α-Elimination Can Be Faster than *β*-Elimination in d^2 Alkyl Complexes of Molybdenum and Tungsten That Contain the Trimethylsilyl-Substituted Triamidoamine Ligand

Richard R. Schrock,* Keng-Yu Shih, Daniel A. Dobbs, and William M. Davis

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Reactivity characteristics of transition metal complexes that contain triamidoamine ligands[1] are beginning to be explored.[2−14] We recently published some unusual reactions of Mo[8] and W[9] complexes containing the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ($[N_3N]^{3-}$) ligand[15] that included (*inter alia*) loss of molecular hydrogen from W alkyls to give alkylidyne complexes. We show here that when α,α-dehydrogenation is blocked (by employing a cyclopentyl ligand), α-elimination to give an alkylidene hydride complex of W (but *not* one of Mo) as well as eventual *β*-elimination to give stable paramagnetic monohydride complexes of both Mo and W can be observed.

Addition of cyclopentyllithium to $[N_3N]WCl$[9] in diethyl ether yields lithium chloride and a pentane-soluble yellow crystalline complex quantitatively. An X-ray study[16] (Figure 1) shows it to be the 18-electron[17] cyclopentylidene hydride complex, $[N_3N]W(C_5H_8)(H)$. The cyclopentylidene ligand is oriented so that it lies (*approximately*) in a plane that passes through W, N(5), and N(8), spreading N(6) and N(7) apart slightly (125.7° versus 112.4° and 105.4°). Electron density ascribable to the hydride ligand also was found approximately in this plane 1.81 Å from the metal, but it would not survive refinement. Since $J_{HW} = 89$ Hz, C(9)···H = 2.43 Å, N(5)···H = 1.68 Å, and the p orbitals on C(9) and N(5) are oriented perpendicular to the C(9)−W−H−N(5) plane, there does not appear to be any significant interaction between H and either C(9) or N(5). The position and observed orientation of the cyclopentylidene ligand are consistent with the nature of the three available bonding orbitals, approximately d_{xz}, d_{yz}, and a σ hybrid pointing along the z ($W-N_{donor}$)-axis.[17] Formation of two σ-bonding hybrid orbitals in either the d_{xz} or the d_{yz} plane leaves an orbital perpendicular to that plane for forming the W═C π bond. This frontier orbital picture contrasts sharply with that for the ubiquitous bent metallocene in which all three orbitals lie *in* the plane passing between the two Cp rings.

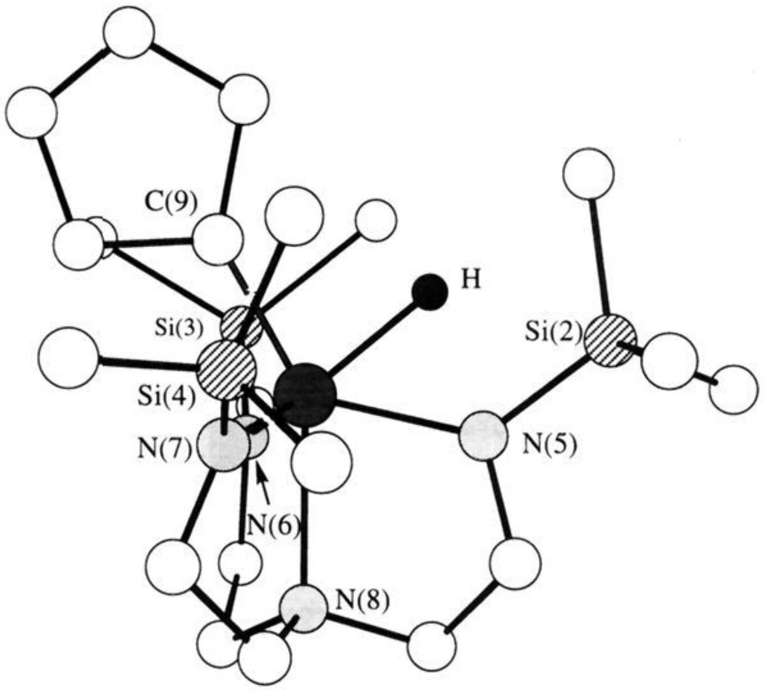
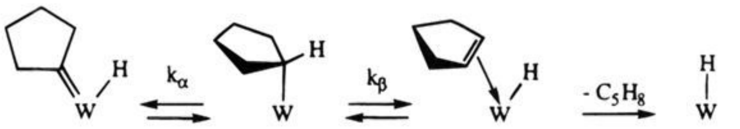


Figure 1. Chem 3D model of the structure of $[N_3N]W(C_5H_8)H$: W−C(9) = 1.97(1) Å, W−H = 1.81Å, $W-N_{eq}$ = 2.02-2.05 Å, $W-N_{ax}$ = 2.346(9) Å, N(6)−W−N(7) = 125.7(4)°, N(5)−W−N(6) = 112.4(4)°, N(5)−W−N(7) = 105.4(4)°, C(9)−W−H = 80°, C(9)···H = 2.43 Å, N(5)···H = 1.68 Å.

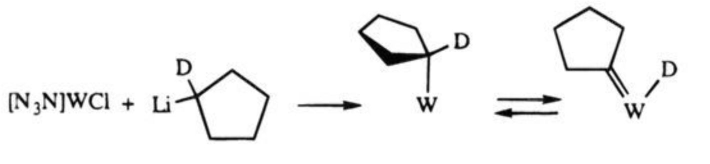
NMR spectra of $[N_3N]W(C_5H_8)(H)$ at −40 °C in toluene-d_8 show the alkylidene C_α resonance at 268.4 ppm and the hydride resonance at 19.4 ppm.[18−20] Other resonances are consistent with the approximate mirror symmetry found in the solid state. Between 25 and 60 °C, the molecule becomes three-fold symmetric on the NMR time scale and begins to decompose to give paramagnetic $[N_3N]WH$. The exact nature of the fluxional process is not known at this stage. Equilibration of $[N_3N]W(C_5H_8)(H)$ with the paramagnetic cyclopentyl complex, $[N_3N]W(C_5H_9)$ (cf. $[N_3N]Mo(C_5H_9)$ below) might explain a downfield shift (to 19.8 ppm) and broadening of the hydride resonance at +60 °C.

Upon heating a solution of $[N_3N]W(C_5H_8)(H)$ in C_6D_6 to 45 °C for 24 h, 1 equiv of cyclopentene is formed and orange, pentane-soluble, paramagnetic $[N_3N]WH$, a 16-e species in which the d_{xz} and d_{yz} orbitals are degenerate,[17] can be isolated in high yield. The presence of the hydride is confirmed by IR ($\nu_{WH} = 1766$ cm^{-1} in Nujol). $[N_3N]WH$ is remarkably stable thermally, surviving sublimation unchanged at 80 °C. We propose that $[N_3N]WH$ is formed via *β*-elimination in intermediate $[N_3N]W(C_5H_9)$ (eq 1; cf. $[N_3N]Mo(C_5H_9)$ below).



(1)

Addition of $LiC_5H_8D_\alpha$ to $[N_3N]WCl$ in toluene-d_8 at −60 °C followed by 0.5 h at −13 °C yields the cyclopentylidene deuteride complex, according to ^2H NMR (eq 2). When this



(2)

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[1] Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

[2] Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.

[3] Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

[4] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.

[5] Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.

[6] Naiini, A. A.; Ringrose, S. L.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 1290.

[7] Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 676.

[8] Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

[9] Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.

[10] Freundlich, J.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

[11] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.

[12] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

[13] Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.

[14] Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

[15] Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.

[16] Space group $P2_12_12_1$ with $a = 9.7636$, $b = 16.467$, and $c = 17.232$ Å, $Z = 4$, FW = 612.73, $V = 2770.6$ Å^3, d(calcd) = 1.469 g/cm^3, $R = 0.030$, $R_w = 0.031$, GOF = 1.09.

[17] The tetradentate $[N_3N]^{3-}$ ligand can form four metal−nitrogen σ bonds and two metal−nitrogen π bonds, leaving three orbitals for binding to a ligand or ligands in the apical position.

[18] Large positive chemical shifts for hydride ligands are rare, but not unknown. See, for example, a hydride chemical shift of 22.87 ppm in $TaCp^*Cl_2(CH_2CMe_3)H$[19] and 21.99 ppm in $TaH_2(OSi\text{-}t\text{-}Bu_3)_3$.[20]

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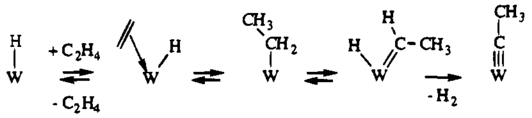
sample is warmed above 0 °C, the deuterium begins to scramble into first the C_β and then also the C_γ sites. The cyclopentene that is formed upon decomposing the D_1-labeled cyclopentylidene complex contains a statistical amount of D throughout. The most plausible method of H/D scrambling to *all* carbon atoms before forming $[N_3N]W(H/D)$ is to reversibly form the cyclopentene hydride complex via the cyclopentyl complex (eq 1). (Solely β-elimination from the cyclopentylidene ligand to give a vinyl dihydride intermediate would result in scrambling only into β carbon positions.) The two most important points are that the equilibrium between the cyclopentyl and the cyclopentylidene hydride complex lies well toward the latter, and that the rate of α-D elimination from the cyclopentyl complex is greater than the rate of β-H elimination.

$[N_3N]WH$ reacts only slowly with H_2 (1 atm) over a period of 1 day to give diamagnetic, white $[N_3N]WH_3$ (ν_{WH} = 1906 and 1886 cm^{-1} in Nujol; δ_H = 10.01 ppm in C_6D_6 with J_{HW} = 23 Hz). Addition of D_2 to $[N_3N]WH$ yields $[N_3N]WHD_2$, and $[N_3N]WH_3$ is unchanged after heating in C_6D_6 to 80 °C for 1 day under an atmosphere of D_2. An X-ray study[21] of $[N_3N]WH_3$ (to be reported fully later) shows the $[N_3N]$ ligand to be coordinated in the "normal" manner ($W-N_{eq} = 2.00-2.01$ Å; $W-N_{ax} = 2.23$ Å), with the three hydrides (located and refined 1.57−1.59 Å from W) approximately staggered with respect to the three amido nitrogen atoms. Addition of ethylene to $[N_3N]WH$ gives known[9] $[N_3N]W{\equiv}CCH_3$ and dihydrogen in minutes at 25 °C, presumably via the sequence shown in eq 3.[9]



(3)

When C_2D_4 is employed, the product is $[N_3N]W{\equiv}CCD_2H$ (according to ^1H NMR integration and ^2H NMR), again consistent with slow H/D scrambling via reversible β-elimination relative to the rate of loss of D_2 from C_α in intermediate $[N_3N]W(CD_2CD_2H)$.

Addition of cyclopentyllithium to $[N_3N]MoCl$ in diethyl ether yields purple, pentane-soluble, paramagnetic $[N_3N]Mo(C_5H_9)$, an analog of other Mo alkyl complexes of this general type[8] and of proposed intermediate $[N_3N]W(C_5H_9)$ shown in eq 1. Upon heating a solution of $[N_3N]Mo(C_5H_9)$ in C_6D_6 to 45 °C for 24 h, it decomposes quantitatively to give cyclopentene and orange $[N_3N]MoH$. Decomposition of the cyclopentyl complex formed by adding $LiC_5H_8D_\alpha$ to $[N_3N]MoCl$ yields cyclopentene that contains a statistical amount of D throughout, according to ^2H NMR. It is worth pointing out that a rapidly attained equilibrium between $[N_3N]Mo(C_5H_9)$ and $[N_3N]Mo(C_5H_8)(H)$ that lies toward the cyclopentyl complex instead of the cyclopentylidene hydride complex would be impossible to detect, i.e., α-elimination could be faster than β-elimination in the Mo case also.

There are several surprising features of the chemistry reported here. First is an observable kinetic preference for α-elimination[22−24] versus β-elimination, a circumstance that may be more general than commonly believed, but rarely observable.[25−28] α-Elimination might be faster than β-elimination in the systems described here as a consequence of steric factors that hinder β-elimination, an explanation that was invoked in order to explain the decomposition of $Cp^*_2Ta(C{=}CH_2)(H)$ via intermediate $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_2)Ta$ to give a mixture of $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH)Ta(H)$ and $Cp^*(\eta^5\text{-}C_5Me_4CH_2\text{-}CH{=}CH_2)Ta(H)$.[27]

Second, it is surprising to us that some relatively simple reactions (e.g., the addition of dihydrogen to $[N_3N]WH$) are so slow. While we have noted previously that dissociation of the apical N donor might serve to regulate the rate of reactions in the three-fold site opposite it,[10] we now want to consider also the possibility that many simple "2-e reactions" are "spin-blocked" as a consequence of very little of the metal being in the low spin state in which an empty d_{xz} (or d_{yz}) orbital and a fully occupied d_{yz} (or d_{xz}) orbital are available.

Finally, it should be noted that we discount at *this* stage the *direct* involvement of the N_3N ligand in removing or adding H to hydrocarbon fragments.

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Supplementary Material Available: Experimental details for the synthesis of all compounds reported here along with a description of the X-ray structure of $[N_3N]W(C_5H_8)(H)$, a summary of crystal data, data collection, and structure refinement, an ORTEP drawing, final positional parameters, final thermal parameters, and tables of bond distances and angles (15 pages); listing of final observed and calculated structure factors (13 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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[19] Belmonte, P. A.; Schrock, R. R.; Day, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 3082.

[20] Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056.

[21] Space group $P2_1/n$ with a = 11.3589, b = 16.0929, and c = 13.4010 Å, Z = 4, FW = 546.65, β = 105.082°, V = 2365.3 $Å^3$, d = 1.535 g/cm^3.

[22] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

[23] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 209.

[24] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761.

[25] Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331.

[26] Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

[27] Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Asselt, A. v.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

[28] Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.