Phosphetanes as Chiral Ligands for Catalytic Asymmetric Reactions: Hydrosilylation of Olefins

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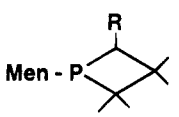
A simple methodology has been developed for the synthesis of P-menthylphosphetanes having known stereochemistry at several chiral centers, including phosphorus. These new electron-rich chiral phosphines have been tested as ligands in olefin hydrogenation reactions and in the palladium-catalyzed hydrosilylation of styrene and cyclopentadiene. High activity and significant enantiomeric excesses have been obtained when using a 1:1 phosphine/Cl_2-$Pd(PhCN)_2$ mixture as the catalyst. Within each set of epimeric phosphetanes, the enantiomeric excesses are highly dependent on the relative configurations of the sequence of chiral centers.

At present, enantioselective catalysis generally makes use of P-aryl-substituted, chelating, chiral phosphines. The properties of these phosphine ligands are principally determined by their donor–acceptor properties and modulated by steric effects.[1] Thus, in transition-metal-based catalysts, one can expect significant differences in both activity and enantioselectivity between trialkyl-substituted phosphines and the less basic arylphosphines. Additionally, it may reasonably be expected that mono(phosphines) have significant potential in the field of catalysis, even though it has been much less investigated than that of chelating bis(phosphines). In fact, some recent literature reports point out a few examples of catalytic processes in which monophosphines are the most suitable ligands.[2]

We intend to develop the *P*-methylphosphetanes **1** as a new class of chiral trialkylphosphines, to explore their potential as ligands in catalytic reactions, and to correlate their properties with changes in the phosphorus environment by varying the α-substituent R.



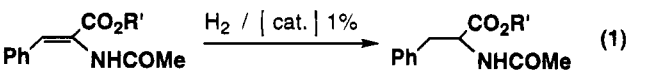
1, Men = L-menthyl

The synthesis of some chiral phosphetanes (**1**, R = H, CH_2Ph, Br) has been reported previously.[3] Here we present a preliminary study of their use as ligands in catalytic processes, as well as the synthesis of some new derivatives.

Results and Discussion

The coordination chemistry of phosphetanes has been very little developed: as far as we know, only dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum[4] and a cationic iron complex[5] and a molybdenum complex[6] of 1-phenylphosphetane have been described. None of these derivatives have ever been tested as catalysts for any known reaction.

Scheme 1[a]



(1)

[a] Reagents and conditions: R′ = H, cat. = $(COD)_2Rh^+PF_6^-$ + 2 **1a**, MeOH, 3.5 bars of H_2, room temperature, 8 days; R′ = Me, cat. = $(COD)Ir(\mathbf{1a})_2^+PF_6^-$, CH_2Cl_2, 2.3 bars of H_2, room temperature, 16 h.

The easily accessible, slightly oxygen-sensitive phosphetane **1a** (R = CH_2Ph, P(*R*) C(*S*) was selected to check the potential of phosphetanes in various catalytic reactions. At first, we targeted the well-known olefin hydrogenations catalyzed by cationic rhodium or iridium complexes (eq 1). Phosphetane **1a** is a very poor ligand for rhodium(I): some $(COD)Rh(\mathbf{1a})_2^+PF_6^-$ complex can be detected by ^{31}P NMR in the reaction mixture formed by adding **1a** to $(COD)_2Rh^+PF_6^-$ ($\delta(^{31}P)$ 62.9 ppm, $^1J_{Rh-P}$ = 158.8 Hz in CH_2Cl_2), but only a left-side-shifted equilibrium with free phosphetane is established. The weakness of the phosphorus–rhodium bond and the subsequent low concentration of catalytic species could be responsible for the very low activity observed in the hydrogenation reaction (Scheme 1).

Iridium(I) is a more suitable complexing agent for phosphetane **1a**, and the cationic $(COD)Ir(\mathbf{1a})_2^+PF_6^-$ has been isolated and fully characterized. It proved to be a more efficient catalyst than the corresponding rhodium derivative. Hydrogenation of the α-acetamidocinnamic acid methyl ester takes place at room temperature, under 2.3 bars of H_2 in about 16 h. In terms of enantioselectivity both of these catalysts were disappointing: neither reaction shown in Scheme 1 gives a significant asymmetric induction (ee values of about 40% and <10%, respectively).

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 4, Chapter 14.

(2) Some examples are as follows. Nickel-catalyzed cross-coupling: Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153. Palladium-catalyzed hydrosilylation of olefins: Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. Palladium-catalyzed reduction of allylic esters: Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y. *J. Am. Chem. Soc.* **1994**, *116*, 775.

(3) Marinetti, A.; Ricard, L. *Tetrahedron* **1993**, *49*, 10291.

(4) Tumas, W.; Huang, J. C.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1992**, *11*, 2944.

(5) Bader, A.; Pathak, D. D.; Wild, S. B.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1751.

(6) Kang, Y. B.; Pabel, M.; Willis, A. C.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1994**, 475.

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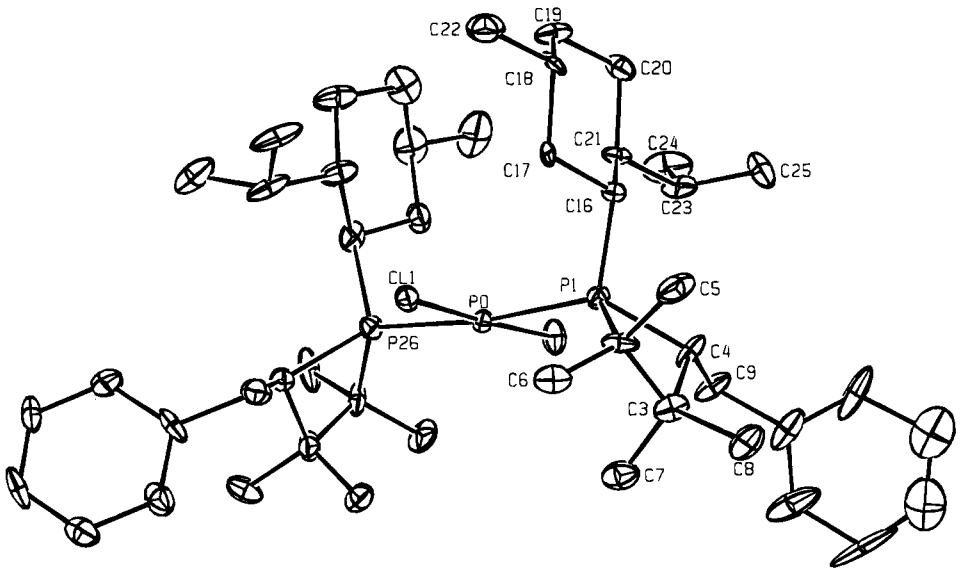
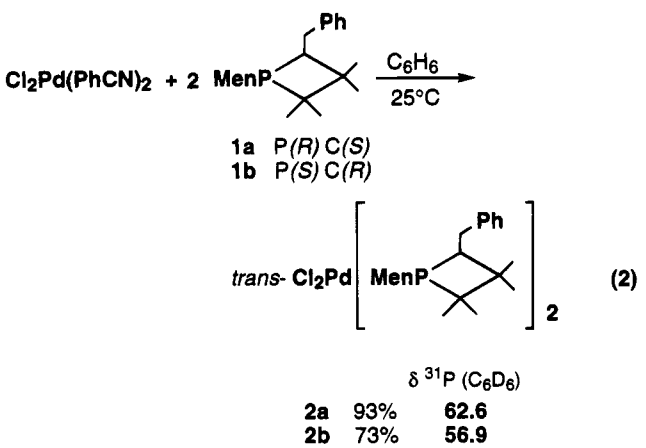


Figure 1. ORTEP drawing of the palladium complex **2b**. Selected bond lengths (Å): Pd—P(1), 2.345(3); Pd—Cl(1), 2.294(3); P(1)—C(4), 1.85(1); C(4)—C(3), 1.57(2); C(3)—C(2), 1.57(2); C(2)—P(1), 1.86(1); P(1)—C(16), 1.85(1). Selected bond angles (deg): P(1)—Pd—Cl(1), 89.6(1); C(2)—P(1)—C(4), 76.2(6); P(1)—C(2)—C(3), 88.9(8); P(1)—C(4)—C(3), 89.4(9); Pd—P(1)—C(4), 123.5(5); Pd—P(1)—C(2), 122.4(5); Pd—P(1)—C(16), 108.9(4).

Scheme 2



Therefore, we turned out our attention to dichlorobis(phosphine)palladium(II) complexes, which are versatile precursors for catalytically active species in a number of important chemical processes[7] including Heck reactions and allylic substitutions. Two equivalents of phosphetane **1a** reacts instantaneously with $Cl_2Pd(PhCN)_2$ in dichloromethane to afford the trans complex **2a**, which was obtained in 93% yield after crystallization from pentane (Scheme 2).

^1H and ^{13}C NMR data for complex **2a** have been reported.[8] The trans disposition of the two phosphine ligands was inferred from NMR data, and this geometry has been confirmed by an X-ray crystal study of the analogous complex **2b**, which contains the epimeric phosphetane **1b**. The molecular structure, together with the main bond distances and angles for complex **2b**, are given in Figure 1. The coordination around the palladium atom is close to square-planar, with the two menthyl groups on the same side of the coordination plane. A similar arrangement of the ligands has been found in the complex $Cl_2Pd(MenPMe_2)_2$.[9]

Among the various palladium-catalyzed reactions, the hydrosilylation of olefins and dienes[10] appeared to be a very attractive one. The asymmetric version of this reaction has been successfully developed by Hayashi and Uozumi, who used MOP (2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl) as the chiral ligand. Excellent regio- and stereoselectivities were obtained in the hydrosilylation of 1-alkenes[2b] or meso-olefins,[11] and the subsequent oxidation of the carbon—silicon bond led to optically active alcohols.[12] Besides the very high regioselectivity and catalytic activity—the substrate to palladium ratio is lower than 1000:1—the most intriguing feature of the Pd-catalyzed hydrosilylation is the specific requirement of monodentate phosphine ligands: chelating bis(phosphine) ligands, such as BINAP, are reported to be totally inactive.[12] Thus, we focused on the development of phosphetanes **1** as chiral ligands for hydrosilylation and selected styrene and cyclopentadiene as substrates for an exploratory study. Asymmetric hydrosilylation of these substrates is not satisfactory at present, with the best enantiomeric excesses being 71% in both cases.[13,14]

According to the usual procedure, cyclopentadiene or styrene (16 mmol) was reacted, without solvent, with 1.1 equiv of trichlorosilane in the presence of the catalysts precursor (5×10^{-3} mmol) (Scheme 3). The

(7) Tsuji, J. *Organic Synthesis via Palladium Compounds*; Springer-Verlag: Heidelberg, Germany, 1980. Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.
(8) Marinetti, A. *Tetrahedron Lett.* **1994**, *35*, 5861.
(9) Kan, K.; Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 733.
(10) Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1969**, 161. Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143.
(11) Uozumi, Y.; Lee, S-Y.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 7185. Uozumi, Y.; Hayashi, T. *Tetrahedron Lett.* **1993**, *34*, 2335.
(12) Hayashi, T.; Uozumi, Y. *Pure Appl. Chem.* **1992**, *64*, 1911 and references therein.
(13) Okada, T.; Morimoto, T.; Achiwa, K. *Chem. Lett.* **1990**, 999.
(14) Uozumi, Y.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1993**, *4*, 2419.

Scheme 3

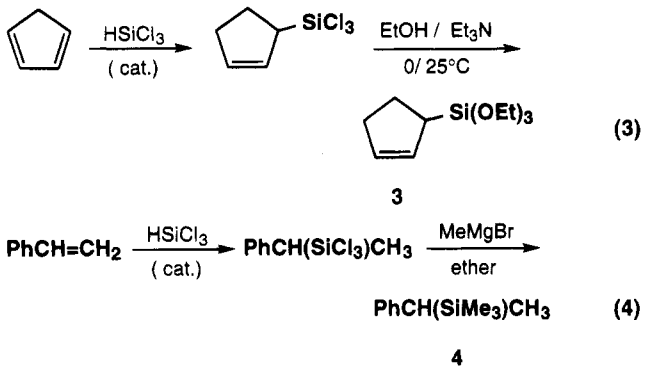


Table 1. Hydrosilylation Reactions with Phosphetane 1a–Palladium Catalysts

catalyst	substrate	reacn conditions	yield, %	ee, % (config)
2a	cyclopentadiene	70 °C, 30 h	26[a]	44 (*S*)
	styrene	90 °C, 24 h	100[b]	19 (*R*)
$Cl_2Pd(PhCN)_2$ + **1a** (1:1)	cyclopentadiene	25–30 °C, 2 h	70[a]	54 (*S*)
	styrene	50 °C, 24 h	100[b]	18 (*R*)

[a] Isolated yield. [b] By ^1H NMR of the reaction mixture.

optical purity of the cyclopentenyltrichlorosilanes was determined by conversion into 3-(triethoxysilyl)cyclopentene (**3**), whose $[\alpha]_D$ measurements were compared with the literature data.[15] Similarly, (1-phenylethyl)trichlorosilane was converted into the corresponding trimethylsilane **4**, of known optical rotation.[16] Complex **2a** is an efficient hydrosilylation catalysts (see Table 1) when operating at 70 and 90 °C for cyclopentadiene and styrene, respectively. Styrene is quantitatively consumed within 24 h, but the yield of reaction 3 (Scheme 3) is lowered by the dimerization of the starting material. Enantiomeric excesses are moderate, but nonetheless significant, in both cases.

In the course of our study, we unexpectedly noticed a considerably higher catalytic activity when a 1:1 phosphetane/$Cl_2Pd(PhCN)_2$ mixture is used instead of **2a** as the catalyst precursor (see Table 1). The implications of this result on the mechanism of the hydrosilylation reaction, which have been discussed in a previous communication,[8] are that a mono(phosphine)–Pd complex must be the catalytically active species. The second phosphine ligand in complex **2a** has rather an inhibitory effect.

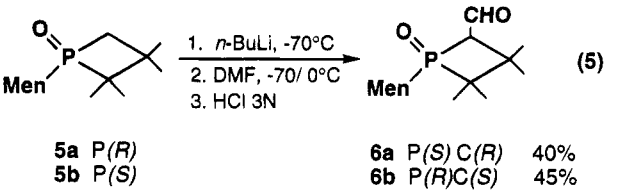
Under the optimized conditions the hydrosilylation of cyclopentadiene gave both an improved yield and a higher enantioselectivity, owing to the lower reaction temperature. Hydrosilylation of styrene is faster than, but the enantiomeric excess is not significantly different from, that described previously.

The 70% yield, 54% ee obtained with ligand **1a** in the hydrosilylation of cyclopentadiene compares with the results obtained with the best catalytic systems: 73% yield, 57% ee is obtained with a chiral aminoferrocenylphosphine[15] and 35% yield, 71% ee is obtained with a sulfonylaminophosphine.[13] Consequently, it was worthwhile to test other known chiral phosphetane ligands

(15) Hayashi, T.; Matsumoto, Y.; Morikawa, I.; Ito, Y. *Tetrahedron: Asymmetry* **1990**, *3*, 151. (*R*)-**3**: 60% optical purity, $[\alpha]_D = +45°$ (c = 1, benzene).

(16) Yamamoto, K.; Kiso, Y.; Ito, R., Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *210*, 9.

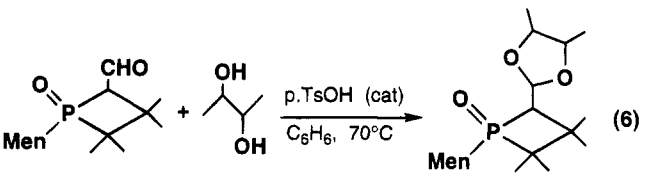
Scheme 4



5a P(*R*)
5b P(*S*)

6a P(*S*) C(*R*) 40%
6b P(*R*)C(*S*) 45%

Scheme 5



	$\delta^{31}P(C_6D_6)$				$\delta^{31}P(C_6D_6)$
6a	**65.6**	(*R,R*)	**7a**	88%	**64.8**
		(*S,S*)	**7b**	81%	**64.2**
6b	**59.1**	(*R,R*)	**7c**	75%	**60.4**
		(*S,S*)	**7d**	70%	**60.1**

in the same catalytic reaction and to expand the family to some new representatives. Considering that the most efficient ligand (MOP) bears an ether functional group, we targeted new phosphetanes with an additional oxygen function. The role of the ether group is not firmly established, but it should have a positive effect in transiently stabilizing the coordinatively unsaturated palladium intermediates.

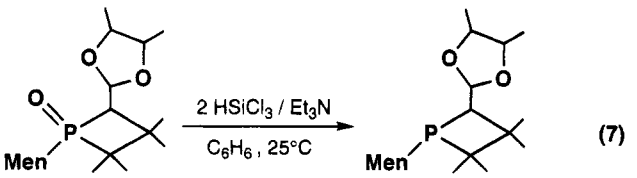
With the phosphetane oxides **5a,b**[3] as starting materials, a formyl group was introduced into the α-position by reaction of the phosphorus-stabilized carbanion with dimethylformamide (eq 5). The reaction leads stereospecifically to a single isomer where the formyl substituent probably lies in the equatorial position, trans to the menthyl group. The analogous alkylations of the same carbanions with benzyl bromide, leading to **1a,b**, proved to be highly stereospecific: the proposed stereochemistry is supported by the X-ray study of the benzyl analogue reported above.

Aldehydes **6** were then reacted separately with both enantiomers of 2,3-butanediol to afford the corresponding acetals **7**, in which two additional chiral centers of known configuration are present (Scheme 5).

Finally, the phosphetane oxides **7** were reduced to the corresponding phosphetanes **8** by using 2 equiv of the$HSiCl_3/Et_3N$ complex in benzene at room temperature (Scheme 6). According to the ^{31}P NMR analysis of the crude reaction mixtures, all reductions are quantitative and stereospecific. The most significant NMR data for compounds **6–8** are reported in Tables 2 and 3.

The new phosphetanes **8**, as well as the previously described phosphetanes **9** and **1** (Table 4), have been used as ligands in the palladium-catalyzed hydrosilylation of cyclopentadiene. Some of these ligands were also evaluated in the hydrosilylation of styrene (eqs 3 and 4 in Scheme 3). All reactions were run in the presence of a palladium–phosphetane catalyst, prepared *in situ* by mixing $Cl_2Pd(PhCN)_2$ and phosphetane. The ratio substrate:$HSiCl_3$:Pd ligand was 1:1.2:0.0003:0.0003. The preformed 2:1 phosphine–Pd complexes showed a lower catalytic activity and a lower asymmetric induction than the 1:1 complex in all cases. This

Scheme 6



(7)

			$\delta^{31}P(C_6D_6)$
7a	**8a**	89%	**20.9**
7b	**8b**	79%	**21.0**
7c	**8c**	66%	**18.9**
7d	**8d**	60%	**18.4**

Table 2. Selected ^{1}H NMR Data[a] for Compounds 6–8

compd	P–CH	CHO	CH(O–)$_2$	CH(Me)O–
6a	2.73 [7.5][b]	9.96 (4.6)[c]		
6b	3.02 [5.4]	10.04 (5.4)		
7a	2.28 [5.8]		5.56 (8.4)[c] [2.2][b]	3.2–3.4
7b	2.25 [5.8]		5.64 (8.4) [3.6]	3.2–3.4
7c	2.58 [5.4]		5.66 (8.3) [4.1]	3.2–3.5
7d	2.60 [5.1]		5.59 (8.5) [3.2]	3.2–3.4
8a	2.33 [6.0]		5.35 (8.3) [1.7]	3.2–3.5
8b	2.31 [6.0]		5.41 (7.6) [3.0]	3.3–3.5
8c	2.56 [6.1]		5.41 (7.6) [2.9]	3.2–3.5
8d	2.57 [6.0]		5.32 (7.8) [2.5]	3.2–3.4

[a] Spectra measured in C_6D_6: chemical shifts in ppm; coupling constants in hertz. [b] J_{HP} coupling constants in brackets. [c] J_{HH} coupling constants in parentheses.

confirms the results obtained with phosphetane **1a** which were discussed above. The hydrosilylation reactions are summarized in Table 4. The catalytic activity is generally high in the case of styrene, but quite variable in the case of cyclopentadiene, where a polymeric material is formed concurrently. The best overall results we obtained with phosphetanes **1a** (70% yield, 54% ee) and **7a** (60% yield, 65% ee). The same phosphetanes give the best, albeit moderate, enantiomeric excesses in the hydrosilylation of styrene.

Phosphetanes **9a,b**, as well as **1a,b** or **8a–d**, are chemically similar but stereochemically distinct compounds of known stereochemistry, having both a chiral phosphorus center and an asymmetric carbon framework. Thus, the results of Table 4 suggest some preliminary conclusions concerning the "cooperativity" between chiral centers[17] with respect to asymmetric induction.

In the hydrosilylation of cyclopentadiene, the *S* enantiomer is mostly favored; the enantioselectivity should be ascribed essentially to the presence of the chiral menthyl group bound to the phosphetane moiety. Nevertheless, regular trends of complementary and opposed effects between the menthyl group and the chiral phosphorus are observed: the phosphetane **9a** (P(*S*), entry 1 in Table 4) and its substituted derivatives (P(*R*) series) give systematically better ee values than the opposite epimers, **9b** (P(*R*)) and its derivatives (P(*S*) series). The effect is more pronounced in the substituted derivatives than in the parent compounds and becomes very important in the acetal series.

(17) Chiral cooperativity has been investigated recently in the case of chiral bis(phosphines) and ferrocenylphosphines: Burgess, K.; Ohlmeyer, M. J.; Whitmire, K. H. *Organometallics* **1992**, *11*, 3588. Nagel, V.; Krink, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1052. Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. Pastor, S. D.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 905. Hayashi, T.; Konishi, M.; Fukushima, M.; Mise T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

The chiral acetal segment has an additional influence on asymmetric induction which may be sufficient to override the effect of the menthyl substituent and to reverse the optical induction. While remembering that chirality is an attribute of the molecule as a whole, it appears that the individual chiral segments—menthyl on one side and the substituted phosphetane on the other—act in a cooperative manner for the P(*R*)C(*R*)-(*R*,*R*) acetal **8a** and in opposition for the P(*S*)C(*S*)(*S*,*S*) configuration. On the basis of qualitative steric criteria we might say that the menthyl group effect largely predominates in the α-unsubstituted phosphetanes **3a,b** but it may be either diminished or reinforced when the other segment reaches a comparable size. More accurate molecular modeling studies should allow rationalization of these experimental data.

In summary, this work confirms that mono(phosphines) play a key role in the Pd-catalyzed hydrosilylation of olefins. It shows that epimeric phosphetane ligands may have dramatically different behavior with respect to both catalytic activity and enantioselectivity. The enantiomeric excesses are still unsatisfactory but nonetheless comparable with those obtained by the most effective phosphines known at present. The flexible synthetic method developed here offers a simple way to create an appropriate sequence of chiral centers and will hopefully lead to the synthesis of new, more efficient phosphetane ligands.

Experimental Section

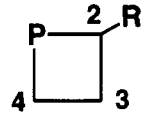
All reactions were carried out under argon in dry solvents. Neutral aluminum oxide was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Mass spectra were obtained at 70 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. The presence of the menthyl group bound to phosphorus made the complete assignment of the NMR signals (^{1}H and ^{13}C) somewhat difficult; only selected NMR data are assigned and reported here.

Phosphetanes **1a,b** and **9a,b** as well as the phosphetane oxides **5a,b** have been prepared according to previously published procedures,[3] starting from (L-menthyl)PCl_2.

Preparation of [(COD)Ir(4-benzyl-1-menthyl-2,2,3,3-tetramethylphosphetane)$_2$]$^+PF_6^-$. To a solution of (R_p,S_c)-4-benzyl-1-menthyl-2,2,3,3-tetramethylphosphetane (**1a**; 90 mg, 0.25 mmol) in CH_2Cl_2 (4 mL) was added $Ir_2Cl_2(COD)_2$ (84 mg, 0.13 mmol). After about 10 min, ammonium hexafluorophosphate (40 mg, 0.25 mmol) was added at room temperature. The solvent was partly removed by evaporation. After addition of pentane (5 mL), the solid AgCl was filtered off, the filtrate evaporated, and the residue dissolved in dichloromethane. Addition of methanol causes crystallization of the final product as an orange solid (225 mg, 88% yield). Recrystallization from a CH_2Cl_2/benzene mixture was eventually performed. Characterization data are as follows: orange solid; mp 180 °C; ^{31}P NMR (C_6D_6) δ 60.1 (broad spectrum); ^{1}H NMR (C_6D_6) δ 0.42 (s, Me), 0.43 (d, $^3J_{HH}$ = 6.7 Hz, Me), 0.91–1.07 (3 Me), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, Me), 1.49 (s, Me), 3.0 (m), 4.0 (m, CH_2Ph), 5.14 and 5.30 (m, CH=CH (cyclooctadiene)), 7.0–7.2 (m, Ph); ^{1}H NMR and ^{13}C NMR are broad, poorly resolved spectra. Anal. Calcd for $C_{56}H_{90}IrP_3F_6{\cdot}CH_2Cl_2$: C, 54.88; H, 7.43. Found: C, 54.99; H, 7.43.

General Procedure for the Hydrogenation Reactions. Hydrogenations were carried out in a constant-volume autoclave (100 mL). Hydrogen was used as received from the suppliers. The substrate (2 mmol) and the catalyst precursors

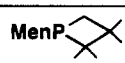
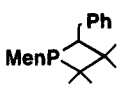
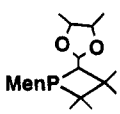
Table 3. Selected ^{13}C NMR Data[a] for Compounds 6–8



compd	C(2)H	C(3)	C(4)	CHO	CH(O–)$_2$	CH(Me)O–
6a	62.4 [39.0][b]	42.2 [17.0]	49.6 [56.0]	198.2 [5.6]		
6b	64.2 [37.0]	44.3 [16.7]	48.4 [60.6]	198.3 [4.6]		
7a	53.6 [48.6]	40.7 [13.6]	48.5 [55.4]		99.9	79.4, 78.3
7b	53.9 [49.3]	40.8 [13.7]	48.4 [56.0]		100.2	79.5, 77.9
7c	55.3 [46.7]	41.7 [13.8]	48.0 [57.9]		100.4	79.4, 78.2
7d	55.0 [45.6]	41.8 [14.8]	47.9 [57.7]		100.1	79.4, 77.8
8a	43.4[c] [–]	41.7 [4.4][d]	36.8 [3.0][d]		104.5 [23.1]	79.4, 78.3
8b	43.7 [–]	41.7 [4.5]	36.6 [4.4]		104.5 [22.1]	79.6, 77.6
8c	45.1 [6.1]	42.9 [3.5]	36.6 [6.2]		105.0 [22.5]	79.4, 78.0
8d	44.7 [6.3]	43.0 [4.4]	36.8 [6.2]		104.6 [22.2]	79.6, 77.8

[a] Spectra measured in C_6D_6: chemical shifts in ppm; coupling constants in hertz. [b] J_{CP} coupling constants in brackets. [c] Tentatively assigned. [d] C(3)/C(4) chemical shifts may be reversed.

Table 4. Asymmetric Hydrosilylation of Cyclopentadiene and Styrene Catalyzed by $Cl_2Pd(PhCN)_2$–L (1:1)

entry no.	ligand		cyclopentadiene: reacn conditions	cyclopentadiene: yield, %	cyclopentadiene: ee, % (config)	styrene[a] ee, % (config)
1		**9a** (P(*S*))	40 °C, 20 h	48	55 (*S*)	
2		**9b** (P(*R*))	40 °C, 20 h	30[b]	27 (*S*)	
3		**1a** (P(*R*),C(*S*))	28 °C, 2 h	70	54 (*S*)	18 (*R*)
4		**1b** (P(*S*),C(*R*))	28 °C, 3 h 30 min	49	16 (*S*)	
5		**8a** (P(*R*),C(*R*)(*R*,*R*))	40 °C, 20 h	60	65 (*S*)	24 (*R*)
6		**8b** (P(*R*),C(*R*)(*S*,*S*))	40 °C, 20 h	62	57 (*S*)	22 (*R*)
7		**8c** (P(*S*),C(*S*)(*R*,*R*))	40 °C, 20 h	30[b]	10 (*S*)	10 (*S*)
8		**8d** (P(*S*),C(*S*)(*S*,*S*))	40 °C, 20 h	30[b]	11 (*R*)	3 (*S*)

[a] Conditions: 50 °C, 24 h. All reactions are quantitative according to ^1H NMR analysis of the reaction mixture. Isolated yields are higher than 90%. [b] Approximate yields.

were placed in the autoclave, which was then evacuated and flushed three times with argon. The solvent was added, and hydrogen was pressurized at 3.5 and 2.5 bars, respectively, for the two reactions of Scheme 1. The solution was stirred at room temperature until gas uptake ceased. The degree of conversion was checked by ^1H NMR, after evaporating the solvent. Published procedures[18] were used to remove the catalyst from the mixture and to isolate the hydrogenation products *N*-acetylphenylalanine and *N*-acetylphenylalanine methyl ester, respectively. Optical yields are calculated with respect to the published values for the optically pure compounds.[18]

Synthesis of the Pd(II) Complexes 2. A 100-mg amount of phosphetane **1a** or **1b** (0.28 mmol) was reacted with 54 mg of $Cl_2Pd(PhCN)_2$ (0.14 mmol) in 3 mL of benzene at room temperature. The reaction was complete after a few minutes, according to ^{31}P NMR analysis of the mixture. The solvent was evaporated under reduced pressure, and 5 mL of pentane was added to the residue. After filtration, the yellow solution was concentrated. Orange crystals separated after keeping the solution at –20 °C overnight.

Spectroscopic characterization of complex **2a** has been reported.[8]

2b: yield 0.18 g (73%); orange crystals; mp 240 °C; ^1H NMR (C_6D_6) δ 0.39 (s, Me), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, Me), 1.06 (d, $^3J_{HH}$ = 5.7 Hz, Me), 1.14–1.17 (2 Me), 1.63 (t, $^3J_{HP}$ = 7.7 Hz, Me), 1.95 (s, Me), 3.08 (m, PC*H*CH$_2$Ph), 3.59 (m, *AB*, $^2J_{AB} \simeq 3J_{HH}$ = 10.9 Hz, $^3J_{HP} \simeq$ 3 Hz, 1H, *CH*$_2$Ph), 3.85 (m, *AB*, $^3J_{HH}$ = 3.7 Hz, $^3J_{HP}$ unresolved, 1H, C*H*$_2$Ph), 7.0–7.2 (m, Ph); ^{13}C NMR (C_6D_6) δ 16.5 (Me), 21.5 (Me), 22.6 (J_{CP} = 3.9 Hz, Me), 23.0 (Me), 23.1 (Me), 24.2 (Me), 24.2 (t, J_{CP} = 8.8 Hz, Me), 25.6 (t, J_{CP} = 4.7 Hz, CH_2), 30.1 (CH), 33.9 (t, J_{CP} = 5.9 Hz, CH), 34.4 (CH_2), 35.6 (CH_2), 41.0 (CH_2), 45.1 (CH), 46.1 (CH), 46.7 (*C*), 49.0 (t, J_{CP} = 14.9 Hz, P*C*Me$_2$), 52.1 (t, J_{CP} = 11.2 Hz, CH), 126.0 (CH (Ph)), 129.1 (CH (Ph)), 142.7 (t, J_{CP} = 6.0 Hz, *C* (Ph)) ppm; $[\alpha]_D$ = –89° (*c* = 0.2, $CHCl_3$). Anal. Calcd for $C_{48}H_{78}Cl_2P_2Pd$: C, 64.46; H, 8.79. Found: C, 64.81; H, 9.16.

Synthesis of the α-Formylphosphetane Oxides 6. nBuLi (1.92 mL, 1.6 M solution in hexane, 3.0 mmol) was added to a THF solution of 1-methyl-2,2,3,3-tetramethylphosphetane oxide (**5a**; 0.80 g, 2.8 mmol) at –70 °C. After a few minutes 0.30 mL (3.8 mmol) of *N*,*N*-dimethylformamide was added. After 10 min at –70 °C the reaction mixture was warmed to 0 °C, hydrolyzed with 3 N HCl (2 mL), and warmed to room temperature. After extraction with ether, the organic phase was dried over $MgSO_4$ and evaporated and the residue recrystallized from pentane. Yield of **6a**: 0.36 g, 40%.

The synthesis of the phosphetane oxide **6b** followed the same procedure, except for the use of a 1:1 nBuLi–LiN(TMS)$_2$ mixture as the metalating agent for **5b**. Yield of **6b**: 0.40 g, 45% after crystallization from pentane.

6a: colorless solid; mp 160 °C; ^1H NMR (C_6D_6) δ 0.64–0.73 (3 Me), 0.84 (d, $^3J_{HH}$ = 6.2 Hz, Me), 0.99 (d, $^3J_{HH}$ = 6.7 Hz, Me), 1.03 (d, $^3J_{HP}$ = 17.6 Hz, PCMe), 1.49 (s, Me); ^{13}C NMR (C_6D_6) δ 16.7 (d, J_{CP} = 4.2 Hz, Me), 17.2 (Me), 20.8 (Me), 22.0 (Me), 22.4 (Me), 23.2 (Me), 24.3 (d, J_{CP} = 11.0 Hz, CH_2), 25.0 (d, J_{CP} = 19.3 Hz, Me), 31.2 (d, J_{CP} = 3.7 Hz, CH), 33.2 (d, J_{CP} = 12.4 Hz, CH), 33.6 (d, J_{CP} = 2.0 Hz, CH_2), 34.1 (CH_2), 40.9 (CH), 41.1 (d, J_{CP} = 43.2, CH) ppm; $[\alpha]_D$ = –218° (*c* = 1, $CHCl_3$). Anal. Calcd for $C_{18}H_{33}O_2P$: C, 69.20; H, 10.65. Found: C, 69.15; H, 10.55.

6b: colorless solid; mp 134 °C; ^1H NMR (C_6D_6) δ 0.66 (s, Me), 0.77 (d, $^3J_{HH}$ = 6.5 Hz, Me), 0.78 (d, $^3J_{HP}$ = 17.5 Hz, PC*Me*), 0.80 (d, $^3J_{HH}$ = 6.6 Hz, Me), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, Me), 1.07 (d, $^3J_{HP}$ = 16.8 Hz, PC*Me*), 1.46 (s, Me); ^{13}C NMR (C_6D_6) δ 15.8 (Me), 17.6 (d, J_{CP} = 5.1 Hz, Me), 20.4 (Me), 21.5 (Me), 22.6 (Me), 23.2 (Me), 24.4 (d, J_{CP} = 10.8 Hz, CH_2), 24.9

(18) Kagan, H.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.

(d, J_{CP} = 19.2 Hz, Me), 29.3 (d, J_{CP} = 4.1 Hz, CH), 32.9 (d, J_{CP} = 12.7 Hz, CH), 34.5 (CH_2), 34.6 (d, J_{CP} = 2.8 Hz, CH_2), 42.4 (CH), 42.9 (d, J_{CP} = 38.4 Hz, CH); mass spectrum *m/e* 312 (M, 4%), 283 (M − CHO, 40%), 228 (M − C_2Me_4, 100%); Anal. Calcd for $C_{18}H_{33}O_2P$: C, 69.20; H, 10.65. Found: C, 69.3; H, 10.68. $[\alpha]_D$ = +92° (*c* = 1, $CHCl_3$).

General Procedure for the Synthesis of the Phosphetane Oxides 7. A solution of **6** (0.3 g 0.96 mmol), (*R*)-(−)-1,3-butanediol (or the corresponding *S* enantiomer; 0.10 mL, 1.1 mmol), and *p*-toluenesulfonic acid (catalytic amount) in benzene was heated to 70 °C for about 6 h. The progress of the reaction was monitored by ^{31}P NMR of the reaction mixture. Molecular sieves or $MgSO_4$ was eventually added in order to remove water. The final product was purified by chromatography on alumina with a hexane−ether gradient (from 90:10 to 100% ether; R_f 0.3 in ether) and crystallized from an ether−hexane mixture.

7a was obtained from **6a** and the *R* diol in 89% yield (0.33 g): colorless solid; mp 186 °C; ^1H NMR (C_6D_6) δ 0.75 (d, $^3J_{HH}$ = 6.8 Hz, Me), 0.88 (d, $^3J_{HP}$ = 17.8 Hz, PCMe), 0.91 (d, $^3J_{HH}$ = 6.4 Hz, Me), ..., 1.60 (s, Me); ^{13}C NMR (C_6D_6) δ 16.9 (d, J_{CP} = 4.0 Hz, Me), 17.1 (Me), 17.3 (Me), 17.5 (Me), 21.6 (Me), 22.2 (Me), 22.3 (Me), 22.7 (Me), 24.6 (d, J_{CP} = 10.8 Hz, CH_2) 25.3 (d, J_{CP} = 21.0 Hz, Me), 30.8 (d, J_{CP} = 2.5 Hz, CH), 33.6 (d, J_{CP} = 12.4, CH), 34.4 (CH_2), 34.9 (CH_2), 39.9 (d, J_{CP} = 43.7 Hz, CH), 41.2 (CH); mass spectrum *m/e* 384 (M, 10%), 301 (M − C_2Me_4 + 1, 100%); $[\alpha]_D$ = −81° (*c* = 1, $CHCl_3$). Anal. Calcd for $C_{22}H_{41}O_3P$: C, 68.72; H, 10.75. Found: C, 68.66; H, 10.55.

7b was obtained from **6a** and the *S* diol in 81% yield (0.30 g): colorless solid; mp 197 °C; ^1H NMR (C_6D_6) δ 0.76 (d, $^3J_{HH}$ = 6.8 Hz, Me), 0.89 (d, $^3J_{HP}$ = 18.0 Hz, PCMe), ..., 1.60 (s, Me); ^{13}C NMR (C_6D_6) δ 16.9 (d, J_{CP} = 4.0 Hz, Me), 17.1, 17.3, 21.6 (Me), 22.2 (2 Me), 22.7 (Me), 24.6 (d, J_{CP} = 11.3 Hz, CH_2), 25.3 (d, J_{CP} = 21.2 Hz, Me), 30.8 (d, J_{CP} = 3.8 Hz, CH), 33.5 (d, J_{CP} = 13.0 Hz, CH), 34.3 (CH_2), 34.8 (CH_2), 39.8 (d, J_{CP} = 44.0 Hz, CH), 41.1 (d, J_{CP} = 2.1 Hz, CH); $[\alpha]_D$ = −52° (*c* = 1, $CHCl_3$). Anal. Calcd for $C_{22}H_{41}O_3P$: C, 68.72; H, 10.75. Found: C, 68.99; H, 10.74.

7c was obtained from **6b** and the *R* diol in 75% yield (0.28 g): colorless solid; ^1H NMR (C_6D_6) δ 0.85 (d, J_{HH} = 6.4 Hz, Me), 0.91 (d, J_{HH} = 6.8 Hz, Me), ..., 1.18 (d, $^3J_{HP}$ = 16.0 Hz, PCMe), 1.61 (s, Me); ^{13}C NMR (C_6D_6) δ 16.4 (Me), 17.0 (Me), 17.2 (Me), 18.0 (d, J_{CP} = 4.4 Hz, Me), 21.0 (Me), 21.8 (Me), 22.0 (Me), 22.8 (Me), 25.0 (d, J_{CP} = 10.9 Hz, CH_2), 25.4 (d, J_{CP} = 21.3 Hz, Me), 28.9 (d, J_{CP} = 4.2 Hz, CH), 33.2 (d, J_{CP} = 10.8 Hz, CH), 34.7 (CH_2), 36.2 (CH_2), 42.5 (d, J_{CP} = 3.3 Hz, CH), 44.6 (d, J_{CP} = 42.0 Hz, CH).

7d was obtained from **6b** and the *S* diol in 78% yield (0.29 g): colorless solid; mp 127 °C; ^1H NMR (C_6D_6) δ 0.8−1.1 (7 Me), 1.18 (d, $^3J_{HP}$ = 16.0 Hz, PCMe), 1.62 (s, Me); ^{13}C NMR (C_6D_6) δ 16.3 (Me), 17.1 (Me), 17.4 (Me), 18.0 (d, J_{CP} = 4.5 Hz, Me), 21.1 (Me), 22.2 (Me), 22.9 (Me), 25.0 (d, J_{CP} = 11.0 Hz, CH_2), 25.3 (d, J_{CP} = 21.6 Hz, Me), 28.6 (d, J_{CP} = 3.2 Hz, CH), 33.2 (d, J_{CP} = 12.3 Hz, CH), 34.7 (CH_2), 36.2 (CH_2), 42.4 (d, J_{CP} = 3.3 Hz, CH), 44.4 (d, J_{CP} = 41.9 Hz, CH); $[\alpha]_D$ = −7° (*c* = 1, $CHCl_3$). Anal. Calcd for $C_{22}H_{41}O_3P$: C, 68.72; H, 10.75. Found: C, 69.01; H, 10.84.

Reduction Procedure (Scheme 6). The phosphetane oxide **7** (0.5 mmol) was dissolved in dry benzene (5 mL), and triethylamine (1 mmol, 0.14 mL) was added. The mixture was heated with trichlorosilane (1 mmol, 0.1 mL). The solution was monitored by ^{31}P NMR; reaction times vary between 1 h (for **7c**) and 3 h (for **7d**). The solution was then cooled to 5 °C, and 20% aqueous sodium hydroxide solution (1 mL) was added dropwise. The organic layer was directly chromatographed on a short alumina column with hexane−ether (95:5) as eluent, under argon. All reductions are quantitative according to ^{31}P NMR analysis of the crude reactions mixtures. Yields ranging from 60% to 89% were obtained after chromatography.

8a: yield 0.17 g (89%); colorless solid; ^1H NMR (C_6D_6) δ 0.77 (d, $^3J_{HH}$ = 6.8 Hz, Me), 0.9−1.2 (7 Me), 1.45 (s, Me); ^{13}C NMR (C_6D_6) δ 16.8 (Me), 17.1 (Me), 17.6 (Me), 22.4 (d, J_{CP} = 10.6 Hz, Me), 22.6 (Me), 23.0 (Me), 23.3 (d, J_{CP} = 4.9 Hz, Me), 23.8 (d, J_{CP} = 23.8 Hz, Me), 25.5 (d, J_{CP} = 10.5 Hz, CH_2), 26.0 (d, J_{CP} = 6.0 Hz, Me), 30.2 (d, J_{CP} = 14.6 Hz, CH), 34.1 (d, J_{CP} = 6.0 Hz, CH), 35.3 (CH_2), 35.9 (d, J_{CP} = 30.3 Hz, CH), 38.1 (d, J_{CP} = 5.2 Hz, CH_2), 48.8 (d, J_{CP} = 24.3 Hz, CH); mass spectrum *m/e* 353 (M − Me, 10%), 311 (M − C_4H_9, 71%), 212 (MenP=CMe_2, 100%); $[\alpha]_D$ = −189° (*c* = 0.8, benzene).

8b: yield 0.15 g (79%); colorless solid; ^1H NMR (C_6D_6) δ 0.77 (d, $^3J_{HH}$ = 6.8 Hz, Me), 0.9−1.2 (7 Me), 1.43 (s, Me); ^{13}C NMR (C_6D_6) δ 16.8 (Me), 17.1 (2 Me), 22.4 (d, J_{CP} = 10.5 Hz, Me), 22.6 (Me), 23.0 (Me), 23.3 (d, J_{CP} = 4.5 Hz, Me), 23.9 (d, J_{CP} = 23.2 Hz, Me), 25.5 (d, J_{CP} = 10.4 Hz, CH_2), 25.9 (d, J_{CP} = 5.8 Hz, Me), 30.1 (d, J_{CP} = 13.9 Hz, CH), 34.0 (d, J_{CP} = 5.9 Hz, CH), 35.2 (CH_2), 35.8 (d, J_{CP} = 30.6 Hz, CH), 38.2 (d, J_{CP} = 4.6 Hz, CH_2), 48.8 (d, J_{CP} = 24.2 Hz, CH); $[\alpha]_D$ = −148° (*c* = 0.8, benzene).

8c: yield 0.12 g (66%); colorless solid; ^1H NMR (C_6D_6) δ 0.8−1.1 (6 Me), 1.15 (d, J_{HP} = 14.7 Hz, Me), 1.26 (d, J_{HP} = 4.2 Hz, Me), 1.46 (Me); ^{13}C NMR (C_6D_6) δ 16.4 (Me), 16.9 (Me), 17.2 (Me), 21.8 (d, J_{CP} = 4.6 Hz, Me), 22.1 (d, J_{CP} = 10.7 Hz, Me), 22.1 (Me), 23.0 (Me), 25.3 (d, J_{CP} = 23.4 Hz, Me), 25.3 (d, J_{CP} = 6.7 Hz, CH_2), 25.7 (d, J_{CP} = 6.0 Hz, Me), 28.8 (d, J_{CP} = 6.2 Hz, CH), 33.2 (d, J_{CP} = 10.8 Hz, CH), 35.3 (CH_2), 39.1 (d, J_{CP} = 34.0 Hz, CH), 39.7 (d, J_{CP} = 17.0 Hz, CH_2), 47.2 (d, J_{CP} = 10.7 Hz, CH); $[\alpha]_D$ = −53° (*c* = 0.8, benzene).

8d: yield 0.11 g (60%); colorless solid; ^1H NMR (C_6D_6) δ 0.8−1.2 (7 Me), 1.25 (d, J_{HP} = 4.2 Hz, Me), 1.46 (s, Me), 2.1 (m, 1H), 2.45 (m, C*H*Me_2); ^{13}C NMR (C_6D_6) δ 16.5 (Me), 17.1 (Me), 17.7 (Me), 21.9 (d, J_{CP} = 5.1 Hz, Me), 22.2 (d, J_{CP} = 10.8 Hz, Me), 22.2 (Me), 23.1 (Me), 25.3 (d, J_{CP} = 25.3 Hz, Me), 25.5 (d, J_{CP} = 7.1 Hz, CH_2), 25.7 (d, J_{CP} = 6.1 Hz, Me), 28.6 (d, J_{CP} = 6.4 Hz, CH), 33.3 (d, J_{CP} = 10.7 Hz, CH), 35.3 (CH_2), 39.1 (d, J_{CP} = 33.7 Hz, CH), 39.8 (d, J_{CP} = 17.8 Hz, CH_2), 47.2 (d, J_{CP} = 10.7 Hz, CH); $[\alpha]_D$ = −15° (*c* = 0.8, benzene).

General Procedure for the Hydrosilylation Reactions (Scheme 3). Most of the reactions were carried out in sealed glass ampules, under argon. In a typical run a glass ampule containing the catalyst (5×10^{-3} mmol) was cooled to 0 °C. The substrate (16 mmol) and $HSiCl_3$ (18 mmol) were added successively. Reaction times and temperatures are given in Tables 1 and 4. For reactions in Table 4 the catalysts were prepared as follows. A solution of phosphetane (5×10^{-3} mmol) in 0.5 mL of CH_2Cl_2 was added dropwise over 20 min to a stirred solution of $Cl_2Pd(PhCN)_2$ (2.0 mg, 5×10^{-3} mmol) in 0.6 mL of CH_2Cl_2, at room temperature. After 1 h, the solvent was evaporated under vacuum and the crude product was used as the catalyst.

(a) Cyclopentadiene. Freshly distilled cyclopentadiene was used. 2-Cyclopentenyltrichlorosilane was purified by distillation at 90−100 °C under vacuum (20 mm Hg) in a kugelrohr apparatus. The distilled product was added to a cooled (0 °C) solution containing EtOH (6 mL) and Et_3N (6 mL) in 40 mL of dry ether. The reaction mixture was warmed to room temperature for about 1 h, and the resulting ammonium salt was filtered. The ether solution was evaporated and the final product, **3**, isolated by distillation (about 150 °C, 20 mmHg).

(b) Styrene. (1-Phenylethyl)trichlorosilane was isolated by distillation at 170 °C (20 mmHg) in a Kugelrohr apparatus. The distilled product was added to a large excess of methylmagnesium bromide (3 M solution in ether, 26 mL) at 0 °C. The mixture was then refluxed for 3 h and stirred at room temperature overnight. Hydrolysis of the excess Grignard reagent was performed by careful addition of aqueous NH_4Cl at 0 °C. The organic layer was separated and dried over magnesium sulfate, and the final product, **4**, was purified by distillation at 110−120 °C (20 mmHg) in a Kugelrohr apparatus.

X-ray Structure Determination for 2b. Crystals of $C_{48}H_{78}Cl_2P_2Pd$ (**2b**) were grown from a solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf-

Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P2_12_12_1$ (No. 19), with a = 13.070(1) Å, b = 19.218(1) Å, c = 19.270(2) Å, V = 4840.4(1.4) Å^3, Z = 4, d_{calc} = 1.227 g/cm^3, μ = 5.8 cm^{-1}, and $F(000)$ = 1904. A total of 5843 unique reflections were recorded in the range $2° \leq 2\theta \leq 54.0°$, of which 3172 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 2671 for solution and refinement. Direct methods yielded a solution for the chlorine and phosphorus atoms. 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 = 0.050, R_w = 0.063, and GOF = 1.10.

Supplementary Material Available: An ORTEP drawing of **2b** giving the complete numbering scheme and tables of X-ray crystal data and experimental details, positional and thermal parameters, and bond distances and angles for **2b** (9 pages). Ordering information is given on any current masthead page.

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