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Redox Reaction of the Pd^0 Complex Bearing the Trost Ligand with *meso*-Cycloalkene-1,4-biscarbonates Leading to a Diamidato Pd^{II} Complex and 1,3-Cycloalkadienes: Enantioselective Desymmetrization Versus Catalyst Deactivation

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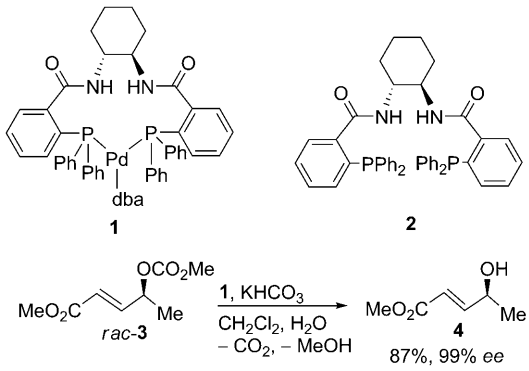
Abstract: The Pd^0 complex **1** that bears the Trost ligand **2** undergoes a facile redox reaction with 1,4-biscarbonates **5b–d** and *rac*-**22** under formation of the diamidato–Pd^{II} complex **7** and the corresponding 1,3-cycloalkadienes **8b–d**. The redox deactivation of complex **1** was the dominating pathway in the reaction of **5b–d** with HCO_3^- at room temperature. However, at 0 °C the six-membered biscarbonate **5b**, catalytic amounts of complex **1**, and HCO_3^- mainly reacted in an allylic alkylation, which led to a highly selective desymmetrization of the substrate and gave alcohol **6b** with $\geq$99 % *ee* in 66 % yield. An increase of the catalyst loading in the reaction of **5b** with **1** and HCO_3^- afforded the bicyclic carbonate **12b** (96 % *ee*, 92 %). Formation of carbonate **12b** involves two consecutive inter- and intramolecular substitution reactions of the π-allyl–Pd^{II} complexes **16b** and **18b**, respectively, with O-nucleophiles and presumably proceeds through the hydrogen carbonate **17b** as key intermediate. The intermediate formation of **17b** is also indicated by the conversion of alcohol *rac*-**6b** to carbonate **12b** upon treatment with HCO_3^- and **1**. The Pd^0-catalyzed desymmetrization of **5b** with formation of **12b** and its hydrolysis allow an efficient enantioselective synthesis of diol **13b**. The reaction of the seven-membered biscarbonate **5c** with *ent*-**1** and HCO_3^- afforded carbonate *ent*-**12c** (99 % *ee*, 39 %). The Pd^0 complex **1** is stable in solution and suffers no intramolecular redox reaction with formation of complex **7** and dihydrogen as recently claimed for the similar Pd^0 complex **9**. Instead, complex **1** is rapidly oxidized by dioxygen to give the stable Pd^{II} complex **7**. Thus, formation of the Pd^{II} complex **10** from **9** was most likely due to an oxidation by dioxygen. Oxidative workup (air) of the reaction mixture stemming from the desymmetrization of **5c** catalyzed by **1** gave the Pd^{II} complex **7** in high yield besides carbonate **12c**.

Keywords: alkylation · oxidation · palladium · redox chemistry · Trost ligand

Introduction

The Pd^0 complex **1** that bears the Trost ligand **2**[1–5] (Scheme 1) is one of the most versatile catalysts for enantioselective allylic alkylation.[6–9] It is applicable to a broad range of cyclic and acyclic allylic substrates and has found extensive use in organic synthesis. Recently, a structure-based rationale had been advanced for the selectivity in the asymmetric allylic alkylation catalyzed by **1**.[5] We had successfully applied catalyst **1** in the kinetic resolution of racemic allylic carbonates[10–15] and enantioselective synthesis of allylic sulfur derivatives.[10–18] Recently, we have described an enantioselective synthesis of allylic alcohols through the



Scheme 1. Deracemization of the allylic carbonate *rac*-**3** with the Pd^0 complex **1** (dba = dibenzylideneacetone) and HCO_3^- in CH_2Cl_2 and H_2O.

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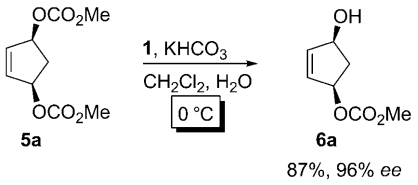
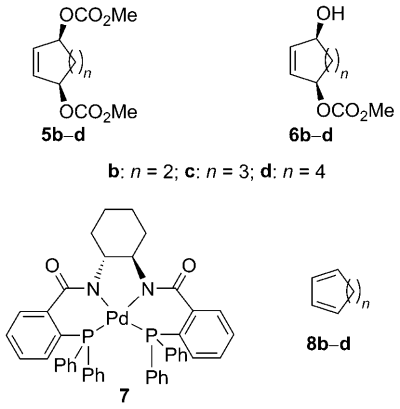
Pd^0-catalyzed deracemization of racemic allylic carbonates with **1** in CH_2Cl_2/H_2O[19,20] as exemplified by the synthesis of alcohol **4** from carbonate *rac*-**3**.[20] The deracemization entails an allylic alkylation of the hydrogen carbonate ion (HCO_3^-),[19–21] which is formed through the ionization of the substrate from $MeCO_3^-$ and H_2O and may also be supplied from an external source. Application of this method to the enantioselective desymmetrization of the *meso*-configured biscarbonate **5a** afforded the allylic alcohol **6a** (Scheme 2), which served as starting material for the synthesis of a key prostaglandin building block.[20]



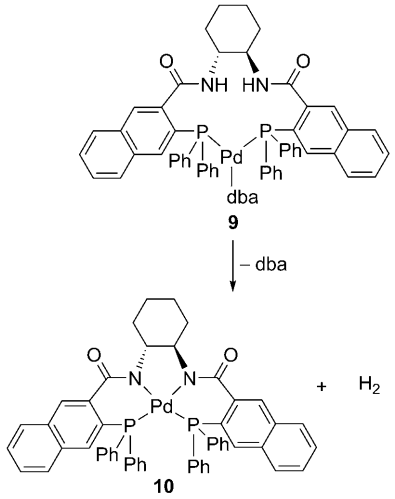
Scheme 2. Pd^0-catalyzed desymmetrization of *meso*-biscarbonate **5a** with complex **1** and HCO_3^-.

The efficient synthesis of **6a** from **5a** prompted us to study the potential of this desymmetrization for the enantioselective synthesis of the cyclic allylic alcohols **6b–d** from the corresponding *meso*-configured allylic carbonates **5b–d**. Alcohols **6b–d**, which had been previously obtained through an enzyme-catalyzed desymmetrization, are, like **6a**, also useful chiral building blocks for the synthesis of natural products.[22–25]



In this paper we describe a new and unexpected redox reaction between the Pd^0 complex **1** and the allylic biscarbonates **5b–d** that leads to the diamidato–bis(phosphanyl)–Pd^{II} complex **7**[26–29] and the corresponding 1,3-dienes **8b–d**. It is furthermore shown that in the case of the allylic biscarbonates **5b** and **5c** the redox reaction can be sufficiently suppressed and a highly enantioselective desymmetrization achieved.

In the course of this work a report had appeared claiming that the analogous Pd^0 complex **9** is unstable and undergoes a facile intramolecular redox reaction with formation of the diamidato–bis(phosphanyl)–Pd^{II} complex **10** and dihydrogen (Scheme 3).[28] Because of the considerable synthetic bearing it would have, should complex **1** also suffer such a redox reaction, its stability was studied. We demonstrate that complex **1** is stable under the conditions used and undergoes no intramolecular redox reaction but instead is rapidly oxidized by dioxygen to the Pd^{II} complex **7**.[26,29]



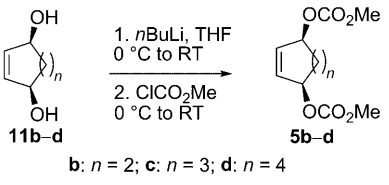
Scheme 3. Alleged intramolecular redox reaction of the Pd^0 complex **9**.[28]

Despite the many applications **1** has found in enantioselective synthesis, a recycling of the complex has not been described. It is shown that an oxidative workup in allylic alkylation with dioxygen allows a high yield recovery of Pd and ligand **2** as complex **7**.

Results and Discussion

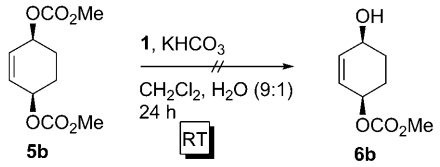
Synthesis of the biscarbonates: The *meso*-configured biscarbonates **5b–d** were synthesized in good yield from the corresponding diols **11b–d** upon treatment of the latter with *n*BuLi and the subsequent quenching of the corresponding dilithium salts with methyl chloroformiate (Scheme 4).

Pd^0-catalyzed desymmetrization: To our surprise, formation of alcohol **6b** could not be observed upon treatment of bis-



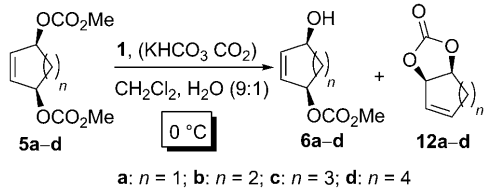
Scheme 4. Synthesis of the cyclic *meso*-biscarbonates **5b–d**.

carbonate **5b** with complex **1** under the standard conditions. A mixture of **5b**, $[Pd_2(dba)_3]\cdot CHCl_3$ (2 mol%; dba = dibenzylideneacetone), ligand **2** (4 mol%), and $KHCO_3$ in CH_2Cl_2/H_2O (9:1; two phases) was rapidly stirred at room temperature (RT) for 24 h under argon (Scheme 5), after which time the biscarbonate was recovered in high yield. Neither a change of the solvent to THF nor an increase of the catalyst loading to 4 mol% resulted in the formation of **6b** at room temperature.



Scheme 5. Attempted Pd^0-catalyzed desymmetrization of *meso*-biscarbonate **5b** with **1** and HCO_3^- at room temperature.

The apparent inertness of **5b** towards **1** and HCO_3^- was very startling because of the following reasons. The allylic alkylation of the biscarbonate with C-nucleophiles catalyzed by **1** has already been described,[30] and various cyclic and acyclic racemic allylic monomethyl carbonates have been successfully converted to the corresponding allylic alcohols by following the standard protocol.[19,20] During an investigation of the Pd^0-catalyzed desymmetrization of the five-membered biscarbonate **5a** with **1** and HCO_3^- under the standard conditions, we had noticed that both the conversion of the substrate and yield of alcohol **6a** significantly increased by running the reaction at 0°C instead of room temperature.[20] Surprisingly, under otherwise identical conditions, conducting the reaction of **5b** with **1** and HCO_3^- at 0°C instead of room temperature for 24 h gave alcohol **6b** with ≥99% *ee* in 66% yield (Scheme 6). However, the conversion of **5b** was still incomplete despite the long reaction time and the biscarbonate was recovered in 30% yield (Table 1, entry 1).



Scheme 6. Pd^0-catalyzed desymmetrization of biscarbonate **5** with complex **1** and HCO_3^- at 0°C.

When the reaction of **5b** with **1** was conducted first at 0°C for 2 h and then at room temperature for 46 h under otherwise identical conditions, **6b** was only obtained in 21% yield with ≥99% *ee* (Table 1, entry 2). Decreasing the catalyst loading to 1 mol% saw no formation of alcohol **6b**. On the other hand, increasing the catalyst loading to 4 mol% resulted in a 85% conversion of the substrate and gave a mixture of the bicyclic carbonate **12b** and alcohol **6b** in a ratio of 1.1:1 (entry 3). The formation of a bicyclic carbonate in the reaction of a *meso*-biscarbonate at a higher loading of **1** had been previously observed in the case of the reaction of **5a**, which gave carbonate **12a** as byproduct.[20] When biscarbonate **5b** was slowly added to catalyst **1** under otherwise identical conditions, a mixture of **12b** and **6b** was formed in the same ratio but in lower yield (entry 4). Reaction of **5b** with **1** in the presence of 1.4 equiv of $KHCO_3$ furnished a mixture of **6b** and **12b** in a ratio of 3.8:1 (entry 5). An efficient synthesis of the bicyclic carbonate **12b** (92% yield, 96% *ee*, 100% conversion of **5b** after 15 h) was accomplished by running the reaction of **5b** with 4 mol% of **1** in the presence of 1.4 equiv of $KHCO_3$ at 0°C (entry 6). Performing this reaction under the same conditions but at room temperature gave alcohol **6b** (≥99% *ee*) in only 20% yield and none of **12b** (entry 7).

Table 1. Pd-catalyzed desymmetrization of biscarbonate **5b** with complex **1** at 0°C.

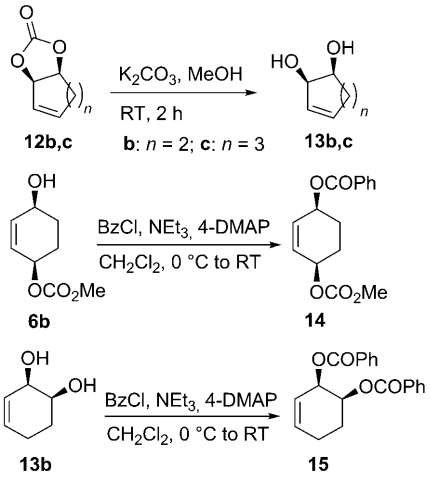
Entry	**1**	**6b**		**12b**	
	[mol%]	Yield [%]	*ee* [%]	Yield [%]	*ee* [%]
1	2	66	≥99	–	–
2[a]	2	21	≥99	–	–
3	4	37	≥99	40	94
4[b]	2	12	≥99	11	94
5[c]	2	38	≥99	10	96
6[c]	4	–	–	92	96
7[c,d]	4	20	≥99	–	–
8[e]	2	30	≥99	11	90
9[e]	4	–	–	88	97

[a] Reaction was run for 2 h at 0°C and then for 46 h at room temperature. [b] Biscarbonate **5b** was slowly added to a solution of **1** within 7 h. [c] Addition of 1.4 equiv of $KHCO_3$. [d] Reaction was performed at room temperature. [e] Reaction was performed under a CO_2 atmosphere.

Treatment of the seven-membered biscarbonate **5c** with catalyst **1** and HCO_3^- under the standard conditions at room temperature saw no formation of alcohol **6c** and/or the bicyclic carbonate **12c**. At a higher catalyst loading and 0°C, carbonate **12c** but not alcohol **6c** was isolated in 23% yield with 91% *ee* (vide infra). However, biscarbonate **5c** was recovered in 70% yield. A conversion of the eight-membered biscarbonate **5d** to **6d** and/or **12d** upon treatment with **1** and HCO_3^- under the standard conditions could not be observed.

The absolute configuration of alcohol **6b** was assigned in analogy to that of alcohol **6a**.[20] The absolute configuration of carbonates **12b** and **12c** was determined by hydrolysis to the corresponding diols **13b** and **13c** (Scheme 7) and comparison of their optical rotation with those reported for *ent*-**13b**[31–34] and *ent*-**13c**,[33–35] respectively. The *ee* values of alcohol **6b** and diol **13b** were determined through conversion to the corresponding benzoates **14** and **15** and analysis by chiral HPLC. The *ee* value of carbonate **12c** was determined by chiral GC.

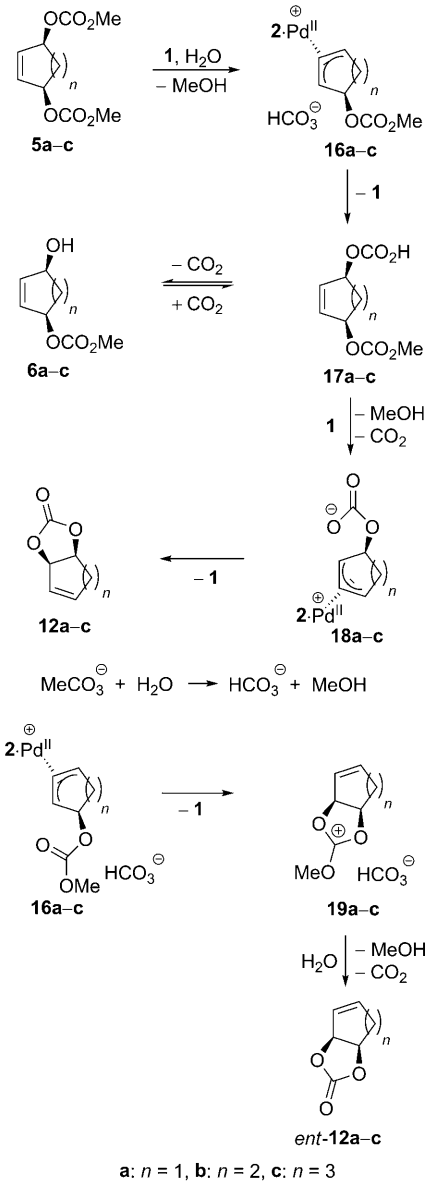
The Pd^0-catalyzed desymmetrization of biscarbonate **5b** with formation of carbonate **12b** allows access to diol **13b**,



Scheme 7. Derivatization of the bicyclic carbonates **12b** and **12c** and alcohol **6b** (4-DMAP = 4-dimethylaminopyridine, Bz = benzoyl).

an efficient enantioselective synthesis of which was not available up to now.[33–35]

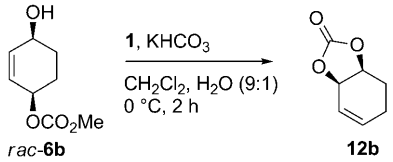
Formation of alcohol **6** and carbonate **12** from **1** and biscarbonate **5** is rationalized as shown in Scheme 8.[20] The enantiotopos-differentiating reaction of the *meso*-biscarbonate with complex **1** involves, with high selectivity, the methoxycarbonyloxy group at the *S*-configured stereogenic center and affords the *trans*-configured π-allyl–Pd^{II} complex **16**.[30,36,37] The methyl carbonate ion, which is formed during the ionization of **5**, is hydrolyzed, thus giving HCO_3^- and MeOH.[19,20] The thus-formed (and eventually externally supplied) HCO_3^- selectively attacks the π-allyl complex **16** to furnish the *cis*-configured hydrogen carbonate **17**, which decomposes because of the presence of water and delivers alcohol **6** and CO_2.[19,20] In a competing reaction, the hydrogen carbonate **17** or its anion reacts with complex **1** to yield the π-allyl–Pd^{II} complex **18**, which undergoes an intramolecular substitution[21] to furnish carbonate **12** and complex **1**. Support for this mechanistic scheme, and in particular for the intramolecular substitution of **18**, comes from the asymmetric synthesis of cyclic 1,2-carbonates through the Pd-catalyzed deracemization of vinyl epoxides with **1** and HCO_3^- in CH_2Cl_2/H_2O.[21] It was proposed that the racemic vinyl epoxide reacts with **1** under formation of the corresponding alkoxy-substituted π-allyl–Pd^{II} complexes. Their reaction with CO_2 generates the corresponding oxycarbonyoxy-substituted π-allyl–Pd^{II} complexes, the intramolecular substitution of which yields the cyclic carbonate and **1**. Whereas the reaction of biscarbonate **5** with catalyst **1** involves a matched ionization, carbonate **17** has to undergo with **1** a mismatched ionization. It had been shown that monomeric **1** is in equilibrium with oligomeric species (see below), which react in mismatched ionization much faster than monomeric **1**.[2–5] Thus, oligomers of **1** are perhaps responsible for the conversion of the hydrogen carbonate **17** to complex **18**. To substantiate the mechanistic proposal of Scheme 8, further cata-



Scheme 8. Proposed mechanism for the Pd^0-catalyzed formation of alcohol **6** and carbonates **12** and *ent*-**12** from biscarbonate **5**.

lytic experiments were performed with **5b**, in which 1) the catalyst loading and the concentration of HCO_3^- were increased, 2) CO_2 was added, or 3) all three parameters were altered (cf. Table 1). These experiments clearly show, in accordance with Scheme 8, that an increase of the catalyst loading (entry 1 vs. 3, entry 5 vs. 6, and entry 8 vs. 9) and an increase of the concentration of HCO_3^- (entry 1 vs. 5, and entry 2 vs. 8) resulted in an increased formation of carbonate **12b**. An inspection of Table 1 (entry 3, without addition of $KHCO_3$ and entry 6, addition of $KHCO_3$) shows that in the reaction of **5b** with **1** not only an increase of the catalyst loading but also the pH from approximately 7 to 9 favors the formation of the bicyclic carbonate **12b**. This observation would also be in accordance with Scheme 8. At pH 9 the concentration of the deprotonated hydrogen carbonate

17b should be higher, a feature which would facilitate the formation of complex **18b** and thus of **12b**. An alternative route to hydrogen carbonate **17** encompasses the reaction of alcohol **6** with CO_2 or HCO_3^- (vide infra).[38,21] Support for this notion comes from an independent but similar experiment with the racemic alcohol *rac*-**6b**, which was obtained from diol **11b** and chloroformiate by using only 1 equiv of *n*BuLi (cf. Scheme 4). Treatment of *rac*-**6b** with 8 mol% of **1** and 1.4 equiv of $KHCO_3$ in CH_2Cl_2/H_2O at 0°C gave carbonate **12b** with 46% *ee* in 88% yield (Scheme 9).

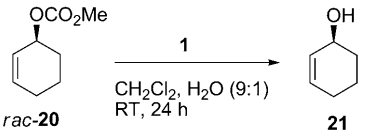


Scheme 9. Pd^0-catalyzed synthesis of carbonate **12b** from alcohol *rac*-**6b** and CO_2 or HCO_3^-.

Another interesting feature of the reaction of biscarbonates **5a–c** with complex **1** in CH_2Cl_2/H_2O in the presence of HCO_3^- is the variation of the *ee* value of **12b** and **12c** depending on the reaction conditions and the relative low *ee* value of **12a** (66%).[20] The first step of the reaction of **5** with **1** to **12**, the formation of the π-allyl–Pd^{II} complex **16**, is generally highly enantioselective.[30,36,37] Since this step determines, according to the mechanistic proposal of Scheme 8, the *ee* value of **12**, there ought also to be a process that leads to the formation of *ent*-**12**. A competing intramolecular substitution of **16** could occur to afford the carbenium ion **19**, the hydrolysis of which would yield the enantiomeric carbonate *ent*-**12**. Indeed, the corresponding π-allyl–Pd^{II} complexes that carry a tosylcarbamoyloxy instead of a methoxycarbonyloxy group exclusively undergo such an intramolecular substitution.[39] However, these complexes are generated from the corresponding *meso*-bis(tosylcarbamoyloxy)cycloalkenes and **1** under nonaqueous conditions in the absence of an external nucleophile. In addition, the nucleophilicity of the tosylcarbamoyloxy group perhaps exceeds that of the methoxycarbonyloxy group.

A recent elegant experimental and theoretical study of a cationic η^3-cyclohexenyl–Pd^{II} complex containing **2** as ligand revealed that the amide groups are placed in close proximity to the Pd atom. It was proposed that the amide N–H plays a crucial role in both directing the attack of the nucleophile at the C atom of the allyl unit and the ionization of the faster reacting enantiomer of the cyclohexenyl ester.[5] The high degree and similar sense of asymmetric induction recorded in the reaction of **1** and nucleophiles with cyclohexenyl esters and the *meso*-configured ester **5** suggest that the selectivities of the reaction of the *meso*-diesters can also be rationalized by this model.[5]

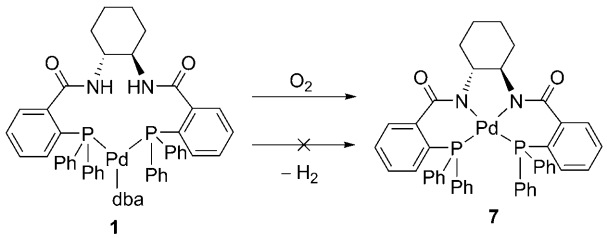
Stability and oxidation of complex 1 by biscarbonates and dioxygen: Having observed a formation of alcohol **6** (as intermediate) upon treatment of biscarbonate **5** with complex **1** and HCO_3^- at 0°C but not at room temperature, the origin of these apparently contradicting results was probed. The reaction of **5** with **1** and HCO_3^- is slow because of the low nucleophilicity of the anion and the conversion of the substrates was not complete. Altogether these results and those listed in Table 1 hinted a competing deactivation of catalyst **1**; they were fast at room temperature and slow at 0°C. A control experiment with the monocarbonate *rac*-**20** and **1** was performed at room temperature under identical conditions to check the activity of the catalyst under the standard reaction conditions (Scheme 10). Here, alcohol **21**



Scheme 10. Pd^0-catalyzed deracemization of the monomethyl carbonate *rac*-**20**.

was obtained in 92% yield with 97% *ee*. In a further experiment, biscarbonate **5b** was added to a solution of 4 mol% of catalyst **1** in CH_2Cl_2/H_2O at room temperature, and after an incubation time of 2 h monocarbonate *rac*-**20** was added to the mixture, which was then kept for 24 h at room temperature. In this case, formation of alcohol **21** could not be detected. Carbonates **5b** and *rac*-**20** were recovered and alcohol **6b** was isolated in only 7% yield (≥99% *ee*).

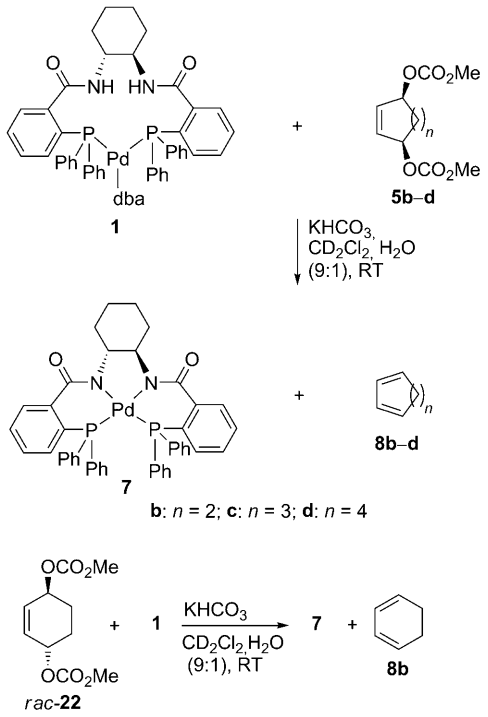
These results strongly suggested that a yet unknown reaction of catalyst **1** with biscarbonate **5b** but not monocarbonate *rac*-**20** caused a deactivation of the catalyst. However, in principle a deactivation of catalyst **1** could also have occurred through an oxidation with dioxygen with formation of the Pd^{II} complex **7** (Scheme 11).[26,29] Although all reactions with biscarbonate **5b** had been conducted in degassed solvents under argon, this possibility could not be rigorously excluded. Finally, a deactivation of **1** through an intramolecular redox reaction with formation of complex **7** and dihydrogen had to be considered since such a reaction had been previously reported for the analogous Pd^0 complex **9** that gave the Pd^{II} complex **10**.[28] To exclude these two modes of deactivation and to see whether complex **1** also undergoes an intramolecular redox reaction, ^{31}P NMR spectroscopic



Scheme 11. Oxidation of the Pd^0 complex **1** to the Pd^{II} complex **7** with dioxygen.

experiments with **1** at room temperature were performed. Solutions of **1** at 9 mM (corresponding to a catalyst loading of 2 mol%) and 18 mM (corresponding to a catalyst loading of 4 mol%) were prepared by dissolving $[Pd_2(dba)_3]\cdot CHCl_3$ (1 equiv) and **2** (2 equiv) in degassed CD_2Cl_2 under argon in an NMR spectroscopy tube, which was closed with a plastic cap. The ^{31}P NMR spectra of both solutions taken after 20 min of their preparation showed the two doublets of the Pd^0 complex **1** with the *P,P*-coordinated ligand **2** at $\delta_P = 20.9$ and 23.9 ppm[28,29] and two broadened signals at $\delta_P = 22.0$ and 27.9 ppm; these stem from oligomers of **1**. In addition, the characteristic singlet of the Pd^{II} complex **7** ($\delta_P =$ 26.1 ppm) with the *P,P,N,N*-tetradentate-coordinated deprotonated ligand **2** was present.[27,28] After the solution containing **1** at an initial concentration of 9 mM was kept for 18 h at room temperature in the NMR spectroscopy tube, a ^{31}P NMR spectrum only showed the presence of the Pd^{II} complex **7** and none of **1** and its oligomers. A ^{31}P NMR spectrum of the solution containing **1** at an initial concentration of 18 mM still showed after 18 h the presence of **1** and oligomers besides **7**, and only after a further 44 h had elapsed had complex **1** completely disappeared and only complex **7** remained. The slower decomposition of **1** at higher concentrations can perhaps be related to the higher stability of the oligomeric catalyst. Formation of the Pd^{II} complex **7** from the Pd^0 complex **1** under these conditions could be ascribed either to an intramolecular redox reaction or oxidation by dioxygen that had entered the NMR spectroscopy tube despite its being closed under argon with a plastic cap or to both reaction pathways. Therefore, the NMR spectroscopic experiments were repeated by using solutions of **1** in CD_2Cl_2 and CD_2Cl_2/H_2O (9:1) contained in NMR spectroscopy tubes, which had been sealed with an acetylene/dioxygen microburner to rigorously exclude a contamination by dioxygen. The solvents, ligand **2**, and $[Pd_2(dba)_3]\cdot CHCl_3$ were degassed by several freeze–thaw cycles and the NMR spectroscopy tubes were sealed at −78 °C under vacuum and argon. The ^{31}P NMR spectra of the solutions of **1** only showed the presence of the monomeric complex **1** and its oligomers and none of the Pd^{II} complex **7**. Even after the solutions of **1** were kept in the sealed NMR spectroscopy tube for three months at room temperature, formation of complex **7** could not be detected. Interestingly, when the sealed NMR spectroscopy tubes that contained the solution of **1** were opened under argon and closed with a plastic cap, a ^{31}P NMR spectrum, which was recorded immediately afterwards, already showed the formation of complex **7**. The ^{31}P and ^1H NMR spectra revealed after approximately 1 d only the signals of complex **7**. These results unequivocally demonstrate that 1) the Pd^0 complex **1** does, under the conditions applied, not undergo an intramolecular redox reaction with formation of the Pd^{II} complex **7** but instead, 2) is very sensitive towards dioxygen and rapidly oxidized to complex **7**. Oxidation of **1**, which is typically used in only catalytic amounts in allylic alkylation, with dioxygen can become a severe side reaction in the case of nucleophiles that have a low nucleophilicity, as, for example, the hydrogen carbonate ion. Our results suggest that the reported formation of the analogous Pd^{II} complex **10** from the Pd^0 complex **9**[28] was most likely due to an oxidation with dioxygen and not caused by an intramolecular redox reaction.

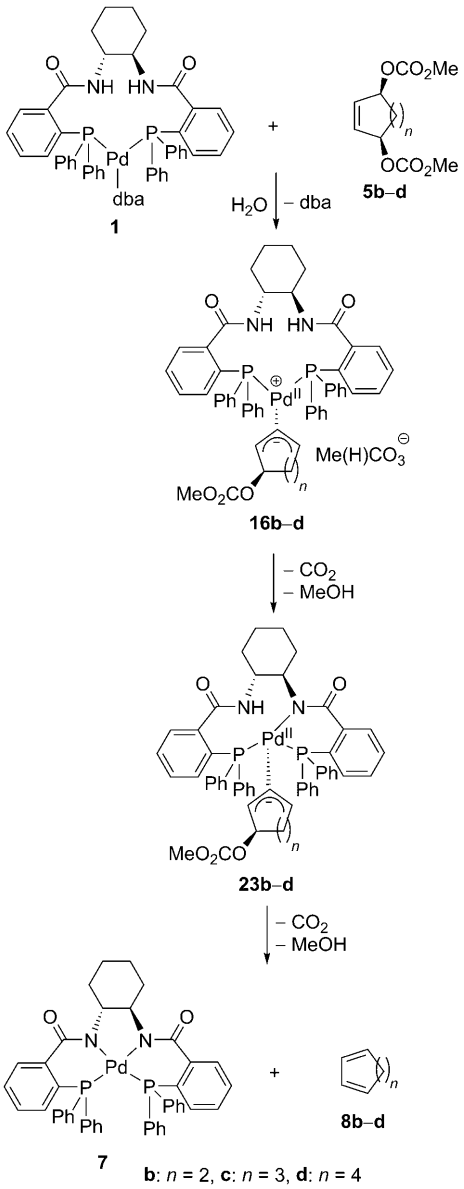
Because of the above results, an intramolecular redox deactivation of complex **1** can be safely dismissed as the cause for its deactivation in the treatment with biscarbonate **5b** and HCO_3^- at room temperature. However, because of the facile oxidation of **1**, the possibility of a dioxygen contamination as the reason for the failure of this experiment remained. Therefore, two preparative stoichiometric experiments with biscarbonate **5b**, complex **1**, and HCO_3^- in CH_2Cl_2/H_2O at room temperature and 0 °C were run in sealed flasks under argon by using degassed solvents and reagents. After a reaction time of 24 h, the flasks were opened and the mixtures were analyzed after standard workup, purification, and derivatization. In the experiment at room temperature, biscarbonate **5b** was recovered in 90% yield. In contrast, the experiment at 0 °C gave alcohol **6b** in 56% yield with 97% *ee*, and carbonate **5b** was recovered in 40% yield. These results unequivocally show that a yet unknown deactivation of catalyst **1** must have occurred upon reaction with biscarbonate **5b**, which is much faster at room temperature than the allylic alkylation of HCO_3^-. To determine the fate of the reagents, the reaction of **5b** with **1** and HCO_3^- was followed by NMR spectroscopy. The NMR spectroscopy tube was successively charged with $[Pd_2(dba)_3]\cdot CHCl_3$, **2**, $KHCO_3$, **5b** (stoichiometric amounts), and CD_2Cl_2/H_2O (9:1) at room temperature under the exclusion of dioxygen. A ^{31}P NMR spectrum, which was taken immediately after the NMR spectroscopy tube was sealed, showed only the presence of the Pd^{II} complex **7** and none of complex **1**. An ^1H NMR spectrum revealed in addition to **7** the presence of diene **8b** in stoichiometric amounts (Scheme 12). Thus, a new and facile stoichiometric redox reaction had occurred between the Pd^0 complex **1** and biscarbonate **5b**. To see whether the redox reaction between **5b** and **1** is a general one for cyclic allylic 1,4-biscarbonates and the Pd^0 complex, the stoichiometric reaction of the seven- and eight-membered biscarbonates **5c** and **5d**, respectively, and the racemic *trans*-configured biscarbonate *rac*-**22** with **1** at room temperature was also followed by ^{31}P and ^1H NMR spectroscopy. The redox reaction of **1** with **5c**, **5d**, and *rac*-**22** was fast in all cases and gave complex **7** together with stoichiometric amounts of the corresponding dienes **8c**, **8d**, and **8b**. Oxidation of complex **1** is confined to allylic 1,4-biscarbonates. An NMR spectroscopic investigation of the deracemization of the monomethyl carbonate *rac*-**20** with catalytic amounts of **1** under standard conditions by using a sealed NMR spectroscopy tube only showed the consumption of the substrate and formation of the allylic alcohol **20**. Neither the formation of diene **8b** nor that of complex **7** could be detected. Complex **1** was still present, the oxidation of which to **7** only started upon opening the NMR spectroscopy tube. The Pd^{II} complex **7** showed no activity in allylic alkylation. Treatment of biscarbonate **5b** with **7** under the standard conditions did not lead to a noticeable reaction.



Scheme 12. Redox reaction of complex **1** with biscarbonates **5** and *rac*-**22** with formation of complex **7** and diene **8**.

Having observed a facile redox reaction of complex **1** with biscarbonates **5c**,**d** and *rac*-**22**, it was of interest to see whether Pd^0 complexes that contain a phosphane and are devoid of an amide group are also amendable to a redox reaction with the biscarbonates. NMR spectroscopy experiments were performed with stoichiometric amounts of biscarbonate **5b** and $[\{Pd(allyl)Cl\}_2]$, $[Pd_2(dba)_3]\cdot CHCl_3$, or $[Pd(PPh_3)_2Cl_2]$ in the presence of 4 and 8 equiv of PPh_3 under standard conditions in CD_2Cl_2 in sealed NMR spectroscopy tubes. In no case could the formation of diene **8b** be observed. This is in contrast to the reported conversion of acyclic and bicyclic allylic 1,4-biscarbonates to the corresponding 1,3-dienes upon treatment with catalytic amounts of $[Pd_2(dba)_3]\cdot CHCl_3$ and nearly stoichiometric amounts of aryl phosphanes including PPh_3, or even better, phosphites including $P(OiPr)_3$.[40] The mechanism of this synthetically useful conversion of allylic 1,4-biscarbonates to the corresponding 1,3-dienes is not known.[40]

The formation of the 1,3-diene **8** and complex **7** in the reaction of the allylic biscarbonate **5** with complex **1** in CH_2Cl_2 or CH_2Cl_2/H_2O is rationalized as shown in Scheme 13. Reaction of complex **1** with **5** furnishes the π-allyl–Pd^{II} complex **16** with methyl carbonate (hydrogen carbonate) as counterion. Intramolecular attack of the amide N atom at the Pd atom delivers the π-allyl–Pd^{II} complex **23**·H^+ (not shown in Scheme 13) with generation of a Pd–N bond, which is deprotonated by the methyl carbonate (hydrogen carbonate) ion to give **23**. Attack of the N atom of complex **16** at the Pd atom is perhaps facilitated by a close proximity of the amide group as observed in the corresponding complex that carries a η^3-cyclohexenyl group.[5] A nucleophilic attack of the second amide N atom of the π-allyl–Pd^{II} complex **23** at the Pd atom instead of at the C atom of the π-allyl–Pd^{II} unit generates the second Pd–N bond and leads under elimination of the Pd atom and the methyl carbonate ion to the formation of diene **8** and the protonated tetracoordinate Pd^{II} complex **7**·H^+ (not shown in Scheme 13), which is deprotonated by the methyl carbonate (hydrogen carbonate) ion with formation of **7**. Attack of the N atom of **23** at the Pd atom may be preceded by a dissociation of a P atom. The facile redox reaction of the *trans*-configured biscarbonate *rac*-**22** with **1**, which should take a similar mechanistic path, shows that the *trans* configuration of complex **16** is not a prerequisite for the reactions depicted in Scheme 13 to occur. The decisive steps according to Scheme 13 are the

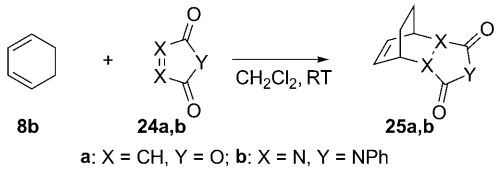


Scheme 13. Proposed mechanism for the redox reaction of the Pd^0 complex **1** with biscarbonate **5**.

intramolecular attack of the N atom of the π-allyl–Pd^{II} complexes **16** and **23** at the Pd atom with formation of the neutral π-allyl–Pd^{II} complex **23** and complex **7**, respectively. The first step is apparently faster at room temperature than the intermolecular substitution of **16** by HCO_3^- to give carbonate **17** (cf. Scheme 8).

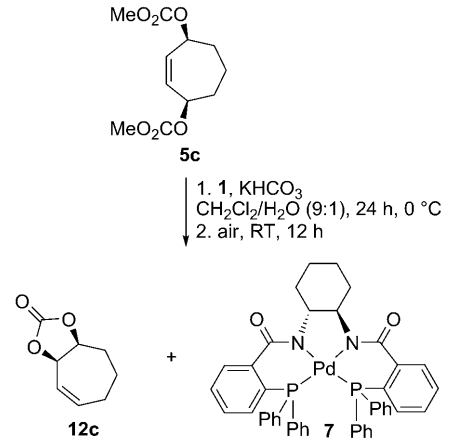
The stoichiometric redox reaction between the Pd^0 complex **1** and biscarbonate **5** with formation of diene **8** and the Pd^{II} complex **7** is mechanistically different from the Pd^0-catalyzed elimination of allylic monocarbonates, which also yields 1,3-dienes.[41,42] It is interesting to note that the reverse transformation to the one depicted in Scheme 12, the generation of 1,4-bisacyloxycycloalk-2-enes and a Pd^0 complex from the corresponding 1,3-cycloalkadienes and a Pd^{II} complex, is well established.[43]

According to NMR spectroscopy, the reaction of equimolar amounts of **1** and biscarbonates **5b–d** gave stoichiometric amounts of the corresponding dienes **8b–d** and complex **7**. Quantitative isolation of dienes **8b–d** proved to be difficult because of their volatility. Therefore, diene **8b**, for example, formed upon reaction of **1** with **5b**, was trapped with dienophiles **24a** and **24b** as the corresponding cycloadducts **25a** and **25b** (Scheme 14). Complex **1** was treated with biscarbonate **5b** (1 equiv) in CH_2Cl_2 at room temperature for 15 min. Addition of diethyl ether and centrifugation of the thus-formed suspension of **7** afforded the Pd^{II} complex in 82% yield. The solution of the diene **8b** in CH_2Cl_2/Et_2O also containing dba was treated with dienophiles **24a** and **24b** following the careful removal of diethyl ether at normal pressure, which furnished cycloadducts **25a**[44] and **25b**[45] in 75 and 80% yield, respectively. Reaction of **8b** with the dienophiles in the presence of diethyl ether was very slow.



Scheme 14. Trapping of diene **8b** as cycloadducts **25a** and **25b**.

Isolation of complex 7 in allylic alkylation: Despite the many applications the Pd^0 complex **1** has found in asymmetric allylic alkylation, a recycling of the catalyst, which would be desirable because of the price of $[Pd_2(dba)_3]\cdot CHCl_3$ and ligand **2**, has not been described. The main obstacle to a recovery of **1** in allylic alkylation is the facile oxidation of the complex to the Pd^{II} complex **7** by dioxygen. A recycling of **1** may perhaps be accomplished by a two-step procedure that includes its oxidation to **7** during workup and a reduction of the latter. Therefore, it was of interest to see whether an oxidative workup in allylic alkylation with **1**[26] would allow the isolation of **7** in high yield. Thus, the desymmetrization of biscarbonate **5c** with **1** was run at a somewhat larger scale and higher catalyst loading followed by an oxidation of the mixture with air (Scheme 15). Biscarbonate **5c** was treated with catalyst **1** (19 mol%) and $KHCO_3$ in degassed CH_2Cl_2/H_2O (9:1) at 0°C under argon for 24 h. Then the mixture was stirred for 12 h under air at room temperature. Addition of diethyl ether to the organic phase and centrifugation of the suspension afforded the slightly impure complex **7** in 90% yield. In addition, carbonate **12c** (68% *ee*) was isolated in 44% yield and biscarbonate **5c** was recovered in 16% yield.



Scheme 15. Isolation of complex **7** in the desymmetrization of biscarbonate **5c** with **1** through oxidative workup.

Conclusion

Catalyst **1** and biscarbonates **5** and *rac*-**22** undergo without the requirement of dioxygen a facile redox reaction whereby the former is oxidized to the Pd^{II} complex **7** and the latter reduced to the 1,3-diene **8**. The redox deactivation of **1** with allylic 1,4-biscarbonates, which involves two intramolecular substitutions at the Pd atom, dominates over the allylic alkylation at room temperature because of the poor nucleophilicity of the hydrogen carbonate ion. The π-allyl–Pd^{II} complex **16** is most likely the key intermediate in both competing reaction paths, the allylic alkylation by means of intermolecular nucleophilic substitution and the redox reaction by means of intramolecular nucleophilic addition/deprotonation. At lower temperatures, allylic alkylation is preferred, which proceeds in the case of the six-membered biscarbonate with high enantioselectivity. The alcohol formed in this manner is activated upon reaction with HCO_3^- to yield the corresponding hydrogen carbonate, which suffers a mismatched ionization by the catalyst, followed by an intramolecular substitution to give the bicyclic carbonate. The Pd^0 complex **1** that bears the Trost ligand undergoes no intramolecular redox reaction with formation of the Pd^{II} complex **7** and dihydrogen under the standard conditions of allylic alkylation. In contrast to what is stated in the literature, monomeric and oligomeric Pd^0 complexes **1** are stable in solution and do not generate the Pd^{II} complex **7** with formation

of dihydrogen. Our results strongly suggest that the reported formation of the analogous Pd^{II} complex **10** from the Pd^0 complex **9** was due to an oxidation with dioxygen and not caused by an intramolecular redox reaction. The facile oxidation of the Pd^0 complex **1** to the Pd^{II} complex **7** by dioxygen allows a recovery of Pd and ligand **2** in allylic alkylation through an oxidative workup. However, a complete recycling of catalyst **1** from complex **7** has to await the development of a procedure for the reduction of the Pd^{II} complex.

Experimental Section

General: All reactions were carried out under an argon atmosphere in dry solvents with syringe and Schlenk techniques in oven-dried glassware. Diols **11b** and **11d** were prepared according to the literature from the corresponding dienes **8b** and **8d** by means of the corresponding *endo*-peroxides,[46,47] which were reduced without isolation with activated Zn in CH_2Cl_2/acetic acid.[48,49] Diol **11c** and (±)-*trans*-cyclohex-2-ene-1,4-diol were prepared according to the literature from the corresponding dienes **8c** and **8b** through a Pd-catalyzed 1,4-diacyloxylation.[50,51] $[Pd_2(dba)_3]\cdot CHCl_3$,[52] bisphosphane **2**,[1] and cycloheptadiene **8c**[53,54] were prepared according to the literature. Carbonate *rac*-**20** was prepared from cylohex-2-en-1-ol by standard procedures. Cyclohexadiene **8b**, cyclooctadiene **8d**, and dieneophiles **24a** and **24b** were obtained from commercial sources. THF and Et_2O were distilled under argon from lead/sodium in the presence of benzophenone. CH_2Cl_2 was distilled from CaH_2. Bulk solvents for column chromatography and extractions were distilled prior to use. Reagents were obtained from commercial sources and used directly without further purification unless otherwise specified. *n*BuLi was obtained from commercial sources and standardized by titration with diphenylacetic acid. TLC was performed on E. Merck precoated plates (silica gel 60 F254, layer thickness 0.2 mm), and chromatography was performed with E. Merck silica gel (0.040–0.063 mm) in the flash mode with a positive nitrogen pressure. HPLC was carried out with a Dynamax SD-1 pump by using Varian 320 UV/Vis and Knauer RI detectors on a Chromasil Si-100 column. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using Varian Mercury 300 and Varian Inova 400 instruments. ^1H and ^{13}C chemical shifts are reported relative to TMS ($\delta=0.00$ ppm) as internal standard and ^{31}P NMR chemical shifts are reported relative to H_3PO_4 in D_2O ($\delta=0.00$ ppm) as external standard. The following abbreviations are used to designate the multiplicity of the peaks in the ^1H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sex = sextet, sep = septet, o = octet, m = multiplet, br = broad, and combinations thereof. Peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two protons attached or as "d" for carbons with one or three attached protons, as determined from the attached proton test (APT) pulse sequence. Assignments in the ^1H NMR spectra were made by gradient multiple quantum (GMQ) COSY and heteronuclear correlation (HETCOR) experiments, and those in the ^{13}C NMR spectra were made by distortionless enhancement by polarization transfer (DEPT) experiments. IR spectra were recorded using a Perkin–Elmer PE 1759 FT instrument, and the abbreviations used to designate the intensity of the peaks are vs = very strong, s = strong, m = medium, and w = weak. Optical rotations were measured using a Perkin–Elmer 241 polarimeter at approximately 22 °C. Specific rotation is given in degrees × (mL per dm) × g, and *c* is in grams per 100 mL. Enantiomer analyses were carried out by HPLC and GC using commercial columns with chiral stationary phases as stated in the experimental procedures.

General procedure for synthesis of the cyclic biscarbonates 5b–d and *rac*-22 (GP1): *n*BuLi (24.2 mL of 1.6 M in hexanes, 38.7 mmol) was added dropwise to a solution of the diol (**11b**, **11d**, and (±)-*trans*-cyclohex-2-ene-1,4-diol; 17.5 mmol) in THF (60 mL). The slurry was stirred first at 0 °C for 10 min and then at room temperature for 20 min. Then the mixture was cooled to 0 °C and methyl chloroformiate (5.4 mL, 70 mmol) was added. After the mixture was stirred at room temperature for 2 h, it was diluted with EtOAc (40 mL). The organic layer was washed twice with water and brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by column chromatography on silica gel (cyclohexane/EtOAc, 7:2) gave the corresponding biscarbonate.

*Biscarbonate **5b***: Biscarbonate **5b** (3.83 g, 95 %) was obtained from diol **11b** according to GP1 as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.96 (m, 4H), 3.79 (s, 6H), 5.09 (m, 2H), 5.98 ppm (d, $J=1.5$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=24.7$ (u), 54.8 (d), 70.9 (d), 130.1 (d), 155.4 ppm (u); IR (capillary): $\tilde{\nu}=3472$ (w), 2959 (vs), 2681 (w), 2374 (w), 2202 (m), 1746 (vs), 1586 (m), 1399 (m), 1343 (s), 1259 (s), 1153 (m), 1110 (s), 1079 (m), 1052 (w), 1009 (s), 940 (s), 867 (m), 845 (m), 792 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 154 (55), 110 (69), 95 (52), 79 (100), 67 (30), 59 (51), 54 (11), 45 (17); elemental analysis calcd (%) for $C_{10}H_{14}O_6$ (230.21): C 52.17, H 6.13; found: C 52.01, H 6.11.

*Biscarbonate **5c***: Biscarbonate **5c** (1.30 g, 70 %) was obtained from diol **11c** according to GP1 as a colorless solid besides the corresponding monocarbonate (340 mg, 24 %). ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.58$–2.13 (m, 6H), 3.79 (s, 6H), 5.23 (m, 2H), 5.75 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=22.8$ (u), 32.3 (u), 54.8 (d), 77.5 (d), 132.1 (d), 155.1 ppm (u); IR (KBr): $\tilde{\nu}=3472$ (w), 2940 (m), 2864 (w), 2192 (w), 2015 (w), 1733 (vs), 1652 (w), 1583 (w), 1448 (s) 1336 (s), 1258 (vs), 1160 (m), 1109 (m), 1062 (m), 966 (vs), 940 (s), 885 (m), 856 (m), 825 (m), 782 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 244 (2) [M^+], 168 (85), 109 (100), 96 (23), 93 (68), 81 (31), 77 (23), 67 (16), 59 (55); elemental analysis calcd (%) for $C_{11}H_{16}O_6$ (244.24): C 54.09, H 6.60; found: C 54.29, H 7.02.

*Biscarbonate **5d***: Biscarbonate **5d** (4.07 g (90 %) was obtained from diol **11d** according to GP1 as a colorless oil, which solidified on standing. M.p. 34–35 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.61$ (m, 6H), 2.03 (m, 2H), 3.78 (s, 6H), 5.45 (m, 2H), 5.63 ppm (dd, $J=4.4$, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=22.9$ (u), 34.7 (u), 54.7 (d), 75.4 (d), 129.5 (d), 154.8 ppm (u); IR (Universal ATR): $\tilde{\nu}=3006$ (w), 2935 (m), 2866 (w), 1744 (vs), 1587 (v), 1444 (s), 1316 (s), 1252 (vs), 1144 (w), 1106 (w), 1077 (w), 996 (s), 947 (m), 925 (s), 864 (m), 791 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 258 (1) [M^+], 182 (54), 141 (7), 123 (24), 109 (26), 106 (100), 97 (16), 95 (29), 91 (44), 78 (42), 71 (18), 67 (27), 59 (62), 55 (26); elemental analysis calcd (%) for $C_{12}H_{18}O_6$ (258.11): C 55.81, H 7.02; found: C 56.13, H 6.97.

*Biscarbonate rac-**22***: Biscarbonate *rac*-**22** (3.91 g, 97 %) was obtained from (±)-*trans*-cyclohex-2-ene-1,4-diol according to GP1 as a colorless solid. M.p. 86–87 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.79$ (m, 2H), 2.19 (m, 2H), 3.79 (s, 6H), 5.18 (m, 2H), 5.99 ppm (d, $J=1.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=25.5$ (u), 54.8 (d), 71.0 (d), 130.0 (d), 155.1 ppm (u); IR (Universal ATR): $\tilde{\nu}=3463$ (w), 2959 (w), 2877 (w), 2195 (w), 2049 (w), 1731 (vs), 1585 (w), 1446 (s), 1400 (w), 1361 (w), 1322 (m), 1246 (vs), 1102 (m), 1003 (s), 930 (s), 897 (m), 790 (s), 758 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 154 (75), 110 (72), 95 (51), 79 (100), 67 (28), 59 (47), 45 (28); elemental analysis calcd (%) for $C_{10}H_{14}O_6$ (230.21): C 52.17, H 6.13; found: C 52.28, H 5.87.

Alcohol 6b: A Schlenk flask was successively charged with $[Pd_2(dba)_3]\cdot CHCl_3$ (41 mg, 0.04 mmol), ligand **2** (55 mg, 0.08 mmol), and degassed CH_2Cl_2 (9 mL). After the mixture was stirred at room temperature for 15 min, it was cooled to 0 °C. Then degassed water (1 mL) and carbonate **5b** (460 mg, 2 mmol) were added. After the mixture was rapidly stirred at 0 °C for 24 h, it was poured into cyclohexane/EtOAc (1:1; 200 mL) and the mixture was filtered through a plug of silica gel (0.0040–0.063 mm; 3 × 2 cm). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) afforded alcohol **6b** (227 mg 66 %) of ≥99 % *ee* (determined by HPLC after benzoylation to **14**) as a colorless oil. $[\alpha]_D=+$ 106.0 ($c=1.0$ in CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.91$ (m, 4H), 2.18 (br s, 1H), 3.78 (s, 3H), 4.17 (m, 1H), 5.06 (m, 1H), 5.85 (m, 1H), 6.00 ppm (m, 1H; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.1$ (u), 27.9 (u), 54.7 (d), 65.4 (d), 71.0 (d), 126.8 (d), 135.7 (d), 155.4 ppm (u); IR (capillary): $\tilde{\nu}=3403$ (s), 3028 (s), 2956 (vs), 2857 (m), 2675 (w), 2460 (w), 2200 (w), 1745 (vs), 1584 (w), 1541 (w), 1444 (s), 1397 (w), 1341 (s), 1264 (vs), 1224 (s), 1149 (m), 1112 (w), 1067 (s), 1010 (s), 970 (s), 943 (s), 913 (s), 867 (w), 831 (w), 792 (s), 757 cm^{-1} (vs); MS (CI, isobutane): *m*/*z* (%): 173 (10) [M^++1], 155 (100), 135 (8), 101 (6), 97 (66), 79 (4), 77 (10); elemen-

tal analysis calcd (%) for $C_8H_{12}O_4$ (172.07): C 55.81, H 7.02; found: C 55.61, H 7.18.

Carbonate 12b: A Schlenk flask was successively charged with [Pd_2(dba)$_3$]·$CHCl_3$ (83 mg, 0.08 mmol), ligand **2** (110 mg, 0.16 mmol), $KHCO_3$ (280 mg, 2.8 mmol), and degassed CH_2Cl_2 (9 mL). Then the mixture was stirred at room temperature for 15 min. After the mixture was cooled to 0 °C, it was treated with degassed water (1 mL) and carbonate **5b** (460 mg, 2 mmol) and the mixture was rapidly stirred at 0 °C for 24 h. Then the mixture was poured into cyclohexane/EtOAc (1:1; 200 mL) and filtered through a plug of silica gel (0.0040–0.063 mm; 3×2 cm). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) afforded carbonate **12b** (258 mg, 92%) of 96% *ee* (determined by HPLC after hydrolysis to **13b** and benzoylation to **15**) as a colorless oil. $[\alpha]_D = +5.0$ (c = 11.0 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (m, 1H), 2.10 (m, 2H), 2.30 (m, 1H), 4.93 (m, 1H), 5.03 (m, 1H), 5.79 (dqtd, J = 10.1, 1.7, 0.5 Hz, 1H), 6.24 ppm (dtd, J = 10.1, 4.0, 0.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (u), 21.2 (u), 72.2 (d), 74.9 (d), 121.3 (d), 135.3 (d), 155.0 ppm (u); IR (capillary): $\tilde{\nu}$ = 3040 (w), 2957 (vs), 2930 (vs), 2859 (s), 1928 (w), 1801 (vs), 1726 (vs), 1652 (w), 1600 (w), 1550 (w), 1459 (m), 1377 (m), 1354 (m), 1280 (s), 1203 (m), 1160 (vs), 1077 (s), 1045 (vs), 1022 (vs), 978 (w), 961 (w), 928 (w), 875 (w), 852 (w), 773 cm^{-1} (m); MS (CI, CH_4): m/z (%): 141 (49) [M^++1], 97 (19), 79 (100), 68 (3), 63 (6); elemental analysis calcd (%) for $C_7H_8O_3$ (140.05): C 59.99, H 5.75; found: C 59.74, H 5.50.

Carbonate 12c: A Schlenk flask was successively charged with [Pd_2(dba)$_3$]·$CHCl_3$ (70 mg, 0.067 mmol), ligand **2** (97 mg, 0.14 mmol), $KHCO_3$ (127 mg, 1.26 mmol), and degassed CH_2Cl_2 (18 mL). After the mixture was stirred at room temperature for 15 min, it was cooled to 0 °C and successively treated with degassed water (2 mL) and carbonate **5c** (200 mg, 0.82 mmol) in degassed CH_2Cl_2 (18 mL). After the mixture was rapidly stirred at 0 °C for 24 h, it was poured into cyclohexane/EtOAc (1:1) (200 mL) and the mixture was filtered through a plug of silica gel (0.0040–0.063 mm; 3×2 cm). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) afforded carbonate **12c** (20 mg, 16%) of 91% *ee* (Lipodex-gamma, H_2, t_R (**12c**) = 94.1 min, t_R (*ent*-**12c**) = 94.7 min) as a colorless oil and biscarbonate **5c** (164 mg, 82%). $[\alpha]_D = -30.0$ (c = 0.5 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–2.32 (m, 6H), 4.77–4.85 (m, 1H), 5.40 (m, 1H), 5.61–5.66 (m, 1H), 5.81–5.89 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (u), 27.5 (u), 27.6 (u), 77.7 (d), 78.3 (d), 123.5 (d), 131.3 (d), 154.1 ppm (u); IR (capillary): $\tilde{\nu}$ = 3569 (w), 2943 (m), 2870 (w), 1786 (vs), 1658 (w), 1545 (w), 1457 (m) 1362 (s), 1263 (w), 1166 (vs), 1055 (vs), 881 (w), 841 (m), 770 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 155 (10), 111 (1), 109 (4), 92 (45), 81 (28), 68 (86), 67 (100), 54 (51); elemental analysis calcd (%) for $C_8H_{10}O_3$ (154.16): C 62.33, H 6.54; found: C 62.54, H 6.41.

Carbonate *ent*-12c: A Schlenk flask was successively charged with [Pd_2(dba)$_3$]·$CHCl_3$ (156 mg, 0.151 mmol), ligand *ent*-**2** (225 mg, 0.33 mmol), $KHCO_3$ (255 mg, 2.55 mmol), and degassed CH_2Cl_2 (15 mL). After the mixture was stirred at room temperature for 5 min, it was cooled to 0 °C and successively treated with degassed water (2.5 mL) and carbonate **5c** (415 mg, 1.70 mmol) in degassed CH_2Cl_2 (8 mL). After the mixture was rapidly stirred at 0 °C for 24 h, it was warmed to room temperature and stirred for 12 h under air. The organic phase was separated from the aqueous phase with a syringe and treated with diethyl ether (360 mL). The suspension was centrifuged and the solid was washed with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) gave carbonate *ent*-**12c** (102 mg, 39%) of 99% *ee* as a colorless oil. $[\alpha]_D = +35.0$ (c = 1.2 in CH_2Cl_2).

Benzoate 14: Alcohol **6b** (52 mg, 0.3 mmol) and 4-DMAP (4-DMAP = 4-dimethylaminopyridine; 1.8 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (2 mL) and the solution was cooled to 0 °C. The mixture was successively treated with NEt_3 (0.06 mL, 0.45 mmol) and PhCOCl (0.037 mL, 0.315 mmol). Then the cooling bath was removed, and after the mixture was stirred for 2 h, it was poured onto a mixture of ice and saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3×10 mL) and the combined organic phases were washed with 1 M HCl, saturated aqueous $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography on silica gel (*n*-pentane/Et_2O, 5:1) gave benzoate **14** (81 mg, 97%) as a colorless oil. HPLC (Chiralpak IA, *n*-heptane/*i*PrOH, 99.9:0.1, flow rate 0.75 mL min^{-1}, λ = 254 nm): t_R (*ent*-**14**) = 18.43 min, t_R (**14**) = 20.70 min, ≥99% *ee*; $[\alpha]_D = -49.5$ (c = 1.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (m, 4H), 3.81 (s, 3H), 5.15 (m, 1H), 5.50 (m, 1H), 6.04 (qd, J = 11.0, 3.0 Hz, 2H), 7,44 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 8.05 ppm (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.9 (u), 25.1 (u), 54.8 (d), 67.7 (d), 71.1 (d), 128.3 (d), 129.5 (d), 129.6 (d), 130.2 (u), 130.9 (d), 133.0 (d), 155.3 (u), 165.9 ppm (u); IR (capillary): $\tilde{\nu}$ = 3421 (w), 2963 (m), 1746 (vs), 1717 (vs), 1601 (v), 1584 (w), 1541 (w), 1445 (m), 1398 (w), 1343 (w), 1315 (w), 1264 (vs), 1212 (w), 1176 (w), 1110 (s), 1071 (w), 1052 (w), 1012 (s), 941 (m), 924 (m), 792 (m), 755 cm^{-1} (w); MS (CI, CH_4): m/z (%): 276 (1) [M^+], 201 (100), 155 (76), 133 (3), 123 (41), 111 (6), 105 (74), 91 (2), 79 (35), 77 (38); elemental analysis calcd (%) for $C_{15}H_{16}O_5$ (276.10): C 65.21, H 5.84; found: C 65.02, H 5.79.

Diol 13b: K_2CO_3 (181 mg, 1.28 mmol) was added portionwise to a solution of carbonate **12b** (30 mg, 0.21 mmol) in MeOH (5 mL) and the mixture was stirred at room temperature for 1 h. The mixture was concentrated in vacuo, the residue was dissolved in water (5 mL), and the solution was extracted with EtOAc (5×10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo, which gave diol **13b** (24.2 mg, 99%) as a slightly yellow oil. The thus-obtained diol was pure enough for benzoylation. Purification by column chromatography (cyclohexane/EtOAc, 1:9) gave diol **13b** (24 mg, 98%) of 96% *ee* (determined by HPLC after benzoylation to **15**) as a colorless oil. $[\alpha]_D = -172.0$ (c = 1 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (m, 1H), 1.72 (m, 1H), 1.96 (m, 1H), 2.14 (m, 1H), 3.56 (brs, 2H), 3.75 (dt, J = 9.3, 3.8 Hz, 1H), 4.05 (brs, 1H), 5.64 (dqt, J = 10.2, 1.9 Hz, 1H), 5.78 ppm (dtd, J = 10.2, 3.7, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.7 (u), 25.8 (u), 66.5 (d), 68.9 (d), 126.9 (d), 131.0 ppm (d); IR (capillary): $\tilde{\nu}$ = 3773 (vs), 3027 (m), 2922 (s), 2655 (w), 1650 (m), 1434 (s), 1404 (s), 1323 (w), 1252 (m), 1226 (m), 1193 (w), 1151 (m), 1080 (vs), 995 (s), 972 (m), 914 (m), 878 (w), 862 (w), 824 (m), 754 cm^{-1} (s); MS (EI, 70 eV): m/z (%): 114 (1) [M^+], 97 (2), 79 (1), 70 (100), 67 (4), 57 (2), 55 (9), 53 (4), 51 (4), 45 (2); elemental analysis calcd (%) for $C_6H_{10}O_2$ (114.07): C 63.14, H 8.83; found: C 63.08, H 8.74.

Diol 13c: A mixture of carbonate **12c** (50 mg, 0.32 mmol) of 68% *ee* and K_2CO_3 (200 mg, 1.45 mmol) in MeOH (5 mL) was stirred at room temperature for 16 h. Then the mixture was concentrated in vacuo, the residue was dissolved in water (5 mL), and the solution was extracted with EtOAc (4×10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/EtOAc, 1:9) gave diol **13c** (20 mg, 45%). $[\alpha]_D = -65.0$ (c = 0.95 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45–1.70 (m, 2H), 1.80 (m, 1H), 1.90–2.15 (m, 2H), 2.23 (m, 1H), 2.55 (brs, 2H), 3.95 (m, 1H), 4.45 (dd, J = 1.7, 1.9 Hz, 1H), 5.55 (dqt, J = 11.5, 1.9 Hz, 1H), 5.91 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 (u), 28.5 (u), 33.9 (u), 72.5 (d), 73.9 (d), 131.8 (d), 132.6 ppm (d); IR (capillary): $\tilde{\nu}$ = 3379 (vs), 3027 (m), 2923 (vs), 2677 (w), 1655 (m), 1442 (s), 1385 (m), 1351 (w), 1273 (s), 1171 (w), 1034 (vs), 994 (vs), 942 (m), 905 (m), 872 (m), 833 (m), 771 (m), 729 (w), 674 cm^{-1} (m); MS (ESI, 70 eV): m/z (%): 111 (1) [M^+−OH], 92 (100), 67 (6).

Dibenzoate 15: The synthesis of dibenzoate **15** (115 mg, 95%) from diol **13b** was performed according to the procedure used for the synthesis of monobenzoate **14** with the exception that 0.1 equiv of 4-DMAP, 3 equiv of NEt_3, and 2.1 equiv of PhCOCl were used. Colorless oil; HPLC (Chiralpak IA, *n*-heptane/*i*PrOH = 99.2:0.8, flow rate 0.75 mL min^{-1}, λ = 254 nm): t_R (*ent*-**15**) = 31.17 min, t_R (**15**) = 32.31 min, 96% *ee*, $[\alpha]_D = -118.0$ (c = 1.0 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (m, 1H), 2.06–2.35 (m, 3H), 5.36 (dt, J = 10.1, 3.5 Hz, 1H), 5.71 (m, 1H), 5.77 (m, 1H), 5.98 (dt, J = 9.6, 3.2 Hz, 1H), 7.24 (t, J = 7.9 Hz, 2H), 7.30 (t, J = 8.2 Hz, 1H), 7.40 (m, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.93 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (u), 24.0 (u), 67.4 (d), 70.3 (d), 123.5 (d), 128.3 (d), 128.4 (d), 129.6 (d), 129.7 (d), 130.3 (u), 130.4 (u), 132.9 (d), 133.0 (d), 133.1 (d), 165.8 (u), 166.0 ppm (u); IR (ca-

pillary): $\tilde{\nu}$ = 3033 (w), 2957 (m), 2854 (w), 1746 (vs), 1716 (vs), 1601 (w), 1584 (w), 1491 (w), 1444 (s), 1398 (w), 1342 (w), 1316 (w), 1263 (vs), 1176 (m), 1109 (s), 1071 (m), 1052 (w), 1012 (s), 980 (w), 939 (m), 924 (m), 857 (w), 792 (m), 7.56 cm^{-1} (m); MS (CI, CH_4): *m/z* (%): 323 (2) [M^++1], 305 (1), 235 (1), 201 (100), 139 (2), 123 (5), 105 (34), 79 (2), 77 (2); elemental analysis calcd (%) for $C_{20}H_{18}O_4$ (322.12): C 74.52, H 5.63; found: C 74.15, H 5.63.

Reaction of alcohol *rac*-6b with 1 and $KHCO_3$: A Schlenk flask was successively charged with [$Pd_2(dba)_3$]·$CHCl_3$ (42 mg, 0.04 mmol), ligand **2** (55 mg, 0.08 mmol), degassed CH_2Cl_2 (9 mL), and $KHCO_3$ (141 mg, 1.4 mmol). After the mixture was stirred at room temperature for 15 min, it was cooled to 0 °C and then degassed water (1 mL) and alcohol *rac*-**6b** (172 mg, 1 mmol) were added. After the mixture was rapidly stirred at 0 °C for 2 h, it was poured into cyclohexane/EtOAc (1:1; 200 mL) and the mixture was filtered through a plug of silica gel (0.0040–0.063 mm; 3 × 2 cm). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) afforded carbonate **12b** (123 mg, 88 %) of 46 % *ee* (determined by HPLC after hydrolysis to **13b** and benzoylation to **15**) as a colorless oil.

General procedure for in situ NMR spectroscopic investigation of the Pd^0 complex 1 in a sealed NMR spectroscopy tube (GP2): A Schlenk-type NMR spectroscopy tube was successively charged with [Pd_2-$(dba)_3$]·$CHCl_3$ (3.2 mg, 0.0031 mmol), ligand **2** (4.3 mg, 0.0062 mmol), and degassed CD_2Cl_2 (0.7 mL) under argon. After the mixture was cooled to −78 °C, the tube was evacuated and sealed under vacuum at −78 °C with an acetylene/oxygen microburner.

General procedure for the in situ NMR spectroscopic investigation of the reaction of the Pd^0 complex 1 with biscarbonates 5b–d and *rac*-22 in a sealed NMR spectroscopy tube (GP3): A Schlenk-type NMR spectroscopy tube equipped with a ground joint was successively charged with [Pd_2-$(dba)_3$]·$CHCl_3$ (3.2 mg, 0.0031 mmol), ligand **2** (4.3 mg, 0.0062 mmol), biscarbonate (**5b**, **5c**, **5d**, and *rac*-**22**; 0.0062 mmol) and degassed CD_2Cl_2 (0.7 mL), and the mixture was cooled to −78 °C. Then the NMR spectroscopy tube was evacuated and sealed under vacuo at −78 °C by using an acetylene/oxygen microburner. Subsequently the mixture was warmed to room temperature. The ^{1}H NMR spectra showed in all cases the signals of the Pd^{II} complex **7**, the corresponding dienes **8b**, **8c**, and **8d**, and dba, whereas the ^{31}P NMR spectra showed in all cases the signal of **7**. Diene **8** and complex **7** were present in a ratio of approximately 1:1. Pd^{II} complex **7**: Contained in all mixtures obtained from biscarbonates **5c**,**d**, *rac*-**22**, and **1** according to GP3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.25 (m, 2H), 1.47 (m, 2H), 1.59 (m, 2H), 2.50 (br d, J = 12.9 Hz, 2H), 3.68 (m, 2H), 6.72 (m, 2H), 7.09 (m, 4H), 7.14–7.23 (m, 14H), 7.37 (t, J = 7.1 Hz, 2H), 7.41 (t, J = 7.1 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 8.51 ppm (dd, J = 8.0, 3.0 Hz, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 26.0 ppm. The NMR spectroscopic data were in complete agreement with those reported in the literature.[27,28] 1,3-Cyclohexadiene (**8b**): Contained in the reaction mixture obtained from biscarbonates **5b** and *rac*-**22** and **1** according to GP3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.12 (m, 4H), 5.78 (m, 2H), 5.87 ppm (m, 2H). 1,3-Cycloheptadiene (**8c**): Contained in reaction mixture obtained from biscarbonate **5c** and **1** according to GP3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.73 (m, 2H), 2.24 (m, 4H), 5.67 ppm (m, 4H). 1,3-Cyclooctadiene (**8d**): Contained in the reaction mixture obtained from biscarbonate **5d** and **1** according to GP3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.50 (m, 4H), 2.17 (m, 4H), 5.61 (m, 2H), 5.79 ppm (m, 2H).

General procedure for the reaction of the Pd^0 complex 1 with biscarbonates 5b–d with formation of the Pd^{II} complex 7 and dienes 8b–d (GP4): A Schlenk flask was successively charged with [$Pd_2(dba)_3$]·$CHCl_3$ (291 mg, 0.28 mmol), ligand **2** (388 mg, 0.56 mmol), biscarbonate **5b–d** (0.56 mmol), and degassed CH_2Cl_2 (5 mL), and the mixture was rapidly stirred at room temperature for 1 h. Then dry diethyl ether (20 mL) was added and the precipitate was separated by centrifugation, washed with diethyl ether (3 × 5 mL) and dried in vacuo. This gave complex **7** (366 mg, 82 %) as a pale yellow powder. All spectroscopic data of **7** were in complete agreement with the literature data.[22] The combined organic phases (diethyl ether/CH_2Cl_2) obtained in the case of **5b** were used for the trapping of **8b** as adducts **25a**,**b**.

General procedure for the trapping of 8b as adducts 24a and 24b (GP5): Diethyl ether was carefully distilled off the combined organic phases, which were obtained according to GP4 from **5b**, at normal pressure by using a column. Then CH_2Cl_2 (10 mL) was added and the remaining diethyl ether was again carefully distilled off (this procedure was repeated twice). Then the mixture was treated with CH_2Cl_2 (10 mL) and the dienophile (**24a** or **24b**). After the mixture was stirred at room temperature for 5 (for **24a**) and 2 h (for **24b**), the solvent was removed in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 3:1) gave adducts **24a** and **24b**.

*Adduct **25a***: Adduct **24a** was synthesized according to GP5 by reaction of diene **8b** obtained according to GP4 with maleic anhydride (**24a**) (55 mg, 0.56 mmol). Adduct **25a** (74 mg, 74 %) was obtained as a slightly yellow solid. All spectral data of **25a** were in complete agreement with those of a sample independently prepared from diene **8b** and **24a** according to the literature.[44]

*Adduct **25b***: Adduct **25b** was synthesized according to GP5 by the reaction of diene **8b** obtained according to GP4 with dienophile **24b** (98 mg, 0.56 mmol). Adduct **25b** (115 mg, 80 %) was obtained as a pale yellow solid. All spectral data of **25b** were in complete agreement with those of a sample independently prepared from diene **8b** and **24b** according to the literature.[45]

Desymmetrization of biscarbonate 5c and isolation of 7 after oxidative workup: A Schlenk flask was successively charged with [Pd_2-$(dba)_3$]·$CHCl_3$ (228 mg, 0.22 mmol), ligand **2** (330 mg, 0.48 mmol), $KHCO_3$ (374 mg, 3.72 mmol), and degassed CH_2Cl_2 (36 mL). Then the mixture was immediately cooled to 0 °C and stirred for 5 min under argon. After the mixture was treated with degassed water (4 mL) and biscarbonate **5c** (608 mg, 2.5 mmol), it was rapidly stirred at 0 °C for 24 h under argon. Then the mixture was warmed to room temperature and stirred for 12 h under air. The organic phase was separated from the aqueous phase with a syringe and treated with diethyl ether (360 mL). Centrifugation of the suspension and washing of the solid with diethyl ether gave after drying in vacuo the slightly impure complex **7** (316 mg, 90 %). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography on silica gel (cyclohexane/EtOAc, 7:2) gave biscarbonate **5c** (100 mg, 16 %) and carbonate **12c** (171 mg, 44 %) of 68 % *ee* as colorless oils. $[\alpha]_D$ = −42.0 (c = 1.8 in CH_2Cl_2).

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