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Catalytic Dimerization of Terminal Alkynes by a Hafnium Carboranyl Complex. A “Self-Correcting” Catalyst

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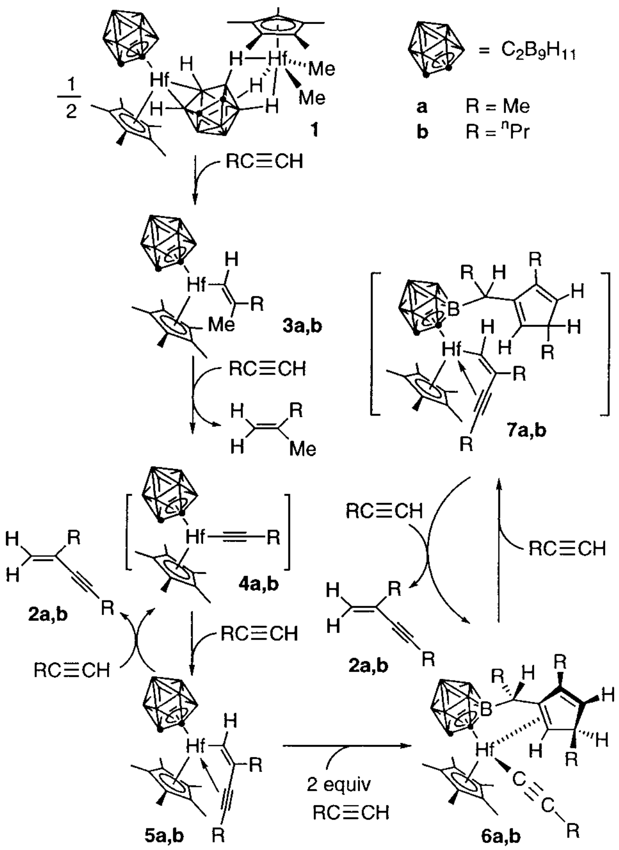
Summary: The dinuclear hafnium dicarbollide methyl complex (Cp)(η^5-$C_2B_9H_{11}$)Hf(μ-η^2:η^3-$C_2B_9H_{11}$)Hf(Cp*)Me_2 (**1**; Cp* = C_5Me_5) catalyzes the regioselective dimerization of terminal alkynes RC≡CH (R = Me, ^{n}Pr, ^{t}Bu) to 2,4-disubstituted 1-buten-3-ynes CH_2=C(R)C≡CR. The selectivity for dimer rather than trimer or higher oligomers results from a “self-correcting” mechanism in which intermediate **8**, which could potentially produce trimers or higher oligomers, undergoes an intramolecular cyclization reaction which ultimately yields the B-alkylated complex **6**, which is too crowded to produce trimer in subsequent cycles.*

One intriguing possibility for achieving high selectivity in catalysis is to design catalysts for which undesired reactions with substrates (*i.e.* chemical, regiochemical, or stereochemical “errors”) induce chemical changes that prevent such errors in subsequent reactions with additional substrate. Here we report the discovery of a novel metallocarborane catalyst which exhibits such “self-correcting” behavior in the catalytic dimerization of terminal alkynes to 1,3-enynes.

Many early-transition-metal/f-element metallocene complexes catalyze the oligomerization of terminal alkynes to 1,3-enynes, dienynes, and higher linear or cyclic oligomers.[1−6] The key steps in the formation of enynes (i.e. dimers) are generation of a MC≡CR alkynyl species, insertion of alkyne to yield MC(H)=C(R)C≡CR alkenyl intermediates, and σ-bond metathesis with additional alkyne to release the dimer and regenerate the MC≡CR species. Higher oligomers are formed by further alkyne insertion into the MC(H)=C(R)C≡CR species or other reactions. The selectivity of these reactions is highly sensitive to the steric and electronic properties of the metallocene complex and the monomer.[1b,4] For example, Cp*$_2$ZrMe$^+$ selectively dimerizes ^{t}BuC≡CH to the head-to-tail dimer but converts ^{n}PrC≡CH and MeC≡CH to mixtures of dimer and trimer.[2] The less bulky Cp_2ZrMe^+ reacts with these alkynes to form catalytically inactive dinuclear compounds.[2b] Catalytic alkyne oligomerization is thus a useful probe of insertion and σ-bond metathesis reactivity of early-metal compounds.

Scheme 1



The unsymmetrical dinuclear hafnium dicarbollide methyl complex (Cp*)(η^5-$C_2B_9H_{11}$)Hf(μ-η^2:η^3-$C_2B_9H_{11}$)-Hf(Cp*)Me_2 (**1**; Scheme 1) reacts with 2-butyne to yield the mononuclear alkenyl complex (Cp*)(η^5-$C_2B_9H_{11}$)-HfC(Me)=CMe_2 and with other substrates to yield products containing (Cp*)(η^5-$C_2B_9H_{11}$)HfX units.[7−9] Thus, **1** is a source of the 14-electron, d^0 fragment “(Cp*)(η^5-$C_2B_9H_{11}$)HfMe”. As part of an effort to compare the reactivity properties of (Cp*)(η^5-$C_2B_9H_{11}$)MR

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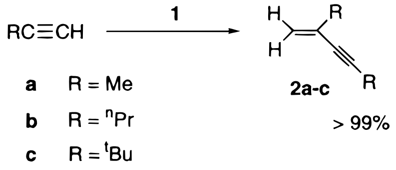
species with those of other d^0 bent metallocenes, we have investigated the reaction of **1** with terminal alkynes.

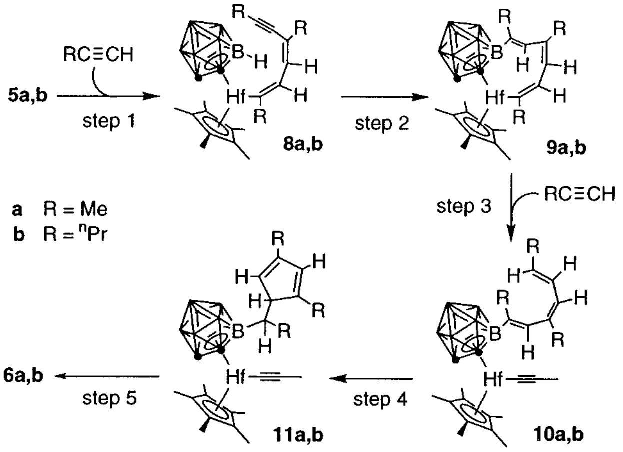
The reactions of **1** with excess (ca. 500 equiv) terminal alkynes RC≡CH (R = Me, ^{n}Pr, ^{t}Bu) in CD_2Cl_2 (23 °C) or $Cl_2CDCDCl_2$ (60 °C) were monitored by ^{1}H NMR spectroscopy. The NMR spectra showed that in each case the alkyne is selectively converted to the corresponding 2,4-disubstituted 1-buten-3-yne (**2a**−**c**; eq 1). This regioselective catalytic dimerization is faster for the bulkier alkynes. Selected data are as follows (t.o. = turnover): MeC≡CH, 19 t.o./h, 23 °C, at 6.9% conversion (65% conversion at 144 h); ^{n}PrC≡CH, 26 t.o./h, 23 °C, at 3.4% conversion; ^{n}PrC≡CH, 630 t.o./h, 60 °C, at 10% conversion (53% conversion at 2 h); ^{t}BuC≡CH, >6500 t.o./h, 60 °C, at 65% conversion (100% conversion at 5.8 h). The dimerization products were identified by GC−MS and comparison of their ^{1}H NMR spectra with literature data.[4]



(1)

Several observations provide insight into the dimerization mechanism (Scheme 1). (i) The reaction of **1** with 8 equiv of MeC≡CH yields an 88/12 mixture of the alkenyl complex (Cp*)(η^5-$C_2B_9H_{11}$)HfC(H)=C(Me)C≡CMe (**5a**) and the unusual B-alkylated alkynyl complex (Cp*)-{η^5-7-CH(Me)(3,5-dimethyl-2-cyclopentadienyl)-1,2-$C_2B_9H_{10}$}HfC≡CMe (**6a**) as the only detectable organometallic species, along with enyne **2a** and 1 equiv of CH_2=CMe_2.[10] **5a** was identified straightforwardly by NMR;[11] the large $^1J_{C_\alpha-H}$ value (147 Hz) suggests that the pendant alkyne is coordinated.[2] The structure of **6a** was deduced by a combination of 1D- and 2D-NMR experiments,[12] which show that **6a** is formed as a single diastereomer[13] and that the C1−C2 double bond of the pendant cyclopentadienyl group is coordinated to hafnium, as illustrated in Scheme 1. (ii) Further reaction of this **5a**/**6a** mixture with 7 equiv of MeC≡CH yields a 34/66 mixture of **5a** and **6a** and additional **2a**, indicating that **6a** is derived from the reaction of **5a** and alkyne. (iii) The reaction of **1** with 20 equiv of MeC≡CH gives **6a** as the only organometallic species, along with **2a** and 1 equiv of CH_2=CMe_2. (iv) Isolated complex **6a** also catalyzes the dimerization of MeC≡CH to **2a**. These observations are consistent with the mechanism in Scheme 1.[14]

Scheme 2



In Scheme 1, **1** first reacts with alkyne to yield 2 equiv of the alkenyl complex (Cp*)(η^5-$C_2B_9H_{11}$)HfC(H)=CRMe (**3**). This species is not observed but is directly analogous to (Cp*)(η^5-$C_2B_9H_{11}$)HfC(Me)=CMe_2, which was characterized previously.[8a] Intermediate **3** undergoes rapid σ-bond metathesis with alkyne to yield the unobserved alkynyl species (Cp*)(η^5-$C_2B_9H_{11}$)HfC≡CR (**4**) and CH_2=CRMe. Rapid alkyne insertion of **4** yields **5**. Complex **5** can react with alkyne in two ways. Simple σ-bond metathesis of **5** and alkyne results in release of dimer **2**, regeneration of **4**, and establishment of one catalytic dimerization cycle. Alternatively, **5** can react with 2 equiv of alkyne by a more complex mechanism (*vide infra*) to yield **6**. Complex **6** catalyzes the dimerization of alkyne by a second insertion/σ-bond metathesis cycle involving the unobserved alkenyl intermediate (Cp*){η^5-7-CH(R)(3,5-R_2-2-cyclopentadienyl)-1,2-$C_2B_9H_{10}$}HfC(H)=C(R)C≡CR (**7**).

A likely mechanism for the formation of **6** from **5** is shown in Scheme 2. Alkyne insertion of **5** yields alkenyl complex **8** (step 1), which undergoes rapid addition of a dicarbollide B−H bond to the pendant alkyne group to yield bridged complex **9** (step 2).[15] Complex **9** undergoes σ-bond metathesis with further alkyne to yield **10** (step 3), which undergoes subsequent insertion of the C5−C6 double bond into the B−C bond to yield **11** (step 4). Finally, **11** undergoes 1,5-H shifts to give **6** (step 5).

Step 2 in Scheme 2 is the key to the self-correcting property of this catalyst system. If **8** were to undergo σ-bond metathesis with alkyne, the trimer HRC=C-(H)C(H)=C(R)C≡CR would be formed and selectivity for the dimer would be low. Alternatively, if **8** were to undergo alkyne insertion, a precursor to tetramer would be formed. However, neither of these reactions occur because the sequence of reactions initiated by step 2 ultimately leads to trapping of the alkyne trimer

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[10] The numbering for the η^5-C_2B_3 ring of the dicarbollide ligand is as follows: C(1)−C(2)−B(7)−B(8)−B(4). See: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 219.

[11] **5a**: unstable off-white waxy solid. ^{1}H NMR (CD_2Cl_2): δ 8.41 (q, J = 1.4 Hz, 1H, HfCH), 3.27 (s, 1H, dicarbollide CH), 2.80 (s, 1H, dicarbollide CH), 2.20 (s, 15H, Cp*), 2.02 (s, 3H, ≡CMe), 1.96 (d, J = 1.4 Hz, 3H, =C(Me)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 214.5 (J_{CH} = 147 Hz, HfCH), 125.2 (Cp*), 112.8 (C), 97.4 (C), 83.8 (C), 56.2 ($C_2B_9H_{11}$), 55.1 ($C_2B_9H_{11}$), 23.2 (CH_3), 12.6 (Cp*), 8.2 (CH_3).

[12] **6a**: unstable brown waxy solid. ^{1}H NMR (CD_2Cl_2): δ 6.73 (q, J = 1.2 Hz, 1H), 4.12 (s, 1H), 3.34 (q, J = 7.4 Hz, 1H), 3.24 (s, 1H), 2.88 (q, J = 6.9 Hz), 2.68 (s, 1H), 2.28 (s, 15H), 1.95 (d, J = 1.2 Hz, 3H), 1.72 (s, 3H), 1.22 (d, J = 7.4 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 196.2 (C), 158.6 (CH), 152.4 (C), 140.8 (C), 124.8 (C), 120.4 (C), 109.8 (CH), 55.1 (CH), 52.3 (CH), 50.2 (CH), 23.9 (CH), 19.4 (CH_3), 18.2 (CH_3), 13.5 (CH_3), 13.2 (CH_3), 5.8 (CH_3). A detailed discussion of the structural elucidation of **6a** by 2-D NMR is presented in the Supporting Information.

[13] The stereochemistry of **6a** is defined by the descriptor (7,*R*,*R*,*S*)/(4,*S*,*S*,*R*), where the entries denote the B atom which is alkylated, the configuration at B*C*H(Me)(cyclopentadienyl), the configuration of the sp^3 carbon in the pendant cyclopentadienyl substituent, and the configuration at Hf, respectively. The (7,*R*,*R*,*S*) enantiomer is shown in Scheme 1. Priority orders used in these stereochemical assignments are discussed in the supporting information.

[14] NMR data for **5b** and **6b** are similar to data for **5a** and **6a**. The mechanism of ^{t}BuC≡CH dimerization was not studied in detail, due to the high reaction rate, but is assumed to be analogous to that for MeC≡CH and ^{n}PrC≡CH dimerization.

[15] For similar B−H activation reactions, see: Anderson, S.; Jeffery, J. C.; Liao, Y.-H.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1997**, *16*, 958.

fragment in the form of the B—CHR(3,5-R_2-cyclopentadienyl) substituent in **6** (and **7**). The bulky B-substituent of **7** favors coordination of RC≡CH through the C—H bond, which leads to σ-bond metathesis and dimer formation, over π-coordination through the C≡C bond, which would lead to insertion and higher oligomers. Thus, the **6**/**7** cycle also produces only dimer.

Several observations provide qualitative information about the switch from the **4**/**5** cycle to the **6**/**7** cycle and the relative rates of the two cycles. (i) The reaction of **5a** with 20 equiv of ^{n}PrC≡CH gives 76% of **6b** and 24% of (Cp*){η^5-7-CH(^{n}Pr)(3,5-dimethyl-2-cyclopentadienyl)-1,2-$C_2B_9H_{10}$}HfC≡C^{n}Pr (**6d**). This result establishes that $k_{\sigma\text{-bond metathesis}}/k_{\text{insertion}}$ for **5a** and ^{n}PrC≡CH is 3/1 and suggests that in the catalytic reactions, after ca. 11 **4**/**5** cycles, 95% of the catalyst will have undergone B-alkylation and switched over to the **6**/**7** cycle. (ii) The turnover frequency decreases at increased reaction times. For example, the turnover frequency for dimerization of MeC≡CH (150 equiv) by **1** (23 °C) decreases from 19 to/h at 6.9% conversion to 6 t.o./h at 10% conversion. Similarly, the turnover frequency for dimerization of ^{n}PrC≡CH (500 equiv) decreases from 26 t.o./h at 3.4% conversion to 8 t.o./h at 4.2% conversion at 23 °C and from 630 t.o./h at 10% conversion to 350 t.o./h at 23% conversion at 60 °C. These results indicate that the **6**/**7** cycle is slower than the **4**/**5** cycle, presumably as a result of inhibition of alkyne coordination and insertion of **6** due to the carboranyl substituent.

This work shows that dinuclear complex **1** catalyzes the regioselective head-to-tail dimerization of terminal alkynes via insertion and σ-bond metathesis reactions of mononuclear species. The selectivity for dimer results from a unique self-correcting mechanism in which the reaction that could potentially produce trimer or higher oligomers (**5a,b** → **8a,b**) triggers a series of steps (**8a,b** → **6a,b**) which modify the catalyst so that it is too crowded to produce trimer in subsequent cycles. We are exploring the possibility of developing other self-correcting catalyst systems through exploitation of dicarbollide B—H bond reactivity.

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Supporting Information Available: Text and tables giving experimental procedures and characterization data for new compounds and details of the structural determination for **6a** (13 pages). Ordering information is given on any current masthead page.

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