J. Am. Chem. Soc. **1995,** *117,* 11015−11016

Mechanism of the Formation of a Tungsten(VI) Alkylidene Complex Which Undergoes Reversible Metalation of an Ancillary Ligand

William M. Vaughan, Khalil A. Abboud, and
James M. Boncella*

Department of Chemistry and Center for Catalysis
University of Florida, Gainesville, Florida 32611-7200

Received June 22, 1995

Changing the ligand environment of a transition metal complex to modify its properties is an important strategy for the development of more efficient or selective catalysts. Recent studies using well-defined metal alkylidene complexes as ring opening metathesis polymerization (ROMP) initiators have shown that this reaction is especially sensitive to the stereoelectronic properties of the ancillary ligands on the catalyst.[1] With manipulation of the ligand environment, both the rates of polymerization and the stereochemical properties of the resultant polymer can be modified.[2] Our interest in using chelating ligands to enhance the properties of alkylidene complexes as catalysts for olefin metathesis polymerization reactions has led to our use of the *N,N'*-bis(trimethylsilyl)-*o*-phenylenediamido (TMS_2pda) ligand as an ancillary ligand for tungsten imido alkylidene complexes.[3]

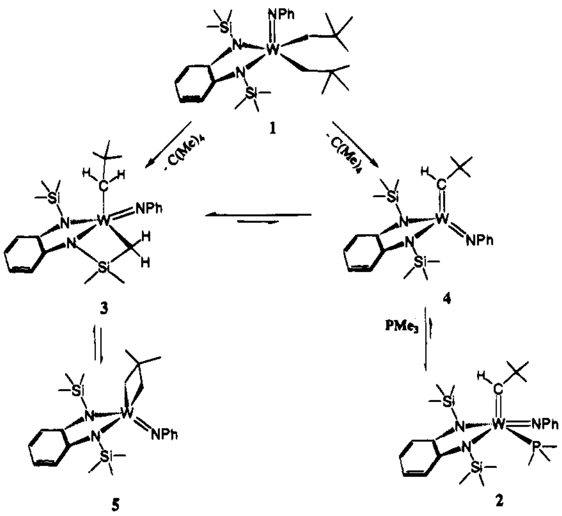
We have previously shown that thermolysis of the dialkyl complex $(TMS_2pda)W(NPh)(CH_2C(CH_3)_3)_2$ (**1**, Scheme 1) in the presence of trimethylphosphine gave the phosphine-bound tungsten alkylidene complex, $(TMS_2pda)W(NPh)(CHC(CH_3)_3)(PMe_3)$ (**2**).[3] Compound **2** is active as an olefin metathesis catalyst which polymerizes cyclic olefins via a ROMP mechanism giving polynorbornene with extremely low polydispersities.[3b] We now report that thermolysis of **1** in the absence of PMe_3 gives complex **3**, in which a trimethylsilyl group of the chelating diamide ligand has been metalated.

Given the predominance of α-abstraction processes in the thermolysis of group 5 and 6 neopentyl complexes,[4] we sought to understand the formation of complexes **2** and **3**, which were *apparently* formed by different reaction mechanisms. Our results indicate that *both* α- and γ-H abstraction processes occur upon thermolysis of **1** in the presence and absence of PMe_3, with the α-H abstraction process predominating under all circumstances. Thus, the intermediate alkylidene complex, **4**, undergoes metalation of the TMS group of the diamide ligand in the absence of PMe_3 giving **3**. The results of our mechanistic studies supporting the mechanism proposed in Scheme 1 are described herein.

Compound **3** has been synthesized by thermolysis of an NMR sample of **1**,[5a] or by the abstraction of PMe_3 from **2** with an electrophilic reagent.[5b] Although a preparative scale isolation of **3** has not yet been successful due its high degree of solubility, **3** has been characterized spectroscopically and its structure has been confirmed with a single-crystal X-ray diffraction study.[6]

Kinetics of the formation of **2** and **3** were followed by ^1H NMR spectroscopy. Plots of ln(peak height) vs time were linear, indicating first-order kinetics.[7] The rate constant for the decay of **1** to give **3** (at 353 K) in the absence of PMe_3 is $6.44(41) \times 10^{-5}\ s^{-1}$. For the thermolysis of **1** in the presence of 20 equiv of PMe_3 to give **2**, the rate constant of $4.52(76) \times 10^{-5}\ s^{-1}$ (353 K). Activation parameters calculated from a plot of the $\ln(k/T)$ versus $1/T$ over the temperature range 353−379 K are $\Delta H^{\ddagger} = 25.2(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7(5)$ eu for the formation of **3**, while for the formation of **2**, $\Delta H^{\ddagger} = 28.1(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1(6)$ eu over the same temperature range. The observation that the addition of PMe_3 has no profound effect on the rate of thermolysis suggests that phosphine is not involved in the rate-determining step of this reaction. The small differences in the rates of reaction in the presence of PMe_3 can be attributed to changes in solvent polarity with the addition of PMe_3 and are consistent with solvent effects observed in other α-H abstraction reactions.[8,9]

Scheme 1



The deuterated neopentane generated in the thermolysis reactions of $(TMS_2pda)W(NPh)(CD_2C(CH_3)_3)_2$, **1**-$d_4$, was analyzed by mass spectrometry in order to determine the extent to which α- or γ-H abstraction occurs during thermolysis.[10-12] The observation of both neopentane-d_3 and d_2 in the presence and absence of added PMe_3 indicates that competing α- and γ-H abstraction processes occur during this reaction. The ratio of neopentane-d_3 to neopentane-d_2, and thus the ratio of α- to γ-H

---

(1) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

(2) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 1423. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (c) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (d) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831. (e) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

(3) (a) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378. (b) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1994**, *35*, 691.

(4) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; John Wiley: New York, 1988.

(5) (a) A toluene solution of **1** (0.152 g, 0.238 mmol) was heated to 110 °C for 75 min. The toluene solvent was rapidly removed under reduced pressure to give a dark red, oily solid. The solid was dissolved in a minimum volume of pentane and cooled to −40 °C for 12 h. The resultant red crystals (*ca.* 15%) were collected by filtration, including one that was suitable for an X-ray diffraction study. Larger scale preparations of **3** have not produced crystalline products, but ^1H NMR spectra of the (oily) solid products of these reactions show that they are 80−90% pure **3**. ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 7.2−6.8 (9H), 2.49, 0.76 (d, 1H each, $WCH_2C(CH_3)_3$); 1.02 (s, 9H, $CH_2C(CH_3)_3$); 0.86, −1.15 (d, 1H each, WCH_2Si); 0.54, 0.20 (s, 3H each, $Si(CH_3)_2$); 0.38 (s, 9H, $Si(CH_3)_3$). 2D NMR experiments show that the doublets at 2.49 and 0.76 ppm are coupled to one another and that the doublets at 0.86 and −1.15 ppm are coupled to one another as is consistent with the X-ray structure of **3**. ^{13}C NMR (75 MHz, C_6D_6, 22 °C): δ 154.9, 150.3, 147.6, 128.6, 128.5, 127.0, 122.9, 120.3, 118.0, 117.2 ($C_6H_4N_2$ and NC_6H_5); 92.9 ($^1J_{W-C} = 103.5$ Hz, WCH_2CMe_3); 37.06 ($^1J_{W-C} = 43.5$ Hz, WCH_2Si), 34.95 (CMe_3); 34.1 (CMe_3); 5.0 ($MeSi$); 4.42 (Me_3Si); 1.55 ($MeSi$). (b) Addition of 1 equiv of $MeSO_3CF_3$ or CuCl to a solution of **2** in toluene results in quantitative conversion to **3** and $[PMe_4][SO_3CF_3]$ or $[CuCl(PMe_3)]_4$, respectively.

(6) See supporting information.

(7) Tables of rate constants and representative kinetics plots are included as supporting information.

(8) Legzdins, P.; Veltheer, J. E.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 407.

(9) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

(10) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

(11) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

0002-7863/95/1517-11015$09.00/0

abstraction, was found to vary slightly with the presence of PMe_3. With 20 equiv of PMe_3, the observed ratio was 92(1) neopentane-d_3 to 8(1) neopentane-d_2. In the absence of PMe_3, the observed ratio was 60(1) neopentane-d_3 to 40(1) neopentane-d_2.

Thermolysis of **1**-d_4 showed significant kinetic isotope effects. At 369 K, the observed k_H/k_D for thermolysis in the absence of PMe_3 is 3.9(4). In the presence of PMe_3, the observed k_H/k_D is 5.2(9). The apparent discrepancy in the k_H/k_D values arises because they are a composite of the α-D abstraction and the γ-abstraction of an $SiMe_3$ proton. From these KIE measurements and the ratio of α- to γ-abstraction rates from the mass spectral data, the ratios of α- to γ-abstraction for the perprotio compound **1** can be estimated.[13] In the absence of PMe_3, k_α/k_γ for the thermolysis of **1** is 9(2), and k_α/k_γ in the presence of 20 equiv of PMe_3 is 64(14).

The above observations indicate a mechanistic scheme (Scheme 1) composed of two competitive, unimolecular abstraction pathways with α-H abstraction being preferred over γ-H abstraction. In the presence of PMe_3, the five-coordinate alkylidene species, **2**, is isolated. In the absence of PMe_3, either **3** is formed directly by γ-abstraction or α-abstraction occurs followed by intramolecular C−H activation of a TMS group by the alkylidene ligand. Compound **3** and the four-coordinate alkylidene species **4** are in equilibrium (as described below), with **3** being highly favored.

The products of the thermolysis of **1**-d_4 were observed by ^2H NMR in toluene. In both the absence and presence of PMe_3, complete scrambling of the deuterium label among the *tert*-butyl and trimethylsilyl groups was observed. In the absence of PMe_3, broad signals were observed in a 1:3:1 ratio at 0.70, 0.53, and 0.36 ppm corresponding to the geminal methyl groups of the silacycle and the free TMS group of **3**. In the presence of PMe_3, a broad resonance was observed at 0.41 ppm corresponding to the TMS groups of **2**. In both cases, no deuterium signals were observed that would be attributed to the methylene groups of **3** or the alkylidene of **2** due to the predominant loss of neopentane-d_3 and the high ratio of TMS and *t*-Bu protons to the other protons in the molecule.

A rapid equilibrium between **3** and **4** is consistent with the incorporation of the deuterium labels into the silyl methyl groups. An additional equilibrium between **3** and the metallacyclobutane complex, **5**, must also be invoked in order to account for the incorporation of deuterium into the *t*-Bu groups of the neopentylidene ligand. Variable temperature NMR studies of **2** indicate that the PMe_3 ligand in **2** has a dissociation rate of *ca.* 45 s^{-1} at 39 °C.[14] Thus, even in the presence of PMe_3, compounds **3**−**5** are accessible and can cause scrambling of the deuterium label into all the observed positions under the conditions of the thermolysis.

Kinetic studies have also been performed on the conversion of **3** to an alkylidene species upon addition of Lewis base. Addition of 7 equiv of PMe_3 to a C_6D_6 solution of **3** gave **2** in a process that is first order in **3** with $k = 5.11(7) \times 10^{-4}\ s^{-1}$ at 295 K. Solutions of **3** also react with CH_3CN to give the CH_3CN adduct of **4**. This reaction is also first order in **3** in the presence of 7, 13, and 25 equiv of CH_3CN with rate constants of 5.95(4), 6.68(4), and 6.30(7) × $10^{-4}\ s^{-1}$, respectively. These results are consistent with rate-determining, unimolecular conversion of **3** to **4** and subsequent trapping of **4** by the added Lewis base.

The mechanism that is outlined in Scheme 1 is consistent with all of the above experimental data. The predominant initial step in the reaction is α-H abstraction giving the base-free alkylidene species, **4**, which either is trapped by a Lewis base or metalates one of the $SiMe_3$ groups of the amide ligand to form **3**. Such intramolecular insertions of early transition metal alkylidenes into the C−H bonds of ancillary ligands have been reported previously[15−19] but are usually irreversible[19] and therefore constitute a catalyst deactivation pathway. It is likely that the equilibrium between **3** and **4** arises from the strained four-membered ring of **3**.

As long as **4** is accessible from **3**, the formation of **3** is not a catalyst deactivation reaction. To the extent that the conversion of **4** to **3** is preferred over other reactions that effect chain transfer or termination, this cyclometalation reaction may actually increase the catalyst lifetime. Indirect evidence for a low rate of chain transfer or termination during ROMP reactions comes from the observed narrow polydispersities of polynorbornene formed when **2** is used as a ROMP catalyst.[20] Experiments are currently underway to test this hypothesis.

Acknowledgment. We wish to acknowledge the National Science Foundation DMR9207358 for the support of this work.

Supporting Information Available: Details of the X-ray results for **3**, representative kinetics plots, and tables of rate constants (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.

JA952030L

---

[12] Methane CIMS was used to ionize the neopentane analytes for mass spectral analysis. This method of analysis is preferable to electron impact MS because the major fragmentation pathway is formation of CMe_3^+ from the loss of methane from protonated neopentane without scrambling of the deuterium labels. Standard samples of neopentane-d_3 and neopentane-d_2 gave 3:1 mixtures of $CMe_2CD_3^+$:CMe_3^+ and $CMe_2CD_2H^+$:CMe_3^+, respectively, thus allowing direct analysis of the MS data without the need to fit the isotopic ratios to standard spectra.

[13] The observed $k_H/k_D = (k_{H\alpha} + k_\gamma)/(k_{D\alpha} + k_\gamma)$ and the ratio of neopentane-d_3 to neopentane-d_2 from the CIMS data gives $k_{D\alpha}/k_\gamma$. Algebraic manipulation of these relationships allows us to estimate $k_{H\alpha}/k_\gamma$ and $k_{H\alpha}/k_{D\alpha}$.

[14] The resonances for the TMS groups coalesce at 312 K, and the $\Delta G^\ddagger$ at coalescence is 15.9(7) kcal mol^{-1}.

[15] Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.

[16] Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847.

[17] Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

[18] Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

[19] van Doorns, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271.

[20] Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.