Experimental Modeling of Selective Alkene Oligomerization: Evidence for Facile Metallacyclopentane Dehydrogenation Mediated by a Transannular β-Hydrogen Agostic Interaction

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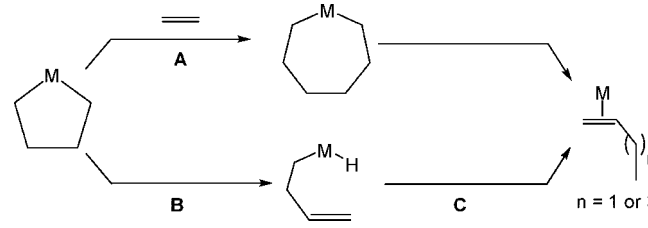
Ring-expansion of the zirconacyclopropane (η^5-C_5Me_5)Zr[N(i-Pr)C(Me)N(i-Pr)](η^2-$CH_2CHC_6H_5$) (**1**) was accomplished through insertion of ethene, propene, and styrene into a metal−carbon bond to yield the series of crystalline zirconacyclopentane derivatives **2**−**4**, respectively, for which solid-state molecular structures have been obtained through single-crystal X-ray analyses. The metallacyclopentane rings of **2** and **4** adopt half-chair conformations that place all β-hydrogens distant from the metal center (cf. nonbonded distances of 3.2−4.0 Å). On the other hand, a twisted-envelope conformation for the zirconacyclopentane ring of **3** features a β-hydrogen agostic interaction with the metal center [cf. a Zr1−H21B distance of 2.38(2) Å]. Unlike **2** and **4**, compound **3** decomposes rapidly in solution at 25 °C to provide the structurally characterized zirconacyclopent-3-ene derivative **5**. Ring-expansion of **1** with 1-(trimethylsilyl)ethene directly provides the zirconacyclopent-3-ene derivative **7**. A mechanism for this facile metallacyclopentane dehydrogenative process is proposed that features an intramolecular allylic β-hydrogen abstraction within a 3-butenyl metal hydride intermediate as a key step. It is further proposed that similar metallacyclopentane to metallacyclopent-3-ene dehydrogenations may be more common than previously thought.

Introduction

Several early transition metal (Ti, Ta, and Cr)-based catalysts have now been developed that are extremely active and highly selective for the trimerization of ethene.[1] Mechanistically, this process is thought to operate through a "metallacycle" mechanism in which the control point for dimerization versus trimerization rests with the relative rates for metallacyclopentane expansion to a metallacycloheptane through alkene insertion (path A) versus that for formal reductive five-membered ring-opening to form a 1-butene metal complex via intramolecular β-hydrogen transfer followed by reductive elimination (path B/C) as presented in Scheme 1.[2] Although isotopic labeling studies,[3] as well as more indirect circumstantial evidence,[4] now provide strong support in favor of this mechanism, to date, experimental precedent for the critical ring-expansion of a metallacyclopentane to a metallacycloheptane through direct alkene insertion into a metal−carbon single bond is still lacking.[5] Furthermore, only scant experimental data still currently exist regarding the structures, thermal stabilities, and decomposition pathways of medium-sized-ring metallacycles containing groups 4−6 metals.[6] Finally, it has long been proposed that metallacyclopentanes lack the degree of conformational flexibility required to engage in transannular β-hydrogen agostic interac-

Scheme 1



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(3) (a) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 808–811. (b) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 14281–14295.

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(5) Insertion into a metal−carbon bond of a conformationally restricted dibenzo-annulated chromacyclopentane (the formal equivalent of a metallacyclopenta-1,3-diene) has been observed; see, ref 3b.

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10.1021/om900132u CCC: $40.75
Publication on Web 03/27/2009

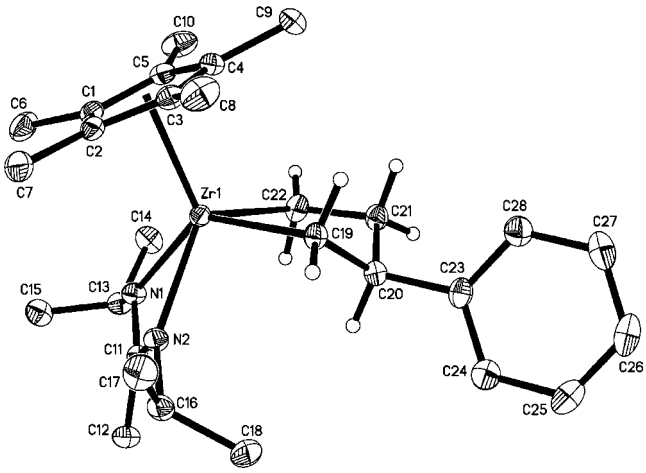
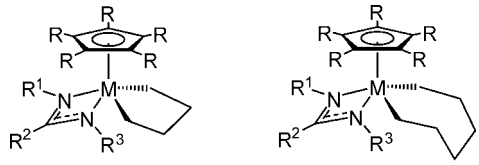


Figure 1. Molecular structure (30% thermal ellipsoids) of compound **2**. Hydrogen atoms have been removed for the sake of clarity except those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.2839(15); C22−C21, 1.527(2); C21−C20, 1.529(2); C20−C19, 1.548(2); C19−Zr1, 2.3073(14); C19−Zr1−C22, 77.21(5); Zr1−C22−C21, 111.39(10); C22−C21−C20, 109.63(12); C21−C20−C19, 106.97(12); C20−C19−Zr1, 105.54(9).

Chart 1



tions that are a prerequisite for lowering the barrier to intramolecular ring-fragmentation according to path B in Figure 1.[2,7,8] Accordingly, with a growing body of work now supporting the ability of the monocyclopentadienyl, monoamidinate (CpAm) ligand environment to impart a high degree of kinetic stability to alkyl substituents bearing β-hydrogens within mid- and high-valent early transition metal complexes,[9] we initiated a program to synthesize and investigate the structures, stabilities, and reaction profiles of group 4 metallacycles of general formula (η^5-C_5R_5)M[$-CH_2(CH_2)_nCH_2-$][N(R^1)C(R^2)N(R^3)] where n = 2 (**I**) and n = 4 (**II**) (see Chart 1). Herein, we now report results for a series of substituted zirconacyclopentane derivatives (M = Zr in **I**) that include support for a ground-state transannular β-hydrogen agostic interaction that further appears responsible for promoting a conformationally dependent facile metallacyclopentane to metallacyclopent-3-ene dehydrogenation pathway in solution. These results further provide a possible alternative explanation for the origin of an anomalous $C_\beta-C_{\beta'}$ bond-length contraction sometimes reported for the solid-state structures of metallacyclopentanes and, significantly, for chroma- and zirconacyclopentanes.[6c,d,f]

Results and Discussion

A. Synthesis and Structural Characterization of Zirconacyclopentanes. As Scheme 2 reveals, formal ring-expansion of the previously reported zirconacyclopropane **1**[10] could be accomplished in modest to excellent yields through insertion of ethene, propene, and styrene into a metal−carbon bond to yield the new zirconacyclopentane derivatives **2**, **3**, and **4**, respectively. Here it is important to note that due to significant differences in thermal stabilities of the compounds, a much lower temperature for the synthesis, isolation, and subsequent handling of solutions of propene-derived **3** is required (*vide infra*). In each case, preliminary ^{1}H NMR spectra indicated formation of a mixture of stereoisomers; however, through recrystallization at −30 °C, a single, analytically pure, crystalline stereoisomer could be isolated and subjected to single-crystal X-ray analysis. Figures 1−3 provide the derived solid-state molecular structures and selected geometric parameters for the isolated stereoisomers of **2**, **3**, and **4**, respectively. Intriguingly, for compounds **2** and **4**, the relative configurations of the exocyclic phenyl substituents appear to enforce half-chair conformations of the five-membered ring that place all β-hydrogens of the zirconacyclopentane ring distant from the metal center (cf. nonbonded distances of 3.2−4.0 Å) (see Figures 1 and 3). On the other hand, the solid-state twisted-envelope conformation for the zirconacyclopentane ring of **3** is notable in that it appears to feature a transannular β-hydrogen agostic interaction with the metal center [cf. a Zr1−H21B distance of 2.38(2) Å].[7] It is reasonable to assume that the magnitude of nonbonded steric interactions that are associated with the relative configurations of the exocyclic substituents for this specific stereoisomer of **3** might be responsible for enforcing a ring-conformation that is conducive for formation of this transannular interaction. Unfortunately, attempts to isolate any other stereoisomer of **3** were not successful owing to the limited stability of this compound in solution (*vide infra*).

Regarding the two different possible regiochemical paths for alkene insertion into the metal−carbon bonds of zirconacyclopropane **1**, it is interesting to note that compound **2** arises from formal insertion of ethene into the phenyl-substituted side of the three-membered ring bond through a pathway that also permits epimerization of the original stereocenter associated with the α-phenyl substituent of **1**. In contrast, the stereoisomer isolated for compound **3** clearly arises from formal alkene insertion into the opposite, unsubstituted zirconium−carbon bond of **1**, which further proceeds with retention of stereochemistry of the α-carbon bearing the phenyl substituent. For zirconacyclopentane **4**, the issue of regiochemistry centers on the task of determining the precursor origins of the two different phenyl substituents. Fortunately, this question could be quickly addressed by utilizing 1,1-[^{2}H]$_2$-labeled styrene (99%, d_2) for insertion. More specifically, after isolation of the corresponding **4**-d_2 material, a ^{1}H NMR spectrum revealed that ring-expansion of **1** is indeed regiospecific and that *it proceeds through styrene insertion into the more substituted zirconium−carbon bond of the metallacyclopropane* according to Scheme 3. Furthermore, monitoring of solution dynamic processes involving **4**-d_2 by ^{1}H NMR at room temperature served to establish that, while rapid reversible epimerization between major and minor stereoisomers (ca. 1.2:1 at 25 °C) is rapidly occurring on the NMR time scale, no exchange of the two styrene fragments of the five-membered ring ever transpires. In dilute solution, thermal decomposition

(7) For reviews of metal−hydrogen agostic interactions, see: (a) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124. (b) Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782–1806. (c) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908–6914.

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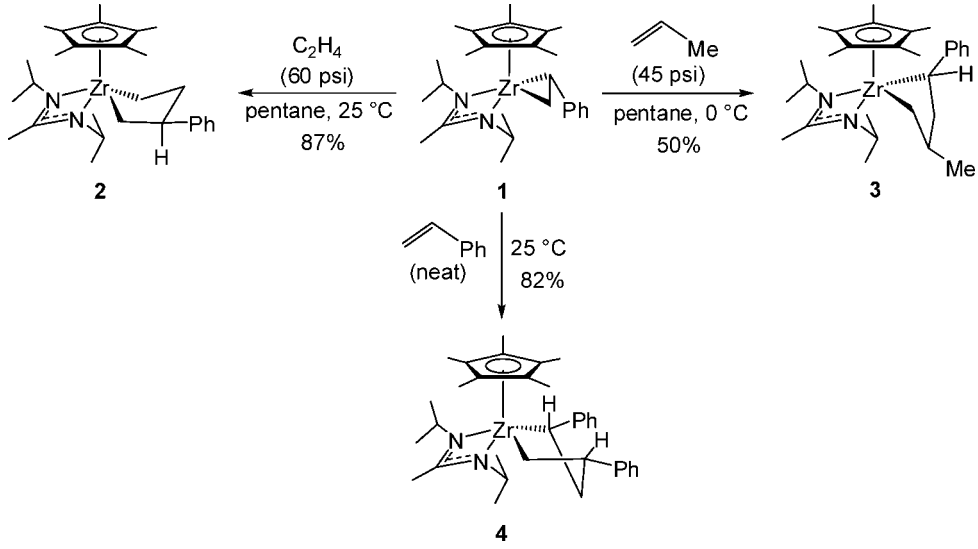
Scheme 2



of **4**-d_2 was also observed to proceed through regiospecific elimination of deuterated styrene to regenerate **1**. On the basis of this information, we tentatively assign the major stereoisomer as being the 2,4-*cis* isomer of **4**, for which the solid-state structure was obtained (see Figure 3), and with the minor isomer then having the corresponding 2,4-*trans* configuration as shown in Scheme 3. Since ^{1}H NMR spectra for **4**-d_2 confirm that dynamic epimerization does not occur at the β-carbon stereocenter, it is further postulated that facile epimerization of the α-carbon stereocenter in **4** might proceed through reversible scission of a zirconium−carbon "weak bond" with generation of a transient "Zr(III)-stabilized" radical species such as that depicted in Scheme 3. A similar transient species derived from reversible bond scission in **1** might then also account for epimerization of the β-carbon stereocenter during ethene insertion to provide compound **2**. Although hard experimental evidence for the Zr(III) species postulated in Scheme 3 has not yet been obtained, we have recently confirmed that the CpAm ligand environment can support the synthesis and isolation of a series of closely related Ti(III) alkyl complexes.[11]

Metallacyclopentanes have long been proposed, or known, to be products of formal oxidative [2+2+1] cyclization of two alkenes coming together at a reduced metal center.[12] Surprisingly, however, the total number of solid-state structures of isolated unsubstituted and substituted metallacyclopentane derivatives remains small.[4,6] Furthermore, within this database of structures, there has sometimes been noted an anomalous

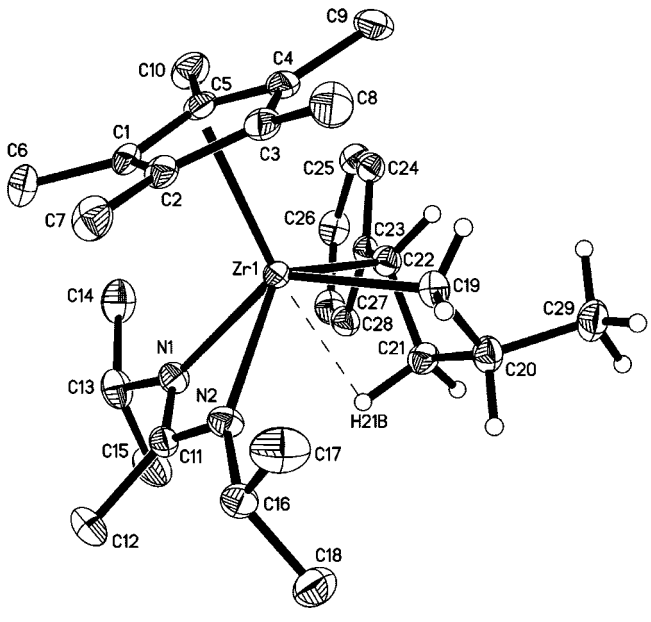


Figure 2. Molecular structure (30% thermal ellipsoids) of compound **3**. Hydrogen atoms have been removed for the sake of clarity except those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.326(2); C22−C21, 1.529(3); C21−C20, 1.545(3); C20−C19, 1.511(3); C19−Zr1, 2.296(2); C19−Zr1−C22, 75.17(8); Zr1−C22−C21,85.10(12);C22−C21−C20,111.70(18);C21−C20−C19, 108.53(17); C20−C19−Zr1, 103.24(13).

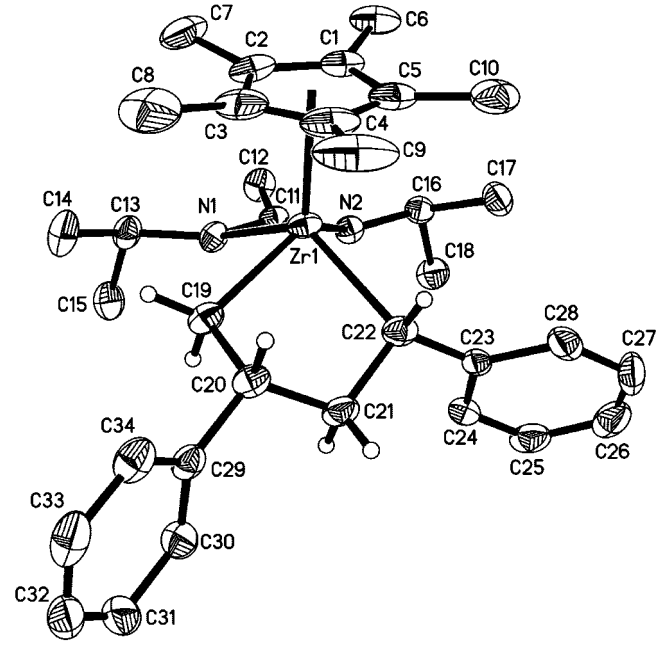


Figure 3. Molecular structure (30% thermal ellipsoids) of compound **4**. Hydrogen atoms have been removed for the sake of clarity except those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.375(2); C22−C21, 1.540(3); C21−C20, 1.516(3); C20−C19, 1.538(3); C19−Zr1, 2.292(2); C19−Zr1−C22, 76.67(8); Zr1−C22−C21,107.09(14);C22−C21−C20,111.98(18);C21−C20−C19, 107.13(18); C20−C19−Zr1, 112.00(16).

Scheme 3

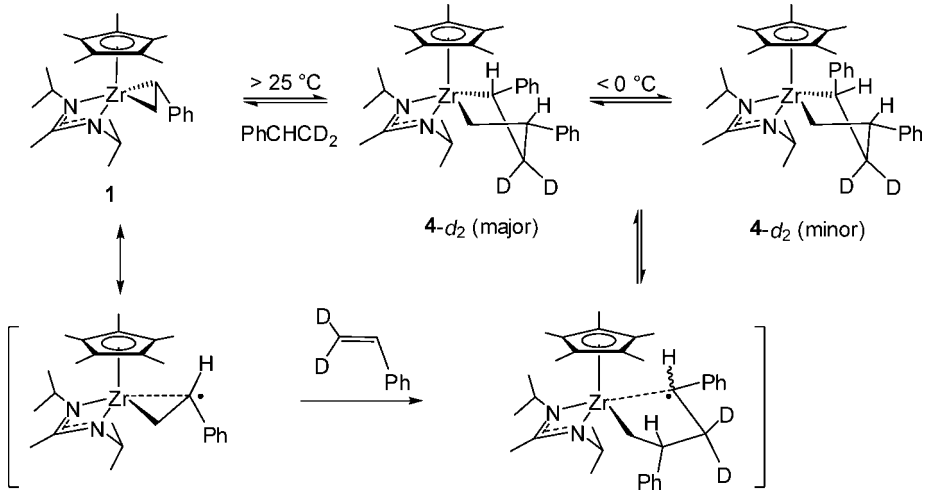
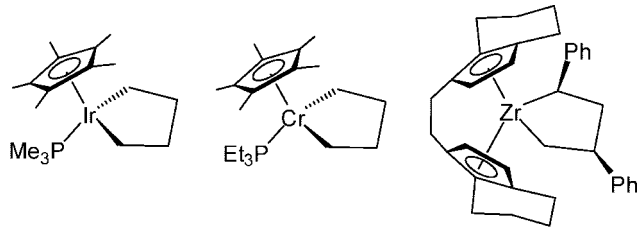


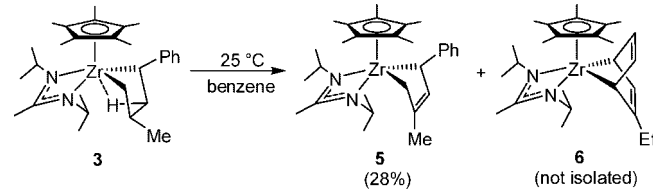
Chart 2



contraction of the carbon−carbon bond between the two cyclic β-carbons that replicates the distance expected for a carbon−carbon double bond, rather than a carbon−carbon single bond and, most notably, for those structures presented in Chart 2.[6c,d,f] In this regard, the bond lengths associated with the five-membered rings of the zirconacyclopentanes **2**−**4** are largely unremarkable. More specifically, as presented in Figures 1−3, all three compounds possess C_β−$C_{\beta'}$ (i.e., C20−C21) bond lengths for the five-membered rings that are within the range expected for carbon−carbon single bonds [cf. for **2**, 1.529(2) Å; **3**, 1.545(3) Å; **4**, 1.516(3) Å]. Furthermore, while it is tempting to assign the slightly longer Zr1−C22 bond length of 2.326(2) Å relative to the Zr1−C19 of 2.296(2) Å in **3** as arising in concert with the previously noted β-hydrogen agostic interaction, a similar disparity in the Zr−C_α bond lengths of **4** suggests that the origin is likely, and largely, steric in nature.

B. Zirconacyclopent-3-enes via Facile Dehydrogenation. Given the wealth of seminal investigations conducted by Negishi and co-workers[12] regarding the reversibility of zirconacyclopentane formation via ring-fragmenting alkene elimination, the relative stabilities of the isolated zirconacyclopentane derivatives **2**−**4** in solution were of significant interest. To begin, ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) spectra quickly revealed that, when monitored within an NMR tube, sealed under an inert atmosphere of dinitrogen, solutions of the three zirconacyclopentanes presented the following relative ordering of stability at room temperature: **2** (indefinitely) ≫ **4** (days) ≫ **3** (hours). Indeed, solutions of compound **3** were found to darken to brown within a few minutes at room temperature, and within hours, a ^{1}H NMR spectrum confirmed that significant decomposition had occurred, as evidenced by new resonances appearing for several different species. Cooling a pentane solution of this mixture to −30 °C surprisingly provided, after several days, a 28% yield of the red-purple zirconacyclopent-3-ene derivative **5** shown in

Scheme 4



Scheme 4. The identity of **5** was unequivocally established through single-crystal X-ray analysis, and Figure 4 provides the solid-state molecular structure of this compound. The most prominent structural feature of **5** is the obvious double bond that exists between the two β-carbon atoms [cf. C20−C21, 1.376(7) Å] that enforces coplanarity with C29 of the exocyclic

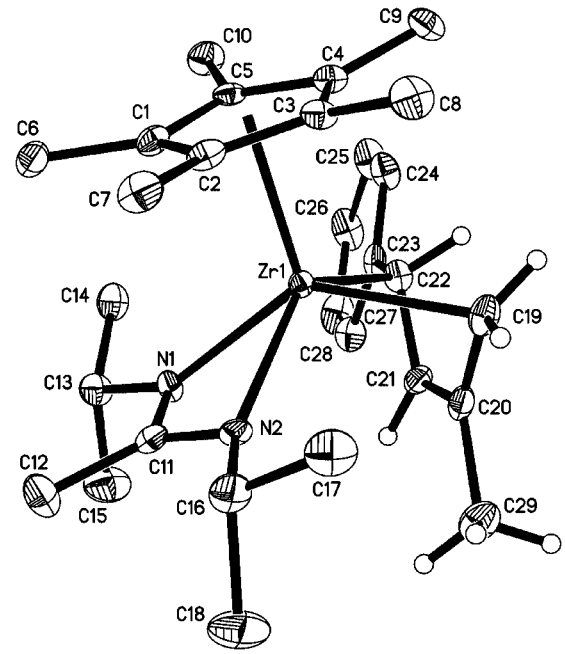
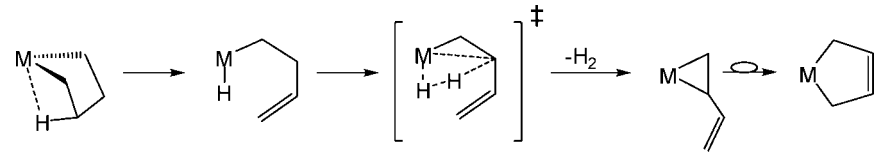
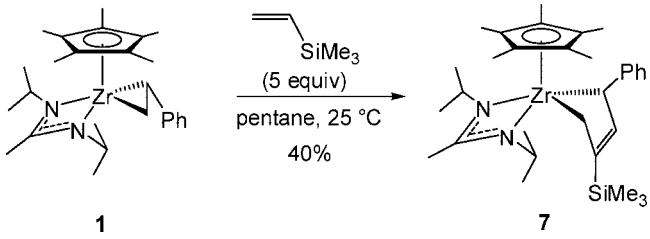


Figure 4. Molecular structure (30% thermal ellipsoids) of compound **5**. Hydrogen atoms have been removed for the sake of clarity except for those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.377(5); C22−C21, 1.463(7); C21−C20, 1.376(7); C20−C19, 1.454(8); C19−Zr1, 2.347(5); C19−Zr1−C22, 75.47(19); Zr1−C22−C21, 75.8(3); C22−C21−C20, 122.6(5); C21−C20−C19, 120.0(5); C20−C19−Zr1, 78.3(3).

Scheme 5



Scheme 6



1 **7**

methyl substituent. Furthermore, in keeping with other zirconacyclopent-3-ene derivatives based on the CpAm ligand environment that we have previously reported.,[9a,13] the five-membered ring adopts an envelope conformation that places the endocyclic double bond within proximity to the metal center, and thereby, in possible support of a secondary π-donor interaction.[9a]

Upon closer inspection, the initial ^{1}H NMR spectrum of the solution decomposition mixture derived from **3** also revealed formation of the zirconanorbornadiene complex **6**, which is depicted in Scheme 4. Compound **6** was previously prepared in near quantitative yield through the low-pressure hydrogenation of zirconacyclopropane **1** in pentane at room temperature.[10] Accordingly, although we do not spectroscopically observe formation of dihydrogen during the decomposition of **3**, facile formation of **6**, which is concomitant with the appearance of **5**, can be viewed as providing circumstantial evidence for transient H_2 production during the **3** → **5** process. On the basis of this hypothesis, together with the greatly reduced stability of **3** vis-à-vis zirconacyclopentanes **2** and **4**, we tentatively conclude that the presence of the conformationally allowed, transannular agostic interaction in **3** significantly lowers the barrier for a ring-fragmenting intramolecular β-hydrogen transfer to the metal to generate a transient 3-butenyl metal hydride intermediate according to Scheme 5. However, in contrast to undergoing reductive elimination according to the B/C pathway of Scheme 1, in the present case, subsequent intramolecular β-hydrogen atom *abstraction* at the "activated" allylic position of the 3-butenyl substituent leads directly to loss of H_2 and formation of an η^2-(1,3-butadiene) metal complex that can rearrange to a metallacyclopent-3-ene according to Scheme 5. Surprisingly, to the best of our knowledge, transformation of a 3-butenyl metal hydride by the process of Scheme 5 has not been previously proposed, but it certainly provides a viable catalyst deactivation process to consider for selective ethene oligomerization.[2,14] The generality of this dehydrogenative process is further supported by observation that reaction of **1** with 5 equiv of 1-(trimethylsilyl)ethene directly provides the structurally characterized zirconacyclopent-3-ene **7** in modest yield according to Scheme 6. The identity and molecular structure of **7** was once again confirmed by single-crystal X-ray analysis, and Figure 5 presents the solid-state molecular structure of this compound along with selected geometric parameters.

(11) Trunkely, E. F.; Epshteyn, A.; Zavalij, P. Y.; Sita, L. R., results to be published.

(12) (a) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124–130. (b) Negishi, E. *Dalton Trans.* **2005**, 827–848.

C. Synthesis and Stability of Methyl ω-Alkenyl Zirconium Complexes. In order to provide more weight to the mechanistic hypothesis of Scheme 5, the series of methyl, ω-alkenyl zirconium complexes **9**−**11** were prepared in straightforward fashion according to Scheme 7. As mentioned previously, the ability of the CpAm ligand environment to impart a high degree of kinetic stability to complexes with alkyl substituents bearing β-hydrogens clearly comes into play to provide for the successful synthesis, isolation, and structural characterization of **9**–**11**. Indeed, Figure 6 presents the solid-state molecular structure as obtained from single-crystal X-ray analysis for the most challenging of these compounds: the 3-butenyl derivative **9**. Regarding the thermal stabilities of these compounds in solution, perhaps not unexpectedly, while compounds **10** and **11** proved to be quite robust in solution toward β-hydrogen transfer processes, **9** was found to quantitatively convert in solution at 25 °C to the zirconacyclopent-3-ene derivative **12** with coproduction of methane according to Scheme 7. For a final comparison, Figure 7 presents the solid-state molecular structure of **12** as obtained from single-crystal X-ray analysis.

Conclusion

In summary, the present results provide considerable support for a simple, but fundamental, low-energy pathway involving 3-butenyl metal hydrides not previously considered as part of

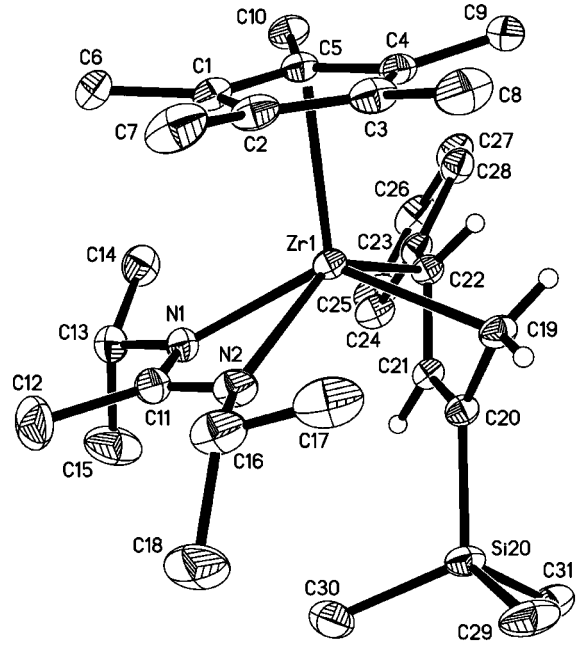
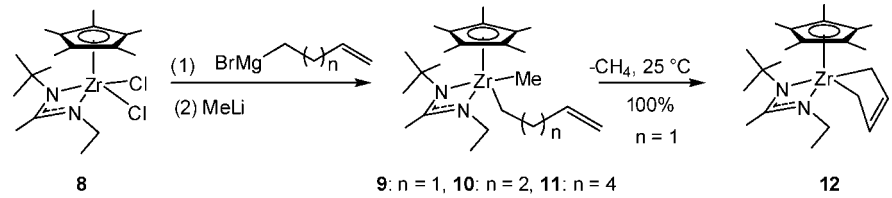


Figure 5. Molecular structure (30% thermal ellipsoids) of compound **7**. Hydrogen atoms have been removed for the sake of clarity except for those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.422(2); C22−C21, 1.432(3); C21−C20, 1.378(3); C20−C19, 1.464(3); C19−Zr1, 2.295(2); C19−Zr1−C22, 76.58(8); Zr1−C22−C21, 75.42(13); C22−C21−C20, 125.4(2); C21−C20−C19, 119.2(2); C20−C19−Zr1, 79.46(13).

Scheme 7



the potential energy surface for metallacyclopentane decomposition. Access to this pathway is guaranteed by the conformational flexibility of the metallcyclopentane ring that can further engage in ground-state transannular β-hydrogen agostic interactions.[8] Furthermore, given the relatively large number of reports of anomalously short $C_\beta-C_{\beta'}$ bond lengths for metallacyclopentanes that are similar in magnitude to those of carbon−carbon double bonds, the occurrence of this dehydrogenative process may actually be more widespread than previously thought. Efforts are currently underway to expand the range of early transition metal-based metallacyclopentanes that are supported by CpAm ligand environments.

Experimental Section

All manipulations were performed under an inert atmosphere of dinitrogen using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Diethyl ether and pentane were distilled from sodium/benzophenone (with a few milliliters of triglyme being added to the pot in the case of pentane), while toluene was distilled from sodium. Benzene-d_6 was vacuum transferred from NaK prior to use for NMR spectroscopy. Ethene and propene were purchased from Matheson Trigas and passed through activated Q5 and molecular sieves (4 Å) and styrene (and styrene-d_2), were vacuumed transferred, and were stored cold under an inert atmosphere prior to use. ^{1}H NMR spectra were recorded at 400 MHz and ambient temperature. Compounds **1** and (η^5-C_5Me_5)Zr[N(i-Pr)C(Me)N-(i-Pr)]Cl_2 (**8**) were prepared according to previously published procedures.[10] The syntheses of compounds **10** and **11** will be reported elsewhere.

(η^5-C_5Me_5)Zr(-CH_2CH(Ph)CH_2CH_2−)[N(i-Pr)C(CH_3)N(i-Pr)] (2). In a 50 mL Schlenk tube fitted with a gastight Teflon valve, 0.10 g (0.21 mmol) of **1** was dissolved in 5 mL of pentane, the dinitrogen atmosphere removed under vacuum, and the tube pressurized with 10 psi of ethene before being sealed. After 30 min, the atmosphere was replaced by N_2, and the solution transferred to a 20 mL vial, whereupon the solvent was partially removed *in vacuo* until the solution volume was approximately 2 mL. After cooling the solution to −30 °C, compound **2** was isolated as yellow crystals. (0.092 g, 87% yield). Anal. Calcd for $C_{29}H_{46}N_2Zr$: C 67.78, H 9.02, N 5.45. Found: C 66.81, H 9.04, N 5.15. Due to stereochemical complexity that prevents simple straightforward assignments, NMR spectra are not presented. The structure of **2** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr(−CH_2CH(Me)CH_2CH(Ph)−)[N(i-Pr)C(CH_3)N-(i-Pr)] (3). In a 50 mL Schlenk tube fitted with a gastight Teflon valve, 0.20 g (0.42 mmol) of **1** was dissolved in 10 mL of pentane, the dinitrogen atmosphere removed under vacuum, and the tube pressurized with 45 psi of propene before being sealed. The tube was then placed at 0 °C for 2 days (until the color of the solution turned from dark green to light yellow). The solution was then

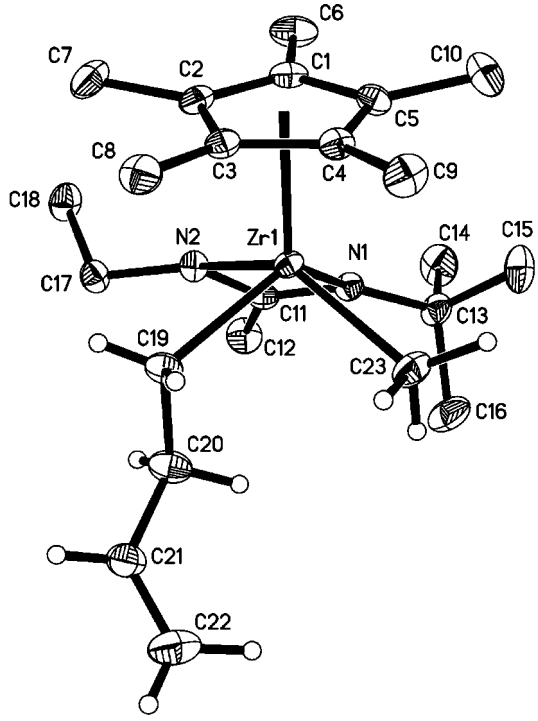


Figure 6. Molecular structure (30% thermal ellipsoids) of compound **9**. Hydrogen atoms have been removed for the sake of clarity except for those for C19−C23, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C19, 2.2582(18); C19−C20, 1.539(3); C20−C21, 1.487(3); C21−C22, 1.302(3); Zr1−C23, 2.285(2).

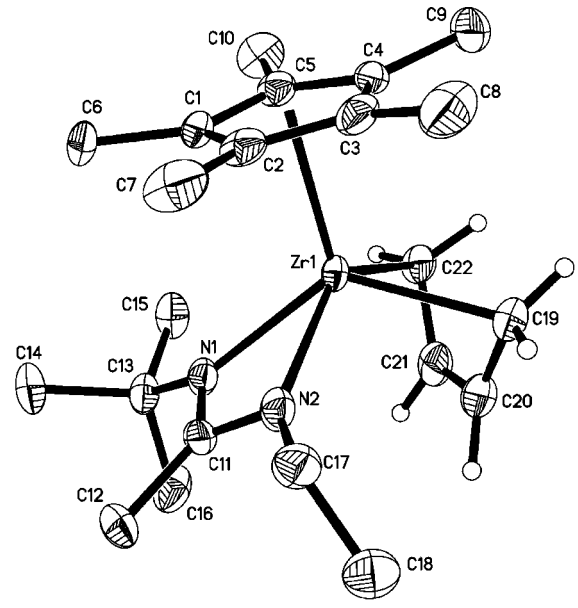


Figure 7. Molecular structure (30% thermal ellipsoids) of compound **12**. Hydrogen atoms have been removed for the sake of clarity except for those for C19−C22, which are represented by small spheres of arbitrary size. Selected bond lengths (Å) and bond angles (deg): Zr1−C22, 2.358(5); C22−C21, 1.427(9); C21−C20, 1.414(10); C20−C19, 1.461(10); C19−Zr1, 2.336(6); C19−Zr1−C22, 77.0(2); Zr1−C22−C21, 78.2(4); C22−C21−C20, 121.6(7); C21−C20−C19, 121.4(7); C20−C19−Zr1, 78.0(4).

transferred to a 20 mL vial, whereupon the solvent was partially removed *in vacuo* until the solution volume was approximately 2 mL. After cooling the solution to −30 °C, compound **3** was isolated as light yellow crystals (0.11 g, 50% yield). Anal. Calcd for $C_{29}H_{46}N_2Zr$: C 67.78, H 9.02, N 5.45. Found: C 66.81, H 9.04, N 5.15. Due to stereochemical complexity that prevents simple straightforward assignments, NMR spectra are not presented. The structure of **3** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr(−CH_2CH(Ph)CH_2CH(Ph)−)[N(i-Pr)C(CH_3)N-(i-Pr)] (4). In a 50 mL round-bottom Schlenk flask 0.25 g (0.53 mmol) of **1** was dissolved in 4 mL of neat styrene at room temperature and allowed to react for 1 h (until there was no visible green color in solution). The reaction mixture was then placed under vacuum, and most of the styrene removed under reduced pressure (0.010 mmHg) for 12 h. The remaining solids were dissolved in 2 mL of Et_2O and recrystallized at −30 °C, yielding **4** as a dark yellow-orange crystalline solid (0.25 g, 82% yield). Anal. Calcd for $C_{34}H_{48}N_2Zr$: C 70.90, H 8.40, N 4.86. Found: C 71.18, H 8.38, N 4.88. The structure of **4** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr(−CH_2C(Me)CHCH(Ph)−)[N(i-Pr)C(CH_3)N-(i-Pr)] (5). In a 20 mL glass vial 0.10 g (0.19 mmol) of **3** was dissolved in 8 mL of pentane and allowed to stand at room temperature overnight, after which time the solution turned from light yellow to dark brown in color. The volatiles were then removed *in vacuo*, and the remaining solids dissolved in a minimal amount of pentane (∼1.5 mL) and cooled to −30 °C, whereupon **5** was isolated as a purple crystalline material (0.02 g, 28% yield). Anal. Calcd for $C_{29}H_{44}N_2Zr$: C 68.04, H 8.66, N 5.47. Found: C 66.11, H 8.51, N 3.65. Due to stereochemical complexity that prevents simple straightforward assignments, NMR spectra are not presented. The structure of **5** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr[−CH_2C($SiMe_3$)CHCH(Ph)−][N(i-Pr)C(CH_3)N-(i-Pr)] (7). In a 50 mL Schlenk tube fitted with a gastight Chemglass Teflon valve, 0.25 g (0.53 mmol) of **1** was dissolved in 8 mL of pentane, followed by addition of 0.26 g (2.65 mmol) of 1-(trimethylsilyl)ethene and the reaction mixture was allowed to stand at ambient temperature for 4 days. Volatiles were then removed *in vacuo*, and the remaining residue dissolved in 2 mL of Et_2O and then cooled to −30 °C, whereupon 0.060 g of the purple crystalline product **6** was isolated in a 40% yield. For **6**, ^{1}H NMR: δ 7.29 (s, 2H), 7.28 (s, 1H), 6.99 (m, 1H), 6.96 (m, 1H), 3.32 (sept, J = 6.0 Hz, 1H), 3.25 (sept, J = 6.2 Hz, 1H), 2.19 (d, J = 8.2 Hz, 1H), 1.92 (s, 15H), 1.70 (d, J = 11.2 Hz, 1H), 1.38 (s, 3H), 1.14 (d, J = 6.1 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 6.2 Hz, 3H), 0.37 (s, 9H). Anal. Calcd for $C_{31}H_{50}N_2SiZr$: C 65.32, H 8.84, N 4.91. Found: C 65.17, H 8.81, N 5.02. The structure of **6** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr(Cl/Br)($CH_2CH_2CH{=}CH_2$)[N(Et)C(CH_3)N-(t-Bu)]. To a solution of 2.12 g (4.8 mmol) of **8** in 100 mL of Et_2O was added dropwise 7.6 mL of 3-butenylmagnesium bromide (0.64 M in Et_2O, 4.8 mmol) over a period of 1 h. The solution was then allowed to warm to room temperature and stirred for another 3 h, whereupon the volatiles were removed *in vacuo*. The yellow product was extracted using 10% toluene in pentane solution, and the extract filtered through a pad of Celite and cooled to −30 °C, whereupon the desired product was obtained as a yellow crystalline material (1.84 g, 79% yield, based on 1.4:1 = Br:Cl product ratio). ^{1}H NMR: δ 6.07 (m, 1H), 5.14 (d, J = 17.1 Hz, 1H), 4.97 (d, J = 9.9 Hz, 1H), 2.99 and 2.87 (two multiplets, 1H (combined integration)), 2.84 (dq, ^2J = 13.9 Hz, ^3J = 7.2 Hz, 1H), 2.63 (dq, ^2J = 14.3 Hz, ^3J = 7.2 Hz, 1H), 2.28 (m, 1H), 1.99 and 1.98 (two singlets, 15H (combined integration), 1.68 and 1.67 (two singlets, 3H (combined integration), 1.32 and 1.30 (two singlets, 9H (combined integration)), 0.79 and 0.77 (two triplets, J = 7.55 Hz, 3H (combined integration)), 0.74 and 0.65 (two multiplets, 1H (combined integration)), 0.23 and 0.11 (two multiplets, 1H (combined integration)). This material was used without further purification for the synthesis of **9**.

(η^5-C_5Me_5)ZrMe($CH_2CH_2CH{=}CH_2$)[N(Et)C(CH_3)N(t-Bu)] (9). To a solution of 0.10 g (0.2 mmol) of (η^5-C_5Me_5)Zr(Br/Cl)($CH_2CH_2CH{=}CH_2$)[N(Et)C(CH_3)N(t-Bu)] in 10 mL of Et_2O, cooled to −30 °C, was added 127 μL of MeLi (1.6 M in Et_2O, 0.2 mmol) via syringe. The reaction mixture was then cooled to −30 °C overnight, after which time, the volatiles were removed *in vacuo*. The crude product was extracted with pentane, and the extract filtered through a pad of Celite. After concentrating *in vacuo*, cooling the solution to −30 °C yielded **9** as white crystals (0.08 g, 89% yield). For **9**, ^{1}H NMR: δ 6.12 (m, 1H), 5.17 (d, J = 16.7 Hz, 1H), 4.99 (d, J = 9.9 Hz, 1H), 2.90 (dq, ^2J = 21.9 Hz, ^3J = 7.2 Hz, 1H), 2.70 (m, 2H), 2.53 (bm, 1H), 1.97 (s, 15H), 1.73 (s, 3H), 1.16 (s, 9H), 0.86 (t, J = 7.2, 3H), 0.44 (m, 1H), 0.16 (s, 3H), 0.05 (bm, 1H). Anal. Calcd for $C_{23}H_{42}N_2Zr$: C 63.10, H 9.67, N 6.40. Found: C 62.85, H 9.52, N 6.37. The structure of **9** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

(η^5-C_5Me_5)Zr(−CH_2CH=CH-CH_2)[N(Et)C(CH_3)N(t-Bu)] (12). A solution of 0.05 g of **9** in 1 mL of pentane was left overnight, after which time the solution turned from clear to a deep red color. After the volatiles were removed *in vacuo*, the crude product was recrystallized from pentane at −30 °C to yield 0.04 g (98% yield). For **12**, ^{1}H NMR: δ 6.17 (dd, ^2J = 18.1 Hz, ^3J = 8.3 Hz, 1H), 6.09 (dd, ^2J = 18.1 Hz, ^3J = 8.0 Hz, 1H), 2.81 (dq, ^2J = 2.4 Hz, ^3J = 7.2 Hz, 2H), 2.05 (s, 15H), 1.96 (dd, ^2J = 9.1 Hz, ^{3}J = 8.3 Hz, 1H), 1.57 (dd, ^2J = 9.1 Hz, ^{3}J = 8.0 Hz, 1H), 1.44 (s, 3H), 1.01 (s, 9H), 0.81 (t, J = 7.2 Hz, 3H), 0.45 (dd, ^2J = 9.1 Hz, ^3J = 8.3 Hz, 1H), 0.34 (dd, ^2J = 9.1 Hz, ^3J = 8.0 Hz, 1H). Anal. Calcd for $C_{22}H_{38}N_2Zr$: C 62.65, H 9.08, N 6.64. Found: C 62.63, H 8.98, N 6.56. The structure of **12** was verified by single-crystal X-ray analysis (see Table 1, Supporting Information).

Acknowledgment. Funding for this work was provided by the NSF (CHE-061794), for which we are grateful.

Supporting Information Available: Details of single-crystal X-ray analyses, including tables of bond lengths, angles, and anisotropic displacement parameters for the solid-state structures and complete X-ray crystallographic data (CIF) for compounds **2**, **3**, **4**, **5**, **7**, **9**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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