Trapping of Acetylene by a Zirconocene Terminal Imido Complex

C. Jeff Harlan, Jon A. Tunge, Brian M. Bridgewater, and Jack R. Norton*

Department of Chemistry, Columbia University, New York, New York 10027

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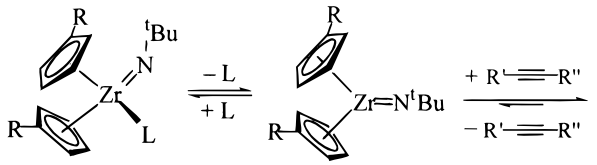
Treatment of the zirconocene terminal imido complex $(CpR)_2Zr{=}N^tBu(THF)$ (**1a-THF**: R = H; **1b-THF**: R = Me) with acetylene results in the formation of a dinuclear product, $[(CpR)_2Zr]_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (**3a**, R = H; **3b**, R = Me), in which the zirconium centers are bridged by nitrogen and carbon. Upon heating, the dinuclear complex **3** is cleaved into the azametallacyclobutene $(CpR)_2Zr(\eta^2\text{-}N^tBuCHCH)$ (**4**) and the terminal imido complex $(CpR)_2Zr{=}N^tBu$ (**1**), which can be trapped with Lewis bases or alkynes. Heating **3** in the absence of traps cleanly produces the alkynyl-bridged species $[(CpR)_2ZrNH^tBu]_2(\mu\text{-}C{\equiv}C)$ (**5**). Kinetic data indicate that the dinuclear complex **3** fragments into the mononuclear species **4** and **1** prior to C−H activation to form **5**. The X-ray structures of $[Cp_2Zr]_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (**3a**) and $[Cp_2ZrNH^tBu]_2(\mu\text{-}C{\equiv}C)$ (**5a**) are reported; the structure of the dinuclear species $[(Cp_2Zr)((CpMe)_2Zr)](\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (**3c**) is included in the Supporting Information.

Introduction

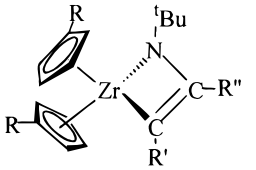
The chemistry of group 4 terminal imido complexes has received considerable attention due to their ability to catalyze imine metathesis[1] and the hydroamination of alkynes.[2,3] A key feature of these transformations is the facile [2+2] cycloaddition of unsaturated substrates across the zirconium imido linkage.[4−6] In addition, in some nonmetallocene cases, the Zr=N bond may activate the C−H bonds of hydrocarbons through σ-bond metathesis.[7,8]

We have recently been examining the reaction of Lewis acids with azazirconacycles[9] such as the azazirconacyclobutene complex **2a**. Such azazirconacyclobutenes are conveniently prepared (eq 1) by treatment of terminal imido complexes of zirconocene, such as **1-L**, with alkynes.[6]



1a-L: R = H
1b-L: R = Me
L = Lewis base

1a: R = H
1b: R = Me



(1)

2a: R' = R" = Ph; R = H
2b: R' = R" = Ph; R = Me

Bergman and co-workers have shown that Lewis bases dissociate from **1-L** to yield the ligand-free imido complex **1** (not observed) prior to reaction with alkyne.[10] The reaction occurs with excellent regioselectivity, yielding azazirconacyclobutenes in which the largest substituent is in the R′ position (α to Zr).[6,10] Azazirconacyclobutenes such as **2** contain a planar ZrNCC ring with bond lengths that are consistent with localization of the double bond between the C atoms,[6] as shown in eq 1. For the cycloaddition of alkynes to **1**, the equilib-

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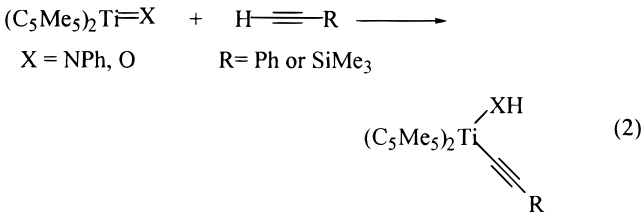
rium lies far in favor of the azazirconacyclobutene, and retrocycloaddition is observable only at elevated temperatures.

The regiochemistry of the cycloaddition of titanocene derivatives and alkynes is opposite that of zirconocene imido complexes,[11,13] a phenomenon that is probably steric in nature. Titanocene imido[12] and oxo[13] complexes (eq 2) also add the C−H bonds of terminal alkynes,[14] but well-defined examples of the activation of C−H bonds of terminal alkynes by zirconocene terminal imido complexes have not been reported.[15]

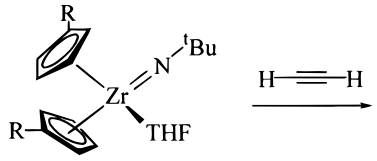


(2)

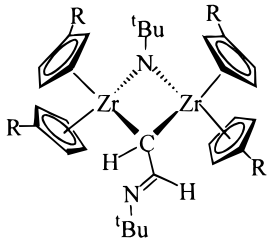
We have found that addition of acetylene to the zirconocene terminal imido complexes **1a-THF** and **1b-THF** leads to an unusual cycloaddition product, which then undergoes C−H activation to give a bridging alkynyl complex.

Results and Discussion

Synthesis and Characterization of $[(CpR)_2Zr]_2$-(μ-CHCHN^{t}Bu)(μ-N^{t}Bu) (3), $(CpR)_2Zr(\eta^2$-N^{t}BuCHCH) (4), and $[(CpR)_2ZrNH^tBu]_2(\mu$-C≡C) (5) (R = H, Me). Treatment of a light yellow toluene solution of the terminal imido species **1a-THF** and **1b-THF** at room temperature with acetylene (eq 3) causes a rapid color change to deep purple. Purple crystals of the dinuclear species **3** were obtained in moderate (**3a**, 63%) and low (**3b**, 18%)[16] isolated yields by addition of hexanes to a concentrated toluene solution. The structures of **3a** and the isostructural complex **3c**, $[(Cp_2Zr)((CpMe)_2Zr)](\mu$-CHCHN^{t}Bu)($\mu$-N^{t}Bu), prepared by a different procedure (eq 4 see below), have been determined by X-ray diffraction.



1a–THF: R = H
1b–THF: R = Me



(3)

3a: R = H
3b: R = Me

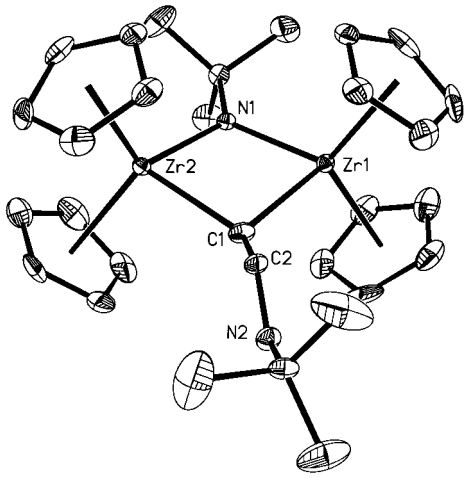


Figure 1. Molecular structure of $[Cp_2Zr]_2(\mu$-CHCHN^{t}Bu)-(μ-N^{t}Bu) (**3a**). Selected bond lengths (Å) and angles (deg): Zr1−N1 2.092(4), Zr2−N1 2.091(5), Zr1−C1 2.267(6), Zr2−C1 2.258(6), C1−C2 1.456(8), C2−N2 1.255(7); C2−C1−Zr1 124.9(5), C2−C1−Zr2 128.7(5), N2−C2−C1 125.3(6), N1−Zr1−C1 81.5(2), N1−Zr2−C1 81.8(2), Zr2−N1−Zr1 103.1(2) Zr2−C1−Zr1 92.8(2).

The molecular structure of complex **3a** is shown in Figure 1 (see Supporting Information for structural data on **3c**). The atoms comprising the $Zr_2(\mu$-C)(μ-N) metallacycle are planar (sum of the angles = 359.2°). The imido group bridges the Zr atoms symmetrically,[17] and the Zr1−N1 (2.092(4) Å) and Zr2−N1 bond lengths (2.091(5) Å) are typical for an imido-bridged zirconium dimer.[6,18] The Zr1−C1 (2.267(6) Å) and Zr2−C1 (2.258-(6) Å) bond lengths are longer than those found with alkylidenes that bridge two Zr atoms[19,20] and slightly shorter than those found in a complex with a methylene bridging Zr and Th.[21] Although the C1−C2 bond (1.456-(8) Å) is shorter than expected for an sp^3-sp^2 C−C

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(14) Related chemistry has been observed in d^0 group 5 complexes. (a) Blake, R. E., Jr.; Antonelli, D. M.; Henling, L. M.; Schaefer, W. P.; Hardcastle, K. I.; Bercaw, J. E. *Organometallics* **1998**, *17*, 718−725. (b) de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493−1496. (c) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903−905.

(15) When [2+2] cycloaddition cannot occur, as with arenes, zirconocene terminal imido complexes give C−H activation products at elevated temperatures.[6]

(16) The isolated yield of **3b** can be improved to 61% by the treatment of **4b** with **1b-THF** in a manner analogous to that used to produce **3c**. Complex **3a** is the major product of treatment of complex **1a** with acetylene, while complex **4b** is the major product of treatment of complex **1b** with acetylene (at room temperature by ^{1}H NMR).

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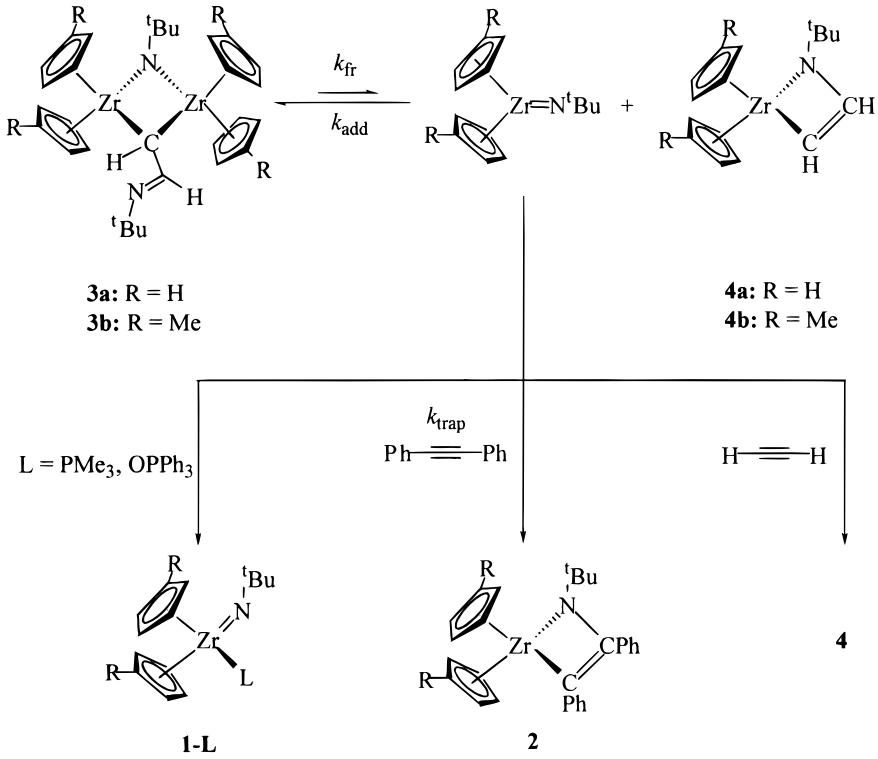
Scheme 1



single bond,[22] the C2═N2 bond (1.255(7) Å) is typical of that found in organic imines.[23] Thus the structural data indicate that C1 is sp^3 hybridized and C2 is sp^2 hybridized.

Complexes **3a** and **3b** are C_s symmetric; the Cp ligands on each Zr are diastereotopic, but undergo exchange on the NMR time scale. Complex **3c** is C_1 symmetric; the four Cp groups are inequivalent, but pairwise exchange between chemically identical Cp ligands (Cp↔Cp and CpMe↔CpMe) is observed. The hydrogen atoms on C1 and C2 were not located in the X-ray structures of **3a** or **3c**, but are readily apparent in the ^{1}H NMR spectra of **3** as two low-field doublets.[24] The resonances of these protons do not exchange, nor do the two separate ^{t}Bu resonances. The ^{13}C NMR resonances of the bridging and imine carbons in complexes **3** have similar chemical shifts (ca. δ 168 and 163 ppm), and we have not attempted to assign them; the carbons of methylene[25] and methine[20,26] ligands that bridge two Zr centers are known to occur in the same region as imine carbons.[27]

Heating solutions of **3** in the presence of trapping agents such as PhC≡CPh, $OPPh_3$, and PMe_3 gives the acetylene-derived azametallacyclobutenes **4** in a one-to-one ratio with products that appear to result from trapping the transiently generated base-free terminal imido complex **1** (Scheme 1).

Thermolysis of the dinuclear complexes **3** in the presence of acetylene allowed complete conversion to the azazirconacyclobutene complexes **4**. Complex **4a** is unstable to standard workup procedures, decomposes slowly at room temperature, and was characterized in solution; complex **4b** is qualitatively more stable than **4a** and could be obtained as an oil. We were not able to purify complexes **4** via crystallization. The best yields (>80% for **4a**; >95% for **4b** by ^{1}H NMR) were obtained at high temperatures (100−110 °C) and short reaction times (<1 min). At lower temperatures the decomposition of **4a** competed with its formation. As expected for the structure shown (Scheme 1), the Cp groups of complexes **4** are equivalent by ^{1}H NMR and the two olefinic protons appear as an AB pattern shifted several ppm upfield from those of complexes **3**.

The fragmentation of complex **3** into **4** and **1** (depicted in Scheme 1) suggests that when **1-THF** is treated with acetylene, the azametallacyclobutene **4** is formed initially and then trapped by a second equivalent of **1-THF** to yield **3**. As evidence, complex **3c** was generated via treatment of **1a-THF** with **4b** (eq 4) and isolated in good yield (73%) as purple crystals. The treatment of **1b-THF** with **4a** also yields **3c** but in lower yield, as **4a** is not formed as cleanly as **4b**.

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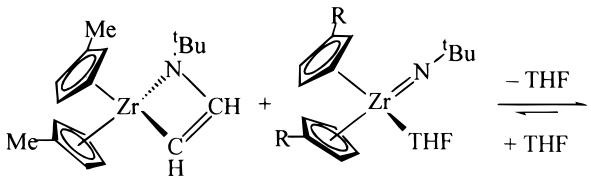
(25) Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1−10.

(26) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979−4981.

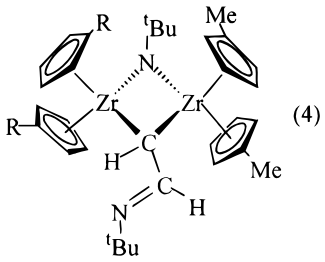
(27) Typical imine carbon ^{13}C NMR resonances are in the range δ 178−154. (a) Inamoto, N.; Kushida, K.; Masuda, S.; Ohta, H.; Satoh, S.; Tamura, Y.; Tokumaru, K.; Tori, K.; Yoshida, M. *Tetrahedron Lett.* **1974**, 3617−3620. (b) Allen, M.; Roberts, J. D. *Can. J. Chem.* **1981**, *59*, 451-458. (c) Fraser, R. R.; Chuaqui-Offermanns, N. *Can. J. Chem.* **1981**, *59*, 3007−3011. (d) Klusener, P. A. A.; Tip, L.; Brandsma, L. *Tetrahedron* **1991**, *47*, 2041−2064.

(28) In THF-d_8 small amounts of complexes **1-THF** and **4a** are observed.

(29) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911−920. (b) Ahlers, W.; Temme, B.; Erker, G.; Fox, T. *J. Organomet. Chem.* **1997**, *527*, 191−201. (c) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158−3167. (d) Varga, V.; Hiller, J.; Thewalt, U.; Polásek, M.; Mach, K. *J. Organomet. Chem.* **1998**, *553*, 15−22. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Organomet. Chem.* **1992**, *428*, 13−47.



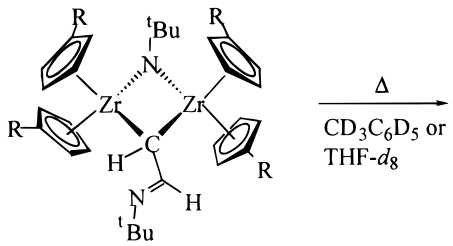
4b **1a–THF:** R = H
1b–THF: R = Me



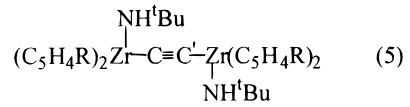
(4)

3c: R = H
3b: R = Me

Upon heating to 60−85 °C in THF[28] or aromatic hydrocarbons, complexes **3a** and **3b** are cleanly converted to the light yellow alkynyl-bridged species (eq 5), $[(CpR)_2ZrNH^tBu]_2(\mu\text{-}C{\equiv}C)$ (**5a** and **5b**). Complex **5a** has been characterized by NMR spectroscopy and X-ray crystallography (Figure 2); complex **5b**, not isolated, has been characterized by ^1H and ^{13}C NMR spectroscopy.



3a: R = H
3b: R = Me



(5)

5a: R = H
5b: R = Me

The Zr−C (2.240(3) Å) bond length in **5a** is comparable to that of the Zr−C σ-bond in $Cp_2Zr(C{\equiv}CMe)_2$ (2.249(3) Å), in which there is no π interaction between the triple bond and the zirconium center.[29] There is a noticeable shortening of the Zr−C bond when π overlap is present,[30,31] for example in $Cp(PMe_3)_2RuC{\equiv}CZrClCp_2$ (d(C−Zr) = 2.141(15) Å).[32] The C1≡C1′ (1.226(7) Å) bond in **5a** is only slightly longer than that in organic and organometallic alkynes,[29a,32] and the Zr−C1−C1′ bond angle (173.8(2)°) in **5a** is close to linear. Thus the Zr−C1−C1′−Zr unit in **5** consists of a C−C′ triple bond and two Zr−C single bonds.

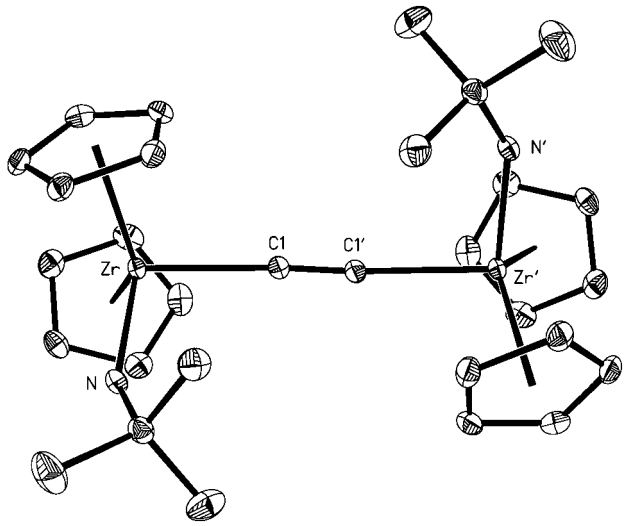


Figure 2. Molecular structure of $[Cp_2ZrNH^tBu]_2(\mu\text{-}C{\equiv}C)$ (**5a**). Selected bond lengths (Å) and angles (deg): Zr−N 2.063(3), Zr−C1 2.240(3), C1−C1′ 1.226(7); N−Zr−C1 96.34(11), C1′−C1−Zr 173.8.

Table 1. Exchange of Cp Resonances of 3

	temp range (°C)	rate[a] (s^{-1}) (25 °C)	relative rate	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
3a	−11 to 17	31(2)	129	12.4(4)	−10(2)
3b	28 to 62	0.24(1)	1	14.1(4)	−14(1)
3c	−16 to 17	17.7(6)	74	12.4(2)	−11(1)

[a] Extrapolated.

In the NMR spectra of **5** the Cp resonances are equivalent and the ^{t}Bu resonances are also equivalent. The bridging alkynyl group displays only one peak in the ^{13}C NMR (**5a**, δ 169.9; **5b**, δ 171.0), comparable in shift to that in $[Cp_2Zr(CPhCPhMe)]_2(\mu\text{-}C{\equiv}C)$ (δ 178.5).[33] The N−H proton resonances (**5a**, δ 5.53; **5b**, δ 5.31) are broad and similar in shift to those observed in other $Cp_2Zr(NHR)R$ complexes.[6,34]

Kinetics of Cp Exchange, Fragmentation, and Isomerization of $[(CpR)_2Zr]_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^t\text{-}Bu)$ (3). Exchange broadening of the ^1H NMR Cp resonances of **3a** and **3c** is readily apparent at room temperature, although those of **3b** are not obviously broadened. The rates of exchange of the Cp groups of **3** were monitored via magnetization transfer and showed good first-order behavior over the temperature ranges specified in Table 1. Most significantly, the rate of exchange of the Cp groups of the tetramethyl-substituted complex **3b** is roughly 2 orders of magnitude slower than those of **3a** and **3c**.

At room temperature and below, addition of excess Lewis bases such as $OPPh_3$ and PMe_3 to solutions of complex **3a** does not affect the rate of exchange and there is no detectable cleavage of **3** into the Lewis base adduct **1-L** and the azametallacyclobutene **4**. Thus, we conclude that the exchange of Cp groups in the complexes **3** does not proceed through dissociation into **1** and **4**. The fact that the relative rates of Cp exchange

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(31) For examples in titanocene chemistry see: Lang, H.; Blau, S.; Nuber, B.; Zsolnai, L. *Organometallics* **1995**, *14*, 3216−3223, and references therein.
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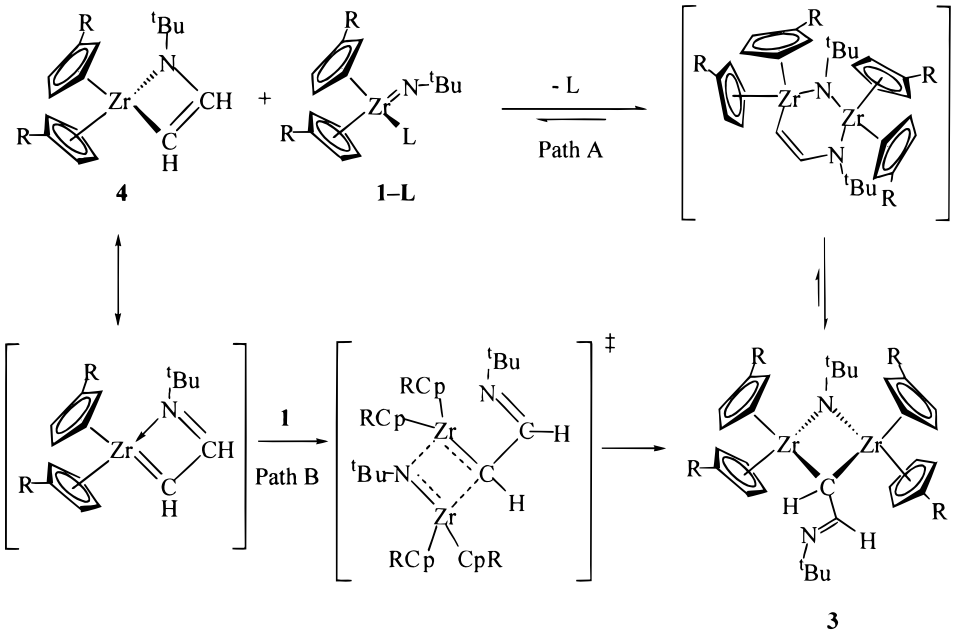
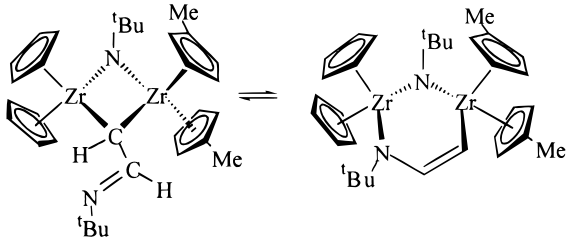
Scheme 2



of the complexes **3** (**3a**:**3b**:**3c** = 129:1:77) are inversely proportional to degree of methyl substitution (**3a**:**3b**:**3c** = 0:4:2) suggests that steric effects are responsible for the observed rate differences.



3c

(6)

The Cp groups could be exchanged by Zr−C bond homolysis in **3** followed by rotation and recombination. However, the steric and electronic effects of an additional methyl group on the Cp ligand should have a negligible effect on the Zr−C bond disruption enthalpy.[35] An intermediate consistent with the observed steric dependence is derived from insertion of the free imine into a Zr−C bond (eq 6). This species contains a plane of symmetry through the atoms comprising the metallacycle; the Cp groups on either side of this plane are equivalent.

As previously shown, the formation of products **3** arises from the reaction of the azazirconacyclobutene **4** with the terminal imido complex **1**. The unusual structure of these complexes raises the possibility that **3** could be derived from a formal [2+2] cycloaddition of the Zr=N bond of **1** across the Zr=C bond of a carbene resonance structure of **4** (Scheme 2, path B). The related rearrangement of metallacyclobutenes to vinyl carbene complexes is a well-known phenomenon.[36,37]

Alternatively, the same intermediate proposed to give rise to magnetization exchange (eq 6) may be on the pathway to formation of **3**. This intermediate could be formed by insertion of the Zr=N bond of imido complex **1** into the Zr−C bond of azametallacyclobutene **4** (path A, Scheme 2). A subsequent step analogous to enamine−imine tautomerization gives the thermodynamically more stable imine complex **3**. Since there is no evidence for path B, and facile Cp exchange implicates the intermediate proposed in eq 6, path A seems more likely than a [2+2] cycloaddition mechanism (path B).

As stated previously, heating complexes **3** in the presence of excess diphenyl acetylene (Scheme 1) gave the products **4** and **2** in a 1:1 ratio. Varying the diphenyl acetylene concentration over a 2-fold concentration range shows that the rate of this transformation is independent of diphenyl acetylene concentration. Therefore diphenyl acetylene functions only as a trap, and the rates monitored are a direct measurement of the rate of fragmentation k_{fr} of **3**. The rate of formation of **2a** from **3a** (Scheme 1) is 1.03×10^{-3} s^{-1} at 333 K. Complex **3b** is transformed in less than 5 min at 333 K, and a rate constant of 9.72×10^{-4} s^{-1} is obtained for **3b** at 318 K.

The addition of THF to solutions of **3** should drive the equilibrium toward **4** and **1-THF** (eq 4). Heating toluene solutions of **3b** containing various amounts of THF for 120 min at 40 °C allows equilibration of the complexes. Integration of the species present in the 318 K ^{1}H NMR spectra shows that $K_{eq} = 709$ (eq 4), favoring **3b**.

The isomerizations of **3** to **5** (eq 5) exhibit good first-order kinetics over the temperature ranges shown in

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(36) (a) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737−738. (b) Han, C. C.; Katz, T. J. *Organometallics* **1985**, *4*, 2186−2195. (c) Schrock, R. R.; Luo, S.; Lee, J. C., Jr.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883−3895. (d) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644−654. (e) Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4742−4744.

(37) Group 4 vinyl carbene complexes have been synthesized via treatment of zirconocene and titanocene equivalents with cyclopropenes and adopt an η^1-vinyl carbene structure. Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610−611.

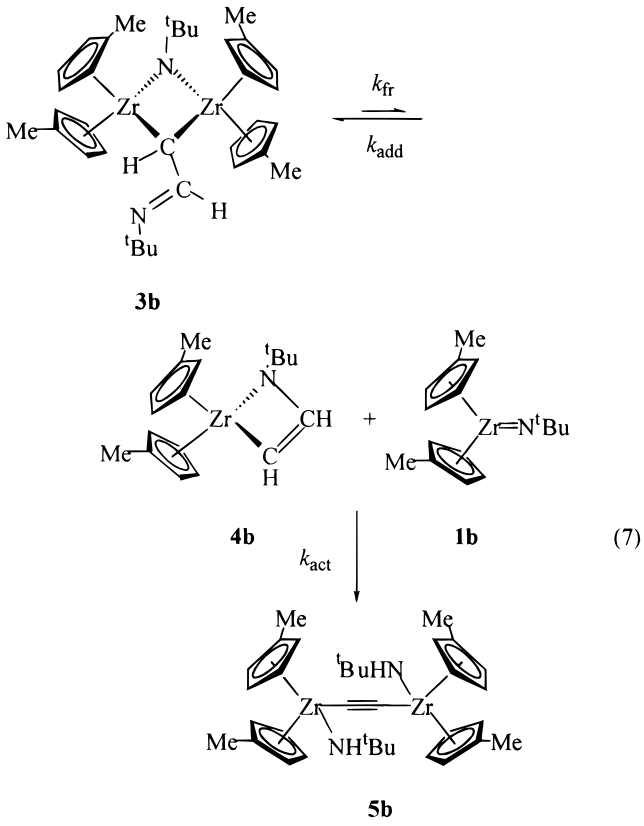
Table 2. Kinetic Data for Conversion of 3 to 5 in $CD_3C_6D_5$

	temp range (°C)	rate[a] (s^{-1}) (25 °C)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
3a	59−85	$4.5(5) \times 10^{-7}$	27.4(5)	4(1)
3b	62−85	$0.3(1) \times 10^{-7}$	39(2)	39(5)

[a] Extrapolated.

Table 2. The rate constants for the isomerization, extrapolated to 25 °C (Table 2), are many orders of magnitude smaller than those for the Cp exchange processes (Table 1), and the isomerization of **3b** to **5b** is 15 times slower than that of **3a** to **5a**.

The rates of formation of **5** from **3** are significantly slower than reversion of **3** into **1** and **4**. For example the rate of formation of **5b** from **3b** extrapolated to 318 K is 3.5×10^{-6} s^{-1}, compared to 9.72×10^{-4} s^{-1} for the formation of **1b** and **4b** from **3b** at the same temperature. Thus, under the conditions of isomerization of **3** to **5**, the equilibrium between **3** and **1**/**4** should be rapidly maintained (eq 7).

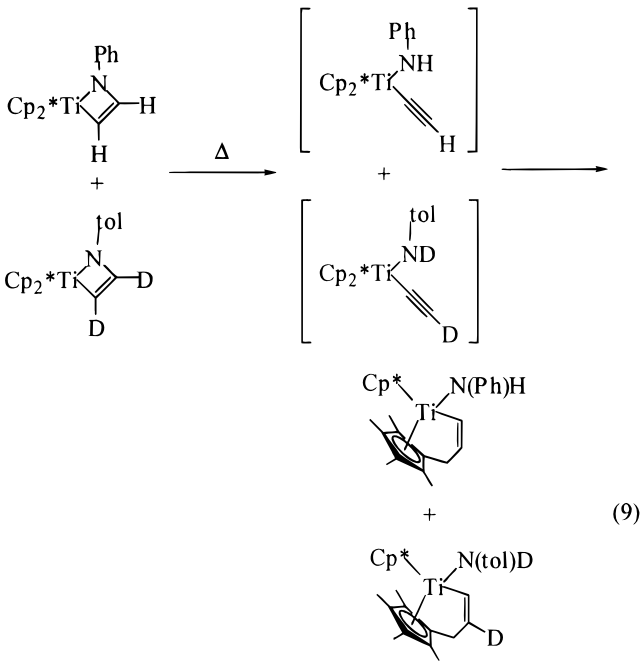


(7)

In C_6D_6 or $CD_3C_6H_5$ there were no intermediates observed in the ^1H NMR spectra during the isomerization of **3a** to **5a** and **3b** to **5b**.[38] In the presence of excess PMe_3 the isomerization of **3a** was suppressed and only small amounts of **5a** were observed; instead the products **1-PMe$_3$** and **4a** were formed in high yield. If **3** fragments into **4** and **1** in a rapid preequilibrium followed by a slow reaction of **4** and **1** to form **5** (eq 7), the rate of the reaction will be given by eq 8, where $K_1 = k_{fr}/k_{add}$. Increasing the concentration of **1b** should accelerate the formation of **5b**, until the saturation rate is reached.[39] The rate of isomerization of **3b** to **5b** with 0.096 M **1b-THF** is $3.0(2) \times 10^{-4}$ s^{-1} at 338 K, whereas the extrapolated rate of formation of **5b** in the absence of **1b-THF** is 1.43×10^{-4} s^{-1}. As thermolysis of **3b** in the presence of excess **1b-THF** *does* result in accelerated conversion to **5b**, we conclude that the formation of **5** is preceded by fragmentation of **3** to the metallacyclobutene **4** and imido complex **1**.

$$\frac{d[\mathbf{5b}]}{dt} = \frac{k_{act}K_1[\mathbf{1b}]}{[\mathbf{1b}] + K_1}([\mathbf{3b}] + [\mathbf{4b}]) \qquad (8)$$

Knowing that **4** and **1** are intermediates in the formation of **5** from **3**, we sought to determine whether extrusion of acetylene from **4** (reverse of eq 1) occurs prior to C−H activation. To investigate this, complex **4b** was heated to 80 °C for 2 h and monitored by ^1H NMR. Although slow decomposition takes place, no evidence for alkyne extrusion was observed. The reported free energy of activation for diphenyl acetylene extrusion from an azazirconacyclobutene is 29.9 kcal/mol,[1c] so at 70 °C the rate of acetylene extrusion from **4** to form **1** is expected to be over 500 times slower than the formation of **5** from **3**. Thus it appears that C−H activation occurs without extrusion of acetylene. Our conclusion is consistent with Bergman's observation that thermolysis of $Cp^*_2Ti(N(Ph)CD{=}CD)$ in the presence of $Cp^*_2Ti(N(tol)CH{=}CH)$ does not result in crossover (eq 9).[12]



(9)

Conclusion

Zirconium azametallacyclobutenes **4**, which have an α-hydrogen (R′ position eq 1), exhibit unusual reactivity. The Zr−C bond is less sterically hindered, allowing insertion of the Zr=N bond of a zirconocene terminal imido complex to form the dinuclear complexes **3**. Additionally, azazirconacyclobutenes **4** react with imido

(38) Similar studies on the unsymmetric species **3c** were confounded by the appearance of multiple doublets between 10 and 8 ppm in the ^1H NMR.

(39) Because the equilibrium between **3b** and **4b**/**1b** already favors **3b**, addition of **1b** will not result in a significant change in the concentration of **3b.** Thus the direct conversion of **3b** to **5b** cannot be accelerated by added **1b**.

complexes **1** to form zirconocene alkynyl complexes **5** through activation of the alkyne C−H bond. This may involve a facile intramolecular rearrangement like that previously proposed by Bergman for $Cp^*_2Ti(N(Ph)CH{=}CH)$, which requires a shift of the α-hydrogen onto nitrogen (eq 9).[12] The results presented here can explain the (apparent) inability of zirconocene terminal imido complexes to catalyze the hydroamination of terminal alkynes. The temperature required for the catalytic process most likely produces small amounts of the unfavored α-hydro regioisomer, which rearranges to the catalytically inactive terminal alkynyl complex.

Experimental Section

Manipulations were conducted under N_2 or Ar using standard Schlenk techniques and inert atmosphere boxes; solvents were dried and degassed. Complex **1a** was prepared according to the published procedure.[6] Cp_2ZrCl_2 and $(CpMe)_2ZrCl_2$ were gifts from Boulder Scientific Co. and used as received. Commercial acetylene was passed through a trap (−78 °C) to remove the bulk of the acetone followed by a column of activated alumina prior to reaction. ^{1}H NMR were recorded at 300 or 500 MHz as noted. ^{13}C NMR were recorded at 75 MHz, and HMQC experiments were recorded at 500 MHz. In cases where both ^{13}C NMR and HMQC data were obtained the results have been combined.

$(CpMe)_2Zr(N^tBu)(THF)$ (1b). Compound **1b** was made in a manner similar to that reported for **1a**. THF solutions (30 mL) of $(CpMe)_2ZrMe(OTf)$ (2.8 g, 6.8 mmol) and $LiNH^tBu$ (0.6 g, 7.6 mmol) were combined (room temperature) and stirred for 1 h. Volatiles were removed under vacuum, and the resulting solid was extracted with hexanes (40 mL) and filtered. The hexanes were removed under vacuum, and the resulting oil was dissolved in THF (50 mL) and heated (90−95 °C) for 5 days in a manner analogous to that for **1a**. The THF solution was concentrated and hexanes (20 mL) were added, forming a gooey precipitate. The solution was heated until the precipitate dissolved; slow cooling to −20 °C overnight produced light yellow plates. Yield = 2.4 g (90%). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.11 (m, 2 H), 6.01 (m, 2 H), 5.91 (m, 2 H), 5.88 (m, 2 H), 3.43 (m, 4 H), 2.23 (s, 6 H), 1.31 (s, 9 H), 1.11 (m, 4 H). Anal. Calcd for $C_{20}H_{31}NOZr$ (392.7): C 61.17; H 7.96; N 3.57. Found: C 60.81; H 7.86; N 3.53.

$(CpMe)_2Zr(\eta^2\text{-}N^tBuCPhCPh)$ (2b). Complex **2b** was prepared in a manner analogous to that reported for **2a**.[6] ^{1}H NMR (C_6D_6, 300 MHz): δ 7.28 (m, 2 H), 7.16−7.07 (m, 5 H), 6.83 (m, 1 H), 6.59 (m, 2 H), 5.92−5.86 (m, 6 H), 5.68 (m, 2 H), 2.05 (s, 6 H), 1.02 (s, 9 H).

$[Cp_2Zr]_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (3a). Acetylene was slowly bubbled through a toluene solution (15 mL, 30 °C) of **1a** (0.7 g, 19.2 mmol) over 10 min. Only a few bubbles per minute were allowed to pass through the solution. After 10 min the solution was saturated with acetylene. The volume was reduced (ca. 5 mL) and hexanes (10 mL) were added, precipitating purple crystalline **3** over the course of 1 h. Yield = 0.37 g (63%). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.76 (d, 1 H, J = 9.1 Hz.), 8.86 (d, 1 H, J = 9.1 Hz), 6.20 (s, 10 H), 6.09 (s, 10 H), 1.40,(s, 9 H), 0.79 (s, 9 H). ^{13}C NMR (C_6D_6): δ 166.7 (*C*H), 163.3 (*C*H), 112.2 (C_5H_5), 111.5 (C_5H_5), 65.5 (*C*CH_3), 54.0 (*C*CH_3), 37.0 (C*C*H_3) 31.8 (C*C*H_3). Anal. Calcd for $C_{30}H_{40}N_2Zr_2$ (611.1): C 58.96; H 6.60; N 4.58. Found: C 59.53; H 6.63; N 4.32.

$[(CpMe)_2Zr]_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (3b). $(CpMe)_2Zr(N^tBu)(THF)$ **1b** (550 mg, 1.4 mmol) was treated as described for the preparation of **3a**. Yield = 170 mg (18%). Alternatively, the procedure used for the synthesis of **3c** can be used to synthesize **3b** in 61% isolated yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 9.35 (d, 1 H, J = 9.2 Hz), 9.03 (d, 1 H, J = 9.2 Hz), 6.79 (m, 2 H), 6.75 (m, 2 H), 6.65 (m, 2 H), 6.36 (m, 2 H), 6.32 (m, 2 H), 5.66 (m, 2 H), 5.61 (m, 2 H), 5.12 (m, 2 H), 2.10 (s, 6 H), 1.76 (s, 6 H), 1.34 (s, 9 H), 0.89 (s, 9 H). ^{13}C NMR ($CD_3C_6D_5$)/HMQC ($CD_3C_6D_5$): δ 168.7/9.35, 163.0/9.03, 123.6 ($H_4C_4CCH_3$), 119.2 ($H_4C_4CCH_3$), 117.0/6.79, 115.2/5.61, 113.9/6.75, 113.5/6.65, 113.4/5.12, 111.3/6.36, 107.3/6.32, 104.3/5.66, 64.7 (*C*CH_3), 53.7 (*C*CH_3), 37.3/0.89, 31.4/1.34, 14.8/1.76, 14.5/2.10. Anal. Calcd for $C_{34}H_{48}N_2Zr_2$ (667.2): C 61.21; H 7.25; N 4.20. Found: C 60.78; H 7.06; N 3.97.

$[(Cp_2Zr)((CpMe)_2Zr)](\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)$ (3c). $(CpMe)_2Zr(N^tBu)(THF)$, **1b** (280 mg, 0.72 mmol), dissolved in toluene (10 mL) was saturated with acetylene via a needle through a septum which was firmly attached to the flask. The acetylene-saturated solution was placed in an oil bath (100 °C) for 1 min, after which time the solution was concentrated under vacuum to about 5 mL. To this solution was added a solution of $Cp_2Zr(N^tBu)(THF)$, **1a** (260 mg, 0.72 mmol), in toluene (12 mL); the mixture was allowed to stir (5 min) at room temperature. The solution was concentrated to about 5 mL, and hexanes (10 mL) were added. After sitting several hours at room temperature and cooling overnight (−20 °C), large purple crystals were isolated by decantation and dried under vacuum. Yield = 330 mg (72%). ^{1}H NMR ($CD_3C_6D_5$, 500 MHz): δ 9.41 (d, 1 H, J = 9.2 Hz), 8.85 (d, 1 H, J = 9.2 Hz), 7.06 (m, 1 H), 6.61 (m, 1 H), 6.60 (m, 1 H), 6.40 (m, 1 H), 6.15 (s, 5 H), 6.10 (s, 1 H), 5.93 (m, 1 H), 5.61 (m, 1 H), 5.41 (m, 1 H), 5.07 (m, 1 H), 2.13 (s, 3 H), 1.70 (s, 3 H), 1.32 (s, 9 H), 0.83 (s, 9 H). ^{13}C NMR ($CD_3C_6D_5$)/HMQC ($CD_3C_6D_5$): δ 167.9/9.41, 162.9/8.85, 124.3 ($H_4C_4CCH_3$), 119.2 ($H_4C_4CCH_3$), 116.0/6.60, 115.6/5.41, 113.8/6.61, 113.3/5.07, 113.2/7.07, 112.3/6.10, 112.0/6.40, 111.5/6.15, 107.0/5.93, 104.6/5.61, 65.1 (*C*$(CH_3)_3$, 53.7 (*C*$(CH_3)_3$, 37.1/0.83, 31.7/1.32, 14.8/2.13, 14.8/1.70.

$Cp_2Zr(\eta^2\text{-}N^tBuCHCH)$ (4a). A solution of complex **3a** (20 mg, 0.033 mmol) in C_6D_6 (0.7 mL) was placed in an NMR tube with a septum firmly attached. The tube was saturated with acetylene, then placed in an oil bath (110 °C) for 60 s. The product **4a** was formed in >80% yield. ^{1}H NMR (C_6D_6): δ 7.10 (d, 1 H, J = 11.7 Hz), 7.02 (d, 1 H, J = 11.7 Hz), 5.81 (s, 10 H), 1.06 (s, 9 H). ^{13}C NMR (C_6D_6)/HMQC (C_6D_6): δ 156.1/7.02 (H*C*CH), 113.7/7.10 (HC*C*H), 110.1 (C_5H_5), 55.5 (N−*C*$(CH_3)_3$), 31.8 (C(*C*$H_3)_3$).

$(CpMe)_2Zr(\eta^2\text{-}N^tBuCHCH)$ (4b). Complex **4b** was formed in a manner analogous to **4a** in >95% yield using toluene-d_8 as the solvent. ^{1}H NMR ($CD_3C_6D_5$): δ 7.25 (d, 1 H, J = 11.8 Hz), 6.66 (d, 1 H, J = 11.8 Hz), 5.75 (m, 2 H), 5.68 (m, 2 H), 5.56 (m, 4 H), 1.91 (s, 6 H), 1.05 (s, 9 H). ^{13}C NMR ($CD_3C_6D_5$): δ 155.5 (H*C*CH), 122.6 (Cp−*C*CH_3), 116.4 (HC*C*H), 112.6 (Cp−*C*H), 111.1 (Cp−*C*H), 107.2 (Cp−*C*H), 106.9 (Cp−*C*H), 55.3 (N−*C*$(CH_3)_3$), 32.0 (C(*C*$H_3)_3$), 15.5 (Cp−*C*H_3).

Table 3. Summary of Crystallographic Data

	2a	**3a·2C_6H_6**
empirical formula	$C_{30}H_{40}N_2Zr_2$	$C_{42}H_{52}N_2Zr_2$
fw	611.08	767.30
temp, K	203(2)	218(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2/n$
a, Å	8.3679(4)	14.5631(18)
b, Å	34.111(2)	8.7651(12)
c, Å	10.0497(5)	14.964(2)
α, deg	90	90
β, deg	108.3430(10)	99.650(3)
γ, deg	90	90
V, Å^3	2722.8(2)	1883.0(4)
Z	4	2
d_{calc}, g/cm^3	1.491	1.353
λ(Mo Kα), Å	0.71073	0.71073
μ, mm^{-1}	0.786	0.584
no. of data collected	18 778	9883
no. of unique data	6177	3890
no. of data/restraints/params	6177/0/316	3890/0/212
GOF on F^2	1.133	1.020
R1, wR2 ($I > 2\sigma(I)$)	0.0686, 0.1245	0.0411, 0.0984
R1, wR2 (all data)	0.1143, 0.1462	0.0636, 0.1099

[$Cp_2ZrNH^tBu]_2$(μ-CC) (5a). A solution of **3a** (20 mg) in C_6D_6 (0.6 mL) was heated to 70 °C for 2 h. Hexanes (ca. 1.5 mL) were added, and the solution was cooled (−20 °C). Over several days benzene and large, very light yellow blocks of **5a** crystallized. The solution was warmed gently to melt the benzene, and the product was isolated by decantation. Yield = 15 mg (75%). ^{1}H NMR (300 MHz, C_6D_6): δ 6.00 (s, 20 H), 5.53 (s, 2 H), 1.30 (s, 18 H). ^{13}C NMR (C_6D_6): δ 169.9 (*CC*), 109.2 (*Cp*), 57.1 (N−*C*(CH_3)$_3$), 34.6 (C(*C*H_3)$_3$).

[($CpMe)_2Zr(NH^tBu)]_2$(μ-CC) (5b). A solution of complex **3b** (15 mg) in $CD_3C_6D_5$ (0.7 mL) was heated to 75 °C for 3 h. ^{1}H NMR (300 MHz, $CD_3C_6D_5$): δ 5.93 (m, 4H), 5.85 (m, 4 H), 5.81 (m, 4 H), 5.73 (m, 4 H), 5.31 (s, 2 H), 2.30 (s, 12H), 1.28 (s, 18 H). ^{13}C NMR ($CD_3C_6D_5$): δ 171.0 (*CC*), 125.1, 111.8, 111.7, 107.9, 105.5, 56.7 (N−*C*(CH_3)$_3$), 34.6 (C(*C*H_3)$_3$), 16.3 (Cp*C*H_3).

X-ray Structure Determinations. Crystal data collection and refinement parameters are summarized in Table 3. Data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures using SHELXTL.[40] Hydrogen atoms on carbon were included in calculated positions.

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Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates of complexes **3a** and **5a** as well as full structural data on complex **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000165G

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