DOI: 10.1002/ange.201007876

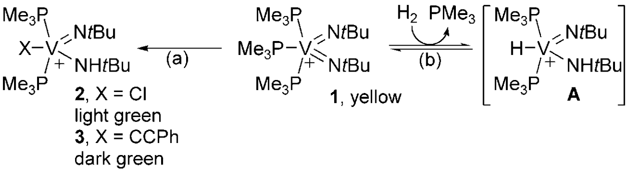
Catalytic Hydrogenation

Z-Selective Semihydrogenation of Alkynes Catalyzed by a Cationic Vanadium Bisimido Complex**

Henry S. La Pierre, John Arnold, and F. Dean Toste**

Early-transition-metal hydrogenation catalysts have received less attention than comparable late-transition-metal systems, particularly since the discovery of Wilkinson's catalyst.[1] This emphasis on late-transition-metal systems has been largely driven by practical concerns including functional-group tolerance and ease of handling. Further examination of early-transition-metal systems is particularly attractive from two viewpoints: 1) the identification and elucidation of unusual mechanisms of dihydrogen activation and 2) the application of the intrinsic properties of early transition metals, in particular high-valent complexes, to the selective hydrogenation of alkynes to *Z* alkenes. This transformation is typically accomplished by Lindlar's catalyst, and is practically difficult to employ and suffers, particularly in the case of conjugated aromatic systems, from *E*/*Z* isomerization and over-hydrogenation.[2] The development of effective molecular catalysts for this transformation remains an area of intense research with recent notable success.[3]

We previously reported the intermediacy of a 1,2-addition of a Si–H σ bond to an oxo ligand of $[ReIO_2(PPh_3)_2]$ in the catalytic hydrosilylation of ketones.[4] We hypothesized that a properly ligated Group 5 analogue of $[ReIO_2(PPh_3)_2]$ could afford the activation of dihydrogen and discriminate between alkenes and alkynes, as alkenes are particularly poor ligands for d^0 complexes. The 1,2-addition of H_2 to metal–ligand multiple bonds (e.g. $L_nM{=}X$; $X{=}O$,[5] S,[6] NR[7]) is a relatively rare transformation and its potential in catalysis has not been rigorously pursued. To combine the previously established early-transition-metal activation of H_2 by polarized metal–ligand multiple bonds with catalytic reduction of organic substrates, we sought a vanadium bisimide supported by labile ligands. Herein we report the synthesis of the cationic vanadium bisimido complex $[V(NtBu)_2(PMe_3)_3][Al(PFTB)_4]$ (**1**, PFTB = perfluoro-*tert*-butoxide, Scheme 1) and its application to the selective catalytic hydrogenation of alkynes to *Z* alkenes.



Scheme 1. Conditions: a) 1.05 equiv 2.0 M HCl in Et_2O, RT, over night, 46%; b) 1.05 equiv phenylacetylene in Et_2O, RT, 71%; c) 1 atm H_2, $PhCF_3$. In complexes **1**, **2**, **3**, and **A** the counteranion, $[Al(PFTB)_4]^-$, is not depicted for clarity.

Addition of a solution of $[VCl(PMe_3)_2(NtBu)_2]$ and 3 equivalents of PMe_3 in chlorobenzene (PhCl) to a slurry of $Li[Al(PFTB)_4]$ in PhCl afforded **1** as bright yellow crystals in 75% yield after crystallization. Complexes **1** and $[VCl(PMe_3)_2(NtBu)_2]$ are rare examples of vanadium bisimido complexes, and **1** is the first cationic Group 5 bisimido complex[8] (Figure 1 depicts complex **1**, see Supporting Information for details and structural characterization of $[VCl(PMe_3)_2(NtBu)_2]$).[9] Notably, **1** does not require bulky ancillary ligands[8e,f] or imides[8b–d] to kinetically stabilize the complex with respect to dimerization.

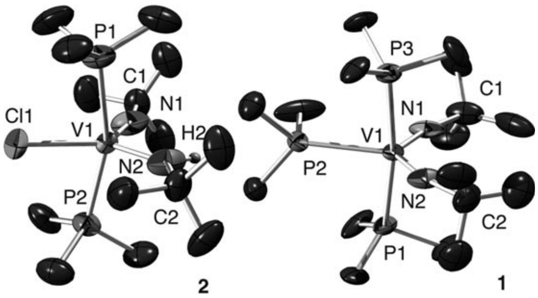


Figure 1. Molecular structures of **1** and **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and counteranions ($[Al(PFTB)_4]^-$) have been removed for clarity.

Treatment of a solution of **1** in $PhCF_3$ with 1 atm of H_2 resulted in recovery of only starting material after workup. Conversely, **1** rapidly decomposed under an atmosphere of H_2 in PhCl. A variable-temperature (VT) ^1H NMR spectrum of complex **1** under N_2 in $PhCF_3$ revealed that the equatorial PMe_3 readily disassociates at 40 °C. Free PMe_3 is not observed due to fast exchange. The remaining axial PMe_3 ligands significantly broadened at 70 °C. Under H_2 in $PhCF_3$, **1** is in

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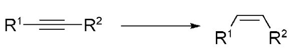
[**] The NIH GMS (R01 GM074774) and NSF (CHE 0848931) are gratefully acknowledged for financial support. We thank Drs. A. Pasquale, C. Canlas, and J. Krinsky for experimental assistance, Profs. R. G. Bergman and S. B. Duckett for helpful discussions, and Prof. A. Pines for a donation of para-H_2. H.S.La.P. is grateful to the NSF for a pre-doctoral fellowship and the UCB Department of Chemistry for the Dauben Fellowship.

Supporting information for this article (detailed descriptions of the syntheses as well as spectroscopic and crystallographic details is available on the WWW under http://dx.doi.org/10.1002/anie.201007876.

equilibrium with at least one other species even at room temperature. At 60 °C the loss of symmetry equivalence of the imido *tert*-butyl resonances (from $\delta = 1.09$ to 1.12 (imide) and 1.19 ppm (amide)) in this new complex, as seen in the $^1H\{^{31}P\}$ spectrum, suggests that reaction with H_2 proceeds through 1,2-, rather than {3+2}-addition, and generates a vanadium hydrido amido complex (**A**). Trace-free PMe_3 is also observed at $\delta = 0.86$ ppm. However, the isolation of **A** either by the direct reaction of **1** with H_2 or by indirect synthetic methods has not been successful to date. Attempts to observe the hydride, **A**, by in situ IR spectroscopy were complicated by the inability to generate a sufficient concentration of the intermediate, as were attempts to observe it by ^1H NMR spectroscopy (presumably further complicated by coupling to ^{51}V ($I = 7/2$) and ^{31}P).

We sought further synthetic evidence for the generation of a vanadium hydride through the 1,2-addition of H_2 to an imido ligand of **1**. To this end, we found complex **1** to be a competent catalyst for the hydrogenation of alkynes. Under standard conditions,[10] methylphenylacetylene was readily and selectively reduced to *cis*-β-methylstyrene in quantitative yield in 24 h. Further reduction to *n*-propylbenzene and isomerization to *trans*-β-methylstyrene or allylbenzene was not observed. The addition of a fresh atmosphere of H_2 and resubmission of the reaction mixture containing the product alkene to reaction conditions also resulted in no further reduction or isomerization. Internal alkyl, aryl, and silyl alkynes were similarly hydrogenated, all yielding the *cis*-alkenes [44–100 % yield, Eq. (1)]. Terminal alkynes (alkyl and aryl) are hydrogenated to the corresponding alkenes, albeit in significantly lower yields (10–52 %) due to competitive addition of the terminal C−H bond.[11]



R^1 = Me, R^2 = Ph; 24 h, 100%
R^1 = R^2 = Et; 72 h, 62%
R^1 = R^2 = TMS; 72 h, 44%
R^1 = *t*Bu, R^2 = H; 72 h, 52%
R^1 = Ph, R^2 = H; 72 h, 10%

(1)

In order to gain further spectroscopic and analytical insight into **A**, **1** was treated with HCl, in order to shift the equilibrium towards the 1,2-addition product. Adding a slight excess of 2.0 M HCl in diethyl ether solution to **1** afforded **2** in 46 % yield after workup as light green blocks. The solid-state structure depicted in Figure 1 clearly shows it to be related to the proposed intermediate **A**. In solution, **2** is a mixture of rotamers about the V−N amide bond and has similar symmetry inequivalence of imido and amide *tert*-butyl groups as in the mixture of **1** and **A**. Furthermore, the ^{27}Al NMR spectrum of **2** exhibits a single sharp resonance at $\delta = 36.01$ ppm ($\Delta\nu_{1/2} = 2.54$ Hz, compared to $\delta = 34.70$ ppm and $\Delta\nu_{1/2} = 2.99$ Hz for **1**). This narrow $\Delta\nu_{1/2}$ indicates that there is no loss of symmetry at $[Al(PFTB)_4]^-$ and that the proton is associated with the vanadium center in solution. While this synthetic work cannot rule out a {3+2}-addition followed by a subsequent 1,2-shift in the activation of H_2, it does further corroborate DFT studies (see below), observed VT NMR behavior, and catalytic reactivity of **1**, as well as previous experimental and DFT studies of σ-bond addition to early-transition-metal imido complexes.[7d,12]

The addition of terminal alkynes in a 1,2-fashion was confirmed by the preparative-scale synthesis of $[V(CCPh)(PMe_3)_2(NtBu)(NH(tBu))][Al(PFTB)]$ (**3**) by the addition of 1.05 equivalents of phenylacetylene to **1** in diethyl ether. Compound **3** was isolated in 71 % yield after crystallization from dichloroethane. In solution, **3**, like **2**, is a mixture of rotamers about the V−N amide bond. Similarly to **1** and **2**, **3** has a single sharp resonance in the ^{27}Al NMR spectrum at $\delta = 34.68$ ppm ($\Delta\nu_{1/2} = 3.81$ Hz).

B3LYP/6-31G(d,p) (LANL2DZ for V) calculations were performed in order to probe the mechanism of H_2-activation by **1** (Figure 2).[10] The reaction proceeds through a 1,2-addition of H_2 to an imido ligand of the four-coordinate complex $[(PMe_3)_2V(NtBu)_2]^+$ generated by the elimination of the equatorial PMe_3. The four-membered, kite-like transition state is similar to those calculated by Cundari et al. for C−H bond addition to $[(RO)_2Ti(NSi(tBu)_3)]$,[12] and Chirik et al. for H_2-addition to $[Cp^*_2Zr(NtBu)]$ ($Cp^* = C_5Me_5$).[7d] Dihydrogen addition to a three-coordinate complex resulting from the loss of two PMe_3 ligands was also considered, but found to be considerably higher in energy. No transition states corresponding to a {3+2}-addition could be located: all attempts collapsed to 1,2-addition transition states, and, furthermore, IRC calculations for these transition states failed to link to the corresponding, hypothetical product $[(PMe_3)_2V(NH(tBu))_2]^+$.

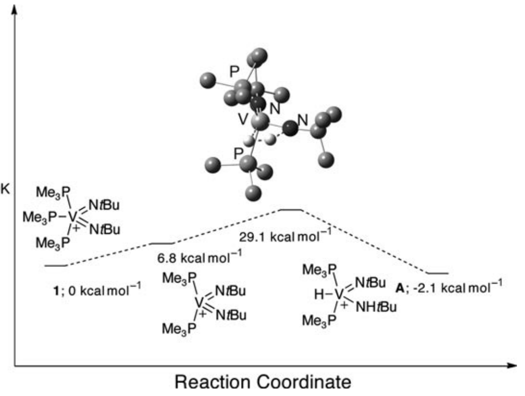
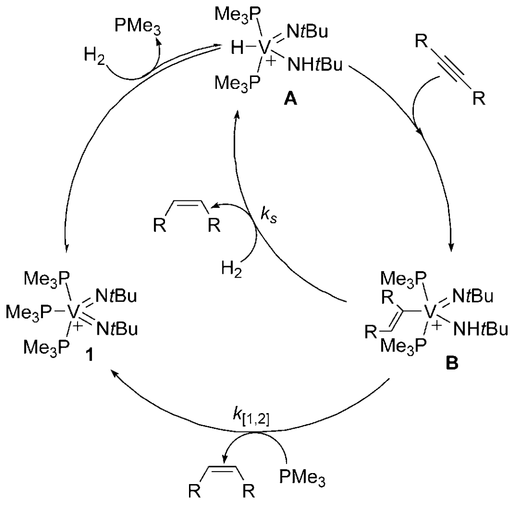


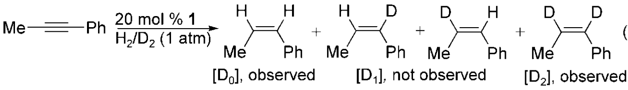
Figure 2. Free enthalpy of H_2 addition to complex **1**.

With these synthetic and DFT results, two reasonable mechanisms may be proposed for the hydrogenation of alkynes by **1** (Scheme 2). Upon insertion of an alkyne into the hydride of **A**, the alkenyl amide, **B**, may undergo σ-bond metathesis with a second equivalent of H_2 (k_σ). Alternatively, intermediate **B** may yield the product and **1** through 1,2-α-NH-elimination ($k_{1,2}$).[13] These two mechanistic possibilities were distinguished by a series of H_2/D_2 crossover experiments in the reduction of methylphenylacetylene (ratio of H_2/D_2, 1:1 and 1:9; ratio of alkyne to **1**, 1:1, 5:1, and 25:1). If $k_\sigma \geq k_{1,2}$, then a mixture of $[D_0]$-, $[D_1]$-, $[D_2]$-*cis*-β-methylstyrene should be observed. However, exclusively $[D_0]$- and $[D_2]$-*cis*-β-methylstyrene are observed by ^1H and $^2H\{^1H\}$ NMR spec-



Scheme 2. Mechanistic hypotheses.

troscopy when there is large excess of alkyne, and early in the course of the reaction [Eq. (2)]. This result implies that $k_{1,2} \gg k_\sigma$, and that, at high concentration, alkyne insertion is faster than the background formation of HD by σ-bond metathesis with **A**. At longer reaction times (12–24 h) and low concentration of alkyne, [D$_1$] isotologues appear in small amounts concomitantly with observation of HD. In sum, these crossover experiments imply that both the 1,2-addition of H$_2$ to an imido ligand and the 1,2-α-NH-elimination of alkene lie on the dominant catalytic cycle.



(2)

Complementary parahydrogen-induced polarization (PHIP)-NMR experiments were also performed.[14] Hydrogenation of methylphenylacetylene (alkyne:**1**, 25:1) by 90% para-H$_2$ at 60°C in protio-PhCF$_3$ afforded two antiphase singlets in the proton spectrum at $\delta = 6.33$ and 5.64 ppm. The transfer of polarization to the product alkene confirms the results of the H$_2$/D$_2$ crossover experiments demonstrating that a single molecule of H$_2$ is involved in the reduction of the alkyne. This result further indicates that possible mechanisms that involve splitting H$_2$ into two distinct molecules, as in hydrogenation by frustrated Lewis pairs, are *not* operative in this system as the H atoms remain *J*-coupled throughout the course of the hydrogenation. Similarly, the transfer of polarization to the product suggests that paramagnetic intermediates or impurities are *not* involved in the hydrogenation or in solution, as such species would rapidly catalyze the conversion of para-H$_2$ to ortho-H$_2$ and prevent the observation of PHIP phenomena.

In summary, we have synthesized the first cationic Group 5 bisimido complex, **1**, and demonstrated its reactivity with H$_2$. We also present evidence for an unusual 1,2-α-NH-elimination of an alkene to regenerate the active catalyst, **1**, in the application of **1** to the selective catalytic semihydrogenation of alkynes to *Z* alkenes. Complementary mechanistic, synthetic, and reactivity studies are ongoing.

Received: December 14, 2010
Revised: February 7, 2011

Keywords: alkynes · bisimides · homogeneous catalysis · hydrogenation · vanadium

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[1] J. F. Young, J. A. Osborn, F. H. Jardine, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* **1965**, 131.

[2] a) H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446; b) A. Molnár, A. Sárkány, M. Varga, *J. Mol. Catal. A* **2001**, *173*, 185.

[3] a) A. M. Kluwer, C. J. Elsevier in *Handbook for Homogeneous Hydrogenation*, *Vol. 1*, (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, p. 375; b) S. Warsink, I. H. Chang, J. J. Weigand, P. Hauwert, J. T. Chen, C. J. Elsevier, *Organometallics* **2010**, *29*, 4555; c) P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier, *Angew. Chem.* **2008**, *120*, 3267; *Angew. Chem. Int. Ed.* **2008**, *47*, 3223.

[4] a) J. J. Kennedy-Smith, K. A. Nolin, H. P. Gunterman, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 4056; b) K. A. Nolin, J. R. Krumper, M. D. Pluth, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 14684; for an enantioselective version see: c) K. A. Nolin, R. W. Ahn, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 12462; K. A. Nolin, R. W. Ahn, Y. Kobayashi, J. J. Kennedy-Smith, F. D. Toste, *Chem. Eur. J.* **2010**, *16*, 9555–9562; for related work see: e) A. Y. Khalimon, R. Simionescu, L. G. Kuzimina, J. A. K. Howard, G. I. Nikonov, *Angew. Chem.* **2008**, *120*, 7815; *Angew. Chem. Int. Ed.* **2008**, *47*, 7701; f) T. I. Gountchev, T. D. Tilley, *J. Am. Chem. Soc.* **1997**, *119*, 12831.

[5] a) G. Parkin, J. E. Bercaw, *J. Am. Chem. Soc.* **1989**, *111*, 391; b) T. E. Hanna, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2007**, *46*, 2359; c) P. M. Reis, P. J. Costa, C. C. Romao, J. A. Fernandes, M. J. Calhorda, B. Royo, *Dalton Trans.* **2008**, 1727; d) W. A. Howard, M. Waters, G. Parkin, *J. Am. Chem. Soc.* **1993**, *115*, 4917; for conceptually related {3+2}-additions of H$_2$ to late-transition-metal *cis*-dioxo compounds see e) J. P. Collman, L. M. Slaugher, T. A. Eberspacher, T. Strassner, J. I. Brauman, *Inorg. Chem.* **2001**, *40*, 6272; f) A. Dehestani, W. H. Lam, D. A. Hrovat, E. R. Davidson, W. T. Borden, J. M. Mayer, *J. Am. Chem. Soc.* **2005**, *127*, 3423, and references therein.

[6] Z. K. Sweeney, J. L. Polse, R. G. Bergman, R. A. Andersen, *Organometallics* **1999**, *18*, 5502.

[7] a) R. E. Blake, D. M. Antonelli, L. M. Henling, W. P. Schaefer, K. I. Hardcastle, J. E. Bercaw, *Organometallics* **1998**, *17*, 718; b) J. L. Polse, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1998**, *120*, 13405; c) T. E. Hanna, I. Keresztes, E. Lobkovsky, W. H. Bernskoetter, P. J. Chirik, *Organometallics* **2004**, *23*, 3448; d) H. E. Toomey, D. Pun, L. F. Veiros, P. J. Chirik, *Organometallics* **2008**, *27*, 872; e) C. C. Cummins, S. M. Baxter, P. T. Wolczanski, *J. Am. Chem. Soc.* **1988**, *110*, 8731.

[8] a) F. Preuss, H. Becker, T. Wieland, *Z. Naturforsch. B* **1990**, 191; b) J. de With, A. D. Horton, A. G. Orpen, *Organometallics* **1990**, *9*, 2207; c) J. de With, A. D. Horton, A. G. Orpen, *Organometallics* **1993**, *12*, 1493; d) J. de With, A. D. Horton, *Angew. Chem.* **1993**, *105*, 958; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 903; e) U. J. Kilgore, J. A. Karty, M. Pink, X. Gao, D. J. Mindiola, *Angew. Chem.* **2009**, *121*, 2430; *Angew. Chem. Int. Ed.* **2009**, *48*, 2394; f) Y. Tsai, P. Wang, K. Lin, S. Chen, J. Chen, *Chem. Commun.* **2008**, 205; for recent related work on reactive niobium bisimides see g) N. C. Tomson, J. Arnold, R. G. Bergman, *Organometallics* **2010**, *29*, 2926.

[9] See Supporting Information for full details.

[10] 1 atm H_2, 700 μL $PhCF_3$, 20 mol% **1**, C_6D_6 insert, 60 °C, 1,3,5-trimethoxybenzene internal standard.

[11] Alkynes are selectively hydrogenated, among other functional groups tolerated by the catalyst. Substrates that are substantially stronger ligands for **1** than PMe_3, such as acetonitrile, undergo exclusive ligand exchange at the equatorial position and are not reduced. Weaker ligands, such as olefins, are also not reduced. Aldehydes and ketones lead to the degradative consumption of catalyst.

[12] T. R. Cundari, T. R. Klinckman, P. T. Wolczanski, *J. Am. Chem. Soc.* **2002**, *124*, 1481.

[13] S. A. Holmes, D. F. Schafer, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2001**, *123*, 10571.

[14] a) D. Blazina, S. B. Duckett, J. P. Dunne, C. Godard, *Dalton Trans.* **2004**, 2601; b) S. P. Millar, D. L. Zubris, J. E. Bercaw, R. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 5329; c) P. J. Carson, C. R. Bowers, D. P. Weitekamp, *J. Am. Chem. Soc.* **2001**, *123*, 11821.