

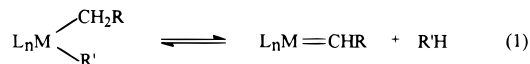
Thermal Alkane C–H Bond Activation by a Tungsten Alkylidene Complex: The Reversal of α -Hydrogen Elimination

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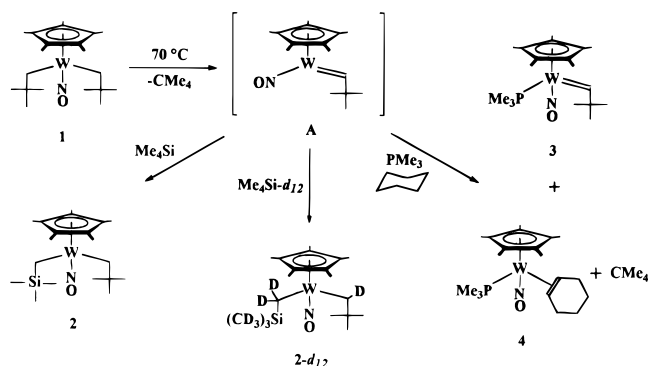
Synthetically useful transition-metal alkylidene complexes are frequently generated by intramolecular α -hydrogen elimination from a bis(alkyl) precursor (eq 1).¹ Although there are now



numerous examples of this process first discovered in 1974 by Schrock,² its reverse, the intermolecular activation of an alkane C–H bond by an alkylidene complex, has not been previously observed.^{3,4} We report here evidence for the generation of a highly reactive alkylidene species, namely Cp*W(NO)(=CHCMe₃) (A), that not only effects such an unprecedented transformation⁵ but does so even in the presence of excess trimethylphosphine.

The chemistry we have observed is summarized in Scheme 1. Thermolysis of the 16-electron bis(alkyl) complex Cp*W(NO)(CH₂CMe₃)₂ (1) in tetramethylsilane at 70 °C for 2 days results in the quantitative formation (as determined by ¹H NMR spectroscopy) of the known mixed bis(alkyl) complex Cp*W(NO)(CH₂SiMe₃)(CH₂CMe₃) (2).⁶ Complex 2, which is formed via C–H bond activation of tetramethylsilane, is thermally stable and does not react further on prolonged heating. Thermolysis of 1 in perdeuterotetramethylsilane demonstrates the fate of the activated hydrogen atom, producing exclusively Cp*W(NO)(CHDCMe₃)[CD₂Si(CD₃)₃] (2-*d*₁₂). Evidence for the monosubstitution of a deuterium atom at the α carbon of the neopentyl ligand of 2-*d*₁₂ is provided by the presence of a broad singlet for one proton at δ 3.19 in its ¹H NMR spectrum in C₆D₆ and a triplet at δ 104.8 (¹J_{CD} = 14.9 Hz) in its ¹³C-¹H NMR spectrum. The fact that a deuterium atom has been incorporated at this position confirms that 2 is formed as a result of C–H bond activation by the initially generated alkylidene intermediate A and not by a σ -bond metathesis reaction between

Scheme 1



1 and tetramethylsilane.⁷ Furthermore, that isolated 2-*d*₁₂ remains unchanged upon heating in protiotetramethylsilane establishes that the C–H(D) activation of this solvent is irreversible. This transformation thus represents an unprecedented example of intermolecular activation of an unactivated aliphatic C–H bond by an alkylidene species, a process which is the reverse of the α -hydrogen elimination reaction.

In an attempt to isolate a base-stabilized form of A, thermolysis of 1 has been effected in a solution of excess trimethylphosphine (10 equiv) in cyclohexane, a relatively inert solvent that has been widely used during the activation of C–H bonds of other hydrocarbons.⁸ As expected, this reaction results in the generation of the phosphine-trapped alkylidene complex Cp*W(NO)(=CHCMe₃)(PMe₃) (3). Surprisingly, a second organometallic compound is also formed, namely Cp*W(NO)(cyclohexene)(PMe₃) (4), a product presumably derived from C–H bond activation of cyclohexane (*vide infra*). The ratio of 3 and 4 depends upon the relative amounts of trimethylphosphine and cyclohexane present in the reaction mixture.⁹

Complexes 3 and 4 are yellow crystalline solids that can be separated by chromatography on alumina I and isolated pure by crystallization from a 3:1 mixture of pentane/Et₂O at –30 °C. A more direct preparation of 3 can be achieved from the thermolysis of 1 in neat trimethylphosphine.¹⁰ Interestingly, no C–H bond activation of the phosphine occurs during this latter reaction. The solution structure of 3 is readily deduced from its ¹H and ¹³C NMR spectra which display diagnostic alkylidene resonances in C₆D₆ at δ 11.25 (³J_{HP} = 3.6 Hz) and δ 282.8 (¹J_{CH} = 111 Hz, ²J_{CP} = 8.9 Hz), respectively, due to the α proton and α carbon of the neopentylidene ligand. Key to the identification of 4 are (1) the isotope patterns at *m/z* 507 and 425 in its mass spectrum which correspond to the molecular ion peak and the molecular ion peak minus cyclohexene and (2) the presence of four CH₂ and two CH signals in the gated ¹³C{¹H} NMR spectrum (C₆D₆) attributable to the cyclohexene ligand. The olefinic CH signals appear at δ 39.6 and δ 40.0; such significantly upfield shifts for these carbon signals is indicative of a high degree of π -back-donation from the tungsten center to the bound cyclohexene.¹¹

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(3) Although transition-metal alkylidene complexes have not been reported to activate C–H bonds of alkanes, they are known to undergo a variety of intra- and intermolecular aliphatic and aromatic C–H bond activations. For intramolecular activation, see: (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1981**, *1*, 1629. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (d) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271. (e) Lockwood, M. A.; Clark, J. R.; Parkin, B. C.; Rothwell, I. P. *Chem. Commun.* **1996**, 1973.

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(9) For example, heating 1 (81 mg, 0.164 mmol) in cyclohexane (2 mL) in the presence of ca. 10 equiv of PMe₃ produces 3 and 4 in a 2:1 ratio. Increasing the amount of cyclohexane to 8 mL while maintaining the other reagents constant changes this ratio to 2:3.

(10) Thermolysis of 1 in cyclohexane in the absence of trimethylphosphine simply led to decomposition.

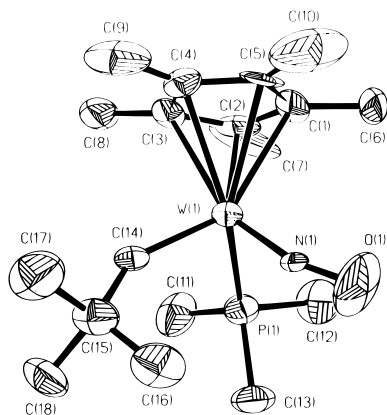


Figure 1. Solid-state molecular structure of **3**.

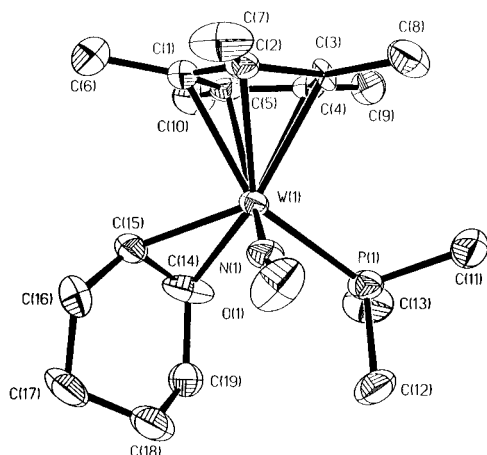


Figure 2. Solid-state molecular structure of **4**.

The solid-state molecular structures of **3** and **4** have been determined by X-ray diffraction and are shown in Figures 1 and 2, respectively.^{12,13} The W(1)–C(14) bond length of 1.960(9) Å in **3** is similar to the analogous M=C distances in isoelectronic molybdenum alkylidene complexes.^{14,15} Furthermore, the orientation of its neopentylidene ligand, with the substituents parallel to the NO ligand (N(1)–W(1)–C(14)–C(15) torsion angle = $-4(2)^\circ$) and the *tert*-butyl group pointing away from the Cp* ligand is as expected for a conformation involving maximum W=C π -bonding and minimum steric interactions.¹⁶ For **4**, the short W(1)–C(14) and W(1)–C(15)

bond distances of 2.246(9) and 2.193(9) Å, respectively, and a long C(14)–C(15) bond length of 1.447(12) Å further substantiate the extensive M \rightarrow L π -back-donation inferred from the spectroscopic data.¹⁷ Additionally, the cyclohexene ligand is coordinated to the metal center such that the C(14)–C(15)–W(1)–N(1) torsion angle is 79.8° with the olefinic hydrogen atoms directed toward the Cp* ligand. Such an orientation again is as expected for a system involving maximal π -back-donation and minimal intramolecular steric repulsions.¹⁵

Preliminary mechanistic investigation by ³¹P NMR spectroscopy has revealed that in the formation of **3** and **4** the ratio of these two complexes remains constant throughout and that isolated **3** does not convert to **4** upon heating in cyclohexane at 70–80 °C for 2 days. This indicates that these products are formed by independent pathways and do not interconvert. This reaction therefore represents a remarkable competition between trimethylphosphine and cyclohexane for irreversible reaction with the electronically unsaturated alkylidene species **A**.¹⁸ We propose that **3** is formed simply by reaction of **A** with trimethylphosphine, while **4** is formed by a multistep mechanism in which the first step involves activation of a cyclohexane C–H bond by **A** to form the unobserved bis(alkyl) species Cp*W(NO)(cyclohexyl)(CH₂CMe₃).¹⁹ This latter species then undergoes β -hydrogen elimination of neopentane to generate the coordinatively unsaturated Cp*W(NO)(cyclohexene) fragment that is subsequently trapped by trimethylphosphine to give **4**. The formation of **4**, which may be regarded as a double C–H bond activation of an alkane to form a complexed alkene fragment, is a rare process that typically occurs in late transition-metal systems.²⁰

In summary, we have discovered the first transition-metal alkylidene complex that can effect intermolecular addition of C–H bonds of alkanes across its metal–carbon double bond. Furthermore, we have demonstrated that this addition can occur even in the presence of excess trimethylphosphine and for alkanes whose C–H bonds are normally difficult to activate. Experiments designed to elucidate the scope and limitations of the reactivity of **A** are underway and will be reported in due course.

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Supporting Information Available: Experimental procedures and complete characterization data for complexes **2–4** and full details of the crystal structure analysis including associated tables for **3** and **4** (20 pages). See any current masthead page for ordering and Internet access instruction.

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(17) Strong π -bonding between the tungsten center and the cyclohexene ligand in **4** is also indicated by the fact that substitution of this cyclohexene by trimethylphosphine to give the known Cp*W(NO)(PMe₃) complex does not occur, even at elevated temperatures (70–80 °C).

(18) The activation of alkane C–H bonds is typically inhibited by the presence of strong two-electron donors; however, there are a few examples where this transformation does occur in the presence of strong Lewis bases, see: (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

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(12) Crystal data for **3**: monoclinic, space group $P2_1$, $a = 8.5740(3)$ Å, $b = 13.9660(5)$ Å, $c = 8.9140(3)$ Å, $\beta = 98.804(1)^\circ$, $V = 1054.83(2)$ Å³, $Z = 2$, $R_1 = 0.0404$, $wR_2 = 0.0916$, and $\text{GOF}(F^2) = 1.059$ for 6896 reflections and 236 variables. This specimen was racemically twinned in a 50:50 ratio; see Supporting Information for details.

(13) Crystal data for **4**: monoclinic, space group $C2/c$, $a = 30.6298(7)$ Å, $b = 9.2908(2)$ Å, $c = 16.6982(4)$ Å, $\beta = 108.4520(10)^\circ$, $V = 4022.4(2)$ Å³, $Z = 8$, $R_1 = 0.0424$, $wR_2 = 0.0760$, and $\text{GOF}(F^2) = 0.963$ for 9770 reflections and 250 variables.

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