Coordination of Alkenes and Alkynes to a Cationic d⁰ Zirconocene Alkoxide Complex

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Zirconium(IV) alkene and alkyne complexes, $(C_5R_5)_2Zr(R)$-(substrate)$^+$, are probable key intermediates in zirconocene-catalyzed alkene polymerization[1] and alkyne oligomerization,[2] but little is known about their structures and properties. These species may exhibit unusual features due to the absence of d–π^* back-bonding. Several d⁰ group 5 and 6 metal alkene[3] and alkyne[4] complexes have been observed by NMR, and *chelated* d⁰ group 3 and 4 metal alkene[5] and alkyne[2,6] complexes have been studied.[7] In particular, X-ray and NMR studies of chelated $(C_5R_5)_2Zr(OCMe_2$-$CH_2CH_2CH=CH_2)^+$ complexes show that the alkene binds to Zr(IV) unsymmetrically $(d(Zr-C_{term}) < d(Zr-C_{int}))$ and suggest that the C=C bond is polarized with positive charge on C_{int}.[5a,b] However, it is not yet clear how the properties of these species are influenced by the chelation, and therefore nonchelated analogues are highly desirable. Here we report the synthesis of base-free $(C_5R_5)_2Zr(O^tBu)^+$ cations, the observation of *nonchelated* alkene and alkyne adducts of these cations, and studies of the thermodynamic and dynamic properties of these novel species.

The alkoxide complex $[Cp'_2Zr(O^tBu)][B(C_6F_5)_4]$ (**1**, Cp' = C_5H_4Me) was synthesized in a one-pot procedure (eq 1). Reaction of Cp'_2ZrMe_2 with *tert*-butyl alcohol followed by $[Ph_3C]$-$[B(C_6F_5)_4]$ in benzene cleanly yields **1**. The Ph₃CMe byproduct can be removed by washing with benzene and hexanes to afford **1** as a bright yellow solid (80%). The analogous complex $[Cp_2Zr(O^tBu)][B(C_6F_5)_4]$ (**2**) was generated in a similar manner.
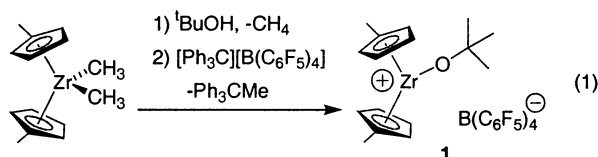
Compound **1** is soluble in halocarbon solvents, forms an oil in benzene or toluene, and is insoluble in alkanes. The ¹H and ¹³C NMR spectra of **1** in C₆D₅Cl at 23 and −35 °C, and in CD₂Cl₂ at −89 °C, contain two CH resonances for the Cp' rings indicative of a C_{2v}-symmetric cation. These data are consistent with either a dinuclear $[Cp'_2Zr(\mu\text{-}O^tBu)]_2^{2+}$ dication[8] or a labile mononuclear ion pair or solvent adduct with fast site epimerization at Zr. The ¹H NMR spectrum of a 1:1 mixture of $Cp'_2Zr(O^tBu)Me$ and $Cp_2Zr(O^tBu)Me$ after treatment with 2 equiv of $[Ph_3C]$-$[B(C_6F_5)_4]$ in C₆D₅Cl exhibits sharp resonances for **1** and **2** but no resonances or line broadening effects indicative of a mixed $[Cp'_2Zr(\mu\text{-}O^tBu)_2ZrCp_2]^{2+}$ dimer. The ¹⁹F NMR spectra of **1** show no evidence of anion coordination down to −89 °C.[9] Additionally, ethylene coordination to **1** in CD₂Cl₂ is influenced by C₆H₅Cl but not by $[Ph_3C][B(C_6F_5)_4]$ (vide infra). These results strongly suggest that **1** forms $Cp'_2Zr(O^tBu)(ClR)^+$ adducts in chlorocarbon solutions.[10]

Addition of ethylene to a CD₂Cl₂ solution of **1** at −89 °C affords an equilibrium mixture of **1**, free ethylene, and the ethylene complex

Table 1. Equilibrium Constants for Eq 2 for Selected Ligands[a]

| L	K_{eq} (−89 °C, M⁻¹)	L	K_{eq} (−89 °C, M⁻¹)
CO	>1500	allene	6.7(3)
propyne (**5**)	360(70)	propylene (**4**)	5.4(2)
2-butyne (**6**)	52(3)	1-hexene	4.8(8)
phenylacetylene	22(1)	*cis*-2-butene	2.2(1)
ethylene (**3**)	7.0(6)	vinyl chloride	<0.1

[a] $K_{eq} = [Zr-L][\mathbf{1}]^{-1}[L]^{-1}$.

Table 2. Thermodynamic Data for Equilibria in Eq 2 and Activation Parameters for Decomplexation (k_{-1}) of L from Adducts **3**−**6**

adduct	$\Delta H°$ (kcal/mol)	$\Delta S°$ (eu)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	$\Delta G^\ddagger$ (kcal/mol)[a]
3	−3.6(1)	−16(4)	7.7(5)	−15(2)	11.1(1)
4	−3.8(2)	−17(1)	8.1(9)	−12(4)	11.0(1)
5	−4.1(3)	−11(1)	8.5(3)	−14(1)	11.8(1)
6	−3.6(3)	−11(1)	13.8(5)	4(2)	12.9(1)

[a] At −39 °C.

$[Cp'_2Zr(O^tBu)(C_2H_4)][B(C_6F_5)_4]$ (**3**, eq 2). The ¹³C NMR spectrum of **3** contains four Cp' CH resonances, consistent with C_s symmetry. The ¹H and ¹³C NMR spectra each contain one coordinated ethylene resonance indicative of fast ethylene rotation. The ethylene ¹H resonance (δ 5.92) is shifted 0.56 ppm downfield, and the ¹³C resonance (δ 119.0) is shifted 3.8 ppm upfield from the free ethylene resonances. The $^1J_{CH}$ value for ethylene is virtually unchanged upon coordination.
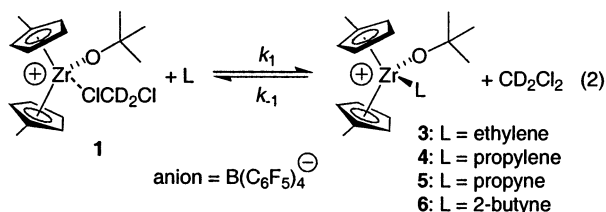
Taking the concentration of CD₂Cl₂ to be constant, we define the equilibrium constant for ethylene coordination in eq 2 by K_{eq} = $[\mathbf{3}][\mathbf{1}]^{-1}[C_2H_4]^{-1}$ = 7.0(6) M⁻¹ (−89 °C, Table 1). This value is unaffected by changing the initial concentrations of **1** (0.038−0.080 M) or ethylene (0.13−0.29 M) or by addition of $[Ph_3C][B(C_6F_5)_4]$ as an excess anion source. However, addition of 30 equiv of C₆H₅Cl shifts the equilibrium to the left, possibly due to C₆H₅Cl coordination.[10b] Raising the temperature also shifts the equilibrium to the left. A van't Hoff plot gives $\Delta H°$ = −3.6(1) kcal/mol and $\Delta S°$ = −16(4) eu for substitution of CD₂Cl₂ by ethylene (Table 2).[11]

The NMR resonances for **1**, **3**, and free ethylene broaden and coalesce as the temperature is raised from −89 °C, consistent with

the exchange of **1** and **3** and of free and coordinated ethylene. The line widths for **3** are independent of the free ethylene concentration, which implies that coordinated ethylene is not directly displaced by free ethylene. Analysis of VT NMR spectra provides first-order rate constants (k_{-1}) and activation parameters (Table 2) for ethylene decomplexation. The negative $\Delta S^{\ddagger}$ value suggests that CD_2Cl_2 displaces the coordinated ethylene in an associative mechanism.[12]

Addition of propylene to **1** results in partial conversion to the propylene adduct $[Cp'_2Zr(O^tBu)(H_2C=CHMe)][B(C_6F_5)_4]$ (**4**, eq 2). The ^{13}C NMR spectrum of **4** contains eight Cp' CH and two Cp' Me resonances, consistent with C_1 symmetry. The ^1H NMR H_{int} resonance of the coordinated propylene (δ 7.34) is shifted far downfield from the free propylene resonance (δ 5.79). The propylene ^{13}C C_{int} resonance (δ 153.5) is shifted 19.6 ppm downfield, and the C_{term} resonance (δ 102.6) is shifted 12.4 ppm upfield by coordination. The propylene J_{HH} and J_{CH} values are virtually unchanged by coordination. These data are very similar to the data for chelated $(C_5R_5)_2Zr(OCMe_2CH_2CH_2CH=CH_2)^+$ olefin complexes, which suggests that the propylene ligand in **4** is bound unsymmetrically and is polarized in the same manner as proposed for the chelated complexes.[5a,b] VT NMR studies show that propylene and ethylene bind with similar strength to **1** and that the barrier to propylene decomplexation is nearly identical to that for ethylene decomplexation from **3** (Tables 1, 2).

Similarly, addition of propyne to **1** yields an equilibrium mixture of **1**, free propyne, and $[Cp'_2Zr(O^tBu)(HC\equiv CMe)][B(C_6F_5)_4]$ (**5**, eq 2). The ^1H and ^{13}C NMR spectra of **5** contain four Cp' CH resonances, consistent with C_s symmetry. The propyne ^{13}C C_{int} resonance (δ 89.1) is shifted 8.9 ppm downfield, and the C_{term} resonance (δ 64.2) is shifted 2.8 ppm upfield upon coordination. These results suggest that the coordinated propyne is unsymmetrically bound and polarized in a similar manner as the propylene of **4**.

The C_s-symmetric 2-butyne adduct $[Cp'_2Zr(O^tBu)(MeC\equiv CMe)]-[B(C_6F_5)_4]$ (**6**, eq 2) is generated by addition of 2-butyne to **1**. At -89 °C, the ^1H and ^{13}C NMR spectra of **6** each contain one 2-butyne C*Me* resonance, which is broadened due to restricted rotation of the in-plane-bound 2-butyne ligand. These resonances sharpen as the temperature is raised to -59 °C due to 2-butyne rotation, and then broaden and coalesce with the free 2-butyne $\equiv$ C*Me* resonances at higher temperatures due to the exchange in eq 2. VT NMR studies show that 2-butyne binds more weakly than propyne, but the barrier to 2-butyne decomplexation is higher than that for propyne decomplexation. These results, and the more positive $\Delta S^{\ddagger}$ value for 2-butyne decomplexation from **6**, are suggestive of a greater degree of dissociative character in the substitution of 2-butyne by CD_2Cl_2 vis-à-vis ligand decomplexation of **3**–**5**. Significant steric crowding is expected in the transition state for associative CD_2Cl_2 displacement of 2-butyne.

Compound **1** forms adducts with a wide variety of other ligands, and equilibrium constants for eq 2 for selected cases are summarized in Table 1. Certain trends can be noted. First, CO binds quite strongly, and NMR studies show that free CO directly displaces coordinated CO.[13] Second, alkynes coordinate more strongly than alkenes of similar structure, but steric crowding can strongly inhibit alkyne binding. Third, ethylene and α-olefins bind with similar strength, which suggests that electronic and steric effects cancel for this series, because α-olefins are expected to be stronger σ-donors on the basis of their higher HOMO energies.[14] The disubstituted olefin *cis*-2-butene binds weakly. Vinyl chloride binds very weakly, and the coordination mode (via C=C vs Cl) is not yet established; in this case, the only evidence for coordination is line broadening of the vinyl chloride ^{13}C NMR signals in the

presence of **1**. Finally, *tert*-butylacetylene, *trans*-2-butene, benzene, N_2, H_2, and, interestingly, 1,3-butadiene do not displace CD_2Cl_2 from **1**.

The $[Cp'_2Zr(O^tBu)][B(C_6F_5)_4]$ system enables, for the first time, direct study of alkene and alkyne coordination to a cationic Zr(IV) center in the absence of chelation. The $Cp'_2Zr(O^tBu)(alkene)^+$ complexes are models for $(C_5R_5)_2ZrR(alkene)^+$ species in zirconocene-catalyzed alkene polymerizations.[1] The use of an alkoxide instead of an alkyl ligand is expected to decrease the metal Lewis acidity, so alkene binding in $Cp'_2Zr(O^tBu)(alkene)^+$ may be weaker than in $Cp'_2ZrR(alkene)^+$ species.[5a] Future studies of alkene coordination to a broader set of $(C_5R_5)_2Zr(O^tBu)^+$ complexes will enable us to probe how the $(C_5R_5)_2Zr$ structure influences olefin coordination, and may provide new insights to the factors which underlie structure/reactivity trends in zirconocene-catalyzed alkene polymerization.

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

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(10) (a) A base free $Cp'_2Zr(O^tBu)^+$ cation is very unlikely in RCl solution. (b) The related chlorobenzene adducts $[Cp_2Zr(CH_2Ph)(ClPh)][B(C_6F_5)_4]$ and $[(C_5Me_5)_2ZrCl(ClPh)][B(C_6F_5)_4]$ have been crystallographically characterized. Wu, F.; Jordan, R. F., unpublished results.

(11) If the solvent term is included, the equilibrium constant for eq 2 is $K'_{eq} = K_{eq}[CD_2Cl_2]$, where K_{eq} is as defined in the text. If the solvent concentration is assumed to be independent of temperature, the value of ΔH° is not affected, but the entropy term becomes $\Delta S^{\circ\prime} = \Delta S^\circ + R(\ln[CD_2Cl_2])$, where $R(\ln[CD_2Cl_2]) \approx 5.5$ eu.

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