Organometallics 1997, 16, 1825−1827

Trapping of Cp*W(NO)(η^2-PhC≡CH), the Key Intermediate in the C−H Activation of Alkanes by Cp*W(NO)(CH$_2$SiMe$_3$)(CPh=CH$_2$)

Peter Legzdins* and Sean A. Lumb

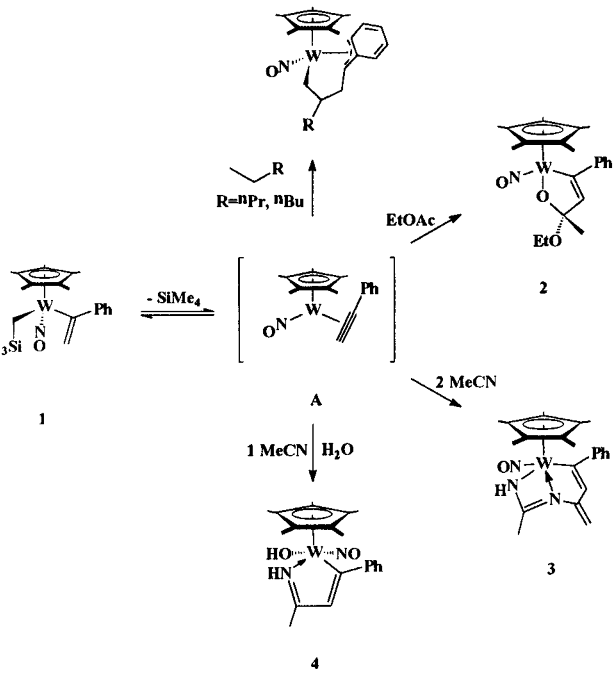
Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Z1

Received February 18, 1997⊗

Summary: Thermolysis of the vinyl nitrosyl complex Cp*W(NO)(CH$_2$SiMe$_3$)(CPh=CH$_2$) (**1**) in ethyl acetate or acetonitrile affords the oxa- or azametallacycles Cp*W(NO)(η^2-OC(Me)(OEt)CH=CPh) (**2**) or Cp*W(NO)(η^3-HNC(Me)=NC(=CH$_2$)CH=CPh) (**3**) and Cp*W(NO)(OH)(η^2-HN=C(Me)CH=CPh) (**4**), respectively. Kinetic and mechanistic studies provide compelling evidence for a pathway involving initial rate-limiting unimolecular elimination of SiMe$_4$ from **1** with concomitant formation of Cp*W(NO)(η^2-CPh≡CH) (**A**).

We recently reported the unique double C−H activation of alkanes under mild thermal conditions by the tungsten vinyl complex Cp*W(NO)(CH$_2$SiMe$_3$)(CPh=CH$_2$) (**1**).[1] The key intermediate invoked to account for this chemistry is the coordinatively unsaturated η^2-phenylacetylene complex **A**, which results from **1** initially undergoing β-H reductive elimination as shown in Scheme 1. Herein we report compelling evidence for the existence of **A** by describing its quantitative trapping by ethyl acetate and acetonitrile via reductive coupling reactions (Scheme 1). Interestingly, the reaction with ethyl acetate affords the expected oxametallacyclopentene complex Cp*W(NO)(η^2-*O*C(Me)(OEt)CH=*C*Ph) (**2**), but the reactions with acetonitrile produce two surprising compounds. Under rigorously anhydrous conditions, 2 equiv of CH$_3$CN is incorporated during the formation of the bicyclic complex Cp*W(NO)(η^3-H*N*C(Me)=*N*C(=CH$_2$)CH=*C*Ph) (**3**). If water is present, only 1 equiv of CH$_3$CN is incorporated to form the hydroxy azametallacyclopentadiene complex Cp*W(NO)(OH)(η^2-H*N*=C(Me)CH=*C*Ph) (**4**), whose solid-state molecular structure has been established by X-ray crystallography.[2] Preliminary kinetic investigations of these reactions indicate that their rates are independent of both the incoming organic substrate and water, thereby implying a mechanism having the unimolecular formation of **A** as the rate-determining step followed by its rapid trapping in subsequent steps to form the observed products.

Scheme 1



At 45 °C in neat ethyl acetate **1** does not effect C−H bond activation as it does in *n*-pentane and *n*-hexane under the same experimental conditions.[3] Instead, reductive coupling of ethyl acetate and phenylacetylene results in the oxametallacyclopentene complex **2**, which is isolated as deep purple needles in >84% yield (Scheme 1).[4] The spectroscopic properties of **2** are consistent with its formulation. Thus, the absence of characteristic C=O and C≡C absorptions in its Nujol-mull IR spectrum implies that the ethyl acetate and acetylene fragments are fused.[5] In addition, a ^{1}H NOEDIFF NMR experiment reveals the close proximity of the acetal methyl substituent to both the vinyl H and the Cp* ring methyl groups, thereby allowing assignment of the stereochemistry at the acetal carbon. Finally, a doublet centered at about δ 152.2 ($^1J_{CH}$ = 159 Hz) in its ^{13}C NMR spectrum in CDCl$_3$ is attributable to the vinylic carbon and is consistent with sp^2 hybridization at that atom.

In rigorously dried acetonitrile **A** reacts with 2 equiv of CH$_3$CN to form the diazametallabicyclic complex **3**, which is isolable as an air-stable, deep red microcrystalline powder in 78% yield. Space-filling models confirm that the imine group is correctly disposed relative to the NO ligand for dative-bond formation as depicted in Scheme 1, thus rendering **3** electronically and coor-

---

⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1997.

[1] Debad, J. D.; Legzdins, P.; Lumb, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 3288.

[2] Coupling reactions of acetylenes and unsaturated organic molecules in metal coordination spheres have been reported previously; see: (a) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696. (b) Buchwald, S. L.; Neilsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Maier, M. E.; Oost, T. *J. Organomet. Chem.* **1995**, *505*, 95. (d) Peulecke, N.; Ohff, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1996**, *15*, 1340.

[3] This contrasts with the activation of a C−H bond in the methoxy group of MeOAc by [Cp*Ir(PMe$_3$)(Me)(ClCH$_2$Cl)]$^+$; see: Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

[4] The three reactions forming complexes **2**−**4** are quantitative, as judged by ^{1}H NMR spectroscopic monitoring.

[5] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986.

S0276-7333(97)00118-0 CCC: $14.00

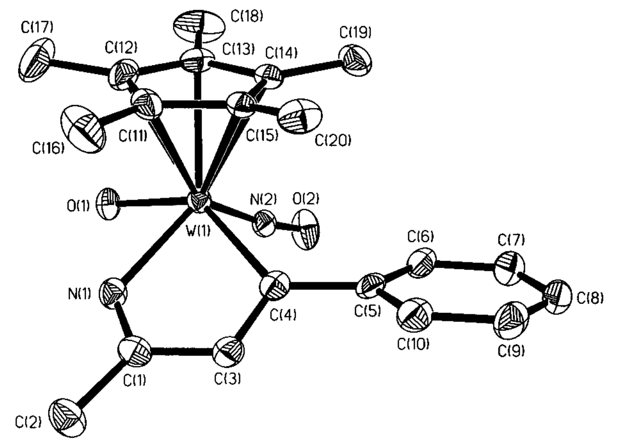
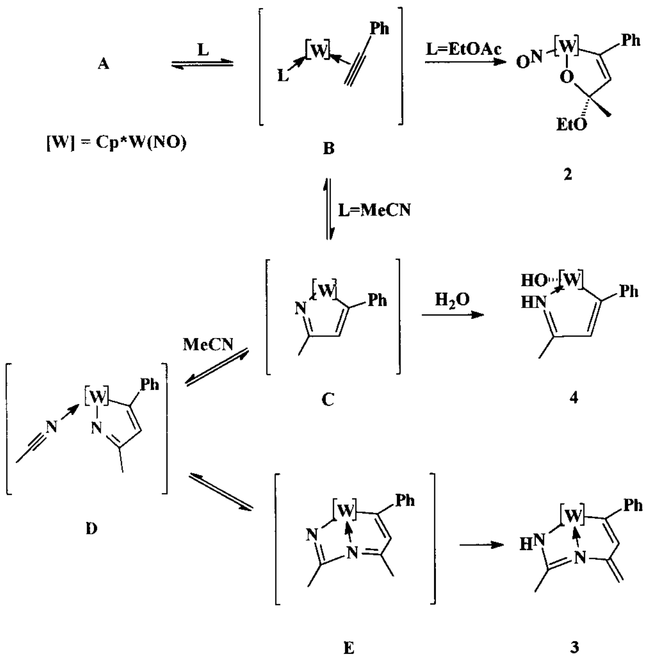


Figure 1. Solid-state molecular structure of **4**. Selected interatomic distances (Å) and angles (deg) W(1)–N(1) = 2.150(3), W(1)–C(4) = 2.227(4), W(1)–O(1) = 2.064(2), N(1)–C(1) = 1.295(5), C(1)–C(3) = 1.434(5), C(3)–C(4) = 1.366(5); W(1)–N(2)–O(2) = 172.7(3), O(1)–W(1)–N(1) = 75.52(11), N(1)–W(1)–C(4) = 72.45(12); N(2)–W(1)–N(1)–C(1) = 84.7(3), N(1)–C(1)–C(3)–C(4) = 6.4(5), N(1)–W(1)–C(4)–C(3) = −3.1(3).

dinatively saturated at the metal center.[6] A broad signal at δ 4.73 in the ^{1}H NMR spectrum of **3** in $CDCl_3$ integrated for one proton is attributable to the amine proton, and a ν_{NH} band at 3258 cm^{-1} in the KBr IR spectrum confirms its existence. In addition, an IR band at 1613 cm^{-1} is attributable to the imide N=C stretching mode.[7] Furthermore, the results of 1D and 2D NMR experiments are consistent with the ring connectivity depicted for **3**. The ^{1}H NMR spectrum of **3** displays signals at δ 6.83, 4.45 and 4.28, and 2.11 which are attributable to the endocyclic vinyl, exocyclic vinyl, and exocyclic methyl environments, respectively, while the results of a short-range ^{1}H–^{13}C HMQC experiment permit the assignment of the carbon nuclei to which these protons are bound. A ^{1}H NOEDIFF NMR experiment yields the spatial relationships of these proton environments, and a long-range ^{1}H–^{13}C HMBC NMR experiment permits the assignment of the quaternary carbon nuclei and hence the carbon backbone of the rings. That the second equivalent of acetonitrile has inserted to form complex **3** and has not simply coordinated to the metal center is indicated both by the absence of characteristic IR[5] and ^{13}C NMR[8] evidence and by a lack of reactivity of **3** with MeCN-d_3 and PMe_3.[9]

In wet acetonitrile **A** incorporates only one CH_3CN molecule during the formation of the hydroxy azametallacyclopentadiene complex Cp*W(NO)(OH)(η^2-H*N*=C(Me)CH=*C*Ph) (**4**; Scheme 1), which is isolable as red crystals in 80% yield.[10] The solid-state molecular structure of **4** clearly reveals the nearly planar azacyclopentadiene ring (Figure 1). Though the hydroxyl hydrogen atom was not located during the structural analysis, the W(1)–O(1) bond distance of 2.064(2) Å is most characteristic of a terminal OH group.[11] The NMR spectroscopic data for **4** indicate that it retains its solid-state structure in solution. For example, a characteristic four-bond coupling constant[12] of 3.5 Hz is observed between the azacyclopentadiene ring proton and the imide proton.[13] Interestingly, a carbenoid signal at 229.5 ppm in the ^{13}C NMR spectrum of **4** in $CDCl_3$ is attributable to the carbon nucleus adjacent to the W center and indicates a degree of aromaticity in the ring.[14]

Scheme 2



The metallacyclic nature of **4** corroborates the structures invoked for complexes **2** and **3** and implies the formation of a common intermediate that results from the reductive coupling of coordinated organic substrate and phenylacetylene in the metal's coordination sphere. Consequently, the mechanism that we propose for the formation of complexes **2**–**4** (Scheme 2) involves the formation of the oxametallacyclopentene complex **3** or the azametallacyclopentadiene complex **C** by reductive coupling of the two unsaturated ligands in intermediate **B** (L = EtOAc, MeCN). Intermediate **C** is probably electronically unsaturated, since the imide fragment cannot adopt the required orientation relative to the M–NO linkage in order to function as a three-electron donor to the metal center[15] and therefore is Lewis basic. In acetonitrile containing trace water, protonation of the

---

(6) Debad, J. D.; Legzdins, P.; Lumb, S. A. *Organometallics* **1995**, *14*, 2543.

(7) Filippou, A. C.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *415*, 375.

(8) Yeh, W.-Y.; Ting, C.-S.; Chih, C.-F. *J. Organomet. Chem.* **1991**, *427*, 257.

(9) Legzdins, P.; Sayers, S. *J. Am. Chem. Soc.* **1994**, *116*, 12105.

(10) Terminal OH ligands in group 6 organometallic complexes are rare, due to their propensity to form very stable bridging oxo ligands by protonolysis of metal–ligand linkages; see: (a) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895. (b) Bergman, R. G. *Polyhedron* **1995**, *14*, 3227.

(11) The complex $[Mo(O)(OH)(CN)_4]^{3-}$ has Mo=O = 1.697(7) Å and Mo–OH = 2.077(7) Å; see: Robinson, P. R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1975**, *14*, 2035. Typical terminal W–oxo bond distances lie in the range 1.68–1.72 Å; see: Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988.

(12) Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics* **1989**, *8*, 930.

(13) An analogous coupling is observed in the iridapyrrole complex recently reported by Carmona *et al.*; see: Alvarado, Y.; Daff, P. J.; Pérez, P. J.; Poveda, M. L.; Sánchez-Delgado, R.; Carmona, E. *Organometallics* **1996**, *15*, 2192.

(14) Aromaticity has been invoked for similar iridium aza- and thiapentadienyl systems; see: (a) Reference 13. (b) Bleeke, J. R.; Ontwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

(15) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730.

basic imide nitrogen in **C** shifts the **D**/**C** equilibrium toward the irreversible formation of the azametallacyclopentadiene **4**.[16] In contrast, in dry acetonitrile an insertion of coordinated CH_3CN in **D** yields the strongly basic amidine group in **E**. A subsequent proton tautomerization such as that observed by Wigley[17] leads to the formation of complex **3**. The extensive conjugation within the ligand backbone in **3** is probably a strong driving force for this reaction.

The use of deuterated solvents provides additional support for these mechanistic proposals. When dry CD_3CN is employed, Cp*W(NO)(η^3-D*N*C(CD_3)=*N*C(=CD_2)-CH=*C*Ph) (**3-*d*$_6$**) results, thereby indicating that the amine proton originates from the methyl substituent through a tautomerization process. In addition, no conversion to **4** is detectable when pure **3** is placed in wet acetonitrile under thermolysis conditions, thereby indicating that both species are formed irreversibly. When D_2O in acetonitrile is employed, Cp*W(NO)(OD)-(η^2-D*N*=C(Me)CH=*C*Ph) (**4-*d*$_2$**) is formed, thereby implying that the amide H originates directly from water since no label is incorporated elsewhere in the ring. In other words, the observed product results from a direct protonation by water similar to that observed by Carmona for the related iridium complex.[14] Complex **4** also exchanges with D_2O to form **4-*d*$_2$** under the same thermolysis conditions. Since the formation of **4** is irreversible (vide supra), this observation implies that the OH ligand is not labile but readily undergoes proton exchange with water in solution.

Further mechanistic insight has been gained through the kinetic analysis of these three transformations. The mechanism we originally proposed for the C—H activation of alkanes by **1** is an E1-type dissociative mechanism independent of substrate that invokes an initial rate-limiting elimination of $SiMe_4$ to generate **A**. However, an alternative bimolecular S_N2-type associative mechanism could also be operative, and the products could be formed by the initial nucleophilic attack of the vinyl β-carbon at the electrophilic quaternary carbon nucleus of the substrate prior to elimination of $SiMe_4$. This would lead to a dependence of the rate on substrate. However, the reactions of **1** with ethyl acetate and dry acetonitrile at 45 °C exhibit first-order rate constants of $[2.93(10)] \times 10^{-5}$ and $[4.71(17)] \times 10^{-5}$ s^{-1}, respectively.[18] The similarity of these two rate constants despite the marked difference in the electrophilicity of these two substrates implies a rate-determining step that is independent of the substrate. The slight variance in the observed rates can be ascribed to the differences in bulk properties of the solvents.[19] Consistently, monitoring the reactions of **1** in wet acetonitrile affords observed rate constants from 4.60×10^{-5} to 4.67×10^{-5} s^{-1} for water concentrations ranging from 0.006 to 0.12 M. The similarity of all these results strongly implies an E1-type mechanism involving a rate-determining loss of alkane from **1**.

Currently we are extending the kinetic analysis to encompass isotope effects and activation parameters. Synthetically, we are expanding the scope of these coupling reactions to include other esters, nitriles, and related organic amides, as well as other protic sources with pK_a values comparable to that of water.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a postgraduate scholarship to S.A.L. We thank Dr. P. J. Daff and Professor E. Carmona for their stimulating discussions of the kinetic and mechanistic analyses. We acknowledge Dr. V. G. Young and the X-ray Crystallographic Laboratory at the University of Minnesota for the structure determination of compound **4**.

Supporting Information Available: Text and tables giving experimental procedures and characterization data for complexes **2**−**4** and full details of the crystal structure analysis, including associated tables, for **4** (11 pages). Ordering information is given on any masthead page.

OM970118X

---

(16) For other examples of imide protonation, see: (a) Lorente, P.; Carfangna, C.; Etienne, M.; Donnadieu, B. *Organometallics* **1996**, *15*, 1090. (b) Reference 13.

(17) Strickler, J. R.; Wigley, D. E. *Organometallics* **1990**, *9*, 1665.

(18) The formation of **2**−**4** was monitored by UV-vis spectroscopy and is cleanly first order in **1**. Monitoring was effected for not less than 3.5 half-lives, and the temperature was controlled to 44.5 ± 0.25 °C.

(19) Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; VCH: New York, 1990; Chapter 8.