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Reactivity of Dimetallapentaboranes—*nido*-$[Cp^*_2M_2B_3H_7]$—with Alkynes: Insertion to Form a Ruthenacarborane (M = RuH) versus Catalytic Cyclotrimerization to Form Arenes (M = Rh)**

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

A significant fraction of modern chemistry incorporates the use of transition metals to modify and control the reactivity of main group moieties, for example, organometallic chemistry, and the use of ligands to modify and control the reactivity at metal sites, for example, supramolecular chemistry. Relative to the other p-block elements, the chemistry of carbon is dominant, however, in principle, a similar wealth of chemistry exists for the other p-block elements.[1] In fact, transition metal promoted main group chemistry[2] and main group element promoted transition metal chemistry[3] has generated more interest recently.

Since developing a practical synthetic route to a class of metallaboranes containing metals ranging from Group 5–9,[4] we have begun to examine the systematic reaction chemistry of these compounds. Thus, thermal elimination reactions as well as reactions with metal fragments, monoboranes, and Lewis bases have been described.[5–11] In these reactions, the distinctive electronic contributions of metal and borane fragments to the cluster structure are seen to be expressed in the overall reactivity. In one case, a new class of metallaborane was revealed, the hypoelectronic rhenaboranes.[12]

In the early days of organometallic chemistry, the reaction of metal species with alkynes yielded a wealth of compounds that helped define structural possibilities.[13] Likewise, the reaction of alkynes with boranes gave rise to carboranes[14] and a subsequent bountiful chemistry of these heteroboranes with metals[15] including catalytic applications.[16] Here we report the comparative reactivity of two isoelectronic *nido*-dimetallapentaboranes with alkynes and demonstrate that a change from Group 8 to Group 9 metal drives a change in the reaction from alkyne insertion to catalytic cyclotrimerization. The latter reaction shows that, with the proper choice of metal, metallaborane clusters provide access to a novel catalytic pathway.

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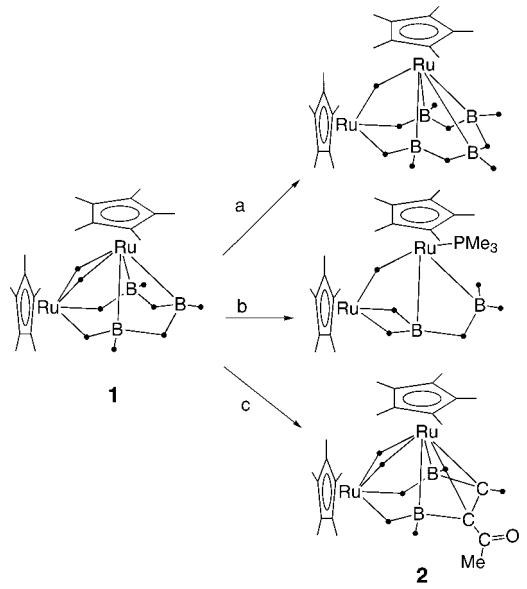
The chemistry of $[1,2\text{-}(Cp^*RuH)_2B_3H_7]$ (**1**; $Cp^* = C_5Me_5$), has been explored by our group[8] and that of Shimoi.[17–19] The results pertinent to this work are shown in Scheme 1 and illustrate a) cluster expansion and b) cluster degradation. Reaction of **1** with $HCCCO_2Me$ leads to $[1,2\text{-}(Cp^*RuH)_2\text{-}3,4\text{-}CHC(CO_2Me)B_2H_4]$ (**2**; Figure 1),[20] which results from combined cluster degradation and expansion (path c in Scheme 1). This reaction is analogous to the reaction of **1** with phosphanes except that ultimately the alkyne base is incorporated into the borane framework rather than coordinated to a metal site. Thermal reaction of metallaboranes with alkynes



Scheme 1. Reactions of **1** with a) monoborane to give cluster expansion, b) with PMe_3 to give cluster degradation, and c) with $HCCCO_2Me$ to yield **2**. The structures shown are schematic representations, for clarity only the H-bridge of the H-bridged bonds is shown, ● = H.

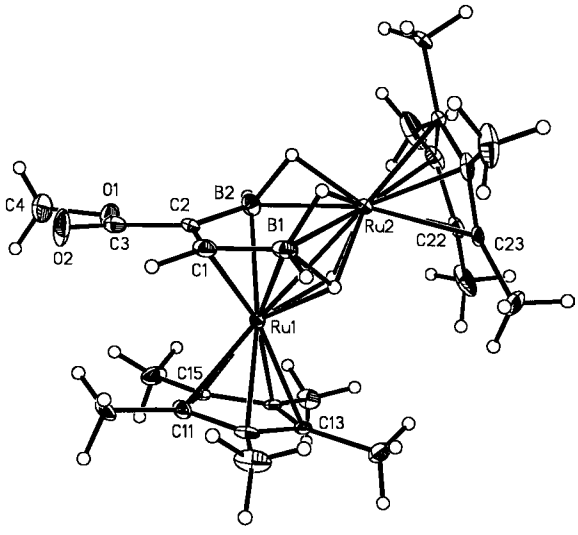


Figure 1. Molecular structure of **2**. Selected bond lengths [Å]: Ru1–Ru2 2.9424(10), Ru1–C1 2.170(8), Ru1–C2 2.180(8), Ru1–B1 2.358(10), Ru1–B2 2.360(10), Ru2–B2 2.385(10), Ru2–B1 2.399(10), B1–C1 1.508(14), B2–C2 1.557(13), C1–C2 1.391(12), C2–C3 1.493(12), O1–C3 1.352(11), O1–C4 1.448(11), O2–C3 1.208(11).

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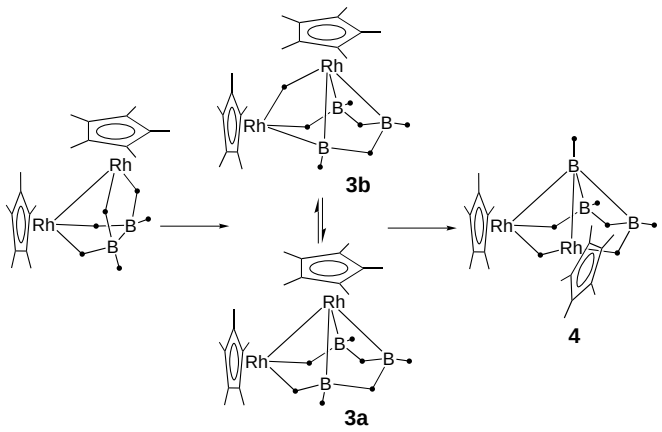
to form metallacarboranes is known[21, 22] as is the metal-catalyzed formation of polyhedral vinyl boranes, which can be precursors to carboranes.[23]

The synthesis of [2,3-(Cp*Rh)$_2$B$_3$H$_7$] (**4**) has been reported.[8, 24] Further work has led to the isolation of [1,2-(Cp*Rh)$_2$B$_3$H$_7$] (**3**; Figure 2)[20] which cleanly converts into **4** on heating. As illustrated in Scheme 2, **3** exists in solution as a equilibrium mixture of two tautomers that differ solely in the placement of one endo hydrogen atom. Isomer **3a**, a direct analogue of B$_5$H$_9$, has an RhHB bridge (abundance 40%) whereas **3b** has a structurally unusual apical–basal RhHRh bridge (abundance 60%).



Scheme 2. Formation of **4**, from [(Cp*Rh)$_2$B$_2$H$_6$] and monoboranes via the intermediate **3** which exists in two tautomeric forms in solution.

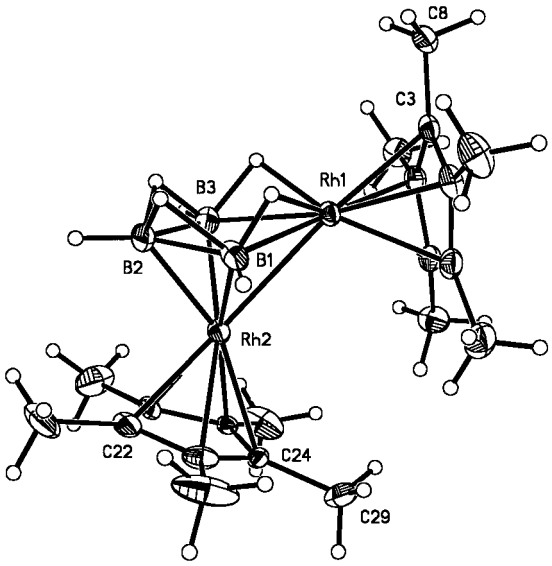


Figure 2. Molecular structure of **3a**. Selected bond lengths [Å]: Rh1–Rh2 2.6892(3), Rh1–B3 2.292(4), Rh1–B1 2.308(3), Rh2–B2 2.061(4), Rh2–B1 2.062(3), Rh2–B3 2.075(4), B1–B2 1.841(5), B2–B3 1.838(5).

The net result of the reaction of either **3** or **4** with a selection of alkynes (Table 1) is the formation of mixtures of 1,2,4- and 1,3,5-substituted benzenes without observable degradation of the rhodaborane. Rates and turnover numbers are modest. Decreasing activities for RC≡CPh, R = H, Me, Ph, suggest a significant steric factor in the reaction. Comparison of rates for HCCCO$_2$Me, catalyzed by **3** and **4** under identical conditions, establishes that **3** is ≈6 times more active at room temperature. The difference in selectivity between **3** and **4** (compare MeC≡CR, R = Ph vs CO$_2$Me) supports catalysis by the rhodaboranes rather than by a fragment derived from degradation. Partial inhibition of the catalysis by triphenylphosphane and pyridine, neither of which degrades the rhodaboranes under the reaction conditions, suggests competition between the alkyne and added Lewis base for the active site on the rhodaborane.

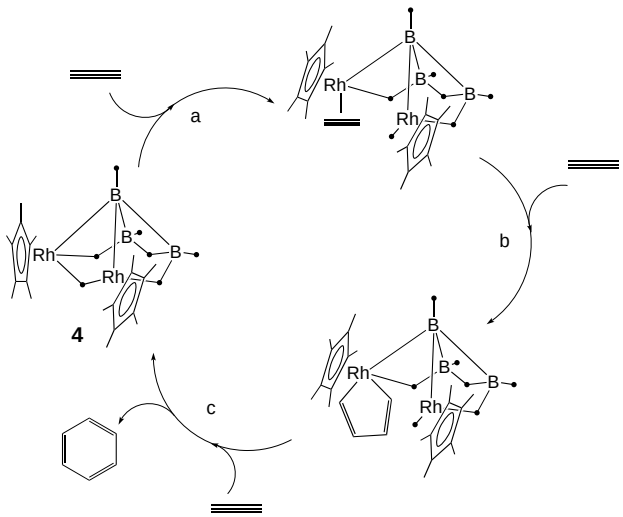
In contrast to, for example, 16 electron rhodium cyclotrimerization catalysts containing chelating carborane ligands,[25] compounds **3** and **4** are formally saturated and have no labile ligands. Hence, the observed catalytic activity may seem puzzling, however, cluster species of this type are intrinsically Lewis acidic relative to non-cluster compounds with saturated electronic structures. Both base-catalyzed framework rearrangements in pentaborane(9)[26, 27] and ligand substitutions in a metal cluster[28] involve addition of a base to open the cluster thereby facilitating rearrangement before base dissociation and cluster closing. Incorporation of this cluster "breathing" process into the "common" mechanism for alkyne cyclotrimerization[29] leads to a reasonable catalytic cycle shown in abbreviated form for **4** (**3** exists as two tautomers each with two different metal sites) in Scheme 3.

The presence of two Cp*RuH fragments in a pentaborane cluster framework leads to insertion whereas Cp*Rh fragments generate catalytic cyclotrimerization. Catalysis by clusters has been an attractive area since its inception[30] but one that has often been frustrated by facile cluster degradation.[31] A metallaborane is electronically, as well as geometrically, similar to a metal cluster of the same nuclearity. Thus, the borane fragment supports the metal atoms in a cluster environment and provides a reaction pathway not available to, for example, an 18 electron organometallic complex.

Table 1. Comparison of selected catalytic data.[a]

Substrate	**3**[a]					**4**[a]				
	Cat:substrate	t[h]	T [°C]	yield [%]	product ratio	Cat:substrate	t [h]	T [°C]	yield [%]	product ratio
HC≡CPh	1:143	24	22	27	1:3	1:36	24	22	39	1:4
MeC≡CPh	1:84	70	22	3	[b]	1:70	24	70	36	[b]
PhC≡CPh	1:12	48	22	NR		1:10	36	70	NR	
HC≡CCO$_2$Me	1:77	48	22	85	1:3	1:260	24	47	42	1:5
MeC≡CCO$_2$Me	1:100	68	22	22	1:1	1:70	24	65	10	3:1

[a] Catalyst to substrate ratio, reaction time, reaction temperature, total yield, ratio of 1,3,5- to 1,2,4-trisubstituted benzene, NR = no reaction. [b] 1,2,4-trimethyl-3,5,6-triphenylbenzene only.



Scheme 3. Proposed catalytic cycle for the cyclotrimerization of alkynes by **4**.

Experimental Section

2: [1,2-(Cp*RuH)$_2$B$_3$H$_7$] (125 mg, 0.24 mmol)[8] in hexane(20 mL) and methyl acetylene monocarboxylate (0.2 mL, 2.24 mmol) were stirred for 8 h at ambient temperature. A yellow solid formed and the suspension became orange. The reaction mixture was concentrated and chromatography (silica gel 60–200) with hexane:toluene = 10:1 afforded the known *nido* cluster [1,2-(Cp*Ru)$_2$(μ-H)B$_4$H$_9$] (8.6 mg, 7%) and with hexane:ether (10:1) the yellow [1,2-(Cp*RuH)$_2$-3,4-CHC(CO$_2$Me)B$_2$H$_4$] (**2**; 74.4 mg, 53%): ^{1}H NMR ([D$_6$]benzene, 22 °C, 600 MHz): δ = 5.53 (s, br, 1H, CH), 3.58 (s, 3H, OMe), 2.72 (br, 2H, B-Ht), 1.78 (s, 15H, Cp*), 1.74 (s, 15H, Cp*), −11.59 (s, 1H, Ru-H-Ru), −11.69 (s, 1H, Ru-H-Ru), −12.25 (s, br, 1H, Ru-H-B), −12.42 (s, br, 1H, Ru-H-B); ^{11}B NMR ([D$_6$]acetone, 22 °C, 128 MHz): δ = −14.2, −15.2 (1:1); ^{13}C NMR ([D$_6$]acetone, 22 °C, 125 MHz): δ = 175.4 (CO), 124.9 (br, *C*=CH), 96.6 (br, C=*C*H), 93.4 (Cp*), 88.8 (Cp*), 50.8 (OMe), 12.1 (Cp*), 10.8 (Cp*); EI-MS: 586.1290 (M^+, found), 586.1297 (calcd); IR (KBr): $\tilde{\nu}$ = 2468(ν_{B-H}), 1604, 1373, and 1222(ν_{COO}^{-1}) cm^{-1}.

3: LiBH$_4$ (0.45 mL, 0.90 mmol) was added to a stirred orange suspension of [Cp*RhCl$_2$]$_2$ (100 mg, 0.16 mmol) in THF (20 mL) at −20 °C. The release of H$_2$ accompanied the formation of a yellow solution (ca. 0.5 h) which was warmed to room temperature for 0.5 h and then heated to 70 °C for 6.5 h. After removal of solvent, the residue was dissolved in hexane and applied to a silica gel column (2 × 10 cm). Elution with hexane:toluene (10:1) gave a red band which contained an inseparable 1:1.25 mixture of *nido*-[-1,2-(Cp*Rh)$_2$B$_3$H$_7$] (**3a**) and *nido*-[-1,2-(Cp*Rh)$_2$(μ-H)B$_3$H$_6$] (**3b**; 30.5 mg, 37% based on Rh). Further elution with hexane:toluene (1:1) afforded **4** (21.4 mg, 26% based on Rh): ^{1}H NMR ([D$_6$]benzene, −60 °C, 400 MHz): **3a**: 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); **3b**: 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); ^{11}B ([D$_6$]benzene, 22 °C, 128 MHz): δ = 5.66, 8.17, 11.02, 22.34 (br); EI-MS: 516.1304 (M^+, 100%, found), 516.1272 (calcd).

Catalytic reactions: In a typical reaction, **4** (8 mg, 15.5 × 10^{-3} mmol) was dissolved in THF (15 mL) and methyl acetylene monocarboxylate (0.36 mL, 4.04 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h gradually generating a white solid on the flask wall. After removal of solvent, the residue was purified by chromatography on silica gel. Elution with hexane:CH$_2$Cl$_2$ (3:1) gave **4** (5 mg) and elution with acetone gave a 5:1 mixture of 1,2,4-and 1,3,5-trimethylbenzenetricarboxylates (142.5 mg, 42%). Data on the trimers (^{1}H, ^{13}C NMR spectroscopy, high resolution mass spectroscopy) corresponded to published spectra.

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(η^3-Allyl)palladium Complexes Bearing Diphosphinidenecyclobutene Ligands: Highly Active Catalysts for the Hydroamination of 1,3-Dienes**

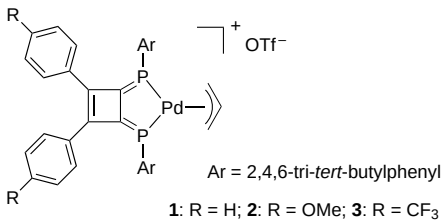
Tatsuya Minami, Hideyuki Okamoto, Shintaro Ikeda, Rika Tanaka, Fumiyuki Ozawa,* and Masaaki Yoshifuji

Dedicated to Prof. François Mathey on the occasion of his 60th birthday

The catalytic hydroamination of unsaturated hydrocarbons is a useful means of synthesizing nitrogen-containing organic molecules.[1] Intramolecular cyclization of aminoalkenes is efficiently catalyzed by lanthanide complexes,[2] and amine-induced telomerization of butadienes[3] and oxidative 1,4-addition of amines to dienes[4] are successfully conducted with palladium catalysts. In contrast, simple intermolecular 1:1 addition of amines to alkenes or dienes is a rather difficult process and has been conducted at high temperature.[5, 6] Hartwig et al. recently reported a significantly improved catalyst, generated from $[Pd(PPh_3)_4]$ and CF_3CO_2H, which performs 1:1 addition of aniline to 1,3-dienes at room temperature.[7] However, even in this case, the reaction takes about a day for completion. Here we report that more efficient catalysts can be prepared by using sp^2-hybridized phosphorus ligands, namely, 1,2-diaryl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutenes.[8]

sp^2-Hybridized phosphorus compounds have a marked propensity to engage in metal-to-phosphorus π backbonding and have a strong π-acceptor property, comparable to that of the carbonyl ligand.[9] Since the catalytic addition of an amine to a 1,3-diene probably involves nucleophilic attack of the amine on an (η^3-allyl)palladium(II) or palladium(II) diene complex,[7a] we expected that diphosphinidenecyclobutene ligands may effectively enhance the electrophilicity of palladium intermediates and thus give highly active catalysts. Although transition metal complexes of sp^2-hybridized phosphorus compounds have been extensively prepared in the last decade,[9] their application to catalysis has been extremely limited,[10] except for phosphaaromatic compounds such as phosphabenzene and phosphaferrocene.[11, 12]

Complexes **1**–**3** were synthesized by treating $[\{Pd(\eta^3\text{-allyl})Cl\}_2]$[13] with the corresponding diphosphinidenecyclobutene ligand and silver trifluoromethanesulfonate (AgOTf) in CH_2Cl_2 at room temperature, and isolated as yellowish orange solids in 66–96% yields.[14] They are fairly stable towards air in solution and as solids; the solid materials can be stored at room temperature for months without notable decomposition.



1: R = H; **2**: R = OMe; **3**: R = CF_3

Figure 1 shows the molecular structure of **1**.[15] The diphosphinidenecyclobutene ligand chelates the (η^3-allyl)palladium moiety through two phosphorus atoms. The aryl rings C and D on the phosphorus atoms are nearly perpendicular to the main framework A, whereas the almost parallel arrangement of phenyl groups E and F and the cyclobutene ring B suggests partial π conjugation between them. The C(53)–C(54) and C(54)–C(55) bond lengths (1.383(8) and 1.376(8) Å) and the C(53)-C(54)-C(55) angle (119.9(5)°) are in the typical ranges for η^3-allyl ligands. The three Pd–C distances (2.168(5)–2.178(4) Å) are comparable to those of diphosphane analogues (2.168–2.201 Å).[16]

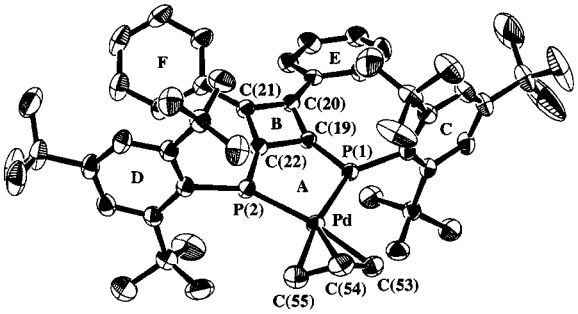
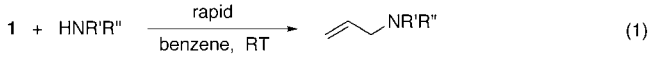


Figure 1. Molecular structure of the cation in crystals of $\mathbf{1}\cdot 2C_6H_6$. Thermal ellipsoids are drawn at the 30% probability level. Triflate anion, benzene molecules (solvent of crystallization), and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-P(1) 2.326(1), Pd-P(2) 2.322(1), Pd-C(53) 2.168(5), Pd-C(54) 2.168(5), Pd-C(55) 2.178(4), P(1)-C(19) 1.667(4), P(2)-C(22) 1.671(4), C(19)-C(20) 1.476(5), C(19)-C(22) 1.499(5), C(20)-C(21) 1.406(5), C(21)-C(22) 1.464(5), C(53)-C(54) 1.383(8), C(54)-C(55) 1.376(8); P(1)-Pd-P(2) 85.50(4), Pd-P(1)-C(19) 107.6(1), Pd-P(2)-C(22) 107.4(1), P(1)-C(19)-C(22) 119.6(3), C(20)-C(19)-C(22) 87.8(2), P(2)-C(22)-C(19) 119.9(3), C(19)-C(22)-C(21) 88.5(3), C(19)-C(20)-C(21) 91.7(3), C(20)-C(21)-C(22) 91.9(3), C(53)-C(54)-C(55) 119.9(5). Dihedral angles between least-squares planes [°]: [A]-[B] 2.3(1), [A]-[C] 93.2(1), [A]-[D] 100.3(1), [B]-[E] 28.2(2), [B]-[F] 147.8(2).

Complex **1** is extremely reactive towards amines [Eq. (1)]. Treatment of **1** with diethylamine (10 mol equiv) in benzene



(1)

at room temperature led to instant formation of 3-(*N*,*N*-diethylamino)propene in 82% yield. Similarly, the reaction with aniline afforded a 45% yield of 3-(*N*-phenylamino)pro-

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