# Ligand-Induced *β*-H Transfer in W(VI) Dialkyl Complexes

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β-Elimination and its microscopic reverse, olefin insertion into the metal−hydride bond, are among the most fundamental transformations that occur in organometallic chemistry.[1,2] There is much evidence[3−6] that provides compelling support for olefin insertion into the metal−hydride bond as an initiation step in Ziegler−Natta polymerization of ethylene and α-olefins, while *β*-H elimination serves as a chain-transfer or termination step in olefin polymerization. In addition, *β*-H elimination is also the most common decomposition route for *β*-hydrogen containing metal alkyls. Indeed, the facility of this pathway often precludes isolation of alkyl complexes with *β*-hydrogen atoms, especially when the complexes are coordinatively unsaturated.[7] We now report the preparation[8] of a series of coordinatively unsaturated tungsten(VI) dialkyl complexes containing *β*-hydrogens (eq 1), from the dichloride precursor, W(NPh)[*o*-(Me₃SiN)₂C₆H₄]Cl₂.[9]

$$\text{eq (1)}$$

R = Et (**1**), *n*-Pr (**2**), *i*-Bu (**3**), CH₂CH₂Ph (**4**)
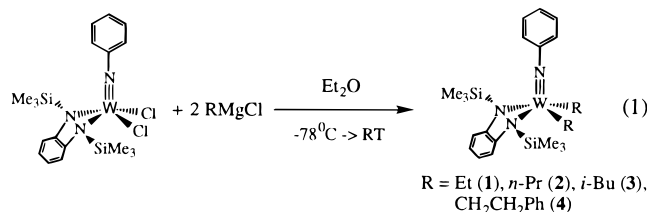
Surprisingly, despite their coordinative unsaturation, complexes **1**−**4** are indefinitely stable at room temperature in the absence of coordinating ligands. Single crystals of **4** that were suitable for X-ray diffraction studies were obtained by slowly cooling a pentane solution of **4** to −20 °C. A thermal ellipsoid plot of **4** is shown in Figure 1.[10] The coordination geometry about W is a square pyramid with the imido N in the axial position and the [*o*-(Me₃SiN)₂C₆H₄]²⁻ ligand and two alkyl ligands in the basal plane. The W−imido bond length is consistent with a W−N triple bond. The geometry about the N atoms of the [*o*-(Me₃SiN)₂C₆H₄]²⁻ ligand is planar as is observed in silyl amines.[11] The ligand is folded about the N−N
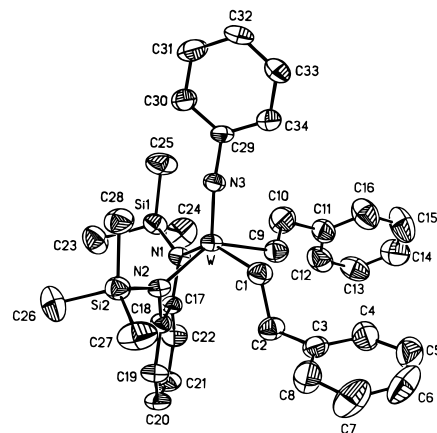
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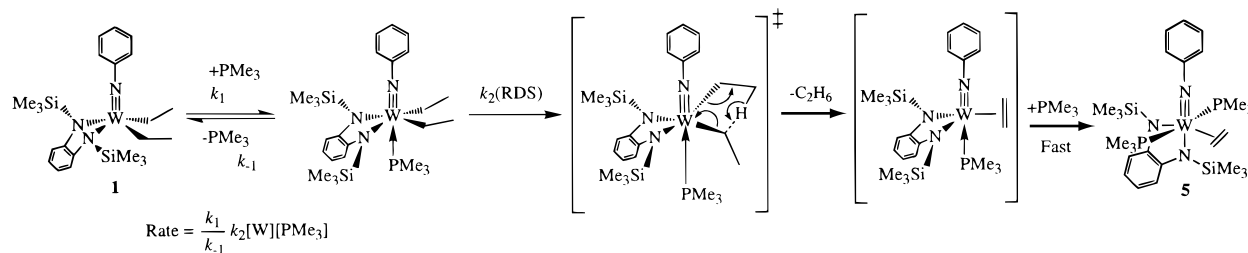(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
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(10) **4**: orange crystals, triclinic, *P*1̄, *a* = 10.0571(1) Å, *b* = 10.1133(2) Å, *c* = 19.1479(4) Å, α = 93.043(1)°, β = 99.667(1)°, γ = 112.048(1)°, *V* = 1765.06(5) Å³, *Z* = 2, *R*₁ = 3.4%, GOF on *F*² = 0.921, *T* = 173 K.

Figure 1. Thermal ellipsoid plot of W(NPh)[(*o*-Me₃SiN)₂C₆H₄](CH₂-CH₂Ph)₂ (**4**). Selected bond distances (Å): W−N(3), 1.728(4); W−N(2), 2.003(4); W−N(1), 2.000(4); W−C(1), 2.189(5); W−C(9), 2.175(5). Selected bond angles (deg): C(29)−N(3)−W, 171.8(3); N(1)−W−N(2), 82.9(2); C(1)−W−C(9), 85.1(2); C(2)−C(1)−W, 117.6(3); C(10)−C(9)−W, 117.7(4).

vector which causes the SiMe₃ groups to be displaced above the basal plane. The folding of the ligand also tilts the N coordination planes by 60−65° relative to the basal plane of the molecule.

The formal electron count at the metal center could be as high as 18 e⁻ if both sets of nitrogen lone pairs of the [*o*-(Me₃-SiN)₂C₆H₄]²⁻ ligand can be donated to the metal center. This is however not possible since there are only three d orbitals that are of the correct symmetry to form π bonds with the ligands. Given that the d$_{xz}$ and d$_{yz}$ orbitals form the π bonds with the imido group, only the d$_{xy}$ orbital is available to overlap with the N π electrons on the diamido ligand. Thus, the maximum electron count at the metal center is 16 e⁻. Furthermore, the structure of **4** shows that the folding of the diamide ligand brings the p orbitals on the N atoms to within *ca.* 25−30° of the *xy* plane, preventing efficient overlap between the d$_{xy}$ orbital and the N lone pairs. The structural constraints imposed by the chelating nature of the [*o*-(Me₃SiN)₂C₆H₄]²⁻ ligand lead us to suggest that these dialkyl complexes are best described as 14 e⁻ or at most 16 e⁻ compounds.

Upon the addition of trimethylphosphine, complexes **1**, **2**, and **4** were converted to the cooresponding olefin complexes **5**, **6**, and **7** (eq 2).[8] It has been shown that the dissociation of

$$\text{eq (2)}$$

R' = H (**5**), Me (**6**), Ph (**7**)
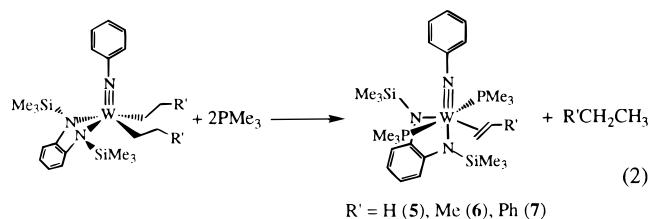
labile ligands (e.g., PMe₃) to generate a coordinatively unsaturated species is often the first step in the *β*-H elimination process.[12] However, the *β*-H transfer chemistry of **1**, **2**, and **4** is promoted by adding a ligand to the metal center. This behavior is clearly unexpected since it implies that *β*-H transfer is induced by increasing the coordination number of the complex. To understand the role of PMe₃ and clarify the mechanism, we have undertaken a kinetic study of the reaction of **1** with PMe₃.

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Scheme 1

$$\text{Rate} = \frac{k_1}{k_{-1}} k_2[\text{W}][\text{PMe}_3]$$

The kinetics of the conversion of **1** to **5** in toluene-d_8 was examined by following the disappearance and appearance of the trimethylsilyl peaks of **1** and **5** using ^{1}H NMR spectroscopy in the presence of a pseudo-first-order excess of PMe$_3$. The reaction is first order with respect to **1** and PMe$_3$, with a pseudo-first-order rate constant at 293 K of $k = 9.61(82) \times 10^{-4}$ s^{-1} ($t_{1/2} = 12$ min). Activation parameters calculated from an Eyring plot over the temperature range 263–293 K are $\Delta H^{\ddagger} = 5.1(2.6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -54.9(9.7)$ cal mol^{-1} K^{-1} for the formation of **5**. The observation that the addition of ethylene has no effect on the rate of thermolysis as well as the large, negative entropy of activation suggests that liberation of ethylene does not occur prior to the rate-determining step in this reaction.

A rapid pre-equilibrium coordination of PMe$_3$ is proposed as the initial step in the reaction because of the first-order dependence on PMe$_3$ and the fact that the PMe$_3$ adduct, W(NPh)[o-(Me$_3$SiN)$_2$C$_6$H$_4$](PMe$_3$)Et$_2$ (**1-P**), has been observed at -50 °C. This adduct exists as a mixture of two isomers as determined by ^{13}C and ^{31}P NMR spectroscopy.[13] The major isomer has *trans* ethyl groups with PMe$_3$ coordinated *cis* to the imido ligand. The minor isomer has the PMe$_3$ coordinated *trans* to the imido ligand, leaving the ethyl groups mutually *cis*. Though saturation of the rate at high concentrations of PMe$_3$ is predicted, we have not been able to observe such behavior even at PMe$_3$ concentrations of 1.6 M. We suggest that this is due in part because the reaction proceeds through the minor isomer of **1-P** in which the *cis* disposition of the ethyl groups is retained.

The β-deuterated analogue, W(NPh)[o-(Me$_3$SiN)$_2$C$_6$H$_4$](CH$_2$CD$_3$)$_2$ (**1-d_6**), was prepared to provide additional information regarding the mechanism. The conversion of **1-d_6** to **5-d_2** was followed by ^{2}H NMR in toluene. In both the absence and presence of PMe$_3$, no scrambling of the deuterium labels among the α- and β-carbons was observed. The products of the reaction are exclusively W(NPh)[o-(Me$_3$SiN)$_2$C$_6$H$_4$](η^2-CH$_2$-CD$_2$)(PMe$_3$)$_2$ (**5-d_2**), and CH$_2$DCD$_3$.[14] The above observation suggests an irreversible β-H abstraction process as proposed by Yamamoto[15] and Buchwald.[22]

At 293 K, the observed k_H/k_D for the thermolysis of **1/1-d_6** is 6.1(5), which strongly suggests a near linear transition state for the β-H transfer process and is consistent with the direct transfer of one β-H to the other α-carbon atom as is proposed in Scheme 1. The large KIE in our system is significantly different from those compounds which decompose by β-elimination followed by reductive elimination, e.g. PdEt$_2$(PMePh$_2$)$_2$ (KIE = 1.4),[15] CoEt$_2$(acac)(PMe$_2$Ph)$_2$ (KIE = 2.3),[16] PtEt$_2$(PEt$_3$)$_2$ (KIE = 1.4–1.7),[17] Cp*$_2$ScCH$_2$CH$_2$Ph (KIE = 2.0),[18] and (CO)(PPh$_3$)$_2$IrCH$_2$-CH$_2$C$_6$H$_{13}$ (KIE = 2.3).[19] Buchwald[20] and Erker[21] have proposed the direct β-hydrogen abstraction process from an sp^2-

hybridized carbon in the formation of alkyne/aryne complexes, while Buchwald[22] and Schrock[23] have proposed direct β-hydrogen abstraction processes in the reactions of Cp$_2$Zr(SCH$_2$-Ph)(Me) and [Me$_3$SiNCH$_2$CH$_2$]$_3$NTa(Et)$_2$, respectively.

The mechanism that is outlined in Scheme 1 is consistent with all of the above experimental data.[24] The initial step in the reaction is coordination of PMe$_3$, which is supported by the observation of the PMe$_3$ adduct, **5-d_2**, and the first-order dependence of the reaction on [**1**] and [PMe$_3$]. The observation of a large kinetic isotope effect and no deuterium scrambling are consistent with the proposed direct β-H abstraction pathway. The combination of the bimolecular nature of this reaction and the highly ordered transition state, imposed by the geometric requirement for the β-H to transfer to the α-C of the other alkyl group, accounts for the large negative entropy value.[22,25]

Supporting Information Available: Full details of the experimental procedures for the syntheses of **1**–**7**, a table of NMR data, representative kinetics plots, a table of rate constants, and a full description of the X-ray structure determination of **4**, including tables of bond lengths and angles and positional and thermal parameters (20 pages). See any current masthead page for ordering and Internet access instructions.

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(24) A reviewer has suggested an alternative mechanism which involves transfer of the β-H atom to the imido nitrogen followed by α-abstraction of the N-H of the resultant amido group by the remaining ethyl group. While we have no direct evidence that excludes this suggestion, we believe that such a mechanism is unlikely because of observations that we have made on the conversion of **4** to the styrene complex **7**. This reaction proceeds very much more slowly ($t_{1/2} = 26$ min at 95 °C) than **2** is converted to **5**, and the data indicate that the conversion of **4** to **7** proceeds via a different mechanism (KIE is 2.3 and $\Delta S^{\ddagger}$ *ca.* -28 cal mol^{-1} K^{-1}) than the conversion of **2** to **5**. When complex **4** binds PMe$_3$, only the isomer with PMe$_3$ *cis* to the imido group and the Et groups *trans* to one another is observed via low-temperature NMR. Apparently, this is responsible for the change in mechanism because the alkyl groups are no longer *cis* to one another. If transfer of the β-H to the imido is the mechanism that is followed, we would expect that changing the geometry of the PMe$_3$ adduct in this fashion would not cause such a dramatic change in the reaction rate because the alkyl groups remain *cis* to the imido group.

(25) (a) The observed value of $\Delta S^{\ddagger}$ is a combination of PMe$_3$ binding and subsequent steps to reach the transition state. Values of $\Delta S^{\ddagger}$ of between -30 and -40 cal mol^{-1} K^{-1} are often observed in purely associative substitution reactions. Thus the majority of the observed value of $\Delta S^{\ddagger}$ is accounted for in the binding of PMe$_3$.[25b] Loss of the remaining 10–20 cal mol^{-1} K^{-1} is accounted for by formation of the highly constrained transition state necessary for the proposed β-H transfer.[22] (b) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991.

(13) Compound **1-P** in the presence of 15 equiv of PMe$_3$ has two isomers at low temperature as observed by ^{31}P NMR in a ratio of *ca.* 20:1. ^{31}P NMR (-80 °C, C$_7$D$_8$): δ -21.9 ($^1J_{P-W} = 240$ Hz, major isomer, PMe$_3$ *cis* to imido and Et groups mutually *trans*), -28.1 (broad, minor isomer with PMe$_3$ *trans* to imido and Et groups mutually *cis*).

(14) The formation of CH$_2$DCD$_3$ is supported by EI-MS, displaying a peak at 34. The same peak is also observed for the product of the reaction between CD$_3$CH$_2$MgCl and D$_2$O.

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