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Metallaboranes from Metal Carbonyl Compounds and Their Utilization as Catalysts for Alkyne Cyclotrimerization

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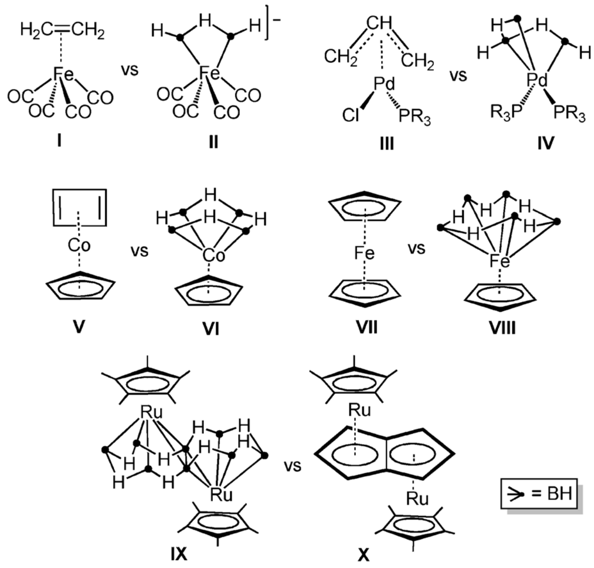
The photolysis of $[M_2(CO)_{10}]$ (M = Re or Mn) with $BH_3{\cdot}thf$ at room temperature yields *arachno*-**1** and **2**, $[(CO)_8M_2B_2H_6]$ (**1**: M = Re, **2**: M = Mn). Both the compounds show a butterfly structure with seven skeletal electron pairs and 42 valence electrons. This result presents a new method for general access to low-boron-content metal–boron compounds without the cyclopentadienyl ligand at the metal centers. This new synthetic route is superior to the existing procedures because it avoids the use of $[LiBH_4]$ and metal polychlorides, for which the synthesis is very tedious. Compound **1** catalyzes the cyclotrimerization of a series of internal and terminal alkynes to yield mixtures of 1,3,5- and 1,2,4-substituted benzenes. The reactivity of **1** with alkynes demonstrates for the first time that the introduction of the $[B_2H_6]$ moiety into the $[Re_2(CO)_{10}]$ framework significantly enhances the catalytic activity. Note that $[Re_2(CO)_{10}]$ catalyzes the same set of alkynes under harsh conditions over a prolonged period of time. Quantum-chemical calculations using DFT methods are applied to afford further insight into the electronic structure, stability, and bonding of **1** and **2**. All the compounds are characterized by IR and ^1H, ^{11}B, and ^{13}C NMR spectroscopy, and the geometry of **1** is established unambiguously through crystallographic analysis.

Introduction

Organometallic chemistry can be regarded as the confluence of coordination chemistry and organic chemistry. The mutually synergistic interactions of metals with organic ligands or fragments and vice versa created new chemistries of both fundamental and practical importance.[1–3] On the other hand, somewhat earlier, metallaborane chemistry provided a close link with organometallic systems, and hence, was rationalized with the 18 electron rule.[4–9] Indeed, many of these clusters, generated from organometallic compounds by replacing C with B plus B–H–B bridging hydrogen atoms, could be related to several classic organometallic complexes that define basic structural and bonding paradigms, for example, $[(CO)_4Fe(\eta^2\text{-}C_2H_4)]$ versus $[\{(CO)_4Fe\}B_2H_5]^-$,[10] $[(PR_3)ClPd(\eta^3\text{-}C_3H_5)]$ versus $[\{(PR_3)_2Pd\}B_3H_7]$,[11] $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)]$ versus $[\{(\eta^5\text{-}C_5H_5)Co\}B_4H_8]$,[12] $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_5)]$ versus $[\{(\eta^5\text{-}C_5H_5)Fe\}B_5H_{10}]$,[13] and $[(Cp^*Ru)B_8H_{14}(RuCp^*)]$ versus $[Cp^*Ru(C_8H_6)RuCp^*]$[14] (Scheme 1). In addition, although the transition metal fragments can be isolobal to borane fragments, they possess bonding capabilities that extend beyond this isolobal analogy.[15–17]



Scheme 1. Metallaborane analogues to π ligands in organometallic complexes. $Cp = \eta^5\text{-}C_5H_5$. $[(CO)_4Fe(\eta^2\text{-}C_2H_4)]$ (I), $[\{(CO)_4Fe\}B_2H_5]^-$ (II), $[(PR_3)ClPd(\eta^3\text{-}C_3H_5)]$ (III), $[\{(PR_3)_2Pd\}B_3H_7]$ (IV), $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)]$ (V), $[\{(\eta^5\text{-}C_5H_5)Co\}B_4H_8]$ (VI), $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_5)]$ (VII), $[\{(\eta^5\text{-}C_5H_5)Fe\}B_5H_{10}]$ (VIII), $[(Cp^*Ru)B_8H_{14}\text{-}(RuCp^*)]$ (IX), $[Cp^*Ru(C_8H_6)RuCp^*]$ (X).

The pioneering studies of Hawthorne and Grimes on the synthesis of metallacarboranes has paved the way for development in the field of metallaborane chemistry. Successively, the contributions of Fehlner,[4,6] Green,[18,19] Kennedy,[7,20] and others[9,21,22] have made significant impacts in this field, which has attracted significant attention owing to the uncommon structures involved as well as their unique bonding, uneven degrees of reactivity, and catalytic activity.[6,18–27] The earliest synthesis methods for metallaboranes were thermolysis or

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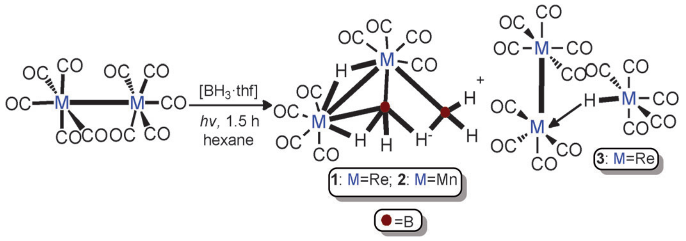
a simple metathesis reactions between preformed polyborane anions and transition-metal halides.[28] However, Fehlner et al. later showed that the addition of monoboranes ($LiBH_4$·thf, BH_3·thf, or $BHCl_2·SMe_2$) to monocyclopentadienyl metal chlorides, $[Cp^*MCl]_n$, is an excellent method for the generation of metallaboranes containing transition metals from Group 5 to Group 9.[29]

Although the methods described above were found to be suitable, and in a few instances, metal hydrides were discovered to be acceptable precursors for metallaboranes,[30–35] the reactions often led to various metallaboranes with low yields. Thus, the greatest challenge for chemists is to find new precursors for metallaboranes. Using the monocyclopentadienyl metal chloride and monoborane reagents, we have formed metallaboranes from Group 4 to Group 9.[36–42] Further, in the search for suitable metal precursors, we found that $[Cp^*MCl(CO)_3]$ (M = Mo, W, Fe) are alternative precursors containing the Cp*M fragment.[43] Metal carbonyl compounds have been found to play a key role in organometallic as well as metallaborane chemistry. Here, we report the synthesis of *arachno*-$[(CO)_8M_2B_2H_6]$ obtained from the UV photolysis of a metal carbonyl $[M_2(CO)_{10}]$ (M = Mn or Re) and BH_3·thf. In addition, we have succeeded in utilizing *arachno*-$[(CO)_8Re_2B_2H_6]$ as an active catalyst for the cyclotrimerization of various terminal and internal alkynes under mild conditions.

Results and Discussion

As shown in Scheme 2, the photolysis of $[M_2(CO)_{10}]$ (M = Re, Mn) and BH_3·thf in *n*-hexane leads to the formation of *arachno*-$[(CO)_8M_2B_2H_6]$ (**1**: M = Re; **2**: M = Mn). The compositions and structures of these compounds were established through X-ray diffraction studies and further confirmed by mass spectral analysis and multinuclear NMR spectroscopy.



Scheme 2. Synthesis of **1** and **2**.

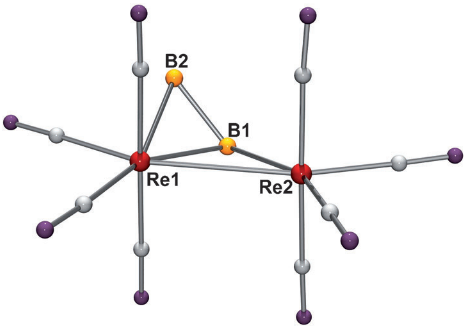


Figure 1. Molecular structure and labeling diagram for **1**. Selected bond lengths [Å] and angles [°] are as follows: Re1–Re2 3.1104(9), B1–B2 1.7600(3), B1–Re1 2.3700(2), B1–Re2 2.500(19), B2–Re1 2.4200(2), B1-Re1-B2 43.1(7), B2-B1-Re2 120.5(14), Re1-B1-Re2 79.4(6), B1-B2-Re1 66.8(9).

The molecular structure of **1**, shown in Figure 1, is very similar to $[B_4H_{10}]$, and can best be described as a butterfly geometry in which one of the wing tips and hinges are replaced by $Re(CO)_4$ fragments. Although the Re–Re bond length of 3.11 Å is longer than those in other rhenaborane clusters,[44–46] it is analogous with the Re–Re bond length of 3.04 Å in $[Re_2(CO)_{10}]$.[47] It has been observed that the axial Re–C distance of 1.92 Å in $[Re_2(CO)_{10}]$ is 0.058 Å shorter than the average equatorial bond length of 1.98 Å. In contrast, the axial Re–C distance in **1** is longer than the equatorial bond length. The Re1–B1 bond length of 2.3700(2) Å is markedly shorter than the Re1–B2 bond length of 2.500(19) Å, as also evident in most *arachno* structures.[48] Note that the UV photolysis of $[M_2(CO)_{10}]$ (M = Mn or Re) in the presence of phosphine or phosphite ligands results in the formation of the disubstituted $[1,2\text{-}M_2(CO)_8L_2]$ (L = PPh_3). Similarly, the room-temperature photolysis of a *n*-hexane or toluene solution of $[Re_2(CO)_{10}]$ in the presence of excess 1-alkene yielded $[(\mu\text{-}H)Re_2(CO)_8\ (\mu\text{-}(\eta^2\text{-}CH{=}CHR))]$ (R = H, CH_3, C_2H_5 or n-C_4H_7).[49] The alkenyl ligand bridges the two metals, forming a σ bond to one Re and a π bond to the other. Compounds **1** and **2** may be considered as direct structural analogues of $[(\mu\text{-}H)Re_2(CO)_8(\mu\text{-}(\eta^2\text{-}CH{=}CH_2)]$. The existence of compound **1** permits structural comparison with other similar compounds of Ru, Ir, and Co without the disruption caused by additional metal fragments or ligands (Table 1).

The spectroscopic data of **1** are consistent with its solid-state X-ray structure. The mass spectroscopic data suggest a molecular formula of $[(CO)_8Re_2B_2H_6]$. The $^{11}B\{^1H\}$ NMR spec-

Table 1. Comparison of structural parameters of *arachno*-$[(CO)_8Re_2B_2H_6]$, **1**, and known dimetallatetraborane complexes.

Metallaborane	spe[a]	d[M–M] [Å]	d_{avg}[M–B] [Å]	d[B–B] [Å]	dihedral angle [°]	δ [ppm] M-H-B, B-H-B	δ [ppm] B1, B2
1	7	3.11	2.43	1.76	128.0	−4.41, −10.63	6.46, −1.12
$[(Cp^*RuCO)_2B_2H_5(C_6H_4O_2H)]$	7	2.92	2.25	1.82	117.1	1.50, −12.71	11.6, 13.5
$[Cp^*Fe(CO)B_3H_8]$	7	–	2.24	1.77	122.7	−1.87, −15.4	−0.5, −41.3
$[(Cp^*RuCO)_2B_2H_6]$	7	2.92	2.28	1.7	119.3	−3.73, −13.15	21.3, −3.0
$[(Cp^*Ru)_2(PMe_3)B_2H_6]$	6	3.00	2.22	1.73	165.9	−2.82, −10.93, −8.45[b]	41.5, −4.8
$[(Cp^*IrH)_2B_2H_6]$	7	2.82	2.19	1.83	115.7	−2.75, −13.99	14.2, −14.6
$[(CpCo)_2(PPh_2)B_2H_5]$	7	2.42	2.09	1.79	–	−5.51, −21.15	24.2, 7.35

[a] Skeletal pair electron. [b] −2.82(B-H-B),−10.93(M-H-B), −8.45(M-H-B).

trum of **1** rationalizes the presence of two types of boron environments in a 1:1 ratio at $\delta = 6.46$ and -1.1 ppm. The chemical shift at lower field is assigned to the boron that bridges two rhenium atoms. In addition, the $^{1}H\{^{11}B\}$ NMR spectrum reveals the presence of B–H–B, Re–H–B, and Re–H–Re protons, which appear at $\delta = -4.41$, -10.63, and -17.20, respectively, in a 1:1:1 ratio. The ^{11}B and ^{1}H NMR chemical shifts of **1** and **2** calculated on the grounds of DFT by using the GIAO-DFT method (Table S2 in the Supporting Information) corroborates the experimental values. The IR spectrum of compound **1** shows an intense band at 1957 cm^{-1}, which is characteristic of the terminal carbonyl groups, and a band at 2403 cm^{-1} attributed to the terminal B–H stretches. The Mn analogue of **1** is highly sensitive to air and moisture, and all our attempts to isolate dimanganaborane selectively failed. As a result, the characterization of **2** is based solely on its limited spectroscopic data. The ^{11}B NMR spectrum of the reaction mixture displays two resonances at $\delta = 31$ and 11.42 ppm in a 1:1 ratio. The ^{1}H NMR chemical shifts at $\delta -3.6$, -10.2, and -20.55 ppm are assigned to B–H–B, Mn–H–B, and Mn–H–Mn protons, respectively. The ^{1}H and ^{11}B NMR chemical shifts show acceptable agreement with the calculated values (Table S2).

In addition to the formation of **1**, the UV photolysis of $[Re_2(CO)_{10}]$ with $BH_3{\cdot}thf$ also yielded the known trirhenium hydride $[Re_3(CO)_{14}H]$, **3**. According to earlier reports, compound **3** is accessible in good yield through the UV photolysis of $[Re(CO)_5H]$. It can also be prepared through the photochemical reaction of dirhenium-docacarbonyl with thiophene and triphenyl silane,[50–52] or the photolysis of $[Re_2(CO)_{10}]$ in THF. Confirmation of the structure of **3** was obtained through single-crystal X-ray structure determination and the reported spectroscopic data.

According to the skeletal electron-counting formalism, cluster **1** is analogous to B_4H_{10} (**A**) or $[(\mu\text{-}H)Re_2(CO)_8(\mu\text{-}(\eta^2\text{-}CH{=}CHR))]$ having seven skeletal electron pairs $([3\{Re(CO)_4\}\times 2 + 2(BH)\times 1 + 3(BH_2)\times 1 + 1(\text{bridging H})\times 3/2 = 14\text{ electrons}])$. The geometries of $[(Cp^*RuCO)_2B_2H_6]$ (**C**), $[Cp^*Fe(CO)B_3H_8]$ (**D**), and **A** are very similar to that of **1**. Interestingly, in **C**, the $[(Cp^*RuCO)_2(\mu\text{-}H)]$ fragment is bridged asymmetrically by a B_2H_5 ligand, whereas in **D**, the BH_2 group is replaced by a $[Cp^*Fe(CO)]$ fragment. Iridaborane $[(CpIr)_2B_2H_8]$ also exhibits a butterfly structure with two triangular wings sharing an edge, that is, the body of the butterfly[53,54] (Scheme 3).

A comprehensive computational study was performed to probe the bonding and stability of **1** and the hypothetically modeled compounds $[(Cp^*Re)_2(CO)_2B_2H_8]$ **1a** and $[(Cp^*Re)_2(CO)_3B_2H_6]$ **1b** (Figures S4 and S5). The geometry optimizations were made with the BP86 functional and mixed basis sets (6–31 g*) for all the main-group elements and LANL2DZ for the Re atom (Table S1). The DFT study shows that there is a considerable bonding interaction in the HOMO−2 of compound **1** (Figure 2). The Wiberg bond index (WBI)[55] of 0.36 (NBO analysis)[56] further confirms that the bonding interaction corresponds to the coupling of two Re centers.

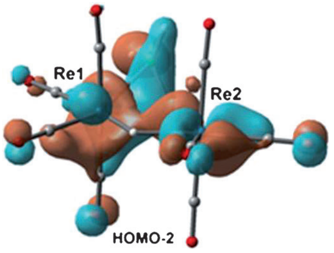
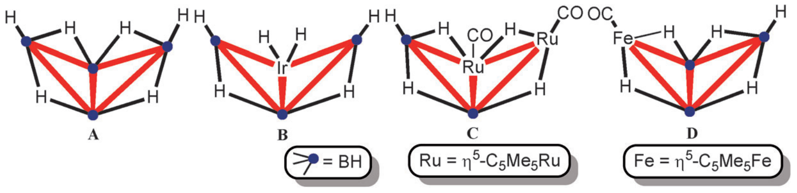


Figure 2. Kohn–Sham orbitals describing Re–Re bonding interactions in HOMO−2 of **1**.

The relative thermodynamic stabilities of **1**, **1a**, and **1b** were calculated to find out if the presence of CO ligands confers any extra stability to **1**. The HOMO–LUMO gap (E_{gap}, 3.17 eV) of compound **1** is significantly larger than that of the model compounds **1a** and **1b** (Figure S1 and Table S3). Further, the first vertical ionization potential (VIP) above 8 eV is consistent with the observed high stability of **1** (Table S3). The high stability of **1** may be caused by the unique features of both σ donation and strong π acceptance of the carbonyl ligands present in the rhenium centers.

[2+2+2] Cycloaddition reactions of alkynes with *arachno*-1 as catalyst

The classic development of a subarea of chemistry begins with the discovery of a new synthetic method and proceeds through structural improvement to a systematic examination of the reactivity. Rhenium complexes are not usually very popular catalysts for organic synthesis except in a few cases such as catalytic reactions with rhenium oxo and rhenium carbonyl complexes.[57] A few accounts of metallaborane reactivity with alkynes have been put forward. For example, 1) a facile reaction occurs between compound $[(Cp^*RuH)_2B_3H_7]$ and a variety of substituted alkynes, leading a range of metallacarboranes,[58] and 2) the reaction of $[(Cp^*Rh)_2B_3H_7]$ or **C** with internal and terminal alkynes leads to catalytic cyclotrimerization.[58,59] Compound **1** is isoelectronic and isostructural with **C**, so we have begun a systematic examination of the reaction chemistry of this compound with alkynes. During our investigation, we recognized that compound **1** plays an important role in the cyclotrimerization of various terminal and internal alkynes. The activities and selectivities for the cyclotrimerization of a variety of terminal and internal alkynes are



Scheme 3. *Arachno*-B_4H_{10} analogues $[CpIrB_3H_9]$, $[Cp^*Fe(CO)B_3H_8]$, and $[(Cp^*RuCO)_2B_2H_6]$.

Table 2. Cyclotrimerization of terminal and internal alkynes catalyzed by compound **1**.

Serial No.	R^1	R^2	Cat./substr.[a]	t [h]	T [°C]	Yield [%][b]	Ratio[c]
1	Ph	Ph	1:60	5	30	60	Hpb[d]
2	Me	Me	1:50	21	60	n/c[h]	–
3	Ph	H	1:70	3	30	70	1:3
4	$SiMe_3$	$SiMe_3$	1:20	25	65	n/c[h]	–
5	CO_2Me	H	1:80	2	30	85	1:6
6	$SiMe_3$	H	1:40	3	30	40	1:3
7	Ph	$SiMe_3$	1:60	9	30	45	Tmsb[e]
8	[g]	H	1:10	5	30	35	1:2
9	CH_3	Ph	1:15	22	60	n/c[h]	Tmpb[f]

[a] Catalyst to substrate ratio, reaction time t, reaction temperature T, total yield, ratio of 1,3,5- to 1,2,4-trisubstituted benzene. [b] Yields are based on product formation as determined by ^{1}H NMR spectroscopy. [c] Single isomer was isolated. [d] Hexaphenylbenzene. [e] 1,2,4-Trimethylsilyl-3,5,6-triphenyl-benzene. [f] 1,2,4-Trimethyl-3,5,6-triphenyl-benzene. [g] $CH_3CH_2CH(SiMe_3)$. [h] No cyclotrimerization.

listed in Table 2. It is evident that the catalytic activity is higher for terminal than for internal alkynes, and that the presence of electron-withdrawing groups enhances the reactivity of an alkyne. The decreasing activities of **1** for $RC{\equiv}CSiMe_3$ (R=H and Ph) imply the presence of a significant steric factor in the reaction pathway. The isomer ratios were determined through ^{1}H NMR measurements taken directly in the reaction mixture after removal of unreacted alkyne and solvent. In all the above the cases, the 1,2,4-isomer was found to be the major product.

Note that Takai and co-workers recently reported the regioselective synthesis of multisubstituted benzene derivatives with the use of rhenium carbonyl as a catalyst.[60,61] Regardless of the excellent regioselectivity, this method has some limitations. It requires a high temperature and exceptionally long reaction time, which narrows the variety of substrates. However, the facile preparation of the four-vertex *arachno*-**1** and its thermal stability makes this system very promising for the catalytic cyclotrimerization of alkynes. In contrast with other transition-metal cyclotrimerization catalysts developed in our laboratory,[59,62] compound **1** has been found to be very efficient, as the reaction is very fast at room temperature.

It was demonstrated earlier by Decker and Klobukowski that the dissociation of CO is the rate-determining step for alkyne cyclotrimerization with a carbonyl-based catalyst.[63,64] Therefore, DFT computational methods were used to understand the catalytic activity of **1**. We calculated the bond dissociation energies (BDEs) for both **1** and the parent $[Re_2(CO)_{10}]$. The first CO BDE value for **1** was found to be 14.7 kcal mol^{-1} lower than that of $[Re_2(CO)_{10}]$, which might mean **1** shows better catalytic activity than $[Re_2(CO)_{10}]$. This was confirmed by the reaction of **1** with various internal and terminal alkynes in the presence of CO gas. No traces of cyclotrimerized products were observed in any of these cases. Further, no cyclotrimerization was observed upon using $[Re_2(CO)_{10}]$ and other labile species such as $[Re_2(CO)_8(PPh_3)_2]$, $[Cp^*Re(CO)_3]$, and $[Re_3(CO)_{14}H]$ at room temperature, so we believe that the active species in the cyclotrimerization process may be a metallaborane species. Note that Schore and others have proposed a common mechanism for the cyclotrimerization of alkynes by a homogenous organometallic catalyst,[65] in which a metallacycle intermediate is proposed by the consecutive addition and coupling of three alkynes into the metal coordination sphere. Recently, we reported a detailed mechanism for the cyclotrimerization of alkynes with ruthenaborane **C** as catalyst.[59] Compound **C** is isoelectronic and isostructural with **1** and has the same number of hydrogen atoms. Therefore, we believe that all the cyclotrimerization reactions reported here involve the initial formation of a metallacycle intermediate and subsequent alkyne insertion.

Conclusion

The reaction of cyclopentadienyl metal polyhalides with monoborane reagents provides a route to a limited class of metallaboranes. In this report, we describe the synthesis of *arachno*-$[(CO)_8Re_2B_2H_6]$ **1** and *arachno*-$[(CO)_8Mn_2B_2H_6]$ **2** through the UV photolysis of $[M_2(CO)_{10}]$ (M=Mn or Re) with $BH_3{\cdot}$thf. The use of these alternative metal carbonyl precursors can overcome the limitation of the monocyclopentadienyl metal-halide route for the synthesis of metallaboranes. Studies of their reactivities demonstrate that, just as organometallic chemistry provides a lucid approach to the chemistry of the M–C bond, so too does metallaborane chemistry. In addition, we have shown that rhenaborane **1** catalyzes the cyclotrimerization of both internal and terminal alkynes under mild conditions. In turn, this fascinating structural and reaction chemistry will fuel interest and lead to rapid progress in this field.

Experimental Section

General procedures and instrumentation

All syntheses were performed under an argon atmosphere by using standard Schlenk and glove-box techniques. Solvents were dried through common methods and distilled under N_2 before use. Chemicals were obtained from Sigma Aldrich and used as received. The external reference for ^{11}B NMR, $[Bu_4N(B_3H_8)]$, was synthesized according to the literature method.[66] Thin-layer chromatography was performed on 250 mm diameter aluminum supported silica gel TLC plates (MERCK TLC Plates). The NMR spectra were recorded on a 400 MHz FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, [D$_6$]benzene, 7.16), and a sealed tube containing $[Bu_4N(B_3H_8)]$ in [D$_6$]benzene (δ_B, ppm, -30.07) was used as an external reference for the ^{11}B NMR spectroscopy. Infrared spectra were recorded on a Nicolet iS10 spectrometer. MALDI-TOF mass spectra of the compounds were obtained on a Bruker Ultraflextreme with 1,2-dihydroxybenzene as a matrix and a ground steel target plate.

Synthesis of *arachno*-1

In a flame-dried Schlenk tube, $[Re_2(CO)_{10}]$ (0.03 g, 0.045 mmol) and $BH_3{\cdot}$thf (1 mL, 1 mmol) in *n*-hexane (10 mL) were irradiated for 1.5 h. The volatile components were removed under vacuum, and the remaining residue was extracted into *n*-hexane and passed through celite. After removal of the solvent, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with *n*-hexane/CH_2Cl_2 (95:5 v/v) yielded very pale yellow **1** (0.010 g, 0.01 mmol, 10%). Mass calcd for $^{12}C_8{}^{1}H_6{}^{11}B_2{}^{16}O_8{}^{186}Re_2$:

624.16; found: 625.18; ^{11}B NMR (22 °C, 128 MHz, $CDCl_3$): $\delta = 6.46$ (s, 1B), −1.12 ppm (s 1B); ^{1}H NMR (22 °C, 400 MHz, $CDCl_3$): $\delta = 7.81$ (B-H$_t$), −4.41 (s, 1H, B-H-B), −10.63 (s, 1H, Re-H-B), −17.20 ppm (s, 1H, Re-H-Re); ^{13}C NMR (22 °C, 100 MHz, $CDCl_3$): $\delta = 188.3$, 183 ppm (CO); IR: $\tilde{\nu} = 2403$ (B-H$_t$), 1957, 2002 cm^{-1} (CO); elemental analysis calcd for $C_8O_8Re_2B_2H_6$: C 15.37, H 0.97; found: C 14.90, H 1.2.

Synthesis of *arachno*-2

In a flame-dried Schlenk tube, [$Mn_2(CO)_{10}$] (0.03 g, 0.079 mmol) and BH_3·thf (1 mL, 1 mmol) in *n*-hexane (10 mL) were irradiated for 1.5 h. The volatile components were removed under vacuum and the remaining residue was extracted into *n*-hexane and passed through celite. ^{11}B NMR (22 °C, 128 MHz, $CDCl_3$): $\delta = 31$ (s, 1B), 11.42 ppm (s, 1B); ^{1}H NMR (22 °C, 400 MHz, $CDCl_3$): $\delta = 7.62$ (B-H$_t$), −3.6 (s, 1H, B-H-B), −10.2 (s, 1H, Mn-H-B), −20.55 ppm (s, 1H, Mn-H-Mn); ^{13}C NMR (22 °C, 100 MHz, $CDCl_3$): $\delta = 205.6$, 199.3 ppm (CO); IR: $\tilde{\nu} = 2434$ (B-H$_t$), 1980, 2014 cm^{-1} (CO).

General procedure for catalytic process

Catalytic data for the alkyne cyclotrimerization are shown in Table 2. All the alkynes were purchased from Sigma Aldrich and used as received. In a typical reaction, **1** (0.015 g) was dissolved in *n*-hexane (12 mL), and alkynes were added to the resulting solution. The reaction mixture was stirred at room temperature for 2–5 h (Table 2). The solvent was evaporated in vacuo. The residue was extracted into *n*-hexane and passed through celite. After removal of the solvent from the filtrate, the residue was subjected to chromatography by using silica gel TLC plates. Elution with *n*-hexane/CH_2Cl_2 yielded the corresponding benzene derivatives.

Note that the formation of the cyclotrimerized products and the ratios of the isomers were confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The yield of the cyclotrimerized products was determined by ^{1}H NMR spectroscopy by employing a reference compound of known weight. The concentration of the analyte in the reaction mixture was determined by comparing the areas of the analyte and reference peaks (ignoring the decomposition of the reference).

X-ray structure determination

The crystal data for **1** were collected and integrated by using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated MoK_α ($\lambda = 0.71073$ Å) radiation at 173 K. The structures were solved by heavy-atom methods by using SHELXS-97 or SIR92 and refined with SHELXL-97.[67]

CCDC 952638 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **1**: $C_8H_6B_2O_8Re_2$; $M_r = 624.15$; monoclinic; $P2_1/n$; $a = 6.5766(4)$, $b = 27.5492(16)$, $c = 8.5288(4)$ Å; $\beta = 109.889(3)°$; $V = 1453.08(14)$ Å^3; $Z = 4$; $\rho_{calcd} = 2.853$ cm^{-3}; $\mu = 16.673$ mm^{-1}; F(000) = 1112; $R_1 = 0.0552$; $wR_2 = 0.1162$; independent reflections 2558 [$2\theta \leq 50.00°$]; 181 parameters.

Theoretical calculations

Quantum chemical calculations were performed on compound **1** and model compounds **1a** and **1b** by using density functional theory (DFT) as implemented in the Gaussian09[68] program package. All the compounds were fully optimized in the gaseous state (no solvent effect) without any symmetry constraints with the BP86[69] functional paired with the LANL2DZ effective core potential (ECP)[70] basis set for the Re atom and 6–31 g* for C, B, O, and H atoms. The optimized geometries are in true minima in the PES diagram. Stationary points were confirmed through analytic computation of harmonic force constants at the aforementioned DFT level. The NMR chemical shifts were calculated by using the BP86/(LANL2DZ,6-31g*) optimized geometries. Computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs),[71,72] using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.[71–77] The projected ^{11}B chemical shielding values determined were referenced to B_2H_6 (BP86/6–31 g* B shielding constant 93.5 ppm) as the primary reference point, and these chemical shift values (δ) were then converted to the standard BF_3·OEt_2 scale by using the experimental value of +16.6 ppm for B_2H_6.

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