Articles

Synthesis of Novel (P,S) Ligands Based on Chiral Nonracemic Episulfides. Use in Asymmetric Hydrogenation

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A strategy for the synthesis of new chiral (P,S) ligands is described. It is based on the opening of chiral nonracemic episulfides using phosphorus nucleophiles. Chiral episulfides, $\overline{CH_2CH(R)S}$, **4**, are derived either from the reaction of thiourea with the corresponding epoxide (**4a**, R = CH_3) or from the stepwise conversion of chiral diols to the episulfide via the thiocarbonate (**4b**, R = cyclohexyl). The reaction of lithium salts of phosphines, $R_2'PLi$ (R = Ph, cyclohexyl), with episulfides is regioselective and gives the ring-opened products **5**−**8**, $PR_2CH_2CH(R')SLi$. Upon treatment with electrophiles, R″Cl (R″ = $-CH_2Ph$, $-CH_2(C_5(CH_3)_5)$, $-CH_2(C_{14}H_9)$, $-CH(C_{14}H_{12})$), they give novel chiral (P,S) ligands, $PR'_2CH_2CH(R')SR''$, **9**−**17** in 31−93% yield. Reactions of $PCy_2CH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$, **11**, with $LMCl_2$ (LM = (DME)Ni, (COD)Pd, and (NBD)Pt; DME = dimethoxyethane, COD = 1,5-cyclooctadiene, NBD = 2,5-norbornadiene) yields the corresponding metal complexes, (**11**)MCl_2, **18**. Variable-temperature ^{1}H NMR spectroscopy indicates that in these complexes sulfur inversion occurs on the NMR time scale. Compound **18b** (M = Pd) was characterized by single-crystal X-ray analysis. Reaction of $PCy_2CH_2CH(CH_3)SCH(C_{14}H_{12})$, **13**, with (COD)$PdCl_2$ results in C−S bond cleavage and produces a dinuclear thiolato-bridged complex, dichlorobis{μ-[2-(dicyclohexylphosphino)-1-(methyl)ethanethiolato]-P,μ-S}-dipalladium(II), **19**. Complex **19** was characterized by single-crystal X-ray analysis. Reactions of ligands **9**−**17** with $Rh(COD)_2^+OTf^-$ (COD = cyclooctadiene, OTf^- = $CF_3SO_3^-$) yields rhodium complexes that have been tested in the asymmetric hydrogenation of α-enamide methyl esters, providing enantioselectivities of up to 51%. The rhodium complex obtained with ligand **11**, (**11**)Rh(COD)OTf, **22**, was characterized by single-crystal X-ray analysis.

Introduction

Chiral bidentate ligands have been used extensively to perform asymmetric transformations.[1] The most commonly employed are bidentate phosphines;[2−4] however, promising catalytic allylic alkylations and Heck reactions have appeared using mixed-donor ligands such as (P,O),[5] (P,N),[6] and (P,S)[7] ligands. Reports on catalytic reactions using the latter class are scarce partially owing to fear of metal poisoning by sulfur. The use of these ligands has been reported for the carbonylation

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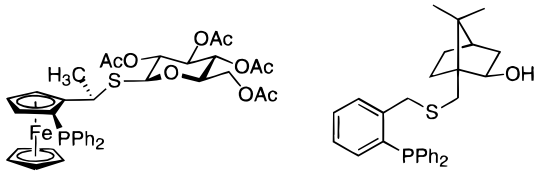
of methanol,[7m] the reduction of ketones by hydrogen transfer (ee up to 20%),[7i,l] and the hydroformylation of styrene.[7i] Pregosin has synthesized and structurally characterized a number of metal complexes bearing chiral P,S-donor ligands. In particular, palladium complexes with ligands such as **1** and **2** were shown to carry out asymmetric allylic alkylation.[7a,c,d]



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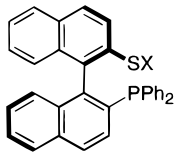
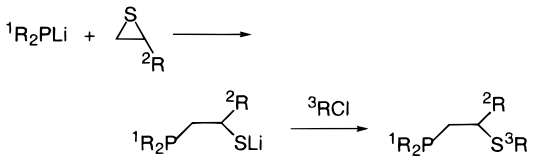


3

Ligand **1** gives 88% ee for the classic test substrate PhCH=CHCH(OAc)Ph, and **2** gives much smaller ee's in the 20−30% range. For chiral hydroformylation of styrene, a maximum of ca. 14% ee was achieved. Most recently, Achiwa has reported the use of (P,S) ligands in asymmetric hydrosilylation of ketones (ee up to 57%).[7p] In these ligand systems it is difficult to tune electronic and steric effects. Here, we report a simple and versatile route to chiral (P,S) ligands amenable to "combinatorial" screening[8] and some preliminary studies of their use in asymmetric hydrogenation.

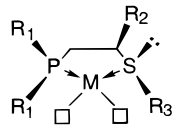
Results and Discussion

The opening of episulfides by phosphorus nucleophiles has been reported and in the case of terminal episulfides proceeds regioselectively to the less hindered site.[9] Subsequent quenching with electrophiles leads to the corresponding (P,S) ligand (eq 1).



(Eq. 1)

The approach shown in eq 1 contains two nearly quantitative steps and allows the introduction of three degrees of molecular diversity represented by ^{1}R, ^{2}R, and ^{3}R. Thus, this strategy seemed adequate for automated synthesis and screening (the first step is byproduct free while the second step generates inert LiCl). Coordination of these ligands to a metal center would place the element of chirality, sulfur, directly next to the metal where the key enantioselective steps occur. In addition, with large groups on phosphorus, one side of the (P, S, metal) plane would be blocked. This in combination with bulky groups both on the backbone and sulfur would cause R_2 and R_3 to be trans to each other upon ligand coordination, thereby limiting the number of coordination modes of alkene substrate. Finally, the electronic dissimilarity of sulfur and phosphorus might lead to electronic effects that have been found to be important in some cases for obtaining favorable ee's.[10] All of the above arguments encouraged us to prepare these ligands.



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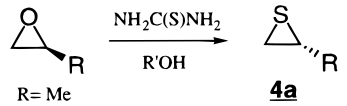
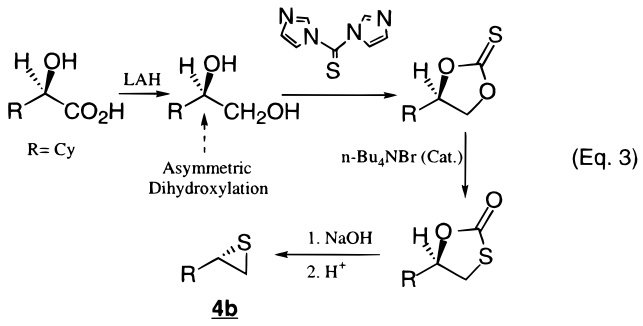
Synthesis of Chiral Episulfides. Literature precedents for the synthesis of chiral nonracemic thiiranes are rare.[11] Episulfides are most commonly synthesized from epoxides using thiourea or potassium thiocyanate.[12] On chiral epoxides, these reactions proceed with inversion of configuration. We synthesized chiral propylene sulfide from commercially available (*S*)-(−)-propylene oxide using thiourea in tetraethylene glycol/water. This procedure was modeled after that reported by Bouda et al.[13] The reaction proceeds smoothly over 12 h at ambient temperature, and the product can be isolated by vacuum transfer from the reaction mixture (eq 2). The enantiomeric purity of chiral propylene sulfide was determined by derivatization of the phosphido ring-opened product (vide infra) with (−)-camphanic chloride and found to be ca. 88%.



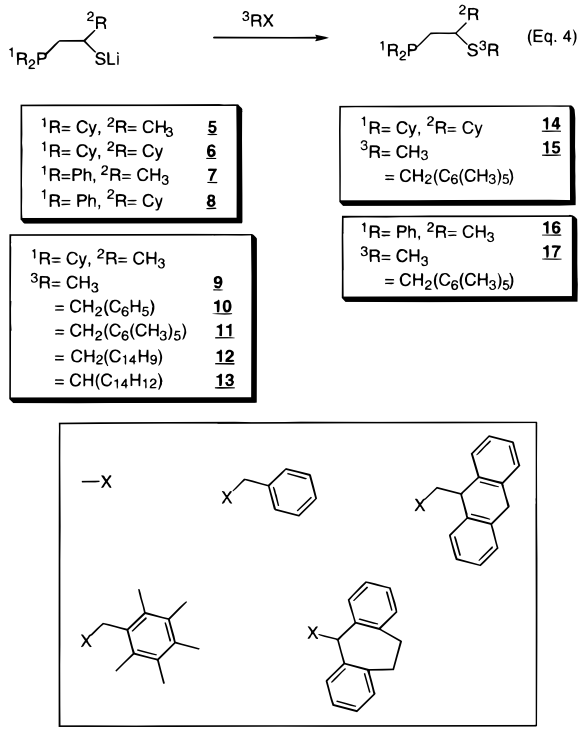
4a (Eq. 2)

Using a procedure of Sharpless et al.,[14] we found that the synthesis of monosubstituted chiral episulfides is more versatile starting from chiral diols. We have synthesized the chiral diol from reduction of enantiomerically pure hexahydromandelic acid, but many more diols should be readily available through the Sharpless dihydroxylation reaction.[15] Reaction of the diol with thiocarbonyldiimidazole yields the corresponding thiocarbonate.[16] Subsequent reaction with a catalytic amount of bromide promotes isomerization to the sulfur-bound carbonate, which upon reaction with hydroxide extrudes carbonate and produces the episulfide with net inversion. All the steps are quantitative except the last one, which occurs in ca. 55% yield.[17] The enantiomeric purity of the episulfide was determined by derivatization with (*S*)-(+)-methoxymethylpyrrolidine and found to be ≥95%.

Synthesis of P,S Ligands. Propylene sulfide or the thiirane of vinyl cyclohexane can be ring-opened using lithium salts of phosphines, $LiPR_2$ (R = Cy, Ph). This reaction takes places at −78 °C and is regiospecific; the opening occurs exclusively at the least hindered carbon. A stoichiometric amount of episulfide is necessary to prevent further oligomerization reactions. Lithium salts **5**−**8** are obtained as white solids (pure by ^{31}P NMR spectroscopy) and were used without further purification. The salts were then reacted with electrophiles (eq 4). Benzyl halide derivatives were the most reactive electrophiles as expected for nucleophilic substitution. All these ligands were obtained in good yields (50−93%) and gave satisfactory elemental analyses and spectroscopic data. The most notable features in the ^1H NMR spectra were the protons α to the sulfur, which were found in the range 3.0−2.5 ppm as complex multiplets resulting from $^1H-^1H$ coupling as well as $^1H-^{31}P$ coupling. In the case of benzyl-like sulfur substituents, the methylene protons α to the sulfur are diastereotopic, coupled to each other, and appear in the 4.0−3.5 ppm region as an AB quartet.



4b (Eq. 3)



(Eq. 4)

Synthesis of Metal Complexes. Owing to the novel nature of these ligands, we first set out to establish their bidentate nature by making various square planar metal complexes of nickel, palladium, and platinum. Their synthesis is outlined in eq 5.

While in the nickel case DME (DME = 1,2-dimethoxyethane) was easily displaced (within minutes), the formation of both the palladium and platinum complexes occurred more slowly over several hours. Spectroscopic data as well as the crystal structure of the

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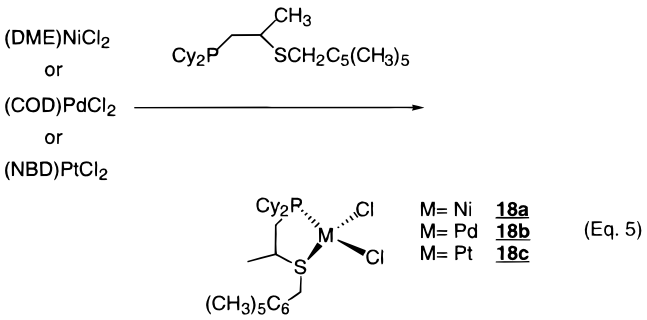
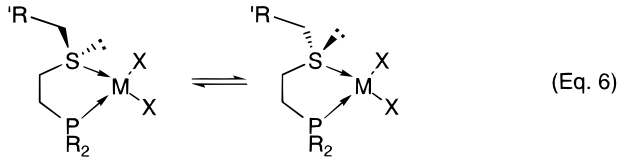
(17) The yield was not optimized; polymerization of the episulfide is a very likely side reaction under these conditions.



(Eq. 5)

palladium complex established the structure shown above. Upon complexation, a shift of the ^{31}P NMR signal was observed going, for example, from −7.6 to +74.2 ppm for complex **18b**. Complex **18c** shows a typical $^{31}P-Pt$ coupling of 3408 Hz.

A noteworthy feature of the Pd and Ni complexes was the broadening of the diastereotopic hydrogens adjacent to sulfur (AB spin system). It is likely that this dynamic process is associated with sulfur inversion. This is a well-known process at metal centers and for this particular system seems to occur on the NMR time scale (see eq 6).[18] To gain more insight into this process, a



(Eq. 6)

low-temperature ^1H NMR study was carried out on the Ni complex where the line broadening was the most noticeable. Since the line broadening was somewhat anomalous (the "A" line was broader than the "B" line), we carried out magnetization transfer experiments at temperatures where the spectra appeared static (−50 to −90 °C). Instead of observing an expected decrease in intensity for B upon irradiating A we noticed a small increase in intensity that could simply be explained by a nuclear Overhauser effect (proximity of the two spins). This indicates that the CH_2 protons are not exchanging with each other. The difference in line width could be associated with different T_2 relaxation at each site or different long-range H−P couplings for the A and B sites (for example, $^4J_{P-H}$). We propose that exchange occurs with another isomer present at very low concentration.[19] If we assume similar shifts and coupling constants for the AB quartet for the Ni, Pd, and Pt complexes, the rate of sulfur inversion appears to increase in the following order: Pt < Pd < Ni, a trend observed previously for Pd and Pt.[18h] The mechanism of sulfur inversion is still controversial, but experimental evidence seems to favor a planar intermediate as opposed to a dissociation−recombination mechanism.[18] These observations were made during the study of metals bound to chelating dithioether ligands, and the proposed "in place" mechanism might not be favored for chelating (P,S) ligands. This inversion at sulfur coupled with the high conformational flexibility of the ligands may be responsible for the moderate enantioselectivities observed in the asymmetric hydrogenations (see below).

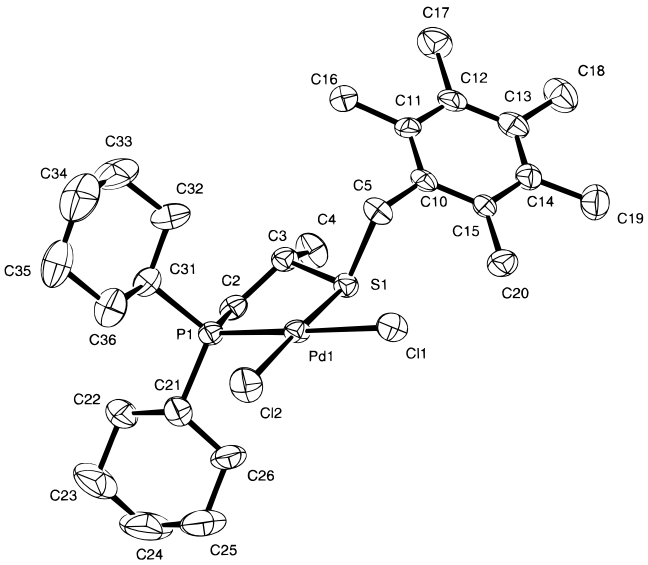


Figure 1. ORTEP drawing of $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)PdCl_2$, **18b**. The hydrogen atoms have been omitted.

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for 18b, 19, and 22

	18b	19	22
mol formula	$PdCl_2SPC_{27}H_{45}$	$Pd_2Cl_2S_2P_2C_{30}H_{56}$	$RhS_3PF_3OC_{35}H_{60}$
fw	610.00	826.56	783.94
cryst dimens (mm)	0.25 × 0.10 × 0.28	0.18 × 0.14 × 0.25	0.44 × 0.29 × 0.39
space grp	$P2_1/n$	$C2/c$	$P2_1/n$
cell param			
a (Å)	8.547(1)	29.125(1)	10.451(2)
b (Å)	24.226(4)	13.340(1)	18.584(3)
c (Å)	14.700(3)	19.740(1)	19.733(4)
β (deg)	103.97(1)	113.71(1)	104.62(1)
V (Å^3)	2953.8	7022.1	3708.5
Z	4	8	4
D_c (g/mL)	1.372	1.564	1.404
temp (°C)	−45	−112	−100
radiation (wavelength, Å)	Mo Kα (0.709 30)	Mo Kα (0.709 30)	Mo Kα (0.709 30)
monochromator	graphite	graphite	graphite
linear abs. coeff (cm^{-1})	9.37	13.89	6.98
scan mode			
2θ limits (deg)	$1.7 \le 2\theta \le 52.0$	$3.1 \le 2\theta \le 48.2$	$4.0 \le 2\theta \le 50.0$
octants collcd	+++, −++	NA	++−, −+−
total no. unique reflns	6179	18069	6963
data with $I \ge x\sigma(I)$	2770 ($x = 3$)	4755 ($x = 3$)	4375 ($x = 3$)
R	0.044	0.038	0.05
R_w	0.037	0.042	0.048
GoF	1.07	2.16	1.63
no. params	289	343	415
max Δ/σ	0.00	0.01	0.20
largest res dens (e/Å^3)	0.80	0.57	1.31

(18) (a) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Sik, V. *J. Organomet. Chem.* **1990**, *394*, 455. (b) Abel, E. W.; Booth, M.; Orrell, K. G.; Pring, G. M. *J. Chem Soc., Dalton Trans.* **1981**, 1944 and references therein. (c) Cross, R. J.; Smith, G. J.; Wardle, R. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 191. (d) Orrell, K. G.; Sik, V.; Brubaker, C. H.; McCulloch, B. *J. Organomet. Chem.* **1984**, *276*, 267. (e) Yamazaki, S.; Ama, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 931. (f) Ascenso, J. R.; Carvalho, M.; Dias, A. R.; Romao, C. C.; Calhorda, M. J.; Veiros, L. F. *J. Organomet. Chem.* **1994**, *470*, 147. (g) Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem Soc., Dalton Trans.* **1981**, 2235. (h) Abel, E. W.; Shamsuddin, A. K. A.; Farrow, G. W.; Orrell, K. G. *J. Chem. Soc., Dalton Trans.* **1977**, *47*. (i) Gladiali, S.; Fabbri, D.; Kollàr, L.; Claver, C.; Ruiz, N.; Alvarez-Larena, A.; Piniella, J. F. *Eur. J. Inorg. Chem.* **1998**, 113.

(19) Under static conditions, we would expect two sets of AB quartets (two diastereomeric complexes); however, the second isomer could not be detected by ^1H NMR spectroscopy. This prevents us from accurately determining the rate at which they interconvert using the slow exchange conditions.

Table 2. Selected Interatomic Distances (Å) for $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)PdCl_2$, 18b[a]

Pd(1)−Cl(1)	2.377(2)	P(1)−C(2)	1.828(6)
Pd(1)−Cl(2)	2.309(2)	P(1)−C(21)	1.826(7)
Pd(1)−S(1)	2.271(2)	P(1)−C(31)	1.834(6)
Pd(1)−P(1)	2.221(2)	C(2)−C(3)	1.513(8)
S(1)−C(3)	1.842(6)	C(3)−C(4)	1.534(9)
S(1)−C(5)	1.833(6)		

[a] Numbers in parentheses are the estimated standard deviations.

Table 3. Selected Bond Angles (deg) for $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)PdCl_2$, 18b[a]

C(3)−S(1)−C(5)	102.3(3)	S(1)−C(5)−C(10)	114.1(4)
Pd(1)−P(1)−C(2)	106.5(2)	P(1)−C(2)−C(3)	114.0(5)
Pd(1)−P(1)−C(21)	113.6(2)	P(1)−C(21)−C(22)	114.0(5)
Pd(1)−P(1)−C(31)	115.9(2)	P(1)−C(21)−C(26)	111.2(5)
C(2)−P(1)−C(21)	105.3(3)	P(1)−C(31)−C(32)	111.4(5)
C(2)−P(1)−C(31)	106.9(3)	P(1)−C(31)−C(36)	113.3(5)
S(1)−C(3)−C(2)	107.7(4)	C(2)−C(3)−C(4)	111.7(6)
S(1)−C(3)−C(4)	110.5(5)	C(21)−P(1)−C(31)	107.8(3)

[a] Numbers in parentheses are the estimated standard deviations.

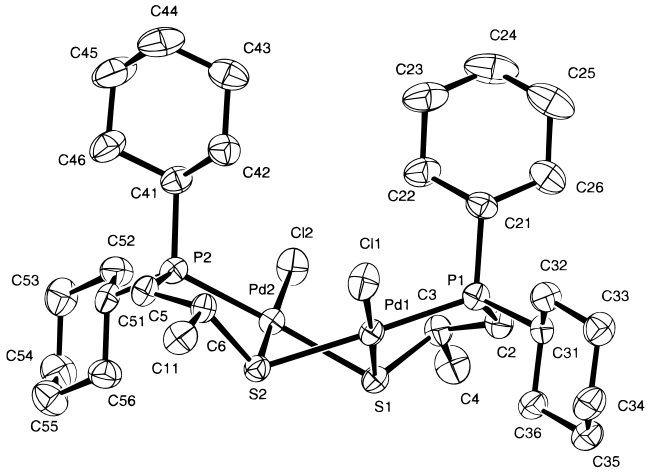
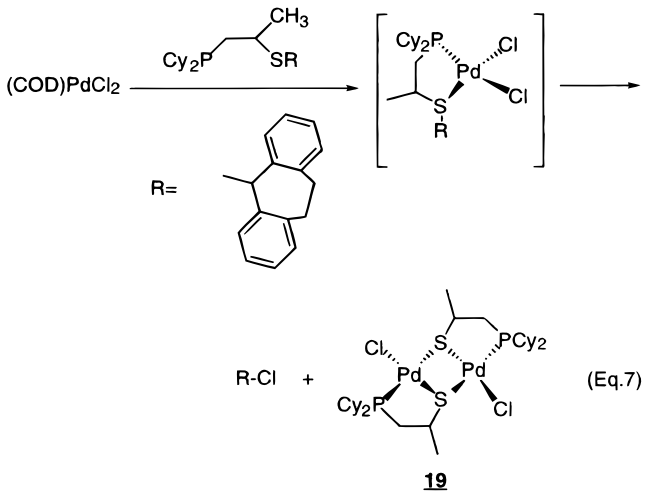


Figure 2. ORTEP drawing of $[(PCy_2CH_2CH(CH_3)SPdCl]_2$, **19**. The hydrogen atoms have been omitted.

The structure of complex **18b** was verified by an X-ray structural determination from crystals grown by slow evaporation of a CH_2Cl_2 solution. An ORTEP diagram is shown in Figure 1. Crystallographic data, collection parameters, and refinement parameters are listed in Table 1; selected interatomic distances and angles are summarized in Tables 2 and 3, respectively. The coordination geometry around the metal center is a slightly distorted square-plane with a P−Pd−S angle of 87.84(7)°. This angle is typical of neutral Pd(II) complexes[7b,20] and smaller than that of cationic (P,S)Pd(II) allyl complexes described by Togni and Pregosin (94.6−96.9°).[7a,e,g,h] Both the Pd−S and Pd−P bond lengths at 2.271(2) and 2.221(2) Å are typical,[7,20] but the two Pd−Cl distances, 2.309(2) Å and 2.377(2) Å, differ significantly. The latter effect is attributed to the larger trans influence of phosphorus versus sulfur. The methyl substituent on the metallacycle is in a pseudoequatorial position trans to the sulfur substituent.[21] This structure is also in accordance with Pregosin's observation that in P,S chelate complexes there is a tendency for pseudoaxial substituents on sulfur.[7c,d]

All attempts to synthesize and recrystallize (**13**)$PdCl_2$ failed and resulted instead in the cleavage of the S−C bond and the formation of the dimeric complex **19** (see eq 7).



The structure of complex **19** was confirmed by X-ray crystallography, and an ORTEP diagram is reported in Figure 2. Single crystals of complex **19** were obtained by recrystallization from CH_2Cl_2/hexane over a period of a few days at ambient temperature. Crystallographic data and collection and refinement parameters are listed in Table 1; selected interatomic distances and angles are summarized in Tables 4 and 5, respectively. The geometry around each palladium is distorted square planar. As observed in other thiolate-bridged complexes of d^8 transition metals, the molecules are folded along the S−S axis leading to a butterfly core structure. This folding brings the two palladium atoms close together (2.9893(6) Å). The chelate bite angles, S−Pd−P, 86.85(4)° and 87.51(4)°, are in the normal range[7q,22a,23] and close to that of the mononuclear complex **18b** (87.84(7)°). The S−Pd−S angles (80.95(4)° and 81.59(4)°) are

Table 4. Selected Interatomic Distances (Å) for $[(PCy_2CH_2CH(CH_3)SPdCl]_2$, 19[a]

Pd(1)−Pd(2)	2.9893(6)	P(1)−C(2)	1.839(4)
Pd(1)−Cl(1)	2.342(1)	P(1)−C(21)	1.838(4)
Pd(2)−Cl(2)	2.327(1)	P(1)−C(31)	1.842(4)
Pd(1)−S(1)	2.278(1)	P(2)−C(5)	1.830(4)
Pd(1)−S(2)	2.415(1)	P(2)−C(41)	1.845(4)
Pd(2)−S(1)	2.3877(10)	P(2)−C(51)	1.519(6)
Pd(2)−S(2)	2.276(1)	C(2)−C(3)	1.512(6)
Pd(1)−P(1)	2.249(1)	C(3)−C(4)	1.525(6)
Pd(2)−P(2)	2.240(1)	C(5)−C(6)	1.514(6)
S(1)−C(3)	1.854(4)	C(6)−C(11)	
S(2)−C(6)	1.842(4)		

[a] Numbers in parentheses are the estimated standard deviations.

(20) Clark, G. R.; Orbell, J. D. *J. Organomet. Chem.* **1981**, *215*, 121.

(21) The structures reported by Pregosin and Togni are all six-membered ring metallacycles, and the methyl substituents in these tend to be equatorial in most cases.

(22) (a) Roundhill, D. M.; Roundhill, S. G. N.; Beaulieu, W. B.; Bagchi, U. *Inorg. Chem.* **1980**, *19*, 3365. (b) Eller, P. G.; Riker, J. M.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 3540. (c) Lockyer, T. N. *Aust. J. Chem.* **1974**, *27*, 259. (d) Marty, W.; Schwarzenbach, G. *Chimia* **1970**, *24*, 431. (e) Kim, J. S.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1996**, *118*, 4115. (f) Aurivillius, K.; Bertinsson, G.-I *Acta Crystallogr.* **1982**, *B38*, 1295. (g) Chooi, S. Y. M.; Leung, P.-H *Bull. Sing. Natl. Inst. Chem.* **1991**, *19*, 69. For a study of electron-transfer induced C−S bond cleavage, see: Mullen, G. E. D.; Went, M. J.; Wocadlo, S.; Powell, A. K.; Blower, P. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1205.

Table 5. Selected Bond Angles (deg) for $[(PCy_2CH_2CH(CH_3)SPdCl]_2$, 19[a]

Pd(2)−Pd(1)−Cl(1)	125.85(3)	Pd(1)−S(2)−C(6)	108.8(1)
Pd(1)−Pd(2)−Cl(2)	123.68(3)	Pd(2)−S(2)−C(6)	102.8(1)
Pd(2)−Pd(1)−S(1)	51.79(3)	Pd(1)−P(1)−C(2)	107.6(1)
Pd(2)−Pd(1)−S(2)	48.39(3)	Pd(1)−P(1)−C(21)	111.8(1)
Pd(1)−Pd(2)−S(2)	52.49(3)	Pd(1)−P(1)−C(31)	116.9(1)
Pd(2)−Pd(1)−P(1)	117.92(3)	Pd(2)−P(2)−C(5)	107.2(1)
Pd(1)−Pd(2)−P(2)	121.49(3)	Pd(2)−P(2)−C(41)	115.3(1)
Cl(1)−Pd(1)−S(1)	177.6(1)	Pd(2)−P(2)−C(51)	114.0(1)
Cl(1)−Pd(1)−S(2)	97.42(1)	C(2)−P(1)−C(21)	108.4(2)
Cl(2)−Pd(2)−S(1)	97.59(4)	C(2)−P(1)−C(31)	104.4(2)
Cl(2)−Pd(2)−S(2)	175.26(4)	C(21)−P(1)−C(31)	107.1(2)
Cl(1)−Pd(1)−P(1)	94.55(6)	C(5)−P(2)−C(41)	106.7(2)
Cl(2)−Pd(2)−P(2)	93.02(4)	C(5)−P(2)−C(51)	106.4(2)
S(1)−Pd(1)−S(2)	80.95(4)	C(41)−P(2)−C(51)	106.7(2)
S(1)−Pd(2)−S(2)	81.59(4)	S(1)−C(3)−C(2)	107.8(3)
S(1)−Pd(1)−P(1)	86.85(4)	S(1)−C(3)−C(4)	108.5(3)
S(2)−Pd(1)−P(1)	165.88(4)	S(2)−C(6)−C(5)	108.6(3)
S(1)−Pd(2)−P(2)	168.69(4)	S(2)−C(6)−C(11)	108.7(3)
S(2)−Pd(2)−P(2)	87.51(4)	P(1)−C(2)−C(3)	111.9(3)
Pd(1)−S(1)−Pd(2)	79.64(3)	P(2)−C(5)−C(6)	111.1(3)
Pd(1)−S(2)−Pd(2)	79.12(3)	C(2)−C(3)−C(4)	114.3(4)
Pd(1)−S(1)−C(3)	104.5(1)	C(5)−C(6)−C(11)	111.9(3)
Pd(2)−S(1)−C(3)	107.5(1)	Pd(1)−Pd(2)−S(1)	48.57(3)

[a] Numbers in parentheses are the estimated standard deviations.

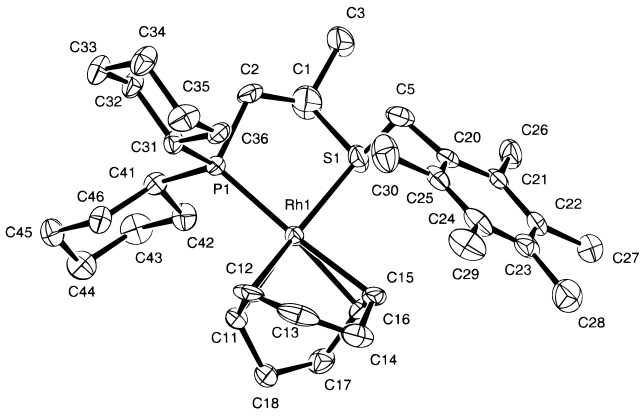
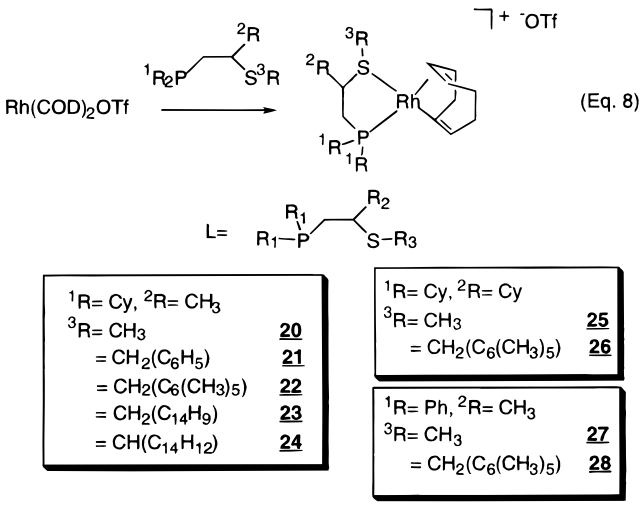


Figure 3. ORTEP drawing of $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)Rh(COD)^+$, **22**. The counterion TfO^- as well as hydrogen atoms have been omitted.

typical, but the Pd−S−Pd angles (79.64(3)° and 79.12(3)°) are about 15° smaller than similar complexes.[7q,22a,23] This latter feature might be due to the fact that most of the structures reported are dicationic,[23] which would widen this angle because of strong electrostatic repulsions. However, in another neutral palladium structure most closely related to this work, $[PdCl(L)]_2$ (L = (*R*)-1-[(S)-diphenylphosphino)ferrocenyl]ethyl mercaptan),[7q] a Pd−S−Pd angle of 92.61(7)° was observed. The Pd−Cl bonds (2.342(1) and 2.327(1) Å) are typical, and again owing to the strong trans influence of the phosphine, the Pd−S distances trans to P are longer (2.415(1) and 2.3877(10) Å) than those trans to Cl (2.278(1) and 2.276(1) Å). The Pd−P distances (2.249(1) and 2.240(1) Å) are typical and close to those of the mononuclear complex **18b** (2.221(2) Å). The cleaveage of C−S bonds has been reported for complexes of this type and may be very relevant to the stability of metal catalysts bearing these ligands.[7q,22]

Synthesis of $LRh(COD)^+TfO^-$ and Their Use as Hydrogenation Catalysts. Treatment of $Rh(COD)_2^+OTf^-$ (COD = 1,5-cyclooctadiene, $OTf^- = CF_3SO_3^-$) with ligands **9**−**17** results in rapid displacement of one cyclooctadiene and formation of $LRh(COD)^+TfO^-$. The ^1H NMR spectra of all these complexes show broad signals corresponding to the coordinated cyclooctadiene. Once again, this fluxional process is probably associated with sulfur inversion and potentially contributes to the moderate enantioselectivities reported below in the asymmetric hydrogenation reactions.



Complex (**11**)$Rh(COD)^+OTf^-$, **22**, was recrystallized from THF/hexane at −30 °C and characterized by X-ray crystallography. An ORTEP diagram is shown in Figure 3. Crystallographic data and collection and refinement

Table 6. Selected Interatomic Distances (Å) for $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)Rh(COD)^+$, 22[a]

Rh(1)−S(1)	2.339(1)	C(1)−C(2)	1.446(9)
Rh(1)−P(1)	2.304(1)	C(1)−C(3)	1.541(8)
Rh(1)−C(11)	2.195(5)	C(5)−C(20)	1.528(8)
Rh(1)−C(12)	2.159(5)	C(11)−C(12)	1.388(8)
Rh(1)−C(15)	2.246(5)	C(11)−C(18)	1.496(7)
Rh(1)−C(16)	2.240(5)	C(12)−C(13)	1.518(9)
S(1)−C(1)	1.819(7)	C(13)−C(14)	1.515(10)
S(1)−C(5)	1.861(7)	C(14)−C(15)	1.505(8)
P(1)−C(2)	1.833(6)	C(15)−C(16)	1.358(9)
P(1)−C(31)	1.840(5)	C(16)−C(17)	1.497(8)
P(1)−C(41)	1.857(5)	C(17)−C(18)	1.524(8)

[a] Number in parentheses are the estimated standard deviations.

Table 7. Selected Bond Angles (deg) for $(PCy_2CH_2CH(CH_3)SCH_2C_5(CH_3)_5)Rh(COD)^+$, 22[a]

S(1)−Rh(1)−P(1)	85.67(6)	Rh(1)−S(1)−C(1)	105.5(2)
S(1)−Rh(1)−C(11)	163.4(1)	Rh(1)−S(1)−C(5)	111.8(2)
S(1)−Rh(1)−C(12)	158.9(2)	C(1)−S(1)−C(5)	105.4(3)
S(1)−Rh(1)−C(15)	93.3(1)	Rh(1)−P(1)−C(2)	107.4(2)
S(1)−Rh(1)−C(16)	90.6(1)	Rh(1)−P(1)−C(31)	116.8(2)
P(1)−Rh(1)−C(11)	97.4(2)	Rh(1)−P(1)−C(41)	117.1(2)
P(1)−Rh(1)−C(12)	96.9(2)	C(2)−P(1)−C(31)	104.2(3)
P(1)−Rh(1)−C(15)	170.5(2)	C(2)−P(1)−C(41)	103.4(3)
P(1)−Rh(1)−C(16)	154.1(2)	C(31)−P(1)−C(41)	106.5(2)
C(11)−Rh(1)−C(12)	37.2(2)	Rh(1)−C(11)−C(12)	70.0(3)
C(11)−Rh(1)−C(15)	86.4(2)	Rh(1)−C(16)−C(17)	106.9(4)
C(11)−Rh(1)−C(16)	79.5(2)	S(1)−C(1)−C(2)	113.7(5)
C(12)−Rh(1)−C(15)	80.8(2)	S(1)−C(1)−C(3)	111.7(5)
C(12)−Rh(1)−C(16)	95.7(2)	S(1)−C(5)−C(20)	110.6(4)
C(15)−Rh(1)−C(16)	35.2(2)	P(1)−C(2)−C(1)	114.0(5)

[a] Numbers in parentheses are the estimated standard deviations.

(23) Capdevila, M.; Clegg, W.; Gonzales-Duarte, P.; Harris, B.; Mira, I.; Sola, J.; Taylor, I. C. *J. Chem. Soc., Dalton Trans.* **1992**, 2817.

Table 8. Rh-Catalyzed Asymmetric Hydrogenation of α-Enamide Esters (R = Ph)[a]

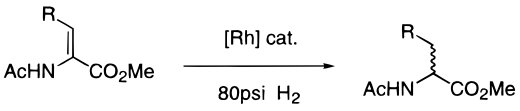
catalyst	% conversion	% ee[b] (confign)[c]
20	100	26.6 (*S*)
21	100	50.1 (*S*)
22	100	18.3 (*S*)
23	100	26.1 (*S*)
24	37	27.7 (*S*)
25	100	29.9 (*R*)
26	100	38.8 (*R*)
27	44	5.1 (*S*)
28	74	24.7 (*R*)
(*R*,*R*)-MeDUPHOS	100	98.0 (*S*)

[a] Reactions were conducted at ambient temperature and a pressure of H_2 of 80 psi using 0.39 M methanol solutions of substrate and the catalyst precursors 2 mol %. Reaction time was 16 h. [b] Enantiomeric excesses were determined by chiral capillary GC using Chrompack's Chirasil-L-Val column (25m). Absolute configurations for the products were confirmed by comparing with that of the product obtained with (*R*,*R*)-MeDUPHOS.

parameters are listed in Table 1; selected interatomic distances and angles are summarized in Tables 6 and 7, respectively.

The (P,S) ligand forms a puckered five-membered chelate ring with the Rh whose geometry is essentially square planar. The bite angle is 85.67(6)°, a typical value for five-membered ring chelates. Both the Rh−S and Rh−P bond lengths at 2.339(1) and 2.304(1) Å are typical,[24] but the Rh−(C_1,C_2) and Rh−(C_3,C_4) differ significantly again due to the stronger trans influence of the phosphorus versus sulfur. Similar to complex **18b**, the methyl substituent on the metallacycle is in a pseudoequatorial position trans to the sulfur substituent, which is in a pseudoaxial position leaving the heteroatom in a very open area.[7c,d]

Complexes **20**−**28** are active catalysts for the enantioselective hydrogenation α-enamide esters (eq 9). Specific results are displayed in Tables 8 and 9.



(Eq. 9)

The results presented in Table 8 do not show obvious trends based on ligand steric or electronic arguments. The ee's obtained are low to moderate, ranging from 5.1% to 50.1%. The results in Table 9 seem to indicate that higher ee's are obtained with more electron-poor substrates. The unusually high ee obtained for (2-thienyl)-CHC(CO_2Me)(NHAc), 51%, could be explained by an additional point of attachment of the substrate via sulfur.

Conclusion

The lack of correlations of the enantioselectivity with phosphorus−sulfur ligand structure and electronics in this study is most likely associated with the possible hemilabile nature of this type of ligand and/or the sulfur inversion processes discussed above. One might expect from previous studies by others that stronger ligand binding and backbone rigidity would yield higher ee's. The apparent flexibility discovered for the ligands in this study is an apparent drawback. On the other hand, the inherent electronic asymmetry generated by the use of two different heteroatoms on the bidentate ligand could possibly compensate for the flexibility of the present ligand systems, generating hope that an appropriate combination of substituents and substrates can be found to obtain higher ee's in the future. We are currently exploring the use of these and related ligands for other asymmetric transformations.

Table 9. Rh-Catalyzed Asymmetric Hydrogenation of α-Enamide Esters Using Catalyst 26[a]

R	% ee[b] (confign)[c]
CH_3	19.0 (*R*)
Ph	38.6 (*R*)
4-F-(C_6H_5)	41.3 (*R*)[d]
3-F-(C_6H_5)	26.3 (*R*)
3-Br-(C_6H_5)	17.6 (*R*)[d]
3,5-F_2-(C_6H_4)	14.8 (*R*)[d]
3,5-$(CF_3)_2$-(C_6H_4)	4.9 (*R*)[d]
2-naphthalene	25.2 (*R*)[d]
3-OMe-(C_6H_5)	35.8 (*R*)[d]
3-thienyl	27.7 (*R*)
2-thienyl	50.9 (*R*)

[a] Reactions were conducted at ambient temperature and a pressure of H_2 of 80 psi using 0.39 M methanol solutions of substrate and the catalyst precursor 2 mol %. Reaction time was 16 h. [b] Enantiomeric excesses were determined by chiral capillary GC using Chrompack's Chirasil-L-Val column (25 m). Absolute configurations for the products were confirmed by comparing with that of the product obtained with (*R*,*R*)-MeDUPHOS. [d] THF had to be added to get most of the substrates in solution.

Experimental Section

General Information. All complexes were manipulated under an atmosphere of dry, oxygen-free nitrogen within a Vacuum Atmospheres drybox, on a high-vacuum line, or on a standard Schlenk line. Methylene chloride was distilled in an N_2 atmosphere from phosphorus pentoxide prior to use. Tetrahydrofuran (THF), toluene, diethyl ether, and hexane were distilled in an N_2 atmosphere from sodium benzophenone ketyl. Methanol was distilled from $Mg(OMe)_2$. Hydrogen (99.9995%) gas was purchased from Matheson and used as received. The compounds (*S*)-(+)-hexahydromandelic acid, thiocarbonyldiimidazole, *n*-butyllithium (1.6 M in hexanes), (*S*)-(−)-propylene oxide, arylbenzyl chlorides, and bis(1,5-cyclooctadiene)rhodium(I) trifluoromethanesulfonate ($(COD)_2Rh^+OTf^-$) were purchased from Aldrich Chemical Co. The complexes (DME)$NiCl_2$ (DME = 1,2-dimethoxyethane) and (COD)$PdCl_2$ (COD = 1,5-cyclooctadiene) were obtained from Strem Chemicals Inc. (NBD)$PtCl_2$ (NBD = norbornadiene) was prepared following a published procedure.[25] The compounds Cy_2PLi and Ph_2PLi were prepared as white solids by deprotonation of the corresponding phosphines with *n*-butyllithium in hexane. All α-(acylamino)acrylate substrates were prepared either by standard Erlenmeyer procedures[26] or by the method of Schmidt et al.[27] Procedures below are given for the preparation of the racemic phosphorus−sulfur ligands, and these same procedures were used to prepare the corresponding *S* and/or *R* enantiomers. All preparative chromatography was done using columns prepared with silica gel. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on either a General Electric 300, Bruker 500, or Varian 500 spectrometer. Chemical shifts for ^{1}H NMR and ^{13}C NMR are reported by reference to protonated or ^{13}C signals of the solvent in ppm downfield from $(CH_3)_4Si$. ^{31}P NMR chemical shifts are positive downfield (and negative upfield) from external 85% H_3PO_4. Elemental

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analyses were performed by Oneida Research Services, Inc. Gas chromatographic analyses were performed using a Hewlett-Packard Model HP 5890 GC. A 25 m × 0.25 mm Chiralsil-L-Val (chiral fused silica, Chrompack) was used to determine enantiomeric excesses in the asymmetric hydrogenation of α-(acylamino)acrylates.

Synthesis of (*R*)-Propylenesulfide (4a). A glass reaction tube sealable with a Teflon stopcock was charged with 3.68 g (48.3 mmol) of thiourea, 24.2 mL of tetraethylene glycol, and 4.79 mL of water. This was placed on a high vacuum line and was freeze−thaw degassed. Into this tube was vacuum transferred 3.03 mL (43.2 mmol) of (*S*)-(−)-propylene oxide. The tube was sealed by closing the stopcock, and the contents were mixed by mechanical rotation of the tube for 12 h. The reaction tube was then placed back onto the high vacuum line, and the product was vacuum transferred out of the reaction mixture into another vessel cooled to −78 °C containing anhydrous sodium sulfate to adsorb water. The propylene sulfide was then vacuum transferred into another vessel containing anhydrous sodium sulfate for further drying. It was then vacuum transferred into a clean vessel for storage and used without further purification or drying. Each of the vacuum transfers was conducted as quickly as possible over a period of time to minimize the amount of water transferred from one vessel to the next. Yield: 2.19 g (68%). NMR data were identical to that of commercially available racemic propylene sulfide.

Synthesis of (*S*)-CyCHOC(S)OCH$_2$. The chiral diol obtained from the lithium aluminum hydride reduction of (*S*)-(+)-hexahydromandelic acid (5.0 g, 31.6 mmol)[28] was dissolved in CH_2Cl_2, and thiocarbonyldiimidazole (8.0 g, 44.9 mmol) was added. It was stirred at ambient temperature for 24 h, after which time the solvent was removed in vacuo. Chromatography of the oily residue (4:1, hexane/ethyl acetate) yielded 4.38 g (74%) of a white crystalline solid after removal of solvent. ^{1}H NMR ($CDCl_3$, 300 MHz, 23 °C): δ 4.66 (m, 2 H, C*H*$_2$O), 4.64 (m, 1 H, C*H*O), 1.78 (m, 6 H), 1.23 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C): δ 192.0 (s, C(S)), 86.1 (d, J = 154 Hz, *C*HO), 71.6 (t, J_{C-H} = 153 Hz, *C*H$_2$O), 40.9 (d, J_{C-H} = 129 Hz, ipso *C*H), 27.6, 27.3, 25.8, 25.3, 25.1 all triplets, J_{C-H} = 140 Hz). C, H Anal. Found (Calcd): C, 58.20 (58.03); H, 7.62 (7.58).

Synthesis of (*S*)-CyCHOC(O)SCH. A 500-mL round-bottomed flask was charged with 4.0 g (21.5 mmol) of (*S*)-CyCHOC(S)OCH$_2$ dissolved in 200 mL of THF. Tetrabutylammonium bromide (1.5 g, 4.7 mmol) was added. It was brought to reflux and kept there overnight. The solvent was then removed in vacuo and the residue chromatographed (4:1 hexane/ethyl acetate). Yield: 3.88 g (97%). ^{1}H NMR ($CDCl_3$, 300 MHz, 23 °C): δ 4.38 (m, 1 H, C*H*O), 3.37 (m, 1 H, C*H*$_2$S), 2.2−0.8 (m, 11 H, Cy). ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C): δ 172.7 (s, *C*(O)), 85.5 (d, J_{C-H} = 150 Hz, *C*HO), 41.7 (d, J_{C-H} = 135 Hz, ipso *C*H), 34.5 (t, J = 143 Hz, *C*H$_2$S), 29.0, 27.9, 26.0, 25.6, 25.4, all triplets, J_{C-H} = 136 Hz). C, H Anal. (Calcd): C, 57.52 (58.03); H, 7.39 (7.58).

Synthesis of (*R*)-2-Cyclohexylthiirane (4b). A 50-mL round-bottomed flask was charged with 1.316 g (7.06 mmol) of (*S*)-CyCHOC(O)SCH dissolved in 15 mL of MeOH. The flask was cooled to 0 °C, and 5.65 mL of a 2 N solution of NaOH was added dropwise. A white precipitate formed immediately. After 2 h most of the solvent was removed in vacuo. The residue was then neutralized with 5% HCl, and the product was extracted with 2 × 30 mL of CH_2Cl_2. Methylene chloride was removed on a rotary evaporator, and the residue was distilled under vacuum (10^{-2} Torr). Yield: 0.550 g (55%). ^{1}H NMR ($CDCl_3$, 300 MHz, 23 °C): δ 2.69 (m, 1 H, C*H*), 2.67 (d, 1 H, J = 6 Hz, CH*H*), 2.46 (d, 1 H, J = 6 Hz, C*H*H), 2.0−0.5 (m, 11 H, Cy). ^{13}C NMR ($CDCl_3$, 75 MHz, 23 °C): δ 44.8 (d, J = 132 Hz), 41.9 (t, J_{C-H} = 163 Hz), 32.9 (t, J_{C-H} = 137 Hz), 32.7 (t, J_{C-H} = 137 Hz), 26.3 (t, J_{C-H} = 134 Hz), 26.0 (t, J_{C-H} = 124 Hz), 25.9 (t, J_{C-H} = 124 Hz), 24.5 (t, J_{C-H} = 170 Hz). HREIMS: m/z = 142.0825 ($C_8H_{14}S$, Δ +0.9 mmu).

Determination of the Enantiomeric Excess of the Thiiranes Derived from Commercial Chiral (*R*)-Hexahydromandelic Acid. A small vial was charged with 110 mg (0.77 mmol) of chiral 2-cyclohexylthiirane (*R* or *S*) and 93 mg (0.81 mmol) of (*S*)-(+)-(methoxymethyl)pyrrolidine (neat). The mixture was heated to 110 °C and kept there for 6.5 h. ^{1}H NMR analysis indicates that the reaction was complete and for each case (*R* or *S*) generated a single diastereoisomer indicating an enantiomeric excess of >95%. Key ^{1}H NMR signals for the single diastereomer are the diastereotopic protons α to oxygen and nitrogen (two AB quartets centered at 2.42 and 3.29 ppm) and the methoxy methyl (s, 3.10 ppm). A 50/50 mixture of both diastereoisomers was obtained by carrying out the above reaction with racemic 2-cyclohexylthiirane. The key ^{1}H NMR signals for the other diastereoisomers are as follows: two AB quartets at 2.46 and 3.38 ppm and a methoxy signal at 3.13 ppm.

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SLi (5). Chiral Version (95% Yield). A 100-mL Schlenk flask was charged with 1.282 g (6.28 mmol) of Cy$_2$PLi dissolved in 20 mL of THF. The flask was cooled to −78 °C, and **4a** (520 mg, 7.01 mmol) was vacuum transferred into the lithium salt solution. It was kept at −78 °C for 45 min, after which time the dry ice/acetone bath was removed and the yellowish solution allowed to reach ambient temperature. After an additional 20 min, the solvent was removed in vacuo. The solid was washed three times with 30 mL of hexane and dried in vacuo. Yield: 1.37 g (78%). The lithium salt was used without further purification. ^{1}H NMR (THF-d_8, 300 MHz, 23 °C): δ 2.80 (m, 1 H, C*H*), 1.31 (d, J = 6 Hz, 3 H, CH$_3$), 2.0−1.0 (m, 24 H). ^{13}C NMR (THF-d_8, 125 MHz, 23 °C): δ 40.1 (brs, *C*H(CH$_3$)), 34.9 (d, J_{P-C} = 20 Hz), 34.6 (d, J_{P-C} = 11 Hz, CH of Cy), 34.3 (d, J_{P-C} = 12 Hz, CH of Cy), 31.5 (d, J_{P-C} = 14 Hz, CH$_2$ of Cy), 31.2 (d, J_{P-C} = 13 Hz, CH$_2$ of Cy), 30.2 (d, J_{P-C} = 8 Hz, CH$_2$ of Cy), 28.6 (m), 27.8 (s). ^{31}P{H} NMR (THF-d_8, 121 MHz, 23 °C): δ −7.6.

Determination of the Enantiomeric Excess of the Ligands Derived from 4a. An NMR tube was charged with 33 mg (0.12 mmol) of Cy$_2$PCH$_2$CH(CH$_3$)SLi (**5**) and (1*S*)-(−)-camphanic chloride (26 mg, 0.12 mmol). The mixture of solids was dissolved in ca. 0.6 mL of THF-d_8. The ^{31}P NMR shows two distincts signals corresponding to two diastereoisomers (−7.3, s, minor, −6.9, s, major). Integration of these signals allows the determination of the enantiomeric excess: 88%. A 50/50 mixture of the diastereoisomers was obtained using racemic propylene sulfide.

Synthesis of Cy$_2$PCH$_2$CH(Cy)SLi (6). A 100-mL Schlenk flask was charged with 509 mg (2.49 mmol) of Cy$_2$PLi dissolved in 15 mL of THF. The flask was cooled to −78 °C and CyCH$_2$SCH (390 mg, 2.74 mmol), **4b**, in 3 mL of THF was added dropwise. It was kept at −78 °C for 5−10 min, after which time the dry ice/acetone bath was removed and the colorless solution allowed to reach ambient temperature. After an additional 30 min, the solvent was removed in vacuo. Yield: 0.765 g (89%). The lithium salt was used without further purification. ^{1}H NMR (THF-d_8, 300 MHz, 23 °C): δ 2.6 (brm, 1 H), 2.1−1.0 (brm, 35 H). ^{13}C{H} NMR (THF-d_8, 125 MHz, 23 °C): δ 49.3 (brs, *C*H(Cy)), 45.4 (d, J_{P-C} = 17 Hz, CH of Cy), 33.9 (d, J_{P-C} = 9 Hz, CH of Cy), 33.7 (d, J_{P-C} = 7 Hz, CH of Cy), 32.0−24.0 (overlapping multiplets corresponding to CH$_2$'s). ^{31}P{H} (THF-d_8, 121 MHz, 23 °C) NMR: δ −7.2.

Synthesis of Ph$_2$PCH$_2$CH(CH$_3$)SLi (7). A Schlenk flask was charged with 2.76 g (14.4 mmol) of Ph$_2$PLi dissolved in 40 mL of THF. The flask was cooled to −78 °C, and **4a** (1.12 g, 15.1 mmol) dissolved in ca. 10 mL THF was added dropwise via syringe. The reaction mixture was kept at −78 °C for 30 min, after which time the dry ice/acetone bath was removed and the colorless solution allowed to reach ambient temper-

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ature. After an additional 25 min, the solvent was removed in vacuo. Yield: 3.55 g. Accounting for 15 mol % of THF in the salt, this corresponds to 3.37 g (88% yield). The lithium salt was used without further purification. ^{1}H NMR (THF-d_8, 300 MHz, 23 °C): δ 8−7 (m, 10 H, arene), 2.85 (m, 1 H, C*H*), 2.46 (ddd, J = 13, 6, 2.3 Hz, 1 H), 2.25 (dd, J = 13, 8 Hz, 1 H), 1.38 (d, J = 6 Hz, 3 H, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 23 °C): δ 141.5 (d, J_{P-C} = 7 Hz, quaternary C Ph), 141.4 (d, J_{P-C} = 7 Hz, quaternary C Ph), 134.0 (dd, J_{P-C} = 13 Hz, J_{C-H} = 142 Hz, CH Ph), 133.8 (dd, J_{P-C} = 13 Hz, J_{C-H} = 142 Hz, CHPh), 128.90 (dd, J_{C-P} = 6 Hz, J_{C-H} = 160 Hz, CHPh), 128.88 (d, J_{C-P} = 6 Hz, J_{C-H} = 160 Hz, CHPh), 128.7 (dd, J_{C-P} = 15 Hz, J_{C-H} = 160 Hz, 2 CH Ph), 46.9 (dt, J_{C-P} = 10 Hz, J_{C-H} = 128 Hz, *C*H_2PPh$_2$), 33.1 (dd, J_{P-C} = 16 Hz, J_{C-H} = 137 Hz, *C*H(CH$_3$)), 31.4 (dq, J_{P-C} = 8 Hz, J_{C-H} = 126 Hz, CH(*C*H$_3$)). ^{31}P{H} NMR (THF-d_8, 121 MHz, 23 °C): δ −17.6.

Synthesis of Ph$_2$PCH$_2$CH(Cy)SLi (8). A 50-mL Schlenk flask was charged with 650 mg (3.38 mmol) of Ph$_2$PLi dissolved in 10 mL of THF. The flask was cooled to −78 °C, and **4b** (505 mg, 3.55 mmol) in 5 mL of THF was added dropwise. It was kept at −78 °C for 30 min, after which time the dry ice/acetone bath was removed and the colorless solution allowed to reach ambient temperature. After an additional 30 min, the solvent was removed in vacuo. Yield: 1.0 g (88%). The lithium salt was used without further purification. ^{1}H NMR (THF-d_8, 300 MHz, 23 °C): δ 7.6−7.4 (m, 4 H, arene), 7.4−7.3 (m, 6 H, arene), 2.62 (m, 1 H, C*H*Cy), 2.54 (ddd, J = 14, 6, 2 Hz, 1 H, C*H*HPPh$_2$), 2.30 (ddd, J = 14 Hz, J = 9 Hz, J = 2 Hz, C*H*HPPh$_2$), 1.9−1.0 (m, 11 H, Cy). ^{13}C{H} NMR (THF-d_8, 125 MHz, 23 °C): δ 140.4 (d, J_{P-C} = 14 Hz, quaternary C Ph), 139.6 (d, J_{P-C} = 15 Hz, quaternary C Ph), 134.2 (d, J_{P-C} = 20 Hz, *C*H Ph), 133.5 (d, J_{P-C} = 19 Hz, CH Ph), 130.0−129.0 (overlapping multiplets accounting for C−H of Ph), 45.1 (d, J_{C-P} = 7 Hz, *C*H), 44.8 (d, J_{P-C} = 16 Hz, *C*H), 38.0 (d, J_{P-C} = 14 Hz, *C*H$_2$PPh$_2$), 31.8 (s, CH$_2$ of Cy), 28.7 (s, CH$_2$ of Cy), 27.52 (s, CH$_2$ of Cy), 27.48 (s, CH$_2$ of Cy), 27.3 (s, CH$_2$ of Cy). ^{31}P{H} NMR (THF-d$_8$, 121 MHz, 23 °C): δ −16.8.

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SCH$_3$ (9). A vial was charged with 462 mg (1.66 mmol) of **5** dissolved in ca. 10 mL of THF. Methyl iodide (127 μL, 2.04 mmol) was then added dropwise. After being stirred at ambient temperature for 15 min, the solvent was removed in vacuo. The product was extracted with hexane (20 mL) followed by toluene (25 mL) and filtered, and the solvent was removed in vacuo from the filtrate. The compound was further purified by oil sublimation in vacuo. Yield: 444 mg (93%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 2.77 (m, 1 H, C*H*), 1.90 (s, 3 H, SCH$_3$), 1−2 (m, 24 H), 1.45 (d, J = 7 Hz, 3 H, CH$_3$). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23 °C): δ 41.5 (d, J_{P-C} = 25 Hz, CH(CH$_3$)), 34.3 (d, J_{P-C} = 14 Hz, CH of Cy), 33.6 (d, J_{P-C} = 14 Hz, CH of Cy), 32.0−25.0 (overlapping multiplets corresponding to CH$_2$'s), 21.8 (d, J_{P-C} = 10 Hz, S*C*H$_3$), 13.8 (s, *C*H$_3$). ^{31}P{H} NMR (THF-d_8, 121 MHz, 23 °C): δ −9.3. C, H Anal. (Calcd): C, 67.40 (67.09); H, 10.84 (10.91).

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SCH$_2$Ph (10). A 100 mL round-bottomed flask was charged with 0.841 g (3.02 mmol) of **5** dissolved in ca. 30 mL of THF. Benzyl bromide (490 mg, 2.87 mmol) was then added dropwise. The initial slurry turned into a clear yellow solution. After the solution was stirred at ambient temperature for 1 h, the solvent was removed in vacuo. The product was extracted with hexane (100 mL) and filtered, and the solvent was removed in vacuo from the filtrate. Yield: 742 mg (71%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 7.5−6.8 (m, 5 H, Ph), 3.57 (AB quartet, 2 H, C*H*$_2$Ph), 2.70 (m, 1 H, C*H*), 1.43 (d, J = 7 Hz, 3 H, CH$_3$), 2.0−0.5 (m, 24 H). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23 °C): δ 139.0 (s), 128.9 (s), 128.6 (s), 126.9 (s), 39.0 (d, J_{P-C} = 24 Hz, CH(CH$_3$)), 35.6 (s, *C*H$_2$Ph), 34.4 (d, J_{P-C} = 16 Hz, CH of Cy), 33.5 (d, J_{P-C} = 15 Hz, CH of Cy), 32.0−26.0 (overlapping multiplets corresponding to CH$_2$'s), 22.1 (d, J_{P-C} = 10 Hz, S*C*H$_3$). ^{31}P{H} NMR (C$_6$D$_6$, 121 MHz, 23 °C): δ −9.8. MS: M + 1 at m/e = 363.39. C, H Anal. (Calcd): C, 73.05 (72.88); H, 9.68 (9.73).

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SCH$_2$(C$_6$(CH$_3$)$_5$) (11). A vial was charged with 355 mg (1.28 mmol) of Cy$_2$PCH$_2$CH(CH$_3$)SLi dissolved in ca. 5 mL of THF. Pentamethylbenzyl chloride (239 mg, 1.21 mmol) dissolved in ca. 5 mL THF was then added dropwise. After the solution was stirred at ambient temperature for 45 min, the solvent was removed in vacuo. The product was extracted with hexane (3 × 30 mL) and filtered and the solvent removed in vacuo from the filtrate. Yield: 416 mg (79%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 3.57 (AB quartet, 2H, C*H*$_2$(C$_6$(CH$_3$)$_5$), 2.99 (m, 1 H, C*H*), 2.42 (s, 6H, 2 CH$_3$'s), 2.05 (s, 3 H, 1 CH$_3$), 2.06 (s, 6 H, 2 CH$_3$'s), 1.60 (d, J = 7 Hz, 3 H, CH$_3$), 2.3−0.5 (m, 24 H). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23 °C): δ 133.7 (s), 132.8 (s), 132.6 (s), 131.6 (s), 41.7 (d, J_{C-P} = 25 Hz, *C*H(S)), 34.5 (d, J_{C-P} = 15 Hz, P cyclohexyl C$_\alpha$), 33.8 (d, J_{C-P} = 15 Hz, P cyclohexyl C$_\alpha$), 32.5 (s, S*C*H$_2$arene), several multiplets due to the cyclohexyl H's were observed in the range 25.0−35.0 ppm, 22.8 (d, J_{C-P} = 9 Hz, CH(*C*H$_3$)(S)), 17.0 (s, CH$_3$), 16.9 (s, CH$_3$), 16.7 (s, CH$_3$). ^{31}P{H} NMR (C$_6$D$_6$, 121 MHz, 23 °C): δ −7.6. C, H Anal. (Calcd): C, 74.78 (74.95); H, 10.50 (10.48).

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SCH$_2$(anthracene) (12). A 250-mL round-bottomed flask was charged with 1.00 g (3.59 mmol) of **5** dissolved in ca. 50 mL of THF. To this was added 9-chloromethylanthracene (810 mg, 3.57 mmol) in small portions. After the solution was stirred at ambient temperature for 5 h (the reaction was complete within an hour), the solvent was removed in vacuo. The product was extracted with toluene (100 mL) and filtered, and the solvent was removed in vacuo from the filtrate. Yield: 1.16 g (70%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 8.49 (dd, J = 9, 0.8 Hz, 2 H), 8.11 (s, 1 H), 7.78 (ddd, J = 9, 0.6, 0.6 Hz, 2 H), 7.31 (m, 4H), 4.71 (s, 2 H, SC*H*$_2$), 3.06 (m, 1 H, C*H*), 1.62 (d, J = 7 Hz, 3 H, CH$_3$), 2.0−0.5 (m, 24 H). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23 °C): δ 132.1 (s), 130.6 (s), 130.2 (s), 129.5 (s), 127.6 (s), 126.3 (s), 125.2 (s), 125.0 (s), 41.8 (d, J_{P-C} = 25 Hz, *C*H(CH$_3$)), 34.2 (d, J_{P-C} = 15 Hz, CH of Cy), 33.6 (d, J_{P-C} = 15 Hz, CH of Cy), 31.3 (d, J_{P-C} = 23 Hz, CH$_2$ of Cy), 30.7−26.0 (overlapping multiplets corresponding to CH$_2$'s of Cy), 23.1 (d, J_{P-C} = 10 Hz, *C*H$_3$). ^{31}P{H} NMR (C$_6$D$_6$, 121 MHz, 23 °C): δ −8.2. C, H Anal. (Calcd): C, 77.30 (77.88); H, 8.14 (8.50). MS: M + 1 at m/e = 463.51.

Synthesis of Cy$_2$PCH$_2$CH(CH$_3$)SCH(suberane) (13). A 250-mL round-bottomed flask was charged with 1.183 g (4.25 mmol) of Cy$_2$PCH$_2$CH(CH$_3$)SLi **5** dissolved in ca. 30 mL of THF. To this was added 5-chlorodibenzosuberane (970 mg, 4.24 mmol) dissolved in ca. 30 mL of THF dropwise. After the solution was stirred at ambient temperature for 1 h, the solvent was removed in vacuo. The product was extracted with hexane and small amounts of diethyl ether. The combined extracts were filtered, and solvent was removed in vacuo from the filtrate. Yield: 1.431 g (73%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 7.5−6.5 (m, 8H, aromatic signals), 5.35 (s, 1 H), 4.12 (m, 1 H), 3.65 (m, 1 H), 2.76 (m, 4 H), 1.62 (d, J = 6.5 Hz), 2.0−1.0 (m, 24 H). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23 °C): δ 141.5 (s), 140.9 (s), 138.7 (s), 138.2 (s), 131.5 (s), 131.2 (s), 130.7 (s), 130.6 (s), 126.2 (s), 125.9 (s), 56.4 (s), 40.7 (d, J_{P-C} = 23 Hz, CH(CH$_3$)), 34.2 (d, J_{P-C} = 15 Hz, CH of Cy), 34.0−25.0 (overlapping multiplets corresponding to CH$_2$'s and a CH of Cy), 23.0 (d, J_{P-C} = 10 Hz, *C*H$_3$). ^{31}P{H} NMR (C$_6$D$_6$, 121 MHz, 23 °C): δ −8.6. MS: M + 1 at m/e = 465.52. C, H Anal. (Calcd): C, 77.72 (77.54); H, 8.86 (8.89).

Synthesis of Cy$_2$PCH$_2$CH(Cy)SCH$_3$ (14). A vial was charged with 217 mg (0.63 mmol) of **6** dissolved in ca. 10 mL of THF. Then methyl iodide (43 μL, 0.69 mmol) was added. After the solution was stirred at ambient temperature for 30 min, the solvent was removed in vacuo. The product was extracted with hexane and filtered, and the solvent was removed in vacuo from the filtrate. Yield: 110 mg (50%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 23 °C): δ 2.58 (m, 1 H), 2.02 (s, 3 H, SCH$_3$), 2.0−1.0 (brm, 35 H). ^{13}C{H} NMR (C$_6$D$_6$, 125 MHz, 23

°C): δ 55.1 (d, J_{P-C} = 22 Hz, *C*H(Cy)), 42.9 (d, J_{P-C} = 9 Hz, CH of Cy), 34.4 (d, J_{P-C} = 16 Hz, CH of Cy), 34.2 (d, J_{P-C} = 16 Hz, CH of Cy), 32.0−26.0 (overlapping multiplets corresponding to CH_2's), 16.2 (d, J_{P-C} = 3 Hz, S*C*H_3). $^{31}P\{H\}$ NMR (C_6D_6, 121 MHz, 23 °C): δ −8.8. We were not able to obtain a satisfactory elemental analysis for this compound. When we submitted this compound for high-resolution mass spectroscopy we observed a molecular ion at 354.2510 ($M^+ - CH_3$).

Synthesis of $Cy_2PCH_2CH(Cy)SCH_2(C_6(CH_3)_5)$ (15). A vial was charged with 252 mg (0.73 mmol) of **6** dissolved in ca. 3 mL of THF. Pentamethylbenzyl chloride (136 mg, 0.69 mmol) dissolved in ca. 7 mL of THF was then added dropwise. After the solution was stirred at ambient temperature for 1 h, the solvent was removed in vacuo. The product was extracted with hexane and filtered, and the solvent was removed in vacuo from the filtrate. Yield: 306 mg (88%). ^1H NMR (C_6D_6, 300 MHz, 23 °C): δ 4.08 (AB quartet, 2 H, C*H*$_2$-($C_6(CH_3)_5$), 2.78 (m, 1 H, C*H*), 2.52 (s, 3 H, CH_3), 2.07 (s, 6 H, 2 CH_3's), 2.2−1.0 (brm, 35 H). $^{13}C\{H\}$ NMR (C_6D_6, 125 MHz, 23 °C): δ 133.6 (s), 132.8 (s), 132.5 (s), 132.0 (s), 54.9 (d, J_{P-C} = 22 Hz, *C*H(Cy)), 44.0 (d, J_{P-C} = 8 Hz, CH of Cy), 35.6 (d, J_{P-C} = 4 Hz, S*C*H_2), 34.4 (dd, J_{P-C} = 15 Hz CH of Cy), 34.3 (d, J_{P-C} = 15 Hz, CH of Cy), 32.0−26.0 (overlapping multiplets corresponding to CH_2's), 16.93 (s, *C*H_3), 16.88 (s, 2 *C*H_3), 16.80 (s, 2 *C*H_3). $^{31}P\{H\}$ NMR (C_6D_6, 121 MHz, 23 °C): δ −7.4. C, H Anal. (Calcd): C, 76.35 (76.75); H, 10.70 (10.67).

Synthesis of $Ph_2PCH_2CH(CH_3)SCH_3$ (16). A vial was charged with 450 mg (1.69 mmol) of **7** dissolved in ca. 10 mL of THF. Methyl iodide (127 μL, 2.04 mmol) was then added dropwise. After the solution was stirred at ambient temperature for 15 min, the solvent was removed in vacuo. The product was extracted with hexane (20 mL) followed by toluene (25 mL) and filtered, and the solvent was removed in vacuo from the filtrate. Yield: 279 mg (60%). ^1H NMR (C_6D_6, 300 MHz, 23 °C): δ 7.3−7.5 (m, 4 H, Ph), 7.15 (m, 6 H, Ph), 2.62 (m, 1 H, C*H*), 2.51 (ddd, J = 14 Hz, J = 5 Hz, J = 1.5 Hz, 1 H), 2.11 (ddd, J = 14 Hz, J = 10 Hz, J = 2.5 Hz), 1.69 (s, 3 H, SCH_3), 1.35 (d, J = 7 Hz, 3 H, CH_3). $^{13}C\{H\}$ NMR (THF-d_8, 125 MHz, 23 °C): δ 139.8 (d, J_{P-C} = 15 Hz, quaternary C Ph), 139.1 (d, J_{P-C} = 15 Hz, quaternary C Ph), 133.4 (d, J_{P-C} = 20 Hz, *C*H Ph), 133.0 (d, J_{P-C} = 19 Hz, *C*H Ph), 129.0−128.0 (overlapping multiplets accounting for C−H of Ph), 39.1 (d, J_{C-P} = 17 Hz, *C*H), 37.3 (d, J_{P-C} = 16 Hz, *C*H_2), 21.9 (d, J_{P-C} = 9 Hz, *C*H_3), 13.2 (s, CH_3). $^{31}P\{H\}$ NMR (C_6D_6, 121 MHz, 23 °C): δ −20.9. C, H Anal. (Calcd): C, 70.05 (70.04); H, 6.74 (6.98).

Synthesis of $Ph_2PCH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$ (17). A vial was charged with 330 mg (1.24 mmol) of **7** dissolved in ca. 5 mL of THF. Pentamethylbenzyl chloride (240 mg, 1.22 mmol) dissolved in ca. 5 mL of THF was then added dropwise. After being stirred at ambient temperature for 1.5 h, the solvent was removed. The product was extracted with hexane/toluene (5 mL/10 mL) and filtered and the solvent removed in vacuo from the filtrate. The oily residue was triturated with small amounts of hexane until a solid was obtained; the white solid was collected by filtration and dried. Yield: 157 mg (31%). ^1H NMR (C_6D_6, 300 MHz, 23 °C): δ 7.44 (m, 4 H, arene), 7.06 (m, 6 H, arene), 3.73 (AB quartet, 2 H, C*H*$_2$($C_6(CH_3)_5$), 2.86 (m, 1 H, C*H*), 2.61 (dd, J = 14 Hz, J = 5 Hz, 1 H, C*H*HPPh$_2$), 2.34 (s, 6 H, 2CH_3's), 2.23 (ddd, J = 14 Hz, J = 9 Hz, J = 2 Hz, 1 H, CH*H*PPh$_2$), 2.05 (s, 3 H, CH_3), 2.04 (s, 6 H, 2 CH_3's), 1.48 (d, J = 7 Hz, 3 H, CH_3). $^{13}C\{H\}$ NMR (THF-d_8, 125 MHz, 23 °C): δ 139.7 (d, J_{P-C} = 15 Hz, quaternary C Ph), 139.4 (d, J_{P-C} = 15 Hz, quaternary C Ph), 133.7 (s), 133.24 (d, J_{P-C} = 19 Hz, *C*H Ph), 133.16 (d, J_{P-C} = 19 Hz, *C*H Ph), 132.7 (s), 132.5 (s), 131.2 (s), 129.0−128.0 (overlapping multiplets accounting for C−H of Ph), 39.3 (d, J_{C-P} = 17 Hz, *C*H), 37.9 (d, J_{P-C} = 16 Hz, *C*H_2PPh$_2$), 31.9 (d, J = 1.5 Hz, S*C*H_2), 22.9 (d, J_{P-C} = 8 Hz, CH*C*H_3), 16.9 (s, CH_3), 16.8 (s, CH_3), 16.5 (s, CH_3). $^{31}P\{H\}$ NMR (C_6D_6, 121 MHz, 23 °C): δ −19.8. C, H Anal. (Calcd): C, 76.38 (77.10); H, 7.50 (7.91).

Synthesis of $(Cy_2PCH_2CH(CH_3)SCH_2(C_5(CH_3)_5)NiCl_2$ (18a). A vial was charged with 50 mg (0.23 mmol) of (DME)-$NiCl_2$. Then 99 mg (0.23 mmol) of **11** dissolved in ca. 3 mL of CH_2Cl_2 was added. A red-purple solution resulted. After the solution was stirred at ambient temperature for 30 min, the solvent was removed. The resulting sticky oil was triturated with hexane until a purple solid was obtained. The solid was collected by filtration, washed with hexane, and dried in vacuo. Yield: 103 mg (69%). ^1H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.14 (brm, 1 H, CH*H*($C_5(CH_3)_5$)), 4.86 (brm, 1 H, C*H*H ($C_5(CH_3)_5$)), 3.0−2.5 (m, 2 H), 2.34 (s, 6 H, 2CH_3's), 2.21 (s, 3 H, CH_3), 2.20 (s, 6 H, 2 CH_3's), 2.0−1.0 (brm, 23 H), 0.61 (brd, J = 6 Hz, 3 H, CH(C*H*$_3$)). ^{13}C NMR (CD_2Cl_2, 23 °C, 75 MHz): δ 136.2 (s), 133.9 (s), 133.5 (s), 127.7 (s), 47.4 (d, J_{C-H} = 146 Hz, *C*H(CH_3)), 40.8 (t, J_{C-H} = 145 Hz, *C*H_2($C_5(CH_3)_5$)), 38.0−26.0 (overlapping broad and sharp multiplets), 21.8 (brq, J_{C-H} = 125 Hz, *C*H_3), 18.0 (q, J_{C-H} = 126 Hz, *C*H_3), 17.3 (q, J_{C-H} = 126 Hz, *C*H_3), 17.0 (q, J_{C-H} = 126 Hz, *C*H_3). $^{31}P\{H\}$ NMR (CD_2Cl_2, 23 °C, 121 MHz): 50−100 very broad signal. C, H Anal. (Calcd): C, 57.53 (57.67); H, 7.87 (8.07).

Synthesis of $(Cy_2PCH_2CH(CH_3)SCH_2(C_5(CH_3)_5)PdCl_2$ (18b). A vial was charged with 102 mg (0.36 mmol) of (COD)-$PdCl_2$, and this was suspended in 10 mL of diethyl ether. Then 162 mg (0.37 mmol) of **11** dissolved in ca. 5 mL of diethyl ether was added. As the reaction proceeded, a very lightly colored yellow solid precipitated. After the solution was stirred at ambient temperature overnight, the solid was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 152 mg (70%). A single crystal was obtained by recrystallization from CH_2Cl_2/hexane at −30 °C. ^1H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.32 (br AB quartet, 2 H, C*H*$_2$S, broadening was due to inversion at S; see text for details), 3.59 (m, 1 H, C*H*(CH_3)), 2.68 (s, 6 H, 2 CH_3's), 2.55 (s, 3 H, CH_3), 2.53 (s, 6 H, 2CH_3's), 2.9−1.4 (brm, 24 H), 1.15 (d, J = 7 Hz, 3H, CH(C*H*$_3$)). $^{13}C\{H\}$ NMR (CD_2Cl_2, 23 °C, 75 MHz): δ 136.3 (s), 133.9 (s), 133.4 (s), 127.4 (s), 48.7 (s, *C*H(CH_3)), 42.6 (s), 37.1 (d, J_{P-C} = 26 Hz), 35.1 (d, J_{P-C} = 29 Hz), 34.1 (d, J_{P-C} = 26 Hz), 30.0−25.0 (overlapping multiplets), 21.4 (d, J_{P-C} = 16 Hz), 18.0 (s, CH_3), 17.3 (s, CH_3), 17.0 (s, CH_3). $^{31}P\{H\}$ NMR (CD_2Cl_2, 23 °C, 121 MHz): 74.2. C, H Anal. (Calcd): C, 53.11 (53.16); H, 6.94 (7.44).

X-ray Structural Analysis of 18b. A single colorless crystal of ($Cy_2PCH_2CH(CH_3)SCH_2(C_5(CH_3)_5)PdCl_2$ (wedge, 0.25 × 0.10 × 0.28 mm^3) was grown by slow evaporation of a CD_2Cl_2 solution at ambient temperature. The crystal was monoclinic ($P2_1/n$, No. 14) with the following cell dimensions determined from 25 reflections (μ(Mo) = 9.37 cm^{-1}): a = 8.547(1) Å, b = 24.226(4) Å, c = 14.700(3) Å; β = 103.97(1)°; V = 2953.8 Å^3; Z = 4; FW = 610.00 ($PdCl_2SPC_{27}H_{45}$); density (calcd) = 1.372 g/cm^3. Data were collected at −45 °C on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator using Mo Kα radiation (λ = 0.7107 Å). A total of 6179 data were collected (1.7° ≤ 2θ ≤ 52.0°; maximum h, k, l = 10, 29, 18; data octants +++, −++; ω scan method; typical half-height peak width = 0.16°ω; scan speed = 1.70−5.00 deg/min). Two standards were collected 28 times (1% fluctuation). There were 2770 unique reflections with $I \geq 3.0\sigma(I)$. The structure was solved by direct methods (SHELXS). The structure was refined by full-matrix least squares on F with scattering factors from the *International Tables for X-ray Crystallography* (Kinoch Press: Birmingham, England, 1974; Vol. 4) including anomalous terms for Pd, Cl, S, and P (biweight·[$\sigma^2(I) + 0.0009I^2]^{-1/2}$) (excluded 5). All non-hydrogen atoms were refined anisotropically; H atoms were refined isotropically. There were 289 parameters, and the data-to-parameter ratio was 9.57; final R = 0.044 (R_w = 0.037). The error of fit was 1.07 with a maximum Δ/σ of 0.00. Because the refinement for a few of the methyl hydrogens gave thermal parameters larger than desired (12.2), all of the hydrogens were idealized close to their previously refined positions. The largest residual density = 0.80 e/Å^3.

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$)$PtCl_2$ (18c). A vial was charged with 43 mg (0.12 mmol) of (NBD)-$PtCl_2$. Then 51 mg (0.12 mmol) of **11** dissolved in ca. 5 mL of CH_2Cl_2 was added. After the solution was stirred overnight at ambient temperature, the solvent was removed. The product was washed with hexane. The crystalline complex has 0.5 equiv of CH_2Cl_2 of solvation. The elemental analysis reflects a somewhat lower content of dichloromethane possibly owing to loss of solvent during transport of the sample. Yield: 57 mg (ca. 64%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 4.96 (AB quartet, 2 H, CH_2S), 3.14 (m, 1 H, CH(CH_3)), 2.36 (s, 6 H, 2 CH_3's), 2.23 (s, 3 H, CH_3), 2.22 (s, 6H, 2 CH_3's), 2.1−1.1 (brm, 24 H), 0.89 (brd, J = 6 Hz, 3 H, CH(CH_3)). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 75 MHz): δ 137.2 (s), 134.0 (brs), 133.4 (brs), 127.4 (s), 49.6 (s, CH(CH_3)), 42.8 (s, CH_2 arene), 35.4 (d, J_{P-C} = 34 Hz, CH of Cy), 32.9 (d, J_{P-C} = 34 Hz, PCH_2), 32.7 (d, J_{P-C} = 36 Hz, CH of Cy), 30.0−26.0 (overlapping multiplets), 20.2 (d, J_{P-C} = 13 Hz), 18.0 (s, CH_3), 17.3 (s, CH_3), 17.0 (s, CH_3). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): 47.3 (t, J_{Pt-P} = 3408 Hz). C, H Anal. (Calcd): C, 45.36 (44.57); H, 6.06 (6.26).

X-ray Structural Analysis of 19. A single gold crystal of $[Cy_2PCH_2CH(CH_3)SPdCl]_2$ (irregular block, 0.18 × 0.14 × 0.25 mm^3) was grown by slow evaporation of a hexane/dichloromethane solution at ambient temperature. The crystal was monoclinic ($C2/c$, No. 15) with the following cell dimensions (μ(Mo)= 13.89 cm^{-1}): a = 29.125(1) Å, b = 13.340(1) Å, c = 19.740(1) Å; β = 113.71(1)°; V = 7022.1 Å^3; Z = 8; FW = 826.56 ($Pd_2Cl_2S_2P_2C_{30}H_{56}$); density (calcd) = 1.564 g/cm^3. One hemisphere of data were collected at −112 °C on a Rigaku RU300, R-AXIS image plate area detector using Mo Kα radiation (λ = 0.7107 Å). A total of 18 069 data were collected (3.1° ≤ 2θ ≤ 48.2°; maximum h, k, l = 33, 15, 22). There were 4755 unique reflections with $I \geq 3.0\sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least squares on F with scattering factors from the *International Tables for X-ray Crystallography* (Kinoch Press: Birmingham, England, 1974; Vol. 4) including anomalous terms for Pd, Cl, S, and P (biweight·[$\sigma^2(I) + 0.0009I^2$]$^{-1/2}$) (excluded 9). All non-hydrogen atoms were refined anisotropically; H atoms were refined isotropically. There were 343 parameters, and the data-to-parameter ratio was 13.84; final R = 0.038 (R_w = 0.042). The error of fit was 2.16 with a maximum Δ/σ of 0.01. Because the refinement for a few of the cyclohexyl hydrogens gave thermal parameters larger than desired, all of the hydrogens were idealized close to their previously refined positions. The largest residual density = 0.57 e/Å^3.

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_3$)$Rh(COD)^+OTf^-$ (20). A vial was charged with 252 mg (0.54 mmol) of $Rh(COD)_2^+OTf^-$, and this was suspended in ca. 5 mL of THF. Then 154 mg (0.54 mmol) of **9** dissolved in ca. 5 mL of THF was added dropwise. After the solution was stirred at ambient temperature for 30 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. The yield of the orange solid was 323 mg (93%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.5−4.5 (brs, 4 H, COD), 3.11 (m, 1 H, CH(CH_3)), 2.40 (s, 3 H, SCH_3), 1.60 (d, J = 6 Hz, 3 H, CH_3), 2.5−1.0 (brm, 24 H). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 103.4 (s, COD olefinic carbon), 98.8 (s, COD olefinic carbon), 86.0 (d, J = 11 Hz, COD olefinic carbon), 84.4 (d, J = 10 Hz, COD olefinic carbon), 49.3 (d, J = 6 Hz, CH(CH_3)), 36.9 (d, J = 21 Hz, CH of Cy), 34.7 (d, J = 23 Hz, CH of Cy), 34.0−25.0 (overlapping multiplets accounting for CH_2's), 19.6 (d, J = 15 Hz, CH(CH_3)), 17.3 (s, SCH_3). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): 51.4 (d, J_{Rh-P} = 139 Hz). C, H Anal. (Calcd): C, 44.84 (46.44); H, 6.54 (6.70).

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_2Ph$)$Rh(COD)^+OTf^-$ (21). A 100-mL round-bottomed flask was charged with 229 mg (0.49 mmol) of $Rh(COD)_2^+OTf^-$, and THF was added until a clear solution was obtained. Then 177 mg (0.49 mmol) of $Cy_2PCH_2CH(CH_3)SCH_2Ph$, **10**, dissolved in ca. 10 mL of THF was added. After the solution was stirred at ambient temperature for 30 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane (2 × 10 mL) and dried in vacuo. The yield of the orange solid was 186 mg (53%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 7.50 (m, 2 H, arene), 7.41 (m, 3 H, arene), 5.07 (brs, 2 H, COD), 4.93 (brs, 1 H, COD), 4.73 (brs, 1 H, COD), AB quartet centered at 4.08 ppm (2 H, CH_2Ph), 2.98 (m, 1 H, CH(CH_3), 2. 7−1.0 (brm, 24 H), 1.54 (d, J = 6 Hz, 3 H, CH_3). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 133.4 (s, quaternary C, arene), 129.7 (s, 2 CH, arene), 129.6 (s, 2 CH, arene), 129.3 (s, CH, arene), 102.0 (dd, J = 16, 7 Hz, COD olefinic carbon), 100.7 (dd, J = 8, 8 Hz, COD olefinic carbon), 85.9 (d, J = 11 Hz, COD olefinic carbon), 85.1 (d, J = 11 Hz, COD olefinic carbon), 46.6 (d, J = 6 Hz, CH(CH_3)), 39.0 (s, CH$_2$Ph), 37.1 (d, J = 21 Hz, CH of Cy), 34.6 (d, J = 23 Hz, CH of Cy), 34.0−25.0 (overlapping multiplets accounting for CH_2's), 20.4 (d, J = 14 Hz, CH(CH_3)). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): 53.3 (d, J_{Rh-P}= 139 Hz). C, H Anal. (Calcd): C, 51.48 (51.52); H, 6.47 (6.56).

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$)$Rh(COD)^+OTf^-$ (22). A vial was charged with 112 mg (0.24 mmol) of $Rh(COD)_2^+OTf^-$ dissolved in ca. 5 mL of THF. Then 104 mg (0.24 mmol) of **11** dissolved in ca. 5 mL of THF was added dropwise. As the addition occurred, the solution turned from red to orange. After the solution was stirred at ambient temperature for 30 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. Yield: 182 mg (96%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.0−4.5 (brm, 3 H, COD), 4.22 (brs, 1 H, COD), 4.15 (d of AB quartet, 1 H, CHH), 4.08 (d of AB quartet, 1 H, CHH), 3.15 (m, 1 H, CH(CH_3)), 2.44 (s, 6 H, $C_5(CH_3)_5$), 2.24 (s, 9 H, $C_5(CH_3)_5$), 1.54 (d, J = 7 Hz, 3 H, CH_3), 2.5−1.0 (brm, 24 H). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 136.8 (s, arene), 134.0 (s, arene), 133.5 (s, arene), 126.3 (s, arene), 103.3 (brs, COD olefinic carbon), 99.9 (brs, COD olefinic carbon), 86.4 (brs, COD olefinic carbon), 85.3 (brs, COD olefinic carbon), 47.7 (d, J = 7 Hz, CH(CH_3)), 36.9 (d, J = 21 Hz, CH of Cy), 36.5 (s, CH_2 arene), 34.7 (d, J = 23 Hz, CH of Cy), 34.0−25.0 (overlapping multiplets accounting for CH_2's), 20.1 (d, J = 13 Hz, CH(CH_3)), 17.9 (brs, CH_3), 17.4 (s, CH_3), 17.1 (s, CH_3). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): 51.8 (d, J_{Rh-P} = 139 Hz). C, H Anal. (Calcd): C, 54.46 (54.54); H, 7.26 (7.25).

X-ray Structural Analysis of 22. A single orange crystal of ($Cy_2PCH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$)$Rh(COD)^+OTf^-$ (irregular block, 0.44 × 0.29 × 0.39 mm^3) was grown from tetrahydrofuran/hexane at −30 °C. The crystal was monoclinic ($P2_1/n$, No. 14) with the following cell dimensions determined from 50 reflections (μ(Mo) = 6.98 cm^{-1}): a = 10.451(2) Å, b = 18.584(3) Å, c = 19.733(4) Å; β = 104.62(1)°; V = 3708.5 Å^3; Z = 4; FW = 783.94 ($RhS_3PF_3OC_{35}H_{60}$); density (calcd) = 1.404 g/cm^3. Data were collected at −100 °C on a Syntex R3 diffractometer with a graphite monochromator using Mo Kα radiation (λ = 0.7107 Å). A total of 6963 data were collected (4.0° ≤ 2θ ≤ 50.0°; maximum h, k, l = 12, 22, 23; data octants ++−, −+−; ω scan method; typical half-height peak width = 0.31°ω; scan speed = 3.90−14.60 deg/min). Two standards were collected 73 times, and adjustments were made for a 3% decrease in intensity. There were 4375 unique reflections with $I \geq 3.0\sigma(I)$. The structure was solved by direct methods (MULTAN) and was refined by full-matrix least squares on F with scattering factors from the *International Tables for X-ray Crystallography* (Kinoch Press: Birmingham, England, 1974; Vol. 4) including anomalous terms for Rh, S, and P (biweight·[$\sigma^2(I) + 0.0009I^2$]$^{-1/2}$) (excluded 4). All non-hydrogen atoms were refined anisotropically; H atoms were refined isotropically. There were 415 parameters, and the data-to-parameter ratio was 10.53; final R = 0.050 (R_w = 0.048). The error of fit was 1.63 with a maximum Δ/σ of 0.20. Because the refinement for a few of the methyl hydrogens gave thermal parameters larger than desired (14.8), all of the hydrogens have been idealized close to their previously refined positions. The largest residual density = 1.31 e/Å^3.

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_2$(anthracene))Rh(COD)$^+$OTf$^-$ (23). A vial was charged with 157 mg (0.34 mmol) of Rh(COD)$_2^+$OTf$^-$, and this was suspended in ca. 2 mL of THF. Then 155 mg (0.34 mmol) of **12** dissolved in ca. 8 mL of THF was added dropwise. During addition, the suspension turned into a clear orange solution. After the solution was stirred at ambient temperature for 30 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. The complex crystallized with two molecules of THF. Yield: 285 mg (88%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 8.58 (s, 1 H, arene), 8.28 (d, J = 9 Hz, 2 H, arene), 8.11 (d, J = 8 Hz, 2 H, arene), 7.69 (ddd, J = 7, 7, 1 Hz, 2 H, arene), 7.59 (dd, J = 8, 8 Hz, 2H, arene), 5.09 (AB quartet, 2 H, CH_2(anthracene)), 4.81 (brs, 1 H, COD), 4.77 (brs, 1 H, COD), 4.52 (brs, 1 H, COD), 3.68 (m, THF), 3.30 (m, 1 H, C*H*Cy), 1.49 (d, J = 6 Hz, CHCH_3), 2.5−1.0 (brm, 32 H). ^{13}C{H} NMR (C_6D_6, 125 MHz, 23 °C): δ 131.8 (s), 130.9 (s), 130.2 (s), 130.1 (s), 127.8 (s), 126.0 (s), 123.7 (s), 123.3 (s), 103.2 (dd, J = 8, 8 Hz, COD olefinic carbon), 99.0 (brs, COD olefinic carbon), 87.2 (d, J = 11 Hz, COD olefinic carbon), 85.4 (d, J = 10 Hz, COD olefinic carbon), 48.2 (d, J_{P-C} = 7 Hz, *C*H(CH$_3$)), 37.0 (d, J_{P-C} = 21 Hz, CH of Cy), 34.7 (d, J_{P-C} = 23 Hz, CH of Cy), 33.0−25 (overlapping multiplets corresponding to CH$_2$'s of Cy), 20.4 (d, J_{P-C} = 13 Hz, *C*H$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): δ 53.2 (d, J_{P-Rh} = 139 Hz). C, H Anal. (Calcd): C, 58.30 (58.38); H, 6.98 (6.45).

Synthesis of ($Cy_2PCH_2CH(CH_3)SCH_2$(suberane))Rh(COD)$^+$OTf$^-$ (24). A vial was charged with 87 mg (0.19 mmol) of Rh(COD)$_2^+$OTf$^-$ and 87 mg (0.19 mmol) of **13**. THF (ca. 10 mL) was then added. After the orange solution was stirred at ambient temperature for 15 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. Yield: 117 mg (76%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 7.5−7.0 (m, 8 H, aromatic), 5.32 (s, 1 H), 5.22 (brs, 1 H, COD), 5.11 (brs, 1 H, COD), 4.63 (brs, 1 H, COD), 3.84 (m, 2 H), 3.45 (brs, 1 H, COD), 3.00 (m, 3 H), 1.12 (d, J = 7 Hz, 3 H), 2.5−1.0 (brm, 32 H). ^{13}C{H} NMR (C_6D_6, 125 MHz, 23 °C): δ 141.4 (s, quaternary C), 141.3 (s, quaternary C), 134.4 (s, quaternary C), 134.3 (s, quaternary C), 132.3 (s), 132.0 (s), 131.5 (s), 131.0 (s), 130.5 (s), 130.3 (s), 127.24 (s), 127.17 (s), 104.0 (dd, J = 7, 7 Hz, COD olefinic carbon), 100.4 (dd, J = 10, 6 Hz, COD olefinic carbon), 86.3 (d, J = 11 Hz, COD olefinic carbon), 86.2 (d, J = 11 Hz, COD olefinic carbon), 64.2 (s, CH), 47.1 (d, J_{P-C} = 7 Hz, *C*H(CH$_3$)), 37.6 (d, J_{P-C} = 21 Hz, CH of Cy), 35.0 (d, J_{P-C} = 21 Hz, CH of Cy), 34.0−25.0 (overlapping multiplets corresponding to CH$_2$'s of Cy and suberane), 22.4 (d, J_{P-C} = 7 Hz, *C*H$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): δ 60.0 (d, J_{P-Rh} = 140 Hz). C, H Anal. (Calcd): C, 55.92 (56.79); H, 6.10 (6.48).

Synthesis of ($Cy_2PCH_2CH(Cy)SCH_3$)Rh(COD)$^+$OTf$^-$ (25). A vial was charged with 213 mg (0.45 mmol) of Rh(COD)$_2^+$OTf$^-$, and this was suspended in ca. 5 mL of THF. Then 161 mg (0.45 mmol) of **14** dissolved in ca. 5 mL of THF was added dropwise. During addition, the solution turned from red to orange. After stirring at ambient temperature for 30 min the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. Yield: 297 mg (91%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.21 (brs, 2 H, COD), 4.87 (brs, 2 H, COD), 2.89 (m, 1 H, C*H*Cy), 2.43 (s, 3 H, SC*H*$_3$), 2.6−1.0 (brm, 35 H). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 104.0 (dd, J = 8, 8 Hz, COD olefinic carbon), 99.4 (dd, J = 7, 7 Hz, COD olefinic carbon), 86.0 (d, J = 11 Hz, COD olefinic carbon), 84.5 (d, J = 10 Hz, COD olefinic carbon), 59.2 (s, *C*HCy), 39.4 (d, J = 12 Hz, CH of Cy), 37.0 (d, J = 21 Hz, CH of Cy), 34.9 (d, J = 23 Hz, CH of Cy), 35.0−22.0 (overlapping multiplets accounting for CH$_2$'s), 17.7 (s, SCH$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 51.3 (d, J_{P-Rh} = 140 Hz). C, H Anal. (Calcd): C, 47.21 (50.41); H, 6.74 (7.19).

Synthesis of ($Cy_2PCH_2CH(Cy)SCH_2(C_6(CH_3)_5)$)Rh(COD)$^+OTf^-$ (26). A vial was charged with 170 mg (0.36 mmol) of Rh(COD)$_2^+$OTf$^-$, and this was suspended in ca. 5 mL of THF. Then 182 mg (0.36 mmol) of **15** dissolved in ca. 15 mL of THF was added dropwise. During addition the solution turned from red to orange. After the solution was stirred at ambient temperature for 45 min, the solvent was removed in vacuo. The resulting oily solid was washed with hexane and dried in vacuo. The solid contained traces of THF as isolated. Yield: 317 mg (ca. 100%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 5.0−4.5 (brm, 3 H, COD), 4.34 (d of AB quartet, 1 H, CH*H*), 4.23 (brs, 1 H, COD), 4.01 (d of AB quartet), 2.41 (s, 6 H, C$_5$(CH$_3$)$_5$), 2.25 (s, 3 H, C$_5$(CH$_3$)$_5$), 2.24 (s, 6 H, C$_5$(CH$_3$)$_5$), 3.0−0.5 (m, 36 H). ^{13}C{H} NMR (CD_2Cl_2, 23 °C, 125 MHz): δ 136.9 (s), 134.1 (s), 133.4 (s), 126.7 (s), 104.0 (dd, J = 7, 7 Hz, COD olefinic carbon), 100.6 (dd, J = 6, 6 Hz, COD olefinic carbon), 86.1 (d, J = 10 Hz, COD olefinic carbon), 84.4 (d, J = 10 Hz, COD olefinic carbon), 68.2 (s, S*C*H$_2$), 58.0 (s, *C*HCy), 40.6 (d, J = 11 Hz, CH of Cy), 37.0 (d, J = 20 Hz, CH of Cy), 35.0 (d, J = 22 Hz, CH of Cy), 35.0−20.0 (overlapping multiplets accounting for CH$_2$'s), 17.9 (brs, CH$_3$), 17.4 (s, CH$_3$), 17.1 (s, CH$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): δ 52.1 (d, J_{P-Rh} = 140 Hz). C, H Anal. (Calcd): C, 57.74 (57.20); H, 7.77 (7.61).

Synthesis of ($Ph_2PCH_2CH(CH_3)SCH_3$)Rh(COD)$^+$OTf$^-$ (27). A vial was charged with 152 mg (0.32 mmol) of Rh(COD)$_2^+$OTf$^-$, and this was suspended in ca. 5 mL of THF. Then 89 mg (0.32 mmol) of **16** dissolved in ca. 5 mL of THF was added dropwise. During addition, the slurry turned into a clear orange solution. After the solution was stirred at ambient temperature for 30 min, the solvent was removed. The resulting oily solid was washed with hexane (ca. 10 mL) and dried in vacuo. Yield: 204 mg (99%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 8.0−7.3 (m, 10 H, arene), 5.43 (brs, 2 H, COD), 4.39 (brs, 1 H, COD), 3.85 (brs, 1 H, COD), 2.51 (s, 3 H, SC*H*$_3$), 1.60 (d, J = 6 Hz, CH(C*H*$_3$), 2.8−1.9 (brm, 11 H). ^{13}C NMR (THF-d_8, 125 MHz, 23 °C): δ 135.0 (d, J = 13 Hz), 133.1 (s), 131.8 (d, J = 2.5 Hz), 131.5 (d, J = 10 Hz), 130.2 (d, J = 11 Hz), 129.8 (d, J = 11 Hz), 106.3 (dd, J = 7, 7 Hz, COD olefinic carbon), 102.7 (dd, J = 9, 9 Hz, COD olefinic carbon), 90.1 (d, J = 11 Hz, COD olefinic carbon), 84.4 (d, J = 10 Hz, COD olefinic carbon), 45.5 (d, J = 9 Hz, *C*H), 37.9 (d, J = 30 Hz, *C*H$_2$), 33.1 (d, J = 3 Hz, *C*H$_2$), 30.5 (s, CH$_2$ of COD), 30.2 (s, CH$_2$ of COD), 28.7 (s, CH$_2$ of COD), 19.6 (s, CH$_3$), 19.1 (d, J = 17 Hz, CH$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): δ 46.2 (d, J_{P-Rh} = 146 Hz). C, H Anal. (Calcd): C, 47.87 (47.32); H, 4.80 (4.92).

Synthesis of ($Ph_2PCH_2CH(CH_3)SCH_2(C_6(CH_3)_5)$Rh(COD)$^+OTf^-$ (28). A vial was charged with 86 mg (0.18 mmol) of Rh(COD)$_2^+$OTf$^-$, and this was suspended in ca. 5 mL of THF. Then 77 mg (0.18 mmol) of **17** dissolved in ca. 5 mL of THF was added dropwise. During addition, the red slurry turned into a clear orange-yellow solution. After the solution was stirred at ambient temperature for 30 min, the solvent was removed. The resulting oily solid was washed with hexane (ca. 10 mL) and dried in vacuo. Yield: 117 mg (82%). ^{1}H NMR (CD_2Cl_2, 23 °C, 300 MHz): δ 7.95 (m, 2 H, Ph), 7.8−7.4 (m, 6 H, arene), 7.35 (m, 2 H, Ph), 5.55 (brs, 1 H, COD), 4.93 (brs, 1 H, COD), 4.67 (brs, 1 H, COD), 4.40 (brs, 1 H, COD), 4.39 (d, J = 12 Hz, C*H*H(C$_6$(CH$_3$)$_5$), 4.03 (d, J = 12 Hz, C*H*H(C$_6$(CH$_3$)$_5$), 3.82 (brs, 1 H, CH(CH$_3$)), 2.23 (s, 3 H, CH$_3$), 2.22 (s, 6 H, 2CH$_3$'s), 2.8−1.9 (brm, 10 H), 1.43 (d, J = 6 Hz, 3 H, CH(C*H*$_3$)). ^{13}C{H} NMR (THF-d_8, 125 MHz, 23 °C): δ 136.9 (s), 134.9 (d, J = 12 Hz), 134.0 (s), 133.5 (s), 133.2 (s), 131.9 (s), 131.6 (d, J = 10 Hz), 130.3 (d, J = 10 Hz), 129.8 (d, J = 10 Hz), 129.0 (s), 126.4 (s), 105.7 (brm, COD olefinic carbon), 104.9 (brm, COD olefinic carbon), 89.9 (d, J = 11 Hz, COD olefinic carbon), 85.1 (d, J = 11 Hz, COD olefinic carbon), 44.4 (d, J_{C-P} = 9 Hz, *C*H), 39.7 (s, S*C*H$_2$ arene), 38.4 (d, J_{P-C} = 32 Hz, *C*H$_2$PPh$_2$), 33.1 (s, CH$_2$ of COD), 30.6 (s, CH$_2$ of COD), 30.2 (s, CH$_2$ of COD), 28.8 (s, CH$_2$ of COD), 20.4 (d, J_{P-C} = 15 Hz, CH*C*H$_3$), 17.5 (s, CH$_3$), 17.4 (s, CH$_3$), 17.0 (s, CH$_3$). ^{31}P{H} NMR (CD_2Cl_2, 23 °C, 121 MHz): δ 47.9 (d, J_{P-Rh} = 145 Hz).

Typical Procedure for the Hydrogenation Runs

Hydrogenation reactions were carried out using 2 mol % catalyst (MeOH solution) and a 0.39 M solution of substrate, RC(H)C(CO_2Me)(NHAc), in MeOH. The reaction vessel was placed at 80 psi H_2 and kept stirring at ambient temperature for 16 h. Conversion analysis was achieved by ^{1}H NMR spectroscopy, and analysis of the enantiomeric excess was done by GC (Chirasil-L-Val). Results can be found in Tables 8 and 9.

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Supporting Information Available: X-ray data for **18b**, **19** and **22**, including tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and intermolecular distances and ORTEP diagrams of **18b**, **19** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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