

ACCOUNTS of CHEMICAL RESEARCH®

APRIL 2003

Registered in U.S. Patent and Trademark Office; Copyright 2003 by the American Chemical Society

Thermal Activation of Hydrocarbon C–H Bonds by Cp*M(NO) Complexes of Molybdenum and Tungsten

CRAIG B. PAMPLIN AND PETER LEGZDINS*

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

Received July 19, 2002

ABSTRACT

Gentle thermolysis of appropriate Cp*M(NO)(hydrocarbyl)₂ complexes (Cp* = η⁵-C₅Me₅) of molybdenum and tungsten results in loss of hydrocarbon and the transient formation of 16-electron Cp*M(NO)-containing complexes such as Cp*M(NO)(alkylidene), Cp*M(NO)(η²-benzynes), Cp*M(NO)(η²-acetylene), and Cp*M(NO)(η²-allene) (M = Mo, W). These intermediates effect the single, double, or triple activation of hydrocarbon C–H bonds intermolecularly, the first step of these activations being the reverse of the transformations by which they were generated. This Account summarizes the various types of C–H activations that have been effected with these nitrosyl complexes and also describes the results of kinetic, mechanistic, and theoretical investigations of these processes.

A long-term goal of our research program has been the development of organometallic nitrosyl complexes as specific reactants or selective catalysts for organic or organometallic transformations of practical significance.

Craig Pamplin was born in 1973 in Victoria, Canada. After receiving his B.Sc. degree from the University College of the Cariboo in Kamloops, British Columbia, in 1996, he carried out his graduate studies at the University of British Columbia under the supervision of B. R. James. He obtained his Ph.D. degree in 2001, and he is currently a postdoctoral fellow in the Legzdins research group investigating the varied roles that coordinated nitric oxide plays in transition-metal chemistry.

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 and a Canada Council Killam Research Fellow. His research interests are centered on transition-metal nitrosyl complexes that can be utilized as specific reactants or selective catalysts in organic or organometallic syntheses.

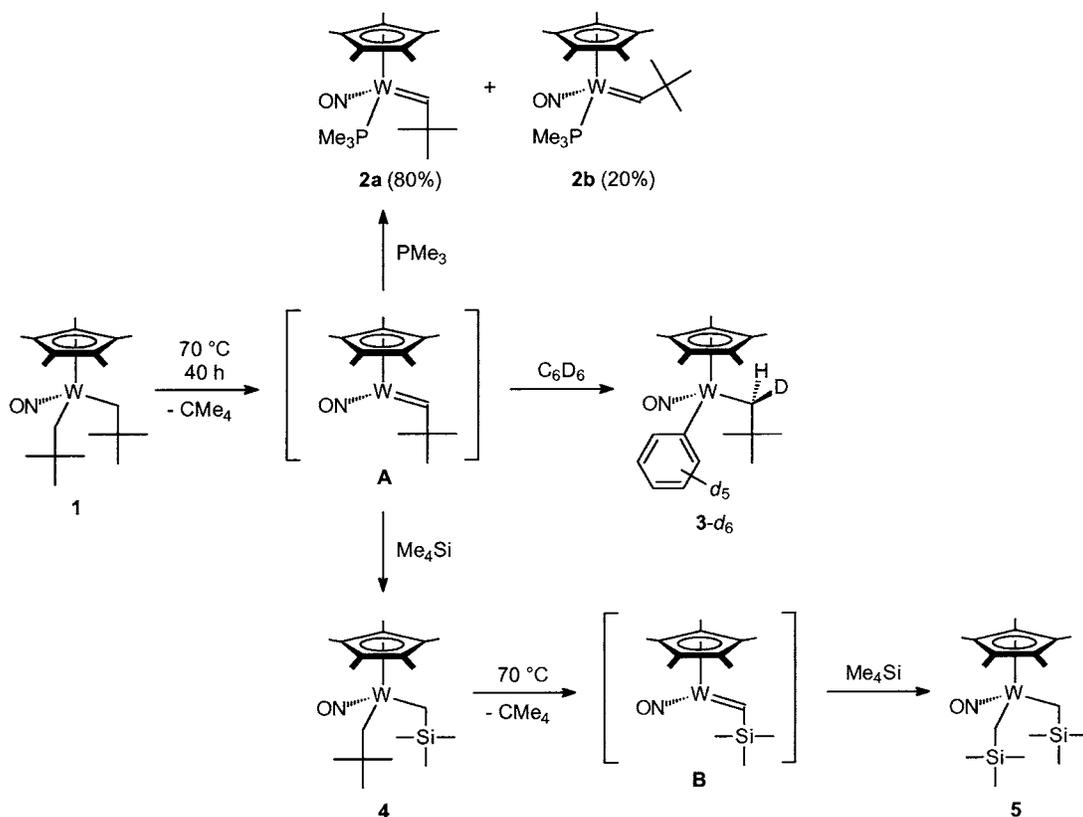
In this regard, we have been investigating in recent years the characteristic chemistry of the pseudooctahedral 16-electron (16e) Cp*M(NO)R₂ systems (Cp* = η⁵-C₅Me₅; M = Mo or W; R = a hydrocarbyl group such as an alkyl or aryl).¹ These complexes are conveniently synthesized by metathesis reactions of their dichloro precursors with appropriate organomagnesium reagents. They are typically monomeric and possess piano-stool molecular structures in which the M–NO linkages are essentially linear. In this configuration, the nitrosyl group functions as a formal three-electron donor to the metal center and is a strong π-acid ligand. This π-acidity of the NO group results in the Cp*M(NO)R₂ complexes having a large HOMO–LUMO gap, with the LUMO being a nonbonding, metal-centered orbital that imparts Lewis acid characteristics to these compounds. Consequently, during our initial investigations of the physical and chemical properties of these complexes, we found that they react with a variety of small molecules, often in an unprecedented manner. More recently, we have discovered that the family of Cp*M(NO)–R₂ compounds also exhibits R-dependent thermal reactivity to form a variety of reactive 16e nitrosyl complexes that are capable of effecting single, double, or triple activation of hydrocarbon C–H bonds intermolecularly, again 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. This thermal activation chemistry is the subject of this Account, and these types of transformations are of considerable current interest, primarily due to the potential for eventual conversion of readily available hydrocarbons into more desirable products.² The chemistry is presented in the following sections in terms of the various reactive intermediates involved, beginning with the most straightforward Cp*M(NO)(alkylidene) systems.

Cp*M(NO)(alkylidene) Intermediates

Tungsten Complexes. These intermediate complexes result from the thermal activation of bis(alkyl) precursors,

* Corresponding author. Phone: 604-822-2987. Fax: 604-822-2847. E-mail: legzdins@chem.ubc.ca.

Scheme 1



the first of which to be identified was the bis(neopentyl) complex $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**1**). The solid-state molecular structure of **1** contains one neopentyl ligand with a “strongly agostic” methylene hydrogen atom [$\text{C}-\text{H} = 1.153(6) \text{ \AA}$; $\text{W}-\text{C}-\text{H} = 80.6(3)^\circ$] and another with a “weakly agostic” interaction [$\text{C}-\text{H} = 1.094(6) \text{ \AA}$; $\text{W}-\text{C}-\text{H} = 99.3(3)^\circ$], as shown by a neutron diffraction analysis at 120 K.³ Its ^1H and gated $^{13}\text{C}\{^1\text{H}\}$ NMR spectra exhibit spectral parameters for the α -H and α -C atoms that indicate that these α -agostic $\text{C}-\text{H}\cdots\text{M}$ interactions persist in the molecular structure of **1** in solutions, as would be expected for an electronically unsaturated organometallic complex.⁴ Complex **1** is thus appropriately configured to undergo cleavage of an α -H bond by a metal-assisted abstraction process.

Thermal activation of **1** at 70°C in neat hydrocarbon solutions transiently generates the highly reactive neopentylidene complex $\text{Cp}^*\text{W}(\text{NO})(=\text{CHCMe}_3)$ (**A**) that can be trapped by PMe_3 as the $\text{Cp}^*\text{W}(\text{NO})(=\text{CHCMe}_3)(\text{PMe}_3)$ adduct in two isomeric forms (**2a,b**) which differ in the orientations of the CHCMe_3 ligand with respect to the Cp^* group (Scheme 1). The principal isomer, **2a**, has been characterized in the solid state by a single-crystal X-ray crystallographic analysis that has established the anticlinal orientation of the ^tBu and Cp^* groups (Figure 1). More importantly, intermediate **A** can effect the single activation of solvent C–H bonds (Scheme 1).^{5,6} Thus, in neat benzene and benzene- d_6 , it cleanly forms the corresponding phenyl complexes $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)$ (**3**) and $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)$ (**3-d6**), and in Me_4Si it forms the unsymmetrical bis(alkyl) complex $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2-$

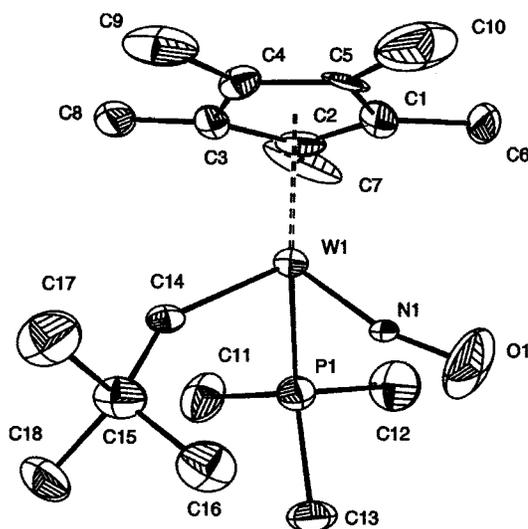
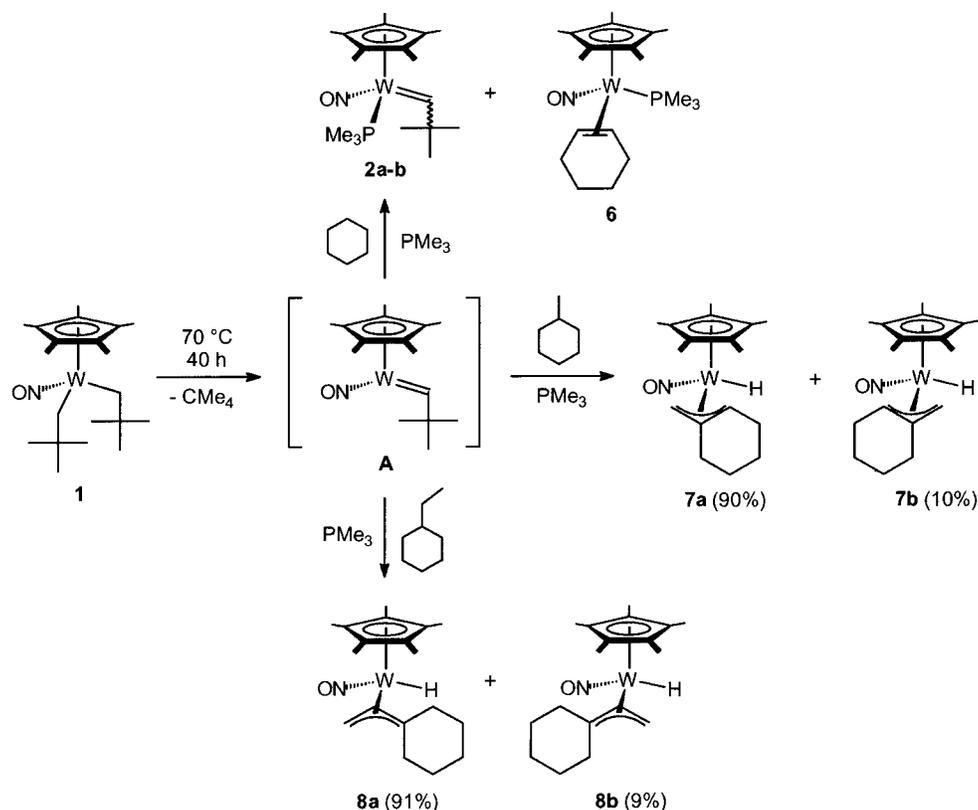


FIGURE 1. Solid-state molecular structure of the principal isomer of $\text{Cp}^*\text{W}(\text{NO})(=\text{CHCMe}_3)(\text{PMe}_3)$ (**2a**).

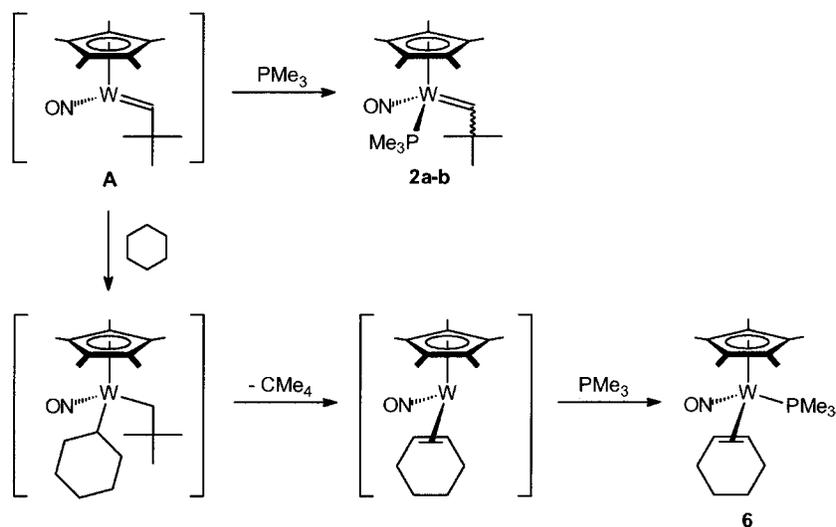
$\text{CMe}_3)(\text{CH}_2\text{SiMe}_3)$ (**4**) in high yields. Interestingly, **4** reacts further with Me_4Si under the thermolysis conditions, albeit very slowly, to form $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (**5**) as a second product. The relative amount of **5** gradually increases upon prolonged heating of the reaction mixture, and its formation implies the transient existence of $\text{Cp}^*\text{W}(\text{NO})(=\text{CHSiMe}_3)$ (**B**) as a reactive intermediate (Scheme 1).

Alkylidene complexes **A** and **B** belong to a small class of complexes that intermolecularly activate C–H bonds via their addition across the $\text{M}=\text{C}$ bond of an alkylidene intermediate.^{7–9} However, **A** is unique in its ability to

Scheme 2



Scheme 3

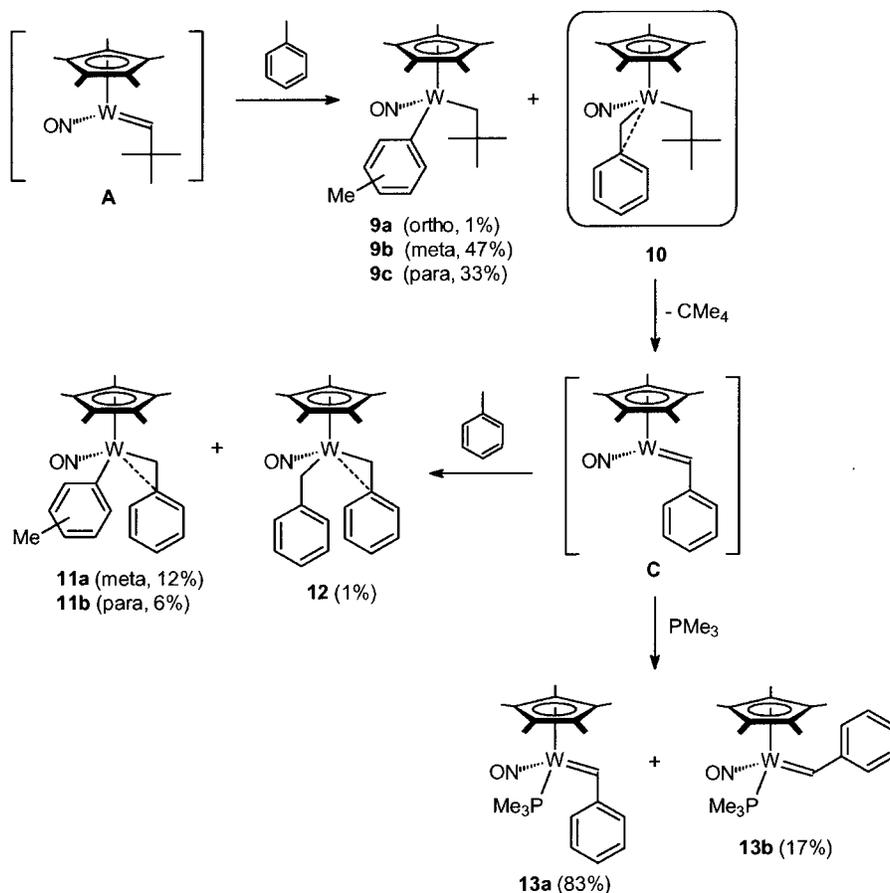


activate aliphatic C–H bonds to form isolable, well-defined products.

Intermediate **A** can also effect multiple C–H bond activations, even in the presence of excess PMe₃ (Scheme 2). Thus, thermolysis of **1** in cyclohexane in the presence of PMe₃ yields **2a,b** as well as the olefin complex Cp*W(NO)(η²-cyclohexene)(PMe₃) (**6**). It is likely that the double C–H activation of cyclohexane by **A** is in direct competition with trapping of **A** by PMe₃, as portrayed in Scheme 3. The competitive C–H activation by an unsaturated intermediate in the presence of a strong Lewis base is remarkable, yet it has been observed before¹⁰ and is aided

by low concentrations of the trapping agent relative to the cyclohexane solvent. In contrast to cyclohexane, methylcyclohexane under identical experimental conditions affords trace amounts of **2a,b** and the exocyclic allyl hydride complex Cp*W(NO)(η³-C₇H₁₁)(H) in two isomeric forms (**7a,b**) whose relative abundances are shown in Scheme 2. Ethylcyclohexane affords similar exocyclic allyl hydride products **8a,b**. The mechanisms for the transformations of **1** into **7a,b** or **8a,b** likely mirror that of cyclohexane (Scheme 3) in that activation of a solvent C–H bond by **A** is followed by β-H activation to release the second neopentyl ligand as neopentane and form a

Scheme 4

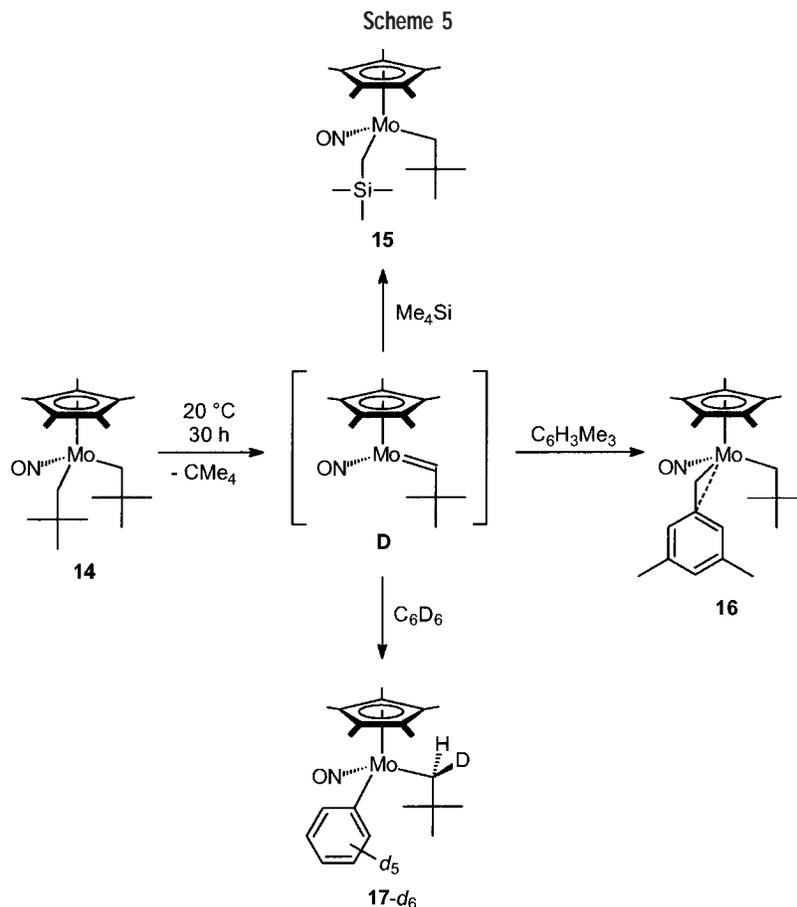


16e alkene complex. Unlike the cyclohexene case, however, the alkene complexes in these systems evidently do not persist long enough to be trapped by PMe_3 . Rather, there is a third γ -H activation by the metal center that results in the conversion of the alkene complexes into the isolable 18e allyl hydride complexes. Thus, these processes involve triple C–H bond activations of the original hydrocarbon substrates.

The thermolysis of $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**1**) in toluene affords a surprisingly complex mixture of six products (Scheme 4).⁶ The major products are the neopentyl aryl complexes $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_4\text{-3-Me})$ (**9a**, ~47%), $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_4\text{-4-Me})$ (**9b**, ~33%), and $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_4\text{-2-Me})$ (**9c**, ~1%). The remaining three products all arise from the incorporation of two molecules of toluene, namely $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\text{C}_6\text{H}_4\text{-3-Me})$ (**11a**, ~12%), $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\text{C}_6\text{H}_4\text{-4-Me})$ (**11b**, ~6%), and $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\text{CH}_2\text{Ph})$ (**12**, ~1%). It has been demonstrated that the formation of these latter complexes involves the transient formation of $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\text{CH}_2\text{CMe}_3)$ (**10**), the product of toluene activation at the methyl position, which subsequently reductively eliminates neopentane to generate the C–H-activating benzyldiene complex $\text{Cp}^*\text{W}(\text{NO})(=\text{CHPh})$ (**C**). Intermediate **C** can also be trapped by PMe_3 to obtain the adduct $\text{Cp}^*\text{W}(\text{NO})(=\text{CHPh})(\text{PMe}_3)$ (**13**), again in two rotameric forms. From their reactions with toluene, it can be deduced that both alkyldiene intermediates **A** and **C** exhibit a preference for activating the stronger aryl sp^2

C–H bonds, thereby reflecting the same qualitative bond selectivity as the majority of the reported metal-based C–H activation systems.^{2c} The C–H-activating ability of **C** also encompasses aliphatic substrates as well, as it reacts with tetramethylsilane and cyclohexanes in a manner similar to that summarized in Schemes 1 and 2 for **A**.⁶ Similarly, thermolyses (70 °C, 40 h) of **1** and **10** in xylenes, mesitylene, and α, α, α -trifluorotoluene generate mixtures of the corresponding aryl and/or benzyl products derived from aromatic sp^2 and benzylic sp^3 C–H bond activations of the solvent molecules by the intermediate alkyldiene complexes **A** and **C**.¹¹ Analyses of the product distributions resulting from the various thermolyses indicate that the benzyl products are increasingly favored over the aryl products as the number of methyl substituents on the solvent molecule increases and that, in general, the least sterically congested regioisomers are formed preferentially. On the basis of these studies, it thus appears that a whole family of such C–H bond-activating tungsten alkyldiene complexes with differing steric and electronic properties should be capable of existence.

Molybdenum Complexes. We have recently extended this work to encompass the congeneric molybdenum precursors, and we began our investigations in this area with $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**14**), since we knew from previous studies that the related $\text{CpMo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ precursor ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) forms an alkyldiene complex that spontaneously dimerizes in CH_2Cl_2 below room temperature.¹² In general, the thermal reactivity of **14**



resembles that of its isostructural tungsten analogue **1** (vide supra), but it occurs under the unusually mild conditions of ambient temperatures and pressures (Scheme 5). For example, the reactions of **14** with tetramethylsilane or mesitylene for 30 h result in the clean formation of free neopentane and Cp*Mo(NO)(CH₂CMe₃)(CH₂SiMe₃) (**15**) or Cp*Mo(NO)(CH₂CMe₃)(η^2 -CH₂C₆H₃-3,5-Me₂) (**16**), respectively.¹³ Neither product undergoes further reactivity under these mild reaction conditions. Similarly, the reaction of **14** with C₆D₆ generates predominantly Cp*Mo(NO)(CHDCMe₃)(C₆D₅) (**17-d₆**) with stereospecific deuterium incorporation at the synclinal methylene position of the neopentyl ligand (just as portrayed for **3-d₆** in Scheme 1).

Mechanistic Aspects. The conversion of Cp*W(NO)(CH₂CMe₃)₂ (**1**) to Cp*W(NO)(=CHCMe₃)(PMe₃) (**2a,b**) can be conveniently monitored by UV–vis spectroscopy in cyclohexane solutions containing an excess of PMe₃. The reaction exhibits first-order kinetics for the loss of **1** over the temperature range of 71–98 °C, and an Eyring plot of the data affords the activation parameters $\Delta H^\ddagger = 114(7)$ kJ mol⁻¹ and $\Delta S^\ddagger = 3(12)$ J mol⁻¹ K⁻¹. Both parameters lie within the range reported for other complexes that undergo rate-determining intramolecular α -H eliminations of alkane. A primary deuterium kinetic isotope effect (KIE) of 2.4(2) is observed when the PMe₃-trapping reaction is conducted with Cp*W(NO)(CD₂CMe₃)₂ (**1-d₄**) at 91 °C, thereby confirming that the rate-determining step involves intramolecular cleavage of a methylene C–H(D) bond. Additional mechanistic information can be gleaned

from the thermolysis of **1** in benzene and benzene-*d*₆. In benzene, **1** cleanly forms the phenyl complex Cp*W(NO)(CH₂CMe₃)(C₆H₅) (**3**) by activation of an aryl sp² C–H bond, and in benzene-*d*₆ it forms Cp*W(NO)(CHDCMe₃)(C₆D₅) (**3-d₆**) with exclusive stereospecific deuterium incorporation at the synclinal methylene position of the neopentyl ligand (Scheme 1). The first-order rate constant of $4.6(1) \times 10^{-5}$ s⁻¹ for this latter conversion at 72.0 °C is of the same magnitude as that determined in cyclohexane/PMe₃ solutions under comparable conditions. In other words, the presence of phosphine and the nature of the solvent do not significantly affect the rate of reaction.

Taken together, the labeling, trapping, and kinetic results verify that the C–H activation chemistry derived from **1** proceeds through two distinct steps: (1) formation of the neopentylidene complex **A** via rate-determining intramolecular α -H elimination of neopentane, and (2) a 1,2-cis addition of R–H across the M=CHR linkage of **A**. Similarly, a kinetic analysis of the reaction of Cp*Mo(NO)(CH₂CMe₃)₂ (**14**) with C₆D₆ to form Cp*Mo(NO)(CHDCMe₃)(C₆D₅) (**17-d₆**) (Scheme 5) in the temperature range 26–40 °C reveals a first-order loss of organometallic reactant, and a linear Eyring plot affords $\Delta H^\ddagger = 99(1)$ kJ mol⁻¹ and $\Delta S^\ddagger = -11(4)$ J mol⁻¹ K⁻¹. These parameters are very similar to those determined at higher temperatures for the tungsten analogue **1** (vide supra) and indicate that a similar mechanism is operative for the molybdenum system.

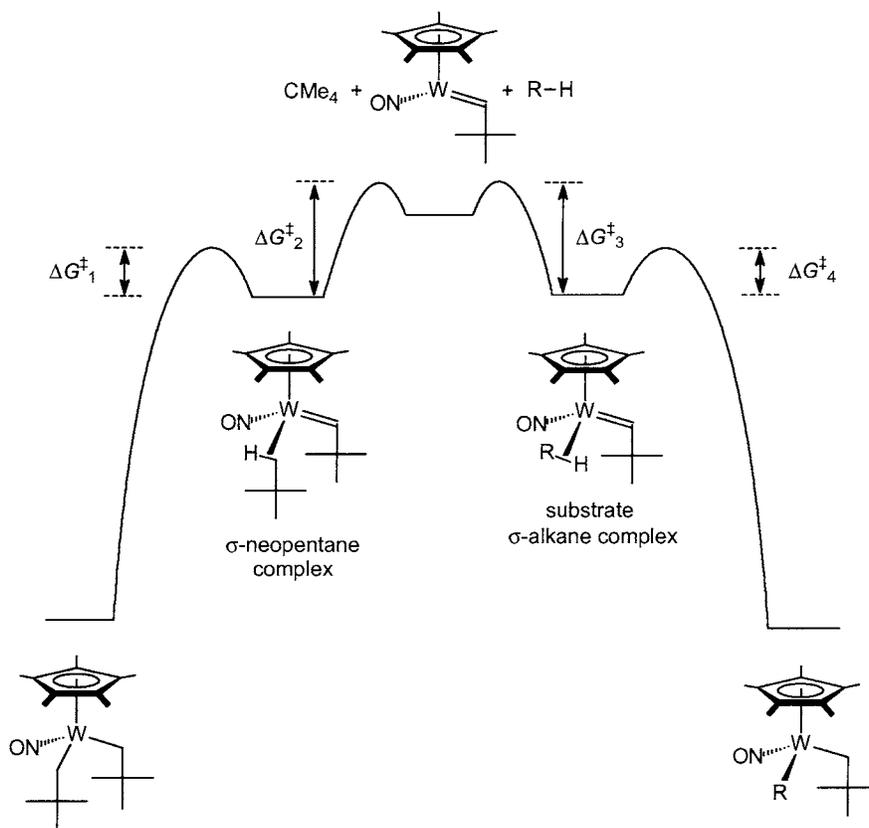
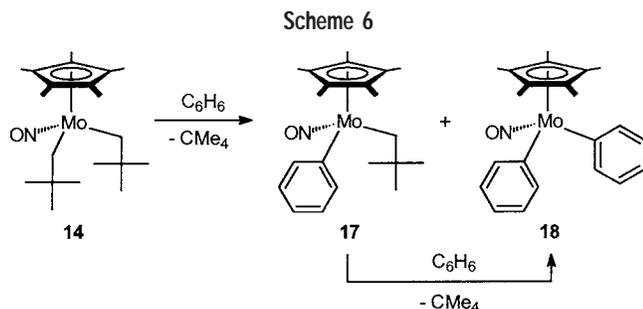


FIGURE 2. Qualitative potential energy surfaces for the activation of an alkane substrate (R–H) by the alkylidene intermediate(s) derived from $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**1**).

We have also carried out additional experimental and B3LYP computational mechanistic studies of the intermolecular C–H activations of hydrocarbons by the tungsten alkylidene complexes.¹⁴ During these studies, it was shown that the α -deuterated derivative $\text{Cp}^*\text{W}(\text{NO})(\text{CD}_2\text{-CMe}_3)_2$ (**1-d**₄) undergoes intramolecular H/D exchange within the neopentyl ligands, a feature consistent with the reversible formation of σ -neopentane complexes prior to neopentane elimination. Microscopic reversibility requires that such σ -complexes also be formed during the reverse process of alkane C–H activation by the alkylidene complexes. In addition, it has been found that thermolysis of $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**1**) at 70 °C for 40 h in a 1:1 molar mixture of tetramethylsilane and tetramethylsilane-*d*₁₂ yields an intermolecular KIE of 1.07(4):1. Similarly, thermolysis of **1** and $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\eta^2\text{-CH}_2\text{Ph})$ (**10**) in 1:1 benzene/benzene-*d*₆ yields intermolecular KIEs of 1.03(5):1 and 1.17(19):1, respectively. The alkylidene intermediates thus exhibit little preference for activating protio over deuterio substrates. Hence, the observed KIE values are inconsistent with C–H(D) bond addition to the W=C linkage being the discriminating factor in alkane and arene intermolecular competitions, but rather they indicate that coordination of the substrate to the metal center is the discriminating event. A possible qualitative potential energy surface for activation of an alkane substrate (R–H) that incorporates this feature is shown in Figure 2, in which **1** is used as an illustrative example, and the energies of closely related complexes are shown as being the same for simplicity.

Evidence that transient π -complexes may also be formed during such processes is provided by the observation that $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{D}_5)$ (**3-d**₅) and $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\text{C}_6\text{D}_5)$ convert to the respective H/D scrambled products under thermolytic conditions, consistent with the occurrence of reversible aromatic sp^2 C–H bond cleavage. These results suggest that the observed discrimination between the aryl and benzyl products of toluene activation by intermediate complexes **A** and **C** (e.g., Scheme 4) originates from the coordination of toluene to the tungsten center in two distinct modes. Supporting DFT calculations (including zero-point-energy and entropy corrections) on the activation of toluene by $\text{Cp}^*\text{W}(\text{NO})(=\text{CH}_2)$ indicate that aromatic sp^2 C–H bond activation proceeds through a π -arene complex, while benzylic sp^3 C–H bond activation proceeds through an $\eta^2(\text{C,H})$ - σ -phenylmethane complex.¹⁴ The principal factor behind the preferential formation of the aryl products appears to be the relative ease of formation of the π -arene intermediates.

Aspects of the alkylidene chemistry outlined in this section have been the subjects of theoretical investigations by other researchers. For instance, mechanisms for generating tungsten carbene complexes from $\text{Cp}'\text{W}(\text{NO})\text{Me}_2$ ($\text{Cp}' = \text{Cp}$ or Cp^*) by methane elimination have been studied by density functional (B3LYP) computations by Fan and Hall.¹⁵ Their calculations suggest that a one-step, metal-assisted (σ -bond metathesis-like) mechanism is preferred for this process. The reactivities of $\text{CpM}(\text{NO})\text{-Me}_2$ ($\text{M} = \text{Mo}, \text{W}$) have also been investigated by DFT



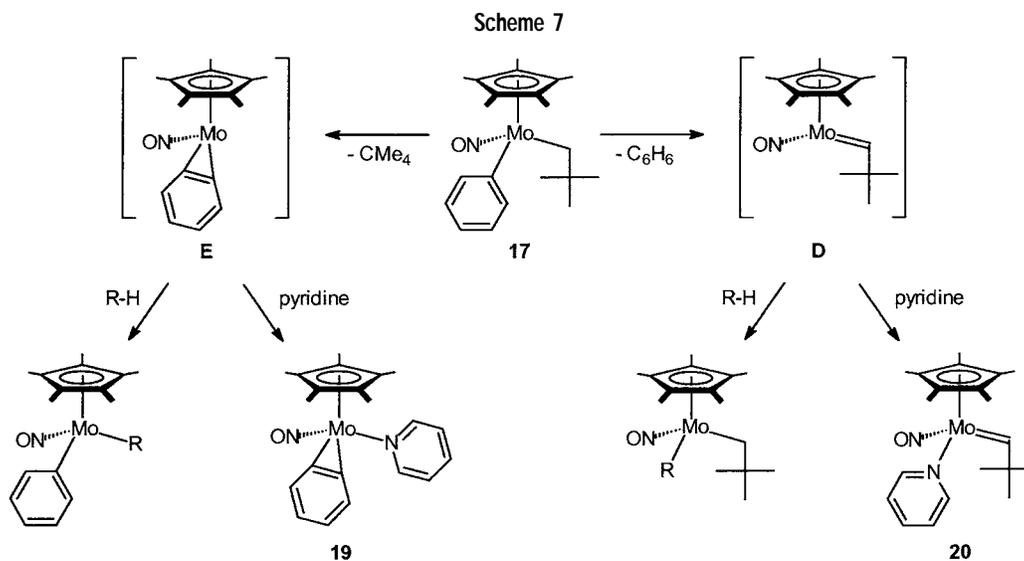
calculations at the B3LYP level by Poli and Smith.¹⁶ While generally in agreement with experimental findings, their computations nevertheless indicate that reaction of the $\text{Cp}^*\text{W}(\text{NO})(=\text{CH}_2)$ model complex with CH_4 is more exothermic and has a lower activation barrier than the corresponding process for $\text{Cp}^*\text{Mo}(\text{NO})(=\text{CH}_2)$, a conclusion contrary to the observed behavior of intermediates **A** and **D** (vide supra).¹⁶ Hence, it is worth noting at this point that while the insights provided by such computations can be useful, the results should be interpreted with caution since simplified models of the organometallic reactants are often being employed. In the cases above, the dimethyl compounds $\text{Cp}^*\text{M}(\text{NO})\text{Me}_2$ are being used in place of the actual (and sterically more demanding) $\text{Cp}^*\text{M}(\text{NO})(\text{CH}_2\text{R})_2$ reactants, even though the dimethyl complexes do not exhibit α -H elimination chemistry, preferring instead to spontaneously convert to their oxo imido isomers, $\text{Cp}^*\text{M}(\text{NMe})(\text{O})\text{Me}$, via nitrosyl N–O bond cleavage under the experimental conditions employed.¹⁷

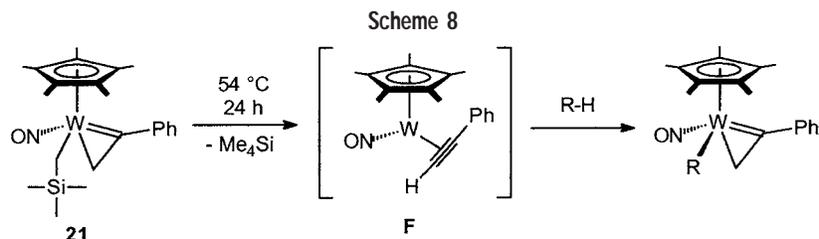
$\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-benzyne})$ Intermediates

To date, only the molybdenum-containing member of these reactive intermediates has been unambiguously identified. Its existence was first inferred from the remarkable reaction of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**14**) with C_6H_6 at room temperature that leads to the sequential activation of two molecules of benzene, as depicted in Scheme 6.¹³ These conversions resemble the sequential activation of two molecules of Me_4Si by the neopentylidene intermediate **A** shown at the bottom of Scheme 1. The intermediacy

of a transient benzyne complex in this benzene activation chemistry (Scheme 7) is confirmed by the fact that thermolysis of independently prepared $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)$ (**17**) in pyridine- d_5 at room temperature for 30 h affords a mixture of the trapped η^2 -benzyne complex $\text{Cp}^*\text{Mo}(\text{NO})(\eta^2\text{-C}_6\text{H}_4)(\text{NC}_5\text{D}_5)$ (**19**- d_5 , ~25%) and the trapped alkylidene complex $\text{Cp}^*\text{Mo}(\text{NO})(=\text{CHCMe}_3)(\text{NC}_5\text{D}_5)$ (**20**- d_5 , ~75%), which can be separated by fractional crystallization. The trapped η^2 -benzyne complex is stereochemically rigid in solutions, and its solid-state molecular structure has been confirmed by a single-crystal X-ray crystallographic analysis. As shown in Scheme 7, the $16e$ $\text{Cp}^*\text{Mo}(\text{NO})(\eta^2\text{-C}_6\text{H}_4)$ intermediate **E** also reacts readily with the aliphatic C–H bonds of various substrates (R–H) to form the corresponding $\text{Cp}^*\text{Mo}(\text{NO})(\text{C}_6\text{H}_5)(\text{R})$ products, but the exact scope of its C–H bond-activating ability remains to be delineated. However, it is not unreasonable to expect that its chemistry may well resemble in some aspects that exhibited by the $\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-acetylene})$ intermediates which are considered in the next section. In this connection, it may be noted that relatively few benzyne complexes have been reported to undergo intermolecular C–H bond activation processes, and then usually at temperatures in excess of 100°C .^{18–20}

It is clear that the gentler reaction conditions required for the molybdenum system permit the isolation of the η^2 -benzyne complex **19**, even though it is not obtainable by thermolysis of the diphenyl complex **18** in pyridine. We have previously proposed similar intermediates for the related tungsten systems, but they have proven to be unisolable, probably because of thermal decomposition under the requisite experimental conditions. For instance, thermolysis of $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)$ in C_6H_6 at 80°C results in the elimination of neopentane, but not in the formation of one principal organometallic product. When effected in the presence of PMe_3 , no reaction occurs at 80°C . However, at 110°C , this thermolysis affords the yellow **18e** adduct of the diphenyl complex, $\text{Cp}^*\text{W}(\text{NO})(\text{C}_6\text{H}_5)_2(\text{PMe}_3)$, which can be isolated in good yields.²¹ Whether PMe_3 coordinates to the tungsten center before or after the putative benzyne complex activates the solvent





is unknown. We presume that this activation would be more facile prior to phosphine coordination, since we have only ever found one such 18e species, namely $\text{Cp}^*\text{W}(\text{NO})(\text{H})(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)$, that is capable of intermolecular C–H bond activation.²² In benzene at 40 °C, this alkyl hydrido complex quantitatively converts to $\text{Cp}^*\text{W}(\text{NO})(\text{H})(\text{C}_6\text{H}_5)(\text{PMe}_3)$ with concomitant elimination of Me_4Si in 22 h. Regrettably, attempts to activate the C–H bonds of cyclohexane in an identical manner result only in the formation of low yields of 18e $\text{Cp}^*\text{W}(\text{NO})(\text{PMe}_3)_2$ as the only identifiable product. In closing this section, we note that we have also invoked similar toluene intermediates to rationalize the thermal isomerization of $\text{CpW}(\text{NO})(o\text{-tolyl})_2$ at 40 °C in benzene to its *m*- and *p*-tolyl-containing isomers.²³

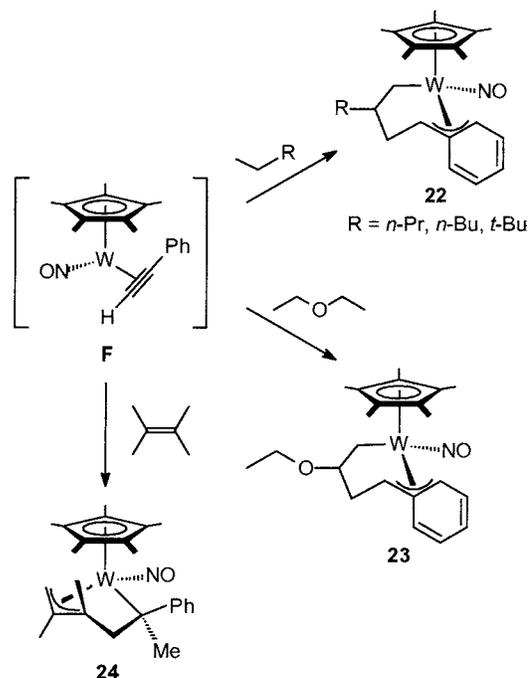
$\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-acetylene})$ Intermediates

These intermediates result from the thermolysis of alkyl vinyl precursors, the most studied of which is $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{CPh}=\text{CH}_2)$ (**21**). The solid-state molecular structure of this complex reveals that its vinyl ligand exists in a distorted form that cannot readily be described by either of the classic η^1 -vinyl or 1-metallacyclopropene limiting structures. However, the NMR parameters for the CPhCH_2 fragment in **21** in solutions are characteristic of those of a 1-metallacyclopropene unit, a feature reflecting the metal center's attainment of the favored 18e configuration.²⁴

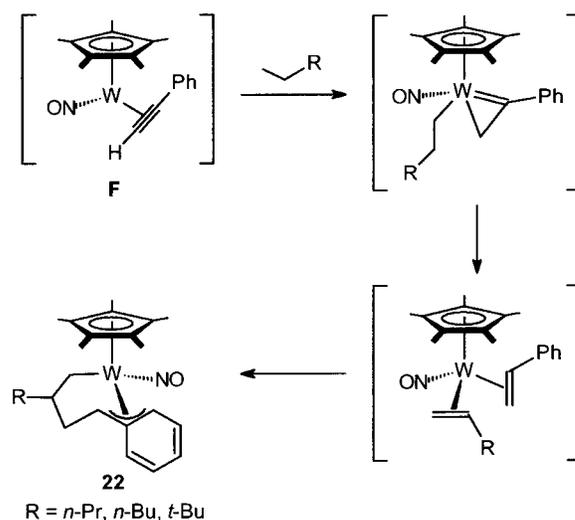
Thermal activation of **21** at 54 °C in neat hydrocarbon solutions transiently generates $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-PhC}\equiv\text{CH})$ (**F**), which subsequently activates solvent C–H bonds.^{25,26} Examples of the single C–H activation processes that have been effected by this complex are summarized in Scheme 8. These activations of substrates R–H [R–H = benzene, methyl-substituted arenes, and $(\text{Me}_3\text{Si})_2\text{O}$] afford the corresponding 18e $\text{Cp}^*\text{W}(\text{NO})(\text{R})(\eta^2\text{-CPh}=\text{CH}_2)$ complexes. As found with other systems^{2c} and the other nitrosyl intermediates considered in this Account, intra- and intermolecular selectivity studies reveal that the strongest C–H bond of R–H (yielding the stronger M–C bond) is the preferred site of reactivity of intermediate **F**. Mechanistic, labeling, and kinetic studies of these conversions are also consistent with the rate-determining step being the reversible formation of **F** from **21** by elimination of Me_4Si and with the involvement of σ - and π -hydrocarbon complexes along the various mechanistic pathways (cf. Figure 2).

The dual C–H bond activations of aliphatic hydrocarbons effected by **21** (Scheme 9) are unique to this complex, and they are particularly interesting for several reasons. First, these processes result in the dehydroge-

Scheme 9

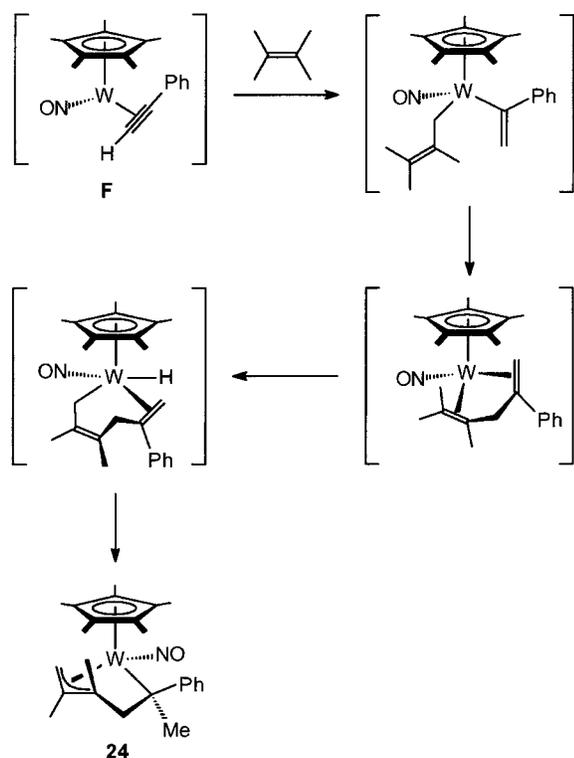


Scheme 10

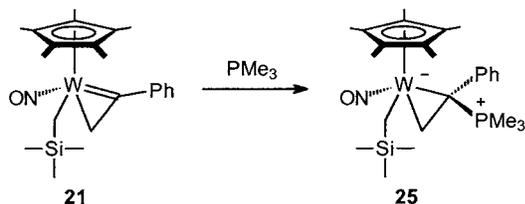


nation of alkanes with β -C–H bonds and their coupling with the alkenyl ligand in the tungsten's coordination sphere to form 18e η^1, η^3 -metallacyclic species. Second, they selectively activate substrates that contain an ethyl substituent (e.g., the reaction with Et_2O to form **23**). A plausible mechanism for these dual C–H activation processes is depicted in Scheme 10 using the formation of the complexes **22** as a particular example. Interestingly, in the absence of alkyl groups with β -C–H bonds, a

Scheme 11



Scheme 12



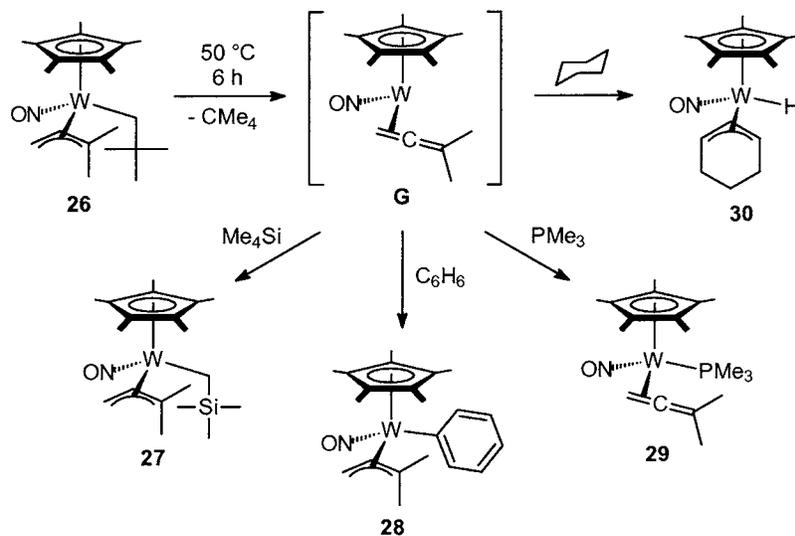
different mode of reactivity results, as illustrated in Scheme 9 for 2,3-dimethyl-2-butene. In this case, fusion of the olefinic fragment to the vinyl fragment occurs at the α -C of the vinyl fragment, and the two C–H bond activations now occur at the trans- γ positions in the

olefinic substrate. The probable mechanism for the formation of complex **24** is depicted in Scheme 11. Unfortunately, the thermolyses of **21** in cyclopentane, cyclopentene, cyclohexane, and cyclohexene each lead to the formation of a plethora of as yet unidentified products. Finally, attempts to trap the intermediate acetylene complex, which has so far defied spectroscopic detection,²⁷ with PMe_3 are foiled by the ready reaction of the trapping agent under ambient conditions with the original reactant **21** to form the metallacyclopropane complex $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-CH}_2\text{CPh})(\text{PMe}_3)$ (**25**, Scheme 12).²⁶

$\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-allene})$ Intermediates

The 16e η^2 -allene intermediate species result from the thermal activation of 18e precursor complexes having η^1 -alkyl and η^3 -allyl ligands. The most studied member of this family of compounds is $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)(\eta^3\text{-1,1-Me}_2\text{C}_3\text{H}_3)$ (**26**), and its chemistry that we have discovered to date is summarized in Scheme 13.²⁸ Thermolysis of **26** in Me_4Si at 50 °C for 6 h results in the evolution of neopentane and the quantitative formation of the 18e alkyl-allyl complex $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^3\text{-1,1-Me}_2\text{C}_3\text{H}_3)$ (**27**). Complex **27** is thermally stable in Me_4Si , and the bis(alkyl) complex $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (**4**, Scheme 1) is not formed after prolonged reaction times. In a similar manner, $\text{Cp}^*\text{W}(\text{NO})(\text{C}_6\text{H}_5)(\eta^3\text{-1,1-Me}_2\text{C}_3\text{H}_3)$ (**28**) is produced quantitatively via thermolysis of **26** under the same conditions in benzene solution. The analogous reaction in C_6D_6 leads to the formation of the corresponding deuterated complex, $\text{Cp}^*\text{W}(\text{NO})(\text{C}_6\text{D}_5)(\eta^3\text{-1,1-Me}_2\text{-allyl-}d_1)$ (**28-}d_6**), in which the deuterium atom in the allyl ligand is incorporated among all three types of carbon atoms. This conversion also exhibits first-order kinetics for the loss of **26** at 50 °C, a feature consistent with the rate-determining step being the intramolecular generation of the intermediate η^2 -allene complex **G** (Scheme 13). Thermolyses of alkyl-allyl complexes of iridium at 120 °C are believed to form similar allene complexes. However, these intermediates have not been characterized or isolated, and

Scheme 13



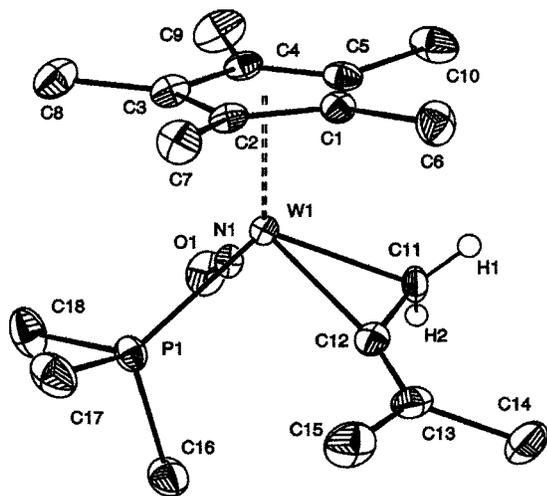


FIGURE 3. Solid-state molecular structure of $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-H}_2\text{C}=\text{C}=\text{CMe}_2)(\text{PMe}_3)$ (**29**).

they are only capable of effecting single C–H bond activations.^{10b}

The thermal reaction of **26** in a solution of excess PMe_3 in cyclohexane cleanly affords the base-stabilized form of the allene complex, namely $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-H}_2\text{C}=\text{C}=\text{CMe}_2)(\text{PMe}_3)$ (**29**), which has been isolated and fully characterized. For instance, its solid-state molecular structure (Figure 3) exhibits metrical parameters [e.g., $\text{C}(11)\text{--}\text{C}(12) = 1.436(7)$ Å, $\text{C}(12)\text{--}\text{C}(13) = 1.324(7)$ Å, and $\text{C}(11)\text{--}\text{C}(12)\text{--}\text{C}(13) = 134.0(5)^\circ$] that indicate considerable back-donation of electron density from the tungsten center to the allene π^* orbitals. This exceptionally strong π -donor ability of the $\text{Cp}^*\text{M}(\text{NO})(\text{PMe}_3)$ ($\text{M} = \text{Mo}, \text{W}$) fragments²⁹ un-

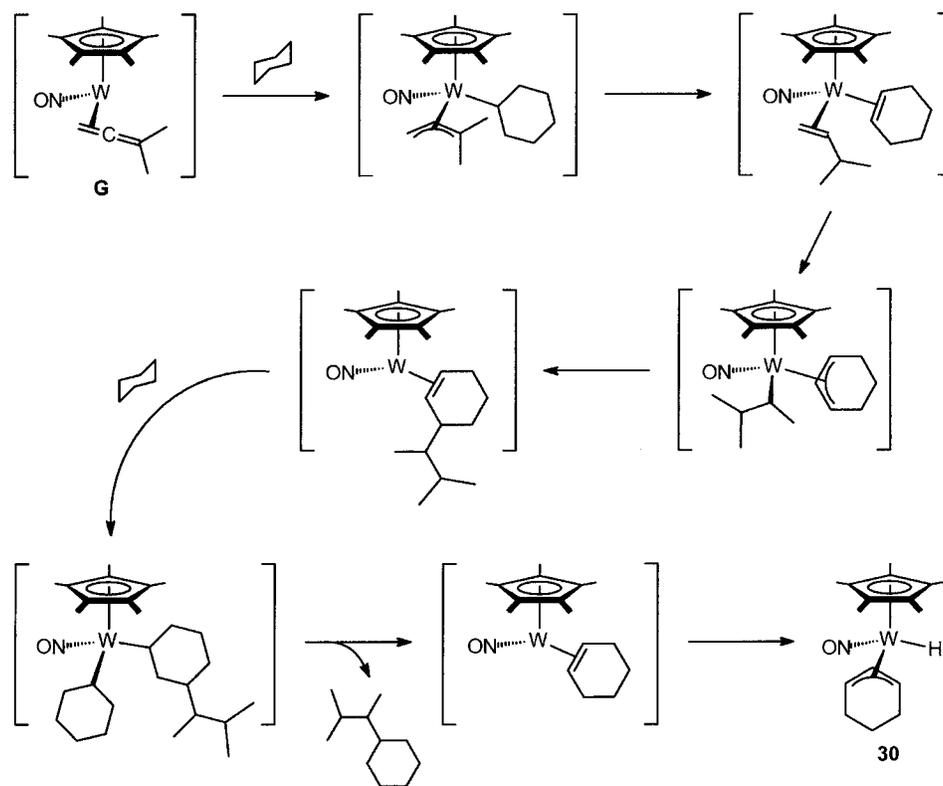
doubtedly stabilizes all the PMe_3 -trapped reactive intermediates considered in this Account.

Most interestingly, the thermolysis of **26** in cyclohexane produces principally the cyclohexenyl hydrido complex $\text{Cp}^*\text{W}(\text{NO})(\eta^3\text{-C}_6\text{H}_9)(\text{H})$ (**30**), which formally results from three C–H bond activations of the hydrocarbon solvent. Its ^1H NMR spectrum in C_6D_6 contains a distinctive hydride resonance at $\delta -0.57$ ($^1J_{\text{WH}} = 131.7$ Hz), and the IR spectrum of it as a KBr pellet exhibits ν_{WH} at 1898 cm^{-1} . GC–MS studies also reveal the presence of the coupled organic product, a dimethylpropylcyclohexane, in the final reaction mixture. Even though the mechanism of this transformation remains to be ascertained, a plausible series of steps that accounts for the formation of the isolated products is shown in Scheme 14. Overall, the conversion of **26** into **30** constitutes a novel mode of multiple C–H activations of cyclohexane, a relatively inert solvent that has frequently been used to study the C–H activations of other hydrocarbons. For comparison, it may be noted that bis(alkyl) species such as $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{-CMe}_3)_2$ (**1**) react with cyclohexane in a different manner to afford $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-cyclohexene})(\text{PMe}_3)$ (**6**) in the presence of PMe_3 (Scheme 2).

Summary

In summary, reactive 16e $\text{Cp}^*\text{M}(\text{NO})$ -containing complexes of molybdenum and tungsten such as $\text{Cp}^*\text{M}(\text{NO})$ -(alkylidene), $\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-benzyl})$, $\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-acetylene})$, and $\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-allene})$ have been successfully generated by the gentle thermolyses of appropriate $\text{Cp}^*\text{M}(\text{NO})(\text{hydrocarbyl})_2$ precursors. In most cases, these com-

Scheme 14



plexes have been isolated and fully characterized by conventional spectroscopic means and X-ray crystallographic analyses as their 18e Lewis base adducts. These 16e intermediate complexes effect single C–H bond activations which are the reverse of the reactions used to generate them while exhibiting a preference for activating stronger arene sp^2 C–H bonds. Furthermore, these reactive 16e intermediates usually effect multiple C–H bond activations of hydrocarbon substrates, some of which are normally difficult to activate by other means. Interestingly, the multiple activations apparently involve the transient formation of labile mono- and bis(olefin) complexes that subsequently convert to the final isolable products. The reactivity differences displayed by the various 16e species presented in this Account suggest that new avenues of alkane activation and eventual functionalization may well be accessible through these and related complexes. Our studies in this regard with these fascinating systems are continuing.

We are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of British Columbia for generously supporting our research efforts over the years. We also gratefully acknowledge the hard work, perseverance, and insight of the various graduate students, postdoctoral fellows, and research associates cited in the references that made this Account possible.

References

- Legzdins, P.; Veltheer, J. E. Cp*M(NO)R₂: 16-Electron Piano-Stool Molecules of Molybdenum and Tungsten. *Acc. Chem. Res.* **1993**, *26*, 41–48.
- The field of C–H bond activation has been extensively reviewed. For leading references, see: (a) Labinger, J. A.; Bercaw, J. E. Understanding and Exploiting C–H Bond Activation. *Nature* **2002**, *417*, 507–514. (b) Shilov, A. E.; Shul'pin, G. B. Activation of C–H Bonds by Metal Complexes. *Chem. Rev.* **1997**, *97*, 2879–2932. (c) Arndtsen, B. A.; Bergman, R. G.; Mobley, A.; Peterson, T. H. Selective Intermolecular Carbon–Hydrogen Bond Activation by Synthetic Metal Complexes in Homogeneous Solution. *Acc. Chem. Res.* **1995**, *28*, 154–162.
- Bau, R.; Mason, S. A.; Patrick, B. O.; Adams, C. S.; Sharp, W. B.; Legzdins, P. α -Agostic Interactions in Cp*W(NO)(CH₂CMe₃)₂ and Related Nitrosyl Complexes. *Organometallics* **2001**, *20*, 4492–4501.
- (a) Brookhart, M.; Green, M. L. H. Carbon–Hydrogen–Transition Metal Bonds. *J. Organomet. Chem.* **1983**, *250*, 395–408. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. Carbon–Hydrogen–Transition Metal Bonds. *Prog. Inorg. Chem.* **1988**, *36*, 1–124. (c) Crabtree, R. H.; Hamilton, D. G. Hydrogen–Hydrogen, Carbon–Hydrogen, and Related Sigma-Bonded Groups as Ligands. *Adv. Organomet. Chem.* **1988**, *28*, 299–338.
- Tran, E.; Legzdins, P. Thermal Alkane C–H Bond Activation by a Tungsten Alkylidene Complex: The Reversal of α -Hydrogen Elimination. *J. Am. Chem. Soc.* **1997**, *119*, 5071–5072.
- Adams, C. S.; Legzdins, P.; Tran, E. Thermal Activation of Hydrocarbon C–H Bonds by Tungsten Alkylidene Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 612–624.
- van der Heijden, H.; Hessen, B. Intermolecular C–H Activation by Reactive Titanocene Alkylidene Intermediates. *J. Chem. Soc., Chem. Commun.* **1995**, 145–146.
- Coles, M. P.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J.; Porelli, P. A. Synthesis and Reactivity of the First Stable Chromium(VI) Alkylidene Complexes. *J. Chem. Soc., Chem. Commun.* **1996**, 1963–1964.
- Cheon, J.; Rogers, D. M.; Girolami, G. S. Mechanistic Studies of the Thermolysis of Tetraneopentyltitanium(IV). 1. Solution Evidence That Titanium Alkylidenes Activate Saturated Hydrocarbons. *J. Am. Chem. Soc.* **1997**, *119*, 6804–6813.
- (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. A Structural, Kinetic, and Thermodynamic Study of the Reversible Thermal C–H Activation/Reductive Elimination of Alkanes at Iridium. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. (b) McGhee, W. D.; Bergman, R. G. Synthesis of an (η^3 -Allyl)(hydrido)iridium Complex and Its Reactions with Arenes and Alkanes. Sequential Intermolecular C–H Oxidative Addition and Hydride-to-Alkene Migratory Insertion Reactions. *J. Am. Chem. Soc.* **1988**, *110*, 4246–4262.
- Adams, C. S.; Legzdins, P.; Tran, E. C–H Activation of Substituted Arenes by Tungsten Alkylidene Complexes: Products, Selectivity, and Mechanism. *Organometallics* **2002**, *21*, 1474–1486.
- (a) Legzdins, P.; Rettig, S. J.; Veltheer, J. E. A Unique $u\text{-}\eta^1\text{-}\eta^2$ -NO Ligand in a Bimetallic Alkylidene Nitrosyl Complex of Molybdenum. *J. Am. Chem. Soc.* **1992**, *114*, 6922–6923. (b) Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. Thermal Chemistry of Molybdenum Complex CpMo(NO)(CH₂CMe₃)₂: Lewis Base Adducts of CpMo(NO)(=CHCMe₃) and a New Bonding Mode for Nitric Oxide. *Organometallics* **1993**, *12*, 3575–3585.
- Wada, K.; Pamplin, C. B.; Legzdins, P. Parallel Modes of C–H Bond Activation Initiated by Cp*Mo(NO)(CH₂CMe₃)(C₆H₅) at Ambient Temperatures. *J. Am. Chem. Soc.* **2002**, *124*, 9680–9681.
- Adams, C. S.; Legzdins, P.; McNeil, W. S. Intermolecular C–H Activation of Hydrocarbons by Tungsten Alkylidene Complexes: An Experimental and Computational Mechanistic Study. *Organometallics* **2001**, *20*, 4939–4955.
- Fan, Y.; Hall, M. B. Carbon–Hydrogen Bond Activation in Cyclopentadienyl Dimethyl Tungsten Nitrosyl and Carbonyl. *J. Chem. Soc., Dalton Trans.* **2002**, 713–718.
- Poli, R.; Smith, K. M. Theoretical Studies of the Reactivity of Cyclopentadienyl Nitrosyl Alkyl Species of Molybdenum and Tungsten. *Organometallics* **2000**, *19*, 2858–2867.
- Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. The Elusive 16-Electron Cp*M(NO)Me₂ (M = Mo, W) Complexes and Their Spontaneous Conversions to Cp*M(NMe)(O)Me Isomers. *J. Am. Chem. Soc.* **2001**, *123*, 6272–6282.
- Erker, G. The Reaction of Intermediate Zirconocene-Aryne Complexes with C–H Bonds in the Thermolysis of Diarylzirconocenes. *J. Organomet. Chem.* **1977**, *134*, 189–202.
- Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. Synthesis and Properties of Bis(pentamethylcyclopentadienyl) Actinide Hydrocarbyls and Hydrides. A New Class of Highly Reactive f-Element Organometallic Compounds. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.
- (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. Synthesis of a Highly Reactive (Benzynes)ruthenium Complex: C–C, C–H, N–H, and O–H Activation Reactions. *J. Am. Chem. Soc.* **1989**, *111*, 2717–2719. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. Structure, Synthesis, and Chemistry of (PMe₃)₄Ru(η^2 -benzynes). Reactions with Arenes, Alkenes, and Heteroatom-Containing Organic Compounds. Synthesis and Structure of a Monomeric Hydroxide Complex. *J. Am. Chem. Soc.* **1991**, *113*, 3404–3418.
- Debad, J. D. Hydride, Alkyl, and Alkenyl Complexes of Tungsten. Ph.D. Dissertation, The University of British Columbia, 1994.
- Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Jones, R. H. New Types of Remarkably Stable Alkyl Hydride Complexes of Tungsten. *Organometallics* **1987**, *6*, 1826–1827.
- Sharp, W. B. Synthesis and Ligand Reactivity of Group 6 Organometallic Nitrosyl Complexes. Ph.D. Dissertation, The University of British Columbia, 2001.
- Legzdins, P.; Lumb, S. A.; Rettig, S. J. 1-Metallacyclopropene Complexes and η^1 -Vinyl Complexes Containing the Cp*W(NO) Fragment. *Organometallics* **1999**, *18*, 3128–3137.
- Debad, J. D.; Legzdins, P.; Lumb, S. A.; Batchelor, R. J.; Einstein, F. W. B. Facile Thermal Reactivity of Cp*W(NO)(CH₂SiMe₃)(CPh=CH₂): Unique Alkane C–H Activation under Mild Conditions. *J. Am. Chem. Soc.* **1995**, *117*, 3288–3289.
- Debad, D.; Legzdins, P.; Lumb, S. A.; Rettig, S. J.; Batchelor, R. J.; Einstein, F. W. B. Hydrocarbon C–H Bond Activation by a Tungsten Acetylene Complex. *Organometallics* **1999**, *18*, 3414–3428.
- Legzdins, P.; Lumb, S. A. Trapping of Cp*W(NO)(η^2 -PhC≡CH), the Key Intermediate in the C–H Activation of Alkanes by Cp*W(NO)-(CH₂SiMe₃)(CPh=CH₂). *Organometallics* **1997**, *16*, 1825–1827.
- Ng, S. H. K.; Adams, C. S.; Legzdins, P. Unusual Thermal C–H Bond Activation by a Tungsten Allene Complex. *J. Am. Chem. Soc.* **2002**, *124*, 9380–9381.
- The strong π -donor ability of the related Cp*W(NO)(PPh₃) fragment has been documented: Burkey, D. J.; Debad, J. D.; Legzdins, P. Unusual Ligand-Induced Reductive Elimination in Cp*W(NO)-(H)[η^2 -PPh₂C₆H₄]: A Route to the Extremely Strong π -Donor Fragment Cp*W(NO)(PPh₃). *J. Am. Chem. Soc.* **1997**, *119*, 1139–1140.

AR0202215