# Synthesis and Structure of Acyclic Bis(ketenimine) Complexes of Zirconium

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*Received October 3, 1997*

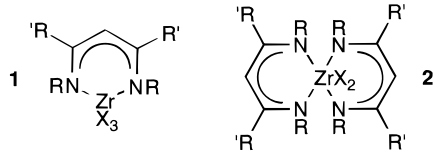
Mono- and disubstituted bis(ketenimine) complexes of zirconium (**1** and **2**, respectively) can be readily prepared by reaction of these ligands (**3**) with $Zr(NMe)_4$ or, in some cases, the homoleptic tetrabenzyl derivative $ZrBn_4$. Treatment of **1** (Ar = Ph, *p*-$CF_3$Ph; X = $NMe_2$) with $Me_2NH{\cdot}HCl$ and of **2** (Ar = Ph, X = $NMe_2$) with either $Me_2NH{\cdot}HCl$ or TMSCl provides the corresponding chloro derivatives in high yield. Alkyl derivatives of **2** (X = Me, Bn) can be readily prepared by reaction of the corresponding chloro derivatives with Grignard or organolithium reagents. Monocyclopentadienyl bis(ketenimine) complexes **4** (Ar = Ph, *p*-$CF_3$Ph; Cp = $\eta^5$-$C_5H_5$, $\eta^5$-$C_9H_7$; X = Cl) were prepared from **1** (Ar = Ph, *p*-$CF_3$Ph; X = Cl) by reaction with CpLi or IndLi in high yield, and methyl derivatives **4** (Ar = Ph, *p*-$CF_3$Ph; Cp = $\eta^5$-$C_5H_5$, $\eta^5$-$C_9H_7$; X = Me) were accessible by treatment of the chloro precursors with methyllithium. The X-ray structure of **2** (Ar = Ph; X = $NMe_2$) reveals a distorted-octahedral geometry in which the bis(ketenimine) ligands are $\sigma$-bound to the metal and the dimethylamido groups are cis to one another, and the corresponding dichloro derivative also adopts a similar structure in the solid state, whereas the bis(ketenimine) ligands adopt a distorted, $\eta^5$ binding mode in the monoindenyl derivative **4** (Ar = Ph; Cp = $\eta^5$-$C_9H_7$; X = Cl). Enantiomers of **2** (Ar = Ph, X = Cl) readily interconvert in solution via a Bailar-twist mechanism, as revealed by variable-temperature $^1$H NMR spectroscopic studies; activation parameters for this process were determined ($\Delta H^{\ddagger}$ = 9.0 ± 0.45 kcal mol$^{-1}$; $\Delta S^{\ddagger}$ = −9.9 ± 1.0 cal mol$^{-1}$ K$^{-1}$).



## Introduction

There is considerable current interest in the preparation and chemistry of electron-deficient complexes of the group 4 transition metals in connection with their use in olefin polymerization and related processes. The vast majority of such studies deal with bis(cyclopentadienyl) complexes of group 4[1] and the related, but more electron deficient, monocyclopentadienyl derivatives.[2] More recently, attention has been focused on the use of isoelectronic alternatives to the cyclopentadienyl anion[3] and other electron-deficient complexes such as bis(amido),[4] bis(amidinato),[5] and porphine derivatives.[6] In contrast, there are few reports concerning the use of acyclic, mono- or disubstituted bis(ketenimine) complexes of group 4 (**1** and **2**, respectively; Chart 1) in olefin polymerization, the work of Jordan and co-workers[3a] being confined to macrocyclic versions of this ligand class.

**Chart 1**




Given the isoelectronic relationship between bis(ketenimine) ligands and cyclopentadienyl anions, the paucity of work in this area seemed surprising, particularly because the steric and electronic properties of the bis(ketenimine) ligand can be readily altered through an appropriate choice of amine and $\beta$-diketone used in

(1) For recent reviewe see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Reiger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.

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(6) (a) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469. (b) Cozz, P. G.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4994.

S0276-7333(97)00862-5 CCC: $15.00 
Publication on Web 03/05/1998

**Table 1. $^1$H NMR Spectral Data for Complexes 1[a]**

| compd (solvent) | Ar | X | $\delta$ (ppm) | appearance | assignt |
|---|---|---|---|---|---|
| **1a** ($C_6D_6$) | Ph | $CH_2Ph$ | 7.07 | m, 10 H | N**Ph** |
| | | | 6.90 | m, 5 H | $ZrCH_2$**Ph** |
| | | | 6.72 | m, 10H | $ZrCH_2$**Ph** |
| | | | 5.01 | s, 1H | PhNC(Me)C**H**C(Me)NPh |
| | | | 2.60 | s, 6H | $ZrCH_2$Ph |
| | | | 1.51 | s, 12H | PhNC(**Me**)CHC(**Me**)NPh |
| **1b** ($C_6D_6$) | Ph | $NMe_2$ | 7.13 | d, $J$ = 8.3 Hz, 2H | N**Ph** |
| | | | 6.90 | t, $J$ = 8.3 Hz, 4H | N**Ph** |
| | | | 6.70 | d, $J$ = 8.3 Hz, 4H | N**Ph** |
| | | | 5.02 | s, 1H | PhNC(Me)C**H**C(Me)NPh |
| | | | 2.73 | s, 18H | N**Me**$_2$ |
| | | | 1.75 | s, 6H | PhNC(**Me**)CHC(**Me**)NPh |
| **1c** ($C_6D_6$) | *p*-$CF_3$Ph | $NMe_2$ | 7.45 | d, $J$ = 10 Hz, 4H | $NC_6$**H**$_4CF_3$ |
| | | | 6.56 | d, $J$ = 10 Hz, 4H | $NC_6$**H**$_4CF_3$ |
| | | | 5.02 | s, 1H | ArNC(Me)C**H**C(Me)NAr |
| | | | 2.58 | s, 18H | N**Me**$_2$ |
| | | | 1.55 | s, 6H | ArNC(**Me**)CHC(**Me**)NAr |
| **1d** ($C_6D_6$) | Ph | Cl | 7.10 | m, 10H | N**Ph** |
| | | | 4.80 | s, 1H | PhNC(Me)C**H**C(Me)NPh |
| | | | 1.84 | s, 6H | PhNC(**Me**)CHC(**Me**)NPh |
| **1e** (THF-$d_8$) | *p*-$CF_3$Ph | Cl | 7.65 | d, $J$ = 8 Hz, 4H | $NC_6$**H**$_4CF_3$ |
| | | | 7.30 | d, $J$ = 8 Hz, 4H | $NC_6$**H**$_4CF_3$ |
| | | | 5.69 | s, 1H | ArNC(Me)C**H**C(Me)NAr |
| | | | 1.70 | s, 6H | ArNC(**Me**)CHC(**Me**)NAr |

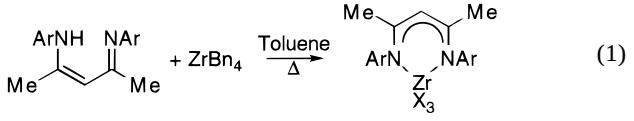
[a] Recorded at 250 MHz in the solvent indicated.



their synthesis.[7] This latter feature prompted us to develop efficient and general synthetic routes to both **1** and **2**, the results of which are reported here.[8] While this work was in progress, Lappert and co-workers[9] independently described the preparation of some examples of complexes **1** (X = Cl); X-ray studies revealed that the bis(ketenimine) ligand is $\eta^5$-coordinated to the metal, thus highlighting the similarity between these ligands and Cp anions.

## Results and Discussion

Our initial synthetic efforts focused on the use of alkane elimination reactions as a route to complexes **1** and **2**, as these had been reported to be successful in the case of macrocyclic versions.[3a] Indeed, reaction of $ZrBn_4$ with ligand **3a** (Ar = Ph, R′ = Me), in toluene solution at 40−50 °C, cleanly furnished the 1:1 complex **1a** (Ar = Ph, R′ = Me, X = Bn) in high yield (eq 1). Quite




**3a**: Ar = Ph **1a**: Ar = Ph; X = Bn (1)

surprisingly, the (much) more acidic ligand **3b** (Ar = p-$CF_3$Ph, R′ = Me) failed to react with $ZrBn_4$ under the same conditions; at higher temperatures, reaction did occur to give a complex analogous to **1a** but, under the conditions employed (toluene, 80−90 °C), this compound competitively decomposed to provide a complex mixture of products. This surprising result seems to indicate that it may be the donor properties of ligand **3** that are important in facilitating alkane elimination reactions (and that, perversely, the thermal lability of complexes **1** appears also to be correlated in the same manner) rather than their thermodynamic acidity.

Spectroscopic data for complex **1a** appear in Table 1. The benzyl groups appear to be conventionally bound to the metal in this complex, and the data obtained are reminiscent of simple monocyclopentadienylzirconium tribenzyl compounds.[10] Attempts to obtain suitable single crystals of this compound to delineate the mode of binding of the bis(ketenimine) ligand to the metal were not successful; we suspect that in complex **1a** the ligand adopts the $\eta^5$ coordination mode, on the basis of structural characterization of related materials.[9]

Attempts to prepare complex **2a** (Ar = Ph, R′ = Me, X = Bn) by reaction of **1a** with an additional 1 equiv of ligand **3a** were not successful; a mixture of several compounds was formed, none of which appears to be **2a**, on the basis of its successful synthesis by another route (vide infra). As alkane elimination reactions did not appear to provide a general method for the synthesis of complexes **1** and to a greater extent **2**, we elected to investigate amine elimination reactions[11] as an alternative approach.

As shown in Scheme 1, this process and allied chemistry appear to offer reasonable access to a range of complexes **1** and **2**. Reaction of 1 or 2 equiv of **3a** (Ar = Ph) with $Zr(NMe_2)_4$ in toluene solution cleanly furnished the tris- and bis(dimethylamido) derivatives **1b** and **2b**, respectively. Similar chemistry was encountered using the *p*-$CF_3$Ph analogue **3b**; although monosubstituted adduct **1c** could be cleanly prepared by this route, the bis(dimethylamido) derivative **2c** could

(7) See e.g.: McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903 and references therein.

(8) We have screened a number of the complexes reported here in olefin polymerization, and the results will be reported elsewhere: Rahim, M.; Collins, S. Manuscript in preparation.

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(10) (a) Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. (b) Pellecchia, C.; Grassi, A.; Zambelli, A. *J. Mol. Catal.* **1993**, *82*, 57. (c) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (d) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 3856.

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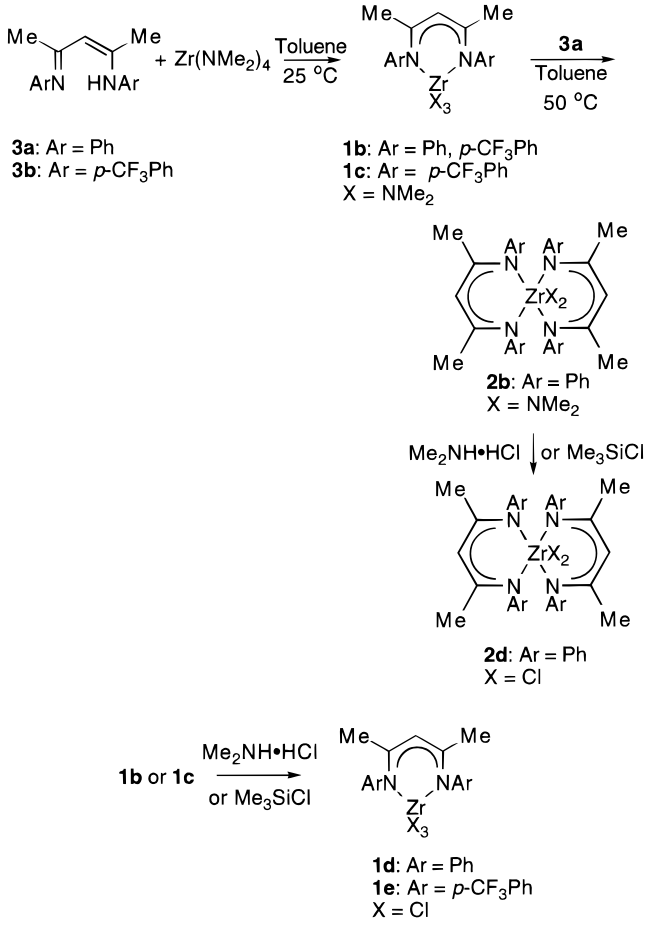
**Scheme 1**



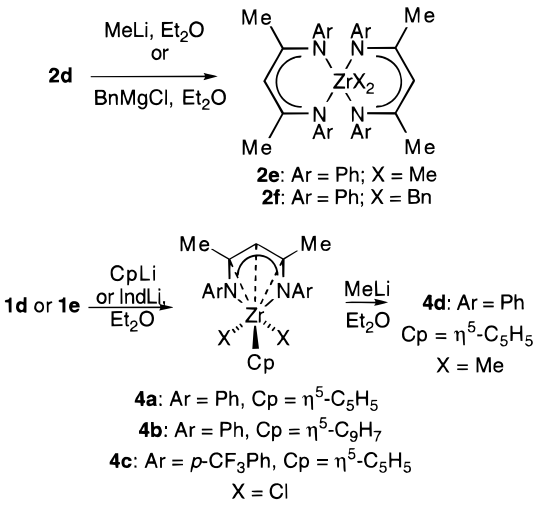

not be isolated in pure form on treatment either of $Zr(NMe_2)_4$ with 2 equiv of **3b** or of **1c** with 1 equiv of this ligand, due to thermal instability in solution. The corresponding chloro derivatives (**1d**,**e**, **2d**) were accessible by treatment of **1b** and **1c** or of **2b** with 3 or 2 equiv of $Me_2NH{\cdot}HCl$, respectively, in dichloromethane solution or, in certain cases, a slight excess of $Me_3SiCl$ in toluene solution.[12]

Direct conversion of **1b** or **2b** to the dimethyl derivatives was attempted using $AlMe_3$ in toluene; unlike their metallocene analogues,[12] complexes **1b** and **2b** proved resistant to alkylation at room temperature in toluene. At higher temperatures, reaction occurred but it proved difficult to obtain the dimethyl derivatives **2** in pure form due to competing decomposition and formation of aluminum amide byproducts. We thus resorted to synthesis of dialkyl derivatives **2** using conventional metathetical reactions on the corresponding chloro derivatives; in this way methyl and benzyl derivatives (**2e**,**f**) were obtained in high yield (Scheme 2).

The $^1H$ NMR spectroscopic data for complexes **1a**−**e** and **2b**−**f** appear in Tables 1 and 2, respectively. Aside from the aromatic region which was, in general, difficult to assign, the spectral data are readily interpreted. The chemical shift of the methine proton of the bis(ketenimine) ligand appears as a sharp singlet at ca. 5 ppm, and the position of this resonance was somewhat insensitive with respect to the identity of the other ligands present on the metal in complexes **2** (Table 2);

(12) Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

**Scheme 2**




the resonance(s) due to the methyl groups were also largely unaffected. Interestingly, in the spectrum of **2b**, a high-field doublet at 5.8 ppm, integrated to two protons, was observed (Table 2, entry 1) and was assigned to aromatic protons ortho to N (vide infra). In addition, two singlets due to methyl groups of the bis(ketenimine) ligand were present. Finally, the signal due to the $NMe_2$ groups was line-broadened, suggesting restricted rotation about the Zr−N bond.[13] In the other complexes, derived from **2b**, only one methyl resonance was present at 298 K and the high-field doublet was absent; in addition, the aromatic protons were line-broadened, which suggested fluxionality in solution.

Finally, mixed cyclopentadienyl-bis(ketenimine) complexes **4a**−**c** could be prepared by reaction of the trichloride complexes **1d**,**e** with either CpLi or IndLi in ether solution. Following purification by recrystallization, the mixed complex **4a** could be converted to the corresponding dimethyl derivative **4d** on reaction with MeLi in ether solution (Scheme 2). Spectroscopic data for these mixed complexes are included in the Experimental Section; the spectroscopic properties of the bis(ketenimine) ligand in these complexes were surprisingly similar to those observed for complexes **1** and **2**.

A number of these bis(ketenimine) complexes were characterized by X-ray crystallography to delineate the binding mode(s) of this ligand to Zr.

The molecular structure of the bis(dimethylamido) derivative **2b** appears in Figure 1, while selected bond lengths and angles appear in Table 3 and crystallographic data are summarized in Table 5. In this complex, the bis(ketenimine) ligands are $\sigma$-bound to the metal and the complex assumes a distorted, cis-octahedral geometry at the metal, in which the N−Zr−N angles involving the bis(ketenimine) ligands and the cis dimethylamido groups differ significantly from 90° (N(5)−Zr-N(6) = 80.3(1)°; N(3)−Zr-N(4) = 79.6(1)°; N(1)−Zr−N(2) = 92.8(1)°). The trans influence of the dimethylamido ligands is clearly seen in the longer Zr−N(4) and Zr−N(6) distances of 2.380(1) and 2.397(2) Å

(13) At low temperatures in toluene-$d_8$, two separate signals in a ratio of 1:1 are observed for the $NMe_2$ protons. Simulation of these spectra[16] provided the activation parameters $\Delta H^{\ddagger} = 16.1 \pm 0.8$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 13.2 \pm 1.3$ cal mol$^{-1}$ K$^{-1}$) for rotation about the Zr−N bond.

**Table 2. $^1$H NMR Spectral Data for Complexes 2[a]**

| compd (solvent) | Ar | X | $\delta$ (ppm) | appearance | assignt |
|---|---|---|---|---|---|
| **2b** ($C_6D_6$) | Ph | $NMe_2$ | 7.10 | m, 14H | N**Ph** |
| | | | 6.85 | m, 4H | N**Ph** |
| | | | 5.80 | d, $J$ = 8 Hz, 2H | N**Ph** (*o*-H) |
| | | | 5.10 | s, 2H | PhNC(Me)C**H**C(Me)NPh |
| | | | 2.50 | br s, 12H | N**Me**$_2$ |
| | | | 1.70 | s, 6H | PhNC(**Me**)CHC(Me)NPh |
| | | | 1.41 | s, 6H | PhNC(Me)CHC(**Me**)NPh |
| **2d** (THF-$d_8$) | Ph | Cl | 6.90 | br m, 20H | N**Ph** |
| | | | 5.10 | s, 2H | PhNC(Me)C**H**C(Me)NPh |
| | | | 1.45 | s, 12H | PhNC(**Me**)CHC(**Me**)NPh |
| **2e** ($C_6D_6$) | Ph | Me | 7.15 | d, $J$ = 8.2 Hz, 8H | N**Ph** |
| | | | 6.90 | t, $J$ = 8.2 Hz, 4H | N**Ph** |
| | | | 6.62 | d, $J$ = 8.2, 8H | N**Ph** |
| | | | 4.90 | s, 2H | PhNC(Me)C**H**C(Me)NPh |
| | | | 1.50 | s, 12H | PhNC(**Me**)CHC(**Me**)NPh |
| | | | 1.32 | s, 6H | Zr**Me**$_2$ |
| **2f** ($C_6D_6$) | Ph | $CH_2Ph$ | 7.20 | m, 6H | N**Ph** |
| | | | 7.05 | m, 8H | N**Ph** |
| | | | 6.90 | m, 10H | Zr$CH_2$**Ph** |
| | | | 6.50 | m, 6H | N**Ph** |
| | | | 5.05 | s, 2H | PhNC(Me)C**H**C(Me)NPh |
| | | | 2.50 | s, 4H | Zr$C$**H**$_2$Ph |
| | | | 1.42 | s, 6H | PhNC(**Me**)CHC(**Me**)NPh |

[a] Recorded at 250 MHz in the solvent indicated at 298 K.



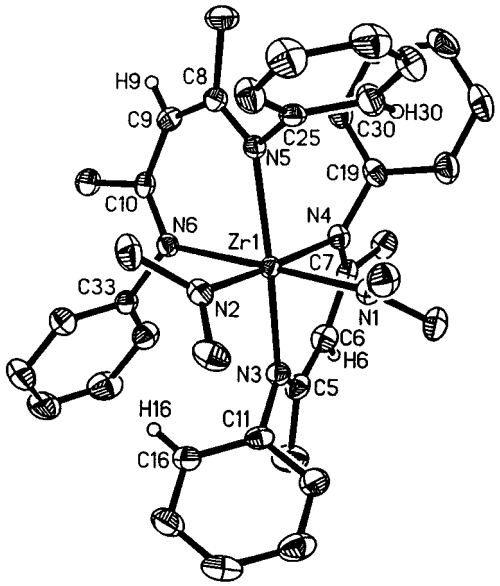



**Figure 1.** Molecular structure of complex **2b** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see Table 3; for crystallographic data see Table 5.

compared with the Zr−N(3) and Zr−N(5) bond lengths of 2.266(1) and 2.263(1) Å, respectively. The dimethylamido ligands are planar at nitrogen (sum of the bond angles 360(2) and 360(2)° at N(1) and N(2), for Zr−N(1) and Zr(2), respectively), suggesting considerable $\pi$-donation to the metal, which is borne out by the significantly shorter Zr−N distances of 2.078(1) and 2.074(2) Å, respectively. The five atoms in the bis(ketenimine) ligands are coplanar, and the two C−C distances of 1.394(2) and 1.399(2) Å and the two C−N distances of 1.337(2) and 1.339(2) Å suggest significant delocalization within the $\pi$-system of these ligands. Overall, the complex has approximate $C_2$ symmetry and the observation of two $^1$H NMR signals for the methyl groups of the bis(ketenimine) ligands in solution is consistent with the solid-state structure. Moreover, the observation of the high-field doublet due to the ortho-H's on the aromatic rings can be rationalized from the solid-state structure; as is evident from Figure 1, H(30) is directly over the shielding cone of the opposite aromatic ring and

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2b and 2d[a]**

| complex **2b** | | complex **2d** | |
|---|---|---|---|
| Bond Lengths | | | |
| Zr(1)−N(1) | 2.078(1) | Zr(1)−Cl(1) | 2.439(1) |
| Zr(1)−N(2) | 2.074(1) | Zr(1)−Cl(2) | 2.426(1) |
| Zr(1)−N(3) | 2.266(1) | Zr(1)−N(1) | 2.216(2) |
| Zr(1)−N(4) | 2.397(1) | Zr(1)−N(2) | 2.275(2) |
| Zr(1)−N(5) | 2.262(1) | Zr(1)−N(3) | 2.197(2) |
| Zr(1)−N(6) | 2.380(1) | Zr(1)−N(4) | 2.279(2) |
| N(5)−C(8) | 1.337(2) | N(1)−C(1) | 1.329(4) |
| C(8)−C(9) | 1.394(2) | C(1)−C(2) | 1.403(4) |
| C(9)−C(10) | 1.399(2) | C(2)−C(3) | 1.399(4) |
| N(6)−C(10) | 1.330(2) | N(2)−C(3) | 1.332(3) |
| Bond Angles | | | |
| N(1)−Zr(1)−N(2) | 92.8(1) | Cl(1)−Zr(1)−Cl(2) | 90.0(1) |
| N(4)−Zr(1)−N(3) | 79.6(1) | N(1)−Zr−N(2) | 79.9(1) |
| N(5)−Zr(1)−N(6) | 80.3(1) | N(4)−Zr(1)−N(3) | 78.9(1) |
| Zr(1)−N(5)−C(8) | 130.1(1) | Zr(1)−N(1)−C(1) | 128.1(2) |
| N(5)−C(8)−C(9) | 124.6(1) | N(1)−C(1)−C(2) | 122.8(3) |
| C(8)−C(9)−C(10) | 130.0(1) | C(1)−C(2)−C(3) | 127.1(3) |
| C(9)−C(10)−N(6) | 124.7 (1) | C(2)−C(3)−N(2) | 124.2(2) |
| C(10)−N(6)−Zr(1) | 126.8 (1) | C(3)−N(2)−Zr(1) | 125.3(2) |

[a] Estimated standard deviations in parentheses.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 4b[a]**

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Zr(1)−Cl(1) | 2.505(1) | Zr(1)−Cl(2) | 2.480(1) |
| Zr(1)−N(1) | 2.201(2) | Zr(1)−N(2) | 2.192(1) |
| Zr(1)−C(1) | 2.515(2) | Zr(1)−C(2) | 2.484(2) |
| Zr(1)−C(3) | 2.463(2) | Zr(1)−C3(a) | 2.554(2) |
| Zr(1)−C7(a) | 2.592(2) | Zr(1)−C(8) | 2.748(2) |
| Zr(1)−C(9) | 2.703(2) | Zr(1)−C(10) | 2.713(2) |
| N(1)−C(8) | 1.318(3) | N(2)−C(10) | 1.328(3) |
| C(8)−C(9) | 1.421(3) | C(9)−C(10) | 1.412(2) |
| Bond Angles | | | |
| Cl(1)−Zr(1)−Cl(2) | 85.8(1) | N(1)−Zr(1)−N(2) | 79.7(1) |
| Zr(1)−N(1)−C(8) | 99.6(1) | Zr(1)−N(2)−C(10) | 97.8(1) |
| N(1)−C(8)−C(9) | 119.1(2) | N(2)−C(10)−C(9) | 119.9(2) |
| C(8)−C(9)−C(10) | 126.0(2) | | |

[a] Estimated standard deviations in parentheses.

**Table 5. Summary of Crystallographic Data**

| compd | **2b** | **2d** | **4b** |
|---|---|---|---|
| formula | $C_{38}H_{46}N_6Zr$ | $C_{34}H_{34}Cl_2N_4Zr$ | $C_{26}H_{24}Cl_2N_2Zr$ |
| mw | 678.0 | 660.8 | 536 |
| $T$ (K) | 180 | 160 | 160 |
| radiation | Mo Kα | Mo Kα | Mo Kα |
| cryst syst | triclinic | orthorhombic | triclinic |
| space group | $P\bar{1}$ | $P2_12_12_1$ | $P\bar{1}$ |
| unit cell | | | |
| $a$ (Å) | 9.26(1) | 11.438(1) | 9.9399(7) |
| $b$ (Å) | 11.565(1) | 16.024(2) | 10.9317(7) |
| $c$ (Å) | 17.352(2) | 16.923(2) | 12.1965(8) |
| α (deg) | 74.376(6) | | 112.560(4) |
| $\beta$ (deg) | 89.059(7) | | 103.200(4) |
| $\gamma$ (deg) | 73.216(7) | | 96.177(6) |
| $V$ (Å$^3$) | 1710.5(5) | 3101.7(6) | 1163.1(2) |
| $Z$ | 2 | 4 | 2 |
| $D$(calcd) (g cm$^{-3}$) | 1.316 | 1.415 | 1.504 |
| abs coeff (cm$^{-1}$) | 3.57 | 5.57 | 7.19 |
| $F$(000) | 712 | 1360 | 536 |
| cryst size (mm) | 0.30 × 0.30 × 0.20 | 0.25 × 0.40 | 0.42 × 0.21 × 0.28 |
| $2\theta$ range (deg) | 4.0−50.0 | 4.0−52.0 | 4.0−52.0 |
| index ranges | $-10 \le h \le 10$ | $0 \le h \le 14$ | $0 \le h \le 12$ |
| | $-12 \le k \le 13$ | $0 \le k \le 19$ | $-12 \le k \le 12$ |
| | $-20 \le l \le 20$ | $0 \le l \le 20$ | $-15 \le l \le 14$ |
| no. of collected rflns | 11 902 | 3414 | 4705 |
| no. of indep. rflns | 5970 ($R_{int}$ = 1.67%) | 3414 | 4433 ($R_{int}$ = 1.07%) |
| no. of obsd rflns ($F > 6.0\sigma(F)$) | 5204 | 3054 | 4045 |
| data to param ratio | 8.8:1 | 6.0:1 | 10.7:1 |
| GOF ($F^2$) | 1.80 | 1.43 | 2.37 |
| final $R$ indices ($I > 2\sigma(I)$) (%) | $R$ = 2.09 | $R$ = 1.94 | $R$ = 2.04 |
| | $R_w$ = 2.44 | $R_w$ = 2.10 | $R_w$ = 2.61 |
| $R$ indices (all data) (%) | $R$ = 2.51 | $R$ = 2.24 | $R$ = 2.27 |
| | $R_w$ = 2.47 | $R_w$ = 2.13 | $R_w$ = 2.62 |
| diff peak, hole (e Å$^{-3}$) | 0.35, −0.20 | 0.24, −0.28 | 0.29, −0.32 |



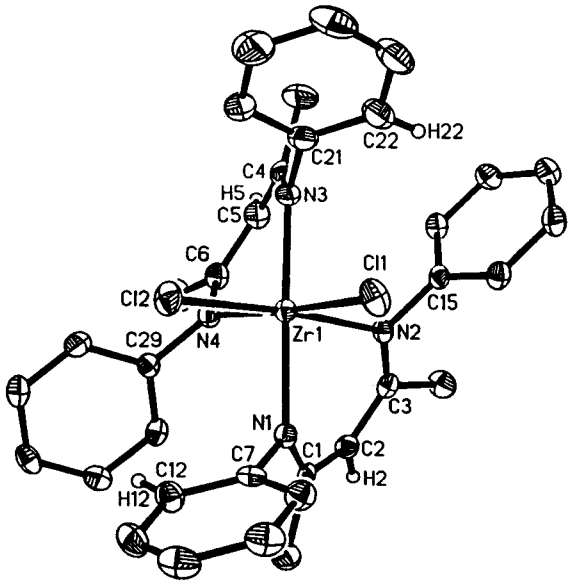



**Figure 2.** Molecular structure of complex **2d** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see Table 3; for crystallographic data see Table 5.

would experience strong deshielding in solution on a time-averaged basis.

Similarly, the dichloride analogue **2d** also shows a distorted-octahedral geometry at the metal center with two cis chloride atoms at an angle of 90.0(1)° (Figure 2, Tables 3 and 5). However, the angles involving the metal center and the bis(ketenimine) ligand deviate significantly from 90° (N(3)−Zr−N(4) = 79.6(1)°; N(1)−Zr−N(2) = 78.9(1)°). The shorter bond distances Zr−N(1) = 2.216(1) Å and Zr−N(3) = 2.197(1) Å as compared to Zr−N(2) = 2.275(1) Å and Zr−N(4) = 2.279(1) Å suggest a similar trans influence, but it is weaker than in **2b**, because the amido is a stronger $\sigma$, $\pi$-donor than chloride. As noted previously, the room-temperature $^1$H NMR spectrum of the dichloride complex **2d** exhibits only one resonance for the methyl groups of the bis(ketenimine) ligand, and this is inconsistent with the solid-state structure. Even the $^1$H NMR spectra of the dialkyl analogues **2e**,**f** were consistent with a more symmetrical structure in a variety of NMR solvents.

To resolve this ambiguity, variable-temperature $^1$H NMR spectra of **2d** were obtained. As the temperature was lowered, the singlet at $\delta$ 1.47 starts to broaden (see Figure 3) and at 237 K the peak starts to decoalesce. Finally, at 200 K two separate singlets appear at $\delta$ 1.32 and 1.53, respectively; the low-temperature spectrum is consistent with the solid-state structure, wherein the two methyl groups on the backbone of the ligand are inequivalent. Note also in the spectrum obtained at 200 K that the characteristic, high-field doublet for two ortho, aromatic protons is observed, suggesting that **2d** adopts a similar conformation in solution as **2b**.[14]

This fluxional process can be explained by a Bailar twist mechanism.[15] At room temperature, the two enantiomers interconvert rapidly on the NMR time scale via a trigonal-prismatic intermediate where all the

(14) The fact that this high-field doublet is integrated to only two protons also implies that rotation about the N−Ph bond is hindered in **2d** at 200 K, and in the case of **2b**, this same process is slow on the NMR time scale even at room temperature.

(15) (a) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165. (b) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 171. (c) Fleischer, E. B.; Gebala, A. E.; Swift, D. R.; Tasker, P. A. *Inorg. Chem.* **1972**, *11*, 2775. (d) Churchill, M. R.; Reis, A. H. *Inorg. Chem.* **1972**, *11*, 1811. (e) Vanquickenborne, L. G.; Pierloot, K. *Inorg. Chem.* **1981**, *20*, 3673. (f) Darensbonrg, D. J.; Kump, R. L. *Inorg. Chem.* **1984**, *23*, 2993.

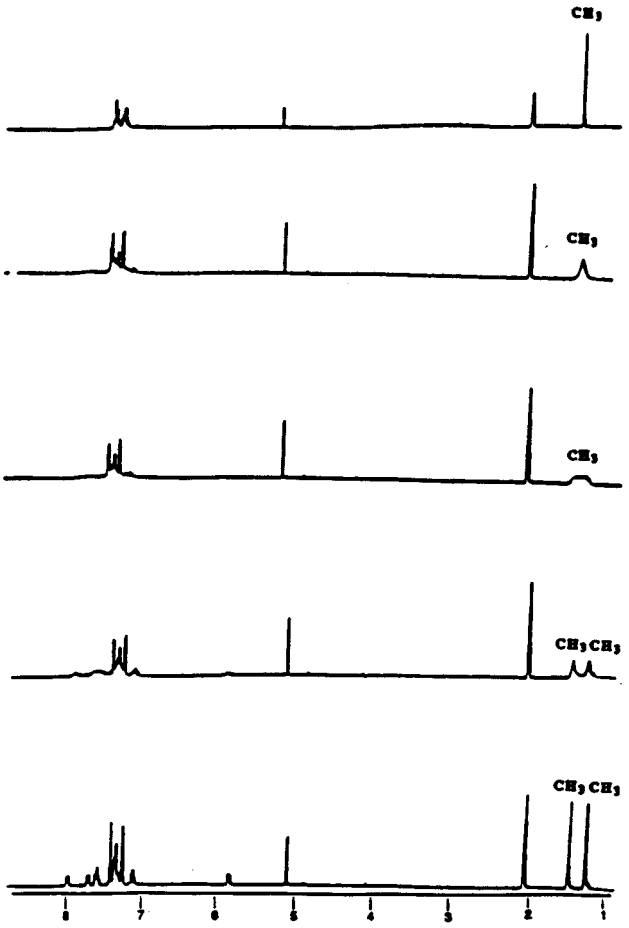
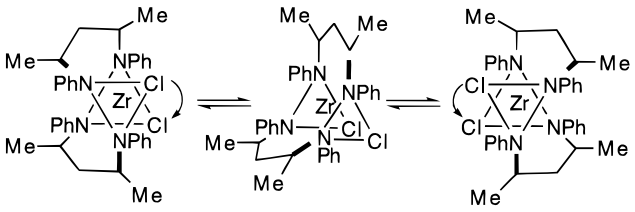


**Figure 3.** Variable-temperature 300 MHz $^1$H NMR spectra of complex **2d** in toluene-$d_8$.

**Scheme 3**



methyl groups are equivalent (Scheme 3). The rate constants of this interconversion process at various temperatures were obtained from spectral simulation by using the DNMR4 program.[16] From an Eyring plot (Figure 5) $\Delta H^{\ddagger} = 9.0 \pm 0.45$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -9.9 \pm 1.0$ cal mol$^{-1}$ K$^{-1}$ were determined. The low value of $\Delta H^{\ddagger}$ and the negative value of $\Delta S^{\ddagger}$ are consistent with an internal twist mechanism and not a dissociative pathway involving the bis(ketenimine) ligand.[15f,17]

The X-ray structure of complex **4b** was also determined for comparison purposes, and the molecular structure is depicted in Figure 4 (data in Tables 4 and 5). The bis(ketenimine) ligand adopts a "$\eta^5$-coordination" mode in this structure, and the N−Ph substitutents are directed toward the rear of the "wedge" defined by the two $\pi$-bound ligands. In this structure, the metal atom distances involving the bis(ketenimine) ligand are significantly longer (Zr−N(1) = 2.201(1) Å, Zr−N(2) = 2.192(1) Å, Zr−C(9) = 2.703(2) Å, Zr−C(10) = 2.713(2) Å, Zr−C(8) = 2.748(2) Å) than those found in Lappert's monoadduct complexes.[9] The indenyl ligand assumes an asymmetric conformation with respect to the bis(ketenimine) and chloride ligands, and the metal−carbon distances within the five-membered ring are significantly different (Zr−C(1) = 2.515(2) Å, Zr−C(2) = 2.480(2) Å, Zr−C(3) = 2.463(2) Å, Zr−C(3a) = 2.554(2) Å, Zr−C7a = 2.592(2) Å), suggesting possible slip distortion[18] of the indenyl ligand in this complex; however, they are roughly comparable to those found in bis(indenyl)zirconium complexes.[19] The Cl−Zr−Cl

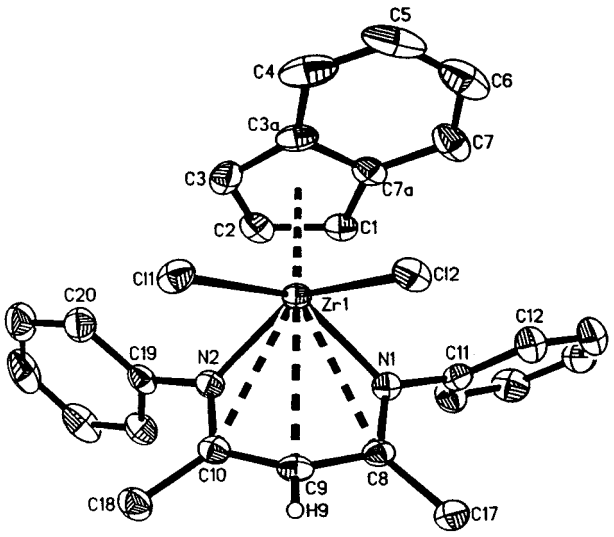



**Figure 4.** Molecular structure of complex **4b** with 50% probability thermal ellipsoids depicted and H-atoms omitted for clarity. For bond lengths and angles see Table 4; for crystallographic data see Table 5.

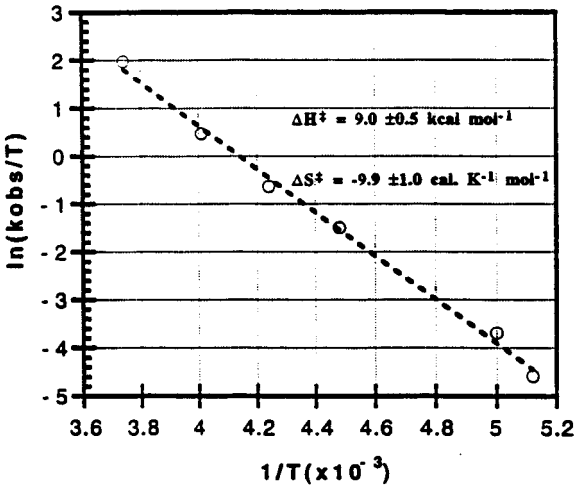



**Figure 5.** Eyring plot for interconversion of the two enantiomers of complex **2d** in toluene-$d_8$.

(16) Bushweller C. H.; Letenare, L. J.; Brunelle, J. A.; Bilorsky, H. J.; Whalon, M. J.; Fiels, S. H. Calculation of Chemically Exchanging Spectra; (QCPE Program No. 466; Department of Chemistry, University of Vermont, Burlington, VT 05401.

(17) Although we cannot rule out a dissociative process for the fluxional behavior, the observation that the barrier to interconversion for the bis(dimethylamido) complex **2b** is higher (i.e. slow exchange on the NMR time scale at 298 K) than that in **2d** seems inconsistent with a dissociative process; the trans effect of the dimethylamido ligands in **2b** should facilitate dissociation of the bis(ketenimine) ligand.

(18) (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev. (Washington, D.C.)* **1987**, *87*, 307. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (c) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

angle of 85.8(1)° is more acute compared to that typically observed in bent-metallocene complexes.[20] Somewhat surprisingly, the chemical shift of the signal due to the methine proton in the bis(ketenimine) ligand is insensitive to the coordination mode adopted by these ligands in solution. It could be that $\pi \rightarrow \sigma$ interconversion is very facile in solution.

It is apparent from a comparison of these various complexes that the bis(ketenimine) ligand can readily modify its mode of coordination to the metal in response to the donor properties of the other ligands bonded to zirconium. Presumably, in the presence of strong $\pi$-donors, as in **2b**, the bis(ketenimine) ligand acts primarily as a $2\sigma$, 4 $e^-$ donor for a formal count of 16 $e^-$ in such complexes, while in the more electron deficient complexes such as **4** it distorts to $\pi$-coordination so as to maintain a 16 $e^-$ count at the metal center, at least in the solid state. While this flexibility is appealing as a mechanism for modifying the reactivity of these complexes, it would appear from the structure of **4b** that the $\pi$-donor ability of this ligand appears to be considerably weaker[21] than in Cp (or even pentadienyl[22]) complexes of group 4. This feature will obviously modify the reactivity of more electron deficient versions of group 4 complexes incorporating this ligand, and studies directed toward elucidating these effects in, for example, olefin polymerization are being actively pursued.[8]



## Experimental Section

All solvents and chemicals were reagent grade and purified as required. All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted. Tetrahydrofuran, diethyl ether, hexanes, and toluene were dried by distillation from sodium−benzophenone ketyl while dichloromethane was dried and distilled from $CaH_2$. The compounds $Zr(Bn)_4$[23] and $Zr(NMe_2)_4$[24] were prepared as described in the literature. The bis(ketenimine) ligand **3a** was prepared as described previously.[7] Routine $^1H$, $^{13}C$, and $^{19}F$ NMR spectra were recorded in THF-$d_8$ or $C_6D_6$ solution on a Bruker AM-250, AC-200, or AM-300 spectrometer; $^1H$ and $^{19}F$ chemical shifts are referenced with respect to residual protonated solvent or internal $CFCl_3$, respectively. Low-temperature NMR spectra were recorded using these spectrometers in toluene-$d_8$ or $CD_2Cl_2$ solution using a solution of methanol in $CD_3OD$ for calibration purposes. IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. Mass spectra were obtained using a VG-7070 instrument at the University of Waterloo. Elemental analyses were determined by M. H. W. Laboratories of Phoenix, AZ, and Oneida Research Services, Inc., New York, NY.

**Synthesis of Ligand 3b. Synthesis of 4-((*p*-(Trifluoromethyl)phenyl)amino)pent-3-en-2-one (5).** A 4 mL amount of *p*-(trifluoromethyl)aniline (0.031 mol) was added to 3.50 mL of 2,4-pentanedione (0.034 mol), and the resulting mixture was heated at 150 °C for 4 h. The water produced from the reaction mixture was collected via a condenser. The resulting solution was left in the freezer overnight, and a bright yellow solid was produced. The compound was recrystallized from hexane (7.46 g, 98%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 13.26 (s, 1H, **H**$NC_6H_4$-*p*-$CF_3$), 7.48 (d, $J_{HH}$ = 9 Hz, 2H, N($C_6$**H**$_4CF_3$)), 6.83 (d, $J_{HH}$ = 9 Hz, 2H, N($C_6$**H**$_4CF_3$)), 5.28 (s, 1H, *p*-$CF_3C_6H_4NHC$(Me)-C**H**COMe), 2.33 (s, 3H, *p*-$CF_3C_6H_4NHC$(**Me**)CHCOMe), 1.81 (s, 3H, *p*-$CF_3C_6H_4NHC$(Me)CHCO**Me**). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 196.5, 157.6, 142.5, 125.5 (q, $J_{CF}$ = 30 Hz), 124.8 (q, $J_{CF}$ = 270 Hz), 126.2, 123.0, 99.5, 29.5, 19.5. $^{19}F$ NMR (188 MHz, $C_6D_6$): $\delta$ −61.90. High-resolution mass spectrum: calcd for $C_{12}H_{12}NF_3O$ 243.0949, found 243.0992. IR (KBr disk): 3037, 3080, 1592, 1535, 1483, 1393, 1021, 824, 704, 690 $cm^{-1}$.

**Synthesis of 4-((*p*-(Trifluoromethyl)phenyl)amino)-2-((*p*-(trifluoromethyl)phenyl)imino)pent-3-ene (3b).** Triethyloxonium tetrafluroborate (2.50 g, 0.013 25 mol) dissolved in 20 mL of $CH_2Cl_2$ was added dropwise to a stirred solution of **5** (3.22 g, 0.013 mol) in the same solvent. The reaction mixture was allowed to react for 20 min, and then 1.8 mL (0.013 mol) of dry *p*-(trifluoromethyl)aniline was added to it. The reaction mixture was stirred overnight. The reaction solution was then evaporated to dryness. The resulting solid was then redissolved in 140 mL of THF and cooled to 0 °C. Excess solid NaH (0.3369 g, 0.014 mol) was added in one portion from a solid addition funnel over 30 min. The reaction mixture was warmed to room temperature after 2 h and then stirred overnight. The solvent was then removed under vacuum, and the resulting yellow solid was extracted with 200 mL of hexane. The volume of the extract was reduced to 25 mL and then cooled to −35 °C overnight to obtain the title compound (4.61 g, 90%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 12.84 (s, 1H, **H**$NC_6H_4$-*p*-$CF_3$), 7.24 (d, $J_{HH}$ = 10 Hz, 4H, N($C_6$**H**$_4$-$CF_3$)), 6.58 (d, $J_{HH}$ = 10 Hz, 4H, N($C_6$**H**$_4CF_3$)), 4.72 (s, 1H, *p*-$CF_3C_6H_4NC$(Me)C**H**C(Me)N$C_6H_4$-*p*-$CF_3$), 1.60 (s, 6H, *p*-$CF_3$PhNC(**Me**)CHC(**Me**)N$C_6H_4$-*p*-$CF_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 159.3, 148.9, 126.4, 125.4 (q, $J_{CF}$ = 34.3 Hz), 125.15 (q, $J_{CF}$ = 279.2 Hz), 121.9, 99.6, 22.7. $^{19}F$ NMR (188 MHz, $C_6D_6$): $\delta$ −61.42. High-resolution mass spectrum: calcd for $C_{19}H_{17}N_2F_6$ 387.1296, found (EI) 387.1282. IR (KBr disk): 3036, 3054, 1652, 1611, 1564, 1387, 1326, 1281, 1193, 1089, 1065, 854, 829, 769, 587 $cm^{-1}$.

**Synthesis of (PhNC(Me)CHC(Me)NPh)Zr($CH_2$Ph)$_3$ (1a).** To a stirred solution of $Zr(CH_2Ph)_4$ (0.302 g, 0.66 mmol) in toluene was added a toluene solution of **3a** (0.157 g, 0.628 mmol). The reaction mixture was stirred with exclusion of light for 8 h at room temperature, and the resulting orange solution was concentrated to dryness in vacuo. The resulting orange oil was extracted with hexane. The hexane solution was concentrated and cooled to −40 °C which resulted in the precipitation of complex **1a** as a yellow solid. The solid was collected by filtration and dried by blowing with nitrogen gas (yield 0.284 g, 60%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 7.07 (m, 10H, N**Ph**), 6.90 (m, 5H, $CH_2$**Ph**), 6.72 (m, 10H, N**Ph**, $CH_2$**Ph**), 5.01 (s, 1H, PhNC(Me)C**H**C(Me)NPh), 2.60 (s, 6H, C**H**$_2$Ph), 1.51 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 160.1, 146.1, 146.04, 128.9, 128.4, 127.2, 126.0, 125.4, 121.5, 101.3, 75.4, 21.31. Anal. Calcd for $C_{38}H_{38}N_2Zr$: C, 71.08; H, 6.23. Found: C, 71.35; H, 6.09. IR (KBr disk): 3060, 3038, 1633, 1593, 1543, 1483, 1449, 1483, 1449, 1373, 1282, 1203, 1117, 1070, 1023, 743, 698, 521 $cm^{-1}$.

**(PhNC(Me)CHC(Me)NPh)Zr($NMe_2$)$_3$ and (*p*-$CF_3$PhNC(Me)CHC(Me)NPh-*p*-$CF_3$)Zr($NMe_2$)$_3$ (1b,c).** A common procedure was employed for the syntheses of these zirconium

(19) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E.; Samuel, E. *J. Organomet. Chem.* **1987**, *327*, 39.

(20) (a) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. (b) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Ress, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290. (c) Lauer, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (d) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (e) Bush, M. A.; Sinn, G. A. *J. Chem. Soc. A* **1971**, 2225.

(21) The nitrogen atoms in the acyclic bis(ketenimine) ligand will lower the energy of the $\pi$-orbitals on N, and indirectly those on adjacent C atoms, compared with an analogous all-C $\pi$ system.

(22) (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) Bleeke, J. R.; Earl, P. L. *Organometallics* **1989**, *8*, 2735. (c) Freeman, J. W.; Hallinan, N. C.; Arif, A. M.; Gedridge, R. W.; Ernst, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1991**, *113*, 6509. (d) Hyla-Kryspin, I.; Waldman, T. E.; Melendez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030.

(23) (a) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *J. Organomet. Chem.* **1973**, *57*, 269.

(24) (a) Bradley, D. C.; Thomas, I. M. *Proc. Chem. Soc., London* **1959**, 225. (b) Bradley, D. C.; Thomas, I. M. *Proc. Chem. Soc., London* **1960**, 3857.

tris(amido) complexes. In each case, 0.374 g (2.8 mmol) of $Zr(NMe_2)_4$ was dissolved in toluene (30 mL). One equivalent of the corresponding bis(ketenimine) ligand **3a** or **3b**, also dissolved in toluene (10 mL), was added to the solution containing the zirconium amide complex, and the solution was stirred for 10 min. During this period, the solution turned from pale yellow to bright yellow. Once the completion of the reaction was ascertained from an NMR spectrum of the reaction mixture, the solution was evacuated to dryness to leave a orange solid. Extraction of the solid with pentane, filtration through Celite, and concentration of the extract precipitated bright yellow, microcrystalline solids. Further precipitation was accomplished by cooling the mixture to −40 °C for 10 h. The supernatant was syringed off and discarded, and the orange solids were pumped to dryness. Yields ranged from 70 to 83%.

Data for **1b** are as follows. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.13 (d, $J_{HH}$ = 8.3 Hz, 4H), 6.90 (t, $J$ = 8.3 Hz, 2H), 6.70 (d, $J_{HH}$ = 8.3 Hz, 4H), 5.02 (s, 1H, PhNC(Me)C**H**C(Me)NPh), 2.73 (s, 18H, N**Me**$_2$), 1.75 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$): $\delta$ 164.6, 160.0, 128.65, 125.41, 124.19, 100.40, 42.46, 24.39. Anal. Calcd for $C_{23}H_{35}N_5Zr$: C, 58.30; H, 7.44; N, 14.78. Found: C, 57.98; H, 7.28; N, 14.60. IR (KBr disk): 2822, 2758, 1631, 1593, 1558, 1513, 1482, 1450, 1383, 1258, 1184, 1160, 1022, 959, 939, 832, 752, 700, 524 cm$^{-1}$.

Data for **1c** are as follows. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.45 (d, $J_{HH}$ = 10 Hz, 4H, N($C_6$**H**$_4$CF$_3$)), 6.56, (d, $J_{HH}$ = 10 Hz, 4H, N($C_6$**H**$_4$CF$_3$)), 5.02 (s, 1H, *p*-$CF_3C_6H_4$NC(Me)C**H**C(Me)-$NC_6H_4$-*p*-$CF_3$), 2.58 (s, 18H, N**Me**$_2$), 1.55 (s, 6H, *p*-$CF_3C_6H_4$-NC(**Me**)CHC(**Me**)$NC_6H_4$-*p*-$CF_3$). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$): $\delta$ 164.7, 153.7, 126.5 (q, $J_{CF}$ = 52.8 Hz), 125.5 (q, $J_{CF}$ = 253.5 Hz), 125.0, 123.3, 100.6, 41.9, 24.2. $^{19}$F NMR (188 MHz, $C_6D_6$): $\delta$ 62.12. Anal. Calcd for $C_{25}H_{33}N_5F_6Zr$: C, 49.29; H, 5.46. Found: C, 49.25; H, 5.50. IR (KBr): 1655, 1610, 1561, 1386, 1325, 1284, 1167, 1108, 1065, 855 cm$^{-1}$.

**Synthesis of (PhNC(Me)CHC(Me)NPh)ZrCl$_3$ (1d).** A solution of $Me_3SiCl$ (0.068 g, 0.63 mmol) in hexane (10 mL) was added dropwise to a toluene solution of **1b** (0.100 g, 0.21 mmol) at room temperature. The yellow solution was then heated at 60 °C for 24 h, resulting in the formation of a yellow slurry. The slurry was cooled to −35 °C, and the solid was collected by filtration, washed with hexane, and dried under vacuum. The yield was 75%. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.10 (m, 10H, NPh), 4.80 (s, 1H, PhNC(Me)C**H**C(Me)NPh), 1.84 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}$C{$^1$H} NMR (75 MHz, THF-$d_8$): $\delta$ 168.4, 148.1, 129.5, 128.9, 127.1, 107.5, 24.6. Anal. Calcd for $C_{17}H_{17}N_2Cl_3Zr$: C, 45.68; H, 3.85; N, 6.26. Found: C, 45.38; H, 4.34; N, 6.24. IR (KBr disk): 2590, 1995, 1580, 1528, 1495, 1482, 1361, 1286, 1197, 1028, 744, 686, 475, 434 cm$^{-1}$.

**Synthesis of (*p*-$CF_3C_6H_4$NC(Me)CHC(Me)$NC_6H_4$-*p*-$CF_3$)-ZrCl$_3$·NHMe$_2$ (1e).** Three equivalents of solid $NHMe_2$·HCl (2.4 mmol) was added to a solution of **1c** (506 mg, 0.796 mmol) dissolved in 20 mL of THF. The solution was stirred overnight, affording a yellow slurry. The yellow solid was collected by filtration, washed with hexane, and dried under vacuum. Yield: 80% (400 mg). $^1$H NMR (250 MHz, THF-$d_8$): $\delta$ 7.65 (d, $J$ = 8 Hz, 4H, N($C_6$**H**$_4$CF$_3$)), 7.30 (d, $J$ = 8 Hz, 4H, N($C_6$**H**$_4$-$CF_3$)), 5.69 (s, 1H, *p*-$CF_3C_6H_4$NC(Me)C**H**C(Me)$NC_6H_4$-*p*-$CF_3$), 3.10 (br s, 1H, N**H**Me$_2$), 2.26 (br s, 6H, NH**Me**$_2$) 1.70 (s, 6H, *p*-$CF_3C_6H_4$NC(**Me**)CHC(**Me**)$NC_6H_4$-*p*-$CF_3$). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$) $\delta$ 165.6, 155.3, 129.6, 127.7 (q, $J_{CF}$ = 234 Hz), 126.5 (q, $J_{CF}$ = 37.5 Hz): 124.19, 115.4, 44.3, 25.0. $^{19}$F NMR (188 MHz, $C_6D_6$): $\delta$ −62.12. Anal. Calcd for $C_{21}H_{22}N_3F_6Cl_3Zr$: C, 40.16; H, 3.53; N, 6.69. Found: C, 39.37; H, 3.68; N, 7.81. IR (KBr disk): 3035, 2950, 1608, 1528, 1378, 1323, 1284, 1167, 1116, 1065, 1015, 943, 876 cm$^{-1}$.

**Synthesis of *cis*-(PhNC(Me)CHC(Me)NPh)$_2$Zr(NMe$_2$)$_2$ (2b).** This complex was prepared by dissolving $Zr(NMe_2)_4$ (0.187 g, 1.4 mmol) in toluene and adding 2 equiv of **3a** (0.7 g, 2.8 mmol), also dissolved in toluene. The resulting bright yellow solution was stirred at 92 °C for 24 h, after which time it was evacuated to dryness. The gummy yellow solid residue was then washed with hexane. The solid was then redissolved in toluene and filtered through a $^1/_2$ in. pad of Celite to give a clear yellow solution. Concentrating the toluene solution under vacuum and cooling to −40 °C for 12 h yielded a bright yellow microcrystalline solid, which was separated by filtration (yield 0.757 g, 80%). $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.10 (m, 14H, N**Ph**), 6.85 (m, 4H, N**Ph**), 5.80 (d, $J_{HH}$ = 8.0 Hz, 2H, NPh *o*-H), 5.10 (s, 2H, PhNC(Me)C**H**C(Me)NPh), 2.50 (br s, 12H, N**Me**$_2$), 1.70 (s, 6H, PhNC(**Me**)CHC(Me)NPh), 1.41 (s, 6H, PhNC(Me)CHC(**Me**)NPh). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$): $\delta$ 164.9, 164.1, 153.2, 150.2, 128.1, 127.9, 127.1, 126, 124.9, 124.1, 100.1, 47.1, 25.2, 25.4. Anal. Calcd for $C_{38}H_{46}N_6Zr$: C, 67.28; H, 6.83; N, 12.39. Found: C, 67.35; H, 6.61; N, 12.18. IR (KBr disk): 1630, 1550, 1436, 1375, 1278, 1186, 1071, 1025, 950, 804, 748, 698 cm$^{-1}$.

**Synthesis of *cis*-(PhNC(Me)CHC(Me)NPh)$_2$ZrCl$_2$ (2d).** Complex **2b** (0.225 g, 0.332 mmol) was dissolved in toluene (10 mL) and was added to a slurry of $[Me_2NH_2][Cl]$ (0.054 g, 0.664 mmol) at room temperature. The mixture was stirred for 24 h at 55 °C. At the end of this period, the cloudy mixture was pumped to dryness. The solid residues were dissolved in a large volume of toluene at 50 °C, and this solution was filtered through Celite to give a clear yellow solution. Concentration of the filtrate yielded bright yellow crystals (0.29 g, 90% yield) of the title compound. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 6.90 (m, 20 H, NPh), 5.10 (s, 2H, PhNC(Me)C**H**C(Me)NPh), 1.45 (s, 12H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}$C{$^1$H} NMR (75 MHz, THF-$d_8$): $\delta$ 167.0, 150.2, 130.3, 128.1, 125.3, 105.2, 25.2. Anal. Calcd for $C_{34}H_{34}N_4Cl_2Zr$: C, 61.79; H, 5.18; N, 10.72. Found: C, 61.54; H, 5.21; N, 10.51. IR (KBr disk): 1597, 1529, 1484, 1442, 1368, 1300, 1256, 1205, 1180, 1072, 1024, 929, 836, 795, 755, 710, 698 cm$^{-1}$.

**Synthesis of *cis*-(PhNC(Me)CHC(Me)NPh)$_2$ZrMe$_2$ (2e) and *cis*-(PhNC(Me)CHC(Me)NPh)$_2$ZrBn$_2$ (2f).** To 150 mg (0.22 mmol) of **2d** dissolved in 2 mL of toluene was added 2 equiv of MeLi (185 $\mu$L of 1.2 M solution). After 10 min the yellow solution became a clear orange solution. The toluene solution was removed under vacuum to give an orange solid. The solid was extracted with hexane and filtered, and the crude product **2e** was recrystallized from hexane or dichloromethane. A similar procedure was followed for synthesizing benzyl derivative **2f** using $PhCH_2MgCl$ as the alkylating agent (yield 75−85%).

Data for **2e** are as follows. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.15 (d, $J_{HH}$ = 8.2, 8H, N**Ph**), 6.90 (t, $J_{HH}$ = 8.2, 4H, N**Ph**), 6.62 (d, $J_{HH}$ = 8.2, 8H, N**Ph**), 4.90 (s, 2H, PhNC(Me)C**H**C(Me)NPh), 1.50 (s, 12H, PhNC(**Me**)CHC(**Me**)NPh), 1.32 (s, 6H, Zr**Me**$_2$). $^{13}$C{$^1$H} NMR (75 MHz, THF-$d_8$): $\delta$ 165.0, 150.8, 129.0, 128.7, 125.1, 106.7, 53.9, 25.0. Anal. Calcd for $C_{36}H_{40}N_4Zr$·$^1/_6CH_2Cl_2$: C, 68.45; H, 6.38. Found: C, 68.32; H, 6.28. IR (KBr disk): 1631, 1595, 1544, 1484, 1439, 1373, 1277, 1184, 1023, 827, 750, 699, 497 cm$^{-1}$.

Data for **2f** are as follows. $^1$H NMR (250 MHz, $C_6D_6$): $\delta$ 7.20 (m, 6H, N**Ph**), 7.05 (m, 8H, N**Ph**), 6.90 (m, 10H, $CH_2$**Ph**), 6.50 (m, 6H, N**Ph**), 5.05 (s, 2H, PhNC(Me)C**H**C(Me)NPh), 2.50 (s, 4H, Zr−C**H**$_2$Ph), 1.42 (s, 12H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}$C{$^1$H} NMR (75 MHz, THF-$d_8$): $\delta$ 165.1, 153.5, 129.3, 127.6, 127.5, 127.3, 125.4, 120.3, 103.1, 93.2, 85.6, 25.5. Anal. Calcd for $C_{48}H_{48}N_4Zr$: C, 74.62; H, 6.26; N, 7.20. Found: C, 74.42; H, 6.21; N, 7.15. IR (KBr disk): 3054 (w), 1636, 1590, 1533, 1482, 1442, 1389, 1254, 1203, 1181, 1025, 990, 935, 827, 798, 748, 702, 514 cm$^{-1}$.

**Synthesis of (PhNC(Me)CHC(Me)NPh)($\eta^5$-Cp)ZrCl$_2$ (4a).** To a stirred solution of **1d** (400 mg, 0.89 mmol) in benzene (50 mL) was added solid CpNa (88 mg, 0.98 mmol) over 30 min. After the solution was stirred for 24 h, the reaction mixture was filtered and the pale yellow filtrate evaporated to give a light yellow solid. The compound was recrystallized from toluene. Yields ranged from 70 to 83%. $^1$H NMR (250

MHz, $C_6D_6$): $\delta$ 6.96 (m, 10H, N**Ph**), 6.16, (s, 5H, **CpH**), 5.23 (s, 1H, PhNC(Me)C**H**C(Me)NPh), 1.70 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 164.0, 150.4, 129.1, 126, 124.2, 117.2, 90.8, 22.0. Anal. Calcd for $C_{22}H_{22}Cl_2N_2Zr\cdot{}^1/_3C_6H_6$: C, 57.35; H, 4.81; N, 5.57. Found: C, 57.44; H, 4.51; N, 5.62. IR (KBr): 1592, 1534, 1483, 1392, 1291, 1237, 1188, 1072, 1020, 825, 755, 706, 690 $cm^{-1}$.

**Synthesis of (PhNC(Me)CHC(Me)NPh)($\eta^5$-$C_9H_7$)$ZrCl_2$ (4b).** This compound was synthesized in a manner analogous to that described above (yield 80%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 7.55 (m, 4H, $H_4-H_7$ of the indene ring), 7.00 (m, 10H, N**Ph**), 6.25 (d, $J_{HH}$ = 2.3 Hz, 2H, $H_1$ and $H_3$ of the indenyl ring), 6.05 (t, $J$ = 2.3 Hz, 1H, $H_2$), 4.90 (s, 1H, PhNC(Me)-C**H**C(Me)NPh), 1.70 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh). $^{13}C\{^1H\}$ NMR (75 MHz, THF-$d_8$): $\delta$ 164.5, 151.1, 129.8, 127.8, 127.3, 126.8, 126.0, 125.1, 121.4, 106.6, 89.9, 22.4. Anal. Calcd for $C_{33}H_{24}N_2Cl_2Zr$: C, 59.10; H, 5.00; N, 5.32. Found: C, 59.25; H, 4.60; N, 5.32. IR (KBr disk): 3050, 3100, 1593, 1484, 1450, 1395, 1237, 1022, 831, 754, 703, 454 $cm^{-1}$.

**Synthesis of (*p*-$CF_3C_6H_4NC(Me)CHC(Me)NC_6H_4$-*p*-$CF_3$)($\eta^5$-Cp)$ZrCl_2$ (4c).** A 320 mg (0.51 mmol) amount of **1e** was slurried in 30 mL of benzene. Solid NaCp (49 mg, 0.55 mmol) was added in portions over 15 min, and the slurry of the complex was stirred overnight. A color change from yellow to orange was observed over 24 h, and the reaction mixture was then filtered. The orange filtrate was evaporated to provide a yellow-orange solid. Recrystallization from toluene at −35 °C yielded a pure yellow-orange, crystalline solid (185 mg, yield 60%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 7.32 (d, $J$ = 10 Hz, 2H, N($C_6$**H**$_4CF_3$)), 6.90 (d, $J$ = 10 Hz, 2H, N($C_6$**H**$_4CF_3$)), 6.00 (s, 5H, CpH), 5.11 (s, 1H, *p*-$CF_3C_6H_4NC(Me)C$**H**$C(Me)NC_6H_4$-*p*-$CF_3$) 1.60 (s, 6H, *p*-$CF_3$PhNC(**Me**)CHC(**Me**)NPh*p*-$CF_3$). $^{13}C\{^1H\}$ NMR (75 MHz, THF-$d_8$) $\delta$ 165.6, 154.3, 128.0 (q, $J_{CF}$ = 32.2), 127.5 (q, $J_{CF}$ = 272.2), 127.2, 125.8, 117.9, 92.5, 22.5. $^{19}F$ NMR (188 MHz, $C_6D_6$): $\delta$ −62.32. Anal. Calc′d for $C_{24}H_{20}N_2Cl_2F_6Zr$: C, 47.06; H, 3.29; N, 4.57. Found: C, 47.10; H, 3.45; N, 4.35. IR (KBr disk): 3027, 2875, 2800, 1610, 1537, 1504, 1406, 1321 $cm^{-1}$.

**Synthesis of (PhNC(Me)CHC(Me)NPh)($\eta^5$-Cp)$ZrMe_2$ (4d).** Compound **4a** (600 mg, 1.25 mmol) was dissolved in 100 mL of benzene and was allowed to react with 2 equiv of MeLi (1.79 mLof 1.4 M solution in ether) for 3 h at room temperature. The light yellow reaction mixture turned brown. The solution was filtered through Celite and the solvent was removed under reduced pressure, yielding an orange solid. The yellow solid residue was extracted with hexane, and cooling the hexane extract at −10 °C produced **4d** as an orange microcrystalline solid (300 mg, yield 60%). $^1H$ NMR (250 MHz, $C_6D_6$): $\delta$ 7.35 (d, 4H, $J_{HH}$ = 8.3, N**Ph**), 7.29 (t, 2H, $J_{HH}$ = 8.3, N**Ph**), 7.13 (d, 4H, $J_{HH}$ = 8.3, N**Ph**), 6.24, (s, 5H, CpH), 5.60 (s, 1H, PhNC(Me)C**H**C(Me)NPh), 1.54 (s, 6H, PhNC(**Me**)CHC(**Me**)NPh), 0.46 (s, 6H, Zr**Me**$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$): $\delta$ 161.7, 150.9, 128.9, 124.8, 124.6, 113.1, 94.0, 27.0, 22.3. Anal. Calcd for $C_{24}H_{28}N_2Zr$: C, 66.17; H, 6.47; N, 6.23. Found: C, 66.37; H, 6.38; N, 6.13. IR (KBr disk): 1620, 1550, 1383, 1312, 1191, 1184, 1088, 1074, 925, 854 $cm^{-1}$.

**Synthesis of (*p*-$CF_3C_6H_4$PhNC(Me)CHC(Me)$NC_6H_4$-*p*-$CF_3$)($\eta^5$-Cp)$ZrMe_2$ (4e).** A similar procedure was followed, as described above for the preparation of **4d**, using **4c**. Yield: 65%. $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 7.35 (d, $J_{HH}$ = 10 Hz, 2H, N($C_6$**H**$_4CF_3$)), 6.55 (d, $J_{HH}$ = 10 Hz, 2H, N($C_6$**H**$_4CF_3$)), 6.82 (s, 5H, CpH), 5.30 (s, 1H, *p*-$CF_3C_6H_4NC(Me)C$**H**$C(Me)NC_6H_4$-*p*-$CF_3$), 1.54 (s, 6H, *p*-$CF_3C_6H_4NC$(**Me**)CHC(**Me**)$NC_6H_4$-*p*-$CF_3$), 0.43 (s, 6H, Zr**Me**$_2$). $^{13}C\{^1H\}$ NMR (THF-$d_8$): $\delta$ 162.5, 153.7, 126.2 (q, $J_{CF}$ = 34.0 Hz), 124.7 (q, $J_{CF}$ = 272 Hz), 122.7, 115.1, 113.2, 94.3, 27.0, 23.3. $^{19}F$ NMR (188 MHz, $C_6D_6$): $\delta$ −62.09. Anal. Calcd for $C_{26}H_{26}N_2F_6Zr$: C, 54.63; H, 4.58; N, 4.90. Found: C, 54.57; H, 4.32; N, 4.78. IR (KBr disk): 2920, 2862, 1610, 1538, 1502, 1395, 1323, 1240, 1166, 1117, 1066, 1012, 873, 805, 737, 691, 598, 550, 458 $cm^{-1}$.

**X-ray Structure Determinations.** Selected crystallographic and refinement data appear in Table 5 for compounds **2b**,**d** and **4b**. In all cases, a suitable single crystal was glued to a glass fiber using epoxy resin, and the fiber was then mounted on a Siemens P4 diffractometer. Unit cell parameters were determined and refined from a set of 25 general reflections ($20.0 < 2\theta < 30.0°$) well distributed in reciprocal space.

Intensity data were collected using graphite-monochromated Mo K$\alpha$ radiation at the temperature indicated in Table 5 by employing the $\omega$-scan technique over the $2\theta$ range indicated in Table 5 with variable scan speeds (3.00−30.00° $min^{-1}$) and a 1.20° scan width. Background measurements using the stationary crystal, stationary counter method were made at the beginning and end of each scan, each for 25% of the total scan time. Three standard reflections were measured after every 100 reflections and showed no significant loss in intensity during data acquisition.

Intensities were corrected for Lorentz and polarization effects. A face-indexed numerical method was employed to correct for adsorption effects in all cases. Collected, independent and observed reflections ($F > 6.0\sigma(F)$) are summarized in Table 5, and the last group was used in the structure solution and refinement. The minimum and maximum transmission factors through the crystals were calculated to be 0.8771 and 0.9367, 0.8519 and 0.8947, and 0.7967 and 0.8843 for **2b**,**d** and **4b**, respectively.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques using the Siemens SHELXTL PLUS software. Anisotropic refinement of all non-H atoms allowed location of all hydrogen atoms from a difference map in all cases. In the final cycles of refinement, the hydrogens were included at their found positions and were refined isotropically.

Scattering factors for non-hydrogen atoms were taken from ref 25, while the data of Stewart et al.[26] were used for hydrogen atoms. Full details of the crystallographic data, solution, and refinement, as well as atomic coordinates, thermal parameters, and bond lengths and angles are included in the Supporting Information.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council and Nova Chemicals Ltd. for financial support of this work. We also acknowledge the donation of $B(C_6F_5)_3$ and [DMANH][$B(C_6F_5)_4$] by Nova Chemicals Ltd and BFGoodrich Co., respectively.

**Supporting Information Available:** Tables of crystallographic data, atomic coordinates with isotropic thermal coefficients, bond lengths, bond angles, anisotropic thermal coefficients, and H-atom coordinates and isotropic thermal coefficients for compounds **2b**,**d** and **4b** (25 pages). Ordering information is given on any current masthead page.

OM970862H

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