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Regio- and stereospecific syntheses and structural characterization of alkyl-substituted 1,3-diene complexes of cyclopentadienylzirconium amidinates of the general formula: $(\eta^5\text{-}C_5Me_5)Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}C_4H_5R)$ (R = Me or Et)

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Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

Abstract

Alkylation of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](Cl)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**4**) with 2 equiv. of *n*-hexyllithium in diethylether at −30 °C provided $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](n\text{-}C_6H_{13})_2$ (**5**) in excellent yield. In solution, **5** undergoes thermally induced loss of "C_6H_{16}" to provide a 35% isolated yield of the 1,3-hexadiene complex, $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](C_4H_5Et)$ (**6**), in regio- and diastereochemically pure form. Ligand substitution of the η^2-styrene group in $Cp^*Zr[\eta^2\text{-}CH_2CH(C_6H_5)][N(^iPr)C(Me)N(^iPr)]$ (**3**) was achieved using an excess of 2-methyl-1,3-butadiene (isoprene) in toluene at 25 °C to provide $Cp^*Zr[N(^iPr)C(Me)N(^iPr)]$(isoprene) (**7**) in regio- and stereochemically pure form. In similar fashion, an excess of *cis*,*trans*-1,3-pentadiene was used to separately prepare the isomeric diene complex $Cp^*Zr[N(^iPr)C(Me)N(^iPr)]$(1,3-pentadiene) (**8**), once again in regio- and stereospecific fashion. Detailed experimental investigations of the molecular and electronic structures of **6**–**8**, as performed in solution by 1D and 2D NMR spectroscopy and in the solid state by single-crystal X-ray analysis, revealed that the best structural description for these compounds is that of the Zr(IV) σ^2,π-metallacyclopent-3-ene limiting resonance form rather than as a Zr(II) η^4-diene complex.

Keywords: Group 4 metals; Conjugated dienes; Regiospecific; Stereospecific; Olefin polymerization catalysts

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1. Introduction

Investigations into the syntheses, molecular and electronic structures, and chemical reactivities of transition metal complexes of conjugated dienes conducted over the past several decades have contributed to a fundamental understanding of the foundations upon which modern organometallic chemistry rests [1]. In this regard, studies performed by Erker and co-workers [2] over the same period of time have played an important role in the development of 1,3-butadiene complexes of zirconocenes, e.g. $Cp_2Zr(\eta^4\text{-}C_4H_6)$ ($Cp = \eta^5\text{-}C_5H_5$), as synthetic precursors having broad applicability for the discovery of new catalytic and stoichiometric transformations that are useful for the construction of complex organic frameworks, as well as, new homogeneous catalysts for large-scale industrial processes. With respect to the latter, results obtained by the Erker group have played a key role in the development of zirconocene 1,3-butadiene complexes, as highly active, and in some cases, stereoselective catalysts for the Ziegler–Natta polymerization of ethene and propene upon 'activation' using a stoichiometric equivalent of the fluorinated borane, $B(C_6F_5)_3$ [3].

Our interest in non-metallocene-based conjugated diene complexes of group 4 and 5 metals stems from recent

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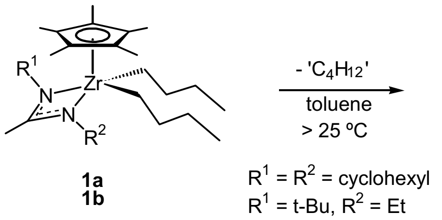


Scheme 1.

efforts made by us [4–7] to further develop monocyclopentadienyl, monoamidinate (CpAm) metal dialkyl complexes of the general formula, $(\eta^5\text{-}C_5R_5)M(R')_2[N(R^1)C(Me)N(R^2)]$ (M = Ti, Zr, Hf, Ta; R = H or Me; R′ = Me, *n*-Bu, *i*-Bu), as highly active and stereoselective initiators for the living Ziegler–Natta polymerization of ethene, propene, and higher α-olefins upon activation by either stoichiometric or substoichiometric amounts of the borates, $[PhNHMe_2][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$. More specifically, one particularly noteworthy observation made during a preliminary study of the solution thermal stabilities of the di(*n*-butyl) derivatives, **1a** and **1b**, was their near quantitative conversion to the isolable CpAmZr(butadiene) complexes, **2a** and **2b**, respectively, that occurs in solution at and above room-temperature (⩾25 °C) according to Scheme 1 [8]. Following the course of this conversion by ^{1}H NMR spectroscopy conducted within a flame-sealed NMR tube confirmed that, in each case, thermolytic production of **2** from **1**, which is strictly first-order in disappearance of the di(*n*-butyl) species ($t_{1/2}$ of ~48 h at 30 °C), proceeds with formation of spectroscopically observable butane and H_2. These latter data were interpreted as being consistent with the overall mechanism shown in Scheme 2 that is further supported by additional literature precedent [9,10]. Finally, single-crystal X-ray analyses of both **2a** and **2b** served to provide solid-state geometric parameters which confirm that the best structural description for **2** is that of the σ^2,π-limiting resonance structure **I** for transition metal diene complexes rather than the other limiting resonance structure of a *cis*-η^4-butadiene depicted by **II** in Chart 1 [2].

Another new and potentially general synthetic route to a wider range of derivatives of CpAmZr(butadiene) complexes represented by **2** arose during preliminary investigations of alkene insertions into a zirconium-carbon bond of the $(\eta^2\text{-styrene})$CpAmZr derivative **3** [11]. As originally concluded by us on the basis of single-crystal X-ray analysis and chemical reactivity data, the structural model for compound **3** seemed to best be represented in the Dewar–Chatt–Duncanson 'σ-bonding, π-back-bonding' model [12] as a zirconacyclopropane with a formal Zr(IV) metal center, rather than as a Zr(II) $(\eta^2\text{-styrene})$ adduct. In new studies, **3** was found to cleanly react with 1-alkenes to provide the expected zirconacyclopentane products that could be viewed as arising from simple 1,2-insertion into a Zr–C bond of the three-membered ring [13]. However, in the presence of an excess of 1,3-butadiene, complete ligand substitution of the η^2-styrene fragment of **3** readily occurred to provide an excellent isolated yield of the CpAmZr(butadiene) (**2c**), which based on ^{1}H NMR spectroscopy, also adopts the σ^2,π-diene resonance form that is depicted in Scheme 3. Thus, from this very preliminary data, it would appear that with conjugated dienes, compound **3** is also capable of functioning as a convenient source of a reduced CpAm Zr(II) synthetic starting material.

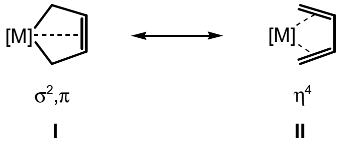
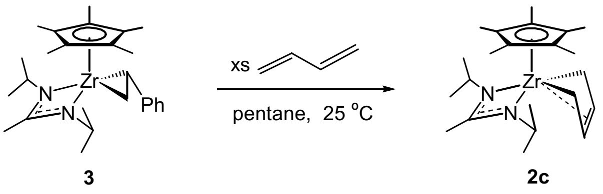
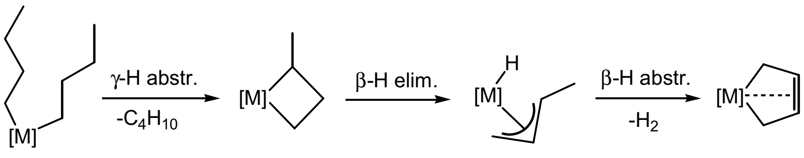


Chart 1.

Given that only a few synthetic routes are still currently available for the synthesis of group 4 metal complexes of conjugated dienes – with even a smaller number of these being applicable when considering the synthesis of metal complexes that are supported by non-metallocene ligands or when alkyl substituents on the diene fragment must be positioned in a highly regio- and stereospecific fashion – the present study was undertaken to map out the possible generality of the reactions presented in Schemes 1 and 3 as viable regio- and stereospecific synthetic routes to a broader range of CpAmZr(butadiene) complexes in which the C_4-butadiene fragment bears alkyl subsitutents.



Scheme 3.



Scheme 2.

2. Experimental

2.1. General procedures

Manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Pentane, diethyl ether, and toluene were distilled from sodium/benzophenone (with a few milliliters of triglyme being added to the pot in the case of pentane). Benzene-d_6 was vacuum transferred from NaK prior to being used for NMR spectroscopy. Celite was oven dried at 150 °C for several days prior to use. $Cp^*Zr[\eta^2\text{-}CH_2CH(C_6H_5)][N(^iPr)C(Me)N(^iPr)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**3**) and $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](Cl)_2$ (**4**) were prepared as previously reported [11]. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 400 MHz and 100 MHz, respectively, using benzene-d_6 as the solvent. 2D HMQC experiments were recorded on a 500 MHz NMR spectrometer. Elemental analyses were performed by Midwest Microlab.

2.2. Synthesis of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}1,3\text{-}hexadiene)$ (**6**)

To a cooled solution of 170 mg (0.39 mmol) of **4** in 25 ml of Et_2O at −30 °C, 0.31 ml (0.77 mmol) of *n*-hexyl lithium (2.5 M in hexanes) was added via a gas tight syringe and the resulting mixture warmed to room temperature and stirred for 12 h. At this time, the volatiles were removed *in vacuo*, and the solid residue taken up in pentane and filtered through a short pad of Celite in a glass frit. After removing the solvent from the filtrate, the crude product was isolated as a pinkish oil (202 mg, 98% yield). A ^1H NMR spectrum of this material showed clean alkylation of **4** to provide **5**, along with ~10% of the CpAmZr (diene) complex **6**. To achieve complete conversion to the latter, the entire amount of **5** was dissolved into ~2 ml of toluene and the resulting solution heated at 50 °C for ~72 h, at which point the volatiles were removed *in vacuo* to provide an oily purple material, from which, 60 mg (35% yield) of the desired compound **6** was obtained as dark purple crystals upon crystallization from pentane at −30 °C. For **5**: ^1H NMR (C_6D_6, 400 MHz): δ 3.36 (2H, sp, $J = 6.4$ Hz), 2.00 (15H, s), 1.90 (4H, m), 1.64 (3H, s), 1.50 (12H, m), 1.10 (12H, d, $J = 6.4$ Hz), 0.96 (6H, t, $J = 7.2$ Hz), 0.55 (2H, td, $J = 4.4$, 12.3 Hz), 0.37 (2H, td, $J = 4.8$, 12.3 Hz). For **6**: ^1H NMR (C_6D_6, 400 MHz): δ 5.89 (2H, m), 3.244 (1H, sp, $J = 6.4$ Hz), 3.238 (1H, sp, $J = 6.4$ Hz), 2.23 (1H, m), 2.03 (15H, s), 1.99 (1H, m), 1.78 (1H, m), 1.40 (3H, s), 1.23 (3H, d, $J = 7.2$ Hz), 1.03 (3H, d, $J = 6.4$ Hz), 1.02 (3H, d, $J = 6.4$ Hz), 0.89 (3H, d, $J = 6.4$ Hz), 0.84 (3H, d, $J = 6.4$ Hz), 0.08 (1H, t), 0.01 (1H, m). ^{13}C NMR (C_6D_6, 100.5 MHz): δ 168.1, 123.6, 118.9, 114.5, 74.1, 56.7, 47.5, 47.3, 27.7, 25.7, 25.4 (2 superimposed resonances), 24.4, 21.2, 13.5, 12.3. Anal. Calc. for $C_{24}H_{42}N_2Zr$: C, 64.08; H, 9.41; N, 6.23. Found: C, 63.42; H, 8.82; N, 6.12%.

2.3. Synthesis of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}2\text{-}methyl\text{-}1,3\text{-}butadiene)$ (**7**)

To a forest green solution of 130 mg (0.28 mmol) of **3** in 2 ml of toluene in a Schlenk tube, 192 mg (2.82 mmol) of 2-methyl-1,3-butadiene was added, the tube stoppered and the mixture stirred at room temperature for 16 h, over which time a deep red color developed. The volatiles were removed *in vacuo*, and the remaining residue taken up in pentane and filtered through a short pad of Celite in a glass frit. After removing the volatiles from the filtrate, the crude product was recrystallized from pentane at −30 °C to provide 85 mg (71% yield) of the desired compound **7** as a dark red crystalline material. Single crystals of **7** that are suitable for X-ray diffraction were obtained from a toluene solution at −30 °C. For **7**: ^1H NMR (C_6D_6, 400 MHz): δ 5.90 (1H, m), 3.32 (1H, sp, $J = 6.4$ Hz), 3.30 (1H, sp, $J = 6.4$ Hz), 2.22 (3H, s), 2.02 (15H, s), 1.78 (1H, m), 1.76 (1H, m), 1.43 (1H, s), 1.06 (3H, d, $J = 6.4$ Hz), 1.02 (3H, d, $J = 6.4$ Hz), 0.88 (3H, d, $J = 6.4$ Hz), 0.84 (3H, d, $J = 6.4$ Hz), 0.41 (1H, d, $J = 7.6$ Hz), 0.29 (1H, t, $J = 8.3$ Hz). ^{13}C NMR (C_6D_6, 100.5 MHz): δ 164.3, 130.3 118.9, 116.4, 58.3, 56.4, 47.3, 46.6, 27.8, 26.2, 25.7, 25.4, 25.3, 12.5, 12.4. Anal. Calc. for $C_{23}H_{40}N_2Zr$: C, 63.39; H, 9.25; N, 6.43. Found: C, 63.67; H, 9.23; N, 6.21%.

2.4. Synthesis of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}1,3\text{-}pentadiene)$ (**8**)

Following the same procedure as that used for the synthesis of **7**, 162 mg (70% yield) of compound **8** was obtained as a purple crystalline material after recrystallization from pentane at −30 °C. For **8**: ^1H NMR (C_6D_6, 400 MHz): δ 5.88 (2H, m), 3.25 (1H, sp, $J = 6.4$ Hz), 3.24 (1H, sp, $J = 6.4$ Hz), 2.03 (15H, s), 1.95 (1H, m), 1.85 (3H, d, $J = 6.4$ Hz), 1.39 (3H, s), 1.04 (3H, d, $J = 6.4$ Hz), 1.02 (3H, d, $J = 6.4$ Hz), 0.90 (3H, d, $J = 6.4$ Hz), 0.84 (3H, d, $J = 6.4$ Hz), 0.07 (1H, m), 0.01 (1H, m). ^{13}C NMR (C_6D_6, 100.5 MHz): δ 168.1, 124.8, 118.8, 114.1, 63.6, 56.7, 47.5, 47.3, 25.8, 25.4 (2 superimposed resonances), 24.4, 18.5, 13.5, 12.3. Anal. Calc. for $C_{23}H_{40}N_2Zr$: C, 63.39; H, 9.25; N, 6.43. Found: C, 63.29; H, 9.09; N, 6.28%.

2.5. Crystal structure determinations

Data were collected on a Bruker SMART CCD system operating at 220 (2) K using a graphite-monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 50 kV. Structures were solved using the SHELX-97 software by direct methods and refined by full-matrix least-squares methods on F^2 [14,15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and refined in the riding mode. Weights were optimized in the final cycles. For **7**, the hydrogen atoms on the C(1)–C(5) 2-methyl-1,3-butadiene fragment were refined using soft restraints on the

Table 1
Crystallographic data and details of refinement for compounds **6**–**8**

Compound	**6**	**7**	**8**
Empirical formula	$C_{24}H_{42}N_2Zr$	$C_{23}H_{40}N_2Zr$	$C_{23}H_{40}N_2Zr$
Formula weight	449.82	435.79	435.79
Temperature (K)	220 (2)	220 (2)	220 (2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$	Pn
a (Å)	8.6815 (7)	10.2229 (15)	10.6540 (7)
b (Å)	9.8075 (8)	15.053 (2)	9.4450 (6)
c (Å)	15.4122 (12)	16.022 (3)	11.4556 (8)
α (°)	95.981 (2)	90	90
β (°)	101.008 (1)	107.982 (3)	94.515 (1)
γ (°)	105.838 (1)°	90	90
V (Å^3)	1222.11 (17)	2345.1 (6)	1149.17 (13)
Z	2	4	2
ρ_{calc} (g cm^{-3})	1.222	1.234	1.259
μ(Mo Kα) (mm^{-1})	0.460	0.477	0.487
Crystal size (mm)	0.42 × 0.21 × 0.11	0.40 × 0.25 × 0.006	0.19 × 0.11 × 0.04
θ Range (°)	2.51–27.50	2.67–22.50	2.51–25.00
Total reflections	21 150	4440	9996
Independent reflections (R_{int})	7067 (0.0252)	2893 (0.0373)	3990 (0.0328)
Data/restraints/parameters	7067/0/283	2893/7/261	3990/7/303
Final R indices:R_1, [$I > 2\sigma(I)$]	0.0225	0.0435	0.0270
wR_2 (all data)	0.0562	0.0988	0.0596
Goodness-of-fit	1.001	0.999	1.000

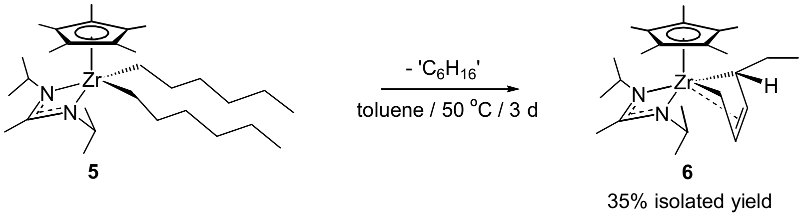
distances and angles to the respective attached atoms (A), where $U_{iso}(H) = 1.5 \times U_{iso}(A)$ for CH_3 and $U_{iso}(H) = 1.2 \times U_{iso}(A)$ for all other hydrogen atoms. For **8**, the hydrogen atoms on the C(1)–C(5) 1,3-pentadiene fragment were clearly located from difference Fourier and refined, for which the C–H distances were restrained to be approximately the same during the final refinement. Crystallographic data for compounds **6**–**8** are given in Table 1.

3. Results and discussion

3.1. Synthesis of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}C_4H_5Et)$ (6) via thermolysis

Following previously reported procedures [8,11], the dichloro CpAmZr derivative, $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](Cl)_2$ (**4**) was alkylated in Et_2O at −30 °C with 2 equiv. of n-hexyllithium to afford an excellent isolated yield of the corresponding di(n-alkyl) derivative, $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](n\text{-}C_6H_{13})_2$ (**5**), as a pink-tinged, pentane-soluble oil. Although this material remained an oil even after repeated attempts at crystallization from different solvents and temperature, a ^1H NMR (400 MHz, benzene-d_6, 25 °C) spectrum of **5** served to confirm the structure shown in Scheme 4. Interestingly, however, this ^1H NMR spectrum also revealed the presence of a small amount (~10%) of a single co-product, which also displayed vinyl resonances consistent with those expected for the σ^2,π-diene complex **6** (see Scheme 4).

The possibility that the small amount of observed **6** is produced through a post-synthesis thermal decomposition of **5** was confirmed by allowing a benzene solution of the latter to stand at room temperature for an extended period of time (~36 h), whereupon the initial pink hue of the solution steadily darkened to an intense purple-red color. Furthermore, by following the course of this thermal transformation by ^1H NMR (400 MHz, benzene-d_6) spectroscopy at 40 °C within a sealed NMR tube, a series of spectra recorded at timed intervals clearly revealed that **5** cleanly decomposes – in strictly first-order fashion with an associated half-life ($t_{1/2}$) of ~11 h – with concomitant growth in the ^1H NMR resonances for **6**. Thus, on the basis of this very preliminary information, it would qualitatively appear that the di(n-butyl)CpAmZr derivatives **1a** and **1b** are somewhat more thermally stable in solution than their



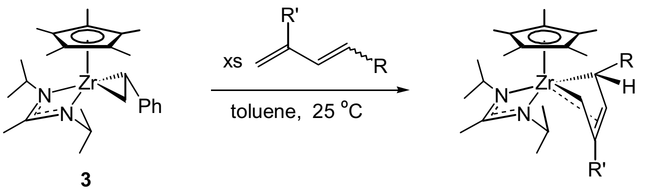
Scheme 4.

di(*n*-hexyl)CpAmZr congener **5**. However, at the present time, it is not known what contributions the difference in steric interactions associated with the amidinate N-substituents for **1a** and **1b** relative to those of **5**, as well as, possible differences in steric and electronic effects associated with an increased *n*-alkyl chain, might play in governing the nature of the rate-determining step, or even potentially, the overall mechanism by which decomposition of these di(*n*-alkyl)CpAmZr compounds occur in solution. In this regard, it must be mentioned that while *n*-hexane production has been confirmed, initial attempts to observe the co-production of H_2 during decomposition of **5** have so far failed. Accordingly, answers to these and other questions must await the quantitative results of further experimental and computational investigations of **1** and **5**.

As presented in Scheme 4, extended thermolysis of toluene solutions of ~100 mg of **5** at 50 °C over a 3 d period provided a red-purple crude material from which a 35% isolated yield of **6** could be obtained after crystallization from pentane at −30 °C. Gratifyingly, analytic and spectroscopic characterization of pure **6**, including spectral assignments obtained from a series of 1D and 2D (^{1}H, ^{1}H COSY and ^{13}C, ^{1}H HMQC) NMR experiments were fully consistent with the solution structure being the σ^2,π-diene structure originally proposed for this compound. In this regard, it is important to mention that, according to ^{1}H NMR spectroscopy, only a single diastereoisomer of **6** is produced from thermolysis of **5**, and further, no irreversible or dynamic structural or stereochemical isomerizations involving the diene fragment of **6** are observed in solution at elevated temperatures or over extended periods of time.

3.2. Syntheses of isomeric $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi$-2-methyl-1,3-butadiene) (7) and $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi$-1,3-pentadiene) (8) via ligand substitution

As Scheme 5 reveals, the (η^2-styrene)CpAmZr complex **3** underwent clean ligand substitution in the presence of an excess of 2-methyl-1,3-butadiene (isoprene) to provide a high yield of $Cp^*Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi$-2-methyl-1,3-butadiene) (**7**). In similar fashion, by employing an excess of *cis,trans*-1,3-pentadiene, the isomeric $Cp^*Zr[N(^iPr)C(Me)$-$N(^iPr)](\sigma^2,\pi$-1,3-pentadiene) (**8**), was obtained. Importantly, data obtained from detailed analytic and 1D and 2D NMR (^{1}H, ^{1}H COSY and ^{13}C, ^{1}H HMQC) NMR experiments are not only fully consistent with the σ^2,π-diene structural assignment shown for each compound, but also, as with **6**, formation of **7** and **8** through ligand substitution of **3** ultimately provides only a single regio- and diastereomerically pure species that does not engage in either irreversible or dynamic structural or stereochemical isomerizations in solution. Although small amounts of styrene were spectroscopically observed by ^{1}H NMR, the sequence and nature of the detailed steps that are involved in this ligand substitution of **3** by 1,3-dienes have not yet been elucidated. It can be noted here, however, that conjugated and non-conjugated dienes that failed to react with **3** up to temperatures of 50 °C include: 2,3-dimethyl-1,3-butadiene, 1,1-dimethyl-1,3-butadiene, 2,4-hexadiene, 1,3- and 1,4-cyclohexadiene, and norbornadiene. In the case of 1,5-hexadiene, only single 1,2-insertion into a Zr–C bond of **3** readily occurred and this is in keeping with prior observations regarding the general reactivity of this compound towards 1-alkenes [13].



3

7: R' = Me, R = H (71%)
8: R' = H, R = Me (70%)

Scheme 5.

*3.3. Solid-state structural characterization of complexes **6–8***

In spite of their fundamental importance to the organometallic chemistry of early transition metals, there are surprisingly few reports detailing the solid-state molecular structures of alkyl [16] or aryl [17] substituted-1,3 diene complexes of the group 4 metals. Accordingly, in order to add to this database and to obtain further information regarding the molecular and electronic structures of the new $CpAmZr(\sigma^2,\pi\text{-}C_4H_5R)$ derivatives, **6–8**, single-crystal X-ray analyses were performed. Figs. 1–3 and Table 2 provide the molecular structures and selected structural parameters for these compounds that were obtained from crystallographic studies. To begin, all three compounds display a remarkably high degree of similarity with respect to both gross overall geometric shape, including structural dispositions of the separate Cp*, amidinate, and 1,3-diene fragments. On a more specific level, as Table 2 reveals, all the bond lengths involving these ligands and the zirconium metal center are also very similar in magnitude.

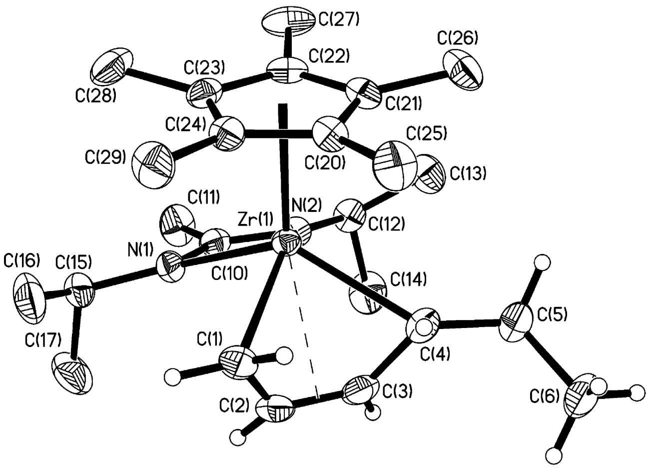


Fig. 1. Molecular structure (30% thermal ellipsoids) of compound **6**. Hydrogen atoms, except for those attached to C(1)–C(6), have been removed for the sake of clarity.

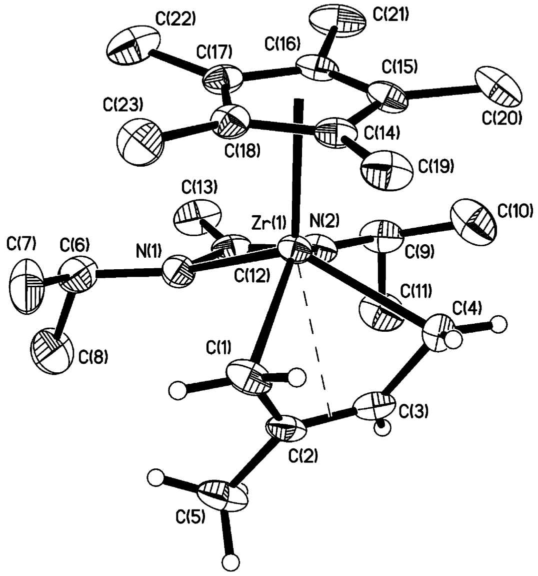


Fig. 2. Molecular structure (30% thermal ellipsoids) of compound **7**. Hydrogen atoms, except for those attached to C(1)–C(5), have been removed for the sake of clarity.

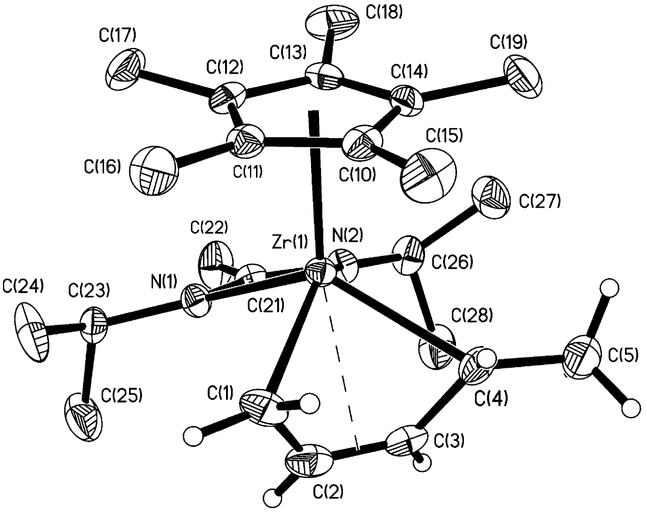


Fig. 3. Molecular structure (30% thermal ellipsoids) of compound **8**. Hydrogen atoms, except for those attached to C(1)–C(5), have been removed for the sake of clarity.

However, upon closer inspection, the formally non-bonding distance between Zr(1) and the midpoint of the C(2)–C(3) bond of the 1,3-diene fragment is somewhat lengthened in **7** relative to both **6** and **8** (cf. 2.374 Å versus 2.358 and 2.355 Å, respectively) and this difference is presumably steric in nature as **7** must accommodate the steric bulk of the methyl substituent on C(2), which from a side-view perspective, is likely to engage in strong non-bonded interactions with the amidinate ligand, thereby, forcing the C(2)–C(3) unit further out from the metal. In this regard, it is interesting to mention that if one assumes the σ^2, π-metallacyclopent-3-ene resonance form as being the dominant one for this series of compounds (vide infra), then the absence of these non-bonded steric interactions in **6** and **8** should manifest in a stronger π-donor interaction of the C(2)–C(3) bond of these compounds with the metal center, and indeed, both **6** and **8** are noticeably more purple than the red color of **7** – thus possibly signifying a bathochromic shift of the lowest energy electronic transition that is associated with this π-donor interaction [11].

Table 2
Selected distances (Å) and angles (°) for compounds **6**–**8**

Compound	**6**	**7**	**8**
Bond distances (Å)			
Zr(1)–N(1)	2.2787 (13)	2.253 (4)	2.267 (3)
Zr(1)–N(2)	2.2611 (13)	2.269 (4)	2.271 (2)
Zr(1)–C(1)	2.3153 (18)	2.334 (6)	2.320 (3)
Zr(1)–C(4)	2.3644 (16)	2.312 (5)	2.366 (4)
Zr(1)···C(2),C(3)$_{\text{midpt}}$	2.358	2.374	2.355
C(1)–C(2)	1.433 (3)	1.428 (8)	1.419 (6)
C(2)–C(3)	1.378 (3)	1.362 (8)	1.367 (6)
C(3)–C(4)	1.437 (3)	1.457 (8)	1.432 (5)
C(4)–C(5)	1.512 (2)	–	1.513 (6)
C(2)–C(5)	–	1.511 (7)	–
C(5)–C(6)	1.527 (3)	–	–
Bond angles (°)			
C(1)–Zr(1)–C(4)	76.88 (7)	75.7 (2)	76.67 (15)
Zr(1)–C(1)–C(2)	77.72 (11)	77.5 (3)	77.6 (2)
C(1)–C(2)–C(3)	121.60 (19)	19.9 (5)	122.4 (4)
C(2)–C(3)–C(4)	122.92 (18)	122.1 (5)	123.1 (4)
C(3)–C(2)–C(5)	–	119.6 (6)	–
C(1)–C(2)–C(5)	–	120.2 (6)	–
C(3)–C(4)–C(5)	118.21 (16)	–	118.3 (3)
C(3)–C(4)–Zr(1)	76.49 (10)	78.8 (3)	76.3 (2)
C(5)–C(4)–Zr(1)	137.19 (12)	–	133.3 (3)
$\sum\theta_{C(1)}$	348	344	336
$\sum\theta_{C(4)}$	342	340	346

Within the 1,3-diene fragment of **6**–**8**, in each case, the C(2)–C(3) bond length is significantly shorter than the other carbon–carbon bond lengths; a structural feature which lends considerable support for the σ^2,π-metallacyclopent-3-ene formalism for this class of compound. However, on the basis of the sums of bond angles about C(1) and C(4) that are provided in Table 2, it must also be pointed out that both of the α-carbons of **6**–**8** are not as pyramidalized as expected if **I** is the single dominant resonance contributor and thus, an argument could also be made for a strong contribution of the η^4-interaction represented by **II**, at least in terms of solid-state bonding interactions. In solution, previous studies conducted by us with **2a** and **2b**, failed to provide any evidence of the ability of these compounds to engage in 1,3-butadiene ligand substitution with an excess of a different 1,3-butadiene even at elevated temperatures. Accordingly, we believe that the bonding picture presented by **I** is the best structural picture to bear in mind as far as chemical stability and reactivity patterns are concerned.

4. Conclusion

The present study has confirmed that additional derivatives of the family of CpAmZr(σ^2,π-1,3-diene) class of compound can be prepared through both thermolysis of di(*n*-alkyl)CpAmZr precursors and ligand substitution of the (η^2-styrene)CpAmZr complex **3** in the presence of an excess of alkyl-substituted 1,3-butadienes. Although steric considerations are likely to limit the scope of the latter process, an important feature of both synthetic routes is that each yields a single regio- and diastereomerically pure product. Investigations are now underway to explore the range of new (stereo)chemical transformations that CpAmZr(σ^2,π-1,3-diene) complexes, such as **2** and **6**–**8**, can engage in that are potentially useful for the construction of complex organic frameworks, including their ability to serve as precatalyts for the Ziegler–Natta polymerization of α-olefins, and possibly, the polymerization of polar functional monomers as well [3a,3c,18].

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Appendix A. Supplementary material

CCDC 649376, 649377 and 649378 contain the supplementary crystallographic data (excluding structure factors) for **6**, **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.018.

References

[1] (a) J.P. Collmann, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987;
(b) H. Alper, Transition Metals Organometallics in Organic Synthesis, vol. 1/vol. 2, Academic Press, New York, 1976/1978;
(c) H. Yasuda, K. Tatsumi, A. Nakamura, Acc. Chem. Res. 18 (1985) 120.

[2] (a) G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1;
(b) G. Erker, G. Kehr, R. Fröhlich, J. Organomet. Chem. 689 (2004) 4305;
(c) G. Erker, G. Kehr, R. Fröhlich, Adv. Organomet. Chem. 51 (2004) 109;
(d) C. Krüger, G. Müller, G. Erker, U. Dorf, K. Engel, Organometallics 4 (1985) 215.

[3] (a) G. Erker, G. Kehr, R. Fröhlich, J. Organomet. Chem. 690 (2005) 6254;
(b) G. Erker, Acc. Chem. Res. 34 (2001) 309;
(c) G. Erker, Chem. Commun. (2003) 1469.

[4] (a) K.C. Jayaratne, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 958;
(b) K.C. Jayaratne, R.J. Keaton, D.A. Henningsen, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 10490;
(c) R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L.R. Sita, J. Am. Chem. Soc. 123 (2001) 6197;
(d) D.A. Kissounko, Y. Zhang, M.B. Harney, L.R. Sita, Adv. Synth. Catal. 347 (2005) 426;
(e) M.B. Harney, Y. Zhang, L.R. Sita, J. Am. Chem. Soc. 128 (2006) 3420.

[5] (a) Y. Zhang, R.J. Keaton, L.R. Sita, J. Am. Chem. Soc. 125 (2003) 9062;
(b) Y. Zhang, L.R. Sita, J. Am. Chem. Soc. 126 (2004) 7776.

[6] (a) M.B. Harney, Y. Zhang, L.R. Sita, Angew. Chem., Int. Ed. 45 (2006) 2400;
(b) M.B. Harney, Y. Zhang, L.R. Sita, Angew. Chem., Int. Ed. 45 (2006) 6140.

[7] A. Epshteyn, P.Y. Zavalij, L.R. Sita, J. Am. Chem. Soc. 128 (2006) 16052.

[8] R.J. Keaton, L.A. Koterwas, J.C. Fettinger, L.R. Sita, J. Am. Chem. Soc. 124 (2002) 5932.

[9] V.K. Dioumaev, J.F. Harrod, Organometallics 16 (1997) 1452.

[10] J. Blenkers, H.J.D. Meijer, J.H. Teuben, J. Organomet. Chem. 218 (1981) 383.

[11] D.A. Kissounko, A. Epshteyn, J.C. Fettinger, L.R. Sita, Organometallics 25 (2006) 1076.

[12] (a) M.J.S. Dewar, Bull. Soc. Chim. Fr. 18 (1951) C79;
(b) J. Chatt, L.A. Duncanson, J. Chem. Soc. (1953) 2939.

[13] A. Epshteyn, D.A. Kissounko, P.P. Fontaine, J.C. Fettinger, P.Y. Zavalij, L.R. Sita, (submitted for publication).

[14] Bruker AXS, SHELXTL version 6.10: Structure Determination Package, Bruker AXS, Madison, WI, USA, 2000.

[15] G.M. Sheldrick, SADABS version 2.03: A Program for Empirical Absorption Correction, Universität Göttingen, Göttingen, Germany, 1997.

[16] (a) J. Blenkers, B. Hessen, F. van Bolhuls, A.J. Wagner, J.H. Teuben, Organometallics 6 (1987) 459;
(b) D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132;
(c) G.J. Pindado, M. Thornton-Pett, M. Bochmann, J. Chem. Soc., Dalton Trans. (1997) 3115.

[17] (a) H. Yamamoto, H. Yasuda, K. Tatsumi, K. Lee, A. Nakamura, J. Chen, Y. Kai, N. Kasai, Organometallics 8 (1989) 105;
(b) L.F. Braun, T. Dreier, M. Christy, J.L. Petersen, Inorg. Chem. 43 (2004) 3976.

[18] (a) J.W. Strauch, J.L. Faure, S. Bredeau, C. Wang, G. Kehr, R. Fröhlich, H. Luftmann, G. Erker, J. Am. Chem. Soc. 126 (2004) 2089;
(b) G. Erker, G. Kehr, R. Fröhlich, Coord. Chem. Rev. 250 (2006) 36.