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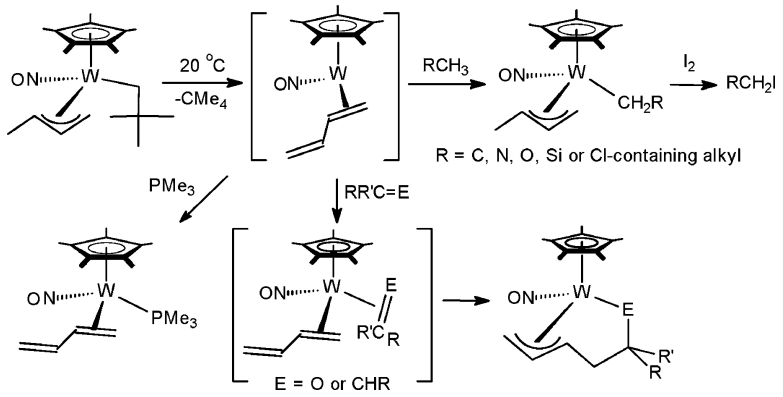

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Facile and Selective Aliphatic C−H Bond Activation at Ambient Temperatures Initiated by Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$)

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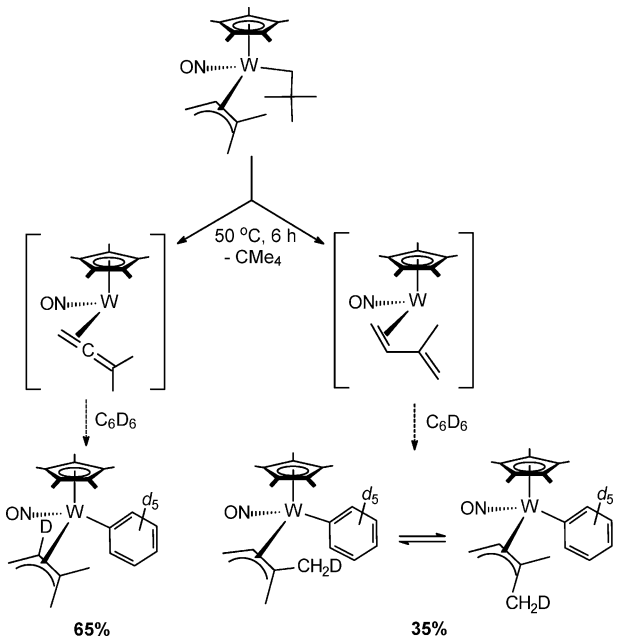
Abstract: Thermolysis of Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$) (**1**) at ambient temperatures leads to the loss of neopentane and the formation of the η^2-diene intermediate, Cp*W(NO)(η^2-CH_2=$CHCH$=CH_2) (**A**), which has been isolated as its 18e PMe_3 adduct. In the presence of linear alkanes, **A** effects C−H activations of the hydrocarbons exclusively at their terminal carbons and forms 18e Cp*W(NO)(*n*-alkyl)(η^3-$CH_2CHCHMe$) complexes. Similarly, treatments of **1** with methylcyclohexane, chloropentane, diethyl ether, and triethylamine all lead to the corresponding terminal C−H activation products. Furthermore, a judicious choice of solvents permits the C−H activation of gaseous hydrocarbons (i.e., propane, ethane, and methane) at ambient temperatures under moderately elevated pressures. However, reactions between intermediate **A** and cyclohexene, acetone, 3-pentanone, and 2-butyne lead to coupling between the η^2-diene ligand and the site of unsaturation on the organic molecule. For example, Cp*W(NO)(η^3,η^1-CH_2-$CHCHCH_2C(CH_2CH_3)_2O$) is formed exclusively in 3-pentanone. When the site of unsaturation is sufficiently sterically hindered, as in the case of 2,3-dimethyl-2-butene, C−H activation again becomes dominant, and so the C−H activation product, Cp*W(NO)(η^1-CH_2CMe=CMe_2)(η^3-$CH_2CHCHMe$), is formed exclusively from the alkene and **1**. All new complexes have been characterized by conventional spectroscopic and analytical methods, and the solid-state molecular structures of most of them have been established by X-ray crystallographic analyses. Finally, the newly formed alkyl ligands may be liberated from the tungsten centers in the product complexes by treatment with iodine. Thus, exposure of a $CDCl_3$ solution of the *n*-pentyl allyl complex, Cp*W(NO)(*n*-C_5H_{11})(η^3-$CH_2CHCHMe$), to I_2 at −60 °C produces *n*-$C_5H_{11}I$ in moderate yields.

Introduction

In recent years we have been investigating the family of Cp*M(NO)R_2 compounds (Cp* = η^5-C_5Me_5; M = Mo, W; R = a hydrocarbyl group) that exhibits R-dependent thermal reactivity to form a variety of reactive 16e nitrosyl complexes that are capable of effecting the single, double, and triple activation of hydrocarbon C−H bonds intermolecularly, often in an unprecedented manner.[1] Of all the Cp*M(NO)R_2 complexes that we have studied to date in this regard, the alkyl allyl complex, Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2),[2] is most interesting because it generates two reactive 16e intermediate species upon thermolysis at 50 °C. One intermediate is a 16e η^2-allene complex, and the other is a 16e η^2-diene complex, both being formed via the loss of neopentane from the precursor compound. Each intermediate reacts with C_6D_6 to form a differently labeled allyl phenyl complex (Scheme 1).

Both intermediates had to be invoked to account for the two organometallic products formed during the reaction of Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) with cyclohexene, but oth-

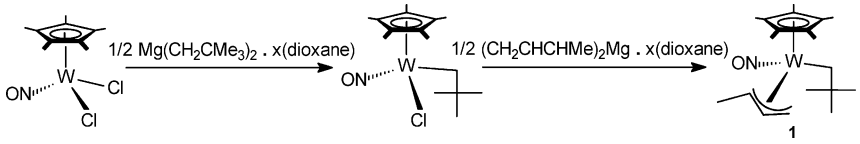
Scheme 1



(1) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223.
(2) Ng, S. H. K.; Adams, C. S.; Hayton, T. W.; Legzdins, P.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 15210.

10.1021/ja710606v CCC: $40.75

Scheme 2



erwise the C−H activation chemistry of this alkyl allyl complex discovered to date could be rationalized solely in terms of the η^2-allene intermediate, which can be isolated and fully characterized as its PMe_3 adduct.[2] Consequently, the exact role of the η^2-diene intermediate in this chemistry has remained unclear until now.

Very recently we synthesized a related alkyl allyl complex, namely Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$) (**1**), in connection with some other chemistry that we were investigating at the time.[3] We soon discovered that **1** is thermally unstable at room temperature and readily converts to a single, selective C−H activating intermediate by losing neopentane. This intermediate turns out to be the 16e η^2-diene complex, Cp*W(NO)(η^2-CH_2═$CHCH$═CH_2) (**A**), which can also be isolated as its PMe_3 adduct. Most importantly, intermediate **A** exhibits selectivities that are different than those displayed by the η^2-allene intermediate in the previous system. For instance, **A** effects facile C−H activations of aliphatic hydrocarbons exclusively at the terminal positions and in so doing it can tolerate amine, halogen, and ether functionalities. Furthermore, many C−H activations that have been difficult to perform with other transition-metal complexes have now become a reality with **1** because of the mild temperatures at which the C−H activation processes are initiated. This paper presents the results of our investigations into the C−H activation of a variety of hydrocarbon substrates initiated by complex **1** and compares them to those that we obtained with the related Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) complex a few years ago. A portion of this work has been previously communicated.[4]

Results and Discussion

The Synthesis and Characterization of Complex 1. Complex **1** may be synthesized via sequential metatheses with magnesium reagents beginning with Cp*W(NO)Cl_2 (Scheme 2), and it is isolable in moderate yields as an orange-yellow solid. As noted earlier, complex **1** is thermally sensitive, especially in solution, and has to be kept cold during its preparation and isolation. As a solid, it can be kept for months at −30 °C without any signs of significant decomposition. In solutions at the same temperature, **1** is stable for a few weeks. However, at room-temperature even under N_2, crystals of **1** decompose into an intractable brown solid over the course of 2 days.

The solid-state molecular structure of **1** has been established by an X-ray crystallographic analysis and is shown in Figure 1. The allyl ligand is in an endo conformation, and its methyl substituent occupies a syn position cis to the smaller nitrosyl ligand instead of the bulkier neopentyl group. As expected, the allyl ligand also exhibits a $\sigma-\pi$ distortion, a manifestation of the electronic asymmetry extant at the metal center.[5] The ^{1}H and ^{13}C NMR spectra of **1** indicate that its solid-state molecular structure persists in solution, but the ^{1}H NMR spectrum in C_6D_6 also exhibits a second set of allyl proton signals that can be attributed to a minor isomer. This minor isomer evidently does not cocrystallize with the major isomer during the growth of X-ray quality crystals of **1**. The minor isomer is probably a coordination isomer that features the methyl substituent of the 1-methylallyl ligand on the opposite end, cis to the CH_2CMe_3 group. In any event, dissolution of a crystalline sample of **1** in C_6D_6 produces a solution containing both isomers in a ca. 4:1 ratio. All solution reactions of **1** have been performed with similar mixtures of these interconverting isomers.

C−H Activation of *n*-Pentane. A yellow *n*-pentane solution of **1** left at room temperature inside an inert-atmosphere glovebox for 1 day darkens in color. The ^{1}H NMR spectrum of the sample redissolved in C_6D_6 reveals a single Cp* Me resonance, the absence of the neopentyl signal, and the appearance of allyl proton signals at slightly different chemical shifts than those of the starting material. Several new broad featureless signals are also evident between 1.30 and 2.00 ppm. This new complex can be chromatographed on alumina and then crystallized from pentane to obtain yellow-orange rods. An X-ray crystallographic analysis has revealed the complex to be Cp*W(NO)(*n*-C_5H_{11})(η^3-$CH_2CHCHMe$) (**2**) whose ORTEP diagram is shown in Figure 2. Complex **2** is isostructural with **1**, apart from the fact that the neopentyl group in **1** has been replaced by an *n*-pentyl group which has been formed by the single C−H activation of *n*-pentane at a terminal position (Scheme 3).

The ability of complex **1** to perform such a clean aliphatic C−H bond activation under ambient conditions is remarkable. Effecting such transformations for linear alkanes is particularly challenging since the activation of aliphatic C−H bonds at transition-metal centers often requires generation of the active species by high-energy thermal or photochemical means.[6] Second, the activations frequently result in the formation of initial organometallic products that are unstable under the experimental conditions employed[7] and undergo decomposition via processes such as β-hydrogen elimination on the newly formed alkyl ligand to form a metal η^2-olefin hydrido complex.[8] Such is the case for our previously reported Cp*Mo(NO)(CH_2CMe_3)$_2$ system which also effects alkane C−H bond activations

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(7) (a) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (c) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (d) Debad, J. D.; Legzdins, P.; Lumb, S. A.; Rettig, S. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1999**, *18*, 3414 and references cited therein.

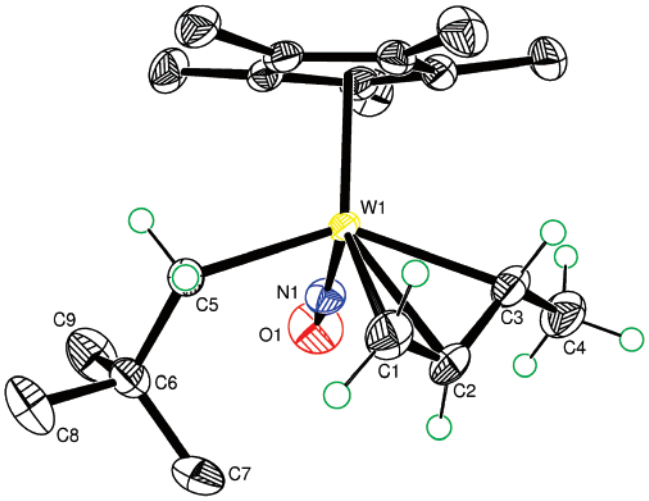


Figure 1. Solid-state molecular structure of **1** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.401(3), W(1)−C(2) = 2.346(3), W(1)−C(3) = 2.282(3), W(1)−C(5) = 2.257(3), W(1)−N(1) = 1.764(2), N(1)−O(1) = 1.221(3), C(1)−C(2) = 1.372(5), C(2)−C(3) = 1.425(4), C(3)−C(4) = 1.509(4), C(1)−C(2)-C(3) = 119.3(3), C(2)−C(3)-C(4) = 120.4(3), W(1)−C(5)−C(6) = 123.4(2), W(1)−N(1)−O(1) = 170.5(2).

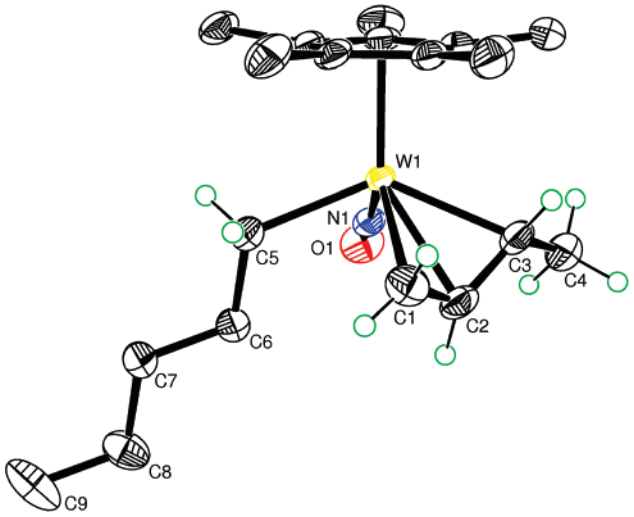
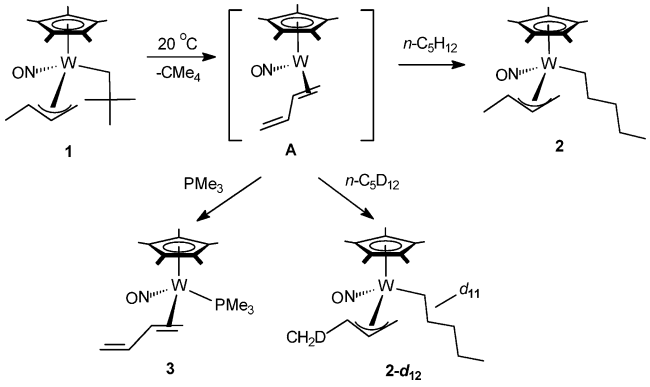


Figure 2. Solid-state molecular structure of complex **2** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.333(4), W(1)−C(2) = 2.313(3), W(1)−C(3) = 2.294(3), W(1)−C(5) = 2.242(3), W(1)−N(1) = 1.788(3), N(1)−O(1) = 1.216(3), C(1)−C(2) = 1.363(5), C(2)−C(3) = 1.414(5), C(3)−C(4) = 1.501(5), C(1)−C(2)−C(3) = 118.8(3), C(2)−C(3)−C(4) = 120.6(3), W(1)−C(5)−C(6) = 116.5(2), W(1)−N(1)−O(1) = 174.9(2).

at room temperature via the Cp*Mo(NO)(=CHCMe$_3$) intermediate but only affords isolable organometallic products when β-hydrogens are absent.[9] Furthermore, at even slightly elevated temperatures, which are the usual conditions during which the initial single C−H activation products are formed, other elimination pathways such as α-hydrogen abstraction or reductive elimination can also become accessible.[10] Finally, the activations can be non-regioselective since several types of C−H activation sites are usually present on most hydrocarbons.[11]

Scheme 3



Complex **1** experiences none of the aforementioned problems. Specifically, the initial pentane C−H activation product is an 18e species; therefore, it does not readily β-hydrogen eliminate despite possessing β-hydrogen atoms on the newly attached *n*-pentyl ligand. Furthermore, the transformation occurs at 20 °C, a temperature at which the 18e allyl *n*-pentyl complex **2** is thermally stable. Finally, the C−H activation is 100% selective for the terminal positions of pentane.

The Reactive Intermediate: Trapping and Labeling Studies. The thermal reaction of **1** in neat PMe$_3$ at 20 °C affords the base-stabilized adduct of the η^2-diene complex, namely Cp*W(NO)(η^2-*trans*-CH$_2$=CHCH=CH$_2$)(PMe$_3$) (**3**) (Scheme 3). The adduct has been isolated in 41% yield by crystallization from pentane at −30 °C since it does not survive chromatography on alumina. This property suggests that if a similar η^2-diene adduct had been formed during the thermolysis of Cp*W(NO)(CH$_2$CMe$_3$)(η^3-CH$_2$CHCMe$_2$) in the presence of PMe$_3$, it would have decomposed during the workup of the final reaction mixture.[2] The solid-state molecular structure of **3** is shown in Figure 3. Complex **3** possesses a three-legged piano-stool geometry, the diene fragment being coordinated in an η^2-fashion with its intramolecular metrical parameters clearly differentiating between the bound and free olefin units.

NMR spectroscopic data indicate that the solid-state molecular structure of complex **3** is maintained in solution. Thus, the ^{1}H NMR spectrum of **3** in C$_6$D$_6$ contains three diagnostic downfield resonances between 4.70 and 6.07 ppm for the protons on the uncoordinated H$_2$C=CH unit and three upfield resonances from 0.32 to 2.04 ppm for the protons on the bound H$_2$C=CH unit. Similarly, in the ^{13}C{^{1}H} NMR spectrum of **3** in the same solvent, the chemical shifts of the signals due to the unbound C=C linkage are much more downfield (149.7 and 102.5 for CH= and CH$_2$=, respectively)[12] than are the chemical shifts for the signals attributable to the bound C=C group (42.7 and

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(12) In our preliminary communication of this work,[4] these two chemical shift values are erroneously switched.

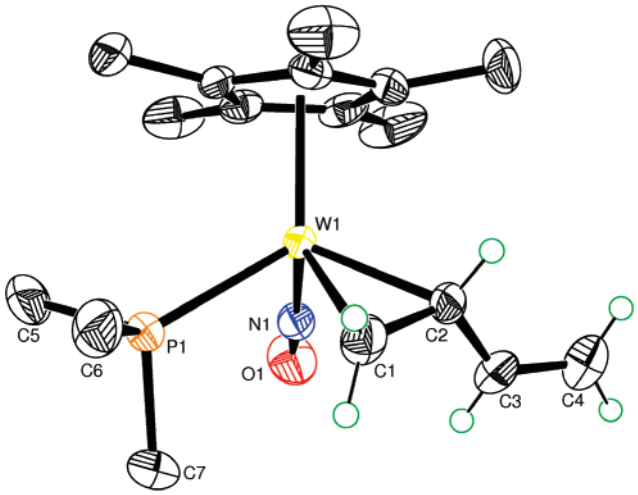

Figure 3. Solid-state molecular structure of **3** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.221(4), W(1)−C(2) = 2.218(3), W(1)−P(1) = 2.4335(8), W(1)−N(1) = 1.774(3), N(1)−O(1) = 1.230(4), C(1)−C(2) = 1.453(5), C(2)−C(3) = 1.456(5), C(3)−C(4) = 1.306(5), C(1)−C(2)−C(3) = 121.4-(3), C(2)−C(3)−C(4) = 126.7(4), W(1)−N(1)−O(1) = 170.1(3).

31.4 for CH═ and CH_2═, respectively). In the IR spectrum of complex **3** as a Nujol mull, the NO-stretching frequency occurs at 1634 cm^{-1}, a relatively high value for compounds of this type. This high wavenumber is probably a reflection of the competition for metal electron density by three π-accepting ligands.

The isolation of complex **3** establishes that the η^2-diene intermediate Cp*W(NO)(η^2-*trans*-CH_2═CHCH═CH_2) (**A**) (Scheme 3) is responsible for the C−H activation chemistry initiated by **1**. It might have been expected that loss of a hydrogen from the terminal methyl group of the allyl ligand in **1** and its metal-mediated transfer to the CH_2CMe_3 ligand resulting in the loss of CMe_4 would lead to the formation of the 18e η^4-diene complex, Cp*W(NO)(η^4-CH_2═CHCH═CH_2), which is a thermally stable yellow compound that we have prepared previously by treating diethyl ether solutions of Cp*W-(NO)(CH_2SiMe_3)$_2$ at −78 °C with H_2 in the presence of 1,3-butadiene.[13] It is unlikely that the η^4-*trans*-diene complex is formed during the C−H activation chemistry initiated by **1** since we have also established previously that such complexes are relatively kinetically inert to substitution by PMe_3,[14] a process that would be required for the formation of **3**. Furthermore, it is highly unlikely that in the presence of *n*-pentane, Cp*W-(NO)(η^4-*trans*-CH_2═CH−CH═CH_2), with its favored 18e configuration at the metal, would open up the coordination position at the tungsten center required for C−H activation by spontaneously converting to the 16e intermediate **A**. Hence, we believe that it is **A** that is formed initially by loss of CMe_4 from **1**. Then, before the η^4-diene complex can be formed, the reactive intermediate **A** comes into contact with a solvent molecule and activates a C−H bond. Such a mechanism of C−H activation has not been established experimentally previously, and it may well be behind the unique C−H activating chemistry initiated by **1**.

(13) Debad, J. D.; Legzdins, P.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1993**, *115*, 2051.
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Dissolution of **1** in *n*-C_5D_{12} for 1 day under ambient conditions results in the clean formation of **2**-d_{12} (Scheme 3). Exactly one deuterium ends up being incorporated into the terminal allyl methyl substituent of **2**-d_{12} as indicated by a conspicuous 1:1:1 triplet at 17.7 ppm in its $^{13}C\{^1H\}$ NMR spectrum. This fact also suggests that the initial C−D activation of *n*-pentane-d_{12} occurs exclusively at the terminal position, and not at a CD_2 position, since subsequent isomerization of 1-methylbutyl ($CD(C_3D_7)(CD_3)$) or 1-ethylpropyl ($CD(C_2D_5)_2$) groups to the observed *n*-pentyl ligand by a chain-walking type mechanism could very well result in the incorporation of more than one deuterium atom into the allyl methyl group. At the same time, the signal due to the allyl middle carbon in complex **2**-d_{12} remains a singlet. This feature indicates that an allene intermediate such as Cp*W(NO)(η^2-H_2C═C═CHMe) is not formed at all during the C−D activation of pentane-d_{12} by **1**, for otherwise deuterium incorporation onto the allyl middle carbon would have occurred. A possible explanation for this phenomenon is that the loss of the middle allyl hydrogen from **1** may well occur only at higher temperatures, such as those employed for Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2).[2] In that connection, it may also be noted at this point that the reaction of Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) with *n*-pentane at 50 °C affords an intractable mixture of products,[2] thereby suggesting that the initial complexes formed via the single C−H activation of *n*-pentane by either the η^2-allene or the η^2-diene intermediate species are thermally unstable under the reaction conditions employed.

Other Aliphatic C−H Activations. (A) Activations of Linear and Branched Hydrocarbons. To investigate the generality of these C−H activation processes, complex **1** has been reacted with a variety of organic substrates. Treatment of **1** with *n*-heptane leads to the formation of Cp*W(NO)(*n*-C_7H_{15})(η^3-$CH_2CHCHMe$) (**4**). As in the case of *n*-pentane, the regioselectivity of *n*-heptane C−H activation is exclusively at the terminal positions. Similarly, exposure of **1** to methylcyclohexane leads to the exclusive terminal C−H activation at the methyl group, Cp*W(NO)(CH_2(cyclohexyl))(η^3-$CH_2CHCHMe$) (**5**) being formed as the only organometallic product. For comparison, the reaction between methylcyclohexane and the related Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) complex at 50 °C leads to the formation of an exocyclic cyclohexenyl hydrido complex, Cp*W(NO)(η^3-C_7H_{11})(H), which is formed after the original allyl ligand is eliminated from the initial C−H activation product.[2] This difference in reactivities between the two alkyl allyl complexes underscores the importance of effecting the initial C−H activation of the hydrocarbon substrate under the mildest possible conditions. Finally, treatment of **1** with cyclohexane under ambient conditions leads to a mixture of as yet unidentified organometallic products. This fact reaffirms that the productive C−H activations of aliphatic hydrocarbons initiated by **1** to date are limited to primary C−H bonds.

A judicious choice of solvents permits the C−H activation of gaseous hydrocarbons at ambient temperatures under moderately elevated pressures. Thus, Cp*W(NO)($CH_2CH_2CH_3$)(η^3-$CH_2CHCHMe$) (**6**) is formed in moderate yields by stirring a C_6F_6 solution of **1** under propane (ca. 150 psi)[15] for 1 day. Similarly, Cp*W(NO)(CH_2CH_3)(η^3-$CH_2CHCHMe$) (**7**) and

(15) The vapor pressure of propane at 300 K is ca. 145 psi; see: Miyamoto, H.; Uematsu, M. *Int. J. Thermophys.* **2006**, *27*, 1052.

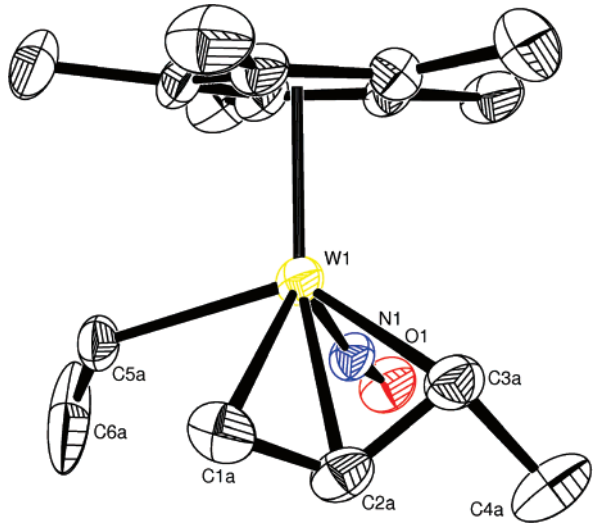


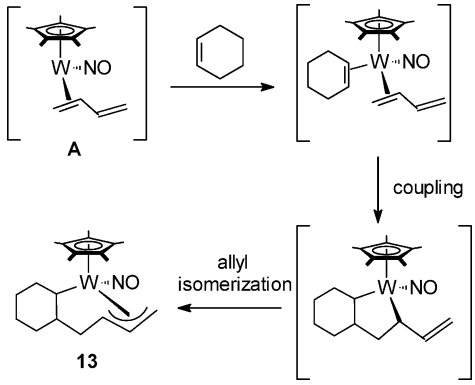
Figure 4. Solid-state molecular structure of **7** with 35% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1a) = 2.368(14), W(1)−C(2a) = 2.285(8), W(1)−C(3a) = 2.174(12), W(1)−C(5a) = 2.332(11), W(1)−N(1) = 1.772(3), N(1)−O(1) = 1.218(4), C(1a)−C(2a) = 1.320(17), C(2a)−C(3a) = 1.398(12), C(3a)−C(4a) = 1.556(16), C(5a)−C(6a) = 1.099(16), C(1a)−C(2a)−C(3a) = 117.4(11), C(2a)−C(3a)−C(4a) = 93.8(9), W(1)−C(5a)−C(6a) = 133.6(11), W(1)−N(1)−O(1) = 169.3(3).

Cp*W(NO)(CH_3)(η^3-$CH_2CHCHMe$) (**8**) can be obtained in moderate yields by pressurizing solutions of **1** in C_6F_6 and cyclohexane, respectively, with ethane (400 psig) and methane (1025 psig) in a stainless steel pressure reactor for the same amount of time. The solid-state molecular structure of complex **7** is shown in Figure 4 as a representative example of these three products. The activation of methane at room temperature by **1** is particularly noteworthy since it is a rare example of the activation of this inert hydrocarbon under very mild conditions.[16]

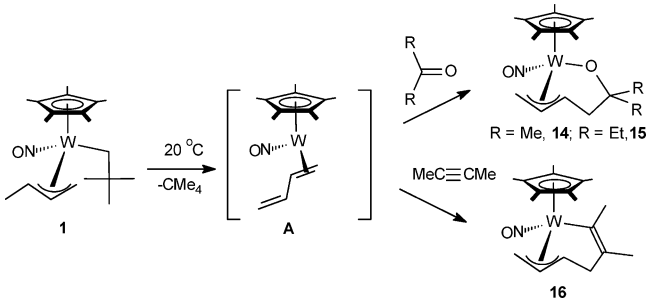
(B) Activations of Heteroatom-Containing Saturated Substrates. Treatment of **1** with tetramethylsilane ($SiMe_4$) leads to the expected formation of Cp*W(NO)(CH_2SiMe_3)(η^3-CH_2-CHCHMe) (**9**). In a similar manner treatments of **1** with 1-chloropentane, diethyl ether, and triethylamine all lead to exclusive formation of the terminal C−H activation products, namely, Cp*W(NO)((CH_2)$_5$Cl)(η^3-$CH_2CHCHMe$) (**10**), Cp*W(NO)($CH_2CH_2OCH_2CH_3$)(η^3-$CH_2CHCHMe$) (**11**), and Cp*W(NO)($CH_2CH_2N(CH_2CH_3)_2$)(η^3-$CH_2CHCHMe$) (**12**), respectively. Particularly notable in the case of the triethylamine reaction is the fact that the 18e Et_3N adduct of the η^2-diene intermediate complex **A**, i.e. Cp*W(NO)(η^2-*trans*-CH_2═CHCH═CH_2)(NEt_3), does not form in detectable amounts.

(C) Attempted Activations of Unsaturated Substrates. Treatment of **1** with cyclohexene at room temperature leads to the exclusive formation of Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C_\beta H$-(C_4H_8)C_αH) (**13**). Complex **13** is analogous to the allyl-containing product formed by the putative η^2-diene intermediate during the thermal reaction of the related Cp*W(NO)(CH_2-CMe_3)(η^3-CH_2CHCMe_2) with cyclohexene at 50 °C.[2] Consistently, the proposed mechanism for the formation of **13** thus involves (a) the coordination of cyclohexene to the metal center, (b) coupling of the two coordinated olefin ligands, and (c) the $\eta^1 \rightarrow \eta^3$ isomerization of the allylic portion of the organic fragment (Scheme 4). A single-crystal X-ray analysis confirms the atom connectivity in **13**, but the effects of twinning prevent meaningful discussion of the metrical parameters.

Scheme 4



Scheme 5



Treatments of **1** with acetone, 3-pentanone, and 2-butyne all lead to the same type of product that arises from the reaction of **1** with cyclohexene. Thus, Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C$-(CH_3)$_2$O) (**14**) is formed as the principal organometallic product in acetone, while Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C(CH_2$-CH_3)$_2$O) (**15**) and Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2CCH_3$═CCH_3) (**16**) are formed exclusively in 3-pentanone and 2-butyne, respectively (Scheme 5). All of these organometallic complexes can be purified by chromatography on alumina. We have previously observed this type of coupling reaction to occur between Cp′Mo(NO)(η^4-diene) complexes (Cp′ = Cp or Cp*) and acetone.[17] The solid-state molecular structures of **15** and **16** have been established by X-ray crystallographic analyses and are shown in Figures 5 and 6, respectively.

When the site of unsaturation is sufficiently sterically hindered, as in the case of 2,3-dimethyl-2-butene, C−H activation again becomes dominant, and so the C−H activation product, Cp*W(NO)(η^1-CH_2CMe═CMe_2)(η^3-$CH_2CHCHMe$) (**17**), is formed exclusively from the alkene and **1**. Figure 7 shows the solid-state molecular structure of **17** in which the newly formed 2,3-dimethyl-2-butenyl ligand exhibits an η^1-binding mode, while the original 1-methylallyl ligand remains η^3-bonded to the metal center.

(D) Attempted Aryl C−H Activation of Aromatic Substrates. During C−H activations by transition-metal complexes,

(16) For other examples of methane activation at ambient temperatures, see: (a) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696 and references cited therein. (b) Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953 and references cited therein. (c) Cui, W.; Zhang, X. P.; Wayland, B. B. *J. Am. Chem. Soc.* **2003**, *125*, 4994 and references cited therein. (d) Fontaine, F.-G.; Tilley, T. D. *Organometallics* **2005**, *24*, 4340 and references cited therein.

(17) Christensen, N. J.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 4021.

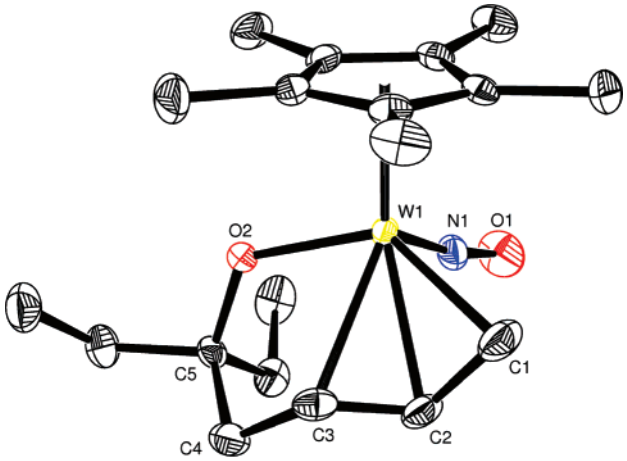


Figure 5. Solid-state molecular structure of **15** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.227(4), W(1)−C(2) = 2.336(3), W(1)−C(3) = 2.437(4), W(1)−O(2) = 2.012(3), W(1)−N(1) = 1.763(3), N(1)−O(1) = 1.230(4), C(1)−C(2) = 1.447(6), C(2)−C(3) = 1.363(6), C(3)−C(4) = 1.488(5), C(4)−C(5) = 1.565(5), C(5)−O(2) = 1.413(4), C(1)−C(2)−C(3) = 117.9-(4), C(2)−C(3)−C(4) = 124.3(4), C(3)−C(4)−C(5) = 109.0(3), C(4)−C(5)−O(2) = 107.8(3), W(1)−O(2)−C(5) = 122.6(2), W(1)−N(1)−O(1) = 171.4(3).

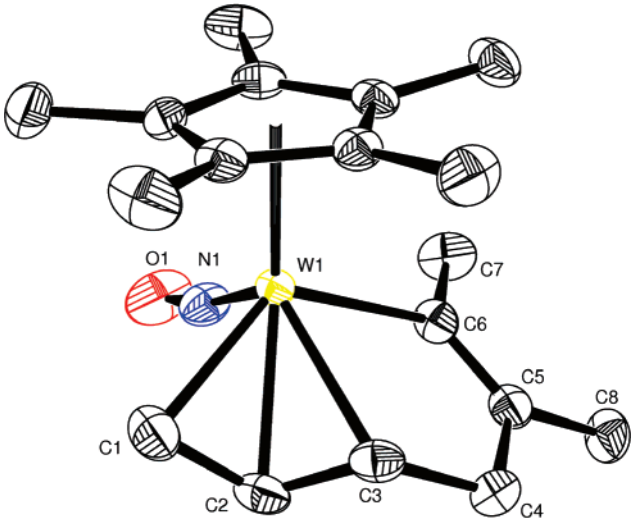


Figure 6. Solid-state molecular structure of **16** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.228(3), W(1)−C(2) = 2.299(3), W(1)−C(3) = 2.360(3), W(1)−C(6) = 2.191(3), W(1)−N(1) = 1.766(3), N(1)−O(1) = 1.212(4), C(1)−C(2) = 1.410(5), C(2)−C(3) = 1.381(5), C(3)−C(4) = 1.488(4), C(4)−C(5) = 1.503(4), C(5)−C(6) = 1.325(4), C(1)−C(2)−C(3) = 117.3-(3), C(2)−C(3)−C(4) = 125.0(3), C(3)−C(4)−C(5) = 108.9(2), C(4)−C(5)−C(6) = 119.4(3), W(1)−C(6)−C(5) = 123.5(2), W(1)−N(1)-O(1) = 169.8(2).

benzene usually yields the cleanest reactions because the resulting metal−phenyl bond is thermodynamically more stable than a metal−aliphatic-carbon bond.[10] However, the same generalization cannot be made in the case of complex **1**. Treatment of **1** with benzene under ambient conditions only affords a brown solution that contains a complex mixture of organometallic compounds that has so far defied our best attempts at separation and identification.

Similarly, treatment of complex **1** with toluene also produces a mixture probably containing aryl- and alkyl-C−H activation products as evidenced by the four allyl meso-proton signals in the ^{1}H NMR spectrum of the final reaction mixture. Heating of

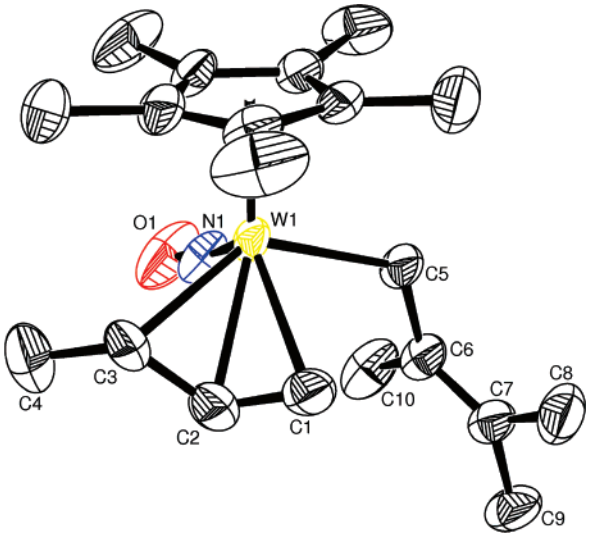


Figure 7. Solid-state molecular structure of **17** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.361(6), W(1)−C(2) = 2.302(6), W(1)−C(3) = 2.290(6), W(1)−C(5) = 2.261(5), W(1)−N(1) = 1.761(6), N(1)−O(1) = 1.224(7), C(1)−C(2) = 1.357(9), C(2)−C(3) = 1.417(8), C(3)−C(4) = 1.485(10), C(5)−C(6) = 1.485(8), C(6)−C(7) = 1.350(8), C(1)−C(2)−C(3) = 120.4-(7), C(2)−C(3)−C(4) = 120.6(7), W(1)−C(5)−C(6) = 121.6(4), C(5)−C(6)−C(7) = 123.7(6), C(6)−C(7)−C(8) = 124.3(6), W(1)−N(1)−O(1) = 170.9(5).

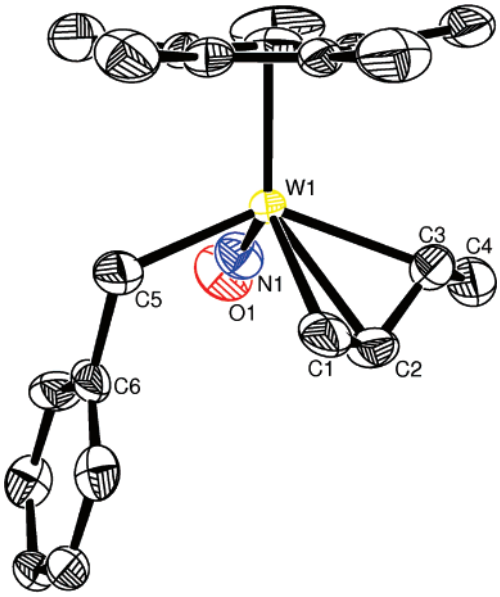


Figure 8. Solid-state molecular structure of **18** with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.410(7), W(1)−C(2) = 2.311(6), W(1)−C(3) = 2.299(6), W(1)−C(5) = 2.216(7), W(1)−N(1) = 1.770(5), N(1)−O(1) = 1.190(6), C(1)−C(2) = 1.395(9), C(2)−C(3) = 1.436(9), C(3)−C(4) = 1.458(10), C(1)−C(2)−C(3) = 120.5(6), C(2)−C(3)−C(4) = 120.5(6), W(1)−C(5)−C(6) = 117.8(4), W(1)−N(1)−O(1) = 170.2(5).

this mixture at 50 °C for 20 h leads only to the isolation of the benzyl allyl complex, Cp*W(NO)(η^1-$CH_2C_6H_5$)(η^3-CH_2-CHCHMe) (**18**). The solid-state molecular structure of **18** has been established by X-ray crystallography, and its ORTEP diagram is shown in Figure 8. The metrical parameters for the allyl ligand in **18** are typical, and the benzyl ligand adopts an η^1-binding motif to the metal center. This feature contrasts with those in related Cp*W(NO)(benzyl)(alkyl) complexes in which

the benzyl ligands are η^2-coordinated to the metals.[18] Complex **18** is formed in 23% NMR yield according to the integration of the meso-proton signals of the various allyl-containing species in the final reaction mixture. This benzyl regioselectivity is similar to that exhibited by Cp*W(NO)(CH_2CMe_3)(η^3-CH_2-$CHCMe_2$) during its C−H activation of toluene.[2] The successful isolation of **18** again reflects the stability of the Cp*W(NO)-(η^1-alkyl)(η^3-$CH_2CHCHMe$) complexes resulting from the activation of sp^3 C−H linkages.

Functionalization of the Newly Created Alkyl Ligands. The new alkyl groups resulting from the C−H activation of the various organic substrates by intermediate **A** may be released from their respective organometallic products by treatment with elemental iodine. Thus, dropwise treatment of a $CDCl_3$ solution of the *n*-pentyl complex **2** at −60 °C with a solution of I_2 in the same solvent affords 1-iodopentane in approximately 70% yield as judged by ^{1}H NMR spectroscopy. The other products are the known Cp*W(NO)I_2[19] and various isomers of methylallyl iodide. The use of heat is not feasible during these functionalizations of **2** since it readily loses *n*-pentane upon warming and reforms the η^2-diene intermediate complex. Thus complex **3** is formed cleanly when **2** is warmed in PMe_3 at 35 °C for 5 days.

Similarly, the treatment of both the benzyl allyl complex **18** and trimethylsilylmethyl complex **9** with I_2 at −60 °C releases the expected iodo-functionalized products (iodomethyl)benzene and (iodomethyl)trimethylsilane in 45% and 57% yields, respectively, as determined by ^{1}H NMR spectroscopy.

Epilogue

In summary, we have discovered a unique tungsten allyl nitrosyl complex (**1**) that selectively activates the terminal C−H bonds of *n*-alkanes under ambient conditions and forms thermally stable *n*-alkyl complexes that may be isolated and fully characterized. Furthermore, a judicious choice of solvents permits the C−H activation of gaseous hydrocarbons (i.e., propane, ethane, and methane) at ambient temperatures under moderately elevated pressures. We have also found that the *n*-alkyl ligands can be released from these complexes in a derivatized form with the functional group at the terminal position. Complex **1** can initiate similar C−H bond activations on saturated organic molecules even in the presence of functional groups containing heteroatoms such as nitrogen, oxygen, silicon, and chlorine. These remarkable C−H activations are manifestations of the fact that the exclusive activating species in this system is the η^2-diene complex, Cp*W(NO)(η^2-CH_2═$CHCH$═CH_2) (**A**). We had previously invoked a similar intermediate to explain some of the thermal chemistry of Cp*W(NO)(CH_2-CMe_3)(η^3-CH_2CHCMe_2). However, on the basis of the present report, we now realize that most of the organometallic products resulting from the η^2-diene intermediate in that system either decomposed under the 50 °C conditions employed or during the workup of the final mixtures by chromatography on alumina. Consequently, as we reported, most of the C−H activating chemistry of Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) could be understood in terms of the other intermediate generated thermally, namely the 16e η^2-allene complex, Cp*W(NO)(η^2-H_2C═C═CMe_2).[2]

Our activations of alkanes initiated by Cp*W(NO)(CH_2-CMe_3)(η^3-$CH_2CHCHMe$) (**1**) at ambient temperatures involve some of the most gentle conditions yet discovered for effecting these transformations. To exploit more fully these unique C−H activations, particularly the preferential intermolecular activations of sp^3 C−H bonds, we are currently endeavoring to discover the conditions for effecting these activations and the subsequent functionalization of the resulting hydrocarbyl ligands in a catalytic manner. As a first step, we are presently examining the reactions of the various Cp*W(NO)(*n*-alkyl)(η^3-CH_2-$CHCHMe$) product complexes with a range of electrophiles and nucleophiles to discover those reagents that react only with the alkyl ligand and not with both the alkyl and allyl ligands as does I_2 (vide supra). Once we have succeeded in releasing the alkyl ligand from the Cp*W(NO)(η^3-$CH_2CHCHMe$) fragment in a functionalized form, we shall then be in a position to complete the catalytic cycle by regenerating the intermediate Cp*W(NO)(η^2-CH_2═$CHCH$═CH_2) (**A**). We shall report our results in this regard in due course.

Experimental Section

General Methods. All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions either under 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 vacuum-line Schlenk techniques were utilized throughout. The gloveboxes used were Innovative Technologies LabMaster 100 and MS-130 BG dual-station models equipped with freezers maintained at −30 °C. Most of the reactions were performed in thick-walled glass vessels possessing Kontes greaseless stopcocks and sidearm inlets for vacuum-line attachment. Small-scale reactions and NMR spectroscopic analyses were conducted in J. Young NMR tubes which were also equipped with Kontes greaseless stopcocks. All solvents were dried with appropriate drying agents under a dinitrogen atmosphere and were distilled prior to use, or they were transferred directly under vacuum from the appropriate drying agent. Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl. Commercially available ($CH_2CHCHMe$)MgCl (Aldrich, 0.5 M in THF) was transformed into the corresponding diallylmagnesium reagents in the usual manner.[1] Cp*W(NO)(CH_2CMe_3)Cl[2] was prepared according to the published procedure. The progress of most reactions was monitored by NMR spectroscopy, but the isolated yields of all new complexes have not been optimized.

All IR samples were prepared as Nujol mulls, and their spectra were recorded on a Thermo Nicolet 4700 FT-IR spectrometer. NMR spectra were recorded at room temperature on Bruker AV-300 or AV-400 spectrometers. All chemical shifts are reported in ppm, and all coupling constants are reported in hertz. ^{1}H NMR spectra are referenced to the residual protio isotopomer present in a particular solvent, and ^{13}C NMR spectra are referenced to the natural-abundance carbon signal of the solvent employed. When necessary, ^{1}H−^{1}H COSY, ^{1}H−^{1}H NOEDS, ^{1}H−^{13}C HMQC, ^{1}H−^{13}C HMBC, 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. Minaz Lakha of the UBC microanalytical facility.

Preparation of Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$) (1). In a glovebox a medium (ca. 250-mL) Schlenk tube was charged with a magnetic stir bar and Cp*W(NO)(CH_2CMe_3)Cl (3.20 g, 7.03 mmol). A second medium Schlenk tube was charged with a magnetic stir bar and ($CH_2CHCHMe$)$_2$Mg·*x*(dioxane) (titer = 112.5 g/mol R, 0.791 g, 0.5 equiv). On a vacuum line, Et_2O (approximately 150 mL and 20 mL) was vacuum-transferred onto the Cp*W(NO)(CH_2CMe_3)Cl and

(18) Adams, C. S.; Legzdins, P.; Tran, E. *Organometallics* **2002**, *21*, 1474.

the diallylmagnesium reagents, respectively. The Et_2O above the Cp*W(NO)(CH_2CMe_3)Cl was allowed to melt while the Schlenk tube was placed in a dry ice/acetone bath. The mixture was stirred to ensure complete dissolution of the Cp*W(NO)(CH_2CMe_3)Cl reagent. The Schlenk glass stoppers were replaced by Suba septa. The second Schlenk tube containing the magnesium reagent was maintained in a liquid N_2 bath, and the purple Cp*W(NO)(CH_2CMe_3)Cl solution was added dropwise via a cannula The rate of addition was slow enough to allow the added solution to freeze upon contact with the frozen Et_2O. Additional cold Et_2O (2 × 10 mL) was used to ensure quantitative transfer of the Cp*W(NO)(CH_2CMe_3)Cl reactant. After the addition of the Cp*W(NO)(CH_2CMe_3)Cl solution was complete, the mixture was stirred for a further 45 min while being maintained in the dry ice/acetone bath. The solution gradually turned brown, with the concomitant formation of a brown suspension of Mg salts. The dry ice/acetone bath was then removed, and the solvent was evaporated from the final mixture in vacuo. Since complex **1** is thermally unstable, cold solvents (−30 °C) have to be employed throughout its extraction and subsequent chromatography in order to minimize its decomposition. The reaction residue was extracted with hexanes (4 × 100 mL), and the combined extracts were transferred to the top of a neutral activated alumina (I) column (2 × 8 cm) made up in hexanes and supported on a medium or high porosity frit. The column was eluted with 1:1 hexanes/Et_2O, the resulting yellow band was collected, and solvents were removed from the eluate in vacuo. The residue from the chromatographic eluate was redissolved and crystallized from pentane at −30 °C overnight to obtain **1** as orange-yellow crystalline, irregularly shaped clusters in multiple crops. The solids were washed with small amounts of cold pentane (−30 °C, 2 × 5 mL) and then dried in vacuo. Yield 2.2 g (43%).

1: IR (cm^{-1}) 1594 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ (major isomer) 0.89 (d, $^2J_{HH}$ = 13.2, 1H, C*H*$_2$CMe$_3$), 1.01 (m, 1H, allyl C*H*Me), 1.32 (s, 9H, CMe$_3$), 1.48 (s, 15H, C_5Me_5), 1.56 (d, $^3J_{HH}$ = 14.0, 1H, allyl CH$_2$), 1.59 (d, $^2J_{HH}$ = 13.2, 1H, C*H*$_2$CMe$_3$), 1.89 (d, $^3J_{HH}$ = 6.0, 3H, allyl Me), 3.67 (d, $^3J_{HH}$ = 7.2 1H, allyl CH$_2$), 4.97 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 9.4, $^3J_{HH}$ = 14.0, 1H, allyl CH). δ (minor isomer) selected signals 0.51 (m, 1H, allyl CH$_2$), 1.35 (s, 9H, CMe$_3$), 2.30 (m, 1H, allyl CH$_2$), 2.67 (m, 1H, allyl CH), 4.47 (m, 1H, allyl CH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 9.5 (C_5*Me*$_5$), 16.9 (allyl Me), 27.9 (*C*H$_2$CMe$_3$), 34.6 (CH$_2$C*Me*$_3$), 39.3 (CH$_2$*C*Me$_3$), 52.4 (allyl *C*HMe), 74.3 (allyl CH$_2$), 106.0 (*C*$_5$Me$_5$), 114.6 (allyl *C*H). MS (LREI, *m/z*, probe temperature 120 °C) 475 [M$^+$]. Anal. Calcd for $C_{19}H_{33}NOW$: C, 48.01; H, 7.00; N, 2.95. Found: C, 47.88; H, 7.32; N, 3.24.

Preparation of Cp*W(NO)(*n*-C_5H_{11})(η^3-$CH_2CHCHMe$) (2). In a glovebox a sample of **1** (60.0 mg, 1.26 mmol) was dissolved in pentane in a 4-dram vial, and the solution was set aside. After 20 h, the solution, which had darkened slightly in color, was transferred to the top of an alumina I column (0.5 × 5 cm) supported by glass wool in a Pasteur pipet. The column was eluted with 3:1 pentane/Et_2O, and the yellow band that developed was eluted and collected. The solvent was removed from the eluate in vacuo, and the oily residue was redissolved in pentane (2 mL). The solution was stored at −30 °C overnight to induce to deposition of orange rods of **2** (48 mg, 81%).

2: IR (cm^{-1}) 1597 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 1.04 (t, $^3J_{HH}$ = 7.3, 3H, *n*-pentyl Me), 1.07 (overlapping m, 1H, *n*-pentyl CH$_2$), 1.11 (overlapping m, 1H, allyl C*H*Me), 1.40 (m, 2H, *n*-pentyl CH$_2$), 1.49 (obscured, 3H, *n*-pentyl CH$_2$), 1.50 (s, 15H, C_5Me_5), 1.51 (obscured, 1H, allyl CH$_2$), 1.59 (m, 1H, *n*-pentyl CH$_2$), 1.93 (d, $^3J_{HH}$ = 5.8, 3H, allyl Me), 2.08 (m, 1H, *n*-pentyl CH$_2$), 3.23 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH$_2$), 4.89 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 9.6, $^3J_{HH}$ = 13.6, 1H, allyl CH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 9.4 (C_5*Me*$_5$), 14.7 (*n*-pentyl Me), 16.2 (*n*-pentyl CH$_2$), 17.7 (allyl Me), 23.0 (*n*-pentyl CH$_2$), 34.0 (*n*-pentyl CH$_2$), 39.3 (*n*-pentyl CH$_2$), 54.1 (allyl *C*HMe), 74.4 (allyl CH$_2$), 105.5 (*C*$_5$Me$_5$), 109.5 (allyl *C*H). MS (LREI, *m/z*, probe temperature 120 °C) 475 [M$^+$]. Anal. Calcd for $C_{19}H_{33}NOW$: C, 48.01; H, 7.00; N, 2.95. Found: C, 47.92; H, 6.91; N, 3.17.

Preparation of Cp*W(NO)(η^2-CH_2=CHCH=CH_2)(PMe_3) (3). In a glovebox a sample of **1** (60.0 mg, 1.26 mmol) was added to a small resealable vessel. At a vacuum line, an excess of PMe_3 (2 mL) was vacuum-transferred onto the solid, and the resulting yellow-orange solution was set aside. After 20 h at room temperature, the solution had lightened in color. The volatiles were then removed in vacuo, and the remaining solid was extracted with cold pentane (−30 °C, 5 × 5 mL), leaving behind an unidentified white residue. The combined extracts were filtered through Celite supported on glass wool in a Pasteur pipet, and the filtrate was reduced in volume in vacuo. Storage of the sample at −30 °C overnight led to the deposition of **3** as a yellow microcrystalline solid (25 mg, 41%).

3: IR (cm^{-1}) 1634 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 0.32 (m, 1H, metal-bound *H*$_2$C=CH), 1.14 (d, $^2J_{HP}$ = 8.4, 9H, PMe_3), 1.59 (m, 1H, metal-bound *H*$_2$C=CH), 1.65 (s, 15H, C_5Me_5), 2.04 (m, 1H, metal-bound H$_2$C=C*H*), 4.70 (dd, $^2J_{HH}$ = 2.0, $^3J_{HH}$ = 10.0, 1H, uncoordinated *H*$_2$C=CH), 5.15 (dd, $^2J_{HH}$ = 2.0, $^3J_{HH}$ = 16.4, 1H, uncoordinated *H*$_2$C=CH), 6.07 (dt, $^3J_{HH}$ = 10.0, $^3J_{HH}$ = 16.4, 1H, uncoordinated H$_2$C=C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 10.1 (C_5*Me*$_5$), 16.3 (d, $^1J_{CP}$ = 32.0, PMe_3), 31.4 (d, $^2J_{CP}$ = 12.0, metal-bound H$_2$*C*=CH), 42.7 (metal-bound H$_2$C≡C*H*), 102.5 (uncoordinated H$_2$*C*=CH), 103.1 (*C*$_5$Me$_5$), 149.7 (uncoordinated H$_2$*C*=CH). MS (LREI, *m/z*, probe temperature 120 °C) 479 [M$^+$]. Anal. Calcd for $C_{17}H_{30}NOPW$: C, 42.61; H, 6.31; N, 2.92. Found: C, 42.67; H, 6.50; N, 2.72.

Preparation of Cp*W(NO)(*n*-C_7H_{15})(η^3-$CH_2CHCHMe$) (4). Complex **4** was prepared from **1** and *n*-heptane in a manner identical to that described above for the synthesis of compound **2** from **1** and *n*-pentane. Compound **4** was isolated as orange irregularly shaped crystals in 42% yield.

4: IR (cm^{-1}) 1593 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 0.92 (t, $^3J_{HH}$ = 7.2, 3H, *n*-heptyl Me), 1.08 (overlapping m, 2H, *n*-heptyl CH$_2$), 1.10 (overlapping m, 1H, allyl C*H*Me), 1.30 (m, 1H, *n*-heptyl CH$_2$), 1.36 (br m, 4H, *n*-heptyl CH$_2$), 1.49 (obscured, 4H, *n*-heptyl CH$_2$), 1.51 (s, 15H, C_5Me_5), 1.52 (obscured, 1H, allyl CH$_2$), 1.93 (d, $^3J_{HH}$ = 5.6, 3H, allyl Me), 2.08 (m, 1H, *n*-pentyl CH$_2$), 3.24 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH$_2$), 4.90 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 9.2, $^3J_{HH}$ = 13.6, 1H, allyl CH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 9.4 (C_5*Me*$_5$), 14.4 (*n*-heptyl Me), 16.4 (*n*-heptyl CH$_2$), 17.7 (allyl Me), 23.3, 29.8, 32.7, 34.4, 38.0 (*n*-heptyl CH$_2$), 54.1 (allyl *C*HMe), 74.4 (allyl CH$_2$), 105.5 (*C*$_5$Me$_5$), 109.5 (allyl *C*H). MS (LREI, *m/z*, probe temperature 120 °C) 503 [M$^+$]. Anal. Calcd for $C_{21}H_{37}NOW$: C, 50.09; H, 7.41; N, 2.78. Found: C, 49.97; H, 7.40; N, 2.70.

Preparation of Cp*W(NO)(CH$_2$(cyclohexyl))(η^3-$CH_2CHCHMe$) (5). Complex **5** was prepared from compound **1** and methylcyclohexane in a manner identical to that described above for the synthesis of compound **2** from **1** and *n*-pentane. Compound **5** was isolated as orange irregularly shaped crystals in 42% yield.

5: IR (cm^{-1}): 1591 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6), selected signals: δ 1.00−1.40 (m, cyclohexylmethyl CH$_2$), 1.49 (s, 15H, C_5Me_5), 1.69−1.79 (m, cyclohexylmethyl CH$_2$), 1.89 (d, $^3J_{HH}$ = 6.0, 3H, allyl Me), 2.62 (br d, cyclohexyl CH), 3.38 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH$_2$), 4.94 (ddd, $^3J_{HH}$ = 13.6, $^3J_{HH}$ = 9.2, $^3J_{HH}$ = 7.2, 1H, allyl CH). ^{13}C $\{^1H\}$ (100 MHz, C_6D_6): δ 9.4 (C_5*Me*$_5$), 17.1 (allyl CH$_3$), 24.1, 27.4, 27.7, 37.1, 42.1 (cyclohexylmethyl CH$_2$), 44.5 (cyclohexylmethyl CH), 54.4 (allyl *C*HCH$_3$), 73.9 (allyl CH$_2$), 105.6, (*C*$_5$Me$_5$), 110.3 (allyl CH). MS (LREI, probe temp 100 °C) *m/z* 501 [M$^+$]. Anal. Calcd for for $C_{21}H_{35}NOW$: C, 50.29; H, 7.04; N, 2.79. Found: C, 50.47; H, 7.28; N, 2.78.

Preparation of Cp*W(NO)($CH_2CH_2CH_3$)(η^3-$CH_2CHCHMe$) (6). In a glovebox a sample of **1** (47.5 mg, 0.100 mmol) was dissolved in C_6F_6 (2 mL) in a ca. 50-mL glass reaction bomb charged with a magnetic stir bar. At a vacuum-N_2 dual manifold, propane (ca. 2 mL) was condensed under a gentle flow of N_2 into the reaction bomb maintained in a liquid N_2 bath. The bomb was sealed and placed above a stirrer located behind a blast shield, and its contents were stirred for 20 h., after which time the volatiles were removed in vacuo. Complex

6 was worked up in a manner identical to that described for **2** (vide supra) and was isolated as orange crystalline clusters (30 mg, 65%).

6: IR (cm^{-1}): 1599 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) selected signals δ 1.00 (m, 1H, allyl C*H*CH_3), 1.28 (t, $^3J_{HH}$ = 7.2, 3H, propyl CH_3), 1.50 (s, 15H, C_5Me_5), 1.94 (d, $^3J_{HH}$ = 6.0, 3H, allyl Me), 2.08 (m, 1H, propyl WCH_2), 3.18 (d, $^3J_{HH}$ = 7.6, 1H, allyl CH_2), 4.78 (ddd, $^3J_{HH}$ = 13.6, $^3J_{HH}$ = 9.8, $^3J_{HH}$ = 7.6, 1H, allyl CH). ^{13}C {^1H} (100 MHz, C_6D_6): δ 9.4 (C_5*Me*$_5$), 17.6 (allyl CH_3), 19.4 (propyl CH_2), 22.5 (propyl CH_3), 27.5 (propyl CH_2), 54.1 (allyl *C*HCH_3), 74.3 (allyl CH_2), 105.4, (C_5Me_5), 109.5 (allyl CH). MS (LREI, probe temp 100 °C) *m*/*z* 447 [M^+]. Anal. Calcd for $C_{17}H_{29}NOW$: C 45.65, H 6.53, N 3.13. Found: C 45.80, H 6.81, N 3.22.

Preparation of Cp*W(NO)(CH_2CH_3)(η^3-$CH_2CHCHMe$) (7). In a glovebox a sample of **1** (34.0 mg, 0.072 mmol) was dissolved in C_6F_6 (1 mL) in a 4-dram vial to obtain a light orange solution. The solution was placed in a stainless steel pressure reactor, removed from the glovebox, and purged with C_2H_6 (99.9%) for 10 min. The reactor was pressurized with C_2H_6 (400 psig) and allowed to warm to room temperature. After 20 h, the pressure was released, and the solution was transferred to the top of an alumina I column (0.5 × 4 cm). The column was eluted with 4:1 pentane/Et_2O, and the light yellow band that developed was collected. The solvent was removed from the eluate in vacuo, and the residue was dissolved in a minimum amount of pentane. The solution was stored overnight at −30 °C to induce the deposition of **7** as flaky orange crystals (20.0 mg, 59%).

7: IR (cm^{-1}) 1600 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 1.15−1.28 (m, 3H, allyl C*H*Me and ethyl CH_2Me, overlapping), 1.48 (s, 15H, C_5Me_5), 1.49 (obs, 1H, allyl CH_2), 1.76 (t, $^3J_{HH}$ = 7.3, 3H, ethyl CH_3), 1.93 (d, $^3J_{HH}$ = 5.6, 3H, allyl CH_3), 3.22 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 4.90 (ddd, $^3J_{HH}$ = 13.7, 9.4, 7.0, allyl CH). ^{13}C{^1H} NMR (100 MHz, C_6D_6) δ 8.4 (ethyl CH_2), 9.8 (C_5*Me*$_5$), 18.1 (allyl *C*H_3 or ethyl *C*H_3), 18.5 (allyl *C*H_3 or ethyl *C*H_3), 54.7 (allyl *C*HCH_3), 74.7 (allyl CH_2), 105.9 (C_5Me_5), 109.5 (allyl CH). MS (LREI, *m*/*z*, probe temperature 120 °C) 433 [M^+]. Anal. Calcd for $C_{16}H_{27}NOW$: C, 44.36; H, 6.28; N, 3.23. Found: C, 44.10; H, 6.26; N, 3.17.

Preparation of Cp*W(NO)(CH_3)(η^3-$CH_2CHCHMe$) (8). In a glovebox a sample of **1** (40.0 mg, 0.084 mmol) was dissolved in C_6H_{12} (1.5 mL) in a 4-dram vial to obtain an orange solution. The solution was placed in a stainless steel pressure reactor, removed from the glovebox, and purged with CH_4 (99.99%) for 10 min. The reactor was pressurized with CH_4 (1025 psig) and allowed to warm to room temperature. After 20 h, the pressure was released, and the solution was transferred to the top of an alumina I column (0.5 × 6 cm). The column was eluted with 2:1 pentane/Et_2O, and the light yellow band that developed was collected. The solvent was removed from the eluate in vacuo, and the oily orange residue was recrystallized from pentane layered onto Et_2O. The mixture was stored overnight at −30 °C to induce deposition of **8** as needle-like orange crystals (25.0 mg, 63%).

8: IR (cm^{-1}) 1600 (s, υ_{NO}). ^1H NMR (300 MHz, C_6D_6) δ 0.14 (s, 3H, WCH_3), 1.45 (obs, 1H, allyl CH_2), 1.51 (s, 15H, C_5Me_5), 1.95 (d, $^3J_{HH}$ = 5.8, 3H, allyl CH_3), 3.02 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH_2), 4.60 (ddd, $^3J_{HH}$ = 13.7, 8.7, 7.8, 1H, allyl CH). ^{13}C{^1H} NMR (150 MHz, C_6D_6) δ 3.2 (WCH_3), 10.1 (C_5*Me*$_5$), 16.1 (allyl *C*H_3), 54.5 (allyl *C*HMe), 74.7 (allyl CH_2), 105.8 (C_5Me_5), 107.9 (allyl *C*H) MS (LREI, *m*/*z*, probe temperature 100 °C) 419 [M^+].

Preparation of Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (9). Complex **9** was prepared from **1** (47.5 mg, 0.100 mmol) and tetramethylsilane (ca. 3 mL) and purified in a manner identical to that described above for the synthesis of complex **2**. Complex **9** was isolated as yellow-orange irregularly shaped crystals (37 mg, 75%).

9: IR (cm^{-1}) 1593 (s, ν_{NO}). ^1H NMR (300 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, C$H_2$$SiMe_3$), −0.09 (d, $^2J_{HH}$ = 13.2, 1H, C$H_2$$SiMe_3$), 0.37 (s, 9H, $SiMe_3$), 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 Me), 3.36 (d, $^3J_{HH}$ = 7.0 1H, allyl CH_2), 5.10 (ddd, $^3J_{HH}$ = 13.8, $^3J_{HH}$ = 9.4, $^3J_{HH}$ = 7.0, 1H, allyl CH). δ (minor isomer) selected signals −0.76 (d, $^2J_{HH}$ = 13.2, 1H, C$H_2$$SiMe_3$), −0.48 (d, $^2J_{HH}$ = 13.2, 1H, C$H_2$$SiMe_3$). 0.40 (s, 9H, $SiMe_3$), 1.34 (d, $^3J_{HH}$ = 5.8, 3H, allyl Me), 1.49 (s, 15H, C_5Me_5), 2.12 (m, 1H, allyl CH_2), 2.24 (m, 1H, allyl CH), 4.61 (m, 1H, allyl CH). ^{13}C{^1H} NMR (75 MHz, C_6D_6) δ −6.2 (CH_2-$SiMe_3$), 4.1 (CH_2Si*Me*$_3$), 10.3 (C_5*Me*$_5$), 17.1 (allyl Me), 53.3 (allyl *C*HMe), 74.5 (allyl CH_2), 106.5 (C_5Me_5), 114.2 (allyl *C*H). MS (LREI, *m*/*z*, probe temperature 100 °C) 491 [M^+]. Anal. Calcd for $C_{18}H_{33}NOW$: C, 44.00; H, 6.77; N, 2.85. Found: C, 44.04; H, 6.90; N, 2.85.

Preparation of Cp*W(NO)($(CH_2)_5Cl$)(η^3-$CH_2CHCHMe$) (10). Complex **10** was prepared from **1** (47.5 mg, 0.100 mmol) and 1-chloropentane (2 mL) in a manner identical to that described above for the synthesis of complex **2**. Complex **10** was not amenable to chromatographic purification and was therefore obtained as an orange-yellow analytically pure solid by crystallization of the crude product from pentane in multiple crops (20 mg, 40%).

10: IR (cm^{-1}): 1598 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6), selected signals: δ 1.10 (m, 1H, allyl C*H*CH_3), 1.49 (s, 15H, C_5Me_5), 1.93 (d, $^3J_{HH}$ = 6.0, 3H, allyl CH_3), 3.14 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH_2), 3.29 (m, 2H, CH_2Cl), 4.87 (ddd, $^3J_{HH}$ = 13.6, $^3J_{HH}$ = 9.6, $^3J_{HH}$ = 7.2, 1H, allyl CH). ^{13}C {^1H} (100 MHz, C_6D_6): δ 9.4 (C_5*Me*$_5$), 15.6 (WCH_2), 17.6 (allyl CH_3), 32.9, 33.5, 34.7 (chloropentyl CH_2), 45.5 (CH_2Cl), 54.3 (allyl *C*HCH_3), 74.3 (allyl CH_2), 105.5, (C_5Me_5), 109.6 (allyl CH). MS (LREI, probe temp 100 °C) *m*/*z* 509 [M^+]. Anal. Calcd for $C_{19}H_{32}$-ClNOW: C 44.77, H 6.33, N 2.75. Found: C 44.66, H 6.49, N 2.69.

Preparation of Cp*W(NO)($CH_2CH_2OCH_2CH_3$)(η^3-$CH_2CHCHMe$) (11). Complex **11** was prepared from **1** (47.5 mg, 0.100 mmol) and Et_2O (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **10**. Complex **11** was obtained as tan solid by crystallization of the crude product from pentane in multiple crops (16 mg, 34%).

11: IR (cm^{-1}): ν(NO) 1595. ^1H NMR (400 MHz, C_6D_6): δ 1.00 (m, 1H, allyl C*H*CH_3), 1.29 (t, $^3J_{HH}$ = 7.0, 3H, C*H*$_3$$CH_2O$), 1.47 (s, 15H, C_5Me_5), 1.49 (obs, 1H, allyl CH_2) 1.88 (d, $^2J_{HH}$ = 5.8, 3H, allyl CH_3), 3.34 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH_2), 3.39 (m, 1H, OCH_2), 3.56 (m, 2H, OCH_2), 4.06 (m, 1H, OCH_2) 4.81 (ddd, $^3J_{HH}$ = 13.6, $^3J_{HH}$ = 9.2, $^3J_{HH}$ = 7.2, 1H, allyl CH). ^{13}C {^1H} (100 MHz, C_6D_6): δ 9.4 (C_5*Me*$_5$), 14.0 (WCH_2), 16.2 (*C*$H_3$$CH_2O$), 17.4 (allyl CH_3), 53.6 (allyl *C*HCH_3), 64.9 (OCH_2), 73.8 (allyl CH_2), 76.8 (OCH_2) 105.8, (C_5Me_5), 110.5 (allyl CH). MS (LREI, probe temp 100 °C) *m*/*z* 477 [M^+]. Anal. Calcd for $C_{18}H_{31}NO_2W$: C 45.30, H 6.55, N 2.93. Found: C 45.48, H 6.71, N 2.67.

Preparation of Cp*W(NO)($CH_2CH_2N(CH_2CH_3)_2$)(η^3-$CH_2CHCHMe$) (12). Complex **12** was prepared from **1** (47.5 mg, 0.100 mmol) and triethylamine (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **10**. Complex **12** was obtained as a viscous yellow oil by precipitation of the crude product from pentane in multiple crops (20 mg, 40%).

12: IR (cm^{-1}) 1596 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) selected signals δ 0.86 (dt, $^3J_{HH}$ = 6.9, $^2J_{HH}$ = 6.9, 1H, W*CH*$_2$), 1.02 (m, 1H, allyl C*H*Me), 1.21 (t, $^3J_{HH}$ = 7.0, 6H, NCH_2*CH*$_3$), 1.49 (s, 15H, C_5-Me_5), 1.89 (d, $^3J_{HH}$ = 5.9, 3H, allyl CH_3), 2.40 (dt, $^3J_{HH}$ = 6.9, $^2J_{HH}$ = 6.9, 1H, W*CH*$_2$), 2.50 (m, 1H, WCH_2*CH*$_2$N), 2.73 (q, $^3J_{HH}$ = 7.0, 4H, N*CH*$_2$$CH_3$), 3.19 (m, 1H, WCH_2*CH*$_2$N), 3.43 (d, $^3J_{HH}$ = 7.0, 1H, allyl C*H*$_2$), 4.86 (ddd, $^3J_{HH}$ = 13.6, $^3J_{HH}$ = 9.4, $^3J_{HH}$ = 7.0, 1H, allyl CH). ^{13}C{^1H} NMR (100 MHz, C_6D_6) δ 9.8 (C_5*Me*$_5$), 11.4 (WCH_2CH_2N), 13.7 (NCH_2*CH*$_3$), 18.0 (allyl *C*H_3), 47.4 (N*CH*$_2$$CH_3$), 54.3 (allyl *C*HMe), 58.0 (NCH_2CH_2W), 73.7 (allyl CH_2), 106.0 (C_5Me_5), 110.4 (allyl *C*H). MS (MALDI-TOF, *m*/*z* 503 [M − 1^+].

Preparation of Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C_\beta H(C_4H_8)C_\alpha H$) (13). Complex **13** was prepared from **1** (47.5 mg, 0.100 mmol) and cyclohexene (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **2**. Complex **13** was obtained as yellow rods by crystallization of the chromatographically purified product from pentane in multiple crops (20 mg, 40%).

13: IR (cm^{-1}) 1588 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 0.37 (dd, $^2J_{HH} = 3.0$, $^3J_{HH} = 9.6$, 1H, allyl CH_2), 1.35−1.45 (overlapping m, 2H, cyclohexyl CH_2), 1.62 (s, 15H, C_5Me_5), 1.72 (dt, 1H, $^3J_{HH} = 12.8$, $^3J_{HH} = 3.0$, 1H, cyclohexyl WCH), 1.77 (m, 2H, cyclohexyl CH_2), 1.90 (m, 1H, cyclohexyl CH_2), 2.07 (m, 1H, $WCH_2CH{=}CHCH_2$), 2.11 (dd, $^2J_{HH} = 3.0$, $^3J_{HH} = 6.4$, 1H, allyl CH_2), 2.39 (m, 1H, cyclohexyl CH), 2.48 (m, 1H, cyclohexyl CH_2), 2.58 (m, 1H, $WCH_2CH{=}CHCH_2$), 2.74 (m, 1H, allyl CH), 5.26 (ddd, $^3J_{HH} = 12.8$, $^3J_{HH} = 9.6$, $^3J_{HH} = 6.4$, 1H, allyl CH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 9.8 (C_5Me_5), 22.5, 32.6, 32.8, 34.4 (cyclohexyl CH_2), 34.2 ($WCH_2CH{=}CHCH_2$), 36.0 (allyl CH_2), 39.7 (WCH), 62.3 (cyclohexyl CH), 102.4 ($WCH_2CH{=}CH$), 105.4 (C_5Me_5), 109.8 ($WCH_2CH{=}CH$). MS (LREI, *m/z*, probe temperature 120 °C) 485 [M^+]. Anal. Calcd for $C_{20}H_{31}NOW$: C, 49.50; H, 6.44; N, 2.89. Found: C, 49.53; H, 6.31; N, 2.71.

Preparation of Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C(CH_3)_2O$) (14). Complex **14** was prepared from **1** (47.5 mg, 0.100 mmol) and acetone (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **2**. Complex **14** was obtained as orange irregularly shaped crystals by storing a concentrated solution of the chromatographically purified product in pentane at −30 °C overnight (18 mg, 39%).

14: IR (cm^{-1}): ν(NO) 1594 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6): δ 0.76 (ddd, $^2J_{HH} = 3.0$, $^3J_{HH} = 9.2$, $^4J_{HH} = 1.2$, 1H, allyl CH_2), 1.35 (s, 3H, $OCMe_2$), 1.40 (s, 3H, $OCMe_2$), 1.52 (dd, 1H, $^2J_{HH} = 12.4$, $^3J_{HH} = 7.6$, $WCH_2CH{=}CHCH_2$), 1.64 (s, 15H, C_5Me_5), 1.71 (dd, $^2J_{HH} = 3.0$, $^3J_{HH} = 6.4$, 1H, allyl CH_2), 1.79 (dd, $^2J_{HH} = 12.4$, $^3J_{HH} = 7.6$, 1H, $WCH_2CH{=}CHCH_2$), 3.98 (dtd, $^3J_{HH} = 12.4$, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.2$, 1H, allyl CH), 6.14 (ddd, $^3J_{HH} = 13.2$, $^3J_{HH} = 9.2$, $^3J_{HH} = 6.4$, 1H, allyl CH). $^{13}C\{^1H\}$ (100 MHz, C_6D_6): δ 10.0 (C_5Me_5), 33.0, 35.8 ($OCMe_2$), 40.8 (allyl CH_2), 42.6 ($WCH_2CH{=}CHCH_2$), 83.5 ($OCMe_2$), 104.7 (C_5Me_5), 111.5 (allyl CH), 118.7 (allyl CH). MS (LREI, probe temp 100 °C) *m/z* 461 [M^+]. Anal. Calcd for $C_{17}H_{27}NO_2W$: C 44.27, H 5.90, N 3.04. Found: C 44.40, H 5.86, N 3.05.

Preparation of Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2C(CH_2CH_3)_2O$) (15). Complex **15** was prepared from **1** (47.5 mg, 0.100 mmol) and 3-pentanone (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **2**. Complex **15** was obtained as orange irregularly shaped crystals by storing a concentrated solution of the chromatographically purified product in pentane at −30 °C overnight (33 mg, 67%).

15: IR (cm^{-1}): 1593 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6), selected signals: δ 0.77 (m, 1H, allyl CH_2), 0.91 (t, $^3J_{HH} = 7.2$, ethyl CH_3), 1.01 (t, $^3J_{HH} = 7.2$, ethyl CH_3), 1.66 (s, C_5Me_5), 1.80 (m, 2H, $CH_2C(C(Et)_2)O$), 3.98 (m, 1H, allyl $CHCH_2$), 6.08 (ddd, $^3J_{HH} = 6.4$, $^3J_{HH} = 8.8$, $^3J_{HH} = 13.2$ 1H, allyl CH_2CH). $^{13}C\{^1H\}$ (100 MHz, C_6D_6): δ 8.5, 10.3 (ethyl CH_3), 10.0 (C_5Me_5), 33.8, 36.9 (ethyl CH_2), 39.3 (allyl CH_2), 40.8 (allyl CH_2), 108.0 (C−O), 109.7 (C_5Me_5), 112.4 (allyl CH), 119.3 (allyl CH). MS (LREI, probe temp 100 °C) *m/z* 489 [M^+]. Anal. Calcd for $C_{19}H_{31}NOW$: C 46.64, H 6.39, N 2.86. Found: C 46.50, H 6.27 11, N 2.83.

Preparation of Cp*W(NO)(η^3,η^1-$CH_2CHCHCH_2CCH_3{=}CCH_3$) (16). Complex **16** was prepared from **1** (47.5 mg, 0.100 mmol) and 2-butyne (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **2**. Complex **16** was obtained as orange rod-shaped crystals by storing a concentrated solution of the chromatographically purified product in pentane at −30 °C overnight (30 mg, 66%).

16: IR (cm^{-1}): 1609 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6), selected signals: δ 0.52 (dd, $^2J_{HH} = 2.4$, $^3J_{HH} = 9.6$, 1H, allyl CH_2), 1.63 (s, 15H, C_5Me_5), 1.71 (s, 3H, 2-buytne CH_3), 2.17 (s, 3H, 2-buytne CH_3), 2.42 (dd, $^3J_{HH} = 2.4$, $^3J_{HH} = 6.8$, 1H, allyl CH_2), 2.48 (dd, $^3J_{HH} = 6.8$, $^2J_{HH} = 16$, 1H, allyl CH_2), 2.68 (dd, $^3J_{HH} = 3.6$, $^2J_{HH} = 16$, allyl CH_2), 3.28 (m, 1H, allyl CH), 5.38 (ddd, $^3J_{HH} = 6.8$, $^3J_{HH} = 9.6$, $^3J_{HH} = 13.2$, allyl CH). $^{13}C\{^1H\}$ (100 MHz, C_6D_6): δ 10.3(C_5Me_5), 18.1, 26.4 (CH_3), 38.8 (allyl CH_2), 41.9 (CH_2), 101.9 (allyl CH), 106.8 (C_5Me_5), 111.9, (allyl CH), 154.5, 158.7 (C=C). MS (LREI, probe temp 100 °C) *m/z* 457 [M^+]. Anal. Calcd for $C_{18}H_{27}NOW$: C 47.28, H 5.95, N 3.06. Found: C 47.20, H 6.21, N 2.75.

Preparation of Cp*W(NO)(η^1-$CH_2CMe{=}CMe_2$)(η^3-$CH_2CHCHMe$) (17). Complex **17** was prepared from **1** (47.5 mg, 0.100 mmol) and 2,3-dimethyl-2-butene (2 mL) and worked up in a manner identical to that described above for the synthesis of complex **2**. Complex **17** was obtained as orange irregularly shaped crystals by storing a concentrated solution of the chromatographically purified product in THF/HMDS at −30 °C overnight (24 mg, 49%).

17: IR (cm^{-1}): 1597 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6), selected signals: δ 1.30 (m, 1H, allyl $CHCH_3$) 1.50 (s, 15H, C_5Me_5), 1.88 (s, 3H, CH_3), 1.93 (br s, 9H, CH_3), 2.14 (d, $^3J_{HH} = 8.8$, 1H, WCH_2), 3.31 (d, $^3J_{HH} = 6.8$, allyl CH_2), 4.8 (ddd, $^3J_{HH} = 13.12$, $^3J_{HH} = 8.8$, $^3J_{HH} = 6.8$, 1H, allyl CH). $^{13}C\{^1H\}$ (100 MHz, C_6D_6): δ 9.5 (C_5Me_5), 17.2 (methylallyl CH_3), 20.9 (WCH_2), 21.0, 21.1, 21.9 (trimethylallyl CH_3), 55.9 (methylallyl $CHCH_3$), 77.0 (methylallyl CH_2), 105.8, (C_5Me_5), 111.0 (methylallyl CH), 116.7, 140.7 (trimethylallyl olefinic C). MS (LREI, probe temp 100 °C) *m/z* 487 [M^+]. Anal. Calcd for $C_{20}H_{33}NOW$: C 49.73, H 6.02, N 2.64. Found: C 49.68, H 6.03, N 2.71.

Preparation of Cp*W(NO)($CH_2C_6H_5$)(η^3-$CH_2CHCHMe$) (18). In a glovebox a sample of **1** (33.0 mg, 0.069 mmol) was dissolved in toluene (1.2 mL) in a 4-dram vial to obtain an orange solution. This solution was left to sit in the glovebox for 20 h at room temperature. The orange solution was heated at 50 °C for 20 h to obtain a brown solution. The brown solution was transferred to the top of an alumina I column (0.5 × 6 cm). The column was eluted with 2:1 pentane/Et_2O, and the light yellow band that developed was collected. The solvent was removed from the eluate in vacuo, and the oily yellow residue was recrystallized from layered 1:1 pentane/Et_2O. The mixture was stored overnight at −30 °C to induce the deposition of **18** as orange crystals (13.0 mg, 39%).

18: IR (cm^{-1}) 1603 (s, ν_{NO}). ^1H NMR (400 MHz, C_6D_6) δ 1.25 (m, 1H, allyl CHMe 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, $^3J_{HH} = 9.1$, 1H, benzyl CH_2), 2.82 (d, $^3J_{HH} = 9.1$, 1H, benzyl CH_2), 3.43 (d, $^3J_{HH} = 7.4$, 1H, allyl CH_2), 4.43 (ddd, $^3J_{HH} = 13.6$, 9.3, 7.0, 1H, allyl CH) 7.00 (d, $^3J_{HH} = 7.4$, 1H, para CH), 7.29 (t, $^3J_{HH} = 7.4$, 2H, meta CH), 7.51 (d, $^3J_{HH} = 7.4$, 2H, ortho CH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 9.8 (C_5Me_5), 17.5 (allyl CH_3), 21.1 (benzyl CH_2), 56.5 (allyl $CHCH_3$), 77.0 (allyl CH_2), 110.4 (allyl CH), 123.5 (Ar C), 128.1 (Ar C), 129.1 (Ar C). MS (LREI, *m/z*, probe temperature 100 °C) 495 [M^+]. 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.

Reaction Between Complex 2 and I_2. In a glovebox, complex **2** (42.0 mg, 0.880 mmol) was dissolved in $CDCl_3$ (3 mL) in a glass bomb containing a small stir bar. HMDS (10 μL) was added via a microsyringe as an NMR integration standard. The ^1H 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 maintained at −60 °C with a dry ice/acetone bath. A solution of I_2 (45.0 mg, 2 equiv) in $CDCl_3$ (15 mL) was prepared in a Schlenk tube, and the solution was added dropwise via a cannula to the resealable vessel maintained at −60 °C. The Schlenk tube was finally rinsed with a small amount of cold $CDCl_3$ (2 × 2 mL) to ensure quantitative transfer. The cold bath was removed after the addition of I_2 was complete, and the reaction mixture was stirred for a further 1 h as it warmed to room temperature. Overall, the reaction mixture changed color from yellow-orange to dark greenish yellow. The resealable vessel was taken into a glovebox, and a small amount of the reaction mixture was transferred into an NMR tube. The sample was analyzed by ^1H NMR spectroscopy, and integration of the area under the triplet at 3.20 ppm (2H, $CH_3CH_2CH_2CH_2CH_2I$) against the HMDS signal revealed that n-$C_5H_{11}I$ had been formed in approximately 73% yield.

Table 1. X-ray Crystallographic Data for Complexes **1**, **2**, **3**, **7**, **15**, **16**, **17**, and **18**

	1	**2**	**3**	**7**
		Crystal Data		
empirical formula	$C_{19}H_{33}NOW$	$C_{19}H_{33}NOW$	$C_{17}H_{30}NOPW$	$C_{16}H_{27}NOW$
crystal habit, color	prism, yellow	rod, yellow	prism, yellow	prism, yellow
crystal size (mm)	0.45 0.30 0.20	0.35 0.20 0.10	0.35 0.20 0.20	0.35 0.30 0.05
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
volume (Å^3)	1940.63(8)	1919.05(17)	1875.15(16)	1622.3(4)
A (Å)	9.0412(2)	8.9209(5)	8.1936(4)	11.7746(16)
B (Å)	14.2430(3)	18.9252(9)	15.3514(8)	9.4294(13)
C (Å)	15.6092(4)	11.3669(6)	14.9078(7)	14.829(2)
α (deg)	90	90	90	90
β (deg)	105.103(1)	90.286(3)	90.020(1)	99.830(7)
γ (deg)	90	90	90	90
Z	4	4	4	4
density (calculated) (mg/m^3)	1.627	1.645	1.698	1.774
absorption coefficient (mm^{-1})	5.955	6.022	6.245	7.114
F_{000}	944	944	944	848
		Data Collection and Refinement		
measured reflections: total	29663	36501	15837	21587
measured reflections: unique	4599	4679	4503	3767
final R indices[a]	R1 = 0.0178, wR2 = 0.0423	R1 = 0.0232, wR2 = 0.0526	R1 = 0.0216, wR2 = 0.0536	R1 = 0.0211, wR2 = 0.0498
goodness-of-fit on F^2 [b]	1.080	1.038	1.014	1.064
largest diff peak and hole (e$^-$ Å^{-3})	1.185 and −0.806	1.619 and −0.774	1.579 and −0.932	0.959 and −0.830

	15	**16**	**17**	**18**
		Crystal Data		
empirical formula	$C_{19}H_{31}NO_2W$	$C_{18}H_{27}NOW$	$C_{20}H_{33}NOW{\cdot}1/2\ (OC_4H_8)$	$C_{21}H_{29}NOW$
crystal habit, color	plate, orange	prism, orange	irregular, orange	prism, yellow
crystal size (mm)	0.5 0.5 0.1	0.5 0.4 0.3	0.40 0.30 0.30	0.20 0.20 0.05
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_12_12_1$
volume (Å^3)	1877.8(2)	1660.9(3)	4391.3(7)	1902.05(12)
a (Å)	9.2125(8)	10.2949(9)	30.129(3)	8.7093(3)
b (Å)	14.4236(12)	12.0055(13)	9.0268(9)	13.8379(5)
c (Å)	14.8434(3)	13.5878(14)	17.0499(13)	15.7822(6)
α (deg)	90	90	90	90
β (deg)	107.809(4)	98.512(5)	108.735(3)	90
γ (deg)	90	90	90	90
Z	4	4	8	4
density (calculated) (mg/m^3)	1.731	1.829	1.583	1.730
absorption coefficient (mm^{-1})	6.161	6.954	5.273	6.080
F_{000}	968	896	2096	976
		Data Collection and Refinement		
measured reflections: total	19800	21396	25263	17222
measured reflections: unique	4493	3834	5277	4538
final R indices[a]	R1 = 0.0256, wR2 = 0.0694	R1 = 0.0186, wR2 = 0.0464	R1 = 0.0322, wR2 = 0.0827	R1 = 0.0273, wR2 = 0.0581
goodness-of-fit on F^2 [b]	1.059	1.063	1.050	1.087
largest diff peak and hole (e$^-$ Å^{-3})	1.625 and −1.802	1.048 and −1.122	2.099 and −1.051	0.931 and −0.877

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

The volatiles from the final reaction mixture were then vacuum-transferred into another Schlenk tube and were analyzed by ^{1}H NMR spectroscopy. Signals at 3.20 ppm (t, 2H, $CH_3CH_2CH_2CH_2CH_2I$), 1.84 ppm (m, 2H, $CH_3CH_2CH_2CH_2CH_2I$), 1.38 ppm (m, 4H, $CH_3CH_2CH_2CH_2CH_2I$, $CH_3CH_2CH_2CH_2CH_2I$), and 0.91 ppm (t, 3H, $CH_3CH_2CH_2CH_2CH_2I$) indicated the presence of 1-iodopentane, as confirmed by comparison with a ^{1}H NMR spectrum of an authentic sample. The volatiles were also analyzed by EI-MS. The presence of 1-iodopentane was indicated by a signal at m/z =197.9 [P$^+$], while a signal at m/z = 181.9 indicated the presence of at least one isomer of methallyl iodide.

The final organometallic residue was extracted with pentane (2 × 20 mL). The extracts were filtered through Celite supported on a medium-porosity frit. The pentane was removed from the filtrate in vacuo, and the green-yellow residue was analyzed by ^{1}H NMR and IR spectroscopy. Spectroscopic data [^{1}H NMR in $CDCl_3$: δ 2.18 (C_5Me_5); IR (Nujol mull): ν 1630 cm^{-1} (ν_{NO}); MS (LREI, probe temp 100 °C) m/z 603 [M$^+$]] were consistent with the residue being principally the well-known Cp*W(NO)I_2.[19]

Reaction between Complex 9 and I_2. In a glovebox, complex **9** (40.0 mg, 0.081 mmol) was dissolved in $CDCl_3$ (1.5 mL) in a glass bomb 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 above. The final mixture was analyzed by ^{1}H NMR spectroscopy, and integration of the area under the singlet at 0.17 ppm (9H, Me_3SiCH_2I) against the C_6H_6 signal revealed that (iodomethyl)trimethylsilane had been formed in approximately 57% yield.

Reaction between Complex 18 and I_2. In a glovebox, complex **18** (24.0 mg, 0.051 mmol) was dissolved in $CDCl_3$ (1.5 mL) in a glass bomb containing a small stir bar. HMDS (10 μL) was added via a microsyringe as an NMR integration standard. The reaction with I_2

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was performed as described above. The final mixture was analyzed by ^{1}H NMR spectroscopy, and integration of the area under the singlet at 4.47 ppm (2H, $(C_6H_5)CH_2I$) against the HMDS signal revealed that (iodomethyl)benzene had been formed in approximately 45% yield.

X-ray Crystallography. Data collection for each compound was carried out at −100 ± 1 °C on a Rigaku AFC7/ADSC CCD diffractometer or on a Bruker X8 APEX diffractometer, using graphite-monochromated Mo Kα radiation.

Data for **1** were collected to a maximum 2θ value of 55.8° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] All non-hydrogen atoms were refined anisotropically; hydrogen atoms H1a, H1b, H2, H3, H5a, and H5b 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 4599 observed reflections and 232 variable parameters.

Data for **2** were collected to a maximum 2θ value of 56.4° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The crystal was a two-component twin. All non-hydrogen atoms were refined anisotropically; hydrogen atoms H1a, H1b, 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 4679 observed reflections and 222 variable parameters.

Data for **3** were collected to a maximum 2θ value of 55.8° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] All non-hydrogen atoms were refined anisotropically; hydrogen atoms H1a, H1b, H2, H3, H4a, and H4b 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 4503 observed reflections and 222 variable parameters.

Data for **7** were collected to a maximum 2θ value of 55.4° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The two (mirror-image) chiral isomers of the compound cocrystallized to produce a crystallographically averaged solution. This was modeled as two disordered components called Part A and Part B for the methylallyl ligand and the ethyl ligand. Each part had 50% occupancy. All non-hydrogen atoms were refined anisotropically. Related bond distances in the two parts were constrained to the same length within a standard deviation of 0.02 for the following pairs: C1a-C2a and C1b-C2b; C2a-C3a and C2b-C3b; C3a-C4a and C3b-C4b; C5a-C6a and C5b-C6b; W1−C5a and W1−C5b; C1a-C3a and C1b-C3b; and C2a-C4a and C2b-C4b. All hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 3767 observed reflections and 235 variable parameters.

Data for **15** were collected to a maximum 2θ value of 56.0° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] All non-hydrogen atoms were refined anisotropically; hydrogen atoms H1a, H1b, 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 4493 observed reflections and 231 variable parameters.

Data for **16** were collected to a maximum 2θ value of 55.2° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] All non-hydrogen atoms were refined anisotropically; hydrogen atoms H1a, H1b, 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 3834 observed reflections and 213 variable parameters.

Data for **17** were collected to a maximum 2θ value of 56.0° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] In the crystal lattice **17** was solvated with THF in a 2:1 ratio. The disordered THF molecule was modeled with constrained, isotropic atoms. All other 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 5277 observed reflections and 237 variable parameters.

Data for **18** were collected to a maximum 2θ value of 56.0° in 0.5° oscillations. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] 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 4538 observed reflections and 223 variable parameters.

For each structure neutral-atom scattering factors were taken from Cromer and Waber.[22] Anomalous dispersion effects were included in F_{calc};[23] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[24] The values for mass attenuation coefficients are those of Creagh and Hubbell.[25] All calculations were performed using the CrystalClear software package of Rigaku/MSC,[26] or Shelxl-97.[27] X-ray crystallographic data for all nine structures are presented in Table 1, and full details of all crystallographic analyses are provided in the Supporting Information.

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Supporting Information Available: CIF files providing full details of crystallographic analyses of complexes **1**, **2**, **3**, **7**, **15**, **16**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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