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Cobalt(I)-Mediated Preparation of Polyborylated Cyclohexadienes: Scope, Limitations, and Mechanistic Insight

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Abstract: A series of 1,3- and 1,4-diboryl-1,3-cyclohexadienes have been prepared by intermolecular CoCp-mediated [2+2+2] cocyclizations of alkynylboronic pinacolate esters with alkenes, followed by oxidative demetallation with iron(III) chloride. The effect of substitution at the borylated alkyne on chemo- and regioselectivities has been studied, suggesting steric control. The proper choice of substituents allowed the preparation of 1,3-diborylated cyclohexadienes in a highly selective manner. Alternatively, 1,4-diborylated cyclohexadienes could be prepared from diborylated diynes. The scope of this reaction has been examined and found to include electron-poor, electron-rich, linear, and cyclic alkenes. The diborylated cyclohexadienes were submitted to single or double Suzuki–Miyaura cross-coupling reactions with haloarenes to afford polyarylated systems. The mechanism of the title reaction, including the regioselectivity of the cycloaddition steps, has been analyzed by means of DFT computations.

Keywords: boron · cobalt · cross-coupling · density functional calculations · diene ligands

Introduction

The transition-metal-mediated [2+2+2] cycloaddition of alkynes and alkenes is one of the most powerful methods for forming three new C–C bonds in a single chemical step.[1] For instance, the cycloaddition of three alkynes, or two alkynes and one alkene, provides benzene or 1,3-cyclohexadiene derivatives (Figure 1). The preferential obtention of the latter requires a considerable degree of chemoselectivity, not only with respect to competitive formation of benzenes by [2+2+2] cyclotrimerization of the starting alkyne, but also alkyne [2+2+2] cyclodimerization, which leads to η^4-cyclobutadiene complexes.[2] 1,3-Cyclohexadienes are good ligands for transition metals, thus catalytic methods for their formation with this methodology are relatively scarce and often restricted to specific substrates.[3] Although used stoichiometrically, cobalt complexes have proven to be reagents of choice for mediating direct alkyne/alkene cocyclizations in a highly chemo-, regio-, and stereoselective way with broad substrate scope.[1] In that vein, complexes of type [CoCpL$_2$] (L = CO, PR$_3$, alkenes) have been employed widely to selectively produce derivatives of furans,[4] benzofurans,[5] thiophenes,[4] indoles,[6] pyrroles,[7] imidazoles,[8] pyrimidines,[9] steroids,[10] and terpenes.[11] Among the cobalt reagents, [CoCp(C$_2$H$_4$)$_2$] (**1**) is one of the most active. It can be prepared on a multigram scale by using standard Schlenk

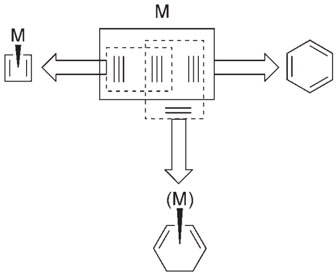

Figure 1. Prototypical generic [2+2] and [2+2+2] cycloadditions of ethyne and ethene.

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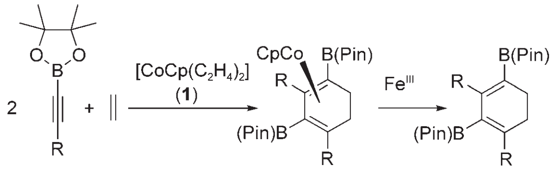
techniques[3c,12] and operates under mild reaction conditions, is compatible with many organic solvents, and tolerates a wide range of functional groups.

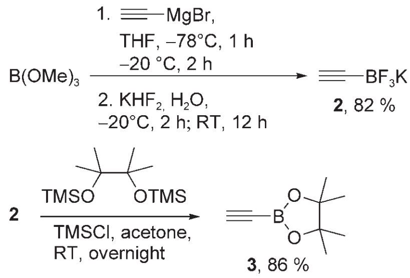
We have disclosed recently that complex **1** successfully converts alkynyl boronates[13] and alkenes to borylated cyclohexadienes in a chemo-, regio-, and diastereoselective manner, as exemplified for ethene in Scheme 1.[14] In this new transformation, we employed disubstituted, pinacol-derived, borylated alkynes, which, unlike their catechol counterparts,[13i] did not undergo cyclotrimerization in the presence of cobalt(0) or (I). The CoCp moiety could be removed readily from the resulting [CoCp(η^4-cyclohexadiene)] complexes by oxidative demetallation with $FeCl_3{\cdot}6H_2O$, affording borylated 1,3-cyclohexadienes as a new class of boranes. Alkenylboranes are useful intermediates for the preparation of a wide range of important organic molecules.[15] The C_{sp2}–B bonds can be subject to coupling reactions[16] and a plethora of other known functional group transformations.[17] Specifically, mono- and diborylated 1,3-dienes have found various applications as dienylation reagents,[18] Diels–Alder partners,[19] and in the synthesis of α,β- or γ,δ-unsaturated ketones.[13c,20] Thus, cyclic dienyl boronates offer promising synthetic opportunities, such as the direct incorporation of cyclohexadiene moieties through cross-coupling reactions.[21] We report herein on the scope of the cobalt(I)-mediated preparation of polyborylated cyclohexadienes and on the cross-coupling of borylated cyclohexadienes with haloarenes. In addition, DFT computations have been executed to pinpoint mechanisms and rationalize the intriguing regioselectivities observed during the cycloaddition steps. For the purpose of listing comparative data, some selected examples from our preliminary communication[14] were included in this paper.



Scheme 1. CoCp-mediated cocyclization of two alkynyl boronates with ethene.

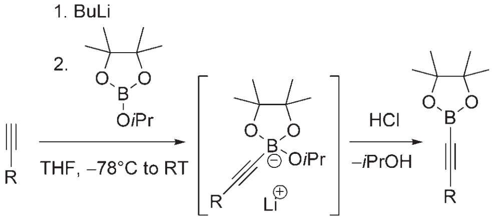
Results and Discussion

Cycloadditions of alkynyl boronates to alkenes: Various alkynyl(pinacol)boronic esters were prepared in order to study the influence of substitution at the triple bond on the product distribution. For the synthesis of the monosubstituted alkyne **3**, ethynylmagnesium bromide was added at −78 °C to a solution of $B(OMe)_3$ in THF, followed by addition of KHF_2 in distilled water (Scheme 2).[22] The resulting potassium salt of ethynyl trifluoroborate (**2**) was then treated with bissilylated pinacol and TMSCl to afford the desired compound in 86 % yield.[23]



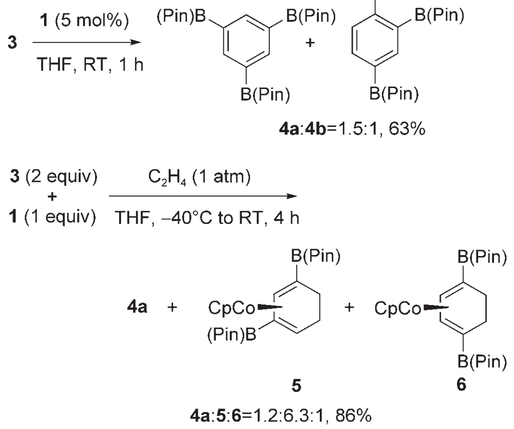
Scheme 2. Synthesis of the alkynyl(pinacol)boronic ester **3**.

All other alkynyl boronates were prepared according to Brown's procedure (Scheme 3).[24] Monosubstituted alkynes or diynes were deprotonated by BuLi and then exposed to isopropyl pinacolylboronic orthoester, which produces lithium alkynyl boronate salts. The mixtures were then treated in situ with HCl to free the desired alkynes.



Scheme 3. General procedure for the synthesis of substituted alkynyl(pinacol)boronic esters.

The behavior of the borylated alkynes toward [2+2+2] cyclodimerization, [2+2+2] cyclotrimerization (both catalytically and stoichiometrically), and cocyclization with ethene was evaluated next. In the presence of 5 mol % of the cobalt complex **1**, compound **3** underwent ready cyclotrimerization giving a 1.5:1 mixture of 1,3,5- and 1,2,4-triborylbenzenes **4a** and **4b** (Scheme 4). These products proved rather unstable

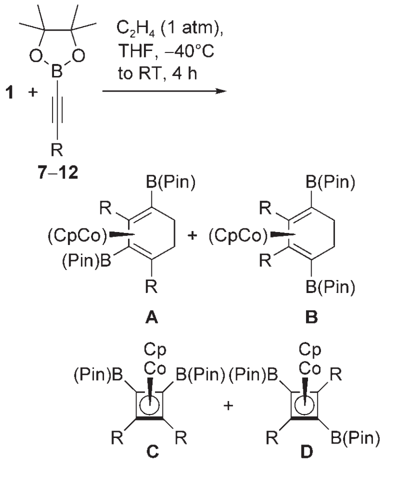


Scheme 4. Cyclotrimerization of **3** and its cocyclization with ethene.

over silica gel and inseparable, but they could be analyzed unambiguously, notably by their ^{1}H NMR spectra [**4a**: $\delta_{\mathrm{Harom}} = 8.36$ ppm (s);[25] **4b**: $\delta_{\mathrm{Harom}} = 8.06$ (brs), 7.78 (dd, J = 7.3, 1.2 Hz), 7.60 (dd, J = 7.3, 0.8 Hz) ppm]. On the other hand, exposing two equivalents of **3** to one equivalent of **1** in THF under ethene (1 atm) gave the 1,3,5-triborylbenzene **4a**, as well as the 1,3- and 1,4-diboryl(η^4-1,3-cyclohexadiene)–CoCp complexes **5** and **6**. In agreement with ^{1}H chemical shifts of CoCp-complexed 1,3-dienes,[26] the internal and terminal diene protons of **5** give rise to broad singlets at 5.81 and 3.56 ppm, respectively. Only one vinylic signal is observed for **6** at 5.67 ppm. Complex **5** was the major component of this inseparable mixture. Notably absent were the 2,3-diboryl(η^4-1,3-cyclohexadiene) isomer and any η^4-cyclobutadiene complexes.

The presence of benzene derivatives was no longer detected when using disubstituted alkynes (Scheme 5). Instead, mixtures of 1,3- and 1,4-diboryl(η^4-1,3-cyclohexadiene)–CoCp complexes of type **A** and **B**, in addition to 1,2- and 1,3-diboryl(η^4-1,3-cyclobutadiene)–CoCp complexes of type **C** and **D** were obtained.[27] Alkynes **7** and **8** gave the best regioselectivities in favor of the 1,3-substitution pattern **A**. Complexes **14** and **15** could be isolated by flash chromatography over silica gel. Although much less regioselective, the cocyclization of alkynes **9** and **10** still provided 1,3-diborylated cyclohexadienes as major products. Complexes **16** and **17** proved unstable over silica; the free cyclohexadienes were obtained directly in 87 and 90% yields, respectively, after chromatography. The reaction of alkyne **11** gave a slight excess of the 1,4-species of type **B**. In this case, regioisomers **18A** and **18B** were separable. A reversal in regioselectivity ensued with the *i*Pr alkyne **12**, likely a steric effect that also directed the outcome of the reaction toward [2+2] dimerization. Thus, the sole cyclohexadiene product was 1,4-complex **19B**, accompanied by a 3.4:1 regioisomeric mixture of 1,2- and 1,3-diborylcyclobutadiene complexes **20C** and **20D**. With the *t*Bu derivative **13**, only the 1,3-diboryl(η^4-cyclobutadiene)–CoCp complex **22D** was obtained in 59% yield. Finally, with R = SiMe$_3$, no product could be isolated.

These results suggest that steric effects influence strongly the reactivity of the postulated intermediate [CoCp(bisalkyne)] complexes and the resulting metallacycles, in turn the origin of the benzene, metalated cyclobutadiene, and cyclohexadiene products (Figure 2).[28] When R is bulky, steric hindrance retards alkene incorporation into the latter, favoring isomerizations to cyclobutadienes.[28d] For less bulky R, cyclohexadiene formation is dominant.



7, R=Ph	92 % (**14A**:**14B**=20:1)
8, R=CH$_2$OMe	84 % (**15A**:**15B**=9:1)
9, R=CH$_2$SPh^a	87 % (**16A**:**16B**=2:1)[a]
10, R=CH$_2$-*i*Pr^a	90 % (**17A**:**17B**=1.8:1)[a]
11, R=Hex	93 % (**18A**:**18B**=1:1.5)
12, R=*i*Pr	72 % (**19A**:**19B**:**20C**:**20D**=0:3:2:7)
13, R=*t*Bu	59 % (**21A**:**21B**:**22C**:**22D**)=0:0:0:1)

Scheme 5. Cocyclizations of ethene with alkynes **7**–**12**. [a] The complexes are unstable over SiO$_2$, and the yields and ratios correspond to the isolated free ligands.

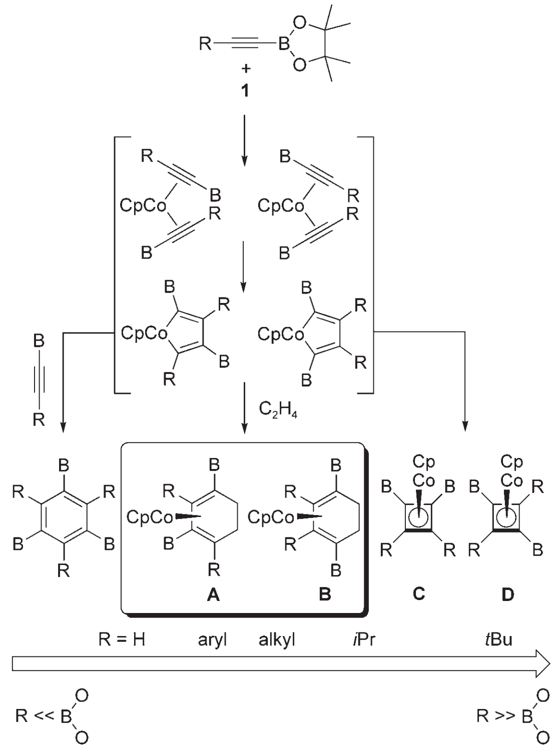
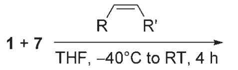


Figure 2. Influence of the steric bulk at the triple bond of alkynyl (pinacol)boronates (increasing from left to right) on the outcome of the reaction.

Next, we turned our attention to the range of alkenes that can take part in these cyclizations. Some acyclic electron-deficient alkenes decomposed under the reaction conditions (e.g., propenenitrile, dimethyl butynedioate, diethylvinylphosphite, and phenylvinylsulfone). On the other hand, a variety of other alkenes converted successfully in the presence of alkyne **7** as a cocyclization partner, some with remarkable selectivity (Table 1). For example, styrene generated complex **22** in 50% isolated yield with complete chemo-, regio-, and diastereoselectivity. This compound serves as an illustrative example for how NMR spectroscopy was used in

Table 1. Cocyclization of **7** with acyclic alkenes.



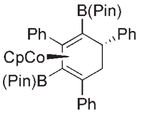
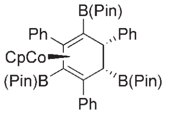
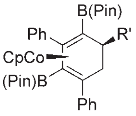
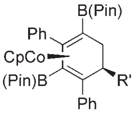
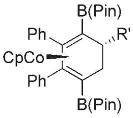
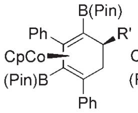
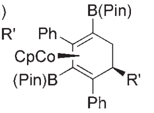
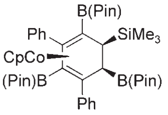
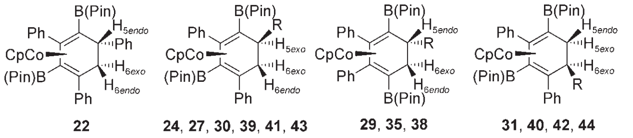
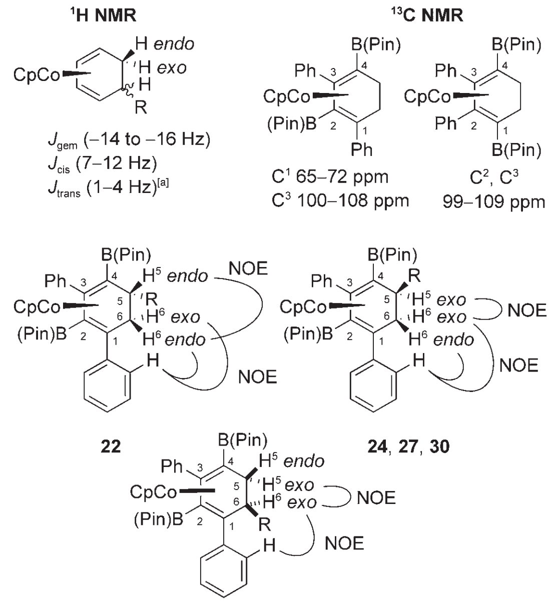
	R	R′	Products	Ratio	Yield [%]
					
1	H	Ph	**22**		50
2	Ph	B(Pin)	**23**		22
					
3	H	O*t*Bu	**24**:**25**:**26**	1:0:0	65
4	H	OTHP	**27**:**28**:**29**	2.5:0:1	69
5	H	$OSiMe_3$	**30**:**31**:**32**	1:1.6:0	35
6	H	OEt	**33**:**34**:**35**	0:0:1	30
7	H	OBu	**36**:**37**:**38**	0:0:1	31
					
8	H	B(Pin)	**39**:**40**	1:1.2	62
9	H	$SiMe_3$	**41**:**42**	2.8:1	68
10	H	S*n*Bu_3	**43**:**44**	3.1:1	45
					
11	$SiMe_3$	B(Pin)	**45**		21

Table 2. ^1H NMR data of the ring protons of the [CoCp(cyclohexadiene)] complexes shown in Table 1.



	Complex	R	H	δ [ppm]	Multiplicity	J_{gem} [Hz]	J_{cis} [Hz]	J_{trans} [Hz]
1	**22**	–	H^5*endo*	3.32	dd	–	11.4	2.0
			H^6*exo*	1.67	dd	–15.7	–	2.0
			H^6*endo*	2.86	dd	–15.7	11.4	–
2	**24**	O*t*Bu	H^5*exo*	2.70	dd	–	6.8	2.8
			H^6*exo*	1.20	dd	–15.4	6.8	–
			H^6*endo*	1.68	dd	–15.1	–	2.8
3	**27**	OTHP	H^5*exo*	3.29	dd	–	6.9	1.6
			H^6*exo*	1.7	m	–	–	–
			H^6*endo*	2.26	dd	–15.1	–	1.3
4	**30**	$OSiMe_3$	H^5*exo*	3.04	dd	–	6.7	2.4
			H^6*exo*	1.3	m	–	–	–
			H^6*endo*	1.58	dd	–15.0	–	2.5
5	**41**	$SiMe_3$	H^5*exo*	–0.05	t	–	8.4	8.4
			H^6*exo*	1.51	dd	–15.4	7.8	–
			H^6*endo*	1.98	dd	–15.3	–	9.2
6	**43**	S*n*Bu_3	H^5*exo*	0.48	t	–	8.1	8.1
			H^6*exo*	1.69	dd	–15.4	8.1	–
			H^6*endo*	2.27	dd	–15.4	8.1	–
7	**39**	B(Pin)	H^5*exo*	0.78	dd	–	9.5	4.4
			H^6*exo*	1.16	dd	–14.9	9.6	–
			H^6*endo*	1.81	dd	–14.8	–	4.6
8	**29**	OTHP	H^5*endo*	3.34	dd	–	11.6	2.8
			H^6*exo*	1.73	dd	–16.2	–	2.8
			H^6*endo*	2.95	dd	–16.2	11.8	–
9	**35**	OEt	H^5*endo*	3.39	dd	–	11.6	2.0
			H^6*exo*	1.72	dd	–15.4	–	2.3
			H^6*endo*	2.95	dd	–15.2	11.6	–
10	**38**	OBu	H^5*endo*	3.38	dd	–	11.6	2.2
			H^6*exo*	1.69	dd	–15.4	–	2.3
			H^6*endo*	2.95	dd	–15.2	11.6	–
11	**42**	$SiMe_3$	H^5*exo*	0.97	dd	–15.7	7.6	–
			H^6*endo*	1.65	dd	–15.6	–	7.6
			H^6*exo*	0.19	t	–	7.6	7.6
12	**44**	S*n*Bu_3	H^5*exo*	0.65	m	–	–	–
			H^6*endo*	2.02	dd	–14.4	–	2.3
			H^6*exo*	0.65	m	–	–	–
13	**40**	B(Pin)	H^5*exo*	1.38	dd	–	8.9	4.3
			H^6*endo*	1.71	dd	–14.1	–	3.8
			H^6*exo*	0.83	m	–	–	–
14	**31**	$OSiMe_3$	H^5*exo*	1.3	m	–	–	–
			H^6*endo*	1.84	dd	–14.9	–	1.8
			H^6*exo*	3.45	dd	–	6.3	1.8

the structural assignments of the cyclization products (see Scheme 6 and Table 2 for selected data and numbering system). Thus, a distinction between the 1,3- and 1,4-diboryl substitution pattern was possible on the basis of the characteristic chemical shifts of the complexed diene carbons,[1i,12c,29] in conjunction with the effect of boron nuclear quadrupole broadening, which frequently precludes the observation of boron-substituted carbons. Hence, for **22**, only two signals were observed: one, at $\delta = 104.2$ ppm, was diagnostic of an aryl-bearing internal quaternary diene carbon (C^3), whereas the other, at $\delta = 65.1$ ppm, was typical of its terminal counterpart (C^1). The absence of a second carbon signal in the vicinity of each of these peaks indicated the 1,3-diboryl structure. The regio- and stereochemistry of sty-



Scheme 6. NMR characteristics of CoCp-complexed cyclohexadiene **22**–**44**. [a] For exceptions, see Table 2.

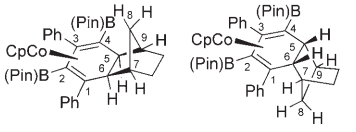
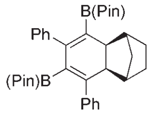
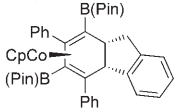
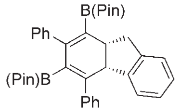
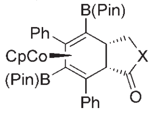
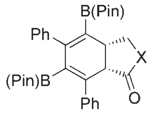
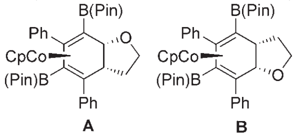
rene incorporation was ascertained by chemical shift, NOE, 2D experiments (COSY, HMBC, HSQC) and coupling data derived from ^{1}H NMR spectroscopy. For example, the methylene hydrogen atoms at C^6 were readily identified by their mutual large geminal coupling ($J_{gem}=-15.7$ Hz) and assigned ($\delta_{Hexo}=1.67$ and $\delta_{Hendo}=2.86$ ppm) on the basis of the characteristic relative chemical shifts of complexed cyclohexadiene hydrogens, which are shielded when located *exo* to cobalt and deshielded when located *endo*.[1i,12c,29,30] Their regiochemistry was established by noting that irradiation of either one of them exerted an NOE effect on the *ortho* protons of the phenyl ring at C^1. The latter could, in turn, be identified by their characteristically deshielded position ($\delta=7.69$ ppm) and appearance as a pseudodoublet, observed uniquely for all diene complexes in this work bearing terminal phenyl substituents. NOE experiments also established the *cis* relationship between H^6*endo* and its neighbor, H^5, the signal for which occurred at the expected low field position of $\delta=3.32$ ppm. This result was corroborated by HMBC, establishing the vicinity of C^1 and H^6. Finally, and as complementary evidence for the stereochemical assignments, the rigidly held complexed cyclohexadiene frame generates a nearly eclipsed ethanediyl fragment,[31] with normally considerably larger J_{cis} than J_{trans} values, in this case 11.4 versus 2.0 Hz (Table 2).[32] The *trans* coupling is relatively large only in those cases in which bulky substituents, such as SiMe$_3$ or SnBu$_3$ (complexes **41**–**43**, Table 2) or constraining ringfusion[33] enforce a pseudoaxial orientation of the tertiary hydrogen.

The reaction of **7** with *tert*-butylvinylether was also completely selective, leading to **24** as a single diastereomer in 65% isolated yield. Puzzlingly, while the regioselectivity is the same as that observed for styrene, the O*t*Bu substituent is now located exclusively *syn* to CoCp. Again, the proximity of the diene phenyl ring with the CH$_2$ moiety was evidenced by NOE experiments. The more deshielded methylene proton ($\delta_{H6endo}=1.68$ ppm) shows *trans* coupling with H^5 (J(H^6*endo*,H^5)$=2.8$ Hz), hence the *cis* relationship with O*t*Bu. That H^5 is located *exo* is corroborated by its chemical shift $\delta=2.70$ ppm, shielded by the appropriate increment of ≈ 1 ppm relative to two known *anti*-methoxy analogues.[34] The replacement of the *t*Bu group by THP gave the *syn* isomer **27** as major compound ($\delta_{H6endo}=2.26$ ppm, $\delta_{H6exo}=1.7$ ppm (by HSQC), J(H^6*endo*,H^5)$=1.6$ Hz), but, surprisingly, the *anti* 1,4-diborylcyclohexadiene **29** was also found in the mixture. The 1,4-arrangement was evidenced by ^{13}C NMR spectroscopy (C^2, C^3: $\delta=99.0$ and 109.0 ppm). Peaks for H^6*endo* and *exo* appear at 2.95 and 1.73 ppm, respectively, in the ^{1}H NMR spectrum, and the former shows a cis relationship with H^5 (J(H^6*endo*,H^5)$=11.8$ Hz). Both complexes were obtained as single diastereomers and separated by flash chromatography on silica gel. Trimethylsilylvinyl ether lead to two *endo* regioisomers **30** and **31** in a 1:1.6 ratio in 35% yield. As a result of the substitution at C^6 in **31**, only two NOE interactions were observed; one between H^5*exo* and H^6*exo* and the other between the phenyl group at C^1 and H^6*exo*. The *trans* relationship between H^5*endo* and H^6*exo* results in small mutual coupling $J=1.8$ Hz. Interestingly, ethyl- and butylvinyl ethers furnished only the 1,4-diborylcyclohexadienes **35** and **38**, respectively, as revealed by the chemical shifts of the external diene carbons (**35**: 97.8 and 108.9 ppm; **38**: 97.8 and 108.9 ppm). The *anti* disposition of the alkoxy groups was ascertained as above for tetrahydropyran-2-yloxy (OTHP) [in both cases, the signals for H^6*endo* appears at 2.95 ppm and shows a *cis* relationship with H^5 (J(H^6*endo*,H^5)$=11.6$ Hz)]. This set of results suggests that the alkene substituent(s) may either influence the regioselectivity of the oxidative coupling of the two alkynes or, considering the reversibility of this step, that they exhibit selectivity for insertion into cobaltacyclopentadienes with specific substituent patterns.[35] Alternatively, electron-rich alkenes might compete with the alkyne in the oxidative coupling step, favoring the formation of a cobaltacyclopentene rather than cobaltacyclopentadiene as the intermediate.[36] This matter will be discussed in the mechanistic section below. Other heteroatom-substituted alkenes (B, Si, Sn) gave better yields, but did not allow for extensive regiocontrol (products **39**–**45**). The structures of these compounds were in accord with ^{13}C and ^{1}H (NOE) NMR experiments, as described above. Although not exhaustively investigated, disubstituted *cis*-alkenes also appear to participate in the cyclization, albeit in lower yields due to competitive insertion of ethene emanating from **1**. The two examples, *cis*-B(Pin)-substituted styrene (Pin = 2,3-dimethylbutane-2,3-dioxy) and trimethylsilylethene,[37] were chosen for comparison with the results obtained for their non-borylated counterparts (**22**, and **41**/**42**, respectively) and because of the additional synthetic versatility imparted by a third, but now allylic, boryl substituent in the potential product.[38] Gratifyingly, the second substituent (boryl) did not affect much the ability of the first to control both regio- and diastereoselectivity, giving **23** and **45**, respectively, as the sole products. The *cis* arrangement of Ph and B(Pin) in **23** was revealed by a *cis* coupling constant between H^5 and H^6 ($J=11.6$ Hz). The relatively large chemical shifts of these two protons ($\delta_{H5}=3.84$ ppm, $\delta_{H6}=2.63$ ppm) pinpoints their *endo* relationship with CoCp. In contrast, an *exo* relationship between the *cis* protons H^5, H^6 ($J=8.1$ Hz) and CoCp is suggested in **45** ($\delta_{H5}=-0.10$ ppm, $\delta_{H6}=1.78$ ppm).

Cyclic alkenes proved equally good cocyclization partners with alkynyl (pinacol)boronates. In our preliminary disclosure of this work,[14] only symmetrical monocyclic alkenes (cyclopentene, cyclohexene, 2,5-dihydrofuran) had been used, which provided stable bicyclic complexes as mixtures of diastereomers, albeit with preference for the *anti* isomer between CoCp and the fused alkene-derived unit. Table 3 expands on this list significantly by addressing further issues of stereo- and regioselectivity. For example, norbornene led to a (separated) mixture of only two out of four possible diastereomers, in both of which the *exo*-face of norbornene reacted. In this case, the *endo* form was somewhat favored over its *exo* analogue (Table 3). Related transformations of norbornene and the NMR assignment of the resulting diastereomers have been described.[29] In analogy, for *syn*-**46**,

Table 3. Cocyclization of **7** with cyclic alkenes.

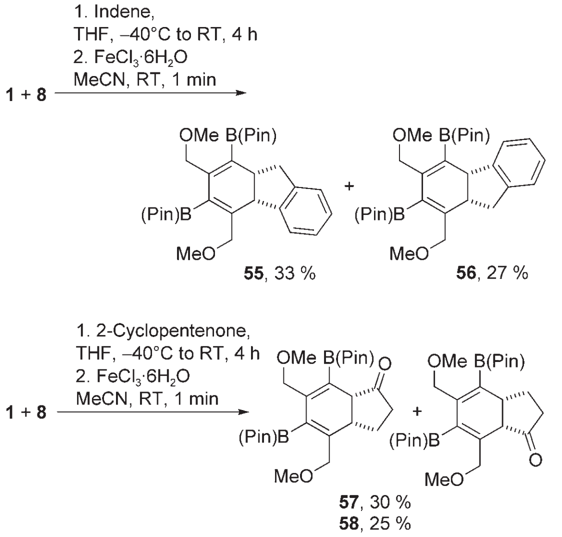
$$1 + 7 \xrightarrow[\text{THF, −40°C to RT, 4 h}]{\text{Cyclic alkene}} \xrightarrow[\text{MeCN, RT}]{FeCl_3 \cdot 6H_2O}$$

	Complexes[a]	Yield [%]	Free ligands	Yield [%]
1	 **46** (*syn*:*anti*=2.3:1)	52	 **47**	78
2	 **48** (*syn*:*anti*=2.1:1)	78	 **49**	86
3	 **50** (X=CH_2)[b]	57	 **51**	77
4	**52** (X=CH_2CH_2, *syn*:*anti*=1.5:1)	52	**53**	59
5	 **54** (**A**:**B**=3.8:1)	66		

[a] Only the major diastereomers are depicted for **48**, **50**, and **52**. [b] The isomers could not be separated and the diastereomeric ratio could not be determined.

the low-field doublet at 3.71 ppm ($J=-8.6$ Hz) is characteristic of the methylene proton directed toward cobalt (H^8*endo*) and the resonance for H^8*exo* is found at high field ($\delta =0.85$ ppm, $J=-8.6$ Hz). Broad singlets at 1.89 and 2.48 ppm corresponding to H^7 and H^9 are also clearly observed. The remaining protons of the norbornane framework, in particular H^5 and H^6, resonate at high field between 0.72 and 1.40 ppm. In sharp contrast, the corresponding protons H^5 and H^6 at the ring junction of *anti*-**46** are detected at low field, as a result of their *endo* relationship with cobalt [$\delta =2.11$ and 2.22 ppm (2d, $J=9.4$ Hz)]. The protons H^7 and H^9 give rise to doublets at 1.78 and 1.88 ppm ($J=3.5$ Hz), all in agreement with the literature analysis of related compounds.[37] Chemical proof for the assigned structures was obtained on oxidative demetalation of the mixture of **46**, which gave a single compound **47** in 78% yield. Unsymmetrical cyclic alkenes (indene, 2-cyclopentenone, 2-cyclohexenone, and 2,3-dihydrofuran) reverted to the preferred formation of *anti* diastereomers as the major or only product. The cyclic enones did so regioselectively, the carbonyl function emerging away from the B(Pin) end of the diene unit in **50** and **51**. In all cases efficient oxidative removal of CpCo was possible (Table 3), except from the regioisomeric mixture **54**, which, upon treatment with iron(III) chloride, gave a complex collection of unidentified compounds.

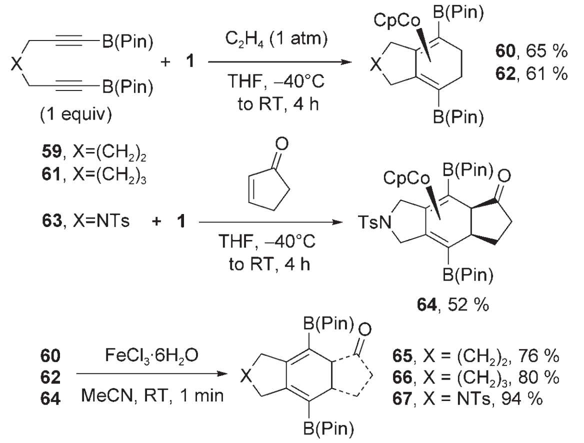
The complete regioselectivity of the cocyclization of **7** with unsymmetrical cycloalkenes summarized in Table 3 could not be reproduced with ether **8**. The reactions with indene and cyclopentenone gave inseparable regioisomeric mixtures of cobalt complexes in 72 and 74% yield, respectively. The NMR spectra of the mixtures were too complicated to be fully analyzable. Nevertheless, the presence of pairs of quaternary carbons within $\delta =$ 70–72 and 100–104 ppm is indicative of the 1,3-arrangement of the boryl groups in the 1,3-cyclohexadienes complexes (Scheme 6). Moreover, the mixtures were subjected to decomplexation using iron(III) chloride, affording the corresponding free ligands, which could be separated by flash chromatography. The incorporation of the alkene in **55**, **56**, **57**, and **58** was poorly controlled (Scheme 7), the two possible regioisomers being generated in similar yield. NOE experiments did not allow the unambiguous assignment of the regiochemistry of these compounds. The structure of compound **55** could be confirmed on the basis of an HMBC experiment which showed a ^3J correlation between H^6 ($\delta =3.84$ ppm (d, $J=10.1$ Hz)) and one OCH_2 ($\delta =72.7$ ppm). On the other hand, H^5 in **56** ($\delta =4.01$ ppm (d, $J=8.6$ Hz)) gave no such interaction. Since the ^{1}H NMR spectra of **57**



Scheme 7. Cocyclizations of **8** with indene and 2-cyclopentenone.

and **58** did not allow for the unambiguous identification of the signals for H^5 and H^6, we were not able to assign the structures from HMBC in this case.

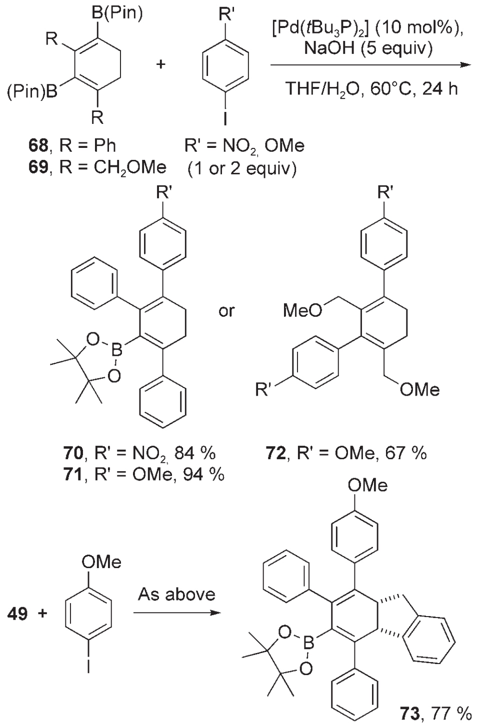
Next, our attention turned to the cocyclization of 1,6- and 1,7-diborylated diynes with alkenes, mechanistically interesting as this constellation enforces the emergence of the normally less favorable (vide supra) 1,4-diborylcyclohexadiene frame, and synthetically important because of the oligocyclic nature of the products. Indeed, for the limited number of cases studied, fairly good yields of fused complexed 1,4-diboryl-1,3-cyclohexadienes were obtained (Scheme 8), the demetallation of which proceeded uneventfully. In the case of the reaction of **63** with **1**, a single diastereomer **64** was obtained, exhibiting a doublet for H^5 at $\delta = 1.57$ ppm. Since analogous *endo* protons resonate at ≈2.7 ppm,[39] a *cis* relationship between the fused cyclopentenone ring and CoCp is indicated.



Scheme 8. Cocyclizations of diboryldiynes with alkenes.

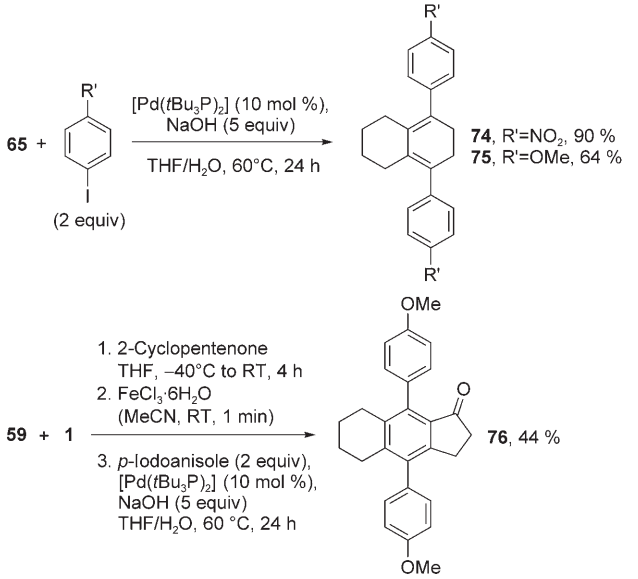
To summarize the above, it is clear that the [2+2+2] cycloaddition of borylalkynes to alkenes has extensive potential in the selective synthesis of polyborylated cyclohexadienes. Further utility should be attainable if a better understanding could be gained of the intriguing regioselectivities observed during alkyne coupling and alkene incorporation. An attempt at doing so with the help of DFT computations is presented after the next section.

Suzuki–Miyaura coupling reactions: With a number of borylated cyclohexadienes in hand, their potential in Suzuki–Miyaura couplings was investigated. Of particular interest was whether such couplings could be executed on the CoCp complexes and whether they would occur stepwise and with regioselectivity. In the event, the complexed cyclohexadienes and cyclobutadienes were unreactive toward bromo- and iodobenzene, respectively, under various catalytic conditions (e.g., $[Pd(PPh_3)_4]$/CsF or NaOH, $[PdCl_2(dppf)]/K_3PO_4$, $[Pd(tBu_3P)_2]$/NaOH; dppf = 1,1′-bis(diphenylphosphino)ferrocene). However, the uncomplexed cyclohexadienes proved to be more forthcoming. Initial experiments with $[Pd(PPh_3)_4]$/CsF or $[PdCl_2(dppf)]/K_3PO_4$ as catalytic systems succeeded in arylating the less hindered, terminal site of the 1,3-diboryl-1,3-cyclohexadienes, but extensive aromatization occurred (^{1}H NMR spectroscopy). This problem was solved with the $[Pd(tBu_3P)_2]$/NaOH system,[40] which kept the cyclohexadiene ring intact. With *p*-iodoanisole and *p*-iodonitrobenzene (1 or 2 equiv), cyclohexadienes **68** and **49** were converted into compounds **70**, **71**, and **73**, respectively, in good yields (Scheme 9). To force reaction of the remaining borylated site, **68** and **49** were subjected to prolonged heating with the same catalyst in the presence of a large excess of iodoarene (5–10 equiv). However, these conditions only provoked reductive deborylation[41] after monoarylation and, eventually, aromatization of the central ring. The same observation was made starting with pure **70**, **71**, and **73**. In contrast, presumably as a consequence of reduced steric protection of the internal boryl group (and also electronic factors, see Mechanistic Insight), diene **69** underwent double coupling with *p*-iodoanisole, giving **72** in 67 % yield.



Scheme 9. Selected Suzuki–Miyaura couplings of 1,3-diborylcyclohexadienes with iodoarenes.

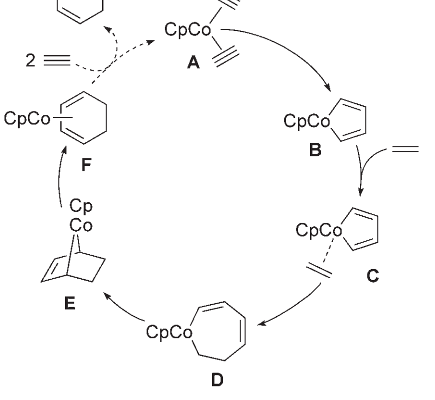
1,4-Diboryl-1,3-cyclohexadienes **65** also gave doubly arylated products under Suzuki coupling conditions (Scheme 10). The [2+2+2] cycloaddition of diyne **59** to cyclopentenone, followed by decomplexation with iron(III) chloride, and application of Suzuki coupling conditions with *p*-iodoanisole lead to **76** in 44 % yield over three steps. Both boryl groups were substituted by the aryl as expected, but the central ring was found completely aromatized.



Scheme 10. Suzuki–Miyaura couplings of 1,4-diborylcyclohexadienes with iodoarenes.

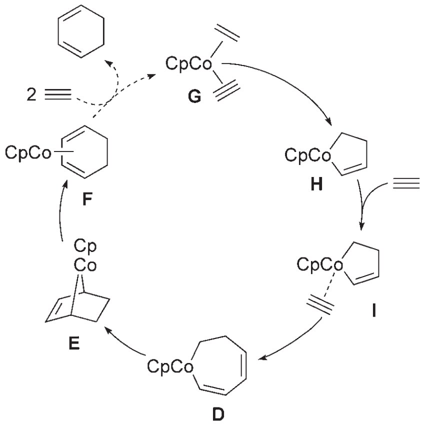
In conclusion, these first attempts at using diborylated cyclohexadienes as coupling partners revealed synthetically useful chemistry. The cyclohexadiene moiety can be kept intact, but seems sensitive to aromatization. In either case, the method appears to be very useful in the regiospecific construction of substituted cyclohexadienes.

Mechanistic insight: We have reported previously on the mechanism of the CoCp-mediated cycloaddition of two alkynes to an alkene to give 1,3-cyclohexadienes by means of DFT computations.[28h] To summarize briefly, when ethyne and ethene are submitted simultaneously to a CoCp source, the bisacetylene cobalt complex **A** forms, which is converted readily into cobaltacyclopentadiene **B** (Scheme 11). Complex **B** then reacts with ethene to give the corresponding 18-electron complex **C**. Compound **D** is obtained after *insertion* of the coordinated alkene into a Co–C σ bond (as opposed to a much invoked Diels–Alder-like pathway). The transformation of this seven-membered complex into the cobaltanorbornene **E**, followed by reductive elimination, gives the expected CoCp-complexed cyclohexadiene **F**. In catalytic reactions,[3a–c] the cyclohexadiene ligand is displaced by two ethynes, which regenerates the species **A**.



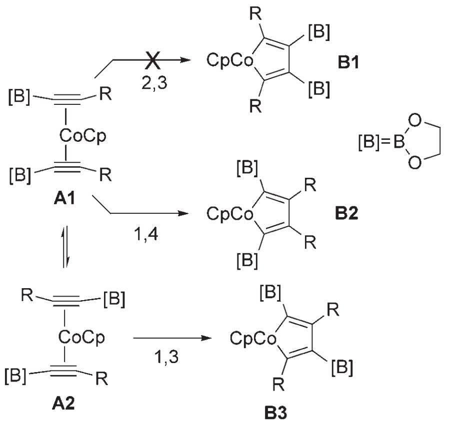
Scheme 11. CoCp-mediated formation of cyclohexadienes via cobaltacyclopentadienes.

An alternative pathway would be the formation of a cobaltacyclopentene **H** by initial alkene/alkyne coupling of the CoCp complex **G** (Scheme 12). Coordination of ethyne follows to give **I**, which subsequently transforms into **D** after regioselective insertion into the Co–C_{sp2} bond. In the unsubstituted series (ethene and ethyne), we found that this option was not favored. However, the experimental data given above were somewhat difficult to rationalize on the basis of the mechanism described in Scheme 11 alone. Indeed, Table 1 indicates that the regioselectivity of the oxidative coupling of the borylalkynes is influenced by the nature of the alkene. With *t*Bu, THP, and $SiMe_3$ enol ethers, 1,3-diborylcyclohexadienes were obtained (at least dominantly), whereas only 1,4-diborylcyclohexadienes were obtained with Et and Bu. The cobaltacyclopentadiene pathway given in Scheme 11 implies that the regiochemistry of the product cyclohexadiene is determined during the oxidative cyclization step converting **A** into **B**, the various permutations of which are depicted in Scheme 13. Therefore no influence of the alkene should manifest, unless the oxidative cyclization step is reversible or the alternative mechanism depicted on Scheme 12 applies. Because, at least in the case of cobaltacyclopentadienes, reversible bisalkyne coupling is rare,[35] we have attempted to quantify the feasibility of these options for some of our substrates.



Scheme 12. CoCp-mediated formation of cyclohexadienes via cobaltacyclopentenes.

The transformations were studied by means of DFT/B3LYP computations at the LACVP(d,p) level (for a selection of structures, see Figure 3). To save computer time, most treatments used boryl 1,2-ethanediolate instead of B(Pin) as the substituent.[42] Presumably because of the high steric repulsion between the boryl groups, a transition state



Scheme 13. The various regiochemical options for the oxidative coupling step from **A**: 2,3, 1,4, and 1,3-coupling.

corresponding to 2,3-coupling could not be optimized, in agreement with experiment. On the other hand, both 1,4- and 1,3-couplings could be modeled.

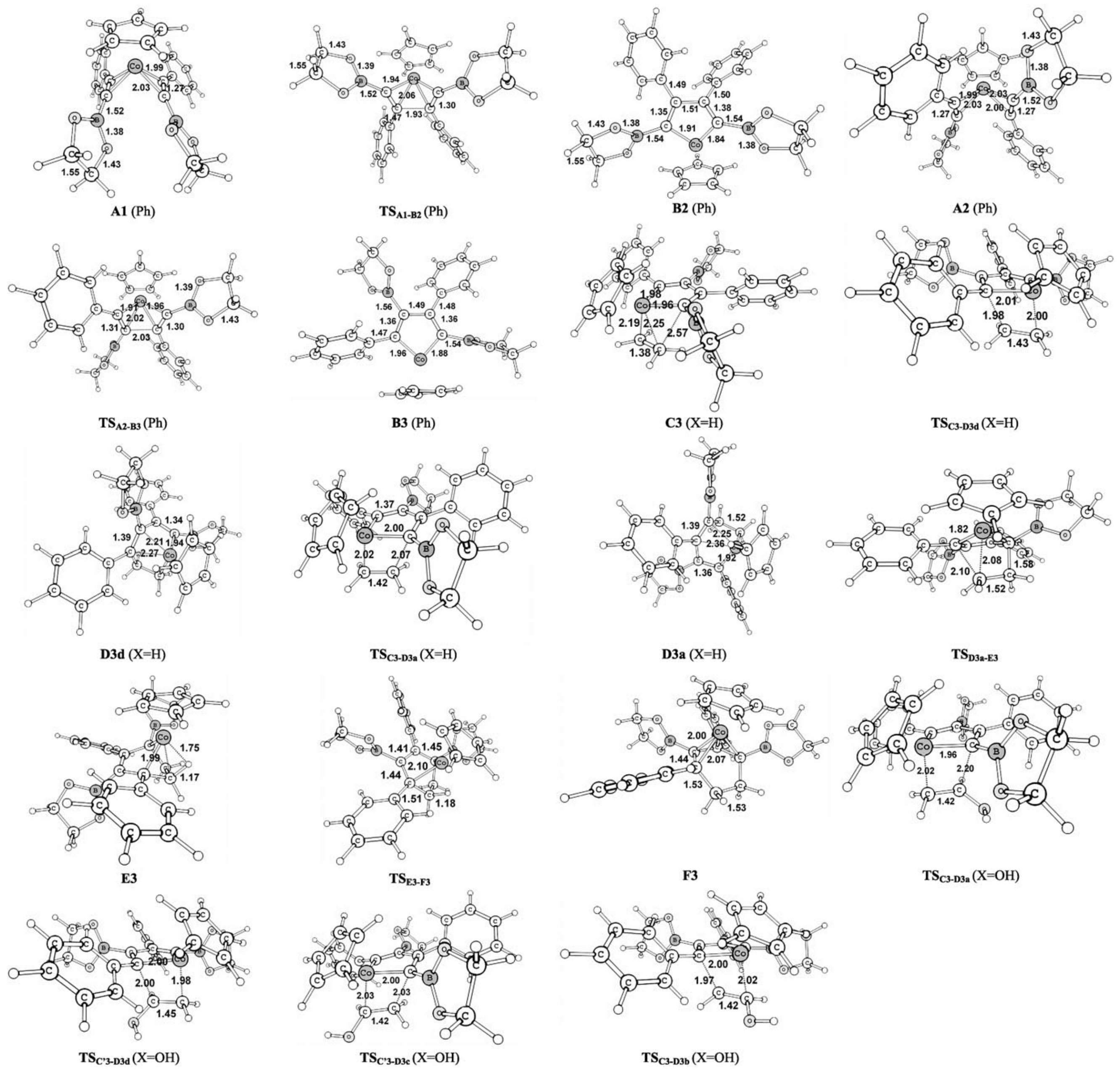
Table 4 depicts the relative energies of species **A** and **B** and of the transition states connecting the former with the latter. It can be seen that 1,3- is favored over 1,4-coupling for R = Ph and CH_2OMe ($\Delta\Delta H^{\neq}=4.0$ and 1.1 kcal mol^{-1}, respectively), as observed experimentally. The attenuation of this preference when going from R = Ph to CH_2OMe is also reproduced by the changes in isomer ratios of products **14** and **15** in Scheme 5. For R = Me, this preference disappears computationally, in good agreement with the experimental result observed for R = Hex.

Next, we studied the conversion of species **B** into **C** and the subsequent insertion step with electron-neutral, -rich, and -poor alkenes. For the former, the picture (Scheme 14) is a priori complicated by a rotation of the ethylenic C–C bond in complexes of type **C** relative to the C_β–C_β bond of the metallacycle (≈23° for ethene)[28h] as a consequence of early bonding between one of the alkene carbons and the juxtaposed C_α of the metallacycle. Because of the asymmetry of the cobaltacycle, this disposition gives rise to regioisomers, **C3** and **C′3**, two for ethene and four for substituted ethenes. In the cases examined for the latter, ethenol and 2-propenal, in turn chosen to model the types of substrates used in the experiments, the regioisomers in brackets of each pair of **C3** or **C′3** (Scheme 14), collapsed to the respective other isomer on attempted geometry optimization, simplifying the problem. An additional simplification was made deliberately, in as much as the choice of *endo* (for X = CHO) and *exo* (for X = OH) complexation was dictated by the experimentally observed stereochemistry of the actual substrates (Table 1 and Table 3).

Overall, the conversions of **B** into **C** are exothermic by 13–20 kcal mol^{-1}, and subsequent insertions to give species **D** require 1–11 kcal mol^{-1} and are exothermic by 8–18 kcal mol^{-1} (Scheme 15). As shown by carrying out a set of constrained geometry optimizations at successively smaller distances between Co and the center of ethene, ethenol, or 2-propenal, the addition of the alkene was found barrierless, whatever regioisomer considered (**C3** or **C′3**). This result is not surprising considering our previous report on this matter.[28h] In complexes of type **C3**, this rotation brings C^5 closer to C^4 with X = H, OH, or CHO, whereas in **C′3**, C^6 comes closer to C^1 (Scheme 14). The preferred orientation of the coordinated alkene in **C3** or **C′3** with disymmetric alkenes seems to depend on charges: the cobalt always bears a strongly positive charge, boron as a substituent imparts a strongly negative charge on C^4, whereas C^1 is only slightly negative (Scheme 16). In coordinated ethenol, C^5 is positive and C^6 negative. In coordinated 2-propenal, both C^5 and C^6 are negatively charged, the former more so than the latter. Thus, charge compensation appears to control the structures of **C3** and **C′3** and the subsequent specific creations of Co–C^6 and C^4–C^5 for ethenol, as reflected in $\mathbf{TS}_{\mathbf{C3\text{-}D3a}}$, and Co–$C^5$ and C^1–C^6 for 2-propenal, as reflected in $\mathbf{TS}_{\mathbf{C3\text{-}D3d}}$.

The most stable isomer **C3**/**C′3** also gives rise to the fastest insertion into Co–C^4/Co–C^1, respectively. When X = OH, **C3** is more stable than **C′3** by 2.6 kcal mol^{-1} (Scheme 15). On the other hand, when X = CHO, **C′3** is more stable than **C3** by 1.4 kcal mol^{-1}. With ethenol, the fastest reaction is that of **C3** to **D3a** ($\Delta H^{\neq}_{298}=1.0$ kcal mol^{-1}), which places the hydroxy group next to boron, as observed experimentally for *t*Bu and THP-substituted enol ethers (Table 1). On the other hand, relative to **C3**, the transition states to **D3b**, **D3c**, and **D3d** are found at higher energies, 10.5, 7.8, and 10.6 kcal mol^{-1}, respectively. For 2-propenal, the transformation of **C′3** into **D3d** requires only 2.2 kcal mol^{-1} and is appreciably exothermic by 18.2 kcal mol^{-1}. This transformation places the formyl group close to Ph, as in compounds **50** and **52** (Table 3).

We found that the charges of the free alkenes may be used to anticipate the best arrangement in complexes of type **C**. Thus, while the coordination of the alkene to cobalt changes the polarization compared to the free ligand, it maintains its direction. For instance, free ethenol shows charges of 0.118 and −0.553 on C^5 and C^6, respectively, as opposed to 0.202 and −0.649 in the complex. Similarly, the charges of −0.359 and −0.332 in 2-propenal become −0.445 and −0.374, respectively, after coordination. Consequently, for the first six examples depicted on Scheme 17, providing that the carbon atom which bears the strongest negative charge binds Co in **C** (as shown in Scheme 14), and that the positive (or moderately negative) charge at the other alkene carbon can accommodate the negative charge at C^4, complexes of type **C3** are expected. Thus, in these cases the carbon atom which bears the strongest negative charge becomes C^6 in the major product (Tables 1 and 2). This treatment nicely accounts for the reversal in regioselectivity between styrene and indene (the aryl group being placed next to C^4 in the former and next to C^1 in the latter). For the last two examples, the two alkene charges are strongly negative, as in the case of 2-propenal. In this case, one would expect the trimethylsilyl-substituted carbon atoms to stay attached to Co, thus linking their neighbors to C^1. After reductive



A1 (Ph) **TS**$_{A1\text{-}B2}$ (Ph) **B2** (Ph) **A2** (Ph)

TS$_{A2\text{-}B3}$ (Ph) **B3** (Ph) **C3** (X=H) **TS**$_{C3\text{-}D3d}$ (X=H)

D3d (X=H) **TS**$_{C3\text{-}D3a}$ (X=H) **D3a** (X=H) **TS**$_{D3a\text{-}E3}$

E3 **TS**$_{E3\text{-}F3}$ **F3** **TS**$_{C3\text{-}D3a}$ (X=OH)

TS$_{C'3\text{-}D3d}$ (X=OH) **TS**$_{C'3\text{-}D3c}$ (X=OH) **TS**$_{C3\text{-}D3b}$ (X=OH)

Figure 3. Structures of selected cobalt species appearing in this study, with selected bond lengths (Å).

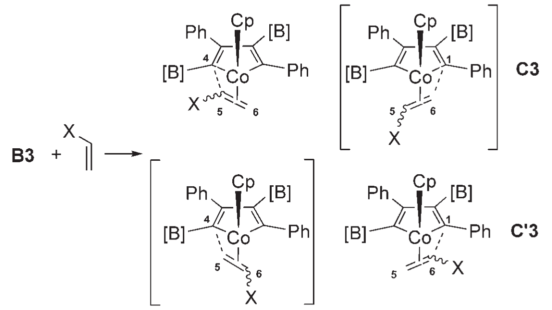
Table 4. Relative enthalpies [kcal mol^{-1}] relevant to the transformations described in Scheme 13, with **A 2** as a reference point.

	Compound	R = Ph	R = CH_2OMe	R = Me
1	**A1**	2.0	0.3	1.6
2	**TS**$_{A1\text{-}B2}$	21.0	16.2	17.6
3	**B2**	2.3	−8.2	−5.1
4	**A2**	0.0	0.0	0.0
5	**TS**$_{A2\text{-}B3}$	17.0	15.1	17.6
6	**B3**	−4.3	−3.4	−3.4

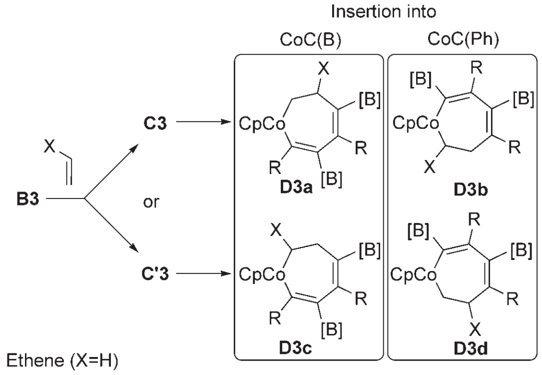
elimination, the Me_3Si groups would be expected at C^5 in the final products, as observed (Table 1).

The study of the mechanism for R = Ph was completed up to the final product **F3** (Scheme 18 and Figure 3): Insertion of ethene is faster into the Co−C(B) bond (**C3**→**D3 a**), rather than into the Co−C(Ph) bond (**C3**→**D3 d**), especially with R = Ph (3.1 vs. 7.5 kcal mol^{-1} of enthalpy of activation). Complex **D3 a** is transformed into the cobaltanorbornene **E3** ($\Delta H^{\ddagger}_{298} = 7.1$ kcal mol^{-1}; $\Delta H_{298} = -4.8$ kcal), which reductively eliminates CoCp to give the final product **F3**, with a large exothermicity of 34.8 kcal mol^{-1} ($\Delta H^{\ddagger}_{298} = 7.4$ kcal mol^{-1}).[43] Thus, the mechanism previously described[28h] could be reproduced successfully for boryl alkynes.

To summarize the above, the classical cobaltacyclopentadiene route to cyclohexadienes appears consistent with the



Scheme 14. Orientation of the coordinated alkene in optimized rotamers of the stereoisomers **C3** and **C′3**.



Ethene (X=H)

	B3 → C3	C3 → D3a		C'3 → D3d	
	ΔH_{298}	$\Delta H^{\ddagger}_{298}$	ΔH_{298}	$\Delta H^{\ddagger}_{298}$	ΔH_{298}
R=Ph	–17.9	3.1	–12.0	7.5	–11.7
R=CH_2OMe	–20.2	4.5	–13.9	5.8	–14.2
R=Me	–15.5	3.2	–15.3	4.2	–12.5

Ethenol (X=OH), R=Ph

	$\Delta H^{\ddagger}_{298}$	ΔH_{298}
B3 → C3	-	–18.0
B3 → C'3	-	–15.4
C3 → D3a	1.0	–10.9
C3 → D3b	10.5	–8.4
C'3 → D3c	5.1 (7.8)	–12.1
C'3 → D3d	8.0 (10.6)	–11.3

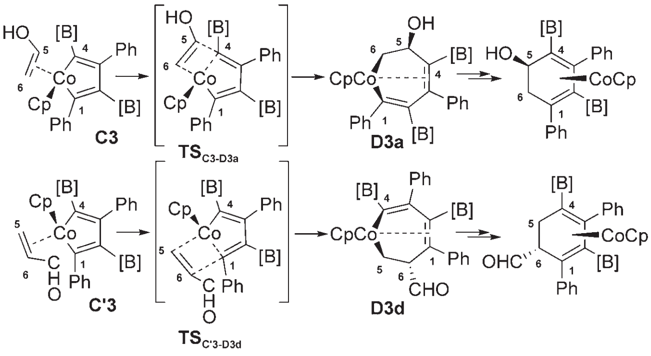
2-Propenal (X=CHO), R=Ph

	$\Delta H^{\ddagger}_{298}$	ΔH_{298}
B3 → C3	-	–12.9
B3 → C'3	-	–14.3
C3 → D3a	6.4 (8.0)	–16.9
C3 → D3b	8.9 (10.5)	–7.0
C'3 → D3c	5.4	–10.3
C'3 → D3d	2.2	–18.2

Scheme 15. Reactions of cobaltacyclopentadienes **B** with ethene, ethenol, or 2-propenal, and subsequent insertions to give cobaltacycloheptadienes **D**. Relative enthalpies are given in kcal mol^{-1}. Enthalpies of activation relative to the most stable isomer **C3** (X = OH) or **C′3** (X = CHO) are given in parentheses.

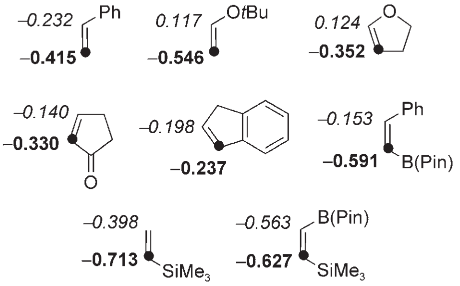
bulk of the experimental results, except for the observation of 1,4-diboryl-1,3-cyclohexadiene complexes **29**, **35**, and **38**. This complication warranted a brief exploration of the mechanism described in Scheme 12. In this pathway, the regioselectivity between the two boryl groups is decided after the oxidative cyclization to **H**, either during complexation of the alkyne to the unsaturated cobaltacyclopentene or during the subsequent insertion.[36] We computed the energetics of CoCp-mediated couplings of borylalkynes with ethene or ethenol (Scheme 19).

The results show that the formation of species **H** requires relatively high enthalpies of activation of 22–27 kcal mol^{-1} and is usually endothermic. Although not depicted in the

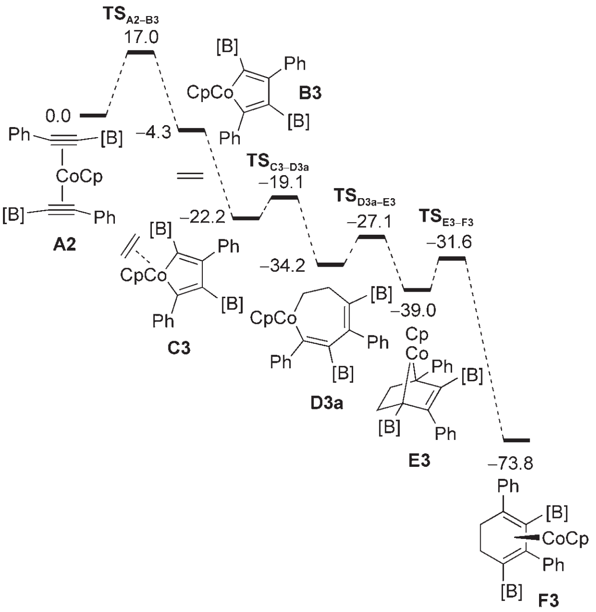


	C3	C'3	$TS_{C3\text{-}D3a}$	$TS_{C'3\text{-}D3d}$
Co	0.609	0.563	0.609	0.581
C^1	–0.064	–0.061	–0.058	–0.096
C^4	–0.482	–0.444	–0.541	–0.501
C^5	0.202	–0.445	0.272	–0.516
C^6	–0.649	–0.374	–0.676	–0.328

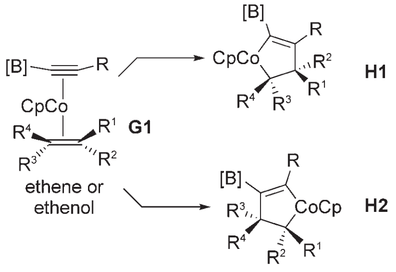
Scheme 16. Examples of natural bond orbital (NBO) charges for the insertion of ethenol and 2-propenal, respectively, in **C3/C′3**.



Scheme 17. Examples of NBO charges (the carbon atom that bears the strongest negative charge is highlighted).



Scheme 18. Energy profile (kcal mol^{-1}) for the formation of complex **F3**.



Ethene

R =	Ph	CH$_2$OMe	Me
G1	0.0	0.0	0.0
TS$_{G1–H1}$	23.4	23.4	22.7
H1	2.6	–0.7	0.6
TS$_{G1–H2}$	23.3	25.0	24.4
H2	4.8	4.2	3.6

Ethenol

R = Ph	R^1=OH	R^2=OH	R^3=OH	R^4=OH
G1	0.0	0.0	0.0	0.0
TS$_{G1–H1}$	22.5	25.6	25.4	26.8
H1	4.5	4.0	–3.1	1.5
TS$_{G1–H2}$	26.4	22.8	22.4	23.6
H2	–10.0	4.2	5.9	5.6

Scheme 19. CoCp-mediated formation of cobaltacyclopentenes. Relative enthalpies are given in kcal mol^{-1}.

scheme, the subsequent complexation of a borylalkyne to give species of type **I** is only modestly exothermic by 0–4 kcal mol^{-1}. Thus, the relatively disfavored energetics of the cobaltacyclopentene pathway led us to discard this option.[44] Thus, we are left with the possibility that in solution the computed energetic distinction between **TS$_{A1-B2}$** and **TS$_{A2-B3}$** are less pronounced, in general or just for enol ethers. Perhaps further experimentation will shed light on this problem.

Conclusion

We have explored the scope of the CoCp-mediated [2+2+2] cocyclization of alkynyl boronates with alkenes. The proper choice of substituents on the alkyne allows the selective formation of 1,3- or 1,4-diboryl-1,3-cyclohexadiene cobalt complexes. The 1,3- or 1,4-arrangement of the boryl groups is dependent on the choice of alkene taking part in the cyclization. The complexes could be demetallated by using iron(III) chloride, and the resulting cyclohexadienes were submitted to cross-coupling with haloarenes yielding polyarylated systems. DFT computations showed that the previously described mechanism of the cyclic 2:1 cooligomerization of alkynes with alkenes to give 1,3-cyclohexadienes remains generally valid, although at present the occasional formation of 1,4-diborylated products is left unexplained. We have rationalized the regioselectivity of alkene incorporation into diphenylated diborylcobaltacyclopentadienes by proposing polarization as the controlling factor.

Experimental Section

General methods: Reactions were carried out under argon by using standard Schlenk techniques. THF was distilled over sodium/benzophenone ketyl. Hexane and toluene were distilled from NaK$_{2.8}$. Thin-layer chromatography (TLC) was performed on Merck 60 F$_{254}$ silica gel. Merck Gerudan SI 60 Å silica gel (35–70 µm) was used for column chromatography. ^{11}B NMR was performed at 96 MHz on a Bruker AC300 spectrometer by using BF$_3$·OEt$_2$ as external standard. ^{1}H and ^{13}C spectra were recorded at room temperature at 400 and 100 MHz, respectively, on a Bruker ARX400 spectrometer. The term *exo* refers to protons in an *anti* relationship with cobalt. The term *endo* refers to protons in a *syn* relationship with cobalt. Chemical shifts are given in ppm, referenced to the residual proton resonance of the solvents (δ = 7.26 ppm for CDCl$_3$) or to the residual carbon resonance of the solvent (δ = 77.16 ppm for CDCl$_3$) Coupling constants (J) are given in Hertz (Hz). The term pin refers to the pinacol group. The terms m, s, d, t, and q refer to multiplet, singlet, doublet, triplet and quartet, respectively; br means that the signal is broad. Due to the boron quadrupole, ^{13}C NMR signals of carbon atoms attached to boron are very broad and may not be observed. When possible, ^{1}H and ^{13}C signals were assigned mostly on the basis of DEPT and 2D-NMR (COSY, HMBC) experiments. In the description of the ^{13}C NMR spectra, a number at the beginning of the information in parentheses refers to accidentally isochronous carbons. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse de l'ICSN-CNRS, Gif-sur-Yvette. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. Absorbance frequencies are given at the peak maximum and at the medium C≡C triple bond band. Melting points were obtained on a Büchi capillary apparatus and were uncorrected.

Starting alkynes: Compounds **7**, **8**, **11**, **12**, **13**, **59**, and **61** were described previously.[13k,14] The same experimental procedure allowed the preparation of the following alkynes:

Alkyne 9: Golden solid; m.p. 72–76 °C; ^{1}H NMR (CDCl$_3$): δ = 1.26 (s, 12H; pin), 3.64 (s, 2H; CH$_2$), 7.20–7.35 (m, 3H), 7.41–7.45 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): δ = 23.4 (CH$_2$), 24.7 (CH$_3$, pin), 84.4 (C, pin), 99.0 (CH$_2$CCB), 127.0 (CH$_{arom}$), 129.1 (CH$_{arom}$), 130.0 (CH$_{arom}$), 135.2 ppm (C); CH$_2$CCB unobserved; ^{11}B NMR (CDCl$_3$): δ = 21 ppm; IR (neat): $\tilde{\nu}$ = 1140, 1336, 2210 (m, C≡C), 2979 cm^{-1}.

Alkyne 10: Colorless oil; b.p. (1 Torr) 93 °C; ^{1}H NMR (CDCl$_3$): δ = 0.97 (d, J = 6.6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.27 (s, 12H; pin), 1.84 (nonet, J = 6.6 Hz, 1H; C*H*(CH$_3$)$_2$), 2.14 ppm (d, J = 6.6 Hz, 2H; CH$_2$); ^{13}C NMR (CDCl$_3$): δ = 22.1 (CH(*C*H$_3$)$_2$), 24.8 (CH$_3$, pin), 27.8 (*C*H(CH$_3$)$_2$), 28.8 (CH$_2$), 84.1 (C, pin), 104.1 ppm (CH$_2$CCB); CH$_2$C*C*B unobserved; ^{11}B NMR (CDCl$_3$): δ = 22 ppm; IR (neat): $\tilde{\nu}$ = 1140, 1309, 1332, 1342, 2207 (m, C≡C), 2960 cm^{-1}.

Alkyne 57: Pink solid; m.p. 178–182 °C; ^{1}H NMR (CDCl$_3$): δ = 1.24 (s, 24H; pin), 2.41 (s, 3H; CH$_3$), 4.20 (s, 4H; CH$_2$), 7.29 (d, J = 7.8 Hz, 2H), 7.70 ppm (d, J = 7.8 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ = 21.9 (CH$_3$), 24.9 (CH$_3$, pin), 37.2 (CH$_2$), 84.7 (C, pin), 95.0 (CH$_2$CCB), 128.3 (CH$_{arom}$), 130.0 (CH$_{arom}$), 135.2 (C), 144.2 ppm (CH$_{arom}$); CH$_2$C*C*B unobserved; ^{11}B NMR (CDCl$_3$): δ = 23 ppm; IR (neat): $\tilde{\nu}$ = 1140, 1163, 1332, 2217 (m, C≡C), 2980 cm^{-1}.

General procedure for ethene insertion: [CoCp(C$_2$H$_4$)$_2$] (**1**) (360 mg, 2 mmol) was dissolved in THF (8 mL). The solution was cooled to −40 °C. The argon atmosphere was replaced by ethene. The alkyne (4 mmol) or the diyne (2 mmol) in THF (4 mL) were transferred by cannula into the cold mixture. The cold bath was removed and the mixture stirred at room temperature for 4 h. The solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography with gradient mixtures of pentane and diethyl ether (deep red bands).

General procedure for alkene insertion: [CoCp(C$_2$H$_4$)$_2$] (**1**) (360 mg, 2 mmol) was dissolved in THF (8 mL). The alkene (5 equiv) was added neat and the mixture allowed to stir for 4 h at room temperature. The alkyne (4 mmol) or the diyne (2 mmol) in THF (2 mL), was transferred by cannula into the mixture at −40°C. The cold bath was removed and the mixture stirred at room temperature for 4 h. The solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography with gradient mixtures of pentane and diethyl ether (deep red bands).

General procedure for oxidative demetallation: The complex (0.4 mmol) was dissolved in acetonitrile (5 mL) in open air. FeCl$_3$·6H$_2$O (162 mg, 0.6 mmol) was added in one portion at room temperature. The color of the solution turned instantly from red to violet. The mixture was promptly evaporated and the residue submitted to flash chromatography over silica gel. Solid compounds were recrystallized in hexane.

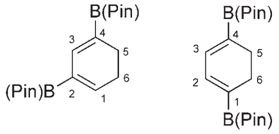
General procedure for Suzuki coupling: A dried flask was charged under argon atmosphere with (tBu$_3$P)$_2$Pd (0.1 equiv), anhydrous THF, and the iodoarene (1 to 2 equiv). After 5 min, a solution of the cyclohexadiene (1 equiv) in THF was added to the mixture. Solid sodium hydroxide (2.7 or 5.4 equiv) and water (2.7 or 5.4 equiv) were introduced at once. The reaction mixture was refluxed overnight and allowed to cool to room temperature. Water and diethyl ether were added and the aqueous layer was separated and extracted with diethyl ether. The combined organic extracts were washed with water, dried over MgSO$_4$, and concentrated. The residue was purified by flash column chromatography with gradient mixtures of pentane and diethyl ether.

Compounds **12**, **14**, **15**, **18–21**, **62**, **65** and **66** were described previously.[14]

1,3,5-Tris(pinacolboryl)benzene (4a)[25] and 1,2,4-tris(pinacolboryl)benzene (4b) (1:1.5 mixture)

*Data for **4a***: ^{1}H NMR (CDCl$_3$): $\delta = 1.31$ (s, 36H; pin), 8.36 ppm (s, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 25.0$ (CH$_3$, pin), 83.8 (C, pin), 144.2 ppm (CH$_{\text{arom}}$); C^1, C^3, and C^5 unobserved.

*Data for **4b***: $\delta = 1.24$ (s, 12H; pin), 1.34 (s, 12H; pin), 1.35 (s, 12H; pin), 7.60 (dd, $J = 7.3$, 0.8 Hz, 1H), 7.78 (dd, $J = 7.3$, 1.2 Hz, 1H), 8.06 ppm (brs, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 24.9$ (CH$_3$, pin), 83.7, 83.8, 83.9 (C, pin), 132.5, 135.4, 139.6 ppm (CH$_{\text{arom}}$); C^1, C^2, and C^4 unobserved; IR (neat): $\tilde{\nu} = 1140$, 1322, 2361, 2977 cm^{-1}; HRMS (ES+): m/z calcd for C$_{24}$H$_{39}$B$_3$O$_6$Na: 479.2924; found: 479.2934.



General numbering of the cyclohexadiene ring used in this section:

Data for 5 and 6 (6.3:1 mixture, admixed with 4a): Red solid; ^{1}H NMR (CDCl$_3$): $\delta = 0.44$–0.51 (m, 1.6H; H^{5,6}*exo* **6** and H*exo* **5**), 0.74–0.85 (m, 1H; H*exo*, **5**), 1.26–1.38 (m, 27.8H; pin, **5** and **6**), 1.57–1.61 (m, 2H; H^{5,6}*endo*, **5**), 2.16–2.20 (m, 0.3H; H^{5,6}*endo*, **6**), 3.55 (s, 1H; H^1, **5**), 4.71 (s, 5H; Cp, **5**), 4.72 (s, 0.8H; **6**), 5.66 (s, 0.3H; H^{2,3}, **6**), 5.80 ppm (s, 1H; H^3, **5**); ^{13}C NMR (CDCl$_3$): $\delta = 24.5$ (CH$_3$, pin), 24.7 (CH$_2$), 24.8 (CH$_3$, pin), 24.9 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.4 (CH$_3$, pin), 25.5 (CH$_3$, pin), 25.9 (CH$_2$), 26.9 (CH$_2$), 59.1 (CH, C^1, **5**), 78.8 (CH, Cp, **6**), 79.0 (CH, Cp, **5**), 81.5 (C, pin, **5**), 81.6 (C, pin, **6**), 82.1 (C, pin, **5**), 82.7 (C, pin, **6**), 85.9 (CH, C^{2,3}, **6**), 89.5 ppm (CH, C^3, **5**); C^2 and C^4 of **5** and C^1 and C^4 of **6** unobserved; IR (neat): $\tilde{\nu} = 731$, 1139, 1318, 2976 cm^{-1}.

Data for 16A: White solid; m.p. 157–159°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.23$ (s, 12H; pin), 1.28 (s, 12H; pin), 1.86–1.95 (m, 2H), 2.02–2.12 (m, 2H), 4.09 (s, 2H; C*H*$_2$SPh), 4.39 (s, 2H; C*H*$_2$SPh), 7.10–7.20 (m, 4H), 7.22–7.30 (m, 4H), 7.42–7.48 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 24.9$ (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.7 (C^5), 27.7 (C^6), 37.0 (CH$_2$S), 40.1 (CH$_2$S), 83.0 (C, pin), 83.4 (C, pin), 126.2 (CH$_{\text{arom}}$), 126.3 (CH$_{\text{arom}}$), 128.2 (CH$_{\text{arom}}$), 128.8 (CH$_{\text{arom}}$), 130.4 (CH$_{\text{arom}}$), 131.8 (CH$_{\text{arom}}$), 135.5 (C), 136.8 (C), 148.3 (C), 153.0 ppm (C); C^2 and C^4 unobserved; ^{11}B NMR (CDCl$_3$): $\delta = 30$ ppm; IR (neat): $\tilde{\nu} = 1140$, 1271, 2978 cm^{-1}; elemental analysis calcd (%) for C$_{32}$H$_{42}$B$_2$O$_4$S$_2$: C 66.68, H 7.34; found: C 66.72, H 7.38.

Data for 16B: White solid; m.p. 100–107°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.24$ (s, 24H; pin), 1.95 (s, 4H; H^{5,6}), 4.33 (s, 4H; C*H*$_2$S), 7.15–7.30 (m, 6H), 7.32–7.40 ppm (m, 4H); ^{13}C NMR (CDCl$_3$): $\delta = 24.9$ (CH$_3$, pin), 25.2 (C^{5,6}), 34.8 (CH$_2$S), 83.3 (C, pin), 126.6 (CH$_{\text{arom}}$), 128.5 (CH$_{\text{arom}}$), 131.9 (CH$_{\text{arom}}$), 135.9 (C), 145.2 ppm (C^{2,3}); C^1 and C^4 unobserved; ^{11}B NMR (CDCl$_3$): $\delta = 31$ ppm; IR (neat): $\tilde{\nu} = 1139$, 1296, 2976 cm^{-1}; elemental analysis calcd (%) for C$_{32}$H$_{42}$B$_2$O$_4$S$_2$: C 66.68, H 7.34; found: C 66.75, H 7.32.

Data for 17A and 17B (1.8:1 mixture): White solid; m.p. 180–185°C; **17A**: ^{1}H NMR (CDCl$_3$): $\delta = 0.82$ (d, $J = 6.6$ Hz, 6H), 0.83 (d, $J = 6.6$ Hz, 6H), 1.25 (s, 12H; pin), 1.31 (s, 12H; pin), 1.44–1.89 (m, 4H), 2.04–2.12 (m, 2H), 2.20 (d, $J = 7.6$ Hz, 2H), 2.50 (d, $J = 7.3$ Hz, 2H); **17B**: 0.89 (d, $J = 6.6$ Hz, 12H), 1.28 (s, 24H; pin), 1.44–1.89 (m, 2H), 1.95 (s, 4H; H^{5,6}), 2.42 ppm (d, $J = 7.1$ Hz, 4H); ^{13}C NMR (CDCl$_3$): $\delta = 22.2$ (CH$_3$), 22.4 (CH$_3$), 22.7 (CH$_3$), 24.8 (CH$_3$), 24.9 (CH$_3$), 25.0 (CH$_3$), 25.2 (CH$_2$), 25.3 (CH$_2$), 27.5 (CH), 28.3 (CH$_2$), 28.4 (CH), 28.7 (CH), 40.1 (CH$_2$), 42.9 (CH$_2$), 46.5 (CH$_2$), 82.6 (C, pin), 82.9 (C, pin), 83.2 (C, pin), 151.4 (C), 153.0 (C), 154.0 ppm (C); **17A**-C^2, **17A**-C^4, **17B**-C^{1,4} unobserved; ^{11}B NMR (CDCl$_3$): $\delta = 31$ ppm; IR (neat): $\tilde{\nu} = 1141$, 1270, 1294, 2868, 2953 cm^{-1}; elemental analysis calcd (%) for C$_{26}$H$_{46}$B$_2$O$_4$: C 70.29, H 10.44; found: C 70.18, H 10.21.

Data for 23: Red solid; m.p. 250°C; ^{1}H NMR (CDCl$_3$): $\delta = 0.53$ (s, 6H; pin), 0.71 (s, 6H; pin), 0.82 (s, 6H; pin), 0.92 (s, 6H; pin), 0.99 (s, 6H; pin), 1.07 (s, 6H; pin), 2.63 (d, $J = 11.6$ Hz, 1H; H^6*endo*), 3.84 (d, $J = 11.6$ Hz, 1H; H^5*endo*), 4.69 (s, 5H; Cp), 6.96–7.26 (m, 13H), 7.72 ppm (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 24.1$ (CH$_3$, pin), 24.4 (CH$_3$, pin), 24.5 (CH$_3$, pin), 24.9 (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.3 (CH$_3$, pin), 49.3 (CH, C^5), 71.3 (C, C^1), 81.8 (C, pin), 82.4 (C, pin), 83.3 (CH, Cp), 83.4 (C, pin) 105.6 (C, C^3), 124.2 (CH$_{\text{arom}}$), 124.9 (CH$_{\text{arom}}$), 125.7 (CH$_{\text{arom}}$), 126.0 (CH$_{\text{arom}}$), 127.1 (2C, CH$_{\text{arom}}$), 128.4 (CH$_{\text{arom}}$), 129.1 (CH$_{\text{arom}}$), 132.2 (CH$_{\text{arom}}$), 142.0 (C), 145.8 (C), 149.2 ppm (C); C^2, C^4 and C^6 unobserved; IR (neat): $\tilde{\nu} = 699$, 1142, 1330, 1371, 1447, 2977 cm^{-1}; HRMS (ES+): m/z calcd for C$_{47}$H$_{58}$B$_3$CoO$_6$Na: 833.3742; found: 833.3719.

Data for 24: Red solid; m.p. 190°C; ^{1}H NMR (CDCl$_3$): $\delta = 0.65$ (s, 9H; tBu), 0.80 (s, 6H; pin), 0.96 (s, 6H; pin), 1.10 (s, 6H; pin), 1.20 (dd, $J = -15.4$, 6.8 Hz, 1H; H^6*exo*), 1.22 (s, 6H; pin), 1.68 (dd, $J = -15.1$, 2.8 Hz, 1H; H^6*endo*), 2.70 (dd, $J = 6.8$, 2.8 Hz, 1H; H^5*exo*), 4.91 (s, 5H; Cp), 7.06–7.26 (m, 8H), 7.51 ppm (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 24.4$ (CH$_3$, pin), 25.3 (2C, CH$_3$, pin), 25.4 (CH$_3$, pin), 28.1 (CH$_3$, tBu), 39.9 (CH$_2$, C^6), 72.4 (C, possibly C^1), 72.6 (C, possibly C^1), 79.2 (CH, C^5), 82.1 (C, pin), 82.8 (CH, Cp), 83.8 (C, pin), 105.8 (C, C^3), 125.2 (CH$_{\text{arom}}$), 126.2 (2C, CH$_{\text{arom}}$), 126.8 (CH$_{\text{arom}}$), 131.1 (CH$_{\text{arom}}$), 132.3 (CH$_{\text{arom}}$), 142.5 (C), 147.1 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu} = 690$, 802, 1139, 1289, 1387, 2973 cm^{-1}; HRMS (ES+): m/z calcd for C$_{39}$H$_{51}$B$_2$CoO$_5$Na: 703.3152; found: 703.3168.

Data for 27: Red oil; ^{1}H NMR (CDCl$_3$): $\delta = 0.85$ (s, 6H; pin), 0.92 (s, 6H; pin), 1.00 (s, 6H; pin), 1.06 (s, 6H; pin), 1.58–1.85 (m, 5H; includes H^6*exo*), 1.94–2.10 (m, 2H), 2.26 (dd, $J = -15.1$, 1.3 Hz, 1H; H^6*endo*), 3.29 (dd, $J = 6.9$, 1.6 Hz, 1H; H^5*exo*), 3.56–3.63 (m, 1H), 4.05–4.13 (m, 1H), 4.83 (s, 5H; Cp), 4.96–4.99 (m, 1H), 7.08–7.27 (m, 8H), 7.62 ppm (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 20.1$ (CH$_2$), 24.5 (CH$_3$, pin), 24.8 (CH$_3$, pin), 24.9 (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.9 (CH$_2$), 31.5 (CH$_2$), 38.8 (CH$_2$), 62.6 (CH$_2$), 66.3 (C, C^1), 79.8 (CH, C^5), 82.1 (C, pin), 83.1 (CH, Cp), 83.8 (C, pin), 100.9 (CH), 106.7 (C, C^3), 124.2 (CH$_{\text{arom}}$), 126.5 (CH$_{\text{arom}}$), 126.7 (CH$_{\text{arom}}$), 127.4 (2C, CH$_{\text{arom}}$), 127.5 (CH$_{\text{arom}}$), 141.2 (C), 149.0 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu} = 699$, 800, 1021, 1142, 1261, 1367, 2954 cm^{-1}.

Data for 29: Red oil; ^{1}H NMR (CDCl$_3$): $\delta = 0.97$ (s, 6H; pin), 1.02 (s, 6H; pin), 1.16 (s, 6H; pin), 1.30 (s, 6H; pin), 1.50–1.67 (m, 4H), 1.73 (dd, $J = -16.2$, 2.8 Hz, 1H; H^6*exo*), 1.78–1.90 (m, 2H), 2.95 (dd, $J = -16.2$, 11.8 Hz, 1H; H^6*endo*), 3.34 (dd, $J = 11.6$, 2.8 Hz, 1H; H^5*endo*), 3.46–3.52 (m, 1H), 3.90–3.97 (m, 1H), 4.83 (s, 5H; Cp), 5.26–5.29 (m, 1H), 7.00–7.26 ppm (m, 10H); ^{13}C NMR (CDCl$_3$): $\delta = 19.8$ (CH$_2$), 24.9 (CH$_3$, pin), 25.0 (2C, CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_2$), 31.4 (CH$_2$), 41.7 (CH, C^5), 43.0 (CH$_2$, C^6), 62.5 (CH$_2$), 81.9 (CH, Cp), 82.0 (C, pin), 83.6 (C, pin), 99.0 (CH), 109.0 (C), 124.9 (CH$_{\text{arom}}$), 125.8 (CH$_{\text{arom}}$), 126.3 (CH$_{\text{arom}}$), 127.4 (CH$_{\text{arom}}$), 127.7 (CH$_{\text{arom}}$), 131.2 (CH$_{\text{arom}}$), 141.8 (C), 147.6 ppm (C); C^1, C^4 and an additional C unobserved; IR (neat): $\tilde{\nu} = 699$, 1142, 1260, 1368, 2925 cm^{-1}.

Data for 30 and 31: Red solid (1:1.6 mixture); ^{1}H NMR (CDCl$_3$): $\delta = -0.25$ (s, 9H; TMS, **30**), 0.20 (s, 14.4H; TMS, **31**), 0.84 (s, 6H; pin, **30**), 0.86 (s, 9.6H; pin, **31**), 0.93 (s, 9.6H; pin, **31**), 1.00 (s, 15.6H; 2 pin, **30** and **31**), 1.04 (s, 9.6H; pin, **31**), 1.14 (s, 6H; pin, **30**), 1.20 (s, 6H; pin, **30**), 1.28–1.35 (m, 2.6H; H^6*exo* **30** and H^5*exo* **31**), 1.58 (dd, *J*=15.0, 2.5 Hz, 1H; H^6*endo* **30**), 1.84 (dd, *J*=−14.9, 1.8 Hz, 1.6H; H^5*endo* **31**), 3.04 (dd, *J*=6.7, 2.4 Hz, 1H; H^5*exo* **30**), 3.45 (dd, *J*=6.3, 1.8 Hz, 1.6H; H^6*exo* **31**), 4.82 (s, 7.9H; Cp, **31**), 4.93 (s, 5H; Cp, **30**), 7.11–7.26 (m, 20.8H; **30** and **31**), 7.54 (d, *J*=7.5 Hz, 2H; **30**), 7.60 ppm (d, *J*=7.1 Hz, 2H; **31**); ^{13}C NMR ($CDCl_3$): δ=−0.1 (CH_3, TMS, **30**), 0.9 (CH_3, TMS, **31**), 24.3 (CH_3, pin, **30**), 24.5 (CH_3, pin, **31**), 24.6 (CH_3, pin, **31**), 24.7 (CH_3, pin, **31**), 25.1 (CH_3, pin, **31**), 25.1 (CH_3, pin, **30**), 25.3 (CH_3, pin, **30**), 25.4 (CH_3, pin, **30**), 38.7 (CH_2, C^6, **30**), 41.4 (CH_2, C^5, **31**), 70.4 (CH, C^6, **31**), 72.8 (CH, C^5, **30**), 65.5 (C, C^1, **30** and **31**), 82.1 (C, pin, **31**), 82.2 (C, pin, **30**), 82.9 (CH, Cp, **30**), 83.2 (CH, Cp, **31**), 83.8 (C, pin, **30** and **31**), 106.1 (C, C^3, **30**), 106.4 (C, C^3, **31**), 124.2 (CH_{arom}, **31**), 125.2 (CH_{arom}, **30**), 126.2 (CH_{arom}, **30**), 126.4 (CH_{arom}, **31**), 126.5 (CH_{arom}, **30**), 126.7 (CH_{arom}, **31**), 126.8 (CH_{arom}, **30**), 127.2 (CH_{arom}, **31**), 127.5 (2C, CH_{arom}, **31**), 131.4 (CH_{arom}, **30**), 131.6 (CH_{arom}, **30**), 141.2 (C, **31**), 142.3 (C, **30**), 146.7 (C, **30**), 149.2 ppm (C, **31**); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$=693, 759, 803, 835, 1070, 1140, 1250, 1292, 2974 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{38}H_{51}B_2CoO_5SiNa$: 719.2922; found: 719.2913.

Data for 35: Red oil; ^{1}H NMR ($CDCl_3$): δ=1.00 (s, 6H; pin), 1.06 (s, 6H; pin), 1.20 (s, 6H; pin), 1.24–1.30 (m, 9H; pin and Et-CH_3), 1.72 (dd, *J*=−15.4, 2.3 Hz, 1H; H^6*exo*), 2.95 (dd, *J*=−15.2, 11.6 Hz, 1H; H^6*endo*), 3.39 (dd, *J*=11.6, 2.0 Hz, 1H; H^5*endo*), 3.72–3.80 (m, 1H), 3.93–4.01 (m, 1H), 4.88 (s, 5H; Cp), 7.00–7.26 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ= 15.7 (CH_3), 24.6 (CH_3, pin), 24.9 (CH_3, pin), 25.0 (2C, CH_3, pin), 40.8 (CH_2, C^6), 41.4 (CH, C^5), 62.8 (CH_2), 81.8 (CH, Cp), 82.0 (C, pin), 83.7 (C, pin), 97.8 (C), 108.9 (C), 124.9 (CH_{arom}), 125.7 (CH_{arom}), 126.3 (CH_{arom}), 127.3 (CH_{arom}), 127.8 (CH_{arom}), 131.2 (CH_{arom}), 141.9 (C), 147.7 ppm (C); C^1 and C^4 unobserved; IR (neat): $\tilde{\nu}$=700, 1143, 1261, 1311, 1379, 2977 cm^{-1}; elemental analysis calcd (%) for $C_{37}H_{47}B_2CoO_5$: C 68.13, H 7.26; found: C 68.12, H 7.59

Data for 38: Red oil; ^{1}H NMR ($CDCl_3$): δ=0.94–0.99 (m, 9H; pin and Bu-CH_3), 1.05 (s, 6H; pin), 1.17 (s, 6H; pin), 1.27 (s, 6H; pin), 1.45–1.54 (m, 2H), 1.56–1.65 (m, 2H), 1.69 (dd, *J*=−15.4, 2.3 Hz, 1H; H^6*exo*), 2.95 (dd, *J*=−15.2, 11.6 Hz, 1H; H^6*endo*), 3.38 (dd, *J*=11.6, 2.2 Hz, 1H; H^5*endo*), 3.61–3.68 (m, 1H), 3.86–3.93 (m, 1H), 4.87 (s, 5H; Cp), 7.00–7.17 (m, 9H), 7.22–7.27 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ=15.1 (CH_3), 19.6 (CH_2), 24.8 (CH_3, pin), 24.9 (CH_3, pin), 25.0 (2C, CH_3, pin), 32.4 (CH_2), 40.9 (CH_2, C^6), 41.4 (CH, C^5), 66.9 (CH_2), 81.7 (CH, Cp), 82.0 (C, pin), 83.6 (C, pin), 97.6 (C), 108.9 (C), 124.9 (CH_{arom}), 125.7 (CH_{arom}), 126.3 (CH_{arom}), 127.3 (CH_{arom}), 127.8 (CH_{arom}), 131.2 (CH_{arom}), 142.0 (C), 147.8 ppm (C); C^1 and C^4 unobserved; IR (neat): $\tilde{\nu}$=700, 1141, 1260, 1309, 1371, 2929 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{39}H_{51}B_2CoO_5Na$: 703.3152; found: 703.3177; elemental analysis calcd (%) for $C_{39}H_{51}B_2CoO_5$: C 68.85, H 7.56; found: C 69.23, H 7.64.

Data for 39: Red solid; m.p. 220°C; ^{1}H NMR ($CDCl_3$): δ=0.72 (dd, *J*= 9.5, 4.4 Hz, 1H; H^5*exo*), 0.89 (s, 6H; pin), 0.90 (s, 6H; pin), 0.98 (s, 6H; pin), 1.04 (s, 6H; pin), 1.16 (dd, *J*=−14.6, 9.6 Hz, 1H; H^6*exo*), 1.36 (s, 6H; pin), 1.37 (s, 6H; pin), 1.81 (dd, *J*=−14.8, 4.6 Hz, 1H; H^6*endo*), 4.77 (s, 5H; Cp), 7.07–7.23 (m, 8H), 7.62 ppm (d, *J*=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=24.4 (CH_3, pin), 24.5 (CH_3, pin), 24.6 (CH_3, pin), 25.1 (CH_3, pin), 25.2 (CH_3, pin), 25.6 (CH_3, pin), 31.6 (CH_2, C^6), 67.3 (C, C^1), 82.3 (C, pin), 82.5 (C, pin), 83.4 (CH, Cp), 83.7 (C, pin), 106.7 (C, C^3), 124.1 (CH_{arom}), 126.1 (CH_{arom}), 127.4 (2C, CH_{arom}), 127.5 (2C, CH_{arom}), 142.0 (C), 149.9 ppm (C); C^2, C^4 and C^5 unobserved; IR (neat): $\tilde{\nu}$=699, 1141, 1310, 1370, 2976 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{41}H_{54}B_3CoO_6Na$: 757.3429; found: 757.3445.

Data for 40: Red solid; m.p. 229°C; ^{1}H NMR ($CDCl_3$): δ=0.81–0.86 (m, 7H; pin and H^6*exo*), 0.97 (s, 6H; pin), 1.00 (s, 6H; pin), 1.14 (s, 6H; pin), 1.18 (s, 6H; pin), 1.19 (s, 6H; pin), 1.38 (dd, *J*=8.9, 4.3 Hz, 1H; H^5*exo*), 1.71 (dd, *J*=−14.1, 3.8 Hz, 1H; H^5*endo*), 4.92 (s, 5H; Cp), 7.05–7.24 (m, 8H), 7.56 ppm (d, *J*=7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=24.2 (CH_3, pin), 24.6 (CH_3, pin), 24.8 (CH_3, pin), 24.9 (CH_3, pin), 25.0 (CH_3, pin), 25.5 (CH_3, pin), 29.1 (CH_2, C^5), 71.8 (C, C^1), 82.1 (C, pin), 82.3 (C, pin), 83.2 (CH, Cp), 83.6 (C, pin), 105.4 (C, C^3), 124.6 (CH_{arom}), 126.0 (CH_{arom}), 126.6 (CH_{arom}), 127.0 (CH_{arom}), 129.2 (CH_{arom}), 131.7 (CH_{arom}), 142.6 (C), 149.6 ppm (C); C^2, C^4 and C^6 unobserved; IR (neat): $\tilde{\nu}$=700, 805, 1142, 1262, 1309, 1371, 2928, 2977 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{41}H_{54}B_3CoO_6Na$: 757.3429; found: 757.3464.

Data for 45: Red solid; m.p. 180°C; ^{1}H NMR ($CDCl_3$): δ=−0.10 (d, *J*= 8.1 Hz, 1H; H^5*exo*), 0.13 (s, 9H; TMS), 0.78 (s, 6H; pin), 0.99 (s, 6H; pin), 1.03 (s, 6H; pin), 1.12 (s, 6H; pin), 1.25 (s, 6H; pin), 1.28 (s, 6H; pin), 1.78 (d, *J*=8.1 Hz, 1H; H^6*exo*), 4.95 (s, 5H; Cp), 7.08–7.26 (m, 8H), 7.62 ppm (d, *J*=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=0.00 (CH_3, TMS), 22.0 (CH_3, pin), 22.8 (CH, C^5), 23.0 (CH_3, pin), 23.2 (CH_3, pin), 24.0 (2C, CH_3, pin), 24.6 (CH_3, pin), 70.2 (C, C^1), 79.9 (C, pin), 80.7 (C, pin), 81.7 (C, pin), 82.1 (CH, Cp), 101.0 (C, C^3), 123.2 (CH_{arom}), 124.1 (CH_{arom}), 124.8 (CH_{arom}), 125.0 (CH_{arom}), 128.2 (CH_{arom}), 129.8 (CH_{arom}), 141.1 (C), 147.1 ppm (C); C^2, C^4 and C^6 unobserved; IR (neat): $\tilde{\nu}$=699, 838, 1139, 1243, 1307, 1371, 2977 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{44}H_{62}B_3CoO_6SiNa$: 829.3825; found: 829.3839.

Data for *syn*-46: Red solid; m.p. 201°C; ^{1}H NMR ($CDCl_3$): δ=0.72–1.40 (m, 6H), 0.76 (s, 6H; pin), 0.85 (d, *J*=−8.6 Hz, 1H; H^8*exo*), 0.88 (s, 6H; pin), 1.11 (s, 12H; pin), 1.89 (bs, 1H; H^7 or H^9), 2.48 (bs, 1H; H^7 or H^9), 3.71 (d, *J*=−8.6 Hz, 1H; H^8*endo*), 4.94 (s, 5H; Cp), 7.13–7.25 (m, 6H), 7.45 (d, *J*=7.6 Hz, 2H), 7.67–7.68 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ= 24.4 (CH_3, pin), 25.1 (CH_3, pin), 25.2 (CH_3, pin), 25.3 (CH_3, pin), 30.3 (CH_2), 30.4 (CH_2), 32.6 (CH_2), 39.3 (CH), 41.6 (CH), 48.4 (CH), 54.0 (CH), 82.2 (C, pin), 83.7 (C, pin), 84.1 (CH, Cp), 103.8 (C^3), 125.2 (CH_{arom}), 126.3 (CH_{arom}), 127.0 (CH_{arom}), 127.1 (CH_{arom}), 130.8 (CH_{arom}), 131.2 (CH_{arom}), 142.8 (C), 148.5 ppm (C); C^1, C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$=696, 787, 1141, 1368, 2341, 2360, 2862, 2974 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{49}B_2CoO_4$: C 71.24, H 7.32; found: C 71.06, H 7.34.

Data for *anti*-46: Red solid; m.p. 230°C; ^{1}H NMR ($CDCl_3$): δ=0.47 (d, *J*=−10.0 Hz, 1H; H^8), 0.86–1.34 (m, 5H), 0.88 (s, 6H; pin), 0.95 (s, 6H; pin), 1.07 (s, 12H; pin), 1.78 (d, *J*=3.5 Hz, 1H; H^7 or H^9), 1.88 (d, *J*= 3.5 Hz, 1H; H^7 or H^9), 2.11 (d, *J*=9.4 Hz, 1H; H^5 or H^6), 2.22 (d, *J*= 9.4 Hz, 1H; H^5 or H^6), 4.62 (s, 5H; Cp), 7.02–7.37 (m, 8H), 7.61 ppm (d, *J*=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=24.8 (CH_3, pin), 24.9 (CH_3, pin), 25.1 (CH_3, pin), 25.4 (CH_3, pin), 29.0 (CH_2), 29.5 (CH_2), 31.6 (CH_2), 40.5 (CH), 43.3 (CH), 50.6 (CH), 53.0 (CH), 71.5 (C^1) 81.9 (C, pin), 82.6 (CH, Cp), 83.6 (C, pin), 106.7 (C^3), 124.2 (CH_{arom}), 126.1 (CH_{arom}), 126.5 (CH_{arom}), 127.4 (CH_{arom}), 128.4 (2C, CH_{arom}), 142.4 (C), 149.1 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$=697, 802, 1141, 2866, 2922 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{49}B_2CoO_4$: C, 71.24; H, 7.32; found: C, 71.11; H, 7.15.

Data for 47: White solid; m.p. 212°C; ^{1}H NMR ($CDCl_3$): δ=0.55 (s, 6H; pin), 0.71 (s, 6H; pin), 0.98 (s, 6H; pin), 1.12 (s, 6H; pin), 1.28–1.31 (m, 2H), 1.52–1.58 (m, 3H), 1.93–2.15 (m, 3H), 2.74–2.91 (m, 2H), 7.17–7.33 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ=24.0 (CH_3, pin), 24.4 (2C, CH_3, pin), 24.9 (CH_3, pin), 30.1 (CH_2), 31.0 (CH_2), 34.7 (CH_2), 43.0 (CH), 46.1 (CH), 47.1 (CH), 47.3 (CH), 82.8 (C, pin), 83.0 (C, pin), 126.4 (CH_{arom}), 126.9 (CH_{arom}), 127.5 (CH_{arom}), 128.0 (2C, CH_{arom}), 128.6 (CH_{arom}), 144.0 (C), 144.3 (C), 144.7 (C), 147.6 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$=697, 802, 1141, 2866, 2922 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{35}H_{44}B_2O_4Na$: 573.3323; found: 573.3358.

Data for *anti*-48: Red solid; m.p. 205°C; ^{1}H NMR ($CDCl_3$): δ=0.86 (s, 6H; pin), 1.00 (s, 6H; pin), 1.08 (s, 6H; pin), 1.12 (s, 6H; pin), 2.51 (dd, *J*=16.7, 4.3 Hz, 1H), 3.08, (dd, *J*=16.7, 9.4 Hz, 1H), 3.36 (dt, *J*=9.8, 4.3 Hz, 1H; H^5*endo*), 4.16 (d, *J*=10.1 Hz, 1H; H^6*endo*), 4.72 (s, 5H; Cp), 6.23 (d, *J*=7.6 Hz, 1H), 6.75 (t, *J*=7.6 Hz, 1H), 6.90–7.00 (m, 2H), 7.15–7.30 (m, 8H), 7.72 ppm (d, *J*=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=24.7 (CH_3, pin), 25.0 (CH_3, pin), 25.1 (CH_3, pin), 25.2 (CH_3, pin), 40.5 (CH_2), 46.3 (CH, C^5), 54.6 (CH, C^6), 72.5 (C, C^1), 82.1 (C, pin), 83.2 (CH, Cp), 83.6 (C, pin), 107.2 (C, C^3), 124.2 (CH_{arom}), 124.6 (CH_{arom}), 124.8 (CH_{arom}), 125.2 (CH_{arom}), 125.9 (CH_{arom}), 126.1 (CH_{arom}), 126.4 (CH_{arom}), 127.5 (CH_{arom}), 129.1 (CH_{arom}), 131.7 (CH_{arom}), 141.9 (C), 142.4 (C), 145.2 (C), 148.7 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$=696, 744, 1140, 1263, 1389, 2978 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{42}H_{47}B_2CoO_4Na$: 719.2890; found: 719.2853.

Data for *syn*-48: Red solid; m.p. 217°C; ^{1}H NMR ($CDCl_3$): δ=0.83 (s, 6H; pin), 0.98 (s, 6H; pin), 1.16 (s, 6H; pin), 1.22 (s, 6H; pin), 2.16–2.26 (m, 2H), 3.38–3.49 (m, 2H), 4.85 (s, 5H; Cp), 5.52 (d, *J*=7.6 Hz, 1H), 6.69 (t, *J*=7.6 Hz, 1H), 7.05 (t, *J*=7.4 Hz, 1H), 7.12–7.30 (m, 9H), 7.71–7.78 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ=24.2 (CH_3, pin), 25.2 (CH_3, pin), 25.3 (2C, CH_3, pin), 42.7 (CH_2), 44.1 (CH, C^5), 53.0 (CH, C^6), 77.3

(C, C^1), 82.4 (C, pin), 82.6 (CH, Cp), 83.8 (C, pin), 107.0 (C, C^3), 123.5 (CH$_{arom}$), 124.2 (CH$_{arom}$), 125.5 (CH$_{arom}$), 125.8 (CH$_{arom}$), 126.3 (CH$_{arom}$), 126.6 (CH$_{arom}$), 127.1 (3C, CH$_{arom}$), 131.2 (CH$_{arom}$), 142.5 (C), 144.2 (C), 144.8 (C), 146.6 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 699, 807, 1142, 1257, 1377, 2975 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{42}H_{47}B_2CoO_5Na$: 719.2890; found: 719.2857; elemental analysis calcd (%) for $C_{42}H_{47}B_2CoO_4$: C 72.44, H 6.80; found: C 72.39, H 6.99.

Data for 49: White solid; m.p. 135 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.52$ (s, 6H; pin), 0.73 (s, 6H; pin), 1.07 (s, 6H; pin), 1.08 (s, 6H; pin), 3.11 (dd, J = 15.1, 8.5 Hz, 1H), 3.25 (dd, J = 15.1, 7.6 Hz, 1H), 3.53 (ddd, J = 8.7 Hz, 1H; H^5), 4.20 (d, J = 10.1 Hz, 1H; H^6), 6.51 (d, J = 7.6 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 7.10–7.30 ppm (m, 11H); ^{13}C NMR (CDCl$_3$): $\delta = 24.3$ (CH$_3$, pin), 24.4 (CH$_3$, pin), 24.5 (2C, CH$_3$, pin), 40.5 (CH$_2$), 42.8 (CH, C^5), 47.3 (CH, C^6), 82.9 (C, pin), 83.0 (C, pin), 123.3 (CH$_{arom}$), 125.4 (CH$_{arom}$), 126.0 (CH$_{arom}$), 126.2 (CH$_{arom}$), 126.6 (CH$_{arom}$), 126.9 (CH$_{arom}$), 127.4 (CH$_{arom}$), 127.7 (CH$_{arom}$), 128.8 (CH$_{arom}$), 129.3 (CH$_{arom}$), 142.3 (C), 142.6 (C), 143.7 (C), 144.1 (C), 146.1 (C), 147.0 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 698, 749, 1140, 1263, 1315, 1370, 2976 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{37}H_{42}B_2O_4Na$: 595.3167; found: 595.3146.

Data for 51: Pale yellow solid; m.p. 121 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.61$ (s, 6H; pin), 0.64 (s, 6H; pin), 0.96 (s, 6H; pin), 1.04 (s, 6H; pin), 1.95–2.03 (m, 1H), 2.10–2.27 (m, 3H), 3.10 (d, J = 9.1 Hz, 1H; H^6), 3.40–3.43 (m, 1H), 7.13–7.37 ppm (m, 10H); ^{13}C NMR (CDCl$_3$): $\delta = 24.6$ (2C, CH$_3$, pin), 24.7 (CH$_3$, pin), 24.8 (CH$_3$, pin), 27.7 (CH$_2$), 36.9 (CH$_2$), 40.6 (CH), 54.3 (CH), 83.3 (C, pin), 83.4 (C, pin), 127.0 (CH$_{arom}$), 127.5 (CH$_{arom}$), 127.6 (CH$_{arom}$), 128.0 (CH$_{arom}$), 128.4 (CH$_{arom}$), 129.3 (CH$_{arom}$), 142.4 (C), 143.1 (C), 143.2 (C), 149.4 (C), 218.1 ppm (C=O); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 698, 1138, 1307, 1740, 2929, 2976 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{33}H_{40}B_2O_5Na$: 561.2960; found: 561.2942.

Data for *anti*-52 *anti*: Red solid; m.p. 108 °C; ^{1}H NMR (CDCl$_3$): δ = 0.83–1.95 (m, 5H), 0.93 (s, 6H; pin), 1.01 (s, 6H; pin), 1.11 (s, 6H; pin), 1.23 (s, 6H; pin), 2.12–2.18 (m, 1H), 2.82–2.85 (m, 1H), 3.35 (d, J = 11.3 Hz, 1H; H^6), 4.70 (s, 5H; Cp), 7.07–7.26 (m, 6H), 7.33–7.37 (m, 2H), 7.54–7.64 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 21.6$ (CH$_2$), 24.9 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_3$, pin), 25.6 (CH$_3$, pin), 31.8 (CH$_2$), 37.4 (CH$_2$), 42.6 (CH), 60.5 (CH), 67.6 (C^1), 82.3 (C, pin), 83.9 (CH, Cp), 84.2 (C, pin), 106.0 (C^3), 125.2 (CH$_{arom}$), 126.5 (CH$_{arom}$), 126.8 (CH$_{arom}$), 127.5 (CH$_{arom}$), 128.8 (CH$_{arom}$), 131.9 (CH$_{arom}$), 141.7 (C), 147.4 (C), 212.8 ppm (C=O); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 698, 1139, 1701, 2926, 2974 cm^{-1}; elemental analysis calcd (%) for $C_{39}H_{47}B_2CoO_5$: C 69.26, H 7.00; found: C 68.99, H 7.25.

Data for *syn*-52: Red solid; m.p. 162 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.85$ (s, 6H; pin), 0.88 (s, 6H; pin), 1.10 (s, 6H; pin), 1.17 (s, 6H; pin), 1.44–1.62 (m, 2H), 1.79–1.82 (m, 1H), 1.97–2.06 (m, 1H), 2.11–2.14 (m, 1H), 2.27–2.40 (m, 2H), 2.53–2.62 (m, 1H), 4.99 (s, 5H; Cp), 7.08–7.30 (m, 8H), 7.64 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 23.5$ (CH$_2$), 24.4 (CH$_3$, pin), 25.0 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_3$, pin), 32.7 (CH$_2$), 42.5 (CH$_2$), 45.0 (CH), 55.4 (CH), 73.9 (C^1), 82.5 (C, pin), 83.7 (CH, Cp), 83.9 (C, pin), 107.0 (C^3), 125.9 (CH$_{arom}$), 126.6 (CH$_{arom}$), 127.2 (CH$_{arom}$), 127.3 (CH$_{arom}$), 130.4 (CH$_{arom}$), 131.2 (CH$_{arom}$), 142.0(C), 145.4 (C), 213.3 ppm (C=O); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 701, 1137, 1701, 2928, 2975 cm^{-1}.

Data for 53: White solid, m.p. 161 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.53$ (s, 6H; pin), 0.76 (s, 6H; pin), 0.98 (s, 12H; pin), 1.53–1.63 (m, 1H), 1.72–1.77 (m, 1H), 1.84–1.99 (m, 4H), 2.84–2.89 (m, 1H), 3.56 (d, J = 7.3 Hz, 1H; H^6), 7.13–7.24 ppm (m, 10H); ^{13}C NMR (CDCl$_3$): $\delta = 24.5$ (CH$_3$, pin), 24.6 (CH$_3$, pin), 24.6 (CH$_3$, pin), 24.7 (CH$_3$, pin), 25.6 (CH$_2$), 25.8 (CH$_2$), 41.2 (CH$_2$), 42.3 (CH), 56.0 (CH), 83.1 (C, pin), 83.4 (C, pin), 127.0 (CH$_{arom}$), 127.5 (CH$_{arom}$), 127.6 (CH$_{arom}$), 128.1 (CH$_{arom}$), 128.4 (CH$_{arom}$), 129.3 (CH$_{arom}$), 141.5 (C), 142.8(C), 143.6 (C), 149.4 (C), 213.2 ppm (C=O); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 699, 1139, 1707, 2930, 2979 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{34}H_{42}B_2O_5Na$: 575.3116; found: 575.3079.

Data for 54A: Red solid, m.p. 210 °C (decomp); ^{1}H NMR (CDCl$_3$): δ = 0.92 (s, 6H; pin), 0.97 (s, 6H; pin), 1.07 (s, 6H; pin), 1.10 (s, 6H; pin), 1.28–1.35 (m, 1H), 1.64–1.74 (m, 1H), 3.31 (dt, J = 9.1, 2.3 Hz, 1H; H^6*endo*), 3.51–3.63 (m, 2H), 4.66 (s, 5H; Cp), 5.05 (d, J = 9.3 Hz, 1H; H^5*endo*), 7.09–7.28 (m, 8H), 7.63 ppm (d, J = 7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 24.3$ (CH$_3$, pin), 24.6 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.5 (CH$_3$, pin), 35.4 (CH$_2$), 46.8 (CH, C^6), 65.1 (C, C^1), 67.2 (CH$_2$), 82.2 (CH, C^5), 82.3 (C, pin), 83.0 (C, Cp), 84.0 (C, pin), 107.6 (C, C^3), 124.5 (CH$_{arom}$), 126.4 (CH$_{arom}$), 126.6 (CH$_{arom}$), 127.6 (CH$_{arom}$), 127.8 (CH$_{arom}$) 132.0 (CH$_{arom}$), 141.3 (C), 148.1 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 702, 803, 1037, 1143, 1295, 1411, 2965 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{37}H_{46}B_2CoO_5$: 651.2863; found: 651.2866 [*M*+H]$^+$.

Data for 54B: Red solid; m.p. 215 °C (decomp); ^{1}H NMR (CDCl$_3$): δ = 0.89 (s, 6H; pin), 0.97 (s, 6H; pin), 1.04 (s, 6H; pin), 1.10 (s, 6H; pin), 1.33–1.41 (m, 1H), 1.85–1.97 (m, 1H), 3.09 (dt, J = 9.3, 3.0 Hz, 1H; H^5*endo*), 3.51–3.59 (m, 2H), 4.70 (s, 5H; Cp), 5.05 (d, J = 9.6 Hz, 1H; H^6*endo*), 7.07–7.13 (m, 1H), 7.16–7.28 (m, 6H), 7.68–7.73 ppm (m, overlapped d, J = 7.6 Hz, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 24.5$ (CH$_3$, pin), 24.6 (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.2 (CH$_3$, pin), 37.3 (CH$_2$), 43.9 (CH, C^5), 65.3 (C, C^1), 67.2 (CH$_2$), 82.3 (C, pin), 82.6 (CH, C^6), 82.9 (C, Cp), 84.0 (C, pin), 107.1 (C, C^3), 124.5 (CH$_{arom}$), 126.4 (CH$_{arom}$), 126.6 (CH$_{arom}$), 127.6 (CH$_{arom}$), 128.2 (2C, CH$_{arom}$), 141.2 (C), 147.4 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 704, 770, 1032, 1141, 1310, 1409, 2971 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{37}H_{46}B_2CoO_5$: 651.2863; found: 651.2878 [*M*+H]$^+$.

Data for 55: White solid; m.p 167 °C; ^{1}H NMR (CDCl$_3$): δ = 1.28–1.30 (m, 24H; pin), 2.73–2.79 (m, 1H), 3.03–3.12 (m, 1H), 3.17 (s, 3H; OCH$_3$), 3.27–3.37 (m, 1H), 3.32 (s, 3H; OCH$_3$), 3.84 (d, J = 10.1 Hz, 1H; H^6), 3.93 (A of AB, J = 11.9 Hz, 1H; C*H*HO), 3.99 (B of AB, J = 11.9 Hz, 1H; CH*H*O), 4.41 (A of AB, J = 12.6 Hz, 1H; C*H*HO), 4.48 (B of AB, J = 12.6 Hz, 1H; CH*H*O), 7.11–7.15 (m, 3H), 7.49–7.51 ppm (m, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 24.8$ (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.3 (CH$_3$, pin), 25.5 (CH$_3$, pin), 40.4 (CH$_2$), 42.4 (CH), 44.4 (CH), 56.0 (OCH$_3$), 57.1 (OCH$_3$), 71.8 (OCH$_2$), 72.7 (OCH$_2$), 83.3 (C, pin), 83.4 (C, pin), 123.3 (CH$_{arom}$), 126.1 (CH$_{arom}$), 126.3 (CH$_{arom}$), 126.5 (CH$_{arom}$), 143.1 (C), 143.1 (C), 144.7 (C), 145.3 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 847, 1078, 1142, 2928, 2975 cm^{-1}; elemental analysis calcd (%) for $C_{29}H_{42}B_2O_6$: C 68.53, H 8.33; found: C 68.21, H 8.49.

Data for 56: Yellow oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.19$ (s, 6H; pin), 1.29 (s, 6H; pin), 1.31–1.33 (m, 12H; pin), 2.97–3.00 (m, 1H), 3.06–3.13 (m, 2H), 3.12 (s, 3H; OCH$_3$), 3.32 (s, 3H; OCH$_3$), 4.01 (br d, J = 8.6 Hz, 1H; H^5), 4.15 (A of AB, J = 12.5 Hz, 1H; C*H*HO), 4.20 (B of AB, J = 12.6 Hz, 1H; CH*H*O), 4.35 (A of ABm, J = 12.6, 1 Hz, 1H; C*H*HO), 4.39 (B of ABm, J = 12.6, 2 Hz, 1H; CH*H*O), 7.06–7.08 (m, 2H), 7.14–7.16 (m, 1H), 7.42–7.44 ppm (m, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 25.0$ (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_3$, pin), 25.4 (CH$_3$, pin), 38.4 (CH$_2$), 41.2 (CH), 46.6 (CH), 56.0 (OCH$_3$), 57.4 (OCH$_3$), 71.8 (OCH$_2$), 73.9 (OCH$_2$), 83.4 (2C, C, pin), 123.7 (CH$_{arom}$), 125.5 (CH$_{arom}$), 126.0 (CH$_{arom}$), 126.1 (CH$_{arom}$), 143.3 (C), 143.8 (C), 146.0 (C), 148.3 ppm (C); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 731, 1081, 1140, 2928, 2976 cm^{-1}.

Data for 57: Yellow oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.29$ (s, 6H; pin), 1.31 (s, 18H; pin), 2.00–2.13 (m, 2H), 2.17–2.23 (m, 2H), 3.15 (s, 3H; OCH$_3$), 3.26–3.28 (m, 2H), 3.32 (s, 3H; OCH$_3$), 4.14 (A of AB, J = 12.4 Hz, 1H; C*H*HO), 4.22 (B of AB, J = 12.4 Hz, 1H; CH*H*O), 4.34–4.35 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 24.7$ (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.4 (CH$_3$, pin), 27.1 (CH$_2$), 36.4 (CH$_2$), 36.8 (CH), 52.0 (CH), 56.0 (OCH$_3$), 57.6 (OCH$_3$), 71.8 (OCH$_2$), 73.1 (OCH$_2$), 83.5 (C, pin), 83.7 (C, pin), 144.4 (C), 146.0 (C), 220.1 ppm (C=O), C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 851, 1139, 1304, 1737, 2976 cm^{-1}.

Data for 58: Yellow oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.24$ (s, 12H; pin), 1.28 (s, 12H; pin), 1.91–2.23 (m, 4H), 2.93–2.95 (m, 1H), 3.09 (s, 3H; OCH$_3$), 3.22 (s, 3H; OCH$_3$), 3.24–3.28 (m, 1H), 4.04–4.38 ppm (m, 4H); ^{13}C NMR (CDCl$_3$): $\delta = 24.7$ (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_3$, pin), 27.6 (CH$_2$), 36.4 (CH$_2$), 39.1 (CH), 50.6 (CH), 56.1 (OCH$_3$), 57.6 (OCH$_3$), 71.7 (OCH$_2$), 72.3 (OCH$_2$), 83.4 (C, pin), 83.5 (C, pin), 139.9 (C), 146.6 (C), 219.0 ppm (C=O); C^2 and C^4 unobserved; IR (neat): $\tilde{\nu}$ = 848, 1139, 1305, 1738, 2976 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{25}H_{40}B_2O_7Na$: 497.2858; found: 497.2887.

Data for 64: Red solid; m.p. 188 °C; ^{1}H NMR (CDCl$_3$): δ = 1.02–1.11 (m, 1H), 1.26 (s, 12H; pin), 1.30 (s, 6H; pin), 1.32 (s, 6H; pin), 1.57 (d, J = 7.6 Hz, 1H; H^5, 1.89–2.05 (m, 2H), 2.17–2.27 (m, 2H), 2.42 (s, 3H; CH$_3$), 4.00 (A of AB, J = 12.6 Hz, 1H; NC*H*H), 4.05 (B of AB, J = 12.6 Hz, 1H;

NCH*H*), 4.49 (A of AB, J=12.4 Hz, 1H; NC*H*H), 4.59 (s, 5H; Cp), 4.84 (B of AB, J=12.4 Hz, 1H; NCH*H*), 7.35 (d, J=8.1 Hz, 2H), 7.80 ppm (d, J=8.1 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=21.6 (CH$_3$), 24.6 (CH$_3$, pin), 24.8 (CH$_3$, pin), 25.1 (CH$_3$, pin), 25.4 (CH$_3$, pin), 27.0 (CH$_2$), 37.0 (CH, C^5), 37.0 (CH$_2$), 53.3 (CH, C^6), 53.3 (CH$_2$, NCH$_2$), 54.1 (CH$_2$, NCH$_2$), 81.9 (CH, Cp), 82.7 (C, pin), 83.3 (C, pin), 101.4 (C), 101.9 (C), 127.7 (CH$_{\mathrm{arom}}$), 129.9 (CH$_{\mathrm{arom}}$), 134.0 (C), 143.6 (C), 218.4 ppm (C=O); C^1 and C^4 unobserved; IR (neat): $\tilde{\nu}$=678, 1106, 1149, 1357, 1736, 2926, 2975 cm^{-1}; elemental analysis calcd (%) for C$_{35}$H$_{46}$B$_2$CoNO$_7$S: C 59.60, H 6.57, N 1.99; found: C 59.58, H 6.75, N 2.11.

Data for 67: Yellow solid; m.p. 105 °C; ^{1}H NMR (CDCl$_3$): δ=1.27 (s, 12H; pin), 1.28 (s, 6H; pin), 1.30 (s, 6H; pin), 1.64–1.75 (m, 1H), 2.03–2.11 (m, 1H), 2.17–2.26 (m, 1H), 2.41 (s, 3H; CH$_3$), 3.09 (d, J=11.1 Hz, 1H; H^6), 3.14–3.19 (m, 1H), 3.96 (A of ABm J=16.0, 2.6 Hz, 1H; NC*H*H), 4.07 (B of ABm, J=15.9, 1.6 Hz, 1H; NCH*H*), 4.18 (A of ABm, J=15.9, 1.6 Hz, 1H; NC*H*H), 4.28 (B of ABm, J=16.0, 2.6 Hz, 1H; NCH*H*), 7.28 (d, J=8.1 Hz, 2H), 7.69 ppm (d, J=8.1 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=21.6 (CH$_3$), 24.5 (2C, CH$_3$, pin), 25.2 (CH$_3$, pin), 25.3 (CH$_3$, pin), 28.8 (CH$_2$), 36.6 (CH$_2$), 37.9 (CH, C^5), 49.5 (CH, C^6), 52.3 (CH$_2$, NCH$_2$), 52.6 (CH$_2$, NCH$_2$), 83.9 (C, pin), 84.0 (C, pin), 127.9 (CH$_{\mathrm{arom}}$), 129.8 (CH$_{\mathrm{arom}}$), 133.1 (C), 143.7 (C), 144.6 (C), 146.5 (C), 219.8 ppm (C=O); C^1 and C^4 unobserved; IR (neat): $\tilde{\nu}$=665, 1131, 1366, 1737, 2924, 2976 cm^{-1}; HRMS (ES+): m/z calcd for C$_{30}$H$_{42}$B$_2$NO$_7$S: 582.2868; found: 582.2884 [M+H]$^+$.

Data for 70: Yellow solid; m.p. 221 °C; ^{1}H NMR (CDCl$_3$): δ=0.76 (s, 12H; pin), 2.70–2.82 (m, 4H), 7.06–7.10 (m, 4H), 7.16–7.18 (m, 3H), 7.26–7.27 (m, 1H), 7.33 (apparent t, J=10.0 Hz, 2H), 7.44 (d, J=8.0 Hz, 2H), 7.92 ppm (d, J=8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=24.7 (2C, CH$_3$, pin), 30.0 (CH$_2$), 30.5 (CH$_2$), 83.6 (C, pin), 123.0 (CH$_{\mathrm{arom}}$), 127.3 (CH$_{\mathrm{arom}}$), 127.4 (CH$_{\mathrm{arom}}$), 127.6 (CH$_{\mathrm{arom}}$), 128.2 (CH$_{\mathrm{arom}}$), 128.3 (CH$_{\mathrm{arom}}$), 129.1 (CH$_{\mathrm{arom}}$), 130.4 (CH$_{\mathrm{arom}}$), 139.5 (C), 140.8 (C), 143.4 (C), 145.5 (C), 148.0 (C), 150.0 ppm (C); C^2 and an additional C unobserved; IR (neat): $\tilde{\nu}$=701, 851, 1319, 1342 cm^{-1}; HRMS (ES+): m/z calcd for C$_{30}$H$_{30}$BNO$_4$Na: 502.2166; found: 502.2175.

Data for 71: White solid; m.p. 155 °C; ^{1}H NMR (CDCl$_3$): δ=0.76 (s, 12H; pin), 2.66–2.78 (m, 4H), 3.72 (s, 3H; OCH$_3$), 6.62 (d, J=8.8 Hz, 2H), 6.89 (d, J=8.8 Hz, 2H), 7.11–7.17 (m, 4H), 7.26–7.33 (m, 2H), 7.44 (d, J=8.0 Hz, 2H), 7.92 ppm (d, J=8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=24.8 (2C, CH$_3$, pin), 30.1 (CH$_2$), 31.0 (CH$_2$), 55.2 (OCH$_3$), 83.4 (C, pin), 113.0 (CH$_{\mathrm{arom}}$), 126.4 (CH$_{\mathrm{arom}}$), 127.1 (CH$_{\mathrm{arom}}$), 127.5 (CH$_{\mathrm{arom}}$), 127.9 (CH$_{\mathrm{arom}}$), 128.1 (CH$_{\mathrm{arom}}$), 129.6 (CH$_{\mathrm{arom}}$), 130.7 (CH$_{\mathrm{arom}}$), 132.1 (C), 135.0 (C), 135.8 (C), 142.1 (C), 144.1 (C), 144.5 (C), 157.6 ppm (C); C^2 unobserved; IR (neat): $\tilde{\nu}$=701, 1140, 1346, 2359 cm^{-1}; HRMS (ES+): m/z calcd for C$_{31}$H$_{33}$BO$_3$Na: 487.2420; found: 487.2435.

Data for 72: Pale yellow oil; ^{1}H NMR (CDCl$_3$): δ=2.44 (AA′m, 2H), 2.62 (BB′m, 2H), 2.90 (s, 3H; OCH$_3$), 3.18 (s, 3H; OCH$_3$), 3.53 (s, 2H; OCH$_2$), 3.78 (s, 2H; OCH$_2$), 3.82 (s, 3H; OCH$_3$), 3.83 (s, 3H; OCH$_3$), 6.90 (d, J=8.8 Hz, 2H), 6.91 (d, J=8.8 Hz, 2H), 7.12 (d, J=8.8 Hz, 2H), 7.32 ppm (d, J=8.8 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=24.6 (CH$_2$), 30.6 (CH$_2$), 55.3 (OCH$_3$), 55.4 (OCH$_3$), 57.5 (OCH$_3$), 57.6 (OCH$_3$), 69.5 (OCH$_2$), 72.5 (OCH$_2$), 113.1 (CH$_{\mathrm{arom}}$), 113.5 (CH$_{\mathrm{arom}}$), 129.5 (CH$_{\mathrm{arom}}$), 130.0 (C), 131.0 (CH$_{\mathrm{arom}}$), 131.2 (C), 132.1 (C), 134.5 (C), 137.9 (C), 139.1 (C), 158.4 (C), 158.7 ppm (C); IR (neat): $\tilde{\nu}$=828, 1241, 1507, 2817, 2921 cm^{-1}; elemental analysis calcd (%) for C$_{24}$H$_{28}$O$_4$: C 75.76, H 7.42; found: C 75.74, H 7.71; HRMS (ES+): m/z calcd for C$_{24}$H$_{28}$O$_4$Na: 403.1885; found: 403.1909.

Data for 73: White solid; m.p. 196 °C; ^{1}H NMR (CDCl$_3$): δ=0.58 (s, 6H; pin), 0.69 (s, 6H; pin), 3.10–3.21 (m, 2H), 3.66–3.77 (m, 1H), 3.72 (s, 3H; OCH$_3$), 4.39 (d, J=9.6 Hz, 1H), 6.62–6.66 (m, 3H), 6.86–6.90 (m, 3H), 7.02–7.13 (m, 8H), 7.21–7.27 ppm (m, 4H); ^{13}C NMR (CDCl$_3$): δ=24.6 (2C, CH$_3$, pin), 39.8 (CH$_2$), 46.1 (CH), 49.6 (CH), 55.3 (OCH$_3$), 88.3 (C, pin), 113.1 (CH$_{\mathrm{arom}}$), 123.4 (CH$_{\mathrm{arom}}$), 125.7 (CH$_{\mathrm{arom}}$), 125.8 (CH$_{\mathrm{arom}}$), 126.1 (CH$_{\mathrm{arom}}$), 126.2 (CH$_{\mathrm{arom}}$), 127.1 (CH$_{\mathrm{arom}}$), 127.7 (CH$_{\mathrm{arom}}$), 127.9 (CH$_{\mathrm{arom}}$), 129.1 (CH$_{\mathrm{arom}}$), 130.2 (CH$_{\mathrm{arom}}$), 130.5 (CH$_{\mathrm{arom}}$), 134.0 (C), 134.4 (C), 135.0 (C), 142.2 (2C, C), 142.5 (C), 143.4 (C), 144.5 (C), 157.6 ppm (C); C^2 unobserved; IR (neat): $\tilde{\nu}$=698, 1139, 1244, 1510, 2928, 2975 cm^{-1}; HRMS (ES+): m/z calcd for C$_{38}$H$_{37}$BO$_3$Na: 575.2733; found: 575.2729.

Data for 74: Yellow solid; m.p. 144 °C; ^{1}H NMR (CDCl$_3$): δ=1.47–1.58 (m, 4H), 2.40 (m, 4H), 2.54 (s, 4H), 7.40 (d, J=8.6 Hz, 4H), 8.22 ppm (d, J=8.6 Hz, 4H); ^{13}C NMR (CDCl$_3$): δ=23.6 (CH$_2$), 28.1 (CH$_2$), 30.0 (CH$_2$), 123.6 (CH$_{\mathrm{arom}}$), 129.3 (CH$_{\mathrm{arom}}$), 131.2 (C), 134.1 (C), 146.2 (C), 149.7 ppm (C); IR (neat): $\tilde{\nu}$=700, 849, 1339, 1509, 2858, 2919 cm^{-1}.

Data for 75: White solid; m.p. 107 °C; ^{1}H NMR (CDCl$_3$): δ=1.54–1.62 (m, 4H), 2.42–2.48 (m, 4H), 2.48 (s, 4H), 3.83 (s, 6H; OCH$_3$), 6.90 (d, J=8.6 Hz, 4H), 7.20 ppm (d, J=8.6 Hz, 4H); ^{13}C NMR (CDCl$_3$): δ=24.0 (CH$_2$), 28.0 (CH$_2$), 30.7 (CH$_2$), 55.4 (OCH$_3$), 113.5 (CH$_{\mathrm{arom}}$), 129.7 (CH$_{\mathrm{arom}}$), 131.0 (C), 131.6 (C), 135.6 (C), 158.0 ppm (C); IR (neat): $\tilde{\nu}$=810, 823, 1030, 1244, 1506, 2851, 2918 cm^{-1}; HRMS (ES+): m/z calcd for C$_{24}$H$_{27}$O$_2$: 347.2011; found: 347.2046 [M+H]$^+$.

Data for 76: White solid; m.p. 207 °C; ^{1}H NMR (CDCl$_3$): δ=1.65–1.67 (m, 4H), 2.49–2.52 (m, 4H), 2.56–2.57 (m, 2H), 2.70–2.73 (m, 2H), 3.87 (s, 3H; OCH$_3$), 3.88 (s, 3H; OCH$_3$), 6.99 (d, J=8.8 Hz, 2H), 7.02 (d, J=8.6 Hz, 2H), 7.12 (d, J=8.6 Hz, 2H), 7.17 ppm (d, J=8.8 Hz, 2H); ^{13}C NMR (CDCl$_3$): δ=22.7 (CH$_2$), 22.8 (CH$_2$), 24.6 (CH$_2$), 28.2 (CH$_2$), 29.6 (CH$_2$), 37.1 (CH$_2$), 55.3 (OCH$_3$), 55.4 (OCH$_3$), 113.6 (CH$_{\mathrm{arom}}$), 114.3 (CH$_{\mathrm{arom}}$), 130.0 (CH$_{\mathrm{arom}}$), 130.1 (CH$_{\mathrm{arom}}$), 131.0 (C), 131.7 (C), 136.1 (C), 138.9 (C), 139.0 (C), 143.0 (C), 151.8 (C), 158.7 (C), 158.8 (C), 206.3 ppm (C=O); one C unobserved; IR (neat): $\tilde{\nu}$=792, 1027, 1242, 1706, 2925, 2956 cm^{-1}; HRMS (ES+): m/z calcd for C$_{27}$H$_{26}$O$_3$Na: 421.1780; found: 421.1781.

Computational details: All geometries of molecules and transition states were optimized fully without symmetry constraints by using the Gaussian 03 program.[45] The DFT computations were carried out by using the B3LYP functional as implemented in Gaussian. The computations were done by using the LACVP(d,p) basis set: The cobalt atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),[46] and the 6–31G(d,p) basis set[47] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate calculations (IRC). Single-point calculations were carried out occasionally at the B3LYP/6–311+G(2d,2p) level without any significant changes of the relative energies. Since most of the transformations described herein are intramolecular, the energy values refer to enthalpies (ΔH_{298} and $\Delta H^{\neq}_{298}$), unless stated otherwise. The Chemcraft program was used to draw the calculated structures.[48]

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[43] The X-ray structure of **14 A** (reference [14]) and its computed version **F3** are in excellent agreement.

[44] The link between the two mechanisms depends on the ability of bisalkyne and alkyne–alkene CoCp complexes to interconvert. We have shown in reference [28h] that the mechanism of ligand exchange in ([CoCp(alkyne)$_2$] + alkene → [CoCp(alkyne)(alkene)] + alkyne) is probably dissociative. An approximation of the energy required for the substitution can be obtained by computing the binding energy of the substituent to be replaced. This was achieved by comparing the energy differences between [CoCpLL′] and the component fragments L′ and CoCpL, the latter being optimized in their triplet ground states. Single points at the B3LYP/6–311+G(2d,2p) level were achieved for better estimations. In the present case, application of this methodology reveals that the dissociation of the coordinated alkene in [CoCp(borylalkyne)(alkene)] complexes require about 2 kcal mol^{-1} and that of a borylalkyne in [CoCp(borylalkyne)$_2$] complexes about 9 kcal mol^{-1}. Therefore, the rate-determining step in either case is oxidative coupling, which always requires more than 15 kcal mol^{-1} (see Table 4 and Scheme 19) of activation energy, and not the ligand substitution.

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