Metallaborane Reaction Chemistry. *nido*-Dirhodapentaborane Isomer Structures and Stabilities and Utilization of Dirhodaboranes as Catalysts for Alkyne Cyclotrimerization

Hong Yan, Alicia M. Beatty, and Thomas P. Fehlner*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670

Received July 16, 2002

The reaction of $(Cp^*Rh)_2B_2H_6$ (**1**) with BH_3THF under mild conditions leads to the intermediate $(Cp^*Rh)_2B_3H_7$, which is shown to exist in the two isomeric forms 1,2-$(Cp^*Rh)_2B_3H_7$ (**2a**) 1,2-$(Cp^*Rh)_2(\mu\text{-}H)B_3H_6$ (**2b**) by a solid-state structure of **2a** and low-temperature NMR data of the mixture. **1** slowly decomposes at room temperature to yield a number of products including *pileo*-$(Cp^*Rh)_3B_4H_4$ (**4**), which has been characterized by a solid-state structure determination. **2** converts on heating to 2,3-$(Cp^*Rh)_2B_3H_7$ (**3**), of known structure. **1**−**3** catalyze the cyclotrimerization of both terminal and internal alkynes with differing activities. The rate of catalysis is inhibited by PPh_3 and pyridine and competition experiments show evidence for a multistep mechanism with concentration-dependent selectivity. The pathway proposed suggests the borane fragment acts in an ancillary role by providing a cluster environment for the dimetal fragment. Metal polyhedral edge opening on alkyne (or base) addition is proposed as the novel activation step thereby making rhodaboranes hybrid cluster catalysts.

Introduction

The broad outlines of metallaborane chemistry have been clearly understood for some time now.[1] In terms of structural chemistry, the cluster electron counting rules[2,3] and the isolobal principle[4] place these compounds securely between borane cages on one hand and transition metal clusters on the other. That the structures of the majority of metallaboranes isolated follow the counting rules is a tribute to the insight of Wade, Mingos, and others. The simple rules function well despite the fact that in a quantitative sense the frontier orbitals of main group fragments and transition metal fragments differ considerably.[5] That is, the electronic structure of a metallaborane differs markedly from that of its main group or transition metal analogues. This is readily evident from a comparison of spectroscopic properties. It follows that the reaction chemistry of metallaboranes will also differ substantially from those of boranes and metal clusters.

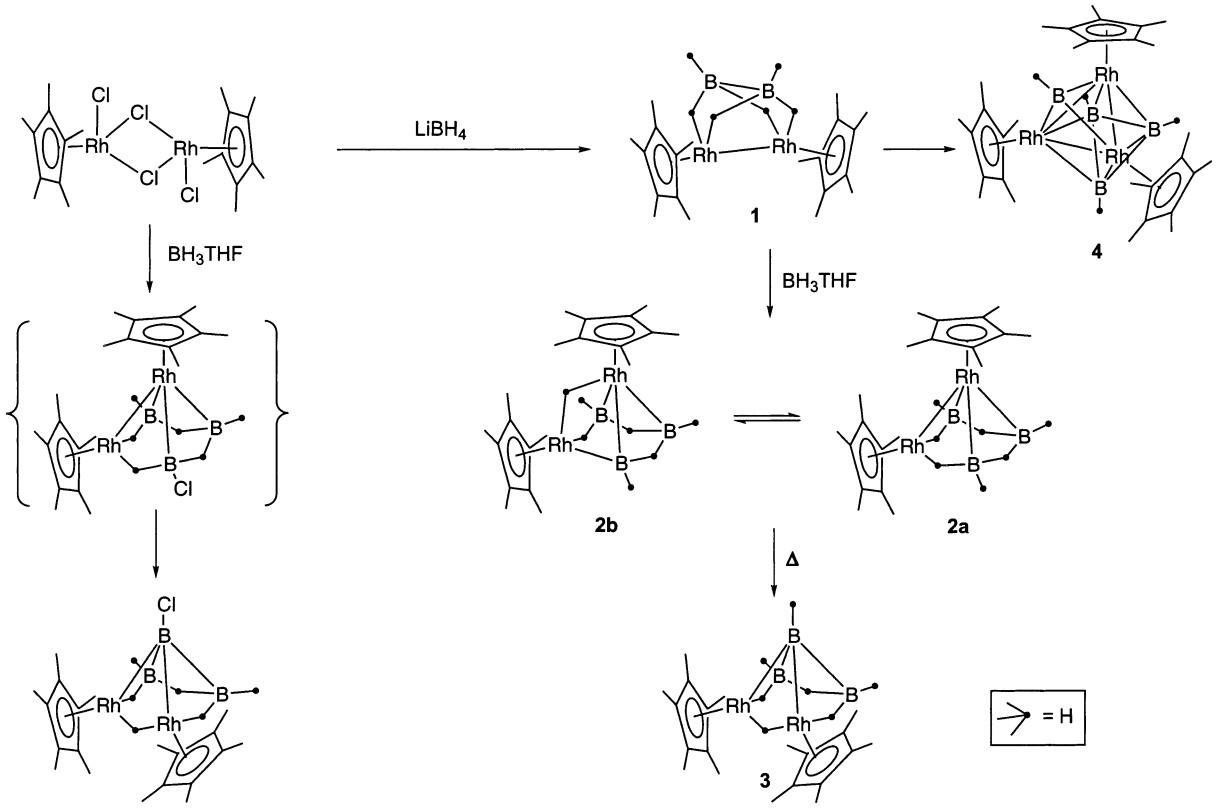
One reason an understanding of the relationship between geometry and composition does not guarantee an understanding of reactivity is that small differences in reaction barriers can change the reaction type observed. Hence, neutral compounds having the same framework geometry but with different ancillary ligands on the metal, different metals, or different numbers of endocluster hydrogens can exhibit qualitatively different reactivities relative to an identical substrate. Certainly the structural work constitutes an impressive accomplishment, but the chemistry of metallaboranes will only become a significant one when the reaction chemistry is equally well understood. Just as with organometallic chemistry, where, for example, an understanding of the unique structural features of olefin coordination preceded the explosive development of the reaction chemistry of coordinated olefins,[6] so too one anticipates similar developments in transition metal−main group element chemistry.

In a series of reports we have defined the systematic preparative and structural chemistry of a class of metallaboranes derived from monocyclopentadienyl metal chlorides.[7] The majority of compounds contain two metal centers and from 1 to 10 boron atoms. Compounds containing metals ranging from groups 5 to 9 have been prepared and for groups 6 and 9 compounds of all three metals have been accessed. Although this work continues, particularly with structurally unique compounds containing group 6 and 7 metals,[8] recent efforts have focused on the reaction chemistry of these compounds. The following is the full report of dirhodapentaborane isomer interconversion and stability as well as a detailed study of the reactivity of these rhodaboranes with a variety of terminal and internal alkynes leading to catalyzed cyclotrimerization.[9]

(1) Barton, L.; Srivastava, D. K. In *Comprehensive Organometallic Chemistry II*; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1.
(2) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
(3) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.
(4) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
(5) Mingos, D. M. P. In *Inorganometallic Chemistry*; Fehlner, T. P., Ed.; Plenum: New York, 1992; p 179.
(6) Mingos, D. M. P. *J. Organomet. Chem.* **2001**, *635*, 1.
(7) Fehlner, T. P. *Organometallics* **2000**, *19*, 2643.
(8) Ghosh, S.; Shang, M.; Li, Y.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1125.

10.1021/om0205694 CCC: $22.00
Publication on Web 10/09/2002

Scheme 1



Results and Discussion

***nido*-Dirhodatetraborane and *nido*-Dirhodapentaborane.** Our original publications on this system described the reaction of $LiBH_4$ and BH_3THF with $[Cp^*RhCl_2]_2$, $Cp^* = \eta^5\text{-}C_5Me_5$.[10,11] With the former, reduction to $[Cp^*RhCl]_2$ preceded formation of $(Cp^*Rh)_2B_2H_6$ (**1**), presumably via the bis-borohydride complex. This metastable compound reacts with BH_3THF to yield the *nido*-dirhodapentaborane 2,3-$(Cp^*Rh)_2B_3H_7$ as shown in Scheme 1. Alternatively, direct reaction of BH_3THF with $[Cp^*RhCl_2]_2$ leads to an intermediate that rearranges to the 1-Cl derivative of 2,3-$(Cp^*Rh)_2B_3H_7$ (**3**). Both derivatives were characterized by solid-state structure studies by single-crystal X-ray diffraction. On the basis of spectroscopic data, the intermediate was identified as the 3-Cl derivative of 1,2-$(Cp^*Rh)_2B_3H_7$ (**2**). As a preliminary to reactivity studies we have explored this system further in terms of reaction conditions and rhodaborane stabilities.

$(Cp^*Rh)_2B_2H_6$ (**1**) is considerably more stable than $(Cp^*Co)_2B_2H_6$,[12] which decomposes rapidly at room temperature to a variety of cobaltaborane clusters including $(Cp^*Co)_3B_4H_4$, a BH fragment capped, a 7 skeletal electron pair (sep), and an octahedral cluster characterized many years earlier in Grimes' laboratory.[13] At room temperature and above **1** slowly deomposes into a number of products. One isolated and structurally characterized is $(Cp^*Rh)_3B_4H_4$ (**4**). Its structure, Figure 1 and Scheme 1, is analogous to that of the cobalt derivative. We reasonably conclude from this that the thermolysis chemistry of **1** is similar to that of the cobalt derivative. The iridium analogue of **1** is not known:

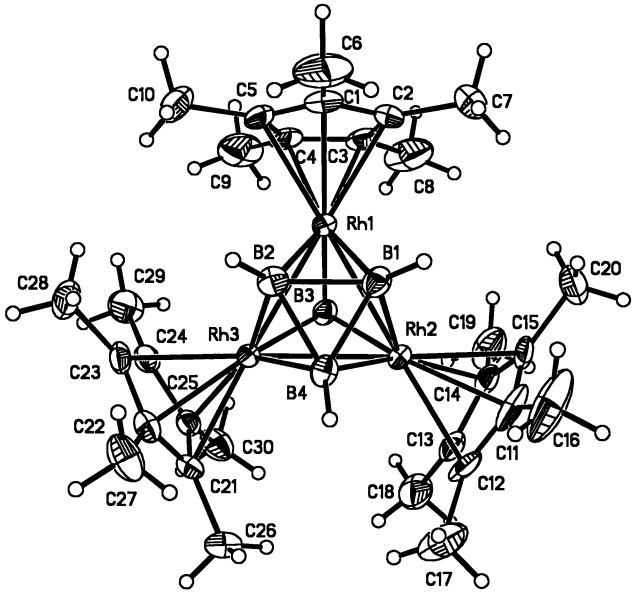


Figure 1. Molecular structure of $(Cp^*Rh)_3B_4H_4$ (**4**). Selected bond distances (Å): Rh(1)−B(3) 2.0622(12), Rh(1)−B(2) 2.119(4), Rh(1)−B(1) 2.128(4), Rh(1)−Rh(3) 2.6634(4), Rh(1)−Rh(2) 2.6741(5), Rh(2)−B(3) 2.0699(13), Rh(2)−B(4) 2.1144(13), Rh(2)−B(1) 2.128(4), Rh(2)−Rh(3) 2.6656(5), Rh(3)−B(3) 2.0768(13), Rh(3)−B(4) 2.1166(13), Rh(3)−B(2) 2.129(4), B(1)−B(4) 1.733(4), B(1)−B(2) 1.741(6), B(2)−B(4) 1.721(5).

(9) Yan, H.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4498.
(10) Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, *120*, 2686.
(11) Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 1275.
(12) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1994**, *13*, 4510.
(13) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 257.

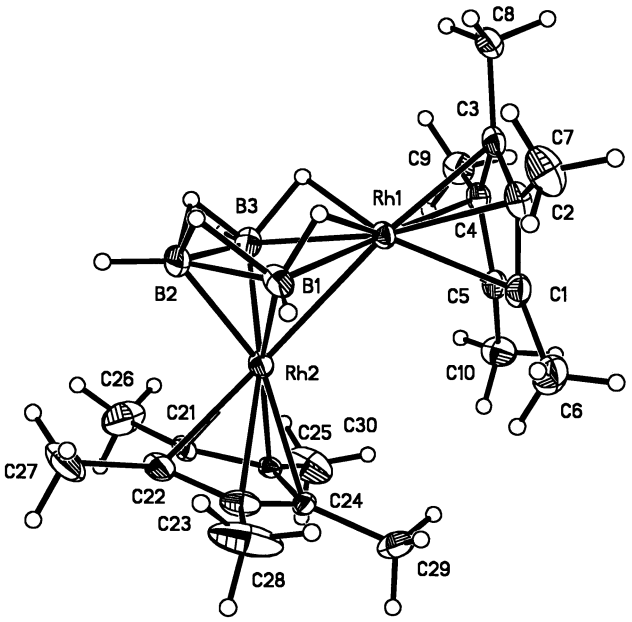


Figure 2. Molecular structure of 1,2-$(Cp^*Rh)_2B_3H_7$ (**2a**). Selected bond distances (Å): Rh(1)−Rh(2) 2.6892(3), Rh(1)−B(3) 2.292(4), Rh(1)−B(1) 2.308(3), Rh(2)−B(2) 2.061(4), Rh(2)−B(1) 2.062(3), Rh(2)−B(3) 2.075(4), B(1)−B(2) 1.841(5), B(2)−B(3) 1.838(5).

arachno-$(Cp^*Ir)_2B_2H_8$, a close relative, does not generate $(Cp^*Ir)_2B_2H_6$ on thermolysis.[14]

Reaction of **1** with the borane produced in situ during the reduction of $[Cp^*RhCl_2]_2$ by $2LiBH_4$ to $[Cp^*RhCl]_2$ allows the isolation of an intermediate which, on heating, converts into **3**. An ca. 1:1 mixture of the intermediate and **3** was successfully separated by column chromatography and the former was crystallized. The solid state structure was obtained. There are two independent molecules in the unit cell. One refines normally as 1,2-$(Cp^*Rh)_2B_3H_7$ (**2a**, Figure 2 and Scheme 1) with a structure analogous to that of 1,2-$\{(CO)_3Fe\}_2B_3H_7$. The second is disordered, but an acceptable solution is qualitatively the same. The structure in the solid state is the expected one and we were therefore surprised that the solution spectroscopic behavior of **2** was not consistent with that of the solid state structure. Fortunately, variable-temperature ^1H and ^{11}B NMR nicely resolved the problem. The high-field region of the proton NMR, shown in Figure 3, is most revealing. At −60 °C the equal intensity signals for the B−H−B and Rh−H−B protons of **2a** can be identified along with other signals corresponding to B−H−B, B−H−B, Rh−H−B, and Rh−H−Rh (triplet) protons in a 1:1:1:1 ratio. These data, along with the other low-temperature NMR data, allow the second species to be identified as a tautomer of **2a**, 1,2-$(Cp^*Rh)_2(\mu\text{-}H)B_3H_6$ (**2b**), shown in Scheme 1. If **2a** is viewed as the borane analogue, then **2b** can reasonably be called the metal cluster analogue. As the temperature is raised the Rh−H−Rh and Rh−H−B protons of **2b** begin to exchange and then, when the temperature reaches 85 °C, the interconversion of **2a** and **2b** becomes rapid on the NMR time scale. The relative abundances show that **2b** is slightly more stable than **2a** (60:40) at −60 °C.

(14) Lei, X.; Shang, M.; Fehlner, T. P. *Chem. Eur. J.* **2000**, *6*, 2653.

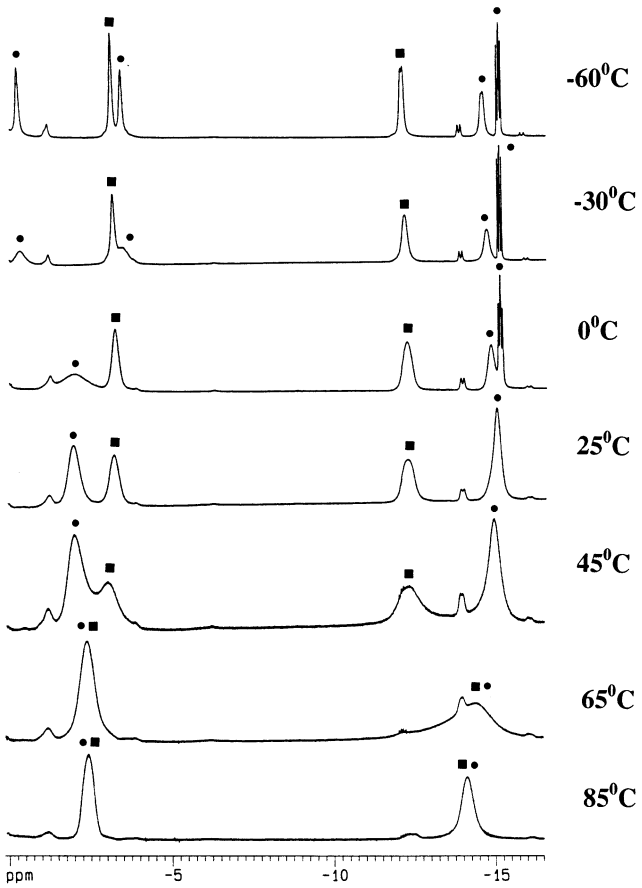


Figure 3. Variable-temperature ^1H NMR spectrum of **2** in the hydride region showing that **2** exists as a mixture of two isomeric forms, **2a** (solid squares) and **2b** (solid dots), in solution. The small unmarked resonances correspond to an unknown impurity.

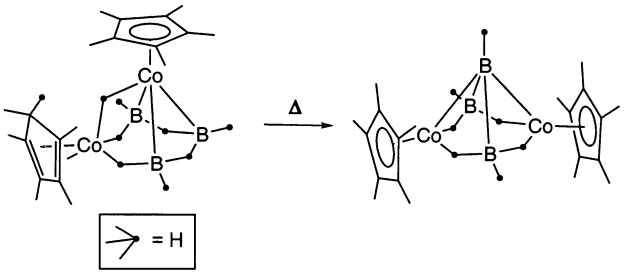
Bridging hydrogen atoms in a *nido*-borane are found on edges of the open face. Clearly in **2** it is the strength of the Rh−H−Rh interaction that leads to a slight preference for the metal cluster analogue **2b** over the borane analogue **2a**. The increased stability of 2,3-$(Cp^*Rh)_2B_3H_7$ (**3**) over **2** then can be attributed to the generation of the preferred skeletal bridging hydrogen placement of a *nido*-borane plus the preferred Rh−H−Rh bridging interaction.

A comparison of the dirhodapentaboranes with dicobaltapentaboranes is also instructive.[12,15] In the cobalt system, the first formed *nido*-dicobaltapentaborane contains a 1,2-Co_2B_3 framework albeit also a Co−H−Co bridge and a η^4-C_5Me_5H dienyl ligand on the Co in the 2-position (Scheme 2). Heating leads to H_2 loss and formation of 2,4-$(Cp^*Co)_2B_3H_7$. In the case of Rh, the isomer with metals in basal positions is unambiguously more stable than that with apical and one basal position occupied. The same appears true for Co, the 2,4-isomer being favored by a somewhat weaker M−H−M bond plus the steric bulk of the Cp* ligand. To date, the Ir analogue of $(Cp^*M)_2B_3H_7$ (M = Co, Rh) has not been isolated as reaction of BH_3THF with $(Cp^*Ir)_2B_2H_8$ leads directly to *arachno*-$Cp^*_2Ir_2B_4H_{10}$.[14]

Reaction with Alkynes. The choice of alkynes as an organic substrate is a natural one. Reaction of

(15) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1993**, *115*, 12224.

Scheme 2



alkynes with boranes leads to carboranes[16−18] and with metal clusters to compounds containing a variety of hydrocarbyl fragments including carbynes.[19] In both polyhedral borane and metal cluster chemistries it was one of the earliest reactions studied. The same reaction outcomes are possible for metallaboranes but, in addition, there is the possibility that adjacent metal and borane fragments will generate new chemistry. A few accounts of reactions of metallaboranes with alkynes have appeared;[20,21] however, we are aware of no systematic study of substituted alkynes with a set of closely related metallaboranes.

The reactions of compounds **1**−**4** with typical alkynes, e.g., PhC≡CH, were surveyed by using ^{1}H and ^{11}B NMR. In no case was a new metallaborane or metallacarborane observed. This is in distinct contrast to the situation with ruthenaboranes where several new types of compounds including metallacarboranes can be accessed.[22] **1** degraded over time whereas **2**, **3**, and **4** remained unchanged (at temperatures above 60 °C, **2** converts into **3**). Although there were no new cluster compounds formed, cyclotrimerization of the alkyne in the presence of **1**, **2**, or **3**, but not **4**, was observed. Product yields indicated catalysis by the rhodaboranes with modest turnover frequencies (TOF) at room temperature (up to 50 turnovers per day).

Although homogeneous catalysis of the cyclotrimerization of alkynes by metal complexes is well understood,[23,24] there is one aspect of the present observations that was surprising. A requirement for metal-catalyzed cyclotrimerization is coordination of the alkyne to a metal center which, in turn, requires the existence of or generation of a coordinatively unsaturated metal site. Excluding catalysis by degradation products for the moment (see also below), catalytic action by the rhodaboranes would demand an essentially different type of activation as none is unsaturated. For this reason, we have explored the cyclotrimerization in some detail to establish the role of the rhodaboranes in the process as well as to examine the dependence of activities and selectivities on catalyst structure and substrate substituents. In the case of **1**, reaction with PhC≡CPh led to a small amount of hydrogenation (*Z*- and *E*-stilbene plus bibenzyl). HC≡C^{t}Bu gave insoluble material but no cyclotrimers. Reactions carried out at temperatures above room temperature also showed signs of side reactions.

Activities and selectivities for the cyclotrimerization of a variety of terminal and internal alkynes are given in Table 1 and the primary data are given in the Experimental Section. Yields ranged from 20% to 80% at catalyst loadings from 0.5% to 30%. No attempt was made to optimize reaction conditions. Some trends are evident. Activities are higher for terminal vs internal acetylenes. Activities decrease in the order **1** > **2** > **3**. In fact, catalysis by **3** requires heating in several cases to allow convenient measurement. Electron-withdrawing substituents enhance activities. In the absence of electron-withdrawing substituents, rates for terminal alkynes with a bulky substituent and rates for internal alkynes are very low. Comparison of the TOF for **2** vs **3** under identical conditions in two separate determinations showed **2** to be 5 and 8 times more active than **3** for the substrate HC≡CCO_2Me at room temperature.

Isomer ratios were measured by ^{1}H NMR directly on the reaction mixture after removing unreacted alkyne and solvent or, particularly in the case where side reactions were observed, by ^{1}H NMR after column chromatography. A couple of comparative observations showed the former to be a more accurate measure of the selectivities. With the exception of MeC≡CCO_2Me, the 1,2,4-isomer predominates but the selectivity is low ranging from ca. 1:1 to 3:1 with changing alkyne substitutent. There are no significant differences between the three catalysts except again for MeC≡CCO_2Me, where **1** leads to the 1,2,4-isomer but **2** and **3** generate the 1,3,5-isomer preferentially.

Mechanistic Considerations. (a) Identity of the Catalyst. There are three pieces of circumstantial evidence that support catalysis by these *nido*-dirhodaboranes. First, the *nido*-dirhodaboranes **1**, **2**, and **3** exhibited catalytic activity but the capped *closo*-trirhodaborane **4** did not. Second, although **1**, which is the least stable of the four compounds, degrades under the reaction conditions, both **2** and **3** could be recovered from the reaction mixtures in high yields (70−80% for **2** and **3**). Third, the measured activities of **1**, **2**, and **3** differ considerably, with **1** being most active and **3** least active. This is particularly important for **2** and **3**, both of which have square-pyramidal structures and identical compositions. It is always very difficult to rule out degradation of the putative catalyst leading to metal moieties which constitute the actual catalyst.[25] However, there is enough evidence to interpret the observations in terms of direct catalysis by the rhodaboranes.

(b) "Common" Mechanism. Although there are exceptions, the "common" mechanism of Schore[23] satisfactorily explains alkyne cyclotrimerization homogeneously catalyzed by metal complexes. As shown in Scheme 3, the mechanism consists of the sequential addition and coupling of three alkynes within the coordination sphere of the metal of the catalyst thereby generating a series of metallacycle intermediates. To initiate the process, a site for alkyne coordination must

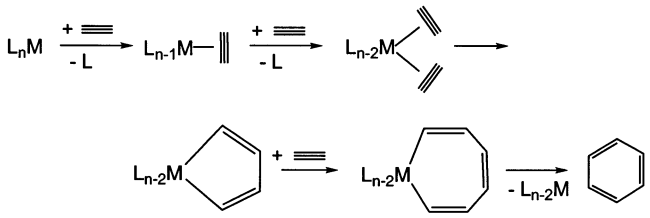
(16) Williams, R. E. *Prog. Boron Chem.* **1970**, *2*, 37.
(17) Hawthorne, M. F. *Pure Appl. Chem.* **1972**, *29*, 547.
(18) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975.
(19) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990.
(20) Grimes, R. N. *Pure Appl. Chem.* **1974**, *39*, 455.
(21) Bould, J.; Rath, N. P.; Barton, L.; Kennedy, J. D. *Organometallics* **1998**, *17*, 902.
(22) Yan, H.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2578.
(23) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
(24) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
(25) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891.

Table 1. Activities and Selectivities for the Catalysis of Terminal and Internal Alkynes by *nido*-Dirhodaboranes[a]

RC≡CR′		1			2			3		
R	R′	TOF[b]	R_1[c]	T (°C)	TOF[b]	R_1[c]	T (°C)	TOF[b]	R_1[c]	T (°C)
terminal alkynes										
H	C(O)Me	50	1.16	22	30	1.19	22		1.15	22
H	C(O)Me							130	1.31	62
H	CO_2Me	30	2.43	22	30	2.44	22		2.56	22
								130	3	62
H	Ph	20	4.6	22	40	3.4	22	14	4.2	22
H	^{t}Bu	c		22	c		22	*d*		22
internal alkynes										
Me	CO_2Me	14	1.3	22	8	0.7	22	7	0.5	65
Me	Ph	6	*e*	22	1	*d*	22	25	*e*	70
Me	Me	6		22		*d*	22	*d*		70
Ph	C(O)Me	7	3[f]	22	2	3[f]	22	12	3[f]	60
Ph	CO_2Me	5	3[f]	22	2	3[f]	22	7	3[f]	60
Ph	Ph	2		22	*c*		22	*d*		70
CO_2Me	CO_2Me	40		22	2		22	0.2		22

[a] Catalyst loadings range from 0.3 to 30% and times from 1 to 3 days. [b] Turnover frequency, day^{-1}. [c] Ratio of 1,2,4- to 1,3,5-isomers. [d] No reaction observed in ca. 1−3 days. [e] 1,2,4-Isomer only (>90%). [f] Measured after chromatography.

Scheme 3



exist on the metal complex. If the complex is saturated, this site must be generated by ligand dissociation.

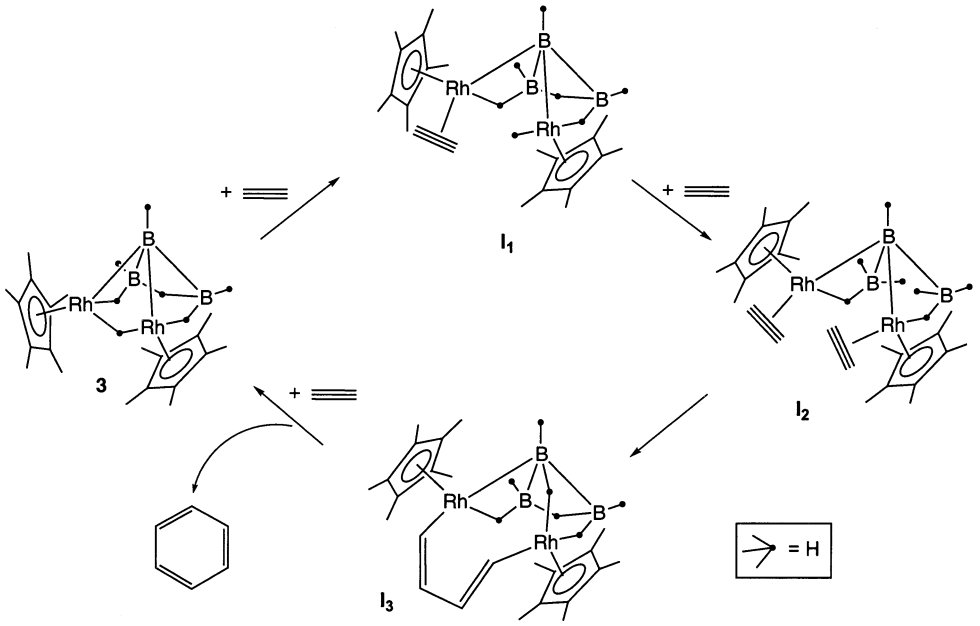
(c) Coordination of the First Alkyne. The dirhodatetraborane, **1**, and dirhodapentaboranes, **2** and **3**, are coordinatively saturated and, in the sense of Wade's rules, electronically saturated as well. Further, there is no simple monodentate ligand that can be lost to generate a coordination site for the alkyne. However, both boranes and metal clusters are susceptible to attack by Lewis bases. In some cases cleavage of borane or metal fragments occurs with concomitant degradation of the cage.[19,26] In other cases, including metallaboranes, base addition occurs leading to cluster opening in response to the increase in cluster sep.[27] These facts have mechanistic significance. For example, reversible base addition has been shown to be responsible for the base-promoted skeletal rearrangements of substituted pentaborane(9)'s.[28] Likewise ligand (Lewis base) addition with edge opening and subsequent loss with edge closure is the favored mechanism for ligand substitution in a class of metal clusters.[29] In the case of the reaction of $(Cp^*ReH_2)_2B_4H_4$ with CO, we were able to isolate the product of CO addition and a structure determination showed rupture of a cluster edge bond (B−B bond in this case).[30] Loss of H_2 resulted in reclosure of the edge bond with an overall reaction of subsitution of H_2 by CO. Thus, a reasonable initiation step in the rhodaborane catalysis is the addition of alkyne to a rhodium center of the *nido*-dirhodaborane thereby generating an 8 sep *arachno*-dirhodapentaborane. This is illustrated in Scheme 4, intermediate $\mathbf{I_1}$, for **3**. The same basic process is envisioned for **2**; however, the existence of two tautomers, as well as two different Rh sites, in each introduces considerable additional complexity.

(d) Inhibition by Lewis Bases. Coordination of the alkyne to rhodium should be inhibited by Lewis bases that coordinate more effectively. Hence, the sensitivity of the cyclotrimerization TOF to three Lewis bases was investigated. PPh_3, which is expected to preferentially coordinate to a rhodium center, pyridine (py), which is expected to preferentially coordinate to a boron center, and the weak base CH_3CN were chosen.[31] The latter could potentially be incorporated into the trimer.[32] No reaction of the Lewis bases with **3** in the absence of alkyne was observed under the conditions used for catalysis. For HC≡CPh inhibition was examined under the same set of conditions (catalyst-to-alkyne ratio, time, temperature, solvent) for each base. More active alkynes, e.g., HC≡CC(O)OMe, could not be used as they react with phosphines. The relative yields of cyclotrimer observed for **3** were 100, 3, 26, 100 for no base, PPh_3 (6 × **3**), py (50 × **3**), and CH_3CN (large excess). The fact that PPh_3 is the most potent inhibitor is consistent with coordination at a metal site.

However, competitive inhibition in the first step requires preferential coordination of the inhibitor to the rhodium site. In addition, the adduct formation constant must be large enough to coordinate most of the rhodaborane to significantly decrease the concentration of the catalyst−substrate complex. Hence we sought evidence for significant levels of coordinated rhodaborane. However, ^{31}P NMR of the reaction in the presence of Ph_3P showed only uncoordinated phosphine. Likewise there was no significant chemical shift change or increase in line width relative to Ph_3P alone ruling out rapid exchange with a rhodaborane coordinated to phosphine. In addition, the ^1H NMR of the reaction mixture during the course of the reaction showed the

(26) Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 79.
(27) Jan, D.-Y.; Workman, D. P.; Hsu, L.-Y.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 5123.
(28) Gaines, D. F. *Acc. Chem. Res.* **1973**, *6*, 416.
(29) Knoll, K.; Huttner, G.; Zsolnai, L.; Jibril, I.; Wasincionek, M. *J. Organomet. Chem.* **1985**, *294*, 91.
(30) Ghosh, S.; Lei, X.; Cahill, C. L.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2900.
(31) Lei, X.; Shang, M.; Fehlner, T. P. *Organometallics* **2000**, *19*, 5266.
(32) Ferre, K.; Toupet, L.; Guerchais, V. *Organometallics* **2002**, *21*, 2578.

Scheme 4



rhodaborane alone and no evidence of a coordinated species. All suggest the concentration of coordinated dirhodaborane (alkyne or base) is below the detection limits of NMR.

Thus, inhibition must occur at a later step of the catalytic cycle. The coordination of a second alkyne is the likely second step. The corresponding increase in sep to 9 requires the generation of a *hypho*-dirhodapentaborane. The known structure of the bis-trimethylphosphine adduct of pentaborane(9) provides a model for intermediate **I_2** in Scheme 4.[33] Coordination to the same metal site is less likely as rhodaborane fragmentation is likely to occur. Effective inhibition by phosphine is subject to the same constraints as the first step; however, now, in contrast to the concentration of the resting catalyst, that of the first intermediate competing for alkyne vs inhibitor is very low.

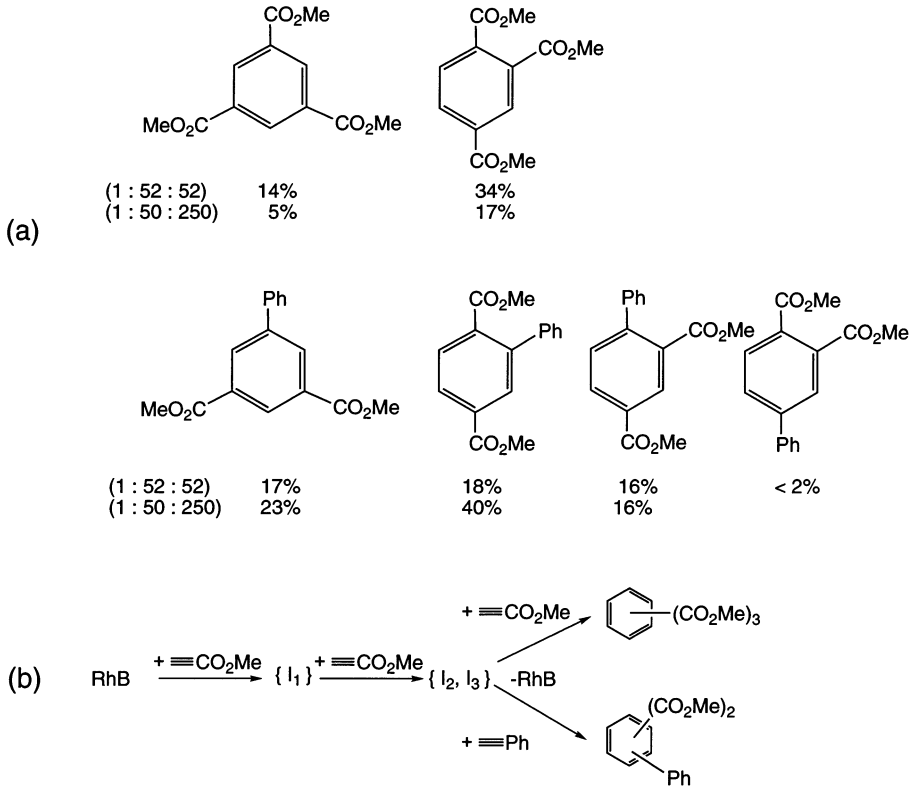
(e) Selectivity. In the "common" mechanism, coordination of the second alkyne is followed by oxidative coupling and carbon−carbon bond formation. For unsymmetrical alkynes oxidative coupling leading to metallacyclopentadienes occurs most readily at the least substituted carbon atoms. In the typical cyclotrimerization process this leads to a preference for the 1,2,4-substituted product. Here the 1,2,4-product dominates for most of the unsymmetrical alkynes, which is consistent with the formation of either metallacyclopentadiene intermediate (not shown) or the bridging diene shown as intermediate **I_3** in Scheme 4. Presumably the last step proceeds through insertion or by direct Diels−Alder type addition, both of which are established pathways in systems catalyzed by organometallic complexes.[34]

To probe the relationship of selectivity and reaction dynamics, a competition experiment was run. The cyclotrimerization of a mixture of **3**, HC≡CCO_2Me, and HC≡CPh (1:52:52) was carried out. Analysis of the mixture of products by mass spectrometry provides evidence for all four stoichiometric combinations of the two monomers. However, analysis of the ^{1}H NMR spectra shows a distribution of products strongly biased in favor of the incorporation of the CO_2Me group over the Ph group. The mixture of products was simple enough so that the spectra of products from the noncompetitive experiments combined with chemical shifts, homonuclear coupling constants, and relative intensities allowed complete assignment. The vast majority of products results from trimerization of three HC≡CCO_2Me and two HC≡CCO_2Me plus one HC≡CPh. The amount of 1,3,5-$C_6H_3Ph_3$ present is ca. 2% of the amount of 1,3,5-$C_6H_3(CO_2Me)_3$ present. The signals attributed to $C_6H_3(CO_2Me)Ph_2$ are at comparable low levels. The results are given in Scheme 5a.

Assuming a consecutive three-step addition of HC≡CCO_2Me or HC≡CPh, one explanation of the results postulates that HC≡CPh is not competitive with HC≡CCO_2Me until the last step (Scheme 5b), where it is equally competitive. That is, the third intermediate (Scheme 4) is formed exclusively from HC≡CCO_2Me. Equal efficiencies in adding the third alkyne lead to a calculated ratio of $C_6H_3(CO_2Me)_3$ to $C_6H_3(CO_2Me)_2Ph$ of 1.0 vs the observed ratio of 0.95. To test this hypothesis, a second mixture of **3**, HC≡CCO_2Me, and HC≡CPh (1:50:250) was allowed to react reasoning that now $C_6H_3(CO_2Me)_2Ph$ should be the dominant product. This is indeed correct as shown in Scheme 5a. The calculated ratio of $C_6H_3(CO_2Me)_3$ to $C_6H_3(CO_2Me)_2Ph$ is 0.2 vs the overall measured ratio of 0.26. Note that comparison of the ratios of individual isomers for the two experiments shows that the assumption of equal rates for all additions is not precisely correct. However, there is insufficient information to attempt a more detailed interpretation. The essential point is that the chemoselectivity of the process can be varied significantly with the concentration ratio of the substrates.

(33) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3013.
(34) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.

Scheme 5



Conclusions

Relative isomer stabilities in *nido*-dirhodapentaboranes are controlled by the balance between the energetics of Rh−H−X, X = B, Rh, three center-two electron interactions vs preferred siting of μ-hydrogens on a square-pyramidal framework. In contrast to related dimetallapentaboranes, these rhodaboranes do not hydroborate or insert alkynes nor do they form adducts with Lewis bases under mild conditions. These characteristics open a pathway for the catalyzed cyclotrimerization of alkynes—a pathway in which the borane fragment acts in an ancillary role by providing a cluster environment for the dimetal fragment. This permits alkyne addition without metallaborane fragmentation, thereby initiating the catalysis. The work demonstrates a new mode of generating catalytic activity—one that is closely related to the often proposed, but seldom realized, catalytic action of transition metal clusters.[35] Despite the number of exisiting studies, the search for catalysts with good chemo- and regioselectivities for cyclotrimerization of two or three different monoynes continues.[36] Although little selectivity is displayed by these parent rhodaboranes, the present results suggest rhodaborane derivatives could be designed to yield more selective catalysts.

Experimental Section

Synthesis. Standard Schlenk line and solvent purification procedures were used.[37] $LiBH_4$ (2.0 M in THF) and $[Cp^*RhCl_2]_2$ were used as received from Aldrich. **1** was prepared as described earlier.[11] Elemental analysis was performed by M-H-W Laboratories, Phoenix, AZ.

***nido*-1,2-$(Cp^*Rh)_2B_3H_7$ (2).** To a suspension of $[Cp^*RhCl_2]_2$ (100 mg, 0.16 mmol) in THF (20 mL) was added $LiBH_4$ (0.45 mL, 0.90 mmol) at −20 °C. Within 30 min the orange suspension became a dark-yellow solution that was accompanied by the release of H_2. Following warming to room temperature and stirring for another 30 min, the solution was heated at 65 °C for 6 h. After removal of solvent, the residue was dissolved in a small amount of hexane and applied to a silica gel column (2 × 10 cm^2). Elution with hexane/toluene (10:1) gave a red band that contained a 1:1.25 mixture of *nido*-1,2-$(Cp^*Rh)_2B_3H_7$ (**2a**) and *nido*-1,2-$(Cp^*Rh)_2(\mu\text{-}H)B_3H_6$ (**2b**) (30.5 mg, 37% based on Rh). The further elution with hexane/toluene (1:1) afforded *nido*-2,3-$(Cp^*Rh)_2B_3H_7$ (**3**) (21.4 mg, 26% based on Rh).

2a: ^1H NMR (400 MHz, C_6D_6, −60 °C) δ 3.95 (br, 1H, B−Ht), 3.66 (br, 2H, B−Ht), 2.07 (s, 15H, Cp*), 1.53 (s, 15H, Cp*), −3.05 (s, 2H, B−H−B), −12.04 (s, 2H, B−H−Rh). **2b**: ^1H NMR (400 MHz, C_6D_6, −60 °C) δ 5.72 (br, 1H, B−Ht), 4.19 (br, 1H, B−Ht), 2.73 (br, 1H, B−Ht), 1.94 (s, 15H, Cp*), 1.70 (s, 15H, Cp*), −0.16 (s, 1H, B−H−B), −3.35 (s, 1H, B−H−B), −14.54 (s, 1H, B−H−Rh), −15.04 (dd, J_1 = 22.1 Hz, J_2 = 28.3 Hz, 1H, Rh−H−Rh); EI-MS 516.1304 (M^+, 100%, obsd), 516.1272 (calcd). **2**: $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 22 °C) δ 3.1 (br), 5.8 (br), 8.2 (br), 11.1 (br), 21.1 (vbr).

***pileo*-$(Cp^*Rh)_3B_4H_4$ (4).** To a suspension of $[Cp^*RhCl_2]_2$ (82 mg, 0.13 mmol) in THF (15 mL) was added $LiBH_4$ (0.4 mL, 0.8 mmol) at −20 °C. In 30 min the mixture changed from an orange suspension to a dark-yellow solution with release of H_2, after which it was slowly warmed to room temperature and stirred for another 20 min. The solvent was removed from the dark-red solution, and the residue was dissolved in toluene and heated at 65 °C for 6 h. Again the solvent was removed and the residue was dissolved in a small amount of hexane and applied to a TLC plate. Elution with hexane/toluene (1:1) gave an orange band that contained $(Cp^*Rh)_3B_4H_4$. All other compounds in the mixture of products decomposed on the

(35) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; p 329.
(36) Mori, N.; Ikeda, S.; Odashima, K. *Chem. Commun.* **2001**, 181.

plate. Crystals suitable for X-ray measurement were grown by slow evaporation of a hexane solution. Yield, 17.8 mg, 27% based on Rh. ^{1}H NMR (400 MHz, C_6D_6, 22 °C) δ 9.05 (br, 1H, B−Ht), 8.05 (d, br, J_{H-B} = 148 Hz, 3H, B−Ht), 1.80 (s, 45H, Cp*); ^{11}B NMR (128 MHz, C_6D_6, 22 °C) δ 125.5 (br, 1B), 73.8 (d, J_{B-H} =148 Hz, 3B); IR (KBr) 2443, 2420 (B−Ht) cm^{-1}; EI-MS 762.1373 (M^+, 100%, obsd), 762.1353 (calcd). Anal. Calcd for $C_{30}H_{49}B_4Rh_3$: C, 47.24; H, 6.43. Found: C, 47.61; H, 5.93.

Molecular Structures. The structure data for **2a** have been deposited in conjunction with the preliminary communication (Cambridge Crystallographic Data Centre no. CCDC-168356).[9] All data were collected on a Bruker Apex CCD diffractometer at 170(2) K with MO Kα radiation (λ = 71073 Å). Full details of the crystallographic analysis are described in the Supporting Information.

Crystallographic data for $C_{30}H_{49}B_4Rh_3$ (**4**): M = 761.66 g/mol; triclinic; space group $P\bar{1}$; a = 10.9363(14) Å, b = 16.767-(2) Å, c = 17.995(2) Å, α = 85.271(2)° β = 89.700(2)°, γ = 71.045(2)°, V = 3109.4(7) Å^3; Z = 4; D = 1.627 g cm^{-3}; μ = 1.627 mm^{-1}; F(000) = 1536. Crystal dimensions = 0.24 × 0.22 × 0.10 mm^3. Total reflections collected = 27668 and 14081. R(int) = 0.0208. Goodness of fit on F^2 = 1.069; $R_1(I > 2\sigma I)$ = 0.0332, wR_2 = 0.0713; maximum/minimum residual density = 0.873/−0.559 e Å^{-3}.

Catalytic Chemistry. (a) General Procedure. To a solution of the catalyst in solvent of volume V was added the alkyne and the reaction mixture was stirred at temperature T for time t. After ^{1}H NMR of the reaction mixture in those cases where spectroscopic information of the products was known, the residue was chromatographed on a silica gel column. Elution with a solvent mixture allowed the band containing 1,3,5- and 1,2,4-trimers to be isolated and characterized (yield and isomer ratio: R_I = the ratio of 1,2,4- to 1,3,5-isomers). All NMR data were obtained with a Varian 500-MHz instrument.

(b) Catalytic Reactions. HC≡CC(O)Me: 1 (32 mg, 0.067 mmol), alkyne (0.3 mL, 3.83 mmol), THF V = 15 mL, T = ambient, t = 24 h, hexane/ether 1:2, R_I = 1.16, yield = 215 mg, 85%. **2** (10 mg, 0.0194 mmol), alkyne (0.3 mL, 3.83 mmol), THF V = 10 mL, T = ambient, t = 48 h, hexane/ether 1:2, R_I = 1.19, yield = 88.5 mg, 34%. **3** (10 mg, 0.0194 mmol), alkyne (0.3 mL 3.83 mmol), toluene V = 15 mL, T = 62 °C, t = 24 h, hexane/ether 1:2, R_I = 1.31, yield = 176 mg, 68%. Spectroscopic data for the 1,3,5-trimer: ^{1}H NMR ($CDCl_3$) δ 2.719 (s, 9H, Me), 8.707 (s, 3H, CH). ^{13}C NMR ($CDCl_3$): 27.1 (Me), 132.0 (CH), 138.1 (C), 196.9 (CO). Spectroscopic data for the 1,2,4-trimer: ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3H, Me), 2.62 (s, 3H, Me), 2.67 (s, 3H, Me), 7.58 (d, J = 7.8 Hz, 1H, CH), 8.11 (dd, J_1 = 2.0 Hz, J_2 = 7.8 Hz, 1H, CH), 8.21 (d, J = 2.0 Hz, 1H, CH); ^{13}C($CDCl_3$) δ 27.0, 28.5, 29.5 (Me), 127.8, 128.01, 131.6 (CH), 138.6, 139.0, 144.4 (C), 196.6, 200.3, 202.2 (CO); EI-MS 204 (M^+, 15%), 189 (M^+ − Me, 100%).

HC≡CC(O)OMe: 1 (40 mg, 0.08 mmol), alkyne (0.32 mL, 3.6 mmol), THF V = 15 mL, T = ambient, t = 24 h, acetone, R_I = 2.43, yield = 227 mg, 75%. **2** (10 mg, 0.0194 mmol), alkyne (0.34 mL, 3.82 mmol), THF V = 10 mL, T = ambient, t = 48 h, hexane/ether 3:1, R_I = 2.44, yield = 98 mg, 31%. **3** (10 mg, 0.0194 mmol), alkyne (0.34 mL, 3.82 mmol), toluene V = 15 mL, T = 62 °C, t = 24 h, hexane/ether 3:1, R_I = 3, yield = 208 mg, 65%. Spectroscopic data: Data on the trimers (^{1}H, ^{13}C NMR, and MS) corresponded to the published values.[38]

HC≡CPh: 1 (40 mg, 0.08 mmol), alkyne (0.3 mL, 2.7 mmol), hexane V = 15 mL, T = ambient, t = 20 h, hexane/CH_2Cl_2 1:1, R_I = 4.6, yield = 140 mg, 51%. **2** (8 mg, 0.016 mmol), alkyne (0.25 mL, 2.28 mmol), hexane V = 15 mL, T = ambient, t = 24 h, hexane/toluene 5:1, R_I = 3.4, yield = 62.8 mg, 27% (**2** recovered, 4 mg). **3** (25.8 mg, 0.05 mmol), alkyne (0.2 mL, 1.8 mmol), hexane V = 15 mL, T = ambient, t = 24 h, hexane/toluene 4:1, R_I = 4.2, yield = 72 mg, 39% (**3** recovered 17 mg).

HC≡C^{t}Bu: 1, **2**, and **3** were mixed with considerable excess of *tert*-butyl acetylene in hexane at ambient temperature. After 40, 72, and 44 h, respectively, no trimers were found in the reaction residue.

MeC≡CC(O)OMe: 1 (32 mg, 0.067 mmol), alkyne (0.25 mL, 2.5 mmol), THF V = 15 mL, T = ambient, t = 25 h, hexane/ether 4:1, R_I = 1.3, yield = 98.1 mg, 40%. **2** (10.5 mg, 0.02 mmol), alkyne (0.2 mL, 2.0 mmol), THF V = 15 mL, T = ambient, t = 68 h, hexane/ether 4:1, R_I = 0.7, yield = 43 mg, 22%. **3** (15 mg, 0.029 mmol), alkyne (0.2 mL, 2.0 mmol), toluene V = 10 mL, T = 65 °C, t = 24 h, hexane/ether 4:1, R_I = 0.5, yield = 20 mg, 10%. Spectroscopic data for the 1,3,5-trimer: ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3H, Me), 2.25 (s, 3H, Me), 2.28 (s, 3H, Me), 3.85 (s, 3H, OMe), 3.87 (s, 3H, Me), 3.92 (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ 16.8, 17.3, 17.7 (Me), 52.49, 52.59, 52.64 (OMe), 129.8, 130.9, 133.0, 133.9, 136.4, 137.6 (C), 168.3, 169.1, 170.1 (CO). Spectroscopic data for the 1,2,4-trimer: ^{1}H NMR ($CDCl_3$) δ 2.206 (s, 9H, Me), 3.902 (s, 9H, Me); ^{13}C NMR ($CDCl_3$) δ 17.5 (Me), 52.4 (OMe), 132.8, 133.5 (C), 169.6 (CO); EI-MS 294 (M^+, 28%), 279 (M^+ − Me, 15%), 263 (M^+ − OMe, 100%]

MeC≡CPh: 1 (32 mg, 0.067 mmol), alkyne (0.2 mL, 1.6 mmol), hexane V = 15 mL, T = ambient, t = 24 h, hexane/CH_2Cl_2 3:1, 1,2,4-trimethyl-3,5,6-triphenylbenzene only, yield = 39 mg, 21%. **2** (10 mg, 0.019 mmol), alkyne (0.2 mL, 1.6 mmol), hexane V = 10 mL, T ambient, t = 70 h, hexane/CH_2Cl_2 4:1, 1,2,4-trimethyl-3,5,6-triphenylbenzene only, yield = 5.6 mg, 3%. **3** (12 mg, 0.023 mmol), alkyne (0.2 mL, 1.6 mmol), toluene V = 10 mL, T = 70 °C, t = 24 h, hexane/CH_2Cl_2 5:1, 1,2,4-trimethyl-3,5,6-triphenylbenzene only, yield = 66.8 mg, 36%. Spectroscopic data: ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3H, Me), 2.09 (s, 6H, Me), 6.93−7.64 (15H, Ph); ^{13}C NMR ($CDCl_3$) δ 18.3 (Me), 18.5 (Me), 19.7 (Me), 125.88, 125.93, 126.7, 127.52, 127.54, 128.6, 129.6, 130.5 (CH), 131.5, 132.1, 134.2, 139.4, 140.8, 141.6, 141.81, 141.83, 142.6 (C); EI-MS 348 (M^+, 100%), 333 (M^+ − Me, 20%), 318 (M^+ − 2Me, 12%).

MeC≡CMe: 1 (30 mg, 0.06 mmol), alkyne (1.3 mL, 16.7 mmol), hexane V = 20 mL, T = ambient, t = 24 h, hexane/CH_2Cl_2 3:1, hexamethylbenzene, yield = 16 mg, 1.8%. **2** (17 mg, 0.033 mmol), alkyne (1.19 mL, 15.2 mmol), THF V = 15 mL, T = ambient, t = 48 h, no trimer by ^{1}H NMR. **3** (15 mg, 0.029 mmol), alkyne (2.27 mL, 29 mmol), toluene V = 15 mL, T = 70 °C, t = 24 h, no trimer by ^{1}H NMR.

PhC≡CC(O)Me: 1 (50 mg, 0.099 mmol), alkyne (0.3 mL, 2.1 mmol), THF V = 20 mL, T = ambient, t = 24 h, hexane/ether 2:1, R_I = 3, yield = 95 mg, 32%. **2** (25 mg, 0.048 mmol), alkyne (0.2 mL, 1.37 mmol), THF V = 15 mL, T = ambient, t = 72 h, hexane/ether 2:1, R_I = 3, yield = 52 mg, 26%. **3** (10 mg, 0.019 mmol), alkyne (0.2 mL, 1.37 mmol), toluene V = 15 mL, T = 60 °C, t = 24 h, hexane/ether 2:1, R_I = 3, yield = 34 mg, 17%. Spectroscopic data for the 1,3,5-trimer: ^{1}H NMR ($CDCl_3$) δ: 1.72 (s, 9H, Me), 6.99−7.40 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 32.7 (Me), 128.5, 128.59, 130.2 (CH), 134.4, 136.4, 142.9 (C), 204.4 (CO). Spectroscopic data for the 1,2,4-trimer: ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 3H, Me), 1.86 (s, 3H, Me), 1.90 (s, 3H, Me), 7.00−7.40 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.8, 32.0, 32.8 (Me), 127.6, 127.8, 128.1, 128.2, 128.9, 129.0, 129.8, 130.2, 130.6 (CH), 134.1, 136.9 137.1, 137.2, 137.7, 138.6, 140.8, 141.9, 144.1(C), 204.8, 206.2, 206.4 (CO); EI-MS 432 (M^+, 20%), 417 (M^+ − Me, 100%).

PhC≡CC(O)OMe: 1 (50 mg, 0.099 mmol), alkyne (0.3 mL, 2.06 mmol), THF V = 20 mL, T = ambient, t = 24 h, hexane/ether 1:2, R_I = 3, yield = 79 mg, 24%. **2** (25 mg, 0.048 mmol), alkyne (0.2 mL, 1.37 mmol), THF V = 15 mL, T = ambient, t = 72 h, hexane/ether 1:2, R_I = 3, yield, 40 mg, 18%. **3** (18 mg, 0.035 mmol), alkyne (0.3 mL, 2.06 mmol), toluene V = 15 mL, T = 60 °C, t = 24 h, hexane/ether 1:2, R_I = 3, yield = 34 mg,

(37) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.
(38) Herberhold, M.; Yan, H.; Milius, W.; Warckmeyer, B. *Organometallics* **2000**, *19*, 4289.

11%. Spectroscopic data for the 1,3,5-trimer: ^{1}H NMR ($CDCl_3$) δ 3.22 (s, 9H, Me), 7.00−7.40 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 52.0 (Me), 128.2, 128.4, 129.0 (CH), 134.8, 137.2, 138.3 (C), 168.0 (CO). Spectroscopic data for the 1,2,4-trimer: ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 3H, Me), 3.48 (s, 3H, Me), 3.52 (s, 3H, Me), 7.00−7.40 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 52.0, 52.57, 52.61 (Me), 127.5, 127.6, 127.7, 127.8, 128.2, 128.3, 128.78, 129.83, 129.9 (CH), 132.0, 134.3, 137.40, 137.45, 137.48, 137.60, 137.61, 139.5, 141.2 (C), 168.0, 168.1, 168.3 (CO); EI-MS 480 (M^+, 100%), 449 ($M^+ - OMe$, 35%), 417 ($M^+ - 2OMe$, 45%), 385 ($M^+ - 3OMe$, 40%).

PhC≡CPh: 1 (50 mg, 0.1 mmol), alkyne (54 mg, 0.3 mmol), hexane $V = 30$ mL, $T =$ ambient, $t = 22$ h, hexamethylbenzene, yield = 24.1 mg, 45%, hexane wash contained three organic species of *Z*- and *E*-stilbene, and bibenzyl with a ratio of about 2.6:2.1:1. **2** (8 mg, 0.016 mmol), alkyne (53.5 mg, 0.3 mmol), hexane $V = 15$ mL, $T =$ ambient, $t = 48$ h, no trimer by ^{1}H NMR. **3** (16 mg, 0.031 mmol), alkyne (53.5 mg, 0.3 mmol), hexane $V = 15$ mL, $T =$ ambient, $t = 36$ h followed by change of solvent to toluene and heating at 75 °C for 27 h gave no trimer by ^{1}H NMR.

MeOC(O)C≡CC(O)OMe: 1 (39 mg, 0.076 mmol), alkyne (0.2 mL, 1.6 mmol), THF $V = 15$ mL, $T =$ ambient, $t = 12$ h, acetone, hexamethylcarboxylate benzene, 204 mg, 90%. **2** (40 mg, 0.077 mmol), alkyne (0.27 mL, 2.18 mmol), THF $V = 15$ mL, $T =$ ambient, $t = 72$ h, hexane/toluene 5:1 gave **2** (27 mg) followed by acetone, hexamethylcarboxylate benzene, yield = 52 mg, 17%. **3** (40 mg, 0.077 mmol), alkyne (0.27 mL, 2.18 mmol), THF $V = 15$ mL, $T =$ ambient, $t = 72$ h, hexane/CH_2Cl_2 (3:1) gave **3** (33 mg) followed by acetone, hexamethylcarboxylate benzene, yield, ca. 6 mg, 2%.

(c) Competitive Reactions. 2 vs 3. Run 1: Methyl propiolate (0.3 mL, 3.375 mmol) was added to **2** (13 mg, 0.0252 mmol) and **3** (13 mg, 0.0252 mmol) in THF (6 mL), respectively. The resulting mixture was stirred for 25 h at ambient temperature. After removal of solvent and unreacted alkyne the respective residue was dissolved in identical volumes of $CDCl_3$. Integration of the ^{1}H NMR spectrum showed the rate of **2** to be 5 times faster than that of **3**. Run 2: Methyl propiolate (0.3 mL, 3.375 mmol) was added to **2** (10 mg, 0.0194 mmol) and **3** (10 mg, 0.0194 mmol) in THF (6 mL), respectively. The resulting mixture was stirred for 26 h at ambient temperature. Analysis in the same fashion showed the rate of **2** to be 8 times that of **3**.

3 with mixtures of HC≡CC(O)OMe and HC≡CPh: 1:52:52: To a solution of **3** (20 mg, 0.039 mmol) in THF (20 mL) were added phenylacetylene (0.22 mL, 2.00 mmol) and methyl acetylene monocarboxylate (0.18 mL, 2.00 mmol). The resultant reaction mixture was stirred for 2 days at room temperature. After removal of solvent, the residue was shown by proton NMR to contain a mixture of $C_6H_3(CO_2Me)_3$ (48%) and $C_6H_3(CO_2Me)_2(Ph)$ (52%). 1:50:250: To a solution of **3** (20 mg, 0.039 mmol) in THF (20 mL) was added methyl acetylene monocarboxylate (0.17 mL, 1.94 mmol) and phenylacetylene (1.06 mL, 9.69 mmol). The resultant reaction mixture was stirred for 43 h at room temperature. After removal of solvent, the residue contained $C_6H_3(CO_2Me)_3$ (22%) and $C_6H_3(CO_2Me)_2$-(Ph) (78%). ^{1}H spectroscopic data (C_6D_6, 22 °C, 400 mHz, δ, J (Hz), trimer ring CH phenyl protons only): 1,3,5-(C(O)-OMe)$_3$C$_6$H$_3$, 8.980 (s); 1,2,4-(C(O)OMe)$_3$C$_6$H$_3$, 8.493 (d, $^4J_{HH} = 1.6$), 7.904 (dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.6$), 7.376 (d, $^3J_{HH} = 8.0$); 1-Ph-3,5-(C(O)OMe)$_2$-C$_6$H$_3$, 8.918 (t, $^4J_{HH} = 1.6$), 8.517 (d, $^4J_{HH} = 1.6$); 2-Ph-1,4-(C(O)OMe)$_2$-C$_6$H$_3$, 8.158 (d, $^4J_{HH} = 1.6$), 7.965 (dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.6$), 7.685 (d, $^3J_{HH} = 7.6$); 1-Ph-2,4-(C(O)OMe)$_2$-C$_6$H$_3$, 8.721 (d, $^4J_{HH} = 2.0$), 8.069 (dd, $^3J_{HH} = 7.2$, $^4J_{HH} = 2.0$), 7.376 (d, $^3J_{HH} = 7$).

3 with HC≡CPh and PPh$_3$: To a solution of **3** (25.8 mg, 0.05 mmol) in hexane (15 mL) were added PPh_3 (80 mg, 0.30 mmol) and phenylacetylene (0.2 mL, 1.8 mmol). The resultant reaction mixture was stirred for 24 h at room temperature. After removal of solvent, the residue was examined with ^{1}H, ^{31}P NMR, and EI-MS. The yield of the trimer was ca. 3% of that of a reaction with no phosphine.

3 with HC≡CPh and pyridine: To a solution of **3** (25.8 mg, 0.05 mmol) in hexane (15 mL) were added pyridine (0.2 mL, 2.5 mmol) and phenylacetylene (0.2 mL 1.8 mmol). The resultant reaction mixture was stirred for 24 h at room temperature. The yield of the trimer was ca. 26% of that of a reaction with no pyridine.

3 with HC≡CPh and acetonitrile: To a solution of **3** (25.8 mg, 0.05 mmol) in hexane (15 mL) were added acetonitrile (2 mL, 38.3 mmol) and phenylacetylene (0.2 mL, 1.8 mmol). The resultant reaction mixture was stirred for 24 h at room temperature. The yield of the trimer was approximately equal to that of a reaction with no acetonitrile.

Acknowledgment. This work was supported by the National Science Foundation (CHE 9986880).

Supporting Information Available: X-ray structure information for **4**, including tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205694