J|A|C|S
COMMUNICATIONS

Published on Web 08/21/2004

Alkyne and Alkene Complexes of a d^0 Zirconocene Aryl Cation

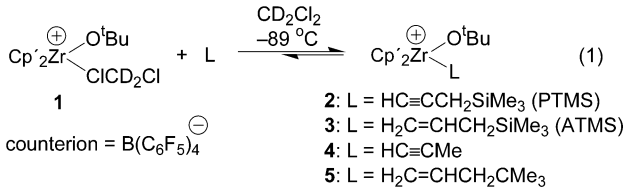
Edward J. Stoebenau, III, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received July 13, 2004; E-mail: rfjordan@uchicago.edu

$(C_5R_5)_2Zr(R)(alkyne)^+$ and $(C_5R_5)_2Zr(R)(alkene)^+$ complexes are probable key intermediates in zirconocene-catalyzed alkyne oligomerization[1] and alkene polymerization.[2] These species are challenging to study because the absence of d−π* 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 $(C_5R_5)_2Zr(OMe_2CH_2CH_2CH{=}CH_2)^+$ complexes,[3] and NMR studies of nonchelated Zr−alkoxide−alkene species,[4] 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_{int}. Several d^0 metal−alkyl−alkene complexes are known,[5] but except for an yttrium system in which alkene coordination can be detected by NMR line broadening,[6] in all cases the coordinated alkene is tethered to another ligand. Here we describe nonchelated Zr−*aryl*−alkyne and Zr−*aryl*−alkene complexes that are stabilized by the presence of β-Si substituents in the alkyne and alkene ligands and fluorination of the aryl ligand.

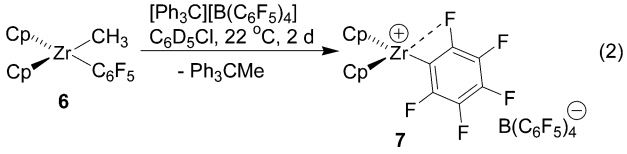
The use of β-Si-substituted alkynes and alkenes should favor the formation of stable d^0 metal−substrate complexes, due to β-Si stabilization of the positive charge on C_{int}.[7,8] To test this idea, we compared the coordination of β-Si-substituted and non-Si-substituted substrates to $[Cp'_2Zr(O^tBu)(ClCD_2Cl)][B(C_6F_5)_4]$ (**1**; Cp′ = C_5H_4Me).[4] Propargyltrimethylsilane (PTMS) and allyltrimethylsilane (ATMS) react with **1** to give robust $[Cp'_2Zr(O^tBu)(L)][B(C_6F_5)_4]$ adducts (L = HC≡CCH$_2$SiMe$_3$ (**2**); H$_2$C=CHCH$_2$SiMe$_3$ (**3**); eq 1). The NMR resonances for the alkyne and alkene units of



2 and **3** are more strongly shifted from free substrate values than those for the non-Si-containing analogues $[Cp'_2Zr(O^tBu)(HC{\equiv}CMe)][B(C_6F_5)_4]$ (**4**, eq 1) and $[Cp'_2Zr(O^tBu)(H_2C{=}CHCH_2CMe_3)][B(C_6F_5)_4]$ (**5**, eq 1), suggesting a greater degree of substrate polarization.[5a] For example, the C_{int} ^{13}C NMR resonance of **3** shifts far downfield ($\Delta\delta = \delta_{coord} - \delta_{free} = +31.6$), 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_{int} +18.8, C_{term} −11.7, H_{int} +1.46). The equilibrium constant for the formation of **2**, $K_{eq} = [\mathbf{2}][\mathbf{1}]^{-1}[HC{\equiv}CCH_2SiMe_3]^{-1} = 1.0(2) \times 10^5$ M^{-1} (CD_2Cl_2, −89 °C, eq 1), is 280 times larger than that for coordination of propyne to **1** to give **4**,[4] 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 β-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.[9] To test this idea, we investigated alkyne and alkene binding to the $Cp_2Zr(C_6F_5)^+$ cation.

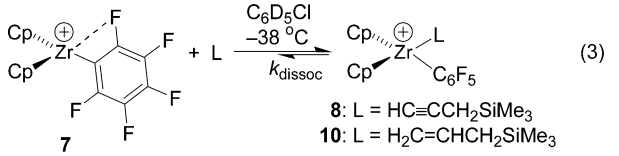
The reaction of $Cp_2Zr(C_6F_5)Me$ (**6**, Cp = C_5H_5)[10] with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ for 2 days (C_6D_5Cl, 22 °C) yields a 1:1 mixture of Ph_3CMe and $[Cp_2Zr(C_6F_5)][B(C_6F_5)_4]$ (**7**, 97%, eq 2). At earlier



reaction times, mixtures of **7**, Ph_3CMe, Ph_3C^+, and $[\{Cp_2Zr(C_6F_5)\}_2(\mu\text{-Me})][B(C_6F_5)_4]$[10] were observed. Compound **7** is stable for 3 weeks in C_6D_5Cl at 22 °C, but decomposes in seconds in CD_2Cl_2 at −78 °C. The −38 °C ^{19}F NMR spectrum of **7** contains two *o*-F resonances, one at δ −118.2 that is typical for $Zr(C_6F_5)$ compounds, and a second at δ −140.0, ca. 20 ppm upfield of the normal range (δ −116 ± 10).[10,11] These results show that the sides of the C_6F_5 ligand are inequivalent, and suggest that one *o*-F is coordinated to Zr.[11a] Additionally, complex **7** may be further stabilized by solvent coordination. VT ^{19}F NMR spectra reveal that the sides of the C_6F_5 ligand exchange as the temperature is raised, due to a lateral pivot of the C_6F_5 ligand and/or Zr−C_6F_5 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).[12] The ^{19}F NMR spectrum of **8** contains two *o*-F resonances in the normal range (δ −114.6, −121.0), which are broadened due to Zr−C_6F_5 rotation. The alkyne C_{int} ^{13}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_{CH} values for the alkyne unit in **8** ($^1J_{CH} = 232$; $^2J_{CH} = 34$ Hz) are 10−15 Hz smaller than the values for free PTMS, **2**, and other terminal alkyne complexes of **1**,[4] but are within the range for sp-hybridized carbons and inconsistent with insertion products in which these carbons would be sp^2-hybridized.[13] PTMS binds strongly to **7** with $K_{eq} = [\mathbf{8}][\mathbf{7}]^{-1}[HC{\equiv}CCH_2SiMe_3]^{-1} = 9.1(6) \times 10^2$ M^{-1} (C_6D_5Cl, −38 °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_6D_5Cl).

Addition of 4 equiv of ATMS to **7** (C_6D_5Cl, −38 °C) results in partial formation of the alkene adduct $[Cp_2Zr(C_6F_5)(H_2C{=}CHCH_2SiMe_3)][B(C_6F_5)_4]$ (**10**, eq 3). The H_{int} ^1H NMR



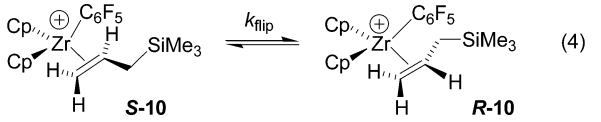
10.1021/ja045794m CCC: $27.50

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 $^1J_{CH}$ 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** (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, $K_{eq} = [\mathbf{10}][\mathbf{7}]^{-1}[H_2C{=}CHCH_2SiMe_3]^{-1} = 8.2(1.4)\ M^{-1}$, 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^{-1}. VT NMR gives $\Delta H° = -5.3(2)$ kcal/mol and $\Delta S° = -18(1)$ eu for binding of ATMS to **7**.

When a solution of **7**, **10**, and free ATMS is warmed from −38 to +2 °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 ATMS[15] 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 ($k_{dissoc} = 5.0(8)\ s^{-1}$; C_6D_5Cl, −38 °C) is in close agreement with that determined from the line broadening of the H_{trans} and *p*-F signals of **10** ($k_{dissoc} = 5.5(2.5)\ s^{-1}$). 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 $\Delta H^‡ = 8.9(6)$ kcal/mol and $\Delta S^‡ = -17(3)$ eu. The negative $\Delta S^‡$ value suggests that solvent or an *o*-F displaces the coordinated alkene in an associative mechanism.[4] This process is much slower than ATMS decomplexation from **3** under the same conditions ($k_{dissoc} \approx 125\ s^{-1}$; C_6D_5Cl, −38 °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).[17]



(4)

This process broadens the Cp and $H_{allylic}$ 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 C=C bond (via a $ZrCH_2-C^+HCH_2SiMe_3$ carbocation intermediate).[18] The rate constant for alkene flipping determined by ^1H EXSY ($k_{flip} = 23(1)\ s^{-1}$; C_6D_5Cl, −38 °C, eq 4) agrees reasonably well with that determined from the NMR line broadening of the $H_{allylic}$ signals of **10** ($k_{flip} = 18(1)\ s^{-1}$), and shows that alkene face exchange is ca. 4 times faster than alkene decomplexation. Alkene flipping was not observed in **3** or other $Cp'_2Zr(O^tBu)(alkene)^+$ 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 $-C_6F_5$ 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^+, $Cp_2ZrCH_2Ph^+$, 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 $(C_5R_5)_2Zr(R)(alkene)^+$ systems in which both alkene coordination and insertion can be directly observed and quantified.

Acknowledgment. We thank the NSF (CHE-0212210) for support and the University of Chicago for a William Rainey Harper Fellowship (E.J.S.).

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.

References

(1) Horton, A. D. *Chem. Commun.* **1992**, 185.
(2) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.
(3) (a) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750. (b) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898.
(4) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222.
(5) (a) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *Organometallics* **2001**, *20*, 4262. (b) Casey, C. P.; Klein, J. F.; Fagan, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 4320. (c) Cano, J.; Gómez-Sal, P.; Heinz, G.; Martínez, G.; Royo, P. *Inorg. Chim. Acta* **2003**, *345*, 15. (d) Brandow, C. G.; Mendiratta, A.; Bercaw, J. E. *Organometallics* **2001**, *20*, 4253.
(6) Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Fagan, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2641.
(7) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
(8) *Chelated* β-Si d^0 metal−alkene complexes are known.[5a,c,d]
(9) (a) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600 and references therein. (b) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728.
(10) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.
(11) (a) Pindado, G. J.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816. (b) Kraft, B. M.; Jones, W. D. *J. Organomet. Chem.* **2002**, *658*, 132.
(12) For a d^0 Ta−hydride−alkyne complex, see: Curtis, M. A.; Finn, M. G.; Grimes, R. N. *J. Organomet. Chem.* **1998**, *550*, 469.
(13) For $H_2C{=}CHC_6F_5$, $^1J_{CH} = 161$ (C_{term}), 163 Hz (C_{int}). All $^2J_{CH} < 2$ Hz.
(14) For C_6F_5Me, $^1J_{CH} = 132$ Hz (Me).
(15) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M.-Y.; Jung, I. N. *Organometallics* **1995**, *14*, 2361.
(16) Schade, C.; Mayr, H. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 477.
(17) (a) Sillars, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **2003**, *125*, 9894. (b) Yoder, J. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 2548. (c) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174. (d) Prosenc, M.-H.; Brintzinger, H.-H. *Organometallics* **1997**, *16*, 3889.
(18) (a) Matchett, S. A.; Schmiege-Boyle, B. R.; Cooper, J.; Fratterelli, D.; Olson, K.; Roberts, J.; Thommen, J.; Tigelaar, D.; Winkler, F. *Organometallics* **2003**, *22*, 5047. (b) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.
(19) (a) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (b) Habaue, S.; Baraki, H.; Okamoto, Y. *Macromol. Chem. Phys.* **1998**, *199*, 2211.

JA045794M