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Migratory Insertion Reactions in Asymmetrical Guanidinate-Supported Zirconium Complexes

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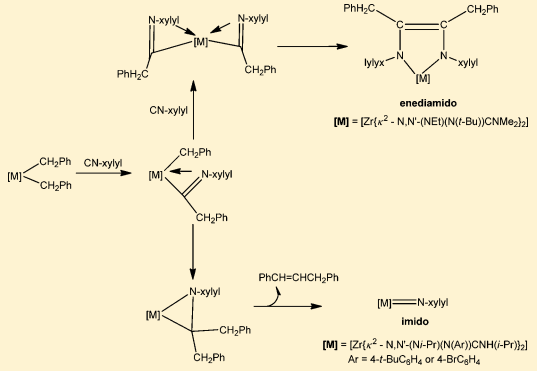
Supporting Information

ABSTRACT: The new diguanidinate-supported dibenzylzirconium complexes $[Zr\{\kappa^2N,N'\text{-}(N\text{-}i\text{-}Pr)(NAr)CNH(i\text{-}Pr)\}_2(CH_2Ph)_2]$ (Ar = 4-*t*-BuC_6H_4 (**1**), 4-BrC_6H_4 (**2**)) and $[Zr\{\kappa^2N,N'\text{-}(NEt)(N\text{-}t\text{-}Bu)\text{-}CNMe_2\}_2(CH_2Ph)_2]$ (**3**) have been prepared. Complexes **1** and **2** were synthesized by protonolysis of $[Zr(CH_2Ph)_4]$ with the guanidine derivatives and complex **3** by treating $[Zr\{\kappa^2N,N'\text{-}(NEt)(N\text{-}t\text{-}Bu)\text{-}CNMe_2\}_2Cl_2]$ (**4**) with $MgCl(CH_2Ph)$. The treatment of **1**−**3** with 2,6-dimethylphenyl isocyanide (XyNC) results in migratory insertion and formation of the terminal imido species $[Zr\{\kappa^2N,N'\text{-}(N\text{-}i\text{-}Pr)(N(Ar))\text{-}CNH(i\text{-}Pr)\}_2\{N(2,6\text{-}Me_2C_6H_3)\}]$ (Ar = 4-*t*-BuC_6H_4 (**7**), 4-BrC_6H_4 (**8**)) with **1** and **2**, respectively, whereas the analogous reaction with **3** leads to the enediamido complex $[Zr\{\kappa^2N,N'\text{-}(NEt)(N\text{-}t\text{Bu})CNMe_2)\}_2\{N(2,6\text{-}Me_2C_6H_3)(CH_2Ph)C{=}C(CH_2Ph)N(2,6\text{-}Me_2C_6H_3)\}]$ (**9**). All the intermediate iminoacyl complexes have been characterized, and the molecular structures of **2**, **4**, and **9** have been determined by single-crystal X-ray diffraction.



INTRODUCTION

Monoanionic chelating guanidinate anions are often used as ancillary ligands, due to their ability to stabilize non-cyclopentadienyl coordination and organometallic compounds of early and late transition metals.[1] Furthermore, the steric and electronic features of these ligands, as well as their coordination to the metal center, can be modified by varying the substituents on the nitrogen atoms (Scheme 1).

Guanidines have been synthesized using a variety of methods, although the catalytic hydroamination of carbodiimides tends to be the most common method due to its 100% atom economy.[2] Indeed, several examples of this type of reaction have been developed over the past few years,[3] and we have recently reported the synthesis of aromatic guanidine derivatives with $ZnEt_2$ as a catalytic precursor.[4]

To the best of our knowledge, the majority of group 4 metal diguanidinate complexes reported to date have the same substituents on the N-donor atoms bonded to the metal center and therefore coordinate symmetrically.[5] The only non-symmetric guanidinate complexes described to date are the zirconium and hafnium complexes $[M\{PhNC(R)NSiMe_3\}_3Cl]$ (R = dimethylamido, 1-piperidino).[6]

As a continuation of our research into group 4 and 5 complexes with guanidinate ligands,[7] herein we report the synthesis and characterization of new asymmetric guaninidinate-supported zirconium complexes and migratory insertion reactions of isocyanide into the resulting M−C bonds to give terminal imido, iminoacyl, or enediamido complexes depending on the guanidinate ligand concerned and the reaction conditions.

RESULTS AND DISCUSSION

We have recently prepared the aromatic guanidine derivatives $(HN\text{-}i\text{-}Pr)_2C{=}NAr$ (Ar = 4-*t*-BuC_6H_4, 4-BrC_6H_4) in good yields by a catalytic process involving $ZnEt_2$ as a catalytic precursor for the addition of aromatic amines to carbodiimides.[4,8]

Although guanidinate-supported complexes are traditionally synthesized by treatment of metal dialkylamide complexes $[M(NR_2)_n]$ with the corresponding guanidines,[9] the insertion of carbodiimide derivatives into a metal−amido[5e,10] or metal−imido bond,[11] or the metathesis reaction of halide metal complexes with lithium guanidinate derivatives,[5a,12] a protonolysis reaction between a guanidine compound and an alkyl metal complex is a clean and easy method to obtain the target complexes.[5b,d,13,14] In addition, to the best of our knowledge, all the dialkyl guanidinate supported zirconium complexes reported to date involve symmetrical coordination of the chelating guanidinate ligands.[5a−e]

The reaction of $Zr(CH_2Ph)_4$ with 2 equiv of the corresponding guanidine derivatives in toluene at room temperature leads to the dibenzyl complexes $[Zr\{\kappa^2N,N'\text{-}(N\text{-}i\text{-}Pr)(NAr)CNH(i\text{-}Pr)\}_2(CH_2Ph)_2]$ (Ar = 4-*t*-BuC_6H_4 (**1**), 4-

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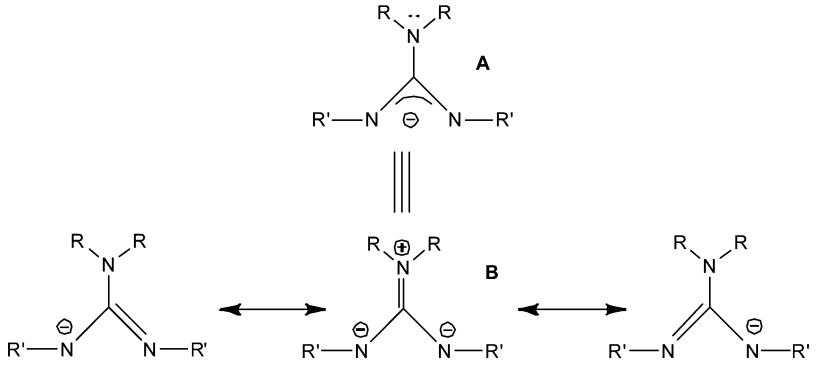
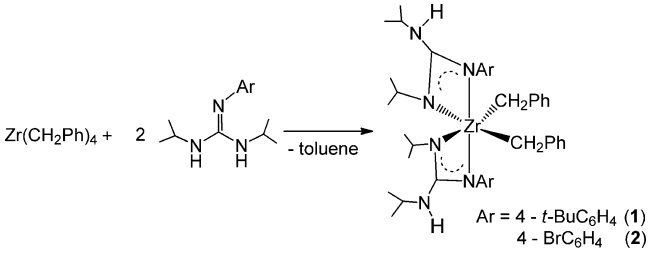
Scheme 1. Resonance Structures for Monoanionic Guanidinate Ligands



BrC_6H_4 (**2**)), which contain asymmetrically coordinated guanidinate ligands, in high yields (see Scheme 2). These complexes are stable for several days in solution under an inert atmosphere at room temperature.

Scheme 2. Synthesis of Complexes 1 and 2



The new benzyl guanidinate complexes **1** and **2** were isolated as yellow crystalline solids and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The room-temperature ^1H NMR spectra for both complexes are similar, exhibiting signals for only one compound. The following common characteristics were found: (i) two groups of signals corresponding to two nonequivalent isopropyl substituents, thus indicating an asymmetrical coordination of the guanidinate ligands to the metal center, (ii) a doublet assigned to the proton of the disubstitued amine group *H*N-*i*-Pr, and (iii) a broad signal for the benzylic protons (see the Experimental Section). These features suggest a fluxional behavior in solution in which the methyl protons of the *i*Pr groups and the benzylic protons exchange on the NMR time scale, whereas the HN(*i*-Pr) moiety does not.

A variable-temperature ^1H NMR experiment (toluene-d_8) with complex **1** revealed the presence of four doublet signals for the isopropyl methyl groups at −25 °C ($\Delta G^{\ddagger}_c$ = 13.23 kcal/mol at a coalescence temperature of 5 °C)[15] and two doublets for the diastereotopic CH_2Ph protons of the benzyl ligands ($\Delta G^{\ddagger}_c$ = 11.06 kcal/mol at a coalescence temperature of −5 °C). Similar results have been reported for the symmetric guanidinate-supported complex $[Zr\{\kappa^2N,N'\text{-}(N\text{-}i\text{-}Pr)_2CNMe_2\}_2(CH_2Ph)_2]$.[5e] The rate constants of this interconversion of **1** at various temperatures were calculated from eq 1 (where $\Delta\nu$ and $\Delta\nu_o$ are frequency differences (Hz) between

$$k = \pi\sqrt{2(\nu_0^2 - \nu^2)} \qquad (1)$$

exchange-broadened sites at temperature T and between the two sites at the slow exchange limit, respectively).[16] The activation parameters of the exchange have been calculated by an Eyring plot giving similar values for the methyl group, $\Delta H^{\ddagger}$ = 1.54 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −65.36 eu, and for the benzyl groups, $\Delta H^{\ddagger}$ = 1.67 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −68.81 eu. This fluxional process has also been observed in hexacoordinated complexes with amidinate or β-diketinimate ligands; moreover, the small differences between the $\Delta H^{\ddagger}$ and the negative $\Delta S^{\ddagger}$ values can be explained by a Bailar twist mechanism.[17]

The room-temperature $^{13}C\{^1H\}$ NMR spectra of **1** and **2** contain signals consistent with the proposed structures, including a signal at ca. 164 ppm corresponding to the central CN_3 carbon of the guanidinate ligands and a resonance at ca. 75.1 ppm for the two benzylic carbon atoms (CH_2). The $^1J_{C-H}$ value of the $-CH_2$ groups (ca. 123.0 Hz) in the room-temperature ^{13}C NMR spectra indicates that the benzylic groups do not exhibit η^2 hapticity in solution.[14c]

The formation of complexes **1** and **2** gives rise to the possibility of different isomers depending on the coordination mode of the guanidinate ligands and the *cis* or *trans* coordination of L ligands to the Zr center in a pseudooctahedral geometry; however, the spectroscopic data of **1** and **2** show the existence of only one of these isomers. In this sense, three isomers with L ligands in *cis* positions are possible (Figure 1).

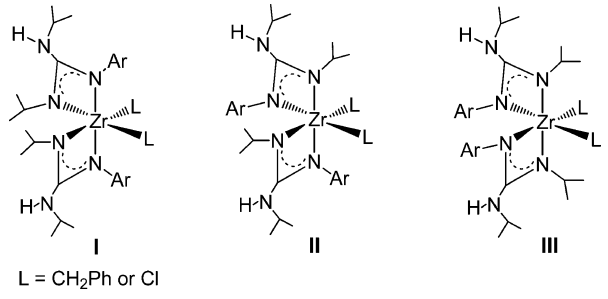


Figure 1. Possible conformations for the asymmetric bis(guanidinate)-supported zirconium complexes with the L ligands in *cis* positions.

The isomers **II** and **III** should be heavily disfavored due to steric effects as in the *trans* isomers, while the isomer **I**, which contains the two aryl amide groups in an *apical* position, is the most favored.

These spectroscopic data were supported by X-ray diffraction studies. Suitable crystals of complex **2** were grown from toluene solution at −30 °C. The molecular structure and atomic numbering scheme of **2** are shown in Figure 2. Selected bond lengths and angles for **2** are given in Table 1.

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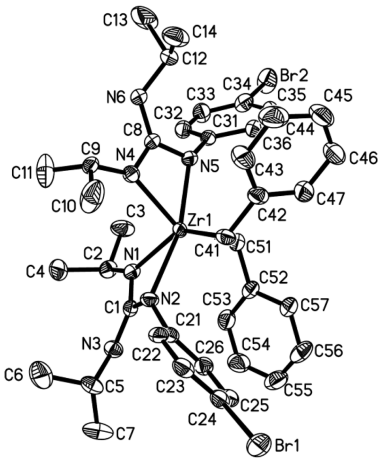

Figure 2. ORTEP drawing of complex **2**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): N1−C1, 1.35(1); N2−C1, 1.31(1); N3−C1, 1.35(1); N4−C8, 1.32(1); N5−C8, 1.35(1); N6−C8, 1.35(1); Zr−N1, 2.20(1); Zr−N2, 2.33(1); Zr−N4, 2.20(1); Zr−N5, 2.23(1); Zr−C41, 2.28(1); Zr−C51, 2.25(1); N1−Zr−N2, 58.0(3); N1−N4−Zr−N5, 59.4(2); N1−C1−N2, 111.5(6); N1−C1−N3, 123.1(7); N2−C1−N3, 125.3(7).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

	molecule A	molecule B
	Bond Lengths	
Zr−N1	2.20(1)	2.20(1)
Zr−N2	2.33(1)	2.30(1)
Zr−N4	2.20(1)	2.23(1)
Zr−N5	2.23(1)	2.28(1)
Zr−C41	2.28(1)	2.30(1)
Zr−C51	2.25(1)	2.26(1)
N1−C1	1.35(1)	1.33(1)
N2−C1	1.31(1)	1.35(1)
N3−C1	1.35(1)	1.38(1)
N4−C8	1.32(1)	1.35(1)
N5−C8	1.35(1)	1.32(1)
N6−C8	1.35(1)	1.36(1)
	Bond Angles	
N1−Zr−N2	58.0(3)	59.1(2)
N2−Zr−N5	164.8(4)	163.0(2)
N2−Zr−N4	105.9(4)	104.8(3)
N2−Zr−C51	112.2(3)	113.8(3)
C41−Zr−C51	94.7(3)	96.5(3)
N1−C1−N2	111.5(6)	111.6(6)
N1−C1−N3	123.1(7)	124.8(6)
N2−C1−N3	125.3(7)	123.5(7)
N4−C8−N5	110.6(6)	112.5(8)
N4−C8−N6	125.6(6)	122.0(9)
N5−C8−N6	123.8(7)	125.5(8)

Complex **2** crystallizes in the $P\bar{1}$ space group, with two molecules per asymmetric unit (A and B), corresponding to the two possible enantiomers. In contrast to the diguanidinate zirconium complexes reported previously, the geometry of **2** shows the Zr atom in a highly distorted octahedral environment that is perhaps better considered as a pseudotetrahedral environment, with the two bidentate guanidinate ligands using one coordination site each in a κ^2N,N'-(N-*i*-Pr)(NAr) coordination mode and the two benzyl groups completing the coordination sphere.

The N1−C1, N2−C1, N4−C8, and N5−C8 bond lengths (ca. 1.33(1) Å) are intermediate between a single and double bond and are similar to the N3−C1 and N6−C8 bond lengths (ca. 1.35(1) Å), thus indicating charge delocalization via the guanidinate atoms and the π-conjugated NCN chelate. The planarity of the "CN_3" core is shown by the sum of the angles around C1 and C8 (360°). The dihedral angles between the two guanidinate ligands (Zr−N1−C1−N2 and Zr−N4−C8−N5) are 87.7 and 86.8° for molecules A and B, respectively. The dihedral angles between the C1−N3−C5 and Zr1−N1−C1−N2 planes (31.7 and 27.8° for molecules A and B, respectively) and between the C8−N6−C12 and Zr1−N4−C8−N5 planes (33.7 and 35.0° for molecules 1 and 2, respectively) indicate a significant contribution from the zwitterionic resonance structure for the guanidinate ligand in this complex (Scheme 1).

Complexes **1** and **2** contain guanidinate ligands with a HNAr group (Ar = 4-*t*-BuC_6H_4 or 4-BrC_6H_4) that does not coordinate to the metal center. As such, we decided to complete our study by synthesizing analogous complexes containing asymmetric guanidinate ligands with an NR_2 group in the noncoordinating position. Thus, we synthesized the dibenzyl complex [Zr{κ^2N,N'-(NEt)(N-*t*-Bu)$CNMe_2$}$_2$(CH_2Ph)$_2$] (**3**) from the new complex [Zr{κ^2N,N'-(NEt)(N-*t*-Bu)$CNMe_2$}$_2$$Cl_2$] (**4**), which we obtained by an insertion reaction of the carbodiimide EtN═C═N-*t*-Bu into the metal−amide bonds of the complex [$ZrCl_2(NMe_2)_2(THF)_2$][18] in very good yields, as described previously[13g,19] (Scheme 3). Complex **4** is stable in solution under an inert atmosphere at room temperature. To the best of our knowledge, only the complex [Ta{κ^2N,N'-(NEt)(N-*t*-Bu)$CNMe_2$}$_2$(NMe_2)$_4$][20] with this guanidinate ligand has been reported. The ^{1}H NMR spectrum of complex **4** contains a single set of resonances for the guanidinate ligand, with resonances for the *tert*-butyl and N*Me*$_2$ protons appearing at 1.37 and 2.27 ppm, respectively, alongside triplet and quartet signals at 1.26 and 3.29 ppm ($^3J_{HH}$ = 6.9 Hz) corresponding to the ethyl fragments.

These spectroscopic data were confirmed by X-ray diffraction studies. Suitable crystals of complex **4** were grown from a toluene solution at −30 °C. The molecular structure and atomic numbering scheme of **4** are shown in Figure 3; selected bond lengths and angles for **4** are given in Table 2.

Complex **4** crystallizes in the $P2_1/n$ space group and is the first structurally characterized dichloro complex of a group 4 metal with the guanidinate ligand (NEt)(N-*t*-Bu)$CNMe_2$, which coordinates to the pseudotetrahedral Zr center in an asymmetrical mode in a manner similar to that for complex **2** above. The coordination sphere of the metal center consists of two chloride ligands and two bidentate guanidinate ligands, each of which occupies one coordination site in a κ^2N,N'-(NEt)(N-*t*-Bu) coordination mode.

The bond lengths of the "CN_3" moieties (N1−C1 = 1.340(5), N2−C1 = 1.347(5), N3−C1 = 1.359(5), N4−C11 = 1.350(5), N5−C11 = 1.329(6), and N6−C11 = 1.369(5) Å) are consistent with a partial double-bond character and a π-conjugated chelate coordination, thus implying that the guanidinate ligand behaves as a strong donor system toward the electron-poor zirconium center. The Zr−N bond distances (2.19−2.20 Å) also support this proposal. Moreover, the guanidinate bite angles of 60.5(1) and 60.0(1)° and the angles between the planes of the NMe_2 moiety and the metal chelate

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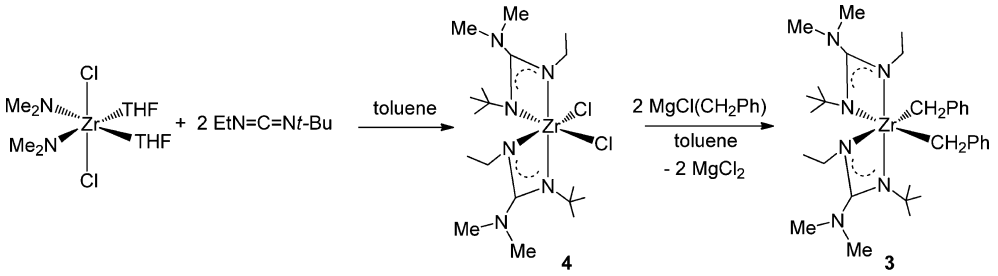
Scheme 3. Synthetic Route to Complexes 3 and 4



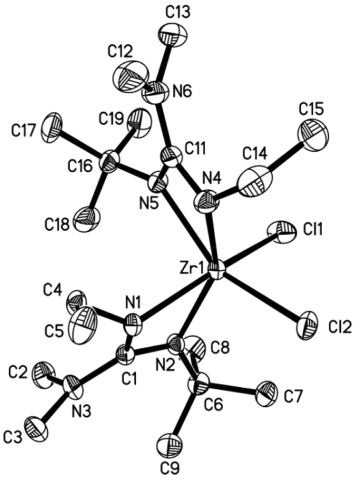


Figure 3. ORTEP drawing of complex **4**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): N1−C1, 1.340(5); N2−C1, 1.347(5); N3−C1, 1.359(5); N4−C11, 1.350(5); N5−C11, 1.329(6); N1−Zr1−N2, 60.5(1); N4−Zr1−N5, 60.0(1).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Bond Lengths			
Zr1−Cl1	2.55(4)	N1−C1	1.340(5)
Zr1−Cl2	2.428(1)	N2−C1	1.347(5)
Zr1−N1	2.186(3)	N3−C1	1.359(5)
Zr1−N2	2.193(3)	N4−C11	1.350(5)
Zr1−N4	2.197(4)	N5−C11	1.329(6)
Zr1−N5	2.204(3)		
Bond Angles			
Cl1−Zr1−Cl2	96.3(8)	N2−C1−N3	125.5(4)
N1−Zr1−N2	60.5(1)	N4−C11−N5	110.5(4)
N4−Zr1−N5	60.0(1)	N4−C11−N6	122.6(4)
N1−C1−N2	110.3(3)	N5−C11−N6	126.9(4)
N1−C1−N3	124.1(4)		

ring of 48.2(3) and 50.3(4)° for Zr1−N1−C1−N2 and Zr1−N4−C11−N5, respectively, indicate a slight overlap between the nitrogen p orbital and the π-conjugated chelate system.[5e] The planarity of the "CN_3" core is also shown by the sum of the bond angles around C1 and C11 (360°). The dihedral angle between the two NCN guanidinate chelate rings is 89.2°.

Alkylation of **4** with 2 equiv of $MgCl(CH_2Ph)$ produces the dibenzyl complex $[Zr\{\kappa^2N,N'\text{-}(NEt)(N\text{-}t\text{-}Bu)\text{-}CNMe_2\}_2(CH_2Ph)_2]$ (**3**) in good yield (Scheme 3). This complex is stable at room temperature under an inert atmosphere. The ^{1}H NMR spectrum at room temperature shows the presence of a broad signal corresponding to the benzylic CH_2Ph protons as well as a broad signal for the methylene protons of the ethyl substituents, indicating a fluxional process in solution. The $^{13}C\{^1H\}$ NMR spectrum of **3** shows only one set of resonances for the guanidinate ligands and two signals for the metal-bonded benzylic carbon atoms, thus confirming the dialkylation process.

In order to study these fluxional processes, we have carried out variable-temperature ^{1}H NMR studies in toluene-d_8. When the temperature was decreased to −50 °C, the spectra showed two doublets at 2.39 and 2.79 ppm for the benzylic protons, with a $^2J_{HH}$ coupling constant of 11 Hz, and two multiplets at 2.96 and 3.09 ppm corresponding to the nonequivalent methylene protons of each ethyl substituent. The signals for the benzylic protons coalesced at 25 °C ($\Delta G^{\ddagger}_c$ = 15.57 kcal/mol),[15] whereas those for the methylene protons of the ethyl groups coalesced at 40 °C ($\Delta G^{\ddagger}_c$ = 16.85 kcal/mol). Raising the temperature to 110 °C led to a single multiplet for the methylene protons of the ethyl substituents. The rate constants of the interconversion in **3** at various temperatures were calculated from eq 1, and the Eyring plot gives similar values for the activation parameters of the exchange for the benzyl protons, $\Delta H^{\ddagger}$ = 3.95 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −54.94 eu, and for the methylene protons, $\Delta H^{\ddagger}$ = 3.78 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −56.97 eu. This fluxional process and small $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values can be explained by a Bailar twist mechanism analogous to that described above for complexes **1** and **2**.

The migratory insertion of alkyl groups toward isocyanide ligands allows the formation of iminoacyl groups, which can coordinate in different modes. Thus, the κ^2C,N coordination of iminoacyl ligands is common for high-valent oxophilic early-transition-metal complexes.[21] Furthermore, their ability to undergo a range of carbon−carbon bond forming reactions has been shown to be particularly interesting in organometallic synthesis,[22] with insertion and intramolecular rearrangement processes leading to the formation of different products and intermediates, The type of ligand present is known to influence the reactivity of the metal center during subsequent insertion and intramolecular C−C coupling.[23] The products and intermediates found in such migratory insertion processes are shown in Scheme 4.

In fact, when two alkyl groups are bonded to the metal center, the addition of 1 equiv of isocyanide ligand produces the migratory insertion of one alkyl group to form iminoacyl complexes which evolve to give the vinylamido derivative (route a) or the imido complexes and the corresponding olefin (route b). If 2 equiv of isocyanide is used, the two alkyl groups undergo insertion (route c) to form the bis(iminoacyl) derivatives, which evolve to the enediamido complexes.

The treatment of **1** and **2** with 2,6-dimethylphenyl isocyanide (XyNC) in a 1:1 stoichiometric ratio in toluene at room temperature gave the monoinsertion reaction products **5** and **6**,

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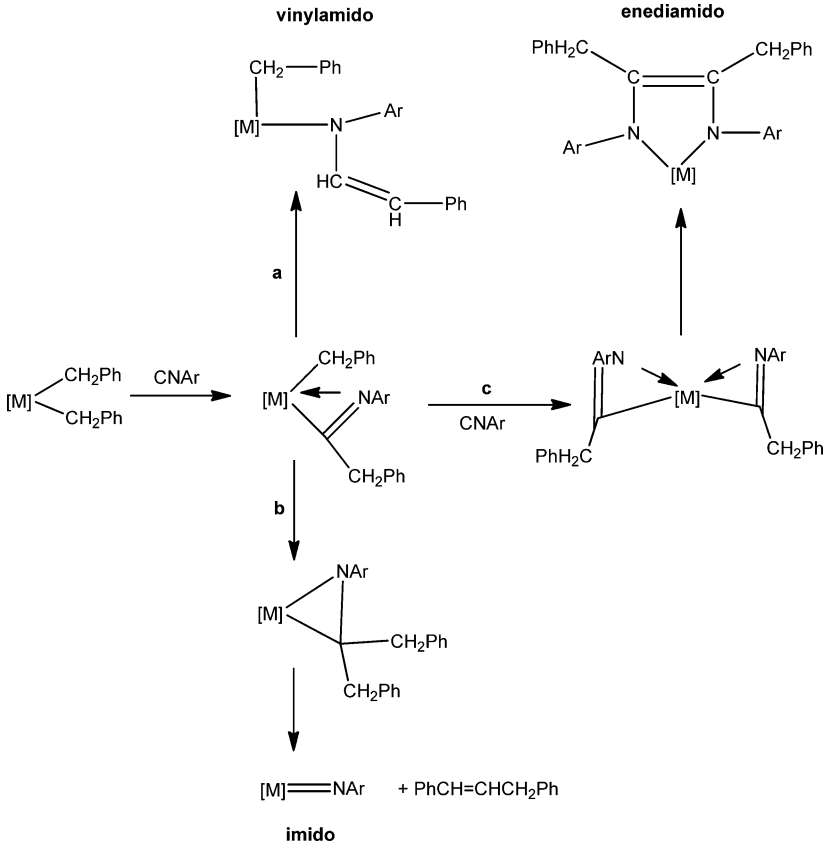
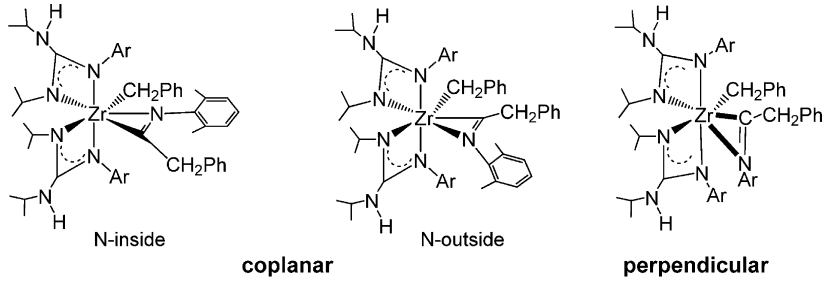
Scheme 4. Reaction Products and Intermediates in the Migratory Insertion of XyCN into Zr−C Bonds



Scheme 5. Possible Isomers for Complexes 5 and 6 (Coplanar and Perpendicular Benzyl and η^2-Iminoacyl Ligands)



with full conversion being reached after 2 days, whereas complexes **5** and **6** were obtained in almost quantitative yield in 16 h when the reaction was carried out at 50 °C. Complexes **5** and **6** were characterized by NMR and FT-IR spectroscopy. The benzyl methylene protons are diastereotopic; thus, the ^{1}H NMR spectrum shows a broad doublet at ca. 2.38 ppm as well as a broad singlet at ca. 3.79 ppm for the inserted benzylic protons. A singlet is also observed at ca. 1.97 ppm for the methyl protons of the 2,6-dimethylphenyl moiety, and the two guanidinate ligands become nonequivalent, with each presenting a set of signals. The κ^2 coordination mode of the iminoacyl group is suggested by ^{13}C{^{1}H} NMR and IR data, with a signal at ca. 252.3 ppm and an absorption at ca. 1561 cm^{-1} being assigned to the iminoacyl quaternary carbon atom and the ν(C═N) stretching vibration, respectively. Moreover, the iminoacyl group can position itself in a perpendicular or coplanar ("*proximal*" or "N-outside" and "*distal*" or "N-inside") geometry with the benzyl ligand (Scheme 5). Although the spectroscopic data do not distinguish between those conformations, it has been demonstrated that the N-outside isomer is the initial kinetic iminoacyl-containing product of the insertion reaction; most group 4 metal derivatives appear as the N-inside isomer, which results from thermodynamic control.[24] As such, we tentatively propose that this complex is the only product resulting from thermodynamic control and that it adopts the N-inside conformation (Scheme 5).

However, heating a solution of this reaction mixture in toluene at reflux for 1 h resulted in a color change from yellow to purple and formation of the imido complex [Zr{κ^2*N*,*N*′-(N-*i*-Pr)(N(Ar)CNH(*i*-Pr)}$_2${N(2,6-Me$_2$C$_6$H$_3$)}] (Ar = 4-*t*-BuC$_6$H$_4$ (**7**), 4-BrC$_6$H$_4$ (**8**)) in very good yield (Scheme 6). Surprisingly, these imido complexes were also obtained when a solution of 1 equiv of **1** or **2** and 2 equiv of XyNC was heated at 70 °C for 4 h, with approximately 1 equiv of XyNC remaining unreacted. This implies that imido formation is favored by the addition of an excess of isocyanide. Moreover, the presence of 2-benzylstyrene was detected when these reactions were carried out in an NMR tube (a doublet at 3.49 ppm for the C*H*$_2$Ph

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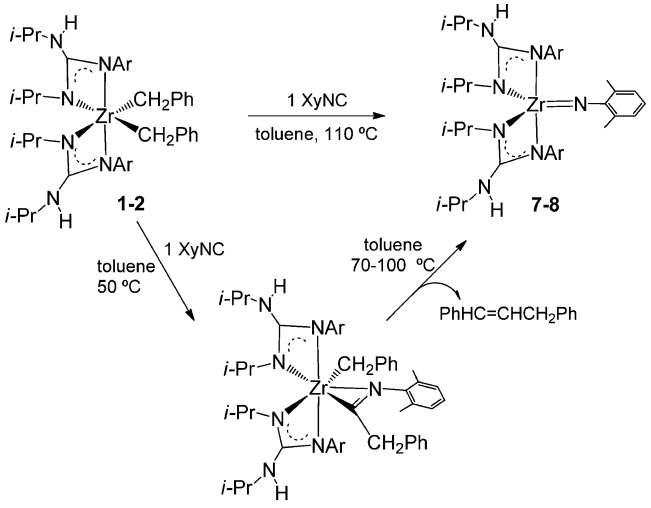
Scheme 6. Reaction of Complexes 1 and 2 with XyNC To Give the Imido Complexes 7 and 8, Respectively



protons and a multiplet at ca. 6.30 ppm for the olefin −C*H*═C*H*− protons), thus indicating that the reaction proceeds via a mechanism similar to that proposed for alkyl complexes with symmetrical guanidinate ligands.[5b]

Complexes **7** and **8** were characterized spectroscopically. The ^{1}H NMR spectra show an absence of resonances corresponding to the benzylic groups and the presence of four doublets for the *i*-Pr methyl groups, as well as two singlets for the two methyl groups of the arylimido ligand, thus indicating that the previously described rotation process is strongly hindered in this complex at room temperature. Variable-temperature ^{1}H NMR studies of **7** in toluene-d_8 showed two broad signals for the methyl protons of the *i*-Pr substituents at 80 °C, with the two singlet resonances corresponding to the methyl groups of the aryl isocyanide being observed as a broad signal. The coalescence temperature was 70 °C, and the calculated free energy of activation was 16.6 kcal/mol. The two guanidinate ligands are equivalent at this temperature, due to the existence of a C_2 axis and a plane containing the Zr═N bond.

Complexes **7** and **8** are imido guanidinate complexes containing asymmetric guanidinate ligands with the Zr atom in a distorted-trigonal-bipyramidal geometry at room temperature similar to that exhibited by the few known examples of terminal imido complexes of group 4 metals with symmetrically coordinated guanidinate ligands.[5b,c] Additionally, the geometry around the Zr atom changed from trigonal bipyramidal to square pyramidal, in agreement with the variable-temperature NMR data at 80 °C.

In contrast to the reactivity outlined above, complex **3** reacted with 2 equiv of XyNC in toluene at reflux over 6 h to yield the enediamido complex [Zr{κ^2*N*,*N*′-(N-*t*-Bu)(NEt)-CNMe$_2$}$_2$}{κ^2*N*,*N*′-N(2,6-Me$_2$C$_6$H$_3$)(CH$_2$Ph)C═C(CH$_2$Ph)-N(2,6-Me$_2$C$_6$H$_3$)}] (**9**). Formation of the new enediamido ligand is supported on the basis of the IR spectrum, which shows a characteristic stretching vibration at 1539 cm^{-1}, and a single-crystal X-ray diffraction study. Suitable crystals of complex **9** were grown from toluene solution at −30 °C. An ORTEP diagram of **9** is shown in Figure 4. Selected bond lengths and angles for **9** are given in Table 3.

Complex **9** is the first structurally characterized enediamido complex of a group 4 metal with guanidinate ligands

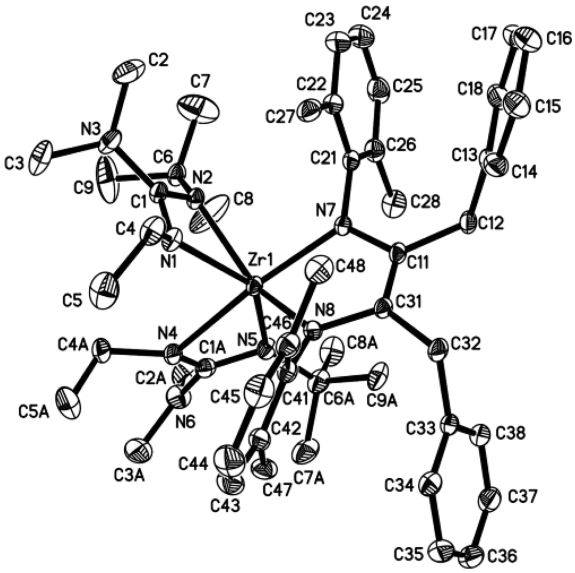


Figure 4. ORTEP drawing of complex **9**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): Zr1−N1, 2.248(2); Zr1−N2, 2.270(2); Zr1−N4, 2.283(2); Zr1−N5, 2.231(2); Zr1−N7, 2.152(2); Zr1−N8, 2.140(2); C11−C31, 1.347(4); N1−C1, 1.327(3); N2−C1, 1.336(3); N3−C1, 1.394(4); N4−C1A, 1.330(4); N5−C1A, 1.346(4); N6−C1A, 1.382(4); N1−Zr1−N2, 58.88(8); N4−Zr1−N5, 58.72(9); N1−C1−N2, 113.0(2); N1−C1−N3, 123.2(3); N2−C1−N3, 123.8(3).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 9

Bond Lengths			
Zr1−N1	2.248(2)	N3−C1	1.394(4)
Zr1−N2	2.270(2)	N4−C1A	1.330(4)
Zr1−N4	2.283(2)	N5−C1A	1.346(4)
Zr1−N5	2.231(2)	N6−C1A	1.382(4)
Zr1−N7	2.152(2)	N7−C11	1.435(3)
Zr1−N8	2.140(2)	N8−C31	1.426(3)
N1−C1	1.327(3)	C11−C31	1.347(4)
N2−C1	1.336(3)		
Bond Angles			
N1−Zr1−N2	58.88(8)	N4−C1A−N6	122.9(3)
N4−Zr1−N5	58.72(9)	N5−C1A−N6	125.5(3)
N7−Zr1−N8	75.44(8)	C1−N3−C2	121.1(3)
N1−C1−N2	113.0(2)	C1−N3−C3	120.3(3)
N1−C1−N3	123.2(3)	C1A−N6−C2A	123.3(3)
N2−C1−N3	123.8(3)	C1A−N6−C3A	121.1(3)
N4−C1A−N5	111.6(2)		

coordinated in an asymmetrical mode. It crystallizes in the $P\bar{1}$ space group. The zirconium atom exhibits a distorted-pseudotetrahedral geometry, with two bidentate guanidinate ligands bonded via two nitrogen atoms in a κ^2 coordination mode and the enediamido group also bonded via two nitrogen atoms. The enediamido group has a bite angle of 75.45(8)°, which is smaller than that typically observed in other compounds (approximately 85°);[5b,25] the guanidinate bite angles are ca. 58.8°. The Zr1−N7 and Zr1−N8 bond distances (2.152(2) and 2.140(2) Å, respectively) corresponding to the Zr−amido linkages are shorter than the average Zr−N guanidinate bond lengths of ca. 2.26(2) Å. The planarity of the "CN$_3$" core, which is seen by the sum of bond angles

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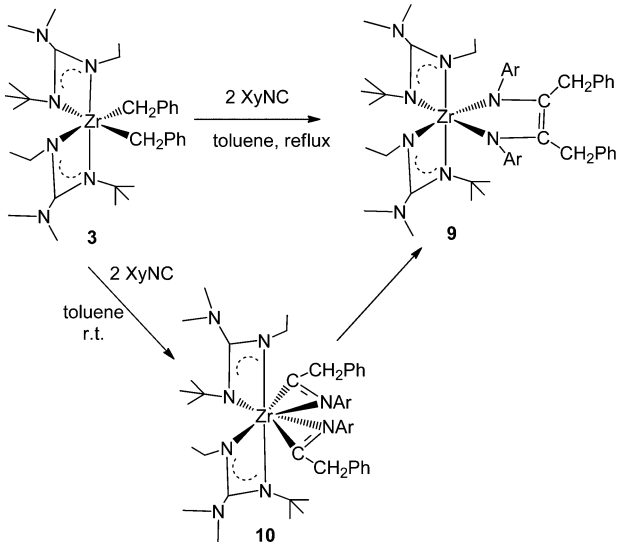
around C1 and C1A (360°), is in contrast with the three different distances found for the N−C bonds. These findings imply a different charge delocalization in this complex, with a less electron donating guanidinate ligand, probably due to the presence of other strong donors, such as enediamido, in the coordination sphere of the metal atom. The C11−C31 distance of 1.347(4) Å corresponds to a C=C bond, whereas the N7−C11 and N8−C31 distances of 1.435(3) and 1.426(3) Å, respectively, are consistent with single bonds between sp^2-hybridized C and N atoms. The dihedral angle of 13.6° between the N7−Zr1−N8 and N7−C11=C31−N8 planes indicates a practically planar chelate ring.

The treatment of **3** with 2 equiv of XyNC at room temperature for 16 h led to formation of the bis(κ^2C,N-iminoacyl) complex [Zr{κ^2N,N'-(N-*t*-Bu)(NEt)CNMe$_2$}$_2$]{κ^2C,N-(2,6-Me$_2$C$_6$H$_3$)N=C(CH$_2$Ph)}$_2$] (**10**) (Scheme 7).

Scheme 7. Migratory Insertion Processes and Evolution to the Enediamido Complex 9 from 10



The formation of **10** was supported by IR and $^{13}C\{^1H\}$ NMR spectroscopy, with the IR spectrum showing a characteristic stretching vibration at 1560 cm^{-1} and the $^{13}C\{^1H\}$ NMR spectrum a signal at 251.9 ppm for the C=N group. In addition, the ^1H NMR spectrum shows an AB system that can be assigned to the diasterotopic methylene protons of the iminoacyl ligands formed by a migratory insertion process.

Although the formation of two isomers (*anti*/*syn*) of the pseudooctahedral metal complex **10** would be expected (Scheme 8), the NMR spectra of complex **10** show only one set of signals, corresponding to a single species.

It is well known that the presence of a guanidinate ligand influences the reactivity of a metal center as a result of its steric and electronic effects on the iminoacyl complex.[5a,15b,23] This factor will lead to formation of the final enediamido complex **9** via an intramolecular coupling of the two iminoacyl groups in the *syn* isomer, as carbon−carbon coupling would be strongly hindered in the *anti* isomer.[23,26] However, this situation is in contrast with the synthesis of the previously described imido complexes **7** and **8**, where the presence of two aryl groups in *apical* positions can block formation of the bis(κ^2-iminoacyl) derivative and favor formation of the less sterically hindered imido complex.

Scheme 8. Possible Isomers (*anti*/*syn*) of the Iminoacyl Complex

CONCLUSIONS

The current work describes new dibenzylzirconium(IV) complexes containing asymmetric guanidinate ligands and their different behaviors with regard to the insertion of aryl isocyanides. Thus, the more hindered complexes **1** and **2** only allow a single insertion reaction to give the imido complexes **7** and **8**, respectively, whereas the enediamido derivative **9** is obtained by an intramolecular coupling reaction of the two iminoacyl ligands in complex **10**. These results show that steric effects resulting from the coordination mode of the guanidinate ligands play a decisive role in the migratory insertion reaction of the aryl isocyanide and the stability of κ^2C,N-iminoacyl intermediates. In addition, we have isolated and identified the monoacyl intermediates **5** and **6**, the bis(iminoacyl) complex **10**, and 2-benzylstyrene as a reaction byproduct.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed using standard Schlenk and glovebox techniques under an atmosphere of dry nitrogen. Solvents were purified by passage through a column of activated alumina (Innovative Technologies) and degassed under nitrogen before use. Microanalyses were carried out using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded using a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent using standard VARIANT-FT software. FT-IR spectra were recorded using a Bruker Tensor 27 spectrophotometer. Zr(CH$_2$Ph)$_4$[27] and [Zr(NMe$_2$)$_2$Cl$_2$(THF)$_2$][21] were prepared according to literature procedures. ZrCl$_4$, ZnEt$_2$, amines, 2,6-dimethylphenyl isocyanide, MgCl(CH$_2$Ph), and the carbodiimide derivatives were purchased from Sigma Aldrich.

Synthesis of [Zr{κ^2N,N'-(N-*i*-Pr)(N4-*t*-BuC$_6$H$_4$)CNH(*i*-Pr)}$_2$(CH$_2$Ph)$_2$] (1). (HN-*i*-Pr)$_2$C=N(4-*t*-BuC$_6$H$_4$) (0.60 g, 2.20 mmol) was added to a solution of Zr(CH$_2$Ph)$_4$ (0.50 g, 1.10 mmol) in toluene (15 mL), and the resulting yellow solution was stirred at room temperature for 30 min. The solvent was then evaporated to dryness to afford a yellow solid, which was redissolved in toluene and cooled to −20 °C to obtain yellow crystals of **1**. Yield: 0.83 g (93%). ^1H NMR (C$_6$D$_6$, 25 °C): δ 0.63 (d, 12H, HNCH(C*H*$_3$)$_2$, $^3J_{H-H}$ = 6.3 Hz), 1.17 (d, 12H, NCH(C*H*$_3$)$_2$, $^3J_{H-H}$ = 6.6 Hz), 1.20 (s, 18H, *t*-Bu), 2.39 (br s, 4H, C*H*$_2$Ph), 3.21 (m, 4H, HNC*H*(CH$_3$)$_2$ and NC*H*(CH$_3$)$_2$), 3.59 (d, 2H, *H*NCH(CH$_3$)$_2$, $^3J_{H-H}$ = 9.15 Hz), 6.77−7.27 (m, 18H, 4-*t*-BuC$_6$*H*$_4$ and CH$_2$*Ph*). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 23.9 (HNCH(*C*H$_3$)$_2$), 24.1 (NCH(*C*H$_3$)$_2$), 31.9, (C-(*C*H$_3$)$_3$), 34.1 (C(CH$_3$)$_3$), 43.8 (HNCH(CH$_3$)$_2$, 44.8 (NCH(CH$_3$)$_2$), 75.1 (CH$_2$Ph), 118.9−149.7 (4-*t*-BuC$_6$H$_4$ and CH$_2$*Ph*), 165.9 (*C*N$_3$). Anal. Calcd for C$_{48}$H$_{70}$ZrN$_6$: C, 70.20; H, 8.53; N, 10.24. Found: C, 70.46; H, 8.49; N, 10.33.

Synthesis of [Zr{κ^2N,N'-(N-*i*-Pr)(N4-BrC$_6$H$_4$)CNH(*i*-Pr)}$_2$(CH$_2$Ph)$_2$] (2). Complex **2** was prepared in a manner identical with that for **1** from Zr(CH$_2$Ph)$_4$ (0.16 g, 0.35 mmol) and (HN-*i*-Pr)$_2$C=N(4-BrC$_6$H$_4$) (0.21 g, 0.70 mmol). Yield: 0.29 g (95%).[1] H NMR (C$_6$D$_6$, 25 °C): δ 0.58 (d, 12H, HNCH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.2 Hz), 1.11 (d, 12H, NCH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.2 Hz), 2.18 (br s, 4H, C*H*$_2$Ph), 3.05 (m, 2H, NC*H*(CH$_3$)$_2$), 3.09 (m, 2H, HNC*H*(CH$_3$)$_2$), 3.49 (d, 2H, *H*NCH(CH$_3$)$_2$, $^3J_{HH}$ = 9.2 Hz), 6.35−7.40 (m, 18H, 4-BrC$_6$*H*$_4$ and CH$_2$*Ph*). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 21.4 (HNCH(*C*H$_3$)$_2$), 23.0 (NCH(*C*H$_3$)$_2$), 44.4 (HNCH(CH$_3$)$_2$, 45.8 (NCH(CH$_3$)$_2$), 75.2 (CH$_2$Ph), 118.0−150.1 (4-BrC$_6$H$_4$ and CH$_2$*Ph*), 163.0 (*C*N$_3$). Anal.

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Calcd for $C_{40}H_{52}ZrN_6Br_2$: C, 55.54; H, 6.02; N, 9.72. Found: C, 55.71; H, 5.98; N, 9.68.

Synthesis of [Zr{κ^2*N,N′*-(N-*t*-Bu)(NEt)CNMe$_2$}$_2$Cl$_2$}] (4). *t*-BuN═C═NEt (0.82 g, 5.27 mmol) was added to a solution of [$ZrCl_2(NMe_2)_2(THF)_2$] (0.90 g, 2.29 mmol) in toluene (50 mL) at −78 °C, and the mixture was stirred at room temperature for 6 h. The resulting pale yellow solution was then dried in vacuo to afford a yellow solid, which was redissolved in THF and cooled to −20 °C to obtain colorless crystals of **4**. Yield: 1.10 g (96%). ^{1}H NMR (C_6D_6, 25 °C): δ 1.26 (t, 6H, NCH_2CH_3, $^3J_{HH}$ = 6.9 Hz), 1.37 (s, 18H, *t*-Bu), 2.27 (s, 12H, NMe_2), 3.29 (q, 4H, NCH_2CH_3, $^3J_{HH}$ = 6.9 Hz).^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 17.3 (NCH_2CH_3), 31.4 (NCH_2CH_3), 40.3($C(CH_3)_3$), 42.7 ($C(CH_3)_3$), 53.9 (NMe_2), 173.8 (CN_3). Anal. Calcd for $C_{18}H_{40}ZrN_6Cl_2$: C, 43.02; H, 7.97; N, 16.73. Found: C, 43.64; H, 8.26; N, 16.99.

Synthesis of [Zr{κ^2*N,N′*-(N-*t*-Bu)(NEt)CNMe$_2$}$_2$(CH$_2$Ph)$_2$] (3). MgCl(CH_2Ph) (2.00 mL, 3.98 mmol, 2 M in THF) was added to a solution of **4** (1.00 g, 1.99 mmol) in THF (50 mL) at −78 °C, and the mixture was stirred at room temperature for 16 h. The resulting yellow solution was dried in vacuo, the residue extracted with *n*-hexane, and the solvent partially removed under vacuum to afford yellow crystals of complex **3**. Yield: 1.17 g (97%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.96 (t, 6H, NCH_2CH_3, $^3J_{HH}$ = 6.9 Hz), 1.20 (s, 18H, *t*-Bu), 2.27 (s, 12H, NMe_2), 2.72 (br s, 4H, CH_2Ph), 3.01 (br s, 4H, NCH_2CH_3), 6.84−7.20 (m, 10H, CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 16.7 (NCH_2CH_3), 31.6 (NCH_2CH_3), 40.6 ($C(CH_3)_3$), 40.7 ($C(CH_3)_3$), 52.7 (NMe_2), 71.2 (CH_2Ph), 120.3−149.9 (CH_2Ph), 176.2 (CN_3). Anal. Calcd for $C_{32}H_{54}ZrN_6$: C, 62.62; H, 8.81; N, 13.70. Found: C, 62.74; H, 8.92.01; N, 13.72.

Synthesis of [Zr{κ^2*N,N′*-(N-*i*-Pr)(N(4-*t*-BuC$_6$H$_4$))CNH(*i*-Pr)}$_2$}-{κ^2*C,N*-(2,6-Me$_2$C$_6$H$_3$)N═C(CH$_2$Ph)}(CH$_2$Ph)] (5). 2,6-Dimethylphenyl isocyanide (0.01 g, 0.11 mmol) was added to a solution of **1** (0.09 g, 0.11 mmol) in toluene (15 mL), and the reaction mixture was stirred at 50 °C for 16 h. The resulting orange solution was dried in vacuo to afford complex **5** as an orange solid. Yield: 0.09 g (89%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.66 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 5.9 Hz), 0.69 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.20 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 5.9 Hz), 1.22 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.23, 1.27 (2s, 18H, *t*-Bu), 1.97 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.39 (d, 2H, ZrCH_2Ph, $^2J_{HH}$ = 20.0 Hz), 3.22 (m, 2H, $HNCH(CH_3)_2$), 3.42 (m, 2H, $NCH(CH_3)_2$), 3.57 (d, 1H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 9.5 Hz), 3.62 (d, 1H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 9.5 Hz), 3.79 (br s, 2H, CH_2Ph), 6.60−7.20 (m, 21H, *t*-BuC_6H_4, 2,6-$(CH_3)_2C_6H_3$ and CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 19.5 (2,6-$(CH_3)_2C_6H_3$), 23.4, 23.5, 24.4, 24.5 ($HNCH(CH_3)_2$ and $NCH(CH_3)_2$), 31.8, ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 46.2 ($HNCH(CH_3)_2$, 45.9 ($NCH(CH_3)_2$), 75.1 (Zr-(CH_2Ph)), 118.0−140.9 (CH_2Ph, $PhCH_2C$═N, 2,6-$(CH_3)_2C_6H_3$, and *t*-BuC_6H_4), 166.2 (CN_3), 252.7 (C═N). Anal. Calcd for $C_{57}H_{79}ZrN_7$: C, 71.83; H, 8.30; N, 10.29. Found: C, 72.01; H, 8.39; N, 10.22.

Synthesis of [Zr{κ^2*N,N′*-(N-*i*-Pr)(N(4-BrC$_6$H$_4$))CNH(*i*-Pr)}$_2$}-{κ^2*C,N*-(2,6-Me$_2$C$_6$H$_3$)N═C(CH$_2$Ph)}(CH$_2$Ph)] (6). Complex **6** was prepared in a manner identical with that for **5** from **2** (0.09 g, 0.11 mmol) and 2,6-dimethylphenyl isocyanide (0.01 g, 0.11 mmol). Yield: 0.10 g (91%). ^{1} H NMR (C_6D_6, 25 °C): δ ^{1}H NMR (toluene-d_8, 25 °C): δ 0.41 (br s, 6H, $HNCH(CH_3)_2$), 0.61 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 1.07 (br s, 6H, $NCH(CH_3)_2$), 1.48 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 2.39 (br s, 4H, CH_2Ph), 2.14 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 3.26 (m, 2H, $NCH(CH_3)_2$), 3.28 (m, 2H, $HNCH(CH_3)_2$), 3.42 (d, 1H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 9.5 Hz), 3.62 (d, 1H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 9.8 Hz), 3.92 (br s, 2H, CH_2Ph), 6.40−7.41 (m, CH_2Ph, BrC_6H_4 and 2,6-$(CH_3)_2C_6H_3$). ^{13}C{^{1}H} NMR (toluene-d_8, 25 °C): δ 19.9 (2,6-$(CH_3)_2C_6H_3$), 23.2, 23.6, 24.3, 24.9 ($HNCH(CH_3)_2$) and ($NCH(CH_3)_2$), 45.0 ($HNCH(CH_3)_2$, 45.7 ($NCH(CH_3)_2$), 72.7 (ZrCH_2Ph), 124.0−140.2 (CH_2Ph, $PhCH_2C$═N, and 2,6-$(CH_3)_2C_6H_3$), 164.6 (CN_3), 251.9 (C═N). Anal. Calcd for $C_{49}H_{61}ZrN_7Br_2$: C, 59.90; H, 6.22; N, 9.99. Found: C, 60.32; H, 6.51; N, 10.42.

Synthesis of [Zr{κ^2*N,N′*-(N-*i*-Pr)(N4-*t*-BuC$_6$H$_4$)CNH(*i*-Pr)}$_2${N-(2,6-Me$_2$C$_6$H$_3$)}] (7). 2,6-Dimethylphenyl isocyanide (0.03 g, 0.25 mmol) was added to a solution of **1** (0.21 g, 0.25 mmol) in toluene (15 mL), and the reaction mixture was stirred at reflux for 1 h. The resulting purple solution was dried in vacuo to afford complex **7** as a dark red solid. Yield: 0.16 g (86%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.44 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 0.56 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 0.91 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 1.08 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.4 Hz), 1.27 (s, 18H, *t*-Bu), 2.08, 2.22 (2s, 6H, 2,6-$(CH_3)_2C_6H_3$), 3.08 (m, 2H, $HNCH(CH_3)_2$), 3.51 (m, 4H, $NCH(CH_3)_2$ and $HNCH(CH_3)_2$), 6.87−7.20 (m, *t*-BuC_6H_4 and 2,6-$(CH_3)_2C_6H_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 18.7 (2,6-$(CH_3)_2C_6H_3$), 23.7, 23.9, 24.2, 24.7 ($HNCH(CH_3)_2$, $NCH(CH_3)_2$), 31.8 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 44.9 ($HNCH(CH_3)_2$, 46.7 (NCH-$(CH_3)_2$), 123.7 - 149.9 (2,6-$(CH_3)_2C_6H_3$ and *t*-BuC_6H_4), 164.0 (CN_3). Anal. Calcd for $C_{42}H_{65}ZrN_7$: C, 66.47; H, 8.57; N, 12.93. Found: C, 66.76; H, 8.88; N, 12.85.

Synthesis of [Zr{κ^2*N,N′*-(N-*i*-Pr)(N4-BrC$_6$H$_4$)CNH(*i*-Pr)}$_2${N(2,6-Me$_2$C$_6$H$_3$)}] (8). Complex **8** was prepared in a manner identical with that for **7** from **2** (0.09 g, 0.11 mmol) and 2,6-dimethylphenyl isocyanide (0.10 g, 0.11 mmol). Yield: 0.08 g (98%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.39 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz), 0.47 (d, 6H, $HNCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz), 0.75 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz), 0.99 (d, 6H, $NCH(CH_3)_2$, $^3J_{HH}$ = 6.1 Hz), 2.04, 2.16 (2s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.87 (m, 2H, $HNCH(CH_3)_2$), 3.37 (m, 4H, $NCH(CH_3)_2$ and $HNCH(CH_3)_2$), 6.60−7.22 (m, BrC_6H_4 and 2,6-$(CH_3)_2C_6H_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 20.2 (2,6-$(CH_3)_2C_6H_3$), 23.2, 23.5, 24.0, 24.6 ($HNCH(CH_3)_2$ and NCH-$(CH_3)_2$), 45.1 ($HNCH(CH_3)_2$), 46.7 ($NCH(CH_3)_2$), 121.2−149.9 (2,6-$(CH_3)_2C_6H_3$ and BrC_6H_4), 163.9 (CN_3). Anal. Calcd for $C_{34}H_{47}ZrN_7Br_2$: C, 50.93; H, 5.87; N, 12.23. Found: C, 51.23; H, 6.14; N, 12.44.

Synthesis of [Zr{κ^2*N,N′*-(N-*t*-Bu)(NEt)CNMe$_2$}$_2$}{κ^2*N,N′*-N(2,6-Me$_2$C$_6$H$_3$)(CH$_2$Ph)C═C(CH$_2$Ph)N(2,6-Me$_2$C$_6$H$_3$)}] (9). 2,6-Dimethylphenyl isocyanide (0.09 g, 0.66 mmol) was added to a solution of **3** (0.20 g, 0.33 mmol) in toluene (10 mL), and the mixture was stirred at reflux temperature for 6 h to give an orange solution. All volatiles were then removed in vacuo to provide a dark orange solid, which was recrystallized from toluene. Yield: 0.21 g (72%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.72 (br s, 6H, CH_2CH_3)), 1.04 (s, 18H, *t*-Bu), 2.08 (s, 12H, 2,6-$(CH_3)_2C_6H_3$), 2.27 (s, 12H, NMe_2), 3.24 (br s, 4H, CH_2Ph), 3.03 (br s, 4H, CH_2CH_3), 6.87−7.20 (m, (2,6-$CH_3)_2C_6H_3$ and CH_2Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 16.1 (2,6-$(CH_3)C_6H_3$), 18.1 (CH_2CH_3), 32.1 (CH_2CH_3), 40.9 ($C(CH_3)_3$), 41.5 ($C(CH_3)_3$),53.2 (NMe_2), 68.2 (CH_2Ph), 121.8−153.4 (2,6-$(CH_3)_2C_6H_3$ and C_6H_5) 168.4 (CN_3). The signal corresponding to the C═C group is not observed. Anal. Calc. for $C_{50}H_{72}ZrN_8$: C, 68.55; H, 8.22; N, 12.79. Found: C 68.72; H, 8.56; N, 12.89.

Synthesis of [Zr{κ^2*N,N′*-(N-*t*-Bu)(NEt)CNMe$_2$}$_2$}{κ^2*C,N*-(2,6-Me$_2$C$_6$H$_3$)N═C(CH$_2$Ph)}$_2$] (10). 2,6-Dimethylphenyl isocyanide (0.07 g, 0.55 mmol) was added to a solution of **3** (0.17 g, 0.27 mmol) in toluene (10 mL) and the mixture allowed to stir at room temperature for 16 h. The resulting orange solution was dried in vacuo to provide orange oil. Yield (0.23 g, 95%). ^{1}H NMR (C_6D_6, 25 °C): 1.06 (t, 6H, NCH_2CH_3, $^3J_{HH}$ = 6.1 Hz), 1.37 (s, 18H, *t*-Bu), 2.01 (s, 12H, NMe_2), 2.05 (s, 12H, 2,6-$(CH_3)_2C_6H_3$), 3.01 (br s, 8H, NCH_2CH_3). 3.96, 4.17 (2d, 4H, CH_2Ph, $^2J_{HH}$ = 13.2 Hz), 6.63−7.24 (2,6-$(CH_3)_2C_6H_3$ and CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 17.4 (NCH_2CH_3), 17.8, 18.8 (2,6-$(CH_3)_2C_6H_3$), 33.1 (NCH_2CH_3), 40.1 ($C(CH_3)$), 41.3 ($C(CH_3)$), 53.1 (NMe_2), 110.5−150.2 ($PhCH_2C$═N, 2,6-$(CH_3)_2C_6H_3$, and CH_2Ph), 176.2 (CN_3), 251.9 (C═N). Anal. Calcd for $C_{50}H_{72}ZrN_8$: C, 68.55; H, 8.22; N, 12.79. Found: C, 68.83; H, 8.36; N, 12.98.

X-ray Structure Analyses for Complexes 2, 4, and 9. Crystals of complexes **2**, **4**, and **9** were obtained from toluene, THF, and diethyl ether/toluene (1/1) solutions at −30 °C, respectively. Crystals were mounted at low temperature in inert oil on a glass fiber. Data were collected using a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å).

The crystal data, data collection, structural solution, and refinement parameters for all three complexes are summarized in the Supporting Information. Data were integrated using SAINT,[28] and an absorption

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correction was performed with the program SADABS.[29] All structures were solved by direct methods using SHELXTL[30] and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Complexes **2** and **4** show some atoms in disordered positions, and complexes **2** and **9** crystallize with toluene molecules as solvates. The toluene molecule in complex **2** shows unsolved disorder.

■ ASSOCIATED CONTENT

Supporting Information

CIF files and a table giving full crystallographic data for **2**, **4**, and **9** and figures giving ^{1}H NMR spectra for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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