

## Communications

Transformations of Aryl Isocyanide on  
Guanidinate-Supported Organozirconium Complexes To  
Yield Terminal Imido, Iminoacyl, and Enediamido  
Ligands

Tiow-Gan Ong, Dayna Wood, Glenn P. A. Yap, and Darrin S. Richeson\*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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**Summary:** Reactions of aryl isocyanide with bis(guanidinate) Zr(IV) hydrocarbyl complexes are presented. With 1 equiv of  $Ar'NC$  the ultimate products are the terminal Zr imido complexes  $[{(R'NR'')C(NR)_2}_2ZrN(2,6-Me_2C_6H_3)]$  (**3**,  $R = R' = iPr$ ,  $R'' = H$ ; **5**,  $R = iPr$ ,  $R' = R'' = Me$ ), which are derived via a unique transformation from intermediate  $\eta^2$ -iminoacyl species. With 2 equiv of  $Ar'NC$ ,  $[{(Me_2N)C(N^iPr)_2}_2Zr(\eta^2-Ar'N=CMe)_2]$  (**6**) was isolated. Mild thermolysis of **6** generates an enediamido complex via intramolecular coupling of the iminoacyl groups.

Guanidinate anions,  $[R'R''NC(NR)_2]^-$ , exhibit versatile and flexible coordination properties and have received increasing attention as ancillary ligands for both main-group and transition-metal complexes.<sup>1–3</sup> These species offer several patterns of substitution, and we are particularly interested in those with either one or two organic substituents on the tertiary  $N(R')R''$  center (e.g.  $N(H)R'$  or  $NR_2'$ ). Most of the efforts in this area have been in the development of new guanidinate complexes, with fewer examples of reactivity studies involving small-molecule activation by complexes supported by

guanidinate ligands. Insertion reactions represent a fundamental reaction type in organometallic chemistry, and isocyanides are among the common substrates of such reactions.<sup>4</sup> We report a sequence of reactions of isocyanide with two bis(guanidinate) Zr(IV) hydrocarbyl complexes that proceed beyond insertion to form new C–C bonds. One of these transformations gives rise to the terminal Zr imido complexes  $[{(R'NR'')C(NR)_2}_2ZrN(2,6-Me_2C_6H_3)]$  ( $R = R' = iPr$ ,  $R'' = H$ ;  $R = iPr$ ,  $R' = R'' = Me$ ) through a novel reaction pathway. A change in reaction stoichiometry produced an enediamido complex via intramolecular coupling of iminoacyl groups. These reactions exemplify the ability of group 4 guanidinate complexes to undergo migratory insertion and to exhibit noteworthy reactivity.

The direct reaction of a 1:2 molar ratio of  $Zr(Bz)_4$  and  $N,N,N'$ -triisopropylguanidine,  $(iPrN)=C(NH^iPr)_2$ , in toluene at room temperature proceeds via proton transfer and toluene elimination to yield the new species  $[{(iPrNH)C(N^iPr)_2}_2ZrBz_2]$  (**1**) in 88% isolated yield. The  $^1H$  and  $^{13}C$  NMR spectra of **1** display two sets of  $^1Pr$  signals in a 2:1 ratio and a single methylene resonance, suggesting a pseudo-octahedral Zr center with freely rotating, cis-oriented benzyl groups. An X-ray crystallographic analysis confirms this hypothesis.<sup>5</sup>

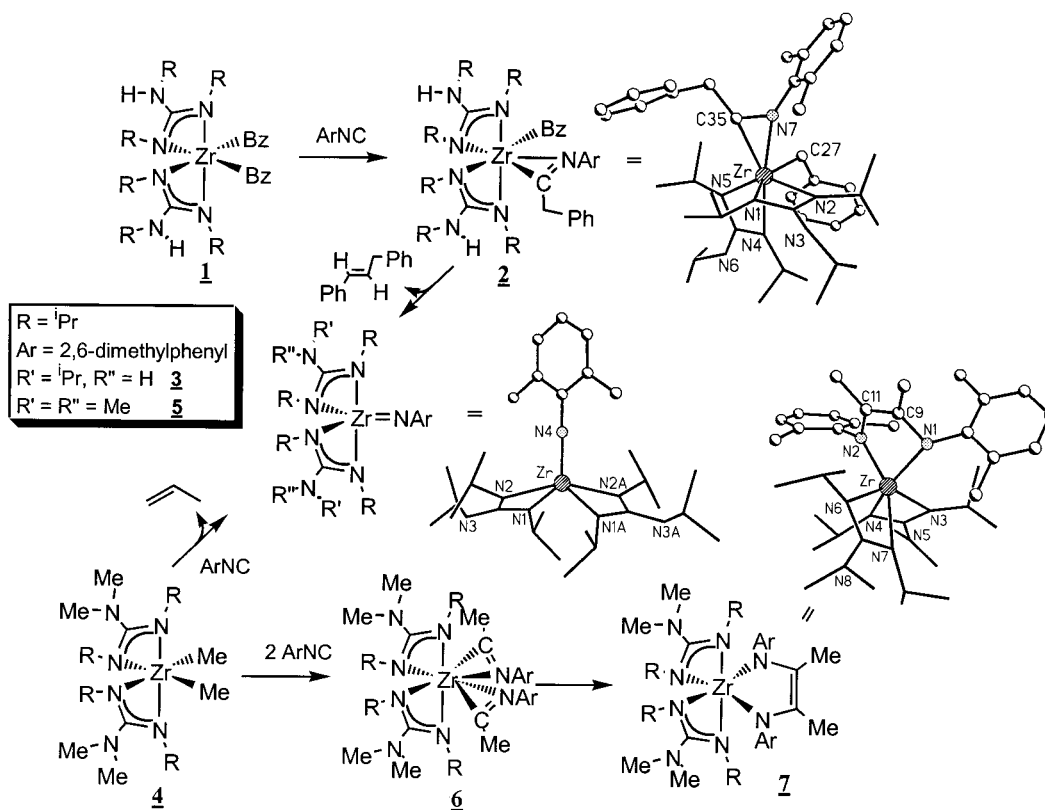
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Scheme 1



Complex **1** reacts rapidly with 1 equiv of 2,6-dimethylphenyl isocyanide, as indicated by a color change from yellow to dark orange to generate compound **2** (Scheme 1). The identity of **2** as the monoinsertion product was indicated by the relative intensity of the aromatic methyl signals and appearance of two equal-intensity resonances for the benzyl methylene protons in the  $^1H$  NMR spectrum at 2.41 ppm (Zr–CH<sub>2</sub>Ph) and 4.06 ppm (Zr– $\eta^2$ -Ar'N=CCH<sub>2</sub>Ph). A characteristic resonance for the iminoacyl C appeared at  $\delta$  252.86.<sup>4</sup>

The molecular structure of **2** confirmed the connectivity of this species and was consistent with our spectroscopic observations (Scheme 1).<sup>6</sup> The Zr(IV) coordination environment consists of two chelating, bidentate guanidinate monoanions, a benzyl ligand, and an  $\eta^2$ -iminoacyl ligand derived from the insertion of the aryl isocyanide into a Zr–Bz bond. Although formally seven-coordinate, the geometry of **2** can be considered distorted octahedral if the  $\eta^2$ -C=N is assigned a single coordination site. The N(7)–C(35) bond length of 1.292(3) Å is consistent with double-bond formation. This moiety is symmetrically bonded to the Zr center (Zr–C(35) = 2.295(3) Å, Zr–N(7) = 2.242 (2) Å). The guanidinate ligands exhibit bonding parameters similar to those of related complexes.<sup>1,3</sup>

Solutions of **2** underwent a transformation at room temperature over several hours, as indicated by the disappearance of the signals attributed to the benzyl

ligand and the appearance of new signals in the olefinic region of the  $^1H$  NMR spectrum (multiplet,  $\delta$  6.2–6.4). The olefin byproduct of this reaction was determined to be *trans*-2-benzylstyrene by comparison of MS and NMR data with literature values.<sup>7</sup> The Zr-containing product exhibited two isopropyl signals in a ratio of 2:1 as well as resonances attributed to a single 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> group. On the basis of these observations, we were able to assign the formula of **3** as [(*i*PrNH)C(*N*<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>-Zr=N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and to suggest the C<sub>2</sub>-symmetric structure depicted in Scheme 1. Compound **3** could be prepared directly by allowing the reaction of **1** and isocyanide to proceed at room temperature for 1 day.

The level of aggregation for **3** was confirmed through structural analysis, which revealed it to be a novel terminal imido complex.<sup>8</sup> Terminal imido complexes of Zr have been isolated and structurally characterized with amido, tetraaza macrocycle, cyclopentadienyl, and aryloxy ligation.<sup>9</sup> Complex **3** is the first example of this moiety supported by guanidinate or amidinate ligation. The geometry of **3** is derived from a trigonal

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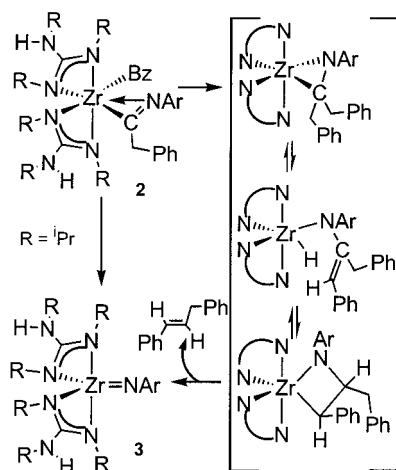
(8) Crystal data: empirical formula C<sub>28</sub>H<sub>53</sub>N<sub>7</sub>Zr, *T* = 203(2) K,  $\lambda$  = 0.710 73 Å, space group *P*4<sub>1</sub>2<sub>1</sub>2, *a* = *b* = 9.8146(13) Å, *c* = 33.688(5) Å,  $\alpha = \beta = \gamma = 90^\circ$ , *V* = 3245.1(8) Å<sup>3</sup>, *Z* = 4, *R* indices (*I* > 2 $\sigma$ (*I*)) *R*1 = 0.0347 and *wR*2 = 0.0983.

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(5) The single-crystal X-ray structures for compounds **1**, **5**, and **6** have been determined. Thermal ellipsoid plots for these complexes can be found in the Supporting Information. Full structural details will be reported in a future paper.

(6) Crystal data: empirical formula C<sub>43</sub>H<sub>67</sub>N<sub>7</sub>Zr, *T* = 203(2) K,  $\lambda$  = 0.710 73 Å, space group *P*2<sub>1</sub>/*c*, *a* = 10.8273(8) Å, *b* = 16.3749(12) Å, *c* = 24.2102(17) Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 90.2690^\circ$ , *V* = 4292.3(5) Å<sup>3</sup>, *Z* = 4, *R* indices (*I* > 2 $\sigma$ (*I*)) *R*1 = 0.0469 and *wR*2 = 0.1063.

Scheme 2



bipyramid, with the imido ligand occupying an equatorial site. Structural and theoretical analysis of five-coordinate Zr imido species along with the Zr–N bond length of 1.863(3) Å and the linearity of the aryl imido group (180.0(2)°) suggest that the Z–N(4) interaction is best viewed as a triple bond.<sup>9f</sup>

The transformation of the  $\eta^2$ -iminoacyl group of **2** to the terminal imido group of **3** is unique.<sup>10</sup> The formation of *trans*-2-benzylstyrene as the byproduct in this reaction suggests a retro 2 + 2 cycloaddition from an azametallacyclobutane as a route to this species. We propose the formation of this metallacycle via the mechanism outlined in Scheme 2. First, **2** forms a metallaziridine complex that undergoes a  $\beta$ -H elimination reaction to yield a transient metal–hydride and a vinyl amido ligand similar to an intermediate in the formation of [(Ar'O)<sub>2</sub>Ta(=NAr){N(Ar')(CH<sub>2</sub>CH<sub>2</sub>Ph)}].<sup>11</sup> An insertion step could produce an azametallacyclobutane, which can proceed to **3** by elimination of observed olefin. The observation of only *trans* olefin requires stereospecific formation of the metallacycle and of the retro-cycloaddition reaction. The closely related conversion of an  $\eta^2$ -imine complex, [Zr(tropocoronand){ $\eta^2$ -Ar'NC(Bz)<sub>2</sub>}] (Ar' = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), to yield a  $\mu$ -imido species apparently proceeds via elimination of a carbene group.<sup>10</sup>

Support for our proposal as well as evidence of the generality of this reaction is provided by the formation of the analogous imido species [(Me<sub>2</sub>N)C(PrN)<sub>2</sub>]<sub>2</sub>Zr=N(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**5**) from the reaction of the tetrasubstituted alkylguanidinate complex [(Me<sub>2</sub>N)C(PrN)<sub>2</sub>]<sub>2</sub>ZrMe<sub>2</sub> (**4**)<sup>3</sup> with CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), as depicted in Scheme 1. An equimolar reaction of these reagents yields **5** over 1 day at room temperature. Furthermore, as would be expected from our proposed mechanism, propene evolution accompanied formation of **5**. The NMR spectra of **5** were similar to those of **1** with appropriate replacements, and the molecular geometry of **5** is similar to that of **3**.<sup>5</sup>

Complex **4** also reacts with CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in a 1:2 stoichiometric ratio. In this case the new bis( $\eta^2$ -

iminoacyl) compound **6** was produced (Scheme 1). Perhaps the clearest spectroscopic indications for **6** are the <sup>13</sup>C NMR resonance at  $\delta$  252.19 assigned to the  $\eta^2$ -iminoacyl moieties and the relative integration intensities for the methyl groups in this species.<sup>5</sup>

The intramolecular coupling between two  $\eta^2$ -iminoacyl groups to yield enediamido ligands has been extensively studied by Rothwell et al. for bis(aryloxy) bis( $\eta^2$ -iminoacyl) group **4** complexes.<sup>12</sup> Coupling reactions have also been observed for group 4 tropocoronand-<sup>10</sup> and calix[4]arene-supported complexes.<sup>13</sup> A recent theoretical treatment of this reaction has also recently appeared.<sup>14</sup> Compound **6** produces the enediamido complex **7** upon mild thermolysis. The clearest spectroscopic evidence for **7** is the appearance of a new carbon signal at  $\delta$  112.0, which was assigned to the C=C carbon centers.

Complex **7** was characterized by crystallographic analysis.<sup>15</sup> The Zr center exhibits a distorted pseudo-octahedral geometry with substantial distortions due to the limitations of the guanidinate bite angles (approximately 58°). The enediamido group has a typical bite angle of 82.96(15)°. The Zr–N(1) and Zr–N(2) bond distances (2.090(4) and 2.108(4) Å) are consistent with Zr amido linkages and are shorter than the average Zr–N<sub>guanidinate</sub> distance of 2.28 Å. The C(9)–C(11) distance (1.358(6) Å) corresponds to a C=C bond, while the N(1)–C(9) and N(2)–C(11) distances (1.427(6) and 1.415(6) Å) are consistent with single bonds between sp<sup>2</sup>-hybridized C and N. As is commonly observed for such species, there is a significant fold angle between the N–Zr–N and N–C=C–N planes of 44.8°.<sup>12,13,16</sup>

We have shown that the bis(guanidinate) framework offers a scaffold for interesting reactivity. We are currently exploring the generality of these reactions with isocyanates and related small molecules as well as the further reactivity of **3** and **5** with various unsaturated substrates.

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**Supporting Information Available:** Text giving experimental details for compounds **1–3** and **5–7**, figures giving thermal ellipsoid plots of compounds **1**, **5**, and **6**, and tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **1**, **3**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Crystal data: empirical formula C<sub>38</sub>H<sub>64</sub>N<sub>8</sub>Zr, *T* = 203(2) K,  $\lambda$  = 0.710 73 Å, space group *P* $\bar{1}$ , *a* = 10.9082(18) Å, *b* = 111.226 76(18) Å, *c* = 18.699(3) Å,  $\alpha$  = 73.361(3)°,  $\beta$  = 86.806(3)°,  $\gamma$  = 61.590(3)°, *V* = 1921.0(5) Å<sup>3</sup>, *Z* = 2, *R* indices (*I* > 2 $\sigma$ (*I*)) *R*1 = 0.0520 and *wR*2 = 0.0815.

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