ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 4115–4125 4115
DOI: 10.1021/om900115v

Zwitterionic and Cationic Titanium and Vanadium Complexes Having Terminal M−C Multiple Bonds. The Role of the *β*-Diketiminate Ligand in Formation of Charge-Separated Species

Debashis Adhikari,[§,†] Falguni Basuli,[§,‡] Justin H. Orlando,[†] Xinfeng Gao,[†]
John C. Huffman,[†] Maren Pink,[†] and Daniel J. Mindiola*[,†]

[†] *Molecular Structure Center and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405.* [§] *First and second author contributed equally to this work.* [‡] *Present address: Nuclear Medicine, Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts 02115*

Received February 12, 2009

Treatment of the neopentylidene complex ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(OTf) (**1**) with a strong base such as an alkyl reagent (lithium or potassium salt) results in deprotonation of the *β*-diketiminate *β*-methyl group to form complex (ArN(Me)CCHC(CH$_2$)NAr)Ti=CH^{t}Bu(THF) (**2**) along with liberation of the alkane. Likewise, ligand deprotonation of ([ArNC(Me)]$_2$CH)V≡C^{t}Bu(OTf) (**3**), in THF or Et$_2$O, results in formation of the alkylidyne−solvent adduct (ArNC(Me)CHC(CH$_2$)NAr)V≡C^{t}Bu(L) (L = THF, **4-THF**; L = Et$_2$O, **4-OEt$_2$**), concomitant with alkane formation. The connectivity in compound **4-Et$_2$O** has been established by single-crystal X-ray diffraction studies. Compounds **2** and **4-THF** react with B(C$_6$F$_5$)$_3$ to produce the first examples of terminal titanium alkylidene and vanadium alkylidyne zwitterions, namely, the borane adducts (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)Ti=CH^{t}Bu(THF) (**5**) and (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)V≡C^{t}Bu(THF) (**6**), respectively. The solid state structure for each zwitterion was also obtained. Compounds **2** and **4-THF** react readily with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] to produce the discrete salts [([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(THF)][B(C$_6$F$_5$)$_4$] (**7**) and [([ArNC(Me)]$_2$CH)V≡C^{t}Bu(THF)][B(C$_6$F$_5$)$_4$] (**8**), respectively, via protonation of the methylene group in the N,N′-chelating ligand ArNC(Me)CHC(CH$_2$)NAr^{2-} to re-form the *β*-diketiminate scaffold. The reactivity of **7** allows for spectroscopic elucidation only at low temperatures, while complex **8** has been fully characterized including a single-crystal X-ray structure.

Introduction

Tebbe's reagent, Cp$_2$Ti(CH$_2$AlCl(Me)$_2$),[1] is a Lewis-acid-stabilized methylidene complex generated from the addition of 2 equiv of AlMe$_3$ to Cp$_2$TiCl$_2$ (eq 1). This complex was perhaps one of the first d^0 transition metal systems to perform olefin metathesis in a catalytic manner and represents a seminal discovery toward the application of high-valent metal−carbon multiple bonds in the realm of organic methodology.[2] In general, Tebbe's complex is a classic stoichiometric Wittig-like reagent for the methylenation of carbonyl-based functional groups.[3,4] The polarized nature of the masked Ti=C multiple bond renders this system more reactive than prototypical phospha-Wittig reactants, and as a result, complex Cp$_2$Ti(CH$_2$AlCl(Me)$_2$) works particularly well for sterically encumbered carbonyls present in reagents such as aldehydes, esters, lactones, and amides.[5] Likewise, the AlMe$_2$Cl moiety in Tebbe's complex reduces nucleophilic character at the methylidene carbon, consequently making this highly polarized group less basic than the more ubiquitous phospha-Wittig compounds.[5] Analogous to Cp$_2$Ti(CH$_2$AlCl(Me)$_2$), treatment of Cp$_2$Ti(Me)$_2$ with AlMe$_3$ does produce chloride-free Cp$_2$Ti(CH$_2$Al(Me)$_3$), but such a complex was never isolated in pure form due to the presence of unreacted dimethyl precursor.[1] Following Tebbe's work, few examples of aluminum-stabilized titanium analogues have been reported. For example, Krüger and co-workers published a rare example of a titanium alkylidene system stabilized by an organoaluminum moiety (eq 2).[6]

---

*Corresponding author. E-mail: mindiola@indiana.edu.

[1] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[2] Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074.

[3] (a) Petasis, N. A.; Hu, Y.-H. *Curr. Org. Chem.* **1997**, *1*, 249. (b) Petasis, N. A.; Hu, Y.-H. *J. Org. Chem.* **1997**, *62*, 782. (c) Petasis, N. A.; Lu, S.-P.; Bzowej, E. I.; Fu, D.-K.; Staszewski, J. P.; Akritopoulou-Zanze, I.; Patane, M. A.; Hu, Y.-H. *Pure Appl. Chem.* **1996**, *68*, 667. (d) Elschenbroich, C. In *Organometallics*, 3rd ed.; Wiley-VCH: Weinheim, 2005; p 343. (e) Pine, S. H. *Org. React.* **1993**, *43*, 1. (f) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2386.

[4] In the absence of Al(CH$_3$)$_3$, complex Cp$_2$Ti(CH$_3$)$_2$, which is fairly tolerant to air and moisture, can extrude CH$_4$ thermolytically: (a) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392. (b) Petasis, N. A.; Bzowej, E. I. *J. Org. Chem.* **1992**, *57*, 1327. (c) Petasis, N. A.; Akritopoulou, I. *Synlett* **1992**, 665. (d) Petasis, N. A.; Lu, S.-P. *Tetrahedron Lett.* **1995**, *36*, 2393.

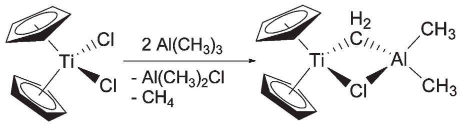
[5] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987; pp 813− 815. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. J. Am. Chem. Soc. 1980, 102, 3270.

[6] Krüger, C.; Mynott, R.; Siedenbiedel, C.; Stehling, L.; Wilke, G. *Angew. Chem., Int. Ed.* **1991**, *30*, 1668.

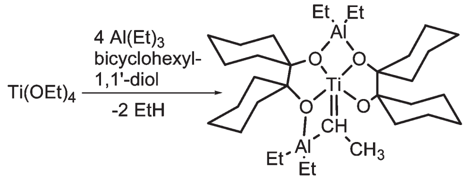
Recently, our group discovered an alkylidyne analogue to Tebbe's complex, namely, the Lewis-acid-stabilized group 4 species (PNP)Ti[C(^{t}Bu)Al(Me)$_3$] (PNP$^-$ = N[2-P-(CHMe$_2$)$_2$-4-MeC$_6$H$_3$]$_2$) (eq 3).[7] Parallel to this contribution, Roesky and co-workers reported an unprecedented "Ti$-$CH$^-$" linkage stabilized by a Al$_2$(Me)$_5^+$ fragment (eq 4).[8] If one excludes the titanium methyl ligand as well as Al$_2$(Me)$_5^+$, compound ([ArNC(Me)]$_2$CH)Ti(Me)=CH(Al$_2$Me$_5$) (Ar = 2,6-^{i}PrC$_6$H$_3$) could be best diagnosed as a parent methylidyne source.[8] Unfortunately, the anionic nature of the TiCH group, coupled with the reactive Ti$-$CH$_3$ linkage and fragile imine group present within the β-diketiminate ligand, precluded clean methylidyne "CH" group transfer chemistry.[8] Roesky and co-workers also complemented work on the heavier congeners of group 4 by preparing [(Cp*M)$_3$Al$_6$Me$_8$(μ_3-CH$_2$)$_2$(μ_4-CH)$_4$(μ_3-CH)] clusters (M = Zr and Hf).[9] A similar "TiCH"-trapped product was reported by Stephan et al., namely, the complex Cp*Ti(μ-Me)(μ-NP^{i}Pr$_3$)(μ_3-CH)(AlMe$_2$)$_2$.[10] If one takes into consideration other groups outside AlMe$_2^+$, then another Lewis-acid-stabilized TiCH group that merits mentioning is Mena's [CpTiO]$_3$(μ_3-CH) cluster as well as its subsequent derivatives.[11]

Although the discovery of Tebbe's complex and its role as a methylidene (e.g., CH$_2$) group transfer reagent was reported over 30 years ago, examples of zwitterionic titanium complexes retaining a terminal alkylidene ligand, to our knowledge, have not been reported. In fact, cationic titanium complexes bearing the terminal alkylidene have also remained elusive, presumably due to the inherent reactivity of the Ti=C bond. This characteristic also applies to vanadium alkylidene[12] and alkylidyne[13] cations, which have been isolated and fully characterized by us only recently.

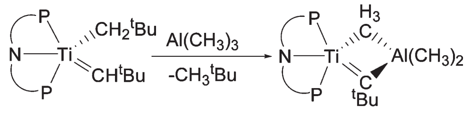
Herein we report in this paper a unique approach to preparing zwitterionic and cationic titanium neopentylidenes as well as zwitterionic and cationic vanadium neopentylidynes. The ability of the β-diketiminate's β-methyl hydrogens to tautomerize in [ArNC(Me)]$_2$CH$^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) allows for facile deprotonation to form the N,N′-chelating, bis-anilide ligand (ArNC(Me)CHC(CH$_2$)NAr)$^{2-}$.[14,15] Due to the nucleophilic nature of the methylene motif in the scaffold (ArNC(Me)CHC(CH$_2$)NAr)$^{2-}$, this ligand can be readily protonated, with reagents such [NHMe$_2$Ph][B(C$_6$F$_5$)$_4$], to reassemble the original β-diketiminate framework on the metal, but as cationic species due to the nature of the weakly coordinating anion. Likewise, Lewis acid coordination to the methylene moiety of (ArNC(Me)CHC(CH$_2$)NAr)$^{2-}$ can yield charge-separated species retaining the terminal M$-$C multiply bonded ligand.



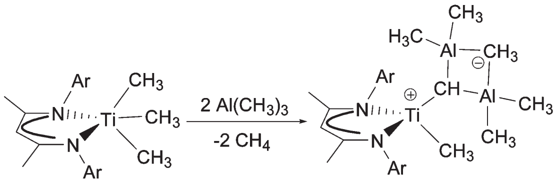
(1)



(2)



(3)



(4)

Results and Discussion

Deprotonation of the β-Diketiminate Ligand [ArNC(Me)]$_2$CH$^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) on Titanium(IV) and Vanadium(V) Complexes. It has been well established that the β-diketiminate ancillary framework has vulnerable sites, especially in the context of early transition metal or main group organometallic chemistry.[16] Of the many different modes of transformation involving the β-diketiminate ligand, perhaps the most common pathway is intramolecular C$-$H bond activation of peripheral groups stemming from the α-nitrogen atoms.[15b,16–22] Other reactions of this ligand type include electrophilic activation at the γ-carbon due to

---

(7) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8246.

(8) Nikiforov, G. B.; Roesky, H. W.; Heisen, B. C.; Grosse, C.; Oswald, R. B. *Organometallics* **2008**, *27*, 2544.

(9) (a) Herzog, A.; Roesky, H. W.; Zak, Z.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **1994**, *33*, 967. (b) Herzog, A.; Roesky, H. W.; Jager, F.; Steiner, A.; Noltemeyer, M. *Organometallics* **1996**, *15*, 909.

(10) Kickham, J. E.; Guerin, F.; Stewart, J. C.; Urbanska, E.; Stephan, D. W. *Organometallics* **2001**, *20*, 1175.

(11) (a) Andrés, R.; Galakhov, M. V.; Martín, A.; Mena, M.; Santamaría, C. *Organometallics* **1994**, *13*, 2159. (b) Andrés, R.; Gomez-Sal, P.; de Jesus, E.; Martín, A.; Mena, M.; Yelamos, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 115. (c) Abarca, A.; Galakhov, M.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J.-M.; Santamaría, C.; Sarasha, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 534. (d) Martín, A.; Mena, M.; Morales-Varela, M.; Santamaria, C. *Eur. J. Inorg. Chem.* **2004**, *9*, 1914. (e) Gracia, J.; Martín, A.; Mena, M.; Morales-Varela, M.; Poblet, J.; Santamaria, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 927.

(12) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156.

(13) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506.

(14) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806.

(15) (a) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003. (b) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 3321.

(16) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.

(17) Qian, B.; Scanlon, W. J.; Smith, M. R.,; Motry, D. H. *Organometallics* **1999**, *18*, 1693.

(18) (a) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533. (b) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622. (c) Knight, L. K.; Piers, W. E.; McDonald, R. *Organometallics* **2006**, *25*, 3289. (d) Conroy, K. D.; Hayes, P. G.; Piers, W. E.; Parvez, M. *Organometallics* **2007**, *26*, 4464.

(19) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.

(20) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2004**, 764.

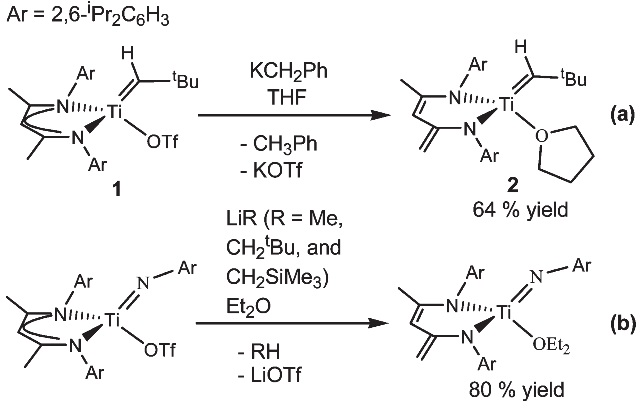
(21) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886.

(22) (a) Eckert, N. A.; Vaddadi, S.; Stoian, S.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6868. (b) Tomson, N. C.; Yan, A.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 11262.

delocalization of charge about the NCCCN ring,[16,23−27] as well as deprotonation of the β-methyl group composing the NCCCN ring.[14,15] Very recently, our group has determined that the imine functionality belonging to the NCCCN ring can undergo smooth cross-metathesis, intramolecularly, with complexes having a titanium[21,28] and vanadium neopentylidene[12] ligand. Other similar groups such as phosphinidenes have been also reported to undergo Wittig/Staudinger-like exchange reaction with the imine group of the β-diketiminate ligand.[29] Although the latter type of intramolecular reaction reveals the parallel reactivity the M−C or M−P multiple bond, such a transformation about the β-diketiminate ligand results in inactivation, by means of a group transfer process, of the functionality that is of interest to us.

Even though the β-diketiminate ligand can readily undergo deprotonation of the β-methyl group, such a transformation can be avoided by incorporating a ^{t}Bu group.[15b,21,30,31] Despite this, we are interested in such a deprotonation reaction taking place in compounds such as ([ArNC(Me)]$_2$CH)Ti=NAr(OTf)[15a] and ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(OTf) (**1**)[15b,21] given that a new, perhaps even more robust ligand framework, such as (ArNC(Me)CHC(CH$_2$)NAr)$^{2-}$ was readily assembled without demetalation (Scheme 1). Intuitively, the nature of the (ArNC(Me)CHC(CH$_2$)NAr)Ti=X(THF) (X = CH^{t}Bu, NAr) scaffold suggested that an intermolecular cross-metathesis reaction was no longer viable given that the vulnerable imine motif was absent. Likewise, the coordination environment at the metal center was relatively unperturbed, concurrent with retention of the functional group of interest: Ti=CH^{t}Bu or Ti=NAr (Scheme 1).[15] In addition, the dianionic nature of the newly formed ligand implied that a more electron rich metal system was accessible, but also having potentially labile ligands such as THF or Et$_2$O. Although Lappert et al. were the first to report deprotonation and protonation reactions of β-diketiminates,[32] only recently have other research groups explored (ArNC(Me)CHC(CH$_2$)NAr)$^{2-}$ as ancillary ligands.[33]

Scheme 1



We were particularly intrigued with the preparation of complex (ArNC(Me)CHC(CH$_2$)NAr)Ti=CH^{t}Bu(THF) (**2**), shown in Scheme 1a,[15b] since this system could offer access to a low-coordinate, electron-rich titanium complex having a terminal alkylidene moiety. Preparation of complex **2** is relatively simple: invoking the use of a strong base, KCH$_2$Ph[34] in THF,[15b] with the alkylidene precursor **1** (Scheme 1a). A similar deprotonation of the ligand backbone has been documented earlier by our group for the titanium imido system ([ArNC(Me)]$_2$CH)Ti=NAr(OTf) (Scheme 1b).[15a] The yield of **2** (64% isolated yield) was relatively unperturbed by using an alternative base such as Li^{t}Bu in THF at −35 °C. The use of a coordinating solvent such as THF was critical to formation of **2** since alkylation of **1** with the same reagents, in pentane or toluene solution at −35 °C, yielded intractable products. Only in the case of LiCH$_2$SiMe$_3$, in pentane, was alkylation successful enough in **1** to allow for isolation of the titanium alkylidene-alkyl ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(CH$_2$SiMe$_3$).[15b] Unfortunately, treating ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(CH$_2$SiMe$_3$) with THF results in complicated mixtures, from which we were unable to identify **2** (Scheme 2). Therefore, we propose that formation of **2** from **1** most likely involves either a tautomerization process promoted by THF or an ionization of the base by THF, which then deprotonates the methyl group of the ligand, concertedly. On the basis of our independent synthetic work, the alkyl complex ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(CH$_2$SiMe$_3$) does not appear to be an intermediate to formation of **2**. THF binding to precursor ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(OTf) is not unreasonable to propose given that the trimethylsilylmethylidene derivative ([ArNC(Me)]$_2$CH)Ti=CHSiMe$_3$(OTf)(THF) readily coordinates THF.[35] We cannot, however, discard the possibility of THF displacing the OTf$^-$ in a precursor such as **1** or the ionization of the alkyl reagent by THF to generate a more powerful base. Therefore, it is evident that THF blocks other, slower, but competitive processes such as double C−H activation of the isopropyl methines as well as intramolecular cross-metathesis with the β-diketiminate imine group to form the products shown in Scheme 2.[15b] The latter two products are observed when ([ArNC(Me)]$_2$CH)Ti=CH^{t}Bu(CH$_2$SiMe$_3$) is allowed

---

(23) (a) Kuhn, N.; Lanfermann, H.; Schmitz, P. *Liebigs Ann. Chem.* **1987**, 727. (b) Kuhn, N.; Kuhn, A.; Boese, R.; Augart, N. J. *Chem. Commun.* **1989**, 975. (c) Kuhn, N.; Kuhn, A.; Speis, M.; Blaeser, D.; Boese, R. *Chem. Ber.* **1990**, *123*, 1301.

(24) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307, and references therein.

(25) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384.

(26) Electrophilic substitution at the γ-carbon of the nacnac backbone with R$_2$P$^+$ has also been reported: (a) Hitchcock, P. B; Lappert, M. F; Nycz, J. E. *Chem. Commun.* **2003**, 1142. (b) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052, and references therein. (c) Carey, D. T.Cope-Eatough, E. K.; Vilaplana-Mafé, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083.

(27) Gregory, E. A.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2005**, *24*, 1803.

(28) (a) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052. (b) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813.

(29) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170.

(30) Basuli, F.; Clark, R. L.; Bailey, B. C.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2005**, 2250.

(31) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.

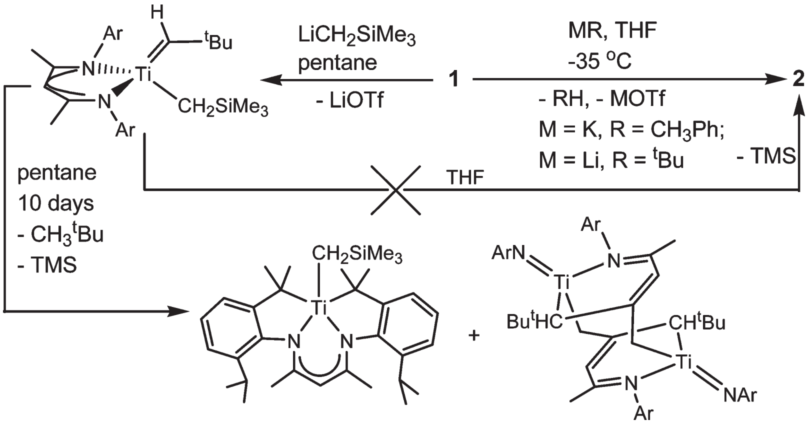
(32) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A V. *Chem. Commun.* **2005**, 951.

(33) (a) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600. (b) Yao, S.; Xiong, Y.; van Wüllen, C.; Driess, M. *Organometallics* **2009**, *28*, 1610. (c) Xiong, Y.; Yao, S.; Matthias Driess, M. *Organometallics* **2009**, *28*, 1927.

(34) (a) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed.* **1973**, *12*, 508. (b) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Lorono-Gonzalez, D.; Parkin, A.; Parsons, S. *Chem.—Eur. J.* **2003**, *9*, 4820.

(35) Basuli, F.; Adhikari, D.; Huffman, J. C.; Mindiola, D. J. *J. Organomet. Chem.* **2007**, *692*, 3115.

Scheme 2



to stir in hexane or pentane for 10 days at room temperature and in the absence of donor solvents (Scheme 2).[15b]

The transformation of **1** to **2** is signified by a drastic upfield chemical shift of the alkylidene C−H group, when judged by both the ^{13}C (from 271 to 254 ppm) and ^{1}H (from 5.69 to 5.05 ppm) NMR spectroscopic resonances. The similarity in the J_{C-H} values for the alkylidene carbons (([ArNC(Me)]$_2$CH)-Ti=CH^{t}Bu(CH$_2$SiMe$_3$), 99 Hz; **2**, 93 Hz) suggests that only a fraction of distortion about the alkylidene moiety group has taken place when the β-diketiminate ligand is deprotonated (Table 1).

The isolobal relationship between ([ArNC(Me)]$_2$CH)-Ti=NAr(OTf) and the vanadium alkylidyne complex ([ArNC(Me)]$_2$CH)V≡C^{t}Bu(OTf) (**3**) prompted us to investigate how an alkyl group would react with the latter. Given that vanadium alkylidynes, until recently,[13] were an unknown class of molecules,[36] we inquired if the alkylidyne functionality would be preserved while transforming the β-diketiminate ligand. Accordingly, treatment of **3** with 1 equiv of KCH$_2$Ph in THF at −35 °C promotes a rapid color change from brown to red. Rapid workup of the reaction after 5−10 min allows for isolation of the alkylidyne−THF complex (ArNC(Me)CHC(CH$_2$)NAr)V≡C^{t}Bu(THF) (**4-THF**) in 46% yield subsequent to recrystallization overnight from pentane at −35 °C (Scheme 3). Complex **4-THF** is sparingly soluble in pentane or hexane, thus allowing for clean crystallization from the reaction mixture. Allowing the reaction to stir longer than 10 min results in lower yields of **4-THF**. Compound **4-THF** reveals a diagnostic alkylidyne resonance in the ^{13}C NMR spectrum centered at 346.7 ppm. The alkylidyne resonance was broad and only observable upon cooling of the NMR probe to −50 °C. Very likely, the lowering of the temperature of an NMR solution containing complex **4-THF** increases the quadrupolar relaxation rate of the vanadium nucleus (^{51}V, I = 7/2, 99.6% abundant), thus resulting in the effective decoupling of the ^{51}V scalar coupling from the ^{13}C nucleus.[37] Other diagnostic spectroscopic features for complex **4-THF** include the observation of two inequivalent protons for the methylene group composing the dianionic ligand, which are centered at 3.52 and 3.29 ppm. The two resonances were clearly correlated to the sp^2-hydridized carbon at 79.78 ppm via an HMQC experiment (J_{C-H} = 158 Hz).[38] Given the breakdown of symmetry in the dianionic ligand, complex **4-THF** belongs to point group C_1, which explains the spectroscopic observation of four inequivalent isopropyl groups on the supporting N,N′-chelating ligand as well as two distinctly different β-carbons composing the NCCC′N ring (^{13}C NMR: 152.6 and 141.1 ppm). Chemically shifted resonances, from that of free THF, are also observed in the ^{1}H NMR spectrum of **4-THF**. Examination of the reaction mixture after separation of **4-THF** suggests a myriad of other products formed from this reaction. In fact, allowing the reaction to stir for longer than 10−20 min results in very low yields of **4-THF** being isolated. Unfortunately, multiple attempts to grow single crystals of **4-THF** suitable for X-ray diffraction studies were unsuccessful. For this reason we turned our attention to preparing a close derivative of **4-THF** by replacing the THF ligand with Et$_2$O. Accordingly, treatment of a cold pentane solution of **3** (having a few drops of Et$_2$O) with 1 equiv of Li^{t}Bu (keeping the solution at −35 °C during the addition and stirring) resulted also in deprotonation of the CH$_3$ group in the β-carbon, to form **4-OEt$_2$** in 58% (isolated) yield after rapid workup of the reaction mixture. Complex **4-OEt$_2$** displays virtually identical spectroscopic signatures to **4-THF**, but the complex can be isolated as single crystals from a hexane solution cooled to −35 °C (see Experimental Section). Table 1 compiles salient NMR spectroscopic data for complexes **4-THF** and **4-OEt$_2$**.

The structure of crystallized **4-OEt$_2$** reveals a rare example of a low-coordinate vanadium alkylidyne confined in a pseudo-tetrahedral environment and displaying C_1 symmetry (Figure 1). The space group, $P2(1)$, also corroborates the chirality present in the system in the solid state. A short V≡C bond length of 1.683(4) Å is consistent with a terminal alkylidyne moiety,[13,36] while the vanadium alkylidyne group is essentially linear (171.0(3)°), where the plane defined by the atoms V≡C−C bisects the N−V−N plane. Although the molecular structure of **4-OEt$_2$** suffered from a highly disordered Et$_2$O ligand (V−O, 2.022(3) Å), connectivity was unambiguously confirmed and was consistent with our NMR spectral data (vide supra). The dianionic nature of the N,N′-chelating ligand in **4-OEt$_2$** is supported by the short V−N bond lengths (1.894(2) and 1.886(3) Å, Table 2), which deviate from V(V)−N$_{\text{nacnac}}$ distances observed in the two examples of four-coordinate vanadium alkylidynes known

---

(36) An example of a Fischer-type carbyne complex of vanadium has been reported. Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564.

(37) Claridge, T. D. W. In *High-Resolution NMR Techniques in Organic Chemistry*; Pergamon: Amsterdam, 1999; pp 40−44.

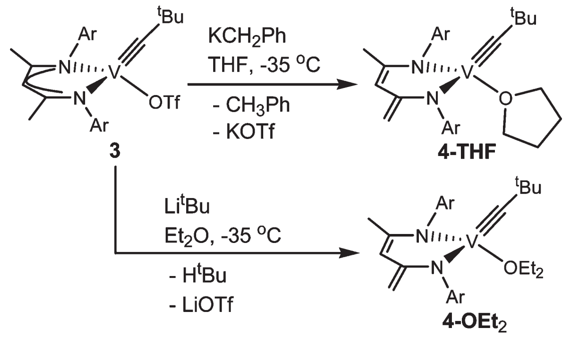
(38) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

Table 1. Selected Multinuclear NMR Spectroscopic Features for Complexes 1−8[a]

	1	2	3	4-THF	4-OEt_2	5	6	7	8-THF
^{1}H NMR: M=CH	5.23	5.05				3.13		3.33	
^{1}H NMR: CH_3 of β carbon in chelate ligand	1.47	1.65	1.49	1.59	1.43	1.53	1.63	1.67	1.84
^{1}H NMR: γ-CH of chelate ligand	4.79	4.92	4.34	4.38	4.33	5.66	5.12	4.99	4.82
^{1}H NMR: β-CH_2 of chelate ligand		3.64, 3.25		3.52, 3.29	3.49, 3.24	2.96, 2.43	2.56, 2.17		
^{13}C NMR: MC (J_{C-H})	271.5 (95)	254.0 (93)	375.1	346.7	343.6	260.0 (na)	365.8	269.3 (na)	374.7
^{13}C NMR: β-carbon of chelate ligand	168.2	153.2	167.2	152.6	153.1	168.0	161.8	168.4	167.5
^{13}C NMR: γ-carbon of chelate ligand (J_{C-H})	95.5 (162)	99.2 (154)	93.8 (na)	94.59 (160)	94.93 (156)	91.05 (na)	89.83 (na)	91.8 (na)	90.47 (na)
^{13}C NMR: β-C, and adjacent CH_2 of chelate ligand (J_{C-H})		141.9, 83.0 (162)		141.1, 79.78 (158)	141.8, 80.23 (158)	181.0, 31.90 (na)	180.2, 30.68 (na)		
^{11}B NMR: $B(C_6F_5)_3$						−14.5	−15.7	−15.6	−15.6
^{19}F NMR	−77.7		−78.2			−131.4, −160.9, −165.3	−131.2, −161.7, −165.9	−132.4, −162.5, −166.4	−133.0, −163.4, −167.3
^{51}V NMR: ($\Delta\nu_{1/2}$)			618(1446)[b]	286(680)	310(741)		489(2671)		548(1966)

[a] Chemical shifts are reported in ppm. Coupling constants and linewidths are reported in Hz. [b] The original value reported at −882 ppm was incorrectly referenced.[13]

Scheme 3



(1.92−1.96 Å).[13] In regard to the N,N′-chelating scaffold in **4-OEt_2**, the N−C_β distances are considerably longer than those reported for the parent β-diketiminate ligand in precursor **3** (Table 2).[13] Due to the conjugated nature of the diene motif in the N,N′-chelating framework, the methylene hydrogens, which were located and refined isotropically, are in the plane defined by the atoms NCCC′N. Table 2 lists selected metrical parameters for the single-crystal structure of **4-OEt_2**.

As noted earlier, the use of a polar solvent such as THF in conjunction with a strong base resulted in deprotonation of the β-diketiminate ligand in **1**. Unfortunately, multiple attempts to alkylate **3** with $LiCH_2SiMe_3$ or KCH_2Ph in nonpolar media (toluene, pentane, hexane) resulted in decomposition mixtures, from which the hypothetical species "([ArNC(Me)]$_2$CH)V≡C^{t}Bu(R)" was never isolated.

Synthesis and Characterization of a Zwitterionic Titanium (IV) Neopentylidene and Vanadium(V) Neopentylidyne. The possibility to transform the β-diketiminate framework, [ArNC(Me)]$_2$CH$^-$, into a more robust N,N′-chelating ligand, ArNC(Me)CHC(CH$_2$)NAr^{2-}, provided the impetus to explore the possibility of abstracting the coordinated Lewis base (THF) or exploiting the chemistry at the Ti=C or V≡C linkage. Accordingly, when a toluene solution of **2** was treated with solid $B(C_6F_5)_3$ and in the absence of coordinating solvents, an oily residue was formed immediately without a significant color change of the solution. Crystallization of this residue from toluene/pentane at −35 °C allowed for isolation of pure (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)Ti=CH^{t}Bu(THF) (**5**) in 86% yield as a brown-red material (Scheme 4). On the basis of ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy, the borane has coordinated to the terminal methylene group to yield a zwitterionic titanium alkylidene species. Specifically, the ^{1}H NMR spectrum of **5** revealed a relatively unperturbed alkylidene α-hydrogen (3.02 ppm) in comparison to **2**, while the ^{13}C NMR spectrum demonstrated that a terminal neopentylidene functionality (260 ppm, J_{C-H} = 85 Hz) and coordinated THF

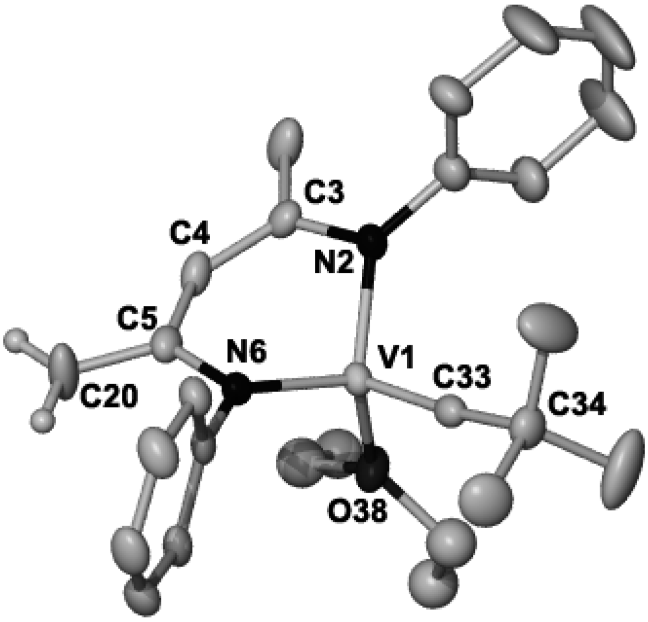


Figure 1. Perspective view of the solid state structure of **4-OEt_2** with thermal ellipsoids at the 50% probability level (for artistic purpose, the ethyl groups on O38 are displayed with isotropic parameters due to disorder). Hydrogens, with the exception of the methylene group, have been omitted for clarity. Isopropyl groups on the bis-anilide aryls have also been omitted for clarity. Table 2 lists pertinent metrical parameters, and crystallographic parameters are listed in Table III (see Supporting Information).

Table 2. Selected Metrical Parameters for the Solid State Structures of Complexes 4, 5, 6, and 8-OEt$_2$[a]

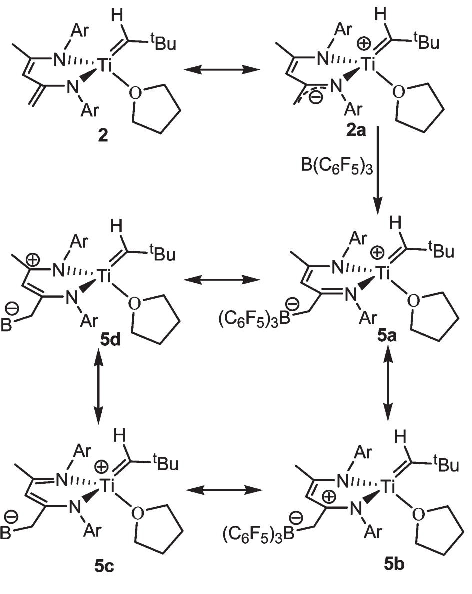
M = Ti or V	**1**	**2**[b]	**3**	**4-OEt$_2$**	**5**·3C_7H_8	**6**·2.25C_7H_8·0.25C_6H_{14}	**8-OEt$_2$**
M−C	1.830(3)	1.86(1)	1.674(2)	1.683(4)	1.830(4)	1.686(3)	1.6809(15)
M−N_α	2.012(3)	1.993(8)	1.924(2)	1.894(2)	1.979(3)	1.932(3)	1.9509(12)
M−N_α	2.025(3)	1.942(9)	1.9364(18)	1.886(3)	2.007(3)	1.941(2)	1.9359(12)
N_α−C_β	1.344(4)	1.42(2)	1.347(3)	1.394(4)	1.354(4)	1.345(4)	1.3379(19)
N_α−C_β	1.343(4)	1.48(2)	1.337(3)	1.410(4)	1.337(4)	1.352(4)	1.3547(18)
C_β−C_γ	1.410(4)	1.51(3)	1.404(3)	1.420(5)	1.429(4)	1.406(4)	1.407(2)
C_β−C_γ	1.403(4)	1.39(3)	1.398(3)	1.422(5)	1.398(4)	1.412(4)	1.419(2)
M−O	1.957(2)	2.130(8)	1.9887(19)	2.022(3)	2.071(2)	2.002(2)	2.0110(11)
B−CH_2					1.657(5)	1.647(5)	
H_2C=C_β		1.413(14)		1.418(5)	1.502(4)	1.514(4)	
M−C−C	163.9(3)	161.7(8)	177.61(19)	171.0(3)	168.3(3)	175.6(3)	174.36(12)
N_α−M−N_α	94.18(10)	101.5(4)	96.83(8)	104.45(13)	97.37(11)	97.67(10)	97.76(5)
N_α−M−C	109.83(13)	115.7(4)	105.58(10)	107.03(15)	113.36(14)	107.36(13)	105.46(6)
N_α−M−C	111.15(13)	114.4(4)	106.65(10)	106.77(16)	106.77(14)	105.11(13)	105.46(6)
N_α−M−O	115.62(10)	107.2(3)	118.08(9)	116.91(11)	112.08(11)	122.54(10)	121.97(5)
N_α−M−O	112.26(10)	113.3(3)	119.64(9)	115.51(12)	121.91(10)	120.28(10)	120.63(5)
O−M−C	112.48(13)	104.9(4)	108.60(10)	105.52(14)	105.45(13)	102.46(13)	103.90(6)
N_α−C_β−C_γ	123.5(3)	125.8(9)	121.8(2)	120.6(3)	123.4(3)	123.1(3)	121.15(13)
N_α−C_β−C_γ	122.8(3)	113.7(9)	121.5(2)	119.9(3)	119.4(3)	119.2(3)	121.85(13)
C_β−C_γ−C_β	129.9(3)	134(1)	130.1(2)	133.8(3)	131.9(3)	130.5(3)	130.11(14)
M deviation	1.129	0.851	1.116	0.990	1.147	1.081	1.112

[a] Metrical parameters for complexes **1**−**3** are included for comparison.[13,15b,21,28a] Distances are reported in angstroms and angles in degrees. N_α, C_β, and C_γ represent the atoms of the NCCCN ring. M deviation represents deviation of the metal ion above or below the plane defined by the NCCC′N or NCCCN ring composing the chelating ligand. [b] The solid state structure was of poor quality due to badly split crystals.[15b]

(resonance at 3.94 and a broad resonance at 1.84 ppm) were retained in **5**. The much lower J_{C-H} versus **1** or **2** suggest a stronger α-hydrogen agostic interaction taking place with the more electron deficient titanium(IV) center. Rehybridization at the former borane group is also evident from the broad ^{11}B NMR chemical shift at −14.5 ppm (relative to $Et_2O{\rightarrow}BH_3$ referenced at 0 ppm), a value upfield shifted from that of free borane (75 ppm). The ^{11}B NMR spectroscopic chemical shift experienced in **5** is analogous to that for methide-abstracted borane zwitterions.[39] Binding of borane to the CH_2 group caused a dramatic upfield shift in the ^{13}C NMR and ^1H resonances for both the methylene carbon and hydrogens (carbon at 31.33 ppm, and diastereotopic hydrogens at ~2.7 and 2.31 ppm, respectively, and having a $^2J_{H-H}$ value of 20 Hz). Other than these diagnostic features, both the ^1H and ^{13}C NMR spectra are consistent with an asymmetrical NCCC′N chelating framework analogous to **2** (two inequivalent β-carbon resonances from the NCCC′N ring as well as inequivalent isopropyl methine and aryl groups, vide supra). Abstraction of THF or chemistry related to the alkylidene moiety was not observed with $B(C_6F_5)_3$, thus suggesting that the most accessible and nucleophilic site for Lewis acid coordination was the "CH_2" group in the new ligand scaffold $(ArNC(Me)CHC(CH_2)NAr)Ti^{2+}$. Formation of **5** can be rationalized on the basis of a charge delocalizing about the butadieneamine "$N_\alpha CC_\gamma C_\beta CH_2$" motif of **2**, to form a zwitterion **2a** shown in Scheme 4.

Charge separation in complex **5** can resonate in several forms (**5a**−**d**), as suggested in Scheme 4. To unambiguously confirm the coordination of borane to **2**, we resorted to single-crystal X-ray analysis (Figure 2). Table 2 lists selected metrical parameters for the single-crystal structure of **5**. While coordination of borane to the methylene group results in an overall fixed negative change at boron, positive charge delocalization can be proposed to be distributed about several atoms in the NCCC′NTi ring, including the Ti center. The metrical parameters observed in the solid state structure of **5** suggest that all resonances, **5a**−**d**, should be considered, given the resemblance for the pair of Ti−N_α and N_α−C_β distances (1.979(3) and 2.007(3) Å; 1.354(4) and 1.337(4) Å, respectively). Although canonical forms **5a** and **5c** seem intuitive based on electropositive character at the metal center, resonances **5b** and **5d** seem the most logical to propose in terms of carbocation character at the β-position being stabilized by N_α-lone pair donation. In fact, ^{13}C NMR spectroscopic data revealed that both β-carbons composing the NCCC′N plane had significantly shifted downfield (181.0 and 168.1 ppm, respectively, with respect to 153.2 and 141.9 ppm in **2**), in accord with these atoms having more carbocation-like character. A compiled list of salient spectroscopic data is shown in Table 1.

Scheme 4



Due to the carbocation character of the β-carbon in complex **5**, the N,N′-chelating scaffold in **2** should, in principle, be a better donor ligand than the chelating ligand in the zwitterion. Judging from the crystallographic data,

---

(39) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

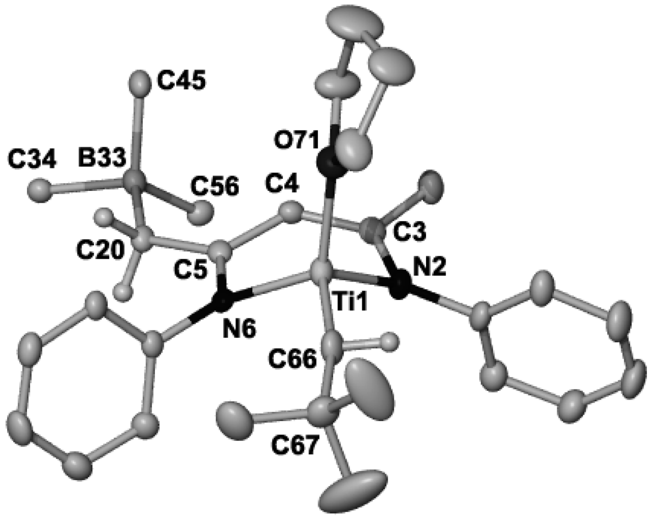
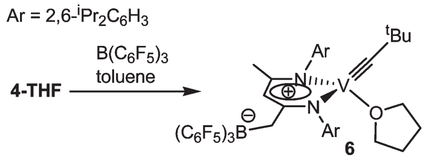


Figure 2. Perspective view of the solid state structure of **5** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of alkylidene and methylene groups (C66 and C20), have been omitted for clarity. Isopropyl aryl groups on the bis-anilide ligand, disordered solvent, and the perfluorophenyl groups on boron (with the exception of the ipso carbons, C34, C45, and C56) have also been omitted for clarity. Table 2 lists pertinent metrical parameters, and crystallographic parameters are listed in Table 3 (see Supporting Information).

Scheme 5



borane coordination to C20 results not only in rehybridization of carbon and boron to sp^3 but elongation of the C20−C5 (1.502(4) Å) from that of its neutral species **2** (Table 2, 1.413 (14) Å).[15] Likewise, the terminal Ti=C linkage is short (1.830 (4) Å) and the angle is distorted significantly from a prototypical sp^2-hybridized carbon, thus suggesting an α-hydrogen agostic interaction taking place with the Ti(IV) center. In addition, the alkylidene hydrogen is oriented perpendicular to the THF, with the metal center deviating 1.147 Å above the NCCC′N plane. The titanium−THF distance in **5** (Ti1−O71, 2.071(2) Å) is significantly shorter than in **2** (2.130(8) Å), thus implying a more electron deficient Ti center.

When a toluene solution containing **4** was added to borane, a similar reaction to that for the formation of **5** was observed. The resulting complex (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)V≡C^{t}Bu(THF) (**6**) was isolated in pure form and good yield (87%) as a red solid after crystallization from a toluene/hexane-layered solution (Scheme 5). Multinuclear NMR spectroscopy and X-ray crystallographic data proved the identity of the complex unambiguously. Several salient spectroscopic features of this new complex are the ^{13}C NMR spectrum displaying a broad resonance for the alkylidyne carbon at 366 ppm (−50 °C) as well as a broad ^{51}V NMR resonance at 489 ppm ($\Delta\nu_{1/2}$ = 2671 Hz). Both of the ^{13}C and ^{51}V NMR spectroscopic features are consistent with a terminal and diamagnetic neopentylidyne vanadium complex.[40] Most notably, the resulting complex shows features of a C_1 symmetric molecule that results from B(C$_6$F$_5$)$_3$ binding to the methylene group in the backbone. The hydrogens on the methylene group are also diastereotopic, showing identical $^2J_{H-H}$ values to that for the titanium analogue **5** (vide supra). The proton and carbon chemical shifts vary remarkably due to a change in hybridization of the center of B(C$_6$F$_5$)$_3$ binding (^{1}H NMR: from 3.52 and 3.29 in **4-THF** to 2.56 and 2.17 ppm in **6**; ^{13}C NMR: from 79.78 in **4-THF** to 31.84 ppm in **6**). In addition, the ^{19}F NMR spectrum reveals the difference between meta and para positions (Δ = 4 ppm), which is indicative of a four-coordinate borate group.[41] On the basis of our data, we confidently propose this new material to be the zwitterionic vanadium alkylidyne depicted in Scheme 5. In fact, addition of donor solvents such as Et$_2$O or THF does not appear to transform **6** back to **4-THF** or **4-OEt$_2$** concurrent with (F$_5$C$_6$)$_3$B←THF ejection.

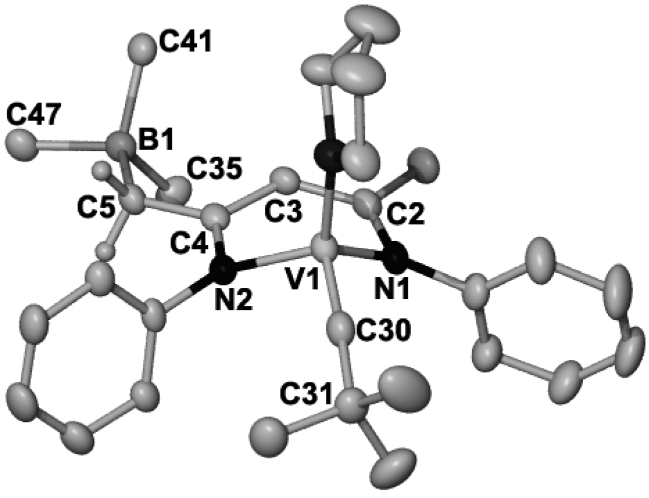


Figure 3. Perspective view of the solid state structure of **6** with thermal ellipsoids at the 50% probability level. Hydrogens, with the exception of the methylene groups (C5), have been omitted for clarity. Isopropyl aryl groups on the bis-anilide ligand, disordered solvent, and the perfluorophenyl groups on boron (with the exception of the ipso carbons, C35, C41, and C47) have also been omitted for clarity. Table 2 lists pertinent metrical parameters, and crystallographic parameters are listed in Table III (see Supporting Information).

A solid state structure of **6** confirms the proposed connectivity (Figure 3) and displays structural features analogous to the titanium derivative **5**. As anticipated, borane coordination to C5 results in rehybridization of carbon and boron to a tetrahedral geometry concurrent with elongation of the C5−C4 bond (1.514(4) Å) from that of its ether analogue of the neutral derivative, namely, **4-OEt$_2$** (Table 2, 1.418(5) Å).[13] The diastereotopic nature of the hydrogen on C5 is clearly visible from the structure. Preservation of the terminal V≡C group is evident from the short bond length of 1.686(3) Å and linear angle of 175.6(3)°. The vanadium−THF distance in **6** (V1−O1, 2.002(2) Å) is comparable to that of **5**, but shorter than that of the borane-free complex **4-THF** (2.022(3) Å, vide supra), again implying a more electron deficient metal center.

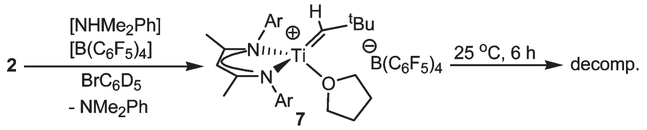
Synthesis and Characterization of a Cationic Titanium(IV) Neopentylidene and a Vanadium(V) Neopentylidyne. Given the nucleophilic nature of the terminal methylene moiety in

---

(40) Rehder, D. *Coord. Chem. Rev.* **2008**, *252*, 2209.

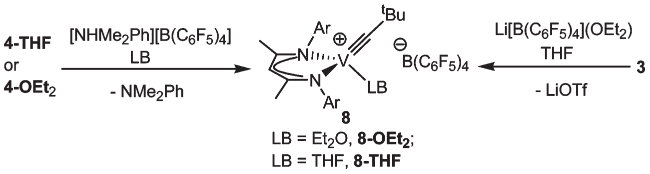
(41) (a) Blackwell, J. M.; Piers, W. E.; Parvez, M. *Org. Lett.* **2002**, *2*, 695. (b) Horton, A. D.; With, J.-D. *Organometallics* **1997**, *16*, 5424.

Scheme 6



compounds **2** and **4**, and the fact that protonation studies occur at this site,[32] we suspected that a similar transformation would happen in our system, to re-form the β-diketiminate ancillary. Accordingly, treatment of **2** in toluene with solid $[HNMe_2Ph][B(C_6F_5)_4]$ at 25 °C rapidly caused an oily product to separate from the medium but without a significant color change in the solution. Examination of the reaction mixture by ^1H NMR spectroscopy of the oily residue revealed formation of the salt that we speculate to be $[([ArNC(Me)]_2CH)Ti{=}CH^tBu(THF)][B(C_6F_5)_4]$ (**7**) along with some other byproducts (Scheme 6). For instance, the ^1H NMR spectrum revealed formation of a C_2 symmetric ligand scaffold, namely, re-formation of the β-diketiminate ligand $[ArNC(Me)]_2CH^-$. Unfortunately, longer time frames (from minutes to hours) resulted in gradual decomposition of **7** to a myriad of products, especially if the solution was kept at room temperature or if an attempt was made to isolate a solid. The thermal instability of **7** is not surprising, since **1** itself has a $t_{1/2}$ of 45 min at 57 °C.[21] In fact, the nature of the pseudo halide or halide affects the rate for the decomposition of the $[([ArNC(Me)]_2CH)Ti{=}CH^tBu]^+$ scaffold to the point where weaker π-donors (Br^- and I^-) result in enhanced rate of decomposition.[21] In the case of **7**, the presence of a more labile ligand such as THF presumably facilitates the rate for decomposition of the latent low-coordinate titanium alkylidene via intramolecular C−H activation as well cross-metathesis pathways among many other possibilities. Our inability to obtain suitable single crystals for diffraction studies as well as the poor characterization of **7** prompted us to conduct an in situ, low-temperature study of this reactive species in bromobenzene-d_5. Hence the ^1H NMR spectrum of **7**, generated in situ at lower temperatures, was greatly improved and confirmed formation of a C_s symmetric system by the presence of diagnostic alkylidene α-hydrogen (3.17 ppm) as well as the methine γ-CH resonance for the β-diketiminate backbone (4.82 ppm) and equivalent β-methyl groups (168.4 ppm). Maintaining the sample cooled to −15 °C allowed us to collect relatively clean ^{13}C, ^{19}F, and ^{11}B NMR spectroscopic data for **7**, for the first terminal alkylidene salt of a group 4 metal (see Experimental Section for all details and Supporting Information for spectra). The ^{13}C NMR spectroscopic data confirmed the presence of a C_s symmetric terminal alkylidene resonance at 269.3 ppm (we were unable, however, to collect reliable J_{C-H} data due to the poor solubility of **7** in bromobenzene-d_5). However, we anticipate a low J_{C-H} value, if not comparable, to that of **5**, most likely due to the unsaturated and thus electron-deficient nature of the Ti(IV) center. Overall, the spectral features for **7** are analogous to **1** and other C_s symmetric neopentylidene complexes supported with the β-diketiminate ligand $[ArNC(Me)]_2CH^-$.[22] Likewise, the similarity of the ^1H NMR spectra of **1** and **7** apparently suggests the α-hydrogen in **7** to be oriented anti with respect to the THF ligand.[21,28a] In contrast, treating **1** with $Li[B(C_6F_5)_4](OEt_2)$ results in complicated mixtures, even when the reaction was performed at low temperatures in bromobenzene-d_5. Likewise, attempts to protonate the alkyl ligand in $([ArNC(Me)]_2CH)Ti{=}CH^tBu(CH_2SiMe_3)$[15b] with a reagent such as $[HNMe_2Ph][B(C_6F_5)_4]$ has not been successful. Therefore, our strategy to reconstruct the β-diketiminate ligand from the chelate scaffold in complex **2** appears to be selective and relatively clean, despite the reactive nature of the product. To our knowledge, complex **7** represents the only documented example of a discrete cationic titanium (or group 4) complex bearing the terminal alkylidene group.

Scheme 7



Because we could not obtain solid state structural information for **7**, we decided to generate a cationic alkylidyne analogue of vanadium. The stability of such a scaffold, $[([ArNC(Me)]_2CH)V{\equiv}C^tBu]^+$, should in principle be greater given the additional M−C π-bond involved, thence providing a higher formal electron count on the V(V) ion as opposed to the Ti(IV) analogue. This hypothesis was further corroborated by the fact that a terminal cationic vanadium alkylidyne complex, $[([ArNC(Me)]_2CH)V{\equiv}C^tBu(THF)][BPh_4]$,[13] has been isolated. This complex was remarkably stable (decomposition occurred only after 20 days at 65 °C) to an intramolecular cross-metathesis transformation of the neopentylidyne with the imine group composing the β-diketiminate NCCCN template.[21,28] In view of that, when a toluene solution of **4-THF** was added to solid $[HNMe_2Ph][B(C_6F_5)_4]$, an immediate product was observed to form upon the dissolution of solid $[HNMe_2Ph][B(C_6F_5)_4]$. Concentrating the solution resulted in gradual precipitation of the salt $[([ArNC(Me)]_2CH)V{\equiv}C^tBu(THF)][B(C_6F_5)_4]$ (**8-THF**) in 81% yield (Scheme 7). The connectivity in complex **8-THF** is assigned on the basis of ^1H, ^{13}C, ^{19}F, ^{11}B, and ^{51}V NMR spectra (Table 1). While the ^1H NMR spectrum confirmed the formation of a C_2 symmetric β-diketiminate ligand by protonation of the methylene moiety in **4-THF**, the ^{13}C NMR spectrum unambiguously established retention of the alkylidyne unit (374.7 ppm, −55 °C). The combination of ^{19}F, ^{11}B, and ^{51}V (548 ppm, $\Delta\nu_{1/2} = 1966$ Hz) NMR spectral data also endorsed the formation of a discrete diamagnetic vanadium salt having the weakly coordinating anion $B(C_6F_5)_4$. Therefore, the solution NMR spectroscopic data for compound **8-THF** suggests a symmetrically identical species to the BPh_4 salt derivative reported earlier by us.[13] Formation of **8-THF** was also achieved by treating **3** with $Li[B(C_6F_5)_4](OEt_2)$ in THF at −35 °C (Scheme 7). Unlike complex **7**, which gradually decayed in solution at room temperature, complex **8-THF** appears to be relatively stable in solutions of THF, bromobenzene, and halogenated solvents such as CH_2Cl_2.

Although we obtained complete NMR spectroscopic data for **8-THF**, single crystals suitable for diffraction analysis were obtained with **8-OEt₂** (multinuclear NMR spectroscopic data is virtually identical to **8-THF**). Single crystals were grown from a toluene/hexane-layered solution cooled to −35 °C over 3 days, and the solid state structure was determined by X-ray diffraction analysis. Figure 4 depicts a four-coordinate vanadium(V) center having overall C_s symmetry consistent with the NMR spectral data (vide supra). The near-linear (174.36(12)°) arrangement of V1−C38−C39

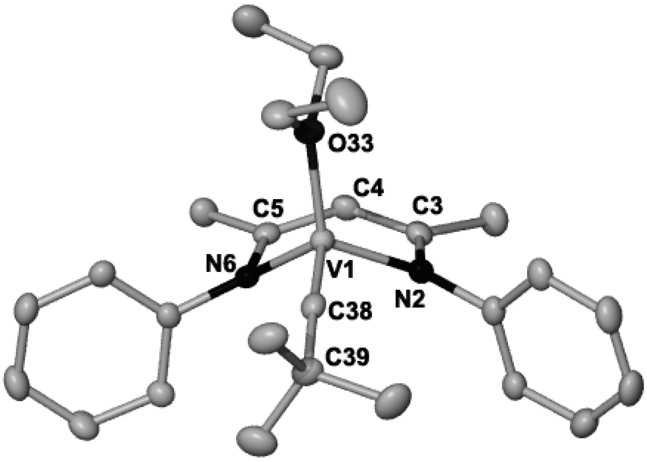


Figure 4. Perspective view of the solid state structure of **8-OEt$_2$** with thermal ellipsoids at the 50% probability level. Hydrogens have been omitted for clarity. Isopropyl groups on the β-diketiminate aryls, disordered solvent, and the borate anion B $(C_6F_5)_4$ have also been omitted for clarity. Table 2 lists pertinent metrical parameters, and crystallographic parameters are listed in Table 3 (see Supporting Information).

and short V1−C38 distance (1.6809(15) Å) in complex **8-OEt$_2$** are clearly indicative of a vanadium alkylidyne as in the BPh_4 salt analogue (1.696(3) Å).[13] The vanadium center is displaced 1.112 Å above the β-diketiminate plane (Table 2 provides salient metrical parameters for the solid state structure of **8-OEt$_2$**). The solid state structure is consistent with the protonation taking place at the formal methylene group since the V−N distances fall within the expected values for a $[ArNC(Me)]_2CH]V$ scaffold (~1.943 Å).[15]

Conclusions

We have demonstrated that deprotonating the β-methyl group of the $(ArNC(Me)]_2CH)M$ (M = Ti(IV) and V(V)) scaffold provides the dianionic N,N′-chelating (ArNC(Me)-CHC(CH$_2$)NAr) ligand. The nucleophilic character at the terminal methylene motif of this ligand has allowed us to convert such an ancillary support to a zwitterion by addition of $B(C_6F_5)_3$ or to a discrete salt by protonation with $[HNMe_2Ph][B(C_6F_5)_4]$. Therefore, the sometimes vulnerable nature of the β-diketiminate ligand, $[ArNC(Me)]_2CH^-$, can play an important role in assembling the first examples of charge-separated species of Ti and V compounds, specifically compounds having terminal metal−carbon multiple bonded ligands. We are currently exploring the reactive nature of the M−C multiple bond in compounds such as **2** and **4** since these systems appear to be more kinetically stable than compounds supported by the original β-diketiminate ligand. This feature is likely due to the fact that the vulnerable imine group is no longer available for the intramolecular Wittig-like rearrangement. We are also beginning to uncover the chemistry offered by unusual alkylidene and alkylidyne zwitterions such as compounds **5** and **6**, given that these systems could be studied as catalysts[42] or as potential sources of zwitterionic, low-coordinate titanium alkylidenes and vanadium alkylidynes by displacement of the neutral ligand THF.

Experimental Details

General Considerations. Unless otherwise stated, all operations were performed in an M. Braun Lab Master double drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[43] Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in Sure Seal reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethyl ether was dried by passage through a column of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into collection vessels before being carried into a drybox. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed, and vacuum transferred to 4 Å molecular sieves. BrC_6D_5 was purchased from CIL and degassed three times. After transferring into the glovebox it was passed through alumina in a pipet column. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. All the starting materials such as **1**, **2**, and **3** were prepared following the literature procedure.[13,15b] $B(C_6F_5)_3$ and $[HNMe_2Ph][B(C_6F_5)_4]$ were purchased from Boulder Scientific. $[HNMe_2Ph][B(C_6F_5)_4]$ was dried at 60 °C for 2 days under reduced pressure to remove traces of CH_2Cl_2. KCH_2Ph was prepared according to the literature procedure.[44] CHN analyses were performed by Midwest Microlab, Indianapolis, IN. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^{1}H NMR spectra are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 ppm). ^{11}B and ^{51}V NMR spectra were collected using a Varian 500 MHz NMR spectrometer. $BF_3 \cdot OEt_2$ (set at 0 ppm) and $VOCl_3$ (set as 0 ppm) were used as external standards for ^{11}B and ^{51}V NMR, respectively. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at low temperatures.[45,46]

Synthesis of the Complex (ArNC(Me)CHC(CH$_2$)NAr) V≡C^{t}Bu(OEt$_2$) (4-OEt$_2$). In a vial was dissolved **3** (80 mg, 0.12 mmol) in pentane (10 mL), and the solution was cooled to −35 °C. To the cold solution was added a cold (−35 °C) pentane (5 mL) solution of ^{t}BuLi [7.46 mg, 0.12 mmol], and the color of the solution changed to brown-red. The solution was stirred for 5 min, and 4 drops of ether were added. The solution was stirred for a further 1 h and dried under vacuum. The residue was extracted with hexane and filtered. The filtrate was reduced in volume in vacuo and cooled to −35 °C to afford **4-OEt$_2$** as dark red crystals [43 mg, 0.07 mmol, 58% yield].

For **4-OEt$_2$**: ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.49−7.25 (m, 6H, C_6H_3), 4.33 (s, 1H, ArNC(Me)C*H*C(CH$_2$)NAr), 4.23 (septet, 1H, C*H*Me$_2$), 4.15 (septet, 1H, C*H*Me$_2$), 4.03−3.92 (m, 5H, C*H*Me$_2$, O(C*H$_2$*CH$_3$)$_2$), 3.86 (septet, 1H, C*H*Me$_2$), 3.49 (s, 1H, ArNC(Me)CHC(C*H$_2$*)NAr), 3.24 (s, 1H, ArNC(Me)-CHC(C*H$_2$*)NAr), 1.67 (d, 3H, CH*Me$_2$*), 1.63−1.58 (overlapping doublets, 9H, CH*Me$_2$*), 1.54 (d, 3H, CH*Me$_2$*), 1.48 (d, 3H, CH*Me$_2$*), 1.43 (s, 3H, ArNC(*Me*)CHC(CH$_2$)NAr), 1.37

---

(42) Borane coordination to remote sites of ancillary ligands has been used to generate efficient catalysts. (a) Azoulay, J. D.; Rojas, R. S.; Serrano, A. V.; Ohtaki, H.; Galland, G. B.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1089. (b) Chen, Y.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108. (c) Lee, B. Y.; Bu, X.; Bazan, G. C. *Organometallics* **2001**, *20*, 5425. (d) Wasilke, J.-C.; Komon, Z. J. A.; Bu, X.; Bazan, G. C. *Organometallics* **2004**, *23*, 4174. (e) Kim, Y. H.; Kim, T. H.; Yeoul, B.; Woodmansee, L. D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082.

(43) For a general description of the equipment and techniques used in carrying out this chemistry see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington D.C., 1987; p 79.

(44) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-González, D.; Parkin, A.; Parsons, S. *Chem.—Eur. J.* **2003**, *9*, 4820.

(45) *SAINT 6.1*; Bruker Analytical X-Ray Systems: Madison, WI.

(46) *SHELXTL-Plus V5.10*; Bruker Analytical X-Ray Systems: Madison, WI.

(d, 3H, CH*Me*$_2$), 1.30 (d, 3H, CH*Me*$_2$), 0.98 (t, 4H, O(CH$_2$C*H*$_3$)$_2$), 0.46 (s, 9H, V≡CC*Me*$_3$). ^{13}C NMR (−50 °C, 100.6 MHz, C$_6$D$_5$CD$_3$): δ 343.6 (V≡*C*CMe$_3$). ^{13}C NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 153.6 (aryl), 153.1 (ArN*C*(Me)CHC(CH$_2$)NAr), 151.6 (aryl), 144.0 (aryl), 143.9 (aryl), 143.5 (aryl), 143.4 (aryl), 141.8 (ArNC(Me)CH*C*(CH$_2$)NAr), 125.3 (aryl), 125.2 (aryl), 124.6 (aryl), 123.8 (aryl), 123.3 (aryl), 122.9 (aryl), 94.93 (d, J_{C-H} = 156 Hz, ArNC(Me)*C*HC(CH$_2$)NAr), 80.23 (t, J_{C-H} = 158 Hz, ArNC(Me)CHC(*C*H$_2$)NAr), 74.41 (O*Et*$_2$), 56.26 (V≡C*C*Me$_3$), 29.30 (V≡CC*Me*$_3$), 29.10 (*C*HMe$_2$), 28.60 (*C*HMe$_2$), 28.56 (*C*HMe$_2$), 28.37 (*C*HMe$_2$), 26.34 (*Me*), 25.89 (*Me*), 25.85 (*Me*), 25.74 (*Me*), 25.41 (*Me*), 25.07 (*Me*), 24.87 (*Me*), 24.35 (*Me*), 23.13 (*Me*), 13.79 (O*Et*$_2$). ^{51}V NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 310 (Δ$\nu_{1/2}$ = 741 Hz). Satisfactory elemental analysis was not obtained due to the thermal instability of the complex.

Synthesis of the Complex (ArNC(Me)CHC(CH$_2$)NAr)V≡C^{t}Bu(THF) (4-THF). In a round-bottom flask was dissolved **3** (160 mg, 0.24 mmol) in THF (20 mL), and the solution was cooled to −35 °C. To the cold solution was added a cold (−35 °C) THF (2 mL) solution of KCH$_2$Ph (30.2 mg, 0.24 mmol), and the color of the solution changed to brown-red immediately after the addition. The solution was stirred for 5 min and dried in vacuo. The dried mass was extracted with 20 mL of pentane and filtered. The filtrate was reduced in volume to 5 mL and stored at −35 °C to yield bright red crystals of **4-THF** within 24 h (65 mg, 0.11 mmol, 46% yield).

For **4-THF**: ^{1}H NMR (23 °C, 399.8 MHz, C$_6$D$_6$): δ 7.51−7.26 (m, 6H, C$_6$*H*$_3$), 4.38 (s, 1H, ArNC(Me)C*H*C(CH$_2$)NAr), 4.23 (septet, 1H, C*H*Me$_2$), 4.15 (br, 4H, THF), 4.00 (overlapping septets, 2H, C*H*Me$_2$), 3.55 (septet, 1H, C*H*Me$_2$), 3.52 (s, 1H, ArNC(Me)CHC(C*H*$_2$)NAr), 3.29 (s, 1H, ArNC(Me)CHC(C*H*$_2$)NAr), 1.70 (d, 3H, CH*Me*$_2$), 1.64 (d, 3H, CH*Me*$_2$), 1.61−1.55 (m, 9H, overlapping singlet of ArNC(*Me*)CHC(CH$_2$)NAr and doublets of CH*Me*$_2$), 1.49 (d, 3H, CH*Me*$_2$), 1.44 (br, 4H, THF), 1.38 (overlapping doublets, 6H, CH*Me*$_2$), 1.27 (d, 3H, CH*Me*$_2$), 0.49 (s, 9H, V≡CC*Me*$_3$). ^{13}C NMR (−50 °C, 100.6 MHz, C$_6$D$_5$CD$_3$): δ 346.7 (V≡*C*CMe$_3$). ^{13}C NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 153.1 (aryl), 152.6 (ArN*C*(Me)CHC(CH$_2$)NAr), 151.6 (aryl), 144.3 (aryl), 143.9 (aryl), 143.5 (aryl), 143.4 (aryl), 141.1 (ArNC(Me)CH*C*(CH$_2$)NAr), 125.5 (aryl), 125.4 (aryl), 124.7 (aryl), 123.9 (aryl), 123.2 (aryl), 123.0 (aryl), 94.59 (d, J_{C-H} = 160 Hz, ArNC(Me)*C*HC(CH$_2$)NAr), 79.78 (t, J_{C-H} = 158 Hz), ArNC(Me)CHC(*C*H$_2$)NAr), 78.67 (THF), 56.24 (V≡C*C*Me$_3$), 29.85 (V≡CC*Me*$_3$), 29.52 (*C*HMe$_2$), 28.60 (*C*HMe$_2$), 28.80 (*C*HMe$_2$), One *C*HMe$_2$ is buried. 26.55 (*Me*), 26.46 (*Me*), 26.31 (*Me*), 26.15 (*Me*), 25.64 (THF), 25.14 (*Me*), 24.96 (*Me*), 24.80 (*Me*), 24.46 (*Me*), 23.31 (*Me*). ^{51}V NMR (23 °C, 100.6 MHz, C$_6$D$_6$): δ 286 (Δ$\nu_{1/2}$ = 680 Hz). Anal. Calcd for C$_{38}$H$_{57}$N$_2$OV: C, 74.97; H, 9.44; N, 4.60. Found: C, 75.22; H, 9.48; N, 4.83.

Synthesis of the Complex (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)Ti=CH^{t}Bu(THF) (5). In a vial **2** (30 mg, 0.50 mmol) was taken in 2 mL of toluene and added to solid B(C$_6$F$_5$)$_3$ (26 mg, 0.50 mmol) along with stirring. No significant color change was observed after the mixing. The solution mixture was stirred for 30 min and then dried in vacuo. Multinuclear NMR proved the identity of the complex.

^{1}H NMR (23 °C, 399.8 MHz, BrC$_6$D$_5$): δ 7.22−6.81 (m, 6H, C$_6$*H*$_3$), 5.52 (s, 1H, ArNC(Me)C*H*C(CH$_2$B)NAr), 4.03−3.81 (m, 4H, THF), 3.02 (s, 1H, Ti=C*H*^{t}Bu, based on HMQC), 2.83−2.72 (m, 2H, C*H*Me$_2$ and ArNC(Me)CHC(C*H*$_2$B(C$_6$F$_5$)$_4$)NAr resonances overlapped with $^2J_{H-H}$ not resolved), 2.60 (septet, 1H, C*H*Me$_2$), 2.51 (septet, 1H, C*H*Me$_2$), 2.42 (septet, 1H, C*H*Me$_2$), 2.31 (d, 1H, ArNC(Me)CHC(C*H*$_2$B(C$_6$F$_5$)$_4$)NAr, $^2J_{H-H}$ = 20 Hz), 1.84 (br, 4H, THF), 1.51 (d, 3H, CH*Me*$_2$), 1.42−1.33 (m, 6H, ArNC(*Me*)CHC(CH$_2$B(C$_6$F$_5$)$_4$)NAr and CH*Me*$_2$ resonances overlapped), 1.30 (d, 3H, CH*Me*$_2$), 1.13 (overlapping doublets, 4H, CH*Me*$_2$), 0.97 (d, 3H, CH*Me*$_2$), 0.76 (d, 3H, CH*Me*$_2$), 0.69 (d, 3H, CH*Me*$_2$), 0.23 (s, 9H, Ti=CH^t*Bu*). ^{13}C NMR (−5 °C, 100.6 MHz, BrC$_6$D$_5$): δ 260.01 (Ti=*C*HCMe$_3$), 180.96 (C(Me)CH*C*(CH$_2$B), 168.04 (*C*(Me)CHC(CH$_2$B), 163.11 (aryl), 149.20 ((C$_6$F$_5$)$_3$B), 146.83 ((C$_6$F$_5$)$_3$B), 145.51 (aryl), 144.82 (aryl), 142.29 (aryl), 141.10 (aryl), 140.35 (aryl), 140.14 (aryl), 139.75 (aryl), 139.54 (aryl), 138.42 ((C$_6$F$_5$)$_3$B), 135.97 ((C$_6$F$_5$)$_3$B), 128.38 (aryl), two aryl peaks are buried under solvent BrC$_6$D$_5$ resonances. 91.05 (C(Me)*C*HC(CH$_2$B)), 78.52 (THF), 51.01 (Ti=CH*C*Me$_3$) 34.37 (*C*HMe$_2$), 31.90 (C(Me)CHC(*C*H$_2$B) 30.46 (*C*HMe$_2$), 29.84 (*C*HMe$_2$), 29.60 (*C*HMe$_2$), 28.69 (Me), 28.32 (Me), 27.75 (Me), 25.92 (THF), 25.66 (Me), 24.49 (Me), 24.20 (Me), 23.71 (Me), 23.26 (Me), 23.04 (Me), 22.74 (Me). ^{19}F NMR (23 °C, 282.3 MHz, BrC$_6$D$_5$): δ −131.35 (B(C$_6$F$_5$)$_3$), −160.94 (B(C$_6$F$_5$)$_3$), −165.27 (B(C$_6$F$_5$)$_3$). ^{11}B NMR (24 °C, 160.61 MHz, BrC$_6$D$_5$): δ −14.45. Satisfactory elemental analysis was not obtained due to the thermal instability of the complex.

Synthesis of the Complex (ArNC(Me)CHC(CH$_2$B(C$_6$F$_5$)$_3$)NAr)V≡C^{t}Bu(THF) (6). In a vial was taken **4-THF** (20 mg, 0.033 mmol) dissolved in 2 mL of toluene. The toluene solution was added to an another vial containing solid B(C$_6$F$_5$)$_3$ (16.9 mg, 0.033 mmol). No color change was observed immediately after the addition. The mixture was stirred for 30 min, after which it was dried in vacuo. The dried mass was washed with 3 mL of pentane and dried again. The dried mass was dissolved in toluene/hexane and stored at −45 °C for 12 h to yield red crystals of **6** (32 mg, 0.029 mmol, 87% yield). Multinuclear NMR of the dried mass proved the identity of the desired complex.

^{1}H NMR (23 °C, 300.07 MHz, CDCl$_3$): δ 7.29−7.19 (m, 6H, C$_6$*H*$_3$), 5.12 (s, 1H, ArNC(Me)C*H*C(CH$_2$B)NAr, 3.10−2.88 (overlapped septets, 2H, C*H*Me$_2$), 2.71−2.56 (overlapped septets, 2H, C*H*Me$_2$), 2.56 (d, 1H, ArNC(Me)CHC(C*H*$_2$B)NAr, $^2J_{H-H}$ = 20 Hz), 2.30 (br, 4H, THF), 2.17 (d, 1H, ArNC(Me)CHC(C*H*$_2$B)NAr), $^2J_{H-H}$ = 20 Hz), 1.63 (s, 3H, ArNC(*Me*)CHC(CH$_2$B)NAr), 1.59−1.44 (overlapping doublets, 9H, CH*Me*$_2$), 1.25−1.16 (m, 13H, overlapped resonance of CH*Me*$_2$ and THF), 1.02 (d, 3H, CH*Me*$_2$), 0.84 (d, 3H, CH*Me*$_2$), 0.10 (s, 9H, V≡CC*Me*$_3$). ^{13}C NMR (−50 °C, 100.6 MHz, CDCl$_3$): δ 366 (V≡*C*CMe$_3$). ^{13}C NMR (23 °C, 125.89 MHz, CDCl$_3$): δ 180.21 (ArNC(Me)CH*C*(CH$_2$B)NAr, 161.83 (ArN*C*(Me)CHC(CH$_2$B)NAr), 149.24 ((C$_6$F$_5$)$_3$B), 148.29 (aryl), 147.38 (aryl), 147.08 ((C$_6$F$_5$)$_3$B), 141.12 (aryl), 140.61 (aryl), 137.72 ((C$_6$F$_5$)$_3$B), 135.19 ((C$_6$F$_5$)$_3$B), 127.70 (aryl), 127.50 (aryl), 124.89 (aryl), 124.65 (aryl), 123.71 (aryl), 123.60 (aryl), 89.83 (ArNC(Me)*C*HC(CH$_2$B)NAr), 65.90 (THF), 60.04 (V≡C*C*Me$_3$), 31.84 (ArNC(Me)CHC(*C*H$_2$B)NAr), 30.54 (*C*HMe$_2$), 28.64 (*C*HMe$_2$), 28.41 (*C*HMe$_2$), 28.13 (V≡CC*Me*$_3$), 27.73 (*C*HMe$_2$), 26.34 (THF), 25.84 (*Me*), 25.04 (*Me*), 24.84 (*Me*), 24.50 (*Me*), 23.88 (*Me*), 23.52 (*Me*), 23.27 (two *Me* overlapped). ^{13}C NMR (−50 °C, 100.6 MHz, CDCl$_3$): δ 365.75 (V≡*C*CMe$_3$). ^{19}F NMR (25 °C, 282.32 MHz, CDCl$_3$): δ −131.22 (B(C$_6$F$_5$)$_3$), −161.65 (B(C$_6$F$_5$)$_3$), −165.89 (B(C$_6$F$_5$)$_3$). ^{51}V NMR (24 °C, 131.58 MHz, CDCl$_3$): δ 489 (Δ$\nu_{1/2}$ = 2671 Hz). ^{11}B NMR (24 °C, 160.61 MHz, CDCl$_3$): δ −14.47. Satisfactory elemental analysis was not obtained due to the thermal instability of the complex.

Synthesis of the Complex [([ArNC(CH$_3$)]$_2$CH)Ti=CH^{t}Bu(THF)][B(C$_6$F$_5$)$_4$] (7). In a vial **2** was taken (15 mg, 0.025 mmol) in 2 mL of toluene and added to the solid [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (21.1 mg, 0.025 mmol). After the addition the color of the mixture remained brown without any change. The mixture was stirred for 30 min, after which it was dried in vacuo. The dried mass was washed with hexane (3 times taking 2 mL each) and dried again. Multinuclear NMR spectroscopy proved the identity of the synthesized complex.

^{1}H NMR (23 °C, 399.8 MHz, BrC$_6$D$_5$): δ 7.21−7.00 (m, 6H, C$_6$H$_3$), 4.82 (s, 1H, ArNC(Me)C*H*C(Me)NAr), 3.84 (br, 4H, THF), 3.17 (s, 1H, Ti=C*H*^{t}Bu, based on HMQC), 2.69 (septet, 2H, C*H*Me$_2$), 2.18 (septet, 2H, C*H*Me$_2$), 1.68 (br, 4H, THF), 1.49 (s, 1H, ArNC(*Me*)CHC(*Me*)NAr), 1.23 (d, 6H, CH*Me*$_2$), 1.08 (d, 6H, CH*Me*$_2$), 0.97 (d, 6H, CH*Me*$_2$), 0.83 (d, 6H, CH*Me*$_2$), 0.18 (s, 9H, Ti=CH^t*Bu*). ^{13}C NMR (−15 °C, 100.6 MHz, BrC$_6$D$_5$): δ 269.31 (Ti=*C*HCMe$_3$), 168.43

(*C*(Me)CH*C*(Me)), 149.75 ($(C_6F_5)_3B$), 147.37 ($(C_6F_5)_3B$), 143.90 (aryl), 140.54 (aryl), 139.27 (aryl), 137.79 ($(C_6F_5)_3B$), 135.36 ($(C_6F_5)_3B$), 128.51 (aryl), 125.27 (aryl), 124.02 (aryl), 91.80 (C(Me)*C*HC(Me), 78.21 (*THF*), 52.51 (Ti=CH-*C*Me$_3$), 31.58 (*C*HMe$_2$), 30.17 (CHMe$_2$), 28.62 (*Me*), 25.85 (*Me*), 25.68 (*THF*), 23.95 (*Me*), 23.82 (*Me*), 24.18 (*Me*), 22.91 (*Me*). ^{19}F NMR (23 °C, 282.3 MHz, BrC$_6$D$_5$): δ −132.41 (B-$(C_6F_5)_4$), −162.51 ($B(C_6F_5)_4$), −166.40 ($B(C_6F_5)_4$). ^{11}B NMR (24 °C, 160.61 MHz, BrC$_6$D$_5$): δ −15.65. Elemental analysis was not obtained due to the thermal instability of the complex.

Synthesis of the Complex [([ArNC(CH$_3$)]$_2$CH)V≡C^{t}Bu-(THF)][B(C$_6$F$_5$)$_4$] (8-THF). In a vial was taken **4-THF** (15 mg, 0.025 mmol), which was dissolved in 3 mL of toluene. The toluene solution was added to an another vial containing solid [NHMe$_2$Ph][$B(C_6F_5)_4$] (20.6 mg, 0.025 mmol). No color change was observed immediately after the addition. The mixture was stirred for 40 min, after which it was dried in vacuo. The dried mass was washed with 3 mL of pentane and dried again. Multinuclear NMR of the dried mass proved the identity of the desired complex (25.6 mg, 0.020 mmol, 81% yield).

^{1}H NMR (23 °C, 400.11 MHz, CDCl$_3$): δ 7.27−7.24 (m, 6H, C$_6$*H*$_3$), 4.82 (s, 1H, ArNC(Me)C*H*C(Me)NAr), 2.97 (septet, 2H, C*H*Me$_2$), 2.59 (septet, 2H, C*H*Me$_2$), 2.21 (br, 4H, THF), 1.84 (s, 6H, ArNC(*Me*)CHC(*Me*)NAr), 1.49 (d, 6H, CH*Me*$_2$), 1.24 (d, 6H, CH*Me*$_2$), 1.13 (d, 6H, CH*Me*$_2$), 1.04 (d, 6H, CH*Me*$_2$),0.73 (br, 4H, THF), 0.05 (s, 9H, V≡CC*Me*$_3$). ^{13}C NMR (−55 °C, 100.6 MHz, CDCl$_3$): δ 374.7 (V≡*C*CMe$_3$). ^{13}C NMR (23 °C, 125.89 MHz, CDCl$_3$): δ 167.53 (ArN*C*(Me)CHC(Me)NAr), 149.30 ($(C_6F_5)_4B$), 147.23 (aryl), 146.92 ($(C_6F_5)_4B$), 140.19 (aryl), 139.50 (aryl), 137.45 ($(C_6F_5)_4B$), 135.02 ($(C_6F_5)_4B$), 128.43 (aryl), 125.12 (aryl), 123.98 (aryl), 90.47 (ArNC(Me)-*C*HC(Me)NAr), 65.86 (*THF*), 61.80 (V≡C*C*Me$_3$), 31.49 (*C*HMe$_2$), 28.79 (*C*HMe$_2$), 27.96 (*Me*), 26.48 (*THF*), 25.71 (*Me*), 24.55 (*Me*), 24.21 (*Me*), 24.11 (*Me*). One −*Me* resonance is buried under other resonances. ^{19}F NMR (25 °C, 282.32 MHz, CDCl$_3$): −133.03 ($B(C_6F_5)_4$), −163.43 ($B(C_6F_5)_4$), −167.31 (B-$(C_6F_5)_4$). ^{51}V NMR (24 °C, 131.58 MHz, CDCl$_3$): δ 548 ($\Delta\nu_{1/2}$ = 1966 Hz). ^{11}B NMR (24 °C, 160.61 MHz, CDCl$_3$): δ −15.63. Multiple attempts to obtain satisfactory elemental analysis failed. The ether analogue, **8-OEt$_2$**, was prepared similarly to **8-THF**, except substituting THF for Et$_2$O.

Acknowledgment. We thank Indiana University−Bloomington, the Dreyfus Foundation, the Sloan Foundation, and the NSF (CHE-0348941) for financial support of this research.

Supporting Information Available: Complete crystallographic data (**4·OEt$_2$**, **5**, **6**, and **8-OEt$_2$**) and synthetic and spectroscopic details (including multinuclear NMR spectra for complexes **4**−**8**) for new compounds are available free of charge via the Internet at http://pubs.acs.org.