Double Isocyanide Insertion and C,C-Coupling Reaction of [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe₂. Structural Characterization of the Two 1,4-Diaza-5-zirconacyclopentene Ring Conformations for [(C₅Me₄)SiMe₂(N-t-Bu)]Zr[N(R)C(Me)=C(Me)N(R)]

Complexes

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The reactions of 2 equiv of CNR (R = (**a**) *tert*-butyl, (**b**) 2,6-xylyl, (**c**) Me) with $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrMe_2$, **1**, proceed sequentially with isocyanide insertion into both Zr-C(methyl) bonds of this 14-electron complex to give the corresponding η^2 -iminoacyl Zr complexes $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrMe[\eta^2-C(Me)NR]$, **2**, and $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[\eta^2-C(Me)NR]_2$, **3**. Subsequent thermolysis of **3** leads to C,C-coupling of the two η^2 -iminoacyl units and proceeds solely with formation of the enediamidate derivative $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrME_2(N-t-Bu)]ZrMe_2(N-t-Bu)]ZrMe_2(N-t-Bu)]$

t-Bu)]Zr[N(R)C(Me)=C(Me)N(R)], **4**. Compounds **2a**, **3a**-**c**, and **4a**-**c** have been observed and characterized by solution NMR measurements, and the molecular structures of **3a**, **3b**, **4a**, and **4b** have been confirmed by crystallographic methods. The nonplanar 1,4-diaza-5zirconacyclopentene rings of **4a** and **4b** are folded by *ca*. 50° in opposite directions along the corresponding N···N line segment and adopt the prone and supine conformations, respectively. The activation parameters for the first-order intramolecular C,C-coupling reaction leading to the conversion of **3a** \rightarrow **4a** are $\Delta H^{\ddagger} = 24.6(2)$ kcal/mol and $\Delta S^{\ddagger} = -11.3(7)$ eu and of **3b** \rightarrow **4b** are $\Delta H^{\ddagger} = 23.9(3)$ kcal/mol and $\Delta S^{\ddagger} = -10.4(8)$ eu.

Introduction

Reactivity studies of the transition-metal-mediated reductive coupling of isocyanides by an electrophilic group 4 metal complex have uncovered two primary reaction mechanisms associated with this C–C bond forming reaction. From their studies of a series of bis(η^2 -iminoacyl)aryloxide complexes, M(OAr)₂[η^2 -C-(R')NR]₂ (M = Ti, Zr, Hf), Rothwell and co-workers¹ observed that these compounds upon thermolysis undergo an intramolecular coupling of the two η^2 -iminoacyl groups to produce the cyclic enediamidate complexes, M(OAr)₂[N(R)C(R')=C(R')N(R)] (eq 1). Our investiga-



tions of the reductive coupling of isocyanides by "stabilized" group 4 metallacyclobutane complexes, $(C_5R_5)_2$ - $M(CH_2SiMe_2CH_2)$ (M = Zr,² Hf;³ R = H, Me) revealed

In the former case an isocyanide inserts sequentially into both M–C(alkyl) bonds, whereas in the latter case the electrophilic character of the η^2 -iminoacyl carbon

 $Cp' = C_5H_5$, C_5Me_5 ; M = Zr, Hf; R = H, Me

that this reaction proceeds via an unusual double insertion reaction that involves the participation of η^2 -

iminoacyl and η^2 -iminoacyl imine intermediates (eq 2).

CNCR₃

Me

Me

(2)

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at this carbenium-type⁴ carbon center. Isocyanide insertion into the remaining metal–carbon bond of the η^2 -iminoacyl intermediate is not observed. Similarly, isocyanide insertion into only one metal–carbon bond occurs for the related d⁰ Zr(IV) complexes (C₅R₅)₂-Zr(alkyl)₂, R = H, Me.⁵

The observed differences in these two C,C-coupling pathways are primarily a consequence of the level of coordinative unsaturation at the early transition metal center in the 12-electron bis(aryloxide) complexes, $M(OAr)_2R'_2$, and in the 16-electron $(C_5R_5)_2Zr(alkyl)_2$ and $(C_5R_5)_2M(CH_2SiMe_2CH_2)$ complexes. The presence of only one vacant metal orbital in these 16-electron complexes led us to hypothesize that a prerequisite for the direct coupling of two iminoacyl fragments is the availability of a minimum of two vacant orbitals at the

electrophilic d⁰ group 4 metal center.⁶ Several years ago, Bercaw and co-workers7 demonstrated that the incorporation of the bifunctional ansamonocyclopentadienylamido ligand [(C5Me4)SiMe2(N-t-Bu)]^{2–} provides an effective strategy for enhancing the Lewis acidity of d⁰ organoscandium complexes. Replacement of a permethylated cyclopentadienyl ring with an appended amido functionality simultaneously reduces steric crowding and lowers the metal's formal electron count by two, thus generating another vacant metal orbital. Researchers at Dow Chemical Co. and Exxon later independently found that the corresponding d⁰ group 4 metal complexes $[(\eta^5 - C_5 R_4)SiR'_2(\eta^1 - NR'')]ML_2$ (M = Ti, Zr, Hf; R = H, alkyl; R', R'' = alkyl, aryl; L =Cl, Me) in the presence of excess methylalumoxane provide commercially viable Ziegler-Natta catalysts for the copolymerization of ethylene and 1-alkenes.⁸

Although the spotlight on 14-electron *ansa*-monocyclopentadienylamido group 4 metal complexes, such as $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrMe_2$, remains primarily focused on their industrial application, far less in known about their reactivity with unsaturated substrates.⁹ To provide an operational test of our working hypothesis, we have undertaken an investigation of the migratory insertion reaction of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrMe_2$, **1**, with various isocyanides. We have found that these reactions indeed proceed with the formation of the

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corresponding bis(η^2 -iminoacyl) complexes [(C₅Me₄)Si-Me₂(N-t-Bu)]Zr[η^2 -C(Me)NR]₂, **3**, which upon thermolysis rearrange to the enediamido isomer [(C₅Me₄)SiMe₂(N-t-Bu)]Zr[N(R)C(Me)=C(Me)N(R)], **4**. Specific details regarding the relevant kinetic and structural aspects of the migratory insertion and intramolecular isocyanide coupling reactions displayed by [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe₂ are described herein.

Experimental Section

Reagents. Reagent grade hydrocarbon and ethereal solvents were purified using standard methods and distilled under nitrogen. Na/K alloy was used to dry pentane, toluene, and tetrahydrofuran. These dried solvents were then transferred to storage flasks containing $[(C_5H_5)_2Ti(\mu-Cl)_2]_2Zn^{10}$ and were freshly distilled prior to use. Hexamethyldisiloxane and diethyl ether were dried over CaH₂. Chlorinated solvents were distilled from P₄O₁₀. The deuterated solvents, C₆H₆-d₆ (Aldrich, 99.5%) and CDCl₃ (Aldrich, 99.8%), were dried over activated 4 Å molecular sieves prior to use; tert-butyl isocyanide (Aldrich), t-butylamine (Aldrich), and SiMe₂Cl₂ (Hüls) were also stored over 4 Å molecular sieves and then introduced by vacuum transfer. Methyllithium (Aldrich, 1.4 M in diethyl ether) and 2,6-xylyl isocyanide (Fluka) were used as received, whereas CNMe¹¹ and [(C₅Me₄)SiMe₂(N-t-Bu)]ZrCl₂¹² were prepared employing literature procedures.

General Considerations. All manipulations and reactions were carried out on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train. Air- and moisture-sensitive compounds were synthesized using pressure equalizing filter frits equipped with high-vacuum Teflon stopcocks. Nitrogen was purified by passage over reduced BTS catalysts and activated 4 Å molecular sieves. All glassware was thoroughly oven-dried or flamedried under vacuum prior to use. NMR sample tubes were sealed under approximately 500 Torr of nitrogen. The NMR spectra were acquired using procedures and instrumentation that has been previously described.^{2b} The NMR assignments for the different methyl protons in 1, 3a, 3b, 4a, and 4b were made on the basis of the cross peaks observed in the corresponding HETCOR NMR spectrum. Elemental analyses were performed either by Robertson Microlit Laboratories, Madison, NJ (RML), or by E+R Microanalytical Laboratory, Corona, NY (E+R).

Synthesis of [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe₂, 1. A solution of [(C5Me4)SiMe2(N-t-Bu)]ZrCl2 (0.75 g, 1.82 mmol) in diethyl ether (50 mL) was cooled down to -78 °C. Methyllithium (3.0 mL, 4.20 mmol) was added dropwise via syringe under a N₂ flush. A white precipitate formed, and the reaction mixture was stirred overnight at room temperature. The solvent was replaced by an equal volume of pentane, and the soluble product was separated from LiCl by filtration. After removal of the pentane, sublimation (10^{-4} Torr, 60 °C) of the crude product yielded a white semicrystalline material. Yield: 0.45 g (76%). ¹H NMR (C_6H_6 - d_6): δ 1.97, 1.91 (C_5Me_4 , s), 1.40 (NCMe₃, s), 0.46 (SiMe₂, s), -0.01 (ZrMe₂, s); (CDCl₃) δ 2.08, 1.98 (C₅Me₄, s), 1.42 (NCMe₃, s), 0.44 (SiMe₂, s), -0.39 (ZrMe₂, s). ¹³C NMR (C₆H₆- d_6 , mult., ¹ J_{CH} in Hz): δ 130.2, 125.3 (proximal and distal carbons of C₅Me₄, s), 95.8 (bridgehead carbon of C₅Me₄, s), 54.9 (NCMe₃, s), 35.8 (ZrMe, q, 114), 34.4 (NCMe₃, q, 125), 14.3, 11.3 (C₅Me₄, q, 127), 6.65 (SiMe₂, q, 118). The ¹H and ¹³C NMR chemical shifts are comparable to those reported in ref 8d. Anal. Calcd for $C_{17}H_{33}$ NSiZr (370.76): C, 55.07; H, 8.97; N, 3.78. Found: C, 55.19; H, 9.15; N, 3.78 (E+R).

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Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[\eta^2-C(Me)N(t-$ **Bu**)₂, **3a.** Initially, this reaction was performed in a sealed NMR tube. Two equiv of tert-butyl isocyanide were added to a solution of 1 (0.032 g, 0.086 mmol) in benzene- d_6 . Periodic NMR measurements indicated that the reaction proceeds initially with rapid insertion of 1 equiv of CN-t-Bu to give the η^2 -iminoacyl adduct [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe[η^2 -C(Me)N(t-Bu)], 2a, and eventually the diinsertion product, 3a, by taking up the second equivalent of CN-t-Bu after 1 day. Because this double isocyanide insertion reaction yields a single product, it was repeated on a larger scale. A 25 mL pentane solution of 1 (0.90 g, 2.43 mmol) was charged with nearly 3 equiv of CN-t-Bu (0.80 mL, 7.08 mmol). The yellow reaction mixture was stirred at ambient temperature for 6 days. Following solvent removal, the product was washed with hexamethyldisiloxane (2 \times 5 mL). Slow removal of pentane from a pentane solution of 3a yielded pale yellow crystals suitable for an X-ray diffraction analysis. Isolated yield: 1.194 g (91%).

Monoinsertion product, **2a**: ¹H NMR ($C_6H_6-d_6$) δ 2.45, 2.26, 1.89 (proximal and distal protons of C₅Me₄ and η^2 -CMe, s), 1.19, 1.09 (NCMe₃, s), 0.69, 0.70 (SiMe₂, s), 0.04 (ZrMe, s). ¹³C NMR ($C_6H_6-d_6$, mult., ¹J_{CH} in Hz): δ 247.9 (η^2 -C, s), 122.3, 121.8 (proximal and distal carbons of C_5Me_4 , s), 100.2 (bridgehead carbon of C_5Me_4 , s), 62.4 (ZrN*C*Me₃, s), 54.5 (SiN*C*Me₃, s), 34.3 (SiN*CMe*₃, q, 126), 30.3 (ZrN*CMe*₃, q, 126), 23.0 (η^2 -*CMe*, q, 127), 20.2 (ZrMe, q, 113), 14.8, 11.3 (C₅Me₄, q, 126), 7.43, 7.28 (SiMe₂, q, 118).

Diinsertion product, **3a**: ¹H NMR ($C_6H_6-d_6$) δ 2.36, 1.76 (proximal and distal protons of C_5Me_4), 2.35 (η^2 -CMe, s), 1.34 (SiNCMe₃, s), 1.22 (ZrNCMe₃, s), 0.79 (SiMe₂, s). ¹³C NMR ($C_6H_6-d_6$, mult., ¹ J_{CH} in Hz): δ 246.0 (η^2 -C, s), 123.8, 122.4 (proximal and distal carbons of C_5Me_4 , s), 104.0 (bridgehead carbon of C_5Me_4 , s), 58.9 (ZrNCMe₃, s), 53.8 (SiNCMe₃, s), 36.1 (SiNCMe₃, q, 126), 30.7 (ZrNCMe₃, q, 126), 23.4 (η^2 -CMe, q, 126), 15.2, 12.0 (C_5Me_4 , q, 126), 8.94 (SiMe₂, q, 118). Anal. Calcd for $C_{27}H_{51}N_3$ SiZr (537.03): C, 60.39; H, 9.57; N, 7.82. Found: C, 60.39; H, 9.59; N, 7.67 (E+R).

Synthesis of [(C₅Me₄)SiMe₂(N-t-Bu)]Zr[N(t-Bu)C(Me)=

C(Me)N(t-Bu)], 4a. A sample of 3a (0.035 g, 0.065 mmol) was added to a NMR tube and dissolved in benzene- d_6 . Periodic ¹H NMR measurements indicated that **3a** upon heating rearranges solely to 4a. On a larger scale, a cylindrical reaction tube equipped with a high-vacuum adapter was charged with 3a (0.232 g, 0.43 mmol) and 10 mL of toluene. The solution was heated to 70 °C for 9 days. The solvent was removed, and the product was extracted with pentane to give a yellow crystalline material. Slow removal of pentane from a saturated pentane solution of 4a afforded single crystals suitable for X-ray structural analysis. Yield: 0.227 g (98%). ¹H NMR (C₆H₆- d_6): δ 2.37, 1.53 (proximal and distal methyl protons of C₅Me₄, s), 1.95 (=CMe, s), 1.37 (ZrNCMe₃, s), 1.34 (SiNCMe₃, s), 0.80 (SiMe₂, s). ¹³C NMR (C_6H_6 - d_6 , mult., ¹ J_{CH} in Hz): δ 125.0, 122.5 (proximal and distal carbons of C_5 Me₄, s), 109.0 (=C, s), 104.2 (bridgehead carbon of C₅Me₄, s), 55.9 (ZrNCMe₃, s), 55.7 (SiNCMe₃, s), 35.3 (SiNCMe₃, q, 124), 34.2 (ZrNCMe3, q, 125), 19.9 (=CMe, q, 126), 15.4, 11.5 (C5Me4, q, 126), 8.81 (SiMe₂, q, 118). Anal. Calcd for C₂₇H₅₁N₃SiZr (537.03): C, 60.39; H, 9.57; N, 7.82. Found: C, 60.18; H, 9.66; N, 7.63 (RML).

Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[\eta^2-C(Me)N(2,6-xylyl)]_2$, **3b**. A NMR tube was charged with **1** (0.030 g, 0.081 mmol) and 2,6-xylyl isocyanide (0.027 g, 0.206 mmol). The solids were dissolved in deuterated chloroform. ¹H NMR measurements indicate that the isocyanide insertion reaction proceeds at ambient temperature with formation of **3b**. On a larger scale, a 25 mL pentane solution of **1** (0.72 g, 1.94 mmol) and 2,6-xylyl isocyanide (0.60 g, 4.57 mmol) was stirred at ambient temperature for 9 days. The solvent was filtered, and the product was washed with pentane (2 × 25 mL), yielding **3b** as a white powder. Slow removal of solvent from a toluene solution yielded single crystals suitable for X-ray analysis.

Yield: 0.984 g (80%). ¹H NMR (CDCl₃): δ 6.96–6.90 (*meta* and *para* CH, m), 2.30, 1.97 (proximal and distal methyl protons of C₅Me₄, s), 1.93, 1.63 (methyl protons of 2,6-xylyl groups, s), 2.18 (η^2 -CMe, s), 0.96 (NCMe₃, s), 0.51 (SiMe₂, s). ¹H NMR (C₆H₆-*d*₆): δ 6.91–6.85 (*meta* and *para* CH, m), 2.37, 1.85 (proximal and distal methyl protons of C₅Me₄, s), 1.96, 1.66 (methyl protons of 2,6-xylyl groups, s), 2.02 (η^2 -CMe, s), 1.21 (NCMe₃, s), 0.79 (SiMe₂, s). ¹³C NMR (CDCl₃, mult., ¹*J*_{CH} in Hz): δ 251.8 (η^2 -*C*, s), 147.2 (N*C*, s), 129.2, 128.6 (xylyl-CMe, s), 127.9, 127.7, 124.3 (*meta* and *para* CH, d, 156, 156, 160), 123.5, 122.8 (proximal and distal carbons of C₅Me₄, s), 104.8 (bridgehead carbon of C₅Me₄, s), 55.0 (N*C*Me₃, s), 35.5 (NC*Me*₃, q, 124), 23.8 (η^2 -C*Me*, q, 126), 19.7, 17.6 (xylyl-C*Me*, q, 127), 14.6, 11.6 (C₅*Me*₄, q, 126), 8.09 (SiMe₂, q, 118). Anal. Calcd for C₃₅H₅₁N₃SiZr (633.12): C, 66.40; H, 8.12; N, 6.64. Found: C, 66.48; H, 8.22; N, 6.60 (E+R).

Synthesis of [(C5Me4)SiMe2(N-t-Bu)]Zr[N(2,6-xylyl)C-

(Me)=C(Me)N(2.6-xvlvl)]. 4b. A NMR tube containing the solution of 3b in deuterated chloroform was heated in an oil bath at 75 °C. Periodic ¹H NMR measurements revealed that 3b rearranges solely to 4b. On a larger scale, a cylindrical reaction tube equipped with a high-vacuum adapter was charged with 3b (0.235 g, 0.371 mmol) and toluene (10 mL). The solution was stirred at 70 °C for 2 days. After the solvent was removed, the product residue was washed with pentane (5 mL). Yellow single crystals of 4b suitable for X-ray diffraction studies were obtained by slow removal of the solvent from a saturated toluene solution. Yield: 0.167 g (71%). ¹H NMR (CDCl₃): δ 7.12-6.92 (meta and para CH, m), 2.37 (=CMe, s), 1.97, 1.36 (C₅Me₄, s), 1.88, 1.68 (xylyl-CMe, s), 1.07 (NCMe₃, s), 0.62 (SiMe₂, s). ¹³C NMR (CDCl₃, mult., ¹ J_{CH} in Hz): δ 148.3 (xylyl-NC, s), 134.5, 132.9 (xylyl-CMe, s), 128.6, 128.2 (proximal and distal carbons of C_5 Me₄, s), 128.0, 127.6, 123.6 (meta and para CH, d, 156, 154, 160), 112.8 (=C, s), 100.1 (bridgehead carbon of C₅Me₄, s), 55.6 (NCMe₃, s), 34.4 (NCMe₃, q, 125), 21.8 (=CMe, q, 126), 19.4, 17.0 (xylyl-CMe, q, 127), 13.6, 9.56 (C₅Me₄, q, 127), 8.34 (SiMe₂, q, 118). Anal. Calcd for C₃₅H₅₁N₃SiZr (633.12): C, 66.40; H, 8.12; N, 6.64. Found: C, 66.34; H, 8.22; N, 6.59 (E+R).

Reductive Coupling of CNMe. A NMR sample tube equipped with a calibrated gas bulb was charged with 1 (0.030 g, 0.081 mmol) and benzene- d_6 . Two equivalents of methyl isocyanide were then introduced. The reaction mixture turned dark brown after a few hours. NMR measurements confirmed the formation of the bis(η^2 -iminoacyl) product **3c**, which gives a characteristic downfield ¹³C NMR resonance at δ 242.2. ¹H NMR (C₆H₆-d₆): δ 2.79 (NMe, s), 2.28, 1.97, 1.79 (proximal and distal methyl protons of C₅Me₄ and η^2 -CMe, s), 1.37 (NCMe₃, s), 0.77 (SiMe₂, s). ${}^{13}C{}^{1}H$ NMR (C₆H₆-d₆): δ 242.2 $(\eta^2$ -C), 124.0, 123.3 (proximal and distal carbons of C_5 Me₄), 90.1 (bridgehead carbon of C₅Me₄), 54.1 (NCMe₃), 35.8 (NC-*Me*₃), 35.6 (NMe), 19.6 (η^2 -C*Me*), 14.4, 11.6 (C₅*Me*₄), 8.96 (SiMe₂). Upon heating the NMR sample tube containing 3c to 65 °C, the proton NMR resonances of the η^2 -iminoacyl product 3c diminished with the formation of the enediamido isomer, **4c**. ¹H NMR (C₆H₆-d₆): δ 3.16 (NMe, s), 2.29, 1.88, 1.71 (proximal and distal protons of C_5Me_4 and =CMe, s), 1.09 (NCMe₃, s), 0.73 (SiMe₂, s).

Kinetic Measurements. The first-order thermal rearrangements of **3a** \rightarrow **4a** and of **3b** \rightarrow **4b** were followed by monitoring the loss of the intensity of the ¹H NMR resonance corresponding to the t-Bu substituents of the η^2 -iminoacyl ligands located at δ 1.22 for **3a** and the t-Bu substituent of the appended amido at δ 1.21 for **3b**. Two standard solutions were prepared by dissolving 0.537g of **3a** and 0.186 g of ferrocene in 8.773 g of C₆D₆ (0.108 M) and by adding 0.3168 g of **3b** and 0.0931 g of ferrocene to 8.332 g of C₆D₆ (0.0571 M). Appropriate aliquots taken from each solution were sealed in a series of NMR tubes. A typical kinetic run involved submerging the NMR tube in an oil bath set at an appropriate temperature (within the range 70–120 °C) maintained to ±0.1

Reaction of [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe₂

Table 1. Rate Constants for the Intramolecular Rearrangement of $3a \rightarrow 4a$ and $3b \rightarrow 4b$

ivearrai	igement of 5a 4a	
<i>T</i> , °C	k, s^{-1}	<i>t</i> _{1/2} , min
	3a → 4a	
70.0	$5.21(4) imes 10^{-6}$	2215(17)
80.0	$1.54(1) imes 10^{-5}$	750(5)
90.0	$4.40(4) imes 10^{-5}$	262(2)
100.0	$1.09(2) imes 10^{-4}$	106(2)
110.0	$2.53(2) imes 10^{-4}$	45.7(4)
120.0	$5.95(11) imes 10^{-4}$	19.4(4)
	$3b \rightarrow 4b$	
70.0	$2.26(6) imes 10^{-5}$	511(14)
80.0	$6.60(8) \times 10^{-5}$	175(2)
90.0	$1.67(2) \times 10^{-4}$	69.4(8)
100.0	$4.26(8) \times 10^{-4}$	27.1(5)
110.0	$1.06(2) \times 10^{-3}$	10.9(2)
120.0	$2.16(6) imes 10^{-3}$	5.3(2)

°C with a Fisher Scientific model 730 isotemp immersion circulator. The NMR tube was removed from the oil bath at a predetermined time and then immediately cooled in an icewater slush bath to quench the rearrangement reaction. Each ¹H NMR spectrum was measured three times with a pulse delay of 20 s in order to obtain reliable peak integrations. The integrated intensity for the *tert*-butyl proton resonance obtained for these three spectra was reproducible to within 5%; the averaged integrated peak intensity for each run was used in the determination of the rate constant *k* at each temperature. The sample was then returned to the constant-temperature oil bath, and the process was repeated for a total time corresponding to a minimum of at least three half-lives. The concentrations of **3a** and **3b** were calculated from the expressions:

$$[\mathbf{3a}] = \frac{10(\text{area of iminoacyl t-Bu resonance of } \mathbf{3a})}{18(\text{area of Cp resonance of } Cp_2Fe)}[Cp_2Fe]$$

and

[**3b**] =

$$\frac{10 (area \ of \ appended \ amido \ t-Bu \ resonance \ of \ \textbf{3b})}{9 (area \ of \ Cp \ resonance \ of \ Cp_2Fe)} [Cp_2Fe]$$

The experimentally determined rate constants and $t_{1/2}$ values for the rearrangements **3a** \rightarrow **4a** and **3b** \rightarrow **4b** are summarized in Table 1. The values of the activation parameters, ΔH^{\ddagger} and ΔS^{\ddagger} , were calculated from the least-squares determined slope ($\Delta H^{\ddagger}/R$) and the *y*-intercept ($-\Delta S^{\ddagger}/R - 23.76$), respectively, of the corresponding plot of $-\ln(k/T)$ vs 1/T, assuming a transmission coefficient of unity in the Eyring equation $\Delta G^{\ddagger}(T) = RT \ln(\kappa k_{\rm B}T/kh)$, Figure 1. The standard errors, which are given in parentheses for the activation parameters, correspond to the errors calculated from the regression analysis.¹³

X-ray Data Collection and Structural Analyses of 3a, 3b, 4a, and 4b. The molecular structures of 3a, 3b, 4a, and 4b were determined following the same general procedure for each X-ray structural analysis. A suitable crystal was sealed in a capillary tube under a nitrogen atmosphere and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The unit cell dimensions were initially determined by indexing a set of reflections whose angular coordinates were obtained either from a rotation photograph or with the automatic peak search routine provided with XSCANS.¹⁴ The corresponding unit cell parameters and orientation matrix were determined from a nonlinear least-squares fit of the orientation angles of at least 20 higher order



Figure 1. Eyring plots for the first-order intramolecular rearrangements of **3a** to **4a** and **3b** to **4b**.

reflections at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2.

Intensity data were measured with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 73 Å) and variable ω scans. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections. The intensity data were corrected for Lorentz–polarization and crystal decay (when appropriate). An empirical absorption correction (when applied) was based upon ψ scans measured for a minimum of eight reflections with $\chi \approx \pm 90^{\circ}$ and 2θ ranging from 5° to 45°.

The structure solution in each case was provided by the first E-map calculated on the basis of the phase assignments made by the SHELXTL direct methods structure solution software. The coordinates of all remaining non-hydrogen atoms that were not revealed on the initial *E*-map were located in the subsequent difference Fourier map. All hydrogen atoms were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of all the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement, based upon the minimization of $\sum W_i |F_0^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (Max(F_0^2, 0) + bP)$ $2F_c^2$)/3, was performed with SHELXL-93¹⁵ operating on a Silicon Graphics Iris Indigo workstation. The final values of the discrepancy indices are provided in Table 2. Their values were calculated from the expressions $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ and wR2 = $[\sum (w_i(F_0^2 - F_c^2)^2) / \sum (w_i(F_0^2)^2)]^{1/2}$, and the standard deviation of an observation of unit weight σ_1 is equal to $[\sum (w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters varied during the last refinement cycle.

Selected interatomic distances and bond angles for the bis(η^2 -iminoacyl) compounds, **3a** and **3b**, and for the cyclic enediamidate complexes, **4a** and **4b**, are compared in Tables 3 and 4, respectively.

Discussion of Results

Migratory Isocyanide Insertion and C,C-Coupling Reactions. The reactions of 2 equiv of CNR (R

⁽¹⁴⁾ XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI. (15) SHELXL-93 is a FORTRAN-77 program developed by Professor

G. Sheldrick (Institut für Anorganische Chemie, University of Göttingen, D-37077 Göttingen, Germany) for single-crystal X-ray structural analyses.

2,6-Xylyl (4b))						
A. Crystal Data						
compound	3a	3b	4a	4b		
emp form	C ₂₇ H ₅₁ N ₃ SiZr	C ₃₅ H ₅₁ N ₃ SiZr	C ₂₇ H ₅₁ N ₃ SiZr	C ₃₅ H ₅₁ N ₃ SiZr		
dimens, mm	$0.20\times0.40\times0.60$	$0.36 \times 0.40 \times 0.48$	0.20 imes 0.30 imes 0.54	$0.20\times0.30\times0.42$		
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic		
space group	Pbca	$P\overline{1}$	Pbca	$P2_{1}/c$		
a, Å	16.957(1)	11.4096(8)	11.968(1)	16.282(1)		
<i>b</i> , Å	11.979(1)	12.0530(9)	17.738(1)	10.611(1)		
<i>c</i> , Å	30.469(3)	13.2952(10)	27.679(2)	19.544(1)		
α, deg	90	83.642(6)	90	90		
β , deg	90	79.413(6)	90	93.352(7)		
γ , deg	90	72.010(6)	90	90		
volume, Å ³	6189.1(7)	1706.5(2)	5875.9(8)	3370.8(4)		
Ζ	8	2	8	4		
fw	537.03	633.12	537.03	633.12		
density, g/cm ³	1.153	1.232	1.214	1.248		
μ , cm ⁻¹	4.11	3.84	4.33	3.88		
F(000)	2304	672	2304	1344		
	B. Data Collec	tion and Structural Analy	ses			
scan type	ω . variable	w. variable	ω . variable	ω . variable		
scan rate. deg/min	2.0 - 10.0	2.0 - 10.0	3.0-10.0	2.0 - 10.0		
2θ range, deg	3.0 - 50.0	3.0 - 50.0	3.0 - 50.0	3.0 - 50.0		
reflns sampled	$h(-1 \le h \le 20)$	$h(-13 \le h \le 12)$	$h(-1 \le h \le 14)$	$h (0 \le h \le 19)$		
I I I	$k(-1 \le k \le 14)$	$k(-14 \le k \le 0)$	$k(-1 \le k \le 21)$	$k(0 \leq k \leq 12)$		
	$l(-36 \le l \le 1)$	$l(-15 \le l \le 15)$	$l(-1 \le l \le 32)'$	$1(-23 \le l \le 23)$		
no. of reflns	6636	6308	6294	6097		
no. of unique data	5433	5990	5137	5879		
agreement factor	$R_{\rm int} = 0.0375$	$R_{\rm int} = 0.0180$	$R_{\rm int} = 0.0429$	$R_{\rm int} = 0.0226$		
no. of data $(I > 2\sigma(I))$	4601	5711	4330	5295		
abs corr	empirical	empirical	none	empirical		
R indices $(I > 2\sigma(I))$	R1 = 0.0497	R1 = 0.0328	R1 = 0.0517	R1 = 0.0420		
	wR2 = 0.0904	wR2 = 0.0750	wR2 = 0.0860	wR2 = 0.0812		
R indices for all data	R1 = 0.1182	R1 = 0.0453	R1 = 0.1257	R1 = 0.0808		
	wR2 = 0.1155	wR2 = 0.0809	wR2 = 0.1097	wR2 = 0.0964		
σ_1 , GOF	1.032	1.026	1.006	1.001		
values of a and b	0.0437. 0.0	0.0384. 0.67	0.0338. 0.0	0.0411. 0.0		
no. of variables	307	376	307	376		
data to parameter ratio	17.7:1	15.2:1	16.7:1	14.1:1		
largest diff peak and hole	0.2540.284	0.2320.209	0.3360.279	0.241 0.217		
6 F						

Table 2. Crystallographic Data for the X-ray Structural Analyses of [(C ₅ Me ₄)SiMe ₂ (N-t-Bu)]Zr[η ² -C(Me)NR] ₂
$(\mathbf{R} = tert$ -Butyl (3a), 2,6-Xylyl (3b), and $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[NRC(Me)=C(Me)NR]$ ($\mathbf{R} = tert$ -Butyl (4a),
9 G V-J-J (Ab))

= (**a**) *tert*-butyl, (**b**) 2,6-xylyl, (**c**) Me) with $[(C_5Me_4)-SiMe_2(N-t-Bu)]ZrMe_2$, **1**, similarly proceed at 25 °C with the sequential migratory insertion of an equivalent of isocyanide into each Zr–C(Me) bond (eq 3) to afford the mono(η^2 -iminoacyl) and bis(η^2 -iminoacyl) complexes $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrMe[\eta^2-C(Me)NR]$, **2**, and $[(C_5-Me_4)SiMe_2(N-t-Bu)]Zr[\eta^2-C(Me)NR]_2$, **3**. For *tert*-butyl



R = (a) t-butyl; (b) 2,6-xylyl; (c) methyl

isocyanide, this insertion reaction proceeds sufficiently slow to observe the formation of the intermediate mono $(\eta^2$ -iminoacyl) complex, **2a**, which was identified in

solution by the presence of a characteristic downfield ¹³C NMR resonance for the η^2 -iminoacyl carbon nucleus at δ 247.9. Whereas two resolved ¹H and ¹³C NMR resonances for the diastereotopic methyl groups of the SiMe₂ linkage are observed for **2a**, only two rather than the expected four ¹H and ¹³C NMR resonances are observed for the proximal and distal methyl groups and the ring carbon atoms. This latter observation may reflect the presence of a dynamic process involving the methyl and η^2 -iminoacyl ligands of **2a**. The bis(η^2 iminoacyl) species 3a-c also exhibit a single downfield ¹³C NMR resonance in solution for the two η^2 -iminoacyl carbons, consistent either with a C_s -symmetric static structure in which both iminoacyls adopt the sterically more favorable N-outside orientation or with a dynamic structure that has the N-inside and N-outside conformations rapidly interconverting on the NMR time scale. The results of the X-ray structure determinations performed on 3a and 3b (vide infra) indicate that the two η^2 -iminoacyl ligands do not adopt the C_s-symmetric structure in the solid state.

Upon thermolysis, the $bis(\eta^2 \text{-iminoacyl})$ complexes $3\mathbf{a}-\mathbf{c}$ rearrange via an intramolecular reaction that involves C,C-coupling of the two iminoacyl ligands to afford solely the cyclic enediamido complexes, $4\mathbf{a}-\mathbf{c}$, respectively (eq 4). These reactions proceed with concomitant disappearance of the downfield η^2 -iminoacyl carbon resonance of $3\mathbf{a}-\mathbf{c}$. The activation parameters for the first-order conversions of $3\mathbf{a} \rightarrow 4\mathbf{a}$ and $3\mathbf{b} \rightarrow 4\mathbf{b}$

Reaction of [(C₅Me₄)SiMe₂(N-t-Bu)]ZrMe₂

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for the $Bis(\eta^2$ -iminoacyl)zirconium Complexes 3a and $3b^{a,b}$

3a		3b				
A Interatomic Distances						
Zr-Cn(c)	2.231	Zr-Cp(c)	2.236			
Zr - N(1)	2.184(3)	Zr - N(1)	2.174(2)			
Zr - N(2)	2.104(0) 2.235(4)	Zr - N(2)	2.316(2)			
Zr - N(3)	2.200(1) 2 304(4)	Zr - N(3)	2.010(2) 2.268(2)			
2r - C(16)	2.001(1) 2.218(5)	7r - C(16)	2.200(2) 2.258(3)			
2r = C(10) 7r = C(22)	2.210(0) 2 242(5)	Zr = C(26)	2,237(3)			
Si - C(1)	1.863(5)	Si - C(1)	1.237(3)			
Si = N(1)	1.003(3) 1 711(A)	Si = N(1)	1.071(3) 1.716(2)			
N(1) = C(12)	1.711(4) 1.485(5)	N(1) = C(12)	1.710(2) 1.485(3)			
N(1) = C(12) N(2) = C(16)	1.405(5)	N(2) - C(16)	1.403(3) 1.989(3)			
N(2) = C(10) N(3) = C(22)	1.270(0)	N(2) = C(26)	1.202(3)			
N(3) = C(22) N(2) = C(18)	1.233(0)	N(3) = C(20) N(2) = C(18)	1.270(3) 1.434(3)			
N(2) = C(10) N(3) = C(24)	1.504(0)	N(2) = C(10) N(3) = C(28)	1.434(3) 1.434(3)			
N(3) C(24)	1.508(0)	N(3) C(20)	1.434(3)			
Cn(c) = 7r - N(1)	99.9	Angles $C_{n}(c) - 7r - N(1)$	99.5			
$C_{n}(c) = 7r - Im(1)$	125.0	$C_{n}(c) = 7r - Im(1)$	121.0			
$C_{n}(c) = 7r - Im(2)$	110 /	$C_{n}(c) = 7r - Im(2)$	115 /			
N(1) - 7r - Im(1)	101 7	N(1) - 7r - Im(1)	105.6			
N(1) = Zr = Im(1) N(1) = Zr = Im(2)	101.7	N(1) = Zr = Im(1) N(1) = Zr = Im(2)	111 0			
$In(1) \ge Inn(2)$ Im(1) = 7r = Im(2)	106 /	In(1) ZI III(2) Im(1) - 7r - Im(2)	103.1			
M(1) = 7r = M(2)	102 61(14)	N(1) = 7r = N(2)	01 26(7)			
N(1) = Zr = N(2) N(1) = Zr = N(3)	98 03(14)	N(1) = Zr = N(2) N(1) = Zr = N(3)	121 13(8)			
N(1) - 7r - C(16)	99 7(2)	N(1) - 7r - C(16)	119 96(9)			
N(1) - 7r - C(22)	129 8(2)	N(1) - 7r - C(26)	101 34(9)			
N(2) - 7r - N(3)	97 1(2)	N(2) - 7r - N(3)	88 53(7)			
N(2) - 7r - C(16)	33 3(2)	N(2) - 7r - C(16)	32 52(8)			
N(3) - 7r - C(22)	85 1(2)	N(2) - 7r - C(26)	116 62(8)			
N(3) - 7r - C(16)	130.0(2)	N(3) - 7r - C(16)	86 29(8)			
N(3) - Zr - C(22)	32.1(2)	N(3) - Zr - C(26)	32.90(8)			
C(16) - Zr - C(22)	111.0(2)	C(16) - Zr - C(26)	119,17(9)			
N(1) - Si - C(1)	96.3(2)	N(1) - Si - C(1)	95.08(11)			
Si-N(1)-Zr	104.2(2)	Si-N(1)-Zr	104.48(6)			
C(12) - N(1) - Si	124.4(3)	C(12) - N(1) - Si	125.5(2)			
C(12) - N(1) - Zr	131.3(3)	C(12) - N(1) - Zr	129.4(2)			
C(16) - N(2) - C(18)	128.3(4)	C(16) - N(2) - C(18)	125.0(2)			
C(16) - N(2) - Zr	72.6(3)	C(16) - N(2) - Zr	71.23(14)			
C(18) - N(2) - Zr	158.5(4)	C(18) - N(2) - Zr	163.8(2)			
C(22) - N(3) - C(24)	131.4(4)	C(26) - N(3) - C(28)	128.8(2)			
C(22) - N(3) - Zr	71.2(3)	C(26) - N(3) - Zr	72.19(14)			
C(24) - N(3) - Zr	157.3(3)	C(28) - N(3) - Zr	158.9(2)			
C(5) - C(1) - C(2)	105.1(4)	C(5) - C(1) - C(2)	105.7(2)			
C(2) - C(1) - Si	125.5(3)	C(2) - C(1) - Si	121.4(3)			
C(5)-C(1)-Si	121.4(4)	C(5) - C(1) - Si	125.6(2)			
N(2)-C(16)-C(17)	128.8(5)	N(2)-C(16)-C(17)	122.2(2)			
N(2)-C(16)-Zr	74.1(3)	N(2)-C(16)-Zr	76.25(14)			
C(17)-C(16)-Zr	156.8(4)	C(17) - C(16) - Zr	161.3(2)			
N(3)-C(22)-C(23)	127.7(7)	N(3)-C(26)-C(27)	124.9(2)			
N(3)-C(22)-Zr	76.6(3)	N(3)-C(26)-Zr	74.90(14)			
C(23)-C(22)-Zr	155.4(3)	C(27) - C(26) - Zr	159.9(2)			

^{*a*} Cp(c) is the centroid of the permethylated cyclopentadienyl ring containing atoms C(1), C(2), C(3), C(4), and C(5). ^{*b*} Im(1) and Im(2) designate the midpoints of the N(2)–C(16) bond and the N(3)–C bond of the two η^2 -iminoacyl ligands, respectively.



R = (a) t-butyl; (b) 2,6-xylyl; (c) methyl

were obtained from an evaluation of the temperature dependence of the rate constant in each case. The corresponding rate constants within the temperature range of 70–120 °C are tabulated in Table 1. The activation parameters of $\Delta H^{\ddagger} = 24.6(2)$ kcal/mol and $\Delta S^{\ddagger} = -11.3(7)$ eu for **3a** \rightarrow **4a** and of $\Delta H^{\ddagger} = 23.9(3)$ kcal/

Table 4. Selected Interatomic Distances (Å) and
Bond Angles (deg) for the Zirconium
Enediamidate Complexes 4a and 4b^a

4a		4b				
A. Interatomic Distances						
Zr-Cp(c)	2.244	Zr-Cp(c)	2.211			
Zr - N(1)	2.138(4)	Zr-N(1)	2.149(3)			
Zr-N(2)	2.068(4)	Zr-N(2)	2.071(3)			
Zr-N(3)	2.064(4)	Zr-N(3)	2.069(3)			
Zr…C(16)	2.564(5)	Zr…C(16)	2.603(4)			
Zr…C(17)	2.563(5)	Zr…C(27)	2.595(4)			
Si-C(1)	1.860(5)	Si-C(1)	1.870(4)			
Si-N(1)	1.733(4)	Si-N(1)	1.723(3)			
N(1)-C(12)	1.501(6)	N(1)-C(12)	1.487(5)			
N(2)-C(16)	1.405(6)	N(2)-C(16)	1.413(5)			
N(3)-C(17)	1.400(6)	N(3)-C(17)	1.417(5)			
N(2)-C(20)	1.491(6)	N(2)-C(20)	1.436(5)			
N(3)-C(24)	1.483(6)	N(3)-C(28)	1.423(5)			
C(16)-C(17)	1.388(7)	C(16)-C(17)	1.373(5)			
	B. Bond	l Angles				
Cp(c)-Zr-N(1)	100.5	Cp(c) - Zr - N(1)	101.5			
Cp(c)-Zr-N(2)	123.6	Cp(c)-Zr-N(2)	115.1			
Cp(c)-Zr-N(3)	123.3	Cp(c)-Zr-N(3)	116.0			
N(1)-Zr-N(2)	110.94(14)	N(1)-Zr-N(2)	120.33(12)			
N(1)-Zr-N(3)	113.2(2)	N(1)-Zr-N(3)	119.84(12)			
N(2)-Zr-N(3)	85.6(2)	N(2)-Zr-N(3)	84.81(12)			
N(1)-Si-C(1)	96.2(2)	N(1)-Si-C(1)	95.9(2)			
Si-N(1)-Zr	103.9(2)	Si-N(1)-Zr	103.3(2)			
C(12)-N(1)-Si	124.2(3)	C(12)-N(1)-Si	123.3(3)			
C(12) - N(1) - Zr	131.9(3)	C(12) - N(1) - Zr	133.4(2)			
C(16) - N(2) - C(20)	123.6(4)	C(16) - N(2) - C(20)	120.6(3)			
C(16) - N(2) - Zr	93.2(3)	C(16) - N(2) - Zr	94.8(2)			
C(20) - N(2) - Zr	141.6(3)	C(20) - N(2) - Zr	142.1(2)			
C(17) - N(3) - C(24)	122.1(4)	C(17) - N(3) - C(28)	119.2(3)			
C(17) - N(3) - Zr	93.5(3)	C(17)-N(3)-Zr	94.4(2)			
C(24) - N(3) - Zr	144.0(3)	C(28)-N(3)-Zr	145.5(3)			
C(5)-C(1)-C(2)	105.8(5)	C(5)-C(1)-C(2)	105.6(4)			
C(2) - C(1) - Si	122.1(4)	C(2) - C(1) - Si	122.5(3)			
C(5) - C(1) - Si	124.5(3)	C(5) - C(1) - Si	124.3(3)			
N(2)-C(16)-C(17)	120.4(4)	N(2) - C(16) - C(17)	119.8(3)			
N(2)-C(16)-C(18)	119.9(5)	N(2) - C(16) - C(18)	117.7(3)			
C(17) - C(16) - C(18)	119.4(5)	C(17) - C(16) - C(18)	122.3(3)			
N(3)-C(17)-C(16)	120.4(5)	N(3) - C(17) - C(16)	120.4(3)			
N(3)-C(17)-C(19)	120.4(5)	N(3) - C(17) - C(19)	117.7(3)			
C(16)-C(17)-C(19)	118.5(5)	C(16) - C(17) - C(19)	121.7(4)			
$2C_{\rm m}(a)$ is the sem	turid of the	nonnestheriteted sealer	اربسه المسير			

 a Cp(c) is the centroid of the permethylated cyclopentadienyl ring containing atoms C(1), C(2), C(3), C(4), and C(5).

mol and $\Delta S^{\ddagger} = -10.4(8)$ eu for **3b** \rightarrow **4b** fall within the ΔH^{\ddagger} range (21.0–25.0 kcal/mol) and ΔS^{\ddagger} range (-2 to -16 eu) reported by Rothwell and co-workers¹⁶ for the analogous intramolecular C,C-coupling reaction observed for Zr(OAr)₂[η^2 -C(Me)NR]₂ complexes, where OAr = 2,6-di-*tert*-butylphenoxide and R = *meta*- or *para* substituted phenyl substituent. The negative entropy of activation is consistent with a mechanism that proceeds toward a more symmetric transition state,¹⁶ and the positive enthalpy of activation presumably reflects the collective energy needed to rotate the two η^2 -iminoacyl groups toward mutually-similar N-outside orientations as well as weaken the two Zr-C(iminoacyl) bonds.

The NMR spectra for the three enediamidate complexes, 4a-c, are consistent with the presence of a mirror plane of symmetry passing through the bridgehead C, Si, and Zr atoms and bisecting the N–Zr–N angle of the 1,4-diaza-5-zirconacyclopentene ring. Each pair of distal and proximal methyl substituents on the permethylated cyclopentadienyl ring, the two methyl groups of the SiMe₂ linkage, and the pair of *cis* methyl

⁽¹⁶⁾ Durfee, L. D.; McMullen, A. K.; Rothwell, I. P. J. Am. Chem. Soc. **1988**, 110, 1463.

groups on the C=C bond exhibit one characteristic ¹H and one ¹³C NMR resonance. As expected, the carbon resonance for the bridgehead carbon¹² of the cyclopentadienyl ring is positioned *ca.* 20 ppm upfield from the corresponding pair of signals for the distal and proximal ring carbons.

The results of our X-ray structural analysis of **4a** and **4b** (vide infra) reveal that their five-membered ZrN_2C_2 rings are significantly folded along the N···N line segment, thereby suggesting the possibility of observing in solution a dynamic equilibrium between two inequivalent folded ring conformations. Rothwell and coworkers^{1b} estimated that the activation energy for the corresponding degenerate process in $Zr(OAr')_2[N(2,6-xylyl)C(Me)=C(Me)N(2,6-xylyl)]$, where OAr' is 2,6-di*tert*-butylphenoxide, is 14.5 (5) kcal/mol at 0 °C. We subsequently found that the activation barrier and coalescence temperature for the analogous process in the related bicyclic enediamidate group 4 metallocene

complexes, $(C_5R'_5)_2M[N(R)C(CH_2SiMe_2CH_2)=CN(R)]$, are highly variable and depend on the substituents R and R' and the metal M.¹⁷ In contrast, upon lowering the temperature of the NMR solutions containing **4a** or **4b**, no noticeable broadening or reduction in the intensities of the ¹H NMR resonances was observed, thereby suggesting either that the activation barrier for this interconversion is small (i.e., $\ll 10$ kcal/mol) or that the ring conformations associated with the molecular structures of **4a** and **4b** remain rigid in solution.

Structural Characterization of the Bis(η^2 -iminoacyl) Complexes, 3a and 3b. Perspective views of the molecular structures of **3a** and **3b** with the corresponding atom labeling schemes are depicted in Figures 2 and 3, respectively. The pseudotetrahedral coordination spheres about the Zr atoms in these complexes are analogous, consisting of a permethylated cyclopentadienyl ring with an appended t-butylamido ligand and two η^2 -bound iminoacyl groups. The angle between the two vectors extending from Zr to the midpoints Im(1) and Im(2) of the two iminoacyl C=N bonds (106.4° (3a) and 103.1° (3b)) compares well with the Cl-Zr-Cl bond angle of 104.92(4)° in [(C₅Me₄)SiMe₂(N-t-Bu)]ZrCl₂.¹² The Zr-N(1) and Cp(c)-Zr distances of 2.184(3) and 2.231 Å in 3a and of 2.174(2) and 2.236 Å in 3b are significantly longer than the corresponding distances of 2.052(2) and 2.163 Å in the 14-electron dichloride derivative. Similar elongations of the Zr-N distance and the Zr-Cp(c) separation are observed in {[(C_5Me_4)-SiMe₂(N-t-Bu)]Zr(η^2 -O₂CMe)(μ -O₂CMe)}₂,⁹ which contains a coordinatively saturated ligand environment at each 18-electron Zr(IV) center. By utilizing two additional metal orbitals for bonding, the two 4-electron donating η^2 -iminoacyl ligands in **3a** and **3b** reduce the electrophilicity at Zr, thereby diminishing the magnitude of the π -donating interaction of the appended amido functionality. The crowded metal coordination environment in **3a** and **3b** is further accompanied by a

(17) The activation barrier and coalescence temperature for the degenerate interconversion of the five-membered ZrN_2C_2 ring in $(C_5-Me_5)_2Zr[N(Me)C(CH_2SiMe_2CH_2)=CN(Me)]$,^{2c} $Cp_2Zr[N(CMe_3)C(CH_2SiMe_2CH_2)=CN(CMe_3)]$,^{2b} $Cp_2Hf[N(CMe_3)C(CH_2SiMe_2CH_2)=CN(CMe_3)]$,^{3a} and $Cp_2Zr[N(2,6-xy]y])C(CH_2SiMe_2CH_2)=CN(CMe_3)]^{2b}$ are $\Delta G^{4}(est.)$



Figure 2. Molecular structure of **3a** with the nonhydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.



Figure 3. Molecular structure of **3b** with the nonhydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

modest decrease¹² in the Cp(c)–Zr-N(amido) angle to 99.2° and 99.5°, respectively.

The structural parameters, such as the C=N distance and the internal angles within the three-membered ZrCN rings, are consistent with those reported for other organozirconium compounds containing one,¹⁸ two,¹⁹ or three¹⁹ η^2 -iminoacyl ligands. Normally, one finds that

and Cp₂Zr[N(2,6-xylyl)C(CH₂SiMe₂CH₂)=CN(CMe₃)]^{2b} are $\Delta G^{*}(\text{est.}) \ll 10 \text{ kcal/mol}, T_{c} < -110 ^{\circ}\text{C}; \Delta G^{*} = 19.5(5) \text{ kcal/mol}, T_{c} = 142 ^{\circ}\text{C}; \Delta G^{*} = 16.9(5) \text{ kcal/mol}, T_{c} = 85 ^{\circ}\text{C}; \text{ and } \Delta G^{*}(\text{est.}) >> 20 \text{ kcal/mol}, T_{c} \gg 150 ^{\circ}\text{C}, \text{ respectively}.$

^{(18) (}a) Reger, D. L.; Tarquini, M. E.; Lebioda, L. Organometallics **1983**, 2, 1763. (b) Erker, G.; Korek, U.; Petersen, J. L. J. Organomet. Chem. **1988**, 355, 121. (c) Bristow, G. S.; Lappert, M. F.; Atwood, J. L.; Hunter, W. E. Unpublished results described in Chemistry of Organozirconium and Hafnium Compounds; Cardin, D. F., Lappert, M. F., Raston, C. L., Eds.; Wiley, New York, 1986.

^{L., Hunter, W. E. Onpublished results described in} *Chemistry on Organozirconium and Hafnium Compounds*; Cardin, D. F., Lappert, M. F., Raston, C. L., Eds.; Wiley, New York, 1986.
(19) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* 1987, *109*, 390.



Figure 4. Molecular structure of **4a** with the nonhydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

for these Zr η^2 -iminoacyl complexes, the Zr–N bond distance is typically equal to or less than the Zr-C bond distance within the same η^2 -iminoacyl ligand. However, the opposite trend is observed in **3a** and **3b**. Here, the Zr-N distance in each three-membered ZrCN ring is ca. 0.02–0.06 Å longer than the corresponding Zr–C distance. The magnitude of $\Delta d (d_{Zr-N} - d_{Zr-C})$ correlates directly with the relative orientation of the iminoacyl group with respect to the plane defined by Zr, Im(1), and Im(2). For **3a**, the acute dihedral angles between the planes containing Zr, N(2), C(16) and Zr, N(3), C(22) with the Zr, Im(1), Im(2) plane are 24.3° and 61.1°, respectively, with N(2) and N(3) positioned inside and outside of the wedge defined by the Zr-Im(1) and Zr-Im(2) directions. For 3b, the acute dihedral angles between the planes containing Zr, N(2), C(16) and Zr, N(3), C(26) with the corresponding Zr, Im(1), Im(2) plane are 90.0° and 14.5°, respectively, with N(3) occupying an inside position. For N(2) in **3a** and N(3) in **3b**, which adopt a nearly N-inside orientation, Δd is 0.017 and 0.031 Å, respectively. In contrast, for the remaining iminoacyl ligand containing N(3) in 3a and N(2) in **3b**, the respective Δd values of 0.062 and 0.058 Å are considerably larger. The relatively long Zr-N(3)distance of 2.304(4) Å in 3a and the Zr-N(2) distance of 2.316(2) Å in 3b probably reflect a poorer orbital match between the available Zr-valence and N-donor orbitals, both of which are directed toward one another from below the Zr, Im(1), Im(2) plane.

Structural Characterization of the Cyclic Enediamidate Complexes, 4a and 4b. The molecular structures of 4a and 4b have also been determined by X-ray crystallography, and perspective views of these two enediamidate complexes with their atom labeling schemes are shown in Figures 4 and 5, respectively. The pseudotetrahedral coordination sphere about the Zr atom in both compounds consists of the permethylated cyclopentadienyl ring, the appended amido N, and the two N-donors of a symmetrically-chelating enediamidate ligand generated by the intramolecular C,C-coupling of the two η^2 -iminoacyl groups of **3a** and **3b**, respectively. The Zr-N(1) distances of 2.138(4) Å in **4a** and 2.149(3) Å in **4b** correspond to the appended t-butylamido functionality and are substantially longer than the



Figure 5. Molecular structure of **4b** with the nonhydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

corresponding Zr-N(2) and Zr-N(3) distances which range from 2.06–2.07 Å in **4a** and **4b**. These latter distances are comparable to the Zr-N distances of 2.060(5) and 2.064(4) Å for the terminal dialkylamido ligands in [(C₅Me₄)SiMe₂(N-t-Bu)]Zr(NMe₂)₂¹² and many other zirconium amido complexes²⁰ in which an appreciable N π -donation to an electrophilic d⁰ Zr center exists. These Zr-N distances for the enediamido ligands of **4a** and **4b** are essentially identical to the values of 2.060(6) and 2.061(6) Å in Zr(OAr)₂[N(2,6-xylyl)C-(Me)=C(Me)N(2,6-xylyl)]^{1b} but are noticeably shorter than the Zr-N distances of 2.111(8), 2.104(6) Å in $Cp_2Zr[N(CMe_3)C(CH_2SiMe_2CH_2)=CN(CMe_3)];^{2b} 2.110(6),$ 2.112(7) Å in Cp*₂ $Zr[N(Me)C(CH_2SiMe_2CH_2)=CN(Me)];^{2c}$ and 2.100(4), 2.123(5) Å in Cp₂Zr[N(Ph)C(Ph)=C(Ph)N-(Ph)1.21

The structural parameters within the 1,4-diaza-5zirconacylopentene rings of **4a** and **4b** are consistent with a dianionic enediamido ligand donating to a d⁰ Zr(IV) center. The C(16)–C(17) bonds of 1.388(7) (**4a**) and 1.373(5) Å (**4b**) fall well within the range 1.35– 1.42 Å observed for the C=C double bond in related enamidolate,¹ enediamidate,^{1.2,6a} and butadiene complexes²² that also conform to the metallacyclopentene resonance structure. The N(2)–C(16) and N(3)–C(17) distances of 1.405(6) and 1.400(6) in **4a** and 1.413(5) and 1.417(5) in **4b** are consistent with C–N single bonds.

A notable structural feature associated with the molecular structures of these compounds is the folding

⁽²⁰⁾ Some representative Zr–N bond distances for Zr(IV) amide complexes: (a) 2.07 Å, Zr(NMe₂)₄ (electron diffraction); Hagen, K.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Inorg. Chem.* **1988**, *27*, 2032. (b) 2.06 Å, $(Me_2N)_2Zr(\mu-N-t-Bu)_2Zr(NMe_2)_2$; Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030. (c) 2.06 Å, *rac*-[C₂H₄-(C₉H₆)₂]Zr(NMe₂)₂; Diamond, G. M.; Jordan, R. F.; Peterssen, J. L. J. *Am. Chem. Soc.* **1996**, *118*, 8024. (d) 2.07 Å, *rac*-[SiMe₂(C₉H₆)₂]Zr(NMe₂)₂; Corda, K.; Jordan, R. F.; Peterssen, J. L. J. *Am. Chem. Soc.* **1996**, *118*, 8024. (d) 2.07 Å, *rac*-[SiMe₂(C₉H₆)₂]Zr(NMe₂)₂; Corda, K.; Jordan, R. F.; Peterssen, J. L. J. *Organometallics* **1996**, *15*, 4038. (e) 2.07 Å, Zr[N(SiMe₃)₂]₃Cl; 2.08 Å, Zr[N(SiMe₃)₂]₃Me; Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibrahim, A. A.; Montevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423. (f) 2.00 Å, (C₅Me₅)Zr[N(i-Pr]₂]Cl₂; Pupi, R. M.; Coalter, J. N.; Petersen, J. L. J. Organomet. Chem. **1995**, *497*, 17.

⁽²¹⁾ Scholz, J.; Dikan, M.; Ströhl, D.; Dietrich, A.; Schumann, H.; Thiele, K.-H. *Chem. Ber.* **1990**, *123*, 2279.

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 $[N(R)C(CH_2SiMe_2CH_2)=CN(R)]$,² the two possible folded conformations represent degenerate structures, and thus only one conformational structure is observed in the solid state. In contrast, the presence of the bifunctional ansa-monocyclopentadienylamido ligand in 4a and 4b offers the possibility of observing two inequivalent conformations for the folded 1,4-diaza-5-zirconacyclopentene ring. If we adopt the analogous nomenclature recently used to define the conformational geometry of the coordinated diene in [(C₅Me₄)SiMe₂(N-t-Bu)]Ti-(diene) complexes,²³ then the ring conformer with the 1,4-diaza-5-zirconacyclopentene ring folded up toward the cyclopentadienyl ring corresponds to the prone structure because the open end of the cup defined by atoms N(2), C(16), C(17), and N(3) is oriented away from the cyclopentadienyl ring. The other ring conformer corresponds to the supine structure because the opening of the cup is directed toward the cyclopentadienyl ring. On the basis of this nomenclature, the 1,4-diaza-5zirconacyclopentene ring of 4a exhibits the prone structure with the acute dihedral angle between the planes containing Zr, N(2), N(3) and N(2), C(16), C(17), N(3) being 50.5° and the corresponding five-membered ring of **4b** adopts the alternative supine structure with the dihedral angle being 49.0°. Given that these folding angles are comparable in magnitude, one might expect that the prone structure should be sterically less favorable. However, the dihedral angle between the plane of the cyclopentadienyl ring and the plane containing Zr, N(2), N(3) of 53.0° for the prone structure is ca. 12° greater than the corresponding dihedral angle of 41.1° associated with the supine structure of 4b. This structural alteration apparently compensates for the steric interactions imposed by the prone conformation.

In both **4a** and **4b**, ring folding moves the internal carbons, C(16) and C(17), of the 1,4-diaza-5-zirconacyclopentene ring closer to the electrophilic Zr center. The corresponding Zr–C(16) and Zr–C(17) distances of 2.564(5) and 2.563(5) Å in **4a** and 2.603(4) and 2.595(4) Å in **4b** imply that both conformers could experience some stabilization from a weak attractive interaction between the filled π -orbital of the C=C double bond and an empty metal orbital that is directed above and below the Zr, N(2), N(3) plane. However, the absence of any significant elongation or notable difference in the C(16)–C(17) bond distances in **4a** and **4b** suggests that this type of π -interaction is probably not a major factor in determining the relative stability and conformational preference of the nonplanar prone and supine structures in **4a** and **4b**, respectively.

The bending of these five-membered rings is more likely a consequence of the presence of the *tert*-butyl or 2,6-xylyl substituent at each N atom of the enediamido ligand. Folding along the N(2)···N(3) line segment (in either direction) enhances the overlap of the p_{π} -orbital at each N with the same laterally disposed vacant metal orbital and thus helps account for the observed reduction in the Zr-N(2) and Zr-N(3) distances mentioned earlier. However, because the magnitude of the ring folding is comparable for **4a** and **4b**, the degree of π -stabilization associated with these Zr-N bonds is expected to be similar and, thus, explains why the Zr-N distances are essentially equal for the prone and supine conformations.

In view of the similar electronic features displayed by these folded metallacylic rings, why do the 1,4-diaza-5-zirconacyclopentene rings of 4a and 4b adopt different conformational structures? The explanation apparently lies in considering the steric features imposed by the different size and shape of the substituents at N(2) and N(3) of the folded ZrN_2C_2 rings. In **4a**, the prone structure directs the bulky tert-butyl substituents away from the methyl substituents at C(2) and C(5) of the cyclopentadienyl ring. In contrast, the supine structure of 4b allows both planar 2,6-xylyl groups to lie parallel to the plane of the cyclopentadienyl ring. By minimizing the steric interactions between the methyl substituents of the 2,6-xylyl and cyclopentadienyl rings, this arrangement reinforces the structural preference for the supine conformation observed for 4b.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, interatomic distances and bond angles, anisotropic displacement parameters, and hydrogen coordinates for **3a**, **3b**, **4a**, and **4b** (29 pages). Ordering information is given on any current masthead page. Structure factor tables for these four compounds are available from the authors upon written request.

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