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New Tertiary Phosphines from Cinnamaldehydes and Diphenylphosphine

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A 1:1 hydrophosphination of the olefinic bond of cinnamaldehyde (and substituted ones) with Ph_2PH, under argon using neat reagents, gives quantitative formation of the new tertiary phosphines $Ph_2PCH(Ar)CH_2CHO$ (**2**) as racemic mixtures (Ar = Ph, *p*-tol, and *p*-OMe–C_6H_4). α-Methylcinnamaldehyde similarly affords $Ph_2PCH(Ph)CH(Me)CHO$, but as a mixture of diastereomers with predominantly *S*,*S*- and *R*,*R*-chirality [diastereomeric ratio (dr) ∼20]. In a 2:1 reaction of Ph_2PH with cinnamaldehyde, hydrophosphination of both the C═C and C═O bonds takes place to give the diphosphine derivative $Ph_2PCH(Ph)CH_2CH(OH)PPh_2$ (**3**) as a diastereomeric mixture with dr ∼2.3. In most organic solvents, the hydrophosphination of the C═O group is reversible, leading to a dynamic equilibrium between **3** and **2**, but **3** is stable in coordinating solvents such as DMSO, DMF, and pyridine. X-ray analysis of a *P*,*P*-chelated $PdCl_2$(**3**) complex, formed from *trans*-$PdCl_2(PhCN)_2$ and **3** in MeOH, reveals that the *S*,*S*/*R*,*R*-enantiomers are favored.

Introduction

Our group has been involved in a collaborative project dealing with development of water-soluble phosphines, particularly tris(hydroxymethyl)phosphine, $(HOCH_2)_3P$, as bleaching and brightness stabilization agents for wood pulps, and interaction of such phosphines with conjugated carbonyl components of lignin is involved in the bleaching process.[1] A commonly used bleaching agent in the pulp industry is the so-called "hydrosulfite", which is in fact sodium dithionite ($Na_2S_2O_4$), the bleaching involving a reasonably well understood reduction process by the dithionite,[2] and notably the collaborative studies have recently revealed a remarkable synergistic effect of the use of a combination of $(HOCH_2)_3P$ and $Na_2S_2O_4$ for the bleaching.[3] This led us to study the complex interaction between these two chemicals, where reactions at ambient conditions in aqueous solution under Ar can lead to formation of bis(hydroxymethyl)phosphine [$(HOCH_2)_2PH$], sodium (hydroxymethane)sulfonate [$HOCH_2S(O)_2ONa$], and sodium (hydroxymethane)sulfinite $HOCH_2S(O)ONa$.[4]

The generation of the $(HOCH_2)_2PH$ encouraged us to investigate the reaction of such secondary phosphines with lignin model compounds, and as cinnamaldehyde possesses the conjugated phenyl−propanoid backbone similar to that present in lignin chromophores,[1b] one such system studied was the reaction of this aldehyde (and substituted ones) with diphenylphosphine. This current paper describes this study, and although there is literature on the interaction of Ph_2PH with α,β-unsaturated carbonyl compounds (including cinnamaldehyde),[5] our findings are very different and have led to the synthesis of new tertiary phosphines and a diphosphine, which result from sequential hydrophosphination of the C═C bond and the C═O bonds of the aldehyde, the respective products being formed at Ph_2PH:cinnamaldehyde ratios of 1 or 2. There is, of course, extensive literature on the hydrophosphination of such moieties by Ph_2PH and other secondary phosphines, including Michael-type addition reactions to activated olefinic substrates, and such studies have been widely used for synthesis of new functionalized

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phosphines.[6−10] An example of the use of the new diphosphine as a ligand at a Pd^{II} center is also presented.

Experimental Section

General. Cinnamaldehyde and α-methylcinnamaldehyde (Aldrich products) were distilled under reduced pressure before use. 4-Methyl- and 4-methoxycinnamaldehyde were prepared by base-catalyzed condensation of acetaldehyde (Aldrich) with *p*-tolualdehyde (Eastman) or 4-methoxybenzaldehyde, respectively (Aldrich). Ph_2PH (Strem Chemicals) was used as received. *trans*-$PdCl_2(PhCN)_2$ was made by a literature procedure[11] from $PdCl_2$ purchased from Colonial Metals, Inc. Organic solvents were dried over the appropriate agents and were distilled under Ar, while $CDCl_3$, CD_3OD, and DMSO-d_6 (Cambridge Isotope Laboratory) were used as received. Syntheses were carried out under Ar either using standard Schlenk glassware or a glovebox. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AV300 spectrometer (121 MHz), at 300 K unless otherwise stated; ^1H and ^{13}C NMR spectra were recorded on an AV400 instrument (400 MHz for ^1H, 100 Hz for $^{13}C\{^1H\}$). All NMR spectra were measured in $CDCl_3$ unless otherwise stated. A residual deuterated solvent proton (relative to external $SiMe_4$) and external 85% aqueous H_3PO_4 were used as references: br = broad, s = singlet, d = doublet, t = triplet, p = pentet, and m = multiplet. *J* values are given in Hertz. When necessary, atom assignments were made by means of $^1H-^1H$, $^1H-^{13}C\{^1H\}$ (HSQC and HMBC), and $^1H-^{31}P\{^1H\}$ NMR correlation spectroscopies. Elemental analyses were performed on a Carlo Erba 1108 analyzer. Mass spectrometry was performed on a Bruker Esquire electrospray (APCI) ion trap spectrometer with samples dissolved in MeOH, with positive ion polarity, scanning from 60 to 1000 *m/z*.

$Ph_2PCH(Ph)CH_2CHO$ (2a). In a glovebox, Ph_2PH (0.88 mL, 0.50 mmol) was added dropwise to stirred cinnamaldehyde (0.66 mL, 0.53 mmol) at room temperature (rt, ∼20 °C). After 15 min, the mixture was heated briefly at 50 °C to yield a pink solid that was triturated with Et_2O (∼6 mL), filtered off, washed once with Et_2O, and dried under vacuum (1.30 g, 82% yield). Anal. Calcd for $C_{21}H_{19}OP$: C, 79.23; H, 6.02. Found: C, 79.44; H, 6.25. $^{31}P\{^1H\}$ NMR: δ 0.50 s. ^1H NMR: δ 9.57 (br s, 1H, C*H*O), 7.67−7.62 (m, 2H), 7.46−7.41 (m, 3H), 7.23−7.10 (m, 10H), 4.10 (ddd, $^2J_{PH} = 5.4$, $^3J_{HH} = 11.1$, $^3J_{HH} = 3.4$, 1H, PC*H*; $^1H\{^{31}P\}$, dd), 3.04 (dddd, $^3J_{PH} = 5.4$, $^2J_{HH} = 17.4$, $^3J_{HH} = 11.1$, $^3J_{HH} = 1.9$, 1H, CH_AH_B; $^1H\{^{31}P\}$, ddd), 2.69 (dddd, $^3J_{PH} = 7.3$, $^2J_{HH} = 17.4$, $^3J_{HH} = 3.3$, $^3J_{HH} = 0.9$, 1H, CH_AH_B; $^1H\{^{31}P\}$, ddd). $^{13}C\{^1H\}$ NMR: δ 200.5 (d, $^3J_{PC} = 12.3$, *C*HO), 139.9 (d, $^2J_{PC} = 8.5$, C_{ipso}-CH), 135.9 (d, $^1J_{PC} = 14.7$, C_{ipso}-P), 135.6 (d, $^1J_{PC} = 16.2$, C'_{ipso}-P), 134.1 (d, $^2J_{PC} = 20.9$, *o*-C of PhP), 133.1 (d, $^2J_{PC} = 18.3$, *o*-C of Ph′P), 129.7 (s, *p*-C of PhP), 128.9 (d, $^3J_{PC} = 7.4$, *m*-C of PhP), 128.8 (d, $^3J_{PC} = 7.4$, *m*-C of Ph′P), 128.6 (s, *p*-C of Ph′P), 128.5 (s, *m*-C of PhC), 128.0 (d, $^3J_{PC} = 6.8$, *o*-C PhC), 126.6 (d, $^5J_{PC} = 2.1$, *p*-C of PhC), 47.2 (d, $^2J_{PC} = 20.1$, *C*H_2), 38.8 (d, $^1J_{PC} = 13.9$, Ph*C*H). APCI (MeOH): *m/z* 319.2 (100%) $[M + H]^+$, calcd 319.1.

$Ph_2PCH(p\text{-}tol)CH_2CHO$ (2b). The procedure used follows that given for **2a**, except that the mixture with 4-Me-cinnamaldehyde generated a red amorphous substance. After the treatment with Et_2O, a pale pink solid was obtained (0.95 g, 57%). The elemental analysis and NMR data ($^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$) for **2b** are given in the Supporting Information (Table S1).

$Ph_2PCH(p\text{-}OMe\text{-}C_6H_4)CH_2CHO$ (2c). The procedure used was as for **2b** but using 4-MeO-cinnamaldehyde (yield 0.82 g, 47%). The elemental analysis and NMR data ($^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$) for **2c** are given in the Supporting Information (Table S1).

$Ph_2PCH(Ph)CH(Me)CHO$ (2d). A mixture of Ph_2PH (0.88 mL, 0.50 mmol) and α-methylcinnamaldehyde (1.40 mL, 1.0 mmol) was heated at 60 °C for 72 h; excess aldehyde was then distilled off at ∼90 °C under reduced pressure (∼0.1 Torr). The resulting colorless, viscous residue was analyzed by ^1H NMR spectroscopy, which revealed a mixture of diastereomers of **2d** in a diastereomeric ratio (dr) of ∼10, along with some remaining aldehyde (15 mol %). The aldehyde was removed by dissolving the residue in Et_2O (5 mL) and keeping the solution for 2 days at −20 °C; the resulting white solid was filtered off and dried under vacuum (0.95 g, 57%). The $^{31}P\{^1H\}$ NMR spectrum revealed two diastereomers with dr ∼20. Anal. Calcd for $C_{22}H_{21}OP$: C, 79.50; H, 6.37. Found: C, 79.71; H, 6.57.

2d-α (major diastereomer; *S,S*- and *R,R*-enantiomers). $^{31}P\{^1H\}$ NMR: δ −8.6 s. ^1H NMR: δ 9.97 (br s, 1H, C*H*O; $^1H\{^{31}P\}$: d, $^3J_{HH} = 1.1$), 7.75−7.68 (m, 2H), 7.46−7.40 (m, 3H), 7.23−7.08 (m, 10H), 3.84 (dd, $^2J_{PH} = 4.7$, 1H, PC*H*; $^1H\{^{31}P\}$, d, $^3J_{HH} = 5.7$), 2.79 (m, 1H, MeC*H*; $^1H\{^{31}P\}$, dp, $^3J_{HH} = 6.9$, $^3J_{HH} = 1.1$), 1.07 (d, $^3J_{HH} = 6.9$, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 203.6 (d, $^3J_{PC} = 10.9$, *C*HO), 138.2 (d, $^2J_{PC} = 8.5$, C_{ipso}-CH), 136.3 (d, $^1J_{PC} = 14.9$, C_{ipso}-P), 135.9 (d, $^1J_{PC} = 13.5$, C'_{ipso}-P), 134.2 (d, $^2J_{PC} = 21.2$, *o*-C of PhP), 133.2 (d, $^2J_{PC} = 19.1$, *o*-C of Ph′P), 129.7 (s, *p*-C of PhP), 129.6 (d, $^3J_{PC} = 8.4$, *m*-C of PhP), 128.8 (d, $^3J_{PC} = 7.4$, *m*-C of Ph′P), 128.5 (s, *p*-C of Ph′P), 128.4 (s, *m*-C of PhC), 127.9 (d, $^3J_{PC} = 7.1$, *o*-C of PhC), 126.8 (d, $^5J_{PC} = 1.4$, *p*-C of PhC), 49.1 (d, $^2J_{PC} = 13.9$, Me*C*H), 48.0 (d, $^1J_{PC} = 17.0$, P*C*H), 13.5 (d, $^3J_{PC} = 7.6$, *C*H_3).

2d-β (minor diastereomer; *S,R*- and *R,S*-enantiomers). $^{31}P\{^1H\}$ NMR: δ −8.2 s. ^1H NMR: δ 9.51 (m, 1H, C*H*O; $^1H\{^{31}P\}$: d, $^3J_{HH} = 1.0$), 7.68−7.64 (m, 2H), 7.52−7.46 (m, 3H), 7.38−7.23 (m, 10H), 4.25 (pseudo t, $^2J_{PH} \approx 4.9$, 1H, PC*H*; $^1H\{^{31}P\}$, d, $^3J_{HH} = 4.5$), 2.54 (m, 1H, MeC*H*), 1.20 (d, $^3J_{HH} = 6.9$, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 203.6 (d, $^3J_{PC} = 10.9$, *C*HO, overlapped with *C*HO of **2d-α**), 48.1 (d, $^2J_{PC} = 15.8$, Me*C*H), 44.7 (d, $^1J_{PC} = 14.2$, P*C*H), 10.8 (d, $^3J_{PC} = 9.6$, *C*H_3). Other $^{13}C\{^1H\}$ signals could not be assigned.

$Ph_2PCH(Ph)CH_2CH(OH)PPh_2$ (3). Dropwise addition of cinnamaldehyde (0.38 mL, 0.30 mmol) to stirred Ph_2PH (1.10 mL, 0.63 mmol) generated a viscous mixture, which was then heated at 60 °C and stirred for 15 min to give a pink glasslike residue. The $^{31}P\{^1H\}$ spectra of the residue in various solvents show mainly two sets of two singlets (corresponding to two diastereomers, **3a** and **3b**), and small amounts (∼7 mol %) of **2a** and Ph_2PH; the $^{31}P\{^1H\}$ data are listed in Table 1. ^1H and $^{13}C\{^1H\}$ NMR data given below pertain to DMSO-d_6 solution.

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Table 1. $^{31}P\{^1H\}$ Singlet Resonances (δ) for Ph_2PH, **3a**, **3b**, and **4** in Various Solvents[a]

		3a		3b		
solvent	Ph_2PH	α-P	γ-P	α-P	γ-P	**4**
DMSO	−39.7	−7.5	−0.8	−5.7	1.5	−6.8
DMF	−39.7	−6.0	−0.4	−4.6	2.1	−
pyridine	−39.6	−5.2	0.4	−4.0	2.2	−4.5
acetone	−39.1	−4.8	0.3	−3.8	2.5	−4.0
CH_3CN	−39.0	−4.5	−0.5	−4.2	1.5	−4.4
Et_2O	−39.7	−3.6	0.4	−3.6	2.4	−3.0
CH_2Cl_2	−39.6	−3.0	−0.8	−4.1	1.0	−2.4[b]
$CHCl_3$	−39.8	−2.4	0.3	−3.9	1.8	−1.6
benzene	−40.1	−1.8	0.1	−3.7	1.6	−1.7
hexane	−39.6	−1.0	−0.3	−3.4	2.0	−
MeOH	−39.8	−6.6	0.3	−4.5	2.6	−5.7
EtOH	−39.8	−6.6	0.4	−4.5	2.7	−5.8
^{i}PrOH	−39.9	−6.5	0.4	−4.7	2.5	−6.1

[a] Spectra measured using 0.05 M solution of the phosphines. [b] The reported value (ref 9) is −6.5 ppm.

3a (*S,S*/*R,R*-enantiomers). ^1H NMR: δ 7.60−7.01 (m, 23H, Ph), 6.92 (d, $^3J_{HH}$ = 7.7, 2H, *o*-H of PhC), 5.45 (pseudo t, $^3J_{PH}$ = 6.7, $^3J_{HH}$ = 6.8, 1H, O*H*; $^1H\{^{31}P\}$, d), 4.07−3.94 (m, 2H, C*H*Ph and C*H*(OH)), 1.91−1.68 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR: δ 138.9 (d, $^2J_{PC}$ = 9.0, C_{ipso}-CH), 137.1 (d, $^1J_{PC}$ = 16.0, C_{ipso}-P), 136.9 (d, $^1J_{PC}$ = 15.4, C_{ipso}-P), 136.4 (d, $^1J_{PC}$ = 16.9, C_{ipso}-P), 136.3 (d, $^1J_{PC}$ = 13.7, C_{ipso}-P), 133.7 (d, $^2J_{PC}$ = 19.2, *o*-C of PhP), 133.5 (d, $^2J_{PC}$ = 20.0, *o*-C of PhP), 132.9 (d, $^2J_{PC}$ = 21.2, *o*-C of PhP), 132.7 (d, $^2J_{PC}$ = 19.1, *o*-C of PhP), 129.2 (d, $^3J_{PC}$ = 7.6, *o*-C of PhC), 129.0 (d, $^4J_{PC}$ = 7.6, *m*-C of PhC), 126.1 (d, $^5J_{PC}$ = 1.8, *p*-C of PhC), 68.2 (dd, $^1J_{PC}$ = 11.2, $^3J_{PC}$ = 3.8, *C*H(OH)), 39.3 (dd, P*C*H, overlapped with intense resonance of $(CD_3)_2SO$), 37.7 (dd, $^2J_{PC}$ = 20.5, $^2J_{PC}$ = 26.1, *C*H_2). Other $^{13}C\{^1H\}$ resonances (and for **3b**, see below) could not be assigned (even using HMQC and HMBC data) because of overlapping signals.

3b (*S,R*/*R,S*-enantiomers). ^1H NMR: δ 7.60−7.01 (m, 25H, Ph, overlapped with Ph-proton signals of **3a**), 5.04 (pseudo t, $^3J_{PH}$ = 5.0, $^3J_{HH}$ = 6.1, 1H, O*H*; $^1H\{^{31}P\}$, d), 4.14 (m, 1H, C*H*(OH)), 3.88 (m, 1H, C*H*Ph; $^1H\{^{31}P\}$, dd, $^3J_{HH}$ = 10.7, $^3J_{HH}$ = 4.1), 2.08 (m, 1H, CH_AH$_B$; $^1H\{^{31}P\}$, ddd, $^3J_{HH}$ = 5.6, $^3J_{HH}$ = 11.1, $^2J_{HH}$ = 14.1), 1.84 (m, 1H, CH$_A$*H*$_B$, overlapped with CH_2 proton signals of **3a**). $^{13}C\{^1H\}$ NMR: δ 140.9 (d, $^2J_{PC}$ = 8.1, C_{ipso}-CH), 134.6 (d, $^2J_{PC}$ = 19.0, *o*-C of PhP), 133.6 (d, $^2J_{PC}$ = 16.5, *o*-C of PhP), 133.1 (d, $^2J_{PC}$ = 19.4, *o*-C of PhP), 133.0 (d, $^2J_{PC}$ = 17.5, *o*-C of PhP), 126.1 (*p*-C of $Ph_2PCH(OH)$,overlapped with *p*-C signal of **3a**), 69.1 (dd, $^1J_{PC}$ = 12.1, $^3J_{PC}$ = 11.4, *C*H(OH)), 40.7 (dd, $^1J_{PC}$ = 13.5, $^3J_{PC}$ = 11.0, *C*HPh), 39.0 (dd, *C*H_2, overlapped with intense resonance of $(CD_3)_2SO$).

$Ph_2PCH(OH)Et$ (4). The synthesis was a modification of a literature procedure.[9] Freshly distilled, oxygen-free propionaldehyde (0.36 mL, 0.50 mmol) was added to stirred Ph_2PH (0.88 mL, 0.50 mmol) under Ar at rt, and after 15 min a pure, white solid product was formed quantitatively. Anal. Calcd for $C_{15}H_{17}OP$: C, 73.76; H, 7.01. Found: C, 73.51; H, 7.03. ^{31}P NMR shifts in different solvents are listed in Table 1. ^1H NMR (DMSO-d_6): δ 7.61−7.27 (m, 10H, Ph), 5.09 (br s, 1H, O*H*), 4.36 (t, $^3J_{HH}$ = 6.0, 1H, C*H*(OH); $^1H\{^{31}P\}$, same), 1.45 (dp, $^3J_{HH}$ = $^3J_{PH}$ = 7.2, 2H, CH_2; $^1H\{^{31}P\}$, p), 0.95 (t, $^3J_{HH}$ = 7.2, 3H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 137.5 (d, $^1J_{PC}$ = 13.9, C_{ipso} of PhP), 137.2 (d, $^1J_{PC}$ = 15.2, C'_{ipso}-P), 133.6 (d, $^2J_{PC}$ = 18.9, *o*-C of PhP), 133.3 (d, $^2J_{PC}$ = 17.2, *o*-C of Ph′P), 128.6 (s, *p*-C of PhP), 128.3 (d, $^3J_{PC}$ = 6.8, *m*-C of PhP), 128.2 (s, *p*-C of Ph′P), 128.0 (d, $^3J_{PC}$ = 6.3, *m*-C of Ph′P), 72.4 (d, $^1J_{PC}$ = 4.6, *C*HOH), 27.7 (d, $^2J_{PC}$ = 23.5, *C*H_2), 10.7 (d, $^3J_{PC}$ = 12.3, *C*H_3).

Decomposition of 3 and 4. In a glovebox, the compound (0.05 mmol) was dissolved in 1 mL of a selected solvent, and ∼0.7 mL of the solution was placed under Ar in a J-Young NMR tube; $^{31}P\{^1H\}$ NMR spectral changes were then monitored.

$PdCl_2[Ph_2PCH(Ph)CH_2CH(OH)PPh_2]$ (5). The diphosphine **3** (39 mg, 0.077 mmol, based on 95% purity) in MeOH (1 mL) was added to a 1 mL MeOH solution of $PdCl_2(PhCN)_2$ (28 mg, 0.073 mmol) under Ar. The immediately formed pale yellow solid subsequently dissolved within 1 min, and the solution was kept for 4 h at rt. Deposited crystals of **5** were filtered off, washed once with MeOH (∼1 mL), and dried overnight under vacuum (25 mg, 50%, dr ∼20). Anal. Calcd for $C_{33}H_{30}Cl_2OP_2Pd$: C, 58.13; H, 4.43. Found: C, 58.26; H, 4.64. Leaving the MeOH solution for 16 h afforded **5** in 80% yield, with dr ∼ 3.3 as estimated by $^{31}P\{^1H\}$ NMR.

5a (*S,S*/*R,R*-enantiomers). $^{31}P\{^1H\}$ NMR (161 MHz on the AV400, CD_2Cl_2): δ 24.1 [d, $^2J_{PP}$ = 16.0, *P*CH(OH)] and 23.6 [d, $^2J_{PP}$ = 16.0, *P*CH(Ph)]. ^1H NMR (resonances in the δ 8.30−6.30 region overlap with corresponding signals of **5b**; see below): δ 8.29−8.22 (m, 2H, *o*-H of PhPCH(OH)), 7.93−7.85 (m, 2H, *o*-H of *Ph*PCH(Ph)), 7.85−7.78 (m, 2H, *o*-H of Ph′PCH(OH)), 7.70−7.35 (m, 10H, *p*-H and *m*-H of $Ph_2PCH(OH)$, *p*-H of Ph_2PCH(Ph), and *m*-H of *Ph*PCH(Ph)), 7.32−7.25 (m, 2H, *o*-H of *Ph*′PCH(Ph)), 7.19−7.07 (m, 3H, *p*-H of PhCH, *m*-H of *Ph*′PCH(Ph)), 6.94 (t, $^3J_{HH}$ = 7.8, *m*-H of *Ph*CH), 6.35 (d, $^3J_{HH}$ = 7.8, *o*-H of PhCH), 5.02 (d, $^3J_{HH}$ = 6.8, C*H*(OH); $^1H\{^{31}P\}$, same), 4.58 (pseudo t, $^2J_{PH}$ = 10.3, 1H, C*H*(Ph); $^1H\{^{31}P\}$, dd, $^3J_{HH}$ = 12.3, $^3J_{HH}$ = 1.6), 2.77 (br s, 1H, O*H*), 2.71−2.20 (m, 2H, CH_2, overlapped with CH_2 signals of **5b**). $^{13}C\{^1H\}$ NMR: δ 138.0 (d, $^2J_{PC}$ = 9.0, C_{ipso} of *Ph*CH), 136.9 (d, $^2J_{PC}$ = 11.1, *o*-C of *Ph*′PCH(Ph)), 135.8 (d, $^2J_{PC}$ = 9.5, *o*-C of PhPCH(OH)), 134.6 (d, $^2J_{PC}$ = 9.8, *o*-C of Ph′PCH(OH)), 133.8 (d, $^2J_{PC}$ = 9.1, *o*-C of *Ph*PCH(Ph)), 132.6 (d, $^4J_{PC}$ = 2.5, *p*-C of PhPCH(OH)), 132.0 (d, $^4J_{PC}$ = 2.6, *p*-C of *Ph*′PCH(Ph)), 131.8 (d, $^4J_{PC}$ = 2.1, *p*-C of Ph′PCH(OH)), 131.2 (d, $^4J_{PC}$ = 2.8, *p*-C of *Ph*PCH(Ph)), 65.3 (dd, $^1J_{PC}$ = 38.2, $^3J_{PC}$ = 7.0, *C*H(OH)), 35.5 (dd, $^1J_{PC}$ = 22.7, $^3J_{PC}$ = 9.0, *C*H(Ph)), 34.2 (overlapping dd, seen as pseudo t, $^2J_{PC}$ = 7.4, $^3J_{PC}$ = 6.8, *C*H_2). Other $^{13}C\{^1H\}$ resonances (and for **5b**, see below) could not be assigned because of overlapping signals.

5b (*S,R*/*R,S*-enantiomers). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.1 [d, $^2J_{PP}$ = 16.8, *P*CH(Ph)] and 28.0 [d, $^2J_{PP}$ = 16.8, *P*CH(OH)]. ^1H NMR: δ 8.32−8.29 (m, 2H, *o*-H of PhPCH(OH)), 7.78−7.71 (m, 2H, *o*-H of *Ph*PCH(Ph)), 7.27−7.21 (m, 2H, *o*-H of *Ph*′PCH(Ph)), 4.98 (ddd, $^2J_{PH}$ = 5.1, C*H*(OH); $^1H\{^{31}P\}$, dd, $^3J_{HH}$ = 11.6, $^3J_{HH}$ = 2.2), 4.12 (ddd, $^2J_{PH}$ = 8.3, C*H*(Ph); $^1H\{^{31}P\}$, dd, $^3J_{HH}$ = 11.8, $^3J_{HH}$ = 2.3). $^{13}C\{^1H\}$ NMR: δ 137.9 (d, $^2J_{PC}$ = 9.6, C_{ipso} of *Ph*CH), 137.0 (d, $^2J_{PC}$ = 10.7, *o*-C of *Ph*′PCH(OH)), 136.7 (d, J_{PC} = 9.9, *o*-C of PhPCH(OH)), 134.4 (d, $^2J_{PC}$ = 9.4, *o*-C of *Ph*PCH(Ph)), 133.9 (d, $^2J_{PC}$ = 9.4, *o*-C of *Ph*′PCH(Ph)), 132.5 (d, $^4J_{PC}$ = 2.5, *p*-C), 132.1 (d, $^4J_{PC}$ = 2.5, *p*-C), 131.8 (presumably d, *p*-C of *Ph*PCH(Ph), overlapped with *p*-C signal of Ph′PCH(OH)), 131.4 (d, $^4J_{PC}$ = 2.9, *p*-C), 71.4 (dd, $^1J_{PC}$ = 31.1, $^3J_{PC}$ = 7.5, *C*H(OH)), 47.6 (br d, $^1J_{PC}$ = 23.3, *C*H(Ph)), 37.2 (br d, $^2J_{PC}$ ≈ 8).

X-ray Crystallographic Analysis of 5. X-ray-quality, pale yellow crystals of **5**·3MeOH were obtained as described above in the synthesis reaction, the $^{31}P\{^1H\}$ NMR revealing two diastereomers (dr ∼ 20). Selected crystallographic data are shown in Table 2, and more details are provided in the Supporting Information. Measurements were made at 173 (±0.1) K on a Bruker X8 APEX diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). Data were collected to a maximum 2θ value of 55.8°, in a series of ϕ and ω scans in 0.50° oscillations with 25.0 s exposures; the crystal-to-detector distance was 36.00 mm. Of the

Table 2. Crystallographic Data for **5**·3MeOH

empirical formula	$C_{36}H_{42}O_4P_2PdCl_2$
cryst color, habit	colorless, blade
cryst size, mm^3	$0.05 \times 0.13 \times 0.40$
cryst syst	primitive
space group	*Pbca* (#14)
a, Å	14.7439(6)
b, Å	21.8538(9)
c, Å	21.9153(9)
V, Å^3	7061.3(5)
Z	8
F(000)	3200.00
μ, cm^{-1}	8.05
total reflns	46556
unique reflns	8420
R_{int}	0.066
no. variables	450
*R*1 ($I > 2\sigma(I)$)	0.055 (5943 obsd reflns)
wR2	0.113 (all data)[a]
gof	1.12 (all data)

[a] $w = 1/[\sigma^2(F_o^2) + (0.00P)^2 + 36.2447P]$, where $P = (F_o^2 + 2F_c^2)/3$.

46 556 reflections collected, 8420 were unique ($R_{int} = 0.066$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package[12] and were corrected for absorption effects using the multiscan technique (SADABS),[13] with minimum and maximum transmission coefficients of 0.703 and 0.961, respectively. Data were corrected for Lorentz and polarization effects, and the structures were solved by direct methods.[14] The material appears to be a mixture of diastereomers, with predominantly *S*,*S* (or *R*,*R*) at C(1) and C(3), respectively, and a small (~5%) fraction of the *S*,*R* (or *R*,*S*) isomer (see Figure 2 for atom labeling). This manifests itself as apparent minor disorder at C(3) as well as minor disorder of the PdP_2Cl_2 fragment. There may be disorder in the positions of the other atoms; however, the minimal disorder and the very small shifts in positions between the major and minor fragments make it impossible to see these fragments. All non-hydrogen atoms except the disordered minor fragments were refined anisotropically, and all disordered fragments were refined isotropically. The hydroxyl hydrogen (H1o) was located in a difference map and refined isotropically, while all other H atoms were placed in calculated positions. Of the three molecules of MeOH found in the asymmetric unit, one is disordered in two orientations.

Results and Discussion

All the reactions involving Ph_2PH were exothermic, as judged by handling of the reaction vessel. Diphenylphosphine reacts with cinnamaldehyde (**1a**) in the absence of solvent at room temperature to afford the tertiary phosphine **2a** (Scheme 1). A pink-colored viscous liquid is first formed rapidly and, to avoid formation of the diphosphine **3** (see below), the reaction mixture was briefly stirred at 50 °C to give a pink solid. After workup, **2a** was obtained in good yield as a racemate; the compound is soluble in acetone, benzene, and $CHCl_3$, but poorly soluble in Et_2O, and in $CDCl_3$ gives a singlet at δ_P 0.50 in the $^{31}P\{^1H\}$ spectrum. The four nonaromatic protons form an X−AB−Y spin system in the $^1H\{^{31}P\}$ spectrum and, as the C*H* and CH_AH_B resonances also show coupling to the P-atom in the ^{31}P spectrum, the ^1H signals are readily assigned (see Experimental Section); the $^{13}C\{^1H\}$ spectrum (which delineates the diastereotopic PPh_2 phenyl groups), MS data, and elemental analysis support the formulation. The *p*-tolyl and anisole derivatives, **2b** and **2c**, were obtained likewise as pink solids in more moderate yields, because of better solubility in Et_2O than **2a**, and were characterized similarly by elemental analysis and NMR spectroscopy (Table S1).

The reaction of Ph_2PH with α-methylcinnamaldehyde to generate **2d** required prolonged heating (see Scheme 2) and a 2:1 excess of the aldehyde, which was largely removed by distillation under vacuum. Further workup from Et_2O yielded **2d** as a white solid in 57% yield; the solution $^{31}P\{^1H\}$ spectrum, which shows just two singlets, means that **2d** (a molecule with two chiral centers) is isolated as a mixture of diastereomers in about a 20:1 ratio as judged by the signal intensities. There is no direct evidence for which diastereomer is favored, but based on reasoning discussed in our earlier paper on attack of PR_3 [R = $(CH_2)_3OH$] on cinnamaldehyde, which is thought to generate the phosphonium cation $[PhCH(PR_3)CH(D)CHO]^+$ as *S*,*S* and *R*,*R* enantiomers,[1b] the same *S*,*S*/*R*,*R*-diastereomer (labeled **2d**-α) is favored. Its aldehydic proton is downfield-shifted (δ_H 9.97) from that of the *S*,*R*/*R*,*S*-diastereomer (**2d**-*β*) (δ_H 9.51) and from that of **2a** (δ_H 9.57), appearing in the $^1H\{^{31}P\}$ spectrum as a doublet with a $^3J_{HH}$ vicinal coupling of 1.1 Hz. On the contrary, the benzyl proton of **2d**-α (δ_H 3.84) is upfield-shifted from that of **2a** (δ_H 4.10), whereas the corresponding signal of **2d**-*β* (δ_H 4.25) is downfield-shifted. The P-atoms of **2d**-α and **2d**-*β* appear in the $^{31}P\{^1H\}$ spectrum as singlets at δ_P −8.6 and −8.2, respectively.

The reaction of **1a** with 2 equiv of Ph_2PH affords a pinkish, glasslike residue which, according to a $^{31}P\{^1H\}$ spectrum in DMSO-d_6, consists of the diphosphine **3** (as a mixture of diastereomers, Scheme 3), some **2a** (~2%), and Ph_2PH (~5%). Attempts to purify **3** revealed its instability in common organic solvents by decomposing into **2a** and Ph_2PH (Scheme 4); such reversibility of the addition of secondary phosphines to carbonyl functions has long been known,[7d,f] but we are unaware of any reports on the solvent dependence (see below). Table 1 summarizes the immediately measured $^{31}P\{^1H\}$ data for **3** in various solvents, while the NMR data given in the Experimental Section are measured in DMSO-d_6, in which **3** is stable (see below). Like compound **2d**, the diphosphine contains two chiral centers, and the $^{31}P\{^1H\}$ spectra reveal two sets of two singlets, each set being attributed to one of two diastereomers (**3a** and **3b**); on the basis of data from a Pd(II) complex containing **3** (see below), the major diastereomer (**3a**) is considered to be the *S*,*S*/*R*,*R* mixture; in DMSO-d_6 the measured dr = 2.3.

The data in Table 1 show that the $^{31}P\{^1H\}$ shift for the α-P atom of **3a** and **3b** (adjacent to the OH group) is markedly solvent-dependent (e.g., a difference of 6.5 ppm between values for **3a** in DMSO and in hexane), while shift values for the *γ*-P atom vary by only 1.2 ppm. A few examples of the $^{31}P\{^1H\}$ spectra of **3** in different solvents

(12) *SAINT*, Version 7.03A; Bruker AXS Inc., Madison, WI, 1997−2003.
(13) *SADABS*. Bruker Nonius area detector scaling and absorption correction−V2.10; Bruker AXS Inc., Madison, WI, 2003.
(14) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

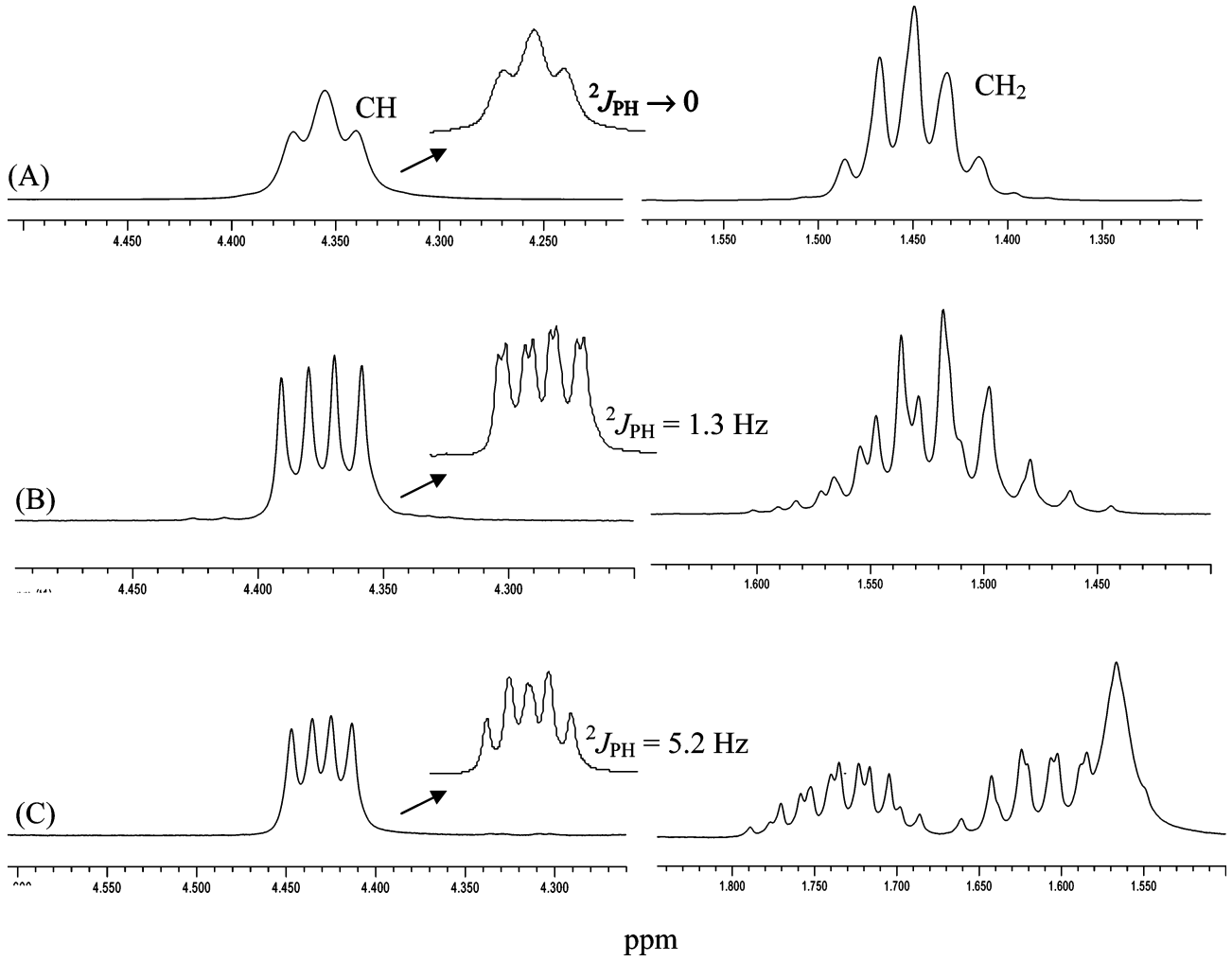


Figure 1. The experimental $^1H\{^{31}P\}$ spectra for the CH- and CH_2-protons of $Ph_2PCH(OH)Et$ (**4**) recorded in (A) DMSO-d_6, (B) CD_3OD, and (C) $CDCl_3$. ^1H NMR spectra for the CH-proton are shown to the right of the $^1H\{^{31}P\}$ spectra.

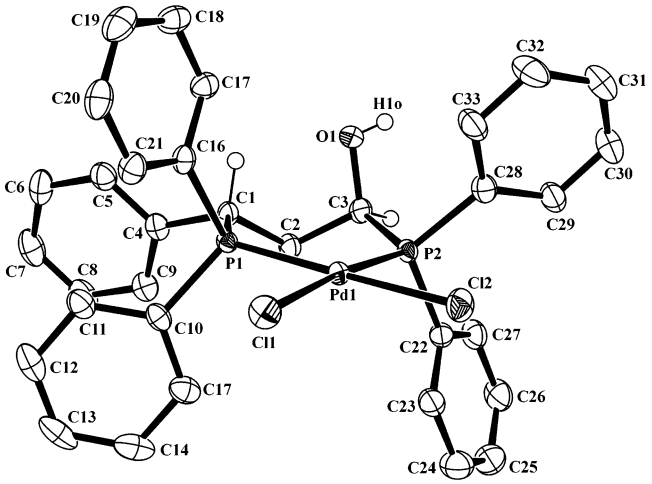
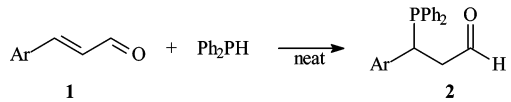


Figure 2. ORTEP diagram of $PdCl_2[S,S\text{-}Ph_2PCH(Ph)CH_2CH(OH)PPh_2]$ (**5**) showing 50% probability thermal ellipsoids; H-atoms are omitted for clarity.

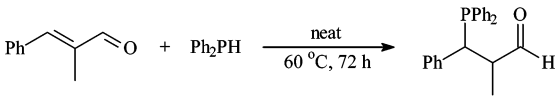
Scheme 1



1 **2**

Ar = Ph (**a**), *p*-tol (**b**), *p*-OMe-C_6H_4 (**c**)

Scheme 2

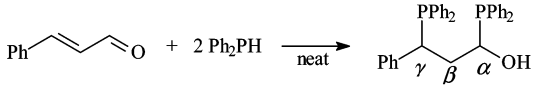


1d

2d-α (*S,S*- and *R,R*-enantiomers)

2d-β (*S,R*- and *R,S*-enantiomers)

Scheme 3



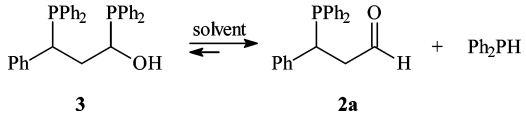
1a

3a (*S,S*- and *R,R*-enantiomers)

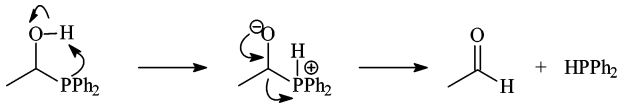
3b (*S,R*- and *R,S*-enantiomers)

are given in the Supporting Information (Figure S1). In DMSO, the α-P atoms of **3a** and **3b** are the most upfield-shifted, while in hexane they are the most downfield-shifted. For **3a**, the α- and γ-protons appear in the $^1H\{^{31}P\}$ spectrum in DMSO-d_6 as overlapping multiplets centered at δ_H 4.0, and the diastereotopic β-protons appear as a multiplet centered at δ_H 1.8. The corresponding spectrum for **3b** is better resolved. The α-H appears as a multiplet at δ_H 4.14 (due to coupling to CH_2 and OH protons), and the γ-H appears as a doublet of doublets at δ_H 3.88 ($^3J_{HH}$ = 10.7, $^3J_{HH}$ = 4.1 Hz); one of the CH_2 protons appears at δ_H 2.08

Scheme 4



Scheme 5



as a doublet of doublets of doublets with two vicinal and one geminal coupling constant ($^3J_{HH}$ = 5.6, $^3J_{HH}$ = 11.1, and $^2J_{HH}$ = 14.1 Hz), while the signal for other proton overlaps with the CH_2 proton signals of **3a**. The individual J_{PH} constants for these protons could not be evaluated, but the J_{PH} and J_{HH} values for the O*H* resonances of **3a** and **3b** (δ_H 5.45 and 5.04, respectively) were readily determined. The $^{13}C\{^1H\}$ resonances for the α-, *β*-, and *γ*-carbon atoms of both diastereomers, including J_{PC} values for both P-atoms, were generally readily measured, although the *γ*-C signal for **3a** (a presumed doublet of doublets) was buried under the DMSO-d_6 resonance and required detection using an HMQC experiment.

We then studied semiquantitatively the decomposition process, which involves loss of Ph_2PH to form the phosphine-substituted aldehyde **2a**—presumably the reverse of the second step of the synthesis of **3** (Scheme 4). The decomposition rate at room temperature was studied in several solvents. Data in Figure S2 show that the rates of, and the degree of, decomposition decrease in the order $CHCl_3$ [donor number (DN) = 4.0] ~ CH_2Cl_2 (1.0) > C_6H_6 (0.1) > MeCN (14.1) > Me_2CO (17.0) > Et_2O (19.2),[15] the trend generally implying increased stability with DN and, as mentioned above, no decomposition was seen in DMSO (DN = 29.8); similarly, solutions of **3** in DMF (DN = 26.6) and pyridine (33.1) are stable. In $CHCl_3/CH_2Cl_2$, an equilibrium showing ~65% conversion to **2a** and Ph_2PH is established with $t_{1/2}$ ~30 min; in acetone, an equilibrium with ~25% conversion occurs with $t_{1/2}$ ~ 20 h, while in Et_2O there is only ~20% conversion after 1 week. Decomposition of **3** in alcohols follows the trend MeOH > EtOH > ^{i}PrOH (see Figure S3) and is faster (e.g., $t_{1/2}$ ~20 h for ~65% conversion in MeOH) than expected from the respective donor numbers (30, 32 and 36),[15] and this might result from the presence of trace water (see below).

In order to test the generality of decomposition of (α-hydroxy)monophosphines, we synthesized $Ph_2PCH(OH)Et$ (**4**) via a room temperature reaction between propionaldehyde and Ph_2PH, a process of the type shown in the reverse reaction of Scheme 4, that is, hydrophosphination of the carbonyl. Phosphine **4** has been synthesized previously by the same reaction carried out at −20 °C but, not mentioned in this report,[9] **4** in solution reversibly decomposes back to its synthetic components (cf. Scheme 4); of note, however, the reversible nature of such a reaction (between benzaldehyde and Ph_2PH) has long been known.[7f] The behavior of **3** in solution is similar to that of **4**, although **3** shows less decomposition at equilibrium than does **4** (Figures S4 and S5 show decomposition data for **4** in the same solvents used in the study of **3**). The variation with solvent of the $^{31}P\{^1H\}$ shifts for **4** is also shown in Table 1 and is very similar to those seen for the α-P atom of **3a** and **3b**; our δ_P value of −2.4 in CH_2Cl_2 is 4.1 ppm to higher field than the reported value.[9] Similar to **3**, **4** is stable in DMSO, and the ^1H NMR data for **4** given in the Experimental are measured in DMSO-d_6; the ^1H data generally agree with those previously reported in $CDCl_3$,[9] but our data are more detailed and there is the complication of rapid decomposition of **4** in $CHCl_3/CDCl_3$.[16]

The solvent also affects the pattern of the ^1H and $^1H\{^{31}P\}$ NMR spectra of **4**. In the latter in DMSO-d_6, the alkyl protons form an $XABY_3$ spin system (Figure 1A), which is well-simulated using J_{XA} = 3.6, J_{XB} = 9.0, J_{AB} = 14.6, J_{YA} = J_{YB} = 7.4 Hz, and the low value of $\Delta\delta_{AB}$ = 1.5 Hz; in the ^1H spectrum, the α-H shows the same broad triplet, implying immeasurable $^2J_{PH}$ coupling (Figure 1A). In CD_3OD (where δ_P = −5.7), the $^1H\{^{31}P\}$ spectrum shows the same spin system, but the *β*-protons are now anisochronous by 14.8 Hz (Figure 1B), and the spectrum is simulated using J_{XA} = 3.4, J_{XB} = 9.2, J_{AB} = 14.0, J_{YA} = J_{YB} = 7.4; in the ^1H spectrum, the α-H resonance now shows $^2J_{PH}$ coupling of 1.3 Hz (Figure 1B). In $CDCl_3$ (where δ_P = −1.6, the most downfield-shifted; see Table 1), the *β*-protons are now anisochronous by 51.2 Hz (Figure 1C) and the $^1H\{^{31}P\}$ spectrum is simulated using J_{XA} = 4.7, J_{XB} = 8.9, J_{AB} = 14.1, J_{YA} = J_{YB} = 7.4); the α-H shows the largest $^2J_{PH}$ coupling of = 5.2 Hz (Figure 1C). A similar analysis of the ^1H and $^1H\{^{31}P\}$ data for the alkyl-chain protons of **3a** and **3b** is more complicated, since there is coupling of the diastereotopic CH_2 protons to both P atoms that cannot be assessed quantitatively.

The decomposition of (α-hydroxy)phosphines could occur via an acid−base interaction between the OH proton and phosphine lone pair to give a phosphonium intermediate, which rearranges to give its component reagents; Scheme 5 shows this as an intramolecular process, while an intermolecular process has been suggested for other rearrangements of (α-hydroxy)phosphines.[17] The better donor solvents likely prevent the OH···P atom interaction by stabilization of the proton; as well as pyridinium, protonated DMSO and DMF cations have been characterized in the solid state.[18] It should be noted that the various solvents were purified by standard procedures, with no special attempts to remove trace water and/or acid, which would be important in the decomposition process; e.g. trace HCl in $CHCl_3$ would certainly promote the decomposition and indeed could account for the faster decomposition in this solvent, but the general observed correlation with DN is nevertheless likely valid, especially

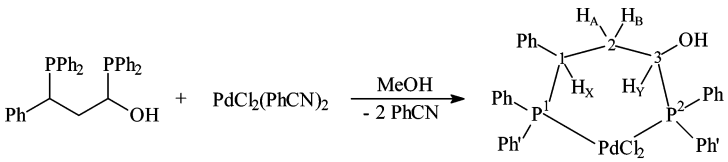
(15) Marcus, Y. *J. Sol. Chem.* **1984**, *13*, 599.

(16) Although not mentioned in ref 9, Muller confirmed via a private communication that his group had observed decomposition of **4** in $CHCl_3$.

(17) Evanelidou-Tsolis, E.; Ramirez, F. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 123.

(18) (a) James, B. R.; Morris, R. H.; Einstein, F. W. B.; Willis, A. *J. Chem. Soc., Chem. Commun.* **1980**, 31. (b) BenedettiMorelli, E.; Di Blasio, B.; Blaine. P. *J. Chem. Soc. Perkin Trans. 2* **1980**, 500.

Scheme 6



5a and **5b** (*S,S*/*R,R*- and *S,R*/*R,S*-enantiomers)

Table 3. Selected Bond Distances and Angles for **5** (Estimated Standard Deviations in Parentheses)

length (Å)		angle (deg)	
P(1)−Pd(1)	2.2599(14)	P(1)−Pd(1)−P(2)	96.43(5)
P(2)−Pd(1)	2.2423(14)	P(1)−Pd(1)−Cl(1)	87.35(5)
Cl(1)−Pd(1)	2.3519(16)	P(2)−Pd(1)−Cl(2)	86.24(5)
Cl(2)−Pd(1)	2.3625(13)	Cl(1)−Pd(1)−Cl(2)	90.15(5)
C(1)−P(1)	1.862(5)	C(1)−P(1)−Pd(1)	120.15(15)
C(3)−P(2)	1.845(5)	C(3)−P(2)−Pd(1)	117.41(15)
C(3)−O(1)	1.408(6)	C(1)−P(1)−C(10)	103.6(2)
		C(1)−P(1)−C(16)	104.5(2)
		O(1)−C(3)−P(2)	111.0(3)

as the measured decomposition rates were reproducible. The downfield-shifted ^{31}P NMR resonances in nondonor solvents (Table 1) are also consistent with favored formation of the phosphonium intermediates, and thus more rapid decomposition (and vice versa). That the relative stability of **3** is greater than that of **4** (Figures S2−S5) perhaps indicates that the γ-P of **3** might interact with the OH proton via an intramolecular interaction and impede protonation of the α-P atom. In a recent report, an analogous dynamic equilibrium between (α-hydroxy)phosphines of the type ArCH(OH)PPh$_2$ and its precursor reagents (e.g, Ph$_2$PH and benzaldehydes) was mentioned in studies describing acid-catalyzed formation of the phosphine oxides ArCH$_2$P(O)Ph$_2$from these reagents, and for the 4-hydroxybenzaldehyde system, the intermediate (α-hydroxy)phosphine was isolated;[10c] in the earlier work with benzaldehyde itself, PhCH(OH)PPh$_2$ had been detected in solution.[7f]

As mentioned in the Introduction, there has been a report on the interaction of Ph$_2$PH with α,β-unsaturated carbonyl compounds including cinnamaldehyde.[5] These reactions, which were catalyzed by Lewis acids in CH$_2$Cl$_2$ solution, included schemes showing hydrophosphination of one or both of the olefinic and carbonyl moieties.[5,19] The schemes incorporated (i) intermediate tertiary phosphines with an aldehyde side chain (including Ph$_2$PCH(Ph)CH$_2$CHO, **2**, synthesized in our studies),[5] (ii) phosphine intermediates with a hydroxy-containing side chain,[19] of the type exemplified by **4** and formed by addition of a second mole of Ph$_2$PH to a phosphino-aldehyde (exemplified by **2**→**3**). However, in neither of these studies by Susuki's group were the intermediates isolated, and no ^{31}P NMR data were presented: only monophosphine oxides were isolated during the workup procedures, or diphosphine dioxides when H$_2$O$_2$ was used as an oxidant to give an isolable product.[5,19]

We have initiated studies on the coordination chemistry of the new tertiary phosphines **2** and **3**, using initially *trans*-PdCl$_2$(PhCN)$_2$ as the metal source, and have isolated and fully characterized complex **5**, PdCl$_2$(*P*,*P*-**3**) (see Scheme 6). A solution ^{31}P{^{1}H} spectrum reveals two sets of resonances, one for each diastereomer pair, the relative intensities being determined by the dr value, which decreases if the crystal-yielding reaction solution is kept for a longer period, presumably because of differences in the solubilities of the diastereomers. Figure S6 shows the spectrum of a CD$_2$Cl$_2$ solution of **5** obtained in 80% yield with dr ∼ 3 after a 16 h reaction; the P^1 and P^2 atoms of the more favorable diastereomer appear at δ_P 23.6 and 24.1, respectively ($^2J_{PP}$ = 16.0 Hz), while the corresponding data for the minor isomer are δ_P 39.1 and 28.0 ($^2J_{PP}$ = 16.8 Hz). A 4 h reaction gave **5** in 50% yield with dr ∼ 20, and an X-ray-quality crystal of **5** with this dr value was analyzed crystallographically (Figure 2, Tables 2 and 3). The compound crystallizes as a mixture of diastereomers, with predominantly *S*,*S*- and *R*,*R*-chirality at C(1) and C(3), respectively, and a small fraction (∼5%) of the *S*,*R*- and *R*,*S*-isomers. The Pd atom shows the expected square-planar coordination, the Pd−P and Pd−Cl distances being close to those reported for the analogous 1,3-bis(diphenylphosphino)propane complex, PdCl$_2$-(dppp),[20] although the P−Pd−P bite angle of **5** (96.43°) is some 6° larger than that of the dppp complex. The C(1)−P(1)−Pd(1) and C(3)−P(2)−Pd(1) angles are similarly about 5° greater than those found for PdCl$_2$(dppp).[20]

The X−AB−Y spin system of the propane-bridge protons seen in the ^{1}H{^{31}P} spectrum of **5** (Figure S7) is simulated using J_{XA} = 1.6, J_{XB} = 12.6, J_{YA} = 7.0, $J_{YB} \leq$ 1.0, and J_{AB} = 15.0 Hz ($\Delta\delta_{AB}$ = 0.273 ppm) for **5a** (Figure S8) and J_{XA} = 12.6, J_{XB} = 2.2, J_{YA} = 11.6, J_{YB} = 2.2, and J_{AB} = 14.0 Hz ($\Delta\delta_{AB}$ = 0.273 ppm) for **5b** (Figure S9). A distinctive feature of **5a** is that the H$_Y$ proton does not couple to the P^2 atom and appears as a doublet at δ_H 5.02 both in the ^{1}H and in ^{1}H{^{31}P} spectra (J_{YB} is unresolved); in contrast, the H$_X$ proton does show $^2J_{PH}$ coupling to the P^1 atom and appears in the ^{1}H spectrum as a pseudotriplet at δ_H 4.58 ($^2J_{PH}$ = 10.3, J_{XB} = 12.3 Hz; J_{XA} 1.6 Hz, seen in the ^{1}H{^{31}P} but being unresolved in the ^{1}H spectrum). For **5b**, however, the H$_Y$ proton couples to P^2 ($^2J_{PH}$ = 5.1 Hz) and appears in the ^{1}H spectrum as a doublet of doublets of doublets at δ_H 4.98 (J_{YA} = 11.6 and J_{YB} = 2.2 Hz), overlapping with the corresponding H$_Y$ proton signal of **5a**. The absence of two-bond coupling between the CH proton and P within an PCH-(OH) moiety has been noted previously.[1b,21] The C(1) and C(3) carbon atoms of **5a** and **5b** do show coupling to both P atoms in the ^{13}C{^{1}H} spectrum, the signals being a doublet of doublets at δ_C 35.5 and 65.3 (for **5a**), and 47.6 and 71.4 (for **5b**). The OH protons of **5a** and **5b** can be seen in a ^{1}H

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spectrum, recorded in DMSO-d_6: dd at δ_H 6.60 ($^3J_{PH}$ = 11.0, $^3J_{HH}$ = 5.6 Hz) and 6.28 ($^3J_{PH}$ = 9.0, $^3J_{HH}$ = 5.6 Hz), respectively. Coordinated **3** shows no decomposition, consistent with the unavailability of phosphorus lone pairs, implying no semilabile character for the ligand (cf. Scheme 5).

Conclusions

New tertiary phosphines $Ph_2PCH(Ar)CH_2CHO$ (Ar = Ph, *p*-tol, and *p*-OMe-C_6H_4), bearing an aliphatic aldehyde group in the side chain, are prepared in good yield by hydrophosphination of the C═C bond of the corresponding cinnamaldehyde in a 1:1 reaction with Ph_2PH at room temperature in the absence of solvent. A similar reaction of Ph_2PH with α-methylcinnamaldehyde, but requiring more severe conditions, affords $Ph_2PCH(Ph)CH(Me)CHO$ as a mixture of diastereomers with predominantly *S*,*S*- and *R*,*R*-chirality, which can be obtained with a dr of ∼20. In a 2:1 reaction of Ph_2PH with cinnamaldehyde, hydrophosphination of both the C═C and C═O bonds gives the diphosphine $Ph_2PCH(Ph)CH_2CH(OH)PPh_2$ as a mixture of diastereomers (dr ∼ 2.3) in which the *S*,*S*/*R*,*R* mixture is dominant. The hydrophosphination of the C═O group is reversible in common organic solvents and leads to an equilibrium between the diphosphine and $Ph_2PCH(Ph)CH_2CHO$; however, the diphosphine is stable in strong donor solvents such as DMSO, DMF, or pyridine, likely due to stabilization of the phosphine-OH proton. X-ray analysis of the complex $PdCl_2[Ph_2PCH(Ph)CH_2CH(OH)PPh_2]$ (with dr ∼ 20) reveals that the *S*,*S*- and *R*,*R*-enantiomers are favored.

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Supporting Information Available: Characterization data for **2b** and **2c** (Table S1); $^{31}P\{^1H\}$ spectra of **3** in various solvents (Figure S1); decomposition of **3** and **4** in aprotic and alcohol solvents (Figures S2−S5); $^{31}P\{^1H\}$ spectrum of **5**, dr ∼ 3 (Figure S6); experimental (Figure S7) and simulated $^1H\{^{31}P\}$ spectra of **5a** (Figure S8) and **5b** (Figure S9); and CIF file for **5**·3MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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