

Amidosilylcyclopentadienyl Monoalkyl Zirconium Compounds: Evidence of a N-Assisted 1,3-Proton Shift Olefin Isomerization Mechanism

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New η^5 -cyclopentadienyl- η^1 -amido monoalkyl zirconium compounds of the type $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{R}')]]$ ($\text{R} = \text{Me, Bn}$; $\text{R}' = \text{H, SiMe}_3, \text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2$) have been synthesized and fully characterized. Allyldimethylsilylcyclopentadienyl derivatives $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ isomerize the allyl fragment bound to the cyclopentadienyl ring to give the corresponding $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}=\text{CHCH}_3)]$ compounds ($\text{R} = \text{Me, Bn}$). Experimental as well as DFT computational studies support an isomerization mechanism based on a N-assisted 1,3-proton shift.

Chelate η^5 -cyclopentadienyl- η^1 -amido group 4 metal complexes such as $[\text{MX}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_5)]^1$ or $[\text{MX}\{\eta^5\text{-C}_5\text{R}_3(\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})_2\}]^2$ ($\text{M} = \text{Ti, Zr}$; $\text{X} = \text{Cl, Me, Bn}$; $\text{R} = \text{H, Me}$), which do not retain an alkyl ligand in their MAO-activated form, have recently proved to be active olefin polymerization precatalysts. This finding has prompted new investigations on such catalytic systems and the possible pathways through which polymerization occurs.^{1–3}

Within this context, well-known alkene isomerization has special relevance, as it takes place very often as a side reaction during olefin polymerization processes mediated by bis-cyclopentadienyl group 4 compounds, and is responsible

for epimerization of chiral centers, stereoerrors, and the so-called *chain walk* of group 4 metallocenes along the alkyl polymer chain.^{4,5} Polymerization and isomerization share fundamental reactions in organometallic chemistry, such as olefin insertion into M-X ($\text{X} = \text{H, alkyl}$) bonds and the reverse, $\beta\text{-X}$ elimination from a transition metal-alkyl. Thus, elucidation of the steric and electronic factors that control H and alkyl insertion/elimination reactions in monoalkyl constrained geometry compounds is of paramount importance for a better understanding of the mechanisms driving their polymerization and isomerization catalytic processes.

Recently, we reported the intramolecular allyl isomerization occurring in group 4 and 6 metal hydride compounds with the allyldimethylsilyl- η^5 -cyclopentadienyl ligand.^{6–8} The design of such model species, which contain cyclopentadienyl units with a hemilabile binding profile, has proven to be a useful strategy to gain insight into their olefin isomerization mechanisms. While group 6 metal compounds of formula $[\text{MH}(\eta^5\text{-C}_5\text{R}_4\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)(\text{CO})_3]$ isomerize the intramolecular pendant allyl unit selectively to the *trans*-prop-1-enyl-dimethylsilyl group,^{6,8} the allyldimethylsilyl cyclopentadienyl Zr hydride compound $[\text{ZrH}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ evolves to the six-membered zirconacycle derivative $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{-}\eta^1\text{-CH}_2)]$.⁷ Despite these remarkable experimental differences between group 4 and 6 metal derivatives, theoretical DFT calculations support a traditional metal hydride addition–elimination mechanism for both systems.^{7,8}

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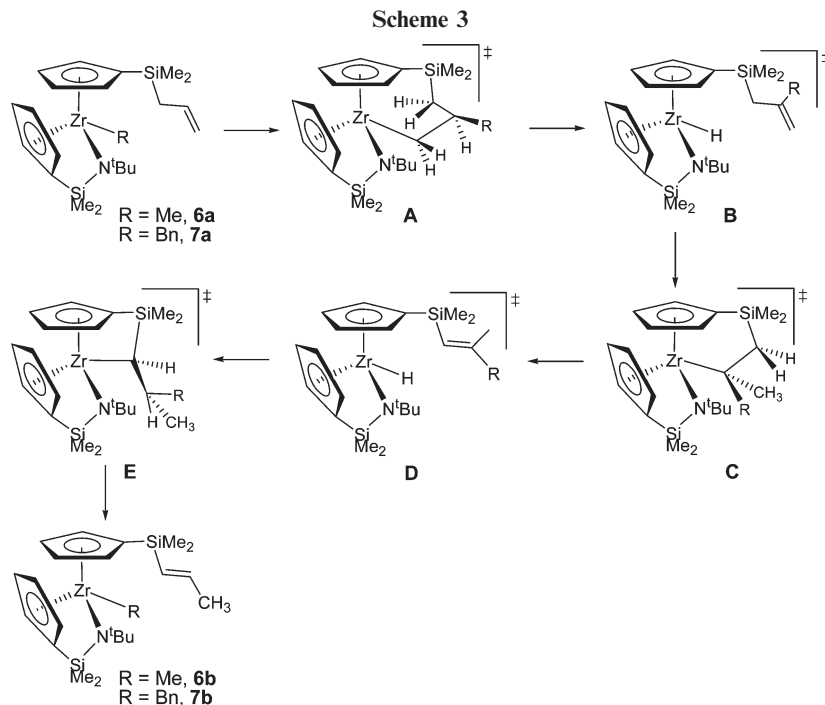
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Table 1. Selected ^1H , ^{13}C , and ^{29}Si NMR Data (δ in ppm, ^{cis}J , $^{trans}J$ in Hz) of Compounds **6a,b** and **7a,b**

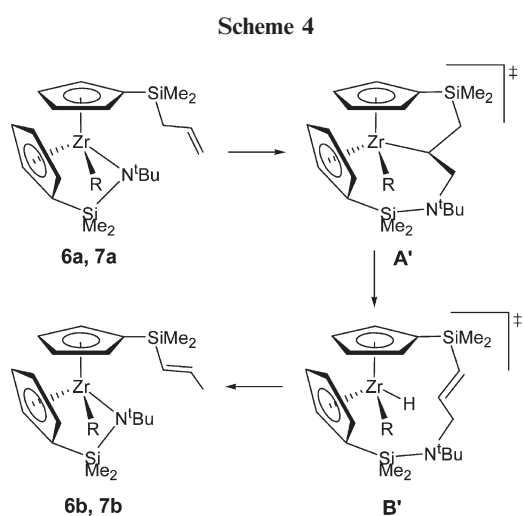
compd	-SiCH ₂ -CH=CH ₂			compd	-SiCH=CHCH ₃			
	Si-CH ₂	=CH	=CH ₂		Si-CH=	=CH-	-CH ₃	
^1H	6a	1.59 (d)	5.72 (m) ($^{trans}J = 16$, $^{cis}J = 10$)	4.90 (d, $^{trans}J = 16$) 4.92 (d, $^{cis}J = 10$)	6b	5.79 (dq) ($^{trans}J = 19$)	6.03 (dq) ($^{trans}J = 19$)	1.70 (dd)
$^{13}\text{C}^{a,b}$		26.3 (-)	135.5 (+)	114.4 (-)		131.0 (+)	144.3 (+)	23.3 (+)
^{29}Si		-7.6				-16.2		
^1H	7a	1.56 (d)	5.66 (m) ($^{trans}J = 18$, $^{cis}J = 11$)	4.92 (d, $^{cis}J = 11$) 4.89 (d, $^{trans}J = 18$)	7b	5.78 (dq) ($^{trans}J = 18$)	6.01 (dq) ($^{trans}J = 18$)	1.71 (dd)
$^{13}\text{C}^a$		26.2 (-)	135.2 (+)	114.6 (-)		130.7 (+)	144.7 (+)	23.3 (+)
^{29}Si		-7.8				-15.6		

^a All NMR data were measured in benzene-*d*₆ at 22 °C. ^b APT ^{13}C NMR experiments showed positive (+) (CH, CH₃) and negative phased signals (-) (CH₂ and quaternary C).



π -allyl-M-hydride intermediate. This hydride ligand migrates to the olefinic C-1 to produce the allyl to 1-propenyl isomerization. For the zirconium system under study, one objection to this π -allylic mechanism is that the required net oxidative addition of a C-H bond to a Zr(IV) metal center is not feasible.

Evidence of a M-N insertion route operating in the intramolecular hydroamination/cyclization, IHC, of aminoalkenes mediated by neutral amido zirconium compounds has been found recently,^{12,13} and the viability of such a M-N insertion pathway in aminoallene IHC catalyzed by bis(amido) zirconium derivatives has been intensely studied by using the DFT method.¹⁴ Thus, an isomerization mechanism involving insertion of the M-N bond into the pendant olefin present in derivatives **6a** and **7a**, shown in Scheme 4, should also be considered. Consistent with the strong M-N bond,¹² the four-membered transition structure constituting the simultaneous Zr-N, C=C bond cleavage and Zr-C, C-N bond formation affords high calculated energy values



(TS_{6a-A'}; $\Delta H^\ddagger = 51.3$ kcal/mol, $\Delta G^\ddagger = 56.1$ kcal/mol)¹⁵ from the DFT method.

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(15) See Supporting Information for details of DFT calculations.

Production of derivative **6b** from the starting **6a** through this M–N insertion mechanism requires formation of a hydride-methyl Zr intermediate species **B'**, which contains a pendant olefin fragment close to the metal center. The evolution of such a species at the working temperatures of 120 °C is expected to follow favored reaction channels different from those required to afford the final **6b** zirconium derivative. The hydrozirconation of such hydride-zirconium compounds with similar pendant alkene fragments has been demonstrated to be an easy process that is favored over double-bond isomerization.^{5,7,16} Furthermore, analogous metallocene hydride-alkyl-zirconium species suffer thermal reductive elimination of alkane,¹⁷ which occur even without addition of any exogenous ligands at temperatures of ca. 75 °C. These reasons, together with the calculated energies by the DFT method, led us to discount an isomerization mechanism involving olefin insertion into the M–N bond.

Metal complexes with metal–oxygen and –nitrogen bonds facilitate H–H and C–H bond activation reactions. The positioning of a nucleophilic/basic heteroatom ligand (amido, alkoxo, imido, oxo, etc.) adjacent to a Lewis-acidic metal center provides opportunities for activation of organic substrates toward controlled bond-breaking and bond-forming reactions.¹⁸ Weak C–H···X interactions are claimed to be responsible for this kind of reactivity.¹⁹ As formation of M–hydride intermediate species can be rejected, we took into account these antecedents and considered the possibility that isomerization of derivatives **6a** and **7a** is initiated through an unusual Zr–N-assisted 1,3-allylic proton shift.

The proposed isomerization pathway would occur in two steps, shown in Figure 1. The first step consists of a net addition of a methylenic C–H bond across the Zr–N bond, via a four-membered transition structure (**TS6a-F**), in which Zr, N, C, and H atoms are involved. The Zr–C(1–3) bond distances (3.94, 5.18, 6.18 Å, respectively) found for **TS6a-F** agree well with a σ -allyl–Zr disposition. An intermediate (**F**) of high energy, containing a secondary amine pendant ligand and a π -allyl–Zr bond, is formed. This disposition is energetically favored over a σ -allyl–Zr system. The following deprotonation of the amine group, which gives rise to the zirconium complex **6b**, takes place through a six-membered transition state (**TSF-6b**), with the three allylic C atoms, Zr, H, and N centers involved. A π -allyl–Zr representation for **TSF-6b** is upheld for the calculated Zr–C(1–3) bond distances (3.37, 3.65, 4.05 Å, respectively) of this transition state.

The activation energies of protonation and deprotonation steps are rather high, both over 40 kcal/mol, but they agree well with the high reaction temperatures required experimentally. Most remarkably, the activation parameters of these pathways are more than 10 kcal/mol lower in energy

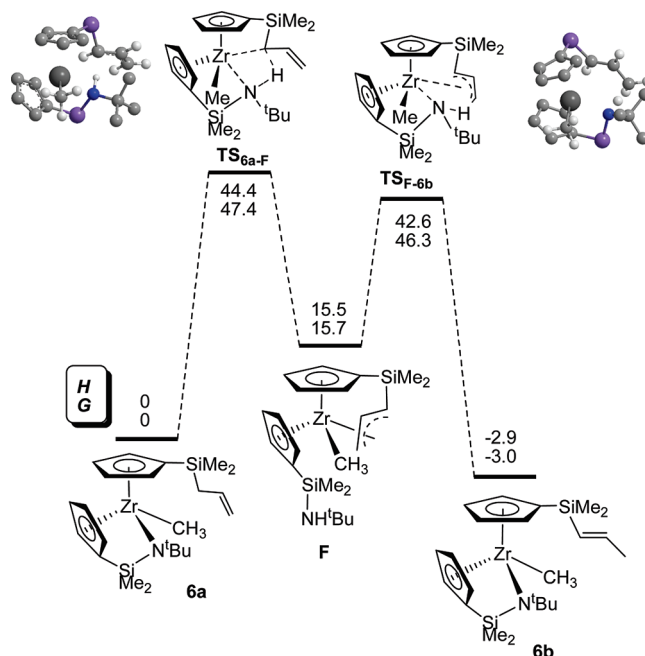


Figure 1. Energy diagram of the proposed pathway for the isomerization of **6a** to **6b** through a N-assisted 1,3-allylic proton shift: ΔH and ΔG , in kcal/mol.

than those calculated for the mechanisms involving insertion/elimination steps into M–alkyl or M–amido bonds. In agreement with the experimental results, the overall process is thermodynamically driven to the formation of the most stable compound, **6b** ($\Delta H = -2.9$ kcal/mol, $\Delta G = -3.0$ kcal/mol). Finally, IRC calculations undoubtedly show the connection between the two transition state structures, **TS6a-F** and **TSF-6b**, and the cyclopentadienyl pendant olefin systems **6a** and **6b** through intermediate **F**.

In summary, new monoalkyl zirconium compounds of the type $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{R}')]]$ have been prepared and fully characterized. Allyldimethylsilylcyclopentadienyl derivatives $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ have been shown to undergo the intramolecular isomerization of the allyl fragment to cleanly afford the corresponding *trans*-1-propenyl $[\text{ZrR}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}=\text{CHCH}_3)]$ ($\text{R} = \text{Me}, \text{Bn}$) compounds. Whichever isomerization mechanism is responsible, selectivity to the *trans*-isomer formation is a consequence of the geometry imposed by the chelating character of the cyclopentadienyl-olefin ligand. On the basis of the experimental work and DFT computational studies reported here, an isomerization mechanism consisting of a 1,3-proton shift mediated by a noninnocent amide ligand is proposed.

Experimental Section

General Information. All manipulations involving syntheses of metal complexes and catalysis were performed at an argon/vacuum manifold using standard Schlenk-line techniques under an argon atmosphere or in a glovebox MBraun MOD system. Solvents were dried by conventional procedures and freshly distilled prior to use. $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{-}\eta^1\text{-N}^t\text{Bu})\text{Cl}_2]$,²⁰ $[\text{ZrCl}$

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(η^5 -C₅H₄SiMe₂- η^1 -N^tBu)(η^5 -C₅H₄R')⁷ (R' = H, SiMe₃, SiMe₂CH₂-CH=CH₂), ¹³C-labeled methyl lithium, ¹³CH₃Li,²¹ and corresponding lithium salts of the substituted cyclopentadiene compounds, [(C₅H₄R')Li] (R' = SiMe₃,²² SiMe₂CH₂CH=CH₂²³), were prepared according to previous reports. Diethyl ether (Et₂O) solutions of MeLi and tetrahydrofuran (THF) solutions of BnMgCl were purchased from Aldrich. NMR spectra were recorded in a Bruker 400 Ultrashield. ¹H and ¹³C chemical shifts are reported relative to tetramethylsilane. Coupling constants *J* are given in Hz. Elemental analyses were performed in our laboratories (UAH) on a Perkin-Elmer 2400 CHNS/O analyzer, Series II.

General Procedure for Preparation of [ZrMe(η^5 -C₅H₄SiMe₂- η^1 -N^tBu)(η^5 -C₅H₄R)] (R = H, **4; SiMe₃, **5**; SiMe₂CH₂CH=CH₂, **6a**).** A 1.5 M solution of MeLi in Et₂O (0.63 mL, 0.94 mmol) was added dropwise to an Et₂O solution of **1** (0.24 g, 0.62 mmol), **2** (0.21 g, 0.47 mmol), or **3** (0.23 g, 0.47 mmol), respectively, and the reaction mixture was stirred for 12 h at room temperature. Solvent was completely removed from the resulting yellow suspension under vacuum, and the solid residue was extracted into hexane (3 × 5 mL). Removal of the hexane from the yellow solution gave yellow to orange foams, which were identified as pure derivatives **4**, **5**, and **6a**, respectively, in isolated yields of 0.21 g of **4** (91%), 0.19 g of **5** (92%), and 0.18 g of **6a** (88%). **6a**: Anal. Calcd for C₂₂H₃₇ZrNSi₂: C, 57.08; H, 8.08; N, 3.03. Found: C, 56.70; H, 7.99; N, 2.90. ¹H NMR (plus HSQC, 400 MHz, C₆D₆): δ 6.55, 6.22, 6.08, 6.07, 5.97, 5.92, 5.81, 5.80 (all m, each 1H, C₅H₄), 5.72 (m, 1H, ^{trans}*J*_{HH} = 16, ^{cis}*J*_{HH} = 10, ³*J*_{HH} = 8, =CH), 4.92 (d, 1H, ^{cis}*J*_{HH} = 10, =CH₂), 4.90 (d, 1H, ^{trans}*J*_{HH} = 16, =CH₂), 1.59 (d, 2H, ³*J*_{HH} = 8, Si-CH₂), 1.17 (s, 9H, C(CH₃)₃), 0.54, 0.41, 0.22, 0.18 (all s, each 3H, Si(CH₃)₂), 0.11 (s, 3H, Zr-CH₃). ¹³C NMR (plus APT, plus HSQC, 100 MHz, C₆D₆): δ 135.5 (+, =CH), 124.5, 120.7, 117.5, 116.2, 115.3, 114.7 (all +, C₅H₄), 114.4 (-, =CH₂), 113.7 (+, C₅H₄), 113.6, 110.4 (-, *ipso*-C₅H₄), 108.4 (+, C₅H₄), 57.7 (-, NC(CH₃)₃), 36.0 (+, C(CH₃)₃), 26.3 (-, -CH₂), 19.7 (+, Zr-CH₃) 5.2, 2.9, -1.5, -1.9 (all +, Si-(CH₃)₂). ²⁹Si HMBC NMR (79.4 MHz, C₆D₆): δ -25.2 (Si-N), -7.6 (Si-CH₂).

Preparation of [ZrBn(η^5 -C₅H₄SiMe₂- η^1 -N^tBu)(η^5 -C₅H₄SiMe₂CH₂CH=CH₂)] (7a**).** A THF solution of BnMgCl (0.52 mL, 1.06 mmol) was added at room temperature to a solution of **3** (0.26 g, 0.53 mmol) in THF (5 mL). Stirring the reaction mixture for 3 days at 50 °C gave a yellow suspension. The solvent was removed under vacuum, hexane (2 × 3 mL) was then added to the oily residue, the resulting suspension was filtered, and the yellow solution was dried under vacuum to produce a yellow oily residue, which was identified as pure derivative **7a**. Yield: 0.26 g (93%). Anal. Calcd for C₂₈H₄₁ZrNSi₂: C, 62.39; H, 7.67; N, 2.60. Found: C, 62.25; H, 8.39; N, 2.22. ¹H NMR (plus HSQC, 400 MHz, C₆D₆): δ 7.28 (dd, 2H, ³*J*_{HH} = 8, ³*J*_{HH} = 7, *m*-C₆H₅), 7.10 (d, 2H, ³*J*_{HH} = 7, *o*-C₆H₅), 6.93 (t, 1H, ³*J*_{HH} = 8, *p*-C₆H₅), 6.28, 6.12, 6.05, 6.02, 5.86, 5.79, 5.77, 5.74 (all m, each 1H, C₅H₄), 5.66 (m, 1H, ^{trans}*J*_{HH} = 18, ^{cis}*J*_{HH} = 11, ³*J*_{HH} = 8, =CH), 4.92 (d, 1H, ^{cis}*J*_{HH} = 11, =CH₂), 4.89 (d, 1H, ^{trans}*J*_{HH} = 18, =CH₂), 2.50 (d, 1H, ²*J*_{HH} = 10, PhCH₂), 1.98 (d, 1H, ²*J*_{HH} = 10, PhCH₂), 1.56 (d, 2H, ³*J*_{HH} = 8, Si-CH₂), 1.25 (s, 9H, C(CH₃)₃), 0.44, 0.36, 0.21, 0.19 (all s, each 3H, Si(CH₃)₂). ¹³C NMR (plus APT, plus HSQC, 100 MHz, C₆D₆): δ 155.9 (-, *ipso*-C₆H₅), 135.2 (+, =CH), 129.0 (+, *m*-C₆H₅), 127.2 (+, *o*-C₆H₅), 125.7 (+, C₅H₄), 121.7 (+, *p*-C₆H₅), 121.5, 118.5, 116.6, 116.2, 116.1, 114.7 (all +, C₅H₄), 114.6 (-, =CH₂), 113.4, 111.4 (-, *ipso*-C₅H₄), 109.6 (+, C₅H₄), 58.6 (-, NC(CH₃)₃), 49.2 (-, -CH₂Ph), 36.0 (+, C(CH₃)₃), 26.2 (-, Si-CH₂), 4.9, 2.9, -1.3, -1.9 (all +, Si-(CH₃)₂). ²⁹Si NMR (79.4 MHz, C₆D₆): δ -23.5 (Si-N), -7.8 (Si-CH₂).

Isomerization Reactions: Synthesis of [ZrR(η^5 -C₅H₄SiMe₂- η^1 -N^tBu)(η^5 -C₅H₄SiMe₂CH=CHCH₃)] (R = Me, **6b; Bn, **7b**).** A toluene (3 mL) solution of **6a** (0.15 g, 0.32 mmol) or a THF (3 mL) solution of **7a** (0.17 g, 0.37 mmol) was heated at 120 °C for ca. 8 (**6a**) or 10 (**7a**) days. Solvent was completely removed from the resulting yellow to dark orange solutions, and the yellow solid residues were identified as pure derivatives **6b** (yield: 0.10 g (69%)) and **7b** (yield: 0.12 g (71%)). **6b**: Anal. Calcd for C₂₂H₃₇ZrNSi₂: C, 57.08; H, 8.08; N, 3.03. Found: C, 56.82; H, 7.96; N, 2.90. ¹H NMR (plus TOCSY, plus HSQC, plus HMBC, 400 MHz, C₆D₆): δ 6.58, 6.20, 6.17, 6.16 (all m, each 1H, C₅H₄), 6.03 (dq, 1H, ^{trans}*J*_{HH} = 19, ³*J*_{HH} = 6, =CH-Me), 5.95, 5.93, 5.87, 5.86 (all m, each 1H, C₅H₄), 5.79 (dq, ^{trans}*J*_{HH} = 19, ⁴*J*_{HH} = 1, =CH-Si), 1.70 (dd, 3H, ³*J*_{HH} = 6, ⁴*J*_{HH} = 1, =CCH₃), 1.18 (s, 9H, C(CH₃)₃), 0.55, 0.43, 0.29, 0.28 (all s, each 3H, Si(CH₃)₂), 0.15 (s, 3H, Zr-CH₃). ¹³C NMR (plus APT, plus HSQC, 100 MHz, C₆D₆): δ 144.3 (+, =CHMe), 131.0 (+, =CHSi), 124.7, 120.5, 117.9, 116.3, 115.1, 114.7, 114.7 (all +, C₅H₄), 112.5 (-, *ipso*-C₅H₄), 108.5 (+, C₅H₄), 105.7 (-, *ipso*-C₅H₄), 57.7 (-, NC(CH₃)₃), 36.0 (+, C(CH₃)₃), 23.3 (+, =CCH₃), 19.5 (+, Zr-CH₃), 5.2, 2.9, -0.1, -0.5 (all +, Si-(CH₃)₂). ²⁹Si HMBC NMR (C₆D₆): δ -25.1 (Si-N), -16.2 (Si-CH=), **7b**: Anal. Calcd for C₂₈H₄₁ZrNSi₂: C, 62.39; H, 7.67; N, 2.60. Found: C, 62.07; H, 7.30; N, 2.71. ¹H NMR (plus HSQC, 400 MHz, C₆D₆): δ 7.29 (dd, 2H, ³*J*_{HH} = 8, ³*J*_{HH} = 7, *m*-C₆H₅), 7.00 (d, 2H, ³*J*_{HH} = 7, *o*-C₆H₅), 6.93 (t, 1H, ³*J*_{HH} = 8, *p*-C₆H₅), 6.35, 6.15, 6.05, 6.05 (all m, each 1H, C₅H₄), 6.01 (dq, 1H, ^{trans}*J*_{HH} = 18, ³*J*_{HH} = 6, =CHMe), 5.87, 5.86, 5.81, 5.81 (all m, each 1H, C₅H₄), 5.78 (dq, 1H, ^{trans}*J*_{HH} = 18, ⁴*J*_{HH} = 1, =CH-Si), 2.52 (d, 1H, ²*J*_{HH} = 10, PhCH₂), 2.01 (d, 1H, ²*J*_{HH} = 10, PhCH₂), 1.71 (dd, 3H, ³*J*_{HH} = 6, ⁴*J*_{HH} = 1, =CCH₃), 1.26 (s, 9H, C(CH₃)₃), 0.45, 0.38, 0.28, 0.26 (all s, each 3H, Si(CH₃)₂). ¹³C NMR (plus APT, plus HSQC, 100 MHz, C₆D₆): δ 156.0 (-, *ipso*-C₆H₅), 144.7 (+, =CH-Me), 130.7 (+, =CH-Si), 129.0 (+, *m*-C₆H₅), 127.2 (+, *o*-C₆H₅), 125.7, 121.7 (both +, C₅H₄), 121.5 (+, *p*-C₆H₅), 118.7, 116.8, 116.2, 116.1, 115.0 (all +, C₅H₄), 113.7, 111.3 (both -, *ipso*-C₅H₄), 109.8 (+, C₅H₄), 58.5 (-, NC(CH₃)₃), 49.1 (-, -CH₂Ph), 36.0 (+, C(CH₃)₃), 23.3 (-, =C-CH₃), 4.9, 2.9, -0.1, -0.3 (all +, Si-(CH₃)₂). ²⁹Si NMR (79.4 MHz, C₆D₆): δ -23.5 (Si-N), -15.6 (Si-CH₂).

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Supporting Information Available: Details of synthetic procedures of ¹³C-labeled derivatives **6a*** and **6b***, full data characterization of compounds **4**, **5**, **6a***, and **6b***, selected NMR spectra, details of computational methods, and coordinates of DFT-optimized compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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