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# Synthesis of Dibromobenzobarrelene Derivatives and Catalytic Activity of Their Rhodium Complexes

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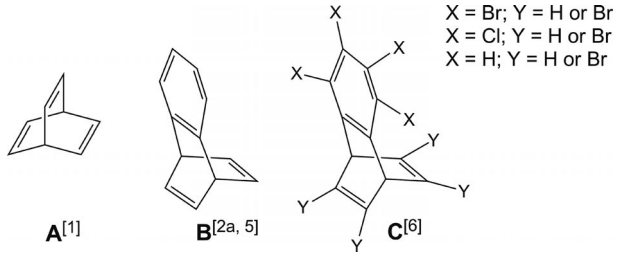
A novel synthetic route based on [4+2] cycloaddition for dibromobenzobarrelene derivatives starting from in situ generated 3,5-dibromo-1,2-didehydrobenzene and mesitylene, 1,2,4,5-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, pentamethylbenzene, 1,3-dimethoxybenzene, and 2,4,6-trimethylbromobenzene, respectively, was developed. Thus, six novel dibromobenzobarrelenes with diverse substitution patterns at the barrelene framework including chiral derivatives are reported. The benzobarrelene 6,8-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**1a**) was functionalized at the annulated benzene ring to give three novel carboxylic acids and two novel phosphonic acid esters. Selected benzobarrelene complexes with $Rh^{I}Cl$ were tested for their catalytic activity in the 1,4-addition of phenylboronic acid towards cyclohex-2-enone. Turnover frequencies up to 3405 $h^{-1}$ were observed, which are among the highest reported so far for Rh–diene complexes in this type of C–C coupling reaction.

## Introduction

Since the first report by Zimmerman and Paufler on bicyclo[2.2.2]-2,5,7-octatriene (Scheme 1, **A**) in 1960,[1] diverse synthetic routes have been developed for this class of bicyclic olefins.[2] In particular, their reactivity as a result of the ring strain has gained considerable interest.[2b,2c] The key step to prepare these so-called barrelenes is a [4+2] cycloaddition of acetylene and benzene derivatives.[2a,3] Recently, alternative synthetic routes starting from *cis*-3,5-cyclohexadiene-1,2-diol have been reported.[4] The replacement of acetylene by benzyne derivatives and the reaction of acetylene derivatives with naphthalene give access to strained olefins attached to a substituted benzene ring, so-called benzobarrelenes (Scheme 1, **B**).[2a,5] The substitution pattern at the olefin as well as at the annulated benzene ring does significantly influence the reactivity of the compounds[6] as well as their electronic properties and thus their coordination behavior (e.g., towards late-transition metals).[7] For example, halogen atoms in perhalogenobenzobarrelene derivatives (Scheme 1, **C**) act as electron-withdrawing groups that enhance the coordination strength of the strained olefins in complexes with late-transition metals, whereas substitution at the double bonds allows the fine-tuning of the bite angle of the dienes and provides steric and stereochemical control of the coordination.[7] Since 1985, a rich coordination chemistry with achiral perfluorinated benzobarrelenes was developed,[8] whereas the growing interest in chiral benzobarrelene ligands and their use in asymmetric catalysis is more recent.[9] With regard to immobilization of diene-based catalysts, it is of interest to post-functionalize the benzene ring of a benzobarrelene ligand (e.g., with carboxylic or phosphonic acid moieties). However, so far only the synthesis of perhalogenated derivatives was reported, which are not suitable for such post-functionalization strategies. Herein, we present a one-pot synthesis for partially bromo-substituted benzobarrelenes, which are subsequently transformed into phosphonic acid esters and carboxylic acids, respectively. The potential of




Scheme 1. Selected examples of different types of barrelenes.[1,2,5,6]

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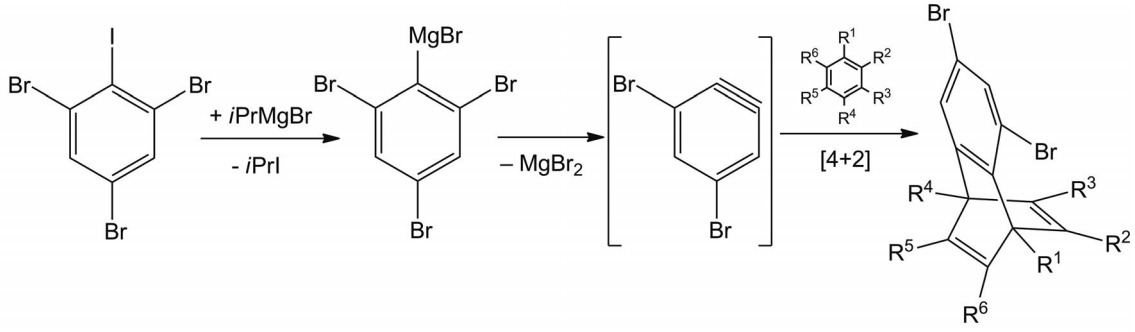
the benzobarrelenes to act as diene ligands is demonstrated by the isolation of the rhodium complex μ-dichloridodi(6,8-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene)dirhodium(I). The 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one was chosen as a catalytic test reaction to study the potential of in situ formed rhodium complexes with benzobarrelene ligands in homogeneous catalysis.

## Results and Discussion

### Synthesis of Benzobarrelene Derivatives

Our synthetic approach towards bromo-substituted benzobarrelene derivatives is based on the Diels–Alder reaction of 3,5-dibromo-1,2-didehydrobenzene with different benzene derivatives. Typically, arynes are accessible either by means of decomposition of anthranilic acid derivatives,[5,10] oxidation of 1-aminobenzotriazole,[11] or elimination of metal salts starting from *ortho*-metalated halobenzenes.[12] With respect to the latter method, and as a result of higher stability, Grignard reagents are much easier to handle than organolithium compounds, especially in the case of a high halogen content in the halobenzenes. Thus, they allow a "controlled" release of the benzyne upon gentle heating, which ensures high conversion rates upon reaction with benzene derivatives. So far, studies on the synthesis of partially substituted benzobarrelenes using benzynes are scarce, presumably because the elimination of metal halides from *ortho*-metalated halobenzenes results in the formation of different isomeric benzynes. These might react with unsymmetrical benzenes to give a large number of benzobarrelene isomers. Thus, we used symmetrically substituted 2,4,6-tribromoiodobenzene as starting material, which reacts with isopropylmagnesium bromide[13] to afford the Grignard reagent 2,4,6-$Br_3C_6H_2MgBr$. The latter is stable in THF at room temperature in the presence of substituted benzene derivatives. Upon heating the Grignard reagent in THF, 3,5-dibromo-1,2-didehydrobenzene is released and reacts with the benzene derivative to give a benzobarrelene as illustrated in Scheme 2.

To identify suitable benzene derivatives for the [4+2] cycloaddition, various diene components such as mesitylene (**1**), 1,2,4,5-tetramethylbenzene (**2**), 1,2,3,5-tetramethylbenzene (**3**), 2,4,6-trimethylbromobenzene (**4**), pentamethylbenzene (**5**), and 1,3-dimethoxybenzene (**6**) were investigated and the degree of conversion was determined by NMR spectroscopy. Electron-rich benzenes such as 1,3-dimethoxybenzene and 1,2,3,5-tetramethylbenzene show a high degree of conversion (58–62%, based on 2,4,6-tribromoiodobenzene) to the respective benzobarrelene derivatives, whereas electron-poor systems (e.g., 2,4,6-trimethylbromobenzene; 17% conversion) did react, but only sluggishly. Depending on the workup procedure, we were able to isolate benzobarrelenes with yields up to 37% (e.g., compound **6**). The number of isomers formed depends on the identity of the starting benzene derivatives. In the case of mesitylene, the two regioisomers **1a** and **1b** (76:24) were separated by precipitation to give 6,8-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene **1a** as solid material, which was additionally purified by sublimation (20% yield). Kugelrohr distillation and column chromatography of the residue afforded 5,7-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**1b**) with a yield of 8%. The NMR spectra of both isomers **1a** and **1b** do not differ significantly except for a signal that is observed at $\delta$ = 4.64 ppm for **1b** and at $\delta$ = 4.00 ppm for **1a**. The latter is assigned on the basis of a NOESY 1D-NMR spectroscopic experiment that revealed an interaction (NOE 1.7%) between the aromatic proton $H^a$(C4) at $\delta$ = 7.18 ppm and the bridgehead proton $H^b$(C7) at $\delta$ = 4.00 ppm (Scheme S1 in the Supporting Information). In the isomer **1b** the bridgehead proton $H^c$ is located in proximity to $Br^d$ and does not show any interaction with an aromatic proton.




**1a**: $R^{1,3,5}$-$CH_3$, $R^{2,4,6}$-H; **1b**: $R^{1,3,5}$-H, $R^{2,4,6}$-$CH_3$
**2a**: $R^{1,4}$-H, $R^{2,3,5,6}$-$CH_3$; **2b**: $R^{1,2,4,5}$-$CH_3$, $R^{3,6}$-H;
**2c**: $R^{1,3,4,6}$-$CH_3$, $R^{2,5}$-H
**3a**: $R^{1,2,3,5}$-$CH_3$, $R^{4,6}$-H; **3b**: $R^{1,3,5,6}$-$CH_3$, $R^{2,4}$-H;
**3c**: $R^{1,5}$-H, $R^{2,3,4,6}$-$CH_3$; **3d**: $R^{1,3}$-H, $R^{2,4,5,6}$-$CH_3$

**4a**: $R^{1,3,5}$-$CH_3$, $R^2$-Br, $R^{4,6}$-H; **4b**: $R^{1,3,5}$-$CH_3$, $R^{2,4}$-H, $R^6$-Br;
**4c**: $R^{1,5}$-H, $R^{2,4,6}$-$CH_3$, $R^3$-Br; **4d**: $R^{1,3}$-H, $R^{2,4,6}$-$CH_3$, $R^5$-Br
**5a**: $R^{1,2,3,5,6}$-$CH_3$, $R^4$-H; **5b**: $R^{1,2,3,5,6}$-$CH_3$, $R^4$-H;
**5c**: $R^{1,3,4,5,6}$-$CH_3$, $R^2$-H; **5d**: $R^{1,2,3,4,5}$-$CH_3$, $R^6$-H
**6a**: $R^{1,3}$-$OCH_3$, $R^{2,4,5,6}$-H; **6b**: $R^{1,5}$-$OCH_3$, $R^{2,3,4,6}$-H;
**6c**: $R^{1,3,5,6}$-H, $R^{2,4}$-$OCH_3$; **6d**: $R^{1,2,3,5}$-H, $R^{4,6}$-$OCH_3$

Scheme 2. Synthesis of dibromo-substituted benzobarrelene derivatives.

The reaction of the in situ prepared 3,5-dibromo-1,2-didehydrobenzene with 1,2,4,5-tetramethylbenzene gave, according to NMR spectroscopic experiments, three different isomers of **2**, two of which were stereoisomers. Conversion into the symmetrical regioisomer **2a** bearing two hydrogen atoms in the bridgehead position is favored, but isolation of the pure compound **2a** was difficult. Thus, a mixture of all isomers with an overall yield of 24% was isolated. Using the more complex 1,2,3,5-tetramethylbenzene gave two chiral regioisomers (**3a/b**; **3c/d**), of which compound **3a/b** was isolated by column chromatography with a yield of 31%. Crystallization from hexane gave single crystals that consisted of a racemic mixture of **3a/b**. $^1$H NMR spectroscopy revealed the absence of an achiral regioisomer with two methyl groups in the bridgehead position. This might be explained as the result of steric hindrance and unfavorable electronic properties in the starting material 1,2,3,5-tetramethylbenzene. According to the frontier orbitals overlap concept developed by Fukui for Diels–Alder reactions, it is most likely that the methyl groups in the 2- and 5-position in 1,2,3,5-tetramethylbenzene disfavor the reaction with 3,5-dibromo-1,2-didehydrobenzene to give the above-mentioned achiral regioisomer.[14] A similar situation was observed upon reaction of 3,5-dibromo-1,2-didehydrobenzene with 2,4,6-trimethylbromobenzene, which results in the formation of two chiral regioisomers, **4a/b** and **4c/d** (62:38). The stereochemical outcome of the reaction does not differ significantly relative to 1,2,3,5-tetramethylbenzene, but the conversion drops to 17%. Single crystals of **4a/b** were isolated with the bromo substituent located at the 2-position of the corresponding benzobarrelene derivative (Figure 1). Bromo-substituted derivatives similar to **4** have been reported earlier. A bromination–elimination sequence starting from unsubstituted or fully halogenated benzobarrelene derivatives was used. Such a reaction sequence might allow additional functionalization of the novel benzobarrelenes reported here.[6a,15] Starting from pentamethylbenzene, the reaction is even more complex and provides three regioisomers of compound **5** including one chiral isomer. After the workup procedure including column chromatography, sublimation, and crystallization, we did obtain single crystals composed of the regioisomers **5a** and **5b** and the stereoisomers **5c/d** with a ratio of 53:25:22 (Figure S1 in the Supporting Information). As expected, the reaction of 3,5-dibromo-1,2-didehydrobenzene with the electron-rich 1,3-dimethoxybenzene gave the best conversion of 76% yield, but isolation of the pure compound **6** was difficult. However, from a mixture of two racemic regioisomers (**6a/b:6c/d**; 84:16) dissolved in hexane/acetone, racemic single crystals of the regioisomer **6a/b** crystallized with low yield (Figure 1).

The molecular structures show different angles at the diene. For example, in compound **1a** the angles C9–C10–C12 105.2(4)° and C8–C7–C11 107.4(4)° differ by 2.20° (Figure 1), which is a consequence of both electronic and steric properties of the diene system. Electron-rich compounds, such as compound **6a**, do not show a significant difference (0.13°), whereas for electron-poor systems (e.g., compound **4a**) a large difference is observed (3.86°). These values demonstrate that a fine-tuning of the bite angle of the dienes is possible through substitution at the barrelene framework.

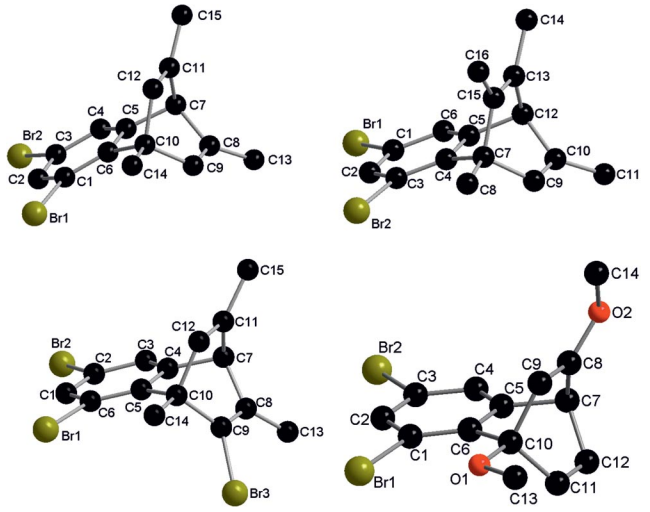
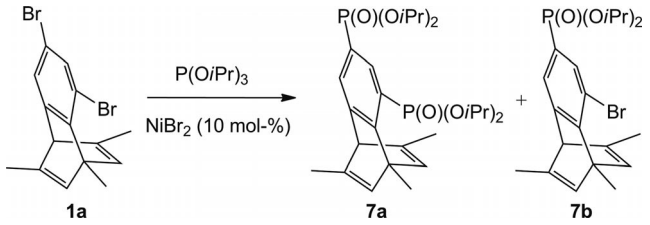



Figure 1. Ball-and-stick representation (DIAMOND) of the molecular structures of compounds **1a** (left top), **3a** (right top), **4a** (left bottom), and **6a** (right bottom). Hydrogen atoms are omitted for clarity.

## Functionalization

The substituent pattern of the dibromobenzobarrelene derivatives reported here allows further substitution at the annulated benzene ring. We have chosen compound **1a** as a model compound to study the reactivity of dibromobenzobarrelenes. With regard to our previous work on organophosphonate synthesis, we have chosen functionalization of compound **1a** by a nickel-promoted phosphonation with triisopropylphosphite (Tavs reaction).[16] Additionally, we studied the synthesis of the corresponding carboxylic acids. The reaction of **1a** with triisopropyl phosphite at a temperature of 160 °C gave tetraisopropyl 1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6,8-diphosphonate (**7a**), which was isolated with a yield of 52% (Scheme 3). Crystallization from ethyl acetate afforded single crystals that were suitable for X-ray diffraction analysis (Figure 2). Purification of the crude product by column chromatography gave a second product, diisopropyl 8-bromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6-phosphonate (**7b**), with an isolated yield of 14%. The $^1$H NMR spec-




Scheme 3. Functionalization of compound **1a** by the Tavs reaction.

tra show a shift to higher frequencies for both aromatic protons from $\delta$ = 7.14 and 7.23 ppm in compound **1a** to $\delta$ = 7.43 and 7.51 ppm in compound **7b**, respectively. Furthermore, both aromatic protons show a $^{3}J(^{1}H,^{31}P)$ coupling of 14.3 Hz. Crystallization from ethyl acetate gave single crystals of **7b**. The molecular structure (Figure S2 in the Supporting Information) confirms the substitution at the sterically less-hindered bromine substituent in the 6-position. It is worth noting that selective substitution of one bromine atom of compound **1a** using the Tavs reaction failed; instead, mixtures of **7a** and **7b** were always obtained.

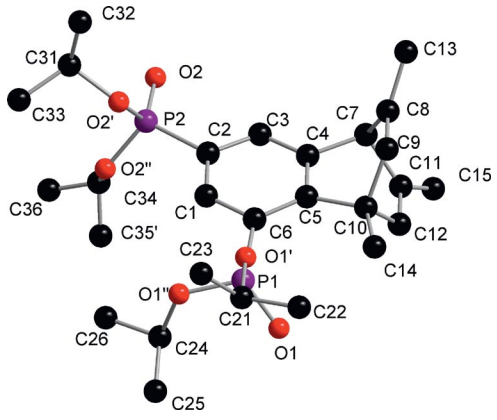
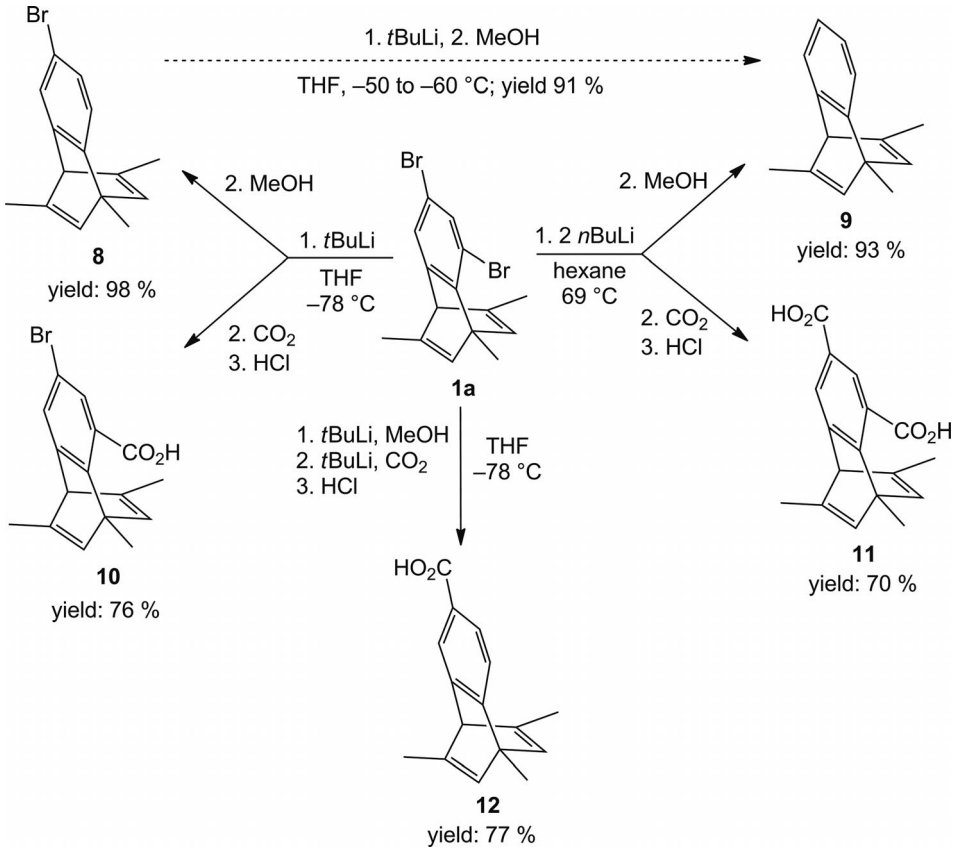



Figure 2. Ball-and-stick representation (DIAMOND) of the molecular structure of compound **7a**. Hydrogen atoms are omitted for clarity.

The reaction of one molar equivalent of *n*-butyllithium with compound **1a** gave a mixture of products as a result of metal/halogen exchange in the 6- and 8-position. Quantitative and selective metal–halogen exchange at the 8-position was realized by the use of *tert*-butyllithium at –78 °C. The addition of methanol gave 6-bromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**8**) with a yield of 98% (Scheme 4). Worthy of note, and in contrast to the synthesis of compound **7b**, substitution at the sterically hindered bromine atom in the 8-position is observed. The bromine atom of compound **8** in the 6-position was removed quantitatively by the reaction of the latter with one equivalent of *tert*-butyllithium at –50 to –60 °C followed by the addition of methanol to give 1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**9**) with a yield of 91%. The latter was directly prepared with a yield of 93% by reaction of 1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**1a**) with two equivalents of *n*-butyllithium in hexane under reflux conditions followed by the addition of methanol. Starting from compound **1a** the use of *tert*-butyllithium even in large excess amount in a one-pot reaction did not result in quantitative metal–halogen exchange of both bromine atoms.

Based on the results of the metal–halogen exchange studies, three benzobarrelene carboxylic acid derivatives (**10**–**12**) were synthesized by the addition of carbon dioxide to the




Scheme 4. Metal–halogen exchange studies of compound **1a**.

organolithium species with yields in the range 70–77% (Scheme 4). The monocarboxylic acid **10** was obtained as a crystalline material (Figure 3). The molecular structure is composed of a dimer as a result of hydrogen bonds with an O1···O2A distance of 2.653 Å. The characteristic absorption band assigned to the asymmetric stretching vibration of the carbonyl group at $\tilde{\nu}$ = 1697 cm$^{-1}$, the broad band at $\tilde{\nu}$ = 2962 cm$^{-1}$, and the O–H···O out-of-plane vibrations at $\tilde{\nu}$ = 960 cm$^{-1}$ support the assignment of strong hydrogen bonds. Furthermore, the $^1$H NMR spectra show a shift to higher frequency for the aromatic proton at C2 from $\delta$ = 7.23 ppm in compound **1a** to $\delta$ = 7.41 ppm in compound **10**, respectively. Similarly, in the $^1$H NMR spectrum of compound **11** the aromatic protons are shifted to $\delta$ = 7.63 and 7.80 ppm. The IR spectrum indicates the formation of hydrogen bonds by the asymmetric stretching vibration of the carbonyl group at $\tilde{\nu}$ = 1688 cm$^{-1}$ and the broad band absorption at $\tilde{\nu}$ = 3040 cm$^{-1}$. The monocarboxylic acid **12**, synthesized starting from compound **1a** by means of **8**, also shows characteristic absorption bands for the asymmetric stretching vibration of the carbonyl group at $\tilde{\nu}$ = 1694 cm$^{-1}$ and a broad absorption band at $\tilde{\nu}$ = 3020 cm$^{-1}$ that is indicative of a supramolecular assembly through hydrogen bonds. The $^1$H NMR spectrum shows a shift to higher frequencies for the corresponding aromatic protons from $\delta$ = 6.95, 7.07, and 7.27 ppm in compound **8** to $\delta$ = 7.15, 7.56, and 7.70 ppm in compound **12**, respectively. These observations are in good agreement with values described in the literature.[17]

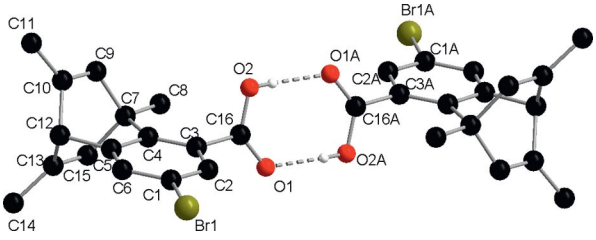



Figure 3. Ball-and-stick representation (DIAMOND) of the molecular structure of compound **10**. Symmetry transformations used: A = –*x* + 1, –*y* + 1, –*z* + 2. O2···O1A 2.653 Å.

## Rh$^I$ Complex

Benzobarrelene derivatives offer the possibility of diene coordination to late-transition metals to give complexes that hold potential in homogeneous catalysis.[9a,9c,9d] Thus, the reaction of compound **1a** with di-μ-chloridotetraethylenedirhodium(I) was studied and gave di-μ-chloridodi-8-Adibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalenedirhodium(I) (**13**) and ethylene. The progress of the reaction was indicated by a disappearance of the $^1$H NMR spectroscopic signal in $CDCl_3$ at $\delta$ = 3.16 ppm (coordinated ethylene) and the appearance of a new signal at $\delta$ = 5.34 ppm (free ethylene). Furthermore, an upfield shift of the signal for the diene hydrogen atoms from $\delta$ = 6.00 ppm in compound **1a** to $\delta$ = 3.18 ppm in compound **13** was observed.

Crystallization from dichloromethane resulted in the formation of single crystals suitable for X-ray diffraction analysis (Figure 4). Formation of a nonsymmetrically chlorido-bridged rhodium dimer [Rh1–Cl1 2.4033(2) Å; Rh1–Cl1A 2.4075(2) Å] is observed. The carbon–carbon double bonds are elongated from 1.315(7) (C8–C9) and 1.321(7) Å (C11–C12) in compound **1a** to 1.4146(1) (C2–C3) and 1.4141(1) Å (C6–C7) in complex **13**. The C3–C4–C6 angle of 98.1(6)° is significantly compressed relative to compound **1a** [C9–C10–C12 105.2(3)°]. This is in good agreement with other known bis(μ-chlorido)bis(benzobarrelene)dirhodium complexes, such as bis(μ-chlorido)-bis{$\eta^2$,$\eta^2$-(*R*,*R*)-5,6,7,8-tetrafluoro-2,9-bis[(–)menthoxymethyl]-1,4-dihydro-1,4-ethenonaphthalene}dirhodium,[9e] which shows a bite angle of approximately 98.2° and a C–C bond length of 1.406 Å.

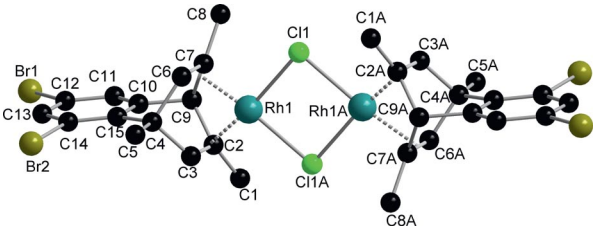


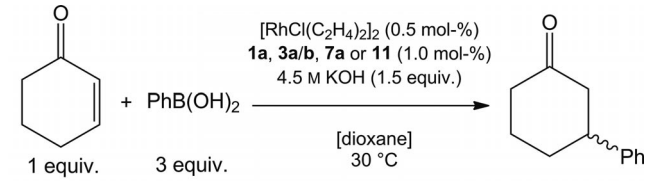

Figure 4. Ball-and-stick representation (DIAMOND) of the molecular structure of complex **13**. Hydrogen atoms are omitted for clarity. Symmetry transformations used: A = –*x* + 1, –*y* + 1, –*z* + 2.

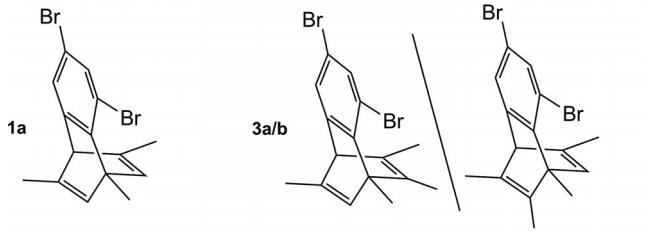
## Catalysis

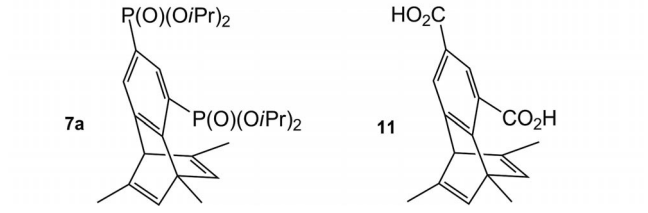
Catalyst screening was performed on the basis of the 1,4-addition of phenylboronic acid towards 2-cyclohexen-1-one (Table 1), a reaction that is catalyzed by rhodium complexes that contain diene ligands (Figure 5).[9b,9d,9e,18] Therefore, compounds **1a**, **3a/b**, **7a**, and **11** were treated with di-μ-chloridotetraethylenedirhodium(I) to induce the exchange of ethylene by the corresponding benzobarrelene ligand. In the case of compound **1a**, this reaction was monitored by $^1$H NMR spectroscopy to reveal quantitative exchange. The complex composed of **1a**–Rh$^I$ gave, after 6 min, quantitative conversion of cyclehex-2-enone to 3-phenylcyclohexenone with a maximum turnover frequency (TOF) of 2900 h$^{-1}$ after 30 s (Table 1). The complexes composed of **7a**–Rh$^I$ and **11**–Rh$^I$, respectively, gave quantitative conversion after 10 min (TOF of 600 h$^{-1}$). The maximum TOF of 3405 h$^{-1}$ after 30 s was observed for **11**–Rh$^I$ (**7a**–Rh$^I$, 2011 h$^{-1}$) and was the highest of all samples tested. The complex **3a/b**–Rh$^I$ gave quantitative conversion after 20 min (TOF of 300 h$^{-1}$) and a maximum TOF of 1821 h$^{-1}$ after 30 s. The lowest catalytic activity was observed for the **3a/b**–Rh$^I$ complex (quantitative conversion after 20 min), which is more sterically hindered at the diene system as a result of the additional methyl group.

Table 1. Rhodium-catalyzed 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one by the use of compounds **1a**, **3a/b**, **7a**, and **11** as diene ligands.




| Time [min] | Conversion [%] (TOF [$h^{-1}$]) 1a | 3a/b | 7a | 11 |
|---|---|---|---|---|
| 0.5 | 24.2 (2900) | 15.2 (1821) | 16.8 (2011) | 28.4 (3405) |
| 1.0 | 36.1 (2163) | 29.5 (1772) | 26.7 (1604) | 46.9 (2812) |
| 1.5 | 49.4 (1977) | 37.2 (1488) | 42.2 (1668) | 59.8 (2392) |
| 2.0 | 59.1 (1699) | 45.2 (1355) | 49.4 (1483) | 79.3 (2379) |
| 3.0 | 71.8 (1437) | 56.0 (1121) | 66.6 (1332) | 85.6 (1713) |
| 4.0 | 94.3 (1414) | 66.1 (992) | 79.6 (1194) | 91.2 (1368) |
| 6.0 | 100 (1000) | 84.0 (840) | 94.6 (946) | 95.2 (952) |
| 10.0 | 100 | 96.5 (579) | 100 (600) | 100 (600) |
| 20.0 | 100 | 100 (300) | 100 | 100 |

Note that the use of complex **1a**–$Rh^{I}$ as catalyst and 0.5 equiv. of KOH, an amount that is typically used in literature procedures, gave a conversion of approximately 85% after 1 h with a maximum TOF of 3142 $h^{-1}$ after 60 s. The amount of conversion is below those reported for other bicyclo[2.2.2]octa-2,5-dienes, which give 96 to 100% yield after a reaction time of 1 h.[18c,18e] However, under optimized reaction conditions (1.5 equiv. KOH) we did observe quantitative conversion within 6 min for complex **1a**–$Rh^{I}$. Thus, the optimized conditions were used for catalytic investigations of the benzobarrelene derivatives reported here and result in high TOFs and quantitative yields.

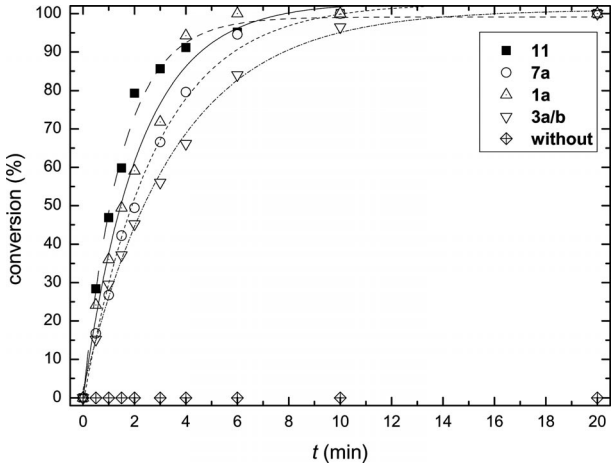



Figure 5. Catalytic activity of $Rh^{I}$ complexes with **1a**, **3a/b**, **7a**, and **11** in the 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one.

## Conclusion

A new synthetic approach towards dibromobenzobarrelene derivatives is reported. The Diels–Alder reaction of 3,5-dibromo-1,2-didehydrobenzene, which was prepared from the Grignard reagent 2,4,6-$Br_3C_6H_2MgBr$, allows the synthesis of dibromobenzobarrelenes including achiral as well as chiral derivatives. Metal–halogen exchange studies using the model compound 6,8-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (**1a**) and butyllithium reagents show a higher reactivity of the bromine atom in the sterically more-hindered 8-position. Interestingly, contrary results were obtained by using the Tavs reaction, which showed a higher reactivity of the bromine atom in the 6-position. By utilizing these two synthetic procedures five additional benzobarrelene derivatives including three carboxylic acids and two phosphonic acid esters were synthesized. They hold potential for the immobilization of benzobarrelenes on solid supports. Exchange experiments with μ-dichloridotetraethylenedirhodium(I) and the benzobarrelene ligand **1a** confirm the straightforward formation of the novel benzobarrelene-substituted rhodium complex [{Rh(**1a**)Cl}$_2$]. Such complexes are very active in the rhodium-catalyzed 1,4-addition of phenylboronic acid to 2-cyclohexen-1-on as exemplified by the use of benzobarrelene ligands **1a**, **3a/b**, **7a**, and **11**. An excellent catalytic performance that resulted in high turnover frequencies with values up to 3405 $h^{-1}$ and quantitative conversions after 6 to 10 min was observed. The catalytic activity was much higher than reported for other diene ligands, which typically give quantitative yields after a reaction time of one to three hours.[18c–18g] Notably, the catalytic reaction tolerates functional groups such as carboxylic acid and phosphonic acid ester.

## Experimental Section

**General:** All solvents were dried and distilled before use. Column chromatography was performed on silica gel 60 (70–230 mesh, Ma-

cherey-Nagel). 2,4,6-Tribromoiodobenzene was synthesized according to literature methods.[19] Melting points were determined with a Büchi Melting Point B-540 melting apparatus and are uncorrected. Infrared spectra were recorded with a Spectromat FTS-165 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500 MHz) at room temperature. NOESY 1D NMR spectroscopic experiments were carried out with a Varian Inova 400 spectrometer. Quantitative gas chromatographic analysis was performed with a 5890 Series II Plus from Hewlett–Packard equipped with a flame ionization detector (FID). An apolar J&W HP-5 column from Agilent Technologies, which consisted of polymethylphenylsiloxane (95% methyl, 5% phenyl groups), was used. The injector temperature was set to 270 °C, a split of 1:50, and a volume flow of the carrier gas nitrogen of 1.8 mL min$^{-1}$ was used. After 5 min at 50 °C, the temperature was increased to 275 °C with a rate of 10 °C min$^{-1}$ and then remained at this temperature for 14.5 min. For each sample a fivefold GC analysis was performed. The data sets for the single-crystal X-ray studies of the compounds **3a/b**, **5a**–**d**, **6a/b**, **7b**, **9**, and **13** were collected with Mo-$K_\alpha$ radiation (0.71073 Å) with an Oxford Gemini S diffractometer at 110 K. The data sets for the single-crystal X-ray studies of the compounds **1a**, **4a/b**, and **7a** were collected with Mo-$K_\alpha$ radiation (0.71073 Å) with a Nonius–Kappa CCD diffractometer at 173 K. All calculations were performed using the SHELXTL program.[20] The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$.

**Comment to Refinement of Structure 13:** The highest unrefined electron-density peak is located approximately 0.50 Å away from atom C17, and the next highest unrefined electron-density peak is located approximately 1.66 Å away from atom Cl5 of one and the same $CH_2Cl_2$ molecule, which acts as packing solvent. Any attempts to refine the mentioned $CH_2Cl_2$ molecule disordered failed or gave unreliable results.

CCDC-817508 (for **1a**), -817512 (for **3a/b**), -817509 (for **4a/b**), -817510 (for **5a**–**d**), -517511 (for **6a/b**), -900721 (for **7a**), -900720 (for **7b**), -900718 (for **10**), and -900719 (for **13**) contain 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.

**General Procedure for the Synthesis of Dibromobenzobarrelene Derivatives:** Isopropylmagnesium bromide was prepared by the reaction of isopropyl bromide (7.4 g, 50.0 mmol) and magnesium turnings (1.8 g, 74.0 mmol) in tetrahydrofuran (100 mL). The solution was added dropwise to a mixture of 2,4,6-tribromoiodobenzene (22.0 g, 50.0 mmol) in tetrahydrofuran (75 mL) and the benzene derivative at 0 °C. After stirring for 48 h under reflux conditions (except for compound **1**), the solvents were evaporated under vacuum at 70 °C. After dissolving the residue in diethyl ether (200 mL), the organic phase was washed three times with water (50 mL) and dried with magnesium sulfate. After removing the latter, evaporation of the solvent provided the crude product that was purified according to the methods presented below.

**6,8-Dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (1a) and 5,7-Dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (1b):** Compounds **1a** and **1b** were prepared according to the general procedure given above by using mesitylene (75 mL). In this case, no additional tetrahydrofuran was used. The reaction mixture was stirred at 130 °C. Compound **1a** was precipitated as solid material by adding hexane. It was removed by filtration and purified by sublimation under high vacuum (<10$^{-3}$ mbar) at 150 °C to give colorless crystals of compound **1a** with a yield of 20% (3.5 g, 9.9 mmol) and a melting point of 144–145 °C. Hexane was evaporated from the filtrate and the residue was purified by Kugelrohr distillation under high vacuum (<10$^{-3}$ mbar) at 180 °C to give crude compound **1b**. Column chromatography (silica, hexane) afforded a colorless oil of compound **1b** with a yield of 8% (1.5 g, 4.2 mmol). Compound **1a**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.93 (d, $J$ = 1.7 Hz, 6 H), 2.11 (s, 3 H), 4.03 (t, $J$ = 1.9 Hz,1 H), 6.00 (m, 2 H), 7.17 (d, $J$ = 1.9 Hz, 1 H), 7.24 (d, $J$ = 1.9 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, $CDCl_3$): $\delta$ = 19.0, 21.8, 52.8, 60.6, 115.2, 116.8, 124.0, 132.1, 138.2, 146.2, 150.3, 153.9 ppm. Calcd. for $C_{15}H_{14}Br_2$ (354.08): C 50.9, H 4.0; found C 50.9, H 3.8. Compound **1b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.93 (d, $J$ = 1.7 Hz, 6 H), 2.29 (s, 3 H), 4.64 (t, $J$ = 1.8 Hz, 1 H), 5.99 (m, 2 H), 7.14 (d, $J$ = 1.5 Hz, 1 H), 7.23 (d, $J$ = 1.6 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, $CDCl_3$): $\delta$ = 19.5, 21.3, 50.9, 58.8, 126.9, 128.3, 137.0, 150.3 ppm. Calcd. for $C_{15}H_{14}Br_2$ (354.08): C 50.9, H 4.0; found 50.6, H 3.9.

**5,7-Dibromo-2,3,9,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (2a), (*S*,*S*)-5,7-Dibromo-1,2,4,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (2b), and (*R*,*R*)-5,7-Dibromo-1,2,4,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (2c):** Compounds **2a**–**c** were prepared according to the general procedure given above using 1,2,4,5-tetramethylbenzene (8.0 g, 60.0 mmol). The crude product was purified by column chromatography (silica, hexane). Sublimation under high vacuum (<10$^{-3}$ mbar) at 85 °C afforded the product as colorless crystals that contained both isomers with a yield of 24% (4.4 g, 12.0 mmol). Compound **2a**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.78 (d, $J$ = 1.1 Hz, 6 H), 1.81 (d, $J$ = 1.1 Hz, 6 H), 4.06 (s, 1 H), 4.54 (s, 2 H), 7.15 (d, $J$ = 1.9 Hz, 1 H), 7.23 (d, $J$ = 1.8 Hz, 1 H) ppm. Compound **2b/2c**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.76 (d, $J$ = 1.2 Hz, 3 H), 1.81 (d, $J$ = 1.2 Hz, 3 H), 2.10 (s, 3 H), 2.20 (s, 3 H), 6.04 (m, 2 H), 7.12 (d, $J$ = 1.6 Hz, 1 H), 7.23 (d, $J$ = 1.6 Hz, 1 H) ppm. Calcd. for $C_{16}H_{16}Br_2$ (368.11): C 52.2, H 4.4; found C 51.9, H 4.2.

**(*S*,*R*)-6,8-Dibromo-1,2,3,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (3a), (*R*,*S*)-6,8-Dibromo-1,2,3,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (3b), (*R*,*S*)-5,7-Dibromo-1,2,3,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (3c), and (*S*,*R*)-5,7-Dibromo-1,2,3,10-tetramethyl-1,4-dihydro-1,4-ethenonaphthalene (3d):** Compounds **3a**–**d** were prepared according to the general procedure given above using 1,2,3,5-tetramethylbenzene (10.0 g, 75.0 mmol). The crude product was purified by column chromatography (silica, hexane). Colorless crystals that contained a mixture of compounds **3a** and **3b** were obtained with a yield of 26% (4.8 g, 13.0 mmol) and a melting point of 115–116 °C. Compounds **3c** and **3d** were not isolated. Compounds **3a/3b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.69 (d, $J$ = 1.2 Hz, 3 H), 1.81 (d, $J$ = 1.2 Hz, 3 H), 1.88 (d, $J$ = 1.2 Hz, 3 H), 2.10 (s, 3 H), 3.98 (d, $J$ = 2.1 Hz, 1 H), 5.89 (m, 2 H),7.14 (d, $J$ = 1.9 Hz, 1 H), 7.22 (d, $J$ = 1.9 Hz, 1 H) ppm. $^{13}$C NMR (125.80 MHz, $CDCl_3$): $\delta$ = 12.6, 17.1, 19.0, 20.4, 55.1, 60.7, 117.0, 123.7, 132.0, 138.3, 140.5, 141.2, 148.7, 153.8 ppm. Calcd. for $C_{16}H_{16}Br_2$ (368.1): C 52.2, H 4.4; found C 51.9, H 4.4. Compounds **3c/3d**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.65 (d, $J$ = 1 Hz, 3 H), 1.85 (d, $J$ = 1.1 Hz, 3 H), 1.91 (s, $J$ = 1.7 Hz, 3 H), 2.25 (s, 3 H), 4.59 (d, $J$ = 1.9 Hz, 1 H), 5.91 (m, 2 H),7.10 (d, $J$ = 1.7 Hz, 1 H), 7.23 (d, $J$ = 1.7 Hz, 1 H) ppm.

**(*R*,*S*)-2,6,8-Tribromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (4a), (*S*,*R*)-2,6,8-Tribromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (4b), (*S*,*R*)-2,5,7-Tribromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (4c), and (*R*,*S*)-2,5,7-Tribromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (4d):** Compounds **4a**–**d** were prepared according to the general procedure given above using 2,4,6-trimethylbromobenzene (10.5 mL,

75.0 mmol). The crude product was purified by column chromatography (silica, hexane). The product was obtained as colorless single-crystalline material with a yield of 7% (1.5 g, 3.5 mmol) and contained all isomers. Compounds **4a**/**4b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.90 (d, $J$ = 1.8 Hz, 3 H), 1.95 (s, 3 H), 2.18 (s, 3 H), 4.15 (d, $J$ = 2.0 Hz, 1 H), 5.98 (m, 1 H), 7.18 (d, $J$ = 1.9 Hz, 1 H), 7.29 (d, $J$ = 1.9 Hz, 1 H) ppm. Compounds **4c**/**4d**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.94 (d, $J$ = 1.7 Hz, 3 H), 1.98 (s, 3 H), 2.21 (s, 3 H), 4.77 (d, $J$ = 2.1 Hz, 1 H), 5.99 (m, 1 H), 7.17 (d, $J$ = 1.6 Hz, 1 H), 7.29 (d, $J$ = 1.6 Hz, 1 H) ppm. Calcd. for $C_{15}H_{13}Br_3$ (432.98): C 41.6; H 3.0; found C 40.9, H 3.3.

**6,8-Dibromo-1,2,3,9,10-pentamethyl-1,4-dihydro-1,4-ethenonaphthalene (5a), 5,7-Dibromo-1,2,3,9,10-pentamethyl-1,4-dihydro-1,4-ethenonaphthalene (5b), (*S*,*R*)-5,7-Dibromo-1,2,3,4,9-pentamethyl-1,4-dihydro-1,4-ethenonaphthalene (5c), and (*R*,*S*)-5,7-Dibromo-1,2,3,4,9-pentamethyl-1,4-dihydro-1,4-ethenonaphthalene (5d):** Compounds **5a**–**d** were prepared according to the general procedure given above using pentamethylbenzene (8.9 g, 60.0 mmol). The crude product was purified by column chromatography (silica, hexane). The product was obtained as colorless crystals with a yield of 29% (5.6 g, 14.6 mmol) and contained all isomers. Compound **5a**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.67 (d, $J$ = 1.2 Hz, 6 H), 1.82 (d, $J$ = 1.2 Hz, 6 H), 2.10 (s, 1 H), 3.96 (s, 1 H), 7.12 (d, $J$ = 1.9 Hz, 1 H), 7.23 (d, $J$ = 1.9 Hz, 1 H) ppm. Compound **5b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.63 (d, $J$ = 1.2 Hz, 6 H), 1.84 (d, $J$ = 1.2 Hz, 6 H), 2.11 (s, 1 H), 4.57 (s, 1 H), 7.10 (d, $J$ = 1.9 Hz, 1 H), 7.23 (d, $J$ = 1.9 Hz, 1 H) ppm. Compound **5c**/**5d**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.73–1.75 (m, 15 H), 6.03 (s, 1 H), 7.05 (d, $J$ = 1.9 Hz, 1 H), 7.22 (d, $J$ = 1.9 Hz, 1 H) ppm. Calcd. for $C_{17}H_{18}Br_2$ (382.13): C 53.4, H 4.8; found C 52.8, H 4.4.

**(*R*,*S*)-6,8-Dibromo-1,3-dimethoxy-1,4-dihydro-1,4-ethenonaphthalene (6a), (*S*,*R*)-6,8-Dibromo-1,3-dimethoxy-1,4-dihydro-1,4-ethenonaphthalene (6b), (*R*,*S*)-5,7-Dibromo-1,3-dimethoxy-1,4-dihydro-1,4-ethenonaphthalene (6c), and (*S*,*R*)-5,7-Dibromo-1,3-dimethoxy-1,4-dihydro-1,4-ethenonaphthalene (6d):** Compounds **6a**–**d** were prepared according to the general procedure given above using 1,3-dimethoxybenzene (10 mL, 77.0 mmol). The crude product was purified by column chromatography (silica, 10:1 mixture of hexane/acetone). The product was obtained as a colorless to light yellow single-crystalline material with a yield of 37% (6.9 g, 18.5 mmol) and contained all isomers. Compounds **6a**/**6b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 3.50 (s, 3 H), 3.74 (s, 3 H), 4.32 (ddd, $J$ = 6.0, 1.6, 2.5 Hz, 1 H), 5.53 (d, $J$ = 2.6 Hz, 2 H), 6.84 (dd, $J$ = 6.1, 7.2 Hz, 1 H), 7.07 (dd, $J$ = 7.3, 1.4 Hz, 1 H), 7.19 (d, $J$ = 1.8 Hz, 1 H), 7.29 (d, $J$ = 1.8 Hz, 1 H) ppm. Compound **6c**/**6d**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 3.50 (s, 3 H), 3.77 (s, 3 H), 4.82 (ddd, $J$ = 6.1, 1.5, 1.9 Hz, 1 H), 5.46 (d, $J$ = 2.4 Hz, 2 H), 6.88 (dd, $J$ = 6.2, 7.2 Hz, 1 H), 7.04 (dd, $J$ = 7.2, 1.4 Hz, 1 H), 7.25 (d, $J$ = 1.8 Hz, 1 H), 7.43 (d, $J$ = 1.8 Hz, 1 H) ppm. Compound **6a**/**6b**: $^{13}$C NMR (125.80 MHz, $CDCl_3$): $\delta$ = 54.3, 56.7, 59.7, 89.5, 101.7, 117.4, 120.5, 124.5, 132.6, 136.1, 139.9, 143.4 ppm. Calcd. for $C_{14}H_{12}Br_2O_2$ (372.05): C 45.2, H 3.3; found C 45.7, H 3.4.

**Tetraisopropyl 1,3,10-Trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6,8-diphosphonate (7a) and Diisopropyl 8-Bromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6-phosphonate (7b):** Compound **1** (5.0 g, 14.1 mmol) was mixed with nickel(II) bromide (1.23 g, 5.6 mmol). After heating to 160 °C, triisopropyl phosphite (8.8 g, 42.3 mmol) was added, and the reaction mixture was stirred over a period of 4 h at the same temperature. Cooling to room temperature afforded the crude product, which was purified by column chromatography (silica, ethyl acetate). Compound **7a** was obtained as colorless crystals with a yield of 52% and a melting point of 86–87 °C as the second phase of the column chromatography. Compound **7b** was obtained as colorless crystals with a yield of 14% and a melting point of 119–121 °C as the first phase of the column chromatography. Compound **7a**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.23 (d, $J$ = 6.2 Hz, 6 H), 1.33 (d, $J$ = 6.2 Hz, 6 H), 1.35 (d, $J$ = 1.5 Hz, 6 H), 1.36 (d, $J$ = 1.5 Hz, 6 H), 1.88 (d, $J$ = 1.6 Hz, 6 H), 2.29 (s, 3 H), 4.17 (q, $J$ = 1.8 Hz, 1 H), 4.65 (m, 4 H), 5.94 (m, 2 H), 7.64 (m, 1 H), 8.07 (m, 1 H) ppm. $^{31}$P NMR (202.53 MHz, $CDCl_3$): $\delta$ = 17.32 (s) ppm. Calcd. for $C_{27}H_{42}O_6P_2$ (524.57): C 61.8, H 8.1; found C 61.5, H 8.2. Compound **7b**: $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.23 (d, $J$ = 1.7 Hz, 6 H), 1.36 (d, $J$ = 6.2 Hz, 6 H), 1.89 (d, $J$ = 6.2 Hz, 6 H), 2.14 (s, 3 H), 4.13 (t, $J$ = 1.9 Hz, 1 H), 4.66 (m, 4 H), 5.98 (m, 2 H), 7.43 (dd, $J$ = 14.0, 1.3 Hz, 1 H), 7.51 (dd, $J$ = 14.0, 1.3 Hz, 1 H) ppm. $^{31}$P NMR (202.53 MHz, $CDCl_3$): $\delta$ = 15.41 (s) ppm. Calcd. for $C_{21}H_{28}BrO_3P$ (439.32): C 57.4, H 6.1; found C 57.0, H 6.1.

**6-Bromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene (8):** Compound **1** (5.0 g, 14.1 mmol) was dissolved in tetrahydrofuran (60 mL), and *tert*-butyllithium (1.6 M, 9.71 mL, 15.5 mmol) was added dropwise at –78 °C. The reaction mixture was stirred for 2 h at –60 to –70 °C. After adding methanol (20 mL), the solvents were evaporated, and the residue was dissolved in diethyl ether (100 mL). The organic phase was extracted three times with water (20 mL) and dried with magnesium sulfate. After removing the latter by filtration, evaporation of the solvent gave the product as a colorless solid with a yield of 98% (3.8 g, 13.8 mmol) and a melting point of 139 °C. $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.82 (s, 3 H), 1.89 (d, $J$ = 1.7 Hz, 6 H), 4.10 (t, $J$ = 1.8 Hz, 1 H), 6.00 (m, 2 H), 6.95 (d, $J$ = 7.8 Hz, 1 H), 7.07 (dd, $J$ = 7.8 Hz, 1.9 Hz, 1 H), 7.27 (d, $J$ = 1.9 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, $CDCl_3$): $\delta$ = 17.3, 19.2, 49.9, 59.9, 119.4, 124.6, 126.1, 137.1, 150.1 ppm. Calcd. for $C_{15}H_{15}Br$ (275.18): C 65.5, H 5.5; found C 65.3, H 5.4.

**1,3,10-Trimethyl-1,4-dihydro-1,4-ethenonaphthalene (9):** Compound **1** (2.0 g, 5.6 mmol) was dissolved in dry hexane (160 mL), and *n*-butyllithium (2.6 M, 4.73 mL, 12.3 mmol) was added dropwise at 0 °C. The reaction mixture was heated at reflux for 1 h. After addition of methanol (50 mL), the solvents were evaporated, and the residue was dissolved in ethyl ether (50 mL). The organic phase was extracted three times with water (20 mL) and dried with magnesium sulfate. After removing the latter by filtration, evaporation of the solvent gave the product as a colorless solid with a yield of 93% (1.0 g, 5.2 mmol) and a melting point of 44–47 °C. $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.85 (s, 3 H), 1.89 (d, $J$ = 1.7 Hz, 6 H), 4.15 (t, $J$ = 1.7 Hz, 1 H), 6.00 (m, 2 H), 6.86 (dt, $J$ = 7.2 Hz, 1.2 Hz, 1 H), 6.94 (dt, $J$ = 7.2 Hz, 1.2 Hz, 1 H), 7.12 (dd, $J$ = 7.2 Hz, 1.2 Hz, 1 H), 7.15 (dd, $J$ = 7.2 Hz, 1.2 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, $CDCl_3$): $\delta$ = 17.6, 19.5, 50.2, 60.6, 118.1, 121.5, 122.8, 123.6, 137.3, 148.4, 150.6, 151.1 ppm. Calcd. for $C_{15}H_{16}$ (196.29); C 91.8, H 8.2; found C 91.4, H 7.7

**6-Bromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene-8-carboxylic Acid (10):** Compound **1** (2.0 g, 5.6 mmol) was dissolved in tetrahydrofuran (35 mL), and *tert*-butyllithium (1.6 M, 3.88 mL, 6.2 mmol) was added dropwise at –78 °C. The reaction mixture was stirred for 2 h at –60 to –70 °C. Gaseous carbon dioxide was dumped through a drain tube over a period of 2 h at the same temperature. After the solvents had been evaporated, the residue was dissolved in diethyl ether (60 mL). The organic phase was extracted three times with diluted hydrochloric acid (20 mL) and dried with magnesium sulfate. After removing the latter by filtration, evaporation of the solvent provided the crude product, which was dissolved in a diluted sodium hydroxide solution and filtered through Celite. Acidification of the filtrate with diluted hy-

drochloric acid gave a colorless precipitate that was removed by filtration and dried under vacuum at 60 °C. The product was obtained as a colorless powder with a yield of 76% (1.4 g, 4.3 mmol) and a decomposition temperature of 189 °C. $^1$H NMR (500.30 MHz, [D$_6$]acetone): $\delta$ = 1.88 (d, $J$ = 1.7 Hz, 6 H), 1.91 (s, 3 H), 4.31 (t, $J$ = 1.8 Hz, 1 H), 5.97 (m, 2 H), 7.05 (d, $J$ = 1.9 Hz, 1 H), 7.41 (d, $J$ = 1.9 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, [D$_6$]-acetone): $\delta$ = 18.1, 18.2, 59.7, 124.4, 125.3, 137.3, 149.9, 169.4 ppm. IR: $\tilde{\nu}$ = 3420 (w), 2970 (m) , 2927 (m), 2902 (m), 2957 (w), 2560 (w), 1694 (s), 1603 (m), 1576 (w), 1508 (w), 1475 (w), 1432 (m), 1378 (w), 1337 (w), 1296 (s), 1262 (s), 1175 (w), 1116 (w), 1092 (w), 1045 (w), 957 (w), 924 (w), 874 (w), 813 (m), 775 (m), 669 (w), 642 (w), 550 (w), 514 (w) cm$^{-1}$. Calcd. for $C_{16}H_{15}BrO_2$ (319.19); C 60.2, H 4.7; found C 60.3, H 4.8.

**1,3,10-Trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6,8-dicarboxylic Acid (11):** *n*-Butyllithium (2.6 M, 4.73 mL, 12.3 mmol) was added dropwise at 0 °C to a solution of compound **1** (2.0 g, 5.6 mmol) in dry hexane (160 mL). The reaction mixture was heated at reflux for 1 h. After cooling to room temperature, gaseous carbon dioxide was added with a drain tube over a period of 2 h. After the solvent had been evaporated, the residue was dissolved in diethyl ether (80 mL). The organic phase was extracted three times with diluted hydrochloric acid (20 mL) and dried with magnesium sulfate. After removing the latter by filtration, evaporation of the solvent provided the crude product, which was dissolved in a diluted sodium hydroxide solution and filtered over Celite. Acidification of the filtrate with diluted hydrochloric acid gave a colorless precipitate that was removed by filtration and dried under vacuum at 60 °C. The product was obtained as a colorless powder with a yield of 70% (1.1 g, 3.9 mmol) and a decomposition temperature of 223 °C. $^1$H NMR (500.30 MHz, [D$_6$]acetone): $\delta$ = 1.91 (d, $J$ = 1.7 Hz, 6 H), 1.96 (s, 3 H), 4.41 (t, $J$ = 1.9 Hz, 1 H), 5.97 (m, 2 H), 7.63 (d, $J$ = 1.7 Hz, 1 H), 7.80 (d, $J$ = 1.7 Hz, 1 H) ppm. $^{13}$C NMR (125.80 MHz, $CDCl_3$): 18.2, 18.3, 51.3, 60.1, 122.4, 125.0, 136.7, 150.4, 151.1, 166.1 ppm. IR: $\tilde{\nu}$ = 3040 (m), 2958 (m), 2930 (m), 2902 (m), 2857 (w), 2647 (w), 2547 (w), 2358 (w), 2325 (m), 1688 (s), 1605 (m), 1461 (w), 1430 (m), 1390 (m), 1259 (s), 1179 (m), 1115 (w), 1047 (m), 903 (w), 874 (w), 811 (m), 766 (m), 702 (w), 668 (w), 646 (m), 536 (w), 208 (w), 479 (w), 422 (w) cm$^{-1}$. Calcd. for $C_{17}H_{16}O_4$ (284.31): C 71.8, H 5.7; found C 71.4, H 6.2

**1,3,10-Trimethyl-1,4-dihydro-1,4-ethenonaphthalene-6-carboxylic Acid (12):** *tert*-Butyllithium (1.6 M, 4.99 mL, 8.0 mmol) was added dropwise at –78 °C to a solution of compound **3** (2.0 g, 7.3 mmol) in tetrahydrofuran (125 mL). The reaction mixture was stirred for 2 h at –50 to –60 °C. Gaseous carbon dioxide was dumped through a drain tube over a period of 2 h at the same temperature. After the solvents had been evaporated, the residue was dissolved in diethyl ether (80 mL). The organic phase was extracted three times with diluted hydrochloric acid (20 mL) and dried with magnesium sulfate. After removing the latter by filtration, evaporation of the solvent provided the crude product, which was dissolved in a diluted sodium hydroxide solution and filtered through Celite. Acidification of the filtrate with diluted hydrochloric acid gave a colorless precipitate that was removed by filtration and dried under vacuum at 60 °C. The product was obtained as colorless powder with a yield of 77% (1.4 g, 5.6 mmol) and a decomposition temperature of 245–250 °C. $^1$H NMR (500.30 MHz, [D$_6$]DMSO): $\delta$ = 1.80 (s, 3 H), 1.83 (d, $J$ = 1.7 Hz, 6 H), 4.32 (t, $J$ = 1.8 Hz, 1 H), 5.96 (m, 2 H), 7.15 (d, $J$ = 7.7 Hz, 1 H), 7.56 (dd, $J$ = 7.7 Hz, 1.7 Hz, 1 H), 7.70 (d, $J$ = 1.7 Hz, 1 H) ppm. $^{13}$C NMR (125.81 MHz, $CDCl_3$): $\delta$ = 17.7, 19.4, 50.4, 59.6, 118.1, 122.1, 125.5, 126.2, 150.3, 167.9 ppm. IR: $\tilde{\nu}$ = 3020 (w), 2970 (m), 2962 (m), 2902 (m), 2657 (w), 2562 (m), 1694 (s), 1603 (m), 1576 (w), 1508 (w), 1475 (w), 1431 (s), 1337 (w), 1296 (s), 1262 (m), 1175 (w), 1093 (w), 1045 (w), 957 (w), 924 (w), 873 (w), 813 (m), 775 (m), 669 (m), 642 (m), 550 (w), 514 (w) cm$^{-1}$. Calcd. for $C_{16}H_{16}O_2$ (240.30): C 80.0, H 6.7; found C 79.2, H 6.7.

**μ-Dichloridodi(6,8-dibromo-1,3,10-trimethyl-1,4-dihydro-1,4-ethenonaphthalene)dirhodium(I) (13):** In a typical synthesis, μ-dichloridotetraethylenedirhodium(I) (50.0 mg, 0.13 mmol) was suspended in dry toluene (5 mL) and then cooled to –70 °C. After compound **1a** (100.1 mg, 0.28 mmol) had been added, the solution was warmed to room temperature and stirred overnight. The precipitate was removed by filtration and dissolved in dry chloroform. Filtration and evaporation of the solvent gave a solid residue that was recrystallized from dry dichloromethane at –40 °C. The product was obtained as yellow-orange crystals with a yield of 96% (122.9 mg). $^1$H NMR (500.30 MHz, $CDCl_3$): $\delta$ = 1.52 (s, 6 H), 2.93 (s, 3 H), 3.18 (s, 2 H), 4.52 (s, 1 H), 7.26 (d, $J$ = 1.9 Hz, 1 H), 7.51 (d, $J$ = 1.9 Hz, 1 H) ppm. IR: $\tilde{\nu}$ = 2960 (w), 2925 (w), 2876 (w), 2853 (w), 1574 (m), 1536 (m), 1417 (m), 1379 (m), 1367 (m), 1252 (s), 1138 (w), 1091 (s), 1015 (s), 912 (w), 870 (w), 839 (w), 789 (s), 774 (s), 751 (s), 693 (m), 674 (m), 663 (m), 617 (m), 567 (w), 537 (m), 521 (w), 495 (w), 464 (w) cm$^{-1}$. Calcd. for $C_{30}H_{28}Br_4Cl_2Rh_2{\cdot}3CH_2Cl_2$ (1239.49): C 32.0, H 2.8; found C 32.0, H 2.6.

**General Procedure for Catalytic Investigations:** Phenylboronic acid (226.8 mg, 1.9 μmol), [{RhCl($C_2H_4$)$_2$}$_2$] (1.2 mg, 3.1 μmol), and the appropriate benzobarrelene derivative (**1a** 2.4 mg, **3a/b** 2.5 mg, **7a** 3.6 mg, **10** 1.9 mg; 6.8 μmol) were dissolved in degassed and dry dioxane (10 mL) and stirred for 45 min at 30 °C. The catalysis was initiated by addition of a degassed, aqueous potassium hydroxide solution (4.5 M, 0.21 mL) and cyclohex-2-enone (0.06 mL, 0.62 mmol). After $t$ = 0.5, 1, 1.5, 2, 3, 4, 6, 10, and 20 min, samples of 0.5 mL were removed, and the catalysis of each sample was stopped by the addition of ice-cold saturated sodium bicarbonate solution (1 mL). The aqueous phase was extracted five times with diethyl ether and then combined. After evaporating the diethyl ether (760 mbar, 40 °C) the GC flame ionization detector (FID) analysis was performed.

**Supporting Information** (see footnote on the first page of this article): It contains Scheme S1, Figure S1, Figure S2, and Table S1 (crystallographic data).

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[1] H. E. Zimmerman, R. M. Paufler, *J. Am. Chem. Soc.* **1960**, *82*, 1514–1515.
[2] a) C. G. Krespan, T. L. Cairns, B. C. McKusick, *J. Am. Chem. Soc.* **1961**, *83*, 3428–3432; b) H. E. Zimmerman, D. Armesto, *Chem. Rev.* **1996**, *96*, 3065–3112; c) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, M. A. Sherwin, *J. Am. Chem. Soc.* **1969**, *91*, 2330–2338.
[3] a) R. S. H. Liu, *J. Am. Chem. Soc.* **1968**, *90*, 215–216; b) R. S. H. Liu, C. G. Krespan, *J. Org. Chem.* **1969**, *34*, 1271–1278.
[4] a) M. W. Wagaman, E. Bellmann, M. Cucullu, R. H. Grubbs, *J. Org. Chem.* **1997**, *62*, 9076–9082; b) M. W. Wagaman, R. H. Grubbs, *Macromolecules* **1997**, *30*, 3978–3985.
[5] R. G. Miller, M. Stiles, *J. Am. Chem. Soc.* **1963**, *85*, 1798–1800.
[6] a) A. Dastan, M. Balci, T. Hokelek, D. Ulku, O. Buyukgungor, *Tetrahedron* **1994**, *50*, 10555–10578; b) M. Balci, O. Cakmak, T. Hokelek, *Tetrahedron* **1992**, *48*, 3163–3182.

 

[7] M. A. Esteruelas, L. A. Oro, *Coord. Chem. Rev.* **1999**, *193–5*, 557–618.
[8] M. Valderrama, M. Scotti, A. Rojas, *Polyhedron* **1985**, *4*, 1585–1588.
[9] a) T. Nishimura, T. Kawamoto, M. Nagaosa, H. Kumamoto, T. Hayashi, *Angew. Chem.* **2010**, *122*, 1682; *Angew. Chem. Int. Ed.* **2010**, *49*, 1638–1641; b) T. Nishimura, Y. Maeda, T. Hayashi, *Angew. Chem.* **2010**, *122*, 7482–7485; c) T. Nishimura, Y. Yasuhara, M. Nagaosa, T. Hayashi, *Tetrahedron: Asymmetry* **2008**, *19*, 1778–1783; d) R. Shintani, M. Takeda, T. Nishimura, T. Hayashi, *Angew. Chem.* **2010**, *122*, 4061; *Angew. Chem. Int. Ed.* **2010**, *49*, 3969–3971; e) T. Nishimura, M. Nagaosa, T. Hayashi, *Chem. Lett.* **2008**, *37*, 860–861.
[10] a) L. Friedman, F. M. Logullo, *J. Org. Chem.* **1969**, *34*, 3089–3092; b) M. Stiles, U. Burckhar, R. G. Miller, *J. Am. Chem. Soc.* **1963**, *85*, 1792–1797.
[11] a) C. D. Campbell, C. W. Rees, *J. Chem. Soc. C* **1969**, 752–756; b) S. E. Whitney, B. Rickborn, *J. Org. Chem.* **1988**, *53*, 5595–5596.
[12] a) G. Wittig, R. W. Hoffmann, *Chem. Ber.* **1962**, *95*, 2729–2734; b) D. J. Berry, B. Wakefield, *J. Chem. Soc. C* **1969**, 2342–2346; c) N. J. Hales, H. Heaney, J. H. Hollinshead, S. M. F. Lai, P. Singh, *Tetrahedron* **1995**, *51*, 7777–7790; d) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, *115*, 518; *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528.
[13] a) L. Shi, Y. Chu, P. Knochel, H. Mayr, *Angew. Chem.* **2008**, *120*, 208; *Angew. Chem. Int. Ed.* **2008**, *47*, 202–204; b) L. Shi, Y. Y. Chu, P. Knochel, H. Mayr, *J. Org. Chem.* **2009**, *74*, 2760–2764.
[14] a) K. Fukui, *Acc. Chem. Res.* **1971**, *4*, 57–64; b) J. Sauer, R. Sustmann, *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779–807.
[15] a) M. E. Sengul, D. D. Gultekin, S. Essiz, E. Sahin, A. Dastan, *Tetrahedron* **2009**, *65*, 4859–4865; b) O. Cakmak, M. Balci, *Tetrahedron Lett.* **1990**, *31*, 2349–2352.
[16] a) M. Henn, K. Jurkschat, D. Mansfeld, M. Mehring, M. Schuermann, *J. Mol. Struct.* **2004**, *697*, 213–220; b) D. Mansfeld, M. Mehring, M. Schuermann, *Inorg. Chim. Acta* **2003**, *348*, 82–90; c) M. Mehring, M. Schuermann, K. Jurkschat, *Organometallics* **1998**, *17*, 1227–1236; d) J. Fischer, M. Schuermann, M. Mehring, U. Zachwieja, K. Jurkschat, *Organometallics* **2006**, *25*, 2886–2893.
[17] L. Iovkova, B. Waengler, E. Schirrmacher, R. Schirrmacher, G. Quandt, G. Boening, M. Schuermann, K. Jurkschat, *Chem. Eur. J.* **2009**, *15*, 2140–2147.
[18] a) T. Nishimura, Y. Maeda, T. Hayashi, *Angew. Chem.* **2010**, *122*, 7482; *Angew. Chem. Int. Ed.* **2010**, *49*, 7324–7327; b) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508–11509; c) F. X. Chen, A. Kina, T. Hayashi, *Org. Lett.* **2006**, *8*, 341–344; d) K. Okamoto, T. Hayashi, V. H. Rawal, *Chem. Commun.* **2009**, 4815–4817; e) Y. Otomaru, K. Okamoto, R. Shintani, T. Hayashi, *J. Org. Chem.* **2005**, *70*, 2503–2508; f) R. Shintani, A. Tsurusaki, K. Okamoto, T. Hayashi, *Angew. Chem.* **2005**, *117*, 3977; *Angew. Chem. Int. Ed.* **2005**, *44*, 3909–3912; g) E. Piras, F. Lang, H. Ruegger, D. Stein, M. Worle, H. Gruetzmacher, *Chem. Eur. J.* **2006**, *12*, 5849–5858.
[19] C. Niemann, C. E. Redemann, *J. Am. Chem. Soc.* **1941**, *63*, 1549.
[20] G. M. Sheldrick, in: *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Siemens Analytical X-ray Instruments, Madison, WI, **1990**.

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