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Investigation of relative stabilities of CPAM zirconium cycloalkylmethyl vs isomeric ω-alkenyl complexes: Crystal structures of the cyclobutylmethyl and cyclopentylmethyl complexes

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ABSTRACT

Investigations of the syntheses, structural characterization, and relative stabilities of the cyclopentadienyl, amidinate Zr cycloalkylmethyl complexes, (CPAM)Zr(X)[CH_2(*cyclo*-C_mH_{2m-1})] (CPAM = (η^5-C_5Me_5)[(*N,N′*)-κ^2-N(Et)-C(Me)N(*t*-Bu)]) for X = Cl and m = 3 (**1a**), 4 (**1b**) and 5 (**1c**) and for X = Me, and m = 4 (**2b**), and of the corresponding isomeric ω-alkenyl complexes, (CPAM)Zr(Cl)[$CH_2(CH_2)_nCH_2CH=CH_2$] for n = 0 (**3a**), 1 (**3b**) and 2 (**3c**), have been conducted. Hydrozirconation of methylenecyclopropane by (CPAM)Zr(X)Cl (X = H or D) (**8**), which is generated in situ through hydrogenolysis of the Zr-Si bond of (CPAM)Zr($SiMe_2$Ph)Cl (**7**), provided a high yield of **3a** due to rapid isomerization of transiently generated **1a**. In contrast, crystalline **1b** could be isolated in high yield via hydrozirconation of methylenecyclobutane by **8**, and it has been structurally characterized by X-ray crystallography. Thermolysis of **1b** in solution provided a quantitative yield of **3b**, while quantitative production of **1c** was achieved through intramolecular cyclization of **3c** by reversible chloride abstraction that was catalyzed by addition of the ion pair, {(CPAM)Zr(Me)}{B(C_6F_5)$_4$} **10**. The cyclobutylmethyl complex **2b** was also prepared from **1b** through traditional methylation using MeLi, and it too was structurally characterized by X-ray crystallography. In solution, **2b** thermally decomposes at 25 °C to an intractable mixture. Finally, reaction of **2b** with a stoichiometric amount of the borate **B1** provided the corresponding ion pair complex, {(CPAM)Zr[$CH_2CH_2CH_2CH=CH_2$]}{B(C_6F_5)$_4$} (**9**) in which the terminal alkenyl group is intramolecularly coordinated to the transition metal center as determined by ^{1}H NMR spectroscopy. The results of a DFT (B3LYP / LANL2DZ (Zr) / 6-31G**) computational investigation for the **1b** to **3b** isomerization and for the structure of **9** are also included.

1. Introduction

Over the past 20 years, we have been developing cyclopentadienyl, amidinate group 4 metal complexes of the general formula, (CPAM)M(X)(R), where CPAM = (η^5-$C_5R^1_5$)[(*N,N′*)-κ^2-N(R^2)C(R^3)N(R^4)], M = Zr or Hf, and X = Cl or Me, (**I**), as pre-initiators for the living coordinative polymerization (LCP) of ethene, propene, longer-chain linear and branched α-olefins, and α,ω-nonconjugated dienes [1–11]. In the case of X = Me, 'activation' of **I** proceeds through chemoselective protonolysis of the methyl group by the borate co-initiator, [PhNHMe_2][B(C_6F_5)$_4$] (**B1**), to generate the corresponding active ion pair initiator, {(CPAM)M(R)}{B(C_6F_5)$_4$} (M = Zr, Hf) (**II**). Living polymerization with **II** then proceeds through 1,2-migratory insertion of the coordinated olefin monomer into the growing polymer chain, which occurs in the absence of irreversible chain termination, to provide a polyolefin product for which a tunable number-average degree of polymerization (DP_n) and a very narrow molar mass distribution (MMD), with a dispersity index, *Đ* (= M_w / M_n), of ≤ 1.1, can be achieved. In the case of C_1-symmetric, chiral (but racemic) derivatives of **I** and **II** (i.e., $R^2 \neq R^4$), propagation also proceeds in a highly stereoselective (stereospecific) fashion to provide an isotactic polyolefin microstructure [1,8].

The robust living character of olefin polymerizations that are

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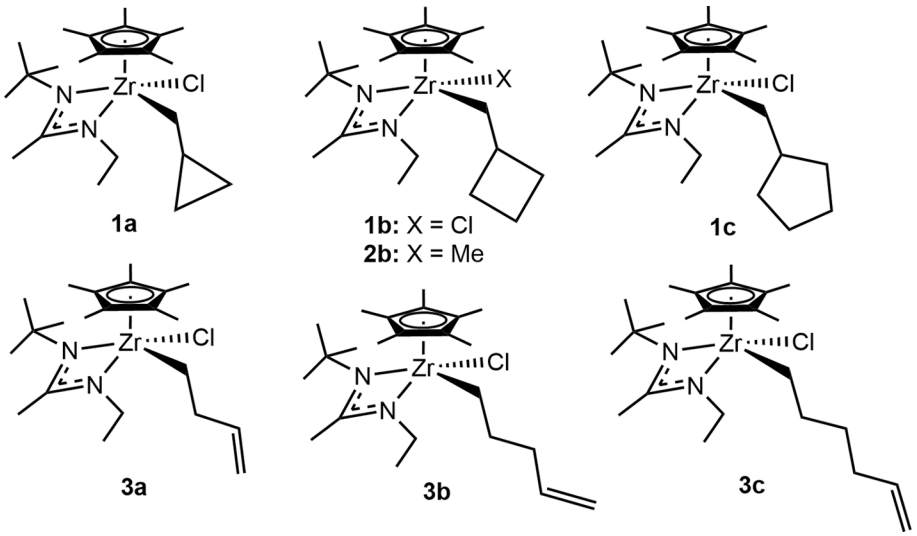
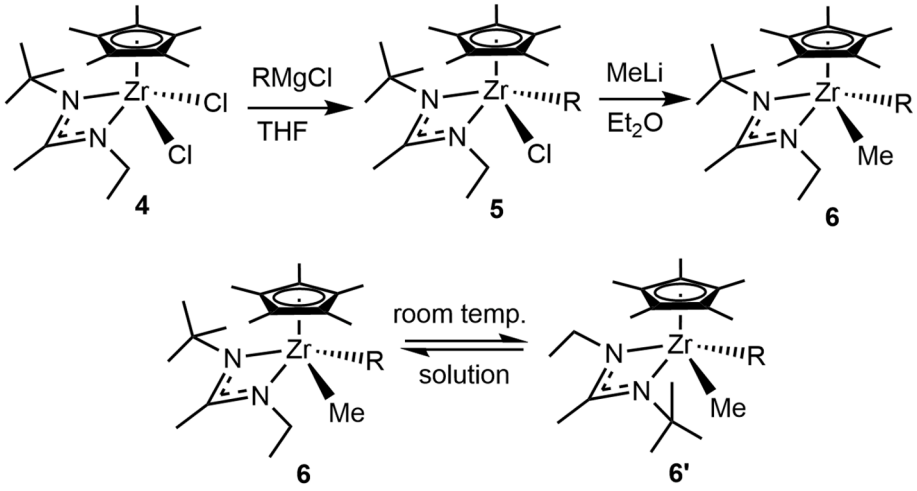
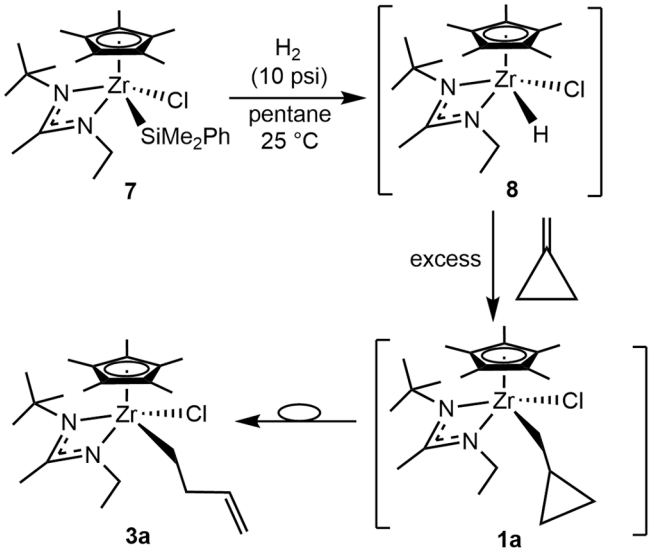


Scheme 1. Structures of the isomeric (CPAM)Zr cycloalkylmethyl and ω-alkenyl complexes investigated.

mediated by **I** and **II** appear to contradict well-established dogma and expectations regarding the anticipated low thermal stability of early transition-metal complexes bearing alkyl substituents with β-hydrogens [12,13]. Accordingly, we have long been interested in exploring the syntheses, solution, and solid-state structures, and relative stabilities of a wide variety of different alkyl substituents bound to group 4 and 5 metal centers that are supported by the CPAM ligand environment in order to not only establish the steric and electronic factors that contribute to the unique stability of these complexes, but also, to potentially discover new and unique decomposition reactions that proceed through novel mechanistic pathways [14–20]. In this regard, organometallic compounds possessing a metal-bonded cycloalkylmethyl group, i.e. M-CH_2(*c*-C_mH_{2m-1}), are notoriously unstable and known to be susceptible to undergoing conversion to the corresponding metal-bound ω-alkenyl structures through isomerization processes that proceed with very low energy barriers for the smallest cycloalkyl rings (e.g., for m = 3 and 4) [21–35]. Particularly relevant to the present report are the seminal contributions made by the groups of Bercaw [25], Casey [26–29], Flood [30–32], and Marks [33] who investigated the relative stabilities of d^0 transition- and lanthanide-metal cyclobutylmethyl and 4-pentenyl complexes in the context of transition-metal coordination polymerization and β-alkyl elimination. For lanthanide- and group 4 metals, cyclobutylmethyl complexes are only presumed to exist as transient intermediates [25–29]. On the other hand, while a few Pt(II) cyclobutylmethyl complexes have been synthesized and isolated, no structure determinations by crystallographic analyses were ever performed [30–32]. Further, thermolysis of these complexes in solution only yielded free diene products through presumed successive β-alkyl and β-hydrogen transfers to the metal. Indeed, to the best of our knowledge, to date, there are no known crystal structures for any cyclopropylmethyl or cyclobutylmethyl lanthanide or transition-metal complexes, nor has the structural isomerization of such complexes into the corresponding isomeric ω-alkenyl complex, or vice-versa, ever been studied. Herein, we now report the results of an experimental evaluation of the relative stabilities of a few examples of (CPAM)Zr(Cl)[CH_2(*c*-C_mH_{2m-1}] complexes, where CPAM = (η^5-C_5Me_5)[(*N,N′*)-κ^2-N(Et)C(Me)N(*t*-Bu)] and m = 3 (**1a**), 4 (**1b**), and 5 (**1c**), as well as, of the isomeric (CPAM)Zr(Cl)[$CH_2(CH_2)_nCH_2CH=CH_2$] complexes, where n = 0 (**3a**), 1 (**3b**) and 2 (**3c**), as presented in Scheme 1. This study also includes an investigation of the synthesis, stability, and chemical reactivity of the corresponding zirconium cyclobutylmethyl, methyl complex, (CPAM)Zr(Me)[CH_2(*c*-C_4H_7)] (**2b**), which upon activation by **B1** in chlorobenzene, cleanly produces a stable ion pair in which isomerization has occurred and the terminal alkenyl group of the resulting 4-pentenyl substituent is



Scheme 2. General synthetic strategy for obtaining C_1-symmetric (CPAM)Zr(X)(R) derivatives that are configurationally-stable for X = Cl (**5**) and configurationally-unstable for X = Me (**6**).



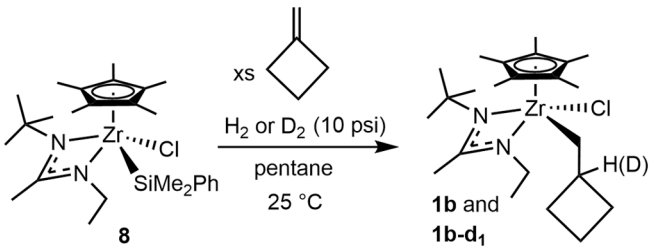
Scheme 3. Hydrozirconation of methylenecyclopropane to provide the known 3-butenyl derivative **3a**.

intramolecularly complexed to the metal center. Finally, the results of a computational DFT (B3LYP / LANL2DZ (Zr) / 6-31G**) investigation for selected transformations and structures are presented.

2. Results and discussion

Scheme 2 summarizes previously reported synthetic methods that have employed the structurally-related C_1-symmetric, chiral (CPAM)Zr(Cl)$_2$ complex (**4**) for the synthesis of a variety of derivatives of (CPAM)Zr(Cl)(R) (**5**) and (CPAM)Zr(Me)(R) (**6**) for R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu, and 3-ethylbutyl [16]. More specifically, reaction of **4** with one equivalent of an alkyl Grignard reagent (RMgCl) routinely provides an excellent yield of **5**, which can then be subjected to a second alkylation using one equivalent of methyl lithium (MeLi) to provide the final mixed alkyl complex **6**. It is important to note that, while all derivatives of **5** investigated to date are configurationally stable towards metal-centered racemization in solution, (CPAM)Zr(R)(R′) dialkyl complexes, such as those represented by **6**, all engage in facile racemization via an amidinate 'ring-flipping' that proceeds rapidly in solution even at low temperatures. The configurational stability of **5** and the energy barrier for racemization of **6** can be easily established by variable temperature ^{1}H NMR spectroscopy in which coalescence of the separate resonances for the two diastereotopic methylene protons of the *N*—C(H$_a$)(H$_b$)CH$_3$ amidinate substituent is tracked as a function of temperature.[1] Additional 2D ^{1}H NMR exchange spectroscopy experiments have further ruled out the alternative possibility that racemization of **6** proceeds by pairwise exchange of the two different alkyl substituents. Finally, the ^{1}H NMR spectra and crystal structures of all these derivatives of **5** and **6** do not show any evidence of the existence of secondary agostic bonding interactions between the electrophilic transition-metal center and protons that are located on any of the C$_\alpha$, C$_\beta$ or C$_\gamma$ positions within the alkyl substituents [12,13]. On the other hand, the existence of these β-hydrogen agostic interactions have been established in solution and the solid state for the corresponding derivatives of **II** that are generated by borate activation of **6** [16].

Given the previously stated instability of organometallic cyclopropylmethyl and cyclobutylmethyl complexes towards undergoing rapid isomerization in solution, the synthetic strategy of Scheme 2 was clearly not applicable for obtaining the desired CPAM Zr complexes **1a** and **1b** of Scheme 1. Accordingly, an alternative strategy was pursued that is based on hydrozirconation of methylenecycloalkanes in which hydrogenolysis of the Zr-Si bond of the CPAM Zr chloro, silyl complex **7** occurs under mild conditions to generate the CPAM Zr hydrido, chloride reagent **8** as presented in Scheme 3. Bercaw [25] and [34] Casey [26] and co-workers have similarly employed the hydrometallation of methylenecyclobutane as a strategic route to transient lanthanide cyclobutylmethyl complexes (vide infra). Importantly, we have previously demonstrated that CPAM Zr chloro, alkyl complexes obtained from the hydrozirconation of internal alkenes by **8** do not undergo subsequent chain-walking of the transition-metal to a terminal position through reversible β-hydride eliminations [34]. As Scheme 3 reveals, when this strategy was employed in the case of the hydrozirconation of methylenecyclopropane, a high yield of a single crystalline product was obtained. A comparison of ^{1}H NMR spectral data, however, established the identity of this material to be the CPAM Zr chloro, 3-butenyl complex **3a**, the synthesis of which we had previously reported by using the standard salt metathesis chemistry of Scheme 2.[19] We postulate that hydrozironation of methylenecyclopropane did, in fact, proceed in high yield as expected, but that the transiently generated CPAM Zr, chloro, cyclopropyl product **1a** has only a very short lifetime due to rapid isomerization according to Scheme 3.



Scheme 4. Hydrozirconation of methylenecyclobutane to provide **1b** and **1b-d$_1$**.

Successful validation of our hydrozirconation synthetic strategy for producing CPAM Zr cycloalkylmethyl complexes was achieved upon moving to methylenecyclobutane as the substrate [25,26]. More specifically, as presented in Scheme 4, hydrogenolysis of **7** in the presence of excess equivalents of methylenecyclobutane now provided a near quantitative yield of the desired crystalline product **1b**. Further, by replacing H_2 with D_2, a similar high yield of **1b-d$_1$** was obtained with the deuterium label now regiospecifically positioned at the β-carbon as depicted in Scheme 4. Analytically pure **1b** and **1b-d$_1$** were obtained through recrystallization from pentane at −30 °C, and the results of chemical and NMR spectroscopic analysis are fully consistent with the assigned structures. In the case of **1b**, unequivocal proof of the cyclobutylmethyl substituent was obtained via single-crystal X-ray analysis, which provided the solid-state molecular structure shown in Fig. 1. As previously noted, to the best of our knowledge, **1b** is now the first transition-metal complex bearing a –CH$_2$(*c*-C$_4$H$_7$) alkyl substituent to be crystallographically characterized. In this respect, the structural features of the supporting CPAM ligand environment are similar to those for a wide range of group 4, group 5, and group 6 metal CPAM derivatives that have similarly been structurally characterized by X-ray analysis. [1–11,14–20,34,35] Furthermore, the steric bulk of the cyclobutylmethyl moiety is once again accommodated on the *N*-Et side of the amidinate group, and there does not appear to be crystallographic evidence for the existence of any secondary hydrogen agostic interaction between this fragment and the zirconium center [12,13]. Finally, all the bond lengths and bond angles for the CH$_2$(*c*-C$_4$H$_7$) group, in which the four-membered ring adopts a planar conformation, are consistent with expectations.

After extended periods of time (>18 h) in hydrocarbon solution at 25 °C, **1b** was observed to cleanly convert to another species as revealed by ^{1}H NMR spectroscopy. A similar transformation for **1b-d$_1$** was also observed, and in this case, no positional scrambling of the deuterium-label was seen to have occurred either within the zirconium-bonded CH$_2$(*c*-C$_4$H$_7$) fragment or in the final product. Diagnostic ^{1}H NMR

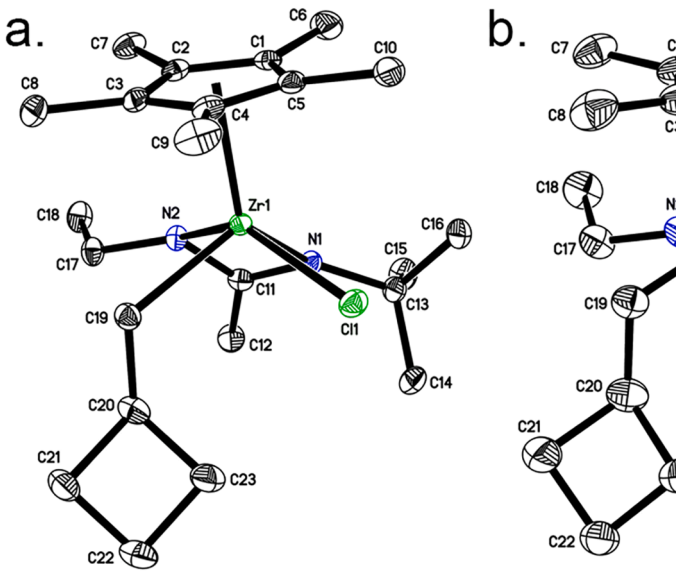
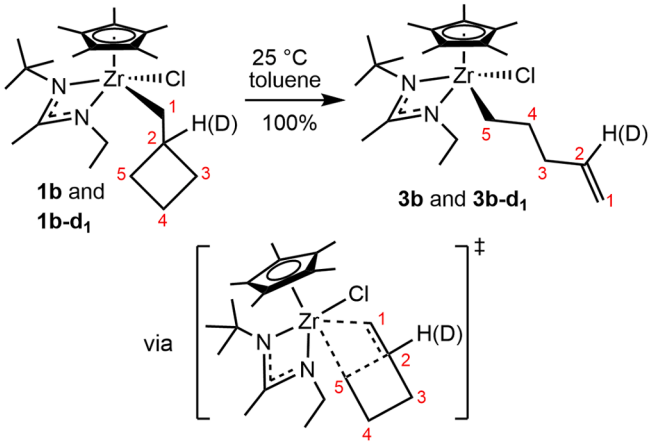


Fig. 1. Molecular structures (30% thermal ellipsoids) of (a) **1b** and (b) **2b**. Hydrogen atoms have been deleted for the sake of clarity. Selected bond lengths (Å) and bond angles (°) for **1b**: Zr1-N1 2.2374(17), Zr1-N2 2.279(17), Zr1-C19 2.273(2), Zr1-Cl1 2.4563 (6), C19-C20 1.523(3), C20-C21 1.555(3), C21-C22 1.514(4), C22-C23 1.531(4), C20-C23 1.534(4), N1-Zr1-N2 59.12(6), C19-Zr1-Cl1 90.76(6), Zr1-C19-C20 114.86(15), C19-C20-C21 120.0(2), C19-C20-C23 121.8(2), C21-C20-C23, 86.9(2), C20-C21-C22 88.8(2), C21-C22-C23 88.5(2), C20-C23-C22 89.0(2) and for **2b**: Zr1-N1 2.266(2), Zr1-N2 2.255 (2), Zr1-C19 2.265(3), Zr1-C24 2.292(3), C19-C20 1.514(4), C20-C21 1.546(5), C21-C22 1.50(2), C22-C23 1.525(19), C20-C23 1.531(5), N1-Zr1-N2 58.46(9), C19-Zr1-C24 90.09(11), Zr1-C19-C20 113.5(2), C19-C20-C21 120.3(3), C19-C20-C23 120.7(3), C21-C20-C23, 86.2(3), C20-C21-C22 90.3(3), C21-C22-C23 87.3(3), C20-C23-C22 89.8(3).



Scheme 5. Thermal isomerization of **1b** to **3b** via a proposed formal intramolecular β-alkyl group migration mechanism.

resonances appearing in the olefinic chemical shift range were highly suggestive that the identity of this compound might be the CPAM Zr chloro, 4-pentenyl derivative **3b** that is shown in Schemes 1 and 5. This hypothesis was further supported by a preparative-scale thermolysis of a solution of **1b** in toluene that was heated at 65 °C for 36 h. Upon removal of the volatiles *in vacuo*, a quantitative yield, by weight, was then obtained of an oily material for which a ^{1}H NMR spectrum confirmed this to consist of a single pure product that had a set of ^{1}H resonances fully consistent with those expected for the structure of **3b**. Similar thermolysis of the singly-deuterium-labeled derivative **1b-d$_1$** in toluene solution, which was maintained at 25 °C for an even longer period of time, also quantitatively provided a corresponding single product that was identifed by ^{1}H NMR spectroscopy to be **3b-d$_1$** in which the deuterium-label was again confirmed to be regiospecifically located at the internal carbon of the ω-alkenyl group as shown in Scheme 5. The lack of evidence for H-D scrambling in the **1b-d$_1$** → **3b-d$_1$** thermal conversion is strongly supportive of a concerted intramolecular rearrangement process. An Eyring analysis of this transformation was performed by ^{1}H NMR spectroscopy at five different temperatures ranging between 48 °C and 90 °C, which yielded the following activation parameters: $\Delta H^{\ddagger}$ = 20.4 ± 0.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −16.3 ± 0.9 eu. The sign and magnitude of these parameters are within the range previously reported for similar isomerizations of organometallic M−cyclobutylmethyl compounds for M = Li and MgCl [22]. Based on these findings, we propose a concerted mechanism that proceeds through formal β-alkyl group migration involving the zirconabicyclo[2.2.0]hexane transitition state structure shown in Scheme 5 [25,26]. It is also notable that no evidence of a competing β-hydrogen atom transfer to the metal center was obtained, and that heating a solution of analytically pure **3b** under identical conditions did not provide any evidence for the establishment of an equilibrium involving reversible formation of **1b**.

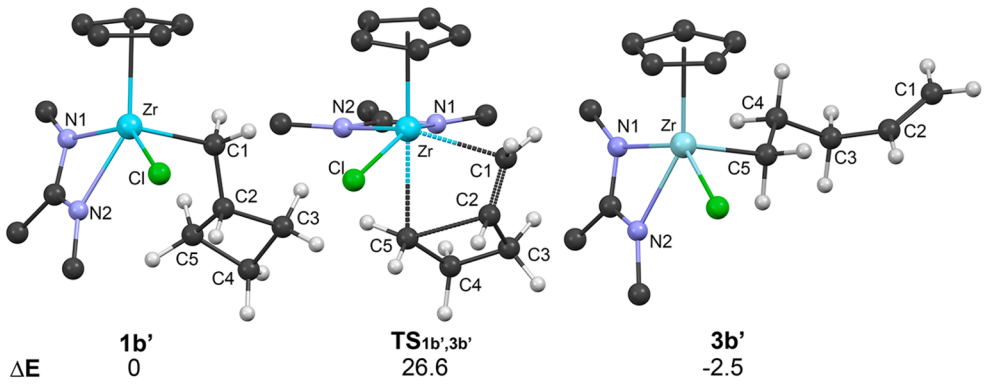
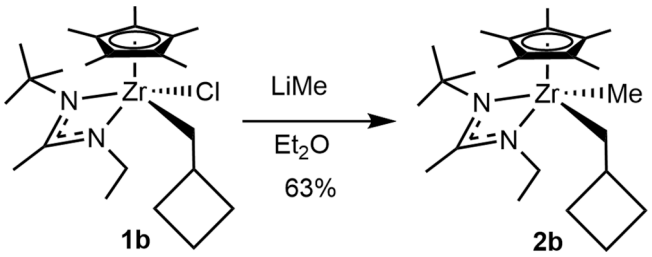


Fig. 2. Optimized structures for **1b′**, **3b′**, and the transition state **TS$_{1b',3b'}$** connecting the two via intramolecular ring-opening β-alkyl migration. Hydrogen atoms are only presented for the cyclobutyl and 4-pentenyl groups for the sake of clarity. Energy is in units of kcal/mol.



Scheme 6. Synthesis of **2b**.

A computational investigation of the **1b** → **3b** isomerization was performed with Gaussion 09 using the DFT method in combination with the B3YLP hybrid functionals and the LANL2DZ effective core potentials for Zr and the 6-31G** basis set for all other elements [36]. To facilitate computational time, a truncated model, CPAM′ = (η^5-C_5H_5)[(*N,N*)-κ^2-N(Me)C(Me)N(Me)], for the supporting ligand set in **1b**′ and **3b**′ was employed, and calculations were performed in the absence of a solvent. Fig. 2 provides the optimized structures obtained for **1b**′ and **3b**′ that were confirmed to be potential energy surface (PES) minima, as well as the optimized structure of the transition-state $\mathbf{TS_{1b',3b'}}$ that was further confirmed to be a saddle point connecting the two. As further revealed in Fig. 2, a calculated activation energy barrier of $\Delta G^{\ddagger} = 26.6$ kcal mol^{-1} was obtained for **1b**′ transforming to **3b**′ via intramolecular β-alkyl

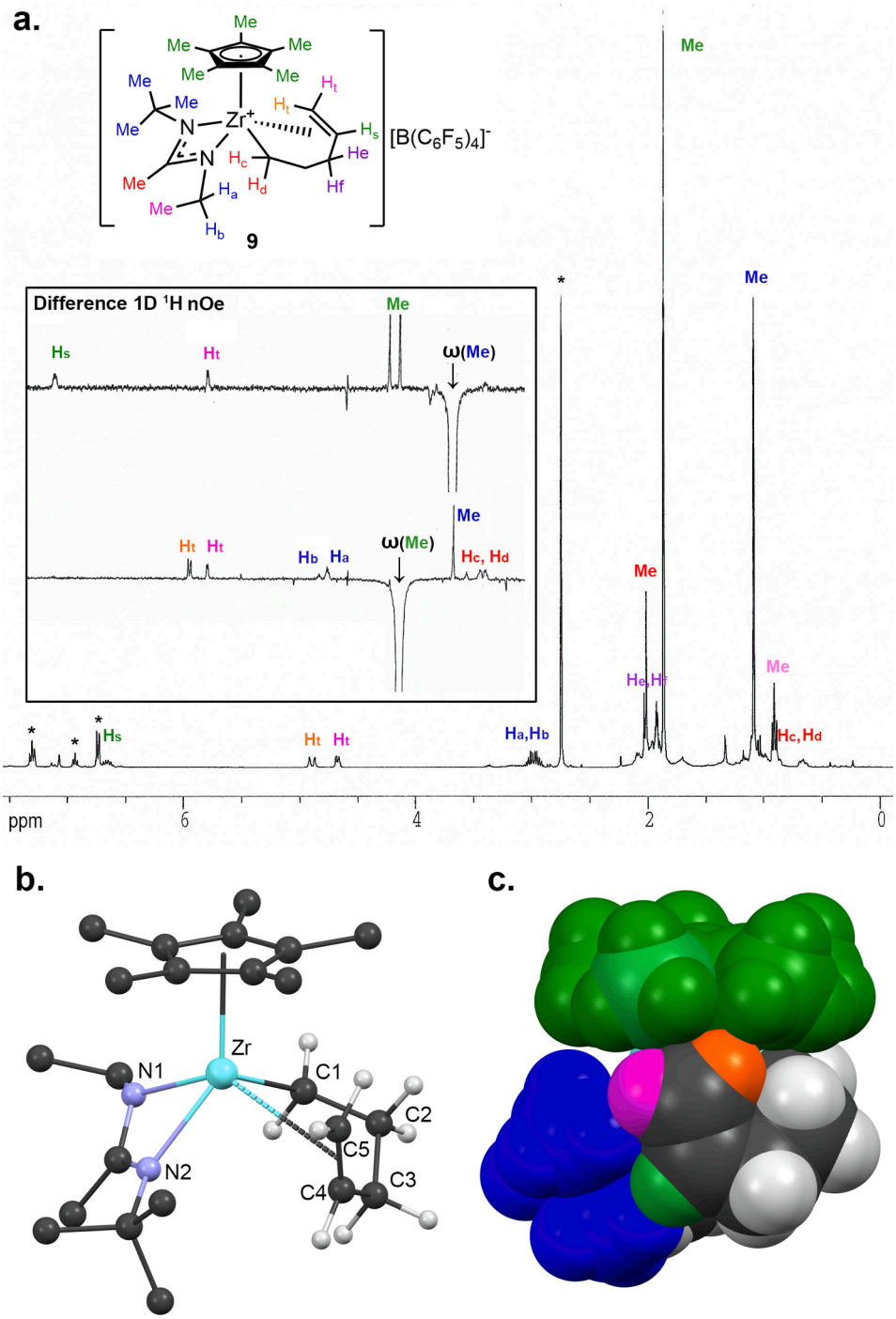
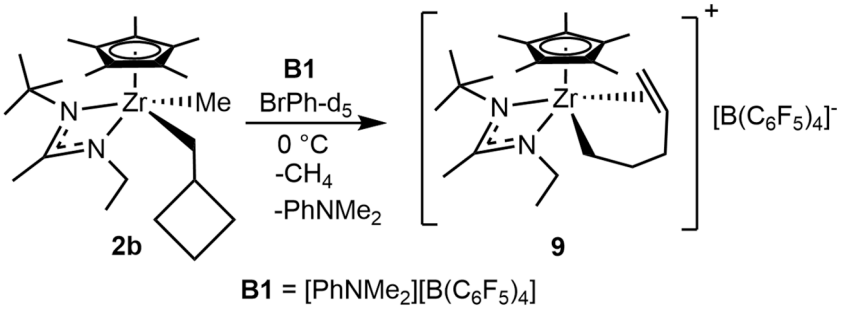


Fig. 3. (a) ^{1}H NMR (500 MHz, BrPh-d_5, 263 K) spectra for the reaction mixture of **2b** and **B1**. Insert presents 1D ^{1}H NMR difference nOe spectra for selective irradition (ω) at the (top) *N*—C(CH_3)$_3$ chemical shift, and (bottom) at the η^5-C_5(CH_3)$_5$ chemical shift, (b) optimized structure of **9** obtained by DFT (B3LYP / LANL2DZ / 6-31G**), minus borate counteranion and solvent, and with hydrogen atoms only being presented for the 4-pentenyl group for the sake of clarity, and (c) space-filling representation of the structure of **9** in (b) with all hydrogen atoms and color-coded according to those assigned for selected ^{1}H NMR resonances of (a). ^{1}H NMR resonances for the $PhNMe_2$ co-product generated upon protonolysis of **2b** by **B1**, are marked with an asterisk in (a).

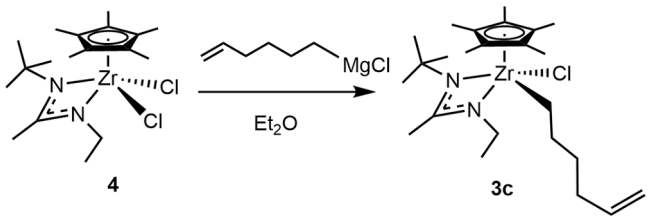


Scheme 7. Chemoselective methyl group protonolysis of **2b** by **B1** to produce the ion pair **9**.

migration. Interestingly, the reverse cyclization process of **3b′** → **1b′** is slightly higher with $\Delta G^{\ddagger}$ = 29.1 kcal mol[1]. While higher theoretical computational models can likely yield more accurate numbers, the current results are nicely in keeping with experimental observations.

Methylation of **1b** with one equivalent of MeLi in Et_2O successfully provided the corresponding CPAM Zr methyl, $CH_2(c\text{-}C_4H_7)$ derivative **2b** in a 63 % yield according to Scheme 6. Analytically pure **2b** could be obtained through recrystallization from pentane solution at low temperature, and single-crystal X-ray analysis revealed that the solid-state molecular structure of this compound, which is presented in Fig. 1, is almost isostructural to that of **1b**. As with other comparisons of CPAM Zr chloro, alkyl and CPAM Zr dialkyl complexes (e.g **5** and **6** in Scheme 2), **2b** displays slightly longer Zr-N bond distances vis-à-vis those of **1b**, and this structural difference strongly correlates with the lower energy barrier to metal-centered racemization via amidinate ring flipping that is seen by ^{1}H NMR spectroscopy. Finally, it is important to note that **2b** is even more thermally unstable in solution than **1b**, but unlike the latter, it decomposes to an intractable mixtue of products for which an absence of olefinic resonances suggests that the β-alkyl group migration mechanism of Scheme 5 is no longer involved [14,15].

With the structure of **2b** confirmed, it was also of interest to determine if chemoselective methyl group protonolysis by the borate **B1** could be achieved to generate the corresponding derivative of **II** with a cyclobutylmethyl substituent. Thus, the reaction between **2b** and one equivalent of **B1** in bromobenzene-d_5 at −10 °C was monitored by ^{1}H NMR (500 MHz, BrPh-d_5, 263 K) spectroscopy while keeping the sample at the same temperature. As presented in Fig. 3, a set of new ^{1}H resonances corresponding to generation of a single product was observed, and through a series of 1D ^{1}H NMR nOe difference spectra (nOe = nuclear Overhauser effect), very strong evidence was obtained in support of this new species being the ion pair **9** in which isomerization of the cyclobutylmethyl group of **2b** has occurred to provide the 4-pentenyl substituent that is intramolecularly coordinated to the zirconium center according to Scheme 7. There has been considerable interest in studying species such as **9** as models for the lanthanide-metal or transition-metal alkyl, alkene intermediate that is involved in the migratory insertion step for the coordination polymerization of olefins [25–29,37–42]. In addition to the difference 1D ^{1}H nOe subspectra (see inset of Fig. 3a), other lines of evidence support the proposed structure that is depicted for **9**. To begin, the secondary ^{1}H resonace of the terminal alkene group is significantly shifted downfield to δ 6.90 ppm due to complexation to the electrophilic zirconium center that places signifcant positive charge at the internal carbon atom of the alkene moiety. Similar downfield shifts have been observed for other intramolecularly coordinated alkenes within neutral and cationic d^0 lanthanide and group 4 metal complexes [25–29,37–42]. Second, a similar computational DFT investigation of **9**, minus the borate counteranion and solvent, provided the optimized PES minimum structure that is shown in Fig. 3b and in which the terminal alkene group is coordinated to the metal center on the *N*-tBu side of the amidinate ligand. Finally, a space-filling representation of this computationally generated structure of **9** that is color-coded according to those assigned to the ^{1}H resonances of Fig. 3a nicely



Scheme 8. Synthesis of **3c**.

conforms to the geometry predicted by the nOe experiments as shown in Fig. 3c.

Interestingly, when activation of **2b** was conducted in the presence of excess equivalents of 1-hexene, polymerization occurred to provide an isotactic poly(1-hexene) product, but with no evidence for the existence of a terminal alkenyl group. This observation can be rationalized by assuming that upon first 1,2-migratory insertion of a 1-hexene monomer into the 4-pentenyl group of **9**, the resulting ω-alkenyl chain is now sufficiently long enough to allow cyclization to a methylenecyclohexyl group to occur. This observation and conclusion are also in keeping with our previous reports that the living cyclopolymerization of 1,5-hexadiene and 1,6-heptadiene can be performed using various derivatives of **II** as initiators to provide poly(methylene-1,3-cyclopentane) (PMCP) and poly(methylene-1,3-cyclohexane) (PMCH), respectively [3,9,43].

Based on the above results establishing that both the CPAM Zr chloro, 3-butenyl and 4-pentenyl complexes, **3a** and **3b**, are thermodynamically more stable than the respective cyclopropylmethyl and cyclobutylmethyl complexes, **1a** and **1b**, it was of interest to determine if this balance could now be tipped in favor of the cycloalkylmethyl structure with a ω-alkenyl substituent that was sufficiently long enough to permit cyclization without incurring an energy penalty due to the introduction of ring strain. Accordingly, synthesis of the CPAM Zr chloro, 5-hexenyl derivative **3c** was undertaken using the conventional salt metathesis route according to Scheme 8. Fortunately, the desired product **3c** could be obtained in high purity as a light yellow oil that proved to be exceedingly stable in solution as assessed by ^{1}H NMR spectroscopy as shown in Fig. 4. Indeed, this stability now raised the question, under what conditions could **3c** be induced to undergo cyclization? To answer this question, a small amount (*ca* 5 mol%) of a pregenerated solution of the ion pair,{(CPAM)Zr(Me)}{$B(C_6F_5)_4$} **10**, in chlorobenzene was added to a solution of **3c** in the same solvent at 25 °C. After a usual workup, a 53 % yield of crystalline **1c** was obtained as verified by both a ^{1}H NMR spectrum and single-crystal X-ray analysis according to the data reproduced in Fig. 4b and Fig. 5, respectively. As presented in Scheme 9, the presumed mechanism for this **3c** → **1c** transformation that occurs under thermodynamically equilibrating conditions, involves chloride abstraction from **3c** by **10** to transiently generate the corresponding ion pair, [(CPAM)Zr(5-hexenyl)][$B(C_6F_5)_4$] (**11**), that then undergoes cyclization to the more thermodynamically favored isomeric species, [(CPAM)Zr(cyclopentylmethyl)] [$B(C_6F_5)_4$]

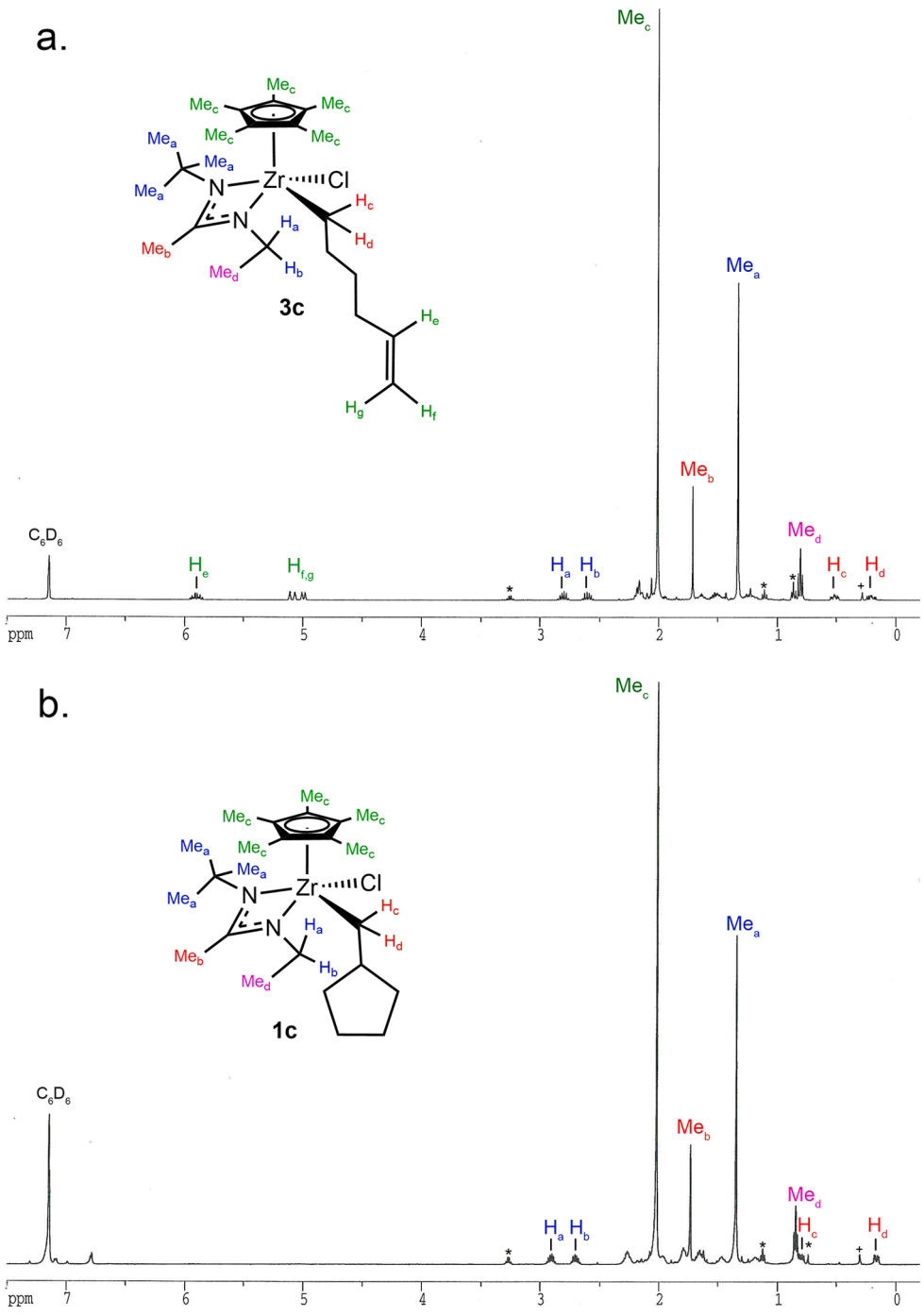


Fig. 4. ^{1}H NMR (500 MHz, benzene-d_6, 298 K) spectra for (a) **3c** and (b) **1c**. Residual solvent and silicon grease resonances are marked with an asterisk (*) and plus (+) symbol, respectively. Structural assignments of selected ^{1}H resonances are provided.

(**12**).[45] Back transfer of a chloride then produces **1c** and regenerates **10**. A similar mechanism of rapid and reversible chloride abstraction is invoked for stereoselective two-state degenerative LCP of α-olefins when substoichiometric activation of (CPAM)Zr(Cl)(R) (**5**) is employed [6,44].

3. 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. Chlorobenzene was distilled from CaH prior to use. Benzene-d_6 and toluene-d_8 were vacuum transferred from NaK prior to being used for NMR spectrscopy. Methylenecyclopropane, methylenecyclobutane, and **B1** were obtained from commercial sources. Compounds **4**, **7**, **3a**, and **10** were prepared as previously reported [1,19,34]. ^{1}H NMR spectra were recorded at 500 MHz at ambient temperature, unless otherwise stated. Elemental analyses were provided by Midwest Labs.

(η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] Zr(Cl) [CH_2(c-C_4H_7)] (1b). In a 50-mL Schlenk tube fitted with a gas tight Teflon valve, 0.30 g (0.54 mmol) of **7** was dissolved into 10 mL of pentane, to which was added, a

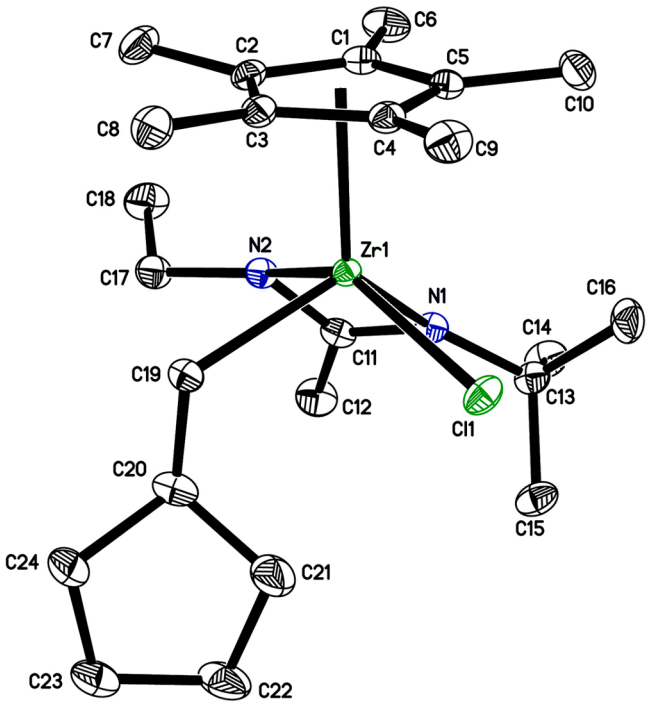


Fig. 5. Molecular structures (30% thermal ellipsoids) of **1c**. Hydrogen atoms have been deleted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Zr1-N1 2.266(2), Zr1-N2 2.255(2), Zr1-C19 2.265(3), Zr1-C24 2.292 (3), C19-C20 1.514(4), C20-C21 1.546(5), C21-C22 1.50(2), C22-C23 1.525 (19), C20-C23 1.531(5), N1-Zr1-N2 58.46(9), C19-Zr1-C24 90.09(11), Zr1-C19-C20 113.5(2), C19-C20-C21 120.3(3), C19-C20-C23 120.7(3), C21-C20-C23, 86.2(3), C20-C21-C22 90.3(3), C21-C22-C23 87.3(3), C20-C23-C22 89.8(3).

5-fold excess of methylenecyclobutane (precooled to −30 °C), and the tube quickly sealed. The tube was then pressurized with H_2 (30 psi) and sealed once more. The mixture was shaken overnight and then the volatiles removed *in vacuo*. The crude product was taken up in a minimum amount of pentane and the yellow solution cooled to −30 °C, to provide yellow crystals of **1b** (0.2 g, 78 % yield). For **1b**: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 2.84 (dq, $J^2 = 13.9$ Hz, $J^3 = 7.2$ Hz, 1H), 2.78 (m, 1H), 2.66 (dq, $J^2 = 14.3$ Hz, $J^3 = 7.2$ Hz, 1H), 2.52 (m, 1H), 2.30 (m, 1H), 2.05 (m, 1H), 2.00 (s, 15H), 1.98 (m, 2H), 1.71 (s, 3H), 1.70 (m, 1H), 1.32 (s, 9H), 088 (dd, $J^2 = 13.1$ Hz, $J^3 = 7.8$ Hz, 1H), 0.81, (t, $J^3 = 7.2$ Hz, 3H), 0.32 (dd, $J^2 = 13.1$ Hz, $J^3 = 5.6$ Hz, 1H). Anal Calcd. for $C_{23}H_{41}N_2ClZr$: %C 58.50, %H 8.75, %N 5.93; Found %C 58.65, %H 8.72, %N 5.86. In a similar fashion, **1b-d$_1$** was obtained using D_2.

Attempted Preparation of (η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] -Zr(Cl) [CH_2(c-C_3H_5)] (1a). The same procedure for the preparation of **1b** was followed, but methylenecyclopropane was used in place of methylenecyclobutane. A ^{1}H NMR spectrum recorded for the crude product revealed this material to be the previously reported **3a** [19].

(η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] Zr(Me) [CH_2(c-C_4H_7)] (2b). To a solution of 0.20 g (0.42 mmol) of **1b** in 6 mL of Et_2O cooled to −30 °C, was added 0.27 mL (0.42 mmol) of MeLi (1.6 M in Et_2O). The initially clear yellow solution was allowed to warm to room temperature over a period of 1 h, after which time, the volatiles were removed *in vacuo*. The crude material was taken up into pentane, the mixture filtered through a pad of Celite, and the volatiles removed once more. Recrystallization of the crude product form pentane at −30 °C provided pale yellow crystals of **2b** (0.12 g, 63 % yield). For **2b**: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 2.90 (m, 3H), 2.71 (m, 1H), 2.46 (m, 1H), 2.37 (m, 1H), 2.22 (m, 1H), 1.97 (s, 15H), 1.96 (m, 1H), 1.80 (s, 3H), 1.78 (m, 1H), 1.19 (s, 9H), 0.88 (t, $J^3 = 7.2$ Hz, 3H), 0.60 (m, 1H), 0.13 (s, 3H), 0.04 (m, 1H). Anal Calcd. for $C_{24}H_{44}N_2Zr$: %C 63.80, %H 9.81, %N 6.20; Found %C 63.50, %H 9.67, %N 6.26.

(η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] Zr(Cl) [$CH_2(CH_2)_2$-CH = CH_2) (3b). In a 50-mL Schlenk tube fitted with a gas tight Teflon valve, 0.10 g (0.21 mmol) of **1b** was dissolved into 2 mL of toluene. After sealing, the tube was placed into an oil bath, maintained at 65 °C, for 36 h, after which time, the volatiles were removed *in vacuo* to provide **3b** as a yellow oil (0.10 g, 100 % yield). For **3b**: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 6.00 (m, 1H), 5.15 (dt, $J^3 = 17.1$ Hz, $J^4 = 1.1$ Hz, 1H), 5.03 (dt, $J^3 = 10.3$ Hz, $J^4 = 1.2$ Hz, 1H), 2.80 (dq, $J^2 = 13.9$ Hz, $J^3 = 6.8$ Hz, 1H), 2.63 (dq, $J^2 = 14.0$ Hz, $J^3 = 6.8$ Hz, 1H), 2.31 (m, 1H), 2.19 (m, 1H), 2.01 (s, 15H), 1.69 (s, 3H), 1.57 (m, 1H), 1.32 (s, 9H), 1.24 (m, 1H), 0.80 (t, $J^3 = 7.2$ Hz, 3H), 0.55 (ddd, $J^2 = 13.1$ Hz, $J^3 = 11.1$ Hz, $J^3 = 3.6$ Hz, 1H), 0.24 (ddd, $J^2 = 13.1$ Hz, $J^3 = 10.7$ Hz, $J^3 = 5.6$ Hz, 1H). Additional proof of structure of **3b** was obtained from a ^{1}H NMR spectrum of this same complex prepared via an alternative synthesis employing addition of $CH_2 = CH(CH_2)_2CH_2MgCl$ to **5**.

(η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] Zr(Cl) [$CH_2(CH_2)_3$-CH = CH_2) (3c). To a solution of 1.317 g (3.0 mmol) of **5** in 120 mL of Et_2O at ambient temperature, was slowly added 2.1 g (3.0 mmol) of $CH_2 = CH(CH_2)_3CH_2MgCl$ in Et_2O. The reaction mixture was stirred for 2 h, after which time, all volatiles were removed *in vacuo*. Extraction of the crude product into a toluene/pentane mixture (1:1) and filtration through a thin pad of Celite afforded a yellow solution, which upon concentration and cooling to −35 °C, provided yellow crystals of **3c** (1.35 g, 98 % yield). For **3c**: ^{1}H NMR (500 MHz, benzene-d_6, 25 °C) (see Fig. 2a): δ 5.89 (m, 1H), 5.01 (m, 2H), 2.80 (dq, 1H), 2.61 (dq, 1H), 2.16 (m, 4H), 2.01 (s, 15H), 1.72 (s, 3H), 1.51 (m, 2H), 1.33 (s, 9H), 0.81 (t, 3H), 0.51 (m, 1H), 0.28 (m, 1H). The purity of **3c**, as determined by this ^{1}H NMR spectrum, was sufficient for the material to be used for the preparation of **1c**.

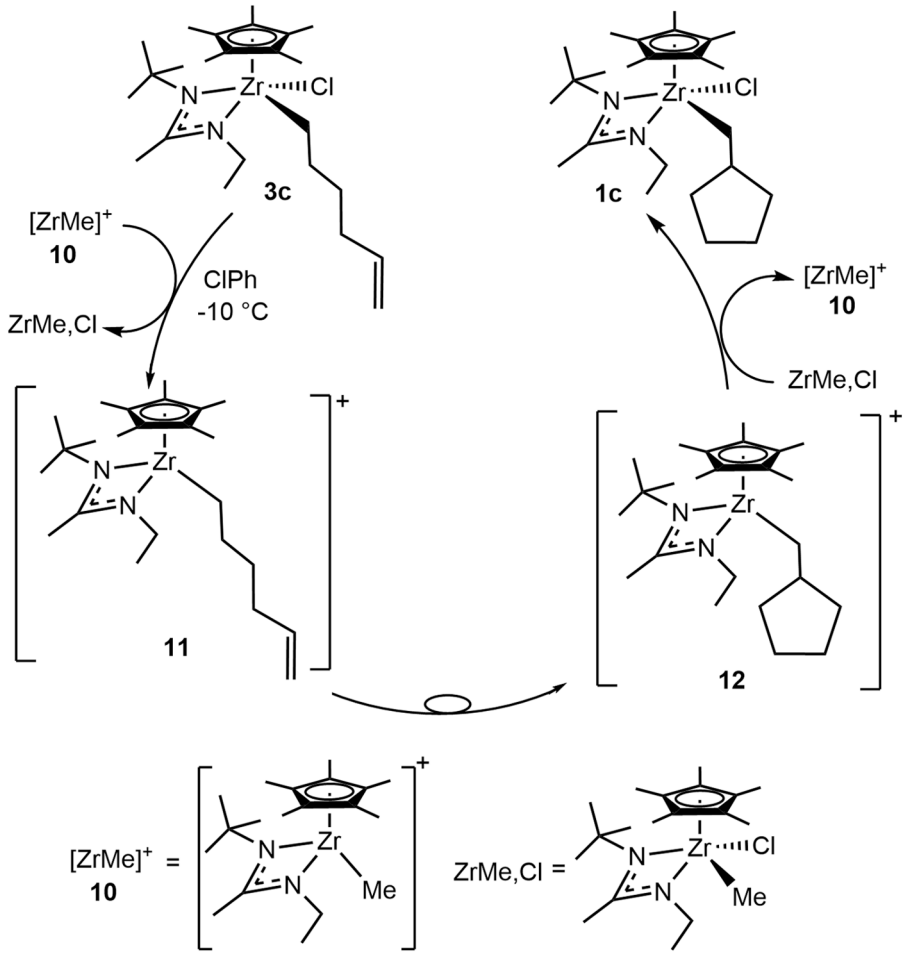
(η^5-C_5Me_5) [N(Et)C(Me)N(tBu)] Zr(Cl) [CH_2(c-C_5H_9)] (1c). A solution of **10** was prepared from 10.0 mg (0.025 mmol) of (η^5-C_5Me_5)[N(Et)C(Me)N(tBu)]Zr($Me)_2$ in 2 mL of chlorobenzene at –10 °C and 20.0 mg (0.025 mmol) of **B1** in 1 mL of chlorobenzene. This yellow solution was then added to 243 mg (0.5 mmol) of **3c** in 20 mL of chlorobenzene at – 30 °C. All volatiles were removed *in vacuo* after 20 h, and the crude product taken up in an Et_2O / pentane solvent mixture (1:1) to afford a yellow solution, which upon concentration and cooling to −35 °C provided yellow crystals (124 mg, 51 % yield). For **1c**: ^{1}H NMR (500 MHz, 25 °C, benzene-d_6) δ 2.89 (dq, 1H), 2.69 (dq, 1H), 2.25 (m, 2H), 2.01 (s, 15H), 1.77 (m, 2H), 1.72 (s, 3H), 1.48 (m, 1H), 1.34 (s, 9H), 1.19 (m, 2H), 0.83 (t, 3H), 0.77 (dd, 1H), 0.17 (dd, 1H) (see Fig. 2b); Anal. Calcd. for $C_{24}H_{43}N_2ClZr$: C 64.20, H 8.93, N 5.76; Found: C 64.12, H 9.02, N 5.84.

4. Summary

The present report serves to extend the unique ability of the CPAM ligand environment for stabilizing group 4 metal complexes with alkyl substituents bearing β-hydrogens. To the best of our knowledge, **1b** and **2b** are now the first examples of a transition-metal cyclobutylmethyl complex to be structurally characterized by X-ray crystallography. While **1b** can be used to further investigate the concerted mechanism by which isomerization to **3b** proceeds, **2b** can be used as a precursor for the structurally unique ion pair initiator **9**. Finally, a novel use of the ion pair **10** to catalyze the **3c** → **1c** cyclization under catalytic and equilibrating reversible chloride abstraction conditions has been reported. Collectively, these results contribute to further knowledge regarding the relative stability and reactivity of CPAM complexes of the early transition metals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Scheme 9. Catalytic cyclization of **3c** to **1c** via reversible chloride abstraction. Borate counterions are not included for sake of clarity.

Data availability

Data will be made available on request.

Acknowledgement

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Author credits

A.E. and Y.Z. performed the experimental work and contributed to data analysis and conclusions, JCF performed the x-ray crystallography of all reported new complexes, and LRS contributed with project management, hypotheses development and conclusions and wrote the manuscript. All authors participated in the review and revision of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.116100.

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