

# Zirconium Chemistry Involving Benzamidinate Ligands. Reduction of $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ To Form an Imido–Iminoacyl Compound by Carbon–Nitrogen Bond Cleavage

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**Summary:** A range of zirconium(IV) derivatives with *N,N'*-bis(trimethylsilyl)benzamidinate ligands has been prepared with  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$  as the starting material. Reduction of the dichloride in the presence of excess diphenylacetylene gave  $[\text{PhCN}(\text{SiMe}_3)_2]_2\text{Zr}(\eta^2\text{-C}_4\text{-Ph}_4)$ . In the absence of acetylene, orange crystals of the  $\mu$ -imido– $\eta^2$ -iminoacyl species  $\{[\text{PhCN}(\text{SiMe}_3)_2]_2\text{Zr}(\eta^2\text{-Ph-CNSiMe}_3)(\mu\text{-NSiMe}_3)_2\}$  were obtained.

Group 4 metallocene compounds have attracted significant interest due to the range of important catalytic and stoichiometric reactions they undergo.<sup>1–3</sup> A number of ligand system alternatives to the ubiquitous Cp<sub>2</sub> fragment have been explored,<sup>2</sup> with most involving alkoxides<sup>4,5</sup> or nitrogen-based donors.<sup>6–12</sup> Due to its ease of preparation, solubility properties, and steric bulk, we were attracted to the *N,N'*-bis(trimethylsilyl)benzamidinate ligand ( $\text{PhC}(\text{NSiMe}_3)_2^-$ ) reported by Dehnicke,<sup>13</sup> Edelmann,<sup>14–16</sup> and others.<sup>17–19</sup> These workers have demonstrated the synthetic utility of this ligand in the preparation of a large variety of transition-metal, main-group, and f-block element complexes, including those of group 4. Here we report the synthesis of several new Ti(IV) and Zr(IV) derivatives and the crystal structure of a novel zirconium compound featur-

ing both  $\mu$ -imido and  $\eta^2$ -iminoacyl functionalities, formed by a rare example of C–N bond cleavage in a formal oxidative-addition reaction.<sup>20</sup>

Multigram quantities of  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ <sup>19</sup> were easily prepared by the reaction of  $[\text{PhC}(\text{NSiMe}_3)_2]\text{Li}(\text{TMEDA})$ <sup>18,21,22</sup> (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) with  $\text{ZrCl}_4(\text{THF})_2$  in hexanes. Colorless crystals of  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$  were obtained in good yields (ca. 70%) from dichloromethane/hexanes. As shown in Scheme 1, the dichloride is an excellent precursor to a wide range of new derivatives. For example, reaction with 1 equiv of  $\text{Me}_2\text{Mg}$  in diethyl ether cleanly yields the dimethyl derivative  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrMe}_2$  as colorless crystals. The compound is air-sensitive but otherwise is stable as a solid for months under nitrogen. The observation of a singlet for the  $-\text{SiMe}_3$  groups in both the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, even down to low temperatures (–90 °C), suggests that rotation of the benzamidinate ligand is rapid on the NMR time scale. The corresponding Ti derivative was also prepared and exhibits similar spectroscopic behavior.

The alkyl–halide complex  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}(\text{CH}_2\text{-SiMe}_3)\text{Cl}$  was easily prepared in moderate yield (47%) from the reaction of  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$  with  $\frac{1}{2}$  equiv of  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  in diethyl ether. Although the methyl chloride complex could be prepared by reaction of  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$  with  $\frac{1}{2}$  equiv of  $\text{Me}_2\text{Mg}$  (or 1 equiv of MeLi), we were unable to isolate this material in pure form, as it always crystallized along with the dimethyl species. Heating a toluene solution containing equimolar amounts of dimethyl and dichloride complexes to 130 °C for 3 days gave only 25% conversion to the methyl chloride. This is in contrast to the analogous titanium chemistry, where we were able to isolate pure  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Ti}(\text{Me})\text{Cl}$  from the reaction of the dichloride with  $\text{Me}_2\text{Mg}$ .

A qualitative measure of the steric demands of the  $[\text{PhC}(\text{NSiMe}_3)_2]$  groups relative to Cp and Cp\* systems was evident from substitution reactions with very bulky chalcogenolate ligands. For example, we have found that while the metallocene bis(chalcogenolate)  $\text{Cp}_2\text{Zr}\{[\text{TeSi}(\text{SiMe}_3)_3]_2\}$  is rapidly formed on mixing  $\text{Cp}_2\text{ZrCl}_2$  and 2 equiv of  $(\text{THF})_2\text{LiTeSi}(\text{SiMe}_3)_3$ , the analogous Cp\* derivative can only be monosubstituted, even under more forcing conditions.<sup>23</sup> The corresponding reaction with  $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$  is interesting, as it follows

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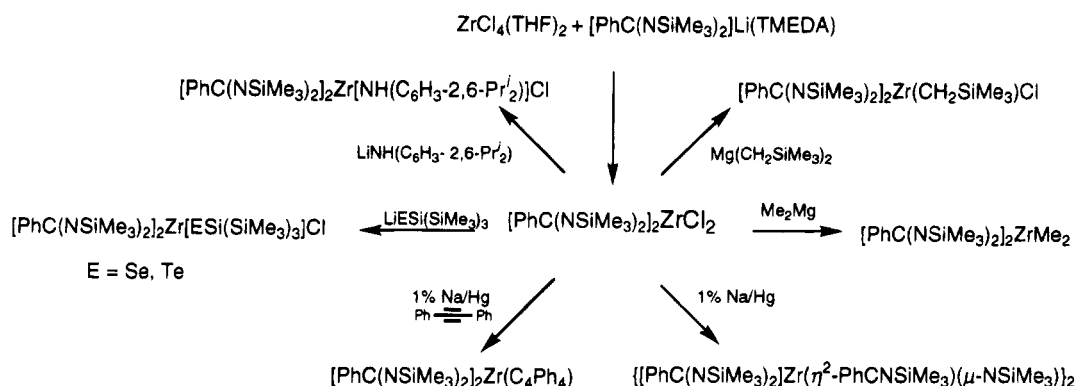
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## Scheme 1



a path similar to that for the Cp\* case, yielding only the orange, monosubstituted complex [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr[TeSi(SiMe<sub>3</sub>)<sub>3</sub>]Cl, even after prolonged treatment with a second equivalent of (THF)<sub>2</sub>LiTeSi(SiMe<sub>3</sub>)<sub>3</sub>. The mono(selenolate) derivative [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr[SeSi(SiMe<sub>3</sub>)<sub>3</sub>]Cl was also isolated in a similar manner, but attempts to prepare titanium derivatives were unsuccessful. Reaction of [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>ZrCl<sub>2</sub> with LiNH(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>f</sup><sub>2</sub>) in toluene gave [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr[NH(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>f</sup><sub>2</sub>)]Cl as yellow crystals. To date, efforts to generate an imido species by dehydrohalogenation using LiN(SiMe<sub>3</sub>)<sub>2</sub>, KN(SiMe<sub>3</sub>)<sub>2</sub>, or MeLi have been unsuccessful.

A benzamidinate analogue of the well-known metalocene derivatives Cp<sub>2</sub>Zr(η<sup>2</sup>-C<sub>4</sub>R<sub>4</sub>)<sup>24</sup> was obtained by reduction of [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>ZrCl<sub>2</sub> using 1% Na/Hg in the presence of excess diphenylacetylene, which gave [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(η<sup>2</sup>-C<sub>4</sub>Ph<sub>4</sub>) as orange crystals from hexanes.<sup>25</sup> The <sup>1</sup>H NMR spectrum of the compound shows multiplets for the aromatic protons from 7.40 to 6.70 ppm (total integration 30 H) and a broad -SiMe<sub>3</sub> resonance at 0.20 ppm (36 H). When the sample was cooled to 0 °C, the latter signal split into two singlets of equal intensity. Evidently, the steric bulk of the η<sup>2</sup>-C<sub>4</sub>Ph<sub>4</sub> ring increases the barrier to rotation of the [PhC(NSiMe<sub>3</sub>)<sub>2</sub>] ligands to the point where, at low temperatures, the inequivalent -SiMe<sub>3</sub> groups can be detected.

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(25) Selected characterization data for new compounds are as follows. [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(η<sup>2</sup>-C<sub>4</sub>Ph<sub>4</sub>): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.32–7.20 (m, 6 H), 7.11 (t, *J* = 7.6 Hz, 4 H), 6.94 (d, *J* = 7.4 Hz, 4 H), 6.89 (t, *J* = 7.3 Hz, 4 H), 6.82–6.70 (m, 12 H), -0.09 (br, 36 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 205.8, 189.0, 153.2, 149.5, 141.0, 139.9, 130.6, 128.9, 127.7, 127.6, 127.2, 126.4, 124.5, 122.7, 2.5 (br). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(η<sup>2</sup>-PhCNSiMe<sub>3</sub>)(μ-NSiMe<sub>3</sub>)<sub>2</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.42 (d, *J* = 7.7 Hz, 4 H), 7.32–7.20 (m, 8 H), 7.18–7.07 (m, 4 H), 6.99 (t, *J* = 7.4 Hz, 4 H), 1.25 (m, hexane, 4 H), 0.86 (m, hexane, 3 H), 0.42 (s, 18 H), 0.18 (s, 18 H), 0.06 (s, 18 H), -0.48 (s, 18 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz) δ 279.5, 184.6, 141.7, 140.6, 129.6, 128.8, 128.3, 128.2, 127.5, 127.4, 127.3, 126.3, 31.6 (hexane), 22.7 (hexane), 14.1 (hexane), 7.1, 4.2, 3.3, 2.7. [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>TiMe<sub>2</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.30–7.25 (m, 4 H), 7.05–7.00 (m, 6 H), 1.96 (s, 6 H), 0.15 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>ZrMe<sub>2</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.22–7.17 (m, 4 H), 7.03–6.97 (m, 6 H), 1.02 (s, 6 H), 0.12 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Ti(Me)Cl: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.30–7.25 (m, 4 H), 7.02–6.98 (m, 6 H), 2.26 (s, 3 H), 0.18 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(CH<sub>2</sub>SiMe<sub>3</sub>)Cl: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.33–7.28 (m, 4 H), 7.00–6.95 (m, 6 H), 1.52 (s, 2 H), 0.51 (s, 9 H), 0.17 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr[SeSi(SiMe<sub>3</sub>)<sub>3</sub>]Cl: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.32–7.28 (m, 4 H), 7.01–6.96 (m, 6 H), 0.54 (s, 27 H), 0.23 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr[TeSi(SiMe<sub>3</sub>)<sub>3</sub>]Cl: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.31–7.27 (m, 4 H), 6.99–6.94 (m, 6 H), 0.57 (s, 27 H), 0.22 (s, 36 H). [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(NHC<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>f</sup><sub>2</sub>)Cl: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz) δ 7.37–7.31 (m, 4 H), 7.22 (d, 2 H, *J* = 7.6 Hz), 7.18 (s, 1 H), 7.07 (t, 1 H, *J* = 7.6 Hz), 7.01–6.96 (m, 6 H), 4.07 (br, 2 H), 1.52 (d, 6 H, *J* = 6.7 Hz), 0.11 (s, 36 H). All compounds gave satisfactory elemental analyses.

A simple analysis of the NMR data gave a Δ*G*<sup>‡</sup> value for [PhC(NSiMe<sub>3</sub>)<sub>2</sub>] rotation of 13(1) kcal mol<sup>-1</sup> at the coalescence temperature (5 °C).

The above reaction takes a very different course in the absence of the acetylene, where reduction of [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>ZrCl<sub>2</sub> gave orange crystals of a new compound with the empirical formula [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr·0.25(hexane) as determined by C, H, and N combustion data. Since a combination of these data and the spectroscopic results discussed below were insufficient to assign a definitive structure, we carried out an X-ray diffraction study, the pertinent details of which are presented as an ORTEP view in Figure 1.<sup>26</sup> The molecular structure was shown to be {[PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(η<sup>2</sup>-PhCNSiMe<sub>3</sub>)(μ-NSiMe<sub>3</sub>)<sub>2</sub>}, with each six-coordinate zirconium being bound to two bridging imido ligands, an η<sup>2</sup>-iminoacyl, and a bidentate [PhC(NSiMe<sub>3</sub>)<sub>2</sub>] ligand. Crystal-packing effects perturb the solid-state structure just enough to destroy a C<sub>2</sub> axis running perpendicular to the plane of the almost planar Zr<sub>2</sub>N<sub>2</sub> four-membered ring. This symmetry feature is restored in solution, as evidenced by the detection, using <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, of four different -SiMe<sub>3</sub> environments of equal intensity and two sets of equivalent phenyl groups. The benzamidinate ligand rotation barrier is higher than in the metallacycle, with *T*<sub>c</sub> = 75 °C and Δ*G*<sup>‡</sup> = 17 kcal mol<sup>-1</sup>. By comparison to relate complexes, the extremely downfield signal at 279.5 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum can be assigned to the η<sup>2</sup>-iminoacyl carbon.<sup>5</sup> In the IR, the η<sup>2</sup>-iminoacyl group gives rise to a relatively low energy ν<sub>C-N</sub> at 1518 cm<sup>-1</sup> as compared to values of 1558 and 1579 cm<sup>-1</sup> reported for Cp<sub>2</sub>Zr[η<sup>2</sup>-C(SiMe<sub>3</sub>)NC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>]Cl and Zr(OC<sub>6</sub>H<sub>3</sub>-2,6-Bu<sup>t</sup><sub>2</sub>)<sub>2</sub>[η<sup>2</sup>-C(Me)NC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>]<sub>2</sub>, respectively.<sup>27,28</sup> The Zr–N bond lengths of 2.068(9), 2.072(9), 2.078(9), and 2.058(9) Å to the bridging imido ligand are effectively identical with related parameters in [(Me<sub>2</sub>N)<sub>2</sub>Zr(μ-NBu<sup>t</sup>)<sub>2</sub> (2.060, 2.071 Å)<sup>29,30</sup> but are slightly shorter than Zr–N bond lengths in [Cp<sub>2</sub>-

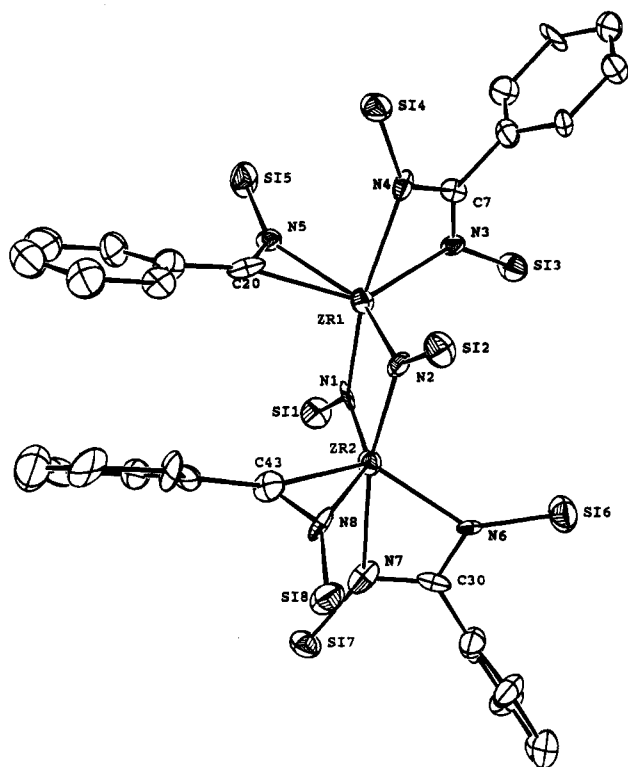
(26) Crystal data for ZrSi<sub>2</sub>ClN<sub>4</sub>C<sub>40</sub>H<sub>60</sub>: space group P2<sub>1</sub>/n, with *a* = 15.553(4) Å, *b* = 20.666(3) Å, *c* = 22.253(3) Å, β = 102.121(16)°, *V* = 6993 Å<sup>3</sup>, *d*<sub>calc</sub> = 2.43 g cm<sup>-3</sup>, and *Z* = 8. Data were collected at -100 °C with Mo Kα radiation (λ = 0.7107 Å). A 2θ range of 3–45° gave 9842 unique data. The heavy-atom positions were determined using Patterson methods and refined by least-squares and Fourier techniques using 628 variables against 3395 observations, for which *F*<sup>2</sup> > 3σ(*F*<sup>2</sup>), to give *R* = 5.14%, *R*<sub>w</sub> = 5.16%, and GOF = 1.27.

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**Figure 1.** ORTEP view of the molecular structure of  $\{-[\text{PhC}(\text{NSiMe}_3)_2]\text{Zr}(\eta^2\text{-PhCNSiMe}_3)(\mu\text{-NSiMe}_3)\}_2$ . Atoms are drawn as 50% thermal ellipsoids. Hydrogen atoms, methyl groups, and hexane are omitted for clarity. Selected distances (Å) and angles (deg): Zr(1)–N(1), 2.068(9); Zr(1)–N(2), 2.072(9); Zr(1)–N(3), 2.284(9); Zr(1)–N(4), 2.385(9); Zr(1)–C(20), 2.235(12); Zr(1)–N(5), 2.321(9); N(5)–C(20), 1.285(16); N(1)–Zr(1)–N(2), 81.8(3); Zr(1)–N(1)–Zr(2), 97.4(3); N(1)–Zr(2)–N(2), 81.9(3); N(3)–Zr(1)–N(4), 58.4(3); N(5)–Zr(1)–C(20), 32.7(4).

$\text{Zr}(\mu\text{-NC}_6\text{H}_4\text{-}p\text{-Bu}^t)_2$  (2.094, 2.098 Å).<sup>31</sup> The Zr–N bonds to the  $[\text{PhC}(\text{NSiMe}_3)_2]$  groups show a trans influence from the imido ligands which results in lengthening of the Zr(1)–N(4) and Zr(2)–N(7) bonds relative to the Zr(1)–N(3) and Zr(2)–N(6) bonds. The  $\eta^2$ -iminoacyl ligands display C=N bond lengths typical for this moiety (1.285(16) and 1.278(15) Å). Our data show no evidence for the formation of a possible alternative structure containing a  $C_2$  axis running along the N–N vector in the bridging imido ligands. This structural preference may simply be dictated by nonbonded repulsions from the bulky groups involved, although we cannot discount some degree of attractive  $\pi$ – $\pi$  interaction between the two iminoacyl phenyl groups that approach within 3.5 Å of each other. Support for the latter suggestion is provided by  $^{13}\text{C}$  NMR data, which show inequivalence

of both the ortho and meta carbons of the iminoacyl phenyl groups. Thus, the structure in solution is consistent with that determined in the solid state.

Formation of the above product most likely occurs via a reduced “ $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}$ ” species which, in the absence of traps such as diphenylacetylene, undergoes intramolecular oxidative addition of a C–N bond to form a monomeric imido–iminoacyl species. Reports of oxidative additions of C–N bonds are rare; examples include cleavage of the C–N multiple bonds of imines, isonitriles, and carbodiimides by Mo(II) and W(II) compounds to form imido–alkylidene, imido, and imido–isonitrile compounds, respectively.<sup>32,33</sup> Also known are the reactions of W=W triple bonds with nitriles yielding nitrido complexes,<sup>34</sup> the oxidative addition of C–N single bonds by zerovalent Ru, Ni, or Fe compounds,<sup>35,36</sup> and the cleavage of R–N bonds in R–NC.<sup>37–39</sup> Following C–N cleavage, dimerization of the putative monomeric imido–iminoacyl intermediate would then give the isolated product. The last step may therefore be related to results obtained by Bergman<sup>31,40</sup> and Wolczanski,<sup>12,41</sup> who were able to trap short-lived terminal imido species ( $\text{Cp}_2\text{ZrNR}$  and  $(\text{RNH})_2\text{ZrNR}$ ) with a variety of reagents. In our case, attempts to trap intermediates by addition of phosphines or carbon monoxide has been unsuccessful. Further synthetic and mechanistic studies of these and related benzamidinate derivatives are in progress.

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**Supplementary Material Available:** Text giving full experimental and characterization data for all new compounds and details of the structure determination for  $\{[\text{PhC}(\text{NSiMe}_3)_2\text{Zr}(\eta^2\text{-PhCNSiMe}_3)(\mu\text{-NSiMe}_3)]_2$ , including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, root-mean-square amplitudes of thermal vibration, bond distances and angles, and least-squares planes (31 pages). Ordering information is given on any current masthead page.

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