Steric and Electronic Ligand Perturbations in Catalysis: Asymmetric Allylic Substitution Reactions Using C_2-Symmetrical Phosphorus-Chiral (Bi)ferrocenyl Donors

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Three series of P-chiral diphosphines based on ferrocene (**1a**−**f**, **2a**−**c**) and biferrocenyl skeletons (**3a**−**c**), including novel ligands **1f** and **3c**, were employed in palladium-catalyzed allylic substitution reactions. Steric effects imposed by the phosphine residues were studied using C_2-symmetrical donors **1** (**1** = 1,1′-bis(arylphenylphosphino)ferrocene with aryl groups **a** = 1-naphthyl, **b** = 2-naphthyl, **c** = 2-anisyl, **d** = 2-biphenylyl, **e** = 9-phenanthryl, and **f** = ferrocenyl), whereas *para*-methoxy- and/or *para*-trifluoromethyl substitution of the phenyl moieties in **1a** enabled investigation of ligand electronic effects applying ferrocenyl diphosphines **2a**−**c**. Ligands **3** (**3** = 2,2′-bis-(arylphenylphosphino)-1,1′-biferrocenyls with aryl substituents **a,c** = 1-naphthyl (diastereomers) and **b** = 2-biphenylyl) allowed for comparison of backbone structure effects (bite angle variation) in catalysis. Linear and cyclic allylic acetates served as substrates in typical test reactions; upon attack of soft carbon and nitrogen nucleophiles on (*E*)-1,3-diphenylprop-2-ene-1-yl acetate the respective malonate, amine, or imide products were obtained in enantioselectivities of up to 99% ee. A crystal structure analysis of a palladium 1,3-diphenyl-η^3-allyl complex incorporating ligand (*S*,*S*)-**1a** revealed a marked distortion of the allyl fragment, herewith defining the regioselectivity of nucleophile addition.

Introduction

Currently, allylic substitution reactions rank among the most thoroughly and intensively studied catalytic transformations. Since the first reports by Tsuji,[1] Trost,[2] and respective co-workers on palladium-mediated C−C bond formations between allylic substrates and carbon nucleophiles, this area has seen fast developments in reaction scope, catalyst structure, nucleophile diversity, and ligand design.[3] Considerable efforts have been devoted to asymmetric reaction variants that provide an access to potentially valuable chiral building blocks.[4] With respect to mechanistic features, enantioselective allylic alkylations and, to some extent, aminations have been studied in detail, mostly using palladium complexes as catalysts.[5] Cyclic or linear 1,3-disubstituted acetates are frequently employed as substrates, which upon oxidative addition give rise primarily to C_s-symmetrical allyl units. Among the various possibilities for enantioface discrimination, irreversible nucleophilic attack on equilibrated palladium(II) allyl complexes plays a dominant role. Consequently, steric and electronic ligand variations were exploited to enhance differentiation between isomeric allyl species as well as enantiotopic allyl termini, and this, indeed, afforded substitution products in high enantiomeric excesses. Prominent examples of successful ligand structures include P−N donors such as phosphinooxazolines,[6] planar-chiral ferrocenyl[7] or atropisomeric binaphthyl[8] derivatives, as well

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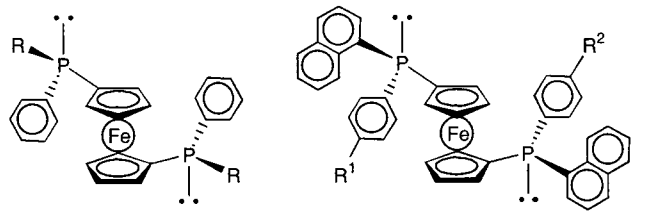
as modularly designed, sterically encumbering diphosphine donors.[9]

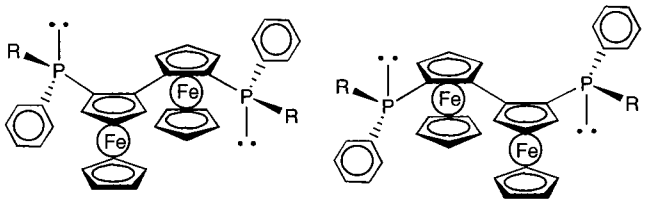
In contrast, the potential of classical C_2-symmetrical diphosphine inducers, devoid of further donor functionalities such as Binap[10] and Chiraphos,[11] is assessed low.[12] To the best of our knowledge, only one contribution describes the successful employment of a propeller-shaped diphospholane ligand in allylic C−C bond forming reactions, using cyclic as well as linear substrates.[13] In that case, molecular mechanics calculations and crystal structure analysis did not indicate a preferred site of nucleophile addition; enantiodiscrimination was therefore assumed to depend on the ease of clockwise or counterclockwise rotation of the allyl moiety upon nucleophilic attack to form the η^2-bonded palladium(0) alkene complex (late transition state). Thus, the stereogenic elements of the ligand had to display their efficacy by creating asymmetric steric congestion in the immediate allyl termini environments, thereby selectively blocking one rotation mode. A possible extension and deeper exploration of the given rationale prompted us to investigate the performance of other P-chiral ligands in allylic substitution reactions.

Recently, we reported the synthesis of a new class of P-chiral diphosphine donors based on dppf (1,1′-bis(diphenylphosphino)ferrocene).[14] Bearing different aryl substituents on phosphorus, these ligands were found to induce high enantioselectivities in rhodium-catalyzed asymmetric hydrogenations of cinnamic acid derivatives.[14a] Preliminary results in allylic substitution reactions seemed also promising[14b] and set the stage for a detailed study of the latter reaction employing several substrates and nucleophiles. Of special interest to us was the investigation of, on one hand, steric effects imposed by the nature of the substituents on chiral phosphorus and the backbone (bite angle variation). On the other hand, we were intrigued by the impact of ligand electronic variations on enantiocontrol. These features were studied by the employment of phosphorus-stereogenic C_2-symmetrical ferrocenyl and biferrocenyl diphosphines, exhibiting steric and electronic perturbations.

In the following we describe the synthesis of two new chiral diphosphine ligands **1f** and **3c**, as well as the performance of these and previously reported ligands **1a**−**e**, **2a**−**c**, and **3a,b**[14] in typical allylic test reactions. Excellent results were obtained in some cases, for which rationalization is attempted by means of a crystal structure determination of a palladium(II) allyl complex as well as two-dimensional variable temperature NMR measurements.



(S_P,S_P)-**1a-f** (S_P,S_P)-**2a-c**



(S_P,R_m,R_m,S_P)-**3a,b** (S_P,S_m,S_m,S_P)-**3c**

1a: R = 1-naphthyl
1b: R = 2-naphthyl
1c: R = 2-anisyl
1d: R = 2-biphenylyl
1e: R = 9-phenanthryl
1f: R = ferrocenyl

2a: $R^1 = R^2$ = methoxy
2b: $R^1 = R^2$ = trifluoromethyl
2c: R^1 = methoxy, R^2 = trifluoromethyl

3a: R = 1-naphthyl
3b: R = 2-biphenylyl
3c: R = 1-naphthyl

Results and Discussion

Ligand Synthesis. An elegant access to enantioenriched borane-protected phosphorus centers was established by nucleophilic displacement reactions controlled by the chiral auxiliary ephedrine. First introduced by Jugé, Genêt, and co-workers,[15] this approach enabled the stereoselective attachment of three different bulky aryl substituents onto phosphorus, which is not easily achieved by utilizing other auxiliaries or different methods such as optical resolutions[16] and direct asymmetric synthesis.[17] In an extension of this work, it was found that nucleophilic attack of 1,1′-dilithioferrocene on enantiopure methyl phosphinite boranes resulted in coupling of two stereogenic phosphorus moieties to the backbone, after decomplexation of borane giving rise to the first P-chiral dppf-analogues.[14a,b,18] The flexibility of this approach was evidenced by the synthesis of ligands **1a**−**e**, bearing sterically demanding aryl moieties on phosphorus. Electronically varied diphosphines **2a**−**c** derived from ligand **1a** by introduction of methoxy and trifluoromethyl groups in *para*-positions of the phenyl rings were synthesized in a similar manner.[14d]

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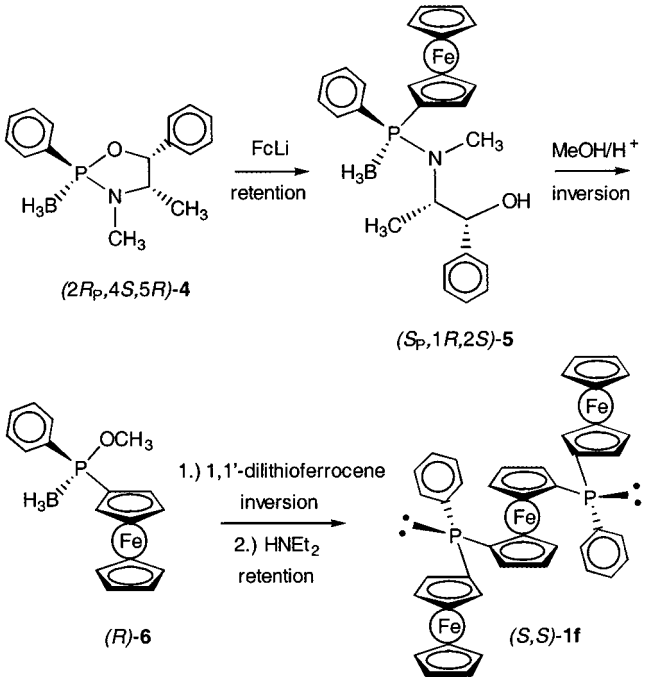
Scheme 1



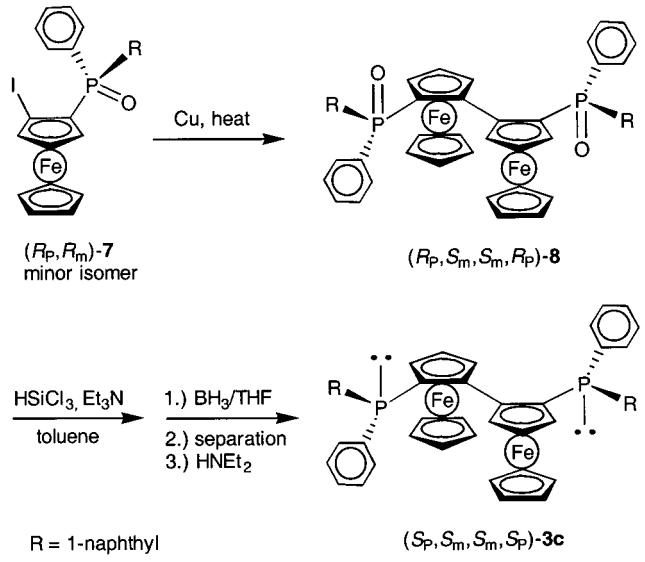
To explore the special aromatic sandwich structure of ferrocene not only as ligand backbone but also as an extraordinarily shaped substituent, we set out to prepare ligand **1f**, incorporating three ferrocene units linked via chiral phosphorus centers. The multistep synthesis was performed in analogy to described procedures; however, diastereoselectivities proved to be somewhat lower than observed during the synthesis of ligands **1a**−**e** (Scheme 1). Nucleophilic attack of monolithioferrocene on (2R_P,-4S,5R)-oxazaphospholidine borane **4** gave rise to the diastereomeric products (S_P,1R,2S)-**5** and (R_P,1R,2S)-**5** in a ratio of 91:9. Yet, column chromatographic separation of these phosphorus amide boranes was successful and enabled continuation of the sequence with diastereomerically pure starting material.

Similarly, the last substitution reaction using dilithioferrocene showed a reduced degree of stereodiscrimination, which was evidenced by the formation of ∼10% of *meso*-configured diphosphine diborane. Since during the synthesis of ligands **1a**−**e** as well as **2a**−**c** the amounts of *meso* product were considerably smaller, if observed at all, we ascribe this lower stereoselectivity to the diminished steric encumbering of the cyclopentadienyl moieties as compared to the aryl substituents. Again, chromatographic separation of the isomeric product mixture and, after deprotection, repeated recrystallizations finally afforded enantiomerically pure (*S*,*S*)-**1f**.

As previously described, the enantiomeric excess of the new ligand was checked by NMR measurements of the derived diphosphine dioxide in the presence of the chiral solvating agent (*S*)-*N*-(3,5-dinitrobenzoyl)-1-phenylethylamine.[19] No splitting of signals due to diastereomeric adduct formation was observed, confirming the enantiomeric integrity of the bis(ferrocenylphenylphosphino)-ferrocene **1f**.

One ligand parameter that has gained increasing attention over the past few years is the natural bite angle.[20] Its pronounced effect on catalyst performance was demonstrated in different applications among which number hydroformylation, hydrocyanation, and allylic substitution reactions.[21] Yet, as a result of their intrinsic conformational flexibility originating from free rotation of the cyclopentadienyl rings around or distortion along the Cp−Fe−Cp axis, calculations of natural bite angles for ligands based on ferrocenyl skeletons are less reliable than for other more rigid donor structures. Nevertheless, we wanted to investigate the steric effects of a backbone alteration in P-chiral diphosphine ligands. Whereas for ligands **2a**−**c** electronic modifications were introduced in *para*-positions of the phenyl rings in order to prevent interference with steric conditions, we chose for a backbone variation by means of a biferrocenyl entity to keep the electronic perturbations with respect to the 1,1′-ferrocenyl skeleton to a minimum.

Scheme 2



In a recent contribution we described the multistep stereoselective approach to enantiopure 2,2′-bis(phenylarylphosphino)biferrocenyls **3a,b**, starting from optically pure methyl phosphinite boranes.[14c] The intermediate 1-naphthylphenyl- and 2-biphenylyl-phenylferrocenylphosphine oxides were subjected to *ortho*-magnesiation and afforded, after quenching with iodine, the substitution products in 50% and 94% de, respectively. In first instance, only the predominantly formed diastereomer of compound **7,** (R_P,S_m)-1-iodo-2-(1-naphthylphenylphosphinoxy)ferrocene, was employed in the further course of the synthesis, which after Ullmann coupling, reduction, and purification via the bisborane complex gave the (S_P,R_m,-R_m,S_P)-configured ligand **3a**. To study the effects of planar chirality, we now also subjected the minor (R_P,R_m)-configured *o*-iodo ferrocenylphosphine oxide **7** to the mentioned procedure (Scheme 2). Thus, we finally obtained the diastereomeric biferrocenyl diphosphine product **3c**, displaying the (S_P,S_m,S_m,S_P) configuration of the four adjacent stereogenic elements.

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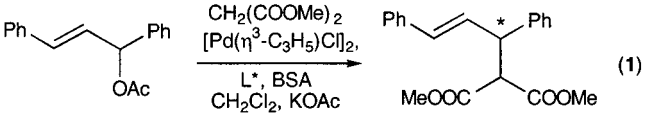
Table 1. Results of Allylic Substitution Reaction 1 with Catalysts Comprising Sterically and Electronically Perturbed P-Chiral Diphosphine Ligands[a]

ligand	temp (°C)	isolated yield (%)	% ee[b] (abs config)
(*R*,*R*)-**1a**	25	88	68 (*R*)
(*R*,*R*)-**1a**	0	73	72 (*R*)
(*R*,*R*)-**1a**	−10	84	73 (*R*)
(*R*,*R*)-**1a**[c]	25	91	63 (*R*)
(*R*,*R*)-**1a**[d]	25	94	61 (*R*)
(*R*,*R*)-**1a**[e]	25	65	64 (*R*)
(*S*,*S*)-**1b**	25	91	10 (*R*)
(*S*,*S*)-**1b**	−20	96	23 (*R*)
(*R*,*R*)-**1c**	25	85	0
(*R*,*R*)-**1c**	0	82	3 (*S*)
(*R*,*R*)-**1d**	25	90	56 (*R*)
(*R*,*R*)-**1e**	25	85	74 (*R*)
(*R*,*R*)-**1e**	0	80	76 (*R*)
(*R*,*R*)-**1e**	−20	82	77 (*R*)
(*S*,*S*)-**1f**	20	84	81 (*R*)
(*S*,*S*)-**2a**	20	88	69 (*S*)
(*S*,*S*)-**2b**	20	87	61 (*S*)
(*S*,*S*)-**2c**	20	65	63 (*S*)
(S_P,R_m,S_P)-**3a**	20	87	88 (*R*)
(S_P,R_m,R_m,S_P)-**3a**	−10	84	88 (*R*)
(S_P,R_m,R_m,S_P)-**3b**	20	89	58 (*R*)
(S_P,S_m,S_m,S_P)-**3c**	25	93	74 (*S*)

[a] Reaction conditions: 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.01 mmol of ligand, 1 mmol of (*E*)-1,3-diphenylprop-2-en-1-yl acetate, 3 mmol of dimethylmalonate, 3 mmol of BSA, and a catalytic amount of KOAc in 1 mL of CH_2Cl_2. Reaction times: 2−48 h (not optimized). [b] Determined by chiral HPLC (Chiralcel OD-H). [c] Ligand/palladium ratio = 2:1. [d] 1,1,3,3-Tetramethylguanidine was used as the base. [e] CH_3CN was used as the solvent.

Catalysis. The first model reaction we investigated employing the P-chiral diphosphines **1a**−**f**, **2a**−**c**, and **3a**−**c** was the allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate (eq 1). Applying



(1)

the Trost protocol[22] with BSA (*N*,*O*-bis(trimethylsilyl)-acetamide) as the base, reaction conditions were optimized for catalysts comprising ligand **1a**; the results for all diphosphine donors are summarized in Table 1.

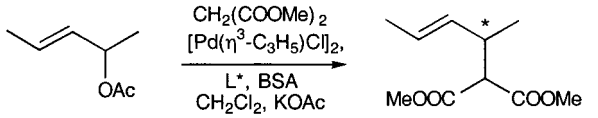
With reaction times between 2 and 20 h at room temperature, isolated product yields typically surpassed 80% for most of the catalysts tested. The chemoselectivity toward the *trans*-configured propenyl diester proved excellent in all runs; no isomerized *cis*-product was identified in the crude reaction mixture. Within the first series of ligands **1a**−**f**, differing from each other by the dissimilar steric demands of the respective aryl substituents on phosphorus, enantiodiscrimination varied considerably. Ligand **1b**, bearing 2-naphthyl moieties, showed a disappointing performance, which might be rationalized by its resemblance with the achiral dppf chelate. Consequently, substitution in *ortho*-position of the aryl group appeared as a necessary, but not sufficient requirement for good asymmetric induction. This was deduced from the undiscriminating behavior of ligand **1c**, contrasting with the excellent performance of the *o*-anisyl substituted derivative in rhodium-catalyzed hydrogenation reactions.

Ligands **1a,d,e,f** as catalyst components induced moderate to good enantioselectivities, herewith emphasizing the importance of bulky aryl units, which markedly contrast with the steric properties of the phenyl group. As evident from screening runs performed in the presence of diphosphine **1a**, a 1:1 ligand/palladium ratio was sufficient and, in combination with CH_2Cl_2 as the solvent and BSA as the base, identified as the optimum reaction conditions. For the structurally similar diphosphine donors **1a** and **1e**, a temperature dependence was found that allowed for a small increase of ee values for reactions run at −10 or −20 °C, respectively. Whereas the slightly higher value of 77% ee for ligand **1e** indicated a beneficial influence of the larger 9-phenanthryl substituents in comparison to the 1-naphthyl moieties, the stereodiscriminating effect of the 2-biphenylyl substituents of compound **1d** was somewhat lower. The best results within this class of dppf-analogues was obtained employing diphosphine **1f** (81% ee). Interestingly, the combination of sandwich-type ferrocenyl moieties and phenyl substituents on phosphorus, if ligated to palladium, favored nucleophilic attack in a different fashion than observed for ligands **1a,d**,**e**, as evidenced by the formation of the (*R*)-configured diester under catalysis by [(*S*,*S*)-**1f**]Pd.

For electronically perturbed ligands **2a**−**c**, the effects of enhanced or diminished donor basicity on enantioselectivities were found to be small. A slightly deleterious influence may be ascribed to the presence of the trifluoromethyl groups, resulting in a decrease of ee values to 61% (**2b**) and 63% (**2c**) in comparison to the unsubstituted diphosphine **1a** (68%). Reactivity was not affected, rendering the reaction profile insensitive to subtle changes of the electron density.[23,24]

The best results in this model reaction, however, were realized employing the biferrocenyl ligand **3a**. For this bulky diphosphine, no further improvement of the 88% ee values was achieved at lower temperatures. Diphosphine **3b** delivered a performance similar to the ferrocenyl-based ligand **1d**; enantioselectivities scarcely depended on backbone structure in these two cases. The new biferrocenyl donor **3c** effected ee values of 74%, hereby revealing the all-(*S*) configuration as the mismatched isomer with respect to the more successful (S_P,R_m,R_m,S_P)-ligand **3a**. Interestingly, the absolute product configuration observed on utilizing diphosphines **3a**−**c** depended on metallocene rather than phosphorus configuration.

The good results obtained with 1,3-diphenylpropenyl acetate could not be repeated with smaller substrates. As summarized in Table 2, pent-3-en-2-yl acetate was, in the presence of palladium complexes of ligands **1a**−**f** as well as **3a**−**c,** converted to the dimethyl malonate adduct with low enantiomeric excesses (eq 2). A similar



(2)

unsatisfactory picture was obtained on utilizing cyclic substrates, such as cyclohex-2-en-1-yl acetate (eq 3, Table

(22) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

(23) In contrast, in the hydroformylation of styrene a correlation between ligand basicity and ee values could be established for diphosphines **1a** and **2a**−**c**: Nettekoven, U.; Kamer, P. C. J.; Widhalm, M.; van Leeuwen, P. W. N. M. *Organometallics* **2000**, *19*, 4596.

(24) Utilizing different ligand systems, electronic effects on reactivity and enantioselectivity have been reported: (a) Saitoh, A.; Misawa, M.; Morimoto, T. *Synlett* **1999**, 483. (b) Chelucci, G.; Deriu, S.; Pinna, G. A.; Saba, A.; Valenti, R. *Tetrahedron: Asymmetry* **1999**, *10*, 3803.

Table 2. Results of Allylic Substitution Reaction 2 with Catalysts Comprising Sterically Perturbed P-Chiral Diphosphine Ligands[a]

ligand	temp (°C)	isolated yield (%)	% ee[b] (abs config)
(*R*,*R*)-**1a**	25	77	9 (*R*)
(*R*,*R*)-**1a**	−10	76	12 (*R*)
(*S*,*S*)-**1b**	25	94	2 (*S*)
(*R*,*R*)-**1c**	25	87	5 (*S*)
(*R*,*R*)-**1d**	25	85	15 (*R*)
(*R*,*R*)-**1e**	25	85	7 (*S*)
(*S*,*S*)-**1f**	25	93	13 (*R*)
(S_P,R_m,R_m,S_P)-**3a**	20	63	15 (*R*)
(S_P,R_m,R_m,S_P)-**3b**	25	95	1 (*S*)

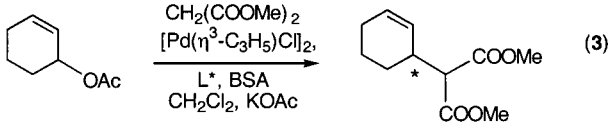
[a] Reaction conditions: 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.01 mmol of ligand, 1 mmol of (*E*)-pent-3-en-2-yl acetate, 3 mmol of dimethylmalonate, 3 mmol of BSA, and a catalytic amount of KOAc in 1 mL of CH_2Cl_2. Reaction times: 3−48 h (not optimized). [b]Determined by chiral GC.

Table 3. Results of Allylic Substitution Reaction 3 with Catalysts Comprising Sterically Perturbed P-Chiral Diphosphine Ligands[a]

ligand	temp (°C)	isolated yield (%)	% ee[c] (abs config)
(*R*,*R*)-**1a**	25	77	26 (*R*)
(*S*,*S*)-**1b**	25	82	1 (*R*)
(*R*,*R*)-**1c**	25	88	4 (*R*)
(*R*,*R*)-**1d**	25	84	29 (*S*)
(*R*,*R*)-**1e**	25	66	17 (*R*)
(*S*,*S*)-**1f**	25	89	11 (*S*)

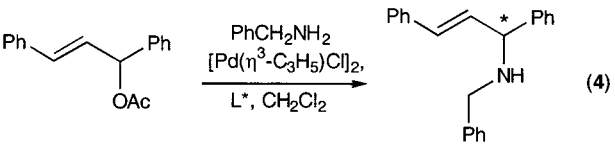
[a] Reaction conditions: 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.01 mmol of ligand, 1 mmol of cyclohex-2-en-1-yl acetate, 3 mmol of dimethylmalonate, 3 mmol of BSA, and a catalytic amount of KOAc in 1 mL of CH_2Cl_2. Reaction times: 20−48 h (not optimized). [b] Determined by optical rotation measurements.

3). With the sense of optical induction caused by ligand **1d** differing from the results of other diphosphines, enantioselectivities were too low to permit decisive conclusions.



(3)

In contrast to substrate variations, alteration of the nucleophile in reactions employing 1,3-diphenylpropenyl acetate gave good results. Using benzylamine, diphosphine palladium complexes catalyzed conversions to the secondary amine product in satisfactory yields (eq 4, Table 4). Enantioselectivities covered a wider range than



(4)

in alkylations; a comparable trend for ligand performances in model reactions 1 and 4, however, could not be deduced for all diphosphines. Ligand **1a** afforded modest enantiodifferentiation, which upon employment of electronically modified derivatives **2a**−**c** did not improve considerably. The sterically more demanding ligand **1e** was, again, shown to promote better asymmetric inductions than the 1-naphthyl containing dppf-analogue **1a**. In the same way, a marked structural dissimilarity of the residues might account for the success of the tris-

Table 4. Results of Allylic Substitution Reaction 4 with Catalysts Comprising Sterically and Electronically Perturbed P-chiral Diphosphine Ligands[a]

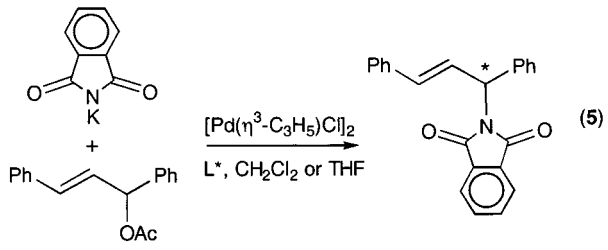
ligand	temp (°C)	isolated yield (%)	% ee[b] (abs config)
(*R*,*R*)-**1a**	20	83	37 (*S*)
(*S*,*S*)-**1b**	20	83	2 (*S*)
(*R*,*R*)-**1c**	20	68	22 (*S*)
(*R*,*R*)-**1d**[c]	20	89	32 (*S*)
(*R*,*R*)-**1d**	20	83	90 (*S*)
(*R*,*R*)-**1d**[d]	20	89	97 (*S*)
(*R*,*R*)-**1d**	−10	90	**99 (*S*)**
(*R*,*R*)-**1e**	20	76	50 (*S*)
(*S*,*S*)-**1f**	20	80	84 (*S*)
(*S*,*S*)-**2a**	20	68	42 (*R*)
(*S*,*S*)-**2b**	20	59	36 (*R*)
(*S*,*S*)-**2c**	20	76	34 (*R*)
(S_P,R_m,R_m,S_P)-**3a**	20	92	89 (*S*)
(S_P,R_m,R_m,S_P)-**3a**	−10	89	93 (*S*)
(S_P,R_m,R_m,S_P)-**3b**	20	17	88 (*S*)
(S_P,S_m,S_m,S_P)-**3c**	20	53	84 (*R*)

[a] Reaction conditions: 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.01 mmol of ligand, 1 mmol of (*E*)-1,3-diphenylprop-2-en-1-yl acetate, and 1.2 mmol of benzylamine in 1 mL of CH_2Cl_2. Reaction times: 12−48 h (not optimized). [b] Determined by chiral HPLC. [c] CH_3CN was used as the solvent. [d] THF was used as the solvent.

(ferrocenyl) ligand **1f**. The top result in this model transformation was due to the biphenylyl-substituted diphosphine **1d**. A value of 97% ee at room temperature could be increased to a remarkable 99% ee for reactions run at −10 °C.

Modification of this successful ligand structure by means of the biferrocenyl skeleton of ligand **3b**, however, seemed to exceed the permissible degree of steric encumbering. Conversions and product yields were found to be low, and enantiocontrol suffered from a decrease of approximately 10% compared to **1d**. On the contrary, in the case of the phenyl-1-naphthyl substitution pattern on phosphorus, exchange of the ferrocenyl for a biferrocenyl backbone bearing planar chirality proved advantageous. Up to 93% ee was achieved employing ligand **3a**, which constituted a remarkable enhancement with respect to the 37% ee obtained for the related diphosphine **1a**. Ligand **3c**, although giving satisfactory enantiomeric excesses of 84%, was, in comparison to compound **3a**, again identified as the configurationally mismatched derivative. Inductions of absolute product configurations followed the trend observed for model reaction 1.

Furthermore, phthalimide potassium salt,[25] a reagent creating interesting precursors for unnatural amino acids,[26] was investigated (eq 5). Diminished reactivity of



(5)

this nucleophile, however, prompted good yields only in the presence of catalysts incorporating ligands **1a,e,f**. In these cases, excellent enantioselectivities were obtained,

(25) Inoue, Y.; Taguchi, M.; Toyofuku, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3021.
(26) Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411.

Table 5. Results of Allylic Substitution Reaction 5 with Catalysts Comprising Sterically Perturbed P-Chiral Diphosphine Ligands[a]

ligand	temp (°C)	isolated yield (%)	% ee[b] (abs config)
(*S*,*S*)-**1a**[c]	reflux	86	85 (*R*)
(*S*,*S*)-**1a**	20	90	81 (*R*)
(*S*,*S*)-**1a**	0	86	87 (*R*)
(*S*,*S*)-**1b**[c]	reflux	<20	nd[d]
(*R*,*R*)-**1c**[c]	reflux	<20	nd
(*R*,*R*)-**1d**[c]	reflux	<20	nd
(*R*,*R*)-**1e**	0	70	92 (*S*)
(*S*,*S*)-**1f**	20	67	93 (*S*)
(*S*,*S*)-**1f**	0	<20	nd
(*S*,*S*)-**2a**	25	91	84 (*R*)

[a] Reaction conditions: 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 0.01 mmol of ligand, 1 mmol of (*E*)-1,3-diphenylprop-2-en-1-yl acetate, and 1.2 mmol of phthalimide potassium salt in 2 mL of CH_2Cl_2. Reaction times: 15−60 h (not optimized). [b] Determined by chiral HPLC (Chiralcel OD-H). [c] THF was used as the solvent. [d] Not determined.

with the top result of 93% ee achieved with the **1f**-modified palladium complex (Table 5).

Crystal Structure of [(1,3-Diphenyl-η^3-allyl)(1a)-Pd]BF_4. Solution Structures of Palladium Complexes [(1,3-diphenyl-η^3-allyl)(1a)Pd]BF_4, [(1,3-diphenyl-η^3-allyl) 1d)Pd]BF_4, and [(1,3-diphenyl-η^3-allyl)(3a)Pd]BF_4. As a result of the C_2-symmetrical nature of the diphosphines and the pro-C_s structure of the allylic acetates employed, enantioface exchange of η^3-allyl complexes should be excluded as stereodiscriminating features. No enantioselective ionization was found to be operative, as indicated by the absence of a kinetic substrate resolution observed for the amination reaction catalyzed by [(*R*,*R*)-**1d**]Pd. Thus, in catalytic runs using 1,3-diphenylpropenyl acetate, regioselective nucleophilic attack on enantiotopic termini of the allyl is assumed as the enantioselectivity determining process. To investigate the factors, rendering one carbon atom the preferred site of nucleophile addition, we performed a crystal structure analysis on the complex {(1,3-diphenyl-η^3-allyl)[(*S*,*S*)-**1a**]-Pd}BF_4, **9a** (Figure 1). This compound was prepared by reaction of $[(1,3\text{-diphenyl-}\eta^3\text{-allyl})PdOAc]_2$ with ligand (*S*,*S*)-**1a** in the presence of $AgBF_4$. Crystals were grown from CH_2Cl_2/benzene with the chiral space group *P*1. The BF_4 anions are orientationally disordered. The crystals additionally contain one molecule of benzene per unit cell. For a summary of selected interatomic distances and angles see Table 1 in the Supporting Information.

As expected, the solid-state structure showed a *syn-syn* configuration of the two phenyl substituents of the allyl moiety; these are engaged in π-stacking interactions with the respective neighboring phenyl and 1-naphthyl groups of the diphosphine ligand.[27] Shortest carbon−carbon nonbonding distances of that kind were identified between C36···C117 (3.256(6) Å) and C31···C112 (3.285-(6) Å), whereas $\pi-\pi$ interactions between the two phenyl rings were found less pronounced (C25···C206 = 3.449-(6) Å, C30···C207 = 3.453(6) Å). Interestingly, a large difference in the palladium−allyl carbon bond lengths (Pd−C22 = 2.302(4) Å, Pd−C24 = 2.208(4) Å) and the respective torsional angles was observed. Whereas the angle for C32−C31−C24−C23 adopts a value of 34.0(6)°, the correspondent angle involving the more loosely

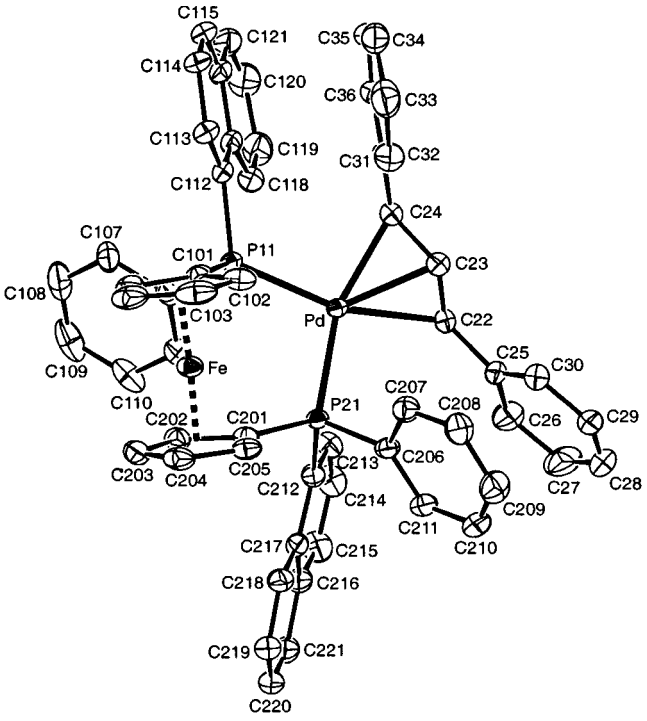


Figure 1. Displacement ellipsoid plot of {(1,3-diphenyl-η^3-allyl)[(*S*,*S*)-**1a**]Pd}BF_4, **9a**, drawn at 50% probability level.

bonded C22 is only 11.4(2)°. Regarding the C_2-symmetrical nature of the ligand, these distortions seem to result from purely steric constraints. Yet, these allyl refinement data are comparable to those of crystal structures of 1,3-diphenyl-η^3-allyl palladium complexes ligated by P−N, P−S, or electronically dissimilar P−P donors displaying strong *trans* influences.[28] Less similarities, however, were found to related complexes bearing other C_2-symmetrical diphosphine ligands such as Binap[29] or Chiraphos.[30] These exhibited approximately the same palladium−carbon bond lengths for the allylic termini and, in the latter case, revealed an almost planar geometry of the allyl ligand, that originated from the pseudo-C_s conformation adopted by the propeller-shaped diphosphine.

Thus, the enforced C_2-symmetry of P-chiral ligands such as **1a** seemed necessary for repulsive steric forces that effectively differentiate between the terminal allylic carbon atoms. The strong $\pi-\pi$ stacking effects, extending toward a favorable offset arrangement of the involved aryl rings,[31] suggested, however, that attractive interactions between ligand and allyl moieties might also participate in determining the preferred allyl coordination geometry.

(27) No significant $\pi-\pi$ interactions involving the benzene solvent molecules were detected.

(28) See, for example: (a) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523. (b) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (c) Baltzer, N.; Macko, L.; Schaffner, S.; Zehnder, M. *Helv. Chim. Acta* **1996**, *79*, 803. (d) Widhalm, M.; Mereiter, K.; Bourghida, M. *Tetrahedron: Asymmetry* **1998**, *9*, 2983. (e) Albinati, A.; Pregosin, P. S.; Wick, K. *Organometallics* **1996**, *15*, 2419. (f) Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Kollner, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 759.

(29) Yamaguchi, M.; Yabuki, M.; Yamagishi, T.; Sakai, K.; Tsubomura, T. *Chem. Lett.* **1996**, 241.

(30) Yamaguchi, M.; Yabuki, M.; Yamagishi, T.; Kondo, M.; Kitagawa, S. *J. Organomet. Chem.* **1997**, *538*, 199.

(31) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

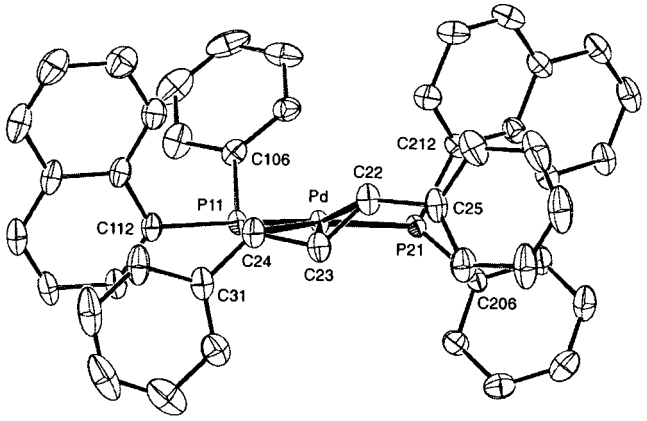


Figure 2. Distortion of the allyl fragment in **9a**. The ferrocene moiety is omitted for clarity.

Assuming the more weakly bonded allyl terminus C22 as the site of nucleophilic attack, the rotation upon $\eta^3-\eta^2$ rearrangement should proceed in a counterclockwise fashion with regard to the incoming nucleophile. We speculate that process to be advantageous in comparison to a clockwise rotation that would involve movement of the C24-phenyl moiety toward the sterically demanding C112-naphthyl group. This hypothesis is further corroborated by the position of the allyl fragment with regard to the coordination plane. The angle between two planes defined by atoms C24, Pd, and C22, as well as P11, Pd, and P21, is 17.3(4)°, whereby the shortest distances of C22 and C24 with respect to the latter plane are 0.44(3) and 0.28(5) Å, respectively (Figure 2). Applying the principle of least motion,[32] the C23−C24 bond is predetermined to move into coplanarity with the phosphine coordination plane. Consequently, attack of dimethyl malonate should preferentially give rise to the (*S*)-configured product, which was, indeed, observed as the reaction outcome.

As evidenced from the crystal structure of **9a**, $\pi-\pi$ interactions between one allyl phenyl group and ligand naphthyl residue exceed those between ligand phenyl and allyl phenyl moieties. P-chiral bidentate donor structures bearing aryl phosphino groups of similar effective electron density (such as, e.g., **1b,c**) can be expected to engage in stacking interactions of the same magnitude, consequently hampering desymmetrization of the allyl fragment and reducing the site selectivity of nucleophilic attack. Assuming the degree of $\pi-\pi$ interactions between allyl phenyl and ligand ferrocenyl moieties to be even lower than the mentioned phenyl−phenyl interactions, predominance of the latter is supposed to be accompanied by a different sense of rotation of the allyl fragment. The resulting inversion of relative reactivities of the allyl termini (with respect to complex **9a**) offers rationalization for the observed (*R*) configuration of the malonate addition product upon employing ligand (*S,S*)-**1f** (vide supra). To elucidate specific catalytic performances, we investigated the solution structures of complexes {(1,3-diphenyl-η^3-allyl)[(*S,S*)-**1a**]Pd}BF_4, **9a**, as well as the analogously prepared {(1,3-diphenyl-η^3-allyl)[(*R,R*)-**1d**]Pd}BF_4, **9d**, and {(1,3-diphenyl-η^3-allyl)[(S_P,R_m,R_m,S_P)-**3a**]Pd}BF_4, **10a**. For all three compounds 400 and 600 MHz 1D and 2D NMR measurements showed a *syn-syn* configuration of the allyl substituents for the predominating isomer, as evidenced by NOEs between the terminal allyl protons. At room temperature, complex **9d** existed as mainly one species in solution (>95%); extensive signal overlap did not allow complete assignment of all resonances.

(32) See, for example: Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

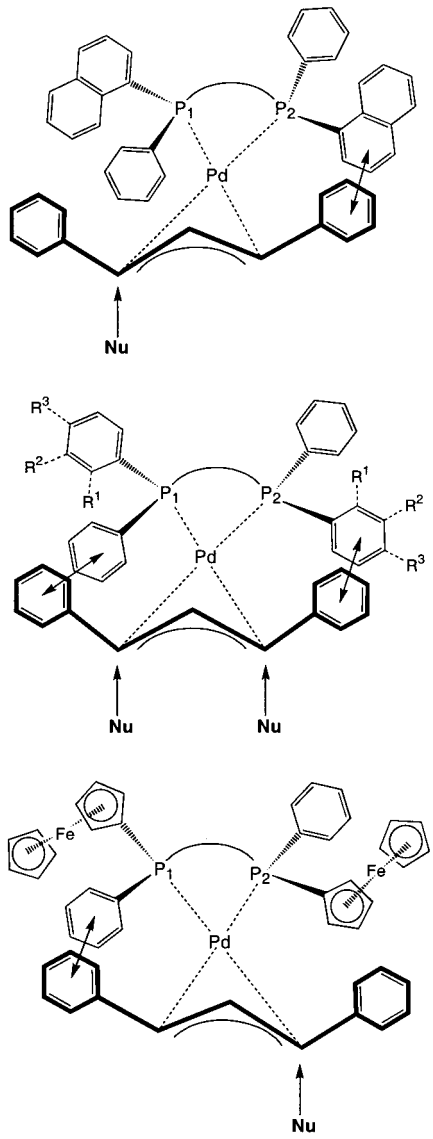


Figure 3. Schematic representation of π-electronic interactions (1-naphthyl/phenyl > phenyl/phenyl > phenyl/ferrocenyl) determining allyl desymmetrization and site of nucleophilic attack (ligand **1b**, R^2,R^3 = Ph; ligand **1c**, R^1 = MeO).

In the case of compound **10a**, $^{31}P\{^1H\}$ NMR spectra revealed the presence of three isomeric complexes in a ratio of 80:16:4. Using homo- and heteronuclear correlation spectroscopy, the signals for the main isomer could be fully assigned; NOESY measurements indicated a pseudoequatorial arrangement of the bulky 1-naphthyl substituents in the seven-membered chelate ring (Figure 4). A less favorable accommodation of these groups in pseudoaxial position might give rise to one of the minor complexes, as could the two possible coordination fashions of a *syn-anti* configured allyl unit. Yet, marked line broadening and low concentration, respectively, did not permit conclusions regarding the precise nature of the minor isomers.

Complex **9a** showed a marked fluxional behavior at ambient temperature, evidenced by a general broadening of all signals in ^1H as well as in $^{31}P\{^1H\}$ NMR. Lowering

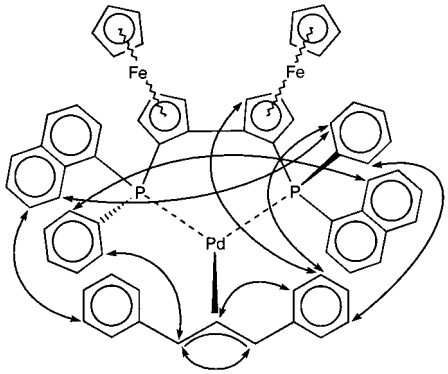


Figure 4. Selected NOEs observed for the main complex **10a**.

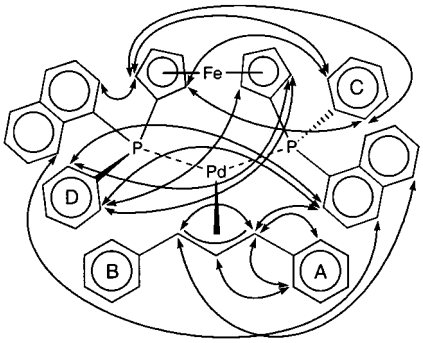


Figure 5. Selected NOEs observed for the major complex **9a**.

the temperature to 223 K, however, gave sufficient decoalescence to enable identification of the major *syn-syn* configured allyl compound and a second isomer in a ratio of 85:15. For the main compound, unequivocal assignment of most signals was possible. Interestingly, allyl phenyl groups as well as phenyl phosphine rings exhibited hindered rotation, resulting in different signals for the respective *ortho*- and *meta*-protons. 2D-TOCSY and exchange spectroscopy allowed for determination of all four connectivity sets. Noteworthy, no NOE contacts were observed between the phenyl rings B and D (Figure 5), suggesting a similar π-stacking as present in the solid state[33] and indicating the major isomer of compound **9a** to match the spatial arrangements displayed in the crystal structure.

The signals of the minor isomer showed a *syn-syn* configuration of the allyl moiety as well and were therefore assumed to originate from a different backbone conformation (pseudoaxial vs. pseudoequatorial arrangement of naphthyl residues). Inspection of the ROESY spectrum evidenced exchange between major and minor isomers via chelate ring inversion. Exchange peaks between the respective ferrocenyl protons were especially marked, whereas no exchange was observed between the allyl protons. Dissolution of crystals of complex **9a** at 200 K and immediate NMR measurement at 223 K did not alter the isomeric distribution, showing fast establishment of equilibrium conditions even at low temperatures.

This sort of conformational flexibility might account for the considerable line broadening observed for compound **9a** at room temperature. Yet, (slow) apparent allyl rotation proceeding via five-coordinate intermediates[34] might occur as additional fluxional process, since decoalescence for the minor isomer was reached at a slightly different temperature (already at 243 K) than for the main complex.

Table 6. Terminal Allyl ^{13}C Chemical Shifts for 1,3-Diphenylallyl Diphosphine Palladium Complexes

complex	δ (ppm)
9a	80.9; 103.3
9d	84.5; 127.5
10a	81.9; 98.1

A further reference to pronounced dissimilar coordination environments of the terminal allyl carbons was provided by the large differences in the ^{13}C chemical shifts of the prevailing isomers in complexes **9a**, **9d**, and **10a** (Table 6). Although these data do not clearly relate to catalytic performances in general, they suggest dissymmetric steric and, possibly, π-electronic influences on complex geometries to be similarly effective as evidenced for **9a** in the solid state.[35]

A comparison of our NMR-assignments of complex **9a** with the crystal structure analysis associates the allylic carbon atoms C22 and C24 with chemical shift values of 80.9 and 103.3 ppm, respectively. As mentioned above, we expect nucleophilic attack to occur at the more shielded carbon atom C22, bearing the lower positive charge distribution. This is in disagreement with literature results, stating that nucleophile addition takes place preferentially at the electronically more deshielded carbon atom.[36] Complex **9a**, comprising a C_2-symmetrical ligand system seems, however, less amenable to electronic preferences commonly observed employing P−N or related chelates. Our findings are among the first to experimentally indicate the theoretically anticipated[37] predominance of steric influences (including π-stacking interactions) over electronic effects in determining the regioselectivity of nucleophilic attack.[38]

The interference of fluxional processes with catalytic conversions might be invoked as possible explanation for the lower ee values obtained with complex **9a** in relation to catalysts incorporating diphosphine (S_P,R_m,R_m,S_P)-**3a**. In this context, effects of the bite angle require consideration. Comparative crystal structure analyses of platinum(II) dichloride complexes bearing ligands (*S*,*S*)-**1a** and (S_P,R_m,R_m,S_P)-**3a** displayed a highly distorted system with a phosphorus−platinum−phosphorus bite angle of 102.97(5)° for the former compound.[14c] In contrast, the geometry of complex [**3a**]$PtCl_2$ displayed less strain and a smaller bite angle of only 92.30(5)°. Extrapolation of these trends onto palladium allyl chemistry might indicate a beneficial effect of a smaller bite angle. Yet, this conclusion presumably holds only for the phenyl-1-naphthyl set of substituents on chiral phosphorus as evidenced by catalysis results. A general trend for the effect of the bite angle cannot be deduced, since the

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structural diversity of 2-biphenylyl and 1-naphthyl groups is too complex to neglect or unify their behavior upon backbone alteration.

Conclusions

Our investigations of allylic substitution reactions using P-chiral diphosphine ligands revealed some interesting trends. Devoid of dissymmetric electronic modeling, the employed C_2-symmetrical ligands (with exception of diphosphine **2c**) were found capable of inducing enantioselectivities of up to 99% ee. Yet, this efficiency depended on several factors, such as substrate structure, type of nucleophile, backbone constitution, and substitution pattern of the chiral phosphorus donors. The smallest effects were observed on varying ligand electronic properties by *para*-methoxy and *para*-trifluoromethyl substitution of the phenyl rings of the phosphines; the latter resulted in a slight decrease of ee values.

In contrast, steric aspects concerning the substituents on phosphorus were found eminently important; a marked difference in spatial requirements, exhibited in proximity to the metal center achieved good asymmetric modeling of the coordination environment. In this context, bulky 9-phenanthryl, 2-biphenylyl, or ferrocenyl moieties were, in combination with phenyl groups, identified as the most efficient substitution arrays. Catalysis results did not show a clear effect of the bite angle; a change of the latter presumably resulted in extensive repositioning of the phosphine residues. NMR spectra indicated, however, that the choice of substituents is crucial to establish a rigid, well-defined chiral pocket.

The crystal structure analysis revealed that marked distortion of the η^3-allyl fragment in complex **9a** and, consequently, determination of the site of nucleophilic attack is imposed by a combination of steric constraints and $\pi-\pi$ interactions. These require the engagement of bulky allyl as well as ligand substituents to induce useful levels of enantiodiscrimination. Thus, purely steric modeling by P-chiral residues could surpass the efficiency of other propeller-shaped ligands bearing carbon or axial chiral elements. In certain cases it even paralleled the good results of P−N or dissymmetric P−P donors, that rely on the exploitation of (stereo)electronic effects[39] in catalysis. Yet, few similarities were established between the ferrocenyl ligands used in this study and the diphospholane donors mentioned in the introductory part. Summarizing, the interesting performance of P-chiral diphosphines in allylic substitutions reactions will prompt further exploration in other catalytic applications soon.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF and Et_2O were distilled from sodium/benzophenone ketyl, CH_2Cl_2 and acetonitrile from CaH_2, and toluene and methanol from sodium wire under nitrogen. Melting points are uncorrected. 1D and 2D NMR spectra were recorded on 250, 300, 400, 500, and 600 MHz instruments; $CDCl_3$ was used as solvent, if not mentioned otherwise. Phosphorus−carbon coupling constants (J_{CP}) were identified by comparison of *J*-modulated ^{13}C (APT) spectra measured at different magnetic field strengths. Optical rotations were measured in a thermostated polarimeter with $l = 1$ dm. Mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Elemental analyses were obtained using an Elementar Vario EL apparatus. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Diethylamine was distilled from KOH under argon. The following compounds were synthesized according to published procedures: ($2R_P$,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine borane **4**,[15a] 1,1′-dilithioferrocene,[40] (R_P,R_m)-1-iodo-2-(1-naphthylphenylphosphinoxy)-ferrocene **7**,[14c] (*E*)-1,3-diphenylprop-2-en-1-yl acetate,[5a] (*E*)-pent-3-en-2-yl acetate,[41] cyclohex-2-en-1-yl acetate,[42] and [(1,3-diphenyl-η^3-allyl)PdOAc]$_2$.[7a] In the nomenclature of ligands **3a**−**c** and their precursor compounds, indices P and m denote absolute configurations of phosphorus and metallocene elements of chirality, respectively.

Synthesis of Ferrocenyl Diphosphine 1f. (S_P,1*R*,2*S*)-(−)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(ferrocenyl)-*P*-(phenyl)-phosphinamide borane, 5. Ferrocene (72 mmol) was dissolved in 80 mL of THF, degassed, and cooled to 0 °C. *t*-BuLi (60 mmol of a 1.7 M solution in pentane) was slowly added via a syringe and the resulting monolithioferrocene suspension was kept at that temperature for 20 min. Then it was added via a Teflon cannula to a precooled (−78 °C) solution of ($2R_P$,4*S*,5*R*)-oxazaphospholidine borane **4** (35 mmol) in 50 mL of THF. The reaction mixture was allowed to reach room temperature over a period of 12 h and quenched with water. THF was evaporated, and the residue was extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The crude product was subjected to column chromatography (SiO_2, toluene/ethyl acetate = 96:4), at which the diastereomeric (R_P)-byproduct (<10%) was eluted first, followed by (S_P)-configured phosphine amide borane. Yield: 81%. Mp: 94 °C. ^1H NMR (400.13 MHz): δ 0.85−1.33 (m, br, 3H); 1.10 (d, 3H, $J = 6.5$ Hz); 1.80 (s, 1H); 2.23 (d, 3H, $J_{HP} = 8.6$ Hz); 4.07 (m, 1H); 4.09 (m, 1H); 4.14 (s, 5H); 4.33 (m, 1H); 4.37 (m 1H); 4.45 (m, 1H); 4.73 (d, br, 1H, $J = 5.0$ Hz); 7.12−7.31 (m, 10H) ppm. ^{13}C NMR (100.62 MHz): δ 13.40 (CH_3); 30.94 (d, CH_3, $J_{CP} = 3.1$ Hz); 58.11 (d, CH, $J_{CP} = 9.2$ Hz); 70.07 (5CH); 70.94 (d, CH, $J_{CP} = 6.9$ Hz); 71.08 (d, CH, $J_{CP} = 8.2$ Hz); 71.80 (d, C, $J_{CP} = 68.7$ Hz); 72.07 (d, CH, $J_{CP} = 13.0$ Hz); 72.37 (d, CH, $J_{CP} = 7.6$ Hz); 78.80 (d, CH, $J_{CP} = 5.4$ Hz); 126.54 (CH); 127.61 (CH); 128.10 (d, CH, $J_{CP} = 10.7$ Hz); 128.37 (CH); 130.36 (d, CH, $J_{CP} = 1.5$ Hz); 131.41 (d, CH, $J_{CP} = 10.7$ Hz); 132.86 (d, C, $J_{CP} = 70.4$ Hz); 142.58 (C) ppm. ^{31}P NMR (121.50 MHz): δ 70.05 (q, br, $J_{PB} = 80.1$ Hz) ppm. $[\alpha]^{20}_D = -118.7$ ($c = 0.59$; CH_2Cl_2). HRMS (FAB$^+$): *m*/*z* calcd for $C_{26}H_{31}$-BFeNOP 471.1586, obsd 471.1598. Anal. Calcd for $C_{26}H_{31}$-BFeNOP: C, 66.28; H, 6.63; N, 2.97. Found: C, 66.24; H, 6.60; N, 2.82.

(*R*)-(+)-Methyl (Ferrocenylphenyl)phosphinite Borane, 6. Phosphinamide borane **5** (27 mmol) was dissolved in 220 mL of degassed methanol. At 0 °C, concentrated sulfuric acid (28.35 mmol, 1.05 equiv) was added dropwise, and the solution was stirred for 15 h at room temperature. The progress of the reaction was monitored by TLC; however, complete conversion could not be obtained. Addition of up to 1.5 equiv of sulfuric acid gave no improvement but, instead, resulted in extensive decomposition. The reaction mixture was concentrated and the residue directly subjected to column chromatography (SiO_2, hexane/ethyl acetate = 95:5). The desired product was eluted first; after a change of the eluent composition (hexane/ethyl acetate = 1:1) unreacted starting material (∼30%) was recovered. Yield: 31%. Mp: 98−100 °C. ^1H NMR (400.13 MHz): δ 0.62−1.37 (m, br, 3H); 3.62 (d, 3H, $J_{HP} = 12.5$ Hz); 4.13 (s, 5H); 4.26 (m, 1H); 4.42 (m, 1H); 4.48 (m, 1H); 4.64 (m, 1H); 7.45−7.56 (m, 3H); 7.83−7.91 (m, 2H)

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ppm. ^{13}C NMR (100.58 MHz): δ 53.71 (d, CH_3, J_{CP} = 3.1 Hz); 69.96 (5CH); 71.15 (d, C, J_{CP} = 70.4 Hz); 71.57 (d, CH, J_{CP} = 10.7 Hz); 71.82 (d, CH, J_{CP} = 9.1 Hz); 71.98 (d, CH, J_{CP} = 13.1 Hz); 72.00 (d, CH, J_{CP} = 7.9 Hz); 128.44 (d, CH, J_{CP} = 9.9 Hz); 131.10 (d, CH, J_{CP} = 11.5 Hz); 131.81 (d, CH, J_{CP} = 2.3 Hz); 131.94 (d, C, J_{CP} = 63.5 Hz) ppm. ^{31}P NMR (121.44 MHz): δ 108.45 (q, br, J_{PB} = 75 Hz) ppm. $[\alpha]^{20}_D$ = +30.5 (c = 0.62; CH_2Cl_2). HRMS (EI$^+$): m/z calcd for $C_{17}H_{20}BFeOP$ 338.0694, obsd 338.0703. Anal. Calcd for $C_{17}H_{20}BFeOP$: C, 60.41; H, 5.96. Found: C, 60.46; H, 5.78.

(*S*,*S*)-(+)-1,1′-Bis(ferrocenylphenylphosphino)ferrocene, 1f. Phosphinite borane (*R*)-**6** (8 mmol) was dissolved in 10 mL of THF and cooled to −40 °C. A suspension of 1,1′-dilithioferrocene (4 mmol) in 7 mL of THF and 35 mL of Et_2O was cooled and added slowly via a Teflon cannula to the phosphinite solution. The reaction mixture was warmed to ambient temperature over a period of 15 h and then quenched with water. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was chromatographed (SiO_2, hexane/CH_2Cl_2 = 1:1) to remove small amounts of monosubstituted and *meso*-configured byproducts. The diastereomerically pure diphosphine diborane complex was then subjected to deprotection using an excess of degassed diethylamine (20 mL). After stirring for 15 h at room temperature, the solvent was evaporated and the crude product was chromatographically purified (SiO_2, hexane/CH_2Cl_2 = 1:1). Repeated recrystallizations from CH_2Cl_2/hexane (diffusion method) removed small amounts of isomerized *meso*-diphosphine and left the enantiopure ligand (*S*,*S*)-**1f**. Yield: 54%. Mp: 75 °C. ^{1}H NMR (400.13 MHz): δ 3.75 (m, 2H); 3.91 (m, 2H); 4.00 (s, 10H); 4.05 (m, 2H); 4.08 (m, 2H); 4.12 (m, 2H); 4.18 (m, 4H); 4.22 (m, 2H); 7.27−7.31 (m, 6H); 7.44−7.50 (m, 4H) ppm. ^{13}C NMR (100.62 MHz): δ 69.00 (5CH); 69.83 (d, CH, J_{CP} = 3.8 Hz); 70.52 (d, CH, J_{CP} = 3.8 Hz); 71.60 (m, CH); 71.95 (d, CH, J_{CP} = 13.7 Hz); 72.16 (m, CH); 72.54 (d, CH, J_{CP} = 10.6 Hz); 72.58 (d, CH, J_{CP} = 15.3 Hz); 73.61 (d, CH, J_{CP} = 16.8 Hz); 77.80 (d, C, J_{CP} = 4.6 Hz); 78.37 (d, C, J_{CP} = 5.4 Hz); 127.84 (d, CH, J_{CP} = 7.6 Hz); 128.77 (CH); 133.83 (d, CH, J_{CP} = 20.7 Hz); 138.98 (d, C, J_{CP} = 9.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ −29.54 (s) ppm. $[\alpha]^{20}_D$ = +36.3 (c = 0.30; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{42}H_{37}Fe_3P_2$ 771.0419, obsd 771.0413. Anal. Calcd for $C_{42}H_{36}Fe_3P_2$: C, 65.49; H, 4.71. Found: C, 65.94; H, 4.50.

Synthesis of Biferrocenyl Diphosphine 3c. (R_P,S_m,S_m,-R_P)-(+)-2,2′-Bis(1-naphthylphenylphosphinoxy)-1,1′-biferrocenyl, 8. The (R_P,R_m)-*o*-iodophosphine oxide **7** (2 mmol) was dissolved in 2 mL of CH_2Cl_2, and activated copper powder (10 mmol) was added under stirring. The solvent was removed in vacuo and the brown residue was heated at 135 °C for 48 h. After this treatment, the crude product was agitated with CH_2Cl_2, filtered over Celite, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/ethyl acetate = 4:1) eluted unreacted starting material first, followed by enantiopure (R_P,S_m,-S_m,R_P)-**8**. Yield: 35% Mp: 180 °C. ^{1}H NMR (400.13 MHz): δ 4.10 (s, 10H); 4.17 (m, 2H); 4.33 (m, 2H); 4.95 (m, 2H); 7.02 (dt, br, 4H, J = 3.0; 8.1 Hz); 7.19−7.24 (m, 2H); 7.29 (ddd, 2H, J = 2.2; 7.2; 8.3 Hz); 7.37−7.48 (m, 8H); 7.82 (dd, br, 2H, J = 6.8; 14.2 Hz); 7.85 (d, br, 2H, J = 7.8 Hz); 7.90 (d, br, 2H, J = 8.1 Hz); 8.68 (d, br, 2H, J = 8.6 Hz) ppm. ^{13}C NMR (100.61 MHz): δ 70.13 (d, CH, J_{CP} = 10.7 Hz); 70.56 (5CH); 73.50 (d, CH, J_{CP} = 13.8 Hz); 74.17 (d, C, J_{CP} = 114.0 Hz); 79.15 (d, CH, J_{CP} = 9.2 Hz); 88.65 (d, C, J_{CP} = 10.7 Hz); 124.40 (d, CH, J_{CP} = 13.8 Hz); 126.04 (CH); 126.50 (CH); 127.72 (d, CH, J_{CP} = 4.6 Hz); 127.91 (d, CH, J_{CP} = 12.2 Hz); 128.71 (d, CH, J_{CP} = 0.9 Hz); 130.92 (d, CH, J_{CP} = 2.3 Hz); 131.01 (d, C, J_{CP} = 102.5 Hz); 131.70 (d, CH, J_{CP} = 10.7 Hz); 132.34 (d, CH, J_{CP} = 3.1 Hz); 133.63 (d, C, J_{CP} = 3.1 Hz); 133.71 (d, C, J_{CP} = 2.3 Hz); 133.90 (d, CH, J_{CP} = 9.9 Hz); 136.01 (d, C, J_{CP} = 105.5 Hz) ppm. ^{31}P NMR (161.98 MHz): δ 33.12 (s) ppm. $[\alpha]^{20}_D$ = +473.9 (c = 0.30; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{52}H_{41}Fe_2O_2P_2$ (MH$^+$) 871.1281; obsd 871.1303. Anal. Calcd for $C_{52}H_{40}Fe_2O_2P_2$: C, 71.75; H, 4.63. Found: C, 71.98; H, 4.82.

(S_P,S_m,S_m,S_P)-(+)-2,2′-Bis(1-naphthylphenylphosphino)-1,1′-biferrocenyl, 3c. Diphosphine dioxide (R_P,S_m,S_m,R_P)-**8** (0.2 mmol) was introduced in a glass tube and toluene (3 mL), trichlorosilane (10 mmol), and triethylamine (15 mmol) were added consecutively. The tube was sealed under vacuum, placed in an autoclave, and heated at 140 °C for 60 h. After treatment, the tube was cooled in liquid nitrogen and opened. NaOH solution (15 M) was carefully added to the crude product mixture, and the resulting solution was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), and the solvent was evaporated. For separation of isomerized byproducts, the residue was dissolved in 5 mL of degassed THF, and BH_3·THF (0.5 mL of a 1 M solution in THF) was added dropwise. After TLC indicated complexation to be complete, the solvent was evaporated and the crude borane complexes were chromatographed (SiO_2, CH_2Cl_2/hexane = 1:1.). The desired C_2-symmetrical diphosphine was eluted first, followed by not further separated epimerized C_1-symmetrical and doubly phosphorus-isomerized byproducts (∼30%). For deprotection, the thus obtained diborane complex of **3c** was dissolved in degassed diethylamine (1 mL) and stirred overnight at room temperature. The solvent was removed in vacuo, and the residual diphosphine was subjected to column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1) to give the enantiopure ligand as orange crystals. Yield: 38%. Mp: 228−230 °C (dec). ^{1}H NMR (400.13 MHz): δ 3.86 (m, 2H); 4.12 (s, 10H); 4.49 (m, 2H); 4.95 (m, 2H); 5.93 (t, br, 2H, J = 7.6 Hz); 6.43 (m 2H); 7.06 (d, 2H, J = 8.1 Hz); 7.19−7.32 (m, 10H); 7.41−7.45 (m, 4H); 7.61 (d, 2H, J = 7.8 Hz); 8.02 (dd, 2H, J = 3.0; 8.1 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 70.06 (d, CH, J_{CP} = 4.0 Hz); 70.14 (5CH); 72.22 (d, CH, J_{CP} = 4.6 Hz); 77.00 (d, CH, J_{CP} = 11.5 Hz); 77.93 (d, C, J_{CP} = 9.2 Hz); 91.05 (d, C, J_{CP} = 31.2 Hz); 124.66 (CH); 125.02 (CH); 125.10 (d, CH, J_{CP} = 2.3 Hz); 126.15 (d, CH, J_{CP} = 24.5 Hz); 127.94 (CH); 127.98 (d, CH, J_{CP} = 8.0 Hz); 128.17 (d, CH, J_{CP} = 1.5 Hz); 128.83 (CH); 130.84 (CH); 133.02 (d, C, J_{CP} = 3.8 Hz); 133.61 (d, C, J_{CP} = 19.9 Hz); 134.68 (d, CH, J_{CP} = 22.1 Hz); 135.79 (d, C, J_{CP} = 13.0 Hz); 138.12 (d, C, J_{CP} = 7.7 Hz) ppm. ^{31}P NMR (121.50 MHz): δ −30.72 (s) ppm. $[\alpha]^{20}_D$ = +181.1 (c = 0.13; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{52}H_{41}Fe_2P_2$ (MH$^+$) 839.1382; obsd 839.1351. Anal. Calcd for $C_{52}H_{40}Fe_2P_2$: C, 74.48; H, 4.81. Found: C, 74.62; H, 4.67.

Asymmetric Allylic Alkylation Reactions 1, 2, and 3 (Typical Procedure). In a Schlenk tube [Pd(η^3-C_3H_5)Cl]$_2$ (0.005 mmol) and the respective ligand (0.01 mmol) were dissolved in 1 mL of CH_2Cl_2 and degassed. (*E*)-1,3-Diphenylprop-2-en-1-yl acetate, (*E*)-pent-3-en-2-yl acetate, or cyclohex-2-en-1-yl acetate (1 mmol) was added as the substrate, and after 20 min of stirring at room temperature, dimethyl malonate (3 mmol), BSA (3 mmol), and a catalytic amount of KOAc were added consecutively. The reaction mixture was degassed again and stirred at the given temperature. If TLC indicated no further conversion, the reaction was quenched by dilution with Et_2O (15 mL); the organic layer was washed twice with saturated NH_4Cl solution and dried over Na_2SO_4. Filtration and removal of solvent left a red oil which was chromatographed (SiO_2; petroleum ether/CH_2Cl_2 = 1:1 (reaction 1), petroleum ether/Et_2O = 3:1 (reactions 2 and 3)) to give analytically pure products.[43] Determination of ee values was performed by chiral HPLC (Chiralcel OD-H, *n*-hexane/2-propanol = 98:2, 0.5 mL·min^{-1}, t_R (*R*) = 15.4 min, t_R (*S*) = 16.8 min; reaction 1), chiral GC (50% octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin, isothermal, T = 55 °C, t_R (*S*) = 95 min, t_R (*R*) = 98 min; reaction 2) and by optical rotation measurements ($[\alpha]^{20}_D$ = −46.1 for (*S*)-dimethyl 2-(cyclohex-2-en-1-yl)malonate,[44] reaction 3).

Asymmetric Allylic Amination/Imidation Reactions 4 and 5 (Typical Procedure). In a Schlenk tube [Pd(η^3-C_3H_5)-Cl]$_2$ (0.005 mmol) and the respective ligand (0.01 mmol) were

(43) Product characterization data were found in agreement with the reported literature; see, for example: Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. Vyskocil, S.; Smrcina, M.; Hanus, V.; Polašek, M.; Kocovsky, P. *J. Org. Chem.* **1998**, *63*, 7738. Widhalm, M.; Wimmer, P.; Klintschar, G. *J. Organomet. Chem.* **1996**, *523*, 167.

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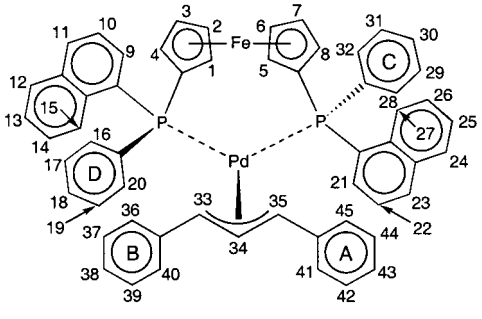
dissolved in 1 mL (reaction 4) or 2 mL (reaction 5) of CH_2Cl_2 and degassed. (*E*)-1,3-Diphenylprop-2-en-1-yl acetate (1 mmol) was added, and the solution was stirred for 20 min at ambient temperature. Subsequently, benzylamine (1.2 mmol) or *N*-phthalimide potassium salt (1.2 mmol) was added, and the reaction was kept at the given temperature until TLC indicated no further progress. The solvent was removed in vacuo, and the residue was purified by column chromatography (SiO_2; petroleum ether/ethyl acetate = 95:5 for reaction 4 or petroleum ether/Et_2O = 4:1 for reaction 5) to give pure products.[45] Determination of ee values was performed by chiral HPLC (Chiralcel-OD; *n*-hexane/2-propanol/diethylamine = 99.55:0.25:0.2, 0.5 mL·min^{-1}, t_R (*R*) = 37.8 min, t_R (*S*) = 41.0 min for reaction 4 and *n*-hexane/2-propanol = 98:2, 0.5 mL·min^{-1}, t_R (*R*) = 26.2 min, t_R (*S*) = 22.8 min for reaction 5).

Synthesis of Allyl Palladium Complexes 9a, 9d, and 10a (Typical Procedure). In a Schlenk tube, [(1,3-diphenyl-η^3-allyl)PdOAc]$_2$ (0.025 mmol) was dissolved in 2 mL of degassed acetone. After addition of $AgBF_4$ (0.05 mmol), the suspension was stirred for 20 min at ambient temperature and then filtered through Celite into a second Schlenk tube containing a solution of the respective ligand (0.05 mmol) in 1 mL of CH_2Cl_2. After stirring for another 20 min, the reaction mixture was concentrated, and the product precipitated by addition of 3 mL of Et_2O. It was collected on a glass filter, washed with hexane, and dried under vacuum.

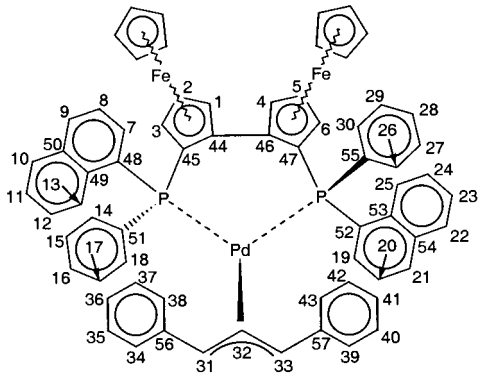
{**(1,3-Diphenyl-η^3-allyl)[(*S,S*)-1a]Pd**}**BF_4, 9a (Major Isomer).** Yield: 86%. ^{1}H NMR (600.13 MHz; CD_2Cl_2, 223 K): δ 3.38 (m, H8); 4.03 (m, H7); 4.14 (m, H5); 4.14 (m, H1); 4.24 (m H6); 4.44 (m, H2); 4.58 (t, J = 11.3 Hz, H33); 4.70 (m H4); 4.96 (m, H3); 5.75 (t, J = 8.7 Hz, H32); 6.08 (t, J = 12.3 Hz, H34); 6.28 (m, H35); 6.42 (m, H9); 6.43 (m, br, H45); 6.53 (m, br, H42); 6.60 (t, J = 7.4 Hz, H31); 6.81 (m, br, H44); 6.89 (t, J = 7.2 Hz, H10); 6.91 (m, br, H16); 6.98 (m, H26); 6.99 (m, H37); 7.00 (m, H43); 7.07 (m, H27); 7.09 (m, H19*); 7.10 (m, H17*); 7.11 (m, H38); 7.28 (m, br, H41); 7.30 (m, H39); 7.31 (m, H18); 7.33 (m, H36); 7.40 (m, H25); 7.40 (m, H30); 7.56 (m, H13); 7.57 (m, H14); 7.64 (m, H40); 7.76 (t, J = 7.2 Hz, H29); 7.80 (d, J = 8.2 Hz, H11); 7.93 (m, H12); 8.01 (d, J = 8.2 Hz, H24); 8.04 (d, br, J = 7.4 Hz, H15); 8.18 (m, H28); 8.24 (t, J = 7.4 Hz, H22); 8.36 (d, J = 8.2 Hz, H23); 8.74 (dd, br, J = 6.9; 15.3 Hz, H20); 9.19 (dd, J = 6.7; 20.5 Hz, H21) ppm. ^{31}P NMR (121.50 MHz, CD_2Cl_2, 230K): δ 24.53 (d, J = 57.5 Hz); 27.82 (d, J = 57.3 Hz) ppm. HRMS (FAB$^+$): *m/z* calcd for $C_{57}H_{46}FeP_2Pd$ (MH$^+$) 954.1427, obsd 954.1401. *Assignment exchangeable.

Minor Isomer 9a. ^{1}H NMR (600.13 MHz; CD_2Cl_2, 223 K) (selected signals, numbering refers to exchange with major isomer): δ 3.46 (m, H5′); 3.74 (m, H1′); 4.09 (m, H6′); 4.16 (m, H2′); 4.28 (m, H7′); 4.28 (m, H8′); 4.48 (m, H3′); 4.86 (m, H4′); 4.91 (t, J = 13.1 Hz, *anti*-allyl-H); 6.06 (m, *syn*-allyl-H); 6.38 (m, *anti*-allyl-H) ppm. ^{31}P NMR (121.50 MHz; CD_2Cl_2, 230K): δ 18.86 (d, J = 59.6 Hz); 26.43 (d, J = 59.7 Hz) ppm.



{**(1,3-Diphenyl-η^3-allyl)[(*R,R*)-1d]Pd**}**BF_4, 9d.** Yield: 73%. ^{1}H NMR (600.13 MHz): δ 2.57 (m, 1H, fc); 3.38 (m, 1H, fc); 3.76 (m, 1H, fc); 3.90 (m, 1H, fc); 4.08 (m, 1H, fc); 4.18 (m, 1H, fc); 4.36 (t, 1H, anti-allyl, J = 11.5 Hz); 4.96 (m, 1H, fc); 5.30 (m, br, 1H, fc); 6.42 (t, 1H, *syn*-allyl, J = 13.0 Hz); 6.53 (m, 1H, *anti*-allyl), 6.54−6.59 (m, 5H); 6.63−6.67 (m, 2H); 6.68−6.85 (m, 12H); 7.01 (t, 2H, J = 7.4 Hz); 7.03−7.09 (m, 3H); 7.14−7.18 (m, 3H); 7.19−7.25 (m, 6H); 7.43−7.47 (m, 3H); 7.57−7.60 (m, 2H) ppm. ^{31}P NMR (161.98 MHz): δ 28.86 (d, J = 72.0 Hz); 31.02 (d, J = 73.2 Hz) ppm. Anal. Calcd for $C_{61}H_{49}BF_4Fe_2P_2Pd\cdot{}^1/_2CH_2Cl_2$: C, 65.05; H, 4.44. Found: C, 64.87; H, 4.53.

{**(1,3-Diphenyl-η^3-allyl)[(S_P,R_m,R_m,S_P)-3a]Pd**}**BF_4, 10a (Main Isomer).** Yield: 81%. ^{1}H NMR (600.13 MHz, CD_2Cl_2): δ 3.11 (m, H3); 3.47 (m, H6); 3.59 (t, J = 11.8 Hz, H33); 4.00 (s, 10H, fc); 4.01 (m, H2); 4.15 (m, H5); 4.69 (m, H1); 4.78 (m, H4); 4.92 (t, J = 10.2 Hz, H31); 5.78 (t, J = 12.8 Hz, H32); 5.91 (m, H39/43); 6.16 (m, br, H34/38); 6.48 (t, br, J = 8.0 Hz, H35/37); 6.87 (m, H36); 6.88 (t, J = 7.7 Hz, H40/42); 7.06 (t, br, J = 7.2 Hz, H41); 7.11 (d, J = 7.1 Hz, H7*); 7.12 (d, J = 7.4 Hz, H19*); 7.20 (t, br, J = 7.1 Hz, H8); 7.25 (m, H27/29); 7.26 (m, H12); 7.37 (m, H26/30); 7.39 (m, H20); 7.44 (t, br, J = 8.2 Hz, H28); 7.47 (t, br, J = 7.2 Hz, H24); 7.59 (m, H11); 7.62 (m, H15/17); 7.65 (m, H16); 7.67 (m, H23); 7.80 (d, J = 8.5 Hz, H9); 7.86 (d, J = 8.8 Hz, H10); 8.06 (dd, J = 7.1; 12.2 Hz, H14/18); 8.09 (d, J = 8.5 Hz, H22); 8.12 (d, J = 8.7 Hz, H21); 8.19 (dd, J = 2.8; 8.2 Hz, H13); 8.39 (d, br, J = 8.7 Hz, H25) ppm. ^{13}C NMR (150.91 MHz, coupling constants not determined): δ 69.0 (C2); 69.2 (C5); 70.7 (10C, fc); 75.4 (C3); 75.5 (C6); 76.0 (C45); 76.4 (C47); 77.4 (C1); 77.7 (C4); 81.9 (C33); 86.8 (C46); 87.0 (C44); 98.1 (C31); 108.7 (C32); 120.1 (C48); 124.3 (C13); 124.5 (C52); 124.7 (C20); 125.7 (C8); 126.3 (C12); 126.4 (C39/43); 126.5 (C34/38); 126.5 (C11); 126.6 (C25); 126.8 (C24); 127.2 (C23); 127.5 (C41); 127.8 (C35/37); 128.1 (C27/29); 128.4 (C36); 128.5 (C40/42); 128.7 (C15/17); 129.8 (C10); 130.1 (C22); 131.3 (C28); 131.5 (C16); 131.7 (C7); 132.1 (C9); 132.2 (C56); 132.2 (C21); 133.2 (C19); 133.4 (C55); 133.5 (C49); 133.6 (C53); 133.9 (C26/30); 134.1 (C14/18); 134.1 (C51); 134.3 (C50); 134.4 (C54); 135.9 (C57) ppm. ^{31}P NMR (161.97 MHz): δ 10.59 (d, J = 74.4 Hz); 11.96 (d, J = 73.2 Hz) ppm. MS (FAB$^+$): *m/z* = 1137.2 (M$^+$); 945.1; 709.1; 603.1. Anal. Calcd for $C_{67}H_{53}BF_4Fe_2P_2Pd\cdot CH_2Cl_2$: C, 62.35; H, 4.23. Found: C, 62.56; H, 4.04. *Assignment exchangeable.



Minor Isomer 10a (16%). ^{31}P NMR (161.97 MHz, CD_2Cl_2): δ −12.93 (m, br); −8.35 (m, br) ppm.

Minor Isomer 10a (4%). ^{31}P NMR (161.97 MHz, CD_2Cl_2): δ 7.81 (d, J = 68.2 Hz); 9.97 (d, J = 67.0 Hz) ppm.

Experimental Details for Crystal Structure Determination of {(1,3-Diphenyl-η^3-allyl)[(*S,S*)-1a]Pd}BF_4, 9a. $C_{57}H_{45}FeP_2Pd\cdot C_6H_6\cdot BF_4$, fw = 1119.04, colorless needle, 0.63 × 0.13 × 0.13 mm^3, triclinic, *P*1 (No. 1), a = 9.7082(1), b = 10.2737(2), c = 13.2188(3) Å, α = 96.039(1)°, β = 95.557(1)°, γ = 99.533(1)°, V = 1284.15(4) Å^3, Z = 1, ρ = 1.447 g cm^{-3}, 22845 measured reflections, 11540 unique reflections (R_{int} = 0.0441). An absorption correction was not considered necessary (μ = 0.751 mm^{-1}); 647 refined parameters, 108 restraints. R ($I > 2\sigma(I)$): R1 = 0.0357, wR2 = 0.0905. R (all data): R1 = 0.0366, wR2 = 0.0913. S = 1.184. Intensities were measured on Nonius Kappa CCD diffractometer with rotating anode (Mo Kα, λ = 0.71073 Å) at a temperature of 150 K up

(45) Product characterization data were found in agreement with the reported literature; see, for example: Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411. Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411.

to a resolution of $(\sin \vartheta/\lambda)_{max} = 0.65$ Å^{-1}. The structure was solved with automated Patterson methods (DIRDIF-97)[46] and refined with the program SHELXL97 [47] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The drawing, structure calculations, and checking for higher symmetry was performed with the program PLATON.[48]

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Supporting Information Available: Crystal structure refinement data for compound **9a** including atomic coordinates, isotropic and anisotropic displacement parameters and a complete listing of bond angles and bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001175U

(46) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF 97 Program System, Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1997.

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