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1-Phosphino-2-sulfenylferrocenes as Planar Chiral Ligands in Enantioselective Palladium-Catalyzed Allylic Substitutions

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The synthesis of a wide structural variety of enantiopure 1-phosphino-2-sulfenylferrocene ligands **1** possessing exclusively planar chirality is described. In the case of the readily available *tert*-butylsulfenyl derivatives very high enantioselectivities were obtained in the palladium-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate (ee's up to 97%) and nitrogen nucleophiles (ee's up to 99.5%). Palladium complexes of these ferrocenes were characterized by NMR and X-ray diffraction, revealing the P,S-bidentate character of the ligands **1** and the formation of a single epimer on the stereogenic sulfur atom resulting from the complexation with palladium. A model justifying the observed asymmetric induction exerted by this novel family of chiral ferrocenes, supported by solution NMR studies on a palladium allylic complex, is discussed.

Introduction

Among the plethora of structurally diverse chiral ligands tested to date in asymmetric catalysis,[1] two different concepts have proven to be very useful: the reduction of the number of possible diastereomeric transition states by using bidentate C_2-symmetrical chiral ligands[1,2] and the use of mixed bidentate ligands equipped with strong and weak donor heteroatom pairs. This second strategy takes advantage of the different electronic properties associated with each heteroatom-metal bond (for instance, the trans effect)[3] and has been widely applied to the design of chiral P,N-bidentate ligands[1] (for instance, phosphine-oxazoline systems). Although much less studied than the mixed P,N-coordination mode, some recent reports indicate that bidentate ligands based on chiral thioethers can also lead to high enantioselectivities in C−C bond-forming metal-catalyzed reactions.[4] In particular, the P,S-bidentate ligands **I**,[5] **II**,[6] and **III**,[7] having several stereogenic carbons, and the chiral ferrocenyl sulfides **IV**[8] and **V**,[9] with both central and planar chirality, have been successfully used in palladium-catalyzed enantioselective allylic substitutions (Figure 1). Within this context, we describe herein that the readily available family of enantiopure P,S-bidentate ferrocenes (*R*)-**1**, having exclusively planar chirality, act as efficient ligands in palladium-catalyzed allylic substitutions with 1,3-diphe-

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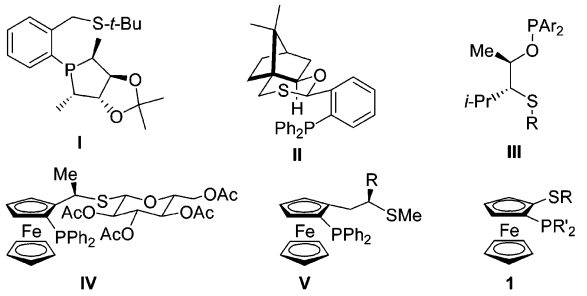


FIGURE 1. Examples of P,S-bidentate ligands used in Pd-catalyzed allylic substitutions.

nylpropenyl acetate.[10] To the best of the authors' knowledge P,S-bidentate ligands possessing planar chirality as the only source of chirality have not been previously tested in asymmetric catalysis.[11]

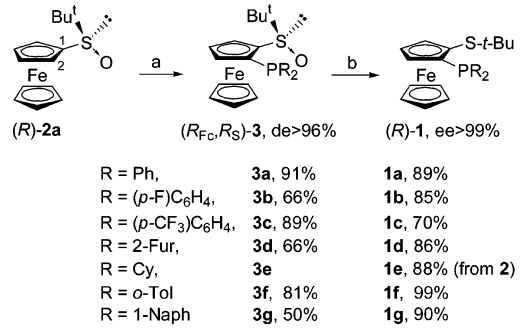
Results and Discussions

Synthesis of the Ligands. On the basis of the remarkable results reported by Evans et al.[7] on the behavior of ligands **III** and our previous results in the enantioselective addition of diethylzinc to aldehydes using catalytic amounts of 2-aminosubstituted 1-sulfinylferrocenes, in which the bulky *tert*-butylsulfoxide gave the best asymmetric inductions,[12] we envisaged that a highly sterically demanding thioether, such as the *tert*-butylsulfenyl group, could be determining in the asymmetric performance exerted by the family of ligands **1**.

The preparation of the enantiopure *tert*-butylsulfinylferrocene (*R*)-**2a**, used as starting material, had been previously reported by Kagan et al. either by sulfinylation of ferrocenyllithium with enantiopure *tert*-butylsulfinates or by asymmetric oxidation of *tert*-butylsulfenylferrocene.[13] Alternatively, we have recently reported[12] that (*R*)-**2a** can be readily prepared on multigram scale by sulfinylation of ferrocenyllithium with (*R*)-*S*-*tert*-butyl *tert*-butanethiosulfinate.[14]

It was well established from the work of Kagan[13a] and Hua[15] that the *ortho*-lithiation of (*R*)-**2a** with strong bases occurs with nearly complete diastereocontrol at C-2.

SCHEME 1. Synthesis of Ferrocene P,S-Ligands (*R*)-1[a]



[a] Reagents and conditions: (a) *t*-BuLi, THF, −78 °C; R_2PCl; (b) $HSiCl_3$, Et_3N, toluene, 110 °C.

Treatment of the resulting lithiated species with different carbon and heteroatomic electrophiles results in a very useful method for the preparation of enantiopure 1,2-disubstituted ferrocenes. In accordance with these results, the treatment of (*R*)-**2a** with *tert*-butyllithium in THF at −78 °C and further quenching with a wide variety of sterically and electronically substituted chlorophosphines led to the corresponding (R_{Fc}, R_S) sulfinylferrocenyl phosphines **3a**−**g** in acceptable to good yields (66−91%) and complete diastereoselectivity (de >96%, Scheme 1).[16] We observed that in solution, the sulfinylferrocenyl phosphines **3** slowly evolve by an intramolecular oxygen transfer process from the sulfoxide to the phosphorus atom to give the corresponding sulfenylferrocenyl phosphine oxide,[17] this process being particularly favorable in the case of the dialkylphosphine **3e**. However, regardless of the extension of this oxygen transfer process, both the sulfinyl and the phosphine oxide moieties were converted to the corresponding sulfenylferrocenyl phosphine **1a**−**g** by reduction with $HSiCl_3$/Et_3N in refluxing toluene. As expected, the enantiopurity of the products **1** proved to be as high as the starting *tert*-butylsulfoxide **2a** (ee > 99%; HPLC, Daicel Chiralcel OD column).

To investigate the effect of the size of the presumed P,S−Pd chelate (five- and six-membered palladium chelates) on the asymmetric performance of this family of chiral ligands, the enantiopure ferrocenes **1h** and **1i**, having the phosphorus atom one position further with regard to the ferrocene backbone, were also prepared (Schemes 2 and 3). The aminophosphine sulfenylferrocene **1h** was readily prepared in two steps from the enantiopure 2-aminosulfinylferrocene **4** previously reported by us[12] through diastereoselective amination of **2a**. Reduction of the sulfoxide moiety of **4** to give the thioether **5** ($HSiCl_3$/Et_3N, toluene, reflux; 71% yield) and further reaction of the amino group with chlorodiphenyl phosphine (Ph_2PCl, *i*-Pr_2NH, CH_2Cl_2, rt; 79% yield) afforded the ligand **1h**. The carbon analogue **1i** was prepared in four steps from the known enantiopure

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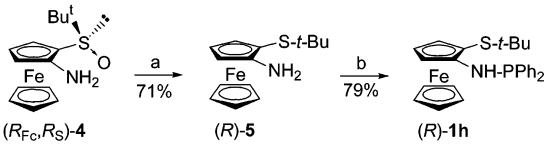
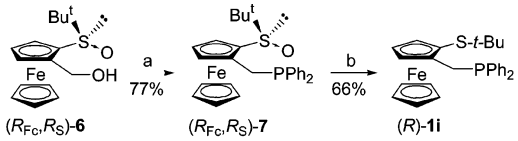
SCHEME 2. Synthesis of Ferrocenyl Aminophosphine (*R*)-1h[a]



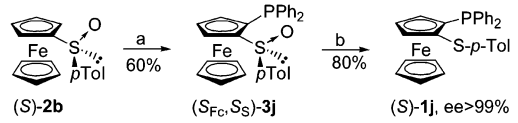
[a] Reagents and conditions: (a) $HSiCl_3$, Et_3N, toluene, 110 °C; (b) *i*-Pr_2NH, CH_2Cl_2, Ph_2PCl, rt.

SCHEME 3. Synthesis of Homologue Ligand (*R*)-1i[a]



[a] Reagents and conditions: (a) (1) Ac_2O, Et_3N, DMAP, rt, (2) Ph_2PH, AcOH, 80 °C; (b) $HSiCl_3$, Et_3N, toluene, 110 °C.

SCHEME 4. Synthesis of Ligand (*S*)-1j[a]



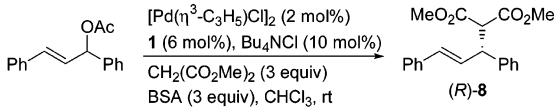
[a] Reagents and conditions: (a) LDA, THF, −78 °C; PPh_2Cl; (b) $HSiCl_3$, Et_3N, toluene, 110 °C.

2-hydroxymethyl sulfinylferrocene **6**[15] (prepared by reaction of **2a** with formaldehyde). Acetylation (Ac_2O, Et_3N, DMAP, CH_2Cl_2, rt; 79%) and nucleophilic substitution at the "benzylic" position with diphenylphosphine (Ph_2PH, AcOH, 80 °C; 98%) afforded the sulfinyl phosphine **7**, which upon reduction under standard conditions ($HSiCl_3$/Et_3N, toluene, reflux; 66% yield) was transformed into the ferrocene **1i**.

As a third structural factor, to study the effect of the nature of the substitution at the sulfur atom, the enantiopure *p*-tolylsulfenylferrocene (*S*)-**1j** was prepared from the known (*S*)-*p*-tolylsufinylferrocene [(*S*)-**2b**][13,15,18] following the same diastereoselective sequence (*ortho*-metalation, phosphination,[18] and sulfoxide reduction) developed for the synthesis of **1a**−**g** (Scheme 4).

Asymmetric Allylic Alkylation. With this sterically and electronically varied set of planar chiral ferrocenes **1a**−**j** in hand, we explored their effectiveness as ligands in enantioselective Pd-catalyzed allylic substitutions[19] (Table 1). As standard test reaction we studied the alkylation of dimethyl malonate with 1,3-diphenyl-2-propenyl acetate, using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) as the base, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %) as palladium source, in the presence of a catalytic amount of ligand **1** (6 mol %) in $CHCl_3$[20] at room temperature. Under these conditions, in the presence of the parent ligand **1a** the reaction was complete in 4 h, affording the substitution product (*R*)-**8** with 93% ee in 99% yield. Interestingly, we found that this transformation was deeply accelerated by addition of a catalytic amount of Bu_4NCl (10 mol %),[21] the reaction being complete within 10 min without any significant change in the enantioselectivity. The high reaction rate observed in the presence of Bu_4NCl as additive made it possible to carry out the transformation at lower temperatures, improving the enantioselectivity of the process. For instance, the enantiomeric excess raised from 93% to 96% ee by performing the reaction at −20 °C instead of room temperature (at temperatures lower than −20 °C the reaction becomes too slow from a practical point of view). The results obtained with the rest of ligands **1** under these optimized conditions are summarized in Table 1.

TABLE 1. Pd-Catalyzed Reaction of 1,3-Diphenyl-2-propenyl Acetate with Dimethyl Malonate in the Presence of Ligands 1



entry	ligand	yield (%)[a]	ee (%)[b]
1	**1a**	92	93 (96)[c]
2	**1b**	94	92 (97)[c]
3	**1c**	90	92 (96)[c]
4	**1d**	60	90
5	**1e**	96	84
6	**1f**	97	73
7	**1g**	95	71
8[d]	**1h**	87	88
9	**1i**	91	85
10	**1j**	92	40[e]

[a] In pure product after chromatography. [b] Determined by HPLC (Chiralcel OD column). [c] Enantiomeric excess at −20 °C instead of room temperature. [d] CH_2Cl_2 as solvent. [e] Enantiomeric excess of (*S*)-**8**.

The ligands **1b** and **1c** (entries 2 and 3) containing electron-withdrawing substituents on the phosphorus atom [*p*-fluorophenyl and (*p*-trifluoromethyl)phenyl, respectively] showed results similar to those of the parent ligand **1a** (ee up to 96−97% at −20 °C), although the reactions were significantly faster. For instance, in the absence of Bu_4NCl, the reaction with **1a** takes 4 h to be completed at room temperature, whereas only 20 min are necessary in the presence of **1b**.

In contrast, ligands containing electron-rich phosphines, as the furyl-substituted ligand **1d** (entry 4, 90% ee) and the dicyclohexylphosphine **1e** (entry 5, 84% ee), as well as the ligands of the homologous series **1h** and **1i** (entries 8 and 9, 88% ee and 85% ee, respectively) gave slightly lower enantioselectivities. A much significant drop in the asymmetric induction was observed in the case of the sterically more demanding diarylphosphines **1f** (entry 6, 73% ee) and **1g** (entry 7, 71% ee), which also showed a decrease in the reaction rates (for instance, the reaction in the presence of **1g** and Bu_4NCl took 50 min to completion, whereas only 10 min were needed in the presence of ligand **1a** under identical conditions).

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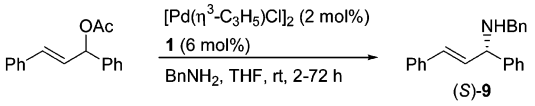
(19) For recent reviews, see: (a) Johannsen, M.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689−1708. (b) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395−422. (c) *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. 2. Chapter 24.

(20) Similar enantioselectivities were observed using THF as solvent, but the reactivity was slower.

(21) For a review on halide effects in transition metal catalysis, see: Fagnou, K.; Lautens, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 26−47.

TABLE 2. Pd-Catalyzed Reaction of 1,3-Diphenyl-2-propenyl Acetate with Benzylamine in the Presence of Ligands 1



entry	ligand	yield (%)[a]	ee (%)[b]
1	**1a**	80	97
2	**1b**	89	98
3	**1c**	91	98
4	**1d**	60[c]	94
5	**1e**	50[d]	40
6	**1f**	82	99.5
7	**1g**	93	99.5
8	**1h**	73[d]	60
9	**1i**	72	98
10	**1j**	88	41[e]

[a] In pure product after chromatography. [b] Determined by HPLC (Chiralcel OD column). [c] Conversion yield after 15 h. [d] Conversion yield after 96 h. [e] Enantiomeric excess of (*R*)-**9**.

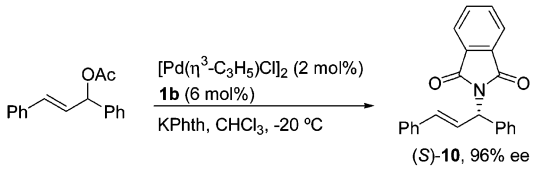
However, the most detrimental effect in the enantioselectivity of the reaction was found in the case of the *p*-tolylsulfenylferrocene **1j** (entry 10), which afforded product **8** in only 40% ee. This result is in agreement with our initial assumption that a high sterically demanding substitution at the sulfur atom in ligands **1** is crucial for reaching a high stereochemical control.[22]

Ligands **1a**−**j** were next evaluated in the palladium-catalyzed reaction of 1,3-diphenyl-2-propenyl acetate with benzylamine. A brief screening of the reaction conditions using the parent ligand **1a** indicated that in this case the addition of Bu_4NCl did not significantly affect the reaction rate and that the reactions in THF gave slightly better enantioselectivities than in $CHCl_3$ or CH_2Cl_2. The results obtained in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mol %) and ligands **1a**−**j** (6 mol %) in THF at room temperature are summarized in Table 2.

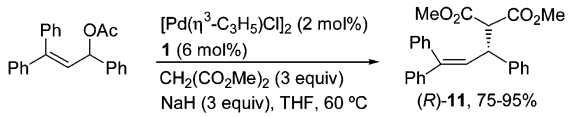
Again very high enantioselectivities, somewhat higher than in the case of the reaction with dimethyl malonate, were observed from the ligands **1a**−**c** [entries 1−3, 97−98% ee for (*S*)-**9**]. Interestingly, in this reaction the bulky diarylphosphines **1f** and **1g** provided even better results, affording (*S*)-**9** with nearly complete enantiocontrol (entries 6 and 7, 99.5% ee). This very high asymmetric performance of ligands **1f** and **1g** in the reaction with benzylamine, compared with that of the reaction with dimethyl malonate (71−73% ee, Table 1), could be tentatively attributed to the high sensitivity of these sterically demanding ligands to the size of the incoming nucleophile. By contrast, the poorest results were obtained using the dicyclohexylphosphine **1e** (entry 5, 40% ee) and the *p*-tolylsulfenylferrocene **1f** (entry 10, 41% ee).

As a second nitrogen nucleophile we briefly studied the palladium-catalyzed reaction of 1,3-diphenyl-2-propenyl acetate with potassium phthalimide (KPhth) in the presence of the ligand **1b** (Scheme 5). As expected, the substitution product [(*S*)-**10**] was obtained in high enantiomeric excess (92.5% ee at room temperature and 96% ee at −20 °C), showing the effectiveness of this family of planar chiral ligands in the palladium-catalyzed substitution reactions of 1,3-diphenyl-2-propenyl acetate.

SCHEME 5. Pd-Catalyzed Reaction of 1,3-Diphenyl-2-propenyl Acetate with Potassium Phthalimide in the Presence of Ligand 1b



SCHEME 6. Pd-Catalyzed Reaction of 1,3,3-Triphenyl-2-propenyl Acetate with Dimethyl Malonate in the Presence of Ligands 1



ligand	ee(%)[a]
1a	59
1b	52
1d	65
1e	82

[a]Determined by HPLC (Chiralcel AD)

As a last example of allylic substitution, we investigated the regio- and stereoselective substitution of 1,3,3-triphenyl-2-propenyl acetate with dimethyl malonate in the presence of several ligands **1**. As in other previously reported studies,[23] this trisubstituted π-allyl precursor proved to be much less reactive than the diphenyl-substituted substrate, harder conditions being required to achieve complete conversions (NaH as base in THF at 60 °C for 3−10 h). Under these conditions (*R*)-**11**[23] was obtained in uniformly lower enantioselectivities (52−82% ee) than those of the analogous (*R*)-**8**. Interestingly, in this reaction the electron-rich phosphine **1e** was found to be the optimal ligand (Scheme 6).

Mechanistic Considerations. To gain mechanistic insight into the origin of the efficiency of ligands **1** in these palladium-catalyzed allylic substitutions, we decided to obtain structural data in the solid state by X-ray diffraction and in solution by NMR spectroscopy. This information could be of great value for future rational ligand design.

Structure of 1a·$PdCl_2$. We first studied the structure of the complex formed from $PdCl_2(CH_3CN)_2$ and ligand **1a**. The stoichiometric reaction of **1a** with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 at room temperature afforded a single complex (**1a**)$PdCl_2$ in 72% yield. Recrystallization from CH_2Cl_2−Et_2O generated X-ray quality crystals of the complex, whose crystallographic analysis[24] proved that **1a** acts effectively as a P,S-bidentate ligand, giving a planar five-membered palladacycle (Figure 2). On the other hand, as expected on steric grounds, in the stereogenic sulfur

(22) A similar trend has been described for the case of the P,S-bidentate ligands **III** (see ref 7).

(23) (a) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033−2046. (b) Dawson, G. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1995**, *36*, 461−462. (c) Dawson, G. J.; Williams, J. M. J.; Coote, S. J. *Tetrahedron*: *Asymmetry* **1995**, *6*, 2535−2536.

(24) The crystallographic data (excluding structure factors) of the complex (**1a**)$PdCl_2$ have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-185296. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

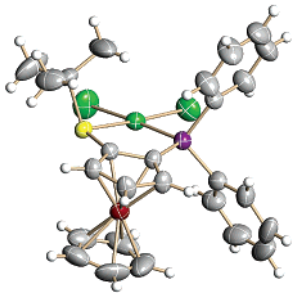


FIGURE 2. Crystal structure of (**1a**)$PdCl_2$.

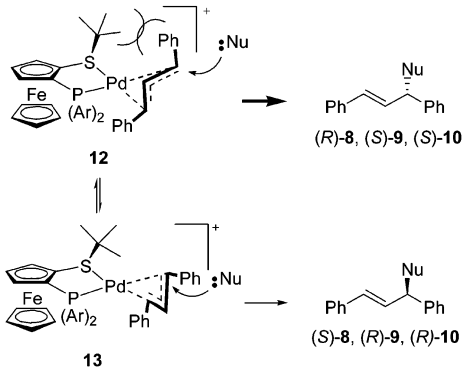


FIGURE 3. Proposed transition state models for the asymmetric allylic substitutions.

center resulting from the S−Pd coordination the bulky *tert*-butyl group is arranged in trans orientation with regard to the iron atom. Interestingly, as in other P,S chelated palladacycles,[7a,4q] the Pd−Cl bond trans to phosphorus is substantially longer than that trans to sulfur (2.35 vs 2.30 Å), reflecting the much stronger trans effect of the phosphine moiety.

Mechanistic Proposal. The plausible key π-allyl palladium intermediates involved in the reaction of 1,3-diphenyl-2-propenyl acetate in the presence of ligands **1** are depicted in Figure 3. Of the four possible Pd−π complex intermediates caused by the chirality of sulfur and the *W*/*M* configuration of the allyl, only those having the *tert*-butyl group on the sulfur oriented trans to the iron of the backbone, **12** and **13**, are assumed to be populated to any extent. The isomers with the opposite configuration at sulfur would possess a severe steric interaction between both moieties. This assumption is consistent with the observed structure of (**1a**)$PdCl_2$. Because the trans effect should direct the nucleophilic addition to the allyl terminus trans to the phosphorus atom, the highly enantioselective formation of the products **8**−**10** with the observed absolute configuration in the presence of ligands (*R*)-**1** indicates a higher reactivity of the cationic (π-allyl)palladium complex intermediate **12** over **13**. According to the Curtin−Hammet principle,[25] it can be reasoned that this (π-allyl)palladium complex **12** (*W*-configuration) would be more reactive than its diastereomer **13** (*M*-configuration), likely because upon nucleophilic addition the steric interaction between the *S*-*tert*-butyl substituent on the ligand and the proximal phenyl group on the π-allyl unit is released.[7] In agreement with this hypothesis, ferrocene ligands with less sterically demanding substituents at the sulfur atom (ligand **1j**) showed a low enantiocontrol.

(25) For a review on Curtin−Hammet kinetics, see: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83−134.

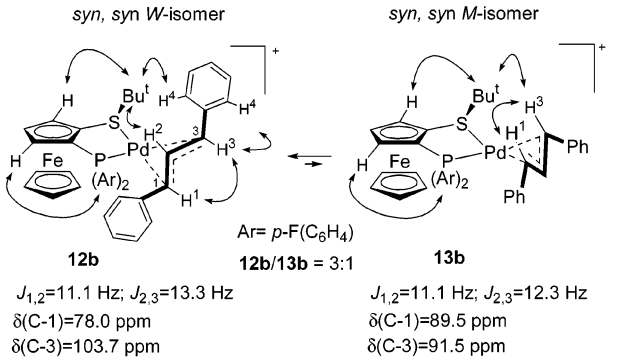


FIGURE 4. Equilibrium of complexes **12b** and **13b** in solution (the SbF_6 counterion has been omitted) and relevant NMR data for their structural assignment (values in CD_3OD).

NMR Study of Pd−Allyl Complexes 12b and 13b. To obtain firm evidence for our mechanistic model, the cationic Pd−allyl complex of one of the most effective ligands, **1b**, was studied. This complex was prepared by reaction of stoichiometric amounts of (*trans*-1,3-diphenylpropenyl) palladium dichloride dimer[26] and ligand **1b** in the presence of silver hexafluoroantimonate. Although we were unable to obtain X-ray quality crystals, the solution structure of the resulting complex was studied by NMR to determine whether **12b** (*W*-type configuration) was the major isomer in the reaction mixture. The ^1H NMR spectrum in $CDCl_3$, CD_2Cl_2, and CD_3OD showed a mixture of two diastereomers in a 3:1 ratio. Their configurations were assigned through a combination of ^1H COSY, ^{13}C, ^1H heteronuclear correlation, and 2D NOESY experiments.[27] As expected, both isomers showed *syn*,*syn* arrangement of the allyl unit, as evidenced by the coupling constants between the allylic protons H^1−H^2 and H^2−H^3, higher than 10 Hz. The strong NOE cross-peak observed between the two terminal allylic protons H^1 and H^3 in both complexes, compared to the weak NOE observed between H^2 and H^1 (or H^3), also supported the *syn*,*syn* configuration. The unambiguous assignment of the major isomer **12b** as *syn*,*syn W*-configuration is based on several critical NOE contacts (Figure 4). A NOE cross signal between the central allylic proton H^2 and the protons on the *tert*-butyl group, coupled with the absence of NOE between the terminal allylic proton H^3 and the *tert*-butyl group, clearly indicates that H^2 and the *tert*-butyl were on the same face of the palladium complex, which means a *W*-conformation of the π-allyl moiety. The observed NOEs cross-peaks of the *ortho* protons H^4 of the phenyl group on the allylic moiety with both the *tert*-butyl group and H^3 also supported this stereochemical assignment. On the other hand, a NOE signal between H^3 and the protons on the *tert*-butyl group in the minor isomer

(26) (a) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301−6311. (b) Von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pflatz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Ruegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265−284.

(27) Because of the low solubility of **12b**/**13b** in $CDCl_3$ and to avoid the overlap of key signals in the CD_2Cl_2 ^1H NMR spectrum, CD_3OD was the solvent of choice for the NMR study.

13b, coupled with the mentioned NOE contact between H^1 and H^3, were the most significant spectral data for its assignment as the *syn*,*syn M*-isomer (Figure 4).

Since the high ee values of the products (96−98% ee) obtained in the palladium-catalyzed reaction of 1,3-diphenyl-2-propenyl acetate in the presence of ligand **1b** do not reflect the isomeric distribution of the intermediate allyl complexes **12b**/**13b**, a fast equilibrium among both components (Curtin-Hammet conditions) must exist, the observed 3:1 ratio of **12b**/**13b** corresponding to the thermodynamic equilibrium mixture.

A correlation between the ^{13}C NMR chemical shifts of the carbons on the π-allyl termini and their electrophilicity, provided by the different trans influences of the heteroatom donors, has been reported[28] and used as a tool for predicting the reactivity.[29] In our case, the ^{13}C NMR data for isomers **12b** and **13b** are also consistent with the observed experimental results. As shown in Figure 4, in both diastereomers the chemical shifts for the terminal carbons of the allyl moiety trans to the phosphorus (C-3) are more deshielded (δ 103.7 ppm for **12b** and δ 91.5 ppm for **13b**) than those trans to the sulfur (C-1; δ 78.0 ppm for **12b** and δ 89.5 ppm for **13b**), which means that C-3 (trans to phosphorus) of both **12b** and **13b** would be more sensitive than C-1 for nucleophilic attack, reflecting therefore the higher trans influence exerted by the phosphine moiety.[30] In addition, the increased downfield observed for C-3 of **12b** (δ 103.7 ppm) versus C-3 of **13b** (δ 89.5 ppm), and the higher difference in chemical shift between C-3 and C-1 in **12b** ($\Delta\delta$ 26 ppm), compared to that observed for the same carbons in **13b** ($\Delta\delta$ 2 ppm), allow us to reason that **12b** is more reactive than **13b**. All these data support the general model proposed in Figure 3 in which nucleophilic addition occurs trans to phosphorus in complex **12** and are consistent with the absolute configuration of the products **8**−**10** and their enantiopurity. In addition, the somewhat higher reactivity exhibited by the fluorosubstituted ligands **1b** and **1c** could be rationalized by the fact that these electron-deficient phosphines would emphasize the electrophilicity of the cationic π-allyl complex intermediate **12**.

Conclusions

A series of bidentate thioether-phosphino ferrocene ligands **1**, having exclusively planar chirality, have been readily prepared from enantiopure sulfinylferrocenes. It has been demonstrated that this family of ligands provides very high enantioselectivities in the Pd-catalyzed allylic substitution of 1,3-diphenylpropenyl acetate with malonate and nitrogen nucleophiles. An attractive feature of the preparation of this ligand system is that it provides easy fine-tuning of its electronic and steric properties by modifying the groups attached to the sulfur and phosphorus atoms. We are currently testing metal complexes of this family of chiral ligands in other asymmetric transformations. A study of the cationic metal complexes of ligands **1** as chiral Lewis acids in asymmetric catalysis is an obvious extension of this work. The results of these investigations will be reported from these laboratories in due course.

Experimental Section[31]

(R_S)-*tert*-Butylsulfinylferrocene (2a).[13b,15] To a suspension of ferrocene (3.01 g, 16.18 mmol) in THF (7.5 mL), cooled to 0 °C, was added dropwise a 1.7 M solution of *t*-BuLi in pentane (9.8 mL, 16.7 mmol). The reaction was stirred at 0 °C for 20 min, and it was diluted with pentane (25 mL). To the resulting mixture was slowly added at 0 °C a solution of a 87% ee sample of (*R*)-*S*-*tert*-butyl *tert*-butanethiosulfinate[14] (1.55 g, 7.97 mmol) in pentane (5 mL). The mixture was stirred at 0 °C for 1 h, and brine (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 1:2) to afford sulfoxide (*R*)-**2a** (1.70 g, 73%) with 87% ee, as a yellow-orange solid. A single recrystallization from CH_2Cl_2−hexane (1:1) afforded (*R*)-**2a** (1.02 g, 60%) with >99% ee. $[\alpha]^{20}_D = -355$ (*c* 0.5, $CHCl_3$) {lit.[15] $[\alpha]^{20}_D = -339$ (*c* 0.5, $CHCl_3$), 95% ee}; mp 150−151 °C (lit.[15] mp 149−150 °C). ^1H NMR (200 MHz): δ 4.68 (m, 1H), 4.41 (m, 2H), 4.38 (s, 5H), 4.35 (m, 1H), 1.12 (s, 9H). HPLC: Daicel Chiralcel OD, *i*-PrOH/hexane 2/98, flow rate 0.70 mL/min, t_R 19.3 min (*R*)-isomer and 24.3 min (*S*)-isomer, 254 nm.

(S_S)-*p*-Tolylsulfinylferrocene (2b).[11i,15,18] To a solution of ferrocene (9.62 g, 51.70 mmol) in THF (85 mL), cooled to 0 °C, was slowly added a 1.7 M solution of *t*-BuLi in pentane (26.0 mL, 44.2 mmol). The solution was stirred at 0 °C for 2 h, then it was cooled to −78 °C and slowly transferred via cannula to a cold (−78 °C) solution of (−)-(*S*)-*l*-menthyl *p*-toluenesulfinate[32] (10.0 g, 34.0 mmol; ≥99% ee) in THF (51 mL). The resulting mixture was stirred at −78 °C for 2 h, and it was treated with brine (100 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 1:1) to afford sulfoxide (*S*)-**2b** (4.4 g, 40%) with 97% ee, as a yellow solid. A single recrystallization from *n*-hexanes−Et_2O 3:1 afforded sulfoxide (*S*)-**2b** (2.2 g, 50%) with >99% ee. $[\alpha]^{20}_D = +303$ (*c* 0.5, $CHCl_3$) {lit.[15] $[\alpha]^{20}_D = +305$ (*c* 0.5, $CHCl_3$), 100% ee}; mp 143−144 °C (lit.[33] mp 142−144 °C). ^1H NMR (200 MHz): δ 7.52 (d, J = 8.3, 2H), 7.25 (d, J = 8.4 Hz, 2H), 4.61 (dt, J = 1.5, 2.3 Hz, 1H), 4.39−4.35 (m, 7H), 4.33−4.31 (m, 1H), 2.37 (s, 3H). HPLC: Daicel Chiralcel OD, *i*-PrOH/hexane 10/90, flow rate 0.80 mL/min, t_R 13.7 min (*R*)-isomer and 15.1 min (*S*)-isomer, 254 nm.

General Procedure for Synthesis of Phosphines 3a−g. To a solution of sulfoxide (*R*)-**2a** (0.70 g, 2.41 mmol) in THF (24 mL) was added a 1.7 M solution of *t*-BuLi in pentane (2.1 mL, 3.62 mmol). The mixture was stirred at −78 °C for 1.5 h, and the corresponding chlorophosphine (3.62 mmol) was added at −78 °C. The reaction mixture was stirred for 30 min, and it was treated with water (20 mL). The organic layer was

(28) (a) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620−628. (b) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133−142. (c) Malet, R.; Moreno-Mañas, M.; Parella, T.; Pleixats, R. *Organometallics* **1995**, *14*, 2463−2469. (d) Macsári, I.; Szabó, K. J. *Organometallics* **1999**, *18*, 701−708.

(29) (a) Aranyos, A.; Szabó, K. J.; Castaño, A. M.; Bäckvall, J.-E. *Organometallics* **1997**, *16*, 1058−1064. (b) Moreno-Mañas, M.; Pajuelo, F.; Parella, T.; Pleixats, R. *Organometallics* **1997**, *16*, 205−209. (c) Macsári, I.; Hupe, E.; Szabó, K. J. *J. Org. Chem.* **1999**, *64*, 9547−9556.

(30) In accordance with the ^{13}C NMR tendency, the chemical shift of the proton on the π-allyl terminus trans to phosphorus (H^3) in the major isomer **12b** was 6.85 ppm, whereas that trans to sulfur was 5.90 ppm (in CD_3OD), indicative of the greater π-accepting ability of the phosphine as compared to the thioether.

(31) General Methods are found within the Supporting Information for ref 10.

(32) Solladié, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173−174.

(33) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502−2505.

separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography or by precipitation (as indicated in each case). For the synthesis and characterization data of ferrocenes **3b**−**j**, see Supporting Information.

(R_{Fc},R_S)-1-(*tert*-Butylsulfinyl)-2-(diphenylphosphino)-ferrocene (3a).[18] Chlorophosphine: PPh_2Cl. Purification by flash chromatography (*n*-hexanes−EtOAc 1:1). Yield: 91%, yellow solid. $[\alpha]^{20}_D = -437$ (*c* 0.4, $CHCl_3$) {lit.[18] $[\alpha]^{20}_D = -303$ (*c* 3.0, benzene)}; mp 162−163 °C (lit.[18] mp 162−163 °C). ^{1}H NMR (300 MHz): δ 7.61−7.52 (m, 2H), 7.35−7.28 (m, 3H,), 7.27−7.14 (m, 5H), 4.60−4.56 (m, 1H), 4.53−4.48 (m, 1H), 4.22−4.18 (m, 1H), 4.10 (s, 5H), 0.98 (s, 9H); ^{13}C NMR (75 MHz): 140.6, 140.4, 138.8, 138.6, 135.8, 135.5, 132.9, 132.7, 129.2, 128.1, 127.9, 127.8, 90.1, 89.8, 76.5, 76.2, 75.3, 75.2, 74.0, 72.5, 71.5, 55.9, 23.7. IE MS: *m*/*z* 474 (M^+, 13), 418 (91), 352 (100), 228 (25), 170 (22).

General Procedure for Reduction with $HSiCl_3$/Et_3N. To a solution of sulfoxide (0.30 mmol) in toluene (4 mL) were successively added Et_3N (400 μL, 3.0 mmol) and $HSiCl_3$ (400 μL, 4.5 mmol). The mixture was heated at reflux for 12 h, and it was poured into a mixture of CH_2Cl_2 (10 mL) and 10% aqueous solution of NaOH (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated. The residue was purified by flash chromatography. For the synthesis and characterization data of ferrocenes **1b**−**j**, see Supporting Information.

(*R*)-2-(*tert*-Butylsulfenyl)-1-(diphenylphosphino)ferrocene (1a). Starting sulfoxide: **3a**. Chromatography: *n*-hexanes−EtOAc 5:1. Yield: 79%, yellow solid. $[\alpha]^{20}_D = -200$ (*c* 0.5, $CHCl_3$); ee > 99%; mp 148−149 °C. ^{1}H NMR (300 MHz): δ 7.68−7.58 (m, 2H), 7.39−7.28 (m, 5H), 7.28−7.20 (m, 3H), 4.71−4.67 (m, 1H), 4.50−4.46 (m, 1H), 4.15−4.12 (m, 1H), 3.98 (s, 5H), 1.00 (s, 9H). ^{13}C NMR (75 MHz): δ 139.9, 138.3, 135.3, 135.0, 133.0, 132.7, 128.9, 127.9, 83.1, 81.0, 80.0, 73.4, 71.5, 70.6, 46.0, 31.0. IE MS: *m*/*z* 458 (M^+, 95), 402 (100), 337 (52), 302 (11), 217 (27), 170 (31), 121 (10). Anal. Calcd for $C_{26}H_{27}$FePS: C, 68.17; H, 5.94; S, 7.00. Found: C, 67.78; H, 6.10; S, 6.75. HPLC: Daicel Chiralcel OD, *i*-PrOH/Hexane 0.2/99.8, flow rate 0.50 mL/min, t_R 22.0 min (*R*)-isomer and 26.1 min (*S*)-isomer, 254 nm.

(R_{Fc},R_S)-2-Amino-1-(*tert*-butylsulfinyl)ferrocene (4).[34] To a cold solution (−78 °C) of sulfoxide **2a** (0.50 g, 1.72 mmol) in THF (12 mL) was added a 1.7 M solution of *t*-BuLi in pentane (1.22 mL, 2.07 mmol) under argon. The mixture was stirred at room temperature for 1.5 h, and then a solution of tosyl azide (0.44 g, 2.24 mmol) was added at −78 °C. The resulting solution was allowed to reach room temperature for 4 h, and a solution of $Bu_4N^+I^-$ (0.25 g, 0.69 mmol) and $NaBH_4$ (0.26 g, 6.88 mmol) in H_2O (5 mL) was added. The reaction mixture was stirred at room temperature for 12 h, and brine was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 30 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated. The resulting mixture was purified by flash chromatography (CH_2Cl_2−EtOAc 3:1) to afford the aminosulfoxide **4** (0.39 g, 75%, orange solid). $[\alpha]^{20}_D = -343$ (*c* 0.1, $CHCl_3$); ee > 98%; mp 163−164 °C. ^{1}H NMR (200 MHz): δ 4.27 (s, 5H), 4.09 (t, *J* = 1.8 Hz, 1H), 4.01 (m, 1H), 3.98 (t, *J* = 2.5 Hz, 1H), 3.64 (bs, 2H), 1.20 (s, 9H). HPLC: Daicel Chiralpak AS, *i*-PrOH/Hexane 5/95, flow rate 0.70 mL/min, t_R 9.9 min (*S*)-isomer and 12.2 min (*R*)-isomer, 254 nm.

(*R*)-2-Amino-1-(*tert*-butylsulfenyl)ferrocene (5). Following the general procedure for the reduction with $HSiCl_3$/Et_3N, compound **5** was obtained from **4** in 79% yield as an orange solid after chromatographic purification (*n*-hexanes−EtOAc 1:1). $[\alpha]^{20}_D = -11$ (*c* 0.15, $CHCl_3$); mp 75−76 °C. ^{1}H NMR (300 MHz): δ 4.13 (m, 2H), 4.06 (s, 5H), 3.96 (s, 1H), 2.94 (bs, 2H), 1.23 (s, 9H). ^{13}C NMR (75 MHz): δ 108.9, 71.3, 70.1, 65.8, 63.3, 57.6, 46.5, 30.8. ApcI MS: *m*/*z* 290.0 (M^++H), 234.0, 232.9, 201.0. Anal. Calcd for $C_{14}H_{19}$FeNS: C, 58.14; H, 6.62; N, 4.48; S, 11.09. Found: C, 58.44; H, 6.47; N, 4.57; S, 11.11.

(R_{Fc},R_S)-1-(*tert*-Butylsulfinyl)-2-[(diphenylphosphino)-methyl]ferrocene (7). To a solution of 2-hydroxymethyl sulfinylferrocene **6**[15] (600 mg, 1.87 mmol) in CH_2Cl_2 (18 mL) were added Ac_2O (400 μL, 2.8 mmol), Et_3N (260 μL, 2.8 mmol), and a catalytic amount of DMAP. The mixture was stirred at room temperature overnight, and NH_4Cl (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was evaporated. The resulting mixture was purified by flash chromatography (*n*-hexanes−EtOAc 2:1) to afford 2-(acetyloxy)methyl-1-(*tert*-butylsulfinyl)ferrocene (540 mg, 79%, orange gummy oil). ^{1}H NMR (200 MHz): δ 5.30 (s, 2H, CH_2), 4.45 (t, *J* = 1.9 Hz, 1H), 4.36 (s, 5H), 4.32 (m, 2H), 2.00 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (50 MHz): δ 170.6, 83.1, 82.4, 72.2, 70.7, 69.9, 60.2, 55.8, 20.8. To a solution of this acetate (400 mg, 1.1 mmol) in AcOH (10 mL) was added $HPPh_2$ (286 μL, 1.65 mmol). The mixture was stirred at 80 °C for 16 h, and the solvent was evaporated. The resulting mixture was purified by flash chromatography (*n*-hexanes−EtOAc 4:1) to afford the phosphine **7** (530 mg, 98%, orange gummy oil). $[\alpha]^{20}_D = -239$ (*c* 0.35, $CHCl_3$). ^{1}H NMR (200 MHz): δ 7.60−7.27 (m, 10H), 4.35 (s, 5H), 4.23 (s, 1H), 4.15 (t, *J* = 2.4 Hz, 1H), 3.92 (s, 1H), 3.84 (dd, *J* = 1.4, 15.4 Hz, 1H), 3.57 (d, *J* = 15.6 Hz, 1H), 1.22 (s, 9H). ^{13}C NMR (50 MHz): δ 139.1 (m), 133.2 (d, J_{P-C} = 19.7 Hz), 132.2 (d, J_{P-C} = 18.3 Hz), 128.7−128.2 (m), 85.9 (d, J_{P-C} = 15.5 Hz), 81.1, 71.5 (d, J_{P-C} = 9.9 Hz), 71.0, 69.5, 68.8, 56.4, 26.8 (d, J_{P-C} = 14.1 Hz), 23.5.

General Procedure for Pd-Catalyzed Allylic Alkylation of 1,3-Diphenyl-2-propenyl Acetate with Dimethyl Malonate. Synthesis of (*R*,*E*)-Methyl 2-Carbomethoxy-3,5-diphenylpent-4-enoate [(*R*)-8].[35] A mixture of ligand **1** (0.02 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 0.006 mmol) [and Bu_4NCl (8.8 mg, 0.03 mmol) when it was used] in dry $CHCl_3$ (1 mL) was stirred at room temperature for 1 h, and it was treated with a solution of 1,3-diphenyl-2-propenyl acetate (80.0 mg, 0.32 mmol) in dry $CHCl_3$ (1 mL). To the resulting mixture were successively added *N*,*O*-bis(trimethylsilyl)acetamide (237 μL, 0.96 mmol) and dimethyl malonate (108 μL, 0.96 mmol). The reaction was monitored by TLC until the starting material was consumed (reaction times varied within a wide range: 10−30 min for ligands **1a**−**d**, **1f**, and **1j**; 50 min and 3 h for ligands **1g** and **1e**, respectively, and 50−96 h for ligands **1h**−**i**). Then it was diluted with diethyl ether and washed with saturated aqueous NH_4Cl solution. The organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-hexane−EtOAc 7:1) to afford (*R*)-**8** as a colorless oil. The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[35] ^{1}H NMR (200 MHz): δ 7.34−7.20 (m, 10H), 6.49 (d, *J* = 16.1 Hz, 1H), 6.33 (dd, *J* = 8.1, 15.6 Hz, 1H), 4.27 (dd, *J* = 8.1, 10.7 Hz, 1H), 3.96 (d, *J* = 10.7 Hz, 1H), 3.71 (s, 3H), 3.52 (s, 3H). HPLC: Daicel Chiralcel OD, *i*-PrOH/Hexane 2/98, flow rate 0.20 mL/min, t_R 44.8 min (*R*)-isomer and 47.2 min (*S*)-isomer, 254 nm.

General Procedure for Pd-Catalyzed Allylic Amination of 1,3-Diphenyl-2-propenyl Acetate with Benzylamine. Synthesis of (*S*,*E*)-*N*-Benzyl-(1,3-diphenyl-2-propenyl)amine [(*S*)-9].[36] A mixture of ligand **1** (0.02 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 0.006 mmol) in THF (1 mL) was

(34) Although compound **4** was previously described by us (see ref 12), an improved procedure has been achieved.

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stirred at room temperature for 1 h, and it was treated with a solution of 1,3-diphenyl-2-propenyl acetate (80.0 mg, 0.32 mmol) in THF (1 mL). To the resulting mixture was added benzylamine (105 μL, 0.96 mmol). The reaction was monitored by TLC until the starting material was consumed. Then it was diluted with diethyl ether and washed with saturated aqueous NH_4Cl solution. The organic layers were dried ($MgSO_4$) and filtered, and the solvents evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 7:1) to afford (*S*)-**9** as a colorless oil. The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[36] ^{1}H NMR (200 MHz): δ 7.52−7.29 (m, 15 H), 6.65 (d, J = 16.1 Hz, 1H), 6.40 (dd, J = 7.0, 15.6 Hz, 1H), 4.46 (d, J = 7.5 Hz, 1H), 3.84 (s, 2H), 1.82 (bs, 1H). HPLC: Daicel Chiralpak AD, *i*-PrOH/Hexane 2/98, flow rate 0.50 mL/min, t_R 16.5 min (*R*)-isomer and 18.0 min (*S*)-isomer, 254 nm.

General Procedure for Pd-Catalyzed Allylic Amination of 1,3-Diphenyl-2-propenyl Acetate with Potassium Phthalimide. Synthesis of 1-(*N*-Phthaloyl)-1,3-diphenylprop-2-ene [(*S*)-10].[37] A mixture of ligand **1** (0.02 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 0.006 mmol) in dry $CHCl_3$ (1 mL) was stirred at room temperature for 1 h, and it was transferred via cannula into a suspension of potassium phthalimide (177.8 mg, 0.96 mmol) in dry $CHCl_3$ (1 mL). The resulting mixture was treated with a solution of 1,3-diphenyl-2-propenyl acetate (80.0 mg, 0.32 mmol) in dry $CHCl_3$ (1 mL). The reaction was monitored by TLC until the starting material was consumed. Then it was diluted with diethyl ether and washed with saturated aqueous NH_4Cl solution. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvents evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 9:1) to afford (*S*)-**10** as a yellow solid. The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[37] ^{1}H NMR (200 MHz): δ 7.87−7.25 (m, 14H), 7.08 (dd, J = 8.6, 16.1 Hz, 1H), 6.72 (d, J = 16.1 Hz, 1H), 6.13 (d, J = 8.6 Hz, 1H). HPLC: Daicel Chiralcel OD, *i*-PrOH/Hexane 2/98, flow rate 0.50 mL/min, t_R 19.0 min (*S*)-isomer and 24.4 min (*R*)-isomer, 254 nm.

General Procedure for Pd-Catalyzed Allylic Alkylation of 1,1,3-Triphenyl-2-propenyl Acetate with Dimethyl Malonate. Synthesis of (*R*)-Methyl 2-Carbomethoxy-3,5,5-triphenylpent-4-enoate [(*R*)-11].[23] A mixture of ligand **1** (0.02 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 0.006 mmol) in dry THF (1 mL) was stirred at room temperature for 30 min, and it was treated with a solution of 1,1,3-triphenyl-2-propenyl acetate (98.5 mg, 0.30 mmol) in dry THF (1 mL). The resulting mixture was transferred via cannula into a solution of sodiodimethylmalonate (103 μL, 0.90 mmol) in THF (1 mL) and heated at 60 °C. The reaction was monitored by TLC until the starting material was consumed. Then it was diluted with diethyl ether and washed with saturated aqueous NH_4Cl solution. The organic layers were dried ($MgSO_4$) and filtered, and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-hexane−EtOAc 4:1) to afford (*R*)-**11** as a white solid. The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[23] ^{1}H NMR (200 MHz): δ 7.50−7.00 (m, 15 H), 6.35 (d, J = 7.3 Hz, 1 H), 4.25 (t, J = 7.3 Hz, 1H), 3.90 (d, J = 7.3 Hz, 1H), 3.70 (s, 3H), 3.50 (s, 3H). HPLC: Daicel Chiralpak AD, *i*-PrOH/Hexane 1/99, flow rate 1.0 mL/min, t_R 16.1 min (*R*)-isomer and 18.7 min (*S*)-isomer, 254 nm.

Synthesis of Complex (1a)·PdCl$_2$. To a solution of **1a** (100 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was added a solution of $Pd(CH_3CN)_2Cl_2$ (57 mg, 0.22 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred 15 min, and then it was concentrated to dryness. The solid was recrystalized from CH_2Cl_2-Et_2O to afford **(1a)**·$PdCl_2$ (100 mg, 72%) as orange crystals. $[\alpha]^{20}_D$ = −423 (*c* 0.1, $CHCl_3$); mp > 200 °C (decomp). ^{1}H NMR (300 MHz): δ 8.03−7.82 (m, 4H), 7.55−7.30 (m, 6H), 4.92 (m, 1H), 4.87 (m, 1H), 4.34 (m, 1H), 4.14 (s, 5H), 1.32 (s, 9H). ^{13}C NMR (75 MHz): 134.6, 134.4, 132.8, 132.6, 132.0, 131.7, 131.6, 130.9, 130.0, 129.1, 129.0, 128.8, 128.5, 128.3, 86.0, 83.6, 80.3, 80.2, 74.9, 74.8, 72.6, 71.9, 59.1, 30.9. Anal. Calcd for $C_{26}H_{27}Cl_2FePPdS$: C, 49.12; H, 4.28. Found: C, 48.76; H, 4.55.

Synthesis of (*R*)-2-(*tert*-Butylsulfenyl)-1-[bis(4-fluorophenyl)phosphino]ferrocene Palladium (1,3-Diphenylpropenyl) Hexafluoroantimonate (12b, 13b). A solution of (*trans*-1,3-diphenylpropenyl) palladium dichloride dimer[26] (51.6 mg, 0.065 mmol) and ligand **1b** (74.1 mg, 0.15 mmol) in CH_2Cl_2/THF/MeOH 5:4:4 (13 mL) was stirred at 50 °C for 3 h, cooled to room temperature, and treated with $AgSbF_6$ (44.7 mg, 0.13 mmol) in 3 mL of THF. After 20 min, the mixture was filtered through a pad of Celite, the filtrate was washed with aqueous saturated NaCl solution and dried ($MgSO_4$), and the solvent was evaporated. The resulting orange solid was recrystalized from CH_2Cl_2−*n*-hexane to afford π-allyl complex **12b/13b** (47 mg, 70%, orange crystals) as a 3:1 mixture of isomers **12b** and **13b**, respectively, that could not be separated by flash chromatography. $[\alpha]^{20}_D$ = −458 (*c* 0.085, CH_2Cl_2); mp > 200 °C (decomp). ^{1}H NMR (300 MHz, CD_3OD): δ (**12b**) 8.03−7.25 (m, 14H), 6.85 (dt, J = 2.2, 8.7 Hz, 2H), 6.63 (dd, J = 9.0, 13.3 Hz, 1H), 630 (ddd, J = 5.5, 8.5, 11.5 Hz, 2H), 5.90 (d, J = 11.1 Hz, 1H), 5.12 (m, 1H), 5.10 (t, J = 2.7 Hz, 1H), 4.58 (m, 1H), 4.25 (s, 5H), 0.75 (s, 9H). ^{1}H NMR (300 MHz, CD_3OD): δ (**13b**) 8.03−7.25 (m, 14H), 7.15 (ddd, J = 5.5, 8.7, 14.2 Hz, 2H), 7.02 (dt, J = 1.8, 8.7 Hz, 2H), 6.13 (d, J = 12.3 Hz, 1H), 5.70 (t, J = 11.1 Hz, 1H), 5.05 (m, 2H), 4.50 (m, 1H), 4.12 (s, 5H), 1.12 (s, 9H). API-ES$^+$ MS *m*/*z* 797 (M^++ 4), 795 (M^++ 2), 793 (M^+), 792 (M^+ − 1), 791 (M^+ − 2).

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Supporting Information Available: Isolation and characterization data of compounds **1b**−**j** and **3b**−**j**, copies of proton and carbon NMR spectra of all new compounds, and X-ray crystallographic studies of (**1a**)$PdCl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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