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## Alkyne and Alkene Complexes of a d<sup>0</sup> Zirconocene Aryl Cation

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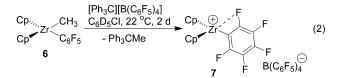
 $(C_5R_5)_2Zr(R)(alkyne)^+$  and  $(C_5R_5)_2Zr(R)(alkene)^+$  complexes are probable key intermediates in zirconocene-catalyzed alkyne oligomerization<sup>1</sup> and alkene polymerization.<sup>2</sup> These species are challenging to study because the absence of  $d-\pi^*$  back-bonding results in weak Zr-substrate binding, and because insertion of the substrate into the Zr-R bond is fast. X-ray and NMR studies of chelated  $(C_5R_5)_2$ Zr(OCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)<sup>+</sup> complexes,<sup>3</sup> and NMR studies of nonchelated Zr-alkoxide-alkene species,<sup>4</sup> show that alkenes bind to Zr(IV) unsymmetrically  $(d(Zr-C_{term}) < d(Zr-C_{int}))$  and that the C=C bond is polarized with positive charge on C<sub>int</sub>. Several d<sup>0</sup> metal-alkyl-alkene complexes are known,<sup>5</sup> but except for an vttrium system in which alkene coordination can be detected by NMR line broadening,<sup>6</sup> in all cases the coordinated alkene is tethered to another ligand. Here we describe nonchelated Zr-arylalkyne and Zr-aryl-alkene complexes that are stabilized by the presence of  $\beta$ -Si substituents in the alkyne and alkene ligands and fluorination of the aryl ligand.

The use of  $\beta$ -Si-substituted alkynes and alkenes should favor the formation of stable d<sup>0</sup> metal—substrate complexes, due to  $\beta$ -Si stabilization of the positive charge on C<sub>int</sub>.<sup>7,8</sup> To test this idea, we compared the coordination of  $\beta$ -Si-substituted and non-Sisubstituted substrates to [Cp'<sub>2</sub>Zr(O'Bu)(ClCD<sub>2</sub>Cl)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1; Cp' = C<sub>5</sub>H<sub>4</sub>Me).<sup>4</sup> Propargyltrimethylsilane (PTMS) and allyltrimethylsilane (ATMS) react with 1 to give robust [Cp'<sub>2</sub>Zr(O'Bu)(L)]-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] adducts (L = HC=CCH<sub>2</sub>SiMe<sub>3</sub> (2); H<sub>2</sub>C=CHCH<sub>2</sub>SiMe<sub>3</sub> (3); eq 1). The NMR resonances for the alkyne and alkene units of

$$\begin{array}{c} \bigoplus_{\substack{C p'_2 Z r \\ C p'_2 Z r \\ C r$$

2 and 3 are more strongly shifted from free substrate values than those for the non-Si-containing analogues [Cp'2Zr- $(O^{t}Bu)(HC \equiv CMe)][B(C_{6}F_{5})_{4}]$  (4, eq 1) and  $[Cp'_{2}Zr(O^{t}Bu) (H_2C=CHCH_2CMe_3)$  [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5, eq 1), suggesting a greater degree of substrate polarization.5a For example, the Cint <sup>13</sup>C NMR resonance of **3** shifts far downfield ( $\Delta \delta = \delta_{\text{coord}} - \delta_{\text{free}} = +31.6$ ), the  $C_{term}$  resonance shifts upfield ( $\Delta \delta$  = -19.7), and the  $H_{int}$ resonance shifts far downfield ( $\Delta \delta = +1.80$ ), compared to the free ligand values. In contrast, much smaller coordination shifts are observed for 5 ( $\Delta\delta$ : C<sub>int</sub> +18.8, C<sub>term</sub> -11.7, H<sub>int</sub> +1.46). The equilibrium constant for the formation of 2,  $K_{eq} = [2][1]^{-1}$ - $[\text{HC} \equiv \text{CCH}_2\text{SiMe}_3]^{-1} = 1.0(2) \times 10^5 \text{ M}^{-1} (\text{CD}_2\text{Cl}_2, -89 \text{ °C}, \text{eq})$ 1), is 280 times larger than that for coordination of propyne to 1 to give 4,<sup>4</sup> even though propyne is smaller than PTMS. Similarly, the equilibrium constant for ATMS binding to 1 ( $K_{eq} = 1.7(4) \times 10^3$  $M^{-1}$ ,  $CD_2Cl_2$ , -89 °C) is 900 times larger than that for coordination of 4,4-dimethyl-1-pentene to 1 to give 5. These results show that the  $\beta$ -Si substituents in 2 and 3 greatly enhance substrate binding. Incorporation of fluorine substituents in the Zr-R group should stabilize a  $(C_5R_5)_2Zr(R)(substrate)^+$  species against insertion, due to the resulting decreased nucleophilicity of the Zr-R group.<sup>9</sup> To test this idea, we investigated alkyne and alkene binding to the  $Cp_2Zr(C_6F_5)^+$  cation.

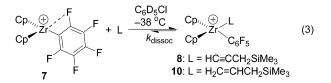
The reaction of  $Cp_2Zr(C_6F_5)Me$  (6,  $Cp = C_5H_5$ )<sup>10</sup> with 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  for 2 days ( $C_6D_5Cl$ , 22 °C) yields a 1:1 mixture of Ph<sub>3</sub>CMe and  $[Cp_2Zr(C_6F_5)][B(C_6F_5)_4]$  (7, 97%, eq 2). At earlier



reaction times, mixtures of **7**, Ph<sub>3</sub>CMe, Ph<sub>3</sub>C<sup>+</sup>, and [{Cp<sub>2</sub>Zr(C<sub>6</sub>F<sub>5</sub>)}<sub>2</sub>-( $\mu$ -Me)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>10</sup> were observed. Compound **7** is stable for 3 weeks in C<sub>6</sub>D<sub>5</sub>Cl at 22 °C, but decomposes in seconds in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C. The -38 °C <sup>19</sup>F NMR spectrum of **7** contains two *o*-F resonances, one at  $\delta$  -118.2 that is typical for Zr(C<sub>6</sub>F<sub>5</sub>) compounds, and a second at  $\delta$  -140.0, ca. 20 ppm upfield of the normal range ( $\delta$  -116 ± 10).<sup>10,11</sup> These results show that the sides of the C<sub>6</sub>F<sub>5</sub> ligand are inequivalent, and suggest that one *o*-F is coordinated to Zr.<sup>11a</sup> Additionally, complex **7** may be further stabilized by solvent coordination. VT <sup>19</sup>F NMR spectra reveal that the sides of the C<sub>6</sub>F<sub>5</sub> ligand exchange as the temperature is raised, due to a lateral pivot of the C<sub>6</sub>F<sub>5</sub> ligand and/or Zr-C<sub>6</sub>F<sub>5</sub> rotation.

Addition of PTMS to 7 ( $C_6D_5Cl$ , -38 °C) yields the alkyne adduct  $[Cp_2Zr(C_6F_5)(HC \equiv CCH_2SiMe_3)][B(C_6F_5)_4]$  (8, eq 3).<sup>12</sup> The <sup>19</sup>F NMR spectrum of 8 contains two o-F resonances in the normal range ( $\delta$  -114.6, -121.0), which are broadened due to Zr-C<sub>6</sub>F<sub>5</sub> rotation. The alkyne Cint <sup>13</sup>C NMR resonance is more strongly shifted in 8 ( $\Delta \delta = +62.5$ ) than in 2 ( $\Delta \delta = +21.7$ ), which may indicate a greater degree of polarization of the alkyne in 8. The  $J_{\text{CH}}$  values for the alkyne unit in 8 ( ${}^{1}J_{\text{CH}} = 232$ ;  ${}^{2}J_{\text{CH}} = 34$  Hz) are 10-15 Hz smaller than the values for free PTMS, 2, and other terminal alkyne complexes of 1,<sup>4</sup> but are within the range for sphybridized carbons and inconsistent with insertion products in which these carbons would be sp<sup>2</sup>-hybridized.<sup>13</sup> PTMS binds strongly to 7 with  $K_{eq} = [8][7]^{-1}[HC \equiv CCH_2SiMe_3]^{-1} = 9.1(6) \times 10^2 M^{-1}$  $(C_6D_5Cl, -38 \text{ °C})$ . THF displaces PTMS from 8 to give  $[Cp_2Zr (C_6F_5)(THF)][B(C_6F_5)_4]$  (9, 100%). Compound 8 is stable for 8 h at -38 °C (C<sub>6</sub>D<sub>5</sub>Cl).

Addition of 4 equiv of ATMS to 7 (C<sub>6</sub>D<sub>5</sub>Cl, -38 °C) results in partial formation of the alkene adduct [Cp<sub>2</sub>Zr(C<sub>6</sub>F<sub>5</sub>)-(H<sub>2</sub>C=CHCH<sub>2</sub>SiMe<sub>3</sub>)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**10**, eq 3). The H<sub>int</sub> <sup>1</sup>H NMR



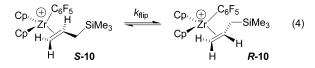
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resonance of the ATMS ligand is shifted far downfield, and the <sup>13</sup>C NMR resonances for C<sub>int</sub> and C<sub>term</sub> are divergently shifted ( $\Delta\delta$ : H<sub>int</sub> +1.89, C<sub>int</sub> +51.2, C<sub>term</sub> -15.4), as expected for unsymmetrical alkene coordination.<sup>3-5</sup> The  $^{1}J_{CH}$  values for the alkene carbons (C<sub>int</sub> 161, C<sub>term</sub> 150 Hz) are typical for an alkene coordinated to a d<sup>0</sup> metal,<sup>3-5</sup> and are inconsistent with insertion products in which those carbons would be sp3-hybridized.14 Addition of THF to 10 ( $C_6D_5Cl$ , -38 °C) gives 9 (100%) and free ATMS. The equilibrium constant for ATMS binding to 7 at -38 °C in  $C_6D_5Cl, K_{eq} = [10][7]^{-1}[H_2C=CHCH_2SiMe_3]^{-1} = 8.2(1.4) M^{-1},$ is 2.8 times larger than the  $K_{eq}$  for ATMS binding to 1, which under these conditions has a value of 2.9(7) M<sup>-1</sup>. VT NMR gives  $\Delta H^{\circ}$ = -5.3(2) kcal/mol and  $\Delta S^{\circ} = -18(1)$  eu for binding of ATMS to 7.

When a solution of 7, 10, and free ATMS is warmed from -38to +2 °C over 4 h, 10 and ATMS are gradually consumed and the ATMS dimer 6,6-dimethyl-4-((trimethylsilyl)methyl)-6-silahept-1ene  $(11)^{15}$  is formed. 11 results from a Lewis acid-mediated dimerization of ATMS<sup>15</sup> due to 7 or trace Ph<sub>3</sub>C<sup>+</sup> in solution.<sup>16</sup> NMR and GC/MS analysis of the organic products from a 7/ATMS mixture maintained at 22 °C for 3 days shows the presence of dimers and trimers of ATMS; while the exact structures of these products have not been determined, none contain C<sub>6</sub>F<sub>5</sub> groups. The trimers likely form by a Lewis acid-mediated allylsilylation of 11.15 There is no evidence for ATMS insertion in 10.

VT NMR and <sup>1</sup>H EXSY studies show that 10 undergoes two dynamic processes. First, 10 undergoes reversible alkene decomplexation (eq 3). This process broadens all of the NMR signals of 10. The rate constant for ATMS decomplexation from 10 found by <sup>1</sup>H EXSY ( $k_{\text{dissoc}} = 5.0(8) \text{ s}^{-1}$ ; C<sub>6</sub>D<sub>5</sub>Cl, -38 °C) is in close agreement with that determined from the line broadening of the H<sub>trans</sub> and *p*-F signals of 10 ( $k_{dissoc} = 5.5(2.5) \text{ s}^{-1}$ ). This value is not affected by the concentration of free ATMS, which indicates that free ATMS does not directly displace bound ATMS from 10. The activation parameters for ATMS decomplexation from 10 are  $\Delta H^{\ddagger} = 8.9(6)$  kcal/mol and  $\Delta S^{\ddagger} = -17(3)$  eu. The negative  $\Delta S^{\ddagger}$ value suggests that solvent or an o-F displaces the coordinated alkene in an associative mechanism.<sup>4</sup> This process is much slower than ATMS decomplexation from 3 under the same conditions  $(k_{\text{dissoc}} \approx 125 \text{ s}^{-1}; \text{ C}_6\text{D}_5\text{Cl}, -38 \text{ }^\circ\text{C}).$ 

Complex 10 also undergoes nondissociative alkene face exchange ("alkene flipping"), i.e., exchange of the  $Cp_2Zr(C_6F_5)^+$  unit between the two alkene enantiofaces without alkene dissociation (eq 4).<sup>17</sup>



This process broadens the Cp and Hallylic resonances of 10 to a greater (and equal) extent compared to the other resonances of 10. No exchange between H<sub>trans</sub> and H<sub>cis</sub> is observed by NMR line broadening or <sup>1</sup>H EXSY, thus ruling out mechanisms involving rotation around the C=C bond (via a ZrCH<sub>2</sub>-C<sup>+</sup>HCH<sub>2</sub>SiMe<sub>3</sub> carbocation intermediate).<sup>18</sup> The rate constant for alkene flipping determined by <sup>1</sup>H EXSY ( $k_{\text{flip}} = 23(1) \text{ s}^{-1}$ ; C<sub>6</sub>D<sub>5</sub>Cl, -38 °C, eq 4) agrees reasonably well with that determined from the NMR line broadening of the H<sub>allylic</sub> signals of **10** ( $k_{\text{flip}} = 18(1) \text{ s}^{-1}$ ), and shows that alkene face exchange is ca. 4 times faster than alkene decomplexation. Alkene flipping was not observed in 3 or other Cp'2Zr(OtBu)(alkene)+ complexes.4 Similar nondissociative alkene face exchanges have been deduced to occur during chain end epimerization in propylene polymerization with Zr catalysts through studies with isotopically labeled propylenes.<sup>17a,b</sup> Alkene flipping likely occurs via an alkene C-H  $\sigma$ -complex intermediate or transition state.17d

These results show that nonchelated d<sup>0</sup> Zr-aryl-alkyne and Zraryl-alkene complexes can be generated using  $\beta$ -Si-substituted alkynes and alkenes to strengthen substrate coordination and the poorly nucleophilic  $-C_6F_5$  group to inhibit insertion. Both tactics are required: non- $\beta$ -Si-substituted substrates such as propyne and 2-butyne do not coordinate to 7, and Cp<sub>2</sub>ZrMe<sup>+</sup>, Cp<sub>2</sub>ZrCH<sub>2</sub>Ph<sup>+</sup>, and Cp<sub>2</sub>HfMe<sup>+</sup> rapidly insert and oligomerize or polymerize ATMS even at -78 °C.<sup>19</sup> Neither 8 (at -38 °C) nor 10 (up to 22 °C) undergoes insertion. The availability of stabilized d<sup>0</sup> metal-carbylalkene species should enable direct study of their structures and dynamics to probe important issues in catalytic alkene polymerization.<sup>2,17</sup> With further adjustment of the nucleophilicity of the Zr-Rgroup, it should be possible to access  $(C_5R_5)_2Zr(R)(alkene)^+$  systems in which both alkene coordination and insertion can be directly observed and quantified.

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Supporting Information Available: Experimental procedures, data for new compounds, and selected NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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