ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Selective Functionalization of a Variety of Hydrocarbon C(sp^3)−H Bonds Initiated by Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHPh$)

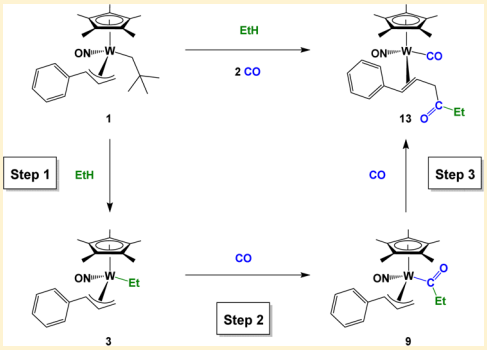
Russell J. Wakeham,[†] Rhett A. Baillie,[†] Brian O. Patrick,[†] Peter Legzdins,*[,†] and Devon C. Rosenfeld[‡]

[†]Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

[‡]The Dow Chemical Company, 2301 North Brazosport Boulevard, Freeport, Texas 77541, United States

Supporting Information

ABSTRACT: Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHPh$) (**1**) effects C(sp^3)−H activations of methane, ethane, propane, and *n*-butane exclusively at their terminal carbons and forms the corresponding Cp*W(NO)(alkyl)(η^3-CH_2-CHCHPh) complexes. It also activates (*n*-Bu)$_2$O, 1-chloropropane, and Me_4Si in a similar manner. Exposure of the Cp*W(NO)(alkyl)(η^3-$CH_2CHCHPh$) complexes to carbon monoxide results in initial 1,1-CO insertion into the newly formed tungsten−alkyl bonds and formation of the corresponding η^1-acyl complexes, some of which can be isolated. Additional functionalization of the C−H activation products occurs upon exposure to CO under more forcing conditions. Such treatment produces η^2-bound unsaturated-ketone complexes resulting from CO insertion into the W−alkyl σ bonds followed by cross-coupling of the η^1-acyl and the η^3-allyl ligands and coordination of CO at the resulting vacant coordination site at tungsten. The unsaturated ketones can be released from the metal's coordination spheres either by photolysis of the complexes in MeCN or by further exposure of them to CO. All new compounds have been characterized by conventional spectroscopic and analytical methods, and the solid-state molecular structures of six of them have been established by single-crystal X-ray crystallographic analyses.



INTRODUCTION

In the preceding article we reported the direct conversion of methane into unsymmetrical, unsaturated ketones and indicated why these conversions are of importance.[1] These transformations are initiated by Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) (Cp* = η^5-C_5Me_5).[1] Thus, sequential exposure of a cyclohexane solution of the alkyl allyl complex to methane and then CO at slightly elevated temperatures and pressures affords a good yield of the unsaturated ketones 5-methylhex-4-en-2-one and 3,3-dimethylpent-4-en-2-one in a 3:2 ratio. Four intermediate organotungsten complexes are involved in these conversions, which proceed in a stepwise manner, and they have all been isolated and fully characterized. However, this chemistry involving Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCMe_2) cannot be extended to encompass other light alkanes, since its thermolysis in aliphatic alkanes affords mixtures of various Cp*W(NO)(H)(η^3-allyl) complexes in which the allyl ligand is derived from three successive C(sp^3)−H activations of the hydrocarbon substrate while the original dimethylallyl ligand is lost.[2,3] In contrast, under similar experimental conditions other Cp*W(NO)(CH_2CMe_3)(η^3-CH_2CHCHR) compounds effect the selective single activation of a terminal C(sp^3)−H bond of the hydrocarbon substrate to produce an isolable η^1-hydrocarbyl complex.[4] These latter compounds would thus appear to be ideal candidates for initiating the selective activation and functionalization not only of methane but also of ethane, propane, and *n*-butane. To test this hypothesis, we have decided to investigate more fully the thermal chemistry of the phenylallyl complex Cp*W(NO)(CH_2CMe_3)(η^3-CH_2-CHCHPh) (**1**) as a representative member of this family of compounds.[5]

We have previously established that thermolysis of **1** at 55 °C leads to the loss of neopentane and the formation of the 16e η^2-allene intermediate complex Cp*W(NO)(η^2-CH_2=C=CHPh). In the presence of *n*-pentane, *n*-heptane, or *n*-octane, this intermediate complex effects C−H activations of the hydrocarbons exclusively at their terminal carbons and forms 18e Cp*W(NO)(*n*-alkyl)(η^3-$CH_2CHCHPh$) complexes.[5] The results of DFT calculations on the model reaction of CpW(NO)(η^2-CH_2=C=CHMe) with propane have confirmed that the rate-determining step is the cleavage of a propane C−H bond and that the lower energy anti conformers favor terminal activation by 11.5 kJ/mol.[5] We have now extended our investigations of the thermal chemistry of **1** to encompass gaseous hydrocarbons as well as hydrocarbon substrates containing heteroatoms such as silicon, oxygen, and halogens. We have also effected the functionalization of the hydrocarbyl complexes resulting from the C−H activation processes by first exposing them to carbon monoxide to form the corresponding η^1-acyl complexes and then releasing the newly formed acyl ligands from the metal's coordination sphere by a combination of

Special Issue: Hydrocarbon Chemistry: Activation and Beyond

Received: September 19, 2016

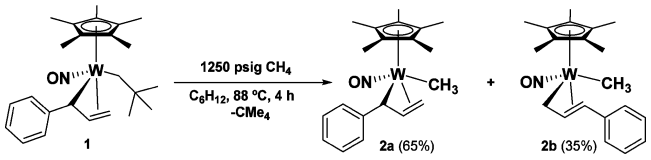
DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

chemical and physical methods. This article reports the results of our investigations.

RESULTS AND DISCUSSION

Selective C−H Activations of Gaseous Alkanes Effected by Complex 1. *Methane.* The C−H activation of methane by **1** in cyclohexane affords Cp*W(NO)(CH_3)(η^3-CH_2CHCHPh) (**2**) (Scheme 1), which has been isolated in

Scheme 1. C−H Activation of Methane by 1



53% yield as a yellow solid that is both air and moisture stable for several days.

In solution, **2** exists as two isomers in a 65:35 ratio which differ in the position of the phenyl substituent of the allyl ligand. In the major isomer (**2a**) the phenyl substituent is distal to the methyl ligand, while in the minor isomer it is distal to the nitrosyl ligand. The orientation of the substituent has been determined by Sel NOE NMR spectroscopy, which has also established that the two isomers exchange in solution. The solid-state molecular structure of **2b** has been confirmed by a single-crystal X-ray crystallographic analysis and is shown in Figure S1 in the Supporting Information.

The family of Cp*W(NO)(alkyl)(η^3-allyl) complexes generally displays a characteristic $\sigma-\pi$ distortion of the allyl ligand in which the allyl ligand does not have equal carbon−carbon bond lengths but rather one longer (σ) and one shorter bond (π). The shorter (π) C−C bond of the allyl is located trans to the nitrosyl ligand (with the σ terminus being proximal to the nitrosyl).[4] The origin of the $\sigma-\pi$ distortion is a result of the electronic asymmetry at the metal center, which is caused by both the nitrosyl and the cyclopentadienyl ligands.[4,6] This effect is manifested in the solid-state molecular structures of the complexes by different allyl C−C bond lengths and in solution by ^{13}C NMR chemical shift values indicating more sp^2 (downfield) or sp^3 (upfield) character of the carbon.[3,7] The latter feature is illustrated for the two isomers of **2** in Figure 1.

Since the $\sigma-\pi$ distortion of the allyl ligand is inherent to the Cp*W(NO)(R)(η^3-allyl) (R = H, alkyl, aryl) complexes,[4,8] the

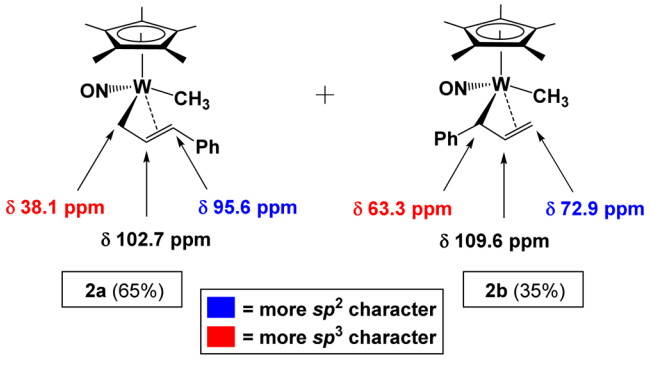
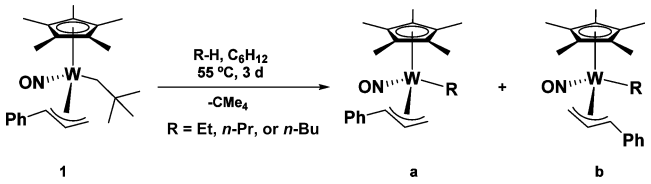


Figure 1. $\sigma-\pi$ distortion of the allyl ligand in the isomers of **2** manifested by the chemical shifts of the signals due to the allyl C atoms in the ^{13}C APT NMR spectrum.

chemical shifts of the allyl carbon signals in the ^{13}C NMR spectrum of a mixture of isomers can be used to determine the orientation of the allyl ligand for the various isomers of a complex.[9] This distortion occurs to some extent in all of the allyl complexes discussed in this report, but they are generally drawn with symmetrical allyl ligands to be consistent with the preceding article.[1]

Ethane, Propane, and n-Butane. The single C−H activation of ethane, propane, and *n*-butane by **1** can be effected in a fashion similar to that described in the preceding section for methane by using cyclohexane as an inert solvent (Scheme 2).

Scheme 2. C−H Activation of Ethane, Propane, and *n*-Butane by 1



Under 250−400 psig of substrate, C−H activation of the C2−C4 alkanes forms the corresponding tungsten complexes Cp*W(NO)(CH_2CH_3)(η^3-CH_2CHCHPh) (**3**), Cp*W(NO)($CH_2CH_2CH_3$)(η^3-CH_2CHCHPh) (**4**), and Cp*W(NO)($CH_2CH_2CH_2CH_3$)(η^3-CH_2CHCHPh) (**5**), respectively, in good yields. All exist as a pair of isomers in solution differing in the orientation of the phenyl substituent of the allyl relative to the nitrosyl and alkyl ligands. The major isomer **a** for all three complexes **3**−**5** (>90%) has the phenyl substituent proximal to the nitrosyl ligand. This observation is consistent with the notion that increasing the steric bulk of the alkyl group from a methyl to an ethyl (or larger) ligand favors the phenyl substituent being distal from the alkyl ligand.

The similar solid-state molecular structures of **3a**−**5a** have been established by single-crystal X-ray crystallographic analyses, and that of **4a** is shown in Figure 2 as a representative example, while those of **3a** and **5a** are shown in Figures S2 and S3 in the Supporting Information. Complex **4a** has a three-legged piano-stool geometry with the allyl ligand attached to the tungsten in an endo fashion. The *n*-propyl ligand is oriented downward relative to the Cp* ligand, and its β-hydrogens have been located in the electron density map, thus allowing the lengths of the C−H bonds at the β carbon to be determined. These bond lengths are 1.11(6) and 1.02(5) Å, which are longer than typical C−H bonds and agree with those reported for β-agostic metal−alkyl complexes.[10,11] There is also evidence for β-agostic interactions between the tungsten and the alkyl β C−H bonds in the ^{1}H NMR spectra of **3a**−**5a**. For instance, the ethyl signal of **3a** is a triplet ($^3J_{HH}$ = 7.34 Hz) with ^{183}W satellites ($^3J_{WH}$ = 5.1 Hz) and has an atypically downfield chemical shift at δ 1.78 ppm. The small value of the tungsten−proton coupling constant is consistent with the existence of longer-range coupling, since tungsten hydride signals of similar Cp*W(NO)(H)(η^3-allyl) complexes have significantly larger coupling constants, typically 120 Hz in magnitude.[3] The β-agostic interaction is an arrested transition state for β-elimination[10,11] and does not commonly persist in complexes, especially at room temperature.[12]

Selective C−H Activations of Heteroatom-Containing Hydrocarbons by 1. *(n-Bu)$_2$O.* Thermolysis of **1** in neat (n-Bu)$_2$O at 55 °C for 3 days affords two isomers of the product

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

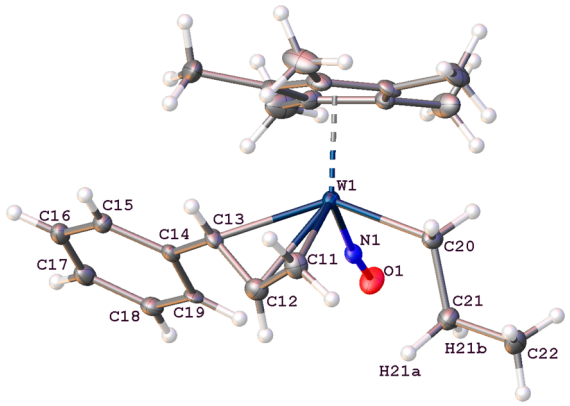
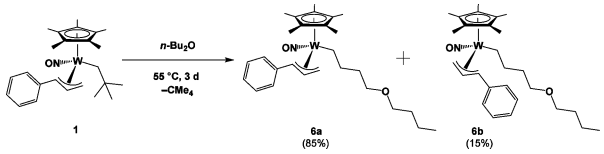


Figure 2. Solid-state molecular structure of **4a** with 50% probability thermal ellipsoids shown. Selected bond lengths (Å) and angles (deg): W(1)−C(11) = 2.341(5), W(1)−C(12) = 2.323(5), W(1)−C(13) = 2.317(4), C(11)−C(12) = 1.390(7), C(12)−C(13) = 1.416(7), C(13)−C(14) = 1.475(6), W(1)−C(20) = 2.230(5), C(20)−C(21) = 1.539(6), C(21)−H(21a) = 1.11(6), C(21)−H(21b) = 1.02(5), C(21)−C(22) = 1.528(7), W(1)−N(1) = 1.776(4), N(1)−O(1) = 1.227(5); C(11)−C(12)−C(13) = 117.3(4), C(12)−C(13)−C(14) = 125.0(4), W(1)−C(20)−C(21) = 116.2(3), C(20)−C(21)−C(22) = 113.1(4), H(21b)−C(21)−H(21b) = 120(4), W(1)−N(1)−O(1) = 169.6(3).

$Cp^*W(NO)((CH_2)_4O(CH_2)_3CH_3)(\eta^3\text{-}CH_2CHCHPh)$ (**6**), which is the result of a single activation of a terminal C−H bond (Scheme 3). The selectivity of the reaction has been

Scheme 3. C−H Activation of $(n\text{-Bu})_2O$ by 1



established by the ^{13}C APT NMR spectrum, which exhibits seven methylene C signals, including two α to the oxygen and only one methyl signal due to the ether ligand. There is no evidence for activation of the weaker C−H bonds α to the oxygen, thereby suggesting that the selectivity is determined by steric considerations.

The ^1H NMR spectrum of **6** indicates that interactions between the tungsten center and the C−H bonds of the ether ligand result in restricted rotation of the four methylene units between the tungsten and the oxygen.[12] The signals due to the α–δ (relative to tungsten) methylene protons of the ether ligand are all diastereotopic and show second-order effects at the α, γ, and δ positions. There is also a pronounced separation in the chemical shifts of the signals due to the β protons (δ 2.14 and 1.63 ppm). Interestingly, the restricted rotation persists all the way to the δ-methylene position (Figure 3a). In contrast, the other CH_2O signal is the expected triplet (Figure 3b), indicating free rotation for the butyl group attached to the oxygen.

1-Chloropropane. The thermolysis of **1** at 55 °C in 1-chloropropane for 3 days affords a dark green mixture which contrasts with the yellow-orange-brown mixtures typically obtained for C−H activation reactions effected by **1**. Spectroscopic analysis of the final reaction mixture reveals the signals for the expected product of C−H activation, Cp^*W

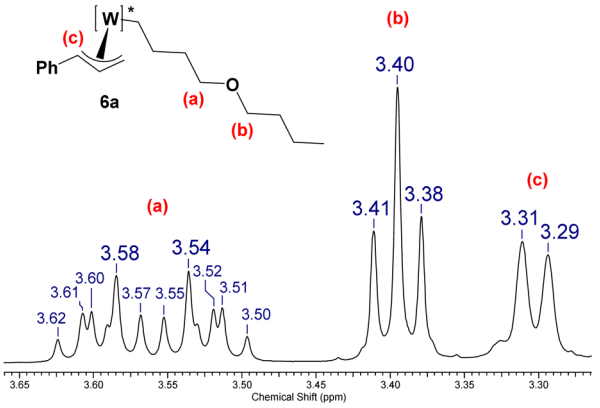
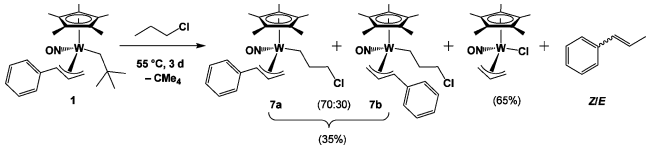


Figure 3. Expansion of the 400 MHz ^1H NMR spectrum of **6** in C_6D_6 from δ 3.66 to 3.27 ppm ([W]* = Cp*W(NO)): (a) multiplet centered at δ 3.56 ppm corresponding to CH_2O proximal to tungsten indicating possible restricted rotation; (b) triplet at δ 3.40 ppm corresponding to CH_2O distal to tungsten indicating free rotation of bonds; (c) doublet at δ 3.30 corresponding to allyl CH_2 (1H).

$(NO)(CH_2CH_2CH_2Cl)(\eta^3\text{-}CH_2CHCHPh)$ (**7**), in addition to $Cp^*W(NO)(Cl)(\eta^3\text{-}CH_2CHCH_2)$, and (*Z*)- and (*E*)-$\beta$-methylstyrene (Scheme 4).

Scheme 4. Reaction of 1 with 1-Chloropropane



Complex **7** can be purified by column chromatography over basic alumina and is isolated as a yellow solid in relatively low yield (22%). In solution, two isomers of **7** are observed in a 70:30 ratio using ^1H NMR spectroscopy. The selectivity for activation of a terminal C−H bond is confirmed by the ^{13}C APT NMR spectrum, which exhibits three methylene signals for the chloropropyl ligand. Crystallization of **7** from a 1:1 mixture of Et_2O/pentane affords only the minor isomer **7b** as a pair of enantiomers not related by one of the space group's symmetry elements. The solid-state molecular structure of each enantiomer viewed from a different angle is shown in Figure 4. Like the structures of the other Cp*W(NO)(alkyl)-$(\eta^3\text{-}CH_2CHCHPh)$ complexes, the metrical parameters of **7b** reveal the σ–π distortion of the allyl ligand and the downward orientation of the 3-chloropropyl ligand such that the β C−H bonds can interact with the tungsten center, a β-agostic interaction[12] that is confirmed by ^1H NMR spectroscopy.

The low yield of **7** and the presence of $Cp^*W(NO)(Cl)(\eta^3\text{-}CH_2CHCH_2)$ are consistent with a proclivity for complex **7** to undergo β-H elimination more readily than other Cp*W-$(NO)(n\text{-alkyl})(\eta^3\text{-}CH_2CHCHPh)$ complexes. The probable mechanism for the transformation of **7a** into $Cp^*W(NO)(Cl)(\eta^3\text{-}CH_2CHCH_2)$ is outlined in Scheme 5. Complex **7a** first undergoes a β-H abstraction that transfers the H from the $n\text{-}CH_2CH_2CH_2Cl$ ligand to the terminus of the phenylallyl ligand to give $Cp^*W(NO)(\eta^2\text{-}PhCH{=}CHMe)(\eta^2\text{-}CH_2{=}CHCH_2Cl)$. Loss of (*E*)-$\beta$-methylstyrene generates the 16e organometallic complex $Cp^*W(NO)(\eta^2\text{-}CH_2{=}CHCH_2Cl)$, which then undergoes an intramolecular C−Cl bond cleavage and converts to $Cp^*W(NO)(Cl)(\eta^3\text{-}CH_2CHCH_2)$.

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

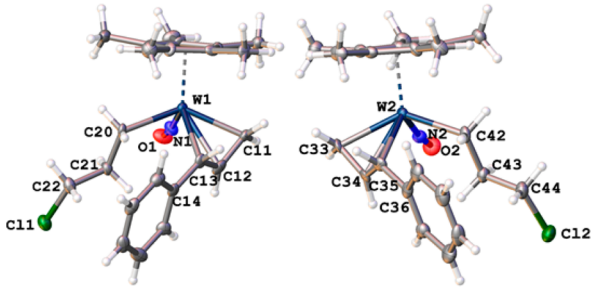
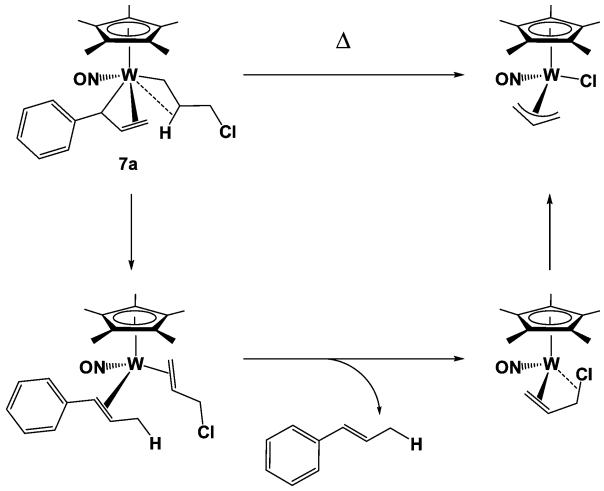


Figure 4. Reoriented solid-state molecular structures for the enantiomers of **7b** with 50% probability thermal ellipsoids shown. Selected bond lengths (Å) and angles (deg): W(1)−C(11) = 2.238(8), W(1)−C(12) = 2.349(8), W(1)−C(13) = 2.524(8), C(11)−C(12) = 1.435(13), C(12)−C(13) = 1.360(13), C(13)−C(14) = 1.482(12), W(1)−C(20) = 2.227(8), C(20)−C(21) = 1.530(12), C(21)−C(22) = 1.520(11), C(22)−Cl(1) = 1.807(9), W(1)−N(1) = 1.763(7), N(1)−O(1) = 1.232(8), W(2)−C(33) = 2.229(8), W(2)−C(34) = 2.344(7), W(2)−C(35) = 2.518(8), C(33)−C(34) = 1.437(12), C(34)−C(35) = 1.374(13), C(35)−C(36) = 1.477(12), W(2)−C(42) = 2.243(8), C(42)−C(43) = 1.521(12), C(43)−C(44) = 1.520(12), C(44)−Cl(2) = 1.814(10); C(11)−C(12)−C(13) = 119.2(9), C(12)−C(13)−C(14) = 126.0(9), W(1)−C(20)−C(21) = 113.5(5), W(1)−N(1)−O(1) = 170.2(7), C(33)−C(34)−C(35) = 117.6(8), C(34)−C(35)−C(36) = 126.4(9), W(2)−C(42)−C(43) = 113.0(5), W(2)−N(2)−O(2) = 170.6(6).

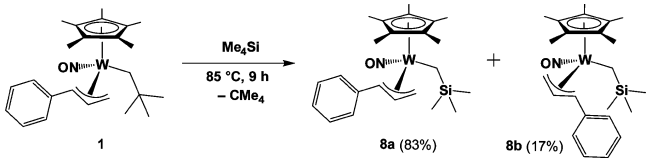
Scheme 5. Probable Mechanism for the Transformation of 7a into Cp*W(NO)(Cl)(η^3-CH_2CHCH_2)



The β-H elimination exemplified by conversion of **7** into Cp*W(NO)(Cl)(η^3-CH_2CHCH_2) through the loss of (*E*)-β-methylstyrene offers some insight into the decomposition of other Cp*W(NO)(*n*-alkyl)(η^3-$CH_2CHCHPh$) complexes. For instance, this fact explains why the C−H activation of C2 and larger alkanes must be carried out at 55 °C to avoid decomposition through β-H elimination. It is also consistent with the C−H activation of methane being able to be effected at a higher temperature without concomitant decomposition.

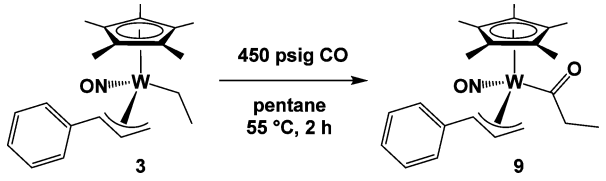
Tetramethylsilane. The C−H activation of Me_4Si by **1** is performed at elevated temperature to obtain two isomers of yellow Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHPh$) (**8**) in a 5:1 ratio (Scheme 6). As with the C−H activation of methane, the lack of β-hydrogens in the product renders **8** more thermally stable, thereby allowing for a shorter reaction time at a higher temperature.

Scheme 6. C−H Activation of Tetramethylsilane by 1



1,1-CO Insertion into the Newly Formed W−Alkyl Bonds. *W−Ethyl Linkage.* The ethyl ligand of complex **3** derived from the C−H activation of ethane can be selectively functionalized by exposing **3** to 450 psig of CO at 55 °C for 2 h (Scheme 7). The acyl complex Cp*W(NO)(C(=O)-CH_2CH_3)(η^3-$CH_2CHCHPh$) (**9**) is formed cleanly and has been isolated in 73% yield by recrystallization.

Scheme 7. Carbonylation of 3 to Produce the Acyl Complex 9



The solid-state molecular structure of **9** is shown in Figure 5, and it verifies the 1,1-insertion of CO into the W−C bond of the ethyl ligand. The allyl ligand has an endo conformation relative to the Cp* ligand, and the phenyl substituent is confirmed to be proximal to the nitrosyl ligand.

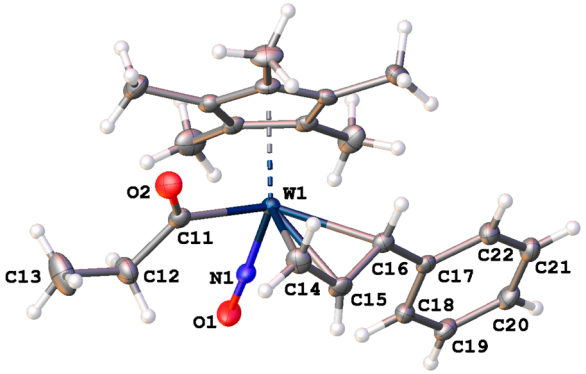
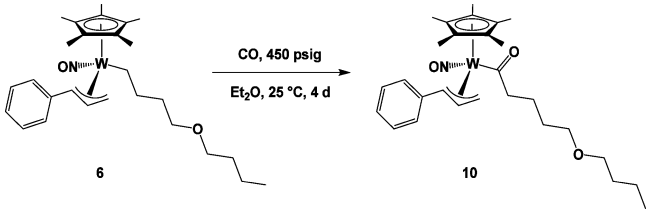


Figure 5. Solid-state molecular structure of **9** with 50% probability thermal ellipsoids shown. Selected bond lengths (Å) and angles (deg): W(1)−C(11) = 2.220(5), C(11)−O(2) = 1.218(6), C(11)−C(12) = 1.536(7), C(12)−C(13) = 1.520(7), W(1)−C(14) = 2.343(5), W(1)−C(15) = 2.328(5), W(1)−C(16) = 2.343(5), C(14)−C(15) = 1.394(7), C(15)−C(16) = 1.407(7), C(16)−C(17) = 1.485(6), W(1)−N(1) = 1.773(4), N(1)−O(1) = 1.223(5); W(1)−C(11)−O(2) = 124.2(4), W(1)−C(11)−C(12) = 116.4(3), O(2)−C(11)−C(12) = 119.4(4), C(14)−C(15)−C(16) = 119.0(5), C(15)−C(16)−C(17) = 123.3(4), W(1)−N(1)−O(1) = 171.3(4).

W−$(CH_2)_4$O-n-Bu Linkage. Exposure of an Et_2O solution of **6** to 450 psig of CO at ambient temperature for a period of 4 days results in the production of the acyl allyl complex Cp*W(NO)(C(=O)$(CH_2)_4O(CH_2)_3CH_3$)(η^3-$CH_2CHCHPh$) (**10**) as a yellow solid (Scheme 8). Attempts to obtain single crystals of **10** suitable for an X-ray diffraction analysis have been unsuccessful to date. Instead, ^1H and ^{13}C APT as well as 2D

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

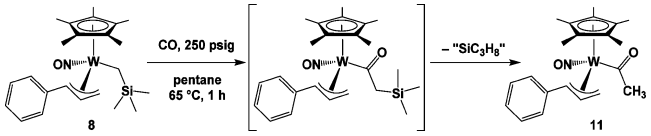
Scheme 8. Carbonylation of 6 To Produce the Acyl Complex 10



NMR spectroscopy, such as {^{1}H−^{13}C} HMBC and {^{1}H−^{13}C} HSQC, have been essential for establishing the 1,1-insertion of CO into the W−C σ bond.

W−CH$_2$SiMe$_3$ Linkage. Exposure of **8** to 250 psig of CO and 65 °C for 1 h does not produce the expected silyl acyl complex but rather Cp*W(NO)(C(=O)CH$_3$)(η^3-CH$_2$CHCHPh) (**11**) (Scheme 9). A similar transformation has been reported for the

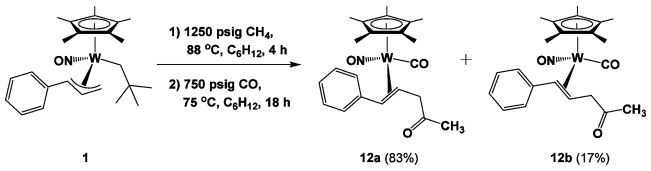
Scheme 9. Conversion of 8 to 11 under CO Pressure



complex Cp*W(NO)(CH$_2$SiMe$_3$)(η^3-CH$_2$CHCHMe).[13] The mechanism of the transformation is not known, but monitoring of the reaction by ^{1}H NMR spectroscopy reveals only the formation of **11**, thereby suggesting that the conversion of the CH$_2$SiMe$_3$ ligand to the C(=O)CH$_3$ ligand on exposure to CO is inherent to the reaction and is not a result of subsequent manipulations. In any event, the transformation shown in Scheme 9 has been used to obtain and characterize compound **11**, which cannot be isolated from the reaction of the methyl complex **2** with CO because of its tendency to undergo further reactions with CO (vide infra).

Additional Functionalization of the C−H Activation Products. Sequential treatment of **1** with methane and then CO at slightly elevated temperatures and pressures produces an η^2-bound olefin complex resulting from CO insertion into the W−CH$_3$ bond followed by cross-coupling to the η^3-allyl ligand and subsequent coordination of CO to the metal center to form the two isomers of complex **12** shown in Scheme 10. Complex

Scheme 10. C−H Activation of Methane and Subsequent Functionalization with CO Initiated by 1



12 probably does result from **2** via 1,1-CO insertion to form compound **11**, which rapidly converts to **12** under the conditions employed.

Efforts to obtain single crystals of **12** for an X-ray diffraction analysis have been unsuccessful to date, and so IR spectroscopy and 1D and 2D NMR spectroscopy have been utilized to characterize the complex, which exists as two isomers in solution differing with respect to the orientation of the η^2-β,γ-ketone ligand. For example, the chemical shifts of the alkene proton resonances in the ^{1}H NMR spectrum can be used to assign the orientation of the unsaturated ketone ligand with respect to the tungsten center. For the major isomer **12a**, the more upfield resonance at δ 2.70 ppm is due to the =C*H* nonbenzylic proton which is oriented toward the Cp* ligand; in addition, the resonance also has satellites due to coupling to the ^{183}W nucleus ($^2J_{WH}$ = 5.6 Hz). In the minor isomer **12b** the η^2-alkene ligand is oriented in the opposite direction, the signal due to the PhC*H*= proton having the more upfield chemical shift at δ 2.41 ppm. These spectroscopic properties resemble those exhibited by the related complexes Cp*W(NO)(CO)(η^2-Me$_2$C=CHCH$_2$C(O)CH$_3$) and Cp*W(NO)(CO)(η^2-CH$_2$=CHCMe$_2$C(O)CH$_3$), the solid-state molecular structure of the latter having been established by a single-crystal X-ray crystallographic analysis.[1]

Similar sequential treatment of **1** with ethane, propane, or *n*-butane followed by CO results in the formation of the corresponding analogues of **12** (Table 1).

Complexes **12**−**15** shown in Table 1 are surprisingly stable and chemically inert, and they can be purified by column chromatography on silica under atmospheric conditions. Like **12**, complexes **13**−**15** exist as two isomers in solution differing with respect to the orientation of the η^2-β,γ-ketone ligand. This feature is clearly evident in the 400 MHz ^{1}H NMR spectrum of **13** in C$_6$D$_6$, a portion of which is shown in Figure 6.

Release of the Bound Unsaturated Ketones from the Tungsten Coordination Sphere. The bound ketone ligands in complexes **12**−**15** can be released in one of two ways, either by photolysis or by further treatment with CO, the optimized conditions for doing so being presented in Scheme 11.

The results for the photolytic releases are shown in Table 2. While the organic products can be readily isolated from the final reaction mixture, the tungsten-containing product is not tractable, and its identity remains unknown. In contrast, release of the bound ketone ligands by treatment with CO at higher pressures and temperatures is accompanied by formation of the well-known Cp*W(NO)(CO)$_2$, which can be reconverted into starting complex **1**.[1] However, the isolated yields of the ketones liberated by carbonylation are somewhat lower than those obtained by photolysis: e.g., 37% vs 48% in the case of **16** being liberated from **12**.

■ EPILOGUE

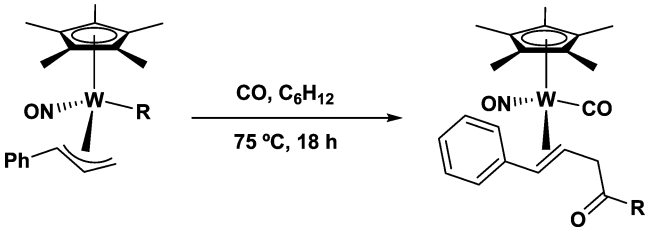
This study has demonstrated that Cp*W(NO)(CH$_2$CMe$_3$)(η^3-CH$_2$CHCHPh) (**1**) initiates the selective functionalization of terminal C(sp^3)−H bonds of lighter alkanes as well as hydrocarbons containing heteroatoms such as O, Cl, and Si. This functionalization involves initial C−H activation and two subsequent C−C bond-forming steps, as illustrated for ethane in Scheme 12. Photolysis of the final complex **13** affords an approximately equimolar mixture of the *Z* and *E* isomers of the β,γ-unsaturated ketone. Methane, propane, and *n*-butane have been functionalized in a similar manner, and steps 1 and 2 have been effected with a long-chain ether as the substrate. It thus appears that Cp*W(NO)(CH$_2$CMe$_3$)(η^3-CH$_2$CHCHPh) is an appropriate platform for the selective functionalization of a broader scope of hydrocarbons both with and without heteroatom constituents.

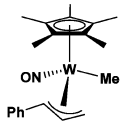
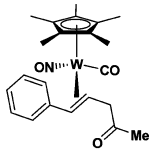
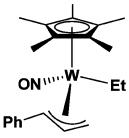
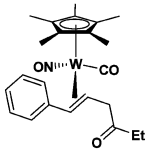
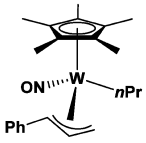
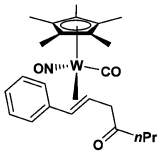
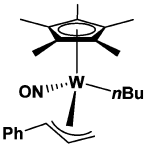
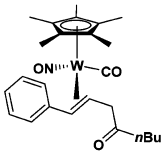
■ EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all reactions involving organometallic reagents were performed under anhydrous and anaerobic conditions. The subsequent manipulations, including column

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

Table 1. C−H Functionalization of C1−C4 Alkanes with Carbon Monoxide



Entry[a]	Intermediate complex	Product[b]	Isolated yield[c] (%)
1	 **2**	 **12**	41
2	 **3**	 **13**	50
3	 **4**	 **14**	45
4	 **5**	 **15**	35

[a]Conditions: 0.558 mmol of starting complex, 75 mL of cyclohexane, 75 °C, reactions run at 750 psig for 18 h in a sealed pressure reactor. [b]Two isomers of each compound that differ with respect to the orientation of the η^2-alkene ligand as shown in Scheme 10 have been characterized. [c]Isolated by column chromatography.

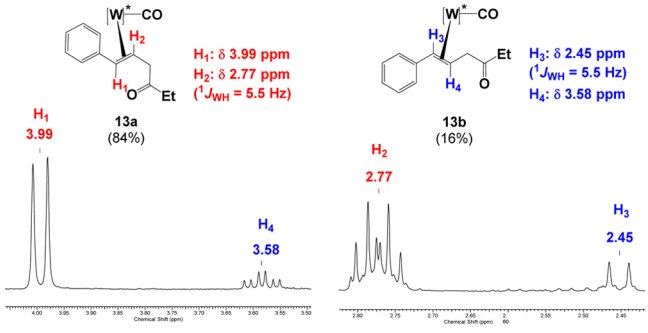


Figure 6. Expansions of the 400 MHz ^{1}H NMR spectrum of **13** in C_6D_6 from δ 4.05 to 3.50 ppm and δ 2.82 to 2.42 ppm showing the signals due to the alkene protons for each isomer ([W]* = Cp*W(NO)).

chromatography and recrystallization, were carried out under aerobic conditions except where otherwise noted. Inert gases were purified by

Scheme 11. Two Routes for the Release of the Bound Ketone Ligands from Complexes 12−15

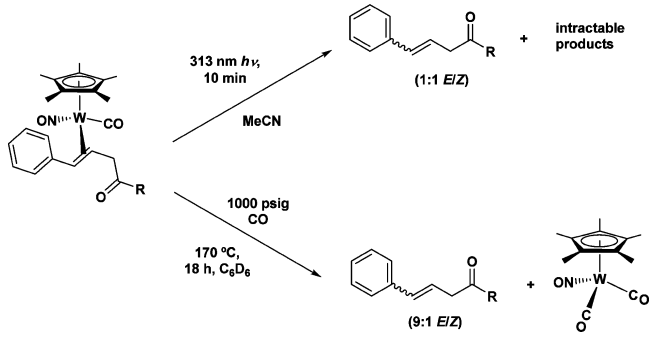
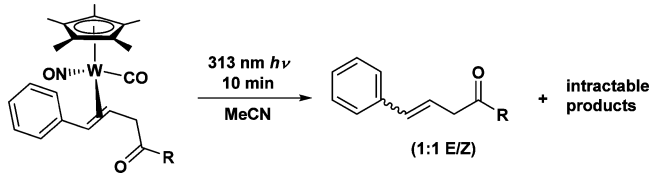
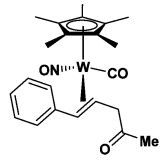
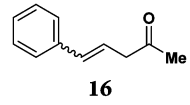
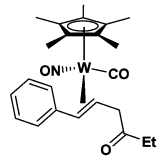
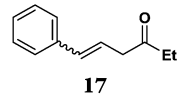
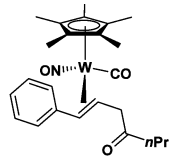
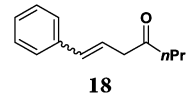
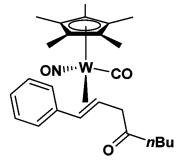
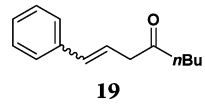


Table 2. Release of the η^2-Bound Ketone Ligands by Photolysis

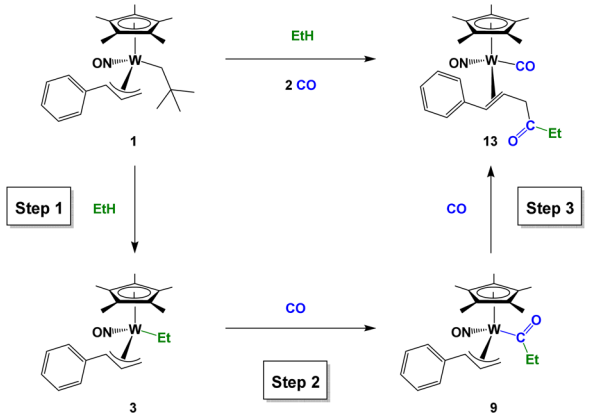


Entry[a]	Starting complex	Product	Isolated yield[b] (%)
1	 **12**	 **16**	48
2	 **13**	 **17**	72
3	 **14**	 **18**	48
4	 **15**	 **19**	69

[a]Starting complex dissolved in 230 mL of MeCN, reactions run for 10 min in a UV reactor using a 313 nm filter. [b]Products isolated by column chromatography.

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

Scheme 12. Stepwise Functionalization of Ethane with CO Initiated by 1



passing them through a column containing MnO and then through a column of activated 4 Å molecular sieves. High-vacuum and inert-atmosphere techniques were performed either using double-manifold Schlenk lines or in Innovative Technologies LabMaster 100 and MS-130 BG dual-station gloveboxes equipped with freezers maintained at −33 °C. Reactions on a preparative scale were performed with Schlenk or round-bottom flasks. Reactions with gases were performed in a Parr 5500 pressure reactor vessel with a capacity of 0.3 L unless otherwise noted. Cyclohexane and pentane were dried over calcium hydride, freshly distilled, and then dried over molecular sieves prior to use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried over sodium/benzophenone ketyl and freshly distilled prior to use. $Cp^*W(NO)Cl_2$ was prepared according to the published procedure.[14] Pentamethylcyclopentadiene was obtained from the Boulder Scientific Company. Methane, ethane, propane, butane, and carbon monoxide were obtained from Praxair and used as received. All other chemicals and reagents were ordered from commercial suppliers and used as received.

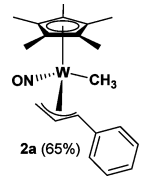
All IR samples were prepared as Nujol mulls sandwiched between NaCl plates, and their spectra were recorded on a Thermo Nicolet Model 4700 FT-IR spectrometer. Except where it has been noted, all NMR spectra were recorded at room temperature on Bruker AV-400 (direct and indirect probes) instruments, and all chemical shifts are reported in ppm and coupling constants are reported in Hz. ^1H NMR spectra were referenced to the residual protio isotopomer present in C_6D_6 (7.16 ppm) or $CDCl_3$ (7.27 ppm).^{13}C NMR spectra were referenced to C_6D_6 (128.39 ppm) or $CDCl_3$ (77.00 ppm). For the characterization of most complexes two-dimensional NMR experiments, $\{^1H-^1H\}$ COSY, $\{^1H-^{13}C\}$ HSQC, and $\{^1H-^{13}C\}$ HMBC, were carried out to correlate and assign ^1H and ^{13}C NMR signals and establish atom connectivity; ^1H NOE NMR and $\{^1H-^1H\}$ NOESY were used for determination of solution structures. Low- and high-resolution mass spectra (EI, 70 eV) were recorded by Mr. Marshall Lapawa of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer, and elemental analyses were performed by Mr. Derek Smith of the UBC microanalytical facility. In some compounds containing W−N bonds (e.g., **4a** and **5a**) lower than expected nitrogen content was measured. X-ray crystallographic data collection, solution, and refinement were performed at the UBC X-ray crystallography facility.

Modified Synthesis of $Cp^*W(NO)(CH_2CMe_3)(\eta^3\text{-}CH_2CHCHPh)$ (1). In a glovebox, a Schlenk flask was charged with $Cp^*W(NO)Cl_2$ (5.01 g, 11.9 mmol), THF (ca. 150 mL), and a magnetic stir bar and then sealed with a rubber septum. A second Schlenk flask was charged with $Mg(CH_2CMe_3)_2$ (titer: 159.5 g/mol, 1.87 g, 11.7 mmol), THF (ca. 100 mL), and a magnetic stir bar and then sealed with a septum. The two Schlenk flasks were transferred to a Schlenk line and placed into a dry ice/acetone bath (−78 °C), and the contents of each flask were stirred while being cooled. The contents of the second flask were cannulated dropwise into the first flask to produce a dark purple mixture. The solvent was removed in vacuo while the Schlenk was maintained in a cold water bath to obtain $Cp^*W(NO)(CH_2CMe_3)Cl$ as a purple residue.

$Cp^*W(NO)(CH_2CMe_3)Cl$ was transferred in Et_2O (ca. 400 mL) to a 1 L round-bottom flask which was maintained at −78 °C in a dry ice/acetone bath. A third Schlenk flask was charged in the glovebox with $Mg(CH_2CH{=}CHPh)$ (titer: 224.5 g/mol, 2.68 g, 11.9 mmol), Et_2O (ca. 200 mL), and a magnetic stir bar. The contents of the third flask were transferred slowly via cannula to the round-bottom flask that was maintained at −78 °C while being stirred. Following the addition, the round-bottom flask was removed from the bath, and its contents were warmed to room temperature while being stirred for 1 h, thereby producing a brown mixture. The volume of the solvent was reduced in vacuo, and the concentrated mixture was added to the top of a basic alumina column. A yellow band was developed and eluted with 0−5% Et_2O in hexanes to obtain an orange eluate. The solvent was removed from the eluate in vacuo to give $Cp^*W(NO)(CH_2CMe_3)(\eta^3\text{-}CH_2CHCHPh)$ (**1**) as an orange solid (1.975 g, 31% yield). Characterization data for **1** have been previously reported.[15]

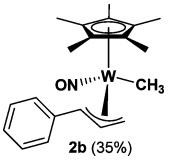
Preparation of $Cp^*W(NO)(CH_3)(\eta^3\text{-}CH_2CHCHPh)$ (2). In a glovebox, a Parr 5500 pressure reactor was charged with a sample of **1** (0.600 g, 1.17 mmol) and cyclohexane (ca. 100 mL) to produce a light orange solution. The reactor was sealed and then removed from the glovebox. It was then purged three times with 500 psig of CH_4 and then pressurized to 1250 psig. The contents were mechanically stirred and heated to 88 °C for 4 h (pressure 575 psig). The gas was then vented from the reactor, and a yellow-brown solution was collected in a 0.5 L round-bottom flask. The solvent was removed in vacuo to give a brown residue which was then dissolved in a minimum volume of Et_2O to give a concentrated solution of the crude product. Purification was performed in the air by column chromatography over an activated basic alumina support. A yellow band was eluted using a gradient of 33−66% Et_2O in hexanes. The solvents were removed in vacuo to give complex **2** as a yellow powder (0.282 g, 53% yield). As a solid the complex is air- and moisture-stable, and in solution it decomposes slowly at room temperature over several weeks. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a 1/1 Et_2O/hexanes solution at room temperature. The complex was found to have a melting point from 106 to 108 °C that was confirmed to be reversible by ^1H NMR spectroscopy. The orientation of the allyl ligand of each isomer was determined using Sel NOE NMR spectroscopy as well the chemical shifts of the allyl C and H signals in the ^1H and ^{13}C NMR spectra.

*Characterization Data for **2a** (65%).*



IR (cm^{-1}): 1559 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 120 °C): 481 [M^+, ^{184}W]. ^1H NMR (400 MHz, C_6D_6): δ −0.18 (s, $^2J_{WH}$ = 5.4, 3H, WCH_3), 0.65 (dd, $^3J_{HH}$ = 9.4, $^2J_{HH}$ = 2.5, 1H, allyl CH_2), 1.53 (s, 15H, C_5Me_5), 2.63 (dd, $^3J_{HH}$ = 7.0, $^2J_{HH}$ = 2.5, 1H, allyl CH_2), 3.01 (d, $^3J_{HH}$ = 13.5, 1H allyl CHPh), 5.44 (ddd, $^3J_{HH}$ = 13.5, 9.4, 7.0, 1H, allyl CH), 6.81 (d, $^3J_{HH}$ = 7.2, 2H, *o*-aryl H), 7.08 (t, $^3J_{HH}$ = 7.4, 1H, *p*-aryl H), 7.13 (t, $^3J_{HH}$ = 7.7, 2H, *m*-aryl H). ^{13}C APT NMR (100 MHz, C_6D_6): δ 6.7 ($^1J_{WC}$ = 81.2, WCH_3), 10.2 (C_5Me_5), 38.1 ($^1J_{WC}$ = 29.4, allyl CH_2), 95.6 (allyl CHPh), 102.7 (allyl CH), 106.2 (C_5Me_5), 127.2 (*p*-aryl C), 127.6 (*o*-aryl C), 128.6 (*m*-aryl C), 137.6 (ipso C). Sel NOE (400 MHz, C_6D_6): δ irrad at −0.18, NOE at 1.53, 3.01, 6.81. Anal. Calcd for $C_{20}H_{27}NOW$: C, 49.91; H, 5.65; N, 2.91. Found: C, 49.97; H, 5.74; N, 2.67.

*Characterization Data for **2b** (35%).*

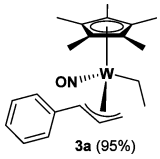


DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

^{1}H NMR (400 MHz, C_6D_6): δ 0.45 (s, $^2J_{WH}$ = 6.0, 3H, WCH_3), 1.43 (s, 15H, C_5Me_5), 1.64 (m, 1H, allyl CH_2), 2.07 (d, $^3J_{HH}$ = 10.0, 1H, allyl CHPh), 2.99 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 5.43 (ddd, $^3J_{HH}$ = 13.5, 10.0, 7.0, 1H, allyl CH), 7.06 (t, $^3J_{HH}$ = 7.2, 1H, *p*-aryl H), 7.30 (t, $^3J_{HH}$ = 7.4, 2H, *m*-aryl H), 7.40 (d, $^3J_{HH}$ = 7.4, 2H, *o*-aryl H). ^{13}C APT NMR (100 MHz, C_6D_6): δ −2.7 (WCH_3), 9.8 (C_5Me_5), 63.3 ($^1J_{WC}$ = 19.4, allyl *C*HPh), 72.9 ($^1J_{WC}$ = 6.6, allyl *C*H$_2$), 106.2 (C_5Me$_5$), 109.6 (allyl *C*H), 125.2 (*p*-aryl *C*), 127.2 (*o*-aryl *C*), 128.4 (*m*-aryl *C*), 143.2 (ipso *C*). Sel NOE (400 MHz, C_6D_6): δ irrad at 0.45, NOE at 1.43, 2.99, 5.42.

Preparation of Cp*W(NO)(CH$_2$CH$_3$)(η^3-CH$_2$CHCHPh) (3). In a glovebox, a Parr 5500 pressure reactor was charged with **1** (0.391 g, 0.728 mmol) and cyclohexane (ca. 75 mL) to give a light orange solution. The reactor was sealed and then removed from the glovebox and purged three times with 400 psig of C_2H_6 before being pressurized to 400 psig. The contents of the reactor were stirred mechanically and heated to 55 °C for 3 days, after which time a yellow solution was obtained. The solvent was removed in vacuo to give a yellow oily residue. The residue was dissolved in a minimum amount of Et_2O to give a concentrated solution of the crude product. Purification of the product was performed using column chromatography on an activated basic alumina support (2.5 × 20 cm). A yellow band was eluted with a gradient of 20−50% Et_2O in hexanes, and the solvent was then removed from the eluate to give **3** as a yellow powder (0.308 g, 86% yield). Yellow crystals suitable for X-ray diffraction were obtained from 1/1 pentane/Et_2O at −33 °C. The complex was found to have a melting point of 108−109 °C that was confirmed to be reversible by ^{1}H NMR spectroscopy. The orientation of the allyl ligand of each isomer was established by using the chemical shifts of the allyl C and H signals in the ^{1}H and ^{13}C NMR spectra, as well as Sel NOE NMR spectroscopy for isomer **3a**.

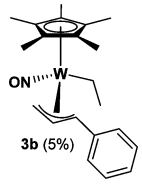
*Characterization Data for **3a** (95%).*



3a (95%)

IR (cm^{-1}): 1553 (s, ν_{NO}). MS (LREI, *m*/*z*, probe temperature 120 °C): 495 [M$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 1.11 (q, $^3J_{HH}$ = 7.2, $^2J_{WH}$ = 7.1, 2H, WCH_2CH$_3$), 1.42 (s, 15H, C_5Me_5), 1.61 (d, $^3J_{HH}$ = 13.3, 1H, allyl CH_2), 1.78 (t, $^3J_{HH}$ = 7.2, $^3J_{WH}$ = 5.2, 3H, WCH$_2$CH_3), 2.17 (d, $^3J_{HH}$ = 9.8, 1H, allyl CHPh), 3.24 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 5.51 (ddd, $^3J_{HH}$ = 13.3, 9.8, 7.0, 1H, allyl CH), 7.05 (t, $^3J_{HH}$ = 7.2, 1H, *p*-aryl *H*), 7.28 (t, $^3J_{HH}$ = 7.6, 2H, *m*-aryl *H*), 7.36 (d, $^3J_{HH}$ = 7.4, 2H, *o*-aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 9.7 (C_5Me_5), 10.1 (WCH$_2$CH$_3$), 18.3 (WCH$_2$CH$_3$), 63.2 ($^1J_{WC}$ = 19.6, allyl *C*HPh), 73.1 ($^1J_{WC}$ = 7.8, allyl *C*H$_2$), 106.2, ($^1J_{WC}$ = 4, C_5Me$_5$), 107.0 (allyl *C*H), 125.6 (*p*-aryl *C*), 127.4 (*o*-aryl *C*), 128.7 (*m*-aryl *C*), 143.2 (ipso *C*). Sel NOE (400 MHz, C_6D_6): δ irrad at 1.78, NOE at 1.11, 1.42, 3.24, 5.51, 7.36. Anal. Calcd for $C_{21}H_{29}$NOW: C, 50.92; H, 5.90; N, 2.83. Found: C, 51.23; H, 5.89; N, 2.66.

*Characterization Data for **3b** (5%).*

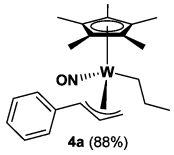


3b (5%)

^{1}H NMR (400 MHz, C_6D_6): δ (selected signals) 0.36 (m, 1H, WCH_2CH$_3$), 0.72 (m, 1H, allyl CH_2), 2.62 (m, 1H, allyl CH_2), 3.19 (m, 1H, allyl CHPh), 5.39 (br s, 1H, allyl CH), 6.96 (br s, 2H, *o*-aryl H), 7.13 (m, 2H, *m*-aryl H). ^{13}C APT NMR (100 MHz, C_6D_6): δ (selected signals) 10.2 (C_5Me_5), 10.5 (WCH$_2$CH$_3$), 16.4 (WCH$_2$CH$_3$), 37.5 (allyl *C*H$_2$), 98.1 (allyl *C*HPh), 101.7 (allyl *C*H), 106.7 (C_5Me$_5$), 128.3 (*o*-aryl H), 138.9 (ipso *C*).

Preparation of Cp*W(NO)(CH$_2$CH$_2$CH$_2$CH$_3$)(η^3-CH$_2$CHCHPh) (4). In a glovebox, a Parr 5500 reactor was charged with **1** (0.300 g, 0.558 mmol) that was then dissolved in cyclohexane (75 mL). The pressure reactor was sealed and purged five times with propane and finally filled to 250 psig. The reactor was connected to the mechanical stirrer and heated to 55 °C, and once stabilized, its contents were stirred for 3 days. The reactor was cooled to room temperature, and the gas was carefully vented. The mixture was transferred to a Schlenk flask, and the volatiles were then removed in vacuo. Purification of the product was performed using column chromatography on an activated basic alumina support (2.5 × 20 cm). A yellow band was eluted with a gradient of 0−50% Et_2O in hexanes, and the solvent was then removed from the eluate to give **4** as an orange solid (0.167 g, 59% yield). The solution structure of the major isomer (**4a**) was inferred on the basis of the Sel ^{1}H NOE NMR spectroscopy performed on the analogous complex **3a**.

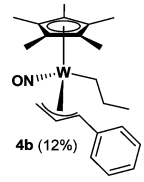
*Characterization Data for **4a** (88%).*



4a (88%)

IR (cm^{-1}): 1598 (s, ν_{NO}). MS (LREI, *m*/*z*, probe temperature 150 °C): 509 [M$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ 1.03−1.08 (m, 2H, WCH_2CH$_2$CH$_3$), 1.29 (t, $^3J_{HH}$ = 7.1, 3H, WCH$_2$CH$_2$CH_3), 1.36−1.48 (obscured, 1H, WCH$_2$CHHCH$_3$), 1.42 (s, 15H, C_5Me_5), 1.61 (d, $^3J_{HH}$ = 13.5, 1H, allyl CH), 2.08−2.22 (obscured, 1H, WCH$_2$CHHCH$_3$), 2.15 (d, $^3J_{HH}$ = 10.0, 1H, allyl CH), 3.19 (d, $^3J_{HH}$ = 7.0, 1H, allyl CHPh), 5.48 (ddd, $^3J_{HH}$ = 13.4, 9.9, 7.1, 1H, *meso* CH), 7.06 (t, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 7.30 (t, $^3J_{HH}$ = 7.7, 2H, *m*-aryl *H*), 7.37 (d, $^3J_{HH}$ = 7.5, 2H, *o*-aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 9.4 (C_5Me_5), 21.0 (WCH$_2$CH$_2$CH$_3$), 22.5 (WCH$_2$CH$_2$CH$_3$), 27.4 (WCH$_2$CH$_2$CH$_3$), 62.7 (allyl *C*H$_2$), 72.8 (allyl PhCH), 105.9 (C_5Me$_5$), 107.1 (*meso* *C*H), 125.3 (*p*-aryl *C*), 127.1 (*o*-aryl *C*), 128.4 (*m*-aryl *C*), 142.8 (ipso *C*). Mp: 104−105 °C (reversible, confirmed by ^{1}H NMR). Anal. Calcd for $C_{22}H_{31}$NOW: C, 51.88; H, 6.14; N, 2.75. Found: C, 52.09; H, 6.30; N, 2.23.

*Characterization Data for **4b** (12%).*

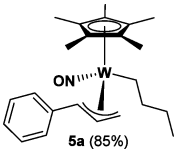


4b (12%)

^{1}H NMR (400 MHz, C_6D_6): δ (selected signals) 0.65 (br s, 1H, allyl CH_2), 5.40 (br s, 1H, allyl CH), 6.96 (br s, 2H, *o*-aryl H), 7.13 (m, 2H, *m*-aryl H). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 9.9 (WCH$_2$CH$_2$CH$_3$), 10.3 (C_5Me_5), 43.0 (allyl *C*H$_2$), 98.6 (allyl *C*HPh), 101.4 (allyl *C*H), 105.9 (C_5Me$_5$), 125.9 (*p*-aryl *C*), 128.5 (*m*-aryl *C*), 128.8 (*o*-aryl *C*), 147.4 (ipso *C*).

Preparation of Cp*W(NO)(CH$_2$CH$_2$CH$_2$CH$_3$)(η^3-CH$_2$CHCHPh) (5). In a glovebox, a Parr 5500 reactor was charged with **1** (0.300 g, 0.558 mmol) dissolved in cyclohexane (75 mL). The pressure reactor was sealed and purged five times with butane and finally filled to 250 psig. The contents of the reactor were stirred at 55 °C for 3 days. The reactor was cooled to room temperature, and the gas was carefully vented. The mixture was transferred to a Schlenk flask, and the volatiles were removed in vacuo. Purification of the product was performed using column chromatography on an activated basic alumina support (2.5 × 20 cm). A yellow band was eluted with a gradient of 0−50% Et_2O in hexanes, and the solvent was then removed from the eluate to give **5** as an orange solid (0.152 g, 52% yield). The solution structure of the major isomer (**5a**) was inferred on the basis of the Sel ^{1}H NOE NMR spectroscopy performed on the analogous complex **3a**.

*Characterization Data for **5a** (85%).*

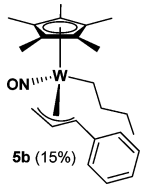


5a (85%)

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

IR (cm^{-1}): 1598 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 150 °C): 523 [M^+, ^{184}W]. ^1H NMR (400 MHz, C_6D_6): δ 1.03−1.11 (m, 2H, $WCH_2CH_2CH_2CH_3$), 1.14 (t, $^3J_{HH}$ = 7.6, 3H, $WCH_2CH_2CH_2CH_3$), 1.36−1.47 (obscured, 1H, $WCH_2CHHCH_2CH_3$), 1.43 (s, 15H, C_5Me_5), 1.53−1.69 (obscured, 2H, $WCH_2CH_2CH_2CH_3$) 1.62−1.69 (obscured, 1H, allyl C*H*), 2.06−2.22 (obscured, 1H, $WCH_2CHHCH_2CH_3$), 2.15 (d, $^3J_{HH}$ = 10.1, 1H, allyl C*H*), 3.23 (d, $^3J_{HH}$ = 7.0, 1H, allyl C*H*Ph), 5.51 (ddd, $^3J_{HH}$ = 13.7, 9.9, 7.0, 1H, *meso* C*H*), 7.05 (t, $^3J_{HH}$ = 6.5, 1H, *p*-aryl *H*), 7.29 (t, $^3J_{HH}$ = 7.6, 2H, *m*-aryl *H*), 7.37 (d, $^3J_{HH}$ = 7.7, 2H, *o*-aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 9.4 (C_5Me_5), 14.4 ($WCH_2CH_2CH_2CH_3$), 17.6 ($WCH_2CH_2CH_2CH_3$), 30.6 ($WCH_2CH_2CH_2CH_3$), 36.4 ($WCH_2CH_2CH_2CH_3$), 62.7 (allyl CH_2), 72.9 (allyl PhCH), 105.9 (C_5Me_5), 107.1 (*meso* CH), 125.3 (*p*-aryl *C*), 127.1 (*o*-aryl *C*), 128.3 (*m*-aryl *C*), 142.8 (ipso *C*); Mp: 106−107 °C (reversible, confirmed by ^1H NMR). Anal. Calcd for $C_{23}H_{33}NOW$: C, 52.78; H, 6.36; N, 2.68. Found: C, 53.06; H, 6.56; N, 2.10.

*Characterization Data for **5b** (15%).*

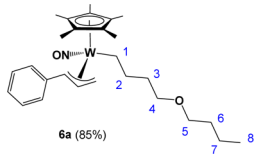


5b (15%)

^1H NMR (400 MHz, C_6D_6): δ (selected signals) 0.57 (m, 1H, allyl CH_2), 1.75−1.85 (m, 2H, butyl CH_2), 5.39 (br s, 1H, allyl C*H*), 6.97 (br s, 2H, *o*-aryl H), 7.10−7.13 (m, 2H, *m*-aryl H). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 9.9 (C_5Me_5), 15.0 ($WCH_2CH_2CH_2CH_3$), 34.2 (allyl CH_2), 99.2 (allyl CHPh), 103.6 (allyl CH), 105.4 (C_5Me_5), 124.9 (*p*-aryl *C*), 142.9 (ipso *C*).

Preparation of Cp*W(NO)($(CH_2)_4O(CH_2)_3CH_3$)(η^3-$CH_2CHCHPh$) (6). In a glovebox a sample of **1** (0.300 g, 0.558 mmol) was dissolved in $(n\text{-Bu})_2O$ (ca. 25 mL) to give a light orange solution, which was transferred to a reaction bomb that was sealed with a Kontes greaseless stopcock. The contents were heated to 55 °C for 3 days to give a dark orange solution. The solvent was removed in vacuo to give an orange oily residue. The crude mixture was dissolved in a minimum amount of Et_2O and purified by column chromatography on activated basic alumina (3 × 7 cm). A yellow eluate was collected using a gradient of 0−40% Et_2O in hexanes. The solvents were removed from the eluate in vacuo to give **6** as a yellow oil (0.165 g, 50% yield). Two isomers of **6** were identified in solution by NMR spectroscopy in an 85:15 ratio. The orientation of the allyl ligand of each isomer was determined using the chemical shifts of the allyl C and H signals in the ^1H and ^{13}C NMR spectra.

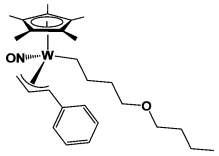
*Characterization Data for **6a** (85%).*



6a (85%)

IR (cm^{-1}): 1589 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 150 °C): 595 [M^+, ^{184}W]. HRMS-EI (*m/z*): [M^+] calcd for $^{184}WC_{27}H_{41}NO_2$ 595.26468, found 595.26501; calcd for $^{182}WC_{27}H_{41}NO_2$ 593.26195, found 593.26206. ^1H NMR (400 MHz, C_6D_6): δ 0.90 (t, $^3J_{HH}$ = 7.4, 3H, C8H_3), 1.01 (dt, $^3J_{HH}$ = 3.3, $^2J_{HH}$ = 11.7, 1H, C1H_2), 1.11 (dt, $^3J_{HH}$ = 5.1, $^2J_{HH}$ = 11.7, 1H, C1H_2), 1.42 (obscured, 2H, C7H_2), 1.43 (s, 15H, C_5Me_5), 1.60 (obscured, 2H, C6H_2), 1.60 (obscured, 1H, C2H_2), 1.63 (obscured, 1H, allyl CH_2), 1.87 (m, 1H, C3H_2), 1.97 (m, 1H, C3H_2), 2.14 (obscured, 1H, C2H_2), 2.15 (d, $^3J_{HH}$ = 9.8, 1H, allyl C*H*Ph), 3.30 (d, $^3J_{HH}$ = 7.2, 1H, allyl CH_2), 3.39 (t, $^3J_{HH}$ = 6.5, 2H, OC5H_2), 3.53 (m, 1H, OC4H_2), 3.59 (m, 1H, OC4H_2), 5.51 (ddd, $^3J_{HH}$ = 13.4, 9.8, 7.2, 1H, allyl CH), 7.04 (t, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 7.27 (t, $^3J_{HH}$ = 7.4, 2H, *m*-aryl *H*), 7.34 (d, $^3J_{HH}$ = 7.7, 2H, *o*-aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 9.7 (C_5Me_5), 14.6 (C8H_3), 17.9 ($^1J_{WC}$ = 78.6, C1H_2), 20.3 (C7H_2), 30.9 (C2H_2), 32.9 (C6H_2), 38.1 (C3H_2), 63.1 ($^1J_{WC}$ = 19.6, allyl CHPh), 71.1 (OC5H_2), 71.6 (OC4H_2), 73.2 (allyl CH_2), 106.2 (C_5Me_5), 107.5 (allyl CH), 125.6 (*p*-aryl *C*), 127.4 (*m*-aryl *C*), 128.7 (*o*-aryl *C*), 143.1 (ipso *C*).

*Characterization Data for **6b** (15%).*

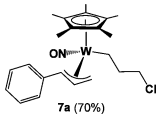


6b (15%)

^1H NMR (400 MHz, C_6D_6): δ (selected signals) 0.14 (t, $^3J_{HH}$ = 11.4, 1H, WCH_2), 0.68 (br s, 1H, allyl CH_2), 0.88 (obscured, 3H, butyl CH_3), 1.56 (br s, 15H, C_5Me_5), 2.58 (d, $^3J_{HH}$ = 6.5, 1H, allyl CH_2), 3.20 (overlapping, 1H, allyl C*H*Ph), 3.23 (overlapping, 2H, CH_2O), 3.32 (obscured, 2H, CH_2O), 5.37 (br s, 1H, allyl C*H*), 6.96 (br s, 1H, *p*-aryl *H*), 7.14 (m, 2H, aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 10.2 (C_5Me_5), 14.7 (butyl CH_3), 23.5 (WCH_2), 37.2 (allyl CH_2), 71.0 (CH_2O), 71.8 (CH_2O), 98.5 (allyl CHPh), 101.8 (allyl CH), 106.3 (C_5Me_5), 128.8 (aryl CH), 136.9 (ipso *C*).

Preparation of Cp*W(NO)($CH_2CH_2CH_2Cl$)(η^3-$CH_2CHCHPh$) (7). In a glovebox, a glass bomb was charged with **1** (0.300 mg, 0.558 mmol), which was then dissolved in 1-chloropropane (ca. 5 mL) to give a dark yellow solution. The bomb was then sealed with a Kontes greaseless stopcock and placed in a 55 °C ethylene glycol bath, whereupon its stirred contents were heated for 3 days to give a dark green mixture. The solvent was removed in vacuo, and the resulting mixture was analyzed by ^1H NMR spectroscopy. Signals attributable to Cp*W(NO)(Cl)(η^3-CH_2CHCH_2) and **7** were evident in the ^1H NMR spectrum of the crude mixture, as were signals corresponding to (*Z*)- and (*E*)-β-methylstyrene, in a 65:35:30:20 ratio, respectively. Complex **7** was purified by column chromatography over basic alumina using a gradient of 0−30% EtOAc in hexanes to give **7** as a yellow solid (67 mg, 22% yield). Two isomers of **7** were detected in solution by NMR spectroscopy. The orientation of the allyl ligand of each isomer was determined using the chemical shifts of the allyl C and H signals in the ^1H and ^{13}C NMR spectra. Crystals suitable for single-crystal X-ray diffraction of the minor isomer, **7b**, were grown by slow evaporation of a 1/1 Et_2O/pentane solution at room temperature. The crystals were dissolved in C_6D_6, and both isomers of **7** were identified by ^1H NMR spectroscopy in solution.

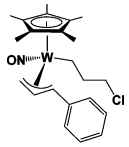
*Characterization Data for **7a** (70%).*



7a (70%)

IR (cm^{-1}): 1602 (s, ν_{NO}). MS (LREI, *m/z*, probe temperature 150 °C): 543 [M^+, ^{184}W]. ^1H NMR (400 MHz, C_6D_6): δ 0.76 (dt, $^3J_{HH}$ = 5.1, $^2J_{HH}$ = 11.2, 1H, WCH_2), 1.05 (dt, $^3J_{HH}$ = 5.1, $^2J_{HH}$ = 11.2, 1H, WCH_2), 1.38 (s, 15H, C_5Me_5), 1.58 (m, 1H, allyl CH_2), 1.70 (m, 1H, WCH_2CH_2), 2.12 (d, $^3J_{HH}$ = 9.9, 1H, allyl C*H*Ph), 2.44 (m, 1H, WCH_2CH_2), 3.12 (d, $^3J_{HH}$ = 7.3, 1H, allyl CH_2), 3.40 (m, 1H, CH_2Cl), 3.53 (ddd, $^3J_{HH}$ = 10.2, 5.9, $^3J_{HH}$ = 7.0, 1H, CH_2Cl), 5.36 (ddd, $^3J_{HH}$ = 13.6, 9.9, 7.3, 1H, allyl CH), 7.07−7.31 (m, 5H, aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 9.7 (C_5Me_5), 12.9 (WCH_2), 37.6 (CH_2), 51.6 (CH_2Cl), 63.4 (allyl CHPh), 73.4 (allyl CH_2), 106.4 (C_5Me_5), 107.8 (allyl CH), 125.8 (aryl *C*), 127.4 (aryl *C*), 128.7 (aryl *C*), 142.8 (ipso *C*).

*Characterization Data for **7b** (30%).*



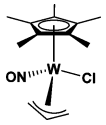
7b (30%)

^1H NMR (400 MHz, C_6D_6): δ (selected signals) −0.24 (dt, $^2J_{HH}$ = 2.3, $^3J_{HH}$= 11.5, 1H, WCH_2), 0.63 (dd, $^3J_{HH}$ = 8.9, $^2J_{HH}$ = 1.9, 1H, allyl CH_2), 1.51 (s, 15H, C_5Me_5), 2.21 (m, 1H, CH_2), 2.47 (obscured, 1H, CH_2), 2.55 (dd, $^3J_{HH}$ = 7.0, $^2J_{HH}$ = 1.9, 1H, allyl CH_2), 2.79 (m, 1H, CH_2Cl), 3.15 (d, $^3J_{HH}$= 14.9, 1H, allyl C*H*Ph), 5.28 (ddd, $^3J_{HH}$ = 14.9,

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

8.9, 7.0, 1H, allyl C*H*) 7.56 (d, $^3J_{HH}$ = 7.4, 1H, *o*-aryl H). ^{13}C APT NMR (100 MHz, C_6D_6): δ (selected signals) 10.2 (C_5Me_5), 98.6 (allyl *C*HPh), 101.9 (allyl *C*H), 131.1 (*o*-aryl *C*H).

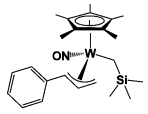
*Characterization Data for Cp*W(NO)(Cl)(η^3-CH_2CHCH_2).*



^{1}H NMR (400 MHz, C_6D_6): δ 0.70 (d, $^3J_{HH}$ = 7.0, 1H, allyl CH_2), 1.53 (s, 15H, C_5Me_5), 1.92 (m, 1H, allyl CH_2), 3.08 (d, $^3J_{HH}$ = 13.9, 1H, allyl CH_2), 4.01 (dd, $^3J_{HH}$ = 7.2, $^2J_{HH}$ = 3.5, 1H, allyl CH_2), 5.86 (m, 1H, allyl C*H*). ^{13}C NMR (100 MHz, C_6D_6): δ 10.3 (C_5Me_5), 43.7 (allyl CH_2), 92.0 (allyl CH_2), 109.6 (C_5Me_5), 115.7 (allyl *C*H). These spectroscopic data are consistent with those reported previously for this complex.[16]

Preparation of Cp*W(NO)(CH_2SiMe_3)(η^3-$CH_2CHCHPh$) (8). In a glovebox, a reaction bomb was charged with **1** (81 mg, 0.15 mmol), $SiMe_4$ (ca. 3 mL), and a magnetic stir bar to give a cloudy orange suspension. The reaction bomb was then sealed with a Kontes greaseless stopcock and placed into an oil bath, whereupon its contents were heated to 85 °C and stirred for 9 h. The solvent was then removed under reduced pressure. Inside a glovebox the contents were transferred to a 4 dram vial with Et_2O (ca. 2 mL). The solvent was removed under reduced pressure to give **8** as a yellow solid (80 mg, 96% yield). Two solution isomers of **8** were identified by ^{1}H NMR spectroscopy. The orientation of the allyl ligand in the major isomer **8a** was determined using the chemical shifts of the allyl C signals in the ^{13}C NMR spectrum.

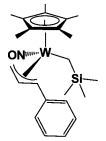
*Characterization Data for **8a** (83%).*



8a (83%)

IR (cm^{-1}): 1574 (s, ν_{NO}). MS (LREI, *m*/*z*, probe temperature 120 °C): 553 [M$^+$, ^{184}W]. ^{1}H NMR (400 MHz, C_6D_6): δ −0.57 (d, $^2J_{HH}$ = 11.7, 1H, SiCH_2), −0.04 (d, $^2J_{HH}$ = 11.7, 1H, SiCH_2), 0.39 (s, 9H, SiMe_3), 1.41 (s, 15H, C_5Me_5), 1.70 (d, $^3J_{HH}$ = 13.2, 1H, allyl CH_2), 2.12 (d, $^3J_{HH}$ = 9.4, 1H, allyl C*H*Ph), 3.42 (d, $^3J_{HH}$ = 5.9, 1H, allyl CH_2), 5.71 (m, 1H, allyl C*H*), 7.05 (br t, $^3J_{HH}$ = 7.2, 1H, aryl *H*), 7.27 (br t, $^3J_{HH}$ = 7.2, 2H, aryl *H*), 7.40 (br d, $^3J_{HH}$ = 7.2, 2H, aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ −4.4 (SiCH_2), 4.3 (SiMe_3), 10.0 (C_5Me_5), 62.2 (allyl *C*HPh), 72.6 (allyl CH_2), 106.8 (C_5Me_5), 111.9 (allyl *C*H), 125.8 (aryl *C*), 128.0 (aryl *C*), 128.7 (aryl *C*), 140.6 (ipso *C*). Anal. Calcd for $C_{27}H_{41}NOW$: C, 49.91; H, 6.37; N, 2.53. Found: C, 49.92; H, 6.25; N, 2.45.

*Characterization Data for **8b** (17%).*

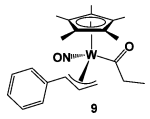


8b (17%)

^{1}H NMR (400 MHz, C_6D_6): δ (selected signals) −0.94 (d, $^2J_{HH}$ = 9.9, 1H, SiCH_2), −0.76 (d, $^2J_{HH}$ = 9.9, 1H, SiCH_2), 0.21 (s, 9H, SiMe_3), 1.51 (s, 15H, C_5Me_5), 2.46 (br s, 1H, allyl *H*), 3.64 (br s, 1H, allyl *H*), 5.26 (br s, 1H, allyl C*H*), 6.98 (m, 1H, aryl *H*).

Preparation of Cp*W(NO)(C(=O)CH_2CH_3)(η^3-$CH_2CHCHPh$) (9). In a glovebox, a Parr 5500 pressure reactor was charged with a sample of **3** (131 mg, 0.264 mmol) and *n*-C_5H_{12} (ca. 75 mL). The reactor was sealed, removed from the glovebox, and then purged three times with 500 psig of CO. The reactor was pressurized with 450 psig of CO, and its contents were stirred mechanically and heated. After 2 h at 55 °C the reactor was cooled in a water bath. The gas was vented, and a light yellow solution was filtered through glass wool and collected in a Schlenk flask. The solvent was removed from the solution under vacuum to give a yellow oily residue. In a glovebox the residue was dissolved in Et_2O (ca. 2 mL) and filtered through an alumina column (0.5 × 4 cm). Addition of pentane to the yellow filtrate induced the precipitation of **9** as a yellow solid (101 mg, 73% yield). Orange crystals of **9** suitable for X-ray diffraction were grown from Et_2O at −33 °C.

*Characterization Data for **9**.*

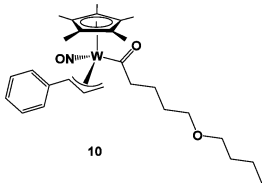


9

IR (cm^{-1}): 1599 (s, ν_{NO}), 1630 (w, ν_{CO}). MS (LREI, *m*/*z*, probe temperature 120 °C): 523 [M$^+$, ^{184}W]. HRMS-EI: (*m*/*z* [M$^+$, ^{182}W]): calcd for $^{182}WC_{22}H_{29}NO_2$ 521.16805, found 521.16761; [M$^+$, ^{184}W] calcd for $^{184}WC_{22}H_{29}NO_2$ 523.17078, found 523.17042. ^{1}H NMR (400 MHz, C_6D_6): δ 1.21 (t, $^3J_{HH}$ = 7.3, 3 H, WC(=O)CH_2CH_3), 1.54 (s, 15H, C_5Me_5), 1.55 (obscured, 1H, allyl CH_2), 2.40 (d, $^3J_{HH}$ = 11.0, 1H, allyl C*H*Ph), 2.99 (q, $^3J_{HH}$ = 7.3, 2H, WC(=O)CH_2CH_3), 3.22 (dd, $^3J_{HH}$ = 7.4, $^2J_{HH}$ = 3.1, 1H, allyl CH_2), 5.39 (ddd, $^3J_{HH}$ = 13.3, 11.0, 7.4, 1H, allyl C*H*), 7.08 (t, $^3J_{HH}$ = 7.4, 1H, aryl *H*), 7.25 (t, $^3J_{HH}$ = 7.4, 2H, aryl *H*), 7.32 (d, $^3J_{HH}$ = 7.4, 2H, aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 10.2 (C_5Me_5), 30.1 (WC(=O)CH_2CH_3), 55.4 (WC(=O)CH_2CH_3), 65.6 (allyl CH_2), 71.2 (allyl *C*HPh), 108.9, (C_5Me_5), 109.7 (allyl *C*H), 126.4 (aryl *C*), 127.7 (aryl *C*), 129.0 (aryl *C*), 141.7 (ipso *C*), 261.0 (acyl *C*). Anal. Calcd for $C_{22}H_{29}NO_2W$: C, 50.49; H, 5.59; N, 2.68. Found: C, 50.74; H, 5.69; N, 3.03.

Preparation of Cp*W(NO)(C(=O)$(CH_2)_4O(CH_2)_3CH_3$)(η^3-$CH_2CHCHPh$) (10). In a glovebox, a Parr 5500 reactor was charged with **6** (30 mg, 0.050 mmol) and Et_2O (ca. 75 mL). The reactor was sealed and purged three times with 450 psig of CO. Then the reactor was pressurized to 450 psig, and the contents were stirred over 4 days at room temperature. The reactor was vented, and a pale yellow solution was collected. Solvent was removed from the solution under reduced pressure to give **10** as a yellow solid (21 mg, 67% yield).

*Characterization Data for **10**.*



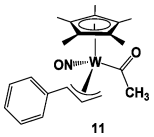
10

^{1}H NMR (400 MHz, C_6D_6): δ 0.88 (t, $^3J_{HH}$ = 7.4, 3H, *n*-butyl CH_3), 1.37 (m, 2H, *n*-butyl CH_2), 1.39 (m, 2H, *n*-butyl CH_2), 1.55 (s, 15H, C_5Me_5), 1.58 (obscured, 1H, allyl CH_2), 1.76 (m, 2H, *n*-butyl CH_2), 1.80 (m, 2H, *n*-butyl CH_2), 2.42 (d, $^3J_{HH}$ = 10.6, 1H, allyl C*H*Ph), 3.08 (t, $^3J_{HH}$ = 6.9, 2H, C(=O)CH_2), 3.27 (m, 1H, allyl CH_2), 3.32 (t, $^3J_{HH}$ = 6.6, 2H, *n*-butyl OCH_2), 3.43 (t, $^3J_{HH}$ = 6.2, 2H, *n*-butyl OCH_2), 5.44 (ddd, $^3J_{HH}$ = 13.3, 10.6, 7.3, 1H, allyl C*H*), 7.05 (t, $^3J_{HH}$ = 7.4, 1H, aryl *H*), 7.25 (t, $^3J_{HH}$ = 7.4, 2H, aryl *H*), 7.33 (d, $^3J_{HH}$ = 7.4, 2H, aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 10.2 (C_5Me_5), 14.6 (*n*-butyl CH_3), 20.2 (*n*-butyl CH_2), 22.7 (*n*-butyl CH_2), 30.6 (*n*-butyl CH_2), 35.5 (*n*-butyl CH_2), 62.3 (C(=O)CH_2), 66.1 (allyl CH_2), 71.1 (*n*-butyl OCH_2), 71.2 (allyl *C*HPh), 71.7 (*n*-butyl OCH_2), 108.9 (C_5Me_5), 109.6 (allyl *C*H), 126.4 (aryl *C*), 127.8 (aryl *C*), 129.0 (aryl *C*), 141.7 (ipso *C*), 260.8 (acyl *C*).

Preparation of Cp*W(NO)(C(=O)CH_3)(η^3-$CH_2CHCHPh$) (11). In a glovebox, a Parr 5500 reactor was charged with **8** (49 mg, 0.089 mmol) and pentane (ca. 75 mL). The reactor was sealed and purged with 500 psig of CO three times. The reactor was then pressurized to 250 psig of CO and heated to 55 °C while its contents were stirred for 2 h. The gas was then vented, and a pale yellow solution was collected. The solvent was removed in vacuo to give a yellow oil. The residue was taken up in 3/1 pentane/Et_2O and transferred to the top of an alumina column (0.5 × 3 cm). A dark yellow band was collected to give a yellow eluate. The solvents were then removed from the eluate in vacuo to give **11** as a yellow oily solid (15 mg, 33% yield).

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

*Characterization Data for **11**.*

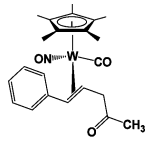


11

IR (cm^{-1}): 1598 (s, ν_{NO}), 1622 (w, ν_{CO}). MS (LREI, *m/z*, probe temperature 150 °C): 553 [M^+, ^{184}W]. ^1H NMR (400 MHz, C_6D_6): δ 1.54 (s, 15H, C_5Me_5), 1.55 (obscured, 1H, allyl CH_2), 2.38 (d, $^3J_{HH}$ = 10.6, 1H, allyl CHPh), 2.73 (s, 3H, C(=O)*Me*), 3.23 (dd, $^3J_{HH}$ = 7.0, $^2J_{HH}$ = 2.5, 1H, allyl CH_2), 5.35 (ddd, $^3J_{HH}$ = 13.3, 10.6, 7.0, 1H, allyl *CH*), 7.05 (t, $^3J_{HH}$ = 7.3, 1H, aryl *H*), 7.26 (t, $^3J_{HH}$ = 7.5, 2H, aryl *H*), 7.31 (d, $^3J_{HH}$ = 7.5, 2H, aryl *H*). ^{13}C APT NMR (100 MHz, C_6D_6): δ 10.2 (C_5Me_5), 48.2 (WC(=O)*Me*), 65.8 (allyl CH_2), 70.9 (allyl CHPh), 109.0 (C_5Me_5), 109.6 (allyl *CH*), 126.5 (aryl *C*), 127.8 (aryl *C*), 129.0 (aryl *C*), 141.7 (ipso *C*), 264.4 (acyl *C*).

Preparation of Cp*W(NO)(CO)(η^2-PhCH=CHCH$_2$C(=O)CH$_3$) (12). In a glovebox, a Parr 5500 reactor was charged with complex **1** (1.123 g, 2.090 mmol) and C_6H_{12} (ca. 125 mL). The reactor was sealed, purged six times with 500 psig of CH_4, and then pressurized to 1250 psig. The contents of the reactor were heated to 88 °C while being mechanically stirred for 4 h. The contents of the reactor were cooled, and the gas was carefully vented. The reactor was purged three times with 500 psig of CO and then pressurized to 750 psig. The contents of the reactor were heated to 75 °C while being stirred for 18 h. The reactor was then cooled, the gas was vented, and a yellow-brown mixture was collected. The solvent was removed in vacuo. The desired product was isolated by column chromatography (2.5 × 6 cm) on a silica support using 0−20% EtOAc in hexanes. Removal of the solvent from the yellow eluate afforded **12** as an orange oil (438.5 mg, 41% yield). The orientation of the η^2-alkene ligand of each isomer was determined using the chemical shifts of the alkene H signals in the ^1H NMR spectrum.

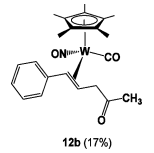
*Characterization Data for **12a** (83%).*



12a (83%)

IR (cm^{-1}): 1606 (s, ν_{NO}), 1714 (w, $\nu_{CO\text{-ketone}}$), 1959 (s, $\nu_{CO\text{-terminal}}$). MS (LREI, *m/z*, probe temperature 150 °C): 537 [M^+, ^{184}W]. ^1H NMR (600 MHz, C_6D_6): δ 1.55 (s, 15H, C_5Me_5), 1.87 (s, 3H, C(=O)*Me*), 2.70 (ddd, $^3J_{HH}$ = 11.0, 7.0, 5.5, $^2J_{WH}$ = 5.6, 1H, =*CH*), 3.01 (dd, $^3J_{HH}$ = 7.0, $^2J_{HH}$ = 16.8, 1H, CH_2C(=O)), 3.10 (dd, $^3J_{HH}$ = 5.5, $^2J_{HH}$ = 16.8, 1H, CH_2C(=O)), 3.96 (d, $^3J_{HH}$ = 11.0, 1H, PhC*H* =), 6.87 (t, $^3J_{HH}$ = 7.2, 1H, aryl *H*), 7.08 (t, $^3J_{HH}$ = 7.4, 2H, aryl *H*), 7.18 (m, 2H, aryl *H*). ^{13}C NMR (150 MHz, C_6D_6): δ 10.3 (C_5Me_5), 29.6 (C(=O)*Me*), 41.6 (=*CH*), 53.3 (CH_2C(=O)), 57.2 (PhCH=), 105.82 (C_5Me_5), 125.9 (aryl *C*), 126.6 (aryl *C*), 128.6 (aryl *C*), 143.52 (ipso *C*), 209.0 (*C*(=O)Me), 224.9 (WCO).

*Characterization Data for **12b** (17%).*

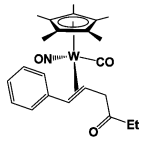


12b (17%)

^1H NMR (600 MHz, C_6D_6): δ 1.52 (obscured, 1H, CH_2C(=O)), 1.56 (s, 15H, C_5Me_5), 1.84 (s, 3H, C(=O)*Me*), 2.41 (d, $^3J_{HH}$ = 10.4, 1H, PhC*H*=), 3.01 (obscured, 1H, CH_2C(=O)), 3.51 (td, $^3J_{HH}$ = 10.8, 5.0, 1H, =*CH*), 6.93 (t, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 6.98 (d, $^3J_{HH}$ = 7.8, 2H, *o*-aryl *H*), 7.23 (m, 2H, *m*-aryl *H*). ^{13}C NMR (150 MHz, C_6D_6): δ (selected signals) 28.2 (C(=O)*Me*), 48.2 (=*CH*), 51.6 (CH_2C(=O)), 53.5 (PhCH=), 105.6 (C_5Me_5), 125.7 (aryl *C*), 146.9 (ipso *C*), 207.5 (*C*(=O)Me).

Preparation of Cp*W(NO)(CO)(η^2-PhCH=CHCH$_2$C(=O)-CH$_2$CH$_3$) (13). In a glovebox, a Parr 5500 reactor was charged with complex **1** (0.300 g, 0.558 mmol) and C_6H_{12} (ca. 75 mL). The reactor was sealed, purged three times with 400 psig of C_2H_6, and then pressurized to 400 psig. The contents of the reactor were heated to 55 °C while being stirred for 3 days. The contents of the reactor were then cooled, and the gas was vented. Then the reactor was purged three times with 500 psig of CO before being pressurized to 750 psig. The contents of the reactor were heated to 75 °C for 18 h while being stirred. The gas was then vented, and a dark yellow mixture was collected. The solvent was removed in vacuo. The desired product was isolated by column chromatography (2.5 × 6 cm) on a silica support using a gradient of 0−20% EtOAc in hexanes. Removal of the solvent from the yellow eluate afforded **13** as an orange oil (153 mg, 50% yield). The orientation of the η^2-alkene ligand of each isomer of **13** was determined using the chemical shifts of the alkene H signals in the ^1H NMR spectrum.

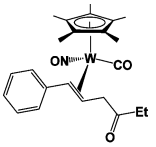
*Characterization Data for **13a** (84%).*



13a (84%)

IR (cm^{-1}): 1608 (s, ν_{NO}), 1711 (w, $\nu_{CO\text{-ketone}}$), 1958 (s, $\nu_{CO\text{-terminal}}$). MS (LREI, *m/z*, probe temperature 150 °C): 551 [M^+ − CO, ^{184}W], 523 [M^+ − CO, ^{184}W]. HRMS-EI (*m/z*, ^{182}W): calcd for $C_{23}H_{29}NO_3{}^{182}W$ 549.16297, found 549.16337. ^1H NMR (400 MHz, C_6D_6): δ 1.00 (t, $^3J_{HH}$ = 7.2, 3H, C(=O)CH_2CH_3), 1.56 (s, 15H, C_5Me_5), 2.20 (m, 1H, C(=O)CH_2CH_3), 2.29 (m, 1H, C(=O)CH_2CH_3), 2.77 (dt, $^3J_{HH}$ = 10.9, 6.5, $^2J_{WH}$ = 5.5, 1H, PhCH=*CH*), 3.10 (d, $^3J_{HH}$ = 6.3, 1H, =CHCH_2C(=O)) 3.99 (d, $^3J_{HH}$ = 10.9, 1H, PhC*H*=CH), 6.89 (t, $^3J_{HH}$ = 7.2, 1H, *p*-aryl *H*), 7.10 (t, $^3J_{HH}$ = 7.6, 2H, *m*-aryl *H*), 7.20 (d, $^3J_{HH}$ = 7.6, 2H, *o*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ 10.2 (C_5Me_5), 30.1 (C(=O)CH_2CH_3), 35.7 (C(=O)CH_2CH_3), 41.8 ($^1J_{WC}$ = 41.0, =*C*HCH$_2$C(=O)), 52.3 (=CHCH$_2$C(=O)), 57.1 ($^1J_{WC}$ = 9.2, PhCH=), 105.9 (C_5Me_5), 125.9 (*p*-aryl *C*), 126.6 (*o*-aryl *C*), 128.2 (*m*-aryl *C*), 143.5 (ipso *C*), 211.4 (*C*(=O)CH_2CH_3), 225.0 ($^1J_{WC}$ = 185.0, W-CO).

*Characterization Data for **13b** (16%).*



13b (16%)

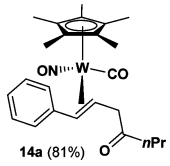
^1H NMR (400 MHz, C_6D_6): δ 0.90 (t, $^3J_{HH}$ = 7.2, 3H, C(=O)C-H_2CH_3), 1.58 (s, 15H, C_5Me_5), 1.59 (obscured, 1H, =CHCH_2C(=O)), 2.28 (m, 2H, C(=O)CH_2CH_3), 2.45 (d, $^3J_{HH}$ = 10.6, $^2J_{WH}$ = 5.5, 1H, PhC*H*=CH), 3.03 (dd, $^3J_{HH}$ = 4.9, $^2J_{HH}$ = 14.5, 1H, =CHCH_2C(=O)) 3.58 (td, $^3J_{HH}$ = 10.6, 4.9, 1H, PhCH=*CH*), 6.92 (tt, $^4J_{HH}$ = 1.1, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 7.00 (dd, $^4J_{HH}$ = 1.1, $^3J_{HH}$ = 8.4, 2H, *o*-aryl *H*), 7.23 (m, 2H, *m*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 10.3 (C_5Me_5), 19.2 (C(=O)CH_2CH_3), 23.4 (C(=O)CH_2CH_3), 48.4 ($^1J_{WC}$ = 11.0, =*C*HCH$_2$C(=O)), 50.5 (=CHCH$_2$C(=O)), 53.7 ($^1J_{WC}$ = 34.9, PhCH=), 105.8 (C_5Me_5), 125.7 (aryl *C*), 127.3 (aryl *C*), 146.8 (ipso *C*), 210.0 (*C*(=O)C-H_2CH_3), 224.1 (W-CO).

Preparation of Cp*W(NO)(CO)(η^2-PhCH=CHCH$_2$C(=O)-CH$_2$CH$_2$CH$_3$) (14). In a glovebox, a Parr 5500 reactor was charged with **1** (0.300 g, 0.558 mmol) and C_6H_{12} (75 mL). The reactor was sealed and purged three times with 150 psig of C_3H_8 and then pressurized to 150 psig. The contents of the reactor were heated to 55 °C while being stirred for 3 days. The contents were then cooled, and the gas was vented. The reactor was purged three times with 500 psig of CO before being pressurized to 750 psig. The contents of the reactor were heated to 75 °C for 18 h while being stirred. The gas was then vented, and a dark yellow mixture was collected. The solvent was removed in vacuo. The desired product was isolated by column chromatography (2.5 × 6 cm) on a silica support using 0−20% EtOAc

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

in hexanes. Removal of the solvent from the yellow eluate afforded **14** as an orange oil (142 mg, 45% yield). The orientation of the η^2-alkene ligand of each isomer was determined using the chemical shifts of the alkene H signals in the ^{1}H NMR spectrum.

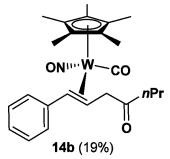
*Characterization data for **14a** (81%).*



14a (81%)

IR (cm^{-1}): 1612 (s, ν_{NO}), 1714 (w, $\nu_{CO\text{-ketone}}$), 1959 (s, $\nu_{CO\text{-terminal}}$). MS (LREI, *m*/*z*, probe temperature 150 °C): 565 [M$^+$, ^{184}W], 537 [M$^+$ − CO, ^{184}W]. HRMS-EI (*m*/*z*, ^{182}W) calcd for $C_{23}H_{31}NO_2{}^{182}W$: 535.18370, found: 535.18345. ^{1}H NMR (400 MHz, C_6D_6): δ 0.81 (t, $^3J_{HH}$ = 7.4, 3H, C(=O)CH$_2$CH$_2$C*H*$_3$), 1.57 (s, 15H, C$_5$*Me*$_5$), 1.57−1.63 (obscured, m, 2H, C(=O)CH$_2$C*H*$_2$CH$_3$), 2.09−2.33 (m, 2H, C(=O)C*H*$_2$CH$_2$CH$_3$), 2.78 (dt, $^3J_{HH}$ = 11.0, 6.4, 1H, PhCH=C*H*), 3.11 (t, $^3J_{HH}$ = 6.3, 1H, =CHC*H*$_2$C(=O)) 4.02 (d, $^3J_{HH}$ = 11.0, 1H, PhC*H*=CH), 6.87 (t, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 7.08 (t, $^3J_{HH}$ = 7.7, 2H, *m*-aryl *H*), 7.20 (d, $^3J_{HH}$ = 7.6, 2H, *o*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ 9.9 (C$_5$*Me*$_5$), 14.0 (C(=O)CH$_2$CH$_2$*C*H$_3$), 17.5 (C(=O)CH$_2$*C*H$_2$CH$_3$), 41.4 (=*C*HCH$_2$C(=O)), 44.2 (C(=O)*C*H$_2$CH$_2$CH$_3$), 52.4 (=CHCH$_2$C(=O)), 56.8 (PhCH=), 105.5 (*C*$_5$Me$_5$), 125.6 (*p*-aryl *C*), 126.4 (*o*-aryl *C*), 128.2 (*m*-aryl *C*), 143.2 (ipso *C*), 210.7 (*C*(=O)CH$_2$CH$_3$), 224.8 (W-*C*O).

*Characterization Data for **14b** (19%).*

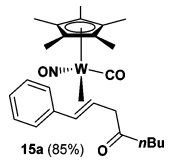


14b (19%)

^{1}H NMR (400 MHz, C_6D_6): δ 0.72 (t, $^3J_{HH}$ = 7.4, 3H, C(=O)CH$_2$CH$_2$C*H*$_3$), 1.44−1.52 (m, 2H, C(=O)CH$_2$C*H*$_2$CH$_3$), 1.59 (s, 15H, C$_5$*Me*$_5$), 2.11−2.15 (m, 2H, C(=O)C*H*$_2$CH$_2$CH$_3$), 2.47 (d, $^3J_{HH}$ = 10.7, $^2J_{WH}$ = 6.2, 1H, PhC*H*=CH), 3.10 (obscured, 2H, =CHC*H*$_2$C(=O)), 3.60 (td, $^3J_{HH}$ = 10.7, 4.8, 1H, PhCH=C*H*), 6.91 (obscured, 1H, *p*-aryl *H*), 7.00 (d, $^3J_{HH}$ = 7.4, 2H, *o*-aryl *H*), 7.22 (obscured, 2H, *m*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 10.2 (C$_5$*Me*$_5$), 14.0 (C(=O)CH$_2$CH$_2$*C*H$_3$), 16.8 (C(=O)CH$_2$CH$_2$*C*H$_3$), 38.1 (C(=O)*C*H$_2$CH$_2$CH$_3$), 41.6 (=CHC*H*$_2$C-(=O)), 47.7 (=CHCH$_2$C(=O)), 52.8 (PhCH=), 105.5 (*C*$_5$Me$_5$), 125.4 (aryl *C*), 126.5 (aryl *C*), 143.0 (ipso *C*).

Preparation of Cp*W(NO)(CO)(η^2-PhCH=CHCH$_2$C(=O)-CH$_2$CH$_2$CH$_2$CH$_3$) (15). In a glovebox, a Parr 5500 reactor was charged with **1** (0.300 g, 0.558 mmol) and C_6H_{12} (ca. 75 mL). The reactor was sealed and purged three times with 150 psig of C_4H_{10} and then pressurized to 150 psig. The contents of the reactor were heated to 55 °C while being stirred for 3 days. The contents of the reactor were then cooled, and the gas was vented. The reactor was purged three times with 500 psig of CO before being pressurized to 750 psig. The contents of the reactor were heated to 75 °C for 18 h while being stirred. The gas was then vented, and a dark yellow mixture was collected. The solvent was removed from the mixture in vacuo. The desired product was isolated by column chromatography (2.5 × 6 cm) on a silica support using 0−20% EtOAc in hexanes. Removal of the solvent from the yellow eluate afforded **15** as an orange oil (108 mg, 35% yield). The orientation of the η^2-alkene ligand of each isomer was determined using the chemical shifts of the alkene H signals in the ^{1}H NMR spectrum.

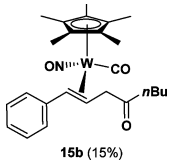
*Characterization Data for **15a** (85%).*



15a (85%)

IR (cm^{-1}): 1610 (s, ν_{NO}), 1712 (w, $\nu_{CO\text{-ketone}}$), 1959 (s, $\nu_{CO\text{-terminal}}$). MS (LREI, *m*/*z*, probe temperature 150 °C): 579 [M$^+$, ^{184}W], 551 [M$^+$ − CO, ^{184}W]. HRMS-EI (*m*/*z*, ^{182}W): calcd for $C_{25}H_{33}NO_3{}^{182}W$ 577.19427, found 577.19496. ^{1}H NMR (400 MHz, C_6D_6): δ 0.81 (t, $^3J_{HH}$ = 7.3, 3H, C(=O)CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.20 (dq, $^3J_{HH}$ = 14.4, 7.3, 2H, C(=O)CH$_2$CH$_2$C*H*$_2$CH$_3$) 1.57 (s, 15H, C$_5$*Me*$_5$), 1.50−1.63 (obscured, m, 2H, C(=O)CH$_2$C*H*$_2$CH$_2$CH$_3$), 2.26 (dt, $^3J_{HH}$ = 17.0, 7.3, 2H, C(=O)C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.80 (dt, $^3J_{HH}$ = 10.8, 6.2, 1H, PhCH=C*H*), 3.13 (t, $^3J_{HH}$ = 6.2, 1H, =CHC*H*$_2$C(=O)) 4.02 (d, $^3J_{HH}$ = 10.8, 1H, PhC*H*=CH), 6.87 (t, $^3J_{HH}$ = 7.3, 1H, *p*-aryl *H*), 7.08 (t, $^3J_{HH}$ = 7.7, 2H, *m*-aryl *H*), 7.21 (d, $^3J_{HH}$ = 7.7, 2H, *o*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ 9.9 (C$_5$*Me*$_5$), 14.1 (C(=O)CH$_2$CH$_2$CH$_2$-*C*H$_3$), 22.7 (C(=O)CH$_2$CH$_2$*C*H$_2$CH$_3$), 26.2 (C(=O)CH$_2$*C*H$_2$-CH$_2$CH$_3$), 41.5 (=*C*HCH$_2$C(=O)), 42.1 (C(=O)CH$_2$CH$_2$*C*H$_2$-CH$_3$), 52.4 (=CHCH$_2$C(=O)), 56.8 (PhCH=), 105.52 (*C*$_5$Me$_5$), 125.5 (*p*-aryl *C*), 126.3 (*o*-aryl *C*), 128.0 (*m*-aryl *C*), 143.2 (ipso *C*), 210.5 (C(=O)CH$_2$CH$_3$), 224.7 (W-CO).

*Characterization Data for **15b** (15%).*

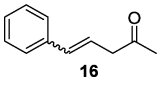


15b (15%)

^{1}H NMR (400 MHz, C_6D_6): δ 0.73 (t, $^3J_{HH}$ = 7.3, 3H, C(=O)CH$_2$-CH$_2$CH$_2$C*H*$_3$), 1.07−1.15 (m, C(=O)CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.46−1.53 (m, 2H, C(=O)CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.59 (s, 15H, C$_5$*Me*$_5$), 2.29−2.39 (m, 2H, C(=O)CH$_2$CH$_2$CH$_2$CH$_3$), 2.47 (d, $^3J_{HH}$ = 10.7, $^2J_{WH}$ = 6.1, 1H, PhC*H*=CH), 2.81−2.90 (obscured, 2H, =CHC*H*$_2$C(=O)), 3.61 (td, $^3J_{HH}$ = 10.6, 4.7, 1H, PhCH=C*H*), 6.86 (obscured, 1H, *p*-aryl *H*), 7.00 (d, $^3J_{HH}$ = 7.4, 2H, *o*-aryl *H*), 7.22−7.26 (obscured, 2H, *m*-aryl *H*). ^{13}C NMR (100 MHz, C_6D_6): δ (selected signals) 10.2 (C$_5$*Me*$_5$), 13.9 (C(=O)CH$_2$CH$_2$CH$_2$CH$_3$), 22.4 (C(=O)-CH$_2$CH$_2$CH$_2$CH$_3$), 26.1 (C(=O)CH$_2$CH$_2$CH$_2$CH$_3$), 41.4 (C(=O)*C*H$_2$CH$_2$CH$_2$CH$_3$), 46.6 (=CHCH$_2$C(=O)), 47.8 (=CHCH$_2$C(=O)), 53.0 (PhCH=), 105.51 (*C*$_5$Me$_5$), 124.9 (aryl *C*), 125.4 (aryl *C*), 126.5 (aryl *C*), 143.2 (ipso *C*), 211.4 (CH$_2$*C*(=O)CH$_2$), 223.9 (W-*C*O).

General Procedure for Effecting the Photolyses. Irradiation was performed in a quartz, UV immersion-well reactor using a mercury high-pressure lamp (Hanovia L, 450 W). The volume of acetonitrile required to fill the reactor was 230 mL. Samples of the organometallic reactants were dissolved in small quantities of acetonitrile prior to addition to the well reactor and then subsequently diluted in acetonitrile to ensure that the reactor was filled.

*Preparation of (E/Z)-5-Phenylpent-4-en-2-one (**16**).*



16

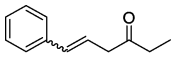
Photolysis was performed by following the general procedure described above. Complex **12** (0.090 g, 0.168 mmol) was irradated in the UV immersion-well reactor for 10 min. The resulting solution was concentrated in vacuo. The crude product was then purified by column chromatography (2.5 × 6 cm) on silica and eluted with gradient 0−30% EtOAc in hexanes to give a yellow oil that was a mixture of approximately 1/1 *E*/*Z* isomers of **16** (0.013 g, 48% yield).

*Characterization Data for (E)-**16**.* IR (cm^{-1}): 1714 (s, ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 3.44 (dd, *J* = 7.2, 1.8, 2H), 5.91 (dt, *J* = 11.6, 7.3, 1H), 6.66 (d, *J* = 11.6, 1H), 7.16−7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.5, 47.1, 122.3, 126.4, 127.7, 128.7, 133.8, 137.1, 209.0.

*Characterization Data for (Z)-**16**.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 1H), 3.34 (dd, *J* = 7.1, 1.3, 2H), 6.31 (dt, *J* = 15.9, 7.1, 1H), 6.47 (d, *J* = 15.9, 1H), 7.16−7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.7, 50.8, 126.1, 126.69, 126.71, 128.4, 134.8, 137.2, 209.0. The spectroscopic data for both isomers of **16** are consistent with that reported in the literature.[17]

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

*Preparation of (E/Z)-6-Phenylhex-5-en-3-one (**17**).*



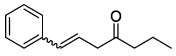
17

Photolysis was performed by following the general procedure described above. Complex **13** (0.018 g, 0.032 mmol) was irradated in the UV immersion-well reactor for 10 min. The resulting solution was concentrated in vacuo. The crude product was then purified by column chromatography (2.5 × 6 cm) on silica, with gradient 0−30% EtOAc in hexanes as eluent, to give a yellow oil consisting of an approximately 1/1 mixture of *E*/*Z* isomers of **17** (0.004 g, 72% yield).

*Characterization Data for (E)-**17**.* IR (cm^{-1}): 1711 (s, ν_{CO}). ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.3, 3H), 2.51 (q, J = 7.3, 2H), 3.37 (d, J = 6.8, 8H), 6.27−6.41 (m, 1H), 6.52 (d, J = 16.5, 1H), 7.13−7.47 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.0, 35.9, 46.8, 122.5, 126.5, 127.8, 128.8, 133.8, 137.1, 209.5.

*Characterization Data for (Z)-**17**.* ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.3, 3H), 2.58 (q, J = 7.2, 2H), 3.47 (dd, J = 7.4, 1.4, 8H), 5.91−6.02 (m, 1H), 6.69 (d, J = 11.4, 1H), 7.13−7.47 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 44.5, 47.1, 122.3, 126.4, 127.7, 128.7, 133.7, 137.2, 207.8. The spectroscopic data for both isomers of **17** are consistent with that reported in the literature.[18]

*Preparation of (E/Z)-1-Phenylhept-1-en-4-one (**18**).*



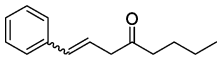
18

Photolysis was performed by following the general procedure described above. Complex **14** (0.110 g, 0.196 mmol) was irradated in the UV immersion-well reactor for 10 min. The resulting solution was concentrated in vacuo. The crude product was then purified by column chromatography (2.5 × 6 cm) on silica, with gradient 0−30% EtOAc in hexanes as eluent, to obtain a yellow oil consisting of an approximately 1/1 mixture of *E*/*Z* isomers of **18** (0.0176 g, 48% yield).

*Characterization Data for (E)-**18**.* IR (cm^{-1}): 1714 (s, ν_{CO}). ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, J = 7.4, 3H), 1.64 (h, J = 7.3, 2H), 2.48 (t, J = 7.3, 2H), 3.32 (d, J = 7.0, 2H), 6.33 (dt, J = 15.8, 7.0, 1H), 6.48 (d, J = 15.9, 1H), 7.24 (t, J = 7.4, 1H), 7.31 (t, J = 7.5, 2H), 7.38 (d, J = 7.3, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 17.3, 44.5, 47.1, 77.2, 122.3, 126.4, 127.7, 128.7, 133.8, 137.1, 209.0.

*Characterization Data for (Z)-**18**.* ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J = 7.8, 3H), 1.57−1.65 (m, 2H), 2.42 (t, J = 7.3, 2H) 3.41 (dd, J = 7.3, 1.8, 2H), 5.92 (dt, J = 11.6, 7.2, 1H), 6.65 (d, J = 11.6, 1H), 7.16−7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.0, 18.4, 38.2, 42.2, 75.5, 122.8, 125.7, 127.1, 128.9, 133.4, 137.2, 207.1. The spectroscopic data for both isomers of **18** are consistent with those reported in the literature.[19]

*Preparation of (E/Z)-1-phenyloct-1-en-4-one (**19**).*



19

Photolysis was performed by following the general procedure described above. Complex **15** (0.018 g, 0.032 mmol) was irradated in the UV immersion-well reactor for 10 min. The resulting solution was concentrated in vacuo. The crude product was then purified by column chromatography on silica eluted with gradient 0−30% EtOAc in hexanes to give a yellow oil consisting of an approximately 1/1 mixture of *E*/*Z* isomers of **19** (0.024 g 69% yield).

*Characterization Data for (E)-**19**.* IR (cm^{-1}): 1712 (s, ν_{CO}). ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.3, 3H), 1.28−1.37 (m, 2H), 1.56−1.64 (m, 2H), 2.49 (t, J = 7.4, 2H), 3.32 (d, J = 8.2, 2H), 6.31 (dt, J = 15.9, 7.1, 1H), 6.47 (d, J = 15.9, 1H), 7.20−7.25 (m, 1H), 7.31 (t, J = 7.5, 2H), 7.37 (d, J = 7.2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 29.9, 42.4, 59.0, 72.8, 122.4, 127.7, 128.7, 129.4, 134.6, 141.5, 209.2.

*Characterization Data for (Z)-**19**.* ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J = 7.6, 3H), 1.29−1.47 (m, 2H), 1.46−1.64 (m, 2H), 2.44 (t, J = 7.4, 1H), 3.42 (dd, J = 7.3, 1.8, 2H), 5.92 (dt, J = 11.5, 7.3, 1H), 6.65 (d, J = 11.7, 1H), 7.16−7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.8, 29.9, 42.1, 57.8, 68.3, 123.4, 126.4, 128.5, 129.4, 133.7, 140.0, 207.8. The spectroscopic data for both isomers of **19** are consistent with those reported in the literature.[20]

Reaction of 7 with CO at 75−170 °C: Preparation of (*E*/*Z*)-5-phenylpent-4-en-2-one (16). In a glovebox, a Parr 5500 reactor was charged with **7** (110 mg, 0.205 mmol) and benzene-d_6 (20 mL) to give a yellow solution. The reactor was sealed and then purged with CO (3 × 500 psig) before being pressurized to 1000 psig. The contents of the reactor were heated to 75 °C for 1 day (to generate complex **12** in situ), and then the heat was increased to 170 °C, at which temperature the contents were mechanically stirred for an additional 18 h. The contents of the reactor were then cooled, and the gas was carefully vented. The final orange reaction mixture was filtered through Celite. The C_6D_6 solvent was removed in vacuo, the resulting orange oily mixture was redissolved in $CDCl_3$ (ca. 2 mL), and ferrocene (39 mg, 0.21 mmol) was added as an internal standard. Analysis of this mixture by ^1H NMR spectroscopy revealed the presence of an approximately 9/1 mixture of (*E*/*Z*)-5-phenylpent-4-en-2-one (**16**), which was obtained in 37% yield (12 mg). The organometallic byproduct Cp*W(NO)$(CO)_2$ was obtained in 24% yield (20 mg).

X-ray Crystallography. Data collection was carried out at −183.0 ± 1 °C on a Bruker APEX DUO diffractometer equipped with a TRIUMPH curved-crystal monochromator using Mo Kα radiation or at −173.0 ± 2 °C on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo Kα radiation.

Data for **2b** were collected to a maximum 2θ value of 55.162° in 0.5° oscillations. The structure was solved by direct methods[21] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in riding coordinates. The final cycle of full-matrix least-squares analysis was based on 4241 observed reflections and 208 variable parameters.

Data for **3a** were collected to a maximum 2θ value of 60.74° in 0.5° oscillations. The structure was solved by direct methods[21] and expanded using Fourier techniques. The complex crystallized as a two-component twin and the twin components were separated using Cell_Now[22] and TWINABS.[23] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares analysis was based on 8507 observed reflections and 225 variable parameters.

Data for **4a** were collected to a maximum 2θ value of 55.06° in 0.5° oscillations. The structure was solved by direct methods[21] and expanded using Fourier techniques. All 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 4542 observed reflections and 241 variable parameters.

Data for **5a** were collected to a maximum 2θ value of 53.1° in 0.5° oscillations. The structure was solved by direct methods[21] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares analysis was based on 4326 observed reflections and 234 variable parameters.

Data for **7b** were collected to a maximum 2θ value of 55.32° in 0.5° oscillations. The structure was solved by direct methods[21] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares analysis was based on 9514 observed reflections and 208 variable parameters.

Data for **9** were collected to a maximum 2θ value of 60.06° in 0.5° oscillations. The structure was solved by direct methods[24] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares analysis was based on 5903 observed reflections and 257 variable parameters.

For each structure neutral-atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_c;[26] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[27] The values for mass attenuation coefficients were those of Creagh and Hubbell.[28] All calculations were performed using either SHELXL-97[29] via the WinGX interface[30] or SHELXL-2014[31] via the OLEX interface.[32] X-ray crystallographic data for all six structures are presented in

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX

Tables S1 and S2 in the Supporting Information, as are full details of all crystallographic analyses.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00739.

Views of the solid-state molecular structures of complexes **2b**, **3a**, and **5a** and tables of X-ray crystallographic data for complexes **2b**, **3a**−**5a**, **7b**, and **9** (PDF)

Full details of the crystallographic analyses of **2b**, **3a**−**5a**, **7b**, and **9** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for P.L.: legzdins@chem.ubc.ca.

ORCID

Peter Legzdins: 0000-0002-3914-3768

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to The Dow Chemical Company for continuing financial support of our work and to our Dow colleagues, Andy Arthur and Brian Kolthammer, for assistance and helpful discussions. R.A.B. acknowledges the NSERC of Canada for the award to him of a PGSD postgraduate scholarship. We also thank Rex Handford for technical assistance.

■ REFERENCES

(1) Baillie, R. A.; Patrick, B. O.; Legzdins, P.; Rosenfeld, D. C. *Organometallics* **2016**, 10.1021/acs.organomet.6b00738.

(2) Ng, S. H. K.; Adams, C. S.; Hayton, T. W.; Legzdins, P.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 15210−15223.

(3) Baillie, R. A.; Tran, T.; Lalonde, K. M.; Tsang, J. Y. K.; Thibault, M. E.; Patrick, B. O.; Legzdins, P. *Organometallics* **2012**, *31*, 1055−1067.

(4) Baillie, R. A.; Legzdins, P. *Acc. Chem. Res.* **2014**, *47*, 330−340.

(5) Baillie, R. A.; Man, R. W. Y.; Shree, M. V.; Chow, C.; Thibault, M. E.; McNeil, W. S.; Legzdins, P. *Organometallics* **2011**, *30*, 6201−6217.

(6) Semproni, S. P.; McNeil, W. S.; Baillie, R. A.; Patrick, B. O.; Campana, C. F.; Legzdins, P. *Organometallics* **2010**, *29*, 867−875.

(7) Baillie, R. A.; Tran, T.; Thibault, M. E.; Legzdins, P. *J. Am. Chem. Soc.* **2010**, *132*, 15160−15161.

(8) Baillie, R. A.; Holmes, A. S.; Lefèvre, G. P.; Patrick, B. O.; Shree, M. V.; Wakeham, R. J.; Legzdins, P.; Rosenfeld, D. C. *Inorg. Chem.* **2015**, *54*, 5915−5929.

(9) Baillie, R. A.; Legzdins, P. *Coord. Chem. Rev.* **2016**, *309*, 1−20.

(10) (a) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 6908−6914. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408.

(11) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, CA, 2010; pp 71−72, 398−407.

(12) Tran, T.; Chow, C.; Zimmerman, A. C.; Thibault, M. E.; McNeil, W. S.; Legzdins, P. *Organometallics* **2011**, *30*, 738−751.

(13) Semproni, S. P.; Graham, P. M.; Buschhaus, M. S. A.; Patrick, B. O.; Legzdins, P. *Organometallics* **2009**, *28*, 4480−4490.

(14) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077−2081.

(15) Tsang, J. Y. K.; Buschhaus, M. S. A.; Fujita-Takayama, C.; Patrick, B. O.; Legzdins, P. *Organometallics* **2008**, *27*, 1634−1644.

(16) Baillie, R. A.; Wakeham, R. J.; Lefèvre, G. P.; Béthegnies, A.; Patrick, B. O.; Legzdins, P.; Rosenfeld, D. C. *Organometallics* **2015**, *34*, 3428−3441.

(17) Trofimov, B. A.; Schmidt, E. Y.; Zorina, N. V.; Ivanova, E. V.; Ushakov, I. A. *J. Org. Chem.* **2012**, *77*, 6880−6886.

(18) Izquierdo, J.; Rodriguez, S.; González, F. V. *Org. Lett.* **2011**, *13*, 3856−3859.

(19) Obora, Y.; Ogawa, Y.; Imai, Y.; Kawamura, T.; Tsuji, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10489−10493.

(20) Hegedus, L. S.; Perry, R. *J. Org. Chem.* **1985**, *50*, 4955−4960.

(21) SIR-92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

(22) *Cell_Now 2008/2*; Bruker AXS Inc., Madison, WI, USA, 2008).

(23) *TWINABS, V2008/4*; Bruker AXS Inc., Madison, WI, USA, 2008.

(24) SIR-97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. *IV*, Table 2.2 A.

(26) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781−782.

(27) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Kluwer Academic: Boston, MA, 1992; Vol. *C*, Table 4.2.6.8.

(28) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*; Kluwer Academic: Boston, MA, 1992; Vol. *C*, Table 4.2.4.3.

(29) SHELXL-97: Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(30) WinGX-V1.70: Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(31) SHELXL-2014: Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8.

(32) OLEX2-V1.2.6: Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.

DOI: 10.1021/acs.organomet.6b00739
Organometallics XXXX, XXX, XXX−XXX