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Chemo-, Regio-, and Stereoselective Cobalt-Mediated [2+2+2] Cycloaddition of Alkynyl Boronates to Alkenes: 1,3- and 1,4-Diboryl-1,3-cyclohexadienes[**]

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Alkenylboranes are useful intermediates for the preparation of a wide range of important organic compounds.[1] Specifically, mono- and diborylated 1,3-dienes have found various applications in dienylations,[2] Diels–Alder reactions,[3] and in the synthesis of α,β- or γ,δ-unsaturated ketones.[4] Their cyclic counterparts, namely boryl-1,3-cyclohexadienes, are as yet unknown. Considering that the 1,3-cyclohexadiene nucleus is a key subunit of many natural and/or biologically active compounds,[5] including those of the didehydroretinol and -carotene families,[6] borylated 1,3-cyclohexadienes constitute valuable reagents with which to introduce this synthon directly. The latter task has been accomplished in the past by using 1,3-cyclohexadienyl–metal complexes,[7] triflates,[8] or phosphates,[9] although these reagents have to be generated in several steps from enolizable cyclohexenone derivatives; this methodology has not been applied to dimetalated 1,3-cyclohexadienes.[10] We report here the preparation of 1,3- and 1,4-diboryl-1,3-cyclohexadienes by means of the cobalt-mediated [2+2+2] cocyclization of alkynyl boronates with alkenes.[11] Alkynyl boronates have recently been used as substrates in various transition-metal-mediated reactions[12] that lead to valuable building blocks, because the newly formed C_{sp^2}–B bonds can be subjected to couplings[13] and a plethora of other functional group transformations.[14] Siebert et al. have shown

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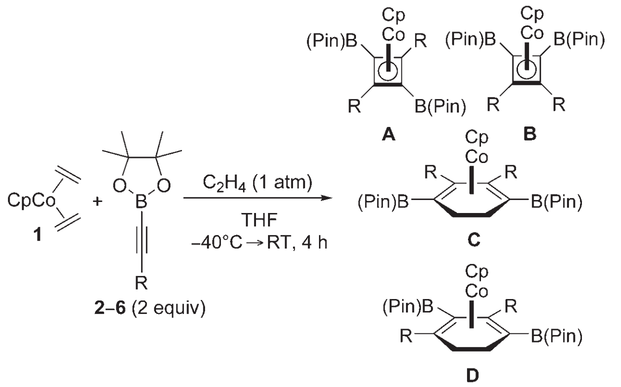
that catechol-substituted mono- and diborylalkynes undergo facile catalytic cyclotrimerization in the presence of cobalt(0) or cobalt(I) complexes to furnish oligoborylarenes.[12g] We have recently disclosed that alkynyl(pinacol)boronic esters add to α,ω-diynes under similar experimental conditions to assemble fused arylboronic esters.[12i]

The success of the present study was predicated on the employment of η^5-cyclopentadienylbis(ethene)cobalt (**1**),[15] which we have employed previously as an active source of CpCo in cooligomerizations of alkynes with alkenes.[11c–e] Preliminary experiments were carried out under an ethene atmosphere by treating **1** with two equivalents of alkynyl(pinacol)boronic esters **2–6** in THF (Table 1).[16] Under these conditions, alkyne cyclotrimerization[12g,i] was suppressed in favour of the formation of mixtures of the regioisomeric 1,2- and 1,3-diboryl(η^4-cyclobutadiene)cyclopentadienylcobalt complexes **A** and **B**, respectively, as well as the 1,4- and 1,3-diboryl(η^4-1,3-cyclohexadiene)cyclopentadienylcobalt complexes **C** and **D**, respectively. The 2,3-diboryl(η^4-1,3-cyclohexadiene) substitution pattern was notably absent.

Table 1: CpCo-mediated cycloaddition of alkynylboronic esters to ethene.



Entry	R	A/B (yield [%])[a]	C/D (yield [%])[a]
1	*t*Bu (**2**)	**7A/7B** 1:0 (59)	–
2	*i*Pr (**3**)	**8A/8B** 3.4:1 (54)[b]	**8C/8D** 1:0 (18)
3	C_6H_{13} (**4**)	–	**9C/9D** 1.5:1 (93)[c]
4	CH_2OMe (**5**)	–	**10C/10D** 1:9 (84)[b]
5	Ph (**6**)	–	**11C/11D** 1:20 (92)[b,d]

[a] Yields of product isolated after flash chromatography. [b] Unseparated mixture. [c] The yield is the sum of those for isolated **9C** (56%) and **9D** (37%). [d] The yield is that for complex **11D**, obtained pure by crystallization from the mixture in hexane. The presence of **11C** was surmised on the basis of the ^1H NMR spectroscopic data of the mixture.

These air-stable products were purified by flash chromatography on silica gel. As shown in Table 1 (entry 1), only the 1,3-diboryl(η^4-cyclobutadiene)cyclopentadienylcobalt complex **7A** was formed for R = *t*Bu. Its structure was confirmed unambiguously by an X-ray analysis (see Supporting Information). Changing the alkynyl substituent to the less bulky *i*Pr group (entry 2) resulted in the formation of a mixture of **8A** and **8B** in 54% yield, accompanied by 18% of the 1,4-diboryl(η^4-1,3-cyclohexadiene)cyclopentadienylcobalt complex **8C**. Following this trend, the reaction with the hexyl-substituted boronic ester **4** afforded products **9C** and **9D** in an excellent 93% yield in the ratio 1.5:1 without side products (entry 3). Similar yields (84% and 92%, respectively), but better regioselectivities for 1,3-diborylated products (9:1 and 20:1, respectively) were obtained with **5** or **6** as starting materials (entries 4 and 5). The less symmetrical structures of isomers **9D–11D** were readily assigned by NMR spectroscopy, and the structure of **11D** was confirmed by a single-crystal X-ray analysis (Figure 1).[17] Interestingly, boryl substitution does not cause significant structural alteration of the CpCo(η^4-1,3-cyclohexadiene) core of the component fragments.[18] The higher symmetry of complexes **8C–10C** was again evident from their NMR spectra, and a distinction between the 2,3- and 1,4-diboryl substitution pattern was possible on the basis of the characteristic chemical shifts of the complexed diene carbons,[11c,e,18a] in conjunction with the effect of boron nuclear quadrupole broadening. Hence, the clearly resolved peaks at $\delta = 110.0$, 105.2, and 100.1 ppm are diagnostic of alkyl-substituted internal quaternary diene carbons in **8C**, **9C**, and **10C**, respectively, whereas the terminal carbons are either unobservable (**8C**, **10C**) or appear as a broad signal at $\delta = 46.7$ ppm (**9C**).

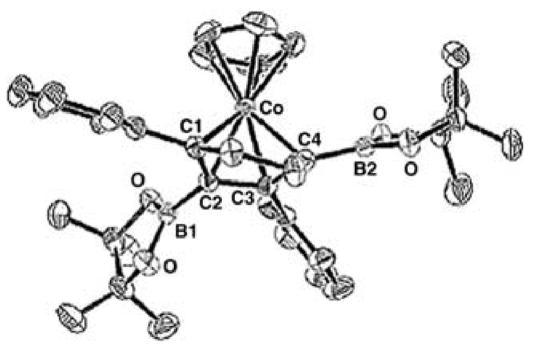
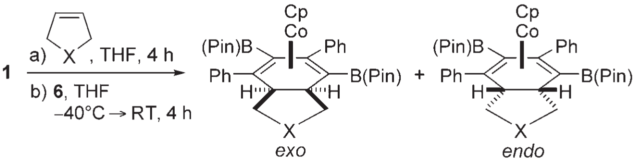


Figure 1. ORTEP view of complex **11D** in the solid state (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Co–C_{Cp} 2.05 (av), C2–B1 1.565(5), C4–B2 1.546(5), B–O 1.37 (av), C–C_{diene} 1.44 (av), Co–C1 2.062(3), Co–C2 1.996(3); C1-C2-C3-C(4) 3.9.

The results in Table 1 are consistent with the notions that steric effects dominate the chemistry of the putative intermediate CpCo(dialkyne) complexes and the resulting metallacycles, which are the relay points on route to the metalated cyclobutadiene and cyclohexadiene products.[11,19] When R is bulky, the route leading to the former is favored[19b] and the steric hindrance retards alkene incorporation to the latter; cyclohexadiene formation is dominant for less bulky R groups. Similarly, the regioselectivity appears to be controlled by the largest substituent, thus favoring the ostensibly least sterically demanding 2,4-substitution in the cobaltacyclopentadiene. When R is larger or smaller than $B(OR)_2$ such control is extensive (**7A**, **10D**, **11D**), whereas when R is comparable to $B(OR)_2$ it is not. Remarkably, an electronic influence of the boryl group is not evident.[20]

The cyclization is not restricted to ethene, and with **6** as the alkyne component and five equivalents of alkene the results summarized in Table 2 and Table 3 were obtained. Specifically, the alkene and **1** were stirred initially in THF at room temperature for 4 h,[21] during which ethene evolution was visible. Subsequently, **6** was added at −40 °C, followed by stirring at room temperature for 4 h. With 2,5-dihydrofuran, cyclopentene, and cyclohexene, the reactions proceeded completely regioselectively in very good overall yields, with moderate to excellent stereoselectivity and no competing ethene insertion (Table 2). Stereochemical assignments were based on the characteristic chemical shifts of the tertiary cyclohexadiene hydrogen atoms, which are shielded when located *anti* to cobalt and deshielded when located *syn*.[11c,e,18a,22] The *endo* diastereomer was favored in all cases, in agreement with the stereochemical preference of cycloadditions of some α,ω-diynes to pyrimidines[23] and indoles.[24]

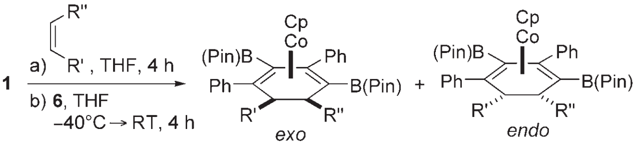
Table 2: CpCo-mediated cocyclizations of **6** with cyclic alkenes.



Entry	X	*exo*/*endo*[a] (yield [%])[b]
1	O	**12**/**13** 1:3.6 (88)
2	CH_2	**14**/**15** 1:1.9 (86)
3	$(CH_2)_2$	**16**/**17** 1:20 (70)

[a] The designations *exo* and *endo* refer to the configuration of the precursor cobaltacyclopentadiene(alkene) complexes and are in analogy to Diels–Alder cycloaddition terminology. [b] Yields of product isolated after flash chromatography on SiO_2. Compounds **13**–**15** could be obtained in pure form, but **12** remained contaminated by some **13**, and **17** by traces of **16.**

Table 3: CpCo-mediated cocyclizations of **6** with acyclic alkenes.

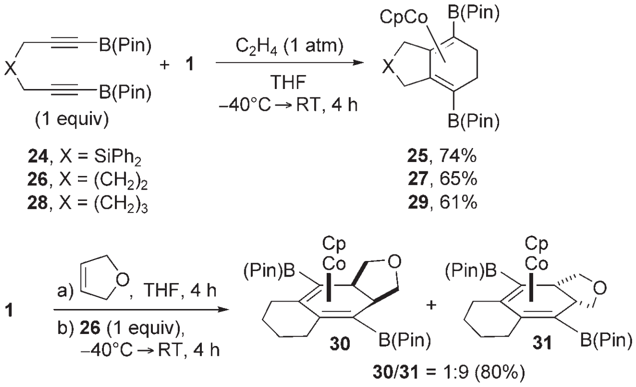


Entry	R′	R″	*exo* or *endo*[a] (yield [%])[b]
1	Ph	Ph	**18**, *endo* (25)
2	H	Ph	**19**, *endo* (50)
3	H	$SiMe_3$	**20**, *exo* (50)
	$SiMe_3$	H	**21**, *exo* (18)
4	H	$SnBu_3$	**22**, *exo* (34)
	$SnBu_3$	H	**23**, *exo* (11)

[a] The designations *exo* and *endo* refer to the configuration of the precursor cobaltacyclopentadiene(alkene) complexes and are in analogy to Diels–Alder cycloaddition terminology. Regio- and stereochemical assignments were made by chemical shift, NOE, DEPT, and 2D-NMR (COSY, HMBC) analyses. [b] Yields of product isolated after flash chromatography on SiO_2, except for **22** and **23**, for which basic alumina was used.

In the case of acyclic, particularly internal, alkenes, competition with ethene becomes an issue (Table 3). For example, *trans*-stilbene failed to undergo cycloaddition, the reaction mixture rendering only **11D** in 70 % yield. On the other hand, *cis*-stilbene provided **18** as a single diastereomer, albeit in moderate yield (entry 1), diminished by the generation of **11D** (50 % yield). Terminal alkenes proved more amenable and revealed interesting stereo- and regioselectivities. For instance, styrene (entry 2) yielded only the *endo*-2,4,6-triphenyl derivative **19** (50 % yield). A similar, but attenuated, preference for placing the substituted ethene carbon adjacent to the boron-substituted terminus was found with vinyltrimethylsilane and vinyl(tributyl)tin (entries 3 and 4, respectively). However, in sharp contrast to styrene, the stereochemistry of addition was exclusively *exo*, an outcome that is most likely caused by steric factors.

The scope of the reaction was expanded to the cycloaddition of various α,ω-diboryldiynes to alkenes (Scheme 1). These substrates enforce the 1,4-orientation of the boryl substituents in the resulting diene and grant access to the first polycyclic 1,4-diborylcyclohexa-1,3-diene derivatives. The reactions proceed in good yield (61–80 %) and, in the case of **26**, high stereoselectivity, which bodes well for synthetic application to more complex structures. The ^{13}C NMR spectroscopic data confirm the location of the boryl groups in complexes **8C**–**11C**. The structure of **27**, while showing some disorder of one of the boryl groups, was confirmed by an X-ray analysis (Figure 2).[25] Again, the effect of the boryl substituents on the remainder of the molecule appears minimal.



Scheme 1. CpCo-mediated cocyclizations of α,ω-diboryldiynes with alkenes leading to bicyclic and tricyclic 1,4-diborylcyclohexadiene complexes.

While the reported cyclizations furnish the desired organic products complexed to cobalt, this outcome is advantageous as it stabilizes the ligands and, at the same time, potentially activates them towards hydride abstraction and further substitution.[11,22,24,26] Nevertheless, the air- and heat-sensitive free dienes could be liberated by rapid oxidative demetalation with iron(III) chloride (1.5 equiv) in acetonitrile (Table 4, entries 1–11). As expected, the respective *endo*- and *exo*-cyclopentadienylcobalt diastereomers

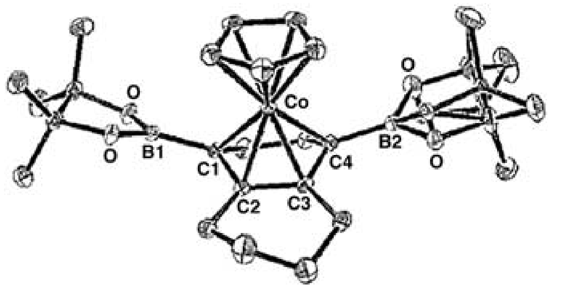
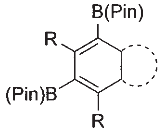
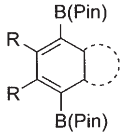
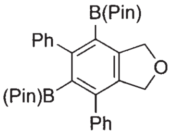


Figure 2. ORTEP view of complex **27** in the solid state (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Co–C$_{Cp}$ 2.07 (av), C1–B1 1.547(4), C4–B2 1.543(4), B–O 1.37 (av), C–C$_{diene}$ 1.44 (av), Co–C1 2.055(3), Co–C2 1.980(3); C1-C2-C3-C4 2.1.

Table 4: Oxidative demetalation of CpCo(cyclohexadiene) complexes with $FeCl_3 \cdot 6H_2O$ and demetalative aromatizations with ceric ammonium nitrate.

Entry	Substrate	Product		Yield [%][a]
				
1	**9D**	**32**		71
2	**9C**		**33**	69
3	**10D**[b]	**34**		74
4	**11D**[b]	**35**		75
5	**14/15**	**37**		79
6	**16/17**	**38**		80
7	**12/13**	**36**		69
8	**25**		**40**	69
9	**27**		**41**	76
10	**29**		**42**	80
11	**30/31**		**43**	82
12[c]	**36**	**39**[e]		45
13[d]	**30/31**		**44**[e]	49

[a] Yields of product isolated after column chromatography. [b] Reacted as a mixture with minor isomer **C**. [c] Treatment with CAN (4×0.5 equiv.) in acetone (RT, 2 h). [d] Treatment with CAN (4×0.75 equiv.) in acetone (RT, 12 h). [e]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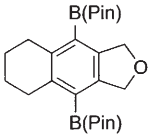
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gave the same diborylcyclohexa-1,3-diene after cobalt removal, thus providing additional proof for the structure of the starting complexes. Aromatization was also accomplished, albeit in only moderate yields so far, using ceric ammonium nitrate (CAN), either starting from the free ligand (entry 12) or directly from the complex (entry 13).

In this work we have described the extensively chemo-, regio-, and diastereoselective assembly of mono-, bi-, and tricyclic 1,3- and 1,4-diboryl-1,3-cyclohexadienes by means of the CpCo-mediated cycloaddition of alkynyl pinacolboronates to alkenes. This method provides a rapid entry into highly functionalized 1,3-cyclohexadiene synthons of potential use in complex molecule synthesis. A mechanistic rationale for the regio- and diastereoselective outcome of this cycloaddition reaction is currently being sought by means of density functional computations.

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Keywords: alkenes · alkynylboronates · cobalt · cycloaddition · diene ligands

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[17] **11D**: $C_{35}H_{43}B_2CoO_4$, $M_r = 608.28$, crystal size $0.10 \times 0.10 \times 0.10\ mm^3$, triclinic, space group $P\bar{1}$ (no. 1), $a = 10.584(3)$, $b = 11.347(4)$, $c = 14.593(3)$ Å, $\alpha = 95.72(2)$, $\beta = 109.511(19)$, $\gamma = 94.51(2)°$, $V = 1632.0(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.238\ g\,cm^{-3}$, scan range $4.00 < 2\theta < 50°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.562\ cm^{-1}$, $T = 295$ K, 5702 unique reflections, of which 3702 were taken as observed ($I > 1.50\sigma(I)$), $R = 0.051$, $R_w = 0.043$. CCDC-272959 (**11D**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[25] **27**: $C_{27}H_{35}B_2CoO_4$, $M_r = 504.13$, crystal size $0.10 \times 0.10 \times 0.10\ mm^3$, triclinic, space group $P\bar{1}$ (no. 1), $a = 10.4024(7)$, $b = 12.1415(11)$, $c = 12.1749(8)$ Å, $\alpha = 100.563(6)$, $\beta = 99.681(6)$, $\gamma = 113.834(6)°$, $V = 1331.6(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.257\ g\,cm^{-3}$, scan range $23.2 < 2\theta < 55°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.674\ cm^{-1}$, $T = 200$ K, 5589 unique reflections, of which 3033 were taken as observed ($I > 3.00\sigma(I)$), $R = 0.038$, $R_w = 0.043$. CCDC-272960 (**27**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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