Synthesis of Optically Active Phosphiranes and Their Use as Ligands in Rhodium(I) Complexes

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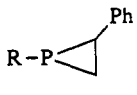
Optically active (phosphirane)$Mo(CO)_5$ complexes have been obtained by starting from chiral styrene oxide. The corresponding tervalent phosphiranes are easily recovered through a stereoselective decomplexation reaction and used as ligands for cationic rhodium complexes. Some preliminary results on the catalytic hydrogenation of olefins show that different diastereoisomers of a phosphirane give a completely different catalytic behavior to their rhodium complexes. Unusually for a monodentate phosphine, significant optical yields are obtained with one of the four diastereoisomers of the *P*-menthylphosphirane. The actual involvement of phosphirane itself in the catalytic cycle is not fully established.

Introduction

Phosphiranes are unusual phosphines, because of their very small intracyclic CPC angle (47–51°),[1] of their bent bonds connecting together the three atoms in the heterocycle, of their high inversion barrier at phosphorus,[2] and of the high s character of their phosphorus lone pair.[3] Cyclic strain makes phosphiranes liable to ring-opening reactions, thus reducing their stability. Nevertheless, phosphiranes bearing bulky substituents are perfectly stable,[4] as are the phosphirane–chromium, –molybdenum, and –tungsten pentacarbonyl complexes.[5]

The high energy required for pyramidal inversion makes phosphiranes potentially worthwhile chiral substrates: very likely no racemization at phosphorus will occur as long as the cyclic structure is untouched. Thus, one could conceive the use of phosphiranes, for example, as chiral ligands in catalytic asymmetric reactions, the critical point being the definition of the reaction conditions where the cyclic structure can be preserved. On the other hand, chiral phosphiranes could be useful starting materials for the synthesis of new chiral phosphines through stereoselective ring-opening or ring-enlargement reactions.[6]

Checking the use of phosphiranes as chiral building blocks and as chiral ligands is the ground of our present interest in this class of heterocycles. Here, we wish to report on the first synthesis of chiral phosphiranes **1**, of the corresponding cationic rhodium complexes **2** and some preliminary results on the catalytic hydrogenation of olefins by using such rhodium/phosphirane complexes.



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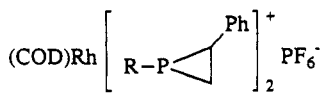

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(1) See for example: Appel, R.; Gaitzsch, T.; Knoch, F.; Lenz, G. *Chem. Ber.* **1986**, *119*, 1977. Hutchings, D. S.; Junk, P. C.; Patalinghug, W. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1989**, 973.

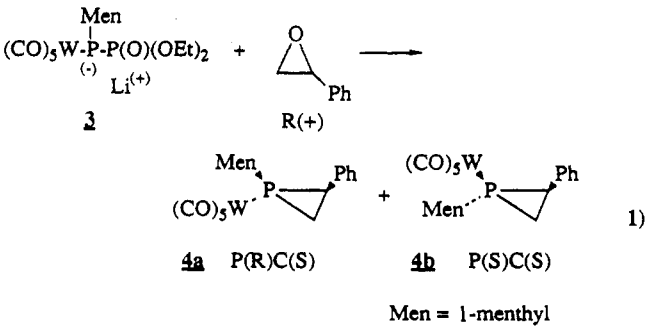
(2) Bachrach, S. H. *J. Phys. Chem.* **1989**, *93*, 7780. Rauk, A.; Andose, J. D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.

(3) Aue, D. H.; Webb, H. M.; Davidson, W. R.; Vidal, M.; Bowers, M. T.; Goldwhite, H.; Vertal, L. E.; Douglas, J. E.; Kollman, D. A.; Kenyon, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 5151.

(4) Oshikawa, T.; Yamashita, M. *Synthesis* **1985**, 290. Yoshifuji, M.; Toyota, K.; Inamoto, N. *Chem. Lett.* **1985**, 441.

Results and Discussion

We have shown recently[7] that the phosphorylphosphane anion **3** (Men = *l*-menthyl) reacts with the pure *R*-enantiomer of styrene oxide to give a mixture of the cis and trans phosphirane complexes **4a,b** with total inversion of the oxirane carbon configuration, as shown in eq 1. The



1)

Men = l-menthyl

two other diastereomeric phosphiranes [P(*R*)C(*R*), P(*S*)C(*R*)] are obtained by starting from the (*S*)-(−)-styrene oxide.

Complexes **4a** and **4b** are obtained separately after chromatography on a silica gel column. As a consequence of the observed inversion at the oxirane carbon, we envisaged the synthesis of a wide range of optically active (phosphirane)$W(CO)_5$ complexes by starting from chiral oxiranes and various phosphorylphosphane anions **3** (R = Ph, PhCH=CH, tBu, ...). The actual enantiomeric excess of the final products **4** could not be established when R ≠ *l*-menthyl (see below).

Tungsten pentacarbonyl complexes are not the best starting material, since we are concerned with free, tervalent phosphiranes: some decomplexation methods are known,[8] but their efficiency is highly dependent on the sensitivity of the phosphine to oxidizing reagents. On the other hand, phosphines are generally easily recovered from their $Mo(CO)_5$ complexes by a ligand displacement reaction (see below). Thus, we investigated at first the synthesis of (phosphirane)$Mo(CO)_5$ complexes by the

(5) See for example: Bausch, R.; Ebsworth, E. A. V.; Rankin, D. W. H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 125. Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(6) For a recent review on the phosphirane chemistry see: Mathey, F. *Chem. Rev.* **1990**, *90*, 997.

(7) Marinetti, A.; Ricard, L.; Mathey, F. *Synthesis* **1992**, 157.

(8) Mathey, F.; Marinetti, A.; Mercier, F. *Synlett* **1992**, 363.

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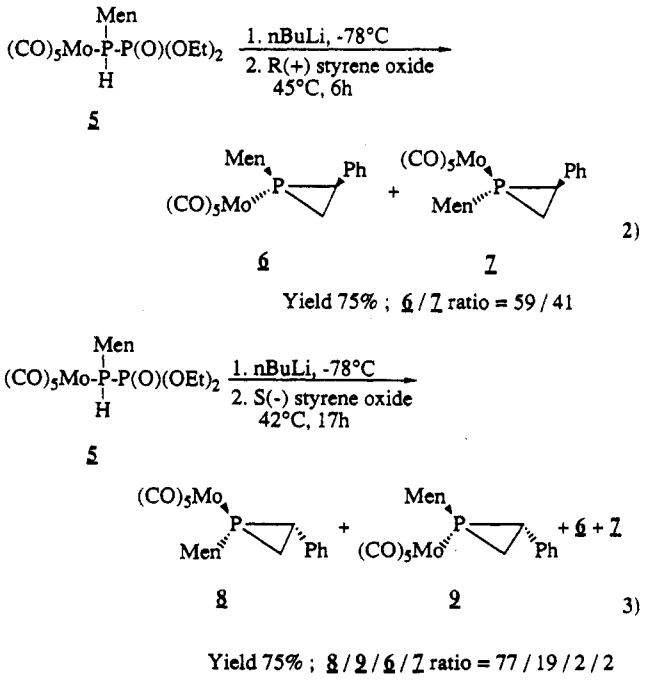
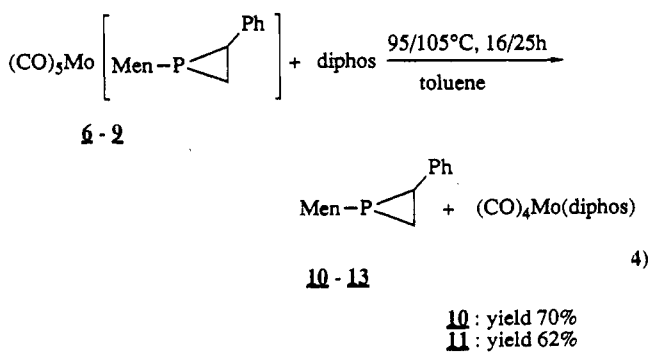
above depicted approach, with special attention to its stereochemical aspects, and then the decomplexation reaction. The phosphorylphosphane anion was formed by addition of butyllithium to complex **5**,[9] and it was reacted with both enantiomers of styrene oxide, as shown in eqs 2 and 3.



The stereochemistry of compounds **6–9** was established by comparison of their spectroscopic data with the known spectra of the analogous tungsten complexes. As expected, the reaction of **5** with (*R*)-(+)-styrene oxide is totally stereospecific with respect to the carbon configuration, while the reaction with the (*S*)-(−)-oxirane is slower and somewhat less selective. Nevertheless the isomeric phosphiranes **8** and **9** have been obtained in the pure form after chromatography and crystallization.

Decomplexation of the four diastereomers of 1-menthyl-2-phenylphosphirane has been performed by heating the molybdenum complexes with 1 equiv of bis(diphenylphosphino)ethane (diphos) at 95 °C for several hours[10] (eq 4).



Phosphiranes seem to be very efficient ligands toward molybdenum; the decomplexation reaction is much slower than for other cyclic phosphines which need, in most cases, 2 or 3 h of heating.[10] We have to point out here the remarkable thermal as well as configurational stability of these phosphiranes: the reaction is quantitative according to the ^{31}P NMR monitoring of the reaction mixture. In spite of the prolonged heating, no phosphorus racemization was observed in the case of the trans isomer **7** and **9**. A small amount of trans phosphirane (2–3%) is formed during the decomplexation of the cis isomers **6** and **8**.

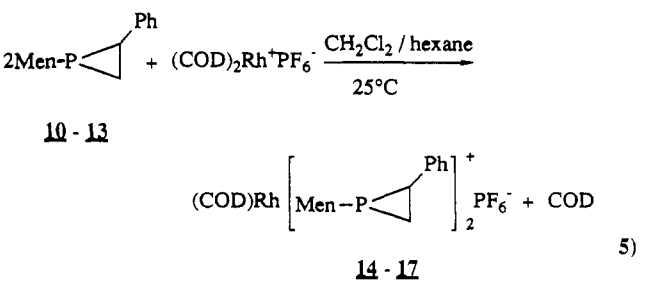
Table I. ^{31}P NMR Data for 1-Menthyl-2-phenylphosphiranes (δ Toluene)

Mo complex	^{31}P NMR (δ)	phosphirane	^{31}P NMR (δ)
6	−120.0	**10**, P(*S*)C(*S*)	−170.2
7	−122.7	**11**, P(*R*)C(*S*)	−182.9
8	−132.7	**12**, P(*R*)C(*R*)	−185.0
9	−125.3	**13**, P(*S*)C(*R*)	−181.8

Table I gives the ^{31}P NMR chemical shifts for the four molybdenum complexes and the corresponding free phosphiranes. All these phosphiranes are very stable in solution at room temperature, but not so stable in the pure state: some less soluble, ring-opening and polymerization products are formed upon storage even at −10 °C. Compounds **10** and **11** have been purified by column chromatography and fully characterized. Solutions of pure **12** and **13** have been obtained, after crystallization of the (diphos)Mo(CO)$_4$ complex from pentane, and used for further reactions.

With a series of new chiral phosphines in hand, we decided to study their behavior as ligands in potential catalytic systems. The coordination chemistry of phosphiranes is very poorly developed; thus, to start with, we turned our attention to the rhodium(I) complexes which are potential hydrogenation catalysts.

Cationic rhodium complexes bearing phosphiranes **10–13** have been prepared by standard methods,[11] as shown in eq 5. The reaction is instantaneous and quantitative,



and the cyclic structure of the phosphine is preserved. The final product is obtained as a pure orange solid (compounds **14** and **15**) or as an oil (**16**, **17**) after addition of ether to the CH_2Cl_2 solution (recrystallization may be required). The structure of **15** was determined by X-ray crystallography and is shown in Figure 1.

The X-ray data show a significant distortion from the expected square planar geometry of the ligand coordination around the rhodium atom. The dihedral angle between the plane defined by the COD olefin midpoints and Rh and the P(1)RhP(2) plane is 17.17(0.16)°. Similar distortions, due to steric interactions, are usually interpreted as a sign for a highly asymmetric environment that should strongly influence the stereoselectivity in catalytic re-

(9) Complex **5** was prepared in 70% yield, by a published procedure (Bauer, S.; Marinetti, A.; Mathey, F. *Heteroatom. Chem.* **1991**, *2*, 277), starting from the (Men*PH$_2$)Mo(CO)$_5$ complex, as described in the Experimental Section.

(10) (a) Maigrot, N.; Ricard, L.; Charrier, C.; Le Goff, P.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 76. (b) De Vaumas, R.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1992**, *114*, 261.

(11) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

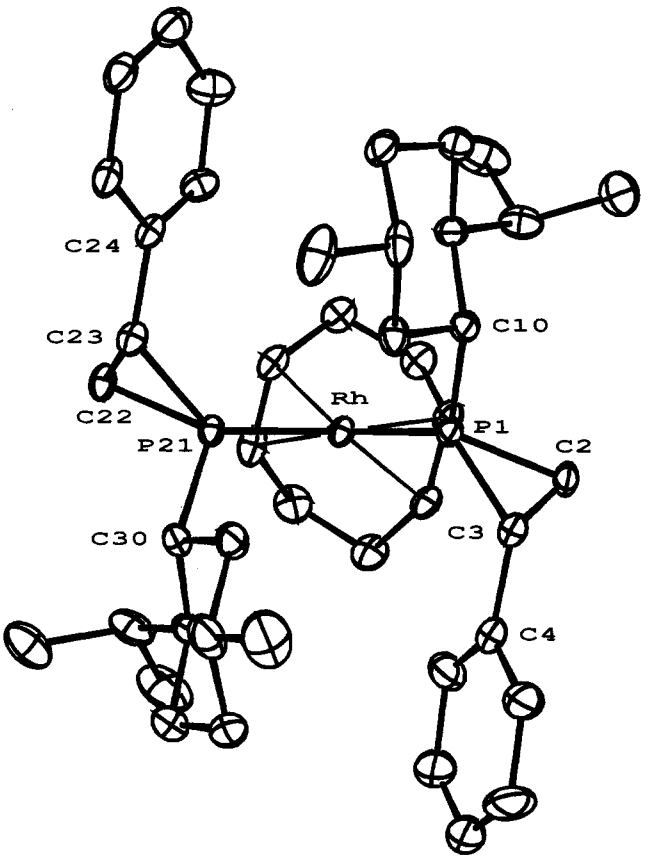


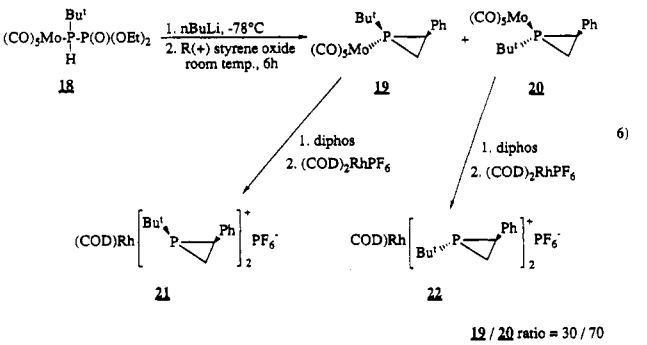
Figure 1. ORTEP drawing of the rhodium complex **15**, $(COD)Rh[11]_2{}^+PF_6{}^-$.

Table II. Selected Bond Distances (Å) and Angles (deg) for Compound 15 and for the Corresponding Phosphirane–Tungsten Complex, (1-Menthyl-2-phenylphosphirane-*P*(*R*),*C*(*S*))W(CO)$_5$ (See Reference 7)

	Rh–phosphirane complex **15**	$(CO)_5W$(phosphirane)
P(1)–M	2.313(1)	2.506(2)
P(1)–C(2)	1.818(4)	1.83(1)
P(1)–C(3)	1.851(5)	1.82(1)
P(1)–C(10)	1.856(5)	1.85(1)
C(2)–C(3)	1.534(7)	1.51(1)
M–P(1)–C(2)	124.3(2)	124.4(4)
M–P(1)–C(3)	133.2(2)	125.2(3)
P(1)–C(3)–C(4)	127.1(4)	123.0(8)
C(2)–P(1)–C(3)	49.4(2)	49.1(4)

actions.[12] The high steric congestion of this complex is also suggested by the significantly distorted geometry of the phosphirane ring with respect to the known geometry of the corresponding (phosphirane)$W(CO)_5$[7] complex. As shown in Table II, the P–C(3) bond is significantly lengthened and the PC(3)C(4) and RhPC(3) angles are increased, as if taking away the phenyl ring from the center of the molecule.

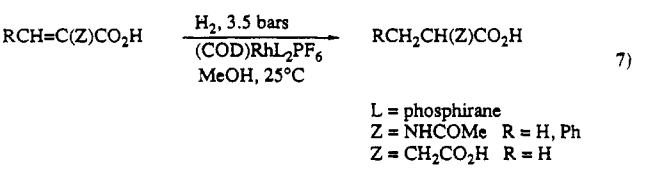
The above depicted approach to chiral phosphirane–rhodium complexes (reactions 2–5) can be extended to some other substrates, especially to phosphiranes with nonchiral substituents on phosphorus. Moreover, the quantitative reaction with the $(COD)_2RhPF_6$ complex (eq 5) suggests an easy way to estimate the enantiopurity of optically active phosphiranes: in fact, this reaction converts any mixture of enantiomeric phosphiranes into a mixture of meso and *dl* diastereomeric rhodium complexes. The relative amount of the two enantiomers can be inferred from ^1H NMR analysis of the final product.[13] An example is given in eq 6.



In both cases more than 95% of a single diastereomer of the rhodium complex is formed. The meso and *dl* diastereomers are perfectly differentiated from each other by ^1H NMR, as checked by starting from a racemic mixture of **20**. With the racemic sample of **20**, we obtained a mixture of the meso and *dl* rhodium complexes in a relative ratio of about 2:1, although the accuracy of the measurement is somewhat limited by the poor resolution. Thus, the meso analogue of **22** seems to be more stable than the *d* or *l* form. Even when statistical behavior is assumed during the formation of **22**, a diastereomeric excess of at least 90% means an ee of at least 95% in the synthesis of the phosphiranes **19** and **20**: as expected, the reaction between the phosphorylphosphane anion **18** and styrene oxide is essentially stereospecific with respect to the carbon configuration and represents a general access to chiral phosphiranes.

More details on the reactions described in eq 6, as well as on the synthesis of the starting material **18**, are given in the Experimental Section.

In order to put in evidence a possible catalytic activity and enantioselectivity of the rhodium complexes **14–17**, **21**, and **22**, we have examined the hydrogenation of some usual unsaturated substrates in standard conditions, as shown in eq 7. The reaction was performed on a 2-mmol



scale with a 1% amount of the rhodium–phosphirane catalyst.

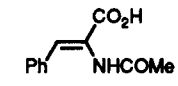
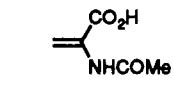
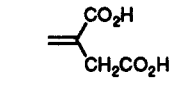
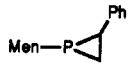
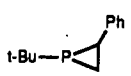
An effective catalytic activity is observed: the starting material is totally hydrogenated after a few hours at room temperature. Nevertheless, a major question needs an answer: does phosphirane itself take part in the catalytic cycle, given that only mixtures of ring-opened oxidized phosphorus derivatives are recovered at the end of the reaction?

Concerning the enantioselectivity, some preliminary results are given in Table III. The optical yields were determined through $[\alpha]_D$ measurements and have to be considered as rather qualitative results. Repeated ex-

(12) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653.

(13) Vigneron, J. P.; Dhaenens, M.; Horeau, A. *Tetrahedron* **1973**, *29*, 1055.

Table III. Enantiomeric Excesses for the Hydrogenation Reactions Catalyzed by the Phosphirane–Rh Complexes [ee, % (Optical Rotation)]

L		catalyst			
	cis	**14**	9 (+)	1 (+)	
	trans	**15**	76 (–)	40 (+)	26 (–)
	cis	**16**	3 (–)		
	trans	**17**	6 (+)	5 (+)	
	cis	**21**	26 (–)	11 (+)	
	trans	**22**	49 (–)	25 (+)	23 (–)

periments in optimized conditions would be required for a more precise data collection.

Optical yields are moderate, but some of them are significant, when one considers that the ligands are monophosphines. More significantly, we observed a close relationship between the phosphirane structure and the observed asymmetric induction: the four diastereomers of the *P*-menthylphosphirane give totally different results, as well as the two isomers of the *tert*-butylphosphirane. The most active ligands are the trans phosphiranes **15** and **22**, as we could expect in light of the relative cis-position of the phenyl group and the rhodium atom (major steric interactions) in their complexes. These remarks seem to indicate the participation of phosphirane itself to the catalytic activity, but do not dismiss definitively the hypothesis of a stereospecific ring-opening reaction during hydrogenation. More detailed study is needed to clarify the role of phosphiranes in this reaction.

As a concluding remark, the search for catalytic activity induced by phosphirane–transition metal complexes seems to be a promising field. The rigid and controlled geometry of the phosphorus environment in phosphiranes could be a valuable tool to better understand the steric tridimensional requirements for high asymmetric induction in the case of monophosphine-based catalysts.

Experimental Section

All reactions were carried out under argon atmosphere in dry solvents, and silica gel (60–200 μm and 15–40 μm) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Mass spectra were obtained at 70 eV with a Shimadzu GC–MS QP 1000 instrument by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS" Gif sur Yvette, France. Hydrogenations were carried out in a constant-volume autoclave (100 mL). Hydrogen and all commercially available reagents were used as received from the suppliers. $(COD)_2RhPF_6$ was prepared according to reported procedures.[14]

[*l*-Menthyl(diethoxyphosphoryl)phosphine]-pentacarbonylmolybdenum (5). (a) *l*-Menthyldichlorophosphine (4.1 g, 1.7 mmol) was reacted in CH_2Cl_2 at room temperature with 8.5 g (1.87 mmol) of the *N*-methylpyridinium salt of $[Mo(CO)_5I]^-$.[15] After 1 h, hexane was added and the reaction mixture was filtered on a short Celite column with hexane as eluent. The crude $(CO)_5Mo(l\text{-menthyl-}PCl_2)$ complex thus obtained was reduced to the corresponding $(l\text{-menthyl-}PH_2)Mo(CO)_5$ complex, as described in ref 10b. The previously reported complexation of $MenPCl_2$ by means of the $(CO)_5Mo(CH_3CN)$ complex gives more often varying amounts (about 10%) of the disubstituted complex $(CO)_4Mo(MenPCl_2)_2$ as side product.

(b) nBuLi (8.7 mL, 1.6 M solution in hexane) was added at –78 °C to a solution of $(MenPH_2)Mo(CO)_5$ (5.4 g, 13.2 mmol) in 10 mL of THF. After a few minutes, diethyl chlorophosphite (1.9 mL, 13.2 mmol) was added. After about 10 min at –78 °C, oxidation was performed by adding a solution of *m*-chloroperbenzoic acid (5.0 g, 50% acid, previously dried over $MgSO_4$) in CH_2Cl_2. The reaction mixture was then warmed to room temperature and hydrolyzed with 6 mL of an aqueous solution of $NaHSO_3$. The THF was removed, the resulting oil was dissolved in ether and washed with a 5% solution of Na_2CO_3 and then with water. The final product was purified by chromatography using an hexane/ether gradient as eluent. *5*: yield 5.0 g (70%), colorless oil, mixture of two isomers in a 80:20 ratio. ^{31}P NMR (C_6D_6) δ –44.3 (*AX*, ^1J(P–P) = 50.7 Hz), 28.6 (*AX*) for the major isomer and δ –33.3 (*AX*, ^1J(P–P) = 32.7 Hz), 27.0 (*AX*) for the minor isomer; mass spectrum (^{98}Mo) *m/z* 546 (M, 6%), 518 (M-CO, 17), 490 (M-2 CO, 49%), 434 (M-4CO, 100%).

[*tert*-Butyl(diethoxyphosphoryl)phosphine]-pentacarbonylmolybdenum (18). The general synthetic method is described in ref 9, but some improvements were carried out, as follows.

(a) A solution of *tert*-butyldichlorophosphane (9 g, 57 mmol) in THF was added slowly at 0 °C to a sodium diethyl phosphite (114 mmol) solution in THF. The reaction mixture was warmed to room temperature and the bis(diethoxyphosphoryl)-*tert*-butylphosphane was characterized by ^{31}P NMR spectroscopy (δ –32.8 (AB_2, ^1J(P–P) = 202 Hz), 31.1 (AB_2) ppm). The THF was evaporated and the residue was taken up with toluene (15 mL) and reacted with $Mo(CO)_6$ (15 g, 57 mmol) at 105 °C for about 3 h. Cooling of the reaction mixture and crystallization at 0 °C from a toluene/hexane mixture gives 27 g (79%) of the molybdenum complex $(CO)_5Mo[tBuP(P(O)(OEt)_2)_2]$, containing some unreacted $Mo(CO)_6$ (^{31}P NMR (THF): δ 24.83 (AB_2, ^1J(P–P) = 9.7 Hz), 27.39 (AB_2) ppm).

(b) A THF solution of the [bis(diethoxyphosphoryl)-*tert*-butylphosphane]$Mo(CO)_5$ complex was added quickly at room temperature to a mixture containing 45 mL of EtONa, 2 N in EtOH, and 45 mL of THF. After 15 min at room temperature, the reaction mixture was hydrolyzed at 0 °C with aqueous hydrochloric acid (pH < 7). After evaporation of the solvents and extraction with ether, the final product was purified by column chromatography with an hexane/ether gradient as eluent. Yield: 13 g (50% from $tBuPCl_2$). The spectroscopic characterization of **18** has already been reported.[16]

General Procedure for the Synthesis of the (phosphirane)$Mo(CO)_5$ Complexes 6–9, 19, and 20. A solution of the phosphorylphosphine complex **5** or **18** (5 mmol) in THF was cooled to –78 °C; butyllithium (3.4 mL, 5.5 mmol) and styrene oxide (0.69 mL, 5.5 mmol) were successively added. The solution was warmed up to room temperature (reaction 6) or to 45 °C (reactions 2 and 3) and monitored by ^{31}P NMR spectroscopy. The final product was purified by chromatography on a silica gel column with hexane/ether (98:2) as eluent. Separation of the cis and trans isomers was performed by column chromatography with hexane as eluent.

(14) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.
(15) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068. Connor, J. A.; Jones, E. M.; McEwen, G. K. *J. Organomet. Chem.* **1972**, *43*, 357.
(16) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.

(1-*l*-Menthyl-2-phenylphosphirane)pentacarbonylmolybdenum (6), Cis: yield 1.1 g (44%), colorless oil; ^{31}P NMR (C_6D_6) δ −120.1; ^1H NMR (C_6D_6) δ −0.37 (d, ^3J(H-H) = 6.7 Hz, CH_3), 0.4–1.7 (m), 0.88 (d, ^3J(H-H) = 6.1 Hz, CH_3), 0.91 (d, ^3J(H-H) = 6.8 Hz, CH_3), 2.65 (t, ^3J(H-H) = 9.9 Hz, CHPh), 6.7–7.1 (m, Ph); ^{13}C NMR (C_6D_6) δ 11.11 (d, ^1J(C-P) = 12.1 Hz, PCH_2), 15.24 (s, CH_3), 22.02 (s, CH_3), 22.49 (s, CH_3), 24.37 (d, J(C-P) = 13.6 Hz, CH_2), 30.04 (d, J(C-P) = 5.5 Hz, CH), 32.19 (d, J(C-P) = 21.6 Hz, CH), 33.25 (d, J(C-P) = 12.1 Hz, CH), 34.43 (s, CH_2), 36.31 (s, CH), 39.11 (s, CH_2), 44.81 (d, J(C-P) = 10.1 Hz, CH), 126.85, 128.92, 135.88 (d, ^2J(C-P) = 5.5 Hz, C(Ph)), 205.75 (d, ^2J(C-P) = 9.6 Hz, cis CO), 208.78 (d, ^2J(C-P) = 30.2 Hz, trans CO) ppm.

(1-*l*-Menthyl-2-phenylphosphirane)pentacarbonylmolybdenum (7), Trans: yield 0.78 g (31%), colorless solid; mp 99 °C; ^{31}P NMR (C_6D_6) δ −122.3; ^1H NMR (C_6D_6) δ 0.59 (d, ^3J(H-H) = 6.8 Hz, CH_3), 0.88 (d, ^3J(H-H) = 6.0 Hz, CH_3), 1.01 (d, ^3J(H-H) = 6.8 Hz, CH_3), 2.2 (m, CHPh); ^{13}C NMR (C_6D_6) δ 14.88 (d, ^1J(C-P) = 17.6 Hz, PCH_2), 15.67 (s, CH_3), 21.64 (s, CH_3), 22.62 (s, CH_3), 24.47 (d, J(C-P) = 11.1 Hz, CH_2), 26.81 (d, J(C-P) = 16.6 Hz, CH), 29.55 (d, J(C-P) = 5.5 Hz, CH), 33.33 (d, J(C-P) = 13.1 Hz, CH), 34.51 (s, CH_2), 39.20 (d, J(C-P) = 5.0 Hz, CH_2), 44.93 (d, J(C-P) = 4.5 Hz, CH), 46.19 (d, J(C-P) = 6.0 Hz, CH), 205.14 (d, ^2J(C-P) = 10.0 Hz, cis CO), 208.10 (d, ^2J(C-P) = 30.2 Hz, trans CO) ppm; mass spectrum (^{98}Mo) m/z 512 (M, 21), 428 (M = 3CO, 53), 290 (87%), 262 (100%). Anal. Calcd for $C_{23}H_{27}O_5PMo$: C, 54.13; H, 5.33. Found: C, 54.28; H, 5.18.

(1-*l*-Menthyl-2-phenylphosphirane)pentacarbonylmolybdenum (8), Cis: yield 1.5 g (58%), colorless solid; mp 105 °C; ^{31}P NMR (C_6D_6) δ −131.2; ^1H NMR (C_6D_6) δ 0.55 (s, br, CH_3), 0.62 (d, ^3J(H-H) = 6.8 Hz, CH_3), 0.97 (d, ^3J(H-H) = 6.8 Hz, CH_3), 1.13 (m, ^3J(H-H) ~ ^2J(H-H) ~ 9.5 Hz, ^2J(H-P) = 2.1 Hz, 1H, PCH_2), 1.67 (q, J(H-H) ~ J(H-P) ~ 9 Hz, 1H, PCH_2), 2.54 (t, ^3J(H-H) = 9.5 Hz, CHPh); ^{13}C NMR (C_6D_6) δ 12.49 (d, ^1J(C-P) = 15.6 Hz, PCH_2), 15.78 (s, CH_3), 21.40 (s, CH_3), 22.29 (s, CH_3), 24.41 (d, J(C-P) = 11.6 Hz, CH_2), 27.45 (d, J(C-P) = 17.6 Hz, CH), 29.48 (d, J(C-P) = 6.0 Hz, CH), 32.88 (d, J(C-P) = 13.6 Hz, CH), 34.40 (s, CH_2), 37.67 (s, CH_2), 38.28 (d, J(C-P) = 5.5 Hz, CH), 44.30 (d, J(C-P) = 4.5 Hz, CH), 205.70 (d, J(C-P) = 10.0 Hz, cis CO), 208.55 (d, J(C-P) = 28.7 Hz, trans CO) ppm.

(1-*l*-Menthyl-2-phenylphosphirane)pentacarbonylmolybdenum (9), Trans: yield 0.4 g (16%), colorless solid; mp 87 °C; ^{31}P NMR (C_6D_6) δ −124.7; ^1H NMR (C_6D_6) δ 0.72 (d, ^3J(H-H) = 6.8 Hz, CH_3), 0.84 (d, ^3J(H-H) = 6.0 Hz, CH_3), 1.02 (d, ^3J(H-H) = 6.8 Hz, CH_3), 2.4 (m, 1H), 2.59 (m, 1H, CHPh); ^{13}C NMR (C_6D_6) δ 12.23 (d, ^1J(C-P) = 14.6 Hz, PCH_2), 16.03 (s, CH_3), 21.54 (s, CH_3), 22.44 (s, CH_3), 24.47 (d, J(C-P) = 11.6 Hz, CH_2), 29.05 (d, J(C-P) = 19.6 Hz, CH), 30.05 (d, J(C-P) = 7.0 Hz, CH), 33.40 (d, J(C-P) = 12.1 Hz, CH), 34.71 (s, CH_2), 38.73 (s, CH_2), 45.05 (d, J(C-P) = 6.0 Hz, CH), 47.13 (d, J(C-P) = 6.0 Hz, CH), 205.2 (d, ^2J(C-P) = 10.0 Hz, cis CO), 208.25 (d, ^2J(C-P) = 30.7 Hz, trans CO) ppm.

(1-*tert*-Butyl-2-phenylphosphirane)pentacarbonylmolybdenum (19), Cis: yield 0.58 g (27%), colorless solid; mp 72 °C; ^{31}P NMR (C_6D_6) δ −115.0; ^1H NMR (C_6D_6) δ 0.58 (d, ^3J(H-P) = 16.8 Hz, CMe_3), 1.14 (m, ^3J(H-H) ~ 10.3 Hz, ^2J(H-H ~ 8.7 Hz, ^2J(H-P) ~ 2.6 Hz, 1H, PCH_2), 1.5 (m, 1H, PCH_2), 2.51 (t, ^3J(H-H) = 10.3 Hz, CHPh), 6.9–7.1 (m, Ph); ^{13}C NMR (C_6D_6) δ 10.18 (d, ^1J(C-P) = 15.6 Hz, PCH_2), 28.51 (d, ^2J(C-P) = 8.0 Hz, CMe_3), 31.94 (d, ^1J(C-P) = 20.6 Hz, CHPh), 32.14 (s, CMe_3), 206.07 (d, ^2J(C-P) = 10.6 Hz, cis CO), 209.29 (d, ^2J(C-P) = 30.2 Hz, trans CO) ppm; $[\alpha]^{25}_D$ = +66 (*c* 1, $CHCl_3$).

(1-*tert*-Butyl-2-phenylphosphirane)pentacarbonylmolybdenum (20), Trans: yield 1.3 g (63%), colorless solid; mp 101 °C; ^{31}P NMR (C_6D_6) δ −107.6; ^1H NMR (C_6D_6) δ 0.73 (d, ^3J(H-P) = 16.0 Hz, CMe_3), 1.16 (m, 2H, CH_2), 2.45 (m, 1H, CHPh); ^{13}C NMR (C_6D_6) δ 11.61 (d, ^1J(C-P) = 19.1 Hz, PCH_2), 24.16 (d, ^1J(C-P) = 21.1, CHPh), 27.59 (d, ^2J(C-P) = 7.5 Hz, CMe_3), 30.63 (s, CMe_3), 205.41 (d, ^2J(C-P) = 9.1 Hz, cis CO) ppm; mass spectrum (^{98}Mo) m/z 430 (M, 36), 346 (M − 3CO, 64), 316 (M − 4CO, 36), 288 (100%). Anal. Calcd for $C_{17}H_{17}MoO_5P$: C, 47.68; H, 4.00. Found: C, 47.69; H, 3.93. $[\alpha]^{25}_D$ = −27 (*c* 1, $CHCl_3$).

Decomplexation of Phosphiranes from Their $Mo(CO)_5$ Complexes. General Procedure. The (phosphirane)$Mo(CO)_5$ complexes **6–9**, **19**, and **20** (1 mmol) and diphos (1 mmol) were heated at 96 °C for 15 h (trans isomers) or at 105 °C for 20 h (cis isomers) in toluene (10 mL) under argon. The reaction is quantitative, according to the ^{31}P NMR spectra of the reaction mixture [$(CO)_4$Mo(diphos) δ 56.6 ppm; δ(^{31}P) for phosphiranes **10–13** are given in Table I; 1-*tert*-butyl-2-phenylphosphirane, cis δ −161.8 ppm; 1-*tert*-butyl-2-phenylphosphirane, trans δ −164.0 ppm]. Most of the $(CO)_4$Mo(diphos) complex was crystallized from the reaction mixture by addition of pentane and cooling at −20 °C. Phosphiranes **10** and **11** were then purified by filtration through a short silica gel column with pentane as eluent and characterized by NMR spectroscopy. Remark: usually, phosphiranes give some unsoluble material when their solutions are evaporated to dryness. Total evaporation is to be avoided.

The crude phosphirane solutions, obtained after total precipitation of the molybdenum–diphos complex, are used directly for the synthesis of the rhodium complexes.

1-*l*-Menthyl-2-phenylphosphirane (10): yield 0.19 g (77%); ^1H NMR (C_6D_6) δ −0.12 (d, ^3J(H-H) = 6.8 Hz, CH_3), 0.86 (d, ^3J(H-H) = 5.8 Hz, CH_3), 0.89 (d, ^3J(H-H) = 6.8 Hz, CH_3), 2.1 (m, 1H), 2.59 (dt, ^3J(H-H) = 9.3 Hz, ^2J(H-P) = 15.1 Hz, CHPh); ^{13}C NMR (C_6D_6) δ 9.28 (d, ^1J(C-P) = 38.2 Hz, PCH_2), 15.65, 22.42, and 22.81 (s, CH_3), 25.17 (d, J(C-P) = 10.6 Hz, CH_2), 27.27 (d, ^1J(C-P) = 43.3 Hz, PCH), 29.51 (d, J(C-P) = 10.6 Hz, CH), 33.49 (s, CH), 33.91 (d, J(C-P) = 26.7 Hz, CH), 34.99 (s, CH_2), 41.28 (d, J(C-P) = 8.6 Hz, CH_2), 47.67 (d, J(C-P) = 23.7 Hz, CH) ppm.

1-*l*-Menthyl-2-phenylphosphirane (11): yield 0.17 g (62%); ^1H NMR (C_6D_6) δ 0.70 (d, ^3J(H-H) = 6.8 Hz, CH_3), 0.84 (d, ^3J(H-H) = 6.0 Hz, CH_3), 0.93 (d, ^3J(H-H) = 6.9 Hz, CH_3), 2.20 (m, 1H CHPh), 2.5 (m, 1H); ^{13}C NMR (C_6D_6) δ 15.97 (s, CH_3), 17.78 (d, ^1J(C-P) = 42.8 Hz, PCH_2), 22.00 and 22.72 (s, CH_3), 25.26 (d, J(C-P) = 7.5 Hz, CH_2), 25.27 (d, ^1J(C-P) = 37.2 Hz, PCH), 29.63 (d, J(C-P) = 9.1 Hz, CH), 33.69 (d, J(C-P) = 8.1 Hz, CH), 35.07 (s, CH_2), 41.34 (d, J(C-P) = 11.1 Hz, CH_2), 44.12 (d, ^1J(C-P) = 32.2 Hz, PCH), 47.47 (d, J(C-P) = 16.1 Hz, CH) ppm; mass spectrum m/z 274 (M, 23), 136 (100%).

General Procedure for the Synthesis of the Rhodium Complexes 14–17, 21, and 22. Solutions of the crude phosphiranes in toluene/pentane mixtures are obtained from the corresponding $Mo(CO)_5$ complexes, as described above. (Excess diphos must be avoided in the decomplexation reaction.) CH_2Cl_2 is added to the phosphirane solution; then solid $(COD)_2Rh^+PF_6^-$ is added gradually at room temperature by monitoring the reaction course by ^{31}P NMR spectroscopy. When phosphirane is totally consumed, ether is added in order to precipitate the final product. Purification is performed by repeated precipitations from CH_2Cl_2/ether mixtures. Compounds **16** and **17** are obtained as amorphous, spongy solids, even after repeated precipitations. Yields were not established. Compounds **14**, **15**, **21**, and **22** are crystalline solids.

(COD)Rh(1-*l*-menthyl-2-phenylphosphirane)$_2PF_6$ (14). Complex **14** was obtained in 52% yield (0.35 g) by starting from 0.76 g (1.5 mmol) of the corresponding molybdenum complex **6**, after decomplexation and reaction with $(COD)_2RhPF_6$ (0.22 g, 0.47 mmol). **14**: orange solid; ^{31}P NMR (CH_2Cl_2) δ −123.9 (d, ^1J(P-Rh) = 158.6 Hz), −143.9 (PF_6); ^1H NMR ($CDCl_3$) δ −0.18 (d, ^3J(H-H) = 6.6 Hz, CH_3), 0.96 (d, ^3J(H-H) = 6.8 Hz, CH_3), 1.02 (d, ^3J(H-H) = 6.3 Hz, CH_3), 3.10 (t, ^3J(H-H) = 9.8 Hz, CHPh), 5.18 (br, 2H, CH(COD)), 5.40 (br, 2H, CH(COD)); ^{13}C NMR ($CDCl_3$) δ 12.69 (br, PCH_2), 15.00 (s, CH_3), 22.26 (s, CH_3), 22.40 (s, CH_3), ..., 95.5 (br, CH(COD)), 102.8 (br, CH(COD)), 127.33, 128.03, 129.06, 133.97 (Ph) ppm. Anal. Calcd for **14**·CH_2Cl_2, $C_{45}H_{68}Cl_2F_6P_3Rh$: C, 54.61; H, 6.92. Found: C, 54.71; H, 6.93. $[\alpha]^{25}_D$ = +277 (*c* 0.2, $CHCl_3$).

(COD)Rh(1-*l*-menthyl-2-phenylphosphirane)$_2PF_6$ (15). Complex **15** was obtained in 75% yield (0.50 g) by starting from 0.76 g (1.5 mmol) of the $Mo(CO)_5$ complex **7**. After decomplex-

ation, 0.27 g (0.58 mmol) of $(COD)_2RhPF_6$, that is about 78% of the required amount, was added to the crude phosphirane solution. The reaction is nearly quantitative with respect to the rhodium derivative. **15**: orange solid; ^{31}P NMR (CH_2Cl_2) δ −125.5 (d, ^1J(P—Rh) = 134 Hz), −143.9 (PF_6); ^1H NMR ($CDCl_3$) very broad signals δ 2.9 (m, 1H, CHPh), 5.0–5.2 (m, HC=CH(COD)); ^{13}C NMR ($CDCl_3$) δ 14.41 (br), 16.08 (s, CH_3), 21.42 (s, CH_3), 21.79 (s, CH_3), 24.36 (s), 27.82 (br), ..., 39.14 (s), 43.82 (br), 98.2 (br, CH(COD)), 127.34, 128.90, 137.14 (Ph) ppm. Anal. Calcd for **15**·CH_2Cl_2, $C_{45}H_{68}Cl_2F_6P_3Rh$: C, 54.61; H, 6.92. Found: C, 54.89; H, 6.88. $[\alpha]^{25}_D$ = +111 (*c* 0.2, $CHCl_3$).

(COD)Rh(1-*l*-menthyl-2-phenylphosphirane)$_2$PF$_6$ (16). Complex **16** (0.22 g containing small amounts of side products) was obtained by starting from 0.51 g (1 mmol) of the corresponding molybdenum complex **8**, after decomplexation and reaction with $(COD)_2RhPF_6$ (0.14 g, 0.30 mmol). **16**: ^{31}P NMR (CH_2Cl_2) δ −129.7 (d, ^1J(P–Rh) = 159.8 Hz), −143.7 (PF_6); ^1H NMR ($CDCl_3$) δ 0.63 (d, ^3J(H–H) = 4.5 Hz, CH_3), 0.93 (d, ^3J(H–H) = 6.8 Hz, CH_3), 0.99 (d, ^3J(H–H) = 6.8 Hz, CH_3), 3.01 (t, ^3J(H–H) = 10.0 Hz, CHPh), 5.16 (br, CH(COD)); ^{13}C NMR ($CDCl_3$) δ 11.21 (PCH_2), 15.91, 21.40, 21.55 (s, CH_3), 24.64 (CH_2), ..., 40.46 (CH_2), 42.13 (CH), 44.63 (CH), 97.65 (CH(COD)), 98.98 (CH(COD)) ppm.

(COD)Rh(1-*l*-menthyl-2-phenylphosphirane)$_2$PF$_6$ (17). ^{31}P NMR ($CDCl_3$) δ −128.0 (^1J(P–Rh) = 158.0 Hz), −143.2 (PF_6); ^1H NMR ($CDCl_3$) very broad spectrum δ 0.92, 0.95, 0.98 (CH_3), 3.12 (CHPh), 4.8 (CH(COD)), 5.14 (CH(COD)); ^{13}C NMR ($CDCl_3$) δ 11.24 (PCH_2), 16.44 (s, CH_3), 21.26 (s, CH_3), 22.15 (s, CH_3), ..., 97.59 (CH(COD)) ppm. Anal. Calcd for $C_{44}H_{66}F_6P_3Rh$: C, 58.41; H, 7.35. Found: C, 59.68; H, 7.28. $[\alpha]^{25}_D$ = −165 (*c* 0.2, $CHCl_3$).

(COD)Rh(1-*tert*-butyl-2-phenylphosphirane)$_2$PF$_6$ (21). Complex **21** was obtained in 45% yield (0.17 g) by starting from 0.43 g (1 mmol) of the corresponding molybdenum complex **19**. After decomplexation, 0.13 g (0.28 mmol) of $(COD)_2RhPF_6$ was added to the crude phosphirane solution. **21**: orange solid; ^{31}P NMR (CH_2Cl_2) δ −108.1 (^1J(P–Rh) = 159.9 Hz), −144.0 (PF_6); ^1H NMR ($CDCl_3$) δ 1.12 (^3J(H–P) = 16.6 Hz, CMe_3), 1.84 (t, J(H–H) = 10.6 Hz, 1H, CH_2), 2.1–2.6 (m, 5H), 2.99 (t, ^3J(H–H) = 10.5 Hz, CHPh), 5.19 (br, 1H, CH(COD)), 5.42 (br, 1H, CH(COD)); ^{13}C NMR ($CDCl_3$) δ 7.90 (PCH_2), 29.34, 30.48, 30.77 (CMe_3), 31.16, 34.85, 97.88 (CH(COD)), 127.48, 128.85, 129.22, and 133.30 (Ph) ppm. Anal. Calcd for $C_{32}H_{46}P_3F_6Rh$: C, 51.90; H, 6.26. Found: C, 51.26; H, 5.84.

(COD)Rh(1-*tert*-butyl-2-phenylphosphirane)$_2$PF$_6$ (22). Complex **22** was obtained in 58% yield (0.32 g) by starting from 0.64 g (1.5 mmol) of the $Mo(CO)_5$ complex **20**, after decomplexation and reaction with $(COD)_2RhPF_6$ (0.24 g, 0.52 mmol). The yield of **22** is about 83% with respect to the rhodium derivative. **22**: yellow-orange solid; ^{31}P NMR (CH_2Cl_2) very broad signal δ −108 (^1J(P–Rh) = 166 Hz), −144.0 (PF_6); ^1H NMR ($CDCl_3$) δ 1.22 (d, ^3J(H–P) = 16.0 Hz, CMe_3), 1.54 (t, J(H–H) = 9.5 Hz, 1H, CH_2), 1.7–2.3 (m, 5H), 2.88 (q, $J \sim$ 9.6 Hz, CHPh), 5.0 (br, 1H, CH(COD)), 5.15 (br, 1H, CH(COD)); ^{13}C NMR ($CDCl_3$) δ 12 (br, PCH_2), 25.53, 25.92, 29.36 (CMe_3), 30.18–30.61 (br), 33.23, 97.51 (CH(COD)), 98.06 (CH(COD)), 127.19, 129.18, and 136.32 (Ph) ppm. Anal. Calcd for $C_{32}H_{46}P_3F_6Rh$: C, 51.90; H, 6.26. Found: C, 52.35; H, 5.95. $[\alpha]^{25}_D$ = +104 (*c* 0.2, $CHCl_3$). When the same reaction was performed by starting from a racemic sample of complex **20**, a mixture of **22** (*d,l* racemic form) and its meso isomer [selected ^1H NMR data ($CDCl_3$): δ 1.77 (t), 3.02 (m, 1H, CHPh), 4.37 (br, 1H, CH(COD)), 5.45 (br, 1H, CH(COD)) ppm] in a 1:2 ratio was obtained.

Hydrogenation Procedure. The substrate (2 mmol) and the rhodium complex, **14–17**, **21**, or **22** (1.6×10^{-2} mmol) were placed in a 100-mL autoclave. The autoclave was evacuated and flushed three times with argon. Then 25 mL of methanol was added and the solution was stirred at room temperature under 3 atm of H_2 (starting pressure) until gas uptake ceased (1–5 h). The conversion degree was checked by ^1H NMR, after evaporating the solvent. Published procedures were used to remove the catalyst from the mixture and to isolate the hydrogenation products, *N*-acetylphenylalanine,[17] *N*-acetylalanine,[17] and methylsuccinic acid,[18] respectively. Optical yields are calculated with respect to the following values for the optically pure compounds: (*S*)-*N*-acetylphenylalanine $[\alpha]_D$ = +47.4 (*c* 1, 95% EtOH);[19] (*R*)-*N*-acetylalanine $[\alpha]_D$ = +66.5 (*c* 2, EtOH);[18] (*R*)-methylsuccinic acid $[\alpha]_D$ = +16.88 (*c* 2.16, EtOH).[20]

X-ray Structure Determination for 15. Crystals of **15**, $C_{48}H_{74}RhF_6OP_3$, were grown at −18 °C from a THF/pentane solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius SDP package. The compound crystallizes in space group $P2_12_12_1$, a = 11.672(1) Å, b = 19.758(2) Å, c = 20.965(2) Å, V = 4834.69(1.36) Å^3, Z = 4; d_{calc} = 1.342 g/cm^3, Mo Kα radiation (λ = 0.710 73 Å) graphite monochromator; μ = 5.0 cm^{-1}; $F(000)$ = 2056. A total of 7354 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$ of which 1512 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 5842 for solution and refinement. Direct methods yielded a solution for the rhodium atom and part of the two phosphirane moieties; the model was completed using standard difference Fourier techniques. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, while anisotropic temperature factors were used for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.042, R_w = 0.058, and GOF = 1.18. The absolute structure was established relative to the known conformation of the menthyl fragment and is also supported by the slightly higher agreement factors for the enantiomer: R = 0.045, R_w = 0.061, GOF = 1.50.

Supplementary Material Available: Tables of experimental details, positional parameters, thermal parameters, and bond angles and distances (8 pages). Ordering information is given on any current masthead page.

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