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Synthesis, Molecular Structure, and Catalytic Evaluation of Centrostereogenic Ferrocenophane Phosphines

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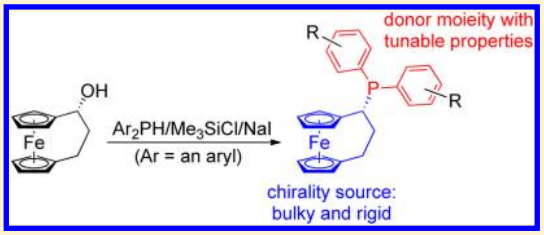
Supporting Information

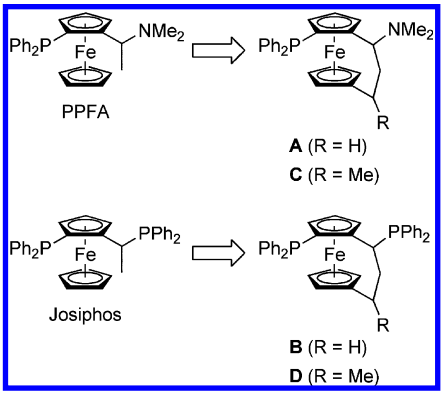
ABSTRACT: 1,1′-[(1*R*)-1-Diarylphosphino-1,3-propanediyl]ferrocenes, where aryl = phenyl, 2-tolyl, 4-tolyl, mesityl, 4-anisyl, 4-(trifluoromethyl)-phenyl, were prepared as new chiral ferrocenophane phosphines featuring only central chirality in good yields by the reaction of the corresponding chiral alcohol, 1,1′-[(1*R*)-1-hydroxy-1,3-propanediyl]ferrocene, and diarylphosphines in the presence of chlorotrimethylsilane and sodium iodide. These phosphines were studied as ligands in palladium(II) complexes and further evaluated in two mechanistically different model catalytic reactions, namely in Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate, and in enantioselective aza-Morita-Baylis-Hillman reactions of aromatic *N*-sulfonyl imines with methyl vinyl ketone.



INTRODUCTION

The enormous practical success of chiral phosphinoferrocene ligands[1,2] has prompted the design of new phosphinoferrocene donors with modified structures. Among these compounds, analogues with bridged cyclopentadienyl rings, typically [3]-ferrocenophane derivatives, emerged as structurally interesting congeners, largely owing to their constrained geometry (Chart 1). Already in 1996, Weissensteiner et al.[3,4] reported the

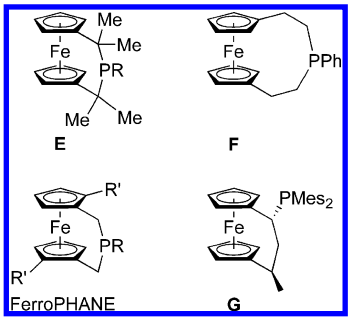
Chart 1



synthesis of ferrocenophane phosphinoamines (**A**) and diphosphines (**B**) as congeners of the archetypical PPFA and Josiphos type ligands (Chart 1), in which one of the two functional moieties available is attached to the ansa bridge. A few years later, Erker and co-workers[5] reported the formally homologous compounds **C** and **D** (Chart 1) possessing an additional chirality center within the butane-1,3-diyl ansa chain. The synthesis of **C**- and **D**-type compounds capitalized upon the newly discovered efficient Mannich-type condensation of 1,1′-diacetylferrocene with secondary amines that provided an elegant route to the parent chiral [3]ferrocenophane.[6] Most recently, Šebesta et al. extended the chemistry of PPFA- and Josiphos-type ferrocenophane ligands to [5]ferrocenophanes,[7] while Takahashi and Ogasawara demonstrated the viability of a ring-closing metathesis route toward bridged phosphaferrocenes.[8]

In parallel, nonchiral ferrocenophane phosphines having the phosphorus atom in the middle of the ferrocenophane bridge of different lengths were developed by Hey-Hawkins (**E** in Chart 2)[9,10] and Curnow (**F** in Chart 2),[11] resulting from metathesis

Chart 2



reactions of the respective dicyclopentadienide salts and iron(II) chloride. C_2-symmetric, planar chiral counterparts of the former compound (FerroPHANE in Chart 2) were introduced by Marinetti et al.[12] and extensively evaluated as organocatalysts (chiral Lewis bases) for enantioselective [3 + 2] cyclization reactions.[13]

From the previous list, it becomes obvious that the vast majority of ferrocenophane phosphines reported to date are either achiral or combine planar and central chirality. The only

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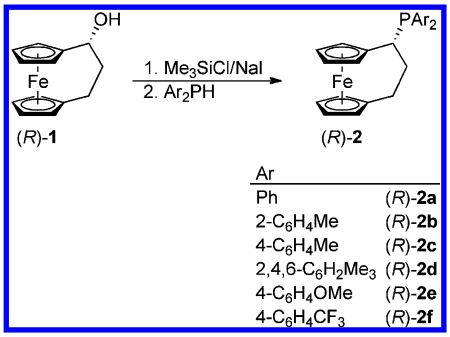
compound possessing only central chirality appears to be 1,1′-[(1*R*,3*R*)-1-(dimesitylphosphino)-3-methyl-1,3-propanediyl]-ferrocene (**G** in Chart 2), which was prepared by Erker et al. and studied for its reactivity toward tris(pentafluorophenyl)-borane.[14] The lack of *C-only chiral* ferrocenophane phosphines led us to design and study C-chiral monophosphine donors derived from [3]ferrocenophane.[15] With this contribution, we report the preparation and structural characterization of these compounds and their Pd(II) complexes and the evaluation of their catalytic performance in model Pd-catalyzed asymmetric allylic alkylations and in Lewis base mediated aza-Morita-Baylis-Hillman reactions.

RESULTS AND DISCUSSION

Synthesis of the Phosphine Ligands. Ferrocene monophosphines featuring only central chirality, viz 1,1′-[(1*R*)-1-(diarylphosphino)-1,3-propanediyl]ferrocenes ((*R*)-**2**), were prepared by a simple one-pot procedure from chiral alcohol (*R*)-**1** (Scheme 1). This alcohol, which was obtained in several steps from [3]ferrocenophane-1-one[16] as described in the literature,[17] was reacted successively with iodotrimethylsilane (generated in situ from chlorotrimethylsilane and sodium iodide)[18] and the appropriate diarylphosphine in dry acetonitrile to afford the corresponding ferrocenophane phosphines **2a**–**f** in good to excellent isolated yields. The phosphinylation reaction[19,4a] proceeded smoothly with the retention of configuration at the stereogenic carbon atom. The secondary phosphine was used in excess, as it prevents the oxidation of the ferrocenophane phosphines during the subsequent workup and chromatographic purification. Attempts at obtaining an analogue bearing the dicyclohexylphosphine moiety were unsuccessful; only the starting alcohol was recovered from the reaction mixture.

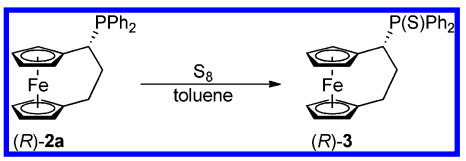
Scheme 1. Preparation of [3]Ferrocenophane Phosphines 2



Ar	
Ph	(*R*)-**2a**
2-C_6H_4Me	(*R*)-**2b**
4-C_6H_4Me	(*R*)-**2c**
2,4,6-$C_6H_2Me_3$	(*R*)-**2d**
4-C_6H_4OMe	(*R*)-**2e**
4-$C_6H_4CF_3$	(*R*)-**2f**

In order to prepare a better crystallizing, simple derivative suitable for structure determination, the parent phosphine (*R*)-**2a** was converted to its corresponding phosphine sulfide (*R*)-**3** by sulfidation with elemental sulfur (Scheme 2). Subsequent crystallization from hot acetonitrile afforded single crystals suitable for X-ray diffraction analysis. The view of the molecular structure of phosphine sulfide (*R*)-**3** shown in Figure 1

Scheme 2. Preparation of Phosphine Sulfide (*R*)-3



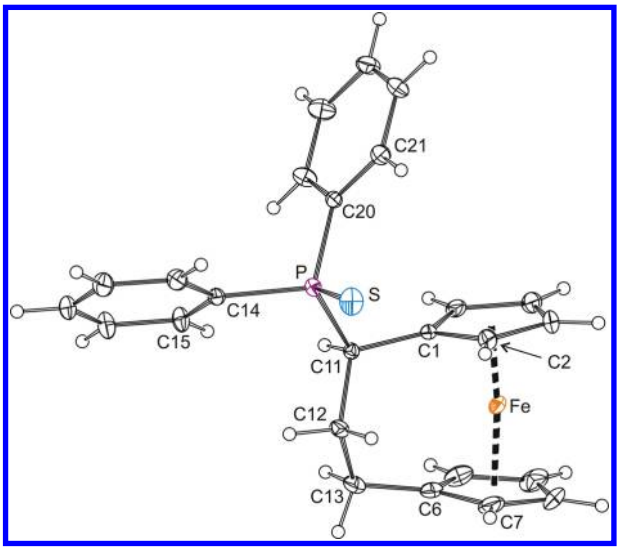


Figure 1. PLATON plot of the molecular structure of compound (*R*)-**3** showing the atom-labeling scheme and displacement ellipsoids at the 30% probability level. Note that carbon atoms in the aromatic rings are numbered consecutively; hence, only the labels of the pivotal carbon atoms and their adjacent carbon atoms are shown for clarity.

corroborates both the formulation and the chirality at the stereogenic carbon atom. Structural data for (*R*)-**3** are presented and discussed below together with those of Pd(II) complexes obtained from phosphine (*R*)-**2a**.

Compounds (*R*)-**2a**–**f** and (*R*)-**3** were characterized by multinuclear NMR spectroscopy and by mass spectrometry with electron impact and electrospray ionization. IR spectra and optical rotations were recorded only for the archetypal representative (*R*)-**2a** and its sulfide (*R*)-**3**, which could be efficiently purified by crystallization.[20] The $^{31}P\{^1H\}$ NMR spectra of phosphines **2a**–**f** display a single resonance, whose position varies with the substituents at the benzene rings (δ_P from ca. −27 for (*R*)-**2b** to ca. −2 for (*R*)-**2a**); the $^{31}P\{^1H\}$ NMR signal of the phosphine sulfide (*R*)-**3** appears shifted to a lower field (δ_P 49.3). The ^1H NMR spectra of **2a**–**f** and **3** comprise signals due to the five nonequivalent hydrogens within the ferrocenephane bridge and eight signals of the diastereotopic ferrocene protons, both forming characteristic patterns (for the "aliphatic" part of the ^1H NMR spectrum of (*R*)-**2a**, see Figure 2). Finally, the $^{13}C\{^1H\}$ NMR spectra of **2a**–**f** and **3** display three characteristic phosphorus-coupled doublets for the carbon atoms constituting the ansa bridge ($C_5H_4CH_2$, δ_C ca. 25 ($^3J_{PC}$ = 11–14 Hz); C_5H_4CHP, δ_C ca. 33–36 ($^1J_{PC}$ = 7–16 Hz); $C_5H_4CH_2CH_2$:, δ_C ca. 39–40 ($^3J_{PC}$ = 24–39 Hz)) and 10 signals for carbons in the ferrocene moiety, among which those due to the pivotal C_{ipso} carbons appear characteristically shifted to lower field (δ_C 85–86). In addition, the ^1H and $^{13}C\{^1H\}$ NMR spectra further comprise signals of the diastereotopic aryl substituents at phosphorus and their substituents (CH_3, OCH_3, and CF_3).[21]

Compounds **2a**–**f** and **3** exert similar fragmentation patterns in their electron impact ionization (EI) mass spectra. The plausible early fragmentation pathway is presented in Scheme 3. In the first step, the molecular cation radical loses its phosphine substituent to afford a relatively stable[22] ferrocenophane cation observed at *m*/*z* 255 (base peak in all spectra). The molecules of phosphine sulfide fragment analogously, eliminating $PSPh_2^+$. The complementary fragment ions are also seen (**2a** and **3**, *m*/*z*

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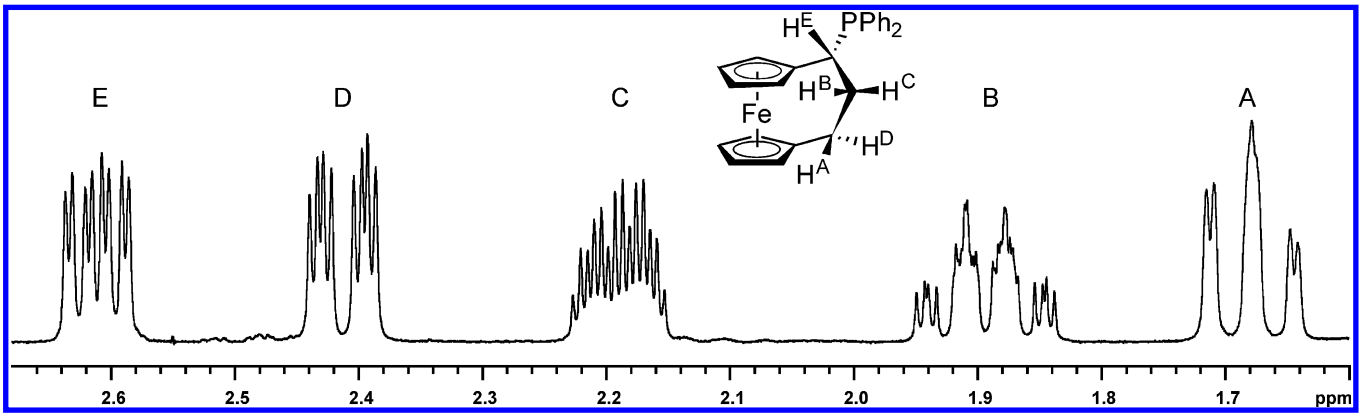
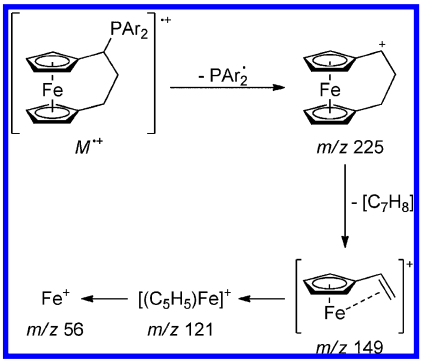


Figure 2. Aliphatic region of ^{1}H NMR spectrum of (*R*)-**2a** showing the assignment of the signals.

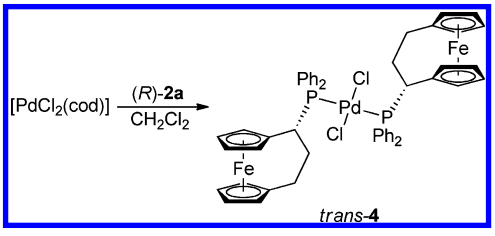
Scheme 3. Plausible Fragmentation Pathway for Phosphines 2



185 (PPh_2^+) and 183 ([PPh_2 − 2 H]$^+$; **2b**−**e**, Ar_2P^+, Ar = an aryl). The ions at *m*/*z* 255 subsequently decompose to give ions at *m*/*z* 149 and, finally, the usual ferrocene fragments such as $[C_5H_5Fe]^+$ and Fe^+. It is noteworthy that the ESI MS spectra of **2** and **3** also display the ions of the dephosphinylated species at *m*/*z* 225 in addition to the expected pseudomolecular ions ([M + X]$^+$, where X = H, Na, K; M^+ was seen for (*R*)-**2a**).

Preparation of Palladium(II) Complexes. In view of catalytic reactions intended for testing, the coordination properties of (*R*)-**2a** as the prototypical representative were assessed in Pd(II) complexes. Thus, the reaction of [$PdCl_2$(cod)] (cod = η^2:η^2-cycloocta-1,5-diene) with 2 molar equiv of the phosphine in dichloromethane proceeded quickly and cleanly to afford the diphosphine complex *trans*-**4** (Scheme 4). An isomeric compound, *cis*-**4**, was isolated serendipitously from the reaction mixture after Pd-catalyzed allylic alkylation (see below). NMR measurements in $CDCl_3$ solution revealed that *cis*-**4** is always accompanied by the thermodynamically favored trans isomer, to which it partially isomerizes upon

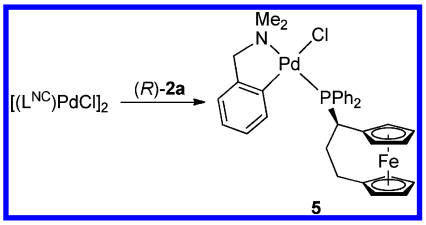
Scheme 4. Preparation of Diphosphine Complex *trans*-4[a]



[a]cod = η^2:η^2-cycloocta-1,5-diene.

standing in solution (see the Supporting Information, Figure S1). Yet another Pd(II) complex containing only one phosphine molecule and an auxiliary 2-[(dimethylamino)-methyl]phenyl C,N-chelating ligand (L^{NC}) was obtained by a bridge-splitting reaction from the dimer [(L^{NC})PdCl]$_2$ (Scheme 5). Complexes *trans*-**4**, *cis*-**4**, and **5** were characterized by

Scheme 5. Preparation of Monophosphine Complex 5[a]



[a]L^{NC} =2-[(dimethylamino-κN)methyl]phenyl-κC^1.

conventional spectroscopic methods and elemental analysis. In addition, their solid-state structures were determined by single-crystal X-ray diffraction analysis (Figures 3−5).

In the ESI mass spectra, the isomeric complexes *cis*- and *trans*-**4** display only weak signals due to the pseudomolecular ions [M + Na]$^+$ at *m*/*z* 1019, the dominant species being ions resulting from the loss of the chloride ligands ([M − Cl − HCl]$^+$ at *m*/*z* 925),[23] all with characteristic isotopic patterns. Complex **5** has a similar response, showing only a weak signal due to [M + Na]$^+$ (*m*/*z* 708) and a strong signal due to fragment ions arising by the loss of Pd-bound chloride ([M − Cl]$^+$ at *m*/*z* 650).

The NMR spectra of the Pd(II) complexes exert several notable features. In ^{1}H NMR spectra of *cis*-**4** and **5**, one of the ferrocene CH protons in a position adjacent to the phosphine substituent[24] appears shifted markedly to higher fields (*cis*-**4**, δ_H 3.05; **5**, δ_H 2.89). This proton is very likely directed toward the center of one phenyl substituent and thus experiences an increased shielding by this magnetically anisotropic aromatic ring. No similar effect is seen for *trans*-**4** (δ_H 3.64), in accordance with the solid-state structural data.[25] In the ^{13}C NMR of *cis*- and *trans*-**4**, the signals of carbons close to the phosphorus atom (phenyl ring and CH_2CHP in the bridge) are observed as apparent and/or nonbinomial triplets that typically arise from virtual coupling in symmetric diphosphine complexes.[26] The spectrum of monophosphine complex **5** obviously lacks such features. In this case, however, the $^3J_{PC}$ and $^4J_{PH}$ coupling constants associated with the signals of the

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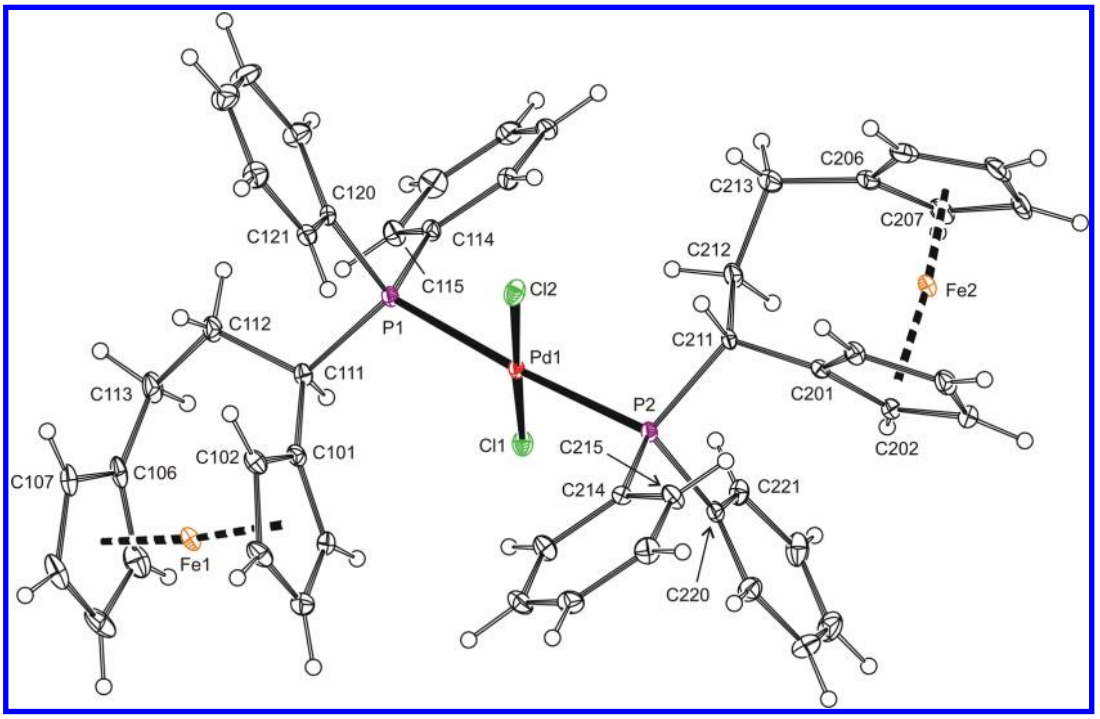

Figure 3. PLATON plot of molecule 1 in the structure of *trans*-**4**. Displacement ellipsoids are scaled to the 30% probability level.

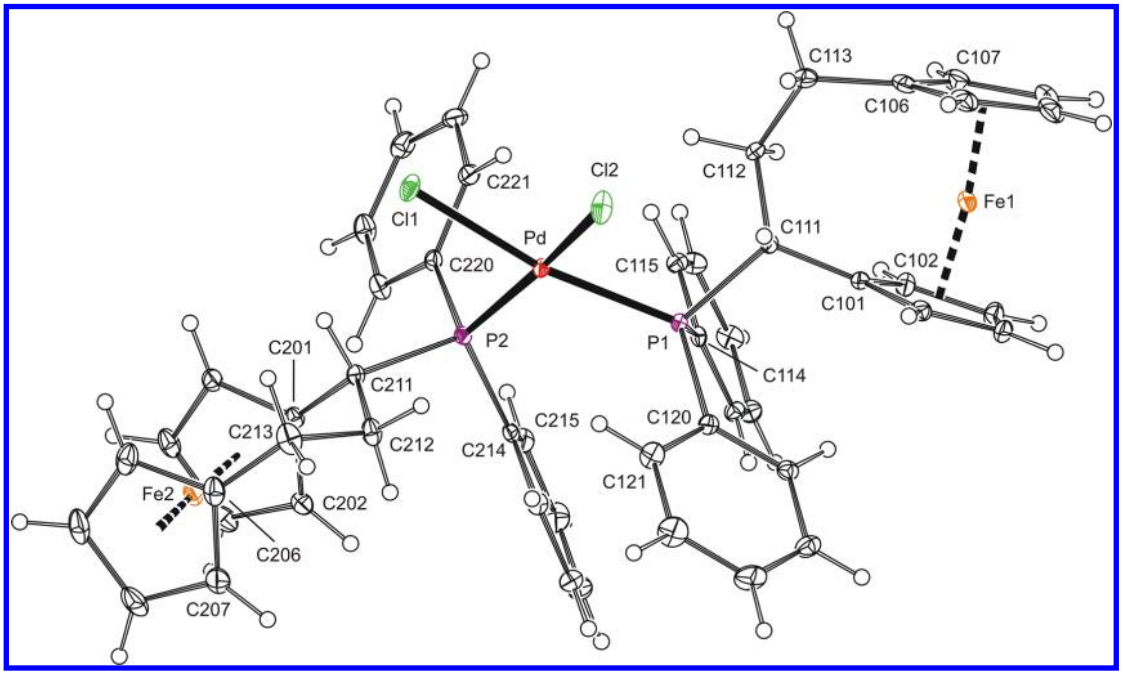

Figure 4. PLATON plot of the complex molecule in the structure of *cis*-**4**·2CH_2Cl_2. Displacement ellipsoids are scaled to the 30% probability level.

CH_2NMe_2 arm indicate a *trans*-P−N arrangement,[27] which is indeed in line with the crystal structure data. The ^{31}P NMR chemical shifts increase in the order *trans*-**4** (δ_P 30.6) < *cis*-**4** (δ_P 42.9) < **5** (δ_P 48.7), thereby reflecting the influence of the donor atom in a trans position.[28]

Description of the Crystal Structures. Views of the molecular structures of (*R*)-**3**, *trans*-**4**, *cis*-**4**·2CH_2Cl_2, and **5**·2$CHCl_3$ are presented in Figures 1 and 3−5, respectively. Parameters describing the geometry of the ferrocenophane moieties in these compounds are summarized in Table 1. The conformations of the ferrocenophane units in all structures are similar to that of pristine 1,1′-(1,3-propanediyl)ferrocene (i.e., the parent [3]ferrocenophane).[29] The cyclopentadienyl rings assume a practically ideal synclinal eclipsed conformation. Perhaps not surprisingly, the largest mutual rotation of the η^5 rings (3.5(1)°) is seen for one ligand moiety in the structure of the sterically congested complex *cis*-**4**. The Fe−ring centroid distances fall into the range 1.6340(7)−1.645(2) Å, while the individual Fe−C distances increase slightly but statistically significantly on going from the pivotal ferrocene C_{ipso} to the opposite CHβ−CHβ' edge (C_{ipso} < C-α < C-β), owing to

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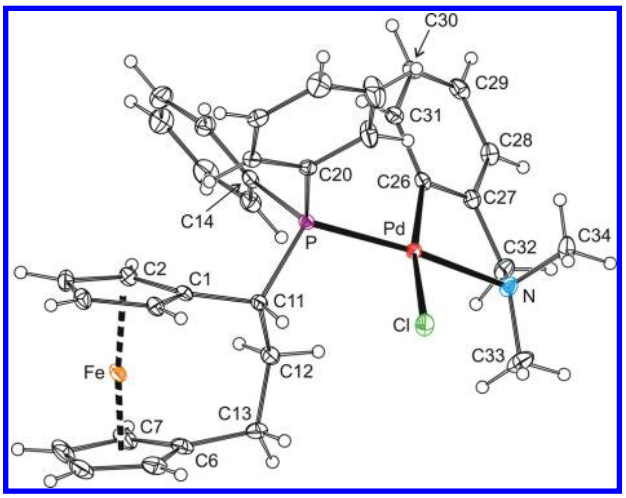

Figure 5. PLATON plot of the complex molecule in the structure of **5**·2CHCl$_3$. Displacement ellipsoids enclose the 30% probability level.

constraints imposed by the three-carbon ansa bridge. This is clearly manifested by the tilt angles being 8.8(1)−10.6(2)°.

The vectors of the C(Cp)−C(bridge) bonds practically bisect the cyclopentadienyl ring and the methylene carbon in the center of the bridge is directed to the side, departing by 0.730(1)−0.748(3) Å from the plane defined by atoms C1, C11, C13, and C6. Because of the chirality, the C−P bond points to the side of the bridge apex in a practically identical position, as indicated by the ψ angles in Table 1. A notable difference among the structures is seen in the orientation of the phosphine moiety toward the pivotal ferrocenophane unit (Figure 6). In the case of (*R*)-**3**, the P═S bond is directed to the apex of the three-carbon bridge, while in all Pd(II) complexes the corresponding P−Pd bonds connecting the ligand to the relatively bulky metal fragments extend away from the ferrocenophane unit.

Compounds *trans*-**4**, *cis*-**4**, and **5** show the expected square-planar-like coordination geometry (Figure 7 and Table 2) typical for Pd(II) complexes,[30] though with a different degree of distortion. The distortion apparently arises from different steric demands of the ligands and, in the case of **5**, also from the presence of the relatively small C,N-chelate ring and unlike Pd−donor distances. The least pronounced deformation is seen for *trans*-**4**, in which the phosphine moieties occupy mutually opposite positions (note that his compound crystallizes with two practically identical but crystallographically independent molecules in the asymmetric unit of the triclinic cell; for an overlap of the independent molecules, see the Supporting Information, Figure S2). In the corresponding cis isomer, the spatial interactions of the bulky phosphine moieties result in twisting of the coordination plane and in changes of the interligand angles (the P1−Pd−P2 angle is the most opened), which then significantly depart from the ideal 90° (see Figure 7). It is also noteworthy that a pair of the phosphorus-bound phenyl groups in *cis*-**4** are rotated so that they allow for a structure-stabilizing intramolecular $\pi\cdots\pi$ stacking interaction (C(114−119) vs C(214−219); see Figure 4). The distance of the centroids of the interacting benzene rings is 3.685(1) Å, and the ring planes are mutually tilted by only 5.17(9)°. The most severe deformation is observed for **5**, where the desymmetrizing effects (i.e., spatial intractions, chelation, and variation of the Pd−donor bond lengths) operate in synergy.

Table 1. Parameters Describing the Geometry of the Ferrocenophane Moieties in (*R*)-3, *trans*-4, *cis*-4·2CH$_2$Cl$_2$, and 5·2CHCl$_3$ (in Å and deg)

		trans-4[c]				*cis*-4·2CH$_2$Cl$_2$[d]		
param[a]	(*R*)-3[b]	Fe1	Fe2	Fe3	Fe4	Fe1	Fe2	5·2CHCl$_3$
Fe−C*gn*1	1.6340(7)	1.645(2)	1.633(1)	1.643(2)	1.633(2)	1.6368(9)	1.6353(9)	1.634(1)
Fe−C*gn*2	1.6391(7)	1.639(2)	1.636(1)	1.641(2)	1.645(2)	1.640(1)	1.638(1)	1.634(2)
Fe−C	2.004(1)−2.055(1)	2.007(3)−2.066(3)	2.010(3)−2.052(4)	2.001(3)−2.072(4)	2.023(3)−2.057(3)	2.007(2)−2.063(2)	2.013(2)−2.055(2)	2.015(3)−2.053(3)
C*n*1−C*n*11	1.507(2)	1.506(4)	1.504(4)	1.502(4)	1.505(4)	1.500(2)	1.501(2)	1.504(3)
C*n*11−C*n*12	1.542(2)	1.539(4)	1.555(4)	1.536(4)	1.563(4)	1.541(2)	1.548(3)	1.549(3)
C*n*12−C*n*13	1.536(2)	1.544(5)	1.542(5)	1.547(5)	1.527(5)	1.532(3)	1.539(3)	1.544(4)
C*n*13−C*n*6	1.498(2)	1.495(4)	1.512(5)	1.503(5)	1.498(4)	1.500(3)	1.502(3)	1.505(4)
ψ	166.95(9)	163.1(2)	160.3(2)	163.5(2)	156.4(2)	159.3(1)	160.1(1)	159.6(2)
P*n*−C*n*11	1.837(1)	1.857(3)	1.861(3)	1.862(3)	1.862(3)	1.876(2)	1.870(2)	1.867(3)
P*n*−C*n*14	1.818(1)	1.824(3)	1.815(3)	1.819(3)	1.816(3)	1.811(2)	1.827(2)	1.817(3)
P*n*−C*n*20	1.816(1)	1.824(3)	1.829(3)	1.827(3)	1.819(3)	1.823(2)	1.819(2)	1.828(2)
∠C*pn*1,C*pn*2	9.73(9)	10.6(2)	9.3(2)	10.6(2)	8.9(2)	9.6(1)	9.0(1)	8.8(1)
τ	−1.1(1)	0.4(2)	−1.1(2)	−0.5(2)	−1.1(2)	−3.5(1)	0.2(1)	−1.2(2)

[a]Definitions: Cp1 = C(*n*01−*n*05), Cp2 = C(*n*06−*n*10) (*n* = molecule number; void for structures featuring only one structurally independent ferrocene moiety), Cg1/2 are the respective centroids. ψ and τ are the torsion angles P*n*−C*n*11−C*n*12−C*n*13 and C*n*01−C*gn*1−C*gn*2−C*n*06, respectively. [b]Further data: P═S = 1.9567(5) Å. [c]Complex *trans*-**4** crystallizes with two complete molecules in the asymmetric molecules (molecule 1, Fe1 and Fe2; molecule 2, Fe3 and Fe4). [d]Data for the two independent ferrocene units comprising atoms Fe1 and Fe2.

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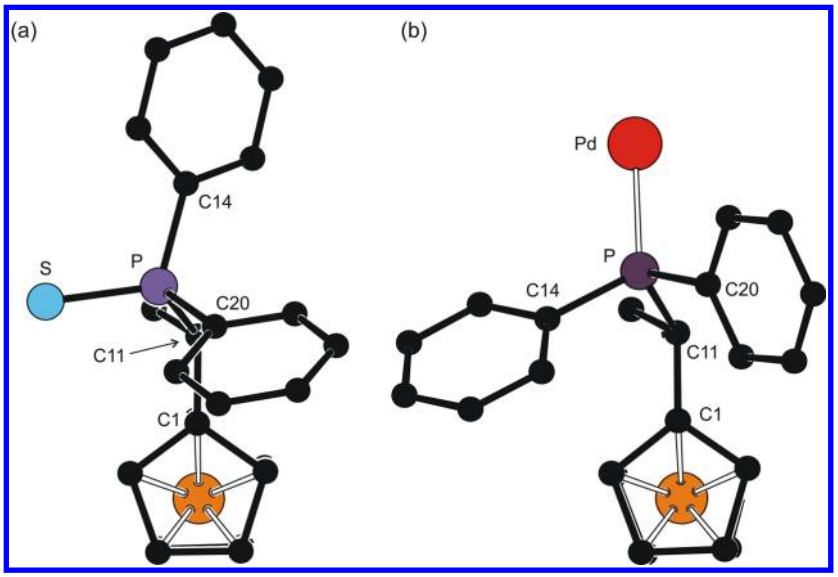


Figure 6. View along the centroid−centroid direction of the ferrocenophane moieties in (a) (*R*)-**3** and (b) **5**, illustrating the conformation of the ferrocenophane unit and the orientation of the "appended moiety" (sulfur or the coordinated metal center), from which only the pivotal atoms are shown for clarity.

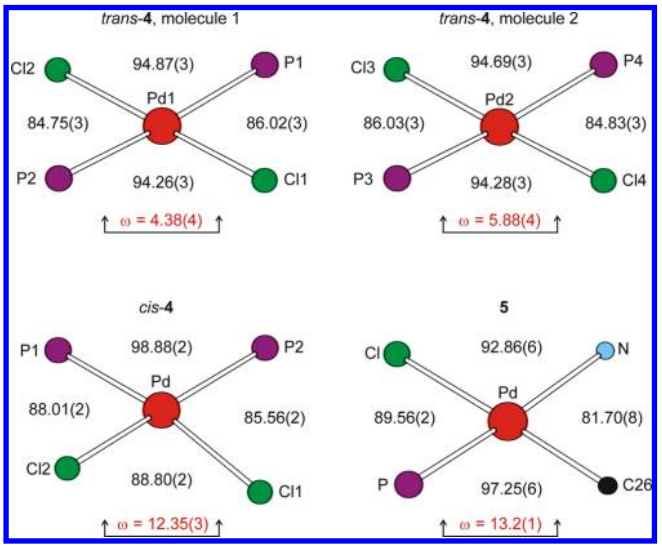


Figure 7. Interligand and interplanar angles describing the coordination geometry of of *trans*-**4**, *cis*-**4** ·$2CH_2Cl_2$, and **5**·$2CHCl_3$. Values are given in degrees. ω (shown in red) is the dihedral angle subtended by the halves of the coordination plane (left vs right as presented in the figure).

Table 2. Coordination Bond Lengths for *trans*-4, *cis*-4·$2CH_2Cl_2$, and 5·$2CHCl_3$ (in Å)

trans-**4**			
molecule 1		molecule 2	
Pd1−P1	2.3285(7)	Pd2−P3	2.3257(8)
Pd1−P2	2.3248(7)	Pd2−P4	2.3340(8)
Pd1−Cl1	2.2980(7)	Pd2−Cl3	2.2984(7)
Pd1−Cl2	2.3064(8)	Pd2−Cl4	2.3093(8)
cis-**4**·$2CH_2Cl_2$		**5**·$2CHCl_3$	
Pd−P1	2.2858(5)	Pd−P	2.2581(7)
Pd−P2	2.2862(5)	Pd−Cl	2.4116(6)
Pd−Cl1	2.3589(5)	Pd−N	2.141(2)
Pd−Cl2	2.3463(5)	Pd−C26	2.000(2)

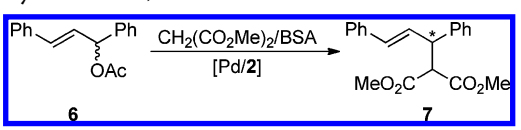
Despite the distortion, however, the Pd−donor distances (Table 2) are found within the common ranges and compare well with those reported for $[(\mu\text{-L})PdCl_2]_2$[31] and for (μ-dppf)$[Pd(L^{NC})Cl]_2$,[32] where L = 1,1′-bis-[(diphenylphosphino)methyl]ferrocene and dppf = 1,1′-bis-(diphenylphosphino)ferrocene. In addition, the observed bond distances clearly demonstrate the structural impact of trans influence.[28] For instance, the Pd−P bond lengths decrease in the order *trans*-**4** > *cis*-**4** > **5**, reflecting the trans influence of the donor atoms in positions trans to phosphorus atom (phosphine > Cl^- > amine). The inverse trend is observed for the Pd−Cl separations, which is again in line with the sequence of the trans-influencing ligands (aryl > phosphine > Cl^-).

Catalytic Tests with Phosphines 2. The series of the newly prepared chiral phosphinoferrocenes **2** has been catalytically evaluated in two chemically dissimilar reactions: as ligands for palladium catalyzed asymmetric allylic alkylation (Tsuji-Trost reaction)[33] and as chiral Lewis bases in the aza variant of the Morita−Baylis−Hillman reaction,[34] which both represent useful tools for the stereoselective construction of new C−C bonds and the preparation of functional molecules.

For testing in palladium-catalyzed asymmetric allylic alkylation, we chose the alkylation of 1,3-diphenylallyl acetate (**6**) with an instant C-nucleophile generated in situ from dimethyl malonate/BSA (BSA = *N*,*O*-bis(trimethylsilyl)-acetamide) to give allylmalonate **7** (Scheme 6), which is usually used as a benchmark test for new ligands. The catalytic results are presented in Table 3.

The reaction performed in the presence of 5 mol % of palladium and 10 mol % of phosphine **2a** afforded the

Scheme 6. Model Allylic Alkylation of Acetate 6 with Dimethyl Malonate/BSA[a]



[a]BSA = *N*,*O*-bis(trimethylsilyl)acetamide.

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Table 3. Summary of Catalytic Results for Pd-Catalyzed Allylic Alkylation of 1,3-Diphenylallyl Acetate (6) with Dimethyl Malonate[a]

entry	ligand	yield (%)[e]	ee (%)[f]
1	**2a**	98	37
2	**2a**[b]	23	36
3	**2a**[c]	95	37
4	**2b**	3	n.d.
5	**2c**	97	29
6	**2d**	1	
7	**2e**	98	50
8	**2f**	44	34
9	*trans*-**4**[d]	<1	
10	*cis*-**4**[d]	<1	

[a]Conditions: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.5 mol %), ligand **2** (10 mol %, **2**:Pd = 2:1), substrate **6** (0.25 mmol), dimethyl malonate and BSA (0.75 mmol each) in 3 mL of dry dichloromethane. The results are an average of two independent runs. [b]Molar ratio **2a**:Pd = 1:1. [c]Reaction in the presence of KOAc (10 mol %). [d]Reaction in the presence of the defined Pd complex (5 mol % Pd). [e]The yield was determined by ^{1}H NMR. [f]Enantiomeric excess was determined by ^{1}H NMR with the aid of chiral lanthanide shift reagent $[Eu(tfc)_3]$. n.d. = not determined.

alkylation product in practically quantitative yield but with only 37% ee (Table 3, entry 1). Decreasing the amount of ligand to 1 molar equiv with respect to palladium (5 mol % Pd, Pd:**2a** = 1:1; entry 2) dramatically decreased the conversion (23% after 24 h), while the enantioselectivity remained practically unchanged. Finally, the addition of potassium acetate (entry 3), which typically accelerates the reaction, had virtually no effect on both the conversion and ee.

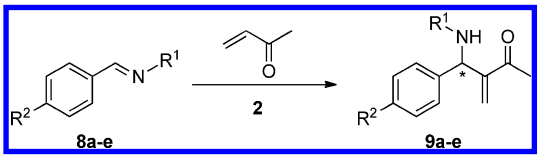
The following experiments carried out with the remaining ligands at a Pd:**2** molar ratio of 1:2 showed that the introduction of substituents at positions 2 and 6 of the phosphorus-bound arene ring has a detrimental effect on the catalyst activity (entries 4 and 6). Substituents in position 4 affected both reaction parameters. Practically complete conversions were obtained with catalysts containing phosphines **2c**,**e**, whereas that based on **2f** as the least electron-rich phosphine furnished a relatively lower yield (42%). In terms of enantioselectivity, the best results were obtained with the catalyst based on **2e**, bearing the electron-donating *p*-anisyl substituents. The generally good catalytic activity (conversions) but relatively poor enantioselectivity of the Pd-**2** catalytic systems are in accordance with previous reports suggesting that electronic discrimination of allylic termini (achieved typically via trans influence of the donor atoms of a chelating ligand) has a decisive influence on the enantioselectivity in the cases where no is sufficient steric differentiation is provided by a rigid, donor-symmetric chelate ligand (chiral pocket).[35] Such discrimination, however, does not occur in the presumed symmetric intermediate $[Pd(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)(\mathbf{2})_2]^+$, containing two identical and mutually movable monodentate donors.

It is also noteworthy that the (defined) dichloride complexes *cis*- and *trans*-**4** did not catalyze the alkylation reaction (Table 3, entries 9 and 10). Indeed, the formation of *cis*-**4**, which was isolated from the reaction mixture, may well represent a deactivation process during which the π-bound allyl is isoeletronically replaced with two chloride anions coming presumably from the palladium precursor and, perhaps, from the halogenated solvent.

Described first in 1968 by Morita[36] and developed by Baylis and Hillman few years later,[37] the addition of C-nucleophiles to electron-poor alkenes catalyzed by Lewis bases (phosphines and amines) came to the fore during the recent development of asymmetric organocatalytic processes.[34] The fact that the Morita–Baylis–Hillman (MBH) reaction is 100% atom economic and affords highly functionalized products makes it synthetically very attractive, particularly in its asymmetric variant. This is turn initiated a search for suitable base catalysts. Among phosphine donors, those recently employed in Morita–Baylis–Hillman reactions include compounds derived from the chiral binaphthyl[38] and spirobiindane units.[39] Chiral ferrocene phosphines have still found only a limited use in this reaction.[40]

For the catalytic evaluation of chiral phosphines **2**, we chose the aza variant of the MBH reaction,[41] namely the commonly used addition of *N*-sulfonyl benzylidene imines **8** to methyl vinyl ketone, affording chiral sulfonamides **9** (Scheme 7).

Scheme 7. Addition of Methyl Vinyl Ketone to Aromatic Imines 8a–e[a]



[a]R^1/R^2 = 4-$CH_3C_6H_4SO_2$/H (**a**), $PhSO_2$/H (**b**), 4-$CH_3C_6H_4SO_2$/Me (**c**), 4-$CH_3C_6H_4SO_2$/MeO (**d**), 4-$CH_3C_6H_4SO_2$/Cl (**e**).

The reaction of *N*-tosylimine **8a** with 2 mol equiv of the ketone in the presence of 10 mol % of chiral phosphine **2a** performed at room temperature for 5 h afforded **9a** in 27% yield and with 97% ee (Table 4, entry 1). Unfortunately, the reaction was only poorly chemoselective, affording various side products, among which the product of double addition **10**[42] and heterocycles **11** and **12**[43] (Scheme 8) were identified by NMR analysis. The formation of such products was observed in reactions mediated by strong Lewis bases (e.g., PBu_3 and

Table 4. Summary of Catalytic Results for the Model Aza-Morita–Baylis–Hillman Reaction[a]

entry	cat.	solvent	additive	yield (%)[b]	ee (%) [config][e]
1	**2a**	$CDCl_3$	none	27	97 [*S*]
2	**2a**	$CHCl_3$	5% $PhCO_2H$	76	32 [*S*]
3	**2a**	CH_2Cl_2	5% $PhCO_2H$	58	33 [*S*]
4	**2a**	MeCN	5% $PhCO_2H$	34	16 [*S*]
5	**2a**	toluene	5% $PhCO_2H$	41	80 [*S*]
6	**2a**	MeOH	5% $PhCO_2H$	12	n.d.
7	**2a**	$CDCl_3$	MS 4 Å	38	94 [*S*]
8	**2b**	$CDCl_3$	MS 4 Å	4 (23[c])	17 [*S*]
9	**2c**	$CDCl_3$	MS 4 Å	traces	n.d.
10	**2d**	$CDCl_3$	MS 4 Å	<1 (traces[c])	n.d.
11	**2e**	$CDCl_3$	MS 4 Å	n.d.	n.d.
12	**2f**	$CDCl_3$	MS 4 Å	67	14 [*S*]
13	**2f**	$CDCl_3$	MS 4 Å	96[d]	12 [*S*]

[a]Conditions: imine (0.5 mmol), methyl vinyl ketone (1.0 mmol), and **2** (50 μmol, 10 mol %) were reacted in 2 mL of solvent at room temperature for 5 h (unless noted otherwise). The results are an average of two independent runs. [b]The yield was determined by ^{1}H NMR spectroscopy using anisole as an internal standard. [c]Conversion after 168 h. [d]Reaction time 24 h. [e]The ee values were determined by HPLC analysis on a chiral column. The configuration was determined by a comparison of optical rotation with literature values (for details, see the Experimental Section). n.d. = not determined.

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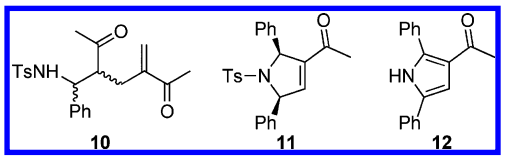
Scheme 8. Side Products Identified in the aza-MBH Reaction of Imine 8a with Methyl Vinyl Ketone



$PhPMe_2$)[34b] and may take place during chromatographic purification if unreacted methyl vinyl ketone is available. The presence of chemically similar byproducts prevented the isolation of pure **9a**, and therefore, the yield of the addition product had to be determined directly by NMR analysis of the reaction mixture using anisole as an internal standard.

Benzoic acid (5 mol %) was then added to the reaction mixture to facilitate proton transfer in an intermediate resulting from addition of the imine to activated ketone, which is believed to be the rate-determining step of the aza-Morita–Baylis–Hillman reaction.[44] Indeed, the yield of **9a** significantly increased, albeit on account of stereoselectivity (entry 2). Both of these reaction parameters varied greatly upon changing the solvent (entries 3–6). A good ee of 80% but still a relatively low yield was obtained in toluene. Other solvents tested afforded considerably worse results.

The reaction in chloroform, which proceeded most rapidly, was chosen for a further optimization. Upon the addition of 4 Å molecular sieves that could prevent the hydrolysis of the imine substrate, the conversion slightly improved while the ee remained nearly the same as in the system without any additive (94%, entry 7). Such conditions were selected for an evaluation of the influence of the ligand structure (entries 7–13).

Surprisingly, none of the compounds completing the series of **2**-type phosphines afforded better results than the parent representative **2a**. For instance, phosphines **2c**,**e** bearing electron-donating groups afforded **9a** in only low yields, while imine **8a** was completely consumed. This can be explained by an acceleration of the followup reactions affording compounds **10**–**12**. In contrast, phosphines with sterically demanding and electron-donating phosphine substituents (**2b**,**d**) reacted much more slowly. The yields of **9a** achieved with these phosphines were low even after extended reaction times (23% for phosphine **2b** after 7 days), but the majority of the starting imine remained unreacted. Finally, compound **2f** bearing the electron-withdrawing trifluoromethyl group reacted rather quickly and chemoselectively. Nonetheless, the enantioselectivity was relatively low. In view of these results, the following experiments with different substrates were carried out only with phosphine **2a** (Table 4).

Reactions with imines **8a**,**b** differing in the sulfonyl protecting group (cf. entries 2 and 7 in Table 4 and entries 2 and 3 in Table 5) revealed similar trends. However, the latter substrate containing the smaller phenylsulfonyl substituent afforded lower yields, a slightly lower enantioselectivity in the reaction performed in the presence of molecular sieves, and a considerably worse ee for the reaction in the presence of 5 mol % of benzoic acid. Introduction of substituents to the benzylidene moiety also affected the reaction outcome. The best results were obtained with unsubstituted imine **8a**. Other *N*-tosylimines bearing methyl, methoxy, and chloro substituents in position 4 of the benzylidene group all gave lower ee's, though not always lower conversions (cf. entry 7 in Table 4 and entries 3–5 in Table 5).

Table 5. Catalytic Results for aza-Morita-Baylis-Hillman Reactions with Different Imine Substrates[a]

imine	R^1	R^2	additive	yield (%)[b]	ee (%)[c] [confign]
8b	$PhSO_2$	H	5% $PhCO_2H$	41	20 [*S*]
8b	$PhSO_2$	H	MS 4 Å	27	91 [*S*]
8c	Ts	Me	MS 4 Å	49	78 [*S*]
8d	Ts	MeO	MS 4 Å	28	ca. 57 [*S*]
8e	Ts	Cl	MS 4 Å	9	n.d.

[a]Conditions: imine (0.5 mmol), methyl vinyl ketone (1.0 mmol), and **2** (50 μmol, 10 mol %) were reacted in 2 mL of $CDCl_3$ at room temperature for 5 h. [b]The yield was determined by ^{1}H NMR using anisole as an internal standard. [c]The enantiomeric excess (ee) was determined by HPLC analysis on a chiral column. The configuration was determined by a comparison of optical rotation with the literature data (for details, see the Experimental Section).

CONCLUSION

Phosphines **2** of the general formula Ar_2PR, where Ar is an aryl group and R is 1,1′-[(1*R*)-1,3-propanediyl-1-yl]ferrocene, reported in this study represent the first ferrocenophane monophosphines containing a stereogenic carbon atom as the sole chirality source. These compounds are structurally modular, combining the rigid chiral ferrocenophane and the diarylphosphino moieties. Since the synthesis of a **2**-type ligand makes use of the readily available diarylphosphines, it allows for easy structural modifications (ligand tailoring) through changing of the diarylphosphine moiety. Compounds **2** form ordinary phosphine complexes from the usual Pd(II) precursors. However, their structural properties often result in distortion of the coordination environments. When applied as chiral donors to Pd-catalyzed asymmetric alkylation, phosphines **2** afford only modest results, which can be rationalized by the absence of electronic discrimination and mobility of the phosphine ligands in the presumed reaction intermediates $[Pd(\eta^3\text{-allyl})(\mathbf{2})_2]^+$. On the other hand, the compounds afford promising results when employed as chiral Lewis bases in aza-Morita–Baylis–Hillman reactions, particularly in terms of enantioselectivity (ee up to 97%). We believe that mechanistically similar reactions are worthy of further investigations aimed mainly at improving the overall chemoselectivity.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses were carried out under an argon atmosphere with exclusion of direct daylight. Compounds (*R*)-**1**,[17] $[PdCl_2(cod)]$,[45] $[(L^{NC})PdCl]_2$,[46] **6**,[47] and **8a**[48] were synthesized according to literature procedures. Toluene and methanol were freshly distilled from sodium metal and sodium methoxide, respectively. Chloroform and chloroform-*d* used for catalytic experiments were distilled from CaH_2. Anhydrous acetonitrile and dichloromethane were purchased from Sigma-Aldrich. Other chemicals (Sigma-Aldrich) and solvents (Lachner) used for crystallizations and chromatography were used as received.

NMR spectra were measured with a Varian UNITY Inova 400 spectrometer at 298 K. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or to external 85% H_3PO_4 (^{31}P). The assignment of the NMR signals is based on COSY-90 and gradient-selected ^{13}C HSQC and ^{13}C HMBC measurements. IR spectra were recorded on an FTIR Nicolet Magna 760 instrument. Electron impact ionization (EI) mass spectra including high-resolution (HR) data were obtained with a GCT Premier spectrometer (Waters). Low-resolution electrospray ionization (ESI) mass spectra were recorded with an Esquire 3000 (Bruker) spectrometer using methanolic solutions. High-resolution ESI MS spectra were obtained with an LTQ Orbitrap XL spectrometer (Thermo Fisher Scientific).

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Optical rotations were determined with an automatic polarimeter Autopol III (Rudolph Research) at room temperature (optical path 2 cm). Melting points were determined on a Büchi B-540 apparatus.

General Procedure for the Synthesis of Phosphines 2. A flame-dried Schlenk tube was charged with the alcohol (*R*)-**1** and sodium iodide, flushed with argon, and sealed with a septum. Dry acetonitrile was introduced, and the mixture was stirred until the solids completely dissolved. Then, neat chlorotrimethylsilane was added, causing an immediate separation of a fine white solid (NaCl). After the mixture was stirred for 15 min, the appropriate phosphine was introduced and the stirring was continued at room temperature overnight (18−20 h).

The reaction was terminated by addition of saturated aqueous NaCl, the orange organic layer was separated, and the milky white aqueous phase was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated with chromatography grade alumina. The crude preadsorbed product was transferred onto the top of a chromatographic column (alumina, hexane) and eluted with hexane to remove excess secondary phosphine. The solvent was then changed to hexane/diethyl ether (1/2), which led to the development of a yellow band. This band was collected and evaporated under vacuum to afford the pure product.

*1,1′-[(1R)-1-(Diphenylphosphino)-1,3-propanediyl]ferrocene ((R)-**2a**).* Following the general procedure, (*R*)-**1** (723 mg, 2.99 mmol), NaI (1.16 g, 7.75 mmol), $ClSiMe_3$ (1.0 mL, 7.9 mmol) and diphenylphosphine (1.3 mL, 7.56 mmol) were reacted in 15 mL of acetonitrile to afford (*R*)-**2a** as an orange solid (1.16 g). This solid product was further crystallized from hot acetonitrile and isolated as orange needlelike crystals (1.01 g, 82%).

Mp: 155.5−157.0 °C dec (MeCN). ^{1}H NMR ($CDCl_3$): δ 1.68 (m, 1 H, $C_5H_4CH_2$), 1.89 (m, 1 H, $C_5H_4CH_2CH_2$), 2.19 (m, 1 H, $C_5H_4CH_2CH_2$), 2.41 (ddd, 1 H, J = 14.3, 4.5, 2.7 Hz, $C_5H_4CH_2$), 2.61 (ddd, 1 H, J = 11.7, 6.4, 2.3 Hz, *CH*P), 3.77 (dt, J' = 2.6, 1.3, 1 H, C_5H_4CHP), 3.90 (td, J' = 2.5, 1.3 Hz, 1 H,$C_5H_4CH_2$), 3.94 (dt, J' = 2.4, 1.3 Hz, 1 H, $C_5H_4CH_2$), 3.99 (dt, J' = 2.6, 1.3 Hz, 1 H, $C_5H_4CH_2$), 4.03 (dt, J' = 2.5, 1.3, 1 H, C_5H_4), 4.06 (m, 2 H, C_5H_4), 4.13 (dt, J' = 2.6, 1.3 Hz, 1 H, C_5H_4CHP), 7.12−7.24 (m, 5 H, PPh_2), 7.38−7.44 (m, 3 H, PPh_2), 7.57−7.63 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.90 (d, $^3J_{PC}$ = 11 Hz, $C_5H_4CH_2$), 36.31 (d, $^1J_{PC}$ = 12 Hz, *CH*P), 39.32 (d, $^2J_{PC}$ = 26 Hz, $C_5H_4CH_2CH_2$), 66.99 (d, J_{PC} = 9 Hz, CH of C_5H_4), 67.42 (CH of C_5H_4), 67.56 (CH of C_5H_4), 67.75 (CH of C_5H_4), 69.03 (CH of C_5H_4), 69.23 (CH of C_5H_4), 71.31 (CH of C_5H_4), 71.63 (d, J_{PC} = 2 Hz, CH of C_5H_4), 85.77 (*C*-CH_2 of $C_5H_4CH_2$), 86.06 (d, $^2J_{PC}$ = 17 Hz, *C*-CH of C_5H_4CHP), 127.72 (d, $^2J_{PC}$ = 7 Hz, CH^{ortho} of PPh_2), 128.20 (CH^{para} of PPh_2), 128.52 (d, $^2J_{PC}$ = 7 Hz, CH^{ortho} of PPh_2), 129.11 (CH^{para} of PPh_2), 133.10 (d, $^3J_{PC}$ = 18 Hz, CH^{meta} of PPh_2), 133.75 (d, $^3J_{PC}$ = 20 Hz, CH^{meta} of PPh_2), 137.61 (d, $^1J_{PC}$ = 16 Hz, C^{ipso} of PPh_2), 137.64 (d, $^1J_{PC}$ = 14 Hz, C^{ipso} of PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −1.7 (s). ESI+ MS: m/z 225 ([M − PPh_2]$^+$), 410 (M^+), 433 ([M + Na]$^+$), 449 ([M + K]$^+$). EI+ MS: m/z (relative abundance) 410 (13, $M^{\bullet+}$), 225 (100, [M − PPh_2]$^+$), 185 (10, PPh_2^+), 183 (11, $C_{12}H_8P^+$), 147 (14, $C_5H_4FeC_2H_3^+$), 121 (14, $C_5H_5Fe^+$), 108 (17, PPh^+), 56 (8, Fe^+). HRMS: calcd for $C_{25}H_{23}FeP$ 410.0887, found 410.0883. IR (DRIFTS): ν_{max} 3071 w, 3024 w, 2937 w, 2908 m, 2841 w, 1479 w, 1433 m, 1223 w, 1194 w, 1039 w, 1031 m, 998 w, 899 w, 857 w, 810 s, 746 s, 738 s, 695 vs, 552 w, 515 s, 506 s, 477 m cm^{-1}. Anal. Calcd for $C_{25}H_{23}FeP$ (410.3): C, 73.19; H, 5.65. Found: C, 72.94; H, 5.78. $[\alpha]_D$ = +36.7°.

*1,1′-{(1R)-1-[Bis(2-methylphenyl)phosphino]-1,3-propanediyl}ferrocene ((R)-**2b**).* Alcohol (*R*)-**1** (450 mg, 1.86 mmol), NaI (696 mg, 4.65 mmol), $ClSiMe_3$ (0.59 mL, 4.65 mmol) and di-2-tolylphosphine (1.0 g, 4.7 mmol) were reacted in 35 mL of acetonitrile according to the general procedure to give phosphine (*R*)-**2b** as an orange solid (762 mg, 93%).

^{1}H NMR ($CDCl_3$): δ 1.76 (m, 1 H, $C_5H_4CH_2$), 1.91 (m, 1 H, $C_5H_4CH_2CH_2$), 2.27 (s, 3 H, CH_3) 2.29 (m, 1 H, $C_5H_4CH_2CH_2$), 2.38 (d, $^4J_{PH}$ = 1.4 Hz, 3 H, CH_3), 2.45 (ddd, J = 14.0, 4.3, 2.4 Hz, 1 H, $C_5H_4CH_2$), 2.57 (ddd, J = 11.5, 5.5, 2.0 Hz, 1 H, CHP), 3.65 (dt, J' = 2.6, 1.3 Hz, 1 H, C_5H_4), 3.83 (td, J' = 2.6, 1.3 Hz, 1 H, C_5H_4), 3.93 (td, J' = 2.4, 1.3 Hz, 1 H, C_5H_4), 3.97−4.02 (m, 2 H, C_5H_4), 4.03 (dt, J' = 2.5, 1.4 Hz, 1 H, C_5H_4), 4.05 (m, 1 H, C_5H_4), 4.18 (dt, J' = 2.5, 1.3 Hz, 1 H, C_5H_4), 6.93 (m, 1 H, C_6H_4), 6.97−7.07 (m, 2 H, C_6H_4), 7.15 (m, 1 H, C_6H_4), 7.18−7.26 (m, 3 H, C_6H_4), 7.43 (m, 1 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.26 (d, $^3J_{PC}$ = 22 Hz, CH_3), 21.50 (d, $^3J_{PC}$ = 21 Hz, CH_3), 24.95 (d, $^3J_{PC}$ = 11 Hz, $C_5H_4CH_2$), 36.47 (d, $^1J_{PC}$ = 12 Hz, *CH*P), 38.77 (d, $^2J_{PC}$ = 27 Hz, $C_5H_4CH_2CH_2$), 67.36 (d, J_{PC} = 8 Hz, CH of C_5H_4), 67.37 (CH of C_5H_4), 67.64 (CH of C_5H_4), 67.78 (CH of C_5H_4), 68.64 (CH of C_5H_4), 69.22 (CH of C_5H_4), 71.33 (CH of C_5H_4), 71.42 (d, J_{PC} = 2 Hz, CH of C_5H_4), 85.55 (*C*-CH_2 of $C_5H_4CH_2$), 85.63 (d, $^2J_{PC}$ = 17 Hz, *C*-CH of C_5H_4CHP), 125.42 (CH of C_6H_4), 125.93 (CH of C_6H_4), 128.21 (CH of C_6H_4), 128.33 (CH of C_6H_4), 129.47 (d, $^2J_{PC}$ = 5 Hz, CH of C_6H_4), 130.22 (d, $^2J_{PC}$ = 4 Hz, CH of C_6H_4), 130.62 (CH of C_6H_4), 132.36 (d, $^3J_{PC}$ = 2 Hz, CH of C_6H_4), 136.37 (d, $^1J_{PC}$ = 13 Hz, *C*-P of C_6H_4), 137.50 (d, $^1J_{PC}$ = 18 Hz, *C*-P of C_6H_4), 142.67 (d, $^2J_{PC}$ = 25 Hz, *C*-Me of $C_6H_4CH_3$), 143.04 (d, $^2J_{PC}$ = 27 Hz, *C*-Me of $C_6H_4CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −27.1 (s). ESI+ MS: m/z 225 ([M − $P(C_6H_4Me)_2$]$^+$), 439 ([M + H]$^+$, 461 ([M + Na]$^+$), 477 ([M + K]$^+$). EI+ MS: m/z (relative abundance) 438 (9, $M^{\bullet+}$), 225 (100, [M − $P(C_6H_4Me)_2$]$^+$), 214 (28, $HP(C_6H_4Me)_2^{\bullet+}$), 147 (9, $C_5H_4FeC_2H_3^+$), 122 (31, $P(C_6H_4Me)^+$), 121 (8, $C_5H_5Fe^+$), 91 (5, $C_7H_7^+$), 78 (35, $C_6H_6^+$), 56 (4, Fe^+). HRMS: calcd for $C_{27}H_{27}FeP$ 438.1200, found 438.1192.

*1,1′-{(1R)-1-[Bis(4-methylphenyl)phosphino]-1,3-propanediyl}ferrocene ((R)-**2c**).* Starting with alcohol (*R*)-**1** (450 mg, 1.86 mmol), NaI (696 mg, 4.65 mmol), $ClSiMe_3$ (0.59 mL, 4.65 mmol) and di-4-tolylphosphine (1.0 g, 4.7 mmol) in 20 mL of acetonitrile, the general procedure gave phosphine (*R*)-**2c** as an orange solid (715 mg, 87%).

^{1}H NMR ($CDCl_3$): δ 1.66 (m, 1 H, $C_5H_4CH_2$), 1.87 (m, 1 H, $C_5H_4CH_2CH_2$), 2.16 (m, 1 H, $C_5H_4CH_2CH_2$), 2.24 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.39 (m, 1 H, $C_5H_4CH_2$), 2.58 (ddd, J = 11.8, 6.4, 2.4 Hz, 1 H, CHP), 3.80 (dt, J' = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.91 (td, J' = 2.4, 1.2 Hz, 1 H, C_5H_4), 3.94 (td, J' = 2.4, 1.2 Hz, 1 H, C_5H_4), 3.98 (dt, J' = 2.5, 1.2 Hz, 1 H, C_5H_4), 4.02 (dt, J' = 2.4, 1.3 Hz, 1 H, C_5H_4), 4.05 (m, 2 H, C_5H_4), 4.12 (dt, J' = 2.5, 1.3 Hz, 1 H, C_5H_4), 6.96 (m, 2 H, C_6H_4), 7.12 (m, 2 H, C_6H_4), 7.20 (m, 2 H, C_6H_4), 7.48 (m, 2 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.22 (CH_3), 21.37 (CH_3), 24.94 (d, $^3J_{PC}$ = 11 Hz, $C_5H_4CH_2$), 36.32 (d, $^1J_{PC}$ = 11 Hz, *CH*P), 39.38 (d, $^2J_{PC}$ = 25 Hz, $C_5H_4CH_2CH_2$), 67.05 (d, $^3J_{PC}$ = 9 Hz, CH of C_5H_4), 67.40 (CH of C_5H_4), 67.60 (CH of C_5H_4), 67.71 (CH of C_5H_4), 69.02 (CH of C_5H_4), 69.20 (CH of C_5H_4), 71.31 (CH of C_5H_4), 71.71 (d, J_{PC} = 2 Hz, CH of C_5H_4), 85.92 (*C*-CH_2 of $C_5H_4CH_2$), 128.63 (d, $^3J_{PC}$ = 7 Hz, CH^{meta} of C_6H_4), 129.34 (d, $^3J_{PC}$ = 8 Hz, CH^{meta} of C_6H_4), 133.02 (d, $^2J_{PC}$ = 18 Hz, CH^{ortho} of C_6H_4), 133.76 (d, $^2J_{PC}$ = 20 Hz, CH^{ortho} of C_6H_4), 138.07 (*C*-Me of C_6H_4), 139.22 (*C*-Me of C_6H_4). The signals due to C-P of C_6H_4 and *C*-CHP of C_5H_4CHP were not found. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −3.4 (s). ESI+ MS: m/z 225 ([M − $P(C_6H_4Me)_2$]$^+$), 439 ([M + H]$^+$, 461 ([M + Na]$^+$), 477 ([M + K]$^+$). EI+ MS: m/z (relative abundance) 438 (9, $M^{\bullet+}$), 225 (100, [M − $P(C_6H_4Me)_2$]$^+$), 214 (10, $HP(C_6H_4Me)_2^{\bullet+}$), 147 (9, $C_5H_4FeC_2H_3^+$), 122 (18, $P(C_6H_4Me)^{\bullet+}$), 121 (8, $C_5H_5Fe^+$), 91 (4, $C_7H_7^+$), 78 (7, $C_6H_6^+$), 56 (4, Fe^+). HRMS: calcd for $C_{27}H_{27}FeP$ 438.1200, found 438.1194.

*1,1′-{(1R)-1-[Bis(2,4,6-trimethylphenyl)phosphino]-1,3-propanediyl}ferrocene ((R)-**2d**).* The reaction of alcohol (*R*)-**1** (358 mg, 1.48 mmol), NaI (554 mg, 3.70 mmol), $ClSiMe_3$ (0.47 mL, 3.7 mmol), and dimesitylphosphine (1.0 g, 3.7 mmol) performed in 60 mL of acetonitrile and isolation as described above afforded phosphine (*R*)-**2d** as an orange foamy solid (691 mg, 94%).

^{1}H NMR ($CDCl_3$): δ 1.79 (m, 1 H, $C_5H_4CH_2$), 2.03 (m, 1 H, $C_5H_4CH_2CH_2$), 2.10 (s, 3 H, CH_3^{para} of $C_6H_2Me_3$), 2.22 (s, 3 H, CH_3^{para} of $C_6H_2Me_3$), 2.34 (s, 6 H, CH_3^{ortho} of $C_6H_2Me_3$), 2.41 (s, 6 H, CH_3^{ortho} of $C_6H_2Me_3$), 2.41−2.53 (m, 2 H, $C_5H_4CH_2$ and $C_5H_4CH_2CH_2$), 3.55 (ddd, J = 11.4, 4.2, 1.7 Hz, 1 H, CHP), 3.68 (dt, J' = 2.6, 1.3 Hz, 1 H, C_5H_4), 3.77 (td, J' = 2.6, 1.3 Hz, 1 H, C_5H_4), 3.89 (m, 1 H, C_5H_4), 3.92 (m, 1 H, C_5H_4), 4.01−4.05 (m, 3 H, C_5H_4), 4.16 (dt, J' = 2.6, 1.3 Hz, 1 H, C_5H_4), 6.59 (dq, $^4J_{HH}$ = 0.6, $^4J_{PH}$ = 2.7 Hz, 2 H, CH of $C_6H_2Me_3$), 6.78 (dq, $^4J_{HH}$ = 0.6, $^4J_{PH}$ = 2.7 Hz, 2 H, CH of $C_6H_2Me_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.65 (CH_3^{para} of $C_6H_2Me_3$), 20.81 (CH_3^{para} $C_6H_2Me_3$), 22.61 (d, $^3J_{PC}$ = 7 Hz, CH_3^{ortho}

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of $C_6H_2Me_3$), 22.75 (d, $^3J_{PC}$ = 6 Hz, CH_3^{ortho} of $C_6H_2Me_3$), 24.95 (d, $^3J_{PC}$ = 14 Hz, $C_5H_4CH_2$), 33.54 (d, $^1J_{PC}$ = 16 Hz, CHP), 40.66 (d, $^2J_{PC}$ = 39 Hz, $C_5H_4CH_2CH_2$), 67.07 (d, J_{PC} = 7 Hz, CH of C_5H_4), 67.79 (CH of C_5H_4), 67.86 (CH of C_5H_4), 68.16 (CH of C_5H_4), 69.19 (CH of C_5H_4), 70.80 (d, J_{PC} = 2 Hz, CH of C_5H_4), 71.25 (CH of C_5H_4), 84.91 (*C*-CH_2 of $C_5H_4CH_2$), 86.40 (d, $^2J_{PC}$ = 18 Hz, *C*-CH of C_5H_4CHP), 129.11 (d, $^3J_{PC}$ = 4 Hz, CH of $C_6H_2Me_3$), 130.45 (d, $^3J_{PC}$ = 2 Hz, CH of $C_6H_2Me_3$), 131.20 (d, $^2J_{PC}$ = 19 Hz, C^{ortho} of $C_6H_2Me_3$), 132.78 (d, $^2J_{PC}$ = 33 Hz, C^{ortho} of $C_6H_2Me_3$), 136.89 (C^{para} of $C_6H_2Me_3$), 137.86 (C^{para} of $C_6H_2Me_3$), 141.68 (d, $^1J_{PC}$ = 13 Hz, *C*-P of $C_6H_2Me_3$), 143.58 (d, $^1J_{PC}$ = 14 Hz, *C*-P of $C_6H_2Me_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −10.1 (s). ESI+ MS: *m*/*z* 225 ($[M - P(C_6H_2Me_3)_2]^+$), 495 ($[M + H]^+$, 517 ($[M + Na]^+$), 549 ($[M + K + O]^+$). EI+ MS: *m*/*z* (relative abundance) 494 (12, $M^{\bullet+}$), 373 (13, $[M - C_5H_5Fe]^+$), 270 (96, $HP(C_6H_2Me_3)_2^{\bullet+}$), 255 (86, $C_{17}H_{19}P^+$), 225 (95, $[M - P(C_6H_2Me_3)_2]^+$), 150 (100, $HPC_6H_2Me_3^{\bullet+}$), 147 (9, $C_5H_4FeC_2H_3^+$), 135 (74, $C_8H_8P^+$), 121 (10, $C_5H_5Fe^+$), 105 (60, $C_8H_8^+$), 91 (26, $C_7H_7^+$), 56 (17, Fe^+). HRMS: calcd for $C_{31}H_{35}FeP$ 494.1826, found 494.1821.

*1,1′-{(1R)-1-[Bis(4-methoxyphenyl)phosphino]-1,3-propanediyl}-ferrocene ((R)-**2e**).* When reacted according to the general procedure, alcohol (*R*)-**1** (392 mg, 1.62 mmol), sodium iodide (608 mg, 4.06 mmol), $ClSiMe_3$ (0.51 mL, 4.06 mmol), and bis(4-methoxyphenyl)-phosphine (1.0 g, 4.1 mmol) in 20 mL of dry acetonitrile gave the crude product, which was isolated as follows. After the excess phosphine was removed by elution with hexane/diethyl ether (95/5), the product was eluted with hexane/diethyl ether (1/1; yellow band). Since the product is highly air sensitive and was partly oxidized, it was chromatographed once again under inert conditions (flash chromatography on alumina with preadsoprtion, elution with diethyl ether) to afford pure (*R*)-**2e** as an orange yellow solid. Yield: 513 mg (67%).

^1H NMR ($CDCl_3$): δ 1.65 (m, 1 H, $C_5H_4CH_2$), 1.87 (m, 1 H, $C_5H_4CH_2CH_2$), 2.15 (m, 1 H, $C_5H_4CH_2CH_2$), 2.40 (ddd, *J* = 14.2, 4.5, 2.6 Hz, 1 H, $C_5H_4CH_2$), 2.52 (ddd, *J* = 11.7, 6.5, 2.2 Hz, 1 H, CHP), 3.72 (s, 3 H, OCH_3), 3.78 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.83 (s, 3 H, OCH_3), 3.90 (td, *J*′ = 2.3, 1.2 Hz, 1 H, C_5H_4), 3.94 (td, *J*′ = 2.4, 1.2 Hz, 1 H, C_5H_4), 3.98 (td, *J*′ = 2.4, 1.3 Hz, 1 H, C_5H_4), 4.02 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 4.05 (m, 2 H, C_5H_4), 4.11 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 6.71 (m, 2 H, C_6H_4), 6.94 (m, 2 H, C_6H_4), 7.16 (m, 2 H, C_6H_4), 7.52 (m, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.96 (d, $^3J_{PC}$ = 11 Hz, $C_5H_4CH_2$), 36.75 (d, $^1J_{PC}$ = 7 Hz, CHP), 39.22 (d, $^2J_{PC}$ = 24 Hz, $C_5H_4CH_2CH_2$), 55.07 (OCH_3), 55.22 (OCH_3), 66.99 (d, J_{PC} = 8 Hz, CH of C_5H_4), 67.43 (CH of C_5H_4), 67.60 (CH of C_5H_4), 67.82 (CH of C_5H_4), 69.07 (CH of C_5H_4), 69.26 (CH of C_5H_4), 71.35 (CH of C_5H_4), 71.73 (d, J_{PC} = 2 Hz, CH of C_5H_4), ca. 85.7 (br s, *C*-CHP of C_5H_4CHP), 85.91 (*C*-CH_2 of $C_5H_4CH_2$), 113.59 (d, $^3J_{PC}$ = 8 Hz, CH of C_6H_4), 114.28 (d, $^3J_{PC}$ = 8 Hz, CH of C_6H_4), 134.48 (d, $^2J_{PC}$ = 19 Hz, CH of C_6H_4), 135.15 (d, $^2J_{PC}$ = 21 Hz, CH of C_6H_4), 160.01 (*C*-OMe of $C_6H_4OCH_3$), 160.70 (*C*-OMe of $C_6H_4OCH_3$). The signals due to *C*-P of PC_6H_4 were not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −4.7 (s). ESI+ MS: *m*/*z* 225 ($[M - P(C_6H_4OMe)_2]^+$), 471 ($[M + H]^+$, 493 ($[M + Na]^+$). EI+ MS: *m*/*z* (relative abundance) 470 (11, $M^{\bullet+}$), 246 (4, $HP(C_6H_4OMe)_2^{\bullet+}$), 225 (100, $[M - P(C_6H_4OMe)_2]^+$), 147 (8, $C_5H_4FeC_2H_3^+$), 138 (16, $HPC_6H_4OMe^+$), 121 (10, $C_5H_5Fe^+$), 91 (4, $C_7H_7^+$). HRMS: calcd for $C_{27}H_{27}FeO_2P$ 470.1098, found 494.1095.

*1,1′-[(1R)-1-{Bis[4-(trifluoromethyl)phenyl]phosphino}-1,3-propanediyl]ferrocene ((R)-**2f**).* Alcohol (*R*)-**1** (125 mg, 0.52 mmol), NaI (116 mg, 0.78 mmol), $ClSiMe_3$ (0.10 mL, 0.78 mmol), and bis[4-(trifluoromethyl)phenyl]phosphine (0.25 g, 0.78 mmol) were reacted in 10 mL of acetonitrile. The reaction mixture was worked up as described above, except that hexane/diethyl ether (3/1) was used to elute the product during column chromatography. Phosphine (*R*)-**2f** was isolated as a yellow solid (165 mg, 58%).

^1H NMR ($CDCl_3$): δ 1.70 (m, 1 H, $C_5H_4CH_2$), 1.92 (m, 1 H, $C_5H_4CH_2CH_2$), 2.16 (m, 1 H, $C_5H_4CH_2CH_2$), 2.44 (ddd, *J* = 13.5, 4.5, 2.6 Hz, 1 H, $C_5H_4CH_2$), 2.64 (ddd, *J* = 11.8, 6.3, 2.3 Hz, 1 H, CHP), 3.78 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.95 (td, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.97 (td, *J*′ = 2.4, 1.2 Hz, C_5H_4), 4.01 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 4.05 (dt, *J*′ = 2.5, 1.3 Hz, 1 H, C_5H_4), 4.07−4.12 (m, 3 H, C_5H_4), 7.25−7.31 (m, 2 H, C_6H_4), 7.39−7.42 (m, 2 H, C_6H_4), 7.65−7.71 (m, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.83 (d, $^3J_{PC}$ = 12 Hz, $C_5H_4CH_2$), 36.34 (d, $^1J_{PC}$ = 13 Hz, CHP), 39.26 (d, $^2J_{PC}$ = 26 Hz, $C_5H_4CH_2CH_2$), 66.98 (d, $^3J_{PC}$ = 9 Hz, CH of C_5H_4), 67.68 (CH of C_5H_4), 67.78 (CH of C_5H_4), 68.23 (CH of C_5H_4), 69.46 (CH of C_5H_4), 69.57 (CH of C_5H_4), 71.47 (CH of C_5H_4), 71.53 (d, J_{PC} = 2 Hz, CH of C_5H_4), 85.10 (d, $^2J_{PC}$ = 16 Hz, *C*-CHP of C_5H_4CHP), 85.38 (*C*-CH_2 of $C_5H_4CH_2$), 123.93 (qd, $^1J_{FC}$ = 272, $^5J_{PC}$ = 4 Hz, CF_3), 124.58 (dq, $^3J_{PC}$ = 7, $^3J_{FC}$ = 4 Hz, CH^{meta} of C_6H_4), 125.46 (dq, $^3J_{PC}$ = 7, $^3J_{FC}$ = 4 Hz, CH^{meta} of C_6H_4), 130.45 (q, $^2J_{FC}$ = 33 Hz, *C*-CF_3 of C_6H_4), 131.47 (q, $^2J_{FC}$ = 33 Hz, *C*-CF_3 of C_6H_4), 133.29 (d, $^2J_{PC}$ = 18 Hz, CH^{ortho} of C_6H_4), 134.04 (d, $^2J_{PC}$ = 20 Hz, CH^{ortho} of C_6H_4), 141.93 (d, $^1J_{PC}$ = 10 Hz, *C*-P of C_6H_4), 142.12 (d, $^1J_{PC}$ = 8 Hz *C*-P of C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.4 (s). ^{19}F NMR ($CDCl_3$): δ −63.1 (s). ESI+ MS: *m*/*z* 225 ($[M - P(CF_3C_6H_4)_2]^+$), 546 (M^+), 585 ($[M + K]^+$). EI+ MS: *m*/*z* (relative abundance) 546 (24, $M^{\bullet+}$), 225 (100, $[M - P(C_6H_4CF_3)_2]^+$), 147 (16, $C_5H_4FeC_2H_3^+$), 145 (8, $C_6H_4CF_3^+$), 121 (14, $C_5H_5Fe^+$), 56 (7, Fe^+). HRMS: calcd for $C_{27}H_{21}F_6FeP$ 546.0640, found 546.0634.

Preparation of 1,1′-[(1*R*)-1-(Diphenylthiophosphinoyl)-1,3-propanediyl]ferrocene ((*R*)-3). Phosphine (*R*)-**2a** (84 mg, 0.20 mmol) and elemental sulfur (7 mg, 0.22 mmol) were allowed to react in dry toluene (5 mL) at room temperature for 20 h. The reaction mixture was evaporated, and the residue was filtered through a plug of silica gel (elution with dichloromethane) to afford pure phosphine sulfide (*R*)-**3** after evaporation. Yield: 89 mg (98%), yellow orange solid. X-ray-quality crystals were grown by slow cooling of an acetonitrile solution.

Mp: 224.7−252.2 °C dec (MeCN). ^1H NMR ($CDCl_3$): δ 1.75 (m, 1 H, $C_5H_4CH_2$), 2.26 (m, 2 H, $C_5H_4CH_2CH_2$), 2.50 (dt, *J* = 14.6, 3.3 Hz, 1 H, $C_5H_4CH_2$), 2.99 (td, *J* = 10.5, 2.8 Hz, 1 H, CHP), 3.77 (m, 1 H, C_5H_4), 3.90 (td, *J* = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.94 (td, *J* = 2.4, 1.3 Hz, 1 H, C_5H_4), 4.04−4.06 (m, 2 H, C_5H_4), 4.06−4.09 (m, 2 H, C_5H_4), 4.60 (m, 1 H, C_5H_4), 7.24−7.30 (m, 2 H, PPh_2), 7.32−7.38 (m, 1 H, PPh_2), 7.48−7.56 (m, 3 H, PPh_2), 7.61−7.68 (m, 2 H, PPh_2), 8.02−8.08 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.16 (d, $^3J_{PC}$ = 14 Hz, $C_5H_4CH_2$), 36.67 (d, $^1J_{PC}$ = 5 Hz, CHP), 40.55 (d, $^2J_{PC}$ = 53 Hz, $C_5H_4CH_2CH_2$), 67.53 (CH of C_5H_4), 67.62 (CH of C_5H_4), 68.01 (d, J_{PC} = 2 Hz, CH of C_5H_4), 68.09 (CH of C_5H_4), 69.61 (CH of C_5H_4), 69.77 (CH of C_5H_4), 71.44 (CH of C_5H_4), 72.07 (d, $^2J_{PC}$ = 4 Hz, CH of C_5H_4), 80.34 (d, $^2J_{PC}$ = 2 Hz, *C*-CHP of C_5H_4CHP), 85.32 (*C*-CH_2 of $C_5H_4CH_2$), 127.90 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} of PPh_2), 128.61 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} of PPh_2), 131.03 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.49 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.51 (d, $^3J_{PC}$ = 9 Hz, CH^{meta} of PPh_2), 131.69 (d, $^3J_{PC}$ = 10 Hz, CH^{meta} of PPh_2), 131.90 (d, $^1J_{PC}$ = 79 Hz, C^{ipso} of PPh_2), 132.44 (d, $^1J_{PC}$ = 80 Hz, C^{ipso} of PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.3 (s). MS EI+: *m*/*z* (relative abundance) 442 (18, $M^{\bullet+}$), 225 (100, $[M - PSPh_2]^+$), 186 (6, $HPPh_2^{\bullet+}$), 147 (9, $C_5H_4FeC_2H_3^+$), 121 (8, $C_5H_5Fe^+$), 108 (11, PPh^+), 56 (4, Fe^+). ESI+ MS: *m*/*z* 225 ($[M - P(S)Ph_2]^+$), 410 ($[M - S]^+$), 442 (M^+), 465 ($[M + Na]^+$), 481 ($[M + K]^+$). HRMS: calcd for $C_{25}H_{23}FePS$ 442.0608, found 442.0616. Anal. Calcd for $C_{25}H_{23}FePS$ (442.3): C, 67.88; H, 5.24. Found: C, 67.75; H, 5.19.

Synthesis of *trans*-4. A solution of $[PdCl_2(cod)]$ (28.5 mg, 0.010 mmol) in dry dichloromethane (6 mL) was added dropwise to a solution of (*R*)-**2a** in the same solvent (82 mg, 0.020 mmol in 1 mL). The resulting deep red solution was stirred for 30 min and then evaporated under vacuum. The residue was treated with pentane (twice, 2 mL) under sonication and then dried under vacuum, yielding *trans*-**4** as a fine orange-red solid (92 mg, 92%). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane/hexane.

^1H NMR ($CDCl_3$): δ 1.66 (dd, *J* = 12.0, 2.5 Hz, 1 H, $C_5H_4CH_2CH_2$), 1.94 (td, *J* = 12.6, 2.5 Hz, 1 H, $C_5H_4CH_2$), 2.46 (dt, *J* = 15, 3.2 Hz, 1 H, $C_5H_4CH_2$), 2.98−3.05 (m, 1 H, $C_5H_4CH_2CH_2$), 3.05 (dt, *J* = 2.6, 1.3 Hz, 1 H, C_5H_4), 3.65 (dt, *J* = 10.6, 4.5 Hz, 1 H, CHP), 3.81 (dt, *J* = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.89 (m, 2 H, C_5H_4), 3.95 (m, 2 H, C_5H_4), 4.08 (dt, *J* = 2.5, 1.3 Hz, 1 H, C_5H_4), 4.14 (dt, *J* = 2.6, 1.3 Hz, 1 H, C_5H_4), 7.29−7.47 (m, 6 H, PPh_2), 7.50−7.57 (m, 2 H, PPh_2), 7.72−7.78 (m, 2 H, PPh_2). $^{13}C\{^1H\}$

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NMR ($CDCl_3$): δ 25.77 (virtual t, J_{PC} = 7 Hz, $C_5H_4CH_2$), 34.93 (virtual t, J_{PC} = 11 Hz, CHP), 39.55 (virtual t, J_{PC} = 6 Hz, $C_5H_4CH_2CH_2$), 67.46 (CH of C_5H_4), 67.79 (CH of C_5H_4), 67.86 (CH of C_5H_4), 68.10 (CH of C_5H_4), 68.93 (CH of C_5H_4), 69.39 (CH of C_5H_4), 71.91 (CH of C_5H_4), 73.26 (CH of C_5H_4), 81.39 (C^{ipso} of C_5H_4), 86.36 (C^{ipso} of C_5H_4), 127.37 (virtual t, J_{PC} = 22 Hz, C^{ipso} of PPh_2), 127.50 (virtual t, J_{PC} = 5 Hz, CH of PPh_2), 127.83 (virtual t, J_{PC} = 5 Hz, CH of PPh_2), 128.44 (virtual t, J_{PC} = 21 Hz, C^{ipso} of PPh_2), 130.34 (CH^{para} of PPh_2), 130.46 (CH^{para} of PPh_2), 134.54 (virtual t, J_{PC} = 6 Hz, CH of PPh_2), 135.11 (virtual t, J_{PC} = 6 Hz, CH of PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.6 (s). ESI+ MS: m/z 25 ($[M - Cl - HCl]^+$), 1019 (weak, $[M + Na]^+$). IR (DRIFTS): ν_{max} 3090 w, 3052 w, 2936 w, 2907 w, 2843 w, 1482w, 1434 s, 1333 w 1290 w, 1156 m, 1102 m, 1043 w, 1031 m 999 w, 903 m, 851 w, 807 m, 751 m 699 s, 660 w, 630 w, 612 w, 518 m, 497 s, 481 w, 454 w, 420 w cm^{-1}. Anal. Calcd for $C_{50}H_{46}Cl_2Fe_2P_2Pd{\cdot}0.6CH_2Cl_2$ (1048.7): C, 57.94; H, 4.54. Found C, 57.93; H, 4.53. The presence of clathrated solvent was verified by NMR spectroscopy.

Isolation of *cis*-4. Complex *cis*-**4** was isolated from the reaction mixture remaining after Pd-catalyzed asymmetric allylic alkylation (see below). A reddish orange band, which remained adsorbed on the top of the chromatographic column after complete removal of the "organic" reaction products (silica gel, hexane/ethyl acetate 3/1), was eluted by increasing the polarity of the mobile phase (hexane/ethyl acetate 1/1). The resulting deep orange band was collected and evaporated. Subsequent crystallization of the evaporation residue from dichloromethane/hexane (liquid-phase diffusion) afforded the solvate *cis*-**4**·$2CH_2Cl_2$ as red prisms. The yield was not determined.

^1H NMR ($CDCl_3$): δ 2.02 (m, 2 H, CH_2), 2.39 (br s, 1 H, CH_2), 2.59 (m, 1 H, CH_2), 3.64 (dt, J = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.73 (m, 1 H, C_5H_4), 3.70−3.86 (m, 4 H, 3× CH of C_5H_4 + CHP), 3.84 (td J = 2.5, 1.2, Hz, 1 H, C_5H_4), 3.87 (td, J = 2.5, 1.3 Hz, 1 H, C_5H_4), 3.98 (dt, J = 2.4, 1.4 Hz, 1 H, C_5H_4), 6.56 (virtual t, J = 7.4 Hz, 2 H, PPh_2), 6.66 (br s, 2 H, PPh_2), 7.00 (virtual t, J = 7.5 Hz, 1 H, PPh_2), 7.41−7.46 (m, 2 H, PPh_2), 7.56−7.61 (m, 1 H, PPh_2), 7.94−8.00 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.70 (nonbinomial t, J_{PC} = 7 Hz, $C_5H_4CH_2$), 40.56 (nonbinomial t, J = 5 Hz, CHP), 43.68 (d, J = 29 Hz, $C_5H_4CH_2CH_2$), 67.00 (CH of C_5H_4), 67.56 (d, J_{PC} = 7 Hz, CH of C_5H_4), 67.86 (CH of C_5H_4), 69.42 (2 C, CH of C_5H_4), 72.01 (CH of C_5H_4), 73.89 (CH of C_5H_4), 77.21 (CH of C_5H_4), 81.00 (C^{ipso} of C_5H_4), 81.15 (C^{ipso} of C_5H_4), 125.41 (d, J_{PC} = 49 Hz, C^{ipso} of PPh_2), 127.43 (virtual t, J_{PC} = 5 Hz, CH of PPh_2), 127.62 (virtual t, J_{PC} = 5 Hz, CH of PPh_2), 128.22 (virtual dd, J_{PC} = 47 and 5 Hz, C^{ipso} of PPh_2), 129.59 (CH^{para} of PPh_2), 131.75 (virtual t, J_{PC} = 6 Hz, CH of PPh_2), 132.05 (CH^{para} of PPh_2), 137.89 (virtual t, J_{PC} = 6 Hz, CH of PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.9 (s). ESI+ MS: m/z 925 ($[M - Cl - HCl]^+$), 1019 (weak, $[M + Na]^+$). Anal. Calcd for $C_{50}H_{46}Cl_2Fe_2P_2Pd{\cdot}0.2CH_2Cl_2$ (1014.8): C, 59.41; H, 4.61. Found: C, 59.39; H, 4.50. The amount of residual solvent was corroborated by NMR spectroscopy.

Preparation of Complex 5. A solution of the dimer $[(L^{NC})PdCl_2]_2$ (20.7 mg, 37.5 μmol) in dichloromethane (2 mL) was added to solid phosphine (*R*)-**2a** (31 mg, 75 μmol). The resulting clear orange solution was stirred for 90 min and evaporated under vacuum. The residue was washed with pentane and dried under vacuum to afford **5** as an orange powdery solid (50 mg, quantitative). X-ray-quality crystals of **5**·$2CHCl_3$ were grown by liquid-phase diffusion of hexane into a solution in chloroform.

^1H NMR ($CDCl_3$): δ 1.79 (m, 1 H, $C_5H_4CH_2CH_2$), 2.04 (td, J = 12.0, 2.7 Hz 1 H, $C_5H_4CH_2$), 2.48 (m, 1 H, $C_5H_4CH_2$), 2.71 (d, $^4J_{HH}$ = 2.4 Hz, 3 H, NCH_3), 2.89 (s, 1 H, C_5H_4), 2.98 (d, $^4J_{HH}$ = 3.1 Hz, 3 H, NCH_3), 3.39 (m, 1 H, $C_5H_4CH_2CH_2$), 3.60 (dd, $^2J_{HH}$ = 13.5, $^4J_{PH}$ = 3.4 Hz, 1 H, NCH_2), 3.66 (t, J = 11 Hz, 1 H, CHP), 3.80 (m, 1 H, C_5H_4), 3.88 (m, 1 H, C_5H_4), 3.91 (m, 1 H, C_5H_4), 3.94 (m, 1 H, C_5H_4), 3.98 (m, 1 H, C_5H_4), 4.09 (m, 2 H, C_5H_4), 4.43 (d, $^2J_{HH}$ = 13.5 Hz, 1 H, NCH_2), 6.25 (td, J = 7.8, 1.3 Hz, 1 H, C_6H_4), 6.32 (br t, J = 7.8 Hz, 1 H, C_6H_4), 6.73 (td, J = 7.3, 1.2 Hz, 1 H, C_6H_4), 6.91 (dd, J = 7.3, 1.4 Hz, 1 H, C_6H_4), 7.21−7.27 (m, 2 H, PPh_2), 7.32−7.40 (m, 3 H, PPh_2), 7.43−7.49 (m, 1 H, PPh_2), 7.56−7.62 (m, 2 H, PPh_2), 7.99−8.05 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.48 (d, $^3J_{PC}$ = 15 Hz, $C_5H_4CH_2$), 39.90 (d, $^1J_{PC}$ = 26 Hz, CHP), 40.76 (d, $^2J_{PC}$ = 11 Hz, $C_5H_4CH_2CH_2$), 49.17 (d, $^3J_{PC}$ = 3 Hz, NCH_3), 51.50 (d, $^3J_{PC}$ = 2 Hz, NCH_3), 67.38 (CH of C_5H_4), 67.48 (d, J_{PC} = 1 Hz, CH of C_5H_4), 67.66 (CH of C_5H_4), 67.97 (CH of C_5H_4), 68.87 (CH of C_5H_4), 69.27 (CH of C_5H_4), 71.91 (CH of C_5H_4), 73.10 (d, $^3J_{PC}$ = 3 Hz, NCH_2), 73.56 (d, $^3J_{PC}$ = 2 Hz, CH of C_5H_4), 81.19 (d, $^2J_{PC}$ = 2 Hz, *C*-CHP of C_5H_4), 86.35 (*C*-CH_2 of C_5H_4), 122.04 (CH of C_6H_4), 123.47 (CH of C_6H_4), 125.07 (d, J_{PC} = 6 Hz, CH of C_6H_4), 127.42 (d, J_{PC} = 10 Hz, CH of PPh_2), 127.88 (d, $^1J_{PC}$ = 43 Hz, C^{ipso} of PPh_2), 127.91 (d, J_{PC} = 10 Hz, CH of PPh_2), 129.32 (d, $^1J_{PC}$ = 43 Hz, C^{ipso} of PPh_2), 130.22 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 131.08 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 134.56 (d, J_{PC} = 11 Hz, CH of PPh_2), 136.51 (d, J_{PC} = 13 Hz, CH of PPh_2), 137.67 (d, $^3J_{PC}$ = 11 Hz, CH of C_6H_4), 147.84 (d, $^2J_{PC}$ = 2 Hz, C^{ipso} of C_6H_4), 152.10 (C^{ipso} of C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.7 (s). ESI+ MS: m/z 650 ($[M - Cl]^+$), 708 (weak, $[M + Na]^+$). IR (DRIFTS): ν_{max} 3459 br w, 3075 m, 3051 m, 2909 m, 2847 m, 1580 m, 1481 m, 1451 m, 1436 s, 1399 w, 1358 w, 1333 w, 1289 w, 1246 w, 1212 w, 1185 w, 1159 w, 1099 m, 1043 m, 1030 m, 997 m, 973 w, 905 m, 861 m, 845 m, 805 m, 740 s, 696 s, 662 w, 630 w, 613 w, 551 w, 520s, 501 s, 501 s, 484 m, 460 m, 421 w cm^{-1}. Anal. Calcd for $C_{34}H_{35}ClFeNPPd{\cdot}2CHCl_3$ (925.0): C, 46.74; H, 4.03; N, 1.51. Found: C, 46.56; H, 3.90; N, 1.34.

Catalytic Tests in Asymmetric Allylic Alkylations. Catalytic experiments were carried out as described in the literature.[49] A flame-dried Schlenk flask was charged with a stirring bar, $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.3 mg, 6.3 μmol), and the appropriate chiral phosphine **2** (25 or 12.5 μmol; see Table 3), flushed with argon, and sealed with a rubber septum. Dry dichloromethane (1 mL) was introduced, and the resulting solution was stirred at room temperature for 30 min. Then, racemic 1,3-diphenylallyl acetate (**6**; 63.1 mg, 0.25 mmol in 1 mL of dichloromethane) was added and the mixture was stirred for another 5 min before a mixture of dimethyl malonate (90 μL, 0.75 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (BSA; 0.19 mL, 0.75 mmol) in dichloromethane (1 mL) was added as the last component. The resulting mixture was stirred at room temperature for 24 h, whereupon it typically turned from yellow to red.

The reaction mixture was diluted with dichlormethane (3 mL) and washed with saturated aqueous NH_4Cl solution (2 × 5 mL). The organic layer was dried over magnesium sulfate and evaporated, leaving a residue which was purified by column chromatography (silica gel, hexane/ethyl acetate 3/1). The first band containing the starting allyl acetate was discarded, and the following one containing the alkylation product and unreacted malonate (if any) was collected and evaporated. Conversion (yield) was obtained by integration of ^1H NMR spectra recorded in C_6D_6. Enantiomeric excess was determined after addition of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) ([Eu(tfc)$_3$]).[50] Analytical data for the alkylation product **7** are given in the Supporting Information.

Catalytic Tests in Asymmetric aza-Morita-Baylis-Hillman Reactions. A flame-dried Schlenk tube was charged with the appropriate imine (0.50 mmol), chiral phosphine **2** (50 μmol), anisole (0.50 mmol, internal standard), and the additive (only if appropriate; either 300 mg of dry 4 Å molecular sieves or 25 μmol of benzoic acid), flushed with argon, and sealed with a rubber septum. Dry solvent (typically $CDCl_3$, 2 mL) was introduced, followed immediately by methyl vinyl ketone (1.0 mmol). The resultant mixture was stirred at room temperature overnight, and a small aliquot was analyzed by ^1H NMR spectroscopy. The rest was evaporated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate 3/1). Following evaporation, the residue was analyzed with HPLC on a suitable chiral column. Stereochemistry of the dominating enantiomer was established by a comparison of optical rotation with the literature values.[51]

Prior to the catalytic experiments with phosphines (*R*)-**2a**−**f**, the reactions were always performed with triphenylphosphine. Following evaporation of the reaction mixture, the racemic products **9a**−**e** were isolated by column chromatography over silica gel using a hexane/ethyl acetate mixture as the eluent (the composition of the mobile phase was gradually changed from 9/1 to 2/1). They were used as reference standards and for calibration of the HPLC analytical

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methods. Characterization data for **9a**–**e** are available as Supporting Information.

X-ray Crystallography. Full-set diffraction data ($\pm h,\pm k,\pm l$; θ_{max} = 27.5°, data completeness ≥99.8%) were collected with a Nonius Kappa diffractometer equipped with an Apex2 detector (Bruker) and Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-87[52]) and refined by full-matrix least squares based on F^2 (SHELXL-97[52]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogens were included in their calculated positions and refined as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq} of their bonding atom. Relevant crystallographic data and structure refinement parameters are presented as Supporting Information (Table S1). Geometric data and structural drawings were obtained with a recent version of the PLATON program.[53] The numerical values are rounded with respect to their estimated deviations (ESDs) given to one decimal place.

■ ASSOCIATED CONTENT

Supporting Information

Text giving analytical data for the products of the catalytic reactions, an NMR profile for the isomerization of *cis*-**4** to *trans*-**4** (Figure S1), an overlap of the crystallographic independent molecules of *trans*-**4** (Figure S2), a summary of crystallographic data (Table S1), figures giving NMR spectra, and CIF files and tables giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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