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Facile Thermal Reactivity of $Cp^*W(NO)(CH_2SiMe_3)(CPh{=}CH_2)$: Unique Alkane C−H Activation under Mild Conditions

Jeff D. Debad, Peter Legzdins,* and Sean A. Lumb

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

Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6

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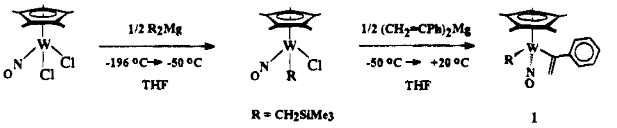
The activation of carbon−hydrogen bonds by coordinatively unsaturated metal complexes continues to be an area of considerable research activity.[1] We now report a unique and selective mode of double C−H bond activation of linear alkanes such as *n*-pentane and *n*-hexane under gentle thermal conditions by the alkenyl complex $Cp^*W(NO)(CH_2SiMe_3)(CPh{=}CH_2)$ (**1**), which attains coordinative unsaturation in an unusual manner. For preparative purposes, complex **1** is best synthesized by the method summarized in eq 1.[2] The solid-state molecular structure of **1** is presented in Figure 1.[3] Its intramolecular dimensions resemble those exhibited by other three-legged piano-stool $Cp^*W(NO)R_2$ complexes[4] and clearly confirm that **1** is a 16-valence-electron complex. The small W−C(19)−C(20) angle of 98.7(5)° is somewhat surprising, but can be attributed to a bending of the alkenyl ligand to relieve steric interactions between the nitrosyl group and the phenyl substituent. Nevertheless, the alkenyl ligand does not bend enough to attain complete η^2-coordination[5] to the Lewis-acidic metal site[6] in the solid state. In C_6D_6 solution the ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**[2] also suggest the existence of a weak interaction between the tungsten center and the π-electron density of the alkenyl group.[7]



(1)

The thermal chemistry of **1** is dominated by its ability to activate aliphatic C−H bonds selectively under mild conditions.

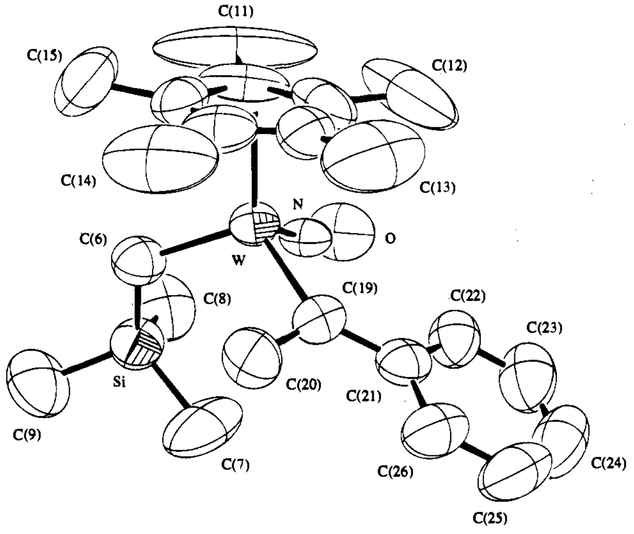
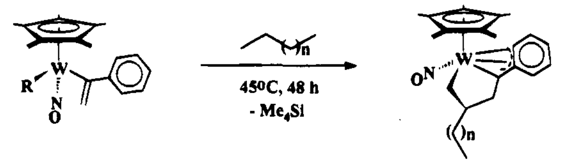


Figure 1. Solid-state molecular structure of **1**; 50% probability thermal ellipsoids are shown. Selected interatomic distances (Å) and angles (deg): W−N = 1.742(8), W−Cp* = 2.048, N−O = 1.234(12), W−C(6) = 2.169(8), W−C(19) = 2.053(7), C(19)−C(20) = 1.347(13), C(19)−C(21) = 1.477(10), N−W−C(6) = 96.5(4), C(20)−C(19)−C(21) = 121.6(7), N−W−C(19) = 96.1(3), C(6)−W−C(19) = 115.2(3), C(6)−W−Cp* = 113.33(21), C(19)−W−Cp* = 111.81(21), W−C(6)−Si = 117.7(4), W−C(19)−C(20) = 98.7(5), W−N−O = 168.6(5), W−C(19)−C(21) = 137.0(7).

Equation 2 summarizes the specific thermal activations of *n*-pentane and *n*-hexane by $Cp^*W(NO)(CH_2SiMe_3)(CPh{=}CH_2)$ to afford complexes **2** and **3** as yellow-orange needles.[2] In forming **2** and **3**, the alkanes have undergone two C−H bond activations and been coupled with the alkenyl ligand in the metal's coordination sphere. It is worth noting that the conversions in eq 2 also occur readily at ambient temperatures, but require longer times to reach completion. The spectroscopic properties of **2** and **3**[8] did not establish their molecular structures unambiguously, and so the pentane-activated thermolysis product, $Cp^*W(NO)(\eta^3,\eta^1\text{-}CHPhCH_2CH(n\text{-}Pr)CH_2)$, **2**, was subjected to a single-crystal X-ray crystallographic analysis,[9] the results of which are displayed in Figure 2. In general, the metrical parameters extant in the solid-state molecular structure of **2** resemble those exhibited by related $Cp^*W(NO)$-containing complexes,[4] and the parent components of the metallacycle in **2** are also easily identifiable (Figure 2). Ring nuclei C(6) and C(7) presumably originate from the hydrocarbon solvent that has been activated by **1**, and C(19) and C(20) originate from the alkenyl ligand. Fusion of the two ligands at C(7) and C(20) results in the formation of the substituted metallacycle. Of



(2)

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[1] (a) Shilov, A. E. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989; Chapter 1. (b) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G *J. Am. Chem. Soc.* **1988**, *110*, 8729. (d) Crabtree, R. H.; Cemou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 6994. (e) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (f) Janowicz, A. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (g) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4346. (h) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620.

[2] Complete experimental details and characterization data for all new complexes isolated during this work are provided as supplementary material.

[3] Crystal data for **1**: triclinic, space group P, $Z = 2$, $a = 8.430(2)$ Å, $b = 9.105(2)$ Å, $c = 16.975(3)$ Å, $\alpha = 88.41(2)°$, $\beta = 89.43(2)°$, $\gamma = 66.63(2)°$, $V = 1195.6$ Å^3, $R_F = 0.034$ for 3021 reflections with $I_o \geq 2.5\sigma(I_o)$ and 244 variables.

[4] Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094 and references cited therein.

[5] For authentic examples of tungsten complexes containing η^2-alkenyl ligands, see: Feng, S. G.; Gamble, A. S.; Templeton, J. L. *Organometallics* **1989**, *8*, 2024 and references cited therein.

[6] Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

[7] Debad, J. D.; Legzdins, P.; Lumb, S. A.; Batchelor, R. J.; Einstein, F. W. B. Submitted for publication.

[8] The $^{13}C\{^1H\}$ and ^1H NMR spectra of **2** and **3**[2] are indicative of the complexes being stereochemically nonrigid in solutions, their aryl groups undergoing an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process with a fast rotation at the η^1 stage. This type of nonrigidity has been documented previously for the η^3-benzyl complexes $CpM(CO)(\eta^3\text{-}CH_2C_6H_5)$ (M = Mo or W); see: Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[9] Crystal data for **2**: monoclinic, space group $C2/c$, $Z = 8$, $a = 19.5492(12)$ Å, $b = 17.8193(20)$ Å, $c = 13.9719(9)$ Å, $\beta = 117.112(6)°$, $V = 4332.3$ Å^3, $R_F = 0.017$ for 2892 reflections with $I_o \geq 2.5\sigma(I_o)$ and 275 variables.

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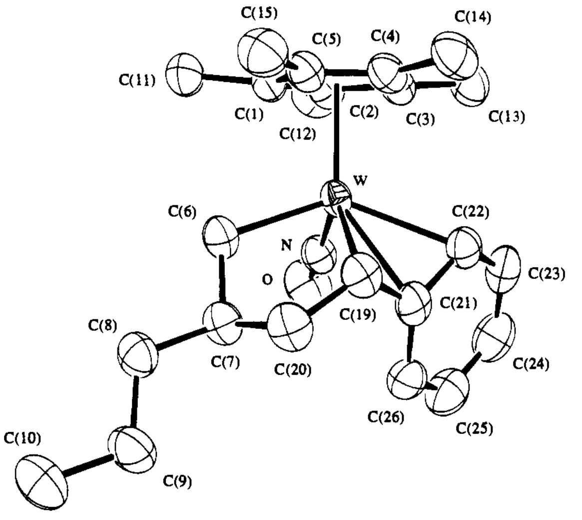
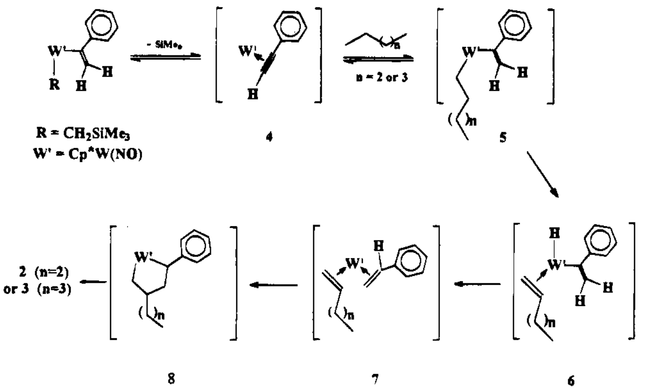


Figure 2. Solid-state molecular structure of **2**; 50% probability thermal ellipsoids are shown. Selected interatomic distances (Å) and angles (deg): W−N = 1.767(4), W−Cp* = 2.051, W−C(6) = 2.226(3), W−C(19) = 2.301(5), W−C(21) = 2.381(4), W−C(22) = 2.371(4), N−O = 1.225(6), C(6)−C(7) = 1.524(6), C(7)−C(20) = 1.535(7), C(19)−C(20) = 1.510(5), C(19)−C(21) = 1.419(5), C(23)−C(24) = 1.349(7), C(21)−C(22) = 1.432(5), C(24)−C(25) = 1.412(6), C(21)−C(26) = 1.440(6), C(25)−C(26) = 1.346(6), C(22)−C(23) = 1.421(6), N−W−C(6) = 88.02(15), C(6)−W−Cp* = 108.35, N−W−C(19) = 111.51(15), N−W−C(21) = 88.19(16), N−W−C(22) = 93.34(16), C(19)−W−Cp* = 124.72, N−W−Cp* = 123.76, C(6)−W−C(19) = 71.82(16), C(21)−W−Cp* = 139.03, C(6)−W−C(21) = 96.51(13), C(22)−W−Cp* = 110.82, C(6)−W−C(22) = 131.34(15), W−N−O = 174.3(3).

particular interest is the tungsten−η^3-benzyl interaction[10] evident in **2**, a feature which undoubtedly stabilizes the 18-valence-electron complex and renders it (and the related complex **3**) isolable.

Our current view of the mechanism resulting in **2** and **3** is depicted in Scheme 1. We propose that the starting material, **1**, initially undergoes β-H elimination to yield a highly reactive, transient η^2-acetylene intermediate, **4**, a unique species in its own right. Being coordinatively unsaturated, **4** is sufficiently reactive to activate a terminal C−H bond of the alkane to regenerate the alkenyl ligand and incorporate the saturated alkyl into the complex (**5**). β-H elimination from the the alkyl ligand to the tungsten forms the η^2-alkene hydrido complex, **6**, which isomerizes to the bis-η^2-alkene complex, **7**, by further transfer of H from the metal to the α carbon of the alkenyl ligand. Cyclization then results in the formation of the metallacyclopentane in **8**. The final products are then stabilized by involvement of the uncomplexed phenyl ring in **8** in an η^3-benzyl interaction with the metal center as observed in complex **2** (Figure 2).

Scheme 1



The selectivity of conversions 2 may well be due to the nature of the proposed alkene hydride intermediate, **6** (Scheme 1). At this point of the proposed mechanism, reversible olefin insertion/hydride elimination could conceivably isomerize the organic group to the more sterically favored α-olefin, even if the alkane is initially activated at an internal position of the hydrocarbon chain. Such isomerization to a terminal olefin is well-known in olefin hydrometalation chemistry.[11]

We are currently endeavoring to obtain experimental evidence in support of our mechanistic proposals. To date we have evidence for the reversibility of the first two steps of our proposed mechanism. Thus, added Me_4Si retards the rate of conversions 2. Furthermore, the activation of benzene-d_6 by **1** under thermolytic conditions results in both the perdeuteration of the alkenyl ligand at the β-position and the incorporation of C_6D_5 as a ligand, thereby forming $Cp^*W(NO)(C_6D_5)(CPh{=}CD_2)$ as the final product. The concomitant perdeuteration of the alkenyl ligand implies the transient existence of the η^2-acetylene intermediate, **4**, since direct addition of a C−D bond in C_6D_6 across the $M-C_{alkyl}$ bond via a four-centered transition state would lead to the elimination of Me_3SiCH_2D and simultaneous incorporation of C_6D_5 as a ligand, but would not effect the deuteration of the alkenyl ligand.

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Supplementary Material Available: Experimental procedures and characterization data for all new complexes and full details of crystal structure analyses including associated tables for **1** and **2** (23 pages); tables of measured and calculated structure factor amplitudes for **1** and **2** (41 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) For other examples of such interactions, see: (a) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (b) Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316. (c) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 188.

(11) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.