ACCOUNTS
of chemical research

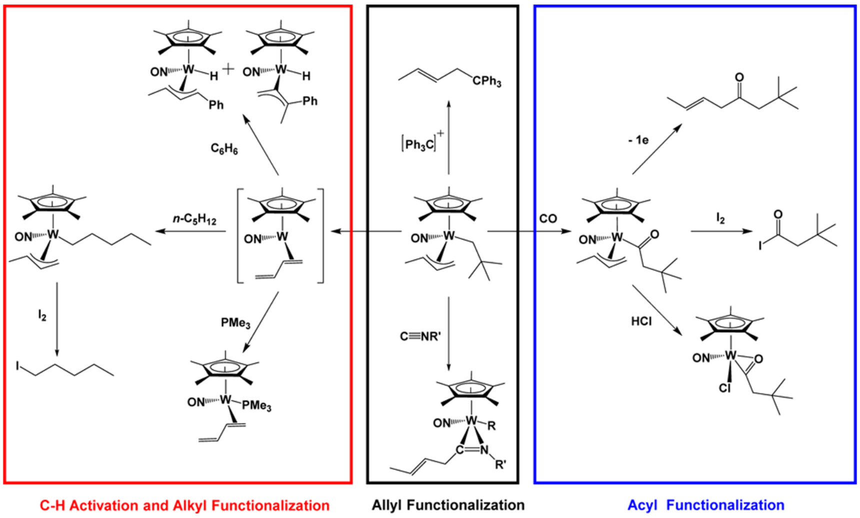
Distinctive Activation and Functionalization of Hydrocarbon C$-$H Bonds Initiated by Cp*W(NO)(η^3-allyl)(CH_2CMe_3) Complexes

RHETT A. BAILLIE AND PETER LEGZDINS*

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

RECEIVED ON APRIL 17, 2013

CONSPECTUS



Converting hydrocarbon feedstocks into value-added chemicals continues to offer challenges to contemporary preparative chemists. A particularly important remaining challenge is the selective activation and functionalization of the C(sp^3)$-$H linkages of alkanes, which are relatively abundant but chemically inert.

This Account outlines the discovery and development of C$-$H bond functionalization mediated by a family of tungsten organometallic nitrosyl complexes. Specifically, it describes how gentle thermolyses of any of four 18-electron Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes (Cp* = η^5-C_5Me_5; η^3-allyl = η^3-$H_2CCHCHMe$, η^3-$H_2CCHCHSiMe_3$, η^3-$H_2CCHCHPh$, or η^3-$H_2CCHCMe_2$) results in the loss of neopentane and the transient formation of a 16-electron intermediate species, Cp*W(NO)(η^2-allene) and/or Cp*W(NO)(η^2-diene). We have never detected any of these species spectroscopically, but we infer their existence based on trapping experiments with trimethylphosphine (PMe_3) and labeling experiments using deuterated hydrocarbon substrates.

This Account first summarizes the syntheses and properties of the four chiral Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes. It then outlines the various types of C$-$H activations we have effected with each of the 16-electron (η^2-allene) or (η^2-diene) intermediate nitrosyl complexes, and presents the results of mechanistic investigations of some of these processes. It next describes the characteristic chemical properties of the Cp*W(NO)(η^3-allyl)(η^1-hydrocarbyl) compounds formed by the single activations of C(sp^3)$-$H bonds, with particular emphasis on those reactions that result in the selective functionalization of the original hydrocarbon substrate. We are continuing development of methods to release the acyl ligands from the metal centers while keeping the Cp*W(NO)(η^3-allyl) fragments intact, with the ultimate aim of achieving these distinctive conversions of alkanes into functionalized organics in a catalytic manner.

Introduction

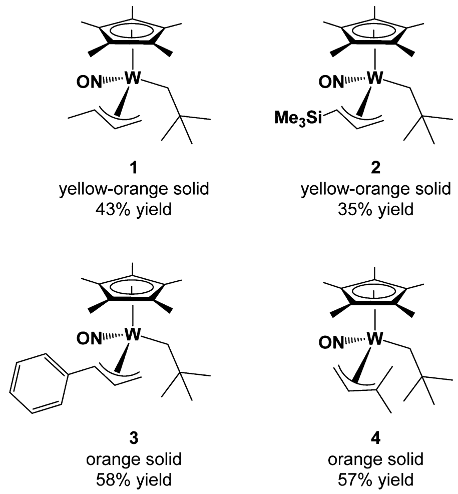
The chemistry involved in the selective activation and functionalization of relatively unreactive C$-$H bonds continues to attract attention from organic, organometallic, biological, and theoretical chemists worldwide.[1] This interest is based, in part, on the desire of researchers to effect the

10.1021/ar400108p

transformation of unactivated C–H linkages into C–X bonds (where X is a desired functional group) in a regio- and chemoselective manner under relatively gentle experimental conditions.[2] One particular area that has received recent attention in this regard has been the conversion of simple hydrocarbons such as alkanes and arenes into value-added chemicals.[3] The development of synthetic methods for these transformations has also been accompanied by kinetic and mechanistic studies that have provided considerable insights as to how these processes may ultimately be effected not only selectively but also in a catalytic manner.[4] Our contributions to this chemistry have involved the development of Group 6 organometallic nitrosyl complexes for the initiation and mediation of various hydrocarbon C–H activations.[5] During these investigations, we have discovered that the family of Cp*M(NO)R_2 compounds (Cp* = η^5-C_5Me_5; M = Mo or W; R = a hydrocarbyl group such as an alkyl or aryl) exhibits R-dependent thermal reactivity to form a variety of reactive 16e nitrosyl complexes that are capable of effecting single, double, or triple activations of hydrocarbon C–H bonds intermolecularly, often in a novel manner. As with their bis(hydrocarbyl) precursors, the NO ligands electronically stabilize these Lewis-acidic intermediate species and render them prone to further reactivity with a variety of hydrocarbon substrates.[5a,b] We have recently extended these investigations to encompass the related 18e Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes, with the neopentyl ligands being employed because of their propensity to participate in intramolecular H-abstraction reactions.[5] The rich C–H activation and functionalization chemistry initiated by four of these allyl complexes is the subject of this Account.

The Cp*W(NO)(η^3-allyl)(CH_2CMe_3) Reactants

The four members of this family of compounds are shown in Figure 1 and, like other Cp*M(NO)(hydrocarbyl)$_2$ (M = Mo, W) complexes,[5a,b] may be synthesized on a large scale and in moderate yields via the sequential metatheses reactions illustrated for **4** in Scheme 1.[6,7]



1
yellow-orange solid
43% yield

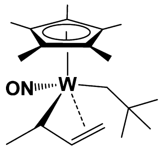
2
yellow-orange solid
35% yield

3
orange solid
58% yield

4
orange solid
57% yield

FIGURE 1. The four Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes whose C–H activation chemistry is the subject of this Account. The yields indicated refer to the second metathesis step shown in Scheme 1

The final yellow-to-orange Cp*W(NO)(η^3-allyl)(CH_2CMe_3) products (**1**–**4**) are separable by chromatography on alumina with Et_2O/pentane as eluant, and concentration of the eluate under reduced pressure affords analytically pure crystals of the desired compounds. Complexes **1**–**4** are 18e species; hence, it is not surprising that they are relatively stable toward oxygen and moisture in the crystalline state. They are chiral and crystallize as enantiomeric pairs in nonchiral space groups. Furthermore, the electronic asymmetry at the metal centers distorts the allyl ligands so as to localize the π-electron density between the carbon atoms trans to NO,[8] as illustrated below for **1**:

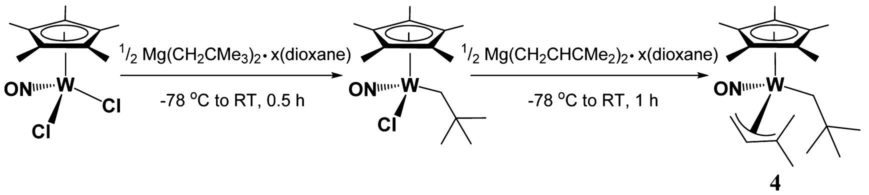


Furthermore, the η^3-allyl ligands may coordinate to the metal centers in an *endo* or an *exo* fashion, and substituents on the terminal carbons of the allyl groups may assume a *syn* or *anti* orientation with respect to the meso hydrogen on the central carbon[8] as illustrated for **1** in Figure 2.

In other words, each Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complex may, in principle, possess several molecular structures in solutions, and some of these isomers are detectable by ^1H NMR spectroscopy.[6,7] However, it has been our experience that steric factors result in one structure usually being markedly more abundant (i.e., >90%) than the others. In general, this molecular structure is the one that the compound exhibits in the solid state, and it is the one that we draw for each of the complexes in this Account. For simplicity, these structures are usually drawn with undistorted allyl ligands.

Complexes **1**–**4** eliminate CMe_4 intramolecularly when thermolyzed at different temperatures, and the reactants are consumed via pseudo-first-order processes. These eliminations leading to the transient C–H activating complexes are the rate-determining steps in the operative mechanisms with all subsequent steps proceeding rapidly. As a result, none of the C–H activating complexes have ever been detected spectroscopically, but their existence has been inferred on the basis of (a) trapping experiments with

SCHEME 1



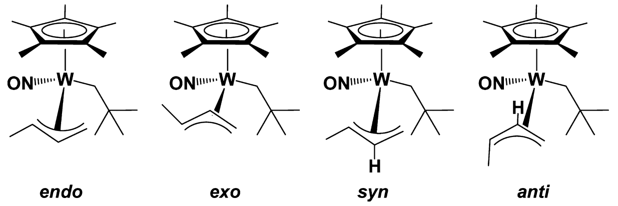


FIGURE 2. Structural isomers of **1**.

PMe_3, as illustrated for **1** and **2** (which form transient η^2-diene and η^2-allene complexes, respectively) in Scheme 2, (b) their reactions with cyclohexene, as illustrated for **3** in Scheme 3, and (c) labeling experiments utilizing deuterated hydrocarbon substrates, as illustrated for **4** in Scheme 4.[7,9–11]

C–H Activations Initiated by the Cp*W(NO)(η^3-allyl)(CH$_2$CMe$_3$) Complexes

The intermolecular C–H activation chemistry of complexes **1**–**4** that has been established to date involves the three distinct types of chemical transformations summarized below.[12,13]

Mode 1. Selective single activation of a terminal C(sp^3)–H bond of the hydrocarbon substrate to produce an isolable η^1-hydrocarbyl complex. Examples of this type of reaction initiated by **1** under ambient conditions and **3** upon thermolysis are illustrated in Scheme 5.[9,10] Complexes **1** and **3** react via different 16e intermediates, namely an η^2-diene (**A**) for **1** and an η^2-allene (**B**) for **3**. That both of these complexes can effect the same single and selective activation of linear alkanes (e.g., to afford products **5** and **6** in Scheme 5) demonstrates that the nature of the 16e intermediate complex is not the key factor in differentiating the mode of reactivity.

Complex **2** is also particularly effective at initiating the very clean activation of the terminal C(sp^3)-H bonds of alkanes or alkyl groups at 55 °C to produce isolable products, and like **3** it does so via an η^2-allene intermediate complex.[7] Interestingly, complexes **1**–**3** do not initiate the clean activation of arene C(sp^2)–H bonds (vide infra). However, as shown in Scheme 4 for C_6D_6, the dimethylallyl complex **4** does effect the activation of a benzene C–H bond at 50 °C and forms the expected phenyl derivative.[11]

Mode 2. The η^1-hydrocarbyl complex initially formed by activation of R–H, Cp*W(NO)(η^3-allyl)(η^1-R), isomerizes by intramolecular exchange of the newly formed hydrocarbyl ligand (R) with a hydrogen atom on the allyl ligand. An example of this type of reaction is the activation of C_6H_6 by **1** as illustrated in Scheme 6.[13,14] As shown in this scheme, the initially formed phenyl complexes (**7a** and **7b**) exhibit electronic asymmetry in their allyl ligands, and the subsequent coupling of the allyl and aryl ligands occurs at the allyl C that has more sp^2 character. In other words, electronic factors seem to determine which allyl hydride complexes [**8a** (minor) and **8b** (major)] are eventually produced.

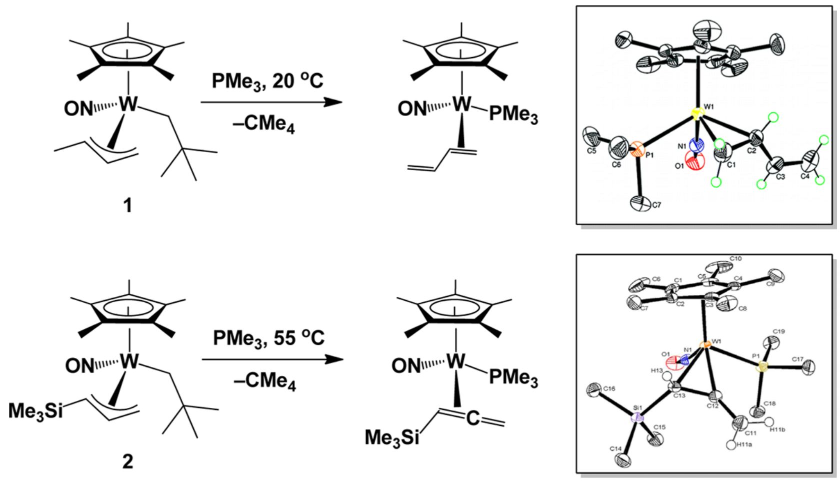
Mode 3. The initially formed η^1-hydrocarbyl complex (which may or may not be detectable) undergoes additional C–H activations and is converted to a new hydrido allyl compound. For instance, thermolyses of **4** in alkane solvents afford mixtures of various allyl hydride complexes resulting from three successive C–H bond activations at different places on the alkanes following loss of the original 1,1-dimethylallyl ligand. The reaction of **4** with pentane to give isomers of Cp*W(NO)(η^3-C_5H_9) is shown in Scheme 7 as a representative example.[13]

Interestingly, as shown in Scheme 8, the phenylallyl complex **3** reacts with methylcyclohexane to produce organometallic complexes resulting from all three possible modes of reactivity.[13] Specifically, complex **3** effects single C–H activation of methylcyclohexane (i.e., mode 1) to afford the product **9**, which can then undergo both mode 2 and mode 3 reactivity intramolecularly to give complexes **10** and **11**, respectively. The reaction of **3** with methylcyclohexane thus provides evidence that both modes 2 and 3 of C–H activation must first occur through single C–H activation (i.e., mode 1) of the organic substrate. For the majority of mode 2 and 3 reactions the initial mode 1 products cannot be isolated.

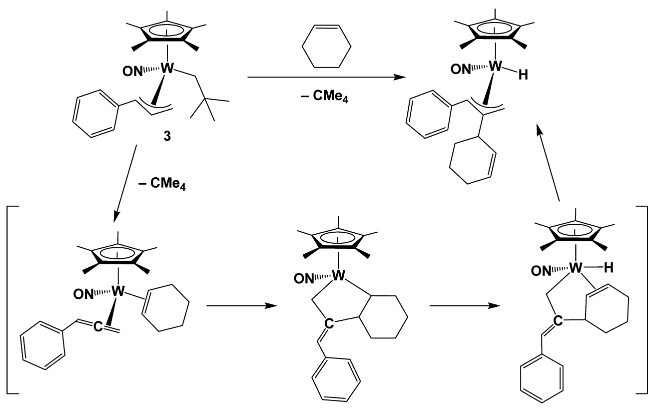
The outcomes of the reactions of complexes **1**–**4** with both C(sp^3)–H and C(sp^2)–H bonds of hydrocarbons are summarized in Table 1.

Interestingly, a correlation exists between the observed thermal chemistry of complexes **1**–**4** and the electron densities at their metal centers as indicated by their infrared nitrosyl-streching frequencies.[13] Thus, **1**, **2**, and **3** exhibit relatively higher ν_{NO}'s as Nujol mulls at 1594, 1589, and 1588 cm^{-1}, respectively, that are indicative of diminished

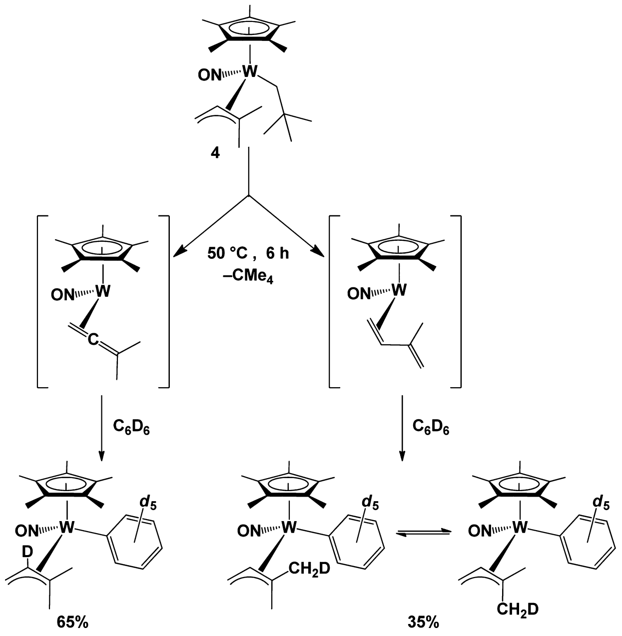
SCHEME 2



SCHEME 3



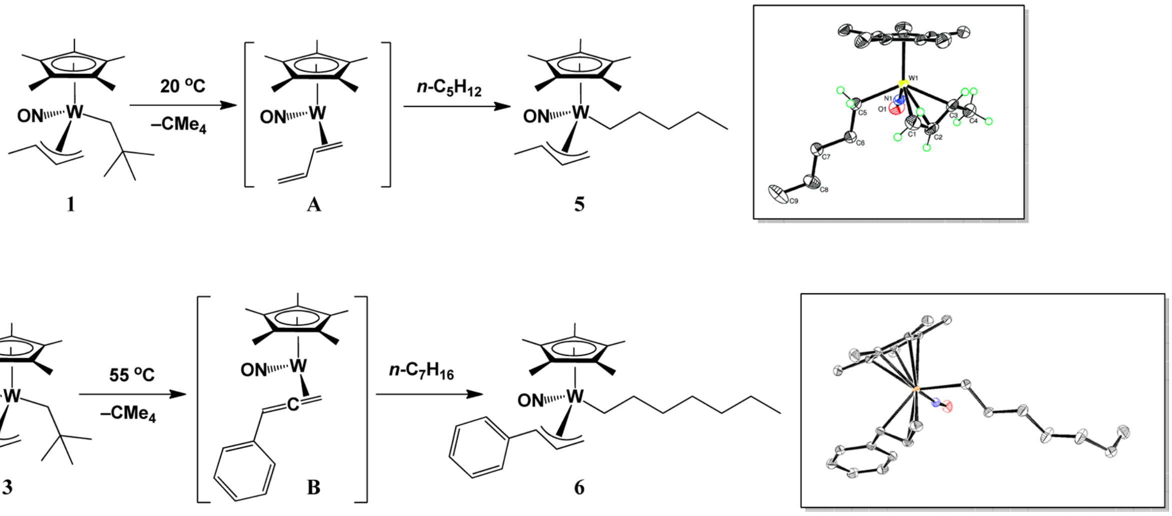
SCHEME 4



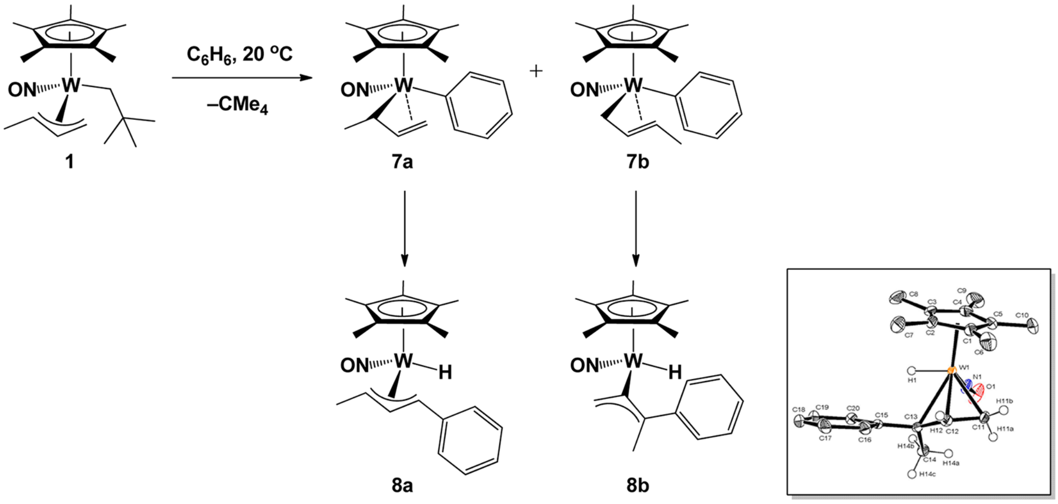
W→NO back-bonding and thus less electron-rich tungsten centers. Consistently, all three complexes display Mode 1 behavior and initiate the activation of only a single primary sp^3 C–H bond of alkanes. In contrast, **4** has a more electron-rich metal center (i.e., a relatively low ν_{NO} of 1546 cm^{-1}), and it facilitates multiple C–H bond activations of alkane substrates (i.e., Mode 3 behavior). This correlation can also be applied to the complexes resulting from the initial C–H activations (e.g., Scheme 10). The other transformation that can occur with a Cp*W(NO)(η^3-allyl)(η^1-R) complex resulting from initial activation of an R–H bond is most commonly encountered when R–H is an arene, and it involves exchange of the aryl ligand with a terminal hydrogen atom of the allyl ligand, with a typical example being shown in Scheme 8 for the reaction of complex **1** with benzene (vide supra). A plausible mechanism for this isomerization involves intramolecular nucleophilic attack by the phenyl ligand on the CH$_2$ terminus of the η^3-allyl group. Such an attack would be favored for a complex having a relatively electrophilic allyl ligand attached to a less electron-rich tungsten center. Consistent with this view is the fact that such isomerizations do indeed occur for the Cp*W(NO)(η^3-allyl)(η^1-Ph) complexes resulting from the activation of benzene by complexes **1**–**3** and exhibiting relatively higher nitrosyl-stretching frequencies of approximately 1590 cm^{-1}.[13]

In order to be of use in a practical sense, the C–H activations initiated by these Cp*W(NO)(η^3-allyl)(CH$_2$CMe$_3$) complexes must be selective and afford single organometallic products in good yields. As summarized in Table 1, our results to date have established that Mode 1 single activations of arenes such as benzene are best effected with the dimethylallyl complex **4** at

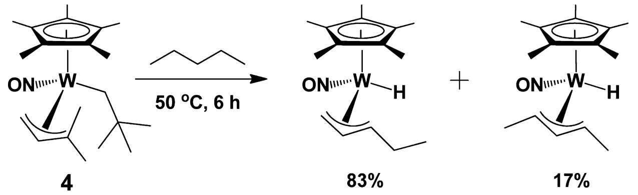
SCHEME 5



SCHEME 6



SCHEME 7



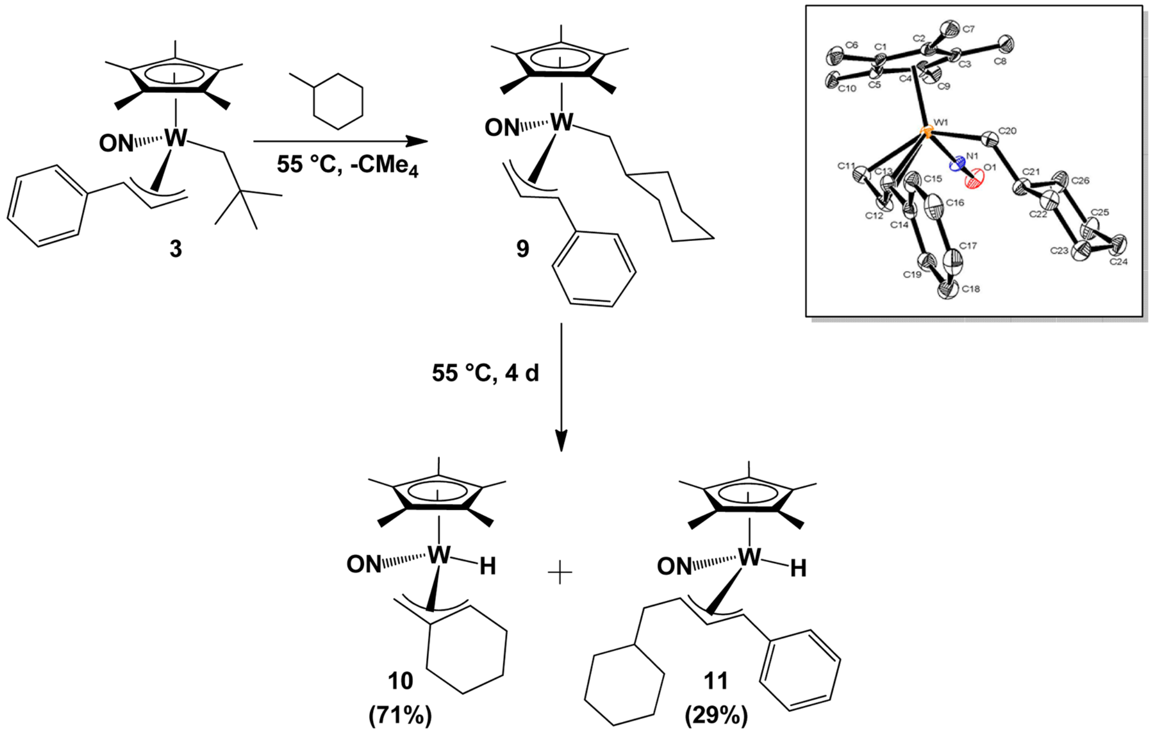
50 °C, whereas the specific activations of terminal C(sp^3)−H bonds of alkanes are best effected with **1** at ambient temperatures or with **2** and **3** at 55 °C. Reactions of the four Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes at temperatures higher than those specified above or with other hydrocarbon substrates begin to afford other undesired products via Modes 2 and 3.

Consequently, our most recent investigations have been centered on releasing the η^1-hydrocarbyl ligands formed by the desired single C−H activation processes from the tungsten's coordination sphere in an appropriately functionalized manner. The results of these studies are presented in the next part of this Account.

Functionalization of the Alkyl Ligands Resulting from the Single C−H Activations of Alkanes

Many C−H activating transition-metal complexes exhibit an inherent preference for the activation of stronger arene C(sp^2)-H bonds.[3c] In contrast, systems which activate the C(sp^3)−H bonds of alkanes remain relatively rare, and those which can combine alkane activation with subsequent functionalization of the alkyl

SCHEME 8



ligand are even more unique.[3a,b] As described in the preceding section, Cp*W(NO)(η^3-allyl)(alkyl) complexes result from the selective activations of the terminal C(sp^3)-H bonds of alkanes initiated by complexes **1**−**3**. Consequently, the reactions of prototypical members of this family of complexes with a range of reagents have been explored with a view to developing methods for functionalizing and releasing the newly formed alkyl ligands. The reactions of the Cp*W(NO)(η^3-allyl)(alkyl) complexes that have been investigated to date are outlined in the next sections.

Typical Reactions of Cp*W(NO)(η^3-allyl)(alkyl) Complexes

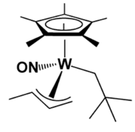
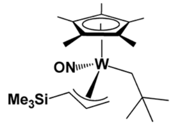
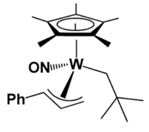
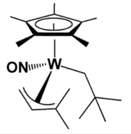
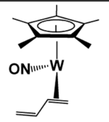
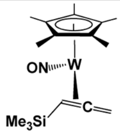
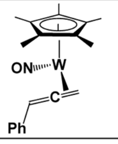
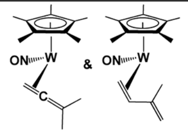
(1). With Iodine. Treatment of Cp*W(NO)(η^3-$CH_2CHCHMe$)(η^1-R) complexes with 2 equiv of the oxidant I_2 at −60 °C produces Cp*W(NO)I_2 (**12**) and terminally functionalized iodoalkanes, RI, as well as iodoalkenes, as illustrated for the *n*-pentyl complex **5** in Scheme 9.[9] Interestingly, the reaction with only a single equivalent of I_2 leads to 50% conversion, thereby indicating that the oxidation is not selective for either the alkyl or allyl ligands.[15]

(2). With Electrophiles. Treatment of Cp*W(NO)(η^3-$CH_2CHCHMe$)(CH_2SiMe_3) (**13**) and Cp*W(NO)(η^3-$CH_2CHCHMe$)($CH_2C_6H_5$) with electrophiles affords the products resulting from addition of the electrophile to the electron-rich terminus of the $\sigma-\pi$ distorted allyl ligands in the reactants. Thus, reagents of the type E−X (E = triphenylcarbenium, H, catecholborane; X = Cl, BF_4) liberate $CH_3CH{=}CHCH_2E$ and/or $CH_2{=}CHC(E)HCH_3$ to form the organometallic products, Cp*W(NO)(X)(CH_2SiMe_3) and Cp*W(NO)(X)($CH_2C_6H_5$), respectively, for example, Scheme 10.[16]

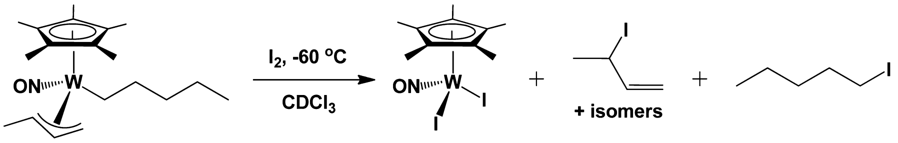
(3). Insertion Reactions. Exposure of the tungsten allyl alkyl complexes to isocyanide reagents leads to the formation of compounds bearing β,γ-unsaturated η^2-iminoacyl ligands that apparently arise from the migratory insertion of isocyanide into the tungsten-allyl linkages (Scheme 11). For instance, reaction of **13** with 2,6-xylylisocyanide produces Cp*W(NO)(CH_2SiMe_3)(η^2-$CH_3CH{=}CHCH_2C{=}NC_6H_3Me_2$) (**14a**). Interestingly, gentle heating or purification of this compound by chromatography on alumina causes isomerization of the olefin and conversion to the conjugated product Cp*W(NO)(CH_2SiMe_3)(η^2-$CH_3CH_2CH{=}CHC{=}NC_6H_3Me_2$) (**14b**). The similar reaction of Cp*W(NO)(η^3-$CH_2CHCHMe$)($CH_2C_6H_5$) with 2,6-xylylisocyanide affords both unconjugated and conjugated isocyanide insertion products while treatment with *n*-butylisocyanide produces primarily the conjugated product.[16]

Finally, exposure of these tungsten allyl alkyl complexes to 1000 psig of CO gas generally results in the desired migratory insertion of the CO into the metal−alkyl linkages to form acyl compounds, as illustrated for **1** that is converted to Cp*W(NO)(C(O)CH_2CMe_3)(η^3-$CH_2CHCHMe$) (**15**) in Scheme 12.[16] An exception to this generalization is **13** which is first converted into Cp*W(NO)(C(O)CH_2SiMe_3)(η^3-$CH_2CHCHMe$) (**16**) that then

TABLE 1. C–H Activation Chemistry of Complexes **1**–**4**

Complex				
Complex Number	**1**	**2**	**3**	**4**
16-electron intermediate				
C-H activation conditions	$\xrightarrow[1\ d]{20\ ^{o}C}$	$\xrightarrow[2\ d]{55\ ^{o}C}$	$\xrightarrow[3\ d]{55\ ^{o}C}$	$\xrightarrow[6\ h]{50\ ^{o}C}$
Modes of activation of C(sp³)-H bonds				
Mode 1	✓	✓	✓	✗
Mode 3	✗	✗	✗	✓
Modes of activation of C(sp²)-H bonds				
Mode 2	✓	✓	✓	✗
Mode 1	✗	✗	✗	✓

SCHEME 9



5

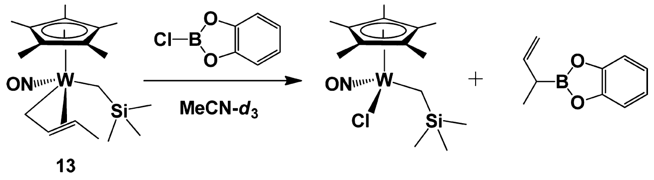
12

subsequently transforms into isolable Cp*W(NO)(C(O)CH$_3$)(η^3-CH$_2$CHCHMe) (**17**) (Scheme 12).[16] How this happens remains to be ascertained. Interestingly, Cp*W(NO)(η^3-CH$_2$CHCHMe)(CH$_2$C$_6$H$_5$) does not react with CO under these experimental conditions.

Summary of the Functionalization Reactions of the Newly Formed Alkyl Ligands

In summary, the allyl ligands of the tungsten allyl alkyl complexes are the preferred sites of reactivity when electrophiles are employed, leading to the liberation of olefinic species. Isocyanides preferentially insert into the W-allyl linkages and initially form complexes containing β,γ-unsaturated η^2-imine ligands. Isomerization to the conjugated α,β-unsaturated η^2-imine complexes occurs spontaneously in solution in some cases. In contrast, CO gas under pressure inserts preferentially into the tungsten-alkyl bonds and affords the desired metalloacyl species. The reactions of the Cp*W(NO)(η^3-allyl)(η^1-acyl) complexes discovered to date that release the newly formed acyl ligands are outlined in the next section. Our development of methods to release the acyl ligands from the metal centers while keeping the Cp*W(NO)(η^3-allyl) fragments intact is continuing with a view to eventually effecting these distinctive activations and functionalizations of alkanes in a catalytic manner.

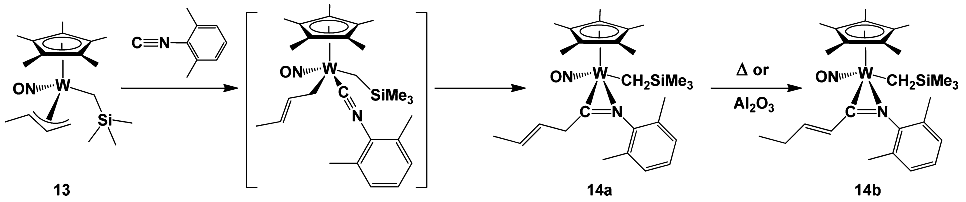
SCHEME 10



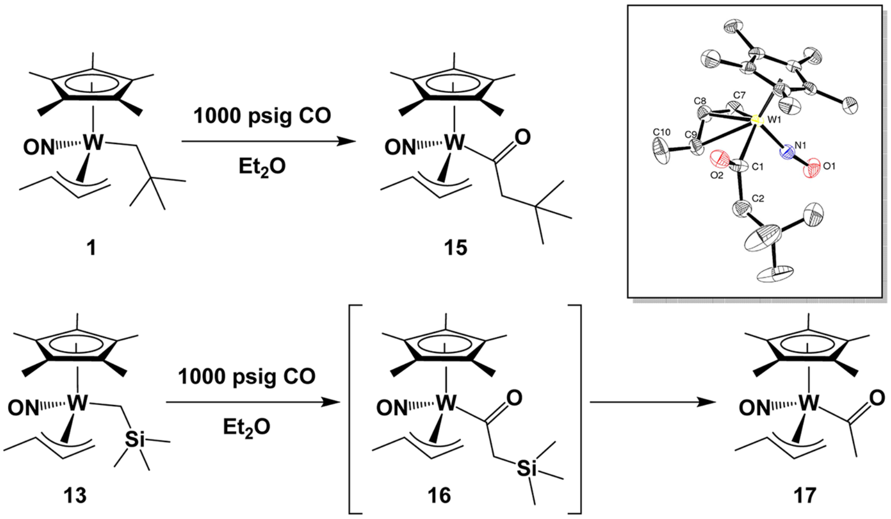
Reactions of Typical Cp*W(NO)(η^3-allyl)(η^1-acyl) Complexes

(1). With Iodine. Treatment of Cp*W(NO)(η^3-$CH_2CHCHPh$)($C(O)CH_2CMe_3$) (**18**) with 2 equiv of the oxidant I_2 at −78 °C produces Cp*W(NO)I_2 (**12**), the acyl iodide $IC(O)CH_2CMe_3$ (**19**), and isomers if the iodo alkene, $ICH_2CHCHPh$ (**20**) (Scheme 13). Just as for the analogous conversion of the alkyl complexes presented in Scheme 9, the reaction with

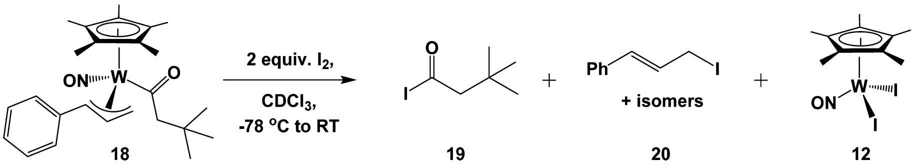
SCHEME 11



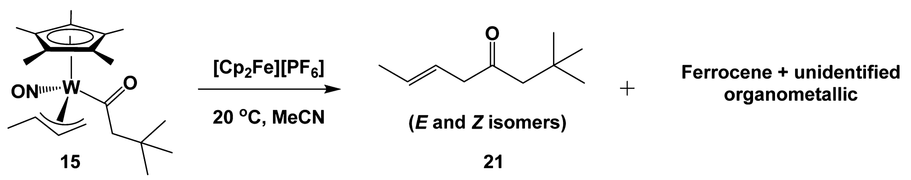
SCHEME 12



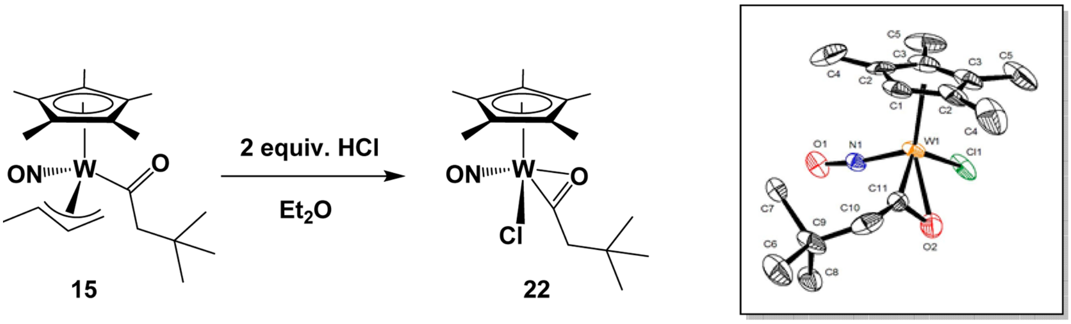
SCHEME 13



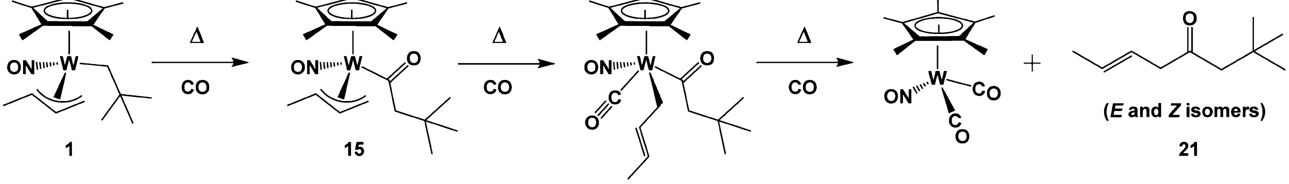
SCHEME 14



SCHEME 15



SCHEME 16



only a single equivalent of I_2 leads to 50% conversion, thereby indicating that the oxidation is not selective for either the acyl or allyl ligands.[15]

(2). With Oxidants. Treatment of **15** with one-electron oxidants such as $[Cp_2Fe]^+$ or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature results in the oxidatively induced reductive elimination of the β,γ-unsaturated ketone formed by the coupling of the acyl and the allyl ligands in the initial reactant (Scheme 14).[15] Not surprisingly, the organic product, $CH_3CH{=}CHCH_2C(O)CH_2CMe_3$ (**21**), is released as a mixture of *E* and *Z* isomers.

(3). With HCl. This reaction was also investigated as a possible means of releasing the acyl ligand from the tungsten's coordination sphere. However, as illustrated in Scheme 15, treatment of **15** with two equivalents of HCl in Et_2O under ambient conditions produces Cp*W(NO)(Cl)(η^2-$C(O)CH_2CMe_3$) (**22**). The conversion evidently involves electrophilic attack by H^+ on the allyl ligand and its release from the metal's coordination sphere as the alkene. The coordinatively unsaturated metal fragment thus formed attains the favored 18-valence-electron configuration by coordinating the residual Cl^- and linking to the acyl ligand in a *dihapto* fashion. This structural feature has been established by a crystallographic analysis of the analogous (η^5-C_5Me_4H)W(NO)(Cl)(η^2-$C(O)CH_2CMe_3$) complex whose solid-state molecular structure is shown in Scheme 15.

(4). With CO. Spectroscopic monitoring of the further carbonylation of **15** by pressures of CO of at least 500 psig and temperatures greater than 55 °C has revealed that this reaction proceeds in the stepwise manner shown in Scheme 16. There are ample literature precedents for carbonylation reactions proceeding in this manner.[17] In the end, the final organometallic product is Cp*W(NO)$(CO)_2$, and the liberated organic product is the same β,γ-unsaturated ketone **21** as released by treatment of the original acyl alkyl complex with one-electron oxidants (Scheme 14).[15]

Conclusions

Several properties of the 18-electron Cp*W(NO)(η^3-allyl)(CH_2CMe_3) complexes lead to the desired C(sp^3)−H bond functionalizations outlined in this Account. Specifically, thermolyses of the compounds having η^3-allyl = η^3-$H_2CCHCHMe$, η^3-$H_2CCHCHSiMe_3$, or η^3-$H_2CCHCHPh$ (i.e., **1**−**3**) first lead to the loss of neopentane and the transient formation of the 16-electron intermediate species, Cp*W(NO)(η^2-allene) or Cp*W(NO)(η^2-diene) (e.g., Scheme 7). Under appropriate experimental conditions, these transient intermediates then effect the selective single activation of hydrocarbon C−H bonds intermolecularly and form new Cp*W(NO)(η^3-allyl)(η^1-hydrocarbyl) complexes. Of particular interest in this regard are the Cp*W(NO)(η^3-allyl)(*n*-alkyl) compounds that result from the activation of the terminal C(sp^3)-H bonds of simple alkanes. The allyl ligands of these tungsten allyl alkyl complexes are the preferred sites of reactivity when electrophiles are employed, but treatment of these compounds with I_2 liberates iodoalkanes from the tungsten's coordination spheres. More importantly, CO gas under pressure inserts preferentially into the tungsten-alkyl bonds of these reactants and affords Cp*W(NO)(η^3-allyl)(η^1-acyl) complexes from which the acyl ligands may be released as functionalized organics such as ketones and acyl iodides. In other words, we have demonstrated that the Cp*W(NO)(η^3-allyl)-(CH_2CMe_3) complexes initiate a stoichiometric cycle of reactions that convert alkanes into oxygen-containing organic molecules. Our investigations with these and related nitrosyl complexes are continuing with a view to expanding the scope of the functionalization chemistry as well as to effecting it in a catalytic manner. In any event, the functionalizations of alkanes mediated by these nitrosyl complexes nicely complement other previously reported conversions of these hydrocarbons such as their selective oxidation,[18] their dehydrogenation,[19] their metathesis,[20] and their borylation.[21]

We are indebted to the various undergraduate and graduate students, postdoctoral fellows, and research associates cited in the references for their hard work, perseverance, and insight that made this Account possible. We also gratefully acknowledge The Dow Chemical Company for continuing financial and material support of our research.

BIOGRAPHICAL INFORMATION

Rhett A. Baillie was born in Nanaimo, British Columbia, Canada in 1984. He received his B.Sc. from the University of British Columbia in 2011. He is presently a graduate student carrying out research leading toward a Ph.D. degree under the supervision of Professor Peter Legzdins at the University of British Columbia. His research interests include the discovery and development of new synthetic routes involving mediation by transition-metal organometallic complexes.

Peter Legzdins was born in Riga, Latvia in 1942. He received his Honours B.Sc. from Carleton University (1964) and his Ph.D. from MIT (1968) with F. A. Cotton. After a postdoctoral year with G. Wilkinson at Imperial College in London, he joined the faculty at the University of British Columbia where he is currently Professor of Chemistry. His research interests are centered on transition-metal nitrosyl complexes that can be utilized as specific reactants or selective catalysts in organic and organometallic syntheses.

FOOTNOTES

*To whom correspondence should be addressed. Phone: 604-822-2987. Fax: 604-822-2847. E-mail: legzdins@chem.ubc.ca.

The authors declare no competing financial interest.

REFERENCES

1 (a) *Acc. Chem. Res.* 2012, *45*, 6 (Special Issue on CH-Functionalization). (b) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. C-H Bond Functionalization: Emerging Synthetic Tools for Natural Products and Pharmaceuticals. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960–9009. (c) *Chem. Soc. Rev.* 2011, *40*, 4 (special issue on C-H functionalization in organic synthesis). (d) *Chem. Rev.* 2010, *110*, 2 (special issue on selective functionalization of C-H bonds).

2 (a) Ramirez, T. A.; Zhao, B.; Shi, Y. Recent advances in transition metal-catalyzed sp^3 C-H amination adjacent to double bonds and carbonyl groups. *Chem. Soc. Rev.* **2012**, *41*, 931–942. (b) Shi, L.; Xia, W. Photoredox functionalization of C-H bonds adjacent to a nitrogen atom. *Chem. Soc. Rev.* **2012**, *41*, 7687–7697. (c) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. Direct Functionalization of Nitrogen Heterocycles via Rh-Catalyzed C-H Bond Activation. *Acc. Chem. Res.* **2008**, *41*, 1013–1025.

3 (a) *Alkane C-H Activation by Single-Site Metal Catalysis*; Pérez, P. J., Ed.; Catalysis by Metal Complexes 38; Springer Science: Dordrecht, 2012. (b) Cavaliere, V. N.; Mindiola, D. J. Methane: a new frontier in organometallic chemistry. *Chem. Sci.* **2012**, *3*, 3356–3365. (c) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. Beyond Directing Groups: Transition-Metal-Catalyzed C-H Activation of Simple Arenes. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236–10254. (d) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. Ruthenium(II)-Catalyzed C-H Bond Activation and Functionalization. *Chem. Rev.* **2012**, *112*, 5879–5918.

4 Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, CA. 2010; Chapter 6.

5 (a) Pamplin, C. B.; Legzdins, P. Thermal Activation of Hydrocarbon C-H Bonds by Cp*M(NO) Complexes of Molybdenum and Tungsten. *Acc. Chem. Res.* **2003**, *36*, 223–233. (b) Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. Intermolecular Activation of Hydrocarbon C-H Bonds under Ambient Conditions by 16-Electron Neopentylidene and Benzyne Complexes of Molybdenum. *J. Am. Chem. Soc.* **2003**, *125*, 7035–7043. (c) Lee, K.; Legzdins, P.; Pamplin, C. B.; Patrick, B. O.; Wada, K. Intermolecular Activation of Hydrocarbon C-H Bonds Initiated by the Tungsten Hydrocarbyl Hydrido Complexes, Cp*W(NO)(R)(H)(PMe_3) [R = Alkyl, Aryl]. *Organometallics* **2005**, *24*, 638–649; Corrections. *Organometallics* **2006**, *25*, 4702–4702. (d) Graham, P. M.; Buschhaus, M. S. A.; Pamplin, C. B.; Legzdins, P. Reactivity of Cp*Mo(NO)(=$CHCMe_3$) with Olefins and Dienes: C-H Activation Reactions of Molybdenacyclobutanes. *Organometallics* **2008**, *27*, 2840–2851.

6 Tsang, J. Y. K.; Buschhaus, M. S. A.; Fujita-Takayama, C.; Patrick, B. O.; Legzdins, P. Different Modes of Reactivity of Cp*W(NO)(alkyl)(η^3-allyl) Complexes with Cyclic Amines: The Influence of the Allyl Ligands. *Organometallics* **2008**, *27*, 1634–1644.

7 (a) Chow, C.; Patrick, B. O.; Legzdins, P. Intermolecular C-H Activations of Hydrocarbons Initiated by a Tungsten Trimethylsilylallyl Complex. *Organometallics* **2012**, *31*, 7453–7466. (b) Chow, C.; Patrick, B. O.; Legzdins, P. Thermal Chemistry of a Tungsten Trimethylsilylallyl Complex in Benzene and Fluorobenzenes. *Organometallics* **2012**, *31*, 8159–8171.

8 Tsang, J. Y. K. Intermolecular C-H Activation Effected by Cp*W(NO)-Containing Complexes. Ph.D. Thesis, The University of British Columbia, Vancouver, Canada, 2008.

9 Tsang, J. Y. K.; Buschhaus, M. S. A.; Graham, P. M.; Semiao, C. J.; Semproni, S. P.; Kim, S. J.; Legzdins, P. Facile and Selective Aliphatic C-H Bond Activation at Ambient Temperatures Initiated by Cp*W(NO)(CH_2CMe_3)(η^3-$CH_2CHCHMe$). *J. Am. Chem. Soc.* **2008**, *130*, 3652–3663.

10 Baillie, R. A.; Man, R. W. Y.; Shree, M. V.; Chow, C.; Thibault, M. E.; McNeil, W. S.; Legzdins, P. Intermolecular C-H Activations of Hydrocarbons Initiated by Cp*M(NO)-(CH_2CMe_3)(η^3-$CH_2CHCHPh$) Complexes (M = Mo, W). *Organometallics* **2011**, *30*, 6201–6217.

11 Ng, S. H. K.; Adams, C. S.; Hayton, T. W.; Legzdins, P.; Patrick, B. O. Thermal Activation of Hydrocarbon C-H Bonds Initiated by a Tungsten Allyl Complex. *J. Am. Chem. Soc.* **2003**, *125*, 15210–15223.

12 Tran, T.; Chow, C.; Zimmerman, A. C.; Thibault, M. E.; McNeil, W. S.; Legzdins, P. Differing Reactions of Functionalized Hydrocarbons with Cp*M(NO)(alkyl)(η^3-allyl) Complexes of Molybdenum and Tungsten. *Organometallics* **2011**, *30*, 738–751.

13 Baillie, R. A.; Tran, T.; Lalonde, K. M.; Tsang, J. Y. K.; Thibault, M. E.; Patrick, B. O.; Legzdins, P. Factors Influencing the Outcomes of Intermolecular C-H Activations of Hydrocarbons Initiated by CpW(NO)(CH_2CMe_3)(η^3-allyl) Complexes (Cp = η^5-C_5Me_5 (Cp*), η^5-C_5Me_4H (Cp′)). *Organometallics* **2012**, *31*, 1055–1067.

14 Baillie, R. A.; Tran, T.; Thibault, M. E.; Legzdins, P. A Beneficial Kinetic Effect of an η^5-C_5Me_4H Ligand. *J. Am. Chem. Soc.* **2010**, *132*, 15160–15161.

15 Baillie, R. A.; Tran, T.; Legzdins, P. Unpublished observations.

16 Semproni, S. P.; Graham, P. M.; Buschhaus, M. S. A.; Patrick, B. O.; Legzdins, P. Toward Alkane Functionalization Effected with Cp*W(NO)(alkyl)(η^3-allyl) Complexes. *Organometallics* **2009**, *28*, 4480–4490.

17 Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, CA. 2010; Chapters 17 and 18.

18 Kirillov, A. M.; Kirillova, M. V.; Pombeiro, A. J. L. Homogeneous Multicopper Catalysts for Oxidation and Hydrocarboxylation of Alkanes. *Adv. Inorg. Chem.* **2013**, *65*, 1–31and references cited therein.

19 Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth, R.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. Rational Design and Synthesis of Highly Active Pincer-Iridium Catalysts for Alkane Dehydrogenation. *Organometallics* **2009**, *28*, 5432–5444.

20 Bailey, B. C.; Schrock, R. R.; Kundu, S.; Goldman, A. S.; Huang, Z.; Brookhart, M. Evaluation of Molybdenum and Tungsten Metathesis Catalysts for Homogeneous Tandem Alkane Metathesis. *Organometallics* **2009**, *28*, 355–360.

21 Wei, C. S.; Jiménez-Hoyos, C. A.; Videa, M. F.; Hartwig, J. F.; Hall, M. B. Origins of the Selectivity for Borylation of Primary over Secondary C—H Bonds Catalyzed by Cp*-Rhodium Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 3078–3091and references cited therein.