J|A|C|S
COMMUNICATIONS

A Terminal and Four-Coordinate Titanium Alkylidene Prepared by Oxidatively Induced α-Hydrogen Abstraction

Falguni Basuli, Brad C. Bailey, John Tomaszewski, John C. Huffman, and Daniel J. Mindiola*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

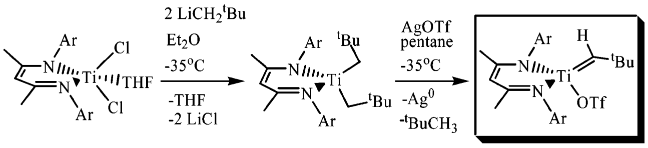
Received February 20, 2003; E-mail: mindiola@indiana.edu

Early-transition-metal alkylidenes play an important role in synthetic transformations such as cross-metathesis, ring-closing metathesis, ring-opening metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, acetylene polymerization, and Wittig-type reactions. A series of reviews[1] and highlights[2] in the literature exemplify the importance and need for metal alkylidene complexes. High oxidation state metal alkylidenes were reported over 25 years ago and are prepared commonly via α-abstraction or α-deprotonation reactions from the corresponding metal alkyl complex.[1] To favor α-deprotonation in such systems, one needs to prepare metal alkyl functionalities lacking *β*-hydrogens. In general, α-hydrogen abstraction to yield high-oxidation state metal alkylidenes is induced thermally, photochemically, or with Lewis bases to promote steric crowding.[1a−d,3,4] In contrast to groups 5 and 6, group 4 terminal metal alkylidene complexes, in particular, Zr and Hf, are exceedingly rare,[5] and the majority of the few examples are titanium based with coordination numbers ≥5.[1c,3,4,6]

Herein, we report a synthetic methodology to access the first four-coordinate titanium complex containing a terminal metal−carbon double bond. Preliminary Wittig-type reactions of the titanium neopentylidene complex with ketone and imine functionalities are also described.

Our opening approach to preparing a low-coordinate and terminal titanium alkylidene complex involved an adaptation for the synthesis of the precursor (Nacnac)$TiCl_2$ ($Nacnac^-$ = [Ar]NC(Me)CHC(Me)-N[Ar], Ar = 2,6-$(CHMe_2)_2C_6H_3$) complex reported by Budzelaar and co-workers.[7] Following Budzelaar's procedure, we recrystallized the THF base adduct (Nacnac)$TiCl_2$(THF) (**1**) from toluene in 70% yield as dark-green blocks (Scheme 1). The isolation of **1** avoids lower yields as well as additional steps to the THF-free complex (Nacnac)$TiCl_2$. Complex **1** was characterized by ^1H NMR spectroscopic methods, elemental analysis, and by single-crystal X-ray diffraction.[8] Ethereal solutions of **1** react rapidly with 2 equiv of $LiCH_2{}^tBu$[9] to afford emerald-green solutions of (Nacnac)-$Ti(CH_2{}^tBu)_2$ (**2**), which was isolated as dark-green blocks in over 75% yield (Scheme 1). Complex **2** was fully characterized,[8] and the molecular structure shows no α-agostic interactions or remarkable features similar to those reported for the bis-methyl complex studied by Budzelaar.[7]

Scheme 1. Synthesis of Titanium Alkylidene **3**



1 **2** **3**

Because complex **2** does not bind Lewis bases such as THF or PMe_3, we reasoned that one-electron oxidation might enhance Lewis acidity and promote deprotonation of the α-hydrogen of one of the neopentyl ligands. In addition, α-abstraction often takes place in five-coordinate d^0 species.[10] A cyclic voltammogram of a solution of **2** (THF/TBAH) showed one irreversible oxidation wave at −0.90 V (referenced vs $FeCp_2/FeCp_2{}^+$) for the Ti(III)/Ti(IV) couple.[8] Chemically, it was found that treatment of pentane solutions of **2** with AgOTf caused a rapid color change from green to red-brown concomitant with precipitation of a Ag^0 mirror and quantitative formation of the alkylidene complex (Nacnac)Ti=CH^tBu(OTf) (**3**) as evidenced by ^1H and ^{13}C NMR spectroscopic methods (Scheme 1). Complex **3** is likely formed from the putative five-coordinate intermediate (Nacnac)$Ti(CH_2{}^tBu)_2$(OTf). On the NMR time scale, compound **3** displays two methine resonances, four diastereotopic methyl groups on the isopropyls, as well as one methyl environment for the *β*-carbons of the Nacnac backbone, all consistent with the molecule having C_s symmetry. A C_α resonance centered at δ 271 ppm with a J_{CH} coupling constant of 95 Hz is diagnostic of **3** having a terminal alkylidene functionality.[3,4] The J_{CH} coupling from the ^{13}C NMR spectral data suggests an α-hydrogen agostic interaction with the metal center.[1c] The ^1H NMR CH_α resonance was located at 5.23 ppm and differentiated unambiguously from the CH_γ resonance for the Nacnac backbone (4.79 ppm) using HMQC NMR methods.[8,11] Large red-brown blocks of **3** were grown from pentane at −35 °C (89% yield), and the single-crystal structure revealed a four-coordinate titanium complex having C_s symmetry and having the shortest Ti=C bond length reported[12] (Ti(1)−C(33) = 1.830(3) Å, Figure 1).[8] The *tert*-butyl group is along the *σ*-plane bisecting N−Ti−N and oriented syn with respect to the triflato ligand. The $C_\alpha H_\alpha$ (H87) hydrogen was located in the Fourier electron map and refined isotropically (Ti(1)−H(87) = 1.92(3) Å). An α-agostic interaction is also substantiated by the large Ti(1)−C(33)−C(34) angle of 163.9(3)°.

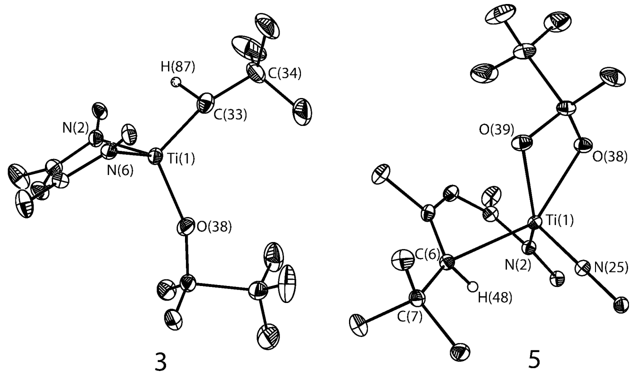


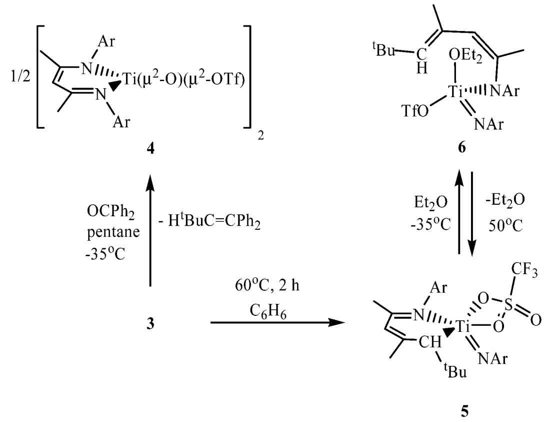
Figure 1. Molecular structures of **3** and **5** showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. H-atoms with the exception of the α-hydrogens and aryl groups with the exception of the *ipso*-carbons on the *β*-diketiminate or imido nitrogens have been omitted for clarity.

Complex **3** reacts rapidly with 1 equiv of benzophenone at room temperature to afford the olefin $H^tBuC=CPh_2$[13] and $^1/_2$ equiv of

10.1021/ja034786n CCC: $25.00

the titanium-oxo dimer $[(\text{Nacnac})\text{Ti}(\mu^2\text{-O})(\mu^2\text{-OTf})]_2$ (**4**)[14] in quantitative yield (Scheme 2).[8] Bridged titanium-oxo complex **4** and the corresponding olefin were isolated in 90% and 91% yield, respectively.[6] The reactivity observed between **3** and benzophenone follows well-established "Wittig-type" reagents studied in organic synthesis.[15]

Scheme 2. Reactivity of Titanium Alkylidene **3**



Although stable as a solid, complex **3** decomposes gradually in solution (room temperature, >2 days) to a new product as evidenced by ^{1}H and ^{13}C NMR spectroscopy. In fact, heating toluene or benzene solutions of **3** to 60 °C for 2 h affords the titanium imido-triflato complex supported by the chelating amido-diene ligand (η^2-H^{t}BuC═C(Me)CHC(Me)N[Ar])Ti═NAr(μ^2-OTf) (**5**) (65% isolated yield, Scheme 2).[8] Complex **5** is likely formed by a Wittig-type reaction between the titanium neopentylidene and the imine-aryl functionality of the Nacnac ligand. The molecular structure of **5** is shown in Figure 1 and displays one of the diastereomers,[8] and the ^{1}H NMR spectrum of **5** also indicates one diastereomer being present in solution at 25 °C. The chelate ligand in **5** exhibits a resonance indicative of an amido-diene because addition of a Lewis base such as Et$_2$O affords crystals in 80% yield of the adduct (η^1-H^{t}BuC═C(Me)CHC(Me)N[Ar])Ti═NAr(OTf)(Et$_2$O) (**6**), in which the olefinic pendant arm of the amide-diene ligand has been displaced by the Lewis base (Scheme 2). Mild heating of **6** under reduced pressure (50 °C, 2 h) regenerates **5** (Scheme 2). The molecular structure of the etherate adduct **6**[8] reveals a rare example of a four-coordinate titanium imido.[16]

In summary, we have shown that one-electron oxidation of a Ti(III) bis-neopentyl complex supported by a Nacnac ligand affords a terminal, and four-coordinate, titanium neopentylidene and titanium imido. In contrast to thermolytic reactions, an oxidatively induced α-abstraction procedure[17] can create a low-coordinate titanium alkylidene complex containing a labile group (e.g., triflate). We are currently exploring the mechanism behind the carbene-imine Wittig reaction to make **5**, as well as the chemical reactivity of **3** with olefins.

Acknowledgment. This work is dedicated to the memory of Professor Richard Koerner. For financial support of this work, we thank Indiana University-Bloomington, the Camille and Henry Dreyfus Foundation, and the Ford Foundation. D.J.M. would like to thank Mr. X. Hu, Dr. R. Isaacson, and Professors K. Meyer, K. G. Caulton, J. M. Zaleski, and C. C. Cummins for insightful discussions.

Supporting Information Available: Experimental preparation and crystallographic data for compounds **1**−**6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (d) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1989. (e) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
(2) (a) Rouhi, A. M. *Chem. Eng. News* **2002**, *80*, 29. (b) Fürstner, A. *Adv. Synth. Catal.* **2002**, *344*, 567. (c) Schrock, R. R. *Adv. Synth. Catal.* **2002**, *344*, 571.
(3) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686.
(4) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7823.
(5) (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336. (b) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 2478. (c) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608.
(6) (a) van Doorn, J. A.; van der Haijden, H. *Organometallics* **1995**, *14*, 1278. (b) Kahlert S.; Gorls, H.; Scholz, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1857. (c) van Doorn, J. A.; van der Haijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271. (d) Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245.
(7) Budzelaar, P. H. M.; von Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.
(8) See the Supporting Information for complete experimental, spectral, and crystallographic details.
(9) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(10) For an example describing α-hydrogen abstraction stemming from a five-coordinate complex, see: Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(11) Summers, M. F.; Marzilli, L. G.; Bax, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 4285.
(12) A search of the Cambridge Crystallographic Database for titanium−alkylidene bond lengths indicated values to be ≥1.884(4) Å.
(13) The formation of the alkene was confirmed by spectroscopic comparison with ^{1}H NMR shifts reported in the literature. Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000.
(14) The molecular structure of **4** showed an edged-sharing bioctahedra geometry composed of two bridging oxo and triflate ligands. See the Supporting Information, ref 8.
(15) For some illustrative "Wittig-type" titanium-based reactions, see: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2001. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (c) Tebbe, F. N.; Parshall, G. W.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (d) Kauffmann, T.; Ennen, B.; Sander, J.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 244. (e) Grubbs, R. H.; Cannizzo, L. F. *J. Org. Chem.* **1985**, *50*, 2316. (f) Wilcox, C. S.; Long, G. W.; Suh, H. *Tetrahedron Lett.* **1984**, *25*, 395. (g) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392.
(16) (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.
(17) One-electron oxidation followed by hydrogen atom abstraction to generate a putative tungsten-alkylidene has been reported. Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747.

JA034786N