Supporting information for:

Mechanism of Alkyne Insertion of a Cationic Zirconocene Aryl Complex

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I. Experimental Details

[Cp₂Zr(2-Me-4-F-C₆H₃)][B(C₆F₅)₄] (1). A chlorobenzene solution (15 mL) of Cp₂Zr(2-Me-4-F-C₆H₃)₂ (150 mg, 0.341 mmol) and Cp₂ZrMe₂ (85.8 mg, 0.341 mmol) was added dropwise to a chlorobenzene solution (5 mL) of [Ph₃C][B(C₆F₅)₄] (629 mg, 0.682 mmol) in the dark. The mixture was stirred for 1 h at 23 °C, the chlorobenzene was removed under vacuum, and the resulting orange oil was washed with benzene (3 x 10 mL) to remove the triphenylethane side product. The orange oil was dried under vacuum yielding [Cp₂Zr(2-Me-4-F-C₆H₃)][B(C₆F₅)₄]·(C₆H₆)_{1.8} as an orange solid (0.54 g, 34 %). In CD₂Cl₂ (1) forms the solvent adduct **A**. ¹H NMR (CD₂Cl₂, -89 °C): δ 6.97 (m, 2H, H3 & H4), 6.31 (s, 10H, Cp), 5.96 (dd, ³J_{HH} = 7.8, ⁴J_{HF} = 4.0, 1H, H6), 2.32 (s, 3H, Me). ¹³C{gated-¹H} NMR (CD₂Cl₂, -89 °C): δ 186.3 (s, C1), 162.5 (d, ¹J_{CF} = 247, C4), 147.8 (d, ³J_{CF} = 6, C2), 118.1 (dd, ¹J_{CH} = 156, ²J_{CF} = 20, C3), 113.0 (d, ¹J_{CH} = 176, Cp), 112.1 (dd, ¹J_{CH} = 162, ²J_{CF} = 21, C5), 97.7 (dd, ¹J_{CH} = 129, ³J_{CF} = 10, C6), 23.0 (q, ¹J_{CH} = 127, Me). ¹⁹F{¹H} (CD₂Cl₂, -89 °C): δ -114.6 (s).

Generation of $[Cp_2Zr(2-Me-4-F-C_6H_3)(2-butyne)][B(C_6F_5)_4]$. (C) An NMR tube was charged with $Cp_2Zr(2-Me-4-F-C_6H_3)][B(C_6F_5)_4]\cdot(C_6H_6)_2$ (15.9 mg, 0.0136 mmol) and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at -78 °C. The tube was vigorously agitated, cooled to -196 °C, and 2-butyne (0.258 mmol) was added by vacuum transfer. The tube was warmed to -94 °C, vigorously agitated and placed in a pre-cooled NMR probe at -85 °C. NMR analysis after 5 min at -85 °C showed formation of $Cp_2Zr(2-Me-4-F-C_6H_3)(2-butyne)^+$ (26.4 %) and $Cp_2Zr\{CMe=CMe(2-Me-4-F-C_6H_3)\}^+$ (31.2 %) and $Cp_2Zr(2-Me-4-F-C_6H_3)^+$ (42.3 %). This distributions was determined from intensities of the corresponding *ortho*-Me resonances. ¹H NMR data for $[Cp_2Zr(2-Me-4-F-C_6H_3)(2-butyne)]^+$ (CD₂Cl₂, -90 °C): δ 6.95 (m, 2 H, H3 and H5), 6.21 (s, 10 H, Cp), 5.98 (m, 1 H, H6), 2.41 (s, 3 H, *o*-Me), 2.10 (s, 6 H, \equiv CMe). ¹³C{¹H} NMR (CD₂Cl₂, -90 °C): Key resonances δ 112.8 (Cp), 78.6 (\equiv C-Me), 20.9 (*o*-Me), 10.0 (\equiv CMe).

Generation of $[Cp_2Zr{CMe=CMe(2-Me-4-F-C_6H_3)}][B(C_6F_5)_4]$ (D). An NMR tube was charged with $Cp_2Zr(2-Me-4-F-C_6H_3)][B(C_6F_5)_4] \cdot (C_6H_6)_2$ (21.0 mg, 0.0180 mmol) and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at -78 °C. The tube was vigorously agitated, cooled to -196 °C, and 2-butyne (0.0913 mmol) was added by vacuum transfer. The tube was warmed to -78 °C, vigorously agitated and placed in a pre-

cooled NMR probe at -70 °C. NMR analysis after 15 min at -70 °C that showed complete conversion to $[Cp_2Zr(C(Me)=C(Me)(2-Me-4-F-C_6H_3)]^+$ had occurred. ¹H NMR (CD₂Cl₂, -70 °C): δ 7.80 (m, 1 H, Ar), 7.51 (m, 1 H, Ar), 6.65 (s, 5 H, Cp), 6.49 (m, 1 H, Ar), 5.90 (s, 5 H, Cp), 2.56 (s, 3 H, *o*-Me), 1.84 (s, 3 H, =CMe), 1.73 (s, 3 H, =CMe). ¹³C{¹H} NMR (CD₂Cl₂, -70 °C): δ 194 (Zr*C*), 165.0 (d, ¹J_{CF} = 259, C4), 137.6, 133.3 115.8 (Cp), 115.4 (Cp), 114.4, 113.8, 112.5 (²J_{CF} = 20, C3 or C5), 111.7 (d, ²J_{CF} = 20, C3 or C5), 21.8, 21.1, 18.8. Addition of several drops of MeOD to a solution of **D** produced MeDC=C(2-Me-4-F-C₆H₃)Me in 83% GC yield; GC-MS: Calcd *m/z* 165, found 165.

II. Kinetic Scheme

The following is a description of the standard method of treating reaction a preequilibrium kinetic system.ⁱ The reaction



consists of a fast equilibrium between **A** and **B** to form **C**, which reacts irreversibly to form **D**. **B** is present in >10-fold excess va. **A**. The rate law is

(1)
$$rate = \frac{d[D]}{dt} = k_{ins}[C]$$

If we define [R] as the concentration of "remaining reactants",

(2)
$$[R] = [A] + [C]$$

and the total concentration of Zr species T as

(3)
$$T = [A] + [C] + [D]$$

then

$$[R] = T - [D]$$

The equilibrium constant is defined as

(5)
$$K_{eq} = \frac{[C]}{[A] \cdot [B]}$$

(6)
$$\frac{1}{K_{eq}} = \frac{[A] \cdot [B]}{[C]}$$

(7)
$$\frac{1}{K_{eq}[B]} = \frac{[A]}{[C]}$$

Adding 1 to each side gives

(8)
$$\frac{1}{K_{eq}[B]} + 1 = \frac{[A]}{[C]} + \frac{[C]}{[C]} = \frac{[A] + [C]}{[C]} = \frac{[R]}{[C]}$$

It follows that

(9)
$$[C] = \frac{[R]}{\left(\frac{1}{K_{eq} \cdot [B]} + 1\right)} = \frac{K_{eq}[B] \cdot [R]}{K_{eq}[B] + 1} = \frac{K_{eq}[B] \cdot (T - [D])}{K_{eq}[B] + 1}$$

therefore

(10)
$$rate = \frac{d[D]}{dt} = k_{ins}[C] = \frac{k_{ins}K_{eq}[B] \cdot (T - [D])}{K_{eq}[B] + 1} = k_{obs}(T - [D])$$

where

(11)
$$K_{obs} = \frac{K_{eq}[B] \cdot k_{ins}}{K_{eq}[B] + 1} = \frac{[C] \cdot k_{ins}}{[A] + [C]}.$$

Or, since

(12)
$$[D] = T - [R]$$

(13)
$$\frac{d[D]}{dt} = \frac{d(T - [R])}{dt} = k_{obs}[R]$$

(14)
$$-\frac{d[R]}{dt} = k_{obs}[R]$$

which corresponds to the first order decay of the total unreacted zirconium containing species [A] + [C] or

(15)
$$\ln\left(\frac{R}{R_0}\right) = -k_{obs} \cdot t$$

III. Kinetic analysis of the reaction of $Cp_2Zr(2-Me-4-F-C_6H_3)][B(C_6F_5)_4]$ with 2-butyne.

Figure S1 shows a representative ¹H NMR spectrum from the beginning of a kinetic run (i.e. immediately following the thermal equilibration period).



Figure S1. ¹H NMR spectrum of the reaction of **A** with 2-butyne at -85 °C. *Peak 1:* benzene, *Peak 2:* Cp resonance of **D**, *Peak 3*: Cp resonance of **C**, *Peak 4*: Cp resonance of **A**, *Peak 5*: Cp resonance of **D**, *Peak 6*: o-tolyl resonance of **D**, *Peak 7*: o-tolyl resonance of **C**, *Peak 8*: o-tolyl resonance of **A**, *Peak 9*: o-tolyl resonance of 4-F-o-toluene (product of C-H activation of 2-butyne), *Peak 10*: Cp₂(ZrCMeCMeCH₂CC*Me*)⁺ resonance of C-H activation product, *Peak 11*: Me groups from coordinated 2-butyne in **C**, *Peak 12*: 2-butyne.

Figure S2 shows a typical series of NMR spectra from a kinetic run (see run 1 below).



Figure S2. ¹H NMR spectra for a typical kinetic run (see run 1 below). The time is the time following completion of the thermal equilibration period. Peaks from left to right: *Green*: Me peak of **D**, *Blue*: Me peak of **C**, *Red*: Me peak of **A**. *Blue*: 2-butyne from **C**, *Green*: overlap of alkenyl Me from **D** and with free 2-butyne ¹³C satellite.

In order to determine the concentration of Zr species, the total amount of benzene must be known since Cp₂Zr(2-Me-4-F-C₆H₃)][B(C₆F₅)₄] is added a benzene solvate. The concentration of **A**-benzene is known from the mass of **A**-benzene added and the volume of the solvent. The concentration of benzene can be determined at each data point or in a separate NMR experiment. There is little difference between the two methods. The average of the concentration of benzene at each point was used in the analysis. Once the concentration of benzene integral was used as an internal standard. The integral regions were set to be identical between all spectra in a kinetic run using XWINNMR. The ratio of the integral of an o-Me peak of a given species to the total integrals of all the o-Me peaks equals the mole fraction of that species; for example the mole fraction of **A** equals the ratio of the o-Me integrals **A**/(**A** + **C** + **D**). The mole fraction was multiplied by [T] to determine the concentration of each species and the concentration of "remaining reactants" [R] (eq 4 and 12-14). The *k*_{obs} was determined from a fit of ln(R/R₀) vs time

(eq 15, see representative plots in Figures S3 and S4). The time = 0 is the first point after the thermal equilibration period (10 and 15 min after immersion in the -85 °C probe respectively for runs 1 and 2 shown below). $K_{eq} = [C] [B]^{-1} [A]^{-1}$ was determined using [A] and [C] determined by the method described above, and [B] determined from the ratio of the integral of **B**. k_{ins} was determined using eq 11. Uncertainties were estimated using standard differential propagation of error, assuming an uncertainty of ± 5% in the NMR integrals and ± 5 K in the temperature.

Table S1 lists the concentration vs. time data for run 1. Figure S3 is a plot of $ln(R/R_0)$ vs. time for run 1.

Time $(\min)^a$	[A] (M)	[C] (M)	[D] (M)	% conversion
0	0.00691	0.00407	0.00978	47
10	0.00634	0.00333	0.0110	53
20	0.00560	0.00285	0.0123	59
30	0.00489	0.00256	0.0133	64
40	0.00435	0.00230	0.0141	67
70	0.00268	0.00109	0.0169	81
90	0.00229	0.00121	0.0172	83
110	0.00176	0.000930	0.0180	87

Table S1. Concentration vs. time data for run 1.

^{*a*} Time after completion of thermal equilibration period.



Figure S3. Plot of $\ln(R/R_0)$ vs time for run 1.

Table S2 lists the concentration vs. time data for kinetic run 2. Figure S4 is a plot of $ln(R/R_0)$ vs time

time $(\min)^a$	[A] M	[C] M	[D] M	% conversion
0	0.00386	0.00204	0.00305	34
5	0.00377	0.00192	0.00326	36
10	0.00370	0.00172	0.00353	39
15	0.00336	0.00176	0.00383	42
25	0.00307	0.00151	0.00438	48
40	0.00261	0.00115	0.00519	57
61	0.00195	0.000910	0.00610	68
80	0.00154	0.000687	0.00673	75

Table S2. Concentration vs. time data for run 2.

^{*a*} Time after completion of thermal equilibration period.



Figure S4. Plot of $ln(R/R_0)$ vs time for run 2.

IV. Computational Details

The computational methods used have been previously shown to accurately predict the structure of cationic zirconocene chlorocarbon adducts and cationic zirconocene species containing agostic interactions.ⁱⁱ Stationary point DFT structures were optimized from the PM3ⁱⁱⁱ level of theory with the BP86 functional^{iv} in Gaussian 03.^v All main group atoms were modeled using the 6-31G* basis set.^{vi} Zirconium was modeled using the LANL2DZ basis set including an effective core potential.^{vii} Transition state structures were located using the QST3 method.^{viii} Frequency calculations were used to determine that there were no negative frequencies for the stationary point structures and one negative frequency for the TS structure corresponding to the reaction coordinate. Corrections to the Gibbs free energy were calculated at 188 K, 1 atm with a frequency scaling factor or 1.

Structures of the van der Walls contact pairs $\mathbf{C} \cdot \mathbf{CD}_2 \mathbf{Cl}_2$ and $\mathbf{A} \cdot (2$ -butyne) were calculated using the methods described above. The difference between the energies of these species (with zero point energy correction at 188 K) is a reasonable estimate of ΔG_{eq} (-1.69 kcal/mol).

NBO analyses were performed using the NBO 5.0 program.^{ix} All figures were rendered using the MOLEKEL 4.3^x software package.

VI. Metrical parameters of the calculated structures of C, TS and D

Table S1. Bond distances (Å) and angles (deg) in calculated structures of $Cp_2Zr(2-tol-4-F-benzene)(2-butyne)^+$ (**C**), $Cp_2Zr\{CMe=CMe(2-Me-4-F-C_6H_3)\}^+$ (**D**) and the transition state (**TS**) linking **C** and **D**.

	С	TS	D
Zr-C(B1)	2.854	2.407	2.276
Zr—C(B2)	2.853	2.778	3.040
Zr—C(Ar1)	2.229	2.335	2.917
Zr—H(agostic)	2.481	3.132	2.652
Zr—C(Ar6)	2.700	3.159	2.559
C(B1) —C(B2)	1.235	1.263	1.372
C(B2)—C(Ar1)	4.030	2.562	1.495
Zr-Cp(1)	2.237	2.261	2.238
Zr—Cp(2)	2.252	2.269	2.240
C(B1) —Me(1)	1.469	1.501	1.512
C(B2) —Me(2)	1.470	1.466	1.523
Cp(1)—Zr—Cp(2)	129.5	125.8	130.0
Zr—C(B1)—C(B2)	77.5	93.1	110.4
Zr—C(B1)—Me(1)	116.1	124.4	127.7
C(B1)—C(B2)—Me(2)	167.0	161.0	125.2
Zr-C(Ar1)-C(Ar6)	93.2	111.6	61.3
C(B1) - C(B2) - C(Ar1)	108.0	108.1	115.5





Figure S5. Transition state (TS) connecting C and D.

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