Articles

PH-Functional Phosphines with 1,1′-Biphenyl-2,2′-bis(methylene) and 1,1′-Binaphthyl-2,2′-bis(methylene) Backbones

Frank Bitterer,[†] Oliver Herd,[†] Michael Kühnel,[†] Othmar Stelzer,*[,†] Norbert Weferling,[‡] William S. Sheldrick,[§] Jutta Hahn,[||] Sabine Nagel,[||] and Notker Rösch[||]

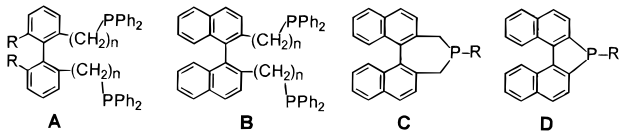
Fachbereich 9, Anorganische Chemie, Bergische Universität-GH Wuppertal, D-42097 Wuppertal, Germany, Clariant GmbH, Werk Knapsack, D-50351 Hürth-Knapsack, Germany, Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany, and Lehrstuhl für Theoretische Chemie, Technische Universität München, D-85747 Garching, Germany

Received March 26, 1998

The first PH-functional phosphines (**1**, **3**, and **5**) containing the 1,1′-binaphthyl-2,2′-bis(methylene) or 1,1′-biphenyl-2,2′-bis(methylene) backbone have been obtained by two-phase phosphination of 2,2′-bis(halomethyl)-1,1′-binaphthyls with PH_3 or in a protected-group synthesis using $P(SiMe_3)_3$ as the starting material. The 4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine (**1**) is configurationally stable, as indicated by the inequivalence of the two CH_2 and naphthyl substituents in the $^{13}C\{^1H\}$ NMR spectra. The X-ray crystal structure of **1**·0.5$C_6H_5CH_3$ shows an intracyclic C−P−C angle of 99.5(2)°, the interplanar angle of the phosphepine ring system being 67.6(5)°. The borane adduct **7** of the secondary phosphine **1** has been employed for the syntheses of atropisomeric mono- and bidentate ligands (**8**−**14**) with the bulky 1,1′-binaphthyl moieties. Results of force field calculations on the conformations of **1**, **3**, and **14** are presented. The ability of these phosphines to form mononuclear and polynuclear complexes with transition-metal centers is discussed. Compound **14** exhibits a large variety of low-energy conformations, and some of them seem to be capable of forming mononuclear transition-metal complexes.

Introduction

Axially disymmetric phosphine ligands, e.g., **A**, **B**,[1−3] **C**,[4] and **D**,[5a] containing the 1,1′-biphenyl or binaphthyl moieties have been extensively employed as chiral auxiliaries for asymmetric syntheses.[6] Ru(II), Pt(II), and Rh(I) complexes of type **A**, **B**, and **C** ligands are highly active enantioselective catalysts for hydrogenation and hydroformylation[7,8] of olefins. With one single exception (**D**, R = H),[5b] only tertiary phosphines containing the 1,1′-binaphthyl backbone have been reported so far in the literature.



PH-functional derivatives of **A**−**D** are of special interest, however, as starting materials and building blocks for the tailor-made syntheses of new tertiary phosphines. Their chirality originates from axial asymmetry rather than from stereogenic carbon or phosphorus centers. In the context of a program aimed at the syntheses of ligands specially designed for water-soluble catalysts, our primary interest was directed toward PH-functional derivatives of **A**−**C**. They may be transformed into tailor-made tertiary phosphines with sulfonated aryl groups using either Pd-catalyzed P−C coupling with *p*- or *m*-iodobenzene

[†] Bergische Universität-GH Wuppertal.
[‡] Clariant GmbH.
[§] Ruhr-Universität Bochum.
[||] Technische Universität München.

(1) Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. *Inorg. Chem.* **1990**, *29*, 3376. Herrmann, W. A.; Kohlpaintner, C. W.; Herdtweck, E.; Kiprof, P. *Inorg. Chem.* **1991**, *30*, 4271. Devon, T. J.; Phillips, G. W.; Puckette, T. A.; Stavinoha, J. L.; Vanderbilt, J. J. U.S. Patent 4,694,109, Sept 15, 1987, Eastman Kodak Co. Puckette, T. A.; Devon, T. J.; Phillips, G. W.; Stavinoha, J. L. U.S. Patent 4,879,416, July 11, 1989, Eastman Kodak Co.

(2) Schmid, R.; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Müller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131.

(3) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389. Puckette, T. A. Eur. Pat. 386,105, Oct 31, 1988, Eastman Kodak Co.

(4) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Manassero, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511.

(5) (a) Gladiali, S.; Fabbri, D. *Chem. Ber./Recueil* **1997**, *130*, 543. Watson, A. A.; Willis, A. C.; Wild, S. B. *J. Organomet. Chem.* **1993**, *445*, 71. Tani, K.; Tashiro, H.; Yoshida, M.; Yamagata, T. *J. Organomet. Chem.* **1994**, *469*, 229. (b) Dore, A.; Fabbri, D.; Gladiali, S.; De Lucchi, O. *J. Chem. Soc., Chem. Commun.* **1993**, 1124. Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Valle, G. *J. Org. Chem.* **1994**, *59*, 6363.

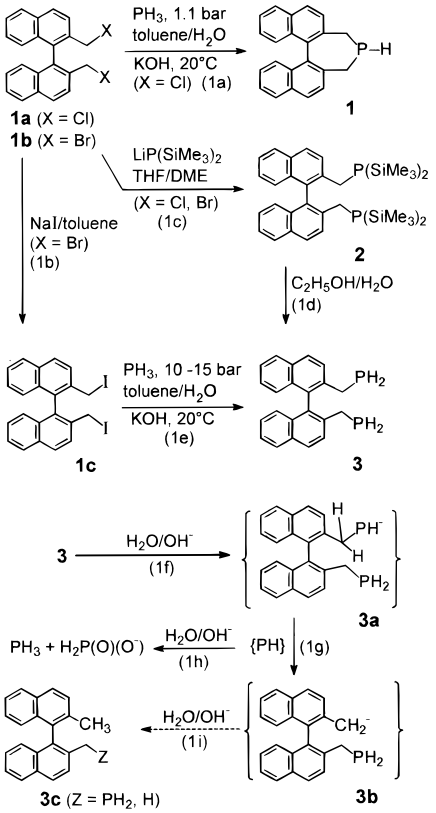
(6) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. Rosini, C.; Franzini, L.; Raffaeli, A.; Salvadori, P. *Synthesis* **1992**, 503.

(7) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3176. Wan, K.; Davis, M. E. *Tetrahedron: Asymmetry* **1993**, *4*, 2461.

(8) Frohning, C. D.; Kohlpaintner, C. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Verlagsgesellschaft mbH: Weinheim, 1996; Vol. 1, p 29. Stille, J. K.; Su, H.; Brechot, P.; Parrinello, G.; Hegedus, L. S. *Organometallics* **1991**, *10*, 1183.

10.1021/ic980346z CCC: $15.00
Published on Web 11/14/1998

Scheme 1

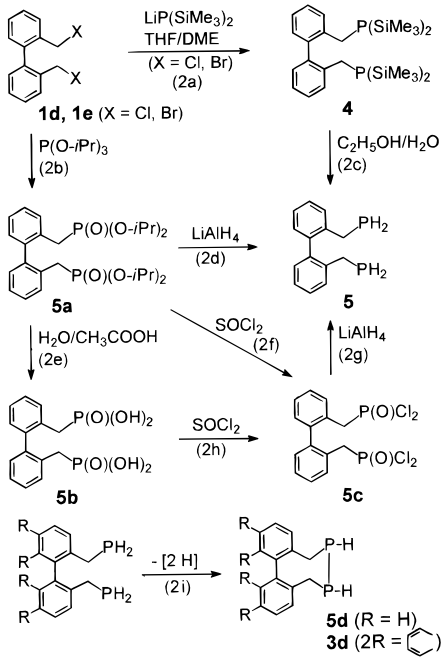


sulfonate or base-assisted reaction with fluorobenzene sulfonates, e.g., FC_6H_4-*p*-SO_3K or FC_6H_3-2,4-$(SO_3K)_2$. These high-yield and selective preparative routes to water-soluble phosphines have been developed by us recently.[9,10]

Results and Discussion

Syntheses of the Ligands 1 and 3. The synthetic procedure which we used first for the preparation of the primary and secondary phosphine with a binaphthyl backbone is based on the two-phase alkylation of PH_3 or primary phosphines in aprotic dipolar solvents such as dimethyl sulfoxide (DMSO). Potassium hydroxide was employed as the base either as a concentrated aqueous solution or as a powdered solid.[10,11] The secondary phosphine **1** was thus obtained in good yields by reaction of the dichloride **1a**[12] with phosphine PH_3 at ca. 1.1 bar in the two-phase system toluene/DMSO/water using concentrated potassium hydroxide solution as the base (eq 1a, Scheme 1). For the preparation of the diprimary phosphine **3**, an increased PH_3 pressure (10−15 bar) has to be used in order to suppress the ring closure reaction leading to the seven-membered ring system in **1**. The concentration of the phosphido anion PH_2^- is increased at higher pressure, favoring the formation of **3**. The 2,2′-bis[iodomethyl]-1,1′-binaphthyl **1c**, prepared by a halogen exchange reaction according to eq 1b, is preferably used instead of the dibromide **1b**.[13] If the phosphination of **1b** or **1c** is run under a low pressure of PH_3, a mixture of the secondary (**1**) and primary (**3**) phosphines is obtained. Inspection of the ^{13}C NMR spectrum of the reaction mixture obtained by high-pressure phosphination according to eq 1e revealed, however, that in addition to **3** the 2,2′-dimethyl-1,1′-binaphthyl (**3c**)[12,13] had been formed in appreciable amounts. Base-catalyzed decomposition of the diprimary phosphine **3** with elimination of phosphinidene {PH}[14] (eqs 1f,g,i), which under the reaction conditions is disproportionated to PH_3 and hypophosphite (eq 1h), may be a plausible way to the methyl and dimethyl derivatives **3c** (Z = H, PH_2).

Scheme 2



The diprimary phosphine **3** was finally obtained in almost pure form by a protective group synthesis using tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$,[15a] as the starting material. Cleavage with *n*BuLi yields the lithium phosphide $LiP(SiMe_3)_2$,[15b] which upon reaction with **1b** gives the silylphosphine **2** (eq 1c). On hydrolytic cleavage of the P−Si bonds in **2**, the diprimary phosphine **3** was formed almost quantitatively (eq 1d). Only very small quantities of the secondary phosphine **1** are obtained as a side product. The synthetic procedure used for **3** can also be employed for the preparation of the 1,1′-biphenyl bridged diprimary phosphine **5**, which is obtained from the intermediate **4** in good yields (eqs 2a,c, Scheme 2). Attempts to prepare **5** alternatively by $LiAlH_4$ reduction of the phosphinyl dichloride **5c** (eq 2g) or the phosphinic ester **5a** (eq 2d) were not successful due to P−C cleavage reactions at the biphenyl-CH_2-P unit leading to side products such as 2-Me-C_6H_4-C_6H_4-2′-CH_2-PH_2

(9) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*, 69. Herd, O.; Hessler, A.; Hingst, M.; Machnitzki, P.; Tepper, M.; Stelzer, O. *Catal. Today* **1998**, *42*, 413.
(10) Bitterer, F.; Herd, O.; Hessler, A.; Kühnel, M.; Rettig, K.; Stelzer, O.; Sheldrick, W. S.; Nagel, S.; Rösch, N. *Inorg. Chem.* **1996**, *35*, 4103. Herd, O.; Langhans, K. P.; Stelzer, O.; Weferling, N.; Sheldrick, W. S. *Angew. Chem., Int. Ed.* **1993**, *32*, 1058. Herd, O.; Hessler, A.; Langhans, K. P.; Stelzer, O.; Sheldrick, W. S.; Weferling, N. *J. Organomet. Chem.* **1994**, *475*, 99.
(11) Langhans, K. P.; Stelzer, O.; Weferling, N. *Chem. Ber.* **1990**, *123*, 995. Stelzer, O.; Langhans, K. P.; Svara, J.; Weferling, N. Eur. Pat. 307,702, Mar 22, 1989; Eur. Pat. 307,717, Mar 22, 1989; U.S. Patent 5,003,108, Mar 26, 1991, Hoechst AG.
(12) Chong, J. M.; MacDonald, G. K.; Park, S. B.; Wilkinson, S. H. *J. Org. Chem.* **1993**, *58*, 1266.
(13) Maigrot, N.; Mazaleyrat, J. P. *Synthesis* **1985**, 317. Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923, 2926.
(14) Mathey, F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; p 33.
(15) (a) Becker, G.; Hölderich, W. *Chem. Ber.* **1975**, *108*, 2484. (b) Fritz, G.; Hölderich, W. *Z. Anorg. Allg. Chem.* **1976**, *422*, 104. Schumann, H.; Rösch, L.; Schmidt-Fritsche, W. *Chem. Ztg.* **1977**, *101*, 156. (c) Maier, L. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, p 1.

Table 1. $^{31}P\{^1H\}$ NMR Data of **1**−**14a**[a,b]

1	−30.55 (188.2)	**10**	−5.81
2	−168.60	**10a**	41.93
3	−129.11 (191.1)	**11**	4.49, 4.16
4	−162.32	**11a**	41.18
5	−125.52 (191.2)	**12**	7.15, 5.45[e]
5a	26.3	**12a**	49.35, 48.23[e]
5b	22.9	**13**	13.97,[e] 13.68 (2.9),[e,f]
5c	44.4		10.34 (2.9),[e,f] 11.63[e]
6	53.15 (349.4)	**13a**	49.66,[e] 51.22, 51.6,[e] 51.87[e]
7	21.17	**14**	10.86, 9.97, 8.83, 8.66[e]
8	9.76 (30.0),[c] −11.66 (30.0)[d]	**14a**	50.86,[e] 50.11, 49.67,[e] 49.19[e]
9	6.31		
9a	48.69		

[a] Chemical shift δP relative to H_3PO_4 (85%); coupling constants ^1J(PH) in hertz in parentheses. [b] Solvents: CD_2Cl_2 (**1**−**5**, **8**, **10a**, **12**−**14**), $CDCl_3$ (**5a**,**c**, **6**, **9a**, **11**, **11a**, **13a**), C_6D_6 (**7**, **9**, **10**, **14a**), DMSO (**5b**). [c] P ring. [d] PPh_2. [e] Diastereoisomers. [f] ^7J(PP).

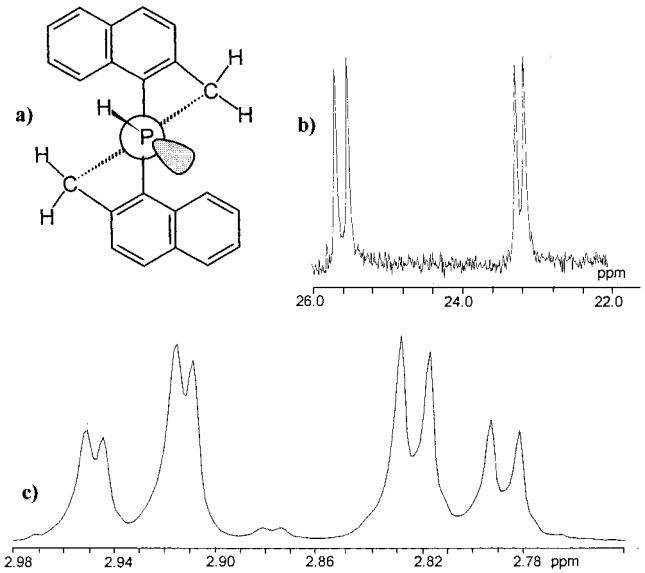
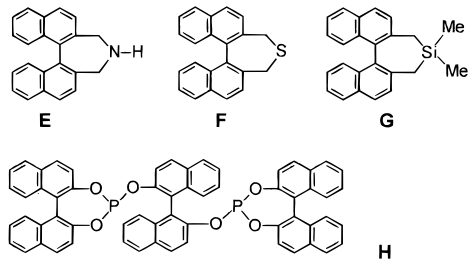


Figure 1. (a) Conformation of **1**, top view. (b) $^{13}C\{^1H\}$ NMR spectrum of **1** (CH_2 groups). (c) ^1H NMR spectrum of **4** (CH_2 groups).

or 2-Me-C_6H_4-C_6H_4-2′-Me,[16] as indicated by resonances at δC = 20.25 and 19.90 ppm in the $^{13}C\{^1H\}$ NMR spectrum of the reaction products (cf. δC = 19.8 ppm for 2-Me-C_6H_4-C_6H_4-2′-Me).[16] The bifunctional phosphonic ester **5a** may be obtained in a straightforward manner by an Arbusov reaction between P(O*i*Pr)$_3$ and **1d** (eq 2b). Treatment of **5a** or **5b** (obtained by hydrolysis of **5a** (eq 2e)) with thionyl chloride yields **5c** (eqs 2f,h).

In the $^{31}P\{^1H\}$ NMR spectra, **1** (δ = −30.55 ppm), **3** (δ = −128.89 ppm), and **2** (δ = −168.68 ppm) exhibit singlets in a δ range typical for secondary and primary phosphines[17a] or silylphosphines of the type $RP(SiMe_3)_2$,[17a] respectively (Table 1). Under proton coupling, the resonances of **1** and **3** are split by PH coupling. Although for **1** a doublet is observed (^1J(PH) = 192.0 Hz), **3** shows a triplet (^1J(PH) = 195.3 Hz). Ten signals should be expected in the $^{13}C\{^1H\}$ NMR spectrum for an isolated α,β-substituted naphthyl moiety, four of which are due to quaternary carbon atoms.[17b] This is true for **2** and **3**, for which four resonances in the $^{13}C\{^1H\}$ NMR spectra could be assigned to quaternary carbon resonances by DEPT experiments.[18] On formation of **1**, however, the C_2 symmetry of the 1,1′-binaphthalene-2,2′-bis(methylene) backbone is lost. The two naphthyl systems are inequivalent now (Figure 1a), as indicated by the increased number of $^{13}C\{^1H\}$ NMR resonances for quaternary and hydrogen-bearing aromatic carbon atoms. According to this, the two CH_2 groups of **1** are diastereotopic, two doublets (δC = 25.5, 23.1 ppm; ^1J(PC) = 17.3, 12.2 Hz) being observed in the $^{13}C\{^1H\}$ NMR spectrum (Figure 1b). The hydrogen atoms of the CH_2 groups of **1** represent the AB and CD parts of an ABCDMX spectrum (A, B = $^1H(CH_2)_a$; C, D = $^1H(CH_2)_b$; M = ^1H; X = ^{31}P) appearing as a complicated line pattern in the ^1H NMR spectrum. A similar result has been reported for the Ph derivative of **1**.[4]

However, in the case of the nitrogen (**E**) and the sulfur (**F**)[19a,b] analogues of **1** and **G**,[19c] the line pattern of only one AB spin



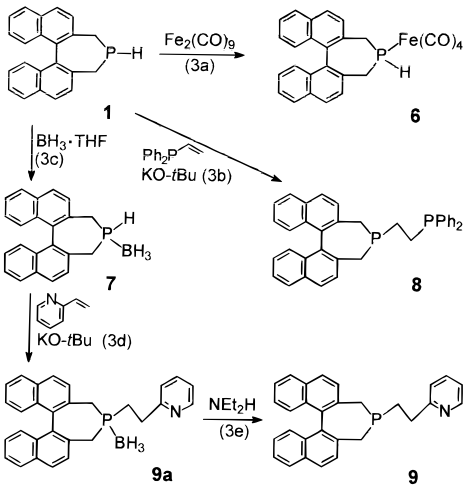
system is observed in the ^1H NMR spectra for the CH_2 groups. This indicates that in contrast to its nitrogen analogue, for which a rapid inversion of configuration at the heteroatom has to be assumed, the secondary phosphine **1** is configurationally stable on the NMR time scale. Also, no configurational change at the central C−C bond has to be taken into account. In the case of **C** (R = Ph), the enantiomeric atropisomers could be separated. The related dinaphtho[2,1-*b*:1′,2′-*d*]phospholes (**D**) are fluxional,[5a,b] the energy barrier for the interconversion of the atropisomeric conformers being 55−60 kJ/mol.

For the diprimary phosphines **3** and **5** and their silyl derivatives **2** and **4**, respectively, only one doublet is observed for the CH_2 groups in the $^{13}C\{^1H\}$ NMR spectra [δC (^1J(PC), Hz): **2**, 19.92 (11.1); **3**, 19.15 (11.1); **4**, 18.32 (11.0); **5**, 18.29 (11.2)]. Under proton coupling, the resonances are split into triplets [^1J(CH), Hz: **2**, ca. 130; **3**, 131.9; **4**, 131.8; **5**, 131.0] with additional fine structure [^3J(C−C═C−H) and ^2J(C−P−H)]. While **3** and **5** show complicated patterns in the ^1H NMR spectra for the CH_2 groups (AB parts of ABMNX spectra; A, B = $^1H(CH_2)$; N, M = $^1H(PH_2)$; X = ^{31}P), for **2** and **4** (Figure 1c), much simpler spectra are observed (AB parts of ABX spin systems).

The syntheses of the diprimary phosphines **3** and **5** obtained according to eqs 1c,d or 2a,c, respectively, are accompanied by the formation of variable but small quantities of side products, which may be assigned to the diphosphine **3d** or **5d**, respectively (eq 2i). In the $^{31}P\{^1H\}$ NMR spectra, they show singlets at δ = −79.4 or −75 ppm, respectively. Under proton coupling, complex line patterns (spin system $[ABMX]_2$; A, B = $H(CH_2)$; M = H(P); X = P) are observed. Analysis as AA′XX′ spin systems (A, A′ = P; X, X′ = H(PH)), neglecting the fine

(16) Fuji, K.; Yamada, T.; Fujita, E. *Org. Magn. Reson.* **1981**, *4*, 250.
(17) (a) Berger, S.; Braun, S.; Kalinowski, H. O. *NMR*−*Spektroskopie von Nichtmetallen*; Georg Thieme Verlag: Stuttgart, 1993; Vol 3. (b) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984.
(18) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed.* **1988**, *27*, 490. Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, New York, Toronto, 1987.
(19) (a) Hawkins, J. M.; Fu, G. C. *J. Org. Chem.* **1986**, *51*, 2820. (b) Stara, I. G.; Stary, I.; Tichy, M.; Zavada, J.; Fiedler, P. *J. Org. Chem.* **1994**, *59*, 1326. (c) Noyori, R.; Sano, N.; Murata, S.; Okamoto, Y.; Yuki, H.; Ito, T. *Tetrahedron Lett.* **1982**, *23*, 2969. Engelhardt, L. M.; Leung, W. P.; Raston, C. L.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 331.

Scheme 3



structure due to coupling to the CH_2 groups, yielded a value of ca. 240 Hz for ^1J(PP) in the case of **5d**, typical for diphosphines.[17a] The formation of diphosphines by oxidative P−P coupling of the PH_2 units in diprimary phosphines containing suitable backbones, e.g., a trimethylene chain under basic conditions, is well established.[20]

Complex Formation, Deprotonation, and Alkylation of 1. The secondary phosphine **1** shows typical donor properties toward transition-metal and main group acceptors as indicated by the formation of the BH_3 adduct **7** and the iron carbonyl complex **6** on reaction with BH_3−THF or $Fe_2(CO)_9$, respectively (eqs 3a,c, Scheme 3). Compared with **1**, the $^{31}P\{^1H\}$ NMR signals of the complexes **6** (53.2 ppm) and **7** (19.2 ppm) are shifted downfield by ca. 80 or 50 ppm, respectively. As for **1**, the CH_2 groups in **6** and **7** are inequivalent, two doublets (**6**, $\delta C = 29.22$, 32.35 ppm, $^1J(PC) = 28.6$, 27.5 Hz; **7**, $\delta C = 26.79$, 25.06 ppm, $^1J(PC) = 32.5$, 34.3 Hz) being observed in the $^{13}C\{^1H\}$ NMR spectra. This is reflected in the ^1H NMR spectrum, which shows complex patterns in the ranges $\delta = 2.8-3.6$ ppm for **6** and $\delta = 2.4-2.5$ ppm for **7**, respectively (AB and CD parts), for the two CH_2 groups with chemically inequivalent H atoms. For the PH units, doublets at $\delta P = 5.70$ (**6**) or 4.70 ppm (**7**) ($^1J(PH) = 349$ (**6**), 350 Hz (**7**)) with additional fine structure due to coupling with the H atoms of the CH_2 groups are observed in the ^1H NMR spectrum. The $Fe(CO)_4$ complex **6** shows four ν(CO) bands at 2051, 2012, 1977, and 1940 cm^{-1} (CH_2Cl_2) in the IR spectrum, indicating the equatorial position of the bulky ligand **1** within the trigonal bipyramidal structure.[21]

The reactivity of the PH functions renders **1** or its BH_3 adduct **7** potentially useful synthons for the preparation of bidentate axially chiral ligands containing the 1,1′-binaphthyl moiety. Thus, 2-vinylpyridine may be added to **7** to give the BH_3 adduct **9a** ($\delta P = 48.69$ ppm). Upon treatment with NEt_2H,[22] the free PN hybrid ligand **9** is obtained (eqs 3d,e). The ditertiary

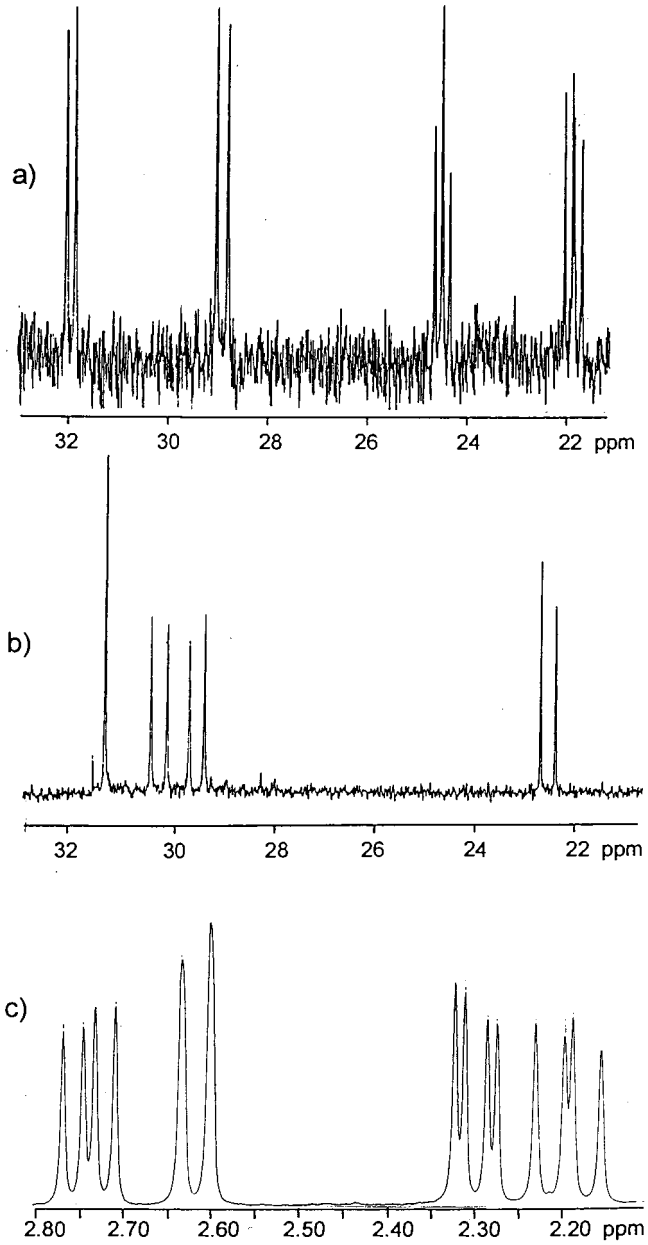


Figure 2. (a) $^{13}C\{^1H\}$ NMR spectrum of **8** (CH_2 groups). (b) $^{13}C\{^1H\}$ NMR spectrum of **9a** (CH_2 groups). (c) ^1H NMR spectrum of **10a** (CH_2 groups).

phosphine **8** was prepared in an analogous manner from **1** and vinyldiphenylphosphine[23] (eq 3b).

For **8**, an AM quartet appears in the $^{31}P\{^1H\}$ NMR spectrum ($\delta P(A) = -11.66$, $\delta P(M) = 9.76$ ppm, $^3J(P(A)P(M)) = 30.0$ Hz),[24] whereas **9** shows only a singlet with a chemical shift $\delta = 6.31$, similar to that of P(M) in **8**. The $^{31}P\{^1H\}$ NMR resonance of **9a** is shifted downfield to 48.69 ppm. Two $^{13}C\{^1H\}$ NMR signals are observed for the C_2H_4 bridge in **8** ($\delta = 24.54$ ppm (15.3 Hz), 21.86 ppm (15.3, 19.8 Hz), appearing as doublets of doublets (spin system AMX; A, M = ^{31}P; X = ^{13}C) (Figure 2a). A doublet (α-carbon) and a singlet (β-carbon) are observed in the $^{13}C\{^1H\}$ NMR spectrum for the C_2H_4 unit in **9a** (Figure 2b). The assignment of the $^{13}C\{^1H\}$ NMR signals

(20) Issleib, K.; Kühne, U.; Thorausch, P. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 275. Issleib, K.; Thorausch, P. *Phosphorus Sulfur Relat. Elem.* **1977**, *3*, 203; **1978**, *4*, 137.

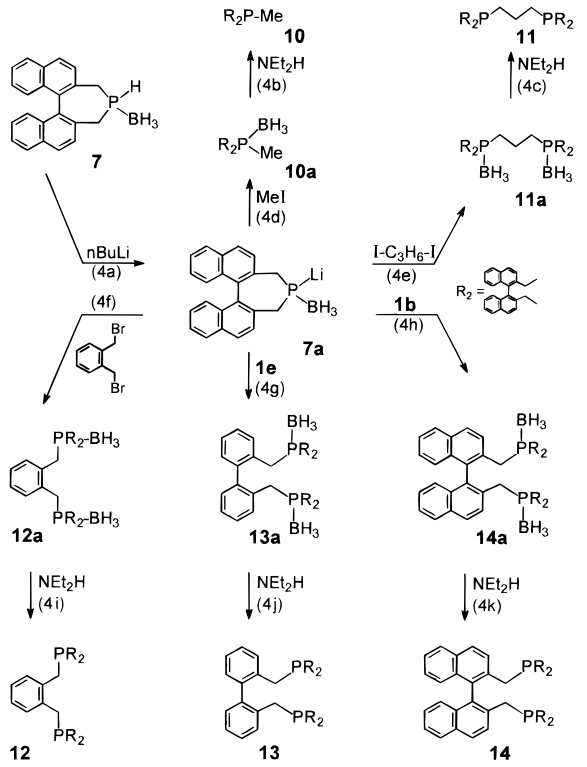
(21) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. Darensbourg, D. J.; Nelson, H. H.; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

(22) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655. Juge, S.; Stephan, M.; Merdes, R.; Genet, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531.

(23) Berlin, K. D.; Butler, G. B. *J. Org. Chem.* **1961**, *26*, 2537. Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623.

(24) (a) Hietkamp, S.; Lebbe, T.; Spiegel, G. U.; Stelzer, O. *Z. Naturforsch.* **1987**, *42b*, 177. (b) Hessler, A.; Fischer, J.; Kucken, S.; Stelzer, O. *Chem. Ber.* **1994**, *127*, 481.

Scheme 4



in **9a** is based on the comparison with pertinent data of **10a** and of transition-metal complexes of P,N hybride ligands with terminal 2-pyridyl donor groups (2-Py-$(CH_2)_2$).[24b] As in the starting material **1**, the two CH_2 groups within the dihydrophosphepine ring systems of **8**, **9**, and **9a** are chemically inequivalent, two $^{13}C\{^1H\}$ NMR resonances with P−C coupling fine structure being observed in all cases.

The deprotonation of **1** with *n*BuLi is accompanied by the formation of unidentified side products. In contrast, the corresponding reaction of the BH_3 adduct **7** proceeds cleanly forming exclusively the BH_3 complex of the lithium phosphide **7a** (eq 4a, Scheme 4). It shows a broad singlet at $\delta = -39.2$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Intermediate **7a** is a useful synthon for the preparation of mono- and bidentate ligands containing the 1,1′-binaphthalene-2,2′-bis(methylene) backbone. Thus, on reaction with methyliodide, the BH_3 adduct **10a** (δP = 41.93 ppm) is formed in high yields, and the protecting group may be removed with NEt_2H,[22] forming **10** (δP = −5.81 ppm) (eqs 4d,b). This reaction sequence may be taken as an identification of the reactive intermediate **7a**. The δP value reported in the literature[4a] for **10** (62.83 ppm) seems to be erroneous and probably corresponds to the oxide. As in the cases of **1** and **6**−**9**, two $^{13}C\{^1H\}$ NMR signals with P−C coupling fine structure are observed for the 1,1′-binaphthalene-2,2′-bis(methylene) backbone in **10** and **10a**. The inequivalence of the two CH_2 groups is reflected in the ^1H NMR spectrum showing the line pattern of the AB parts of two ABX spin systems (A, B = H; X = P) (see Figure 2c for **10a**).

Coupling of **7a** with α,ω-organodihalides yields borane complexes of bidentate ligands containing two (**11a**, **12a**) or three units (**13a**, **14a**) of axial asymmetry (eqs 4e−h). Ligand **12a** obtained from reaction of **7a** with α,α′-dibromo-*o*-xylylene shows two broadened $^{31}P\{^1H\}$ NMR signals (δ = 49.35, 48.23 ppm) corresponding to the two diastereoisomers (meso form and racemate). In the case of **11a**, due to signal overlap, only one broad signal is observed (δ = 41.18 ($CDCl_3$), 47.75 ppm (CD_2Cl_2)). Deprotection of **11a** and **12a** (eqs 4c,f) yields the diphosphines **11** and **12**, respectively, showing $P\{^1H\}$ NMR resonances at δ = 4.49 and 4.16 ppm or δ = 7.15 and 5.45 ppm for the two pairs of diastereoisomers (*SS*(*RR*), *SR*(*RS*)). If for the coupling reactions of **7a** the axially chiral α,ω-organodihalides **1b** and **1e** are employed, the products formed according to eqs 4g and 4h should exist as three enantiomeric pairs of diastereoisomers *SSS*(*RRR*), *SRS*(*RSR*), and *RRS*(*SSR*). Taking into account the chemical inequivalence of the phosphorus atoms in the *RRS*(*SSR*) diastereoisomer, then the appearance of four $^{31}P\{^1H\}$ NMR signals seems to be sensible of the products (**13a**, **14a**). The same number of $^{31}P\{^1H\}$ NMR signals (two of them being split by long-range through-space P−P coupling (^7J(PP) = 17 Hz)) has been found very recently by Huttner et al.[25] for the cyclic phosphite **H**, the oxo analogue of the phosphine ligand in **14a**. The product **13a** obtained according to eq 4g shows four partially overlapping $^{31}P\{^1H\}$ NMR signals (δ = 51.87, 51.22, and 49.66 ppm and a shoulder at ca. 51.6 ppm), which we assign to the signals of the diastereoisomers *SSS*(*RRR*), *SRS*(*RSR*), and *RRS*(*SSR*). By deprotection of **13a**, the phosphine **13** was obtained. Four intense signals at δP = 13.97, 13.68 (2.9 Hz), 11.63, and 10.34 ppm (2.9 Hz) were observed in addition to some signals of low intensity due to impurities. As for **13a**, the $^{31}P\{^1H\}$ NMR spectrum of **14a** showed four resonances (δ = 50.86, 50.11, 49.67, and 49.19 ppm, C_6D_6), two of them being of about equal intensity (δ = 50.11 and 49.19 ppm). Deprotection of **14a** with NEt_2H to give **14** (eq 4k) (δ = 10.86, 9.97, 8.83, and 8.66 ppm) requires longer reaction times, and side products are formed showing $^{31}P\{^1H\}$ NMR resonances in the range typical for free ligands **12**−**14** and the corresponding borane complexes.

The mass spectra of **12**−**14** feature molecular ions M at *m*/*e* = 726, 803, or 903, respectively. Intense signals with *m*/*e* at 591, 577, 446, 415 (**12**); 522, 491, 477 (**13**); and 621, 592, 577 (**14**), respectively, are observed, corresponding to fragment ions due to cleavage of the molecular ions at the P−CH_2 bonds of the bridging units and within the terminal 4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine groups. The basis peak for **13** corresponds to the fragment ion M^+-CH_2-PR_2-H (*m*/*e* = 477), whereas for **14** it may be assigned to the fragment PR_2 (*m*/*e* = 311) (for indication of R, see Scheme 4). The basis peak of **12** (*m*/*e* = 265, 266) may be derived from the PR_2 fragment by elimination of a P-CH_n unit (*n* = 2, 3).

The oxide of **1** and the butane-1,4-diyl analogue of **11** have been obtained in low yield using the lithium derivative of 2,2′-dimethyl-1,1′-binaphthyl and the elusive 1,4-bis(dichlorophosphino)butane as starting materials.[26] Diphosphine ligands related to **12**−**14** are claimed in the same patent, although no spectroscopic or preparative details are given, however.

Molecular Structure of 1. Crystals of composition **1**·$0.5C_7H_8$ suitable for X-ray structural analysis were obtained by recrystallization of **1** from toluene. **1**·$0.5C_7H_8$ crystallizes in the space group $P2_1/c$ with four molecules of **1** in the asymmetric unit. The structure (Figure 3, Tables 2 and 3) reveals the cisoid arrangement around the C(10)−C(20) bond, the interplanar dihedral angle being 67.6(5)°. For the torsion angles P−C(1)−C(11)−C(10) and P−C(2)−C(21)−C(20), the values of 77.5(5)° and 73.7(5)° were found, indicating that the

(25) Scherer, J.; Huttner, G.; Büchner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.
(26) Regnat, D. D.E. 4,433,952, 1996, Hoechst AG.

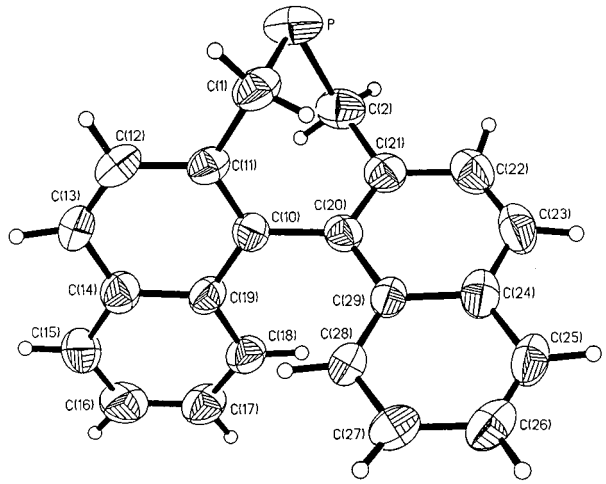


Figure 3. Molecular stucture of **1** (side view).

Table 2. Crystal Data of **1**·0.5$C_6H_5CH_3$

$C_{25.5}H_{21}P$	formula weight 358.39
$a = 9.723(2)$ Å	space group $P2_1/c$
$b = 25.746(5)$ Å	$T = 20$ °C
$c = 7.892(2)$ Å	$\lambda = 0.710\ 73$ Å
$\beta = 101.35(3)°$	$\rho_{calcd} = 1.229$ g cm^{-3}
$V = 1937(7)$ Å^3	$\mu = 14.8$ cm^{-1}
$Z = 4$	$R(F_o) = 0.073^a$
	$wR_2(F_o^2) = 0.225^b$

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Interatomic Distances and Angles for **1**·0.5$C_5H_5CH_3$

	Bond Lengths (Å)		
P−C(1)	1.860(6)	C(20)−C(21)	1.368(6)
C(1)−C(11)	1.498(7)	C(21)−C(22)	1.423(7)
C(10)−C(11)	1.390(6)	P−C(2)	1.862(6)
C(11)−C(12)	1.406(7)	C(2)−C(21)	1.510(7)
C(10)−C(20)	1.498(6)		
	Bond Angles (deg)		
C(1)−P−C(2)	99.5(2)	C(11)−C(1)−P	109.9(3)
C(11)−C(10)−C(20)	118.5(4)	C(21)−C(2)−P	114.5(3)
C(10)−C(11)−C(12)	119.3(4)	C(10)−C(11)−C(1)	120.2(4)
C(21)−C(20)−C(10)	119.4(4)	C(20)−C(21)−C(2)	120.3(4)
C(20)−C(21)−C(22)	119.9(5)		

P−C−C−C skeletons adopt the gauche conformation.[27] Similar structural features have been obtained for the sulfur analogue (**F**)[28a] of **1** and the *S*-(+)-2,2′-(2,2-dimethyl-2-silapropane-1,3-diyl)-1,1′-binaphthalene (**G**).[19c]

The phosphorus−carbon distances (P−C(1) = 1.860(6) Å, P−C(2) = 1.862(6) Å) are in the range typical for P−C(alkyl) bond lengths.[28b] Within the dihydrophosphepine ring of **1** the C−C−P angles (C(11)−C(1)−P = 109.9(3)°, C(21)−C(2)−P = 114.5(3)°) are slightly different. The C(1)−P−C(2) bond angle at the phosphorus atom subtended by the bidentate backbone is narrowed to 99.5(2)°, a value identical to the corresponding angle at the sulfur atom in **F** (C−S−C = 99.5(1)°).[28a] The increase above the tetrahedral values expected for the other angles within the seven-membered ring system is absorbed largely in P−C(2)−C(21) (114.5(3)°). At all aromatic ring junctions, the angles do not deviate notably from the expected trigonal values. The central C(10)−C(20) distance within the 1,1′-binaphthyl backbone of **1** (1.498(6) Å) does not differ significantly from that in the sulfur compound **F** (C(4)−C(5) = 1.491(3) Å).

Results of Quantum Chemical and Force Field Calculations. The goal of the computational investigations was to check if bulky phosphine ligands, like **14**, are able to enforce the formation of mononuclear complexes when coordinating to transition metals, since polynuclear complexes are assumed to be less active as catalysts. Molecular mechanics (CFF91 force field)[29,30] was applied to study the structure of **14** and of the smaller building blocks **1** and **3**.

The geometries and energies of the low-energy conformations of **1**, as calculated with both the CFF91 force field and the semiempirical method PM3,[31] are in good agreement with experimental results (Table 4). Due to the loss of C_2 symmetry of the 1,1′-binaphthyl moiety by introduction of the PH group, both methylene groups are inequivalent, as is confirmed by $^{13}C\{^1H\}$ NMR spectroscopy. The quantum chemical results are taken to validate the CFF91 force field approach for further conformational studies.

The following discussion will focus on the angle between the two naphthyl planes of the binaphthyl phosphines; a convenient measure for this critical quantity is the dihedral angle C(11)−C(10)−C(20)−C(21) viewed along the bond C(10) → C(20). We follow the definition of the Biosym software,[30] which takes the trans conformation of the bonds C(11)−C(10) and C(20)−C(21) as 0° reference for the dihedral angle.

The seven-membered phosphepine ring in **1** restricts the torsion angle C(11)−C(10)−C(20)−C(21) to about 60° (Table 4). In the lowest-energy structure of **3**, this restriction is not present and the torsion angle relaxes to 86° (Table 5). The bond angles C(11)−C(1)−P and C(21)−C(2)−P exhibit values of about 110° which are comparable to the corresponding values for **1** (109.9(3)° and 114.5(3)°), and the bond lengths for **1** and **3** are very similar, with differences below 0.01 Å.

For **3**, the high-energy conformation ($\Delta E = 2.5$ kcal/mol) is appropriate for forming chelating bidentate transition-metal complexes without any significant changes in the structural features of the ligand conformation. Here, the term "chelating" is used to characterize the orientation of the lone pairs located at both phosphorus centers, i.e., if both lone pairs are essentially directed toward each other, the structure will be termed as "chelating" and will be designated by an asterisk (see Table 5). All other arrangements of the phosphorus lone pairs will be called "nonchelating". It is worth noting that the torsion angle C(11)−C(10)−C(20)−C(21) increases from 86° in the nonchelating to 99° in the chelating structures.

From the force field calculations, we predict a mixture of many kinds of low-energy conformations of **14** (with ΔE values below about 5 kcal/mol). Some typical conformations, selected from more than 50 local minimum structures identified, are listed in Table 6. For the three units of axial symmetry in **14a** and **14**, the distinct diastereomers are of the types *SSS*, *SSR*, and *RSR*. The lowest-energy conformation of **14** belongs to the type *SSR* and features a nonchelating structure (Figure 4); therefore, mononuclear coordination of a transition metal is not expected

(27) Desper, J. M.; Gellmann, S. H.; Wolf, R. E.; Cooper, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8663. Desper, J. M.; Vyvyan, J. R.; Mayer, M. J.; Ochrymovycz, L. A.; Gellman, S. H. *Inorg. Chem.* **1993**, *32*, 381.

(28) (a) Bandarage, U. K.; Hanton, L. R.; Smith, R. A. J. *Tetrahedron* **1995**, *51*, 787. (b) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; J. Wiley and Sons: Chichester, 1990; Vol. 1, p 9.

(29) Maple, J.; Dinur, U.; Hagler, A. T. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5350.

(30) Program Discover, Version 2.3.5; Biosym Technologies: San Diego, 1993.

(31) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221; **1991**, *12*, 320.

Table 4. Geometries of the Lowest-Energy Conformations of **1** from Force Field (CFF91) and Semiempirical (PM3) Calculations in Comparison with Experimental Results

	distances (Å)		angles (deg)			
method	C(10)−C(20)	P−C(1), P−C(2)	C(11)−C(10)−C(20)−C(21)	C(1)−P−C(2)	H−P−C(1)−C(11)	H−P−C(2)−C(21)
CFF91	1.51	1.85	60	99	56	−143
PM3	1.48	1.91	64	101	61	−148
X-ray	1.498(6)	1.862(6)	67.6(5)	99.5(2)		

Table 5. Geometries and Relative Energies ΔE for Two Conformations of **3** from Force Field (CFF91) Calculations

ΔE	P−P	angles (deg)			
(kcal/mol)	distance (Å)	C(11)−C(10)−C(20)−C(21)	P−C(1)−C(11)−C(12)	H−P−C(1)−C(11)	
0.0[a]	6.59	86	−101	75	169
2.5* [b]	3.66	99	72	118	−148

[a] Energy reference. [b] Chelating conformation.

Table 6. Geometries and Relative Energies ΔE of Various Typical Low-Energy Conformations of **14** from Force Field (CFF91) Calculations

		angles[b] (deg)						distances (Å)	
	ΔE	C(11)−C(10)−	P−C(1)−	C(1′)−P−	C(2′)−P−	C(1)−P−	C(1)−P−		
	kcal/mol	C(20)−C(21)	C(11)−C(12)	C(1)−C(11)	C(1)−C(11)	C(1′)−C(11′)	C(2′)−C(21′)	P−P	d[c]
SSR[a]	0.0[d]	97	72	−120	135	64	−152	5.38	
			108	68	173	−71	157		
RSR	0.1	91	−101	72	−159	91	−163	6.72	
SSS	0.3	91	99	−92	163	67	−153	6.97	
			84	−113	141	67	−154		
*RSR**	0.9	108	97	−69	−174	72	−159	3.29	3.8
*SSS**	1.2	104	82	−106	148	−76	163	3.38	3.7
SSS	2.5	97	95	95	160	−68	156	6.40	
			−101	61	166	−72	157		
*SSR**	2.8	102	76	−98	158	66	−152	3.59	
			78	−110	145	−73	160		
*RSR**	4.0	106	80	−93	163	64	−150	3.42	4.1
			118	−92	163	68	−154		
*RSR**	4.1	105	85	−125	131	63	−151	3.65	7.2

[a] Chelating conformations are designated by an asterisk. [b] Centers of the secondary phosphines are distinguished from centers of the primary unit by a prime. [c] Distance of stacking naphthyl units. [d] Energy reference.

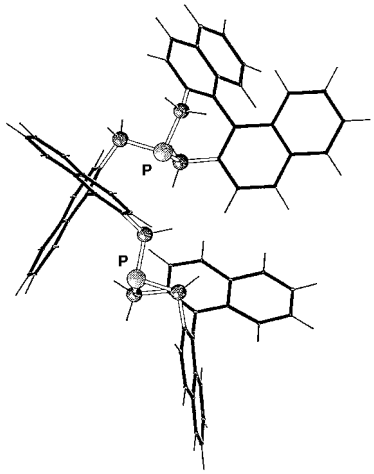


Figure 4. Lowest-energy conformation (nonchelating) of **14** (*SSR*, see Table 6).

to be favored in this case. The lowest-energy conformations of diastereomers of types *RSR* and *SSS* also exhibit nonchelating structures; their energies are almost degenerate with the *SSR* "ground state" conformer ($\Delta E \approx 0.3$ kcal/mol). The lowest-energy candidate for forming a mononuclear transition-metal complex is a chelating conformer of structure *RSR** found at $\Delta E \approx 0.9$ kcal/mol.

The nearest-neighbor bond lengths of all these distinct conformations of **14** are all quite similar. On comparison of these data with the corresponding values for **1** and **3**, no significant differences are found in the calculations. The nonbonded phosphorus distance P···P in **14** strongly correlates with the torsion angle C(11)−C(10)−C(20)−C(21) of the primary unit: the larger this angle, the smaller the P−P distance (Table 6). All calculated chelating structures show a significantly larger torsion angle C(11)−C(10)−C(20)−C(21) of the primary phosphine unit than the nonchelating ones, similar to the results for **3**. The values for the adjacent dihedral angle P−C(1)−C(11)−C(12) of **14** vary from 72° to 118°. However, two exceptional nonchelating structures were found where this angle is −101°, just as for a nonchelating structure of **3**.

Continuing the discussion of the calculated structures of **14**, we now turn to the secondary phosphine units. All central torsion angles C(11′)−C(10′)−C(20′)−C(21′) of the secondary phosphine substituents are calculated to be about 60° (if necessary, we distinguish centers of the secondary phosphines by a prime from those of the primary unit). However, different from **3** and the primary unit of **14**, this torsion angle between the naphthyl planes is not sufficient to characterize the conformation of the secondary phosphine units, in particular of the seven-membered dihydrophosphepine rings. To this end, we also include the torsion angles C(1)−P−C(1′)−C(11′) and C(1)−P−C(2′)−C(21′), as well as the corresponding angles C(2)−P−C(1′)−C(11′) and C(2)−P−C(2′)−C(21′) (Table 6). The calculated angles deviate by at most ±30° from the ideal values of ±60° and ±180°, showing that the energetically preferred conformations are more or less of a staggered type at the central P−C bonds. These structures are, therefore, to some extent related to those obtained for **1** (Table 4). In general, the

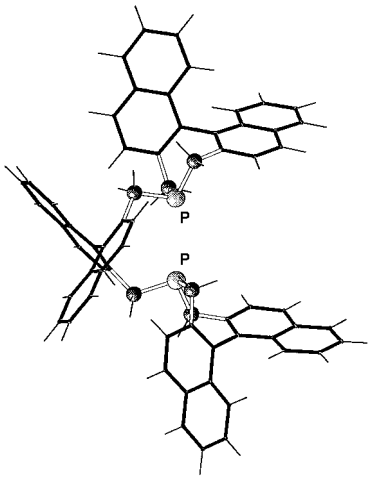


Figure 5. *RSR** conformation (chelating) of **14** at $\Delta E = 4.1$ kcal/mol (see Table 6).

distortions of the secondary phosphine units with respect to the structures of **1** are less significant than those of the primary unit compared to the structures of **3**.

In contrast, the torsions around the bonds P−C(1) and P−C(2) connecting the central primary unit of **14** to the secondary units vary over a wide range. The corresponding torsion angles are C(1′)−P−C(1)−C(11) and C(2′)−P−C(1)−C(11), as well as C(1′)−P−C(2)−C(21) and C(2′)−P−C(2)−C(21) (Table 6). Both staggered and eclipsed conformations are found.

Ligand **14** is similarly flexible with respect to rotations around the bonds of C(11)−C(1) and C(21)−C(2) of the primary fragment, a behavior which is also detected in **3**. No correlation between these torsion angles and the energy of a conformation was found.

Diastereomers with secondary phosphine fragments of the same axial symmetry may exhibit a special structural feature. Both secondary phosphine fragments of **14** may display a stacking arrangement of the naphthyl units. The distances between these units range over a broad interval, from 3.7 to 7.2 Å (Table 6). The lowest-energy structure among these conformers is *RSR** at $\Delta E \approx 0.9$ kcal/mol, with the PC(1′)C(2′) moiety in close to a staggered conformation with respect to the H atoms of the methylene group $C(1)H_2$ of the secondary phosphine unit. A rotation around the P−C axis to an eclipsed conformation leads to the conformer with the highest energy of the three chelating *RSR** analyzed at $\Delta E \approx 4.1$ kcal/mol. This conformer seems to be particularly well set up for a chelating coordination at a transition-metal center (Figure 5). In this case, the distance between the naphthyl units is quite large, 7.2 Å. Thus, a transition-metal atom may find enough space to pass between them "from the right-hand side" to reach a position where it may be able to simultaneously coordinate at both phosphorus centers.

Finally, we try to connect the findings of this molecular modeling-based analysis of the conformations of the various binaphthyl-substituted phosphines and of their flexibility to experimental information from ^{31}P NMR spectroscopy. In our analysis of **14** (Table 6), we found a large variety of chelating and nonchelating conformations. One might assume that they induce variations in the chemical environments of the two P centers, which result in a corresponding number of different NMR peaks. For **14** and **14a**, one finds four distinct ^{31}P NMR signals (see above). However, they are not necessarily connected to the number of diastereoisomers, as comparison with **11** shows where two narrow resonances (δP = 4.49, 4.16 ppm) collapse into one broad signal at δP = 41.18 ppm in the BH_3 adduct **11a**. Nevertheless, at low enough temperatures, the various conformers of **14** and **14a** may lead to a splitting or broadening of the NMR signals.

Experimental Section

Physical Measurements and General Procedures. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX400 at 400.1, 100.6, and 162.0 MHz, respectively. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported relative to tetramethylsilane, and for ^{31}P{^{1}H} NMR spectra, external phosphoric acid was used as reference. Mass spectra were run on a Varian MAT 311A. Air-sensitive materials were manipulated in an inert gas atmosphere using Schlenk techniques. Solvents were purified using standard methods.[32] DMSO was purchased from Aldrich Chemicals and was used as obtained. PH_3 was prepared by hydrolysis of P_4 and was stored in steel cylinders. It was used without further purification. Pressure reactions were performed in a 5 L steel autoclave fitted with a manometer, a gas inlet system, and a mechanical stirrer.

Materials. 2,2′-Bis(bromomethyl)-1,1′-binaphthyl (**1b**) was synthesized by literature methods.[13] The dichloro[12] and diiodo derivatives were obtained by Cl/Br or I/Br exchange, respectively, using LiCl/DMF or NaI/toluene. Vinyldiphenylphosphine[23] was obtained by reaction of diphenylchlorophosphine with vinylmagnesium chloride. $P(SiMe_3)_3$[15a] was prepared as reported in the literature. 2-Vinylpyridine was purchased from Aldrich Chemicals and was used without further purification.

Syntheses. 4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine (1). The two-phase system formed on addition of 40 mL of aqueous KOH (56%) to a mixture of 200 mL of DMSO and 40 mL of toluene was saturated with PH_3 under a pressure of 1.1 bar at 20 °C. A solution of 30.0 g (0.085 mol) of **1a** in 150 mL of toluene was added within 1.5 h, with the PH_3 pressure kept constant. After the addition was complete, the reaction mixture was stirred for an additional 1 h. The organic phase was separated, washed three times with 100 mL aliquots of water, and dried over $MgSO_4$. The solvent was removed under reduced pressure (20 °C, 0.1 mbar), and the remaining residue was recrystallized from toluene. **1** was obtained as a colorless powder (20.0 g, 75%). Anal. Calcd for $C_{22}H_{17}P$ ($M_r = 312.3$): C, 84.60; H, 5.49. Found: C, 84.95; H, 5.55. MS: 312 (M^+). ^{1}H NMR (CD_2Cl_2): δ 7.22−7.99 (aromatic H, 12 H), 4.00 (^1J(PH) = 188.2 Hz, PH, 1 H), 3.01, 2.74, 2.66, 2.51 (m, CH_2, 4 H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 137.75, 135.32 ($J = 1.8$ Hz), 133.79 ($J = 5.1$ Hz), 132.99 ($J = 1.6$ Hz), 132.56, 132.50, 132.36 ($J = 2.0$ Hz), 132.17 (ipso-C), 128.99, 128.63 ($J = 1.5$ Hz), 128.39 ($J = 1.3$ Hz), 127.14 ($J = 1.8$ Hz), 126.58 ($J = 1.0$ Hz), 126.49, 126.23, 126.05 ($J = 0.5$ Hz), 125.18 ($J = 1.0$ Hz), 124.99, 25.56 ($J = 17.3$ Hz, CH_2), 23.11 ($J = 12.2$ Hz, CH_2).

2,2′-Phosphinomethyl-1,1′-binaphthyl (3) and 2,2′-Phosphinomethyl-1,1′-biphenyl (5). (a) Protected-Group Synthesis of 3 and 5. To a solution of 4.29 g (17.1 mmol) or 6.75 g (26.96 mmol) of $P(SiMe_3)_3$ in 25 or 50 mL of DME was added 10.7 or 16.8 mL of a 1.6 M solution of *n*BuLi (17.1 or 26.9 mmol) in *n*-hexane at −30 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 48 h. Thereafter, 3.5 g (8.0 mmol) of **1b** or 4.59 g (13.5 mmol) of **1e** dissolved in 20 mL of DME was added, and the reaction mixture was stirred for 12 h at room temperature. After filtration, the solvent was evaporated in vacuo and replaced by 50 mL of toluene. The precipitate formed was filtered off. After evaporation of the filtrate, the silylphosphine **2** or **4** was obtained as an oily liquid. The protecting silyl groups in **2** and **4** were split off by hydrolysis with a mixture of 20 mL of ethanol and 5 mL of water. All volatiles were removed under reduced pressure (20 °C, 0.01 mbar) to yield 2.32 g (84%) of **3** or 2.21 g (67%) of **5** as a colorless powder. **3**. Anal. Calcd for $C_{22}H_{20}P_2$ ($M_r = 346.3$): C, 76.29; H, 5.82. Found: C, 76.22; H, 6.29. MS: 346 (M^+). **5**. Anal. Calcd for $C_{14}H_{16}P_2$ ($M_r = 246.2$): C, 68.29; H, 6.53. Found: C, 67.89; H, 6.44. MS: 246 (M^+), 244 ($M^+ - 2$ H), 213 ($M^+ - PH_3$). **2** and **4** were characterized by ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{1}H NMR spectroscopy. **2**. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 138.99 ($J = 9.5$ Hz), 134.62, 132.95, 132.56 (ipso-C), 128.45 ($J = 12.1$ Hz), 127.97, 127.57, 126.28, 126.14, 125.06, 19.92 ($J = 11.1$ Hz)

(^{1}H coupled, t, ^1J(CH) ca. 130 Hz), 0.74 (J = 8.1 Hz, $SiMe_3$). ^{1}H NMR (CD_2Cl_2): δ 7.97−7.09 (aromatic H, 12 H), 3.01, 2.97, 2.80, 2.79, 2.76, 2.75 (^2J(HH) = 14.9 Hz, CH_2, 4 H), 0.04 (J = 4.2 Hz, $SiMe_3$, 36 H). **3**. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 138.99, 133.16, 132.41 (ipso-C), 128.66, 128.10, 127.40, 126.53, 126.36, 125.50 (C−H), 19.15 (J = 11.1 Hz) (^{1}H coupled, t, ^1J(CH) = 131.9 Hz). ^{1}H NMR (CD_2Cl_2): δ 7.09−8.04 (aromatic H, 12 H), 3.12, 3.10, 3.09, 2.64, 2.62, 2.61 (^1J(PH) = 194 Hz, PH_2), 2.76−2.72, (m, CH_2, 4 H). **4**. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 140.89 (J = 4.0 Hz, ipso-C), 140.38 (J = 8.1 Hz, ipso-C),130.7, 129.73 (J = 11.2 Hz), 127.24, 125.50 (J = 2.0 Hz, C−H), 18.32 (J = 11.0 Hz, CH_2) (^{1}H coupled, t, ^1J(CH) = 131.8 Hz). ^{1}H NMR (CD_2Cl_2): δ 7.55−7.19 (aromatic H, 8 H), 2.95, 2.94, 2.91, 2.90, 2.82, 2.81, 2.79, 2.78 (CH_2, 4 H), 0.14 (J = 7.4 Hz, $SiMe_3$, 36 H). **5**. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 140.66 (ipso-C), 139.58 (ipso-C), 130.40, 128.94 (J = 4.0 Hz), 128.13, 125.77 (C−H), 18.29 (J = 11.2 Hz, CH_2) (^{1}H coupled, t, ^1J(CH) = 131.0 Hz). ^{1}H NMR (CD_2Cl_2): δ 7.39−7.16 (aromatic H, 8 H), 2.9 (PH_2, ^1J(PH) = 191 Hz, 4 H), 2.82−2.62 (CH_2).

(b) Attempted Multistage Synthesis of 5. Preparation of 5a. A 45.5 g portion (133.8 mmol) of **1e** was added to 76.0 g (365.0 mmol) of triisopropyl phosphite at ambient temperature in a three-necked flask fitted with a distillation head. The mixture was heated to 120 °C for 12 h. During this time, 20 mL of isopropyl bromide was distilled off and collected in a flask. The remaining triisopropyl phosphite was removed under reduced pressure (100 °C, 0.1 mbar). Yield: 68.3 g (99%). Anal. Calcd for $C_{26}H_{40}O_6P_2$ (M_r = 510.5): C, 61.17; H, 7.90. Found: C, 61.80; H, 8.20. MS: 510 (M^+). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.01 (J = 9.2 Hz, ipso-C), 130.61 (J = 7.1 Hz, ipso-C), 130.02 (J = 5.1 Hz), 126.48 (J = 3.1 Hz), 130.85, 127.59 (J = 3.10 Hz), 31.57 (J = 141.4 Hz), 70.6 (J = 7.1 Hz), 70.2 (J = 7.1 Hz), 42.1 (J = 4.0 Hz), 24.03 (J = 4.0 Hz), 23.96, 23.72 (J = 5.0, 4.0 Hz).

Preparation of 5b. A 1.1 g portion (2.2 mmol) of **5a** was dissolved in 10 mL of toluene and 1 mL of acetic acid. The solution was heated to 95 °C for 12 h. After completion of the reaction as indicated by ^{31}P{^{1}H} NMR spectroscopy, all volatiles were removed in vacuo. Yield: 0.75 g (99%). Anal. Calcd for $C_{14}H_{16}O_6P_2{\cdot}H_2O$ (M_r = 360.2): C, 46.68; H, 5.04. Found C, 47.0; H, 4.80. ^{13}C{^{1}H} NMR (d_6-DMSO): δ 141.32 (J = 8.1 Hz, ipso-C), 132.68 (J = 7.1 Hz, ipso-C), 130.73 (J = 4.1 Hz), 126.26, 130.86, 127.62, 32.50 (J = 133.3 Hz). ^{1}H NMR (d_6-DMSO): δ 7.6−7.14 (aromatic H, 8H), 2.85, 2.78 (ABX, ^2J(HH) = 15.3 Hz, CH_2, 2H), 9.76 ($P(O)(OH)_2$).

Preparation of 5c. A 5.0 g portion (9.8 mmol) of **5a** was dissolved in 50 mL of thionyl chloride. After the addition of 0.3 g (4.0 mmol) of dimethylformamide, the solution was heated under reflux for 72 h. The yellowish solid obtained after removing all volatiles in vacuo (50 °C, 0.1 mbar) was dissolved in 5 mL of CH_2Cl_2 and precipitated by the addition of 20 mL of *n*-pentane. Yield: 3.54 g (87%). Anal. Calcd for $C_{14}H_{12}Cl_4O_2P_2$ (M_r = 416.0): C, 40.42; H, 2.91. Found: C, 40.50; H, 3.00. MS: 414, 416, 418, 420 (M^+, ^{35}Cl/^{37}Cl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.53 (J = 11.2, 2.0 Hz, ipso-C), 127.04 (J = 11.2 Hz, ipso-C), 131.11 (J = 6.1 Hz), 128.88 (J = 5.1 Hz), 129.01 (J = 5.1 Hz), 131.44 (J = 4.1, 2.0 Hz), 47.4 (J = 95.60 Hz). ^{1}H NMR ($CDCl_3$): δ 7.76−7.40 (aromatic H, 8H), 3.95, 3.74 (ABX, J(AB) = 15.3, J(AX) = 17.3, J(BX) = 18.0 Hz; A, B = ^{1}H, X = ^{31}P, CH_2, 4H).

Attempted Synthesis of 5 by Reduction of 5a with $LiAlH_4$. To a suspension of 17.0 g (33.3 mmol) of **5a** in 50 mL of diethyl ether was added 67 mL (67 mmol) of a 1 M solution of $LiAlH_4$ at a rate to keep the solvent refluxing. After addition of the $LiAlH_4$ solution, the reaction mixture was heated for 2 h at reflux. The reaction mixture was cooled to ambient temperature, and 20 mL of a 2 N HCl solution was added. The inorganic salts were separated by filtration, and all volatiles were evaporated in vacuo (20 °C, 0.01 mbar). After evaporation, 5.0 g of a colorless oily product was obtained, which showed in the ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) two narrow signals at −125.57 and −125.65 ppm, split into triplets under proton coupling (^1J(PH) = ca. 190 Hz).

Synthesis of the Iron Carbonyl Complex 6. A solution of 1.0 g (3.2 mmol) of **1** in 25 mL of toluene was added to a suspension of 1.16 g (3.2 mmol) of $Fe_2(CO)_9$ in 25 mL of toluene. After 60 h of stirring at ambient temperature, the reaction mixture was filtered and the filtrate was evaporated in vacuo (20 °C, 0.1 mbar). The residue (1.0 g) was dissolved in 5 mL of CH_2Cl_2 and purified by preparative thin-layer chromatography (silica gel, toluene) using Merck PSC plates (20 × 20 mm with a 2 mm layer). The yellow zone was isolated and extracted with CH_2Cl_2 to give **6** (100 mg). Anal. Calcd for $C_{26}H_{17}FeO_4P$ (M_r = 480.2): C, 65.02; H, 3.57. Found: C, 65.30; H, 3.80. MS: 480 (M^+), 452 (M^+ − CO), 396 (M^+ − 3 CO), 368 (M^+ − 4 CO). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 211.63 (J = 19.92 Hz), 132.85 (J = 4.9 Hz), 132.50 (J = 4.9 Hz), 132.69 (J = 3.0 Hz), 132.57, 132.45, 132.3 (J = 1.5 Hz), 132.02 (J = 1.7 Hz), 131.22 (J = 1.5 Hz), 131.09 (J = 1.0 Hz, ipso-C), 128.48, 128.16 (J = 1.7 Hz), 127.50, 127.34, 127.13 (J = 3.0 Hz), 125.89, 125.66, 125.45, 124.94 (J = 7.0 Hz), 124.85 (J = 3.0 Hz, C−H), 32.35 (J = 27.5 Hz), 29.22 (J = 28.6 Hz, CH_2). ^{1}H NMR ($CDCl_3$): δ 8.15−7.07 (aromatic H, 12 H), 5.70 (^1J(PH) = 349 Hz, PH, 1 H), 3.48, 3.15, 2.92 (m, CH_2, 4 H).

Synthesis of the Borane Adduct 7. To a solution of 25.0 g (80.0 mmol) of **1** (in 80 mL of THF) was added an equimolar amount of the borane/THF complex (1 M solution in THF), and the mixture was stirred for 12 h. After the solvent was removed in vacuo (20 °C, 0.05 mbar), **7** was obtained as a colorless powder in quantitative yield (26.1 g). Anal. Calcd for $C_{22}H_{20}BP$ (M_r = 326.2): C, 81.01; H, 6.18. Found: C, 81.39; H, 5.82. MS: 326, 325 (M^+, ^{11}B/^{10}B). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 133.92, 133.85, 133.71 (J = 2.6 Hz), 133.53 (J = 2.1 Hz), 133.31, 133.28, 132.38 (J = 11.0 Hz), 132.38 (J = 6.8 Hz, ipso-C), 129.85 (J = 7.7 Hz), 129.55 (J = 1.7 Hz), 129.03 (J = 2.0 Hz), 128.71 (J = 3.4 Hz), 128.63 (J = 1.5 Hz), 128.57 (J = 1.0 Hz), 126.87 (J = 0.8 Hz), 126.73, 126.72, 126.57, 126.54 (J = 1.0 Hz), 126.06 (J = 1.3 Hz, CH), 26.79 (J = 32.5 Hz, CH_2), 25.06 (J = 34.3 Hz, CH_2). ^{1}H NMR (C_6D_6): δ 7.73−6.91 (aromatic H, 12 H), 4.70 (J = 350 Hz, PH, 1 H), 2.49−2.42 (m, CH_2, 4 H), 1.8−0.9 (BH_3, 3 H).

Synthesis of 8 by Addition of Vinyldiphenylphosphine to 1. To a solution of 1.0 g (3.2 mmol) of **1** in 50 mL of THF were added 0.7 g (3.3 mmol) of vinyldiphenylphosphine and 0.1 g (0.9 mmol) of *t*BuOK. The reaction mixture was stirred at room temperature for 72 h. The residue remaining after evaporation of the solvent in vacuo was extracted twice with 30 mL of methanol, yielding 1.2 g (71%) **8** as a colorless powder. Anal. Calcd for $C_{36}H_{30}P_2$ (M_r = 524.6): C, 82.44; H, 5.76. Found: C, 82.25; H, 5.91. MS: 524 (M^+). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 138.78−124.97 (aromatic C), 32.13 (J = 17.3 Hz, CH_2), 29.02 (J = 22.4 Hz, CH_2), 24.54 (dd, J = 15.3, 15.3 Hz, CH_2), 21.86 (dd, J = 15.3, 19.8 Hz, CH_2).

Syntheses of 9a and 9 by Addition of 2-Vinylpyridine to 7. 2-Vinylpyridine (2.44 g, 23.2 mmol) and 7.57 g (23.2 mmol) of **7** were dissolved in 100 mL of toluene. After the addition of 0.5 g (4.5 mmol) of *t*BuOK the solution was stirred for 16 h at ambient temperature. The solvent was removed under reduced pressure, and the resulting yellow colored solid was extracted three times with 60 mL of MeOH and then dried in vacuo. Yield: 7.6 g (76%) **9a**. Anal. Calcd for $C_{29}H_{27}BNP$ (M_r = 431.32): C, 80.76; H, 6.30; N, 3.24. Found: C, 80.56; H, 6.25; N, 3.13. MS: 431, 430 (M^+, ^{10}B/^{11}B). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.23 (J = 11.8 Hz, Py), 149.59 (Py), 136.79 (Py), 123.30 (Py), 121.90 (Py), 133.89−125.80 (J = 3.0 Hz, aromatic C), 31.31 (CH_2), 30.25 (J = 32.5 Hz, CH_2), 29.48 (J = 30.5 Hz, CH_2), 22.65 (J = 28.5 Hz). ^{1}H NMR (CD_2Cl_2): δ 8.7−7.2 (aromatic H, 16 H), 3.3−2.0 (CH_2, 8 H), 1.0−0.1 (BH_3, 3 H).

The product obtained above was suspended in an excess of diethylamine and stirred for 2 h at 50 °C. The product **9** remaining after removing all volatiles under reduced pressure (50 °C, 0.1 mbar) was washed with methanol and dried in vacuo. It was identified by its mass spectrum and ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra. MS: 417. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.02 (J = 11.1 Hz), 149.48 (J = 6.7 Hz, Py), 136.39 (Py), 133.90−121.36 (aromatic C); (C_6D_6): δ 35.19 (J = 17.6 Hz), 32.62 (J = 18.0 Hz), 29.37 (J = 23.0 Hz), 26.39 (J = 19.3 Hz, CH_2).

Syntheses of 10[4] and 10a. A solution of 3.3 g (10.0 mmol) of **7** was metalated with 6.3 mL of a 1.6 N solution of *n*BuLi in *n*-hexane at −78 °C. After the addition of 1.42 g (10.0 mmol) of MeI, the reaction mixture was allowed to warm to ambient temperature and was stirred for 1 h. The solvent was evaporated in vacuo. The borane adduct **10a** was identified by its ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra. For deprotection, it was suspended in diethylamine, and the mixture was stirred for 2 h at 50 °C. All volatiles were removed under reduced

pressure yieding **10**[4] as a colorless solid. Anal. Calcd for $C_{23}H_{19}P$ (M_r = 326.4) (**10**): C, 84.64; H, 5.87. Found C, 83.97; H, 6.14. MS: 326 (M^+). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 136.2−132.8 (ipso-C), 127.34−125.15 (C−H), 34.22 (J = 16.6 Hz, CH_2), 30.96 (J = 21.1 Hz, CH_2), 10.16 (J = 21.4 Hz, Me). ^1H NMR (C_6D_6): δ 7.78−6.98 (aromatic H, 12 H), 2.60−2.47, 2.05−1.96 (m, CH_2, 4 H), 0.73 (J = 1.0 Hz, Me, 3 H). Anal. Calcd for $C_{23}H_{22}BP$ (M_r = 340.2) (**10a**): C, 81.20; H, 6.52. Found: C, 81.17; H, 5.88. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.05−131.23 (ipso-C), 128.97−125.78 (C−H); ($CDCl_3$): δ 31.06 (J = 32.2 Hz, CH_2), 30.56 (J = 30.1 Hz, CH_2), 8.59 (J = 30.5 Hz, Me). ^1H NMR ($CDCl_3$): δ 7.82−6.95 (aromatic H, 12 H), 2.76−2.59, 2.31−2.15 (m, CH_2, 4 H), 1.56−1.20 (BH_3, 3 H), 0.86 (J = 9.5 Hz, Me, 3 H).

Synthesis of 11a and 11 by Coupling of the Borane Adduct 7. The borane adduct **7** (20.0 g, 61.3 mmol) was dissolved in 60 mL of THF. At −78 °C, 30.7 mL of a 2.0 M solution of *n*BuLi was added with stirring within 0.5 h. To the red-brown colored solution was added 9.08 g (30.7 mmol) of 1,3-diiodopropane, and the mixture was stirred for 2 h. The reaction mixture was allowed to warm to room temperature, and the solvent was evaporated under reduced pressure (20 °C, 0.1 mbar). The remaining residue was washed with 100 mL of methanol and dried in vacuo. The BH_3 groups in **11a** could be removed by heating a suspension in an excess of NEt_2H at 50 °C for 6 h to give **11**. All volatiles were removed under reduced pressure, and the remaining residue was washed with methanol and dried in vacuo (20 °C, 0.01 mbar). Yield: 18.2 g (86%) **11a**. Anal. Calcd for $C_{47}H_{44}B_2P_2$ (M_r = 692.4) (**11a**): C, 81.53; H, 6.40. Found: C, 82.64; H, 6.72. MS: 677, 678 ($M^+ - BH_3$, $^{10}B/^{11}B$), 664 ($M^+ - 2BH_3$), 665 ($M^+ - 2BH_3 + H$), 666 ($M^+ - 2BH_3 + 2H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.9−130.50 (ipso-C), 129.1−125.8 (C−H), 30.11 (J = 31.5 Hz), 29.99 (J = 31.53 Hz), 29.30 (t, J = 15.3 Hz), 24.81 (dd, J = 11.7, 27.5 Hz, CH_2). Anal. Calcd for $C_{47}H_{38}P_2$ (M_r = 664.8) (**11**): C, 84.92; H. 5.76. Found: C, 84.86; H, 5.75. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.6−28.9 (m, CH_2), 25.33−24.7 (m, CH_2).

Synthesis of 12a−14a and 12−14 by Coupling of the Borane Adduct 7 with α,ω-Dihalogen Compounds. General Procedure for 12a−14a. First, 1.21 g (3.71 mmol), 1.28 g (3.94 mmol), or 1.17 g (3.59 mmol) of the borane adduct **7** was dissolved in 30 mL of THF. Next, 2.32 mL, 2.46 mL, or 2.24 mL of a 1.6 M *n*BuLi solution in *n*-hexane was added at −78 °C with stirring. After 2 h, the α,ω-dihalogen compound [0.49 g (1.86 mmol) *o*-dibromoxylene, 0.67 g (1.97 mmol) **1e**, or 0.79 g (1.8 mmol) **1b**] in 15 mL of THF was added within 2 h. The reaction mixtures were evaporated in vacuo (20 °C, 0.1 mbar). The remaining residues were washed with 100 mL of methanol and dried in vacuo. Yields: 1.1 g (78%) **12a**, 0.80 g (49%) **13a**, 1.10 g (66%) **14a**. Anal. Calcd for $C_{52}H_{46}B_2P_2$ (M_r = 754.5) (**12a**): C, 82.78; H, 6.15. Found: C, 82.52; H, 5.89. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.30−130.36 (ipso-C), 129.6−125.80 (C−H), 30.43 (J = 30.5 Hz, CH_2), 29.86 (J = 30.5 Hz, CH_2), 29.18 (J = 26.3 Hz, CH_2), 29.09 (J = 23.3 Hz, CH_2), 27.74 (J = 22.2 Hz, CH_2). Anal. Calcd for $C_{58}H_{50}B_2P_2$ (M_r = 830.6) (**13a**): C, 83.87; H, 6.07. Found: C, 83.19; H, 6.14. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.6−26.6 (m, CH_2). Anal. Calcd for $C_{66}H_{54}B_2P_2$ (M_r = 930.7) (**14a**): C, 85.17; H, 5.85. Found: C, 85.04; H, 5.91. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 31.93−27.36 (m, CH_2).

General Procedure for Deprotection of 12a−14a. A suspension of 1.0 g (1.32 mmol) of **12a**, 0.60 g (0.72 mmol) of **13a**, or 1.0 g (1.07 mmol) of **14a** in an excess of NEt_2H was heated at 50 °C for 8 h. After filtration, all volatiles were removed under reduced pressure. The remaining residue was washed with 100 mL of methanol and dried in vacuo. Yields: 0.82 g (86%) **12**, 0.46 g (79%) **13**, 0.72 g (75%) **14**. Anal. Calcd for $C_{52}H_{40}P_2$ (M_r = 726.8) (**12**): C, 85.93; H, 5.54. Found: C, 86.75; H, 5.89. MS: 726 (M^+), 727 ($M^+ + H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 136.16−132.36 (ipso-C), 130.29−125.05 (C−H), 32.26−30.83 (m, CH_2), 29.68 (J = 24.4 Hz, CH_2). ^1H NMR (CD_2Cl_2): δ 8.06−7.08 (aromatic H, 28 H), 2.80−2.29 (m, J = 12 Hz, CH_2, 12 H). Anal. Calcd for $C_{58}H_{44}P_2$ (M_r = 802.9) (**13**): C, 86.76; H, 5,02. Found: C, 86.98; H, 5.23. MS: 802 ($M^+ - H$). $^{13}C\{^1H\}$NMR (CD_2Cl_2): δ 32.69−29.95 (m, CH_2). ^1H NMR (CD_2Cl_2): δ 8.01−6.72 (aromatic H, 32 H), 2.69−2.00 (m, J = 12 Hz, CH_2, 12 H). Anal. Calcd for $C_{66}H_{48}P_2$ (M_r = 903.1) (**14**): C, 87.78; H, 5.36. Found: C, 88.15; H, 5.40. MS: 902 ($M^+ - H$).

X-ray Crystallography. Diffraction data for **1** were collected at 293 K on a Siemens P4 diffractometer in the ω scan mode using graphite-monochromated Mo Kα radiation. Experimental data are presented in Table 2. The structure was solved by direct methods and refined by full matrix least squares against F_o^2 using the SHELX-97 software package. Scattering factors and corrections for anomalous dispersion were taken from ref 33. H atoms were included in geometrically calculated positions (riding model, C−H = 0.95 Å).

Computational Computational Details. The conformations of **1**, **3**, and **14** were studied using the CFF91 force field[29] as provided by the program DISCOVER.[30] For comparison, the semiempirical method PM3[31] as implemented in the program VAMP (version 5.5)[34] was used to determine the structure of **1** in order to check the suitability of the force field method for the study of phosphines. The CFF91 force field parameters[29,30] were supplemented by the following torsional parameters for bridging carbon atoms C(10)−C(20): torsion angle Θ = 120.05°, force constants $k_1 = k_3 = 0.0$ (kcal/mol)/deg^2, k_2 = 0.325 (kcal/mol)/deg^2.[35]

Acknowledgment. This work was supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, the Fonds der Chemischen Industrie, and the Bayerische Forschungsverbund Katalyse (FORKAT). Hoechst AG is thanked for financial support and generous gifts of chemicals. The authors are grateful to T. Clark for making the program VAMP available and to S. Köstlmeier for helpful discussions.

Supporting Information Available: An X-ray crystallographic file in CIF format for complex **1**·0.5$C_5H_5CH_3$ is available on the Internet only. Access information is given on any current masthead page.

IC980346Z

(32) Perrin, D. D.; Amarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1966.
(33) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.
(34) Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Sauer, W.; Beck, B.; Clark, T. VAMP 5.5 Manual, Centrum für Computer-Chemie der Universität Erlangen-Nürnberg, 1994.
(35) Herrmann, W. A.; Schmid, R.; Kohlpaintner, C. W.; Priermeier, T. *Organometallics* **1995**, *14*, 1961.