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**DOI**

[10.1021/acs.organomet.6b00265](https://doi.org/10.1021/acs.organomet.6b00265)

**Publication date**

2016

**Document Version**

Final published version

**Published in**

Organometallics

**License**

Article 25fa Dutch Copyright Act

[Link to publication](#)

**Citation for published version (APA):**

Théveau, L., Bellini, R., Dydio, P., Szabo, Z., van der Werf, A., Sander, R. A., Reek, J. N. H., & Moberg, C. (2016). Cofactor-Controlled Chirality of Tropoisomeric Ligand. *Organometallics*, 35(11), 1956-1963. <https://doi.org/10.1021/acs.organomet.6b00265>

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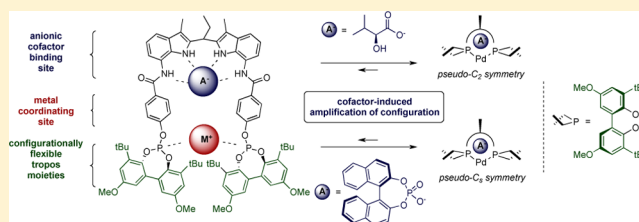
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## Cofactor-Controlled Chirality of Tropoisomeric Ligand

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## Supporting Information

**ABSTRACT:** A new tropos ligand with an integrated anion receptor site has been prepared. Chiral carboxylate and phosphate anions that bind in the anion receptor unit proved capable of stabilizing chiral conformations of the achiral flexible bidentate biaryl phosphite ligand, as shown by variable temperature <sup>1</sup>H and <sup>31</sup>P NMR spectroscopical studies of palladium(0) olefin complexes. Palladium allyl complexes of the supramolecular ligand-chiral cofactor assemblies catalyzed asymmetric allylic substitutions of *rac*-(*E*)-1,3-diphenyl-2-propenyl carbonate and *rac*-3-cyclohexenyl carbonate with malonate and benzylamine as nucleophiles to provide nonracemic products. Although moderate enantioselectivities were observed, (*ee*s up to 66%), the results confirm the ability of the anionic guests to affect the conformation of the ligand.



## INTRODUCTION

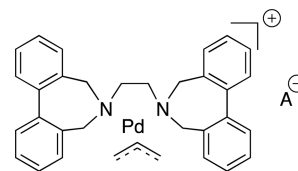
Metal complexes with chirally flexible, tropos, ligands are known to induce high levels of enantioselectivity in a variety of catalytic reactions.<sup>1</sup> Such complexes are convenient to prepare since no resolution or asymmetric synthesis is required. The configuration is instead controlled by a chiral motif covalently attached to the flexible function<sup>2</sup> or present in a separate unit bound to the metal center,<sup>3</sup> and may as well be affected by the substrate undergoing reaction.<sup>4</sup> It has also been shown that chiral ionic liquids are able to favor one enantiomeric conformation of tropos ligands.<sup>5</sup>

An alternative way to control ligand conformation, which is limited to charged complexes, is by means of a chiral counterion.<sup>6</sup> The axial chirality in a tropos biaryl (BIPHEP) ligand has in this way been controlled by chiral anions capable of ion pairing, thereby allowing the preparation of enantiomerically highly enriched gold complexes with either aR or aS configuration<sup>7</sup> and subsequent use of such ion pairs in enantioselective hydroalkoxylation of allenes.<sup>8</sup> In other examples, one of the axially chiral atropos BINAP enantiomers in a racemic mixture has been selectively activated by a chiral borate anion.<sup>9</sup>

Configurational control in bidentate ligands containing two tropos elements is more challenging than in ligands containing a single tropos structural element since such ligands can adopt up to four different geometries, with (aR,aR), (aR,aS), (aS,aR), and (aS,aS) configurations. So far, control of the absolute configuration of bistropos bidentate ligands has been achieved by connecting the two flexible elements via a chiral backbone.<sup>2a,b,d</sup> The possibility to influence the stereochemistry by instead relying on noncovalent interactions with an external

chiral additive would facilitate structural variations and permit efficient combinatorial catalyst screening.<sup>10</sup>

Encouraged by our previous observation that a chiral anion resulted in enantio-differentiation of stereotopic nuclei in palladium allyl complexes with a configurationally labile bisazepine ligand, 1,2-bis[4,5-dihydro-3*H*-dibenzo[*c-e*]-azepino]ethane (Figure 1),<sup>11</sup> we decided to explore the use



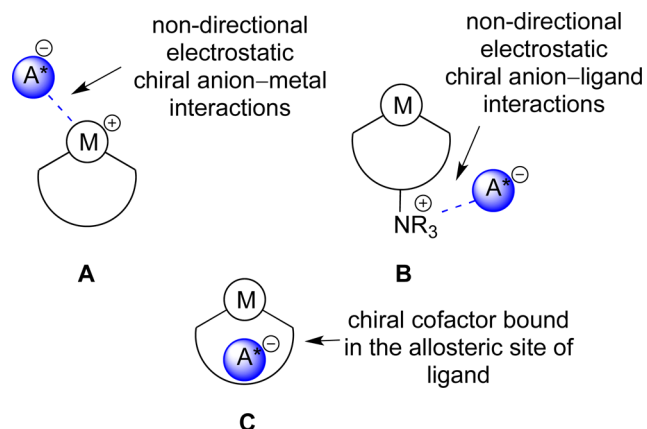
**Figure 1.** Bistropos ligand with chiral anion capable of enantio-differentiation.

of supramolecular interactions for configurational control of ligands with two stereochemically flexible units. Palladium-catalyzed asymmetric allylic alkylation has proven to serve as a useful probe for monitoring the stereochemistry of chirally flexible ligands, since “broad” substrates, such as 1,3-diphenylpropenyl acetate, prefer ligands with *pseudo*-C<sub>2</sub> structure whereas “narrow” substrates like cyclohexenyl acetate react with higher selectivity in the presence of a catalyst with *pseudo*-C<sub>s</sub> symmetry.<sup>11</sup> This reaction was therefore selected as a model reaction to study the influence of chiral additives on the symmetry of self-adaptable ligands.

Received: April 4, 2016

Published: May 23, 2016

Control of nucleophilic attack on  $\eta^3$ -allyl palladium complexes by a chiral counteranion (A, Figure 2) was



**Figure 2.** (A): Cationic complex with chiral counteranion. (B): Complex with cationic substituent and chiral counteranion. (C): Achiral ligand with binding site for chiral anion.

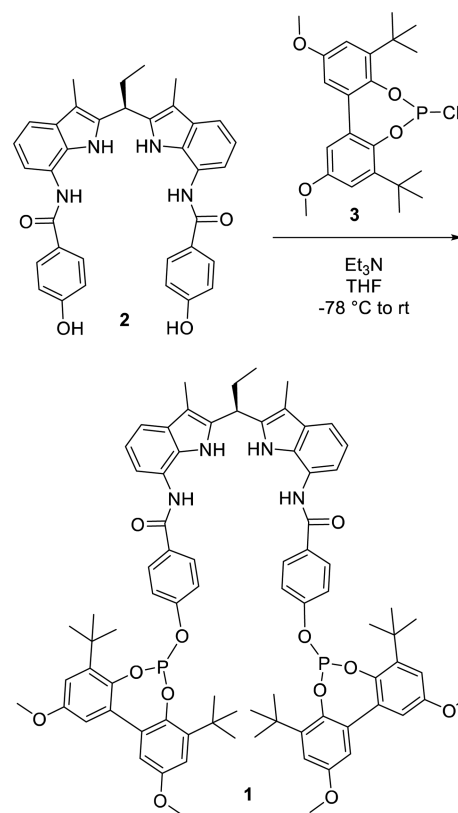
considered inefficient since a neutral complex is formed along the reaction coordinate, resulting in loss of ion pairing. Furthermore, use of an anionic nucleophile may result in replacement of the chiral counterion with the achiral nucleophile. To circumvent this problem, Ooi and co-workers used a ligand assembled from an achiral monodentate phosphine equipped with an ammonium group and chiral biphenolates or phosphates via electrostatic interactions (B, Figure 2).<sup>12</sup> An alternative approach, with more general applications, consists of the use of cofactor-controlled ligands containing a receptor unit<sup>13</sup> capable of supramolecular interaction with a chiral anion (C, Figure 2);<sup>14</sup> such ligands have been developed by some of us and successfully applied in enantioselective catalysis.<sup>15</sup> We anticipated that this strategy could be efficient for conformational control of bistropos ligands, which is demonstrated in studies presented here.

## RESULTS AND DISCUSSION

**Preparation and Properties of Cofactor Ligand.** Ligand **1** was prepared and used for studies of the influence of chiral anions on the atropisomeric behavior of a bidentate biaryl phosphite. The ligand consists of a bis(indolylamide)methane (DIM) unit, which is known to serve as an efficient anion receptor,<sup>13</sup> and which has also previously been used for the preparation of cofactor-controlled ligands.<sup>15</sup> The anion-binding pocket is equipped with four N–H functions, suitably positioned to allow all four of them to participate in hydrogen bonding to oxyanions. The ligand was prepared by a method analogous to that previously used for the preparation of a rigid binaphthyl analogue,<sup>15c–e</sup> by reaction of the known phenolic derivative **2**<sup>16</sup> with chlorophosphite **3**<sup>17</sup> (Scheme 1).

The time-averaged structure of **1** has a mirror plane ( $C_s$  symmetry), and as a result of the low barrier to inversion of the biphenyl units, pairwise identical NH signals were observed in the <sup>1</sup>H NMR spectrum and a single phosphorus signal appeared in the <sup>31</sup>P NMR spectrum collected at room temperature. Upon cooling, the signals broadened but, whereas the central methylene proton started to split at  $-79$  °C (194 K), the NH and phosphorus signals did not split even at this low temperature, suggesting a barrier to inversion  $\leq 10$  kcal mol<sup>-1</sup> (Figures S1 and S2). This behavior is similar to that of other

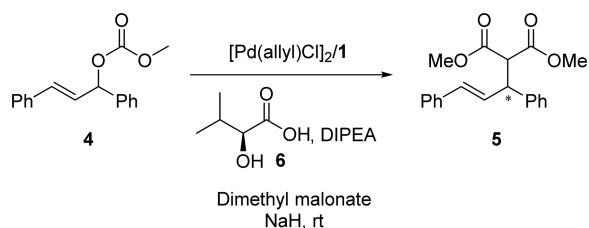
## Scheme 1. Preparation of Ligand 1



ligands containing the same biphenyl phosphite moiety, which have inversion barriers around 10 kcal mol<sup>-1</sup>.<sup>17,18</sup> An analogous phosphine ligand has been found to have a considerably higher barrier, 19.3 kcal mol<sup>-1</sup> at 298 K;<sup>19</sup> the ability to undergo rapid configurational change might render flexible phosphites more useful than their phosphine analogues for catalytic applications.

**Catalytic Reactions.** The ability of the chiral anions bound to the DIM pocket to stabilize chiral conformations of the ligand was first evaluated by analysis of the results of palladium-catalyzed allylic alkylations. Allylic carbonates were chosen as substrates for the catalytic experiments. As might be expected, these substrates are more suitable than the allylic acetate analogues, which release acetate anions during the catalytic reaction. These achiral anions can displace the chiral anion from the binding pocket of the catalyst, leading in consequence to the formation of the racemic product. A range of chiral anions were assessed in the reaction of *rac*-(*E*)-1,3-diphenyl-2-propenyl carbonate **4** with sodium dimethyl malonate as the nucleophile (see Supporting Information). In contrast to previously studied catalytic reactions with cofactor-controlled ligands, where the substrate has a direct interaction with the chiral anion,<sup>15</sup> the conformation of **1** relies solely on long distance interactions between the tropos units and the chiral cofactor. Among the anions evaluated, (*S*)-2-hydroxy-3-methylbutyric carboxylate, obtained from **6** by treatment with *N,N*-diisopropylethylamine (DIPEA), appeared as the most promising chiral cofactor, resulting in a high yield of product with 36% ee in CH<sub>2</sub>Cl<sub>2</sub> (Table 1, entry 1). Optimization of the reaction conditions by modification of the order of addition of reagents, the solvent (entries 1–4), and the palladium to ligand ratio (entries 4 and 5) led to somewhat improved selectivity (46% ee, entry 5). Considering that nucleophilic attack might be faster than the ability of the ligand to adapt its conformation

**Table 1. Asymmetric Allylic Alkylation of 4 Catalyzed by Pd-1 in the Presence of 6, Optimization of Reaction Conditions<sup>a</sup>**



entry	[Pd]:1	solvent (ratio)	yield (%)	ee (%) (config)
1	1:1.5	CH <sub>2</sub> Cl <sub>2</sub>	89	36 (S) <sup>b</sup>
2	1:1.5	CH <sub>2</sub> Cl <sub>2</sub> /THF (2:1)	85	29 (S)
3	1:1.5	CH <sub>2</sub> Cl <sub>2</sub> /THF (1:2)	100	35 (S)
4	1:1.5	THF	100	43 (S)
5	1:1.1	THF	100	46 (S) <sup>c</sup>
6	1:1.1	THF	97	57 (S) <sup>d</sup>
7	1:1.1	THF	98	57 (S) <sup>e</sup>

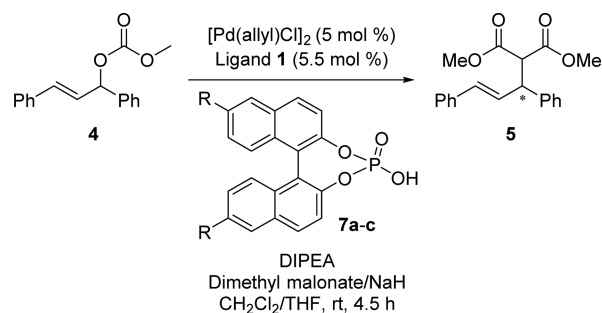
<sup>a</sup>Reaction conditions: 4 (0.055 mmol), [Pd(allyl)Cl]<sub>2</sub> (5 mol %), ligand 1 (5.5–7.5 mol %), cofactor 6 (0.9 equiv based on 4), DIPEA (0.7 equiv), dimethyl malonate (3.6 equiv), NaH (3 equiv), solvent (1 mL), room temperature, 30 min. A solution of 4 and a solution of sodium dimethyl malonate were prepared separately and added successively to the catalyst mixture. Full conversion of 4 was observed in all experiments. Yields and ee were determined by <sup>1</sup>H NMR using 1-methoxynaphthalene as internal standard and by chiral HPLC, respectively. <sup>b</sup>A solution of the catalyst and 4 was added to the sodium dimethyl malonate solution. <sup>c</sup>Average of three experiments. <sup>d</sup>The sodium dimethyl malonate solution was added over 4 h. <sup>e</sup>The sodium dimethyl malonate solution was added over 8 h.

to the substrate, slow addition of the nucleophile to the catalyst/substrate mixture was thought to be beneficial for the enantioselectivity of the reaction. Thus, different rates of addition of the nucleophile to the catalyst/substrate mixture were studied under the otherwise optimum reaction conditions. Addition of the nucleophile to the catalyst/substrate mixture over 4 h did indeed lead to improved results and afforded the product with 57% ee and in excellent yield, whereas further decrease of the rate had no effect (entries 6–7).

Dihydrogen phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) has been shown to bind strongly to the DIM receptor,<sup>13b,15a,c</sup> and for this reason chiral phosphates were considered as suitable cofactor candidates. Several nonsubstituted, 3,3-, and 6,6'-disubstituted chiral BINOL-derived phosphates<sup>20</sup> were studied as chiral cofactors (Table 2). Noteworthy, 3,3'-substituted chiral phosphates were shown to be inefficient, presumably as a result of severe steric hindrance, and slightly inferior enantioselectivities were observed with this new class of chiral cofactors.

As a result of the different conformational preferences of different types of substrates, it was assumed that different cofactors might be preferred for different types of substrates. In order to study the ability of the flexible ligand to adapt its conformation to a different kind of substrate, *rac*-3-cyclohexenyl carbonate 8 was also studied in the asymmetric alkylation (Table 3). In contrast to carbonate 4, which is considered as a "broad" substrate, carbonate 8 represents a "narrow" substrate, and as such requires a different complex geometry for efficient induction of selectivity. The highest selectivity in reactions with this substrate was observed with phosphate 7a (43% ee, entry 4). Notably, the reaction with carbonate 8 in the presence of the anion of (*S*)-2-hydroxy-3-

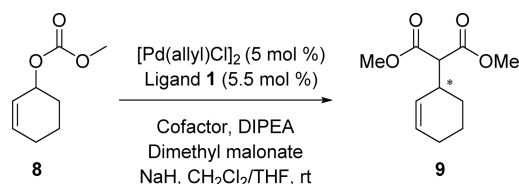
**Table 2. Asymmetric Allylic Alkylation of 4 Catalyzed by Pd-1 in the Presence of BINOL-Derived Phosphate Cofactors<sup>a</sup>**



entry	R (config)	yield (%)	ee (%) (config)
1	H (R), 7a	89	39 (R) <sup>b</sup>
2	Ph (S), 7b	87	38 (S)
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> (S), 7c	85	28 (S) <sup>b</sup>

<sup>a</sup>Reactions were performed and analyzed as described in Table 1 but the catalyst solution was prepared in CH<sub>2</sub>Cl<sub>2</sub> since the phosphate was insoluble in THF; solutions of 4 and sodium dimethyl malonate were prepared separately in THF. The sodium dimethyl malonate solution was added over 4 h. Full conversion of 4 was observed in all experiments. <sup>b</sup>Average of two or three experiments.

**Table 3. Asymmetric Allylic Alkylation of 8 Catalyzed by Pd-1 in the Presence of Different Chiral Cofactors<sup>a</sup>**



entry	cofactor	yield (%)	ee (%) (config)
1	6	94	5 (S) <sup>b,c</sup>
2	6	80	6 (S) <sup>c</sup>
3	7a	100	15 (R) <sup>b</sup>
4	7a	73	43 (R) <sup>d</sup>
5	7a	14	35 (R) <sup>e</sup>
6	7b	63	20 (S)
7	7c	76	19 (S) <sup>d</sup>

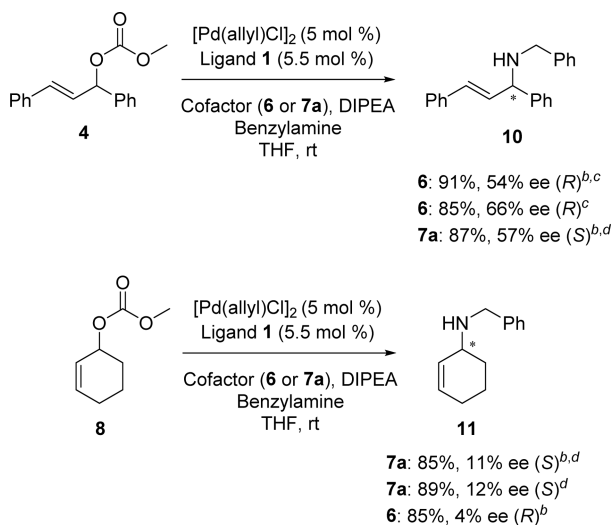
<sup>a</sup>Reactions were performed and analyzed as described in Table 2. Full conversion of 8 was observed in all experiments. <sup>b</sup>The sodium dimethyl malonate solution was added in one portion. <sup>c</sup>The catalyst solution was prepared in THF. <sup>d</sup>Average of two experiments. <sup>e</sup>The sodium dimethyl malonate solution was added over 8 h.

methylbutyric acid 6 gave close to racemic product (entries 1 and 2), which is in sharp contrast to the reaction of carbonate 4, which in the presence of the same chiral anion occurred with the highest selectivity. This demonstrates that the selectivity of the same complex can be optimized for substantially different substrates through the choice of an appropriate guest.

Finally benzylamine was used as the nucleophile in reactions with both types of substrates, employing the reaction conditions developed before (Scheme 2). The highest selectivity, 66% ee, was observed in the reaction of *rac*-(*E*)-1,3-diphenyl-2-propenyl carbonate 4, whereas reactions with the cyclic substrate gave the product with low selectivity.

To evaluate the importance of the noncovalent interactions between the receptor and the chiral anion, control experiments were performed in which ligand 1 was replaced by 12, which lacks the anion binding site. The ligand was prepared as shown

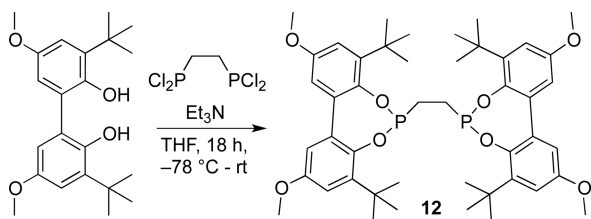


Scheme 2. Use of Benzylamine as Nucleophile<sup>a</sup>

<sup>a</sup>Reactions were performed and analyzed as described in Table 1. Full conversion of **4** or **8** was observed in all experiments. <sup>b</sup>The benzylamine solution was added over 4 h. <sup>c</sup>Average of two experiments. <sup>d</sup>The catalyst solution was prepared in CH<sub>2</sub>Cl<sub>2</sub> since the phosphate was insoluble in THF.

in Scheme 3 and used together with the silver salt of **7a** in reactions of *rac*-(*E*)-1,3-diphenyl-2-propenyl carbonate (**4**)

## Scheme 3. Preparation of Ligand Devoid of Anion Binding Site



with both sodium dimethyl malonate and benzylamine. In both cases, racemic product was obtained, thus demonstrating that anion binding to the ligand is crucial for configurational control of the tropos moieties.

From previous studies it is known that allylic alkylation of *rac*-**4** in the presence of palladium complexes with rigid binaphthyl analogues of 1,2-bis[4,5-dihydro-3*H*-dibenzo[*c-e*]azepino]ethane (Figure 1), containing nitrogen as well as phosphorus donor atoms, with (*S,S*) configuration yield (*S*)-**5** as the major product.<sup>4</sup> Since a product with the same absolute configuration was obtained from the complex containing (*S*)-2-hydroxy-3-methylbutyric acid, it is assumed that the ligand in the presence of this cofactor adopts (*S,S*) configuration in the product olefin complex (Figure 3).

<sup>1</sup>H and <sup>31</sup>P NMR Studies. Cofactor Complexes with Ligand **1**. In order to gain insight into the effect of chiral anions on the conformation of ligand **1**, its complexes with the most efficient anions, **6** and **7a**, were studied in detail by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy (Figures 4, S3, and S4). Addition of anions resulted in characteristic downfield shifts for the four NH protons. The presence of chiral anions causes loss of the mirror symmetry of the ligand, and as a result separate signals were observed for diastereotopic NH indolyl and amide protons in

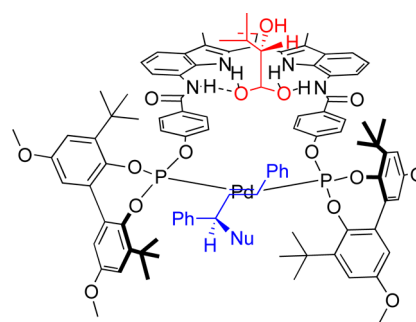


Figure 3. Predicted structure of palladium olefin complex of ligand **1** in the presence of the anion of (*S*)-2-hydroxy-3-methylbutyric acid.

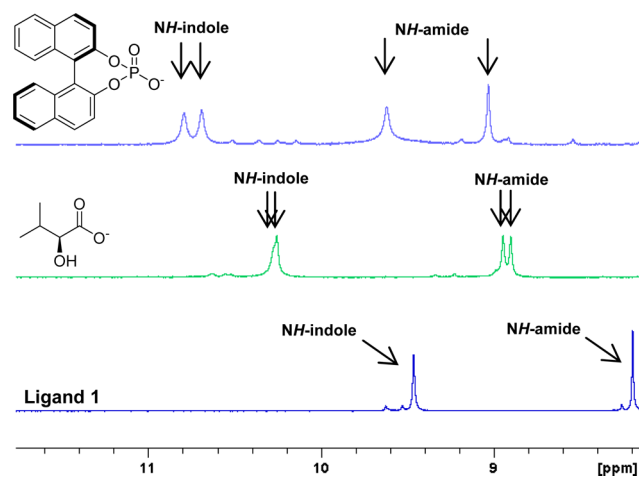


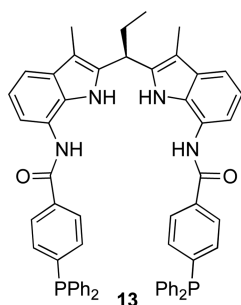
Figure 4. Part of the <sup>1</sup>H NMR spectra of ligand **1** in the absence and in the presence of chiral cofactors **6** or **7a** and DIPEA in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) at 21 °C. Minor signals originate from impurities.

the <sup>1</sup>H NMR spectrum; the largest separation of signals was observed for the complex with **7a**. In the <sup>31</sup>P NMR spectra in the presence of the chiral anions, the phosphorus nuclei appeared at chemical shifts different from that of **1**. In the presence of **7a**, two signals were observed as a result of the absence of mirror symmetry, whereas in the presence of **6** only one signal appeared at room temperature. In low temperature NMR spectra of the complex with **7a** no separation of signals due to the presence of different isomers was observed (Figures S5 and S6), but separate signals for free and bound phosphate cofactor appeared; at room temperature the exchange between free and bound cofactor was fast (Figure S6).

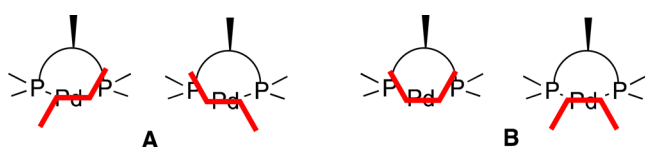
*Palladium Olefin Complexes with Ligand 13.* It is usually assumed that the transition state in palladium-catalyzed asymmetric allylic substitution has a structure closer to that of the product olefin complex rather than that of the precursor allyl complex,<sup>21</sup> and analysis of the structure of Pd(0)-olefin complexes of ligand **1** is therefore considered informative to study the stereochemistry-determining step.<sup>11</sup> Notably, previous work has demonstrated the tendency of palladium complexes of bidentate tropos ligand to adapt their conformation to linear and cyclic olefins with a structure with C<sub>2</sub> and C<sub>s</sub> symmetry, respectively.<sup>11</sup>

In order to mimic the transition states in reactions with linear and cyclic allylic substrates, complexes with *trans* and *cis* olefins, respectively, were studied. Initially, palladium complexes of the previously reported ligand **13**, which was used for rhodium-catalyzed hydrogenation<sup>15b</sup> and hydroformylation,<sup>15a</sup>

with acetate as the counterion and fumaronitrile as the olefin in  $\text{CD}_2\text{Cl}_2$  were studied (Figures S7 and S8).



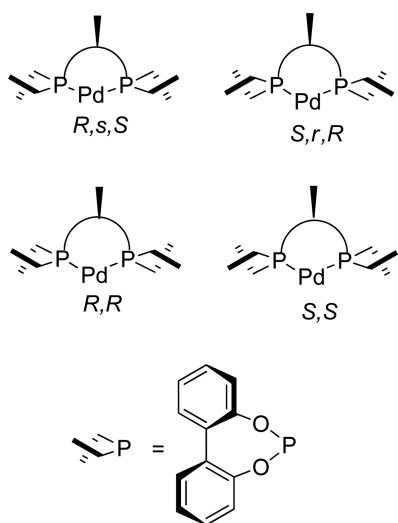
Coordination to the enantiotopic faces of the trans olefin is expected to give rise to two enantiomeric complexes, each with diastereotopic phosphorus centers (Figure 5). This was verified



**Figure 5.** (A) Two enantiomeric complexes with achiral ligand and trans olefin. (B) Two diastereomeric meso complexes with cis olefin. Cis and trans olefins are shown in red.

by the presence of two doublets at  $\delta = 24.05$  and  $24.25$  ppm in the  $^{31}\text{P}$  NMR spectrum and four signals for the pairwise diastereotopic NH protons in the  $^1\text{H}$  NMR spectrum. In contrast, coordination of the two faces of maleic anhydride leads to two diastereomeric meso complexes, and the  $^{31}\text{P}$  NMR spectrum accordingly showed two singlets at  $\delta = 26.40$  and  $26.45$  ppm with unequal intensity (3:2), and the  $^1\text{H}$  NMR spectrum showed two sets of two NH protons (Figures S7 and S8).

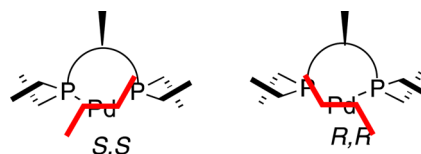
**Palladium Olefin Complexes with Ligand 1.** Ligand 1 can adopt four different conformations, two achiral meso structures,  $R_sS$  and  $S_rR$ , where  $r$  and  $s$  refer to pseudoasymmetric centers,<sup>22</sup> and two homochiral structures, with  $RR$  and  $SS$  configuration, respectively (Figure 6). Each kind of olefin can,



**Figure 6.** Four conformations of ligand 1-Pd complex. Two have achiral meso structures ( $R_sS$  and  $S_rR$ ) and two are chiral ( $RR$  and  $SS$ ).

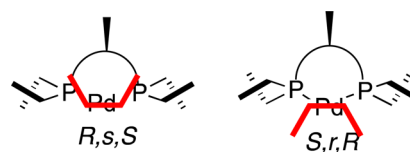
just as with 13, coordinate in two different ways, giving rise to a total of eight complexes with each olefin. For each olefin, four of the complexes are interconvertible via flipping of the ligand, whereas interconversion between the two sets of complexes (coordinating with different faces of the olefin) requires decoordination–recoordination of the olefin (Figure S30).

The  $^{31}\text{P}$  NMR spectrum of the Pd(0) fumaronitrile complex of the phosphite ligand 1 containing acetate showed, as did the spectrum with the corresponding triphenylphosphine ligand 13, two doublets at  $\delta = 137.8$  and  $142.2$  with  $J = 41$  Hz and four N–H proton signals in the  $^1\text{H}$  NMR spectrum (Figures S9 and S10). The  $^{31}\text{P}$  NMR pattern was unchanged upon cooling to  $-90$  °C but characteristic shifts to lower field were observed and the signals gradually broadened; upon subsequent heating to room temperature a spectrum identical to that recorded before cooling was obtained, demonstrating that the processes are reversible (Figures S11 and S12). This result is compatible only with an enantiomeric mixture of complexes with diastereotopic phosphorus atoms (Figure 7).



**Figure 7.** Enantiomeric complexes with symmetrically substituted trans olefin.

In contrast, the  $^{31}\text{P}$  NMR spectrum of the analogous complex with dimethyl fumarate showed two broad signals of equal intensity at room temperature, which separated into two major and two minor signals upon cooling (Figures S13 and S14). At  $-30$  to  $-40$  °C the major signals appeared as doublets with  $J = 19$  Hz. The original spectrum was restored upon subsequent heating to room temperature. This result is compatible with the presence of two complexes, which equilibrate rapidly at room temperature (Figure 8).

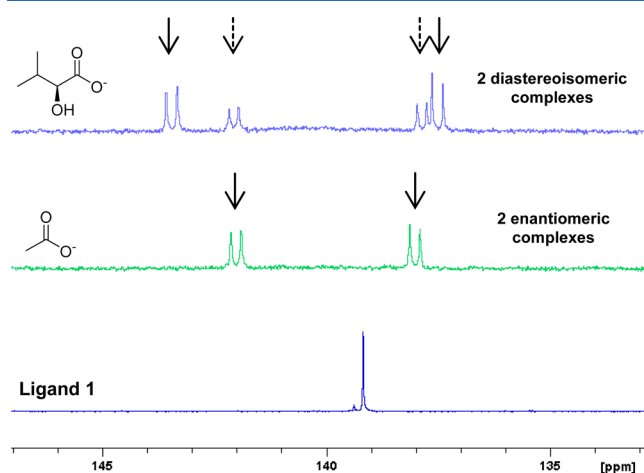


**Figure 8.** Diastereomeric complexes with symmetrically substituted cis olefin.

The NMR spectra of the complexes with maleic anhydride are somewhat more complicated, probably due to ring opening of the anhydride (Figures S15 and S16). At room temperature, one major broad signal was observed in the  $^{31}\text{P}$  NMR spectrum. At lower temperatures, this signal was split into several signals. The  $^1\text{H}$  NMR spectrum showed two NH signals at room temperature. Also these signals were split into several signals at lower temperatures. These results indicate a flexible structure of the complex at room temperature.

**Palladium Olefin Complexes of 1 Binding Chiral Anions.** In order to study whether nonequal amounts of diastereomeric complexes were formed in the presence of chiral cofactors, further studies were performed with the anions that induced the highest enantioselectivities in the catalytic experiments (Tables 1–3). The  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra of the Pd(0) fumaronitrile

complex of ligand **1** containing deprotonated (*S*)-2-hydroxy-3-methylbutyric acid **6** showed two sets of two doublets and two sets of four N–H protons, respectively, corresponding to two diastereoisomeric complexes (Figures 9, S17, and S18). The

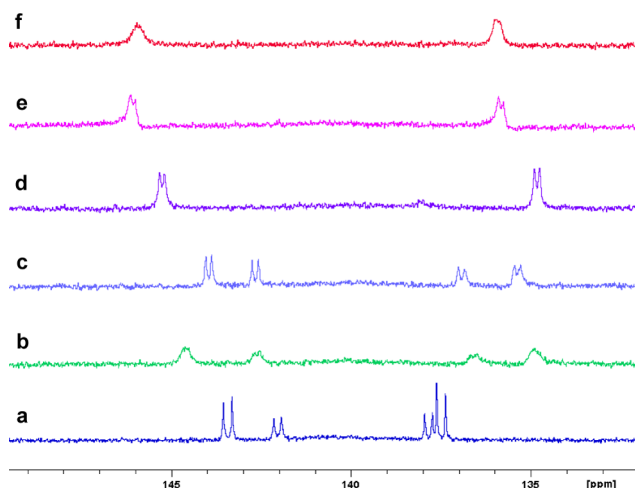


**Figure 9.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the  $[\text{Pd}(\text{fumaronitrile})\mathbf{1}]$  complex in the presence of acetic acid or (*S*)-2-hydroxy-3-methylbutyric acid **6** and DIPEA in  $\text{CD}_2\text{Cl}_2$  (162 MHz).

two complexes were present in unequal amounts, according to  $^1\text{H}$  NMR spectrum in a ratio of approximately 1.5:1, thus demonstrating the ability of the chiral anion to influence the conformation of the flexible biaryl units. A NOESY experiment confirmed the presence of two different complexes, which did not undergo mutual exchange (Figure S19). No splitting of the signals, which remained in the same ratio, was observed upon cooling to  $-79^\circ\text{C}$  further supporting the presence of two stable complexes (Figures S20 and S21). Moreover, broadening of the isopropyl signals of the cofactor **6** at lower temperature showed that free cofactor and cofactor bound in the DIM pocket of the ligand, which are in fast exchange at room temperature, are in slow exchange at these low temperatures (Figure S20). These results are in accordance with the assumed preference for homochiral structures of the ligand (*RR* and *SS*) in the presence of a trans olefin, with one of the configurations being slightly more stable due to coordination of the chiral cofactor.

$\text{Pd}(0)$  fumaronitrile complexes of ligand **1** with other chiral cofactors were also studied (Figures 10, S22, and S23). As observed with the anion of (*S*)-2-hydroxy-3-methylbutyric acid **6**, the presence of chiral carboxylates of *N*-*boc*-*N*- $\alpha$ -methyl-L-isoleucine and *N*- $\alpha$ -acetyl-L-valine led to the formation of two diastereoisomeric complexes in unequal amounts (approximately the same ratio as for (*S*)-2-hydroxy-3-methylbutyric acid). Surprisingly, the presence of BINOL-derived phosphates **7a–c** led to the formation of single complexes.

Low temperature NMR of the  $\text{Pd}(0)$  fumaronitrile complex of ligand **1** with the parent BINOL-derived phosphate **7a** did not show any splitting of neither the NH signals, nor the phosphorus signal of the ligand (broadening of one of the two P signals was observed) (Figures S24 and S25). However, separate signals could be observed for the bound and unbound phosphate cofactor at low temperature ( $-50^\circ\text{C}$ ) by  $^{31}\text{P}$  NMR, demonstrating that the phosphate cofactor is in fast exchange with the DIM pocket of the ligand at room temperature.



**Figure 10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the  $[\text{Pd}(\text{fumaronitrile})\mathbf{1}]$  complex in the presence of chiral cofactors and DIPEA in  $\text{CD}_2\text{Cl}_2$  (162 MHz). (a) (*S*)-2-Hydroxy-3-methylbutyric acid **6**; (b) *N*-*boc*-*N*- $\alpha$ -methyl-L-isoleucine; (c) *N*- $\alpha$ -acetyl-L-valine; (d) (*R*)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate **7a**; (e) (*S*)-6,6'-bisphenyl-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate **7b**; (f) (*S*)-6,6'-bis(4-methoxyphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate **7c**.

In order to compare the affinities of the different anions to the binding pocket, one equivalent of the anion of (*S*)-2-hydroxy-3-methylbutyric acid **6** was added to the Pd-fumaronitrile complex of the ligand **1** containing the non-substituted BINOL-based phosphate **7a**. The NMR spectra recorded at  $-50^\circ\text{C}$  showed complete displacement of the phosphate from the DIM pocket by the carboxylate (Figures S26 and S27).

The nature of the  $\text{Pd}(0)$  cofactor complexes formed with a cis olefin was then investigated. The  $\text{Pd}(0)$  diethyl maleate complex of ligand **1** with acetate as the cofactor showed four N–H signals (2 overlapped)—two pairs of NH indole and NH amide signals in a ratio of 1:1 and a broad signal at 143.21 ppm in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra, respectively (Figures S28 and S29). According to the result obtained with the  $\text{Pd}(0)$  cis olefin complex of the corresponding phosphine ligand containing acetate, those signals evidenced the formation of two diastereoisomeric complexes from a meso conformation (*RsS* or *SrR*) of the ligand coordinating two different faces of the olefin. The  $\text{Pd}(0)$  diethyl maleate complex of **1** with (*S*)-2-hydroxy-3-methylbutyric carboxylate (**6**) and BINOL-based phosphate **7a** showed eight N–H signals and two sets of broad doublets in  $^1\text{H}$  and  $^{31}\text{P}$  NMR, respectively, with unequal intensities showing the ability of chiral phosphate cofactor to stabilize one conformation of the ligand.

## CONCLUSIONS

A new tropos ligand (**1**) with an integrated anion receptor site has been prepared with the aim to provide control over the chirality of a metal complex formed by the binding of a chiral cofactor in the binding pocket.  $^1\text{H}$  and  $^{31}\text{P}$  NMR studies of a palladium(0) complex of ligand **1** with coordinated fumaronitrile, selected as a model for the *E*-olefin product obtained in palladium-catalyzed substitution of (*E*)-1,3-diphenyl-2-propenyl carbonate, and with acetate in the anion-binding pocket, revealed the formation of a racemic mixture of complexes. Replacement of acetate by (*S*)-2-hydroxy-3-methylbutyric carboxylate resulted in the formation of two diastereomeric



complexes with homochiral biaryl phosphite units in a ratio of 1.5:1, presumably with the (*S,S*)-isomer as the major isomer, as judged by the absolute configuration of the product formed in the catalytic reaction. In contrast, replacement of acetate with (*R*)-binol phosphate **7a** did not give rise to diastereomeric complexes under the conditions of the NMR experiments. The analogous maleic anhydride complex used to model the olefin palladium complex from nucleophilic substitution of 3-cyclohexenyl carbonate with acetate in the anion-binding cavity appeared as a mixture of two diastereomeric meso compounds. In the presence of chiral anions, a complex mixture of isomers was observed.

The ability of the chiral anions to influence the conformation of the chirally flexible biaryl phosphite units was also demonstrated by the formation of nonracemic products from palladium-catalyzed substitutions of allylic carbonates with sodium dimethyl malonate and benzylamine.

The work described here demonstrates that the geometry of metal complexes of tropos ligands can be controlled through tailored noncovalent interactions with chiral guest molecules. Considering the privileged nature of axially chiral ligands, the rich chemistry of supramolecular receptors, and the ease of preparation of wide libraries of chiral catalysts by the methodology demonstrated here, that is, combinatorial mixing of a metal precursor, a pool of tropos ligands equipped with a receptor unit and a variety of potential chiral guests, this methodology should seed the formation of many selective catalysts for desired transformations.

## ■ EXPERIMENTAL SECTION

**General Information.** All commercially available reagents were used as received, unless otherwise specified. Chiral carboxylic or phosphoric acid-derived cofactors were obtained from chemical suppliers or synthesized according to previously reported procedures.<sup>15b,23</sup> *rac*-(*E*)-1,3-Diphenylallyl methyl carbonate and *rac*-cyclohex-2-en-1-yl methyl carbonate were synthesized according to previously reported procedures.<sup>24</sup> Dry CH<sub>2</sub>Cl<sub>2</sub>, THF, toluene, and hexane were taken from a glass-contour solvent dispensing system. CD<sub>2</sub>Cl<sub>2</sub> was dried over 3 Å molecular sieves before use. Et<sub>3</sub>N, DIPEA, and benzylamine were distilled from potassium hydroxide under nitrogen. Dimethyl malonate was distilled under reduced pressure. Column chromatography was performed using silica gel 40–63 μm (230–400 mesh). TLC was performed using TLC silica gel 60 F254 and products revealed by UV irradiation (λ = 254 nm). <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR spectra were recorded at room temperature at 400 or 500 MHz, 100 MHz, and 162 or 202 MHz, respectively. Low temperature <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded at 400 and 162 MHz, respectively. Chemical shifts (δ) are given in ppm relative to the residual solvent peak. Splitting patterns are indicated as follows: br: broad; s: singlet; d: doublet; t: triplet; dd: doublet of doublet; m: multiplet. Yields were determined by <sup>1</sup>H NMR using 1-methoxynaphthalene as internal standard and enantiomeric excesses were measured by HPLC using a UV detector and a chiral column, Daicel Chiralpak IC (0.46 cm × 25 cm) or Daicel Chiralcel OD-H (0.46 cm × 25 cm), or by GC using a FID detector and a chiral column, CYCLOSIL B (30 m × 0.25 mm × 0.25 μm).

**Synthesis of Ligand 1.** Compound **2** was synthesized according to a previously reported procedure.<sup>15b</sup> The final step affording ligand **1** was performed in analogy to the procedure described for a similar compound.<sup>16</sup> Chlorophosphite **3** was synthesized as follows and engaged directly in the final step: 5,5'-Dimethoxy-3,3'-di-*tert*-butylbiphenyl-2,2'-diol (428 mg, 1.19 mmol), synthesized according to the procedure of Jana and Tunge,<sup>25</sup> was placed in an oven-dried Schlenk flask and put under argon. Dry and degassed toluene (3 mL) was added and the volatiles were evaporated using an argon-vacuum dual manifold before the addition of dry and degassed THF (6 mL). In

another oven-dried Schlenk flask under argon was placed dry and degassed THF (6 mL) and Et<sub>3</sub>N (333 μL, 2.39 mmol) and the mixture was cooled to –78 °C before the dropwise addition of PCl<sub>3</sub> (118 μL, 1.37 mmol) and then the 5,5'-dimethoxy-3,3'-di-*tert*-butylbiphenyl-2,2'-diol solution prepared before. The reaction mixture was stirred at the same temperature for 20 min, then allowed to reach room temperature and stirred for another 45 min. Volatiles were evaporated using the argon-vacuum dual manifold and, dry and degassed toluene (3 mL) was added, and then the volatiles were evaporated again. Compound **3** was finally dissolved in dry and degassed THF (9 mL) under argon.

Compound **2** (342 mg, 0.597 mmol) was placed in an oven-dried Schlenk flask and put under argon. Dry and degassed toluene (3 mL) was added and the volatiles were evaporated using the argon-vacuum dual manifold. The solid was then dissolved in dry and degassed THF (6 mL), Et<sub>3</sub>N (833 μL, 5.97 mmol) was added, and the solution was cooled to –78 °C. The freshly prepared solution of compound **3** in THF was then added dropwise, the reaction mixture was stirred at –78 °C for 30 min, and then allowed to progressively reach room temperature overnight. Volatiles were evaporated using the argon-vacuum dual manifold then dry and degassed THF (6 mL) and Et<sub>3</sub>N (0.6 mL) were added. The solution was rapidly filtered under argon through a short pad of oven-dried and degassed silica. The silica pad was then washed with another portion of dry and degassed THF. The combined organic fractions were concentrated to approximately 3 mL of solution, using the argon-vacuum dual manifold, then dry and degassed hexane (6 mL) was added before total evaporation of volatiles. After drying under vacuum ligand **1**:THF·C<sub>6</sub>H<sub>14</sub> was obtained as a pale yellow solid (444 mg, 55% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.44 (s, 2H, NH), 8.18 (s, 2H, NH), 7.74 (d, 4H, J = 8.6 Hz), 7.38 (d, 2H, J = 7.5 Hz), 7.08–7.04 (m, 6H), 7.01 (d, 4H, J = 3.1 Hz), 6.96 (d, 2H, J = 7.5 Hz), 6.75 (d, 4H, J = 3.1 Hz), 4.48 (t, 1H, J = 7.7 Hz), 3.81 (s, 12H), 2.30 (s, 6H), 2.23–2.16 (m, 2H), 1.43 (s, 36H), 1.00 (t, 3H (overlap with Et<sub>3</sub>N), J = 7.1 Hz). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 165.4 (2 CO), 156.5 (4 COP), 155.6 (4 C), 143.1 (2 C), 141.4 (4 C), 136.3 (2 C), 134.0 (4 C), 132.4 (2 C), 130.3 (2 C), 129.6 (4 C–H), 128.1 (2 C), 122.4 (2 C), 120.5 (2 C–H), 120.4 (2 C–H), 119.3 (2 C–H), 116.2 (2 C–H), 114.9 (4 C–H), 113.9 (2 C–H), 113.4 (4 C–H), 108.3 (2 C), 56.0 (4 O–CH<sub>3</sub>), 37.2 (C–H), 35.8 (4 C–CH<sub>3</sub>), 31.2 (12 C–CH<sub>3</sub>), 27.8 (CH<sub>2</sub>), 12.6 (CH<sub>3</sub>), 8.9 (2 CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 138.4. HRMS (ESI-Orbitrap) *m/z*: [M]<sup>+</sup> calcd for C<sub>79</sub>H<sub>86</sub>N<sub>4</sub>O<sub>12</sub>P<sub>2</sub> 1344.5712, found 1344.5747.

**Synthesis of Ligand 12.** Ligand **12** was prepared according to a procedure used for an analogous compound<sup>26</sup> by the addition of a solution of 5,5'-dimethoxy-3,3'-di-*tert*-butyl-2,2'-diol (308.3 mg, 0.86 mmol) in THF (4.3 mL) to a solution of 1,2-(dichlorophosphino)ethane (65 μL, 0.43 mmol) and triethylamine (263 μL, 4.4 equiv) in THF (3 mL) at –78 °C under Ar. The reaction mixture was allowed to reach room temperature overnight, then THF (10 mL) was added and the mixture filtered under Ar. The solvent was evaporated to give 288 mg (0.36 mmol, 84%) of **12**. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.10 (d, 4H, J = 2.9 Hz), 6.63 (d, 4H, J = 2.9 Hz), 3.33 (s, 12H), 1.42 (s, 36H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 157.0, 145.3, 143.2, 135.7, 115.5, 114.3, 55.8, 36.3, 32.1, 30.3. <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 202.67 (t, J = 24.3 Hz).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00265.

Procedures for the preparation of phosphate anions and palladium olefin complexes; procedures for catalytic reactions; results from screening of chiral cofactors; stereochemical analyses; and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra (PDF)



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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support from the Wenner-Gren Foundations (L.T.) and from NRSCC (P.D.) are gratefully acknowledged. Dr Anna Laurell Nash contributed with skillful experimental work.

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