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Unusual Thermal C−H Bond Activation by a Tungsten Allene Complex[1]

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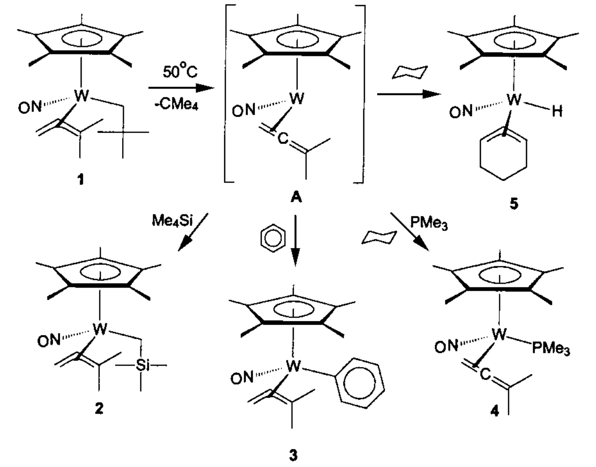
The search for complexes that exhibit selective C−H bond activation is the focus of considerable research in organometallic chemistry at the present time, primarily due to the potential for functionalization of readily available hydrocarbons into more desirable products.[2,3] Our previous contributions to this area have included the development of 16e alkylidene[4,5] and acetylene[6−9] nitrosyl complexes of tungsten that activate aliphatic and aromatic C−H bonds selectively under mild conditions. We now wish to report the generation of a reactive 16e allene complex, Cp*W(NO)(η^2-$H_2C{=}C{=}CMe_2$) (**A**), that effects single and triple C−H bond activations of hydrocarbon substrates under thermal conditions.[10]

The chemistry we have discovered is summarized in Scheme 1.

Scheme 1



Thermolysis of the 18e complex Cp*W(NO)(CH_2CMe_3)(η^3-3,3-$Me_2C_3H_3$) (**1**)[11] in Me_4Si at 50 °C for 6 h results in the evolution of neopentane and the quantitative formation (as determined by ^1H NMR spectroscopy) of the 18e alkyl−allyl complex, Cp*W(NO)(CH_2SiMe_3)(η^3-3,3-$Me_2C_3H_3$) (**2**). Complex **2** is thermally stable in Me_4Si, and the known[12] bis(alkyl) complex, Cp*W(NO)(CH_2SiMe_3)$_2$, is not formed on prolonged reaction times. **2** is an orange air-stable solid that can be isolated in 60% yield by crystallization from the final reaction mixture at −30 °C. Its solid-state molecular structure[13] (Figure 1) exhibits metrical parameters that are consistent with solution NMR data[14] and reflect $\sigma-\pi$ distortion[15] of the dimethylallyl ligand (i.e., C(11)−C(12) = 1.46(1) Å and C(12)−C(13) = 1.348(9) Å). Furthermore, the asymmetric allyl ligand is rotated away from the idealized exo or endo orientations to maximize the π-interaction between the nonbonding orbital of the allyl ligand and the metal center.[16]

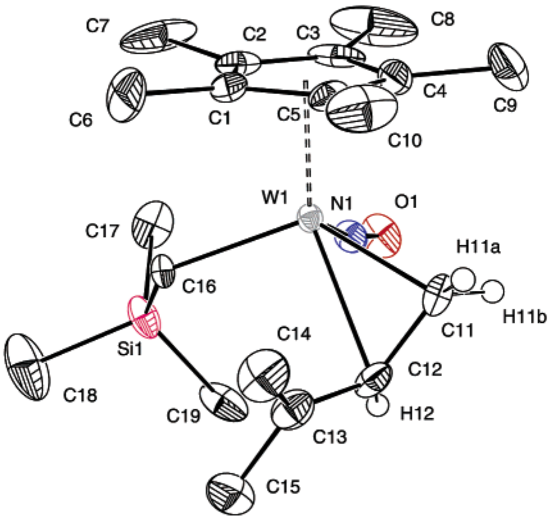


Figure 1. Solid-state molecular structure of **2** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−N(1) = 1.760(5), W(1)−C(16) = 2.217(6), W(1)−C(11) = 2.182(6), W(1)−C(12) = 2.433(6), N(1)−O(1) = 1.237(7), C(11)−C(12) = 1.46(1), C(12)−C(13) = 1.348(9), W(1)−N(1)−O(1) = 170.7(5), N(1)−W(1)−C(16) = 96.7(2), W(1)−C(11)−C(12) = 81.2(4), C(11)−C(12)−C(13) = 124.9(7), C(12)−C(13)−C(14) = 125.6(7), C(12)−C(13)−C(15) = 120.1(7).

In a similar manner, Cp*W(NO)(C_6H_5)(η^3-3,3-$Me_2C_3H_3$) (**3**) is produced quantitatively via thermolysis of **1** under the same conditions in benzene solution. **3** is isolable as orange blocks in 69% yield by recrystallization from ether/hexanes at −30 °C. Consistently, a similar thermal reaction of **1** in C_6D_6 leads to the formation of the corresponding deuterated complex, Cp*W(NO)(C_6D_5)(η^3-3,3-Me_2-allyl-d_1) (**3**-d_6). Interestingly, **3**-d_6 exists as a mixture of three isotopomers, with deuterium being incorporated at the two methyl groups and the central allyl carbon, whose exact modes of formation remain to be ascertained. The thermolysis reaction in C_6D_6 exhibits first-order kinetics for the loss of **1** at 50 °C (k_{obs} = 2.2(1) × 10^{-4} s^{-1}), a feature consistent with the rate-determining step being the intramolecular generation of intermediate **A**.

The thermal reaction of **1** in a solution of excess trimethylphosphine (10 equiv) in cyclohexane cleanly affords the base-stabilized form of **A**, Cp*W(NO)(η^2-$H_2C{=}C{=}CMe_2$)(PMe_3) (**4**), which has been isolated in 24% yield. The solution molecular structure of **4** is readily inferred from its ^{13}C {^1H} and ^1H NMR spectra (C_6D_6), which display a central allene carbon resonance at δ 165.67 and CH_3 (δ = 2.44, 1.78), CH_2 (δ = 0.67, 1.97), and PMe_3 (δ = 1.27) proton resonances which also exhibit the expected NOE enhancements (as determined by selective NOE spectroscopy).[17,18] A single-crystal X-ray crystallographic analysis of **4** has been conducted, and the resulting ORTEP of its solid-state molecular structure is shown in Figure 2.[19] The nonlinear nature of the dimethylallene carbon backbone (C(11)−C(12)−C(13) = 134.0(5)°) and the relatively long C(11)−C(12) bond length of 1.436(7) Å are

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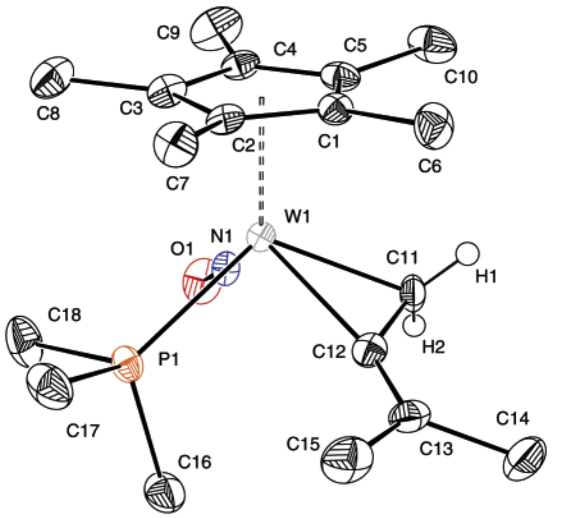

Figure 2. Solid-state molecular structure of **4** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−N(1) = 1.795(4), W(1)−C(11) = 2.205(4), W(1)−C(12) = 2.148(5), W(1)−P(1) = 2.4660(12), N(1)−O(1) = 1.224(5), C(11)−C(12) = 1.436(7), C(12)−C(13) = 1.324(7), W(1)−N(1)−O(1) = 175.0(4), N(1)−W(1)−C(11) = 91.00(18), C(12)−W(1)−C(13) = 38.49(18), C(11)−C(12)−C(13) = 134.0(5), C(12)−C(13)−C(14) = 121.8(5), C(12)−C(13)−C(15) = 124.3(5).

manifestations of the considerable back-donation of electron density from the metal to the alkene π^* orbitals.[20]

Most interestingly, the thermolysis of **1** in cyclohexane produces principally the cyclohexenyl hydrido complex, Cp*W(NO)(η^3-C_6H_9)(H) (**5**), which can be isolated in 32% yield. **5** formally results from three C−H bond activations of the hydrocarbon solvent.[21] Its ^{1}H NMR spectrum (C_6D_6) contains a distinctive hydride resonance at δ −0.57 ($^1J_{WH}$ = 131.7 Hz), and its IR spectrum as a KBr pellet exhibits a ν_{WH} stretch at 1898 cm^{-1}.[4] GC-MS studies also reveal the presence of the coupled organic product, 1,1-dimethylpropylcyclohexane, in the final reaction mixture. This transformation 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.[22−24] For comparison, the well-studied bis(alkyl) species such as Cp*W(NO)(CH_2CMe_3)$_2$ reacts with cyclohexane in a completely different manner. Their thermolyses in the presence of an excess of trimethylphosphine in cyclohexane at 70 °C for 40 h result in the formation of two base-stabilized complexes, the alkylidene and the cyclohexene adducts. However, in the absence of a suitable Lewis base, only decomposition occurs to afford intractable products.[4]

In summary, we have succeeded in generating a reactive 16e allene complex by the gentle thermolysis of an alkyl−allyl precursor. We have isolated and fully characterized this allene complex as its 18e PMe_3 adduct. In addition to effecting single C−H bond activations which are the reverse of the reaction used to generate it, the 16e allene complex also effects multiple C−H bond activations of a substrate that is normally difficult to activate. These reactivity differences suggest that new avenues of alkane activation chemistry may well be accessible through alkyl−allyl complexes such as **1**. Studies in this regard are ongoing, and the results of these investigations will be reported in due course.

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Supporting Information Available: Experimental procedures and complete characterization data for complexes **1**−**5** and full details of the crystal structure analysis including associated tables for **2** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Presented in part at the 223rd National Meeting of the American Chemical Society, Orlando, FL, April 2002, Abstract INOR 0113.

(2) Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(3) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: Norwell, MA, 2000; Vol. 21.

(4) Adams, C. S.; Legzdins, P.; Tran, E. *J. Am. Chem. Soc.* **2001**, *123*, 612.

(5) Adams, C. S.; Legzdins, P.; McNeil, W. S. *Organometallics* **2001**, *20*, 4931.

(6) Legzdins, P.; Lumb, S. A. *Organometallics* **1997**, *16*, 1825.

(7) Legzdins, P.; Lumb, S. A.; Young, V. G. *Organometallics* **1998**, *17*, 854.

(8) Legzdins, P.; Lumb, S. A.; Rettig, S. J. *Organometallics* **1999**, *18*, 3128.

(9) Debad, J. D.; Legzdins, P.; Lumb, S. A.; Rettig, S. J.; Batchelor, R. J.; Einstein, W. B. *Organometallics* **1999**, *18*, 3414.

(10) Thermolyses of alkyl−allyl complexes of iridium at 120 °C are believed to form similar allene intermediates. However, these intermediates have not been isolated or characterized, and they are only capable of effecting single C−H bond activations; see ref 22.

(11) **1** is prepared by the metathesis reaction of the chloro precursor with the appropriate allyl Grignard reagent.

(12) Bau, R.; Mason, S. A.; Patrick, B. O.; Adams, C. S.; Sharp, W. B.; Legzdins, P. *Organometallics* **2001**, *20*, 4492.

(13) Crystal data for **2**: monoclinic, space group $C2/c$, a = 15.3944(6) Å, b = 8.4977(3) Å, c = 32.326(1) Å, β = 90.753(3)°, V = 4228.4(3) Å^3, Z = 8, R_1 = 0.053, wR_2 = 0.0107, and GOF(F^2) = 1.60 for 4410 reflections and 221 variables.

(14) For instance, the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) of **2** exhibits a resonance at 101.93 ppm (allyl-CH) characteristic of an sp^2-like carbon and a signal at 39.31 ppm (allyl-CH_2) indicative of an sp^3-like terminal carbon. In addition, the orientation of the Me_2C allyl terminus trans to NO (as shown in Scheme 1 and Figure 1) is further supported by evidence gathered from selective NOE spectroscopy experiments.

(15) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268.

(16) Schilling, B. E. R.; Hoffman, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(17) Chetcuti, M. J.; Fanwick, P. E.; McDonald, S. R.; Rath, N. N. *Organometallics* **1991**, *10*, 1551.

(18) Lee, L.; Wu, I. Y.; Lin, Y. C.; Lee, G. H.; Wang, Y. *Organometallics* **1994**, *13*, 2521.

(19) Crystal data for **3**: monoclinic, space group $P2_1/c$, a = 9.1458(5) Å, b = 13.6500(7) Å, c = 15.9576(9) Å, β = 98.724(3)°, V = 1969.10(18) Å^3, Z = 4, R_1 = 0.0358, wR_2 = 0.0667, and GOF(F^2) = 0.946 for 4135 reflections and 217 variables.

(20) The exceptionally strong π-donor ability of the related Cp*W(NO)(PPh_3) fragment has been documented, see: Burkey, D. J.; Debad, J. D.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 1139.

(21) Preliminary single-crystal X-ray crystallographic analysis of **5** has confirmed the atomic connectivity shown in Scheme 1. However, the quality of the diffraction data collected precludes meaningful discussion of its metrical parameters.

(22) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

(23) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(24) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591.

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