interconversion concomitant with the coordination of a

Scheme 4



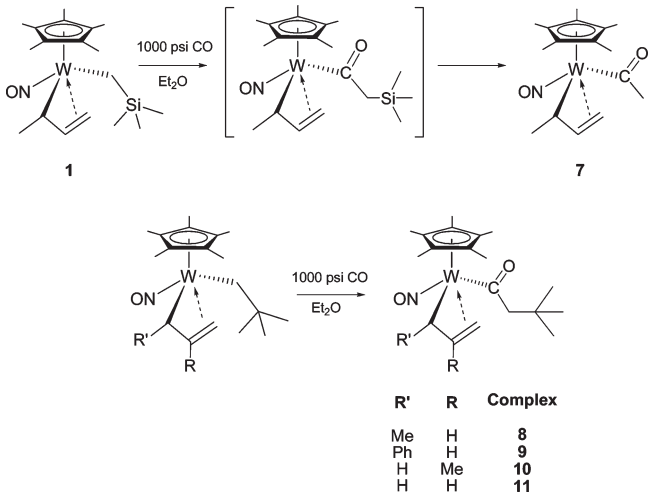
R = CH_2SiMe_3, R' = 2,6-$Me_2C_6H_3$ (**4a, 4b**)
R = $CH_2C_6H_5$, R' = 2,6-$Me_2C_6H_3$ (**5a, 5b**)
R = $CH_2C_6H_5$, R' = C_4H_9 (**6b**)

Lewis base to the metal center as required for the first step of the mechanism presented in Scheme 4 is provided by the formation of the related Cp*Mo(NO)(CH_2CMe_3)(η^1-C_3H_5)(PMe_3) adduct upon the addition of PMe_3 to the parent alkyl allyl complex in benzene at 35 °C.[15] Migratory insertion of the isocyanide into the tungsten−allyl bond then produces an 18-electron η^2-iminoacyl complex. Isocyanide insertion into the allyl ligand does not appear to be influenced by the bulk of either the alkyl ligand or the isocyanide itself.

Carbonylation Reactions of Various Cp*W(NO)(alkyl)(η^3-allyl) Complexes. Synthesis of the Corresponding Metalloacyl Complexes. Given the reactivity exhibited by the various Cp*W(NO)(alkyl)(η^3-allyl) complexes toward isocyanides described in the preceding section, we anticipated that their reactions with CO would probably proceed in a similar manner. We were therefore pleasantly surprised to discover that even though migratory insertion of the CO did occur, it did not involve the tungsten−allyl linkages (as for the isocyanides) but rather the desired tungsten−alkyl bonds (Scheme 5). For instance, reaction of **1** with 1000 psi of CO for 24 h at room temperature leads to insertion exclusively into the W−CH_2SiMe_3 linkage. However, the trimethylsilyl unit is subsequently released from the metalloacyl complex, and the acetyl complex, **7**, is the final complex formed. How this happens remains to be ascertained. Compound **7** has been fully characterized by conventional spectroscopic techniques. Thus, its mass spectrum exhibits a signal with a tungsten isotopic pattern at m/z = 447, corresponding to the parent ion, and its IR spectrum as a Nujol mull displays two strong bands at 1594 and 1615 cm^{-1}, attributable to ν_{NO} of a terminal nitrosyl and ν_{CO} of an η^1-acyl ligand, respectively. Consistently, its $^{13}C\{^1H\}$ NMR spectrum contains a downfield peak at 258.6 ppm characteristic of a tungsten-acetyl species.[16] An X-ray crystallographic analysis of **7** has been attempted; even though the atom connectivity of the complex could be confirmed, neither an acceptable ORTEP plot nor meaningful metrical parameters could be generated due to the presence of significant disorder in the crystal.

(15) Chow, C.; Semproni, S. P.; Legzdins, P. Unpublished observations.
(16) Sakaba, H.; Tsukamoto, M.; Kabuto, C.; Horino, H. *Chem. Lett.* **2000**, *12*, 1404.

Scheme 5



Nevertheless, the first step of the reaction with CO is probably similar to that presented for isocyanides in Scheme 4; namely, the allyl group must first undergo an $\eta^3 \rightarrow \eta^1$ haptotropic shift to open up a coordination position at the metal center, thereby allowing coordination of CO and subsequent insertion into the metal−alkyl bond. Following insertion, the allyl group then undergoes an $\eta^1 \rightarrow \eta^3$ haptotropic shift to form the final 18e metalloacyl complex.

Somewhat surprisingly, similar treatment of **2** with 1000 psi of CO at 20 °C leaves the starting material unchanged. This lack of reactivity probably reflects the fact that the CO simply cannot gain access to the metal center in the presence of a benzyl ligand that can also coordinate in an η^3-fashion to the metal center should the allyl ligand undergo an $\eta^3 \rightarrow \eta^1$ haptotropic shift.[17] Nevertheless, four other Cp*W(NO)-(CH_2CMe_3)(η^3-allyl) complexes that have been studied to date form the corresponding acyl complexes **8**−**11** when exposed to pressures of CO (Scheme 5). Compounds **8**−**11** have been fully characterized by customary spectroscopic techniques, and the solid-state molecular structures of **8**−**10** have been established by single-crystal X-ray crystallographic analyses (Figures 4−6). Interestingly, complex **8** is the only one of these compounds to exist as the exo, syn isomer in the solid state.[18]

The carbonylation reactions of these tungsten alkyl allyl complexes have not yet been optimized. Careful adjustment of solvents, pressures, and reaction times may well lead to significant improvements in the yields of these transformations. Nevertheless, since the tungsten−alkyl bonds result from the activation of the terminal C−H bonds of hydrocarbons, the synthesis of the desired tungsten acyl complexes in this manner represents a significant step toward the selective functionalization of alkanes mediated by these tungsten compounds.

Epilogue. In summary, the characteristic reactivity of a number of tungsten alkyl allyl complexes with a variety of electrophilic and nucleophilic reagents has been investigated. The allyl ligand is the preferred site of reactivity when electrophiles are employed, leading to the liberation of olefinic species. Isocyanides preferentially insert into the W−allyl linkages and form initially complexes containing β,γ-unsaturated η^2-imine ligands. Isomerization to the conjugated α,β-unsaturated η^2-imine complexes occurs spontaneously in solution. In contrast, CO gas under pressure inserts preferentially into the tungsten−alkyl bonds and affords the desired metalloacyl species. Future investigations will focus on optimizing the yields of the carbonylation products by modification of the reaction conditions. Additionally, the development of methods to release the newly formed acyl ligands from the metal centers while keeping the Cp*W(NO)(η^3-allyl) fragments intact is also a high priority for further studies. We shall report our results in these regards in due course.

(17) Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 986.

(18) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388. (b) Bi, S.; Ariafard, A.; Jia, G.; Lin, Z. *Organometallics* **2005**, *24*, 680.

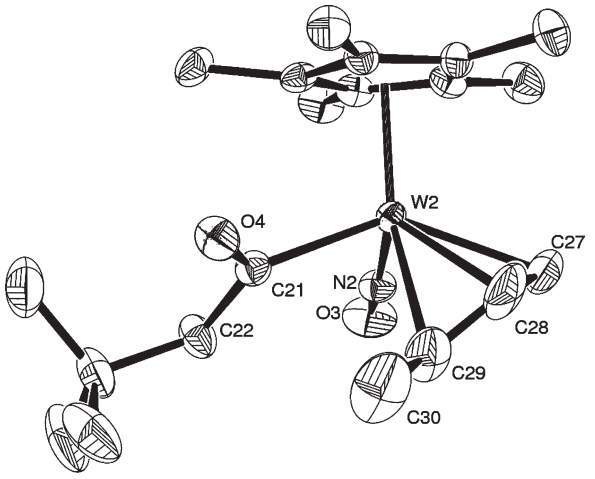


Figure 4. Solid-state molecular structure of **8** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(2)−C(21) = 2.203(3), W(2)−C(29) = 2.459(4), W(2)−C(28) = 2.272(4), W(2)−C(27) = 2.272(4), C(21)−O(4) = 1.221(4), W(2)−N(2)−O(3) = 169.1(3).

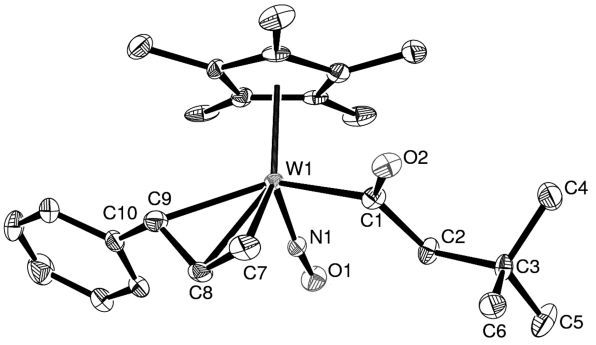


Figure 5. Solid-state molecular structure of **9** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.240(5), W(1)−C(7) = 2.377(6), W(1)−C(8) = 2.345(5), W(1)−C(9) = 2.342(6), C(7)−C(8) = 1.409(8), C(8)−C(9) = 1.429(8), C(1)−O(2) = 1.222(6).

Experimental Section

General Methods. All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions under either high vacuum or an inert atmosphere of prepurified dinitrogen. Purification of inert gases was achieved by passing them first through a column containing MnO and then a column of activated 4 Å molecular sieves. Conventional glovebox and Schlenk techniques were utilized throughout. The gloveboxes utilized were

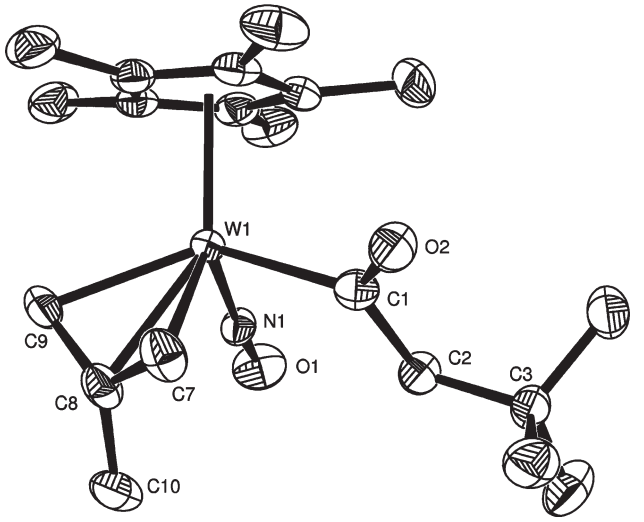


Figure 6. Solid-state molecular structure of **10** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.220(5), W(1)−C(7) = 2.333(4), W(1)−C(8) = 2.349(4), W(1)−C(9) = 2.262(4), C(1)−O(2) = 1.214(5), C(7)−C(8)−C(9) = 116.7(4).

Innovative Technologies LabMaster 100 and MS-130 BG dual-station models equipped with freezers maintained at −30 °C. All glassware was heated in an oven to 275 °C to remove any moisture and then cooled to room temperature under vacuum. Small-scale reactions and NMR spectroscopic analyses were conducted in J. Young NMR tubes equipped with Kontes greaseless stopcocks. Pentane, diethyl ether (Et_2O), benzene, benzene-d_6, and tetrahydrofuran (THF) were dried over sodium/benzophenone ketyl and freshly distilled prior to use. Acetonitrile (MeCN), acetonitrile-d_3, and chloroform-*d* ($CDCl_3$) were dried over CaH_2 and distilled prior to use. Pyridinium chloride was prepared by addition of a 1.0 M solution of hydrochloric acid (HCl) in Et_2O to a solution of pyridine in Et_2O. The powdery white solid that precipitated from Et_2O was collected on a medium-porosity frit, then washed with pentane, and finally dried in vacuo. Commercially available ($CH_2CHCHMe$)MgCl (Aldrich, 0.5 M in THF), ($PhCH_2$)MgCl (Aldrich, 1.0 M in Et_2O), and (Me_3SiCH_2)MgCl (Aldrich, 1.0 M in Et_2O) were transformed into the corresponding diallyl and dialkyl magnesium agents according to literature procedures.[19,20] Cp*W(NO)Cl_2,[21] Cp*W(NO)(CH_2SiMe_3)Cl,[22] and Cp*W(NO)($CH_2C_6H_5$)Cl[23] were prepared according to the published procedures. All other chemicals were ordered from commercial suppliers and used as received.

All IR samples were prepared as Nujol mulls sandwiched between NaCl plates, and their spectra were recorded on a Thermo Nicolet model 4700 FT-IR spectrometer. NMR spectra were recorded at room temperature on Bruker AV-300 or AV-400 instruments, and all chemical shifts and coupling constants are reported in ppm and in Hz, respectively. ^{1}H NMR spectra were referenced to the residual protio isotopomer present in C_6D_6 (7.15 ppm), CD_3CN (1.94 ppm), or $CDCl_3$ (7.24 ppm). ^{13}C NMR spectra were referenced to C_6D_6 (128.4 ppm). When necessary, ^{1}H−^{1}H COSY and ^{13}C APT experiments were carried out to correlate and assign ^{1}H and ^{13}C NMR signals. Low-resolution mass spectra (EI, 70 eV) were recorded by the staff of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Elemental analyses were performed by Mr. David Wong of the UBC microanalytical facility.

Synthesis of Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (1). Complex **1** was first prepared by the C−H activation of $SiMe_4$.[7] However, on a preparative scale it is best synthesized in the following manner: Cp*W(NO)(CH_2SiMe_3)Cl (2.420 g, 5.138 mmol) was dissolved in Et_2O (25 mL) in a Schlenk flask to obtain an ink blue solution. Mg($CH_2CHCHMe$)$_2\cdot x$(dioxane) (titer = 112 g/mol R, 0.575 g, 5.139 mmol) was dissolved in Et_2O (30 mL) in a separate Schlenk flask to obtain a colorless solution. The latter solution was then frozen at −196 °C under a flow of dinitrogen, and the dark blue solution was cannulated onto it dropwise over a period of 20 min. The mixture was allowed to warm to room temperature over the course of 1 h while being stirred, whereupon it became dark brown. The volatile components were removed from the final reaction mixture in vacuo. The remaining brown residue was dissolved in pentane, and the solution was transferred to the top of an alumina I column (3 × 6 cm). Elution of the column with pentane developed a yellow band, which was eluted. The solvent was removed from the eluate in vacuo to obtain **1** as a bright yellow powder (1.73 g, 71% yield).

Anal. Calcd for $C_{18}H_{33}NOSiW$: C, 44.00; H, 6.77; N, 2.85. Found: C, 44.04; H, 6.90; N, 2.85. IR: ν_{NO} 1593 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6), two isomers are present in an approximately 3:1 ratio: δ (major isomer) −0.62 (d, $^2J_{HH}$ = 13.2, 1H, CH_2SiMe$_3$), −0.09 (d, $^2J_{HH}$ = 13.2, 1H, CH_2SiMe$_3$), 0.37 (s, 9H, CH$_2$SiMe_3), 1.01 (m, 1H, allyl C*H*Me), 1.48 (s, 15H, C$_5Me_5$), 1.58 (d, $^3J_{HH}$ = 13.8, 1H, allyl CH_2), 1.88 (d, $^3J_{HH}$ = 5.8, 3H, allyl CH_3), 3.36 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 5.10 (ddd, $^3J_{HH}$ = 13.8, 9.4, 7.0, 1H, allyl C*H*), δ (minor isomer) selected signals −0.76 (d, $^2J_{HH}$ = 13.2, 1H, CH_2SiMe$_3$), −0.48 (d, $^2J_{HH}$ = 13.2, 1H, CH_2SiMe$_3$), 0.40 (s, 9H, CH$_2$SiMe_3), 1.34 (d, $^3J_{HH}$ = 5.8, 3H, allyl CH_3), 1.49 (s, 15H, C$_5Me_5$), 2.12 (m, 1H, allyl CH_2), 2.24 (m, 1H, allyl C*H*), 4.61 (m, 1H, allyl C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ −6.2 (*C*H$_2$SiMe$_3$), 4.1 (CH$_2$Si*Me*$_3$), 10.3 (C$_5$*Me*$_5$), 17.1 (allyl *C*H$_3$), 53.3 (allyl *C*HMe), 74.5 (allyl *C*H$_2$), 106.5 (*C*$_5$Me$_5$), 114.2 (allyl *C*H). MS (LREI, *m*/*z*, probe temperature 100 °C): 491 [P$^+$, ^{184}W].

Synthesis of Cp*W(NO)($CH_2C_6H_5$)(η^3-$CH_2CHCHMe$) (2). Complex **2** was initially prepared by the C−H activation of toluene.[7] Large-scale synthesis was effected by metathesis as follows: Cp*W(NO)($CH_2C_6H_5$)Cl (0.505 g, 1.062 mmol) and Mg($CH_2CHCHMe$)$_2\cdot x$(dioxane) (titer = 112 g/mol R, 0.118 g, 1.054 mmol) were reacted in the manner described in the preceding section for **1**. A yellow-green band was collected by elution from alumina with a 1:1 pentane/Et_2O mixture. The solvent was removed in vacuo to obtain **2** as a light orange powder (0.22 g, 43% yield).

Anal. Calcd for $C_{21}H_{30}NOW$: C, 50.82; H, 6.09; N, 2.82. Found: C, 50.97; H, 5.97; N, 2.82. IR: ν_{NO} 1603 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 1.25 (m, 1H, allyl C*H*Me buried), 1.47 (s, 15H, C$_5Me_5$), 1.52 (d, $^3J_{HH}$ = 13.6, 1H, allyl CH_2) 1.76 (d, $^3J_{HH}$ = 5.9, 3H, allyl CH_3), 1.95 (d, $^2J_{HH}$ = 9.1, 1H, benzyl CH_2), 2.82 (d, $^2J_{HH}$ = 9.1, 1H, benzyl CH_2), 3.43 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 4.43 (ddd, $^3J_{HH}$ = 13.6, 9.3, 7.0, 1H, allyl C*H*), 7.00 (d, $^3J_{HH}$ = 7.4, 1H, para C*H*), 7.29 (t, $^3J_{HH}$ = 7.4, 2H, meta C*H*), 7.51 (d, 2H, $^3J_{HH}$ = 7.4, ortho C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 9.8 (C$_5Me_5$), 17.5 (allyl *C*H$_3$), 21.1 (benzyl *C*H$_2$), 56.5 (allyl *C*HMe), 77.0 (allyl *C*H$_2$), 110.4 (allyl *C*H), 123.5 (Ar *C*), 128.1 (Ar *C*), 129.1 (Ar *C*). MS (LREI, *m*/*z*, probe temperature 100 °C): 495 [P$^+$, ^{184}W].

Reaction of 2 with I_2. Complex **2** (24.0 mg, 0.051 mmol) was dissolved in $CDCl_3$ (1.5 mL) in a resealable glass vessel equipped

(19) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094.

(20) There were instances when the isolation of the bis(allyl)magnesium reagent was unsuccessful, such as when removal of solvent left behind an intractable oily material. In such cases the oily residue was redissolved in Et_2O, and the solution was used as such after the concentration of the allylating reagent had been established by an HCl titration. The Et_2O solution was stored in a resealable glass bomb.

(21) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077.

(22) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1992**, *11*, 6.

(23) Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857.

with a Kontes greaseless stopcock and containing a small stir bar. HMDS (10 μL) was added via a microsyringe as an NMR integration standard. The ^{1}H NMR spectrum of a sample of the mixture was recorded, and the area under the doublet at 3.40 ppm (1H, allyl CH_2CHCHCH$_3$) was integrated against the singlet at 0.10 ppm (18H, HMDS). The NMR sample was recombined with the rest of the solution, and the resealable vessel was attached to a vacuum line and was maintained at −60 °C with a dry ice/acetone bath. A solution of I_2 (25.0 mg, 2 equiv) in $CDCl_3$ (5 mL) was then introduced dropwise via a cannula into the chilled resealable vessel. The cold bath was removed after the addition of I_2 was complete, and the reaction mixture was stirred for 1 h as it warmed to room temperature. Overall, the reaction mixture changed color from yellow to red-orange. A small amount of the final reaction mixture was transferred to an NMR tube, and the sample was analyzed by ^{1}H NMR spectroscopy. Integration of the area under the singlet at 4.47 ppm (2H, (C$_6$H$_5$)CH_2I) against the HMDS signal revealed that (iodomethyl)benzene had been formed in approximately 45% yield.

Reaction of 1 with I_2. Complex **1** (40 mg, 0.081 mmol) was dissolved in $CDCl_3$ (1.5 mL) in a resealable glass vessel equipped with a Kontes greaseless stopcock and containing a small stir bar. C_6H_6 (10 μL) was added via a microsyringe as an NMR integration standard. The reaction with I_2 was performed as described in the preceding paragraph. The final mixture was analyzed by ^{1}H NMR spectroscopy, and integration of the area under the singlet at 0.17 ppm (9H, Me$_3$SiCH$_2$I) against the C_6H_6 signal revealed that (iodomethyl)trimethylsilane had been formed in approximately 57% yield. The solvent was removed in vacuo, and the yellow-green oil was triturated with pentane (2 × 5 mL) to obtain a yellow-green solution. The solution was transferred to the top of a Celite column (5 cm × 0.5 cm). Elution of the column with pentane produced a green band, which was collected. The solvent was removed from the eluate in vacuo, and the green residue was analyzed by EI-MS. The presence of Cp*W(NO)I$_2$ was confirmed by a signal at m/z = 603 [P$^+$].[24]

Reaction of 1 with H_2O_2. A sample of **1** (16 mg, 0.033 mmol) was dissolved in ethanol (5 mL) in a resealable glass vessel equipped with a greaseless stopcock and a magnetic stirbar to obtain a yellow solution. H_2O_2 (1.5 mL, 30% solution in H_2O, 13.2 mmol) was added via pipet. The vessel was sealed, and the mixture was stirred for 72 h at room temperature, whereupon a gradual color change from yellow to colorless occurred. The final reaction mixture was taken to dryness *in vacuo*, and the white residue was subjected to ^{1}H NMR spectroscopic analysis. Diagnostic ^{1}H NMR signals reveal the principal product to be the previously reported Cp*W(O)(η^2-O$_2$)(CH$_2$SiMe$_3$).[8]

^{1}H NMR (400 MHz, C_6D_6): δ 0.45 (s, 9H, CH$_2$SiMe_3), 0.52 (d, 1H, $^2J_{HH}$ = 12.5, CH_2SiMe$_3$) 0.93 (d, 1H, $^2J_{HH}$ = 12.5, CH_2SiMe$_3$), 1.58 (s, 15H, C$_5Me_5$).

Reaction of 1 with HCl. A sample of **1** (30 mg, 0.061 mmol) was dissolved in MeCN-d_3 (1 mL) in a J. Young NMR tube equipped with a Kontes greaseless stopcock to obtain a yellow solution. To this solution was added a solution of HCl in Et$_2$O (0.1 mL, 2.0 M, 0.2 mmol), whereupon an immediate color change from light yellow to dark blue occurred. A ^{1}H NMR spectrum of the crude reaction mixture confirmed the formation of previously characterized Cp*W(NO)(CH$_2$SiMe$_3$)Cl.[22]

^{1}H NMR (400 MHz, CD_3CN): δ 0.08 (s, 9H, CH$_2$SiMe_3), 1.91 (s, 15H, C$_5Me_5$), 2.06 (m, 2H, CH_2SiMe$_3$).

Reaction of 1 with Pyridinium Chloride. A sample of **1** (30 mg, 0.061 mmol) was dissolved in MeCN-d_3 (1 mL) in a J. Young NMR tube equipped with a Kontes greaseless stopcock to obtain a yellow solution. A solution of pyridinium chloride (14 mg, 0.12 mmol) in MeCN-d_3 (0.5 mL) was added all at once, and the NMR tube was sealed. A gradual color change from yellow to dark blue occurred over the course of 30 min. ^{1}H NMR spectroscopic analysis of the reaction mixture again confirmed the formation of Cp*W(NO)(CH$_2$SiMe$_3$)Cl (vide supra).[22]

Reaction of 1 with *B*-Chlorocatecholborane. In the manner described above, complex **1** (10 mg, 0.020 mmol) and *B*-chlorocatecholborane (4 mg, 0.026 mmol) were dissolved in MeCN-d_3 (1 mL) and combined. A color change from yellow to green-blue occurred over the course of 1 h. NMR spectroscopic analyses of the reaction mixture confirmed the formation of Cp*W(NO)(CH$_2$SiMe$_3$)Cl[22] and an olefinic species, the borane-functionalized alkene (cf. eq 3).

^{1}H NMR (400 MHz, CD_3CN): δ 0.43 (s, 9H, CH$_2$SiMe_3), 1.30 (d, 3H, $^3J_{HH}$ = 7.3, *Me*CHB), 1.90 (s, 15H, C$_5Me_5$), 2.06 (br s, 2H, CH_2SiMe$_3$), 2.42 (dt, 1H, $^3J_{HH}$ = 14.5, 7.5, C*H*B) 5.07 (ddt, 2H, $^3J_{HH}$ = 17.3, 10.2, 1.6, CHCH_2), 6.10 (ddd, 1H, $^3J_{HH}$ = 17.3, 10.2, 7.31, C*H*CH$_2$), 6.96 (dd, 1H, $^3J_{HH}$ = 5.7, 3.4, aryl CH), 7.07 (dd, 1H, $^3J_{HH}$ = 5.7, 3.4, aryl CH), 7.11 (dd, 1H, $^3J_{HH}$ = 5.9, 3.2, aryl CH), 7.25 (m, 1H, aryl CH). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN): selected signals δ 3.6 (CH$_2$SiMe_3), 10.4 (C$_5Me_5$), 15.0 (*Me*CH), 112.5 (*C*$_5$Me$_5$), 112.7 (aryl C), 113.6 (aryl C), 115.7 (olefin C), 122.9 (aryl C), 124.0 (olefin C), 124.1 (aryl C), 150.2 (aryl C).

Reaction of 1 with Ph_3CBF_4. A sample of **1** (22 mg, 0.045 mmol) was dissolved in MeCN-d_3 (0.5 mL) in a J. Young NMR tube equipped with a Kontes greaseless stopcock to obtain a yellow solution. To this solution was added a dark orange solution of Ph_3CBF_4 (16 mg, 0.049 mmol) in MeCN-d_3 (0.5 mL). The mixture was stored for 18 h at ambient temperatures before being subjected to a ^{1}H NMR spectroscopic analysis.

^{1}H NMR (400 MHz, C_6D_6): δ −1.15 (d, 1H, $^2J_{HH}$ = 11.4, CH_2SiMe$_3$) 0.01 (d, 1H, $^2J_{HH}$ = 11.4, CH_2SiMe$_3$), 0.36 (s, 9H, CH$_2$SiMe_3) 1.37 (d, 3H, $^3J_{HH}$ = 6.3, *Me*CHCH), 1.63 (s, 15H, C$_5Me_5$), 3.32 (d, 2H, $^3J_{HH}$ = 6.7, CH_2CPh$_3$), 5.37 (m, 1H, MeC*H* or CHC*H*CH$_2$), 5.40 (m, 1H, MeC*H* or CHC*H*CH$_2$), 7.02 (d, 3H, $^3J_{HH}$ = 7.4, para aryl C*H*), 7.09 (t, 6H, $^3J_{HH}$ = 7.6, meta aryl C*H*), 7.26 (d, 6H, $^3J_{HH}$ = 8.2, ortho aryl C*H*).

Removal of the volatile components from the final reaction mixture in vacuo afforded an orange oil. Crystals of CH$_3$CHCHCH$_2$CPh$_3$ (**3**) suitable for X-ray crystallographic analysis were grown by storing a concentrated MeCN solution of the oil at −30 °C overnight.

Reaction of 2 with Ph_3CBF_4. A sample of **2** (7 mg, 0.014 mmol) was dissolved in MeCN (1 mL) to obtain an orange solution. To this was added a solution of Ph_3CBF_4 (7 mg, 0.021 mmol) in MeCN (1 mL). The mixture was left undisturbed for 18 h before the volatile components were removed in vacuo. The orange residue was subjected to ^{1}H NMR spectroscopic analysis, which confirmed the formation of **3** (vide supra).

^{1}H NMR (400 MHz, C_6D_6): δ 1.38 (d obscured, 3H, *Me*CHCH), 1.63 (s, 15H, C$_5Me_5$), 1.70 (d, 1H, $^2J_{HH}$ = 5.3, benzyl CH_2), 2.90 (d, 1H, $^2J_{HH}$ = 5.3, benzyl CH_2), 3.32 (d, 2H, $^3J_{HH}$ = 6.3, CH_2CPh$_3$), 5.30 (m, 1H, MeC*H* or CHC*H*CH$_2$), 5.41 (m, 1H, MeC*H* or CHC*H*CH$_2$), 7.01 (m overlapping, 3H, aryl C*H*), 7.07 (m overlapping, 6H, aryl C*H*), 7.28 (m overlapping, 6H, aryl C*H*).

Preparation of Cp*W(NO)(CH$_2$SiMe$_3$)(η^2-CH$_3$CHCHCH$_2$-C=NC$_6$H$_3$Me$_2$) (4a). A sample of **1** (21.0 mg, 0.043 mmol) was dissolved in Et$_2$O (1 mL) in a 4-dram vial to obtain a yellow solution. To this was added a solution of CNC$_6$H$_3$Me$_2$ (5.0 mg, 0.038 mmol) in Et$_2$O (1 mL), and the mixture was left to stand for 2 h. The solvent was then removed from the solution in vacuo, and the residue was redissolved in a minimum amount of Et$_2$O. The Et$_2$O solution was stored overnight at −30 °C to induce deposition of **4a** as yellow microcrystals (17.0 mg, 80% yield).

Anal. Calcd for C$_{27}$H$_{42}$N$_2$OSiW: C, 52.09; H, 6.80; N, 4.50. Found: C, 52.24; H, 6.85; N, 4.43. IR: ν_{NO} 1553 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ −0.44 (d, $^2J_{HH}$ = 13.3, 1H, CH_2SiMe$_3$), 0.12 (d obscured, 1H, CH_2SiMe$_3$), 0.30 (s, 9H, CH$_2$SiMe_3), 1.40 (d, $^3J_{HH}$ = 6.3, 3H, CH*Me*), 1.64 (s, 3H, aryl *Me*), 1.77 (s, 15H, C$_5Me_5$), 2.04 (s, 3H, aryl *Me*), 2.95 (dd, $^2J_{HH}$ = 17.2, 5.5, 1H, CCH_2CH), 3.54

(24) Dryden, N. H.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Can. J. Chem.* **1988**, *66*, 2100.

(dd, $^2J_{HH}$ = 18.4, 5.9, 1H, CCH_2CH), 5.26 (m, 1H, C*H*Me), 5.39 (m, 1H, C*H*CH$_2$), 6.88 (m overlapping, 3H, aryl C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 2.5 (*C*H$_2$SiMe$_3$), 3.8 (CH$_2$Si*Me$_3$*), 10.6 (*C$_5$Me$_5$*), 18.9 (CH*C*H$_3$), 19.4 (aryl *C*H$_3$), 37.4 (*C*H$_2$CH), 108.3 (*C$_5$*Me$_5$), 123.0 (CH$_2$*C*H), 126.8 (Ar *C*), 129.6 (Ar *C*), 130.6 (Ar *C*), 131.0 (Ar *C*), 138.4 (Ar *C*), 156.6 (CH*C*H), 214.8 (*C*NCH). MS (LREI, *m*/*z*, probe temperature 100 °C): 622 [P$^+$, ^{184}W].

Preparation of Cp*W(NO)(CH$_2$SiMe$_3$)(η^2-CH$_3$CH$_2$CHCH-C=NC$_6$H$_3$Me$_2$) (4b). A sample of **1** (24.0 mg, 0.049 mmol) was dissolved in MeCN (0.5 mL) in a 4-dram vial to obtain a yellow solution. To this was added dropwise a solution of CNC$_6$H$_3$Me$_2$ (6.0 mg, 0.046 mmol) in MeCN (0.25 mL), and the mixture was placed in the freezer for 1 h. The mixture was then transferred to the top of an alumina I column (0.5 × 5 cm), the column was eluted with 4:1 pentane/Et$_2$O, and the dark orange band that developed was collected. The solvent was removed from the eluate in vacuo, and the residue was redissolved in a minimum amount of Et$_2$O. The Et$_2$O solution was stored overnight at −30 °C to induce the deposition of **4b** as irregularly shaped red crystals (19.0 mg, 79% yield).

Anal. Calcd for C$_{27}$H$_{42}$N$_2$OSiW: C, 52.09; H, 6.80; N, 4.50. Found: C, 52.16; H, 6.78; N, 4.48. IR: ν_{NO} 1554 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ −0.30 (d, $^2J_{HH}$ = 13.5, 1H, C*H*$_2$SiMe$_3$), 0.21 (d, $^2J_{HH}$ = 13.5, 1H, C*H*$_2$SiMe$_3$), 0.35 (s, 9H, CH$_2$Si*Me$_3$*), 0.73 (t, $^3J_{HH}$ = 14.9, 3H, CH$_2$C*H$_3$*), 1.79 (m, 2H, C*H*$_2$CH$_3$), 1.81 (s, 15H, C$_5$*Me$_5$*), 2.05 (s, 6H, aryl C*H$_3$*), 6.30 (d, $^3J_{HH}$ = 15.5, 1H, NCC*H*), 6.84 (m, $^3J_{HH}$ = 15.3, 6.9, 6.5, 1H, CHC*H*), 6.9−6.95 (m, 3H, aryl *H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 2.9 (*C*H$_2$SiMe$_3$), 3.8 (CH$_2$Si*Me$_3$*), 10.8 (C$_5$*Me$_5$*), 12.8 (CH$_2$*C*H$_3$), 19.2 (aryl *C*H$_3$), 27.1 (*C*H$_2$CH$_3$), 108.5 (*C$_5$*Me$_5$), 122.3 (C*C*H), 127.1 (Ar *C*), 130.0 (Ar *C*), 131.4 (Ar *C*), 132.3 (Ar *C*), 138.4 (Ar *C*), 156.6 (CH*C*H), 214.8 (*C*NCH). MS (LREI, *m*/*z*, probe temperature 100 °C): 622 [P$^+$, ^{184}W].

Preparation of Cp*W(NO)(CH$_2$C$_6$H$_5$)(η^2-CH$_3$CHCHCH$_2$-C=NC$_6$H$_3$Me$_2$) (5a). A sample of **2** (19.0 mg, 0.039 mmol) was dissolved in THF (2 mL) in a 4-dram vial to obtain an orange solution. To this solution was added dropwise a solution of CNC$_6$H$_3$Me$_2$ (16.0 mg, 0.124 mmol) in THF (1 mL), and the mixture was left to sit for 20 h. The solvent was removed from the red-orange solution in vacuo, and the residue was recrystallized from Et$_2$O at −30 °C to obtain **5a** as irregularly shaped, orange-brown crystals (15.0 mg, 79% yield).

IR: ν_{NO} 1560 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 1.71 (s, 3H, aryl *Me*), 1.77 (s, 3H, aryl *Me*), 1.86 (d, $^3J_{HH}$ = 9.0, 3H, *Me*CH) 2.05 (s, 15H, C$_5$*Me$_5$*), 2.41 (d, $^2J_{HH}$ = 10.6, 1H, benzyl C*H*$_2$), 2.69 (d, $^2J_{HH}$ = 10.6, 1H, benzyl C*H*$_2$), 2.78 (dd, $^2J_{HH}$ = 17.8, 6.5, 1H, NCC*H*$_2$), 3.33 (dd, $^2J_{HH}$ = 18.0, 6.3, 1H, NCC*H*$_2$), 5.23 (m, 1H, MeC*H*), 5.38 (m, 1H, MeCHC*H*), 6.95−7.35 (m, 8H, aryl C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.8 (C$_5$*Me$_5$*), 18.4 (*Me*), 18.6 (*Me*), 19.2 (*Me*), 36.0 (*C*H$_2$C$_6$H$_5$), 110.0 (*C$_5$*Me$_5$), 122.3 (CH$_2$*C*H), 126.4 (Ar *C*), 127.4 (Ar *C*), 127.8 (Ar *C*), 128.7 (Ar *C*), 130.0 (Ar *C*), 130.6 (Ar *C*), 136.2 (*C*HMe), 153.0 (Ar (i) *C*), 221.4 (N*C*). MS (LREI, *m*/*z*, probe temperature 100 °C): 626 [P$^+$, ^{184}W]. MS (HREI, *m*/*z*, probe temperature 120 °C): P$^+$ calcd for C$_{30}$H$_{38}$N$_2$OW 626.24937, found 626.24936.

Preparation of Cp*W(NO)(CH$_2$C$_6$H$_5$)(η^2-CH$_3$CH$_2$CHCH-C=NC$_6$H$_3$Me$_2$) (5b). A sample of **2** (25.0 mg, 0.051 mmol) was dissolved in Et$_2$O (5 mL) in a 4-dram vial to obtain an orange solution. To this solution was added dropwise a solution of CNC$_6$H$_3$Me$_2$ (8.0 mg, 0.062 mmol) in Et$_2$O (1 mL). After 20 h, the final red solution was transferred to the top of an alumina I column (0.5 × 5 cm). The column was eluted with Et$_2$O, and the red band that developed was collected. The solvent was removed from the eluate in vacuo, and the residue was recrystallized from Et$_2$O at −30 °C to obtain **5b** as plate-like red crystals (18.0 mg, 72% yield).

IR: ν_{NO} 1560 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.87 (t, $^3J_{HH}$ = 7.4, 3H, *Me*CH$_2$CH), 1.57 (s, 3H, aryl *Me*), 1.92 (m overlapping, 2H, MeC*H*$_2$CH), 1.99 (s, 15H, C$_5$*Me$_5$*), 2.09 (s, 3H, aryl *Me*), 2.75 (d, $^2J_{HH}$ = 10.2, 1H, benzyl C*H*$_2$), 2.98 (d, $^2J_{HH}$ = 10.2, 1H, benzyl C*H*$_2$), 6.45 (d, $^3J_{HH}$ = 15.3, 1H, NCC*H*), 6.88 (m, 1H, CH$_2$C*H*CH), 7.00−7.41 (m, 8H, aryl C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.6 (C$_5$*Me$_5$*), 12.8 (CH$_2$*Me*), 18.4 (Ar*Me*), 19.6 (Ar*Me*), 27.0 (MeCH2), 34.8 (*C*H$_2$C$_6$H$_5$), 108.4 (*C$_5$*Me$_5$), 122.2 (*C*HCHCN), 126.6 (Ar *C*), 127.4 (Ar *C*), 129.7 (Ar *C*), 131.4 (Ar *C*), 132.9 (Ar *C*), 152.9 (Ar *C*), 157.9 (*C*HCN), 214.7 (N*C*). MS (LREI, *m*/*z*, probe temperature 100 °C): 626 [P$^+$, ^{184}W]. MS (HREI, *m*/*z*, probe temperature 120 °C): P$^+$ calcd for C$_{30}$H$_{38}$N$_2$OW: 626.24937, found 626.24936.

Preparation of Cp*W(NO)(CH$_2$C$_6$H$_5$)(η^2-CH$_3$CH$_2$CHCH-C=NC$_4$H$_9$) (6b). A sample of **2** (19.0 mg, 0.038 mmol) was dissolved in Et$_2$O (1 mL) and THF (5 mL) in a 4-dram vial to obtain an orange solution. To this solution was added a solution of C$_4$H$_9$NC (11.0 mg, 0.133 mmol) in Et$_2$O (1 mL). After 20 h, the final orange solution was transferred to the top of an alumina I column (0.5 × 6 cm). The column was eluted with Et$_2$O, and the yellow band that developed was collected. The solvent was removed from the eluate in vacuo, to obtain **6b** as a viscous red oil (14.0 mg, 74% yield).

IR: ν_{NO} 1548 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 0.79 (m overlapping, 6H, butyl C*H*$_3$ and CHCH$_2$C*H*$_3$), 1.07 (m, 2H, butyl C*H*$_2$), 1.29 (m, 2H, butyl C*H*$_2$), 1.72 (s, 15H, C$_5$*Me$_5$*), 1.88 (t, $^3J_{HH}$ = 7.0, 2H, CHC*H*$_2$CH$_3$), 2.71 (d, $^2J_{HH}$ = 10.6, 1H, benzyl C*H*$_2$), 2.94 (d, $^2J_{HH}$ = 10.6, benzyl C*H*$_2$), 2.96 (m overlapping, 2H, NC*H*$_2$CH$_2$), 6.36 (d, $^3J_{HH}$ = 14.9, 1H, NCC*H*), 6.82 (dt, $^3J_{HH}$ = 15.2, 6.5, 1H, CH$_2$C*H*CH), 6.95 (t, $^3J_{HH}$ = 7.2, 1H, para aryl CH), 7.25 (t, $^3J_{HH}$ = 7.4, 2H, meta aryl CH), 7.83 (d, $^3J_{HH}$ = 7.4, 2H, ortho aryl CH). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.4 (C$_5$*Me$_5$*), 12.7 (*Me*CH$_2$CH), 14.3 (*Me*CH$_2$), 21.1 (MeCH$_2$CH$_2$), 27.1 (MeCH$_2$CH), 32.3 (*C*H$_2$CH$_2$), 32.8 (*C*H$_2$C$_6$H$_5$), 44.2 (NCH$_2$), 108.1 (*C$_5$*Me$_5$), 123.0 (*C*HCHCN), 128.3 (Ar *C*), 128.7 (Ar *C*), 129.8 (Ar *C*), 154.7 (Ar (i) *C*), 157.8 (*C*HCN), 208.1 (*C*N). MS (LREI, *m*/*z*, probe temperature 100 °C): 578 [P$^+$, ^{184}W]. MS (HREI, *m*/*z*, probe temperature 100 °C): P$^+$ calcd for C$_{26}$H$_{38}$N$_2$OW 578.24910, found 578.24937.

Preparation of Cp*(W)(NO)(C(O)Me)(η^3-CH$_2$CHCHMe) (7). A sample of **1** (97.0 mg, 0.198 mmol) was dissolved in C$_6$H$_6$ (6 mL) in a Schlenk tube. The yellow solution was cannulated into a stainless steel pressure vessel containing additional C$_6$H$_6$ (12 mL). The vessel was pressurized with 1000 psig of CO gas, and the solution was stirred for 72 h. The pressure was then released, and the solution was transferred by pipet to a Schlenk tube. The solvent was removed in vacuo, the yellow residue was dissolved in pentane, and this solution was transferred to the top of an alumina I column (2 × 5 cm). The column was eluted with 4:1 pentane/Et$_2$O, and the yellow band that developed was collected. The volume of the eluate was reduced in vacuo, and the concentrated solution was stored at −30 °C overnight to induce the deposition of **7** as yellow prisms (51 mg, 53% yield).

IR: ν_{NO} 1594 cm^{-1}, ν_{CO} 1615 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 1.28 (m obscured, 1H, allyl C*H*Me), 1.63 (s, 15H, C$_5$*Me$_5$*), 1.65 (d obscured, 2H, allyl C*H*$_2$), 1.91 (d, $^3J_{HH}$ = 5.5, 3H, CH*Me*), 2.50 (s, 3H, C(O)*Me*), 4.57 (ddd, $^3J_{HH}$ = 13.8, 9.9, 7.2, 1H, allyl C*H*). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.3 (C$_5$*Me$_5$*), 17.9 (allyl *Me*), 46.4 (C(O)*Me*), 61.1 (Me*C*HCH), 66.1 (*C*H$_2$CH), 108.7 (*C$_5$*Me$_5$), 111.1 (MeCH*C*H), 258.6 (*C*(O)Me). MS (LREI, *m*/*z*, probe temperature 100 °C); 447 [P$^+$, ^{184}W].

Preparation of Cp*(W)(NO)(C(O)CH$_2$CMe$_3$)(η^3-CH$_2$CHC-HMe) (8). In a glovebox, a sample of Cp*(W)(NO)(CH$_2$CMe$_3$)-(η^3-CH$_2$CHCHMe)[6] (65.0 mg, 0.137 mmol) was dissolved in pentane (6 mL) in a 4-dram vial. The orange solution was transferred to a stainless steel pressure vessel. The vessel was pressurized with 850 psig of CO gas, and the solution was stirred for 20 h. The pressure was then released, the solvent was removed in vacuo, and the vessel was brought into the glovebox. The yellow residue was dissolved in pentane and transferred to the top of a Celite column (2 × 3 cm). The column was eluted with pentane, and the orange band that developed was collected. The eluate was taken to dryness in vacuo, and the residue was redissolved into a minimal amount of pentane. Slow evaporation

Table 1. X-ray Crystallographic Data for Complexes 3, 4a, 4b, and 8−10

	3	4a	4b
Crystal Data			
empirical formula	$C_{23}H_{22}$	$C_{27}H_{42}N_2OSiW$	$C_{27}H_{42}N_2OSiW$
cryst habit, color	needle, yellow	irregular, yellow	prism, red-orange
cryst size (mm)	0.45 × 0.30 × 0.20	0.15 × 0.125 × 0.075	0.50 × 0.40 × 0.25
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
volume (Å^3)	1672.13(17)	1338.0(4)	2821.1(4)
a (Å)	16.0109(10)	9.8708(16)	9.7644(8)
b (Å)	14.4336(9)	11.1838(17)	16.7802(14)
c (Å)	7.2497(4)	12.928(2)	17.2285(15)
α (deg)	90	84.215(8)	90
β (deg)	93.563(2)	87.804(9)	91.998(4)
γ (deg)	90	70.445(8)	90
Z	4	2	4
density(calcd) (Mg/m^3)	1.185	1.545	1.466
absorp coeff (mm^{-1})	0.067	4.382	4.157
F_{000}	640	628	1256
Data Collection and Refinement			
measd reflns: total	9091	35 982	54 722
measd reflns: unique	3260	6344	8712
final R indices[a]	R1 = 0.0404, wR2 = 0.1061	R1 = 0.0421, wR2 = 0.1211	R1 = 0.0181, wR2 = 0.0419
goodness-of-fit on F^2[b]	1.017	1.055	1.045
largest diff peak and hole (e$^-$ Å^{-3})	0.223 and −0.189	1.962 and −2.460	0.950 and −0.920

	8	9	10
Crystal Data			
empirical formula	$C_{20}H_{33}NO_2W$	$C_{25}H_{35}NO_2W$	$C_{20}H_{33}NO_2W$
cryst habit, color	irregular, yellow	block, yellow	prism, yellow
cryst size (mm)	0.6 × 0.4 × 0.25	0.4 × 0.35 × 0.12	0.50 × 0.40 × 0.20
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$Pbca$
volume (Å^3)	4349.7(14)	2377.4(17)	4034.5(5)
a (Å)	18.610(3)	21.981(5)	9.2523(8)
b (Å)	8.8162(15)	11.708(5)	17.8946(13)
c (Å)	26.648(5)	9.402(5)	24.3680(17)
α (deg)	90	90	90
β (deg)	95.810(8)	100.724(5)	90
γ (deg)	90	90	90
Z	8	4	8
density(calcd) (Mg/m^3)	1.537	1.580	1.657
absorp coeff (mm^{-1})	5.322	4.878	5.738
F_{000}	2000	1128	2000
Data Collection and Refinement			
measd reflns: total	84 036	5534	25 939
measd reflns: unique	9994	5534	4847
final R indices[a]	R1 = 0.0297, wR2 = 0.0864	R1 = 0.0353, wR2 = 0.0942	R1 = 0.0264, wR2 = 0.0574
goodness-of-fit on F^2[b]	1.109	1.282	1.043
largest diff peak and hole (e Å^{-3})	2.500 and −0.829	1.957 and −2.552	2.143 and −0.810

[a] R1 on $F = \sum(|F_o| - |F_c|)|/\sum|F_o|$ ($I > 2\sigma(I)$); wR2 = $[(\sum(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$ (all data); $w = [\sigma^2 F_o^2]^{-1}$. [b] GOF = $[\sum(w(|F_o| - |F_c|)^2)/$degrees of freedom $]^{1/2}$.

of the pentane solution maintained at −30 °C overnight induced deposition of **8** as yellow hedgehog-like crystals (32 mg, 49%).

Anal. Calcd for $C_{20}H_{33}NO_2W$: C, 47.73; H, 6.61; N, 2.78. Found: C, 47.78; H, 6.59; N, 2.80. IR (cm^{-1}): 1598 (s, ν_{NO}), 1626 (s, ν_{CO}). MS (LREI, m/z, probe temperature 100 °C): 503 [P$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 1.21 (s, 9H, CH_2CMe_3), 1.5 (d, $^3J_{HH}$ = 5.85, 1H, allyl C*H*Me), 1.64 (s, 15H, C_5Me_5), 1.89 (d, $^3J_{HH}$ = 5.55, 3H, allyl CH*Me*), 2.57 (d, $^3J_{HH}$ = 12.6, 1H, allyl CH_2), 2.74 (d, $^2J_{HH}$ = 16.6, 1H, CH_2CMe_3), 2.89 (d, $^2J_{HH}$ = 16.6, 1H, CH_2CMe_3), 3.36 (d, $^3J_{HH}$ = 18.1, 1H, allyl CH_2), 4.65 (ddd, $^3J_{HH}$ = 13.5, 10.0, 7.16, 1H, allyl C*H*), δ (secondary isomer) selected signals 1.23 (s, 9H, CH_2CMe_3), 1.58 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 10.3 (C_5Me_5), 17.8 (allyl CH*Me*), 30.3 (CMe_3), 32.4 (CMe_3), 61.6 (allyl *C*HMe), 72.5 (CH_2CMe_3), 75.4 (allyl CH_2), 108.6 (C_5Me_5), 111.4 (allyl *C*H), 263.0 (*C*(O)), δ (secondary isomer) selected signals 10.2 (C_5Me_5), 30.5 (CMe_3), 107.2 (C_5Me_5).

Preparation of Cp*(W)(NO)(C(O)CH$_2$CMe$_3$)(η^3-CH$_2$CHCHPh) (9). In a glovebox, a sample of Cp*(W)(NO)(CH_2CMe_3)(η^3-$CH_2CHCHPh$)[6] (31.0 mg, 0.058 mmol) was dissolved in diethyl ether (3 mL) in a 4-dram vial. The yellow solution was transferred to a stainless steel pressure vessel. The vessel was pressurized with 850 psig of CO gas, and the solution was stirred for 20 h. The pressure was then released, the solvent was removed in vacuo, and the vessel was taken into the glovebox. The yellow residue was dissolved in diethyl ether and transferred to the top of a Celite column (2 × 5 cm). The column was eluted with diethyl ether, and the yellow band that developed was collected. The eluate was taken to dryness in vacuo, and the residue was redissolved in a minimal amount of diethyl ether. The ether solution was stored at −30 °C overnight to induce deposition of **9** as square yellow crystals (25 mg, 81%).

Anal. Calcd for $C_{25}H_{35}NO_2W$: C, 53.11; H, 6.24; N, 2.48. Found: C, 52.73; H, 6.19; N, 2.45. IR (cm^{-1}): 1591 (s, ν_{NO}), 1637 (s, ν_{CO}). MS (LREI, m/z, probe temperature 100 °C): 565 [P$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 1.22 (s, 9H, CH_2CMe_3), 1.54 (s, 15H, C_5Me_5), 1.60 (s, 2H, C(O)CH_2), 2.42 (d, 1H, $^3J_{HH}$ = 10.5, PhC*H*), 3.25 (m, 2H, allyl CH_2), 5.45 (ddd, 1H, $^3J_{HH}$ = 12.9, 10.9, 7.2, allyl C*H*CH_2), 7.03 (t, 1H, aryl C*H*), 7.23 (t, 2H, aryl C*H*), 7.30 (d, 2H, aryl CH). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 10.2 (C_5Me_5), 30.1 (CH_2CMe_3), 32.1 (CH_2CMe_3), 67.1 (allyl CH_2), 71.5 (allyl *C*HPh),

75.0 (C(O)*C*H_2), 108.8 (*C*$_5$Me$_5$), 109.8 (allyl *C*H), 126.4 (aryl C), 127.8 (aryl C), 129.0 (aryl C), 141.7 (ipso C), 261.6 (*C*(O)CH_2).

Preparation of Cp*(W)(NO)(C(O)CH_2CMe$_3$)(η^3-CH_2CMeCH_2) (10). This compound was prepared from Cp*(W)(NO)(CH_2CMe$_3$)(η^3-CH_2CMeCH_2)[6] and CO in a manner identical to that described in the preceding paragraph for **9**. The yellow eluate from the Celite column was taken to dryness in vacuo, and the residue was redissolved in a minimal amount of a 1:1 pentane/diethyl ether mixture. Slow evaporation of the solution stored at −30 °C overnight induced deposition of **10** as square yellow crystals (31 mg, 78%).

Anal. Calcd for $C_{20}H_{33}NO_2W$: C, 47.73; H, 6.61; N, 2.78. Found: C, 47.35; H, 6.48; N, 2.78. IR (cm^{-1}): 1596 (s, ν_{NO}), 1634 (s, ν_{CO}). MS (LREI, *m*/*z*, probe temperature 100 °C): 503 [P$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 0.97 (br s, 1H, allyl CH_2), 1.19 (s, 9H, $CH_2C\mathit{Me}_3$), 1.66 (s, 15H, $C_5\mathit{Me}_5$), 2.28 (s, 3H, allyl CH_3), 2.57 (s, 1H, allyl CH_2), 2.85 (d, 1H, CH_2CMe_3), 3.06 (d, 1H, CH_2CMe_3), 3.26 (br s, 2H, allyl CH_2). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.6 (*C*$_5\mathit{Me}_5$), 23.0 (allyl *Me*), 30.3 ($CH_2C\mathit{Me}_3$), 32.2 (CH_2CMe_3), 51.0 (allyl *C*H_2), 70.8 (allyl *C*H_2), 77.5 (C(O)*C*H_2), 108.6 (*C*$_5$Me$_5$), 128.2 (obscured, *C*Me), 264.3 (*C*(O)CH_2).

Preparation of Cp*(W)(NO)(C(O)CH_2CMe$_3$)(η^3-CH_2CHCH_2) (11). This complex was prepared from Cp*(W)(NO)(CH_2CMe$_3$)(η^3-CH_2CHCH_2)[6] and CO and was isolated in a manner identical to that described for **9** above. The final ether solution was stored at −30 °C overnight to induce deposition of **11** as square yellow crystals (42 mg, 86%).

Anal. Calcd for $C_{19}H_{31}NO_2W$: C, 46.64; H, 6.39; N, 2.86. Found: C, 46.46; H, 6.36; N, 2.90. IR (cm^{-1}): 1599 (s, ν_{NO}), 1631 (s, ν_{CO}). MS (LREI, *m*/*z*, probe temperature 100 °C): 489 [P$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 1.22 (s, 9H, $CH_2C\mathit{Me}_3$), 1.57 (s, 15H, $C_5\mathit{Me}_5$), 2.15 (br s, 2H, CH_2CMe_3), 2.65 (d, 1H, $^2J_{HH}$ = 13.3, allyl CH_2), 2.96 (d, 1H, $^2J_{HH}$ = 14.1, allyl CH_2), 3.09 (br s, 1H, allyl CH_2), 3.49 (d, $^3J_{HH}$ = 18, allyl CH_2), 4.91 (br s, 1H, allyl CH). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 10.2 (*C*$_5\mathit{Me}_5$), 23.1 ($CH_2C\mathit{Me}_3$), 30.2 ($CH_2C\mathit{Me}_3$), 32.1 (CH_2CMe_3), 50.9 (allyl CH_2), 77.9 (allyl CH_2), 101.4 (allyl CH), 107.3 (*C*$_5$Me$_5$), 268.0 (W*C*(O)).

Other Attempted Reactions of 1. Treatment of **1** with the following gaseous reagents at the noted pressures resulted in no reaction: dihydrogen (1 atm), dioxygen (1 atm), nitric oxide (1 atm), and carbon monoxide (1 and 6 atm).

X-ray Crystallography. Data collection for each compound was carried out at −100 ± 1 °C on a Bruker X8 APEX diffractometer, using graphite-monochromated Mo Kα radiation.

Data for **3** were collected to a maximum 2θ value of 54.8° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] Due to equipment failure, only a partial data set was collected (~80%). Nevertheless, the connectivity and *R* values are sufficiently good to merit the inclusion of this crystallographic analysis. All non-hydrogen atoms were refined anisotropically. Hydrogens H2 and H3 were refined isotropically, and all other hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 3260 observed reflections and 217 variable parameters.

Data for **4a** were collected to a maximum 2θ value of 56.4° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] The C1−C2−C3 fragment was disordered in two orientations, modeled as two parts (A and B) each with 50% occupancy. As a result of their proximity, C3a and C3b were refined isotropically, while all other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 6344 observed reflections and 318 variable parameters.

Data for **4b** were collected to a maximum 2θ value of 61.4° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] All non-hydrogen atoms were refined anisotropically. Hydrogens H3 and H4 were refined isotropically, and all other hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 8712 observed reflections and 308 variable parameters.

Data for **8** were collected to a maximum 2θ value of 55.2° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] The Me_3Si fragment of one molecule in the asymmetric unit was disordered and was modeled in two orientations (one with 80% occupancy and one with 20% occupancy). The carbons of the 20% fragment were refined isotropically. All other non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The SQUEEZE program[27] was used to remove one-half of a molecule of disordered diethyl ether solvent during structure solution. The final cycle of full-matrix least-squares analysis was based on 9994 observed reflections and 467 variable parameters.

Data for **9** were collected to a maximum 2θ value of 55.4° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] The crystal was a two-component twin that was separated into its components using Cell_Now,[28] SAINTPLUS,[29] and TWINABS.[30] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 5534 observed reflections and 270 variable parameters.

Data for **10** were collected to a maximum 2θ value of 56.0° in 0.5° oscillations. The structure was solved by direct methods[25] and expanded using Fourier techniques.[26] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 4847 observed reflections and 242 variable parameters.

For each structure neutral-atom scattering factors were taken from Cromer and Waber.[31] Anomalous dispersion effects were included in F_{calc};[32] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[33] The values for mass attenuation coefficients are those of Creagh and Hubbell.[34] All calculations were performed using Shelxl-97.[35] X-ray crystallographic data for the six structures are presented in Table 1 and in the cif files.

Acknowledgment. We are grateful to Dr. Chris Wallis for assistance with the high-pressure CO reactions, and we acknowledge NSERC Canada for funding.

Supporting Information Available: CIF files providing full details of crystallographic analyses of complexes **3**, **4a**, **4b**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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