

Communication

Alkyne and Alkene Complexes of a d Zirconocene Aryl Cation

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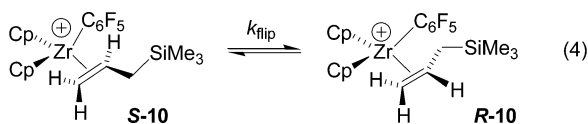


resonance of the ATMS ligand is shifted far downfield, and the ^{13}C NMR resonances for C_{int} and C_{term} are divergently shifted ($\Delta\delta$: H_{int} +1.89, C_{int} +51.2, C_{term} -15.4), as expected for unsymmetrical alkene coordination.^{3–5} The $^1J_{\text{CH}}$ values for the alkene carbons (C_{int} 161, C_{term} 150 Hz) are typical for an alkene coordinated to a d^0 metal,^{3–5} and are inconsistent with insertion products in which those carbons would be sp^3 -hybridized.¹⁴ Addition of THF to **10** ($\text{C}_6\text{D}_5\text{Cl}$, -38°C) gives **9** (100%) and free ATMS. The equilibrium constant for ATMS binding to **7** at -38°C in $\text{C}_6\text{D}_5\text{Cl}$, $K_{\text{eq}} = [\mathbf{10}][\mathbf{7}]^{-1}[\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3]^{-1} = 8.2(1.4) \text{ M}^{-1}$, is 2.8 times larger than the K_{eq} for ATMS binding to **1**, which under these conditions has a value of $2.9(7) \text{ M}^{-1}$. VT NMR gives $\Delta H^\circ = -5.3(2) \text{ kcal/mol}$ and $\Delta S^\circ = -18(1) \text{ eu}$ for binding of ATMS to **7**.

When a solution of **7**, **10**, and free ATMS is warmed from -38 to $+2^\circ\text{C}$ over 4 h, **10** and ATMS are gradually consumed and the ATMS dimer 6,6-dimethyl-4-((trimethylsilyl)methyl)-6-silahept-1-ene (**11**)¹⁵ is formed. **11** results from a Lewis acid-mediated dimerization of ATMS¹⁵ due to **7** or trace Ph_3C^+ in solution.¹⁶ 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_6F_5 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 ^1H 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 ^1H EXSY ($k_{\text{dissoc}} = 5.0(8) \text{ s}^{-1}$; $\text{C}_6\text{D}_5\text{Cl}$, -38°C) is in close agreement with that determined from the line broadening of the H_{trans} and $p\text{-F}$ signals of **10** ($k_{\text{dissoc}} = 5.5(2.5) \text{ s}^{-1}$). 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 $\Delta H^\ddagger = 8.9(6) \text{ kcal/mol}$ and $\Delta S^\ddagger = -17(3) \text{ eu}$. The negative ΔS^\ddagger value suggests that solvent or an $o\text{-F}$ displaces the coordinated alkene in an associative mechanism.⁴ 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°C).

Complex **10** also undergoes nondissociative alkene face exchange (“alkene flipping”), i.e., exchange of the $\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)^+$ unit between the two alkene enantiofaces without alkene dissociation (eq 4).¹⁷



This process broadens the Cp and $\text{H}_{\text{allylic}}$ resonances of **10** to a greater (and equal) extent compared to the other resonances of **10**. No exchange between H_{trans} and H_{cis} is observed by NMR line broadening or ^1H EXSY, thus ruling out mechanisms involving rotation around the $\text{C}=\text{C}$ bond (via a $\text{ZrCH}_2\text{-C}^+\text{HCH}_2\text{SiMe}_3$ carbocation intermediate).¹⁸ The rate constant for alkene flipping determined by ^1H EXSY ($k_{\text{flip}} = 23(1) \text{ s}^{-1}$; $\text{C}_6\text{D}_5\text{Cl}$, -38°C , eq 4) agrees reasonably well with that determined from the NMR line broadening of the $\text{H}_{\text{allylic}}$ 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

$\text{Cp}'_2\text{Zr}(\text{O}^i\text{Bu})(\text{alkene})^+$ 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.^{17a,b} Alkene flipping likely occurs via an alkene C-H σ -complex intermediate or transition state.^{17d}

These results show that *nonchelated* d^0 Zr–aryl–alkyne and Zr–aryl–alkene complexes can be generated using β -Si-substituted alkynes and alkenes to strengthen substrate coordination and the poorly nucleophilic $-\text{C}_6\text{F}_5$ group to inhibit insertion. *Both tactics are required*: non- β -Si-substituted substrates such as propyne and 2-butyne do not coordinate to **7**, and Cp_2ZrMe^+ , $\text{Cp}_2\text{ZrCH}_2\text{Ph}^+$, and Cp_2HfMe^+ rapidly insert and oligomerize or polymerize ATMS even at -78°C .¹⁹ Neither **8** (at -38°C) nor **10** (up to 22°C) undergoes insertion. The availability of stabilized d^0 metal–carbyl–alkene species should enable direct study of their structures and dynamics to probe important issues in catalytic alkene polymerization.^{2,17} With further adjustment of the nucleophilicity of the Zr–R group, it should be possible to access $(\text{C}_5\text{R}_5)_2\text{Zr}(\text{R})(\text{alkene})^+$ 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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