Diphosphines Containing Stereogenic P Atoms: Synthesis of (*S,S*)-*C,C′*-Tetramethylsilanebis-(1-naphthylphenylphosphine) and Applications in Enantioselective Catalysis

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The diphosphine (*S,S*)-$Me_2Si(CH_2P(1\text{-}Np)(Ph))_2$ (1-Np = 1-naphthyl) (**1**), containing stereogenic P atoms, is prepared with high diastereo- and enantiomeric purity by a multistep asymmetric synthesis via its borane adduct (*S,S*)-$Me_2Si(CH_2P(1\text{-}Np)(Ph)(BH_3))_2$ (**2**), obtained by selective methyl lithiation of the enantiomerically pure phosphine borane (*S*)-P(1-Np)(Ph)(Me)(BH_3) (**3**) and coupling onto Me_2SiCl_2. The absolute configuration of **3** is established by X-ray studies. Reacting **2** with morpholine gives free diphosphine (*S,S*)-**1** with a (*S,S*):(*R,R*) enantiomeric ratio better than 99:1. The Rh(I) and Ru(II) derivatives [Rh(diene)((*S,S*)-**1**)] (diene = norbornadiene, **4a**; 1,5-cyclooctadiene, **4b**) and [$RuCl_2(PPh_3)$((*S,S*)-**1**)] (**5**) are prepared and tested as catalyst precursors in enantioselective reactions with standard substrates. In the presence of **4b** as catalyst precursor, a series of dehydroamino acid derivatives are hydrogenated with up to 97.7% ee. Complex **5** catalyzes the hydrogenation of pentane-2,4-dione to (*S,S*)-pentane-2,4-diol with up to 56% ee. Ligand **1** gives enantioselection also in the Pd-catalyzed allylic alkylation of 1,3-diphenyl-3-acetoxypropene with dimethyl malonate (27% ee).

Introduction

During the amazing development of metal-catalyzed enantioselective reactions, and in spite of the early success achieved with dipamp,[1] diphosphines containing stereogenic P atoms have been outnumbered by ligands based on alternative chiral elements.[2] Among these, the atropisomeric ligands of the BINAP family, the planar chiral ferrocenyl phosphines, and those of the DuPHOS group have brought about the long-awaited breakthrough in enantioselective catalysis with respect to industrial application.[3] However, the very recent preparation of BIPNOR and its successful application in enantioselective catalysis[4] suggest that the potential of diphosphines containing stereogenic P atoms has not been exhaustively investigated.

Apparently, both synthetic problems and the widespread prejudice about the low stability of the configuration at the P atom have hampered the development of phosphine ligands containing stereogenic P atoms.[5] However, lately several groups have been developing new methods for the asymmetric synthesis of chiral diphosphines that fulfill the requirements of large-scale preparation.[6−8] The general strategy encompasses three steps, namely, (a) the synthesis of an enantiomerically pure, borane-protected phosphine, (b) coupling of two of these moieties to form the protected diphosphine ligand, and (c) its deprotection to give the free diphosphine. All the methods exploit the diastereoselective formation of a cyclic phospholidine intermediate with a bifunctional chiral auxiliary that bears two different heteroatoms, such as O and N,[6,7] or O and S.[8] The two heteroatoms are then stepwise substituted diastereospecifically by nucleophilic aryl or alkyl groups. The chirality at the P atom needs to be stabilized by a protecting group X, which can be BH_3,[6,8] sulfide,[8] or oxide.[7]

Starting from Imamoto's work on phosphine boranes,[9] Jugé and co-workers have developed a methodology for

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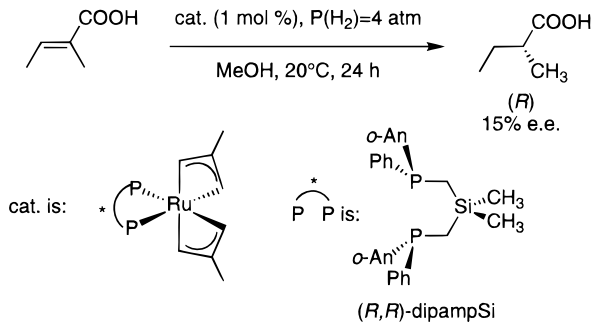
Chart 1



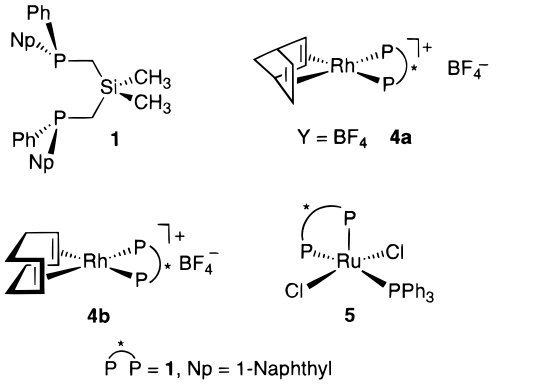
the synthesis of enantiomerically pure, borane-protected P-chiral phosphines of the type P(Ph)(R)(Me)(BH_3),[6a] which can be selectively lithiated at the methyl group. The resulting P(Ph)(R)(BH_3)CH_2Li gives the borane-protected diphosphine either by oxidative coupling or by nucleophilic substitution at R_2SiCl_2. The borane adducts appear to be particularly versatile intermediates in that they are crystalline, chemically and configurationally stable under vigorous reaction conditions, and easily converted into the free diphosphine by reaction with an amine. A different approach is the selective deprotonation of the enantiotopic methyl groups of the borane-protected dimethylarylphosphines P(Ar)-$(Me)_2(BH_3)$ in the presence of a chiral auxiliary, followed by coupling onto the diphosphine framework.[10]

The new protocols for the synthesis of enantiopure P-chiral ligands allow one to screen systematically diphosphines containing stereogenic P atoms in asymmetric catalysis. However, in spite of the effort invested in the development of such diphosphines, reports concerning their catalytic applications are still rare. Genêt et al. reported that the ruthenium-catalyzed asymmetric hydrogenation of tiglic acid using the ligand (*R*,*R*)-Me_2-$Si(CH_2P(o\text{-}An)(Ph))_2$ (*o*-An = *o*-$MeOC_6H_4$) (dipampSi) gives 2-methylbutyric acid with 15% ee (Chart 1).[11] To explore the potential of these ligands further, we prepared the new diphosphine (*S*,*S*)-*C*,*C*′-tetramethylsilanebis(1-naphthylphenylphosphine), (*S*,*S*)-**1**.[12] We report herein a full experimental account of the synthesis of **1** and of its derivatives [Rh(diene)((*S*,*S*)-**1**)] (diene = norbornadiene, **4a**; 1,5-cyclooctadiene, **4b**) and [$RuCl_2(PPh_3)$((*S*,*S*)-**1**)] (**5**) (Chart 2), as well as preliminary catalytic results.

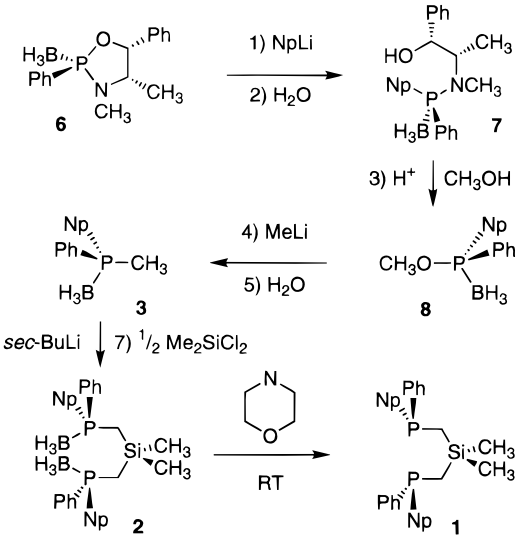
Results and Discussion

Synthesis of (*S*,*S*)-$Me_2Si(CH_2P(1\text{-}Np)(Ph))_2$ ((*S*,*S*)-1). The synthesis of the P-chiral diphosphine (*S*,*S*)-**1** follows the methodology used by Jugé (Scheme 1)[6] and starts from oxazaphospholidine borane (*R*)-**6**, which is prepared from (+)-(1*S*,2*R*)-ephedrine according to the literature.[6a] The new intermediate products **3**, **7**, and **8** are easily purified by conventional methods (recrystallization and column chromatography). The overall (recrystallized) yield is 35%, whereby the acid methanolysis **7** → **8** (60%, recrystallized) and the deprotection step **2** → **1** (78%) give the lower yields.

Chart 2



Scheme 1



Treatment of (*R*)-**6** with 1-naphthyllithium gives the aminophosphine borane diastereomer (*S*)-**7**, whose configuration is attributed by analogy.[6a] Acid-catalyzed methanolysis yields the phosphinite borane P(OMe)(1-Np)(Ph)(BH_3), (*R*)-**8**; inversion of configuration at the phosphorus atom is assumed.[6a] Recrystallization of the crude product from hexane yields enantiomerically pure (*R*)-**8** in 60% yield. Methylation of the phosphinite borane (*R*)-**8** with MeLi and recrystallization from hexane produces enantiomerically pure (*S*)-P(1-Np)(Ph)-(BH_3), (*S*)-**3**, in 81% yield. The enantiomeric purity of **3** and **8** is determined by chiral HPLC; the analytical conditions were optimized using racemic P(OMe)(1-Np)-(Ph)(BH_3) ((*rac*)-**8**) and (*rac*)-P(1-Np)(Ph)(Me)(BH_3) ((*rac*)-**3**), which were prepared as described in Scheme 2.

The predicted[6a] *S* configuration of **3** is confirmed by an X-ray crystallographic investigation. Crystals were grown from CH_2Cl_2/hexane. An ORTEP drawing is shown in Figure 1, and selected bond distances and angles are reported in Table 1. The crystal contains discrete P(1-Np)(Ph)(Me)(BH_3) molecules with normal nonbonded interactions. The geometry of the P atom is approximately tetrahedral, with normal P−C and

(10) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075.

(11) (a) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño De Andrade, M. C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 665. (b) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño De Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675. (c) Genêt, J. P.; Jugé, S.; Laffitte, J. A.; Pinel, C.; Mallart, S. (Elf Aquitaine). PCT Int. Appl. WO 01390, **1994**; *Chem. Abstr.* **1994**, *121*, P156763d.

(12) Absolute configuration at the P atom is expressed in terms of the Cahn−Ingold−Prelog sequence rules[13] and, in the case of **1**, refers to the uncoordinated ligand.

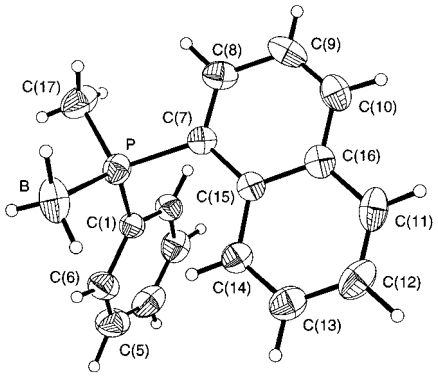


Figure 1. ORTEP view of (*S*)-P(1-Np)(Ph)(BH_3) (**3**).

Scheme 2

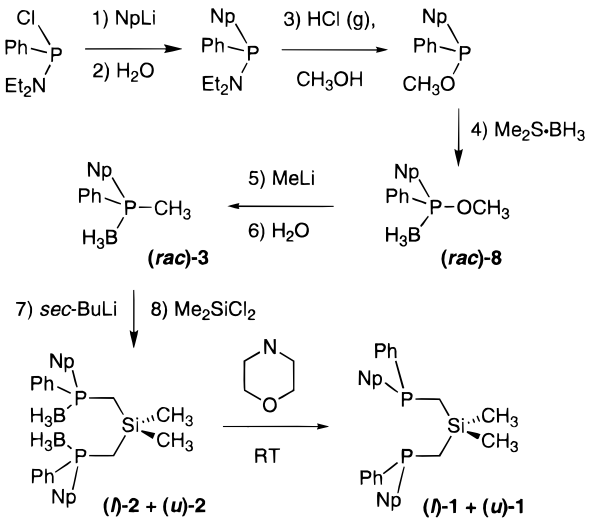


Table 1. Selected Bond Lengths (Å) and Angles (deg) for (*S*)-P(1-Np)(Ph)(Me)(BH_3)

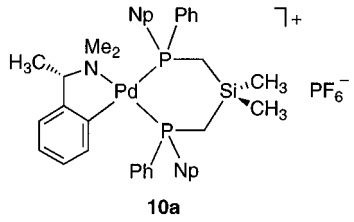
P−C(1)	1.807(3)	P−C(17)	1.810(4)
P−C(7)	1.823(3)	P−B	1.920(4)
C(1)−P−C(7)	104.9(1)	C(7)−P−C(17)	106.0(2)
C(1)−P−C(17)	103.2(2)	C(7)−P−B	116.9(2)
C(1)−P−B	115.8(2)	C(17)−P−B	108.9(2)

P−B distances and slightly opened C−P−B angles, as found in other phosphine borane adducts.[14] The planes of the naphthyl and phenyl rings are approximately perpendicular to one another. Least-squares refinement of the sign of $\Delta f''$ ($\eta = +1.0(2)$) supports the *S* configuration.[15] This is consistent with retention of configuration in step **6** → **7** and inversion in both steps **7** → **8** and **8** → **3** (Scheme 1).[6]

Deprotonation of phosphine borane **8** with *sec*-BuLi yields $LiCH_2P$(1-Np)(Ph)(BH_3), which is then reacted in situ with Me_2SiCl_2 (0.5 equiv) to give the borane-protected diphosphine $Me_2Si(CH_2P(Ph)(1\text{-}Np)(BH_3))_2$ (**2**). Compound **2** is obtained as an amorphous solid by evaporation of a CH_2Cl_2/hexane solution. The low solubility of **2** in hexane/^{i}PrOH mixtures prevents determination of its enantiomeric purity using chiral HPLC. However, the *l*:*u* diastereomeric ratio[16] of 99:1 found for crude **2** affords indirect evidence that the coupling step does not affect significantly the configuration at the P atom. Column chromatography does not improve further this diastereomeric ratio, and the crude product is used for the deprotection step.

Reaction of **2** with morpholine *at room temperature* gives free diphosphine **1** as the method of choice.[17] As borane decomplexation reactions are known to occur with retention of configuration at the phosphorus atoms,[6] the absolute configuration *S,S* is assigned to **1**. Integration of the ^{1}H NMR signals of the $SiMe_2$ groups of crude **1** gives a diastereomeric ratio of 99:1.[19] A lower *l*:*u* diastereomeric ratio of 93:7 is achieved under conditions generally used for similar ligands (refluxing in $HNEt_2$ overnight).[6a] Removal of excess amine (Et_2NH or morpholine) under vacuum yields **1** as a viscous oil. Pure **1** is obtained by chromatography over alumina, which efficiently removes traces of the amine borane adduct. By contrast, free **1** partially decomposes on silica gel, apparently due to the cleavage of one Si−CH_2−P bond. Together with unidentified products, large amounts of the free phosphine **3** (up to 24%) are detected in the ^{31}P NMR spectra of samples of **1** recovered after chromatography on silica gel.

The enantiomeric purity of **1** is determined by integration of the ^{31}P NMR spectra of its (*S*)- and (*R*)-*N*,*N*-dimethyl-1-phenylethylamine ((*S*)- and (*R*)-**9**) palladium(II) complexes [Pd((*S*)-**9**-*C*,*N*)((*S*,*S*)-**1**)]PF_6 (**10a**) and [Pd((*R*)-**9**-*C*,*N*))((*S*,*S*)-**1**)]PF_6 (**10b**) by a modification of the procedure reported by Kyba and Rines.[20] In a



10a

preliminary experiment, the signals of diastereomers (S_C,S_P,$S_{P'}$)-, (S_C,S_P,$R_{P'}$)-, and (S_C,R_P,$R_{P'}$)-**10** are assigned by comparison of the ^{31}P NMR spectra of **10a** and **10b** prepared using a 92:8 *l*:*u* diastereomer mixture of **1** obtained from crude **3** (93% ee). Then, the enantio- and diasteromeric purity of the free ligand (*S*,*S*)-**1** is determined by reaction of (*S*,*S*)-**1** (obtained from (*S*,*S*)-**3** (ee > 99%) using the procedure reported above) with (*S*)-**9** and ^{31}P NMR analysis of the diastereomer mixture of **10a**. The ^{31}P NMR spectrum of crude **10a** exhibits, along with the signals of the main diastereomer [Pd((*S*)-**9**-3*C*,*N*)((*S*,*S*)-**1**)]PF_6, (S_C,S_P,$S_{P'}$)-**10a**, two resolved doublets for each (minor) isomer (S_C,R_P,$S_{P'}$)-, (S_C,-

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(15) Jones, P. G. *Acta Crystallogr.* **1984**, *A43*, 660.

(16) By integration of the ^{1}H NMR signals of the $SiMe_2$ groups, assigned by comparison with the spectra of a 1:1 mixture of (*l*)-**2** and (*u*)-**2** prepared by coupling racemic phosphine borane (*rac*)-**3** onto Me_2SiCl_2 (Scheme 2).

(17) Both deprotection with 1,3,5,7-tetraazaadamantane or 1,4-diazabicyclo[2.2.2]octane (DABCO) and acid workup with $[Et_2OH]BF_4$[18] resulted in extensive decomposition of **1** to P(1-Np)(Ph)(Me) and other unidentified products.

(18) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.

(19) The signals of (*l*)- and (*u*)-**1** were assigned by comparison with the ^{1}H NMR spectrum of a 1:1 mixture of (*l*)-**1** and (*u*)-**1**, obtained by deprotection of a mixture of (*l*)- and (*u*)-**2** with morpholine (Scheme 2).

(20) Kyba, E. P.; Rines, S. P. *J. Org. Chem.* **1982**, *47*, 4800.

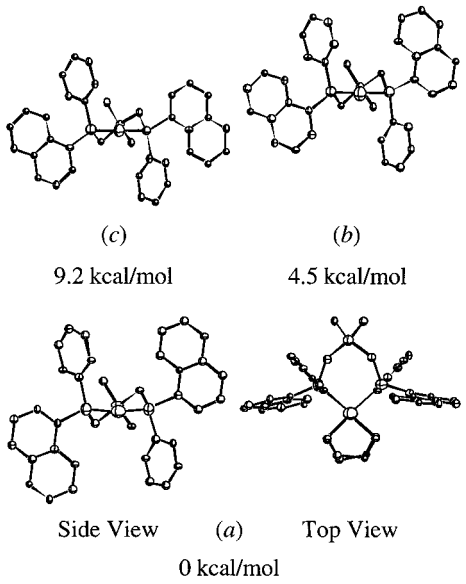


Figure 2. Lowest energy rotamers calculated for **4b** and relative energies. (COD not drawn in *a*, side view, and *b* and *c* for clarity.)

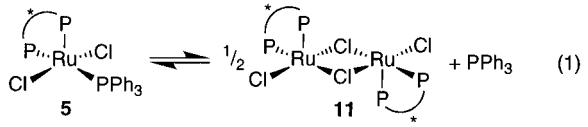
$S_P,R_{P'}$)-, and ($S_C,R_P,R_{P'}$)-**10a**. Integration of the signals of ($S_C,S_P,S_{P'}$)- and ($S_C,R_P,R_{P'}$)-**10a** shows that the *S,S*:*R,R* enantiomeric ratio of **1** is better than 99:1. The value of 99:1 found for the *l*:*u* diastereomeric ratio, independently found by ^{1}H NMR, is confirmed by the integration of the signals of ($S_C,R_P,S_{P'}$)- and ($S_C,S_P,R_{P'}$)-**10a**.

Solution NMR Studies of 1. The resonances of the naphthyl H atoms in the ^{1}H NMR spectrum of free **1** were assigned by means of 2D NMR experiments, in order to check whether complexation to a metal center leads to hindered rotation of the 1-Np groups about the P−C^1 bond. The signals of naphthyl, phenyl, methylene, and methyl H atoms were attributed by means of ^{31}P−^{1}H and ^{13}C−^{1}H correlation and NOESY experiments. The NOESY spectrum indicates that the 1-Np group freely rotates in uncomplexed **1** in $CDCl_3$ at room temperature, as both naphthyl protons on C^2 and C^8 exhibit cross peaks to CH_2P and (CH_3)$_2$Si.

Rhodium and Ruthenium Derivatives. The rhodium derivatives [Rh(diene)((*S,S*)-**1**)]BF_4 (diene = norbornadiene, **4a**; diene = 1,5-cyclooctadiene, **4b**) are prepared from [Rh(diene)$_2$]BF_4 and **1** in THF solution and characterized by ^{1}H and ^{31}P NMR spectroscopy, FAB$^+$ mass spectrometry, and microanalysis. Molecular modeling (UFF calculations based on the Cerius^2 program)[21] shows that the chelate ring of **4b** adopts a twist conformation with equatorial 1-naphthyl groups (Figure 2). Hindered rotation of the 1-naphthyl groups about the P−C^1 bonds gives rise to three rotamers, *a*, *b*, and *c*, with increasing calculated energies as reported in Figure 2. The less crowded NBD derivative **4a** exhibits an analogous situation, but the energy differences among rotamers *a*−*c* are smaller.

The solution behavior of **4a,b** is consistent with naphthyl group rotation being slow on the NMR time scale. The room temperature ^{31}P NMR spectrum of **4a** shows a broad doublet ($w_{1/2} \approx 430$ Hz, $^2J_{PP'} \approx 160$ Hz, $CDCl_3$, 101.3 MHz), which splits up by lowering the temperature and is resolved at −60 °C in a singlet and an AX system (intensity ratio 58:42) for the symmetric and asymmetric rotamers. In the ^{1}H NMR spectrum at −60 °C, the inequivalent naphthyl C^2 protons of the asymmetric rotamer give rise to well-resolved signals at δ 9.50 and 10.18, whereas those of the symmetric one appear as a multiplet centered at δ 9.39. The more crowded **4b** exhibits resolved ^{31}P NMR signals for the two rotamers at room temperature already.

Reaction of (*S,S*)-**1** with [$RuCl_2(PPh_3)_3$] (1:1 mole ratio) in toluene at room temperature gives the ruthenium derivative [$RuCl_2(PPh_3)$((*S,S*)-**1**)] (**5**), whose dark red color is indicative of a five-coordinate structure. The ^{31}P NMR spectrum recorded in CD_2Cl_2 is highly temperature dependent; PPh_3 partially dissociates from **5** in solution giving dimer **11**, as previously observed for other complexes of the type [$RuCl_2(PPh_3)$(P-P)] (P-P= diphosphine) (eq 1).[22]



The room temperature ^{31}P NMR spectrum displays a broadened ABX system, a broadened singlet at δ −6 ($w_{1/2}$ = 30 Hz), attributable to free PPh_3 in chemical exchange with **5**, and broad signals in the δ 19−25 and 41−54 regions, which are assigned to dimer **11**. The PPh_3 exchange process becomes slow on the NMR time scale at low temperature: the ^{31}P NMR spectrum at −40 °C consists of a sharp PPh_3 singlet ($w_{1/2}$ = 2.5 Hz) and a well-resolved ABX system. The integrated intensities of these signals indicate that about 25% of starting **5** is present as dimeric species,[22] but the complicated pattern of low-intensity signals in the δ 19−25 and 41−54 regions of the low-temperature ^{31}P NMR spectra was not analyzed. The ^{31}P NMR parameters of **5** support a trans arrangement of PPh_3 and of one of the diphosphine P atoms, which is compatible with both a square-pyramidal and a trigonal-bipyramidal structure.[23] However, the red color of **5** is suggestive of a trigonal-bipyramidal structure both in the solid state and in solutions of noncoordinating solvents such as CH_2Cl_2. The related species [$RuCl_2(L_3)$] (L_3 = PhP[$(CH_2)_3P(c\text{-}C_6H_{11})_2]_2$) undergoes a solvent-dependent isomerization between a red trigonal-bipyramidal isomer and a green square-pyramidal one,[24] whereas [$RuCl_2(PPh_3)$(biphemp)] is green in the solid state and dark brown in CD_2Cl_2 solution.[22b]

Rhodium-Catalyzed Hydrogenation. Rhodium(I) derivative **4b** (0.5 mol %) catalyzes the asymmetric hydrogenation of (acylamino)cinnamate derivatives with high enantioselectivity (Table 2). *Z*-1-Methylacetamidocinnamate (**12a**) is converted to (*R*)-*N*-acetylphenylalanine methylester (**13a**) with 97.7% enantiomeric excess under 1 atm of H_2 at 30 °C. *Z*-1-Methylacetamidocinnamic acid (**12b**) is hydrogenated under similar

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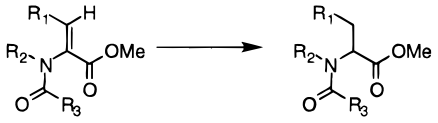
(24) Jia, G.; Lee, I.; Meek, D. W.; Gallucci, J. C. *Inorg. Chim. Acta* **1990**, *177*, 81.

Table 2. Asymmetric Hydrogenation of 12 to 13



12 **13**

entry	R_1	R_2	R_3	ee (%)	config
a	Ph	H	Me	97.7	*R*
b[a]	Ph	H	Me	97.1	*R*
c	H	H	Me	64.1	*R*
d	Ph	Me	Me	96.2	*R*
e	Ph	Me	Ph	96.5	*R*
f[b]	Ph	Me	Ph	0	

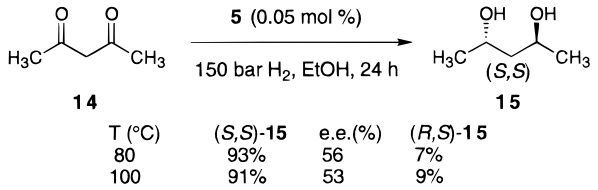
[a] Free acid as substrate. [b] (*E*) isomer as substrate.

conditions to (*R*)-*N*-acetylphenylalanine (**13b**) with about the same enantioselectivity. These values are even better than found with the dipamp/rhodium system on the same substrates.[1] High enantioselection is retained when the free acid **12b** is used provided that a *small amount* of triethylamine is added (4 equiv vs **4b**), a procedure largely used in the catalytic hydrogenation of 1-(acylamino)acrylic acids as an alternative to the use of the corresponding esters.[25] The use of the free acid leads to a decline of the ee values in the rhodium-catalyzed hydrogenation with the recently reported planar chiral diphosphine 4,12-bis(diphenylphosphino)-[2.2]-paracyclophane ([2.2]PHANEPHOS), but the authors do not specify whether the addition of NEt_3 improves the enantioselectivity.[26]

The system is sensitive to the substitution pattern at the β-C atom, as often observed in related systems. When Ph is replaced by H the enantioselectivity drops from 97.7 (**12a**) to 64.1% ee (**12c**). The closely related [Rh(COD)((*l*)-bnpe)] (bnpe=1,2-bis(1-naphthylphenylphosphino)ethane) hydrogenates acetamido acrylic acid with 76% ee.[27] Interestingly, increasing the steric hindrance at the amido group by N-methylation and introducing a benzamido group (**12d,e**) is not detrimental to activity and enantioselectivity, whereas the dipamp system hydrogenates the free acid analogue of **12e** sluggishly and with moderate enantioselectivity.[1] Reports of catalytic hydrogenation of N-substituted enamides are still rare, and the best enantioselectivity achieved does not exceed 75%.[28] The well-known loss of enantioselectivity observed on changing from the *Z* to the *E* configuration is particularly dramatic here: the *E* isomer **12f** yields racemic **13f**.

Other Catalytic Applications. The ruthenium(II) derivative **5** catalyzes the hydrogenation of pentane-2,4-dione (**14**) to (*S,S*)-pentane-2,4-diol (**15**) with moderate enantioselectivity (Scheme 3). The reaction catalyzed by **5** is generally slower than with the binap and biphemp analogues.[29] At 50 °C, the monohydrogenated product 2-hydroxypentan-4-one is formed as the major product (95% yield at 38% conversion) with very low

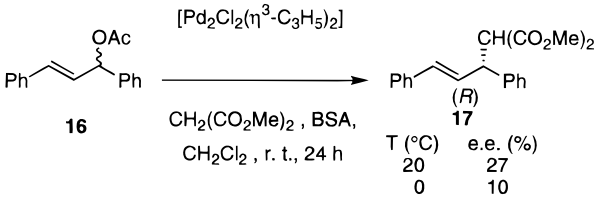
Scheme 3



14 **15**

T (°C)	(*S,S*)-**15**	e.e.(%)	(*R,S*)-**15**
80	93%	56	7%
100	91%	53	9%

Scheme 4



16 **17**

T (°C)	e.e. (%)
20	27
0	10

enantioselectivity (8% ee). Quantitative conversion to (*S,S*)-**15** (56% ee) is achieved at 80 °C under 150 bar of H_2 (Scheme 3).

Ligand **1** was also tested in the palladium-catalyzed substitution reaction of racemic allylic acetates by soft carbon nucleophiles. Racemic 1,3-diphenyl-3-acetoxypropene (**16**) was treated with dimethyl malonate under standard conditions[30] in the presence of 1 mol % of the catalyst (generated in situ from $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ and (*S,S*)-**1**) (Scheme 4). The alkylation product (*R*)-**17** was obtained in nearly quantitative yield after 4 h of reaction time at room temperature, but with low enantioselectivity (27% ee). Decreasing the reaction temperature to 0 °C lowers the enantioselectivity (10% ee).[31]

Conclusion

Homochiral diphosphine ligands can be prepared in good overall yields with high diastereomeric and enantiomeric purity from the corresponding enantiomerically pure phosphine boranes. Bulky substituents are found to be effective in stabilizing the configuration of the stereogenic P atoms. The excellent results obtained in the rhodium-catalyzed enantioselective hydrogenation indicate that placing a stereogenic P atom *in the immediate proximity of the metal* is a successful strategy even with a motif other than P(*o*-An)(Ph)(CH_2R). Improvements in the ligand design would involve the chemical stability and conformational rigidity of the diphosphine bridge. Our efforts are presently directed to developing more stable and rigid linkages between the stereogenic P atoms and to studying the effect of the bite angle of the diphosphine on its stereodifferentiating properties, in order to enlarge the scope of these ligands.

Experimental Section

General Comments. Reactions with air- or moisture-sensitive materials were carried out under an argon atmo-

(25) Zhu, G.; Cao, P.; Jiang, Q.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 1799 and references cited therein.

(26) Pye, P. J.; Rossen, K.; Reamer, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 6207.

(27) Yoshikuni, T.; Bailar, J. C., Jr. *Inorg. Chem.* **1982**, *21*, 2129.

(28) (a) Glaser, R.; Geresh, S.; Twaik, M. *Tetrahedron* **1978**, *34*, 3617. (b) Buser, H. P.; Pugin, B.; Spindler, F.; Sutter, M. *Tetrahedron* **1991**, *47*, 5709.

(29) Mezzetti, A.; Tschumper, A.; Consiglio, G. *J. Chem. Soc, Dalton Trans.* **1995**, 49 and references therein.

(30) (a) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (b) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062, and references therein.

(31) During the preparation of this paper, a communication has appeared on the synthesis of the related ligand (*R,R*)-1,1′-bis(1-naphthylphenylphosphino)ferrocene. Its application in the palladium-catalyzed allylic alkylation gave ee values up to 73%.[32]

(32) Nettekoven, U.; Widhalm, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3185.

sphere using Schlenk techniques. Solvents were purified according to standard procedures; **6** was prepared according to the literature.[6a] ^{1}H and ^{31}P positive chemical shifts in ppm are downfield from tetramethylsilane and external 85% H_3PO_4, respectively. The ^{1}H and ^{31}P NMR spectra of the P→BH_3 borane adducts **2**, **3**, **7**, and **8** are partially relaxed, nonbinomial 1:1:1:1 quartets due to coupling to ^{11}B (80.1% natural abundance); $^1J_{BH}$ and $^1J_{PB}$ were measured between the central peaks. 2D NMR experiments (^{31}P−^{1}H and ^{13}C−^{1}H correlation, NOESY) were carried out on a Bruker DRX 400 spectrometer using standard pulse sequences; the phase-sensitive NOESY experiments used mixing times of 600 ms. Mass spectra were measured by the MS service of the Laboratorium für Organische Chemie (ETH Zürich). A 3-NOBA (3-nitrobenzyl alcohol) matrix and a Xe atom beam with a translational energy of 8 keV were used for FAB$^+$ MS. HPLC was performed on a Hewlett-Packard 1050 chromatograph equipped with a variable-wavelength detector and Daicel Chiralcel OD-H or OB−H columns (0.46 × 25 cm). Optical rotations were measured using a Perkin-Elmer 341 polarimeter with a 1-dm cell. Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich). Melting points were measured in open capillaries with a Büchi-510 apparatus and are uncorrected.

(*S*$_P$,1*R*,2*S*)-P(N(Me)CH(Me)CH(Ph)OH)(1-Np)(Ph)-(BH_3) (7). A cooled THF solution (−78 °C) of 1-naphthyllithium (82.9 mmol) (freshly prepared from 17.2 g of 1-bromonaphthalene (82.9 mmol) dissolved in THF (17 mL) and 51.8 mL of a 1.6 M hexane solution of BuLi (82.9 mmol) at −78 °C) was added by cannula to a THF solution (53 mL) of **6** (18.1912 g, 63.8 mmol) precooled at −78 °C. After stirring for 30 min at −78 °C, the resulting yellow creamy mixture was allowed to warm to room temperature. The cloudy orange solution was quenched with H_2O (40 mL), and the THF was then evaporated. The product was extracted with CH_2Cl_2 and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (silica gel, toluene/AcOEt (95:5)) yielded crude **7** as a pale yellow oil. Yield: 26.01 g (99%). Recrystallization from toluene/hexane yielded pure **7**: yield 22.70 g (82%); mp 115 °C; ^{1}H NMR ($CDCl_3$) δ 8.27−7.17 (m, 17 H, Ph, 1-Np), 5.03−5.01 (m, 1 H, C*H*(Ph)OH), 4.58−4.44 (m, 1 H, NC*H*Me), 2.64 (d, 3 H, NCH_3, $^3J_{PH}$ = 7.5 Hz), 1.31 (d, 3 H, CH_3NHCCH_3, $^3J_{HH'}$ = 6.9 Hz); ^{31}P NMR ($CDCl_3$) δ 70.2 (br q, 1 P, $^1J_{PB}$ = 54 Hz); $[\alpha]^{20}_D$ = 78.9 ± 0.26 ($CHCl_3$, *C* = 1). Anal. Calcd for $C_{26}H_{29}$NOBP: C, 75.56; H, 7.07; N, 3.39. Found: C, 75.69; H, 7.16; N, 3.29.

(*R*)-P(OMe)(1-Np)(Ph)(BH_3) ((*R*)-8). Concentrated H_2SO_4 (6.13 g, 3.35 mL, 62.5 mmol) was added to a MeOH solution (500 mL) of **7** (25.81 g, 62.5 mmol), and the solution was stirred overnight. Evaporation of the solvent and flash chromatography (silica gel, hexane/AcOEt (95:5)) gave the analytically pure product as a thick oil. Yield: 13.10 g (75%, crude). Enantiomeric purity: 92.1% ee (HPLC, OD-H; hexane/^{i}PrOH (99.5:0.5), t_R [(*R*)-**8**] = 17.8 min, t_R [(*S*)-**8**] = 19.1 min). Enantiomerically pure (*R*)-**8** (only the *R* enantiomer detected) was obtained by recrystallization from hot hexane: yield 10.50 g (60%); mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 8.33−7.36 (m, 12 H, Ph, 1-Np), 3.79 (d, 3 H, POCH_3, $^3J_{PH}$ = 12.2 Hz), 1.95−0.5 (q, 3 H, BH_3, $^1J_{BH}$ = 82 Hz); ^{31}P NMR ($CDCl_3$) δ 110.4 (br q, 1 P, $^1J_{PB}$ = 79 Hz); $[\alpha]^{20}_D$ = −22.9 ± 0.25 ($CHCl_3$, *C* = 1); MS (EI), *m*/*z* 277.1 (M$^+$ − 3H, 9), 266.1 (M$^+$ − BH_3, 100), 251.1 (M$^+$ − BH_3 − CH_3, 54). Anal. Calcd for $C_{17}H_{18}$OBP: C, 72.89; H, 6.48. Found: C, 72.66; H, 6.19.

(*S*)-P(1-Np)(Ph)(Me)(BH_3) (3). A hexane solution (49.4 mL, 1.6 M) of MeLi (79.0 mmol; 1.6 equiv vs **8**) was added dropwise to a THF solution (42 mL) of **8** (13.83 g, 49.4 mmol) at −40 °C. After 1 h of stirring at −40 °C, the solution was allowed to slowly reach room temperature (10 h). The reaction was quenched with H_2O (60 mL), and the THF was removed under vacuum. The crude product was extracted with CH_2Cl_2 and dried over $MgSO_4$: removal of the solvent gave a white paste. Yield: 12.54 g (96%, crude), 93% ee (HPLC, OD-H; hexane/^{i}PrOH = 99.5:0.5, t_R [(*S*)-**3**] = 39.4 min, t_R [(*R*)-**3**] = 33.2 min). Enantiomerically pure (*R*)-**3** (only the *R* enantiomer detected) was obtained by recrystallization from hot hexane: yield 10.58 g (81%); mp 110 °C; ^{1}H NMR ($CDCl_3$) δ 8.10−7.34 (m, 12 H, Ph, 1-Np), 2.02 (d, 3 H, PCH_3, $^2J_{PH}$ = 9.9 Hz), 2.05−0.5 (br q, 3 H, BH_3, $^1J_{BH}$ = 93 Hz); ^{31}P NMR ($CDCl_3$) δ 9.5 (br q, 1 P, $^1J_{PB}$ = 68 Hz); $[\alpha]^{20}_D$ = +43.6 ± 0.17 ($CHCl_3$, *C* = 1); MS (EI), *m*/*z* 264.1 (M$^+$, 0.3), 261.1 (M$^+$ − 3H, 13), 249.1 (M$^+$ − CH_3, 100). Anal. Calcd for $C_{17}H_{18}$BP: C, 77.31; H, 6.87. Found: C, 77.55; H, 6.93.

X-ray Structure of (*S*)-P(1-Np)(Ph)(Me)(BH_3) (3). Colorless prismatic crystals (0.5 × 0.6 × 0.8 mm) were grown from CH_2Cl_2/hexane, orthorhombic, $P2_12_12_1$, *a* = 7.406(6) Å, *b* = 8.630(8) Å, *c* = 24.38(2) Å, *V* = 1558(2) Å^3, *Z* = 4, M_w = 264.1, d_c = 1.126 Mg m^{-3}, μ = 0.160 mm^{-1}, *F*(000) = 560, Syntex P21 diffractometer, Mo Kα (λ = 0.710 73 Å, graphite monochromated), 3 ≤ 2θ ≤ 40°, ω-scan, scan speed 1.0−4.0 deg min^{-1} in ω, scan range 1.0°, 1 standard reflection measured every 120 reflections. Index ranges: −7 ≤ *h* ≤ 7, −8 ≤ *k* ≤ 8, −23 ≤ *l* ≤ 23, 3488 reflections collected, of which 1445 were independent (R_{int} = 3.3%) and 1374 observed ($F \geq 4.0\,\sigma$). No correction for absorption was performed. The structure was solved and refined using direct methods with Siemens SHELXTL PLUS (VMS). In the full-matrix least squares, the quantity minimized was $\sum w(F_o - F_c)^2$. The absolute structure was determined by the η method using atomic scattering factors of the type $f_o^{anomal} = f_o + \Delta f' + i\eta\Delta f''$; refinements gave η = 1.0(2) for the *S* configuration irrespective of the starting value of η (+1 or −1). An extinction correction was performed according to $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$, where χ = 0.0064(9). The H atom contribution was held constant (riding model, fixed anisotropic *U*). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0051F^2$, and 246 parameters were refined. The final refinement cycle gave *R* = 2.7%, R_w = 3.6% (observed data), goodness of fit 0.50, largest and mean Δ/σ 0.331 and 0.048, data-to-parameter ratio 5.6:1, largest positive and negative difference peaks 0.20 and −0.27 e Å^{-3}.

(*S*,*S*)-Me_2Si(CH_2P(1-Np)(Ph)(BH_3))$_2$ (2). A hexane solution (15.2 mL, 1.38 M) of *sec*-BuLi (21.0 mmol; 1.1 equiv vs **3**) was added dropwise over a period of 20 min to a THF solution (54 mL) of **3** (5.05 g, 19.1 mmol) at −78 °C. After the solution was stirred for 2 h, Me_2SiCl_2 (1.153 mL, 9.56 mmol; 0.5 equiv vs **3**) was added rapidly via syringe, and the resulting solution was allowed to reach room temperature (17 h). The reaction was quenched with 2 M HCl (30 mL), and the THF was removed under vacuum. The product was extracted with CH_2Cl_2 from the aqueous phase, washed with K_2CO_3, and dried over $MgSO_4$. Evaporation of the solvent gave **2** as an oil. Evaporation under vacuum of a hexane/CH_2Cl_2 solution gave a hard white foam: yield 5.48 g (98%); ^{1}H NMR ($CDCl_3$) δ 8.2−7.2 (m, 24 H, Ph, 1-Np), 1.89 (d × d, 2 H, SiC*H*H′P, $^2J_{HH'}$ = 14.0 Hz, $^2J_{PH}$ = 16.1 Hz), 1.68 (d × d, 2 H, SiCH*H*′P, $^2J_{HH'}$ = 14.0 Hz, $^2J_{PH'}$ = 13.6 Hz), −0.37 (*s*, 6 H, Si(CH_3)$_2$); $[\alpha]^{20}_D$ = −34.7 ± 0.15 (*C* = 1); ^{31}P NMR ($CDCl_3$) δ 12.9 (br s, 2 P); MS (EI), *m*/*z* 584.5 (M$^+$, 0.2), 569.3 (M$^+$ − BH_3, 2), 556.3 (M$^+$ − 2BH_3, 2), 479.2 (M$^+$ − Ph, 3), 429.2 (M$^+$ − 1-Np, 11), 353.2 M$^+$ − 1-Np − Ph, 4), 321.2 (M$^+$ − P(1-Np)(Ph), 5), 307.2 (M$^+$ − P(1-Np)(Ph)(CH_2), 7), 249.2 (M$^+$ − P(1-Np)(Ph)(CH_2SiMe_2), 9), 171.1 (P(1-Np)(CH_2), 28), 135.1 ($SiMe_2$(Ph), 100), 185.2 ($SiMe_2$(1-Np), 61). Anal. Calcd for $C_{36}H_{40}B_2P_2Si$: C, 73.99; H, 6.90. Found: C, 73.99; H, 7.13.

(*S*,*S*)-Me_2Si(CH_2P(1-Np)(Ph))$_2$ ((*S*,*S*)-1). Compound **2** (1.32 g, 2.26 mmol) was dissolved in morpholine (70 mL), and the colorless solution was stirred overnight at room temperature. The resulting white precipitate was filtered off, and the yellowish solution was evaporated to dryness. Flash chromatography (alumina, toluene as eluent) yielded **1** as a colorless oil: yield 0.98 g (78%); ^{1}H NMR ($CDCl_3$) δ 8.60−8.54 (m, 2 H, naphthyl C^2-*H*), 7.85−7.17 (m, 22 H, Ph, other 1-Np), 1.6−1.2 (m, 4 H, SiCH_2P), −0.19 (*s*, 6 H, Si(CH_3)$_2$); ^{31}P NMR

($CDCl_3$) δ −35.74 (*s*, 2 P); MS (EI), *m*/*z* 556.3 (M^+, 19), 479.2 (M^+ − Ph, 20), 429.2 (M^+ − 1-Np, 60), 352.4 M^+ − 1-Np − Ph, trace), 321.4 (M^+ − (1-Np)P(Ph), 12), 307.4 (M^+ − CH_2P(1-Np)(Ph), 16), 249.3 (M^+ − $Me_2Si(CH_2P(1\text{-}Np)(Ph))$, 19), 171.1 ($CH_2$P(1-Np), 36), 135.1 ($Me_2$Si(Ph), 100), 185.2 ($Me_2$Si(1-Np), 95).

(*rac*)-P(NEt$_2$)(1-Np)(Ph). A cooled (−78 °C) THF solution of 1-naphthyllithium (44 mmol) (prepared by dropwise addition of a 1.6 M hexane solution of BuLi (27.9 mL, 44.6 mmol) to a cooled (−78 °C) THF solution (17 mL) of 1-bromonaphthyl (9.2 g, 44.4 mmol)) was added by cannula to a solution of P(Cl)-(NEt_2)(Ph) (9.0 g, 41.5 mmol) in THF (53 mL) at −78 °C. The mixture was stirred for 30 min at −78 °C; the resulting yellow creamy mixture was then allowed to warm to room temperature. The reaction was quenched with H_2O (5 mL), and THF was removed under vacuum. The crude product was extracted with CH_2Cl_2, dried over $MgSO_4$, and distilled: yield 10.6 g (82%); ^{1}H ($CDCl_3$) δ 8.25−7.26 (m, 12 H, Ph, 1-Np), 3.24−3.11 (m, 4 H, P(NCH_2CH_3)$_2$), 0.91 (t, 6 H, P(NCH_2CH_3)$_2$, $^3J_{HH'}$ = 7.1 Hz); ^{31}P NMR ($CDCl_3$) δ 53.5 (s, P); MS (EI), *m*/*z* 307.2 (M^+, 85), 235.1 (M^+ − NEt_2, 91), 233.1 (M^+ − NEt_2 − 2H, 100), 180.1 (M^+ − 1-Np, 39), 166.1 (M^+ − 1-Np − CH_2, 89). Anal. Calcd for $C_{20}H_{22}NP$: C, 78.15; H, 7.21; N, 4.56. Found: C, 77.61; H, 7.45; N, 4.56.

(*rac*)-P(OMe)(1-Np)(Ph)(BH_3) ((*rac*)-8). HCl gas was bubbled through a MeOH solution (50 mL) of P(NEt_2)(1-Np)-(Ph) (10.0 g, 32.5 mmol) until complete esterification was achieved as evidenced by ^{31}P NMR spectroscopy. The solvent was evaporated, the residue was dissolved in toluene (20 mL), and dimethyl sulfide borane (3.2 mL, 32.5 mmol) was then added at room temperature. The resulting solution was stirred for 2 h and then concentrated. The crude product was recrystallized from toluene at 4 °C. Yield: 7.0 g (77%). Analytic and spectroscopic properties are as given for (*R*)-**8**.

(*rac*)-P(1-Np)(Ph)(Me)(BH_3) ((*rac*)-3). A 1.6 M hexane solution of MeLi (14.5 mL, 23.2 mmol) was added dropwise to a solution of (*rac*)-**8** (6.00 g, 21.4 mmol) in 20 mL of THF at −78 °C. The mixture was allowed to reach room temperature within 2 h. The reaction was quenched with 50 mL of H_2O, and the THF was removed under vacuum. The crude product was extracted with CH_2Cl_2, dried over $MgSO_4$, and recrystallized from Et_2O/hexane. Yield: 5.3 g (94%). Analytic and spectroscopic properties are as given for (*S*)-**3**.

(*l*)- + (*u*)-$Me_2Si(CH_2P(1\text{-}Np)(Ph)(BH_3))_2$ ((*l*)- + (*u*)-2). A 1.6 M hexane solution of BuLi (8.0 mL, 12.8 mmol) was added dropwise to a THF solution (15 mL) of (*rac*)-**3** (3.0 g, 11.4 mmol). After stirring for 2 h at −78 °C, Me_2SiCl_2 (0.65 mL, 5.4 mmol) was added thereto, and the resulting solution was allowed to reach room temperature. Workup was the same as for (*S*,*S*)-**2**. Yield: 2.5 g (79%). ^{1}H NMR ($CDCl_3$): *u* isomer (50%) δ −0.29 (s, 3 H, $SiCH_3$), −0.46 (s, 3 H, $SiCH'_3$); *l* isomer (50%) δ −0.37 (s, 6 H, Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$): δ 13.4 (br, *l* and *u* isomers not resolved). Analytic and MS properties are as given for (*S*,*S*)-**2**.

(*l*)- + (*u*)-$Me_2Si(CH_2P(1\text{-}Np)(Ph))_2$ ((*l*)- + (*u*)-1). Deprotection was carried out as described above for (*S*,*S*)-**1**. ^{1}H NMR ($CDCl_3$): *u* isomer (50%) δ −0.18 (s, 3 H, $SiCH_3$), −0.22 (s, 3 H, $SiCH'_3$); *l* isomer (50%) δ −0.19 (s, 6 H, Si(CH_3)$_2$). ^{31}P NMR ($CDCl_3$): *l* isomer (50%) δ −35.74 (s, 2 P); *u* isomer (50%) δ −35.67 (s, 2 P). Analytic and MS properties are as given for (*S*,*S*)-**1**.

[Pd((*S*)-dimethyl(1-methylbenzyl)aminato-*C*,*N*)((*S*,*S*)-1)]PF_6 (10a). A solution of **1** (114 mg, 0.205 mmol) in 5 mL of CH_2Cl_2 was added to a solution of bis(μ-chloro)bis[(*S*)-dimethyl(1-methylbenzyl)aminato-*C*,*N*]dipalladium(II) (60 mg, 0.102 mmol) in 5 mL of MeOH. After the resulting clear yellow mixture was stirred for 12 h, $TlPF_6$ (43 mg, 0.122 mmol) was added. Additional stirring overnight, filtration over Celite, and evaporation to dryness gave a pale yellow solid. The residue was extracted with CD_2Cl_2, and the ^{31}P NMR spectrum of the solution was recorded. ^{31}P NMR ($CDCl_3$): $S_C,S_P,S_{P'}$ isomer δ 33.21 (d, 1 P, $^2J_{PP'}$ = 45.0 Hz), 11.82 (d, 1 P, $^2J_{PP'}$ = 45.0 Hz); $S_C,R_P,R_{P'}$ isomer δ 26.05 (d, 1 P, $^2J_{PP'}$ = 41.0 Hz), 4.24 (d, 1 P, $^2J_{PP'}$ = 41.0 Hz); $S_C,S_P,R_{P'}$ + $S_C,R_P,S_{P'}$ isomers δ 30.6 (d, 1 P, $^2J_{PP'}$ = 41.1 Hz), 29.8 (d, 1 P, $^2J_{PP'}$ = 41.7 Hz), 7.8 (d, 1 P, $^2J_{PP'}$ = 41.1), 7.1 (d, 1 P, $^2J_{PP'}$ = 41.7). MS (FAB$^+$): *m*/*z* 810.2 (M^+, 64), 661.1 (M^+ − $C_{10}H_{15}N$, 35), 391.2 ($C_{23}H_{25}P_2Si^+$, 100). [Pd-((*R*)-**9**-*C*,*N*)((*S*,*S*)-**1**)]PF_6 (**10b**) was prepared and characterized analogously.

[Rh(NBD)((*S*,*S*)-1)]BF_4 (4a). [Rh(NBD)$_2$]BF_4 (95 mg, 0.26 mmol) and (*S*,*S*)-**1** (142 mg, 0.26 mmol) were dissolved in CH_2Cl_2 (8 mL), and the resulting solution was stirred overnight at room temperature. ^{t}BuOMe (10 mL) was added, and the solution was then concentrated under vacuum. A yellow precipitate was formed, filtered off, and dried in vacuo. The ^{1}H NMR spectrum shows the presence of 0.5 mol of ^{t}BuOMe/mol of **1**: yield 181 mg (81%); mp 154 °C; ^{1}H NMR ($CDCl_3$, 293 K) δ 9.1 (br, 2 H, naphthyl C^2-*H*), 8.23−7.15 (m, 22 H, Ph, other 1-Np), 4.76 (br, 2 H, bridgehead C*H*), 4.07 (br, 2 H, =C*H*), 3.98 (br, 2 H, =C*H*), 1.97−1.60 (m, 4 H, PCH_2), 1.53 (br s, 2 H, bridging CH_2), −1.17 (br *s*, 6 H, Si(CH_3)$_2$); ^{31}P NMR ($CDCl_3$, 293 K) δ 18.0 (br d, 2 P, $^1J_{RhP}$ = 160 Hz). ^{1}H NMR (CD_2Cl_2, 213 K): rotamer *a* δ 9.43−9.35 (m, 2 H, naphthyl C^2-*H*), 4.87 (br, 2 H, bridgehead C*H*), 3.91 (br, 2 H, =C*H*), 3.78 (br, 2 H, =C*H*), −1.38 (*s*, 6 H, Si(CH_3)$_2$); rotamer *b* δ 10.18 (br d, 1 H, naphthyl C^2-*H*), 9.50 (br dd, 1 H, naphthyl C^2-*H'*), 4.56 (br, 1 H, bridgehead C*H*), 3.95−3.57 (m, 4 H, =C*H*), −1.08 (*s*, 3 H, Si(CH_3)), −1.39 (*s*, 3 H, Si(CH'_3)). ^{31}P NMR (CD_2Cl_2, 213 K): rotamer *a* (58%) δ 21.26 (d, 2 P, $^1J_{RhP}$ = 157.6 Hz); rotamer *b* (42%) δ 21.21 (dd, 1 P, $^1J_{RhP}$ = 151.3 Hz, $^2J_{PP'}$ = 36.8 Hz), 11.00 (dd, 1 P, $^1J_{RhP}$ = 159.6 Hz, $^2J_{PP'}$ = 36.8 Hz). MS (FAB$^+$) *m*/*z* 751.2 (M^+, 100), 657.1 (M^+ − NBD − H, 30). Anal. Calcd for $C_{44}H_{46}BF_4P_2SiRh\cdot 0.5C_5H_{12}O$: C, 61.92; H, 5.48. Found: C, 61.20; H, 5.61.

[Rh(COD)((*S*,*S*)-1)]BF_4 (4b). [Rh(COD)$_2$]BF_4 (190 mg, 0.467 mmol) and (*S*,*S*)-**1** (260 mg, 0.467 mmol) were dissolved in THF (8 mL), and the resulting solution was stirred for 7 h at room temperature. Evaporation of the solvent gave a yellow solid, which was washed with hot hexane and dried in vacuo: yield 0.37 g (92%); mp 181 °C. ^{1}H NMR ($CDCl_3$): rotamer *a* δ 9.68−9.59 (m, 2 H, naphthyl C^2-*H*), 4.86 (br, 2 H, =C*H*), 4.01 (br, 2 H, =C*H*), −1.35 (*s*, 6 H, Si(CH_3)$_2$); rotamer *b* δ 10.65 (br, 1 H, naphthyl C^2-*H*), 9.74 (br, 1 H, naphthyl C^2-*H'*), 4.90 (br, 1 H, =C*H*), 4.61 (br, 1 H, =C*H*), 4.23 (br, 1 H, =C*H*), 3.84 (br, 1 H, =C*H*), −0.92 (*s*, 3 H, $SiCH_3$). ^{31}P NMR ($CDCl_3$): rotamer *a* (61%) δ 17.60 (d, 2 P, $^1J_{RhP}$ = 144.7 Hz); rotamer *b* (39%) δ 15.36 (dd, 1 P, $^1J_{RhP}$ = 144.7 Hz, $^2J_{PP'}$ = 33.2 Hz), 7.09 (dd, 1 P, $^1J_{RhP}$ = 144.7 Hz, $^2J_{PP'}$ = 33.2 Hz). MS (FAB$^+$): *m*/*z* 767.2 (M^+, 100), 659.1 (M^+ − COD, 86). Anal. Calcd for $C_{44}H_{46}BF_4P_2SiRh\cdot H_2O$: C, 60.56; H, 5.54. Found: C, 60.46; H, 5.58. The presence of water was evidenced by IR spectroscopy (3420 cm^{-1}, br, KBr pellet).

[$RuCl_2(PPh_3)$((*S*,*S*)-1)] (5). [$RuCl_2(PPh_3)_3$] (1.018 g, 1.061 mmol) and (*S*,*S*)-**1** (0.650 g, 1.17 mmol) were dissolved in toluene, and the resulting solution was stirred at room temperature for 24 h. Addition of hexane and partial evaporation of the solvent yielded dark red microcrystals, which were recrystallized from CH_2Cl_2/hexane: yield 1.05 g (89%); mp 140 °C; ^{1}H NMR ($CDCl_3$) δ 8.1−6.0 (m, 39 H, Ph, 1-Np), 2.0−1.4 (m, 4 H, (PCH_2)$_2$Si), −0.2 (s, 6 H, (CH_3)$_2$Si); ^{31}P NMR (CD_2Cl_2, −40 °C) ABX system, δ_A 39.7 ($^2J_{AB}$ = 303.5 Hz, $^2J_{AX}$ = 28.7 Hz), δ_B 35.2 ($^2J_{BX}$ = 39.6 Hz), δ_X 103.8; MS (FAB$^+$), *m*/*z* 919.18 (M^+ − 2Cl − H, 43), 692.06 (M^+ − Cl − H − PPh_3, 34), 657.09 (M^+ − 2Cl − H − PPh_3, 100). Anal. Calcd for $C_{54}H_{49}Cl_2P_3SiRu$: C, 65.45; H, 4.98; Cl, 7.16. Found: C, 65.85; H, 5.02; Cl, 6.99.

Enantioselective Hydrogenation with 4b. The standard procedure was as follows: the substrate (1.64 mmol) and **4b** (6.9 mg, 8.2 μmol, 0.5 mol %) were dissolved in 10 mL of MeOH under argon. The solution was stirred for 15 min and then transferred via a steel capillary into a 180-mL glass reactor thermostated at 30 °C. The inert gas was then

replaced by hydrogen (three cycles), and the pressure was set at 1.0 bar. After completion of the reaction (total reaction times 16−65 h), the conversion was found to be quantitative by gas chromatography, and the product was isolated in ca. 100% yield after filtration of the reaction solution on a plug of silica to remove the catalyst. An analogous procedure was followed for the hydrogenation of **12b** using 1 mol % of catalyst and adding NEt_3 (5 μL, 4 equiv vs Rh) to the reaction solution. The enantiomeric purities of **13a**−**c** were determined by GC (L-Chirasil-Val column, on column injection), those of **13d**−**f** by HPLC (Chiracel OD-H column, eluent: hexane/^{i}PrOH). The enantiomeric purity of **13b** was determined by GC after conversion to the methyl ester **13a**. Further details are given in the Supporting Information.

Enantioselective Hydrogenation with 5. All manipulations involving solutions of **5** were performed in a glovebox under an atmosphere of purified nitrogen. A typical procedure consisted of transferring **5** (49.5 mg, 50 μmol), weighed in a glass insert, into the glovebox, adding pentane-2,4-dione (10.0 g, 99.9 mmol) and ethanol (10.0 g), and inserting the glass vessel into a 250-mL steel autoclave, which was then closed off and taken out of the box. The lines were flushed several times with hydrogen before the autoclave was connected to the hydrogen source (99.9999%). The nitrogen in the autoclave was then replaced by three cycles of pressurization with 50 bar of hydrogen followed by careful ventilation. The required pressure was introduced, the autoclave was transferred into a thermostatic oil bath equipped for mechanical stirring, and the hydrogen pressure vs time data collection was started. After initial equilibration of the system (about 15−30 min), the progress of the reaction was monitored by the decrease of the H_2 pressure.

The clear, red reaction solutions were then analyzed by GC using a Carlo Erba GC 6000 gas chromatograph equipped with a 50-m cross-linked methyl silicon gum capillary column. The enantiomeric excesses were determined by GC analysis of the distilled products using an HP 5890 gas chromatograph equipped with a 50-m Lipodex C chiral column (T = 90 °C, isothermic, 120 kPa H_2 carrier, split 1:50, t_R[(*R*,*S*)-**15**] = 28.20 min, t_R[(*R*,*R*)-**15**] = 30.40 min, t_R[(*S*,*S*)-**15** = 32.61 min). The absolute configuration of the hydrogenation products was determined by comparison of the sign of optical rotation (Perkin-Elmer 241 polarimeter) with that reported.[33]

Palladium-Catalyzed Allylic Alkylation. The ligand (*S*,*S*)-**1** (8.2 mg, 0.015 mmol) and $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (1.8 mg, 4.9 μmol) were dissolved in 5 mL of freshly distilled CH_2Cl_2 under an Ar atmosphere. Racemic 1,3-diphenyl-1-acetoxypropene (81.2 mg, 0.322 mmol), dimethyl malonate (85.0 mg, 0.644 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (131 mg, 0.644 mmol), and potassium acetate (4.7 mg, 0.048 mmol) were then added in that order, and the reaction was monitored by thin-layer chromatography (eluent: ethyl acetate/hexane, 1:5 by volume; product **17**, R_f 0.29). No starting material **16** was detected after 4 h. After 24 h the orange slurry was filtered and the filtrate was concentrated under reduced pressure. Column chromatography on silica gel (same eluent as for TLC) yielded 99.2 mg (0.306 mmol, 95%) of **17** as a colorless oil, which solidified upon standing at −20 °C. The enantiomeric purity was determined by HPLC (Daicel Chiralcel OD-H column, hexane/^{i}PrOH (98:2), flow 0.5 mL/min, t_R[(*R*)-**17**] = 18.3 min, t_R[(*S*)-**17**] = 19.6 min). The absolute configuration was determined by the sign of optical rotation. Enantiomeric excesses were 27% (20 °C) and 10% (0 °C).

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Supporting Information Available: A listing of atomic coordinates, anisotropic displacement coefficients, bond distances and angles, and H atom coordinates (5 pages). Ordering information is given on any current masthead page.

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