Nonchelated Zr^{IV}−Alkoxide−Alkyne Complexes

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Received November 3, 2005

Addition of alkynes to $[Cp'_2Zr(O^tBu)][B(C_6F_5)_4]$ ($Cp' = C_5H_4Me$, **2**) at low temperature in CD_2Cl_2 solution yields equilibrium mixtures of $Cp'_2Zr(O^tBu)(RC{\equiv}CR')^+$ (**3a**−**g**), **2**, and free alkyne. The ^{13}C NMR C_{int} resonance of terminal alkynes shifts far downfield upon coordination, while the C_{term} resonance shifts upfield, consistent with polarization of the C≡C bond with partial positive charge on C_{int} and partial negative charge on C_{term}, probably due to unsymmetrical coordination. Alkynes bind more strongly to **2** than do similar alkenes, but are readily displaced by Lewis bases such as THF. Increasing the steric bulk of the alkyne decreases the coordination strength. Propargyltrimethylsilane coordinates particularly strongly, due to β-Si stabilization of the positive charge on C_{int} of the coordinated alkyne. Compounds **3a**−**g** undergo two dynamic processes: reversible alkyne decomplexation and rotation around the metal−(alkyne centroid) axis.

Introduction

Alkyne complexes of d^0 metals are proposed intermediates in alkyne dimerization and oligomerization reactions (Scheme 1)[1] and are potential models for the d^0 metal−alkene complexes that are intermediates in alkene polymerization.[2] d^0 metal−alkyne complexes are challenging to study because alkyne coordination is weak due to the absence of d−π* back-bonding, and facile alkyne insertion can occur if M−H, M−R, or other reactive groups are present. These properties limit the range of ancillary ligands, solvents, and counterions that may be used with these species.

Alkyne complexes of d^0 metals are very rare. Erker prepared chelated $Cp_2M(CMe{=}C\{B(C_6F_5)_3\}C{\equiv}CMe)$ (M = Zr, Hf) alkenyl−alkyne complexes (**A**, Chart 1) by the reaction of $Cp_2M(C{\equiv}CMe)_2$ with $B(C_6F_5)_3$.[3] Horton prepared $Cp^*_2Zr(CH{=}CRC{\equiv}CR)^+$ species (**B**, $Cp^* = C_5Me_5$), which are intermediates in Zr-catalyzed alkyne oligomerization, by insertion of alkynes into Zr−alkynyl compounds.[1a] Jordan reported similar (η^5-$C_2B_9H_{11}$)(Cp*)Hf(CH=CRC≡CR) compounds (**C**), which were generated by analogous reactions.[1e]

Scheme 1

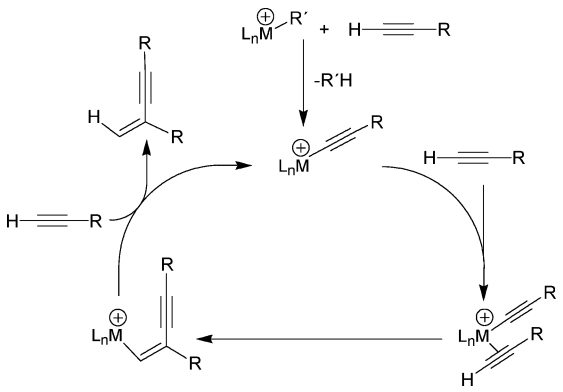
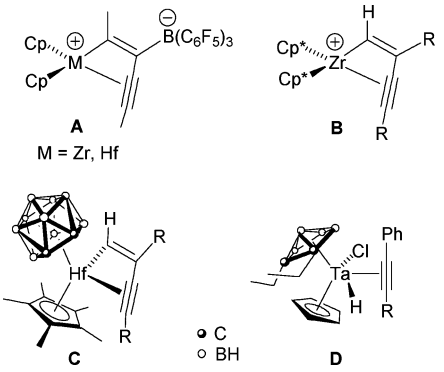


Chart 1



The C≡C NMR resonances of **B** and **C** are 5−10 ppm downfield from the resonances in typical enynes.[1b] Finn and Grimes reported that the reaction of $\{(\eta^5\text{-}Et_2C_2B_4H_4)CpTaH\}_2(\mu\text{-}Cl)_2$ with diphenylacetylene or 1-phenylpropyne yields *nonchelated* alkyne complexes (η^5-$Et_2C_2B_4H_4$)CpTa(H)(Cl)(PhC≡CR) (**D**; R = Ph, Me).[4] ^{13}C NMR chemical shifts for the C≡C carbons in these species were not reported. Theoretical

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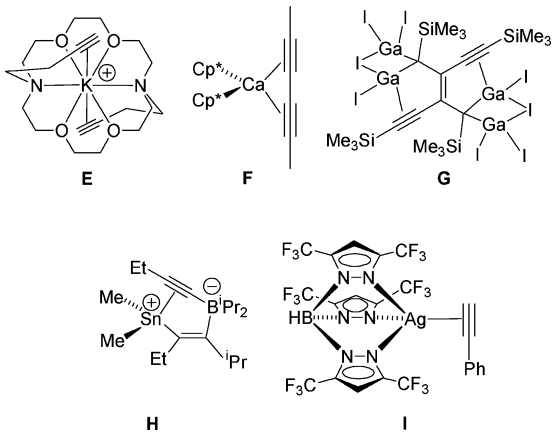
10.1021/om050947f CCC: $33.50
Publication on Web 06/06/2006

Chart 2



studies of $Cp_2ZrMe(HC{\equiv}CH)^+$, $Cl_2ZrH(HC{\equiv}CH)^+$, and $Cl_2ZrMe(HC{\equiv}CH)^+$ predict an unsymmetrical bonding mode for Zr^{IV}−alkyne complexes.[5] For example, the $Zr-C_{alkyne}$ distances in $Cp_2ZrMe(HC{\equiv}CH)^+$ were calculated to be 2.640 and 2.787 Å (Δd(Zr−C) = 0.147 Å).

Alkyne complexes of s- and p-block elements have also been characterized. Gokel reported that crown ethers with tethered alkynes exhibit Na^+− or K^+−alkyne interactions in the solid state (**E**, Chart 2),[6] and Hanusa described the diyne complex $Cp^*_2Ca(Me_3SiC{\equiv}CC{\equiv}CSiMe_3)$ (**F**).[7] The NMR resonances of the alkyne units in these compounds are only slightly shifted from the free alkyne positions.[6b,7] Jones reported that the reaction of "GaI" with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ yields a novel Ga^{III}_4 cluster with two Ga−alkyne units (**G**).[8] Wrackmeyer has studied $Sn^{IV}-\eta^2$-alkynylborate adducts that are intermediates in stannole formation (e.g., **H**)[9] and has reported similar $Pb^{IV}-\eta^2$-alkynylborate compounds.[10]

Group 11 and 12 metal−alkyne complexes in which d−π^* back-bonding is very weak have also been studied. For example, d^{10} Ag^I compounds normally exhibit only minimal d−π^* back-bonding, as exemplified by (HB{(3,5-CF_3)$_2$pz}$_3$)Ag(CO), for which a very high ν_{CO} value (2162 cm^{-1}) was observed.[11] Dias prepared Ag^I−alkyne adducts such as (HB{(3,5-CF_3)$_2$pz}$_3$)Ag(HC≡CPh) (**I**; pz = pyrazolyl).[11] Compound **I** exhibits unsymmetrical Ag−alkyne bonding in the solid state ($d(Ag-C_{term})$ = 2.263(5) Å; $d(Ag-C_{int})$ = 2.407(5) Å; Δd(Ag−C) = $d(Ag-C_{int}) - d(Ag-C_{term})$ = 0.144(7) Å). The coordination shifts ($\Delta\delta = \delta_{coord} - \delta_{free}$) of the alkyne C≡C NMR resonances of **I** are opposite in sign ($\Delta\delta$ C_{term} = −11.1; $\Delta\delta$ C_{int} = 2.8), which may be a consequence of the unsymmetrical coordination. Other Ag^I alkyne adducts have been reported.[12] Starowieyski has studied ω-alkynyl zinc compounds that have chelated structures with alkyne−zinc interactions.[13]

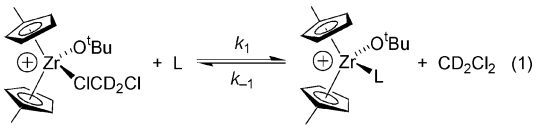
This paper describes the synthesis and properties of nonchelated $Cp'_2Zr(O^tBu)(alkyne)^+$ (Cp′ = C_5H_4Me) complexes, which are models for the putative $(C_5R_5)_2Zr(R')(alkyne)^+$ intermediates in Zr-catalyzed alkyne oligomerization reactions.[14]

Results and Discussion

Targets. The objective of this work was to prepare $[Cp'_2Zr(O^tBu)(RC{\equiv}CR')][B(C_6F_5)_4]$ alkyne complexes in order to probe Zr^{IV}−alkyne bonding. The *tert*-butoxide ligand was used to generate an electrophilic three-coordinate Zr species that cannot undergo alkyne insertion due to the strong Zr−O bond.[15] The Cp′ ligand was chosen because it provides a useful symmetry probe and neutral precursors to $Cp'_2Zr(OR)^+$ are readily available. The $B(C_6F_5)_4^-$ anion was chosen for its high stability and weak coordinating ability.[16] Halocarbon solvents were used to solubilize the ionic species, albeit at the cost of competitive solvent coordination.[17]

Synthesis of $[Cp'_2Zr(O^tBu)][B(C_6F_5)_4]$. The reaction of Cp'_2ZrMe_2 with ^{t}BuOH yields $Cp'_2Zr(O^tBu)Me$ (**1**).[18] The reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ affords $[Cp'_2Zr(O^tBu)][B(C_6F_5)_4]$ (**2**).[14a]

Generation of $Cp'_2Zr(O^tBu)(alkyne)^+$ Complexes. Addition of excess alkyne to a CD_2Cl_2 solution of **2** at low temperature results in the formation of an equilibrium mixture of **2**, free alkyne, and $[Cp'_2Zr(O^tBu)(alkyne)][B(C_6F_5)_4]$ (**3a**−**g**), as shown in eq 1. In a typical experiment, the desired alkyne was added by vacuum transfer to a frozen solution of **2** in CD_2Cl_2 in an NMR tube. The tube was thawed, stored at −78 °C, and transferred to a precooled NMR probe with minimal transfer time (<1 min) to prevent side reactions, and the equilibrium in eq 1 was studied by NMR spectroscopy. The $Cp'_2Zr(O^tBu)(alkyne)^+$ species are thermally sensitive, which precluded isolation or ESI-MS analysis.



cpd	L
a	HC≡CMe
b	HC≡CPh
c	HC≡CSiMe$_3$
d	HC≡CCH$_2$SiMe$_3$
e	MeC≡CMe
f	MeC≡CEt
g	EtC≡CEt

anion = $B(C_6F_5)_4^-$

NMR Properties and Solution Structures of $Cp'_2Zr(O^tBu)(alkyne)^+$ Complexes. The ^1H and $^{13}C\{^1H\}$ NMR spectra of

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Table 1. NMR Coordination Shifts ($\Delta\delta$) for $Cp'_2Zr(O^tBu)(HC{\equiv}CR)^+$ Complexes (3a−d)[a]

cpd	alkyne	C_{int}	C_{term}	C_{prop}[b]	H_{term}	H_{prop}[b]
3a	HC≡CMe	8.9	−2.8	4.5	1.16	0.46
3b	HC≡CPh	13.3	−2.1		1.23	
3c	HC≡$CSiMe_3$	4.8	−2.9		0.98	
3d	HC≡CCH_2SiMe_3	21.7	−0.9	7.0	1.58	0.48

[a] In CD_2Cl_2 solution, −89 °C; $\Delta\delta = \delta_{coord} - \delta_{free}$. [b] $HC{\equiv}CC\mathit{H}_nR_{3-n}$ resonance.

3a−**g** each contain four CH resonances and one set of CMe resonances for the Cp′ ligands, and one set of O^{t}Bu resonances, characteristic of C_s symmetry. In most cases, the Cp′ resonances are only slightly shifted from those of **2**. The Zr−O^{t}Bu ^{1}H NMR resonance appears at δ 1.22 for **2** and shifts less than 0.05 ppm from this position for **3a**,**c**−**g**. However, the Zr−O^{t}Bu ^{1}H NMR resonance of the phenylacetylene adduct **3b** is shifted upfield to δ 0.80, which is ascribed to anisotropic shielding of the O^{t}Bu hydrogens by the phenyl ring of the coordinated alkyne.

The NMR spectra of *terminal* alkyne complexes **3a**−**d** each contain one set of alkyne resonances, which are shifted from the free alkyne positions. The C_s symmetry and the presence of only one set of alkyne signals are consistent with the presence of a single rotamer of **3a**−**d** in which the alkyne lies in the plane between the Cp′ ligands or with fast rotation around the Zr−(alkyne centroid) axis.

The NMR spectra of *symmetrical*-alkyne adducts **3e**,**g** each contain one set of alkyne ≡CR resonances. The C_s symmetry of **3e**,**g** and the presence of only one set of ≡CR signals are consistent with the presence of a single rotamer of **3e**,**g** in which the alkyne lies perpendicular to the plane between the Cp′ ligands or with fast rotation around the Zr−(alkyne centroid) axis. The 2-butyne ^{1}H and ^{13}C NMR resonances of **3e** have approximately the same line widths as the other signals of **3e** at −59 °C, where intermolecular alkyne exchange is slow on the NMR time scale, but broaden as the temperature is lowered to −89 °C, while the other resonances of **3e** remain sharp. Similar NMR line-broadening effects are observed for the 2-pentyne (**3f**) and 3-hexyne (**3g**) adducts. These results indicate that rotation around the metal−(alkyne centroid) axis is fast on the NMR time scale at higher temperatures, but decreases in rate at lower temperatures.

The alkyne NMR resonances of the terminal alkyne complexes **3a**−**d** exhibit characteristic coordination shifts ($\Delta\delta = \delta_{coord} - \delta_{free}$), which are listed in Table 1. The H*C*≡ (C_{term}) ^{13}C resonance shifts upfield by 1−3 ppm, while the ≡*C*R (C_{int}) resonance shifts significantly downfield ($\Delta\delta$ = 5−22) upon coordination. The alkyne region of the $^{13}C\{^1H\}$ NMR spectrum of **3a** is shown in Figure 1 and illustrates the divergent coordination shifts of the Me*C*≡*C*H resonances. The ≡C*H* (H_{term}) ^{1}H NMR resonance of **3a**−**d** shifts downfield by 1−2

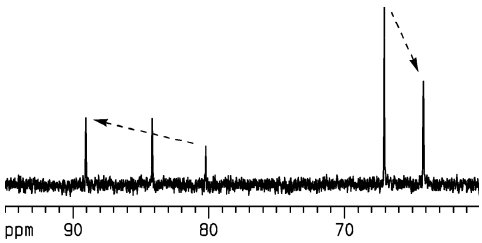

Figure 1. Partial $^{13}C\{^1H\}$ NMR spectrum of **3a** (CD_2Cl_2, −89 °C). Assignments: δ 89 (C_{int} of **3a**), 84 (O*C*Me$_3$ of **2** and **3a**), 80 (C_{int} of free propyne), 67 (C_{term} of free propyne), 64 (C_{term} of **3a**). The coordination shifts (free to coordinated) for the alkyne resonances are shown by arrows.

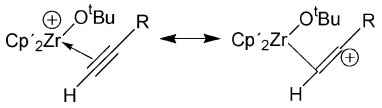

Figure 2. Polarization of d^0 metal−alkyne complexes.

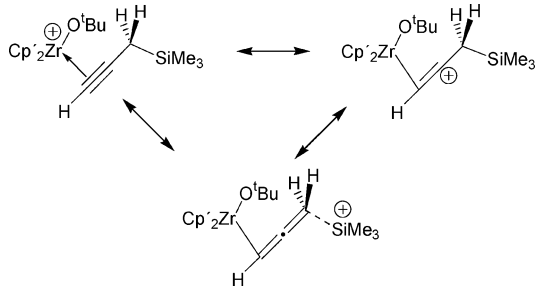

Figure 3. Stabilization of propargyltrimethylsilane adduct **3d** by the β-Si effect.

ppm upon coordination. For **3a**,**d**, the propargylic ≡CH_n ^{1}H and ^{13}C resonances are shifted downfield by ca. 0.5 and 5−7 ppm, respectively.

The ^{13}C $\Delta\delta$ values are reminiscent of the divergent coordination shifts in chelated $(C_5R_5)_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ complexes[19] and the $Ag^I(HC{\equiv}CPh)$ adduct **I**,[11] for which X-ray crystallographic analyses establish that the alkene and alkyne ligands are unsymmetrically bound. Therefore, the alkyne ligands in **3a**−**d** are also probably unsymmetrically coordinated with d(Zr−C_{int}) > d(Zr−C_{term}). Unsymmetrical alkyne coordination will polarize the C≡C triple bond, resulting in positive charge buildup on C_{int} and negative charge buildup on C_{term} (Figure 2), which explains the NMR data in Table 1. Consistent with this picture, propargyltrimethylsilane complex **3d** exhibits the largest $\Delta\delta$ value for C_{int}, which is a consequence of β-Si stabilization of the positive charge on C_{int}, as shown in Figure 3.[20,21] In contrast, the trimethylsilylacetylene adduct **3c** exhibits the smallest $\Delta\delta$ value for C_{int}, because the α-Si is better at stabilizing an anionic charge than a positive charge at C_{int}, resulting in reduced alkyne polarization.

The $^1J_{CH}$ and $^2J_{C{\equiv}\mathit{C}H}$ coupling constants for the alkyne units in **3a**−**d** are only slightly perturbed from the free alkyne values, as summarized in Table 2. These results suggest that the alkyne structure and the hybridization at the alkyne carbons are not strongly perturbed by coordination.

The coordination shifts of internal alkyne complexes **3e**−**g** are listed in Table 3. The C_{alkyne} NMR resonances of **3e**−**g** shift

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Table 2. Coupling Constants for Free Alkynes and Alkynes Coordinated to 2[a]

		$^1J_{CH}$ (Hz)		$^2J_{C\equiv CH}$ (Hz)	
cpd	alkyne	coord	free	coord	free
3a	HC≡CMe	251	249	47	50
3b	HC≡CPh	246	252	41	50
3c	HC≡CSiMe$_3$	244	237	*x*[b]	41
3d	HC≡CCH$_2$SiMe$_3$	244	247	43	50

[a] In CD_2Cl_2 solution, −89 °C. [b] Determination of this coupling constant was precluded by spectral overlaps.

Table 3. NMR Coordination Shifts ($\Delta\delta$) for Cp′$_2$Zr(O^{t}Bu)(RC≡CR′)$^+$ Complexes (3e−g)[a]

cpd	alkyne	C_{alkyne}	C_{prop}[b]	H_{prop}[b]
3e	MeC≡CMe	5.4	6.6	0.35
3f	MeC≡CEt	7.3[c]	6.8[c]	0.36[c]
		3.8[d]	7.2[d]	*x*[d,e]
3g	EtC≡CEt	6.1	7.0	*x*[e]

[a] In CD_2Cl_2 solution, −89 °C; $\Delta\delta = \delta_{coord} - \delta_{free}$. [b] ≡C$CH_nR_{3-n}$ resonance. [c] MeC≡ resonances. [d] EtC≡ resonances. [e] Resonance not detected due to spectral overlaps.

Table 4. Equilibrium Constants (K_{eq}) for Alkyne Coordination to Cp′$_2$Zr(O^{t}Bu)(ClCD$_2$Cl)$^+$ in Eq 1[a]

cpd	alkyne	K_{eq} (M^{-1})[b]
3d	HC≡CCH$_2$SiMe$_3$	$1.0(2) \times 10^5$
3a	HC≡CMe	360(70)
3e	MeC≡CMe	52(3)
3f	MeC≡CEt	49(9)
3g	EtC≡CEt	47(4)
3b	HC≡CPh	22(1)
3c	HC≡CSiMe$_3$	8.1(5)
	HC≡C^{t}Bu	*x*[c]

[a] In CD_2Cl_2 solution, −89 °C. [b] $K_{eq} = [\mathbf{3}][\mathbf{2}]^{-1}[L]^{-1}$. [c] No complex observed; $K_{eq} \leq 0.1\ M^{-1}$.

downfield by 4−7 ppm and the C_{prop} resonances shift downfield by ca. 7 ppm upon coordination. The H_{prop} resonances also display moderate downfield coordination shifts ($\Delta\delta$ = ca. 0.4 ppm).

The NMR properties of **3e**−**g** can be rationalized by the unsymmetrical coordination/alkyne polarization model proposed above for terminal alkyne complexes, coupled with fast exchange of the ends of the alkyne by rotation around the metal−(alkyne centroid) axis. Under slow alkyne rotation conditions, one alkyne carbon resonance of an unsymmetrically bound symmetrical alkyne would shift slightly upfield, while the other would shift significantly downfield, as observed for terminal alkyne adducts **3a**−**d**. Alkyne rotation would average these resonances, resulting in a net downfield shift, as observed for **3e**−**g**. The proposed unsymmetrical alkyne coordination in **3e**−**g** is consistent with the computational results for Cp$_2$ZrMe(HC≡CH)$^+$ noted above.[5]

Oxymetallocyclobutene-type structures derived from alkyne insertion, i.e., Cp′$_2$Zr(κ^2-*C*,*O*-CR=CRO^{t}Bu)$^+$, are ruled out for **3a**−**g** because such structures would display much larger $\Delta\delta$ values for the alkyne fragment than are observed, analogous to those for azametallocyclobutene species, i.e., Cp$_2$Zr(κ^2-*C*,*N*-CR=CRNR).[22]

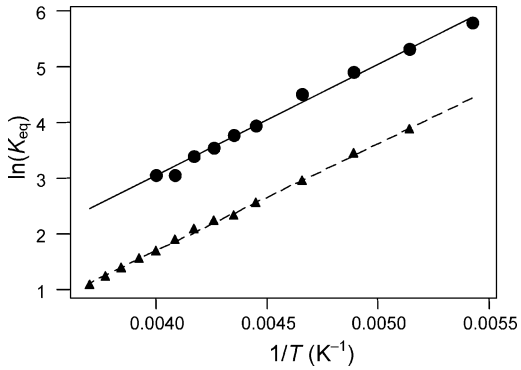


Figure 4. van't Hoff plot for propyne (circles, solid line) and 2-butyne (triangles, dashed line) coordination in **3a**,**e** in CD_2Cl_2 solution (eq 1).

Thermodynamics of Alkyne Binding to 2. Equilibrium constants for alkyne binding to **2** in eq 1, $K_{eq} = [\mathbf{3}][\mathbf{2}]^{-1}[L]^{-1}$, were determined by ^{1}H NMR and are listed in Table 4.[23] K_{eq} values for **3a**−**c**,**e**−**g** were found by studies of eq 1. The K_{eq} value for propargyltrimethylsilane binding was too large to be determined directly and, therefore, was determined by a competition experiment with propyne. In certain cases, K_{eq} values were determined over a sufficiently wide temperature range to enable accurate determination of binding enthalpies and entropies. These values are listed in Table 5.

The binding of 2-butyne to **2** to form **3e** in eq 1 will be described as a representative case. The equilibrium constant for 2-butyne coordination in CD_2Cl_2 solution at −89 °C is K_{eq} = 52(3) M^{-1}. At $[\mathbf{2}]_{initial} = 0.08$ M and [2-butyne]$_{initial} = 0.10$ M, ca. 75% of the total Cp′$_2$Zr(O^{t}Bu)$^+$ exists as **3e**. The K_{eq} value is constant over the concentration ranges $[\mathbf{2}]_{initial} = 0.035-0.078$ M and [2-butyne]$_{initial} = 0.043-0.10$ M. Addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (ca. 4 equiv per Zr) as an anion source does not affect the equilibrium constant at −91 °C in CD_2Cl_2, indicating that the anion is not explicitly involved in eq 1. Under these conditions, Ph$_3$C$^+$ does not interact with 2-butyne or **2**. At −38 °C, K_{eq} for 2-butyne binding is larger in CD_2Cl_2 (8.8(4) M^{-1}) than in C_6D_5Cl (2.9(1) M^{-1}). While solvent polarity may influence the K_{eq} value,[24] it is likely that PhCl binds to **2** more strongly than CD_2Cl_2 does,[17a] which would result in a reduced K_{eq} value in the former solvent. As the temperature is raised, the 2-butyne complex **3e** becomes less favored, and the equilibrium shifts to free alkyne and **2**. A van't Hoff analysis (Figure 4) gives $\Delta H° = -3.6(3)$ kcal/mol and $\Delta S° = -11(1)$ eu (Table 5).[23]

The data in Table 4 show how the steric and electronic properties of the alkyne influence K_{eq}. Steric crowding close to the alkyne triple bond inhibits alkyne coordination. Propyne binds more strongly than 2-butyne or other internal alkynes, and *tert*-butylacetylene does not bind to **2** in CD_2Cl_2 solution. Propyne coordination is strong enough to observe NMR line broadening in a **2**/propyne mixture at 22 °C. Internal alkynes must have one alkyl group in the vicinity of the Cp′ rings in the Cp′$_2$Zr(O^{t}Bu)(RC≡CR)$^+$ adduct, while propyne does not.

Stabilization of the partial positive charge on C_{int} of the coordinated alkyne enhances alkyne binding. Thus, due to the

Table 5. Thermodynamic Data for Equilibria in Eq 1 and Activation Parameters for Decomplexation (k_{-1})[a]

cpd	alkyne	$\Delta H°$ (kcal/mol)	$\Delta S°$ (eu)	$\Delta H^‡$ (kcal/mol)	$\Delta S^‡$ (eu)	$\Delta G^‡$ (kcal/mol)[b]
3a	HC≡CMe	−4.1(3)	−11(1)	8.5(3)	−14(1)	11.8(1)
3e	MeC≡CMe	−3.6(3)	−11(1)	13.8(5)	4(2)	12.9(1)

[a] In CD_2Cl_2 solution. [b] At −39 °C.

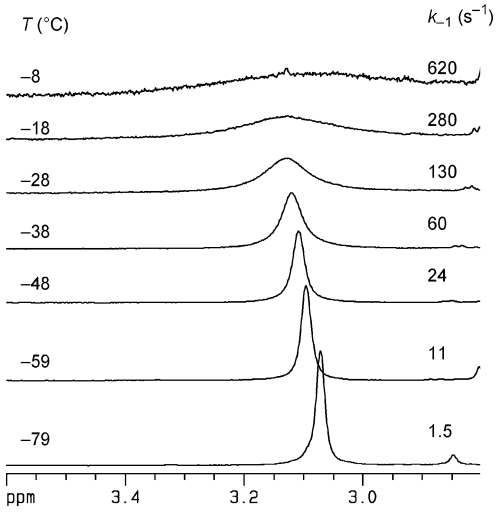


Figure 5. Partial variable-temperature ^{1}H NMR spectra (500 MHz) of an equilibrium mixture of **3a**, **2**, and propyne in CD_2Cl_2 solution illustrating the broadening of the H_{term} resonance of **3a** (δ 3.1) due to reversible propyne decomplexation. The k_{-1} values are first-order rate constants for propyne decomplexation. The peak at δ 2.85 is due to an unidentified impurity.

operation of the β-Si effect, propargyltrimethylsilane coordinates very strongly to **2** to give **3d** (Table 4), and the presence of just 1 equiv of propargyltrimethylsilane results in quantitative formation of **3d** up to −8 °C.[20]

The binding enthalpies in Table 5 show that the Zr−alkyne bonds in **3a**,**e** are only ca. 4 kcal/mol stronger than the Zr−$ClCD_2Cl$ bond in **2**, which underscores the point that the absence of d−π* back-bonding results in weak alkyne coordination. Alkyne binding is substantially weaker than coordination of typical Lewis bases. For example, 1 equiv of THF (per Zr) completely displaces propyne from **3a** to give $[Cp'_2Zr(O^tBu)(THF)][B(C_6F_5)_4]$ (**4**). Compound **4** can be independently generated by addition of THF to a solution of **2**. The properties of **4** are similar to those of $Cp_2Zr(O^tBu)(THF)^+$ and *rac*-$(EBTHI)Zr(O^tBu)(THF)^+$ (EBTHI = 1,2-ethylenebis(tetrahydroindenyl)).[25]

Intermolecular Alkyne Exchange. The NMR resonances for **3a**, **2**, and free propyne in an equilibrium mixture of these species broaden as the temperature is raised above −69 °C. The Cp′ CH ^{1}H NMR signals of **3a** coalesce with those of **2** between −38 and −18 °C, and the bound propyne signals of **3a** coalesce with the free propyne signals between −8 and +22 °C. These dynamic effects are consistent with the exchange of **3a** and **2** and of free and coordinated propyne. The broadening of the H_{term} resonance of **3a** is shown in Figure 5.

First-order rate constants for propyne decomplexation from **3a** (k_{-1} in eq 1) were determined from the excess line broadening of the H_{term} resonance of **3a** under slow NMR exchange conditions. The line width of the H_{term} resonance and

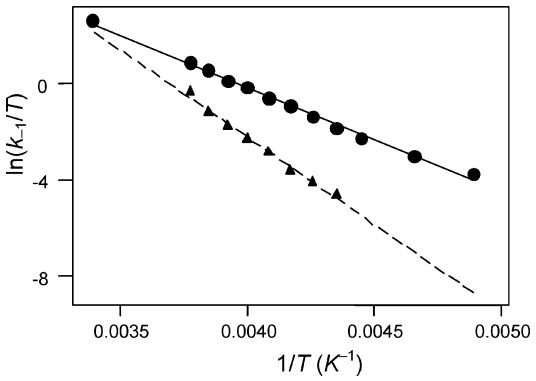
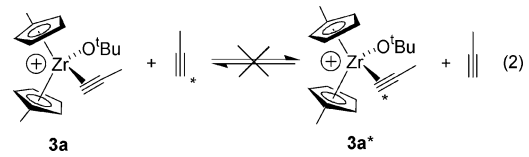


Figure 6. Eyring plot for propyne (circles, solid line) and 2-butyne (triangles, dashed line) decomplexation (k_{-1}) from **3a**,**e** in CD_2Cl_2 solution.

hence the propyne decomplexation rate constant is independent of the free propyne concentration over the range [propyne] = 0.017−0.048 M. Therefore, direct associative displacement of coordinated propyne by free propyne (eq 2) does not occur to a significant extent. Instead, the data imply that propyne is lost from **3a** to give **2**, and propyne coordinates to **2** to give **3a** (eq 1).



An Eyring analysis (Figure 6) for propyne decomplexation from **3a** gives the activation parameters listed in Table 5. The negative $\Delta S^{\ddagger}$ value suggests that a CD_2Cl_2 molecule displaces the coordinated propyne by an associative mechanism.

Similarly, when a solution of **3e** is warmed above −48 °C, the NMR signals of **3e** broaden and coalesce with the signals for **2** and free 2-butyne. First-order rate constants for 2-butyne decomplexation (k_{-1}) were determined from the excess line broadening of the 2-butyne ^{1}H NMR resonance of **3e**. The first-order rate constants are independent of the free 2-butyne concentration over the range [MeC≡CMe] = 0.037−0.079 M. Therefore, free 2-butyne does not directly displace coordinated 2-butyne in the exchange process.

An Eyring analysis for 2-butyne decomplexation from **3e** (Figure 6) gives the activation parameters listed in Table 5. The small, positive $\Delta S^{\ddagger}$ value and larger $\Delta H^{\ddagger}$ value compared to that for propyne decomplexation from **3a** are consistent with a greater degree of dissociative character for 2-butyne decomplexation versus propyne decomplexation. Significant steric crowding is expected in the transition state for associative CD_2Cl_2 displacement of 2-butyne from **3e**.

A free energy diagram comparing propyne and 2-butyne coordination to **2** is shown in Figure 7. 2-Butyne binds more weakly, but exchanges more slowly than propyne. These differences reflect the greater steric crowing in the 2-butyne adduct.

Comparison of Properties of d^0 and d^2 Group 4 Alkyne Complexes. Due to the absence of d−π* back-bonding in alkyne adducts **3a**−**g**, the properties of these compounds are quite different from those of "classical" d^n metal−alkyne complexes, in which back-bonding is present. These differences can be illustrated most clearly by comparing d^0 Zr^{IV}−alkyne adducts to d^2 Zr^{II}−alkyne adducts. Buchwald studied the hexyne adducts $Cp_2Zr(HC{\equiv}C^nBu)(PMe_3)$ (**J**) and $Cp_2Zr(EtC{\equiv}CEt)$-

(22) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705. (b) Harlan, C. J.; Tunge, J. A.; Bridgewater, B. M.; Norton, J. R. *Organometallics* **2000**, *19*, 2365.

(23) If the solvent term is included, the equilibrium constant for eq 1 is $K'_{eq} = K_{eq}[CD_2Cl_2]$, where K_{eq} is defined as in the text. If the solvent concentration is assumed to be independent of temperature, the value of $\Delta H°$ is not affected, but the entropy term becomes $\Delta S°' = \Delta S° + R(\ln[CD_2Cl_2])$, where $R(\ln[CD_2Cl_2]) \approx 5.5$ eu.

(24) The dielectric constants (20 °C) are CH_2Cl_2 9.08, C_6H_5Cl 5.71. *CRC Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1986; pp E-50−51.

(25) (a) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092. (b) Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964.

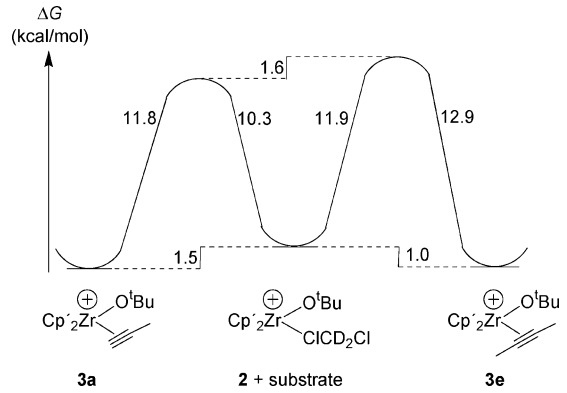


Figure 7. Free energy diagram (−39 °C) comparing propyne and 2-butyne coordination to **2**.

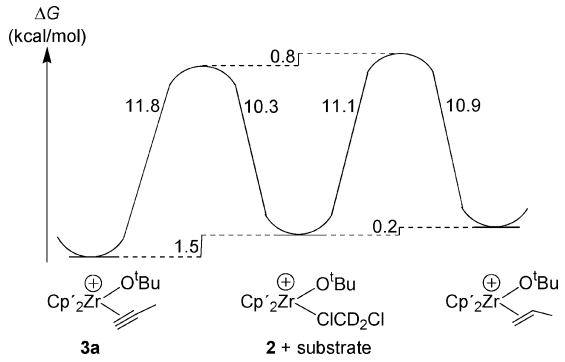


Figure 8. Free energy diagram (−39 °C) comparing propyne and propylene coordination to **2**.

(PMe_3) (**K**).[26] An X-ray crystallographic analysis of 1-hexyne adduct **J** revealed the presence of a symmetrically bound alkyne ligand ($d(Zr-C_{int}) = 2.211(3)$ Å; $d(Zr-C_{term}) = 2.244(3)$ Å; $\Delta d(Zr-C) = 0.033(4)$ Å), with a C≡C distance of 1.286(5) Å and a C≡C−C angle of 135.8(3)°. The C≡C NMR resonances of **J** and **K** are shifted far *downfield* from the free alkyne positions ($\Delta\delta = 60-120$), and the H_{term} resonance of **J** is also shifted significantly downfield upon coordination ($\Delta\delta \approx 5$). These results show that the alkyne ligands in **J** and **K** are symmetrically coordinated, the C≡C bonds are not polarized, but the alkyne is strongly structurally distorted such that the "alkyne" carbons are sp^2 hybridized. The d^2 compounds Cp*$_2$Ti(MeC≡CMe),[27] Cp*$_2$Ti(HC≡CMe),[28] Cp_2Nb(Et)(HC≡CMe), and Cp_2Nb(H)(HC≡CSiMe$_3$)[29] display similar properties. These effects are all characteristic of strong d−π* back-bonding, and these compounds are best described as d^0 metallocyclopropenes. In contrast, the absence of back-bonding in the d^0 metal−alkyne complexes **3a**−**g** results in weak unsymmetrical coordination, substantial polarization of the C≡C bond, but little perturbation of the alkyne structure and hybridization of the alkyne carbons.[30] Other metal−alkyne complexes with weak or nonexistent d−π* back-bonding (e.g., **B**, **C**, **E**, **F**, **H**, and **I**; Charts 1 and 2) also show only minor coordination shifts and thus show a similar contrast to metal−alkyne complexes with back-bonding.

Comparison of d^0 Metal−Alkyne and d^0 Metal−Alkene Complexes. Alkynes bind more strongly to **2** than structurally similar alkenes do.[14] For example, propyne binds to **2** almost 70 times stronger than propylene does, and propargyltrimethylsilane binds about 60 times stronger than allyltrimethylsilane does, based on the measured K_{eq} values. Steric effects probably contribute significantly to this difference, as the linear structure of alkynes creates less steric crowding with the Cp′$_2$Zr backbone compared to alkenes. The ligand exchange behavior of alkyne and alkene complexes of **2** is quite similar. In both cases substrate decomplexation occurs by displacement by solvent in CD_2Cl_2 solution.

A free energy diagram comparing propylene and propyne coordination to **2** is shown in Figure 8. Propyne binds more strongly than propylene by ca. 1.7 kcal/mol. The barrier for propyne decomplexation is higher than that for propylene decomplexation by ca. 0.9 kcal/mol, while the propyne complexation barrier is lower than that for propylene by ca. 0.8 kcal/mol. Thus, the stronger ligand propyne comes off more slowly, but binds more rapidly than the weaker ligand propylene.

Implications for Alkyne Oligomerization. Catalytic dimerization of terminal alkynes by Zr^{IV} compounds normally occurs via 1,2-alkyne insertion to give "head-to-tail" H_2C=CHRC≡CR dimers as the major or exclusive product (Scheme 1). This selectivity implies that the Zr−C≡CR group migrates to C_{int} of the coordinated alkyne.[1] Polarization of the C≡C bond of the alkyne ligand in the key $Cp_2Zr(C{\equiv}CR)(HC{\equiv}CR)^+$ intermediate in the same manner as implied by the NMR data for the Cp′$_2$Zr(O^{t}Bu)(HC≡CR)$^+$ models **3a**−**d** provides a reasonable explanation for this regiochemistry, as the partial positive charge on C_{int} of the alkyne renders this carbon susceptible to nucleophilic attack and thus insertion. It is also possible that steric crowding between the alkyl group of a terminal alkyne and the Cp ligands in the $Cp_2Zr(C{\equiv}CR)(HC{\equiv}CR)^+$ intermediate would favor the alkyne rotamer in which C_{int} is oriented toward the M−R bond, which would increase the preference for 1,2-alkyne insertion. The shielding of the O^{t}Bu hydrogens of **3b** by the phenyl ring of the HC≡CPh ligand suggests that such a rotamer is the favored one.

Experimental Section

General Procedures. All reactions were performed using glovebox or Schlenk techniques under a purified N_2 atmosphere or on a high-vacuum line. N_2 was purified by passage through columns of activated molecular sieves and Q-5 oxygen scavenger. CD_2Cl_2 and C_6D_5Cl were distilled from P_2O_5, while THF was distilled from Na/benzophenone. The synthesis of **2** was described previously.[14a] Other reagents were obtained from standard commercial sources. $[Ph_3C][B(C_6F_5)_4]$ and propyne were used as received. Trimethylsilylacetylene and phenylacetylene were dried over CaH_2. Propargyltrimethylsilane, 2-butyne, and 2-pentyne were dried over 3 Å molecular sieves. 3-Hexyne was dried over Na and stored over 3 Å molecular sieves prior to use.

NMR spectra were recorded on Bruker DRX 500 or 400 spectrometers in Teflon-valved NMR tubes at ambient probe temperature unless otherwise noted. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were referenced to the residual solvent signals. ^{19}F NMR spectra are reported and referenced relative to external neat $CFCl_3$. NMR probe temperatures were calibrated by a MeOH thermometer.[31] Coupling constants are reported in Hz. Where ^{13}C-gated-{^1H} NMR spectra are reported, standard $^{13}C\{^1H\}$ NMR spectra were also recorded to assist in interpretation.

(26) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.
(27) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.
(28) Brinkmann, P. H. P.; Luinstra, G. A.; Saenz, A. *J. Am. Chem. Soc.* **1998**, *120*, 2854.
(29) Yasuda, H.; Yamamoto, H.; Arai, T.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1991**, *10*, 4058.
(30) Structural and vibrational spectroscopic data for Ti^{II} and Ti^{III} alkyne adducts substantiate the weakening of alkyne coordination upon loss of d electrons. Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Burlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed.* **2003**, *42*, 1414.
(31) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

NMR spectra of ionic compounds contain $B(C_6F_5)_4^-$ anion resonances at the free anion positions, as listed in the Supporting Information. ^{19}F NMR spectra were obtained for all compounds that contain this anion. NMR data for free alkynes are given in the Supporting Information.

General Procedure for Generation of [Cp′$_2$Zr(O^{t}Bu)(alkyne)][B(C$_6$F$_5$)$_4$] (3a−g). An NMR tube was charged with **2** (25−50 mg), and CD_2Cl_2 (0.5−0.7 mL) was added by vacuum transfer at −78 °C. The tube was shaken at −78 °C, giving a yellow solution. The tube was cooled to −196 °C, and alkyne (excess) was added by vacuum transfer. The tube was warmed to −78 °C and shaken, yielding a yellow solution. The tube was placed in an NMR probe that had been precooled to −89 °C. NMR spectra were obtained and showed that a mixture of **3a**−**g**, **2**, and free alkene was present. The detailed procedure for propyne adduct **3a** and NMR data for all compounds are given below. The procedure for generation of **3b**−**g** is similar to that for **3a**.

Generation of [Cp′$_2$Zr(O^{t}Bu)(HC≡CMe)][B(C$_6$F$_5$)$_4$] (3a). An NMR tube was charged with **2** (25.5 mg, 0.0255 mmol), and CD_2Cl_2 (0.70 mL) was added by vacuum transfer at −78 °C. The tube was shaken at −78 °C, giving a yellow solution. The tube was cooled to −196 °C, and propyne (0.0265 mmol) was added by vacuum transfer. The tube was warmed to −78 °C, shaken at −78 °C, and placed in an NMR probe that had been precooled to −89 °C. NMR spectra showed the presence of **3a** (0.026 M), **2** (0.0073 M), and free propyne (0.011 M). Raising the temperature from −89 °C has the effect of decreasing the concentration of **3a**, increasing the concentrations of **2** and free propyne, and broadening the signals for **3a** and to a lesser extent those of **2** and free propyne. As the temperature is raised, the signals for **3a** eventually coalesce with those of **2** and free propyne. Data for **3a**: ^1H NMR (CD_2Cl_2, −89 °C): δ 6.42 (m, 2H, Cp′ CH), 6.37 (m, 2H, Cp′ CH, overlaps with signal for **2**), 6.19 (m, 2H, Cp′ CH), 6.06 (m, 2H, Cp′ CH), 3.08 (q, J = 1.8, 1H, ≡C*H*), 2.23 (d, J = 1.5, 3H, ≡C*Me*), 2.17 (s, 6H, Cp′*Me*), 1.23 (s, 9H, O^{t}Bu, overlaps with signal for **2**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 128.2 (ipso Cp′), 118.0 (Cp′ CH), 116.1 (Cp′ CH), 115.1 (Cp′ CH), 110.5 (Cp′ CH), 89.1 (d, $^2J_{C\equiv CH}$ = 47, C_{int}), 84.2 (O*C*Me$_3$), 64.2 (d, $^1J_{CH}$ = 251, C_{term}), 30.8 (OC*Me*$_3$), 14.8 (Cp′*Me*), 7.6 (q, $^1J_{CH}$ = 135, ≡C*Me*).

[Cp′$_2$Zr(O^{t}Bu)(HC≡CPh)][B(C$_6$F$_5$)$_4$] (3b). ^1H NMR (CD_2Cl_2, −89 °C): δ 7.83 (d, J = 7.3, 2H, *o*-Ph), 7.78 (t, J = 7.3, 1H, *p*-Ph), 7.56 (t, J = 7.4, 2H, *m*-Ph), 6.34 (br s, 2H, Cp′ CH, overlaps with signal for **2**), 6.30 (br s, 2H, Cp′ CH), 6.09 (br s, 2H, Cp′ CH), 6.06 (br s, 2H, Cp′ CH), 4.46 (s, 1H, ≡CH), 2.22 (s, 6H, Cp′*Me*), 0.80 (s, 9H, O^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 136.3 (*m*-Ph), 135.8 (*p*-Ph), 129.6 (*o*-Ph), 127.6 (ipso Cp′), 117.8 (Cp′ CH), 115.7 (Cp′ CH), 114.4 (Cp′ CH), 110.9 (Cp′ CH), 96.1 (d, $^2J_{C\equiv CH}$ = 41, C_{int}), 83.5 (O*C*Me$_3$), 75.0 (d, $^1J_{CH}$ = 246, C_{term}), 30.2 (OC*Me*$_3$), 15.0 (Cp′*Me*). The ipso-Ph resonance was not detected.

[Cp′$_2$Zr(O^{t}Bu)(HC≡CSiMe$_3$)][B(C$_6$F$_5$)$_4$] (3c). ^1H NMR (CD_2Cl_2, −89 °C): δ 6.36 (br m, 2H, Cp′ CH), 6.33 (br m, 2H, Cp′ CH), 6.24 (br m, 2H, Cp′ CH), 6.02 (br m, 2H, Cp′ CH), 3.47 (s, 1H, CH), 2.14 (s, 6H, Cp′*Me*), 1.24 (s, 9H, O^{t}Bu), 0.44 (s, 9H, SiMe$_3$). $^{13}C\{^1H$-gated$\}$ NMR (CD_2Cl_2, −89 °C): δ 126.9 (s, ipso Cp′), 118.3 (d, $^1J_{CH}$ = 177, Cp′ CH), 117.1 (d, $^1J_{CH}$ = 170, Cp′ CH), 114.7 (d, $^1J_{CH}$ = 177, Cp′ CH), 109.5 (d, $^1J_{CH}$ = 179, Cp′ CH), 94.3 (C_{int}),[32] 90.1 (d, $^1J_{CH}$ = 244, C_{term}), 84.8 (s, O*C*Me$_3$), 30.9 (q, $^1J_{CH}$ = 125, OC*Me*$_3$), 14.8 (q, $^1J_{CH}$ = 129, Cp′*Me*), −0.5 (q, $^1J_{CH}$ = 122, SiMe$_3$).

[Cp′$_2$Zr(O^{t}Bu)(HC≡CCH$_2$SiMe$_3$)][B(C$_6$F$_5$)$_4$] (3d). ^1H NMR (CD_2Cl_2, −89 °C): δ 6.33 (br m, 2H, Cp′ CH), 6.31 (br s, 2H, Cp′ CH), 6.13 (br m, 2H, Cp′ CH), 5.99 (br m, 2H, Cp′ CH), 3.46 (br s, 1H, ≡CH), 2.13 (s, 6H, Cp′*Me*), 1.91 (br s, 2H, C*H*$_2$SiMe$_3$), 1.19 (s, 9H, O^{t}Bu), 0.21 (s, 9H, SiMe$_3$). ^{13}C-gated-$\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 127.5 (s, ipso Cp′), 117.4 (d, $^1J_{CH}$ = 169, Cp′ CH), 115.6 (d, $^1J_{CH}$ = 171, Cp′ CH), 114.5 (d, $^1J_{CH}$ = 174, Cp′ CH), 110.1 (d, $^1J_{CH}$ = 173, Cp′ CH), 104.3 (d, $^2J_{C\equiv CH}$ = 43, C_{int}), 83.4 (s, O*C*Me$_3$), 65.5 (d, $^1J_{CH}$ = 244, C_{term}), 30.8 (q, $^1J_{CH}$ = 126, OC*Me*$_3$), 14.8 (q, $^1J_{CH}$ = 129, Cp′*Me*), 12.7 (t, $^1J_{CH}$ = 131, *C*H$_2$SiMe$_3$), −2.6 (q, $^1J_{CH}$ = 121, SiMe$_3$).

[Cp′$_2$Zr(O^{t}Bu)(MeC≡CMe)][B(C$_6$F$_5$)$_4$] (3e). ^1H NMR (C_6D_5Cl, −35 °C): δ 5.95 (br s, 2H, Cp′ CH), 5.61 (br s, 2H, Cp′ CH), 1.92 (s, 6H, Cp′*Me*), 1.55 (s, 6H, MeC≡CMe), 0.97 (s, 9H, O^{t}Bu). The other Cp′ CH resonances are obscured by signals for **2**. ^1H NMR (CD_2Cl_2, −89 °C): δ 6.33 (br s, 2H, Cp′ CH, overlaps with signal for **2**), 6.30 (br s, 2H, Cp′ CH), 6.23 (br s, 2H, Cp′ CH), 6.00 (br s, 2H, Cp′ CH), 2.23 (s, 6H, Cp′*Me*), 2.03 (br s, 6H, MeC≡CMe), 1.23 (s, 9H, O^{t}Bu, overlaps with signal for **2**). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, −35 °C): δ 118.1 (Cp′ CH), 116.4 (Cp′ CH), 114.4 (Cp′ CH), 111.5 (Cp′ CH), 84.4 (O*C*Me$_3$), 80.0 (C≡C), 31.2 (OC*Me*$_3$), 14.3 (Cp′*Me*), 8.8 (*Me*C≡C*Me*). The ipso Cp′ resonance is obscured by a solvent resonance. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 128.5 (ipso Cp′), 118.2 (Cp′ CH), 116.1 (Cp′ CH), 113.7 (Cp′ CH), 110.7 (Cp′ CH), 84.3 (O*C*Me$_3$), 79.6 (C≡C), 31.1 (OC*Me*$_3$), 14.5 (Cp′*Me*), 9.7 (br, *Me*C≡C*Me*).

[Cp′$_2$Zr(O^{t}Bu)(MeC≡CEt)][B(C$_6$F$_5$)$_4$] (3f). ^1H NMR (CD_2Cl_2, −89 °C): δ 6.35 (br s, 2H, Cp′ CH), 6.29 (br s, 2H, Cp′ CH), 6.23 (br m, 2H, Cp′ CH), 6.00 (br s, 2H, Cp′ CH), 2.23 (s, 6H, Cp′*Me*), 2.06 (unresolved m, 3H, ≡C*Me*, partially overlaps with a resonance for free 2-pentyne), 1.27 (br t, J = 8, 3H, CH$_2$*Me*, partially obscured by O^{t}Bu resonances of **3f** and **2**), 1.23 (s, 9H, O^{t}Bu, overlaps with resonance for **2**). The ≡CC*H*$_2$ signal is obscured by the Cp′*Me* signal for **2**. $^{13}C\{^1H$-gated$\}$ NMR (CD_2Cl_2, −89 °C): δ 128.3 (s, ipso Cp′), 118.2 (d, $^1J_{CH}$ = 177, Cp′ CH), 116.0 (d, $^1J_{CH}$ = 171, Cp′ CH), 113.8 (d, $^1J_{CH}$ = 174, Cp′ CH), 110.7 (d, $^1J_{CH}$ = 174, Cp′ CH), 84.3 (s, O*C*Me$_3$), 84.0 (slightly br s, C≡C), 81.6 (slightly br s, C≡C), 31.1 (q, $^1J_{CH}$ = 126, OC*Me*$_3$), 19.0 (br t, $^1J_{CH}$ = 135, ≡C*C*H$_2$), 14.6 (q, $^1J_{CH}$ = 128, Cp′*Me*), 14.5 (partially obscured br q, CH$_2$*Me*), 9.9 (br q, $^1J_{CH}$ = 134, *Me*C≡).

[Cp′$_2$Zr(O^{t}Bu)(EtC≡CEt)][B(C$_6$F$_5$)$_4$] (3g). ^1H NMR (CD_2Cl_2, −89 °C): δ 6.33 (br m, 2H, Cp′ CH), 6.28 (br m, 2H, Cp′ CH), 6.20 (br m, 2H, Cp′ CH), 5.98 (br m, 2H, Cp′ CH), 2.22 (s, 6H, Cp′*Me*), 1.29 (br t, J = 7, 6H, *Me*CH$_2$C≡), 1.22 (s, 9H, O^{t}Bu, overlaps with O^{t}Bu signal of **2**). The MeC*H*$_2$C≡ signal is obscured by the Cp′*Me* signal of **3g** and **2**. $^{13}C\{^1H$-gated$\}$ NMR (CD_2Cl_2, −89 °C): δ 128.2 (s, ipso Cp′), 118.1 (d, $^1J_{CH}$ = 172, Cp′ CH), 115.8 (d, $^1J_{CH}$ = 171, Cp′ CH), 113.8 (d, $^1J_{CH}$ = 172.4, Cp′ CH), 110.6 (d, $^1J_{CH}$ = 181, Cp′ CH), 86.5 (s, C≡C), 84.3 (s, O*C*Me$_3$), 31.1 (q, $^1J_{CH}$ = 127, OC*Me*$_3$), 19.0 (br t, $^1J_{CH}$ = 135, *C*H$_2$C≡), 14.6 (*Me*CH$_2$C≡),[33] 14.6 (q, $^1J_{CH}$ = 128, Cp′*Me*).

Competitive Coordination of Propyne and THF to 2. A solution of **2** (0.0270 mmol) in CD_2Cl_2 (0.71 mL) in an NMR tube was generated as described above. The tube was cooled to −196 °C, and THF (0.0292 mmol, 1.08 equiv) was added by vacuum transfer. The tube was warmed to −78 °C and shaken to give a yellow solution. The tube was cooled to −196 °C, and propyne (0.41 mmol, 15 equiv) was added by vacuum transfer. The tube was warmed to −78 °C, shaken to give a yellow solution, and then placed in a precooled NMR probe. NMR spectra recorded at −89 and −38 °C revealed the presence of [Cp′$_2$Zr(O^{t}Bu)(THF)][B(C$_6$F$_5$)$_4$] (**4**; 100%), along with free THF (0.097 equiv) and free propyne (15 equiv). [Cp′$_2$Zr(O^{t}Bu)(HC≡CMe)][B(C$_6$F$_5$)$_4$] (**3a**) was not observed.

Independent Generation of [Cp′$_2$Zr(O^{t}Bu)(THF)][B(C$_6$F$_5$)$_4$] (4). A solution of **2** (0.0701 mmol) in C_6D_5Cl (0.6 mL) was cooled to −196 °C, and THF (0.0717 mmol, 1.02 equiv) was added by vacuum transfer. The tube was warmed to 22 °C and shaken to give a yellow-orange solution. NMR spectra showed that **4** had formed quantitatively. Data for **4**: ^1H NMR (C_6D_5Cl): δ 5.94−5.91 (m, 4H, Cp′ CH), 5.79 (q, J = 2.5, 2H, Cp′ CH), 5.73 (q, J =

(32) While the resonance is clear in the $^{13}C\{^1H\}$ NMR spectrum, the coupling pattern in the $^{13}C\{$gated-$^1H\}$ spectrum is obscured by a free alkyne resonance.

2.9, 2H, Cp′ CH), 3.51 (m, 4H, THF), 1.85 (s, 6H, Cp′*Me*), 1.65 (m, 4H, THF), 1.01 (s, 9H, O^{t}Bu). ^{1}H NMR (CD_2Cl_2, −89 °C): δ 6.36 (br s, 2H, Cp′ CH), 6.31 (br s, 2H, Cp′ CH), 6.15 (br s, 2H, Cp′ CH), 6.07 (br s, 2H, Cp′ CH), 3.96 (br m, 4H, THF), 2.13 (s, 6H, Cp′*Me*), 2.10 (br m, 4H, THF), 1.21 (s, 9H, O^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_5Cl): δ 127.6 (ipso Cp′), 117.6 (Cp′ CH), 116.2 (Cp′ CH), 115.3 (Cp′ CH), 111.2 (Cp′ CH), 78.0 (THF), 31.6 (OC*Me*$_3$), 25.7 (THF), 14.4 (Cp′*Me*); the O*C*Me$_3$ resonance was not detected. ^{13}C{^{1}H} NMR (CD_2Cl_2, −89 °C): δ 126.9 (ipso Cp′), 117.0 (Cp′ CH), 115.0 (Cp′ CH), 114.9 (Cp′ CH), 109.9 (Cp′ CH), 82.3 (O*C*Me$_3$), 78.0 (THF), 31.0 (OC*Me*$_3$), 25.7 (THF), 14.3 (Cp′*Me*).

Influence of [Ph$_3$C][B(C$_6$F$_5$)$_4$] on 2-Butyne Coordination to 2. An NMR tube was charged with **2** (19.3 mg, 0.0193 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (48.9 mg, 0.0530 mmol, 2.75 equiv), and CD_2Cl_2 (0.71 mL) was added by vacuum transfer at −78 °C. The tube was shaken at −78 °C to give a deep yellow solution and was then cooled to −196 °C. 2-Butyne (0.0241 mmol, 1.25 equiv) was added by vacuum transfer. The tube was warmed to −78 °C, shaken, and placed in an NMR probe that had been precooled to −91 °C. NMR spectra showed that **3e** (0.015 M), **2** (0.013 M), free 2-butyne (0.028 M), and Ph_3C^+ (0.084 M) were present. The $B(C_6F_5)_4^-$ concentration was 0.11 M (sum of [**3e**] + [**2**] + [Ph_3C^+]). The equilibrium constant, $K_{eq} = [\mathbf{3e}][\mathbf{2}]^{-1}[MeC{\equiv}CMe]^{-1} = 41(9)\ M^{-1}$, agrees with the value found without added [Ph$_3$C][B(C$_6$F$_5$)$_4$] (52(3) M^{-1}). ^{1}H, ^{19}F, and ^{13}C NMR spectra of a CD_2Cl_2 solution containing [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.042 M) and 2-butyne (0.037 M) showed that there is no detectable interaction between these species at −86 °C.

Competitive Coordination of Propargyltrimethylsilane and Propyne to 2. A solution of **2** (0.0206 mmol) in CD_2Cl_2 (0.63 mL) was generated as described above. The tube was cooled to −196 °C, and propargyltrimethylsilane (0.026 mmol) was added by vacuum transfer. The tube was warmed to −78 °C and shaken, yielding a yellow solution. The tube was cooled to −196 °C, and propyne (0.085 mmol) was added by vacuum transfer. The tube was warmed to −78 °C and shaken, yielding a yellow solution. The tube was placed in an NMR probe that had been precooled to −89 °C. NMR spectra showed that a mixture of [Cp′$_2$Zr(O^{t}Bu)(HC≡CCH$_2$SiMe$_3$)][B(C$_6$F$_5$)$_4$] (**3d**, 0.032 M), [Cp′$_2$Zr(O^{t}Bu)(HC≡CMe)][B(C$_6$F$_5$)$_4$] (**3a**; 0.0017 M), free propargyltrimethylsilane (0.0089 M), and free propyne (0.13 M) was present. **2** was not present. This equilibrium was studied in three experiments, in which the initial concentrations were $[\mathbf{2}]_{initial}$ = 0.033(1) M, $[HC{\equiv}CMe]_{initial}$ = 0.14−0.26 M, and $[HC{\equiv}CCH_2SiMe_3]_{initial}$ = 0.040−0.089 M, and the order of alkyne addition was reversed in one experiment.

Reaction of 2 with *tert*-Butylacetylene. An NMR tube was charged with **2**, and CD_2Cl_2 (ca. 0.60 mL) was added by vacuum transfer at −78 °C. The tube was shaken at this temperature, giving a yellow solution. The tube was cooled to −196 °C, and excess *tert*-butylacetylene was added by vacuum transfer. The tube was warmed to −78 °C, shaken, and placed in an NMR probe cooled to −89 °C. NMR spectra showed that mixtures of **2** and free *tert*-butylacetylene were present. No resonances or line broadening effects indicative of ligand coordination to **2** were observed.

Determination of Thermodynamic Parameters and Exchange Rates. (A) General Variable-Temperature NMR Procedure. NMR samples were prepared as described above. The NMR tube was stored at −78 °C and placed in a precooled NMR probe. The probe was maintained at a given temperature for 20−30 min to allow the sample to reach thermal equilibrium, and then NMR experiments were conducted. The temperature was raised 5 or 10 °C and the procedure repeated until the desired temperature range had been studied.

(B) Equilibrium Constant Measurements. Equilibrium constants for eq 1, $K_{eq} = [\mathbf{3}][\mathbf{2}]^{-1}[alkyne]^{-1}$, were determined by multiple (typically 2−4) ^{1}H NMR experiments in which $[\mathbf{2}]_{initial}$ and $[alkyne]_{initial}$ were varied. For **3a**−**c**,**e**−**g**, K_{eq} values were determined by direct study of the equilibria in eq 1.

For the equilibrium involving **3a**, the relative amounts of **3a**, **2**, and free propyne were determined from the integrals of the H_{term} resonance of **3a**, the O^{t}Bu resonance of **2** after the contribution from **3a** was subtracted, and both free propyne resonances. The number of moles of **3a** and **2** was determined by finding their respective mole fractions and multiplying by the original amount of **2** used. The number of moles of free propyne was determined from the ratio of the integrals of the free and coordinated propyne resonances. Concentrations were determined by dividing the number of moles by the solution volume. K_{eq} values for **3a** were measured between −89 and −8 °C.

The methodology for determining the K_{eq} values for **3b**−**c**,**e**−**g** was similar. Calculations of molar amounts and K_{eq} values for **3b**−**g** were determined as described for **3a**. K_{eq} values for **3b**−**d**,**f**,**g** were measured at −89 °C. K_{eq} values for **3e** were measured between −89 and −3 °C. The choices for integrals for the relative amounts involving **3b**,**c**,**e**−**g** are given below.

For the equilibrium involving **3b**, relative amounts of **3b**, **2**, and free phenylacetylene were determined from the integrations of the H_{term} signal of **3b**, the Cp′*Me* and O^{t}Bu resonance after the contribution from **3b** was subtracted for **2**, and the H_{term} resonance for free phenylacetylene.

For the equilibrium involving **3c**, relative amounts of **3c**, **2**, and free trimethylsilylacetylene were determined from the integrations of the $SiMe_3$ resonance of **3c**, the O^{t}Bu resonance after the contribution from **3c** was subtracted for **2**, and the H_{term} resonance of free trimethylsilylacetylene.

For the equilibrium involving **3e**, relative amounts of **3e**, **2**, and free 2-butyne were determined from the integrations for coordinated 2-butyne, the O^{t}Bu resonance after the contribution from **3e** was subtracted for **2**, and the free 2-butyne resonance. K_{eq} values were found between −89 and −3 °C.

For the equilibrium involving **3f**, relative amounts of **3f**, **2**, and free 2-pentyne were determined from the most upfield Cp′ CH resonance of **3f**, the O^{t}Bu resonance after the contribution from **3f** was subtracted for **2**, and both Me resonances of free 2-pentyne.

For the equilibrium involving **3g** relative amounts of **3g**, **2**, and free 2-hexyne were determined from the two most upfield Cp′ CH resonances of **3g**, the Cp′*Me* resonance after the contribution from **3g** was subtracted for **2**, and the Me resonance for free 3-hexyne.

The K_{eq} value for formation of propargyltrimethylsilane adduct **3d** in eq 1, $K_{eq,\mathbf{3d}} = [\mathbf{3d}][\mathbf{2}]^{-1}[HC{\equiv}CCH_2SiMe_3]^{-1}$, was determined by competition experiments with propyne in CD_2Cl_2 solution at −89 °C. The equilibrium constant for the reaction

$$\mathbf{3a} + HC{\equiv}CCH_2SiMe_3 \leftrightarrows \mathbf{3d} + HC{\equiv}CMe$$

was defined to be $K_1 = [\mathbf{3d}][propyne][\mathbf{3a}]^{-1}[HC{\equiv}CCH_2SiMe_3]^{-1}$ and was determined by ^{1}H NMR studies of this equilibrium. The relative concentrations of **3d**, **3a**, free propargyltrimethylsilane, and free propyne were found from the integrals of the H_{term} resonance of **3d**, the H_{term} resonance of **3a**, the CH_2 and $SiMe_3$ resonances of free propargyltrimethylsilane, and the Me resonance of free propyne. The equilibrium constant for propyne coordination to **2** to form **3a** is $K_{eq,\mathbf{3a}} = [\mathbf{3a}][\mathbf{2}]^{-1}[HC{\equiv}CMe]^{-1}$ and was determined as described above. $K_{eq,\mathbf{3d}}$ is given by $K_{eq,\mathbf{3d}} = K_1K_{eq,\mathbf{3a}}$.

Thermodynamic parameters ($\Delta H°$ and $\Delta S°$) were determined from van't Hoff plots of ln(K_{eq}) versus $1/T$ for each variable-temperature NMR run. The reported values are the weighted average of results from at least three runs in which the initial concentrations of **2** and alkyne were varied.[34]

(33) While the resonance is clear in the ^{13}C{^{1}H} NMR spectrum, the coupling pattern in the ^{13}C{gated-^{1}H} spectrum is obscured by the Cp′*Me* resonance of **3g**.

(C) Exchange Rate Measurements. Rate constants for alkyne decomplexation (k_{-1}) for **3a** and **3e** were determined by variable-temperature ^{1}H NMR spectroscopy. For **3a**, the rate of propyne decomplexation was determined from the line shape of the ≡C*H* resonance of coordinated propyne by fitting simulated spectra to experimental spectra using gNMR to perform an iterative full line shape analysis.[35] The line width at half-height of the benzene resonance (ω_0) was used as the line width in the absence of exchange. The $^4J_{HH}$ value for propyne was set at 1.8 Hz and assumed to be temperature-independent. The rate values were converted to first-order rate constants k_{-1} by the formula rate = k_{-1}[**3a**]. Measurements were made over a temperature range of −69 to +22 °C.

For **3e**, rate constants for 2-butyne decomplexation were determined from the line widths of the coordinated 2-butyne resonance. The line width at half-height of the benzene resonance was used as the line width in the absence of exchange (ω_0) for coordinated 2-butyne at each temperature. First-order rate constants for 2-butyne decomplexation (k_{-1}) were determined by the formula $k_{-1} = \pi(\omega - \omega_0)$, where ω is the line width at half-height of the coordinated 2-butyne resonance. All measurements were made in the slow exchange region between −48 and −8 °C.

For **3a**,**e**, k_{-1} values were determined in at least three experiments with different initial concentrations of **2** and alkyne. The k_{-1} values were found to be independent of the concentrations of **2**, free alkyne, and **3a** or **3e**, consistent with the rate law rate = k_{-1}[**3**]. Activation parameters for decomplexation were determined from Eyring plots of ln(k_{-1}/T) versus 1/*T*. The reported values are the weighted averages of results from at least three runs.[34]

(34) The weighted average $\bar{x}$ is defined as $(\sum w_i x_i)/(\sum w_i)$ and the weighted standard deviation (σ) is defined by $\sigma^2 = \{\sum w_i(x_i - \bar{x})^2\}/\{\sum w_i\}$, where the weighing factors are $w_i = 1/\sigma_i^2$.

(35) *gNMR*, v. 4.1.2; Adept Scientific: Letchworth, UK, 2000.

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

Supporting Information Available: NMR data for free alkynes (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

OM050947F