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Dialkyl and Methyl-Alkyl Zirconocenes: Synthesis and Characterization of Zirconocene-Alkyls That Model the Polymeryl Chain in Alkene Polymerizations

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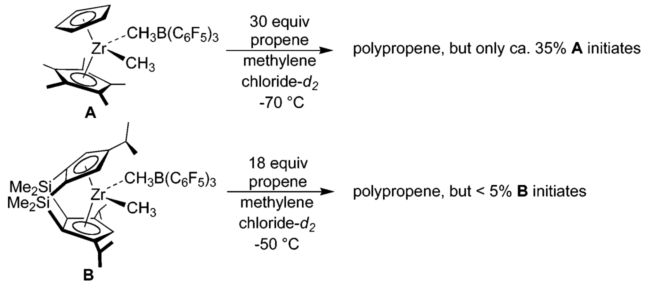
Zirconocene precatalysts with sterically bulky alkyl groups were designed as model systems for the propagating species in zirconocene-catalyzed alkene polymerization. Specialty alkyllithium reagents Li(CH_2CEt_3) and Li($CH_2CMe_2CH_2Ph$) were prepared and utilized in the synthesis of dialkyl and methyl-alkyl zirconocenes of the form $CpCp^*ZrR_2$, $Cp_2Zr(CH_3)(R)$, and $CpCp^*Zr(CH_3)(R)$ ($Cp = (\eta^5\text{-}C_5H_5)$; $Cp^* = (\eta^5\text{-}C_5Me_5)$; $R = CH_2CMe_3$, CH_2SiMe_3, CH_2CEt_3, $CH_2CMe_2CH_2Ph$). These new zirconocene alkyls were isolated and fully characterized by NMR spectroscopy and in some cases by X-ray diffraction. The molecular structures determined display the bent-sandwich coordination mode common for zirconocenes. The steric influence of the alkyl group on the observed structural parameters is reflected in slightly expanded C−Zr−C or C−Zr−Cl angles in the equatorial plane and long zirconium−alkyl bond distances.

Introduction

The propagating catalyst species in metallocene-catalyzed alkene polymerization has been identified as a metallocenium-polymeryl ion having a weakly coordinating anion.[1] Traditionally, propagating species are generated in situ starting from a neutral metallocene precatalyst, generally a dichloride or dimethyl species.[2] The first step is reaction with an activator to generate an ion-paired, cationic, 14-electron metal-alkyl initiator. This initiating species then reacts with alkene in the initiation step, followed by additional alkene insertions to form the propagating species.

Our interest in developing models for the early propagating species arose from a project examining fundamental aspects of zirconocene-catalyzed alkene polymerization using kinetic and mechanistic studies. Initial attempts focused on propagation kinetics for propene polymerization and utilized anion-stabilized methyl-zirconocenium and hafnocenium catalysts of the type $[Cp^x{}_2M(CH_3)]^+[CH_3B(C_6F_5)_3]^-$ ($Cp^x = (\eta^5\text{-}C_5R_nH_{5-n})$; M = Zr, Hf). While this work suggested that propene propagation kinetics could be directly examined at low temperatures using direct ^1H NMR monitoring, limitations associated with the use of methyl-based initiators for these experiments were identified. In particular, these $[Cp^x{}_2M-CH_3]^+$ cations displayed poor initiation behavior for propene polymerization, where only a small, but continually increasing percentage of initiating complex was converted to the propagating species under typical experimental conditions. For example, when excess propene (18−30 equiv) was added to catalyst solutions at low temperatures, incomplete initiation occurred in all cases, as both $[Cp^x{}_2M-\text{polymeryl}]^+[CH_3B(C_6F_5)_3]^-$ and unreacted $[Cp^x{}_2M-CH_3]^+[CH_3B(C_6F_5)_3]^-$ were present after consumption of all monomer (Scheme 1).[3]

Scheme 1



Specifically, only 30−35% initiation was observed (^1H NMR, −70 °C, CD_2Cl_2) for $[CpCp^*Zr-CH_3]^+[CH_3B(C_6F_5)_3]^-$ ($Cp = (\eta^5\text{-}C_5H_5)$; $Cp^* = (\eta^5\text{-}C_5Me_5)$) (**A**) after polymerization of 30 equiv of propene. Similarly, the *ansa*-zirconocene catalyst $[{}^iPrThpZr-CH_3]^+[CH_3B(C_6F_5)_3]^-$ (${}^iPrThp = [(1,2\text{-}SiMe_2)_2(\eta^5\text{-}4\text{-}CHMe_2-C_5H_2)(\eta^5\text{-}3,5\text{-}(CHMe_2)_2-C_5H)]$) (**B**) showed less than 5% initiation after polymerization of 18 equiv of propene (^1H NMR, −50 °C, CD_2Cl_2). These observations may be attributed to a kinetic situation where $k_p \gg k_i$ (where k_p and k_i are the rate constants for propagation and initiation). Similar slow initiation versus propagation behavior has been reported for 1-hexene polymerization by other metallocene[4] and nonmetallocene[5] group 4 $[M-CH_3]^+$ initiators.

These findings prompted us to consider zirconocene initiators bearing polymeryl-like alkyl groups, where k_i may be on the same order as k_p. These compounds may model the propagating species formed in propene polymerization, if the alkyl group more closely resembles the polypropene polymeryl in both Zr−C bond strength and steric influence on ion pairing. Well-

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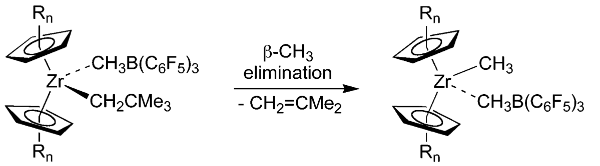
defined initiators suitable for use in kinetic studies may be produced directly from the activation step by reaction with an appropriate zirconocene precatalyst. Therefore, the synthesis of dialkyl and methyl-alkyl zirconocene precursors having more sterically demanding polymeryl-like alkyl groups has been undertaken.

Considerable efforts in both academic and industrial laboratories have produced a rich body of literature precedence for the synthesis and activation of group 4 dimethyl metallocene precatalysts.[6] These efforts offer great diversity with respect to choice of ancillary ligands and activating reagents, but are more limited with respect to variations in alkyl groups. Examples using zirconium and hafnium precatalysts of the form $(Cp-R_n)_2MR'_2$ have generally been restricted to a small number of bulky alkyl groups ($R' = CH_2CMe_3$ (Np), CH_2SiMe_3 (CH_2-TMS), $CH(SiMe_3)_2$, or $CH_2C_6H_5$),[1,2,7] and mixed methyl-alkyl complexes $Cp_2M(CH_3)(R')$ are even fewer in number.

For eventual use in kinetic studies, the thermal stability of the dialkyl zirconocene precatalysts, as well as the generated zirconocene-alkyl cations, toward decomposition, especially via β-hydride elimination,[8,9] must also be considered. These reactions are expected to be more facile for the active polymerization catalysts. These cationic species display increased electrophilicity at the metal center, and accordingly, β-hydride elimination has been identified as a major chain termination pathway for propagating species in metallocene-catalyzed alkene polymerization.[2] In order to avoid complications arising from this type of reactivity, we chose to investigate dialkyl and methyl-alkyl zirconocenes with bulky alkyl groups having no β-hydrogens as precursors to models of the propagating species. Decomposition pathways involving other β-elimination reactions may occur for the cationic alkyl initiators generated from these zirconocenes. Studies by Horton,[10] Marks,[7] and our research group[11] have demonstrated that $[(Cp-R_n)_2Zr(CH_2CMe_3)]^+[CH_3B(C_6F_5)_3]^-$ compounds decompose to zirconocene-methyl cations and isobutene via β-methyl elimination (eq 1).



(1)

For alkyl-zirconocenium ions, the rate of β-methyl elimination[10] and the relative rates of β-hydride elimination versus β-methyl elimination appear to be sensitive to the steric influence of the cyclopentadienyl ancillary ligands.[12] β-Hydride elimination is the primary chain termination pathway for the propagating catalyst produced in propene polymerization using Cp_2ZrCl_2/methylaluminoxane (MAO) systems, while $Cp^*_2ZrCl_2$/MAO-derived catalyst chain terminates largely via β-methyl elimination. In the latter case, the increased rate of β-methyl compared to β-hydride elimination can be rationalized by considering steric interactions between the Cp* ligand and the β-substituents on the polymeryl chain in the respective transition-state structures.[12] These findings suggested that the steric environment might be tuned using both the influence of the bulky alkyl group and the ancillary ligand framework to potentially inhibit β-methyl elimination for the proposed alkyls that model the propagating polymeryl group.

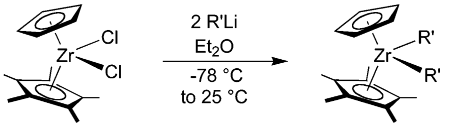
We report herein the syntheses and characterization of a series of zirconocene precatalysts with sterically bulky alkyl groups. The preparation of the mixed methyl-alkyl complexes proved to be less than straightforward, and some more efficient synthetic procedures have been devised that should prove useful in the synthesis of other, related bulky alkyl zirconocene derivatives.

Results and Discussion

Synthesis of Mixed Cyclopentadienyl Ligand Dialkyl Zirconocenes. The mixed cyclopentadienyl/pentamethylcyclopentadienyl ligand dialkyl zirconocenes $CpCp^*ZrNp_2$ (**1**) and $CpCp^*Zr(CH_2TMS)_2$ (**2**) are precursors to catalyst initiators of the form $[CpCp^*ZrR']^+[B(C_6F_5)_4]^-$ or $[CpCp^*Zr(R')(NMe_2Ph)]^+[B(C_6F_5)_4]^-$ ($R' = Np$, CH_2TMS), by activation of the precatalyst with $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $[PhNMe_2H]^+[B(C_6F_5)_4]^-$, respectively.[6] The dialkyl zirconocenes rather than the methyl-alkyl zirconocenes were targeted for use with these activators as multiple cationic species, such as mixtures of $[Zr-CH_3]^+$ and $[Zr-Np]^+$, could potentially be generated upon protonative activation of the methyl-alkyl zirconocenes. Although methyl abstraction appears to be generally favored, other alkyls, including neopentyl, are abstracted from nonmetallocene zirconium(IV) and hafnium(IV) dialkyl compounds using $[Ph_3C]^+[B(C_6F_5)_4]^-$.[13-15]

Horton has shown that the stability of zirconocene-neopentyl cations toward decomposition via β-methyl elimination is sensitive to the cyclopentadienyl ancillary ligands.[10] While $[Cp^*_2ZrNp]^+[CH_3B(C_6F_5)_3]^-$ undergoes rapid decomposition at temperatures as low as -80 °C, $[Cp_2ZrNp]^+[CH_3B(C_6F_5)_3]^-$ is stable up to 0 °C. Therefore, the mixed ring cyclopentadienyl ligation was chosen to provide an intermediate steric influence. Additionally, it was thought that the Si-substituted alkyl group might serve as a neopentyl analogue stable toward β-methyl elimination, as silylene formation is unfavorable.[7]

Compounds **1** and **2** are prepared according to the methodology reported by Lappert for the parent Cp_2ZrR_2 compounds.[16] The reaction of 2 equiv of the appropriate lithium reagent with $CpCp^*ZrCl_2$ proceeds cleanly in diethyl ether solvent to afford **1** or **2** as tan or off-white powders, respectively, in good yields (eq 2).



(2)

1 R' = CH_2CMe_3 (66%)
2 R' = CH_2SiMe_3 (70%)

Cooling a saturated pentane solution of **1** to -35 °C resulted in the formation of pale yellow crystals that were suitable for X-ray diffraction analysis. The molecular structure of **1** displays a bent-sandwich coordination mode common among zir-

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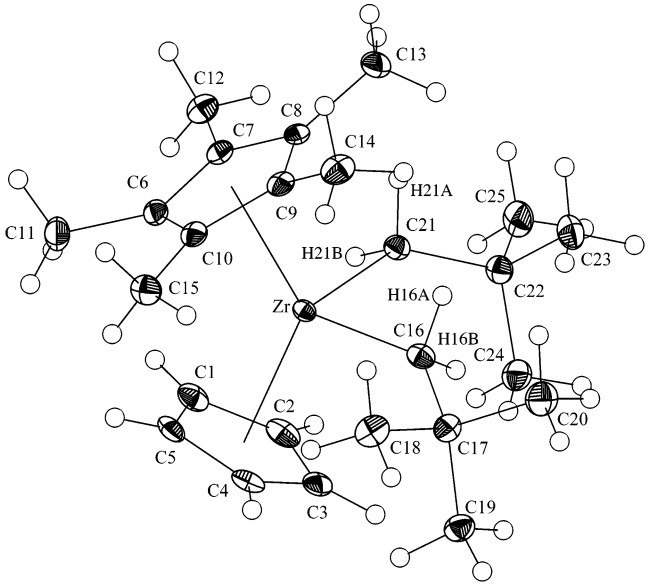

Figure 1. Structural drawing of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr(CH_2CMe_3)_2$ (**1**) with thermal ellipsoids at the 50% probability level.

Table 1. Selected Structural Parameters for CpCp*Zr(CH$_2$CMe$_3$)$_2$ (1) and CpCp*Zr(CH$_2$SiMe$_3$)$_2$ (2)

1		2	
	Distances (Å)		
Zr−Ct(1)[a]	2.241(1)	Zr−Ct(1)[a]	2.246(1)
Zr−Ct(2)[b]	2.260(1)	Zr−Ct(2)[b]	2.247
Zr−C(16)	2.2651(14)	Zr−C(16)	2.2691(16)
Zr−C(21)	2.3524(14)	Zr−C(20)	2.3066(16)
	Angles (deg)		
Ct(1)−Zr−Ct(2)	129.1(1)	Ct(1)−Zr−Ct(2)	131.1(1)
C(16)−Zr−C(21)	99.61(5)	C(16)−Zr−C(20)	98.09(6)

[a] Ct(1) is defined as the centroid of the ring made up of C(1)−C(5). [b] Ct(2) is defined as the centroid of the ring made up of C(6)−C(10).

conocenes (Figure 1). The Zr−Cp and Zr−Cp* centroid distances (2.241(1), 2.260(1) Å) and Cp centroid−Zr−Cp* centroid angle (129.1(1)°) are similar to those found for Cp_2ZrNp_2 (2.25 Å; 128.3°).[17] All of the hydrogen atoms were located in the difference map and have been refined. Details of the data collection and solution and refinement of the structure can be found in Table 2.

The neopentyl groups are oriented to direct the bulky *tert*-butyl substituents away from each other and away from the Cp* group in the solid-state structure. The *tert*-butyl group of C(21) is directed toward the front, more open region of the zirconocene wedge, while that of C(16) is pushed back into the wedge. Two distinct bond lengths are found for Zr−C(σ) bonding to the neopentyl groups (Zr−C(16) = 2.2651(14), Zr−C(21) = 2.3524(14) Å). These short and long bond distances are within the range typically observed for $Cp^x{}_2$Zr-alkyl compounds (2.251−2.388 Å).[18,19] The molecular structure of **1** does not indicate any ground-state γ-agostic interactions; the closest zirconium−γ-hydrogen distance found is 3.82 Å. A close contact is found between zirconium and α-hydrogen H(B), located on C(16) (Zr−α-H(B) = 2.38 Å, Zr−α-H(A) = 2.58 Å; for C(21) Zr−α-H(A) = 2.77 Å, Zr−α-H(B) = 2.71 Å), but even this contact is longer than could reasonably be attributed to an agostic interaction. Moreover, the orientation of α-H(B) does not appear correct for an interaction with zirconium, as it lies 34.5° out of the C(21)−Zr−C(16) equatorial plane, the location of the LUMO for the zirconocene moiety. The absence of low-energy ν(C−H) expected for an α-agostic structure in the IR spectrum of **1** also argues against a substantial interaction between Zr and α-H(16B). Further, the ^{1}H and ^{13}C spectra of **1** at ambient temperature in benzene-d_6 are not indicative of a static α-agostic structure in solution, where two doublets integrating to 2H are observed for the α-hydrogens and $^1J_{C-\alpha H}$ = 109 Hz. The NMR equivalence of the two neopentyl groups further signifies that their asymmetric orientation observed in the crystal structure is not maintained in solution, at least on the ^{1}H NMR time scale.

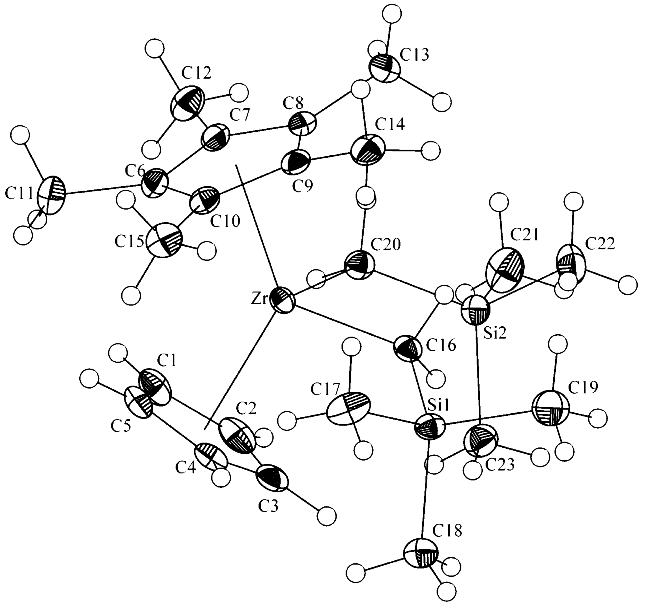

Figure 2. Structural drawing of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Zr(CH_2SiMe_3)_2$ (**2**) with thermal ellipsoids at the 50% probability level.

The structure of compound **2** has also been established by X-ray crystallography. This compound crystallized as colorless blocks from pentane at −35 °C. The molecular structure of **2** (Figure 2), including orientation of the bulky alkyl groups, is remarkably similar to **1**. All hydrogens were located in the difference map and have been refined. No ground-state agostic interactions are observed, as the closest zirconium−α-hydrogen and −γ-hydrogen distances found in **2** are 2.518(0) and 4.219(1) Å, respectively. Details of the data collection and solution and refinement of the structure can be found in Table 2.

The key structural parameters, including Zr−Cp centroid distances and angles and Zr−CH$_2$TMS bond lengths (Table 1), are close to those found for $Cp_2Zr(CH_2TMS)_2$ (2.24 Å; 128.3°; 2.278(4), 2.281(4) Å) respectively.[17] While two unequal bond distances are also found for Zr−CH$_2$TMS σ bonding in **2**, the difference in bond lengths (0.0375 Å) is much smaller than that observed for **1** (0.0873 Å). The Zr−C(21) bond in **1** (relative to Zr−C(20) in **2**) may be elongated to avoid a close contact between the *tert*-butyl substituent of C(21) and C(16) (Figure 1). In **2** however, the longer C−Si bond length may alleviate this interaction. Effectively, the trimethylsilylmethyl group is larger than neopentyl, as the unit cell of **2** is larger by 200 Å^3. This might argue that the neopentyl group is smaller by 25 Å^3.

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Table 2. Crystal and Refinement Data for Complexes $CpCp^*Zr(CH_2CMe_3)_2$ (1), $CpCp^*Zr(CH_2SiMe_3)_2$ (2), $CpCp^*Zr(Np)(Cl)$ (6), and $Cp_2Zr(CH_3)(CH_2CEt_3)$ (22)

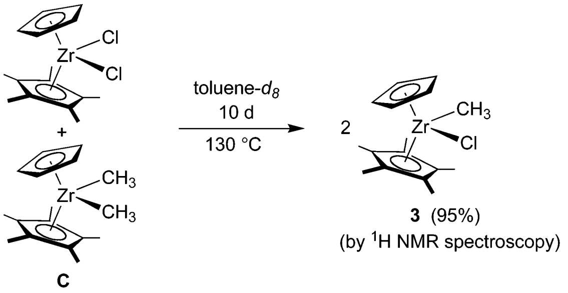
	1	**2**	**6**	**22**
empirical formula	$C_{25}H_{42}Zr$	$C_{23}H_{42}Si_2Zr$	$C_{20}H_{31}ClZr$	$C_{19}H_{30}Zr$
fw	433.81	465.97	398.12	349.65
T (K)	98(2)	98(2)	100(2)	98(2)
a, Å	9.7467(4)	9.9621(5)	8.9772(2)	17.658(3)
b, Å	25.9839(12)	26.8264(13)	13.5673(4)	8.2098(13)
c, Å	10.2031(5)	10.4769(5)	17.2242(5)	25.878(4)
α, deg			101.6260(10)	
β, deg	116.6710(10)	116.3020(10)	104.3560(10)	109.532(2)
γ, deg			100.4190(10)	
volume, Å^3	2309.07(18)	2510.0(2)	1930.85(9)	3535.7(10)
Z	4	4	4	8
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/$n	$P\bar{1}$	$P2/c$
d_{calc}, g/cm^3	1.248	1.233	1.370	1.314
θ range, deg	1.57 to 28.37	1.52 to 28.36	1.58 to 46.45	1.71 to 28.52
μ, mm^{-1}	0.482	0.539	0.704	0.613
abs corr	none	none	none	none
GOF	2.059	2.088	1.157	1.217
R_1,[a] wR_2[b] $[I > 2\sigma(I)]$	0.0247, 0.0475	0.0302, 0.0514	0.0390, 0.0748	0.0571, 0.0876

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Precursors for Methyl-alkyl Zirconocene Compounds. Methyl-alkyl zirconocene compounds of the form $(Cp-R_n)_2Zr(CH_3)R'$ potentially serve as precursors for $[(Cp-R_n)_2Zr(R')]^+[CH_3B(C_6F_5)_3]^-$-type initiators formed via methide abstraction using the strongly Lewis acidic activator $B(C_6F_5)_3$.[6] Again, the mixed ring ancillary ligation was targeted for its potential steric influence on initiator speciation. The steric demand of the Cp* group should discourage formation of bimetallic methyl-bridged monocations, such as $[\{(Cp-R_n)_2Zr(R')\}_2(\mu\text{-}CH_3)]^+[A]^-$ ($[A]^- = [CH_3B(C_6F_5)_3]^-$, $[B(C_6F_5)_4]^-$), which are often observed for zirconocene systems with open coordination environments.[6,20]

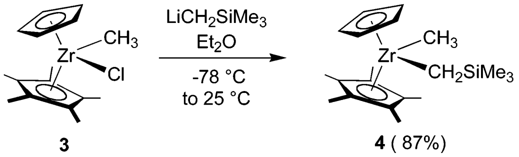
Key starting materials for the formation of methyl-alkyl complexes in zirconocene systems are $(Cp-R_n)_2Zr(CH_3)Cl$. These compounds, however, are not cleanly obtained from the reaction of $(Cp-R_n)_2ZrCl_2$ with 1 equiv of methyllithium.[8] Conventional routes to obtain $(Cp-R_n)_2Zr(CH_3)Cl$ compounds from $(Cp-R_n)_2Zr(CH_3)_2$ utilize HCl,[11] $[(CH_3)_3NH]^+[Cl]^-$,[21] $[(CHMe_2)_2NH_2]^+[Cl]^-$,[22] or $PbCl_2$,[23] as chlorinating reagents. Reagents HCl, $[(CHMe_2)_2NH_2]^+[Cl]^-$, and $PbCl_2$ were tested for the preparation of $CpCp^*Zr(CH_3)Cl$ (**3**) from $CpCp^*Zr(CH_3)_2$; however, in all cases **3** was contaminated with at least 5% $CpCp^*ZrCl_2$ as well as starting material. Separation of mixtures of dialkyl zirconocenes and chloro-alkyl zirconocenes is difficult due to their extreme solubility and similar physical properties, as well as the limited number of compatible purification methods available. Because we found that the purity of **3** plays an important role in the successful isolation of pure $CpCp^*Zr(CH_3)R$ compounds, it was essential to devise a procedure that affords very pure **3**.

A method was developed for the synthesis of clean samples of **3** that is based on the ligand redistribution chemistry reported by Jordan.[24] A solution containing 0.5 M $CpCp^*ZrCl_2$ and 0.5 M $CpCp^*Zr(CH_3)_2$ (**C**) in toluene-d_8 was heated at 130 °C in a J. Young NMR tube. After 10 days, 95% conversion to **3** was observed by ^1H NMR spectroscopy (eq 3). These conditions were subsequently employed on preparative scale reactions and afforded **3** contaminated with less than 3% $CpCp^*ZrCl_2$ as a white powder or pale yellow needles after purification from toluene−petroleum ether at −35 °C.



(3)

Synthesis of $CpCp^*Zr(CH_3)(CH_2TMS)$ and $CpCp^*Zr(CH_3)(Np)$. The mixed ring zirconocene methyl-alkyl compounds $CpCp^*Zr(CH_3)(CH_2TMS)$ (**4**) and $CpCp^*Zr(CH_3)(Np)$ (**5**) were prepared by the reaction of **3** with 1 equiv of the appropriate lithium reagent. The synthesis of **4** proceeded smoothly by this route in diethyl ether, and **4** was isolated as a pale yellow oil in good yields (eq 4). Lyophilization or trituration techniques, as well as a variety of solvent systems, failed in attempts to obtain **4** as a powder or crystalline material. This oil, as isolated, was judged to be >95% pure by ^1H NMR spectroscopy and suitable for use in further transformations.



(4)

The reaction of **3** with neopentyllithium was more sensitive to reaction conditions, including concentration, solvent, temperature, and reaction time. Reactions following the above methodology yielded **5** as a yellow oil (contaminated with other zirconocene compounds including **1** and $CpCp^*Zr(CH_3)_2$ (**C**)) that resists purification by recrystallization or precipitation. Under the reaction conditions shown in eq 5 the product mixture could be driven to **1**, **C**, and **5** in a 1:1:3 ratio, respectively, as

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[23] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155−164.

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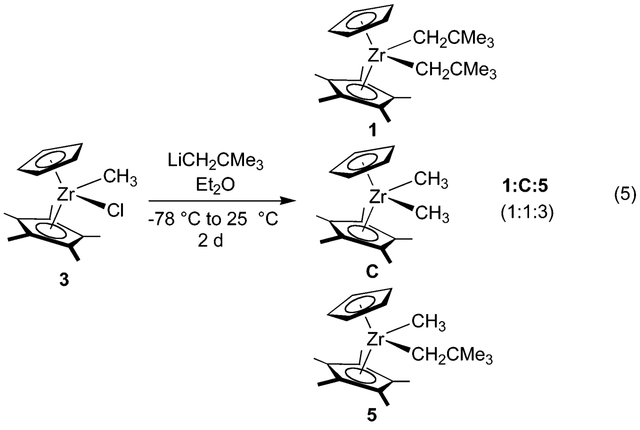
identified by comparison with the ^{1}H NMR spectra of independently synthesized compounds. This observation suggests

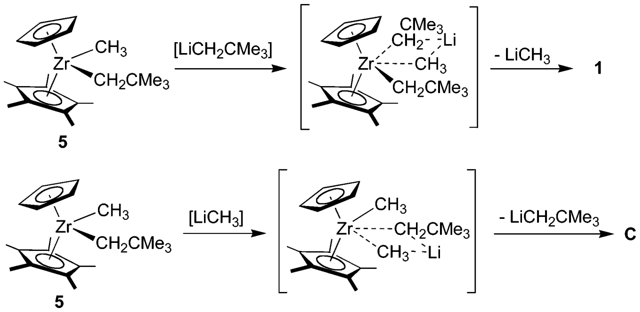


3 **1** **C** **5**

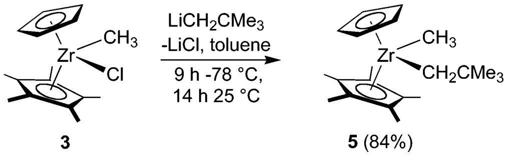
(5)

the alkylation of **3** with alkyllithium reagents may be reversible. Reversible alkylation catalyzed by trace neopentyllithium would provide a pathway for alkyl exchange, potentially explaining the product mixture (Scheme 2). Alkyl exchange between group 4 centers via an intermolecular mechanism involving the formation of bridging alkyl groups has been documented for both metallocene[24] and nonmetallocene compounds.[25] While this process is facile for methyl groups, which readily bridge metal centers, it is likely slower for exchange of a bulky neopentyl group between zirconocene centers having sterically demanding ancillary ligation such as that in **5**.

Scheme 2



A successful set of reaction conditions were eventually identified. Preparation in toluene along with careful control of reaction temperature afforded a clean and reproducible methodology (eq 6) and allowed isolation of **5** as an analytically pure yellow powder after removal of lithium chloride by filtration.



3 **5** (84%)

(6)

Alternate Routes for the Synthesis of CpCp*Zr(CH_3)(Np). A methodology to synthesize **5** utilizing successive monoalkylation reactions starting from CpCp*ZrCl_2 is desirable, as it would remove one step from the overall sequence and eliminate the long reaction time required to prepare **3**. Additionally, this type of strategy would also be preferable in the preparation of isotopically labeled versions of **5**, such as CpCp*Zr(CD_3)(Np) or CpCp*Zr($^{13}CH_3$)(Np), since a 15 mol % excess of CpCp*Zr(CH_3)$_2$ is used in the preparative scale synthesis of **3**. As monomethylation of CpCp*ZrCl_2 is not possible with the lithium reagent, we explored a route via the monoalkylated compound CpCp*Zr(Np)(Cl) (**6**).

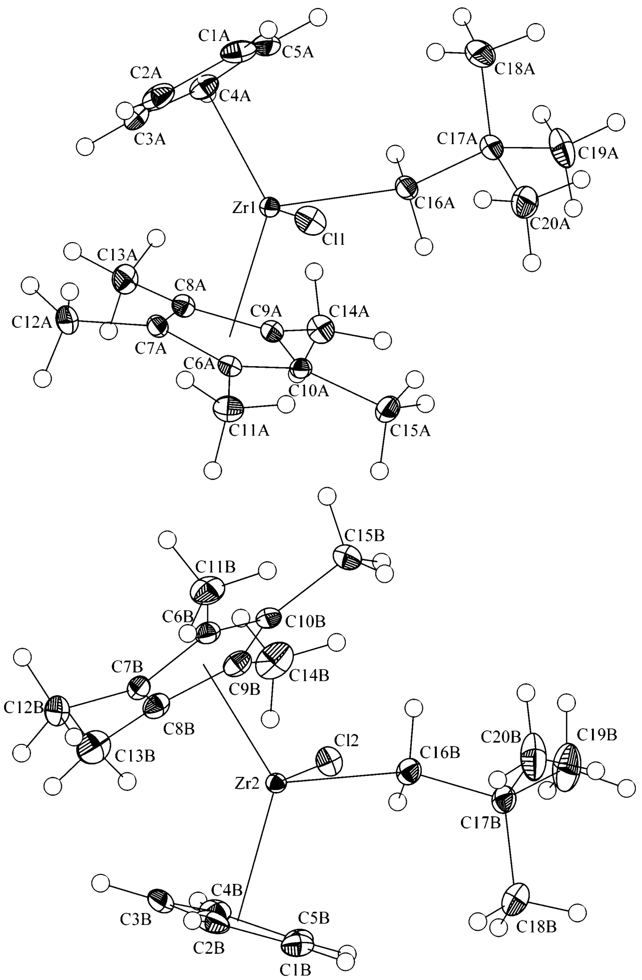
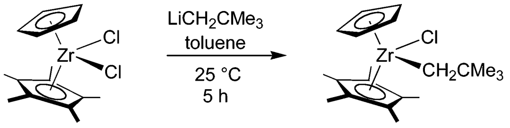


Figure 3. Structural drawing of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2-CMe_3)Cl (**6**) showing the unique molecules found in the asymmetric unit with thermal ellipsoids at the 50% probability level.

Compound **6** is prepared by reaction of CpCp*ZrCl_2 with 1 equiv of neopentyllithium in toluene (eq 7).[26] Although initially **6** is obtained as a sticky, bright yellow solid, it can be isolated as a yellow powder after trituration with petroleum ether.



6 (72%)

(7)

Yellow crystals of **6** were obtained by slow diffusion of petroleum ether into diethyl ether solutions at −35 °C, and the molecular structure was determined by X-ray diffraction (Figure 3). Overall, the structural parameters for **6**, including Zr−Cl

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[25] Mehrkhodavandi, P.; Schrock, R. R.; Bonitatebus, P. J. *Organometallics* **2002**, *21*, 5785−5798.

[26] (a) Chirik, P. J.; Bercaw, J. E. Unpublished results. (b) For related synthetic strategy utilizing Grignard reagents see: Song, F. Q.; et al. *Organometallics* **2005**, *24*, 1315−1328.

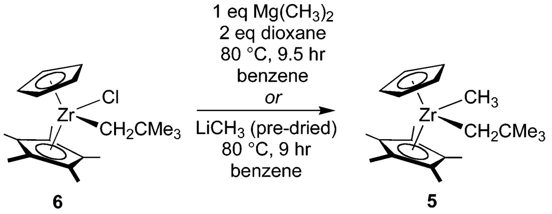
Table 3. Selected Structural Parameters for 6 and 22

6		22	
	Distances (Å)		
Zr(1)−Ct(1A)[a]	2.232	Zr(1)−Ct(1A)[a]	2.23
Zr(1)−Ct(2A)[b]	2.241	Zr(1)−Ct(2A)[b]	2.24
Zr(2)−Ct(1B)[a]	2.224	Zr(2)−Ct(1B)[a]	2.25
Zr(2)−Ct(2B)[b]	2.240	Zr(2)−Ct(2B)[b]	2.24
Zr(1)−C(16A)	2.3258(12)	Zr(1)−C(11A)	2.294(3)
Zr(1)−Cl(1)	2.4503(3)	Zr(1)−C(12A)	2.248(3)
Zr(2)−C(16B)	2.3287(12)	Zr(2)−C(11B)	2.306(3)
Zr(2)−Cl(2)	2.4432(3)	Zr(2)−C(12B)	2.252(3)
	Angles (deg)		
Ct(1A)−Zr(1)−Ct(2A)	129.5	Ct(1A)−Zr(1)−Ct(2A)	130.9
Ct(1B)−Zr(2)−Ct(2B)	129.8	Ct(1B)−Zr(2)−Ct(2B)	130.9
C(16A)−Zr(1)−Cl(1)	100.18(3)	C(11A)−Zr(1)−C(12A)	94.54(12)
C(16B)−Zr(2)−Cl(2)	99.91(3)	C(11B)−Zr(2)−C(12B)	95.07(12)

[a] Ct(1A) is defined as the centroid of the ring made up of C(1A)−C(5A); Ct(1B) is defined as the centroid of the ring made up of C(1B)−C(5B). [b] Ct(2A) is defined as the centroid of the ring made up of C(6A)−C(10A); Ct(2B) is defined as the centroid of the ring made up of C(6B)−C(10B).

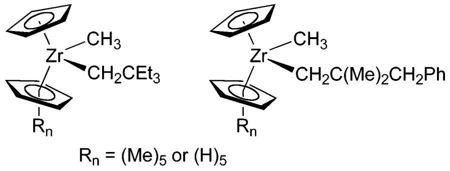
bond lengths, are comparable to those in CpCp*$ZrCl_2$ (2.4421(9) Å).[27] The observed zirconium−neopentyl carbon bond distances (2.3258(12), 2.3287(12) Å for the two independent molecules in the asymmetric unit) are on the long end of the range typically found in alkyl zirconocenes and are roughly intermediate of the range observed in **1** (Table 3).[18,19] Evidence for crowding in the equatorial plane of **6** is suggested by the expanded C(16)−Zr−Cl angles (100.18(3)°, 99.91(3)°) as compared with the Cl−Zr−Cl angle (97.78(5)°) found in CpCp*$ZrCl_2$. No special zirconium−hydrogen interactions are evident in **6**, as the closest Zr−H contact is 2.75 Å. Details of the data collection and solution and refinement of the structure can be found in Table 2.

NMR scale reactions were used to explore methylation of **6** with several alkylating agents. Promising conditions were observed with pre-dried, ether-free methyllithium, as **5** formed cleanly in benzene-d_6 after heating for 9 h at 80 °C (eq 8). Reaction of **6** with $(CH_3)_2Mg$ in benzene-d_6 containing roughly 2 equiv of 1,4-dioxane at 80 °C also formed compound **5** cleanly, as assessed by ^1H NMR spectroscopy. The addition of dioxane to the reaction mixture appeared to minimize formation of products arising from alkyl or halide exchange (possibly by precipitation of magnesium halide salts) while increasing the solubility of $(CH_3)_2Mg$. Reactions of **6** with $(CH_3)_2Mg$ conducted in the absence of dioxane (benzene-d_6, 9 h, 80 °C) resulted in multiple zirconocene species including **3** and **C**, along with **5** and unreacted **6** after heating. Similarly, reaction of **6** with solid $Li^{13}CH_3{\cdot}LiI$ (benzene-d_6, 9 h, 80 °C) complex afforded multiple zirconocene species, including **5** and unreacted **6**, after heating. $Li^{13}CH_3$ and $LiCD_3$ are commonly prepared or purchased commercially as 1:1 complexes with lithium iodide, and this additive appeared detrimental under these conditions.[28] One of the new species is likely CpCp*Zr(Np)(I) on the basis of the chemical shift of a new Cp resonance in the ^1H NMR spectrum as compared with that in CpCp*ZrI_2. The reaction of **6** with CH_3MgBr resulted in the formation of unreacted **6**, **5**, and what appeared to be CpCp*ZrNpBr in a 2:1:2 ratio after 2 h at room temperature in diethyl ether, as determined by ^1H NMR spectroscopy. Thus, it appears that lithium or magnesium methylating agents having halide present are not suited to clean preparation of **5**.



(8)

Design and Synthesis of Specialty Alkyllithium Reagents. One strategy to stabilize the alkyl zirconocene cation formed upon activation toward decomposition via β-methyl elimination is to utilize a bulky alkyl group having no β-methyl groups. Another approach is to design a catalyst where unfavorable steric interactions between β-alkyl substituents and the cyclopentadienyl framework in the transition structure for β-methyl elimination inhibit this reaction. Therefore, syntheses of methyl-alkyl zirconocenes of the type shown below were targeted.



Although catalysts derived from zirconocenes of type Cp($Cp-R_n$)Zr(CH_3)(CH_2CEt_3) might decompose via β-ethyl elimination, generally this reaction has not been observed in related systems. Previously in our group, we noted that whereas $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}Sc\{CH_2CH(CH_3)_2\}$ decomposes by fast, reversible β-H and slower β-methyl elimination, the decomposition of $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}Sc\{CH_2CH(CH_2CH_3)_2\}$ proceeds with no evidence for β-ethyl elimination.[29] Resconi has also found that chain transfer by β-ethyl elimination did not occur during the polymerization of 1-butene by $Cp^*_2MCl_2$/MAO (M = Zr, Hf) catalysts.[12] Activated compounds based on Cp($Cp-R_n$)Zr(CH_3)($CH_2CMe_2CH_2Ph$) could decompose via β-methyl elimination; however this reaction may be inhibited for catalysts with CpCp* ancillary ligation. Unfavorable steric interactions between the benzyl substituent of the alkyl and the cyclopentadienyl ligands might sufficiently destabilize the transition state for this reaction relative to that for $[CpCp^*Zr(Np)]^+[CH_3B(C_6F_5)_3]^-$.

The synthetic methodology used to prepare 2,2-diethylbutyllithium ($Li(CH_2CEt_3)$) (**13**) and 2,2-dimethyl-3-phenylpropyllithium ($Li(CH_2CMe_2CH_2Ph)$) (**19**) is shown in Scheme 3. 2,2-Diethylbutanol (**10**) was prepared conveniently in three steps from commercially available 2-ethylbutric acid (**7**) using standard procedures.[30] A similar sequence gave 2,2-dimethyl-3-phenylpropanol (**16**) from commercially available 2-methylpropionoic acid ethyl ester (**14**). Precedented reaction conditions for the conversion of neopentyl-type alcohols (PPh_3/Br_2, CH_3CN, heat) to alkylbromides failed for **10** and **16**; low yields of products were isolated for both substrates, 30% and 10% respectively. The methane sulfonate esters 2,2-diethylbutyl mesylate (**11**) and 2,2-dimethyl-3-phenylpropyl mesylate (**17**) were prepared after the methodology for hindered primary substrates of Servis.[31] Compounds **11** and **17** were converted to alkyl iodides **12** and **18** using conditions based on those reported by Stevens for the preparation of (−)-9-iodocamphor

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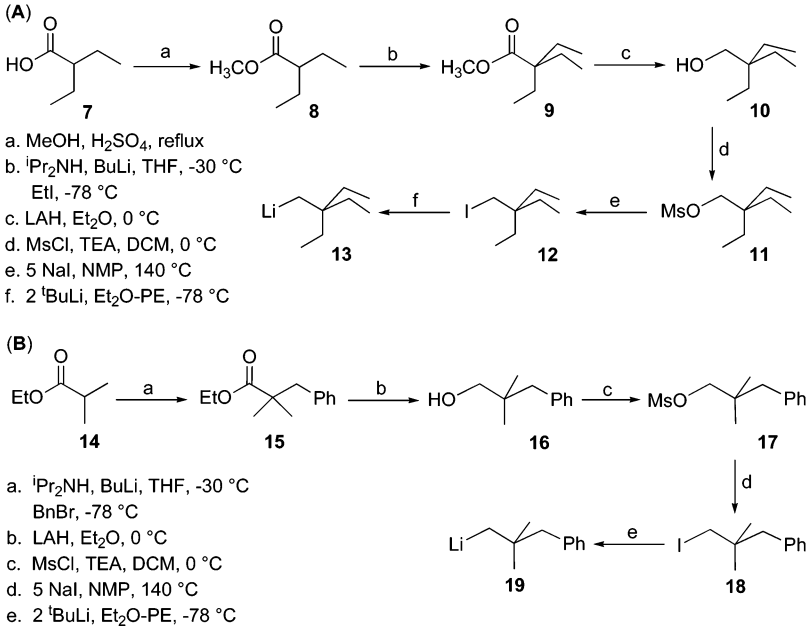
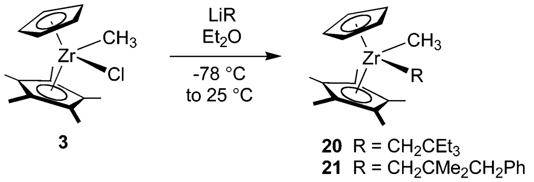
Scheme 3



from (−)-9-bromocamphor.[32] This transformation required forcing conditions, again reflecting the steric inhibition of S_N2 reactivity at the primary carbon center. The desired alkyllithium reagents, **13** and **19**, were synthesized from **12** and **18**, respectively, using the lithium−halogen exchange procedure developed by Bailey[33] and Negishi.[34]

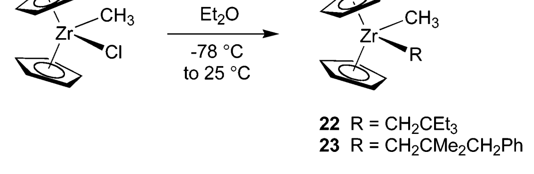
Methyl-alkyl Zirconocene Synthesis Using Specialty Alkyllithium Reagents. Syntheses of methyl-alkyl zirconocenes with the specialty alkyl groups, $CpCp^*Zr(CH_3)(CH_2CEt_3)$ (**20**), $CpCp^*Zr(CH_3)(CH_2CMe_2CH_2Ph)$ (**21**), $Cp_2Zr(CH_3)(CH_2CEt_3)$ (**22**), and $Cp_2Zr(CH_3)(CH_2CMe_2CH_2Ph)$ (**23**), were explored using the conditions shown in eqs 9 and 10. Reaction of **3** with 1 equiv of either **13** or **19** resulted in formation of **20** and **21**, respectively, along with additional zirconocene products as determined by analysis of the isolated material by ^1H NMR spectroscopy. These additional compounds are likely $CpCp^*Zr(CH_3)_2$ (**C**) and $CpCp^*ZrR_2$, possibly formed via the reversible alkylation process postulated for alkyl exchange in **5**. Unfortunately, the oils containing **20** and **21** resisted purification by crystallization or precipitation from pentane, even at temperatures below −35 °C. This difficulty is attributed to the extreme solubility of these compounds.



(9)

3

20 R = CH_2CEt_3
21 R = $CH_2CMe_2CH_2Ph$



(10)

22 R = CH_2CEt_3
23 R = $CH_2CMe_2CH_2Ph$

Compounds **22** and **23** are readily formed under these conditions and are isolated in modest yields after crystallization from pentane at −35 °C. While pale yellow X-ray quality crystals of **22** were obtained, the brown pellets of **23** recovered always showed extremely poor diffraction. This zirconocene complex crystallizes as a radial cluster and maintains this preference under a variety of crystallization conditions.

The pale yellow blocks of **22** crystallized in the *P*2/*c* space group having two independent molecules in the asymmetric unit, differing in orientation of the bulky alkyl group (Figure 4). The zirconium−Cp centroid and zirconium−methyl distances as well as the Cp centroid−zirconium−Cp centroid and carbon−zirconium−carbon angles found for **22** are in line with those observed for $Cp_2Zr(CH_3)(Np)$ (2.232, 2.2980(13) Å; 130.6°, 94.99°) (Table 3).[11] The Zr−C(12) bond lengths (2.248(3) and 2.252(3) Å) in **22** are short in comparison to those found in **1** and **2** and to the range typically seen for zirconocenes having bulky alkyl groups (2.251−2.388 Å).[17−19] No close zirconium−hydrogen contacts are found, as the nearest zirconium−hydrogen distance found in **22** is 2.79 Å. Details of the data collection and solution and refinement of the structure can be found in Table 2.

Conclusions

Synthesis and characterization of precatalysts that will likely generate models for the propagating species in zirconocene-catalyzed alkene polymerizations have been described. In this regard, we have subsequently examined the activation of $CpCp^*Zr(CH_3)(Np)$ with $B(C_6F_5)_3$ at low temperatures and found that it does indeed initiate propene polymerization rapidly, allowing for convenient studies of the kinetics. A full report of those studies, along with that using $CpCp^*Zr(CH_3)(CH_2TMS)$, is forthcoming.[35] The intermediate steric demand of the mixed ring CpCp* ancillary ligation allows preparation of dialkyl zirconocenes with two bulky alkyl groups. A convenient general starting material for preparation of $CpCp^*Zr(CH_3)R'$ is $CpCp^*Zr(CH_3)Cl$. Its preparation using ligand redistribution chemistry minimizes product contamination by $CpCp^*ZrCl_2$. Synthesis on the [CpCp*Zr] framework is often sensitive to the reaction

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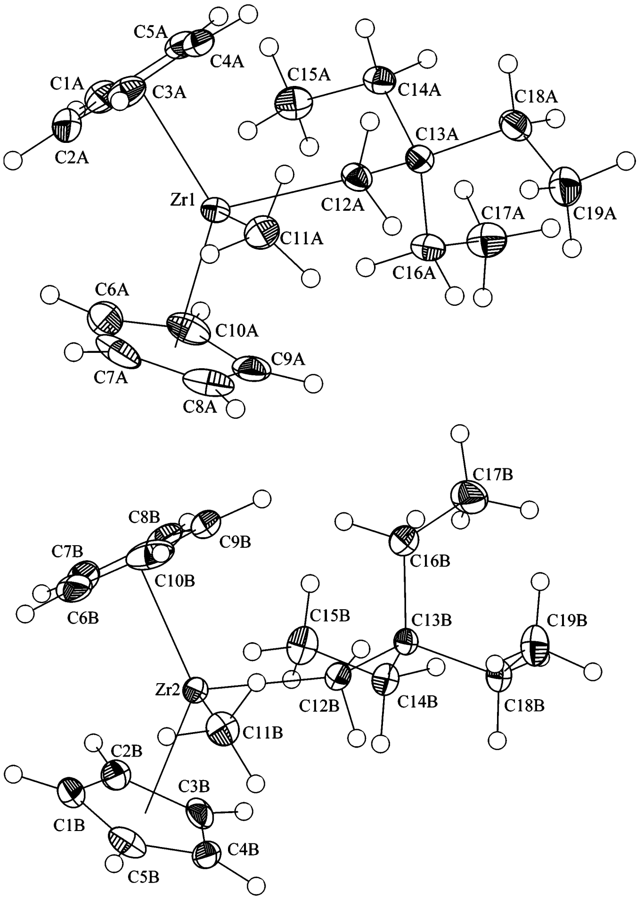

Figure 4. Structural drawing of (η^5-C_5H_5)$_2$Zr(CH_3)($CH_2C(CH_2CH_3)_3$) (**22**) showing the unique molecules found in the asymmetric unit with thermal ellipsoids at the 50% probability level.

conditions, resulting in side-product formation via facile salt-mediated alkyl or halide exchange processes. This undesirable reactivity can be minimized under optimized reaction conditions. X-ray diffraction studies on CpCp*Zr(Np)$_2$, CpCp*Zr(CH_2-TMS)$_2$, CpCp*Zr(Np)(Cl), and $Cp_2Zr(CH_3)(CH_2CEt_3)$ indicate minimal perturbation of the bent-sandwich coordination mode in the molecular structures. In some cases however, the steric bulk of the alkyl group is reflected in (a) a slightly contracted Cp−Zr−Cp centroid angle, (b) an expanded carbon−Zr−carbon(chloride) angle, and (c) zirconium−carbon bond lengths on the long end of the range commonly observed in (Cp−R$_n$)$_2$-ZrR′$_2$ and (Cp−R$_n$)$_2$Zr(CH_3)R′ compound types.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques, or in a drybox under a nitrogen atmosphere as described previously.[36] Argon gas was purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. Solvents for air- and moisture-sensitive reactions were dried by the method of Grubbs[37] and were stored under vacuum over sodium benzophenone ketyl (diethyl ether, pentane, tetrahydrofuran), titanocene[38] (toluene, petroleum ether), or calcium hydride (methylene chloride). 1,4-Dioxane was vacuum distilled from calcium hydride and stored in a Schlenk flask under nitrogen. *N*-Methylpyrrolidinone was purchased anhydrous from Aldrich in a Sure/Seal bottle. Benzene-*d*$_6$ and toluene-*d*$_8$ were purchased from Cambridge Isotopes and vacuum distilled from sodium benzophenone ketyl. Methylene chloride-*d*$_2$ was purchased from Cambridge Isotopes and vacuum distilled from calcium hydride. $CDCl_3$ was purchased from Cambridge Isotopes and stored over molecular sieves. The syntheses of CpCp*ZrCl$_2$, CpCp*Zr-(CH_3)$_2$,[39] $Cp_2Zr(CH_3)Cl$,[40] LiNp,[41] and $LiCH_2TMS$[42] were carried out as previously reported. Li$^{13}CH_3$·LiI[28] and $(CH_3)_2Mg$[43] were prepared using standard procedures. NEt_3 and $HN(CHMe_2)_2$ were vacuum transferred from calcium hydride and stored in a Schlenk flask under argon. Butyllithium was purchased from Aldrich and stored under argon. Benzylbromide was purchased from Aldrich and distilled before use. NaI was dried under vacuum for 6 h at 70 °C and stored under nitrogen in the drybox.

NMR spectra were recorded on Varian Mercury (300 MHz for ^{1}H) and Varian UNITY Inova (500.13 MHz for ^{1}H) spectrometers. Chemical shifts are given in ppm downfield from TMS using residual proton (C_6D_5H 7.16; $CHCl_3$ 7.26; $C_6D_5CD_2H$ 2.09; $CDHCl_2$ 5.32) or carbon (C_6D_6 128.39; $CDCl_3$ 77.23; CD_2Cl_2 54.00) signals of the deuterated solvents. Elemental analyses were performed at Midwest MicroLab LLC.

Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)$_2$ (1)-(CpCp*ZrNp$_2$). In an inert atmosphere glovebox, a 50 mL round-bottom flask equipped with a stir bar was charged with (η^5-C_5H_5)(η^5-C_5Me_5)ZrCl$_2$ (0.502 g, 1.38 mmol) and $LiCH_2CMe_3$ (0.239 g, 3.06 mmol) and attached to a small swivel frit assembly. On the vacuum line, diethyl ether (25 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. Stirring for 36 h resulted in a yellow-brown solution and an off-white precipitate. The solvent was removed in vacuo, leaving a tan solid. Petroleum ether (25 mL) was added to the solids by vacuum transfer. The resulting off-white precipitate was filtered away from the yellow-brown filtrate and washed once with recycled solvent. Removal of all volatiles and drying in vacuo yielded a tan powder. In the glovebox the solid was dissolved in pentane and the solution concentrated to 8 mL. The solution was cooled to −35 °C to recrystallize the desired product; pale yellow crystalline material suitable for X-ray diffraction was isolated and dried in vacuo. Yield: 0.398 g (66%). Anal. Calcd. for $C_{25}H_{42}Zr$: C, 69.21; H, 9.76. Found: C, 68.97, 69.24; H, 9.64, 9.62. ^{1}H NMR (500 MHz, C_6D_6): δ 5.94 (s, C_5H_5, 5H), 1.71 (s, $C_5(CH_3)_5$, 15H), 1.18 (s, $CH_2C(CH_3)_3$, 18H), 0.81 (d, $CH_2C(CH_3)_3$, 2H, $J = 11.6$ Hz), −0.47 (d, $CH_2C(CH_3)_3$, 2H, $J = 11.6$ Hz). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 117.7 ($C_5(CH_3)_5$), 109.7 (C_5H_5), 78.4 (Zr−$CH_2C(CH_3)_3$), 37.1 ($CH_2C(CH_3)_3$), 35.6 ($CH_2C(CH_3)_3$), 12.5 ($C_5(CH_3)_5$). ^{13}C NMR (125 MHz, C_6D_6): δ 117.7 (s, $C_5(CH_3)_5$, 5C), 109.7 (d, C_5H_5, 5C, $^1J_{CH} = 174.8$ Hz), 78.4 (t, Zr−$CH_2C(CH_3)_3$, 2C, $^1J_{CH} = 109.1$ Hz), 37.1 (s, $CH_2C(CH_3)_3$, 2C), 35.6 (q, $CH_2C(CH_3)_3$, 6C, $^1J_{CH} = 123.3$ Hz), 12.5 (q, $C_5(CH_3)_5$, 5C, $^1J_{CH} = 126.2$ Hz).

Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2SiMe_3)$_2$ (2) (CpCp*Zr-(CH_2TMS)$_2$). In an inert atmosphere glovebox, a 50 mL round-bottom flask equipped with a stir bar was charged with (η^5-C_5H_5)(η^5-C_5Me_5)ZrCl$_2$ (1.170 g, 3.23 mmol) and $LiCH_2SiMe_3$ (0.639 g, 6.78 mmol) and attached to a small swivel frit assembly.

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On the vacuum line, diethyl ether (30 mL) was vacuum transferred onto the solids at −78 °C, and the apparatus was backfilled with Ar. The reaction mixture was allowed to warm to room temperature with stirring, and an off-white precipitate was observed. After stirring for 12 h, the solvent was removed in vacuo, leaving a colorless, oily paste. Pentane (35 mL) was added to the mixture by vacuum transfer. The resulting off-white precipitate was filtered away from the colorless filtrate and washed two times with recycled solvent. Removal of all volatiles and drying in vacuo yielded an off-white powder. In the glovebox the solid was dissolved in pentane and the solution concentrated to 8 mL. The solution was cooled to −35 °C to recrystallize the desired product; colorless crystalline material suitable for X-ray diffraction was isolated and dried in vacuo. Yield: 1.051 g (70%). Anal. Calcd. for $\text{C}_{23}\text{H}_{42}\text{Si}_2\text{Zr}$: C, 59.28; H, 9.08. Found: C, 59.45, 59.37; H, 9.20, 8.95. ^{1}H NMR (500 MHz, C_6D_6): δ 5.89 (s, C_5H_5, 5H), 1.70 (s, $\text{C}_5(\text{C}H_3)_5$, 15H), 0.21 (s, $\text{CH}_2\text{Si}(\text{C}H_3)_3$, 18H), −0.25 (d, $\text{C}H_2\text{Si}(\text{CH}_3)_3$, 2H, J = 10.7 Hz), −0.54 (d, $\text{C}H_2\text{Si}(\text{CH}_3)_3$, 2H, J = 10.9 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): δ 118.2 ($C_5(\text{CH}_3)_5$), 110.8 ($C_5\text{H}_5$), 46.0 (Zr−$C\text{H}_2\text{Si}(\text{CH}_3)_3$), 12.4 ($\text{C}_5(C\text{H}_3)_5$), 4.10 ($\text{CH}_2\text{Si}(C\text{H}_3)_3$).

NMR Scale Synthesis of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ (3) (CpCp*Zr(CH$_3$)Cl). In an inert atmosphere glovebox, $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2$ (45 mg, 0.12 mmol) was weighed into a small vial. To this was added 0.25 mL of a 0.5 M solution of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)_2$ (40 mg, 0.12 mmol) in toluene-d_8. The contents of the vial were transferred via pipet to a J. Young NMR tube, and the vial was rinsed with an additional 0.45 mL of solvent. The reaction was heated in an oil bath regulated at 130 °C, and the reaction progress was monitored by ^{1}H NMR spectroscopy. The solution was pale yellow and a solid crystallized out upon cooling the sample to room temperature to acquire ^{1}H NMR data. After 10 days of heating at this temperature, clean formation of **3** was observed in 95% yield (by ^{1}H NMR).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ (3) (CpCp*Zr(CH$_3$)(CI)). In an inert atmosphere glovebox, a thick walled glass vessel equipped with a stir bar was charged with $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2$ (2.001 g, 5.52 mmol) and $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)_2$ (2.048 g, 6.37 mmol). Toluene (24 mL, vacuum transferred from titanocene) was added, giving a mixture consisting of a yellow solution and remaining solid $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2$. The vessel was sealed with an 8 mm Kontes needle valve, and the mixture was stirred in the box to break up the solid. In the hood, the reaction was heated with stirring in an oil bath regulated at 130 °C for 11.64 days. At this temperature a homogeneous solution was observed. The reaction was removed from the oil bath and cooled to room temperature, resulting in a green solution and an off-white precipitate. In the glovebox, a small heterogeneous sample was dried in vacuo for analysis by ^{1}H NMR spectroscopy and confirmed clean conversion to product ($<$5% $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_2$). At this point toluene was added, and the reaction mixture was transferred to a flask and was concentrated and dried in vacuo. The resulting solid was stirred in petroleum ether (100 mL) and filtered. The precipitate was isolated and was purified by precipitation from a concentrated toluene−petroleum ether solution at −35 °C. Removal of all volatiles gave 0.340 g of an off-white solid identical (by ^{1}H NMR spectroscopy) to that obtained using the literature procedure. An additional 2.953 g of product was obtained by concentration of the combined organic filtrates and several repetitions of the purification procedure. Yield: 3.293 g (87%). Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{ClZr}$: C, 56.19; H, 6.78. Found: C, 56.49, 56.29; H, 6.72, 6.82. ^{1}H NMR (300 MHz, C_6D_6): δ 5.79 (s, C_5H_5, 5H), 1.71 (s, $\text{C}_5(\text{C}H_3)_5$, 15H), 0.22 (s, $\text{C}H_3$, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 120.5 ($C_5(\text{CH}_3)_5$), 113.6 ($C_5\text{H}_5$), 35.3 (Zr−$C\text{H}_3$), 12.2 ($\text{C}_5(C\text{H}_3)_5$).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)(\text{CH}_2\text{SiMe}_3)$ (4) (CpCp*Zr(CH$_3$)(CH$_2$TMS)). In an inert atmosphere glovebox, a 50 mL round-bottom flask equipped with a stir bar was charged with $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ (0.866 g, 2.53 mmol) and $\text{LiCH}_2\text{SiMe}_3$ (0.240 g, 2.54 mmol) and attached to a small swivel frit assembly. On the vacuum line, diethyl ether (25 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The reaction mixture was allowed to warm to room temperature over 12 h with stirring. At this time a colorless solution with a white precipitate was observed. The solvent was removed, and resultant paste was dried in vacuo. Pentane (20 mL) was added to the mixture by vacuum transfer. The resulting white precipitate was filtered away from the colorless filtrate and washed twice with recycled solvent. Removal of all volatiles and drying in vacuo resulted in a pale yellow oil. Repeated attempts to solidify the product by trituration with pentane or lyophilization with benzene failed. Yield: 0.865 g (87%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.79 (s, C_5H_5, 5H), 1.68 (s, $\text{C}_5(\text{C}H_3)_5$, 15H), 0.21 (s, $\text{CH}_2\text{Si}(\text{C}H_3)_3$, 9H), −0.29 (s, $\text{C}H_3$, 3H) −0.31 (d, $\text{C}H_2\text{Si}(\text{CH}_3)_3$, 1H, J = 9.5 Hz), −0.38 (d, $\text{C}H_2\text{Si}(\text{CH}_3)_3$, 1H, J = 9.5 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 117.9 ($C_5(\text{CH}_3)_5$), 111.4 ($C_5\text{H}_5$), 44.9 (Zr-$C\text{H}_2\text{Si}(\text{CH}_3)_3$), 34.0 (Zr−$C\text{H}_3$), 12.4 ($\text{C}_5(C\text{H}_3)_5$), 4.3 ($\text{CH}_2\text{Si}(C\text{H}_3)_3$).

Reaction of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ and $\text{LiCH}_2\text{CMe}_3$ Leading to Multiple Dialkyl Zirconocene Products. In an inert atmosphere glovebox, a 50 mL round-bottom flask equipped with a stir bar was charged with $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ (0.500 g, 1.46 mmol) and $\text{LiCH}_2\text{CMe}_3$ (0.126 g, 1.60 mmol) and attached to a small swivel frit assembly. On the vacuum line, diethyl ether (30 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The cooling bath was removed, and the reaction mixture was stirred for 48 h at room temperature. At this time a bright yellow solution with a white precipitate was observed. The solvent was removed in vacuo, leaving an oily residue. Pentane (15 mL) was added to the mixture by vacuum transfer. The resulting white precipitate was filtered away from the yellow filtrate and washed with recycled solvent. Removal of all volatiles and drying in vacuo resulted in a yellow-brown oil. Characterization of the crude oil by ^{1}H NMR indicated three compounds in the product mixture. $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)_2$, $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)(\text{Np})$, and $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(Np)}_2$ were present in a 16:66:18 ratio, respectively.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)(\text{CH}_2\text{CMe}_3)$ (5) (CpCp*Zr(CH$_3$)(Np)). In an inert atmosphere glovebox, a 100 mL round-bottom flask equipped with a stir bar was charged with $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Zr(CH}_3)\text{Cl}$ (0.592 g, 1.73 mmol) and $\text{LiCH}_2\text{CMe}_3$ (0.136 g, 1.74 mmol) and attached to a small swivel frit assembly. On the vacuum line, toluene (70 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The reaction mixture was stirred for 9 h at −78 °C, then allowed to warm to room temperature over 14 h with stirring. At this time a yellow-green solution was observed. The solvent was removed in vacuo, leaving an oily paste. Pentane (25 mL) was added to the mixture by vacuum transfer. The resulting white precipitate was filtered away from the yellow filtrate and washed with recycled solvent. Removal of all volatiles and drying in vacuo resulted in a yellow oil. In the glovebox this oil was dissolved in petroleum ether (20 mL) and filtered via pipet through Celite directly into a 50 mL Kjeldahl flask equipped with a stir bar. The flask was attached to a needle valve, and on the vacuum line the volatiles were removed. Pentane (15 mL) was added by vacuum transfer to dissolve the oil and was removed slowly in vacuo with rapid stirring. Further trituration with pentane (generally 3 cycles) gave a yellow powder, which was dried in vacuo. Yield: 0.550 g (84%). Anal. Calcd. for $\text{C}_{21}\text{H}_{34}\text{Zr}$: C, 66.78; H, 9.07. Found: C, 66.52, 66.76; H, 8.97, 9.01. ^{1}H NMR (300 MHz, C_6D_6): δ 5.86 (s, C_5H_5, 5H), 1.67 (s, $\text{C}_5(\text{C}H_3)_5$, 15H), 1.13 (s, $\text{CH}_2\text{C}(\text{C}H_3)_3$, 9H), 0.45 (d, $\text{C}H_2\text{C}(\text{CH}_3)_3$, 1H, J = 12.6 Hz), −0.18 (d, $\text{C}H_2\text{C}(\text{CH}_3)_3$, 1H, J = 12.6 Hz), −0.27 (s, $\text{C}H_3$, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 117.9 ($C_5(\text{CH}_3)_5$), 111.3 ($C_5\text{H}_5$), 70.9 (Zr−$C\text{H}_2\text{C}(\text{CH}_3)_3$), 36.5 (Zr−$C\text{H}_3$), 36.3 ($\text{CH}_2C(\text{CH}_3)_3$), 36.0 ($\text{CH}_2\text{C}(C\text{H}_3)_3$), 12.3 ($\text{C}_5(C\text{H}_3)_5$).

Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (6) (CpCp*Zr(Np)Cl). In an inert atmosphere glovebox, a 50 mL round-bottom flask equipped with a stir bar was charged with (η^5-C_5H_5)(η^5-C_5Me_5)$ZrCl_2$ (0.385 g, 1.06 mmol) and $LiCH_2CMe_3$ (0.088 g, 1.13 mmol) and attached to a small swivel frit assembly. On the vacuum line, toluene (25 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. Stirring for 5 h resulted in a bright yellow solution and a white precipitate. The reaction was filtered, and the precipitate was washed twice with recycled solvent. The solvent was removed in vacuo, leaving a bright yellow oil that began to solidify. Petroleum ether (10 mL) was added to the isolated material by vacuum transfer followed by stirring at room temperature. Removal of all volatiles and drying in vacuo yielded a bright yellow powder. The product may be crystallized by slow diffusion of petroleum ether into a diethyl ether solution cooled to −35 °C; yellow crystalline fragments suitable for X-ray diffraction were obtained via this method. Yield: 0.303 g (72%). Anal. Calcd. for $C_{20}H_{31}ClZr$: C, 60.33; H, 7.85. Found: C, 60.10, 60.41; H, 7.73, 7.87. ^1H NMR (300 MHz, C_6D_6): δ 5.94 (s, C_5H_5, 5H), 1.69 (s, $C_5(CH_3)_5$, 15H), 1.26 (s, $CH_2C(CH_3)_3$, 9H), 1.21 (d, $CH_2C(CH_3)_3$, 1H, $J = 13.2$ Hz), 0.16 (d, $CH_2C(CH_3)_3$, 1H, $J = 13.2$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 121.0 ($C_5(CH_3)_5$), 113.3 (C_5H_5), 68.9 (Zr−$CH_2C(CH_3)_3$), 36.5 ($CH_2C(CH_3)_3$), 35.5 ($CH_2C(CH_3)_3$), 12.4 ($C_5(CH_3)_5$).

Alternate Methods for the Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_3)(CH_2CMe_3) (5): Reaction of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl with $LiCH_3$. In an inert atmosphere glovebox, a J. Young NMR tube was charged with (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (12 mg, 0.03 mmol) and dry, ether-free solid $LiCH_3$ (1.5 mg, 0.07 mmol). Benzene-d_6 (0.78 mL) was added to give a yellow solution; $LiCH_3$ was not soluble in C_6D_6 at room temperature. The reaction was heated at 80 °C and monitored by ^1H NMR spectroscopy. After 4 h of heating, the ^1H NMR spectrum indicated a 30:70 mixture of **6** and **5**, respectively. The reaction was complete (by ^1H NMR) after an additional 5 h of heating at this temperature to yield **5** cleanly as the only product.

Alternate Methods for the Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_3)(CH_2CMe_3) (5): Reaction of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl with $Li^{13}CH_3\cdot LiI$. In an inert atmosphere glovebox, a J. Young NMR tube was charged with (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (12.8 mg, 0.03 mmol) and dry, ether-free solid $Li^{13}CH_3\cdot LiI$ (7.0 mg, 0.04 mmol). Benzene-d_6 (0.81 mL) was added to give a yellow solution; $Li^{13}CH_3\cdot LiI$ was not soluble in C_6D_6 at room temperature. The reaction mixture was heated for 9 h in an oil bath regulated at 80 °C. At this time the sample was cooled to room temperature and a yellow-green solution with a white precipitate was observed. Analysis by ^1H NMR spectroscopy indicated three compounds were present. Compounds **6**, (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)I (**6-I**), and **5** were observed in roughly a 7:1:12 ratio, respectively.

Alternate Methods for the Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_3)(CH_2CMe_3) (5): Reaction of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl with CH_3MgBr. In an inert atmosphere glovebox, (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (31 mg, 0.08 mmol) was dissolved in diethyl ether (5 mL) and cooled to −35 °C. A 3.17 M ethereal solution of CH_3MgBr (0.04 mL, 0.12 mmol) was diluted in diethyl ether (2 mL) and cooled to −35 °C. The chilled solution of CH_3MgBr was added dropwise to the bright yellow solution of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl. The reaction mixture was stirred for 2 h, over which time it became a darker yellow color. 1,4-Dioxane (2 mL) was added and a white solid precipitated from the yellow solution. The reaction mixture was filtered, and removal of all volatiles followed by drying in vacuo yielded a yellow, oily residue. Analysis of the isolated material by ^1H NMR spectroscopy revealed three compounds were present. Compounds **6**, (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Br (**6-Br**), and **5** were observed in roughly a 2:2:1 ratio respectively.

Alternate Methods for the Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)(CH_3) (5): Reaction of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(Cl)(CH_2CMe_3) with $Mg(CH_3)_2$. In an inert atmosphere glovebox, a J. Young NMR tube was charged with (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (13 mg, 0.03 mmol) and $Mg(CH_3)_2$ (1.4 mg, 0.02 mmol). Benzene-d_6 (0.82 mL) was added, giving a yellow solution. The reaction mixture was heated at 80 °C and was allowed to proceed for 9 h, over which time the solution became more yellow-green in color and a precipitate was observed. The ^1H NMR spectrum indicated a 60:35:5:1 mixture of compounds **6**, **5**, **3**, and (η^5-C_5H_5)(η^5-C_5Me_5)Zr$(CH_3)_2$ respectively.

Alternate Methods for the Synthesis of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_3)(CH_2CMe_3) (5): Reaction of (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl with $Mg(CH_3)_2$−1,4-Dioxane. In an inert atmosphere glovebox, a J. Young NMR tube was charged with (η^5-C_5H_5)(η^5-C_5Me_5)Zr(CH_2CMe_3)Cl (10 mg, 0.02 mmol), $Mg(CH_3)_2$ (1.5 mg, 0.02 mmol), and 1,4-dioxane (5 μL, 0.06 mmol). The addition of benzene-d_6 (0.83 mL) gave a yellow solution. The reaction mixture was heated at 80 °C, and the reaction was allowed to proceed for 9.5 h, over which time the solution became more yellow-green in color and a precipitate was observed. Analysis of the reaction mixture by ^1H NMR spectroscopy indicated clean formation of compound **5**.

2-Ethylbutyric Acid Methyl Ester (8). A 500 mL round-bottom flask was charged with 2-ethylbutyric acid (**7**) (92.4 g, 795 mmol) and methanol (275 mL, 6760 mmol). Concentrated H_2SO_4 (23 mL) was added, and a reflux condenser was attached. The mixture was heated to reflux for 24 h. Methanol was distilled off on a water bath. The residue was diluted with water (500 mL), and the layers were separated. Organics remaining in the aqueous layer were extracted with diethyl ether. The combined organic phases were washed with saturated $NaHCO_3$, water, and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was distilled (137 °C, 1 atm) to produce a clear liquid. Yield: 51.65 g (50%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, OCH_3, 3H), 2.21 (m, $CH(CH_2CH_3)_2$, 1H), 1.56 (m, $CH(CH_2CH_3)_2$, 4H), 0.88 (t, $CH(CH_2CH_3)_2$, 6H, $J = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 176.89, 51.61, 49.19, 25.45, 12.24. DEPT (75 MHz, $CDCl_3$): δ 176.89 (quaternary C), 49.18 (CH), 25.43 (CH_2), 51.58, 12.23 (CH_3).

2,2-Diethylbutyric Acid Methyl Ester (9). A 1 L Schlenk flask with addition funnel was purged with argon and charged with $HN(CHMe_2)_2$ (47.4 mL, 338 mmol). THF (250 mL) was added via cannula and the solution cooled to 0 °C. Butyllithium (211 mL, 338 mmol) was transferred to the addition funnel by cannula and was added to the reaction mixture over 40 min with stirring. The reaction mixture was then cooled to −30 °C, and **8** (40.0 g, 307 mmol) was added slowly by syringe. The yellow solution was stirred for 30 min at this temperature. Ethyl iodide (27.3 mL, 338 mmol) was added at −78 °C. The mixture was stirred at this temperature for 5 h and then at room temperature overnight. The reaction mixture was added to a separatory funnel with diethyl ether and water, and the phases were separated. The aqueous layer was extracted with additional diethyl ether. The combined organic layers were washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting yellow liquid was distilled under full vacuum (30−31 °C, ∼1 mmHg), and a clear liquid was collected in two fractions. Yield: 39.3 g (81%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, OCH_3, 3H), 1.57 (q, $C(CH_2CH_3)_3$, 6H, $J = 7.5$ Hz), 0.75 (t, $C(CH_2CH_3)_3$, 9H, $J = 7.3$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.90, 51.66, 50.32, 26.40, 8.71. DEPT (75 MHz, $CDCl_3$): δ 177.90, 50.32 (quaternary C), 26.40 (CH_2), 51.67, 8.71 (CH_3).

2,2-Diethylbutanol (10). In the glovebox, a 3 L three-neck flask was charged with $LiAlH_4$ (7.19 g, 190 mmol). Outside the glovebox, an addition funnel was attached under a flow of argon. All joints were sealed with Teflon tape and all adaptors secured with wire and rubber bands. The flask was cooled in an ice−NaCl bath, and diethyl ether (750 mL) was added through the addition funnel by cannula. Compound **9** (30.0 g, 190 mmol) was poured into the addition funnel and dissolved in diethyl ether against a strong flow of argon. This solution was added dropwise over 1 h and the temperature maintained at 0 °C. Stirring continued overnight. The reaction was quenched using Fieser conditions: water (8 mL), 15% NaOH (8 g of solution), water (24 mL). The liquids were removed from the sludgy, white precipitate with additional diethyl ether. The phases were separated, and the aqueous layer was washed three times with diethyl ether. The combined organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting cloudy liquid was distilled from $CaSO_4$ under reduced pressure (80−82 °C, 20 mmHg), producing a white liquid. Yield: 22.0 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.34 (d, $C\mathit{H}_2C(CH_2CH_3)_3$, 2H, $J = 3.9$ Hz), 1.30 (br, OH, 1H), 1.22 (q, $CH_2C(C\mathit{H}_2CH_3)_3$, 6H, $J = 7.5$ Hz), 0.77 (t, $CH_2C(CH_2C\mathit{H}_3)_3$, 9H, $J = 7.6$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 65.99, 39.79, 25.26, 7.73. DEPT (75 MHz, $CDCl_3$): δ 39.79 (quaternary C), 65.96, 25.25 (CH_2), 7.72 (CH_3).

(2,2-Diethyl)butyl Mesylate (11). A 250 mL round-bottom flask was charged with **10** (7.07 g, 54.3 mmol) and purged with argon. CH_2Cl_2 (125 mL) was added via cannula. NEt_3 (11.4 mL, 81.7 mmol) was added by syringe, and the mixture was cooled to 0 °C. CH_3SO_2Cl (4.8 mL, 62.0 mmol) was added dropwise. The solution became pale yellow and a precipitate formed. Stirring continued at this temperature for 1 h. For workup, additional CH_2Cl_2 was added and organics were washed with ice water (250 mL), chilled 10% HCl (250 mL), saturated $NaHCO_3$, and saturated NaCl. After drying over Na_2SO_4 the solvent was removed under reduced pressure to yield a thick, yellow liquid that was >95% pure by NMR. Yield: 11.3 g (quantitative). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, $C\mathit{H}_2C(CH_2CH_3)_3$, 2H), 2.30 (s, $C\mathit{H}_3$, 3H), 1.30 (q, $CH_2C(C\mathit{H}_2CH_3)_3$, 6H, $J = 7.5$ Hz), 0.81 (t, $CH_2C(CH_2C\mathit{H}_3)_3$, 9H, $J = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 72.71, 39.13, 37.35, 25.34, 7.58. DEPT (75 MHz, $CDCl_3$): δ 39.13 (quaternary C), 72.69, 25.32 (CH_2), 37.35, 7.59 (CH_3).

2,2-Diethyl-1-iodobutane (12). A 50 mL flask with condenser was charged with **11** (2.91 g, 13.9 mmol) and anhydrous NaI (10.45 g, 69.7 mmol) and was purged with argon. *N*-Methylpyrrolidinone (30 mL) was added via syringe. The reaction mixture was heated to 140 °C for 4 h under argon. The reaction mixture was cooled, and water and pentane were added. The phases were separated, and the aqueous layer was extracted with pentane. The combined organic phases (400 mL) were washed with saturated $Na_2S_2O_3$, twice with saturated $CuSO_4$, and water. After drying over $MgSO_4$, the pentane was removed under reduced pressure. The yellow liquid was purified by column chromatography on silica with hexanes. The product was a clear liquid that was homogeneous by TLC. Yield: 2.40 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.12 (s, $C\mathit{H}_2C(CH_2CH_3)_3$, 2H), 1.30 (q, $CH_2C(C\mathit{H}_2CH_3)_3$, 6H, $J = 7.8$ Hz), 0.76 (t, $CH_2C(CH_2C\mathit{H}_3)_3$, 9H, $J = 7.35$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 38.04, 27.38, 20.25, 8.15. DEPT (75 MHz, $CDCl_3$): δ 38.04 (quaternary C), 27.38, 20.25 (CH_2), 8.14 (CH_3).

Synthesis of $LiCH_2C(CH_2CH_3)_3$ (13) ($LiCH_2CEt_3$). 2,2-Diethyl-1-iodobutane (0.102 g, 0.43 mmol) was weighed into a 25 mL round-bottom flask equipped with a 180° needle valve and was degassed with two freeze−pump−thaw cycles at 77 K on the high-vacuum line. Pentane and then diethyl ether were added by vacuum transfer at −78 °C in a 3:2 ratio, respectively, to give a total solvent volume of 12 mL. (Note: this reaction also worked effectively in 3:1 pentane−diethyl ether solvent.) The apparatus was backfilled with Ar and stirred briefly at room temperature. The Kontes needle valve was replaced with a septum using a positive Ar counterflow. The solution was then cooled to −78 °C, and a 1.7 M solution of *tert*-butyllithium (0.56 mL, 0.95 mmol) was added dropwise using an Ar-flushed syringe. During the addition, formation of a white precipitate was observed. The reaction mixture was stirred at −78 °C for 40 min. The dry ice−acetone bath was removed, and the reaction mixture was allowed to warm to room temperature with stirring for 30 min, after which time a colorless solution was observed. The septum was replaced with a Kontes needle valve, and the solvent was removed. Drying in vacuo yielded a glassy, white solid. In the glovebox the reaction flask was attached to a small swivel frit assembly. On the vacuum line, pentane (12 mL) was vacuum transferred onto the glassy solid at −78 °C. Warming to room temperature and stirring to break up the solids resulted in a colorless solution with a white precipitate. This solution was filtered and the precipitate washed one time with recycled solvent. The solvent was removed to yield a pale yellow, almost colorless, oil, which was dried in vacuo. Yield: 0.045 g (88%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.34 (br q, $CH_2C(C\mathit{H}_2CH_3)_3$ 6H, $J = 7.2$ Hz), 0.90 (t, $CH_2C(CH_2C\mathit{H}_3)_3$, 9H, $J = 7.5$ Hz), −0.71 (br s, $C\mathit{H}_2C(CH_2CH_3)_3$, 2H).

2,2-Dimethyl-3-phenylpropionoic Acid Ethyl Ester (15). A 1 L Schlenk flask with addition funnel was purged with argon and charged with $HN(^iPr)_2$ (66.4 mL, 473 mmol). THF (300 mL) was added via cannula and the solution cooled to 0 °C. Butyllithium (296 mL, 474 mmol) was transferred to the addition funnel by cannula and was added to the reaction mixture over 40 min with stirring. The reaction mixture was then cooled to −30 °C, and 2-methylpropionoic acid ethyl ester (**14**) (50.0 g, 430 mmol) was added slowly by syringe. The yellow solution was stirred for 30 min at this temperature. Benzyl bromide (56.3 mL, 473 mmol) was added at −78 °C. The mixture was stirred at this temperature for 5 h and then at room temperature overnight. The reaction mixture was added to a separatory funnel with diethyl ether and water, and the phases were separated. The aqueous layer was extracted with additional diethyl ether. The combined organic layers were washed with saturated NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting yellow liquid was distilled under full vacuum (55−57 °C, ∼1 mmHg), yielding a faintly yellow liquid. Yield: 74.8 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (m, *m*- and *p*-PhH, 3H), 7.11 (dd, *o*-PhH, 2H, $J =$ 1.65, 7.65 Hz), 4.11 (q, $OC\mathit{H}_2CH_3$, 2H, $J = 7.2$ Hz), 2.85 (s, $C(CH_3)_2C\mathit{H}_2Ph$, 2H), 1.23 (t, $OCH_2C\mathit{H}_3$, 3H, $J = 7.2$ Hz), 1.17 (s, $C(C\mathit{H}_3)_2CH_2Ph$, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 177.54, 138.13, 130.33, 128.09, 126.54, 60.65, 46.59, 43.79, 25.30, 14.53. DEPT (75 MHz, $CDCl_3$): δ 177.54, 138.13, 43.79 (quaternary C), 130.32, 128.10, 126.56 (CH), 60.69, 46.58 (CH_2), 25.30, 14.57 (CH_3).

2,2-Dimethyl-3-phenylpropanol (16). In the glovebox, a 3 L three-neck flask was charged with $LiAlH_4$ (10.41 g, 274 mmol). Outside the glovebox, an addition funnel was attached under a flow of argon. All joints were sealed with Teflon tape and all adaptors secured with wire and rubber bands. The flask was cooled in an ice−NaCl bath, and diethyl ether (850 mL) was added through the addition funnel by cannula. Compound **15** (50.0 g, 242 mmol) was poured into the addition funnel and dissolved in diethyl ether against a strong flow of argon. This solution was added dropwise over 1 h and the temperature maintained at 0 °C. Stirring continued overnight. The reaction was quenched using Fieser conditions: water (11 mL), 15% NaOH (11 g of solution), water (33 mL). The liquids were removed from the sludgy, white precipitate with additional diethyl ether. The phases were separated, and the aqueous layer was washed three times with diethyl ether. The combined organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting cloudy liquid was distilled from $CaSO_4$ under full vacuum (68−72 °C, ∼0.2 mmHg), producing a white liquid that later solidified to a hard white solid. Yield: 35.20 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (m, *m*- and *p*-PhH, 3H), 7.17 (dd, *o*-PhH, 2H, $J = 1.5, 7.35$ Hz), 3.32 (d, $C\mathit{H}_2C(CH_3)_2$-

$\mathrm{CH_2Ph}$, 2H, $J = 5.4$ Hz), 2.58 (s, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 2H), 1.54 (t, O$\mathit{H}$, 1H, $J = 5.4$ Hz), 0.89 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 6H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CDCl_3}$): δ 138.95, 130.68, 128.03, 126.13, 71.41, 44.97, 36.77, 24.35. DEPT (75 MHz, $\mathrm{CDCl_3}$): δ 138.95, 36.77 (quaternary C), 130.68, 128.02, 126.12 (CH), 71.40, 44.98 ($\mathrm{CH_2}$), 24.51 ($\mathrm{CH_3}$).

(2,2-Dimethyl-3-phenyl)propyl Mesylate (17). A 250 mL round-bottom flask was charged with **16** (5.82 g, 35.4 mmol) and purged with argon. $\mathrm{CH_2Cl_2}$ (110 mL) was added via cannula. $\mathrm{NEt_3}$ (7.6 mL, 54.5 mmol) was added by syringe, and the mixture was cooled to 0 °C. $\mathrm{CH_3SO_2Cl}$ (3.2 mL, 41.3 mmol) was added dropwise. The solution became pale yellow and a precipitate formed. The reaction mixture stirred at this temperature for 1 h. For workup, additional $\mathrm{CH_2Cl_2}$ was added and the organics were washed with ice water (250 mL), chilled 10% HCl (250 mL), saturated $\mathrm{NaHCO_3}$, and saturated NaCl. After drying over $\mathrm{Na_2SO_4}$ the solvent was removed under reduced pressure to yield a yellow liquid that was >95% pure by NMR. Yield: 8.50 g (quantitative). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 7.28 (m, *m*- and *p*-PhH, 3H), 7.14 (dd, *o*-PhH, 2H, $J = 2.1$, 7.35 Hz), 3.87 (s, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2CH_2Ph}$, 2H), 3.02 (s, $\mathrm{C}\mathit{H}_3$, 3H), 2.62 (s, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 2H), 0.98 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 6H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CDCl_3}$): δ 137.47, 130.66, 128.26, 126.61, 77.05, 44.81, 37.47, 35.67, 24.39. DEPT (75 MHz, $\mathrm{CDCl_3}$): δ 137.47, 35.67 (quaternary C), 130.65, 128.25, 126.60 (CH), 77.05, 44.79 ($\mathrm{CH_2}$), 37.46, 24.39 ($\mathrm{CH_3}$).

2-Methyl-2-benzyl-1-iodopropane (18). A 50 mL flask with condenser was charged with **17** (1.86 g, 7.67 mmol) and anhydrous NaI (5.75 g, 38.4 mmol) and was purged with argon. *N*-Methylpyrrolidinone (16 mL) was added via syringe. The reaction mixture was heated to 140 °C for 7 h under argon. The reaction mixture was cooled, and water and pentane were added. The phases were separated and the aqueous layer was extracted with pentane. The combined organic phases (250 mL) were washed with saturated $\mathrm{Na_2S_2O_3}$, twice with saturated $\mathrm{CuSO_4}$, and water. After drying over $\mathrm{MgSO_4}$, the pentane was removed under reduced pressure. The yellow liquid was purified by column chromatography on silica with hexanes, and the product was a clear liquid that was homogeneous by TLC. Yield: 1.77 g (84%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 7.25 (br m, *o*-, *m*-, and *p*-PhH, 5H), 3.13 (s, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2CH_2Ph}$, 2H), 2.65 (s, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 2H), 1.04 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 6H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CDCl_3}$): δ 138.36, 130.46, 128.15, 126.50, 46.63, 35.08, 27.44, 24.53. DEPT (75 MHz, $\mathrm{CDCl_3}$): δ 138.46, 35.08 (quaternary C), 130.45, 128.14, 126.49 (CH), 46.62, 24.67 ($\mathrm{CH_2}$), 27.44 ($\mathrm{CH_3}$).

Synthesis of $\mathbf{Li(CH_2C(CH_3)_2CH_2Ph)}$ (19) ($\mathbf{LiCH_2CMe_2CH_2Ph}$). 2-Methyl-2-benzyl-1-iodopropane (0.365 g, 1.33 mmol) was weighed into a 25 mL round-bottom flask equipped with a 180° needle valve and was degassed with two freeze−pump−thaw cycles at 77 K on the high-vacuum line. Pentane and then diethyl ether were added by vacuum transfer at −78 °C in a 3:1 ratio, respectively, to give a total solvent volume of 12 mL. The apparatus was backfilled with Ar and stirred briefly at room temperature. The Kontes needle valve was replaced by a septum using a positive Ar counterflow. The solution was then cooled to −78 °C, and a 1.7 M solution of *tert*-butyllithium (1.80 mL, 2.92 mmol) was added dropwise using an Ar-flushed syringe. A white precipitate was observed immediately following the addition. The reaction mixture was stirred at −78 °C for 35 min. The dry ice−acetone bath was removed, and the reaction mixture was allowed to warm to room temperature with stirring for 45 min, during which time the solution turned yellow. The septum was replaced with a Kontes needle valve, the solvent was removed, and the oily residue was dried in vacuo. In the glovebox the reaction flask was attached to a small swivel frit assembly. On the vacuum line, pentane (12 mL) was vacuum transferred onto the oil at −78 °C. Warming to room temperature and stirring to break up the solids resulted in a yellow solution with a white precipitate. This solution was filtered and the precipitate washed three times with recycled solvent. The solvent was removed, yielding a yellow oil, which was dried in vacuo. (Note: this compound was generally isolated as a diethyl etherate.) Yield: 0.185 g (90%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.05−7.25 (m (partially obscured by $\mathrm{C_6D_6}$), $\mathrm{C_6}\mathit{H}_5$, 5H), 2.55 (s, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 2H), 1.07 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 6H), −1.01 (br s, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2CH_2Ph}$, 2H).

Synthesis of ($\boldsymbol{\eta^5}$-$\mathbf{C_5H_5}$)($\boldsymbol{\eta^5}$-$\mathbf{C_5Me_5}$)$\mathbf{Zr(CH_3)(CH_2C(CH_2CH_3)_3)}$ (20) ($\mathbf{CpCp^*Zr(CH_3)(CH_2CEt_3)}$). In an inert atmosphere glovebox, (η^5-$\mathrm{C_5H_5}$)(η^5-$\mathrm{C_5Me_5}$)$\mathrm{Zr(CH_3)Cl}$ (0.129 g, 0.38 mmol) was added to the 25 mL round-bottom flask equipped with a stir bar containing $\mathrm{LiCH_2CEt_3}$ (0.045 g, 0.38 mmol) and attached to a small swivel frit assembly. On the vacuum line, diethyl ether (12 mL) was vacuum transferred onto the reaction mixture at −78 °C. The apparatus was backfilled with Ar, and the yellow solution was allowed to warm to room temperature over 14 h with stirring. A yellow solution with a white precipitate was observed. The solvent was removed, and the oily residue was dried in vacuo. Pentane (10 mL) was added to the oil by vacuum transfer, and the reaction mixture was stirred briefly at room temperature to break up the solids. The resulting white precipitate was filtered away from the yellow filtrate and washed once with recycled solvent. Removal of all volatiles and drying in vacuo resulted in a yellow-brown oil (0.130 g) that was 59% product **20** as judged by ^{1}H NMR spectroscopy. Repeated attempts to purify this material by crystallization or precipitation from concentrated pentane solutions at −35 °C failed. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 5.89 (s, $\mathrm{C_5}\mathit{H}_5$, 5H), 1.69 (s, $\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$, 15H), 1.43 (m, $\mathrm{CH_2C(C}\mathit{H}_2\mathrm{CH_3)_3}$, 3H, $J = 7.8$ Hz), 1.35 (m, $\mathrm{CH_2C(C}\mathit{H}_2\mathrm{CH_3)_3}$, 3H, $J = 7.8$ Hz), 0.83 (t, $\mathrm{CH_2C(CH_2C}\mathit{H}_3\mathrm{)_3}$, 9H, $J = 7.4$ Hz), −0.13 (d, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_2CH_3)_3}$, 1H, $J = 13.4$ Hz), −0.16 (d, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_2CH_3)_3}$, 1H, $J = 13.4$ Hz), −0.28 (s, $\mathrm{C}\mathit{H}_3$, 3H).

Synthesis of ($\boldsymbol{\eta^5}$-$\mathbf{C_5H_5}$)($\boldsymbol{\eta^5}$-$\mathbf{C_5Me_5}$)$\mathbf{Zr(CH_3)(CH_2CMe_2CH_2Ph)}$ (21) ($\mathbf{CpCp^*Zr(CH_3)(CH_2CMe_2CH_2Ph)}$). In an inert atmosphere glovebox, (η^5-$\mathrm{C_5H_5}$)(η^5-$\mathrm{C_5Me_5}$)$\mathrm{Zr(CH_3)Cl}$ (0.410 g, 1.19 mmol) was added to the 25 mL round-bottom flask equipped with a stir bar containing $\mathrm{LiCH_2CMe_2CH_2Ph}$ (0.185 g, 1.19 mmol) and attached to a small swivel frit assembly. On the vacuum line, diethyl ether (18 mL) was vacuum transferred onto the reaction mixture at −78 °C. The apparatus was backfilled with Ar, and the reaction mixture was allowed to warm to room temperature. After stirring for 36 h a yellow-brown solution with an off-white precipitate was observed. The solvent was removed, and the oily residue was dried for 1 h in vacuo. Pentane (15 mL) was added to the oil by vacuum transfer, and the reaction mixture was stirred briefly at room temperature to break up the solids. The resulting white precipitate was filtered away from the dark brown filtrate and washed once with recycled solvent. Removal of all volatiles and drying in vacuo for 1.5 h at 50 °C resulted in a dark brown oil (0.396 g) that was 71% product **21** as judged by ^{1}H NMR spectroscopy. Repeated attempts to purify this material by crystallization or precipitation from concentrated pentane solutions at −35 °C have failed. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.15−7.25 (m (partially obscured by $\mathrm{C_6D_6}$), $\mathrm{C_6}\mathit{H}_5$, 5H), 5.82 (s, $\mathrm{C_5}\mathit{H}_5$, 5H), 2.58 (d, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 1H, $J = 12.6$ Hz), 2.54 (d, $\mathrm{CH_2C(CH_3)_2C}\mathit{H}_2\mathrm{Ph}$, 1H, $J = 12.1$ Hz), 1.64 (s, $\mathrm{C_5(C}\mathit{H}_3\mathrm{)_5}$, 15H), 1.15 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 3H), 0.92 (s, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)_2CH_2Ph}$, 3H), 0.44 (d, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2CH_2Ph}$, 1H, $J = 12.0$ Hz), −0.27 (s, $\mathrm{C}\mathit{H}_3$, 3H), −0.33 (d, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2CH_2Ph}$, 1H, $J = 12.7$ Hz).

Synthesis of ($\boldsymbol{\eta^5}$-$\mathbf{C_5H_5}$)$_\mathbf{2}$$\mathbf{Zr(CH_3)(CH_2C(CH_2CH_3)_3)}$ (22) ($\mathbf{Cp_2Zr(CH_3)(CH_2CEt_3)}$). 2,2-Diethyl-1-iodobutane (0.274 g, 1.14 mmol) was weighed into a 25 mL round-bottom flask equipped with a 180 ° needle valve and was degassed at 77 K on the high-vacuum line. Pentane (8 to 10 mL) and then diethyl ether (2 to 4 mL) were added by vacuum transfer at −78 °C. The apparatus was backfilled with Ar and stirred briefly at room temperature. The Kontes needle valve was replaced by a septum using a positive Ar counterflow. The solution was then cooled to −78 °C, and a 1.7 M solution of *tert*-butyllithium (1.50 mL, 2.51 mmol) was added dropwise using an Ar-flushed syringe. A white precipitate was observed in the colorless solution before the addition was completed. The reaction mixture was stirred at −78 °C for 30 min. The dry ice−acetone bath was removed and the reaction mixture stirred at room temperature for 30 min. The septum was replaced with a Kontes needle valve, and the solvent was removed. Drying in vacuo yielded a glassy, white solid. In an inert atmosphere glovebox, $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$ (0.310 g, 1.14 mmol) was added to the flask containing this solid, which was then attached to a small swivel frit assembly. On the vacuum line, diethyl ether (13 mL) was vacuum transferred onto the solids at −78 °C and the apparatus was backfilled with Ar. The reaction mixture was allowed to warm to room temperature over 20 h with stirring. At this time a brown-green solution with a white precipitate was observed. The solvent was removed, and the resulting yellow-brown oil was dried at 30 °C in vacuo. Pentane (10 mL) was vacuum transferred onto the oil at −78 °C. Stirring at room temperature gave a yellow-brown solution with an off-white precipitate. Filtration followed by removal of solvent yielded a yellow-brown oil, which was dried at 30 °C in vacuo. In the glovebox this oil was dissolved in pentane, giving a yellow solution, which was filtered via pipet through Celite and concentrated to less than 10 mL. The solution was cooled to −35 °C to recrystallize the desired product; pale yellow crystalline material suitable for X-ray diffraction was isolated and dried in vacuo. Yield: 0.128 g (32%). Anal. Calcd. for $C_{19}H_{30}Zr$: C, 65.26; H, 8.65. Found: C, 64.50, 64.39; H, 8.65, 8.42. ^{1}H NMR (500 MHz, C_6D_6): δ 5.78 (s, C_5H_5, 10H), 1.29 (q, $CH_2C(CH_2CH_3)_3$, 6H, $J = 7.4$ Hz), 0.80 (t, $CH_2C(CH_2CH_3)_3$, 9H, $J = 7.4$ Hz), 0.15 (s, $CH_2C(CH_2CH_3)_3$, 2H), −0.015 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 110.3 (C_5H_5), 76.8 (Zr−$CH_2C(CH_2CH_3)_3$), 46.5 ($CH_2C(CH_2CH_3)_3$), 33.0 ($CH_2C(CH_2CH_3)_3$), 25.9 (Zr−CH_3), 9.3 ($CH_2C(CH_2CH_3)_3$).

Synthesis of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)(CH_2C(CH_3)_2CH_2Ph)$ (23) ($Cp_2Zr(CH_3)(CH_2CMe_2CH_2Ph)$). 2-Methyl-2-benzyl-1-iodopropane (0.448 g, 1.63 mmol) was weighed into a 25 mL round-bottom flask equipped with a 180° needle valve and was degassed at 77 K on the high-vacuum line. Pentane (8 to 10 mL) and then diethyl ether (2 to 4 mL) were added by vacuum transfer at −78 °C. The apparatus was backfilled with Ar and stirred briefly at room temperature. The Kontes needle valve was replaced by a septum using a positive Ar counterflow. The solution was then cooled to −78 °C, and a 1.7 M solution of *tert*-butyllithium (2.15 mL, 3.60 mmol) was added dropwise using an Ar-flushed syringe. A white precipitate was observed in the colorless solution before the addition was completed. The reaction mixture was stirred at −78 °C for 30 min. The dry ice−acetone bath was removed and the reaction mixture stirred at room temperature for 30 min. The septum was replaced with a Kontes needle valve, and the solvent was removed. Drying in vacuo yielded a bright yellow, oily residue. In an inert atmosphere glovebox, $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$ (0.445 g, 1.14 mmol) was added to the flask containing this solid, and it was attached to a small swivel frit assembly. On the vacuum line, diethyl ether (13 mL) was vacuum transferred onto the solids at −78 °C, and the apparatus was backfilled with Ar. The reaction mixture was allowed to warm to room temperature over 19 h with stirring. At this time a yellow-brown solution with a white precipitate was observed. The solvent was removed, and the resulting brown oil was dried at 45 °C in vacuo. Pentane (10 mL) was vacuum transferred onto the oil at −78 °C. Stirring at room temperature gave a yellow-brown solution with an off-white precipitate. Filtration followed by removal of solvent yielded a brown oil, which was dried at 30 °C in vacuo. In the glovebox this oil was dissolved in pentane, giving a yellow-brown solution, which was filtered via pipet through Celite and concentrated to less than 10 mL. The solution was cooled to −35 °C to recrystallize the desired product as brown pellets, which were isolated and dried in vacuo. Yield: 0.208 g (33%). Anal. Calcd. for $C_{22}H_{28}Zr$: C, 68.87; H, 7.35. Found: C, 68.56, 68.62; H, 7.26, 7.28. ^{1}H NMR (300 MHz, C_6D_6): δ 7.16−7.25 (m (partially obscured by C_6D_6), C_6H_5, 5H), 5.73 (s, C_5H_5, 10H), 2.49 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), 0.98 (s, $CH_2C(CH_3)_2CH_2Ph$, 6H), 0.45 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), −0.043 (s, CH_3, 3H). ^{1}H NMR (500 MHz, C_7D_8): δ 7.10−7.20 (m (partially obscured by C_7D_8), C_6H_5, 5H), 5.73 (s, C_5H_5, 10H), 2.43 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), 0.94 (s, $CH_2C(CH_3)_2CH_2Ph$, 6H), 0.41 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), −0.12 (s, CH_3, 3H). ^{1}H NMR (500 MHz, C_7D_8, 193 K): δ 7.15−7.25 (m (partially obscured by C_7D_8), C_6H_5, 5H), 5.63 (s, C_5H_5, 10H), 2.49 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), 1.00 (s, $CH_2C(CH_3)_2CH_2Ph$, 6H), 0.40 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), 0.024 (s, CH_3, 3H). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.24 (t, *m*-C_6H_5, 2H, $J = 7.0$ Hz), 7.17 (t, *p*-C_6H_5, 1H, $J = 7.3$ Hz), 7.08 (d, *o*-C_6H_5, 2H, $J = 7.25$ Hz), 6.08 (s, C_5H_5, 10H), 2.40 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), 0.89 (s, $CH_2C(CH_3)_2CH_2Ph$, 6H), 0.37 (s, $CH_2C(CH_3)_2CH_2Ph$, 2H), −0.31 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 141.2 (*i*-C_6H_5), 131.2 (*m*-C_6H_5), 127.8 (*o*-C_6H_5), 126.0 (*p*-C_6H_5), 110.6 (C_5H_5), 75.6 (Zr−$CH_2C(CH_3)_2CH_2Ph$), 55.0 ($CH_2C(CH_3)_2CH_2Ph$), 41.4 ($CH_2C(CH_3)_2CH_2Ph$), 31.8 ($CH_2C(CH_3)_2CH_2Ph$), 27.6 (Zr-CH_3). DEPT (75 MHz, CD_2Cl_2): δ 141.2, 41.4 (quaternary C), 131.2, 127.8, 126.0, 110.6 (CH), 75.6, 55.0 (CH_2), 31.8, 27.6 (CH_3).

X-ray Crystal Data: General Procedure. Crystals grown from pentane (**1**, **2**, and **22**) at −35 °C were isolated and dried in vacuo, then transferred to a microscope slide coated with Paratone N oil. Crystals grown from Et_2O−petroleum ether (**6**) at −35 °C were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker Smart 1000 CCD diffractometer. The structures were solved by direct (**1**, **2**, **6**) or Patterson methods (**22**) (SHELXTL-97, Sheldrick, 1990) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Some details regarding refined data and cell parameters are available in Table 2. Selected bond distances and angles are supplied in Tables 1 and 3.

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Supporting Information Available: Tables of bond lengths, angles, and anisotropic displacement parameters for **1**, **2**, **6**, and **22**. X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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