

Dynamic NMR Studies of Cationic Bis(2-phenylindenyl)zirconium Pyridyl Complexes: Evidence for *syn* Conformers in Solution

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The conformationally dynamic unbridged metallocene (2-PhInd)₂ZrMe₂ (**1**) was activated with trispentafluorophenylborane (B(C₆F₅)₃, **B2**) or trityl tetrakis(pentafluorophenyl)borate (“trityl borate”, [Ph₃C⁺][B(C₆F₅)₄[−]], **B4**) to generate the ion pair [(2-PhInd)₂ZrMe⁺][MeB(C₆F₅)₃[−]] (**2a**) or [(2-PhInd)₂ZrMe⁺][B(C₆F₅)₄[−]] (**2b**), respectively. Activation parameters for ion-pair separation were determined by line-shape analysis (**2a**: $\Delta H_{\text{ips}}^{\ddagger} = 20 \pm 1$ kcal/mol, $\Delta S_{\text{ips}}^{\ddagger} = 17 \pm 4$ eu; **2b**: $\Delta H_{\text{ips}}^{\ddagger} = 15 \pm 2$ kcal/mol, $\Delta S_{\text{ips}}^{\ddagger} = 13 \pm 7$ eu). For **2a**, a much slower B(C₆F₅)₃ dissociation–reassociation process was also observed ($\Delta G_{83^{\circ}\text{C}}^{\ddagger} = 18.9 \pm 0.1$ kcal/mol). Both **2a** and **2b** were treated with a series of *o*-substituted pyridines, and the behavior of the resulting zirconocenium-pyridyl complexes (**3a–8b**) was studied by ¹H, ¹³C, and ¹⁹F NMR over the temperature range −100 to 100 °C. Below room temperature, ¹H NMR NOESY spectra revealed signals characteristic of a C_s-symmetric *syn* conformation.

Introduction

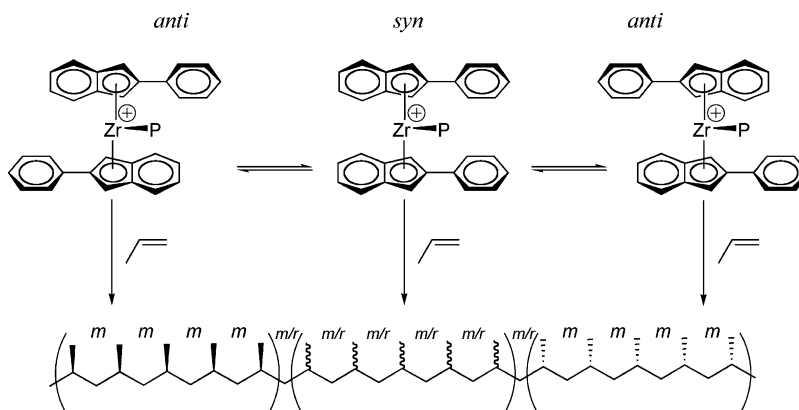
Conformationally dynamic group 4 bis(2-aryindenyl) are an intriguing class of olefin polymerization catalysts that generate polypropylenes with stereosequence distributions ranging from rigid isotactic to amorphous atactic to stereoblock elastomeric plastics depending on the experimental conditions.^{1–3} For the neutral precatalyst (2-PhInd)₂ZrCl₂, X-ray crystallography and theoretical studies indicate that the C₂-symmetric *anti* and C_s-symmetric *syn* conformers represent low-energy conformations, with the *anti* conformer slightly more stable. The *anti* conformation becomes considerably more stable as the steric bulk on the aryl substituent increases.^{1,4–6} We had proposed that the temperature and monomer concentration dependence of the stereospecificity of these catalysts is due to a competition between monomer insertion and conformational isomerization of the metallocene and proposed that the interconversion between enantiomeric *anti* conformers and at least one *syn* conformer was responsible for the generation of isotactic and atactic stereosequences (Scheme 1). Indirect support for this proposal was provided by the polymerization behavior of the MAO-activated silyl-bridged *rac* (*anti*) and *meso* (*syn*) analogues, which produce isotactic and atactic polypropylene, respectively.^{7,8} Recently, Busico has proposed, on

the basis of microstructural analysis of these polymers, that the achiral *syn* isomer can be disregarded as a source of the atactic stereosequences and that the generation of isotactic and atactic stereosequences is the results of the interconversion of chiral *anti* isomers at a rate competitive with propylene insertion. According to this proposal, short atactic stereosequences are generated by kinetic states where the rate of conformational isomerization is faster than propylene insertion.^{9–11}

To provide more evidence for the accessible conformations, direct observation of the conformational states of the active species would be highly informative; however, this has proven extremely challenging. Activation of the dichloro or dialkyl metallocene precursors in the presence of olefin generates very small concentrations of the cationic catalyst that have thus far been observed by NMR only in a few specific cases.^{12–17} Additionally, the lifetime of the polymer-bound complex is short, with the complex undergoing rapid chain transfer and β-hydride elimination. For this reason, much of our understanding of the conformational dynamics of 2-aryindenyl metallocenes stems from studies of the rotation rates of the neutral precatalysts in solution, which have been esti-

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Scheme 1. Expected Low-Energy Conformations of [(2-PhInd)₂Zr(polymeryl)⁺] Based on Calculated Low-Energy Conformations of the Neutral Catalyst Precursor (2-PhInd)₂ZrCl₂^a

^a For simplicity, the counteranion has not been depicted here.

mated previously from ¹H NMR data using line-shape analysis and on-resonance spin–lattice relaxation in the rotating frame (*T*_{1ρ}).^{18–21} These studies reveal rapid rotation of the indenyl ligands at and below room temperature for **1** and its dichloro analogue, (2-PhInd)₂ZrCl₂, with the substitution pattern of the ligands playing a major role in determining the rotation rate. For example, the rate constant *k_r* for the isomerization of (2-PhInd)₂ZrMe₂ **1** was 14 000 ± 4500 s^{−1} at −121 °C, the rate constant for the dibenzyl analogue, (2-PhInd)₂ZrBn₂, approaches this value only at 25 °C (*k_r* = 24 000 ± 4300 s^{−1}).¹⁸ Modifying the indenyl framework has a similar if less pronounced effect (*k_r* for (2-(3',5'-di-*tert*-butyl)PhInd)₂ZrBn₂ at 89 °C = 11 700 ± 3000 s^{−1}).

For (2-PhInd)₂ZrBn₂,²¹ (2-phenylcyclopenta[1]phenanthrene)₂ZrBn₂,¹⁹ and (2-aminoindenyl)₂ZrCl₂ complexes,²² dynamic NMR studies implicate the rapid interconversion of two enantiomeric *anti* conformers at low temperatures; these studies provided no evidence for the achiral *syn* isomer in solution. This is consistent with calculations that imply that the *anti* conformers are slightly lower in energy; however for the dibenzyl derivatives, it may also be a consequence of the preference of the two benzyl groups to adopt an *anti* conformation, thereby stabilizing the *anti* configuration of the two arylindene ligands. The steric demands of the two benzyl groups might also interfere with π -stacking of the phenyl ligands,²³ which was proposed to play a significant role in stabilizing the *syn* conformer.^{5,6} In any case, the results of the dynamic NMR studies for the neutral metallocenes imply that the conformational dynamics are much too fast to be competitive with reasonable estimates for the monomer insertion rates (approximately 10–100 insertions s^{−1}).^{2,9}

It is important to emphasize that the neutral catalyst precursor (**1**) and the actively polymerizing cationic

species differ significantly both structurally and electronically, and their conformational dynamics cannot be assumed to be the same. The catalyst precursor is neutral and relatively sterically unhindered. The active catalyst is cationic, ligated by the growing polymer chain, and associated with a counteranion; the latter two features are likely to influence the catalyst's conformational dynamics. In fact, Busico had proposed that the close association of B(C₆F₅)₄[−] anions in nonpolar solvents leads to the stabilization of chiral *anti* conformations (the “locked-rac” hypothesis), which are responsible for the generation of long isotactic sequences in these metallocenes.⁹ Thus, it is clear that a better understanding of the accessible conformations requires an understanding of the interplay between ion-pairing dynamics^{24–30} and conformational dynamics.

In this work, we sought to examine cationic 2-arylindene metallocenes that might provide more appropriate models for active catalysts; in particular we report NMR investigations of a series of 2-arylindene zirconocene methyl cations (**2a,b**) and cationic zirconocenium-pyridyl complexes (**3a–8b**, Scheme 2). The pyridyl complexes are generated by activation of **1** with B(C₆F₅)₃ or [Ph₃C⁺][B(C₆F₅)₄[−]] and subsequent reaction with *o*-substituted pyridines, eliminating methane.³¹ They approximate an actively polymerizing zirconocene catalyst in several key aspects: the complexes have been activated by typical polymerization cocatalysts, possess cationic metal centers, and have ligands that bring steric bulk proximate to the metal center similar to that of a growing polymer chain (Scheme 3). We here describe a series of variable-temperature one- and two-dimensional ¹H, ¹³C, and ¹⁹F NMR experiments carried out in order to estimate the activation parameters for

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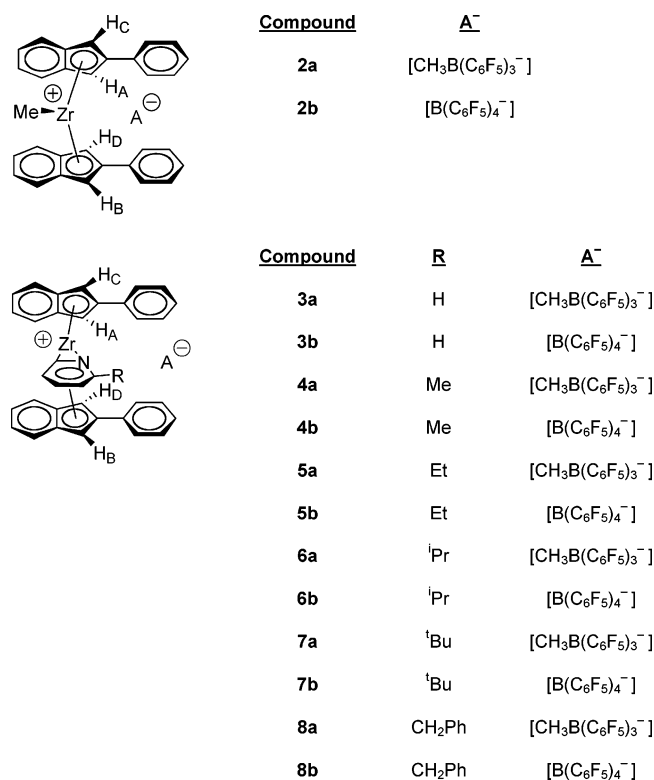
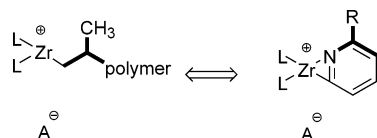
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Scheme 2. Bis(2-phenylindenyl)zirconocene Complexes Studied**Scheme 3. Steric and Electronic Similarities between the Pyridyl Model Complexes and an Actively Polymerizing Zirconocene Catalyst**

the relevant processes of ion-pair separation and dissociation–reassociation for catalysts **2a** and **2b** and studies that reveal the presence of achiral *syn* conformations of zirconocenium-pyridyl complexes in solution.

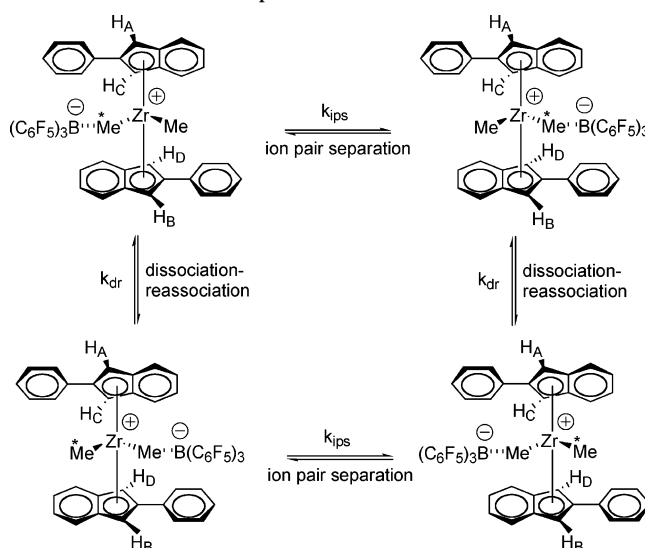
Results and Discussion

Variable-Temperature Behavior of **1**, **2a**, and **2b**.

The unbridged metallocene **1** was prepared by a slight modification of the literature procedure.¹ Treatment of **1** with B(C₆F₅)₃ (**B2**) or [Ph₃C⁺][B(C₆F₅)₄]⁻ (**B4**) at room temperature cleanly generated [(2-PhInd)₂ZrMe⁺][MeB(C₆F₅)₃]⁻ (**2a**) or [(2-PhInd)₂ZrMe⁺][B(C₆F₅)₄]⁻ (**2b**), respectively, within minutes as determined by ¹H and ¹³C NMR spectroscopy in C₆D₅Cl.

The dynamic behavior of the neutral metallocene **1** was evaluated over the temperature range –40 to 100 °C in 10 °C increments and compared to that of the cation–anion pairs **2a** and **2b**. In this temperature range, the ¹H NMR spectrum of **1** exhibits a singlet (4H) at ~6.0 ppm for the cyclopentadienyl (Cp) protons and a singlet (3H) at ~–1.0 ppm for the Zr–CH₃ protons. These observations are consistent with the known rapid rotation of the indenyl ligands in this temperature range.¹⁸

In *d*₈-toluene at 100 °C, the ¹H NMR spectrum of **2a** exhibits one singlet for the cyclopentadienyl protons at

Scheme 4. Intramolecular B(C₆F₅)₃ (*k_{dr}*) and [MeB(C₆F₅)₃]⁻ (*k_{ips}*) Exchange Processes in **2a**

6.12 ppm and a singlet for the Zr–CH₃ protons at –0.30 ppm. As the temperature is decreased, the cyclopentadienyl resonances broaden and decoalesce. At –40 °C, complex **2a** shows two singlets arising from the cyclopentadienyl protons (δ = 5.94 ppm, 5.65 ppm, 2H each), a sharp singlet from the Zr–CH₃ protons (δ = –0.29 ppm), and a quadrupolar-broadened singlet from the methyl group bridging the zirconocenium cation and the borate anion (δ = –0.58 ppm), consistent with a zirconium-bound CH₃B(C₆F₅)₃⁻. A small singlet from CH₃B(C₆F₅)₃⁻ (δ = 1.35 ppm) was also observed. These observations indicate the occurrence of one or more dynamic processes, which we attribute to ion-pair dynamics coupled with rotation of the indenyl ligands in analogy with the work of Marks on related metallocenes.^{28,32–35}

The variable-temperature ¹H NMR spectra of **2a** are most consistent with rapid ligand rotation coupled to two ion-pair exchange processes: (1) an ion-pair symmetrization process, characterized by the rate constant *k_{ips}* in which the CH₃B(C₆F₅)₃⁻ anion reversibly associates at the two diastereotopic coordination sites, and (2) the reversible association of B(C₆F₅)₃ to the two Zr–CH₃ groups, characterized by the rate constant *k_{dr}* (Scheme 4).³³ The first process is characterized by exchange of cyclopentadienyl protons H_A and H_B and of H_C and H_D (Scheme 2). Reversible association of B(C₆F₅)₃ exchanges not only the cyclopentadienyl protons but also the two Zr–CH₃ protons.

The rate constants and activation energies of ion-pair separation and MeB(C₆F₅)₃⁻ dissociation–reassociation were determined by line-shape analysis of the spectra (Table 1). The enthalpy and entropy of activation for ion-pair separation were found by least-squares fitting of an Eyring plot to be $\Delta H^\ddagger_{\text{ips}} = 20 \pm 1$ kcal/mol and $\Delta S^\ddagger_{\text{ips}} = 17 \pm 4$ eu. The rate of ion-pair separation was

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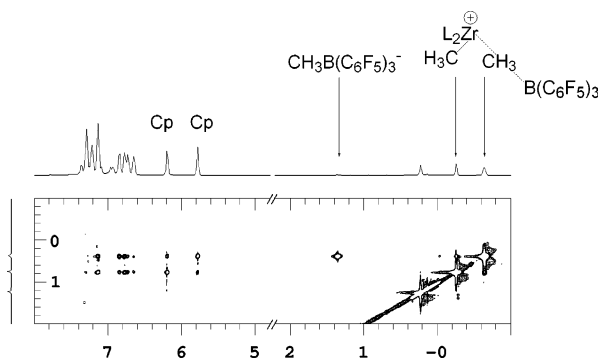


Figure 1. Room-temperature ^1H - ^1H NOESY spectrum for **2a** in $\text{C}_6\text{D}_5\text{Cl}$.

Table 1. Kinetic Data for Ion-Pair Reorganization Processes of **2a in d_8 -Toluene**

T ($^\circ\text{C}$)	k_{ips} (s^{-1})	$\Delta G^\ddagger_{\text{ips}}$ (kcal/mol)	k_{dr} (s^{-1})	$\Delta G^\ddagger_{\text{dr}}$ (kcal/mol)
0 ± 0.5	6 ± 1	15.0 ± 0.1		
10	20 ± 1	14.9		
24	80 ± 4	14.8		
34	300 ± 14	14.5		
44	900 ± 50	14.3		
55	$3,000 \pm 150$	14.0		
64	$8,600 \pm 430$	13.7	24 ± 1	17.8 ± 0.1
73	$18,000 \pm 900$	13.6	46 ± 2	18.4
83	$27,000 \pm 1,400$	13.7	78 ± 4	18.9
98	$68,000 \pm 3,400$	13.7	160 ± 8	19.8

much faster than the rate of $\text{B}(\text{C}_6\text{F}_5)_3$ dissociation, but the temperature range we could access with these experiments precluded a reliable estimation of the activation parameters for reversible association of $\text{B}(\text{C}_6\text{F}_5)_3$. Both processes occurred more rapidly ($k_{\text{ips}, T=83^\circ\text{C}} = 27\,000\text{ s}^{-1}$, $\Delta G^\ddagger_{\text{ips}, T=83^\circ\text{C}} = 13.7\text{ kcal/mol}$; $k_{\text{dr}, T=83^\circ\text{C}} = 78\text{ s}^{-1}$, $\Delta G^\ddagger_{\text{dr}, T=83^\circ\text{C}} = 18.9\text{ kcal/mol}$) than those observed in the compound $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}^+][\text{MeB}(\text{C}_6\text{F}_5)_3^-]$, for which Marks calculated $k_{\text{ips}} = 30\text{ s}^{-1}$ and $k_{\text{dr}} = 4\text{ s}^{-1}$ at 80°C with $\Delta H^\ddagger_{\text{ips}} = 24 \pm 1\text{ kcal/mol}$ and $\Delta S^\ddagger_{\text{ips}} = 17 \pm 2\text{ eu}$ ($\Delta G^\ddagger_{\text{ips}, T=80^\circ\text{C}} = 18.3\text{ kcal/mol}$, $\Delta G^\ddagger_{\text{dr}, T=80^\circ\text{C}} = 19.7\text{ kcal/mol}$).³³ Siedle and Newmark reported similar dynamics for $[(\text{Ind})_2\text{ZrMe}^+][\text{MeB}(\text{C}_6\text{F}_5)_3^-]$ with $\Delta G^\ddagger_{\text{ips}} = 15.8\text{ kcal/mol}$ and $\Delta G^\ddagger_{\text{dr}} = 18.1\text{ kcal/mol}$.³⁶

Further evidence for ion-pair separation was obtained from the low-temperature (-40°C) NOESY spectrum of complex **2a** (Figure 1) in $\text{C}_6\text{D}_5\text{Cl}$. This spectrum reveals a cross-peak between the Zr-CH_3 resonance at $\delta = -0.58\text{ ppm}$ and the free $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ resonance at 1.35 ppm , consistent with exchange between free and bound $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$. Moreover, the cross-peaks between both cyclopentadienyl protons and both the $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ resonances and the Zr-CH_3 resonances indicate that rotation of the indenyl ligands remains rapid at -40°C .

The room-temperature spectrum of the ion pair **2b** in a 1:1 mixture of d_5 -chlorobenzene and d_8 -toluene shows one cyclopentadienyl singlet ($\delta = 6.01\text{ ppm}$) and one Zr-Me singlet ($\delta = -0.32\text{ ppm}$). Below -30°C , the cyclopentadienyl resonance decoalesces into two singlets ($T = -50^\circ\text{C}$: $\delta = 6.15, 5.66\text{ ppm}$). Line-shape analysis was used to determine the activation energies of this phenomenon (Table 2). The enthalpy and entropy of activation were determined to be $\Delta H^\ddagger_{\text{ips}} = 15 \pm 2\text{ kcal/}$

Table 2. Kinetic Data for Ion-Pair Reorganization Processes of **2b in d_8 -Toluene/ d_5 -Chlorobenzene**

T ($^\circ\text{C}$)	k (s^{-1})	$\Delta G^\ddagger$ (kcal/mol)
-58 ± 0.5	5 ± 1	11.81 ± 0.07
-48	16 ± 1	11.81 ± 0.04
-39	63 ± 3	11.69 ± 0.03
-29	360 ± 60	11.34 ± 0.09
-19	970 ± 250	11.31 ± 0.13
0	7200 ± 2200	11.13 ± 0.17
20	$31\,000 \pm 14\,000$	11.11 ± 0.25

mol and $\Delta S^\ddagger_{\text{ips}} = 13 \pm 7\text{ eu}$. The observed dynamic behavior is consistent with the reversible coordination of either the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion or a solvent molecule.^{37,38} Variable-temperature ^{19}F NMR studies of **2b** in chlorobenzene show slight broadening of the *para*-fluoro resonance ($\delta = -162.5\text{ ppm}$) upon cooling from room temperature to -40°C , which is suggestive but not definitive evidence of reversible association of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion. The lower activation barriers for the ion-pair dynamics for the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion are in agreement with previous observations that $\text{B}(\text{C}_6\text{F}_5)_4^-$ coordinates more weakly than the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion to zirconocene cations. These observations are also consistent with our³⁹ and others'¹⁷ observations that catalysts derived from the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anions exhibit much lower activities in olefin polymerization. Moreover, NMR analysis of metallocene cations **2a** and **2b** provides no evidence that the association of the anions with the $(2\text{-PhInd})_2\text{ZrMe}^+$ cations leads to locked conformations at temperatures above -40°C .

Synthesis of Zirconocenium-Pyridyl Complexes.

While the zirconocenium methyl cations provide good models for the initiating species in olefin polymerization, they are not good models for the catalytic species responsible for propagation, as the growing polymer chain is likely to be important for its influence both on stereodifferentiation of monomer insertion^{40–43} and on the ligand rotation dynamics.¹⁸ As we had previously observed that the nature of the zirconium-alkyls have a significant influence on the rotation dynamics of the indenyl ligands, we sought more sterically hindered cations that might be more representative of a steric environment featuring a growing polymer chain. For this reason, we were attracted to the work of Jordan, who demonstrated that pyridines react rapidly with zirconocene cations to provide stable η^2 -coordinated pyridine adducts.³¹

At room temperature, the reaction of **2a** or **2b** with a variety of *ortho*-substituted pyridines in $\text{C}_6\text{D}_5\text{Cl}$ rapidly generates methane and $[(2\text{-PhInd})_2\text{Zr}(2\text{-R-pyridyl})^+][\text{MeB}(\text{C}_6\text{F}_5)_3^-]$ or $[(2\text{-PhInd})_2\text{Zr}(2\text{-R-pyridyl})^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$, respectively, for $\text{R} = \text{H}, \text{Me}, \text{Et}, \text{iPr}, \text{Bn}, \text{tBu}$.⁴⁴

For **2a**, coordination of 2-isopropylpyridine is rapid at room temperature, as evidenced by the immediate

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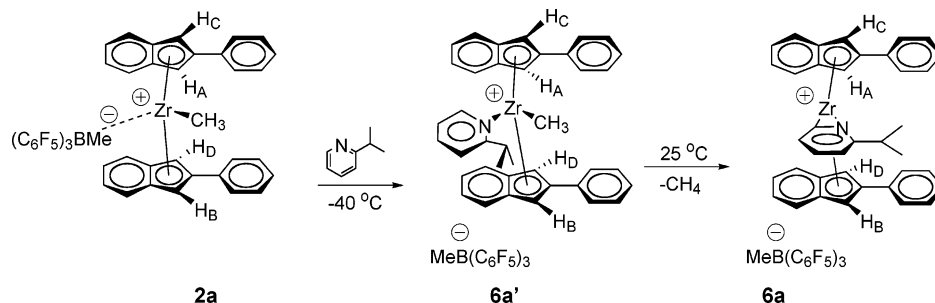
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Scheme 5. Proposed Reaction Observed on Addition of *o*-Isopropylpyridine to 2a

appearance of a Zr-CH₃ singlet at 0.18 ppm, two cyclopentadienyl singlets at 6.20 and 5.68 ppm, a broad singlet at 8.40 ppm due to the *ortho*-proton of the zirconium-bound pyridine, and a resonance (d, 6H) for the isopropyl methyl groups at 0.73 ppm. At room temperature, the subsequent elimination of methane (δ = 0.10 ppm) could be monitored by ¹H NMR over approximately 30 min to give the η^2 -coordinated 2-isopropylpyridyl adduct characterized by two cyclopentadienyl resonances at 6.02 and 5.82 ppm and a resonance (d, 6H) for the isopropyl methyl groups at 0.81 ppm (Scheme 5).

Variable-Temperature Behavior of Zirconocenium-Pyridyl Complexes. The temperature-dependent behavior of the pyridyl complexes **3a–8b** was explored by ¹H NMR spectroscopy between –40 and 100 °C in C₆D₅Cl. At 100 °C, the spectra of the protio-, methyl-, ethyl-, isopropyl-, *tert*-butyl-, and benzyl-pyridyl complexes each exhibit two cyclopentadienyl proton singlets at roughly 6 and 5.8 ppm. Below 100 °C, the two cyclopentadienyl resonances of **3a–8b** exhibit striking asymmetric temperature-dependent chemical shifts: the upfield cyclopentadienyl resonance moves slightly downfield, whereas the downfield cyclopentadienyl resonance moves significantly upfield (e.g., Figure 2). The temperature at which the cyclopentadienyl proton resonances cross one another follows a steric trend, specifically **3a,b** (50–60 °C), **4a,b** (20 °C), **5a,b** (0 °C), **6a,b** (–10 °C), and **7a,b** and **8a,b** (do not overlap as low as –40 °C). At low temperature (between –30 and –40 °C), the methyl- and isopropyl-pyridyl complexes undergo noticeably asymmetric broadening of their upfield cyclopentadienyl signals, while their down-

field cyclopentadienyl signals remain sharp. These observations suggest the electronic environments of the cyclopentadienyl protons differ markedly as the temperature is decreased to –40 °C.

Variable-temperature (–40 to –90 °C) ¹H NMR spectra of the methylpyridine complex **4a** in CDCl₂F⁴⁵ yield similar temperature-dependent chemical shifts for the cyclopentadienyl resonances, but the temperature at which the cyclopentadienyl resonances cross over is lower for **4a** in CDCl₂F (–40 °C) than in chlorobenzene (20 °C). Thus, the crossover temperature is sensitive not only to the steric demands of the substituent on the pyridine ligand but also to the nature of the solvent.²⁸

The observation of two cyclopentadienyl resonances in the low-temperature spectra of the pyridine complexes **3a–8b** and the observation of a single resonance for the isopropyl methyl groups for **6a,b** at all temperatures suggests either that rotation of the phenylindenyl ligands is rapid (time-averaged *C_s* symmetry) or that only one *C_s*-symmetric *syn* conformer predominates at low temperature.

To provide further information about the conformational behavior of these cationic pyridyl complexes, a series of variable-temperature 2D ¹H/¹H NOESY experiments were performed (Figure 3). The room-temperature NOESY spectrum of the isopropylpyridyl complex **6a** in *d*₅-chlorobenzene shows a correlation of the isopropyl CH₃ proton resonance to both cyclopentadienyl proton resonances. No correlation is seen between the cyclopentadienyl resonances and the isopropyl CH proton. These observations are most consistent with rapid phenylindenyl ligand rotation at room temperature. In contrast, the NOESY spectrum of **6a** at –35 °C shows strong correlation between the isopropyl CH₃ protons and only the sharper downfield cyclopentadienyl resonance. A weaker correlation is also seen between the downfield cyclopentadienyl resonance and the isopropyl CH proton at 2.15 ppm.⁴⁶ Thus, the correlation

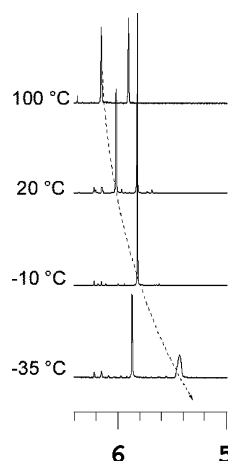


Figure 2. Variable-temperature ¹H NMR showing the cyclopentadienyl resonances for compound **6a** between –35 and 100 °C in C₆D₅Cl.

(44) Pyridine-B(C₆F₅)₃ adducts are also generated in trace amounts. Interestingly, the borane adducts of the ethyl-, isopropyl-, and benzylpyridines exhibit restricted rotation; the ethyl CH₂ resonance is a diastereotopic doublet of multiplets (2.67 and 62.80 ppm), the isopropyl CH₃ resonances are a doublet of doublets (60.13 and 61.04 ppm), and the benzyl CH₂ resonance is a doublet of doublets (64.15 and 64.45 ppm). Such restricted rotation is not observed for the zirconocenium-pyridyl complexes.

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(46) It is possible that the breadth of the upfield cyclopentadienyl resonance might cause similar broadening in the NOE cross-peak such that a correlation may not be observed even if both cyclopentadienyl resonances experience correlation with the isopropyl methyl resonance. However, the broad upfield cyclopentadienyl resonance exhibits correlation to other resonances with a strength comparable to the downfield cyclopentadienyl resonance; for example, both cyclopentadienyl proton resonances correlate to a signal at 7.0 ppm (the proton of the phenyl protons nearest in space to the cyclopentadienyl protons).

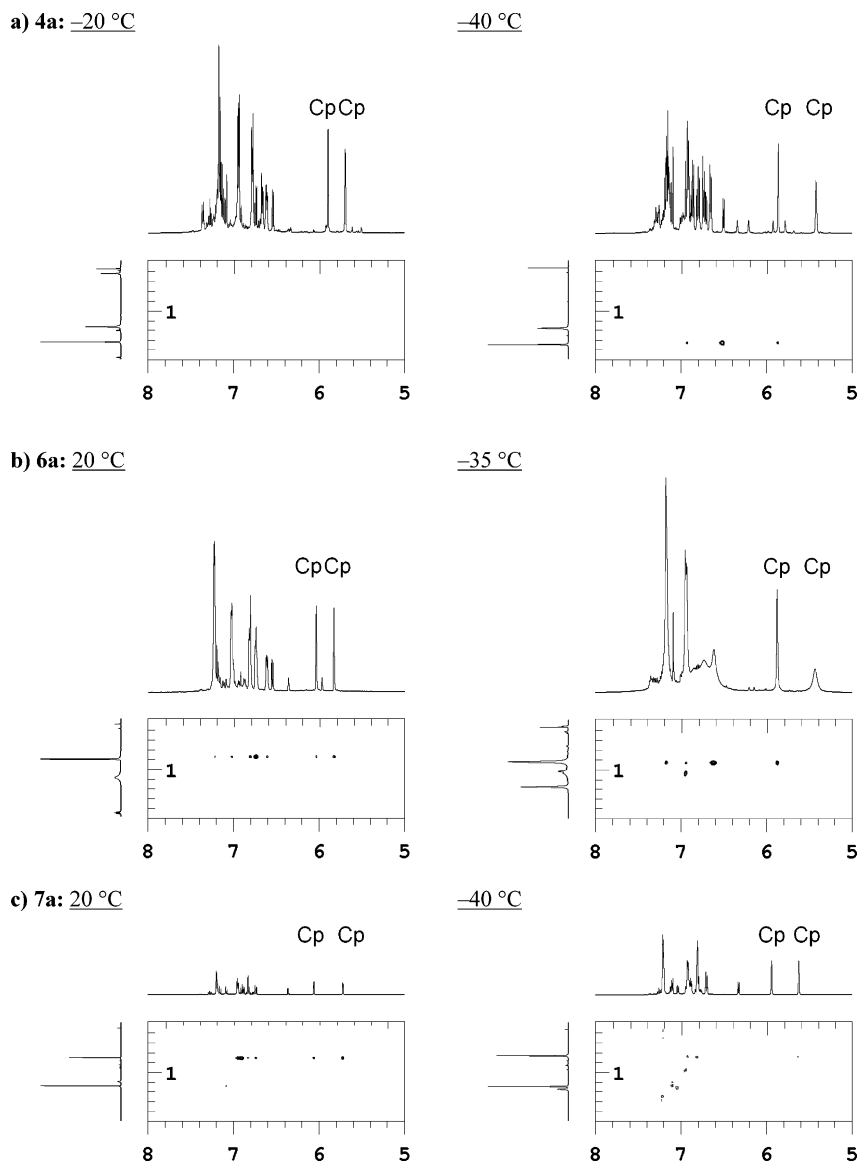


Figure 3. Room-temperature and low-temperature ^1H - ^1H NOESY spectra for the (a) methyl, (b) isopropyl, and (c) *tert*-butyl complexes in $\text{C}_6\text{D}_5\text{Cl}$.

between only one of the cyclopentadienyl resonances with resonances corresponding to the pyridine isopropyl resonances indicates that at $-35\text{ }^\circ\text{C}$ rotation of the indenyl ligands is slow and leads to the predominance of a single *syn* conformer. As this is one of the first indications of the presence of a *syn* isomer in solution, we sought to confirm these observations for the related methylpyridyl complex **4a** and the *tert*-butylpyridyl complex **7a**.

For the methylpyridyl complex **4a**, the cyclopentadienyl resonances have nearly identical chemical shifts at room temperature, which precludes carrying out an analogous NOESY experiment at this temperature. At $-20\text{ }^\circ\text{C}$, the NOESY spectrum of **4a** shows no NOE transfer between the cyclopentadienyl resonances and the pyridyl methyl resonance (Figure 3). Presumably, at this temperature the dynamics of the indenyl ligands are such that the cyclopentadienyl protons and methyl protons are not held in close proximity for a time sufficient for efficient NOE transfer. However, at $-40\text{ }^\circ\text{C}$, the NOESY spectrum of **4a** shows correlation between the pyridyl CH_3 protons and only the downfield cyclopentadienyl resonance, consistent with the pre-

dominance of only one *syn* conformer.⁴⁷ This is consistent with the observation of a correlation between the isopropyl methyl resonances of **6a** (vide supra) at $-40\text{ }^\circ\text{C}$ but not at room temperature. Closer inspection of the $-40\text{ }^\circ\text{C}$ NOESY spectrum of **4a** (Supporting Information) reveals a correlation between the pyridine methyl resonances at 1.75 ppm and the *ortho* protons of the phenyl group at 6.90 ppm (Figure 3), implicating that the predominant *syn* isomer is that which positions the 2-phenyl and methyl substituents in close proximity (Scheme 2).

The variable-temperature NMR spectra of the *tert*-butyl-substituted pyridine complexes **7a** and **7b** are slightly different than those of their less sterically hindered congeners; in contrast to the variable-temperature behavior of complexes **3a**–**6b**, the cyclopentadienyl proton signals for the *tert*-butyl complexes **7a** and **7b** exhibit temperature-dependent chemical shifts but do not cross over in the temperature range studied. Nevertheless, the NOESY spectrum of **7a** shows a

(47) As for **6a**, the strength of the cross-peaks observed for both cyclopentadienyl protons to the phenyl ring protons was similar.

correlation between the *tert*-butyl resonance and both cyclopentadienyl resonances at room temperature, whereas the *tert*-butyl resonance shows a correlation to only the upfield cyclopentadienyl resonance at $-40\text{ }^{\circ}\text{C}$ (Figure 3). At this temperature, a correlation analogous to that observed in the low-temperature **6a** NOESY spectrum is observed between the *tert*-butyl protons and the *ortho* protons of the 2-phenyl substituent, again suggesting that the predominant *syn* isomer holds these groups in close proximity.

Finally, to better characterize the $[(2\text{-PhInd})_2\text{ZrMe}-(2\text{-iPr-pyridine})^+][\text{MeB}(\text{C}_6\text{F}_5)_3^-]$ intermediate (**6a'**), 2-isopropylpyridine was added to **2a** at $-40\text{ }^{\circ}\text{C}$ and a NOESY experiment was performed prior to the elimination of methane to generate **6a**. This spectrum reveals a correlation between the Zr-CH_3 resonance at 0.20 ppm and both cyclopentadienyl resonances, and a correlation between both the isopropylpyridine methyl resonance ($\delta = 0.70\text{ ppm}$) and methine resonance ($\delta = 1.07\text{ ppm}$) and only the downfield cyclopentadienyl resonance ($\delta = 6.14\text{ ppm}$) (Figure 3). Such behavior is also consistent with the presence of only one *syn* conformer.

Thus, the low-temperature NOESY spectra of the cations **4a**, **6a**, **6a'**, and **7a** reveal that 2-phenylindene metallocene cations ligated by cyclometalated 2-alkyl pyridines exist primarily as the achiral *syn* conformers at $-40\text{ }^{\circ}\text{C}$. These results imply that the achiral *syn* isomers are accessible conformations not only in the solid state¹ but also in solution. Moreover these results suggest that the nature of the accessible conformations of these conformationally dynamic catalysts is a complicated function of the nature of the arylindene ligands, the cation/anion interactions, and the nature of the alkyl group bound to the metallocene cation.

Conclusions

NMR investigations of conformationally dynamic unbridged zirconocenium methyl cations $[(2\text{-PhInd})_2\text{ZrMe}^+][\text{RB}(\text{C}_6\text{F}_5)_3^-]$ ($\text{R} = \text{Me}, \text{C}_6\text{F}_5$) reveal that association of sterically hindered counterions $[\text{RB}(\text{C}_6\text{F}_5)_3^-]$ does not provide a sufficient steric barrier to inhibit the conformational dynamics of the 2-arylindene ligands. No evidence was found that suggests the association of the anions with the $(2\text{-PhInd})_2\text{ZrMe}^+$ cations leads to "locked" conformations at temperatures above $-40\text{ }^{\circ}\text{C}$. The activation barrier for ion-pair separation of the zirconocene cations and $\text{RB}(\text{C}_6\text{F}_5)_3^-$ was shown to be slightly higher but in the range observed for related zirconocene methyl cations. The higher activation barriers for ion-pair separation of $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ relative to $\text{B}(\text{C}_6\text{F}_5)_4^-$ are consistent with polymerization data that indicate the $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion coordinates more weakly to the metal center than the $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ anion, leading to higher productivities.

Cationic *o*-substituted pyridyl complexes were prepared as steric analogues to active cationic species ligated to a growing polymer chain. Low-temperature NOESY spectra of the cyclometalated pyridine zirconocene cations provide the first evidence for the presence of C_s -symmetric *syn* conformations in solution.

Experimental Section

General Procedures. Standard Schlenk techniques and a Vacuum Atmospheres drybox were used to handle air- and

moisture-sensitive compounds. Dichlorofluoromethane⁴⁵ and 2-isopropylpyridine⁴⁸ were synthesized according to the literature procedures. Dichlorofluoromethane, all pyridines used, *d*₅-chlorobenzene (Fisher), and *d*₈-toluene were stirred over calcium hydride for at least 6 h under a nitrogen blanket and distilled and degassed prior to use. Tris(pentafluorophenyl)-borane and trityl tetrakis(pentafluorophenyl)borate (Strem) were used as delivered. All chemicals were obtained from Aldrich unless otherwise noted.

Synthesis of (2-Phenylindene)₂ZrMe₂. The compound was prepared following a slight modification of the literature procedure reported by Coates and Resconi.^{1,49} Methylolithium (24.0 mL, 1.6 M in diethyl ether, 38.4 mmol) was added dropwise to a stirred solution of 2-phenylindene (3.85 g, 20.0 mmol) in 250 mL of diethyl ether at $-78\text{ }^{\circ}\text{C}$. The resulting dark brown solution was allowed to warm to room temperature and stirred in the dark for 12 h. The solution was then transferred to a suspension of zirconium tetrachloride (2.55 g, 11.0 mmol) in 50 mL of pentane. When the lighter brown solution began to darken after 1 h, the solvent was removed in vacuo, leaving a dark brown residue. The product was dissolved in toluene, filtered through Celite, and concentrated in vacuo to 50 mL. The product crystallized from this solution at $-50\text{ }^{\circ}\text{C}$ as a pale yellow solid (3.3 g, 6.5 mmol, 65% yield). ¹H NMR (C_6D_6 , 500 MHz): δ (ppm) 7.31 (d, $J = 0.01\text{ Hz}$, 4H), 7.20 (d, $J = 0.01\text{ Hz}$, 4H), 7.10 (t, $J = 0.02\text{ Hz}$, 2H), 7.04 (q, $J = 0.08\text{ Hz}$, 4H), 6.94 (q, $J = 0.08\text{ Hz}$, 4H), 6.90 (t, $J = 0.10\text{ Hz}$, 4H), 5.96 (s, 4H, Cp), -1.05 (s, 6H, Zr-CH_3).

Preparation of Methyl Cations. Compounds **2a** and **2b** were prepared for NMR analysis as follows. Under nitrogen, both **1** and $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$ were weighed directly into a 5 mm Teflon-capped (J. Young) NMR tube, dissolved in $\text{C}_6\text{D}_5\text{Cl}$, and allowed to react for at least 20 min prior to use in NMR experiments unless otherwise indicated. The rate of decomposition of the methyl cations has prevented their characterization by elemental analysis or X-ray crystallography. The methyl cations have also proven insufficiently stable toward appropriate solvents to permit characterization by mass spectroscopy. In lieu of such analyses, the ¹H NMR spectra of **2a** and **2b** at room temperature and below are included in the Supporting Information, and their ¹H and ¹³C chemical shifts are recorded in Tables 3 and 4.

Preparation of Zirconocenium Pyridyl Cations. The *o*-substituted pyridyl cations **3a–8b** were prepared for NMR analysis as follows. Under nitrogen, stock solutions of pyridine or 2-alkylpyridines ($\sim 50\text{ mg/1 mL C}_6\text{D}_5\text{Cl}$) were prepared, and slightly less than 1 equiv was added by micropipet to a Teflon-capped (J. Young) NMR tube containing the appropriate methyl cation (**2a** or **2b**) in $\text{C}_6\text{D}_5\text{Cl}$. The sample was allowed to react for at least 20 min prior to use in NMR experiments unless otherwise indicated. When preparing the pyridyl, methylpyridyl, and ethylpyridyl complexes, slightly less than 1 equiv of the pyridine was used, as these complexes are prone to coordination of a second equivalent of pyridine; in the ¹H NMR spectra, this slight imbalance is manifested in resonances near -0.2 ppm due to $[(2\text{-PhInd})_2\text{ZrCH}_3^+][\text{MeB}(\text{C}_6\text{F}_5)_3^-]$ and near -0.6 ppm due to $[(2\text{-PhInd})_2\text{Zr}^{+}-\text{CH}_3^-][\text{MeB}(\text{C}_6\text{F}_5)_3]$. Attempts to isolate the pyridyl complexes produce oils from which solvent cannot be removed completely; their characterization by elemental analysis or X-ray crystallography has thus been prevented. The pyridyl cations have also proven insufficiently stable toward appropriate solvents to permit characterization by mass spectroscopy. In lieu of such analyses, the room-temperature ¹H NMR chemical shifts of **3a–8a** are recorded in Table 3, and for the representative complexes **4a**, **6a**, and **7a**, the room-temperature ¹³C NMR chemical shifts

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(49) Balboni, D.; Camurati, I.; Prini, G.; Resconi, L.; Galli, S.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2001**, *40*, 6588–6597.

Table 3. Room-Temperature ^1H NMR Chemical Shifts for 1, 2a, 2b, and 3a–8a (500 MHz, $\text{C}_6\text{D}_5\text{Cl}$)

	δ (ppm)	multiplicity	integration	assignment
1	−1.05	s	3	ZrCH ₃
	5.96	s	4	Cp
	6.85–7.35	m	18	Ar–H
2a	−0.37	bs	3	ZrCH ₃
	−0.37	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
	6.10	bs	4	Cp
2b	6.65–7.45	m	18	Ar–H
	−0.28	s	3	ZrCH ₃
	1.97	s	3	Ph ₃ CMe
3a	6.09	s	4	Cp
	6.65–7.45	m	18	Ar–H
	0.10	s	4	CH ₄
4a	1.18	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
	5.87	d ($J = 2.4$ Hz)	2	Cp
	6.23	d ($J = 2.4$ Hz)	2	Cp
5a	6.55–7.80	m	21	Ar–H
	0.10	s	4	CH ₄
	1.19	bs	3	CH ₃ B(C ₆ F ₅) ₃ [−]
6a	1.56	s	3	CH ₃
	5.98	qd ($J_1 = 2.4$ Hz, $J_2 = 0.7$ Hz)	4	Cp
	6.50–7.35	m	21	Ar–H
7a	0.10	s	4	CH ₄
	0.79	t ($J = 7.6$ Hz)	3	CH ₃
	1.21	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
8a	1.85	q ($J = 7.4$ Hz)	2	CH ₂
	5.88	d ($J = 2.05$ Hz)	2	Cp
	5.95	bs	2	Cp
6a	6.50–7.40	m	21	Ar–H
	0.10	s	4	CH ₄
	0.81	d ($J = 7.0$ Hz)	6	iPr CH ₃
7a	1.21	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
	1.92	sept ($J = 7.0$ Hz)	1	iPr CH
	5.82	d ($J = 2.1$ Hz)	2	Cp
8a	6.02	d ($J = 2.1$ Hz)	2	Cp
	6.50–7.35	m	21	Ar–H
	0.10	s	4	CH ₄
7a	1.20	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
	1.29	s	9	tBu CH ₃
	5.70	dd ($J_1 = 7.8$ Hz, $J_2 = 0.7$ Hz)	2	Cp
8a	6.04	dd ($J_1 = 2.4$ Hz, $J_2 = 0.5$ Hz)	2	Cp
	6.30	dd ($J_1 = 2.4$ Hz, $J_2 = 0.9$ Hz)	1	Ar–H
	6.70–7.30	m	21	Ar–H
7a	0.10	s	4	CH ₄
	1.22	s	3	CH ₃ B(C ₆ F ₅) ₃ [−]
	3.22	s	2	CH ₂
8a	5.30	bs	2	Cp
	5.69	d ($J = 1.8$ Hz)	2	Cp
	5.85–7.65	m	26	Ar–H

are recorded in Table 4; ^1H NMR spectra at and below room temperature are also included for **4a**, **6a**, and **7a** in the Supporting Information.

Variable-Temperature ^1H NMR. Samples for use in variable-temperature ^1H NMR experiments were prepared as above. Spectra were recorded on either a Varian Unity Inova 300 MHz NMR spectrometer equipped with a 5 mm broadband switchable probe, a Varian Mercury AS400 MHz NMR equipped with a 5 mm 4-nucleus ($^{13}\text{C}/^{31}\text{P}\{^1\text{H}/^{19}\text{F}\}$) broadband probe, or a Varian Unity Inova 500 MHz NMR equipped with a 5 mm 4-nucleus ($^{13}\text{C}/^{31}\text{P}\{^1\text{H}/^{19}\text{F}\}$) broadband z -axis pulsed field gradient probe. The temperature was calibrated using a methanol or ethylene glycol sample for data collection below or above ambient temperature, respectively. Data were collected first at 20 °C and then in decreasing 10 °C intervals to −40 °C. The samples were then warmed to 20 °C, and spectra were recorded in increasing 10 °C intervals to 100 °C. Upon changing the temperature, samples were allowed 1 min/ $^{\circ}\text{C}$ -changed to come to thermal equilibrium. All ^1H NMR spectra

Table 4. Room-Temperature ^{13}C NMR Chemical Shifts for 1, 2a, 2b, and Representative Zirconocenium Pyridyl Complexes (500 MHz, $\text{C}_6\text{D}_5\text{Cl}$)

	δ (ppm)	multiplicity	integration	assignment
1	35.0	s	2	ZrCH ₃
	98.4	s	4	Cp
	124–130	m	26	Ar–C
2a	39.0	s	1	CH ₃ B(C ₆ F ₅) ₃ [−]
	52.1	s	1	ZrCH ₃
	101.3	bs	4	Cp
2b	121–151	m	44	Ar–C
	30.5	s	1	Ph ₃ CCH ₃
	52.7	s	1	ZrCH ₃
4a	56.1	s	1	Ph ₃ CCH ₃
	102.2	s	4	Cp
	124–151	m	50	Ar–C
6a	1.35	s	1	CH ₄
	20.9	s	2	CH ₃
	39.0	s	1	CH ₃ B(C ₆ F ₅) ₃ [−]
7a	98.9	s	2	Cp
	100.2	s	2	Cp
	121–156	m	48	Ar–C
8a	1.35	s	1	CH ₄
	23.4	s	2	iPr CH ₃
	33.9	s	1	iPr CH
9a	39.0	s	1	CH ₃ B(C ₆ F ₅) ₃ [−]
	100.0	s	2	Cp
	100.6	m	2	Cp
10a	120–166	m	50	Ar–C
	1.35	s	1	CH ₄
	29.5	s	1	tBu C
11a	30.3	s	3	tBu CH ₃
	39.0	s	1	CH ₃ B(C ₆ F ₅) ₃ [−]
	100.2	s	2	Cp
12a	100.4	s	2	Cp
	115–170	m	51	Ar–C

were referenced to toluene, which appears in trace amounts in all samples ($\delta = 2.11$ ppm).

NOESY Experiments. Samples were prepared as above and allowed to equilibrate at the experimental temperature for 30 min prior to acquisition unless otherwise noted. Two-dimensional NOESY NMR experiments were performed on the 500 MHz NMR spectrometer using a slightly modified standard three-pulse sequence; specifically, a pulse was added before the relaxation delay to eliminate residual x/y magnetization. Either 8 or 16 scans of 4096 complex data points ($2 \times \text{np}$) in the t_2 dimension were acquired with between 200 and 256 complex data points in F1. The data were multiplied by cosine-squared weighting functions and zero-filled to a 4096 by 4096 matrix (fn and fn1). The 90° ^1H pulse widths varied with the experimental conditions (sample and temperature) from 15 to 28 μs . A spectral width of 8000 Hz, a mixing time of 0.3 ms, an acquisition time of 128 ms, and a relaxation delay time of 4 s were used. The number of transients and data points were chosen on the basis of the sample concentration. Baseline correction was used. All NOESY spectra were referenced to toluene, which appears in trace amounts in all samples ($\delta = 2.11$ ppm).

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Supporting Information Available: Pertinent room-temperature and low-temperature 1-D ^1H and ^{13}C NMR spectra and 2-D ^1H – ^1H NOESY spectra of the methyl cations and pyridyl complexes are available free of charge via the Internet at <http://pubs.acs.org>.

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