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Iminophosphines: synthesis, formation of 2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salts and *N*-(pyridin-2-yl)-2-diphenylphosphinoylaniline, coordination chemistry and applications in platinum group catalyzed Suzuki coupling reactions and hydrosilylations

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Abstract

The aprotic and protic bi- and multidentate iminophosphines 2-$Ph_2PC_6H_4N{=}CR^1R^2$ ($R^1 = H$, $R^2 = Ph$ = **2a**; $R^1 = Me$ $R^2 = Ph$ = **2b**; $R^1 = H$, R^2 = 2-thienyl = **2c**; $R^1 = H$, $R^2 = C_6H_4$-2-PPh_2 = **2d**; $R^1 = H$, $R^2 = C_6H_4$-2-OH = **2e**, $R^1 = H$, $R^2 = C_6H_4$-2-OH-3-Bu^t = **2f**; $R^1 = H$, $R^2 = CH_2C(O)Me$ = **2g**) have been prepared by the acid catalyzed condensation of 2-(diphenylphosphino)aniline with the corresponding aldehyde–ketone. Iminophosphine **2d** can be reduced with sodium cyanoborohydride to give the corresponding amino-diphosphine 2-$Ph_2PC_6H_4N(H)CH_2C_6H_4$-2-$PPh_2$ (**2h**). In the presence of a stoichiometric quantity of acid, 2-(diphenylphosphino)aniline reacts in an unexpected manner with benzaldehyde, salicylaldehyde, or acetophenone to give the corresponding 2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salts and with pyridine-2-carboxaldehyde to give *N*-(pyridin-2-ylmethyl)-2-diphenylphosphinoylaniline, the latter of which has been characterized by single-crystal X-ray crystallography, as its palladium dichloride derivative. The attempted condensation of 2-(diphenylphosphino)aniline with pyridine-2-carboxaldehyde to give the corresponding pyridine-functionalized iminophosphine resulted in an unusual transformation involving the diastereoselective addition of two equivalents of aldehyde to give 1,2-dipyridin-2-yl-2-(*o*-diphenylphosphinoyl)phenylamino-ethanol, which has been characterized by a single-crystal X-ray structure determination. The bidentate iminophosphine 2-$Ph_2PC_6H_4N{=}C(H)Ph$ reacts with [(cycloocta-1,5-diene)PdClX] X = Cl, Me) to give [Pd{2-$Ph_2PC_6H_4N{=}C(H)Ph$}ClX] and the imino-diphosphine 2-$Ph_2PC_6H_4N{=}C(H)C_6H_4$-$PPh_2$ reacts with [(cycloocta-1,5-diene)PdClMe] to give [Pd{2-$Ph_2PC_6H_4N{=}C(H)C_6H_4$–$PPh_2$}ClMe] and each has been characterized by single-crystal X-ray crystallography. The monobasic iminophosphine 2-$Ph_2PC_6H_4N{=}C(Me)CH_2C(O)Me$ reacts with $[Ni(PPh_3)_2Cl_2]$ in the presence of NaH to give the phosphino–ketoiminate complex [Ni{2-$Ph_2PC_6H_4N{=}C(Me)CHC(O)Me$}Cl], which has been structurally characterized. Mixtures of iminophosphines **2a**–**h** and a palladium source catalyze the Suzuki cross coupling of 4-bromoacetophenone with phenyl boronic acid. The efficiency of these catalysts show a marked dependence on the palladium source, catalysts formed from $[Pd_2(OAc)_6]$ giving consistently higher conversions than those formed from $[Pd_2(dba)_3]$ and $[PdCl_2(MeCN)_2]$. Catalysts formed from neutral bi- and terdentate iminophosphines **2a**–**d** gave significantly higher conversions than those formed from their monobasic counterparts **2e**–**f**. Notably, under our conditions the conversions obtained with **2a**–**c** compare favorably with those of the standards; catalysts formed from tris(2-tolyl)phosphine and tris(2,4-di-*tert*-butylphenyl)phosphite and a source of palladium. In addition, mixtures of $[Ir(COD)Cl]_2$ and **2a**–**h** are active for the hydrosilylation of acetophenone; in this case catalysts formed from monobasic iminophosphines **2e**–**f** giving the highest conversions.

Keywords: Iminophosphines; Multidentate; Template synthesis; Platinum group catalysis; Suzuki coupling reactions; Hydrosilylation

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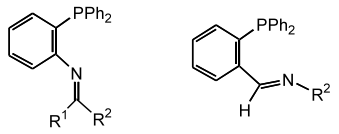
1. Introduction

Iminophosphines are an interesting class of ligand due to the combination of the weak π-accepting nature of the imine and the strong σ-donor properties of the phosphine [1]. Recently, there have been a number of noteworthy reports of the use of these ligands in palladium-mediated catalysis. Shirakawa has shown that palladium complexes of iminophosphine form remarkably active catalysts for the cross coupling of organostannanes with aryl halides [2], the addition of alkynylstannanes to alkynes leading to the regio- and stereoselective formation of conjugated (stannyl)enynes [3] and the carbostannylation of arynes [4]. The steric bulk of the imino phosphine was found to influence both the regioselectivity and rate of alkyne alkynylstannation, those with bulky imino substituents affording higher yields and regioselectivities. Feringa, reasoning that the strongly coordinating soft P-donor and weakly coordinating hard nitrogen donor of imino phosphines could be used to tune the reactivity of palladium complexes in alkene coupling reactions, found that the high temperature oligomerization of ethene in polar solvents gave higher alkenes (C_6–C_{16}) with an oligomer selectivity that was determined by the nature of the ligand substituents [5]. The iminophosphine complex [Pd{*o*-(diphenylphosphino)-*N*-benzaldimime}Me(MeCN)]-[BF_4] catalyses the copolymerization of CO–ethylene and CO–norbornylene and several intermediates of sequential CO and ethylene insertion have been isolated and characterized including [Pd{*o*-(diphenylphosphino)-*N*-benzaldimime}{$CH_2CH_2C(O)CH_2CH_2C(O)CH_3$}][$BF_4$] [6a]. A novel route to a family of bulky iminophosphine ligands [$Ph_2PCH_2C(Ph)$–$N(2,6\text{-}Me_2C_6H_3)$] has recently been developed by Green and co-workers and shown to form active catalysts for CO–ethylene copolymerization [6b]. Turnover numbers as high as 10^6 have been achieved using palladium (**II**) complexes of neutral bidentate iminophosphines to catalyze the Heck reaction between iodobenzene with methyl acrylate, in the presence of *N*-methylpyrrolidinone [7]. Palladium complexes of iminophosphines have also been shown to catalyze the alkoxycarbonylation of terminal alkynes, albeit with much lower rates and regioselectivity than their pyridyldiphenylphosphine counterparts [8]. Five and six-coordinate ruthenium complexes containing the iminophosphine 2-$Ph_2PC_6H_4CH{=}N^tBu$ are active for the transfer hydrogenation of alkyl–aryl and dialkyl ketones in propan-2-ol [9]. Surprisingly, the iminophosphine complexes are more efficient than those based on the corresponding amino-phosphine derivatives, 2-Ph_2P-$C_6H_4CH_2NH^tBu$. Excellent levels of asymmetric induction (95%) have been obtained in the palladium-catalyzed enantioselective allylic alkylation of 1,3-diphenyl-2-propenyl acetate using the chiral iminophosphine (2*S*)-*N*[(1-diphenylphosphino-3-methyl-2-butyl)]-*N*,*N*-dimethylformamidine [10].



A B

One of the most attractive features of iminophosphines is their ease of synthesis, which involves either condensation of 2-(diphenylphosphino)benzaldehyde with an appropriate amine or condensation of 2-(diphenylphosphino)aniline with an aldehyde or ketone to give (A) and (B), respectively. In principle this methodology is extremely versatile and could be used to generate an extensive library of new bi- and multidentate ligands, since a wide range of amines and aldehydes of varying steric bulk and with additional donor groups are either commercially available or can be readily synthesized. The increasing number of reports of the use of iminophosphines in palladium-catalyzed reactions has prompted us to describe the preliminary results of our own study involving the synthesis of iminophosphines, their coordination chemistry and applications in platinum group catalyzed Suzuki coupling reactions and the hydrosilylation of ketones.

2. Experimental

2.1. General procedures

All manipulations involving air sensitive materials were carried out in an inert atmosphere glove box or using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from potassium–sodium alloy, THF from potassium, CH_2Cl_2 from CaH_2 and MeOH from magnesium. Unless otherwise stated commercially purchased materials were purchased and used without further purification. Deuteriochloroform was pre-dried with CaH_2 and vacuum transferred and stored over 4 Å molecular sieves. ^{1}H- and ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR spectra were recorded on a JEOL LAMBDA 500 or Bruker AC 200, AMX 300 and DRX 500 machines. GC analyses were conducted on a Varian CP3800 connected to a Varian C8400 auto sampler. Response factors were determined by injection of samples containing known quantities of authentic sample. The palladium complexes [(cycloocta-1,5-diene)$PdCl_2$] [11a,11b] and [(cycloocta-1,5-diene)PdClMe] [11c], 2-(diphenylphosphino)aniline [12] and its nickel nitrate complex were prepared according to literature methods.

2.2. Synthesis

2.2.1. Synthesis of [2-$Ph_2PC_6H_4N$=C(H)C_6H_5] (2a)

A methanol solution (ca. 30 ml) of 2-(diphenylphosphino)aniline (0.5 g, 1.8 mmol), formic acid (one drop) and benzaldehyde (1.8 mmol, 0.18 ml) was stirred for 18 h after which time the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, washed with water, separated, dried with Na_2SO_4, and filtered. The solvent was removed under reduced pressure to give iminophosphine **2a** as a colorless solid in 66% yield (0.44 g). $^{31}P\{^1H\}$ (202.0 MHz, $CDCl_3$, δ): -13.0 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 8.06 (s, 1H, N=C*H*), 7.14 (m, 19H, C_6H_5 and C_6H_4). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 160.0 (s, N=*C*, 140–122 (m, C_6H_5 and C_5H_4N). *m*/*z* (EI): 365 [M^+]. Anal. Calc. for $C_{25}H_{20}NP$: N, 3.83; C, 82.26; H, 7.18. Found: N, 4.11; C, 82.55; H, 7.48%.

Iminophosphines **2b**–**h** were prepared according to the procedure described above for **2a**.

2.2.2. Synthesis of [2-$Ph_2PC_6H_4N$=C(Me)C_6H_5] (2b)

Iminophosphine **2b** was isolated as a colorless solid in 77% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): -14.1 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 7.19 (m, 22H, C_6H_5 and C_6H_4), 3.41 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 160.0 (N=*C*), 142–128 (m, C_6H_5), 17.5 (*C*H_3). *m*/*z* (EI): 379 [M^+].

2.2.3. Synthesis of [2-$PPh_2C_6H_4N$=C(H)C_3H_3S] (2c)

Iminophosphine **2c** was isolated as a colorless solid in 67% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): -13.0 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 8.15 (d, $J = 1.0$ Hz, 1H, N=C–*H*), 7.71 (dd, $J = 1.0$, 4.1 Hz, 1H, C_3H_3S), 7.24–6.98 (m, 15H, C_6H_5, C_6H_4 and C_3H_3S), 6.94 (dd, $J = 4.1$ Hz, $J = 7.1$ Hz, 1H, C_3H_3S). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 154.0 (s, N=*C*), 153.0 (S*C*=CH), 152.1 (s, *C*–H), 143.3 (s, *C*–H), 137.2 (s, *C*–H), 141–131 (m, C_6H_5). *m*/*z* (EI): 359 [M^+]. Anal. Calc. for $C_{22}H_{18}NPS$: N, 3.90; C, 73.61; H, 5.05. Found: N, 4.09; C, 73.67; H, 5.22%.

2.2.4. Synthesis of [2-$PPh_2C_6H_4N$=C(H)$C_6H_4PPh_2$] (2d)

Iminophosphine **2d** was isolated as a pale yellow solid in 56% yield. $^{31}P\{H\}$-NMR (121.5 MHz, $CDCl_3$, δ): -13.1 (s), -13.7 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 8.82 (d, $J = 5.5$ Hz, 1H, N=C*H*), 7.21–6.82 (m, 29H, C_6H_5 and C_6H_4). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 155.0 (s, N=*C*), 143–132 (m, C_6H_5), 115.1 (d, $^3J_{PC} = 13.3$ Hz). *m*/*z* (EI): 549 [M^+]. Anal. Calc. for $C_{37}H_{29}NP_2$: N, 2.55; C, 80.85; H, 5.32. Found: N, 2.79; C, 81.17; H, 5.43%.

2.2.5. Synthesis of [2-$PPh_2C_6H_4N$=C(H)C_6H_4OH] (2e)

Iminophosphine **2e** was isolated as a pale yellow solid in 61% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ) -13.9 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 12.41 (s, 1H, O*H*), 8.32 (s, 1H, *H*C=*N*), 7.28–6.95 (m, 18H, C_6H_5 and C_6H_4). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ) 160.0 (s, N=*C*) 143–129 (m, C_6H_5). *m*/*z* (EI): 381 [M^+]. Anal. Calc. for $C_{25}H_{20}NOP$: N, 3.67; C, 78.7; H, 5.29. Found: N, 3.71; C, 78.48; H, 5.48%.

2.2.6. Synthesis of [2-$PPh_2C_6H_4N$=C(H)$C_6H_4(Bu^t)OH$] (2f)

Iminophosphine **2f** was isolated as a pale yellow solid in 83% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): -12.6 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 12.9 (s, 1H, O*H*), 8.31 (s, 1H, N=C*H*), 7.11–6.9 (m, 17H, C_6H_5 and C_6H_4), 1.34 (s, 9H, C*Me*$_3$). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 163.0 (s, *C*=N), 141–132 (m, C_6H_5), 34.9 (s, *C*CH_3), 29.3 (s, *C*H_3). *m*/*z* (EI): 437 [M^+]. Anal. Calc. for $C_{29}H_{29}NOP$: N, 3.19; C, 79.42; H, 6.66. Found: N, 2.92; C, 79.58; H, 6.36%.

2.2.7. Synthesis of [2-$PPh_2C_6H_4N$=C(Me)$CH_2C(O)CH_3$] (2g)

Iminophosphine **2g** was isolated as a pale yellow solid in 56% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): -14.5 (s). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 7.25–6.89 (m, 14H, C_6H_5 and C_6H_4), 4.93 (s, 2H, CH_2), 1.94 (s, 3H, CH_3), 1.54 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 196.0 (*C*=O), 160.0 (s, *C*=N), 141–131 (m, C_6H_5), 97.5 (s, *C*H_2), 29.1 (s, *C*H_3), 19.5 (s, CH_3). *m*/*z* (EI): 359 [M^+]. Anal. Calc. for $C_{23}H_{22}NOP$: N, 3.90; C, 76.86; H, 6.17. Found: N, 4.14; C, 77.14; H, 6.44%.

2.2.8. Reduction of [2-$PPh_2C_6H_4N$=C(H)$C_6H_4PPh_2$] (2d)

To a THF solution (ca. 10 ml) of [2-$PPh_2C_6H_4$N=C(H)$C_6H_4PPh_2$] (0.40 g, 0.73 mmol) was added $NaCNBH_3$ (0.046 g, 0.73 mmol) portion wise over 5 min and the resulting mixture allowed to stir overnight. The solvent was removed under reduced pressure and the resulting oily residue was extracted into CH_2Cl_2. The organic phase was washed with water (2×10 ml) separated, dried over Na_2SO_4, filtered and the solvent removed to afford **2i** in 80% yield (0.32 g). ^{1}H-NMR (500.1 MHz, $CDCl_3$, δ): 4.30 (s, br, 2H), 5.22 (s, br, 1H, N–*H*), 7.0 (m, 28H, C_6H_5). $^{13}C\{^1H\}$-NMR (125.65 MHz, $CDCl_3$, δ): 141–130 (m, C_6H_5), 45.9 ($^3J_{PC} = 26.7$ Hz, *C*H_2).

2.2.9. Synthesis of the 2-phenyl-2,3-dihydro-1H-benzo-[1,3]azaphosphol-3-ium salt (3a)

Concentrated sulfuric acid (1 ml) was added dropwise to a rapidly stirred solution of 2-(diphenylphos-

phino)aniline (0.5 g, 1.8 mmol) in methanol (30 ml). Benzaldehyde (0.19 g, 1.8 mmol) was added and the reaction mixture was allowed to stand overnight. The resulting precipitate was filtered and washed with a little methanol to give **3b** in 70% isolated yield (0.58 g) as colorless crystals, after crystallization by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature (r.t.). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 37.7 (s). ^1H-NMR (200.1 MHz, $CDCl_3$, δ); 7.4–6.9 (m, 19H, C_6H_5 and C_6H_4). 6.28 (d, $^2J_{PH} = 10.3$ Hz, $NCHC_6H_5$). m/z (EI): 365 [M^+]. Anal. Calc. for $C_{25}H_{22}NPSO_4$: N, 3.02; C, 64.8; H, 4.79. Found: N, 2.82; C, 65.3; H, 5.08%.

2.2.10. Synthesis of the 2-phenyl-2-methyl-2,3-dihydro-1H-benzo[1,3]azaphosphol-3-ium salt (3b)

Rapid stirring of a methanol solution (ca. 40 ml) of **1** (0.5 g, 1.8 mmol), concentrated H_2SO_4 (ca. 1 ml) and salicylaldehyde (0.2 g, 1.87 mmol) gave **3b** in 58% isolated yield (0.49 g) as colorless crystals, after crystallization by slow diffusion of hexane into the reaction mixture. $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 41.5 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 8.2 (s br, 1H, N*H*), 7.3 (m, 14H, C_6H_5 and C_6H_4), 1.73 (d, $^3J_{P-H} =$ 16.7 Hz, 3H, CH_3), $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.65 MHz, δ): 141–129 (m, C_6H_5 and C_6H_4), 68.8 (d, $^1J_{PC} = 55.9$ Hz, $CC_6H_5CH_3$), 25.5 (d, $^2J_{PC} = 131.3$ Hz, CH_3). Anal. Calc. for $C_{26}H_{24}NPSO_4$: N, 2.93; C, 65.4; H, 5.06. Found: N, 2.77; C, 65.31; H, 4.9%.

2.2.11. Synthesis of the 2-phenol-2-methyl-2,3-dihydro-1H-benzo[1,3]azaphosphol-3-ium salt (3c)

Azaphosphol-3-ium salt **3c** was prepared according to the procedure described above for **3a** and isolated as colorless crystals in 65% yield. $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 38.88 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 10.9 (s, 1H, O*H*), 9.8 (s, 1H, N*H*), 7.7–6.8 (m, 18H, C_6H_5 and C_6H_4), 1.1 (m, 1H, C*H*). Anal. Calc. for $C_{25}H_{22}NPSO_5$: N, 2.92; C, 62.6; H, 4.63. Found: N, 2.95; C, 62.3; H, 4.43%.

2.2.12. Preparation of [Ph2P(O)}C6H4N(H)CH2-2-C5H4N] (4)

Pyridine-2-carboxaldehyde (0.19 g, 1.8 mmol) was added to a stirred solution of 2-(diphenylphosphino)aniline (0.5 g, 1.8 mmol) and formic acid (ca. three drops) in methanol (10 ml). The mixture was allowed to stir overnight and the solvent removed under reduced pressure. Purification of the crude material by column chromatography (CH_2Cl_2:MeOH, 20:1) gave phosphine oxide **4** as a foam in 48% yield (0.33 g). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 37.4. ^1H-NMR (500 MHz, $CDCl_3$, δ): 8.45 (dd, $J = 0.9$, 4.9 Hz, 1H), 7.61 (m, 12H), 7.03 (dd, $J = 5.0$, 6.7 Hz, 1H), 6.94 (d, $J = 7.9$ Hz, 2H), 6.73 (ddd, $J = 1.5$, 7.7, 14.7 Hz, 1H), 6.48 (dd, $J = 4.6$, 7.5 Hz, 2H), 4.44 (d, 2H, $J = 5.9$ Hz), m/z (EI): 384 [M^+]. Anal. Calc. for $C_{23}H_{21}N_2OP$: N, 7.29; C, 75.07; H, 5.51. Found: N, 7.03; C, 74.83; H, 5.18%.

2.2.13. Preparation of [PdCl2{PPh2(O)C6H4N(H)CH2-2-C5H4N}] (5)

A solution of [(cycloocta-1,5-diene)$PdCl_2$] (0.1 g, 0.35 mmol) in CH_2Cl_2 (8–10 ml) was treated with a CH_2Cl_2 solution of **4** (0.13 g, 0.35 mmol) and stirred vigorously overnight. The reaction mixture was filtered, the solvent removed and the residue washed with *n*-hexane and dried under vacuum to give **5** as a yellow solid (0.14 g, 70%). Crystallization by slow diffusion of a CH_2Cl_2 solution layered with *n*-hexane gave X-ray quality crystals of **5**. $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 40.73 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 10.7 (m br, 1H, N*H*), 7.5 (m, 18H, C_6H_5 and C_5H_4N), 4.57 (AB quartet, $^2J_{HH} = 16.5$ Hz, 1H, CHa*H*b), 4.49 (AB quartet, $^2J_{HH} = 16.5$ Hz, 1H, C*H*aHb). Anal. Calc. for $C_{24}H_{21}N_2PPdCl_2O$: N, 4.98; C, 51.3; H, 3.77. Found: N, 4.86; C, 50.91; H, 3.45%.

2.2.14. Reaction of 2-(diphenylphosphino)aniline with pyridine-2-carboxaldehyde in toluene

A toluene solution (ca. 30 ml) of **1** (0.5 g, 1.8 mmol) and pyridine-2-carboxaldehyde (0.19 g, 1.8 mmol) was stirred rapidly for 30 min and then allowed to stand overnight, during which time colorless crystals of **6** formed in 36% yield (0.32 g). The reaction mixture was filtered, the crystals washed with *n*-hexane and dried under vacuum. $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, δ): 35.8 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 4.9 (dd, $J = 8.2$, 2.4 Hz, ArH, 2-pyH, 1H), 5.11 (d, $J = 2.2$ Hz, 1H, ArH, 2-pyH), 6.35 (m, 2H, Ar*H*, 2-Py*H*), 6.68 (ddd, $J = 1.6$, 7.7, 14.4 Hz, 1H, Ar*H*, 2-Py*H*), 6.92 (ddd, $J = 1.0$, 4.9, 7.4 Hz, 1H, Ar*H*, 2-Py*H*), 7.05 (m, 2H, Ar*H*, 2-Py*H*), 7.17 (d, $J = 8$ Hz, 1H, Ar*H*, 2-Py*H*), 7.1–7.6 (m, 15H, Ar*H*, 2-Py*H*), 7.83 (d, $J = 8.3$ Hz, 1H, Ar*H*, 2-Py*H*), 8.23 (d, $J = 4.6$ Hz, 1H, Ar*H*, 2-Py*H*) 8.45 (m, 1H, Ar*H*, 2-Py*H*). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 150–120 (m, C_6H_5), 62.9 (s, CH), 75.1 (s, CH). Anal. Calc. for $C_{30}H_{26}N_3PO_2$: N, 8.54; C, 5.33; H, 5.06. Found: N, 8.34; C, 73.2; H, 5.39%.

2.2.15. Preparation of [Ni(PPh2C6H4N=C(H)-2-C5H4N)2][NO3]2 (7)

A solution of $[Ni(2\text{-}Ph_2PC_6H_4NH_2)_2][NO_3]_2$ (0.5 g, 0.7 mmol) in CH_2Cl_2 (ca. 30 ml) was treated with pyridine-2-carboxaldehyde (0.15 g, 0.7 mmol). The reaction mixture was left to stir overnight to give a deep purple solution, which was filtered and layered with Et_2O to give deep purple crystals of **7** in 43% yield (0.27 g). Anal. Calc. for $C_{48}H_{38}N_4NiO_6P_2 \cdot 5CH_2Cl_2$: N, 6.27; C, 47.48; H, 3.61. Found: N, 6.44; C, 47.79; H, 3.77%.

*2.2.16. Synthesis of [Pd{$Ph_2PC_6H_4N$=C(H)C_6H_5}Cl_2] (**8a**)*

A solution of [(cycloocta-1,5-diene)$PdCl_2$] (0.15 g, 0.52 mmol) in CH_2Cl_2 (ca. 10 ml) was treated with a CH_2Cl_2 solution of **2a** (0.19 g, 0.52 mmol) and stirred vigorously overnight. The reaction mixture was filtered, the solvent removed and the residue washed with *n*-hexane and dried under vacuum to give **8a** as a yellow solid (0.22 g, 78%). Crystallization by slow diffusion of a CH_2Cl_2 solution layered with hexane at r.t. gave X-ray quality crystals of **8a**. $^{31}P\{^1H\}$-NMR (36.4 MHz, $CDCl_3$, δ): 35.6 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 8.66 (s, 1H, *H*–C=N), 7.2–6.9 (m, 19H, C_6H_5 and C_6H_4), $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 164.4 (N=*C*–H), 140–129 (m, C_6H_5). Anal. Calc. for $C_{25}H_{20}Cl_2NPPd$: N, 2.58; C, 55.36; H, 3.71. Found: N, 2.76; C, 55.65; H, 3.99%.

*2.2.17. Synthesis of [Pd{$Ph_2PC_6H_4N$=C(H)C_6H_5}ClMe] (**8b**)*

A solution of [(cycloocta-1,5-diene)PdClMe] (0.1 g, 0.38 mmol) in CH_2Cl_2 (ca. 10 ml) was treated with a CH_2Cl_2 solution of **2a** (0.14 g, 0.38 mmol) and stirred vigorously overnight. The reaction mixture was filtered, the solvent removed and the residue washed with *n*-hexane and dried under vacuum to give **8b** as a yellow solid (0.19 g, 70%). Crystallization by slow diffusion of a CH_2Cl_2 solution layered with Et_2O gave X-ray quality crystals of **8b**. $^{31}P\{^1H\}$-NMR (36.4 MHz, $CDCl_3$, δ): 36.1 (s). ^1H-NMR (500.1 MHz, $CDCl_3$, δ): 8.59 (s, 1H, *H*–C=N), 7.45–6.80 (m, 19H, C_6H_5 and C_6H_4), 1.49 (d, $^3J_{PH} = 7.5$ Hz, 3H, CH_3). $^{13}C\{^1H\}$-NMR (33.9 MHz, $CDCl_3$, δ): 164.0 (N=*C*–H), 141–130 (m, C_6H_5), 3.69 (d, $^2J_{PC} = 22.3$ Hz, 3H, CH_3). Anal. Calc. for $C_{25}H_{20}Cl_2NPPd$: N, 2.58; C, 46.45; H, 3.72. Found: N, 2.77; C, 46.78; H, 4.07%.

*2.2.18. Preparation of [Pd{$Ph_2PC_6H_4N$=C(H)$C_6H_4PPh_2$}Me][$SnMe_3Cl_2$ (**9a**)*

A solution of [(cycloocta-1,5-diene)PdClMe] (0.1 g, 0.38 mmol) in CH_2Cl_2 (ca. 10 ml) was treated with a CH_2Cl_2 solution of **2d** (0.20 g, 0.38 mmol) and stirred vigorously overnight. The reaction mixture was filtered, the solvent removed and the residue washed with *n*-hexane and dried under vacuum to give **9a** as a yellow solid in 64% yield. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): 38.4 (AB quartet, $^2J_{PP} = 392.1$ Hz), 31.4 (AB quartet, $^2J_{pp} = 392.1$ Hz). ^1H-NMR (500.1 MHz $CDCl_3$, δ): 8.47 (dd, $J = 4.2$, 7.0 Hz, 1H, N=C*H*), 7.5–6.9 (m, 28H, C_6H_5 and C_6H_4), 0.69 (s, 9H, SnMe_3), 0.53 (t, $^3J_{PH} =$ 6.1 Hz, 3H, Pd–CH_3). $^{13}C\{^1H\}$-NMR (125.65 MHz, $CDCl_3$, δ): 142.0 (d, $^2J_{P-C} = 9.0$ Hz), 140–130 (m, C_6H_5), 5.68 (s, *C*H_3), −1.85 (*C*H_3). Anal. Calc. for $C_{42.5}H_{45}NP_2PdCl_5Sn$: N, 1.35; C, 49.40; H, 4.38. Found: N, 1.23; C, 49.12; H, 4.13%.

*2.2.19. Preparation of [Pd{$Ph_2PC_6H_4N$=C(H)$C_6H_4Ph_2$]Me]Cl (**9b**)*

A sample of **9a** (0.30 g, 0.33 mmol) and [PPN][Cl] (0.20 g, 35 mmol) was dissolved in CH_2Cl_2 (ca. 15 ml) and the resulting solution stirred for 3 h after which time the solvent was removed and the resulting pale yellow solid was washed with petrol and dried under vacuum. Crystallization from a CH_2Cl_2 solution layered with *n*-hexane at r.t. gave X-ray quality crystals of **9b**. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): 38.4 (AB quartet, $^2J_{pp} = 392.1$ Hz), 31.4 (AB quartet, $^2J_{pp} = 392.1$ Hz). ^1H-NMR (200 MHz, $CDCl_3$, δ): 8.71 (dd, $J = 5.1$, 8.0 Hz, 1H, N=C*H*), 7.3–6.8 (m, 28H, C_6H_5 and C_6H_4), 0.53 (t, $^3J_{PH} = 6.1$ Hz, 3H, PdCH_3). Anal. Calc. for $C_{38}H_{32}ClNP_2Pd$: N, 1.98; C, 64.63; H, 4.57. Found: N, 2.22; C, 64.97; H, 4.83%.

*2.2.20. Reaction of [$NiCl_2(PPh_3)_2$] and [{$PPh_2(C_6H_4)$}N=C(Me)$CH_2C(O)CH_3$] (**10**)*

Addition of sodium hydride (0.004 mg, 0.17 mmol) to a CH_2Cl_2 solution (ca. 20 ml) of iminophosphine **2g** (0.06 g, 0.17 mmol) and [$NiCl_2(PPh_3)_2$] (0.17 mmol, 0.1 g) resulted in an immediate color change from deep green to intense amber. After stirring over night the solvent was removed and the residue was washed with a small amount of THF and then crystallized from THF–hexane to give **10** as an orange crystalline solid in 44% yield (0.038 g). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$, δ): 22.7(s). ^1H-NMR (200.1 MHz, $CDCl_3$, δ): 7.20–6.9 (m, 14H, C_6H_5 and C_6H_4), 5.23 (s, 1H, methane C*H*). 2.10 (s, 3H, CH_3) 1.90 (s, 3H, CH_3). *m*/*z* (EI): 451 [M^+]. Anal. Calc. for $C_{23}H_{22}ClNNiOP$: N, 3.09; C, 66.90; H, 4.89. Found: N, 2.92; C, 66.64; H, 4.43%.

2.3. Catalysis

2.3.1. General procedure for the Suzuki coupling of aryl bromides

A test tube was charged with phenyl boronic acid (0.122 g, 1 mmol), K_2CO_3 (0.19 g, 1.3 mmol), 4-bromoacetophenone (1 mmol), [$Pd_3(OAc)_6$] (0.1 mmol) and dioxane (2 ml). The reaction mixture was stirred at 70 °C for 2 h after which time it was cooled, diluted and a sample removed and diluted with toluene and filtered through celite before being analyzed by gas chromatography. GC conditions: CP-sil5 10 m × 0.53 mm capillary, temperature ramp from 130 to 230 °C, ramp rate 8 °C min^{-1}.

2.3.2. General procedure for the hydrosilylation of acetophenone

A test tube was charged with acetophenone (120 μl, 1 mmol), Ph_2SiH_2 (220 μl, 1.2 mmol), the respective ligand (1 ml of a 10 mM solution), [Ir(COD)Cl]$_2$ (0.5 ml of 20 mM solution) and THF (2 ml). Separate test tubes were charged with the same reactants and the

control ligands. Catalytic runs were performed both in air and under argon. The reaction mixture was stirred for 18 h at ambient temperature and MeOH–2 M HCl (1:1, 0.5 ml) was added and the solution left to stand for 2 h after which time a sample (0.5 ml) of the reaction mixture was removed for analysis by GC.

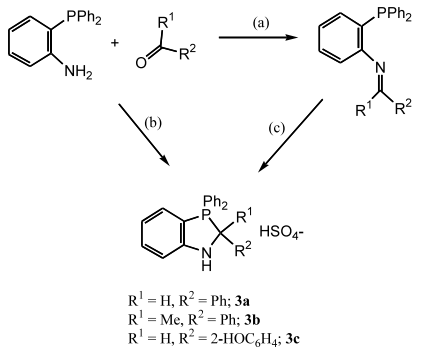
2.4. Crystal structure determinations of *3b*, *3c*, *5*, *6*, *7*, *8a*, *8b*, *9b* and *10*

All measurements were made on a Bruker AXS SMART IK CCD area-detector diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda =$ 0.71073 Å), except for **9b**, for which the very small crystal size required the use of synchrotron radiation (Daresbury SRS station 9.8; $\lambda = 0.6890$ Å). Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved and refined by standard methods, with most H atoms constrained [13a]. Crystal data and other information are given in Table 1. Disorder was resolved and refined for one solvent molecule in **7**, and some of the more highly disordered solvent molecules in this structure were treated by the PLATON SQUEEZE procedure [13b]. There is also two-fold disorder of orientation for the ligand in **9b**, equivalent to exchange of the central N and C atoms of the imido linkage.

3. Results and discussion

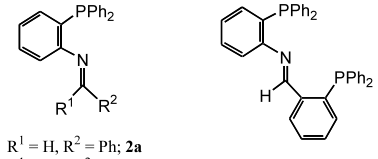
3.1. Acid mediated reactions of 2-(diphenylphosphino)aniline with aromatic carbonyl compounds: synthesis of iminophosphines and formation of 2,3-dihydro-1H-benzo[1, 3]azaphosphol-3-ium salts and N-(pyridin-2-yl)-2-diphenylphosphinoylaniline

Iminophosphines **2a**–**d** were prepared by the acid catalyzed condensation of 2-(diphenylphosphino)aniline (**1**) with the appropriate aldehyde–ketone [14]. Thus, 2-(diphenylphosphino)aniline reacted with benzaldehyde, acetophenone, 2-thiophene carboxaldehyde and 2-(diphenylphosphino)benzaldehyde in methanol in the presence of a catalytic quantity of either formic or sulfuric acid to give the corresponding iminophosphines **2a**–**d**, shown in Chart 1. Similarly, 2-(diphenylphosphino)aniline reacted with salicylaldeyhde, 3-*tert*-butyl-2-salicylaldehyde and 2,4-pentanedione under similar conditions to give the corresponding monobasic terdentate iminophosphines, **2e**–**g**. Reduction of iminophosphine, **2d**, using sodium cyanoborohydride [15] gave the corresponding amino-diphosphine, **2h**, in near quantitative yield. Interestingly, Noyori has recently reported that the iminophosphine complex [$RuCl_2$\{*N*,*N*′-(*S*,*S*)-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diimine\}] is almost inactive for the transfer hydrogenation of acetophenone whereas its amino-phosphine counterpart [$RuCl_2$\{*N*,*N*′-(*S*,*S*)-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine\}] gives high conversions [16]. The ligands are soluble in a range of organic solvents and stable to hydrolysis and aerial oxidation in the solid state over several weeks. Each of the iminophosphines **2a**–**g** and amino-diphosphine **2h** has been characterized using conventional spectroscopic and analytical methods.



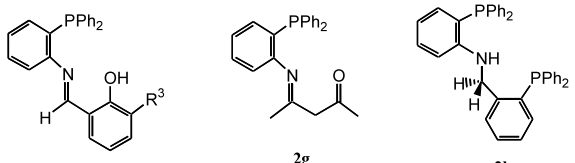
R^1 = H, R^2 = Ph; **3a**
R^1 = Me, R^2 = Ph; **3b**
R^1 = H, R^2 = 2-HOC_6H_4; **3c**

Scheme 1. (a) HCO_2H cat. or H_2SO_4 cat., MeOH, rt, 18 h; (b) H_2SO_4 (ca. five equivalents), MeOH, rt, 18 h; (c) H_2SO_4 (ca. five equivalents), MeOH, rt, 18 h.



R^1 = H, R^2 = Ph; **2a**
R^1 = Me, R^2 = Ph; **2b**
R^1 = H, R^2 = 2-thienyl; **2c**

2d



R^3= H; **2e**
R^3 = Bu^t; **2f**

2g

2h

During our attempts to optimize the conditions required for the condensation we found that, in the presence of excess H_2SO_4 in methanol, the condensation between 2-(diphenylphosphino)aniline and benzaldehyde, acetophenone or salicylaldehyde gave rise to the corresponding benzoazaphospholium salts, **3a**–**c**, rather than the desired iminophosphines (Scheme 1, pathway b). The first evidence for this unexpected transformation was the absence of a low-field ^{1}H-NMR signal associated with the imine N–H. The $^{31}P\{^1H\}$-NMR spectrum of **3a** contains a singlet at δ 37.7 ppm, shifted to low-field of that for the corresponding

Table 1
Crystallographic data for compounds **3b**, **3c**, **5**, **6**, **7**, **8a**, **8b**, **9b** and **10**

Compound	**3b**	**3c**	**5**	**6**	**7**	**8a**	**8b**	**9b**	**10**
Chemical formula	$[C_{26}H_{23}NP][SO_4H]$	$[C_{25}H_{21}NP][SO_4H]$	$C_{24}H_{21}Cl_2N_2OPPd{\cdot}CH_2Cl_2$	$C_{30}H_{26}N_3O_2P$	$[C_{48}H_{38}N_4NiP_2](NO_3)_2{\cdot}5CH_2Cl_2$	$C_{25}H_{20}Cl_2NPPd{\cdot}0.5CH_2Cl_2$	$C_{26}H_{23}ClNPPd$	$[C_{38}H_{32}NP_2Pd]Cl{\cdot}2CH_2Cl_2$	$C_{23}H_{21}ClNNiOP$
Formula weight	477.5	479.5	646.6	491.5	1340.1	585.2	522.3	876.3	452.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$I2/a$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.2574(4)	9.5250(10)	15.1791(10)	11.5624(9)	26.4581(19)	9.7684(8)	7.5030(8)	10.6708(19)	9.424(2)
b (Å)	21.5826(8)	17.0938(18)	10.2385(7)	17.7171(14)	18.0064(14)	9.9703(8)	17.3948(17)	13.746(3)	14.335(3)
c (Å)	19.2286(7)	14.7432(16)	34.199(2)	12.9916(10)	24.2331(18)	14.1133(12)	17.1950(18)	14.364(3)	16.319(4)
α (°)						87.688(2)		114.016(4)	104.915(6)
β (°)	95.014(2)	108.473(2)	101.773(2)	108.596(2)	102.211(2)	77.834(2)	91.663(2)	91.669(5)	102.582(6)
γ (°)						62.871(2)		95.879(4)	91.557(5)
V (Å^3)	4654.0(3)	2276.8(4)	5203.2(6)	2522.4(3)	11283.8(15)	1193.39(17)	2243.2(4)	1908.6(6)	2071.1(8)
Z	8	4	8	4	8	2	4	2	4
D_{calc} (g cm^{-3})	1.363	1.399	1.651	1.294	1.578	1.628	1.546	1.525	1.451
μ (mm^{-1})	0.24	0.25	1.21	0.14	0.93	1.20	1.03	0.95	1.16
Crystal size (mm)	$0.94 \times 0.44 \times 0.34$	$0.16 \times 0.14 \times 0.12$	$0.68 \times 0.12 \times 0.06$	$0.64 \times 0.40 \times 0.20$	$0.78 \times 0.44 \times 0.26$	$0.24 \times 0.22 \times 0.20$	$0.25 \times 0.08 \times 0.06$	$0.06 \times 0.04 \times 0.01$	$0.38 \times 0.30 \times 0.01$
θ_{max} (°)	29.2	29.1	28.8	29.1	25.0	28.6	28.8	25.0	25.0
Reflections measured	44 342	14 460	16 197	15 961	28 894	8906	14 044	13 912	11 179
Unique reflections	11 459 ($R_{int} = 0.0243$)	5620 ($R_{int} = 0.0483$)	6257 ($R_{int} = 0.0254$)	6196 ($R_{int} = 0.0368$)	9875 ($R_{int} = 0.0409$)	5377 ($R_{int} = 0.0206$)	5327 ($R_{int} = 0.0608$)	7324 ($R_{int} = 0.0508$)	7230 ($R_{int} = 0.0812$)
Transmission	0.791–0.908	0.961–0.971	0.550–0.647	0.915–0.972	0.531–0.794	0.573–0.647	0.483–0.928	0.677–0.962	0.668–0.989
Number of parameters	605	307	308	330	654	298	272	463	510
R (F, $F^2 > 2\sigma$)	0.0434	0.0445	0.0305	0.0453	0.0637	0.0296	0.0438	0.0596	0.0686
R_w (F, all data)	0.1226	0.1044	0.0687	0.1172	0.1841	0.0719	0.0887	0.1448	0.1702
Goodness-of-fit on F^2	1.098	0.920	1.049	0.928	1.032	1.023	0.966	0.949	0.911
El. density extremes (e Å^{-3})	1.09 and −0.75	0.40 and −0.41	0.81 and −0.77	0.36 and −0.22	0.86 and −0.95	0.85 and −0.86	1.10 and −1.32	1.72 and −1.56	0.97 and −0.61

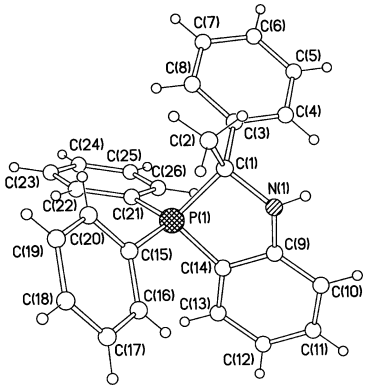


Fig. 1. Molecular structure of one of the two independent molecules of the 2-phenyl-2-methyl-2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salt (**3b**).

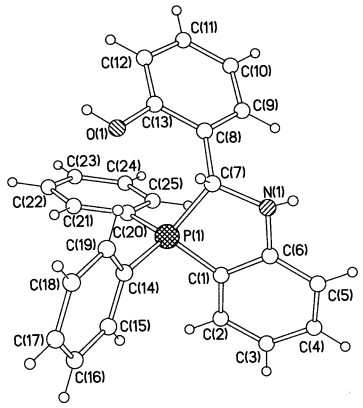


Fig. 2. Molecular structure of the 2-phenol-2-methyl-2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salt (**3c**).

iminophosphine, which in the case of **2a** appears at δ −13.0 ppm. The identity of the salicylaldehyde- and acetophenone-derived salts **3b** and **3c** has been confirmed by single-crystal X-ray structure determinations. Perspective views of the molecular structures of **3b** and **3c**, together with their atomic numbering schemes, are shown in Figs. 1 and 2, respectively, and a selection of bond lengths and angles for both molecules is listed in Table 2. The structure of **3c** reveals that individual ions are linked through intermolecular H-bonding interactions: between the azaphospholium N–H and the oxygen atom of one hydrogen sulfate [N(1)···O(4′) = 2.974 Å and an N–H···O angle of 164°] and the alcohol group of the benzo ring and the oxygen atom of another hydrogen sulfate [O(1)···O(3′) = 2.638 Å and an O(1)···H···O(3′) angle of 162°], together with double hydrogen bonds between pairs of HSO_4^- ions across inversion centers [O(5)–O(2′) = 2.618 Å and an O···H···O angle of 170°]. These hydrogen-bonding interactions propagate through the crystal to form linear 1D arrays along the *c*-axis. Similar N–H···O(anion) and (anion)O–H···O (anion) hydrogen bonds are found in the structure of **3b,** but the resulting anion pairing is not centrosymmetric, as it involves two symmetry-independent anions. Relevant distances are N(1)···O(8) 2.822, N(2)···O(3) 2.853, O(2)···O(6) 2.581,O(4)···O(5) 2.542 Å, with angles of 168, 169, 171, and 169° at the respective hydrogen atoms. In the absence of the alcohol group, further hydrogen bonding interactions are not possible, and only discrete groups of two anions with two cations are formed rather than chains.

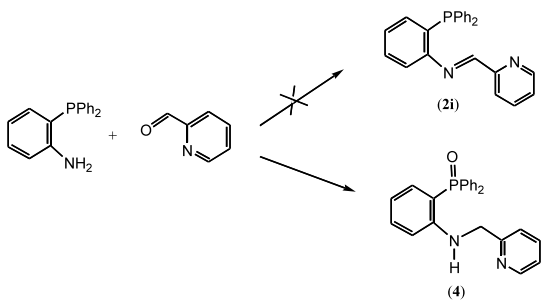
Table 2
Selected bond distances (Å) and angles (°) for **3b** and **3c**

3b		**3c**	
Bond lengths			
P(1)–C(14)	1.7669(17)	P(1)–C(1)	1.767(2)
P(1)–C(1)	1.8941(17)	P(1)–C(7)	1.865(2)
P(1)–C(15)	1.7915(17)	P(1)–C(14)	1.796(2)
P(1)–C(21)	1.7885(17)	P(1)–C(20)	1.789(2)
C(1)–N(1)	1.458(2)	C(7)–N(1)	1.455(2)
N(1)–C(9)	1.367(2)	N(1)–C(6)	1.372(3)
C(9)–C(14)	1.407(2)	C(1)–C(6)	1.404(3)
Bond angles			
C(1)–P(1)–C(14)	943.77(8)	C(1)–P(1)–C(7)	93.87(10)
C(1)–P(1)–C(15)	110.29(8)	C(1)–P(1)–C(14)	112.31(10)
C(1)–P(1)–C(21)	116.51(8)	C(1)–P(1)–C(20)	111.84(10)
C(14)–P(1)–C(15)	111.64(8)	C(7)–P(1)–C(14)	112.61(10)
C(14)–P(1)–C(21)	110.81(8)	C(7)–P(1)–C(20)	114.74(10)
C(15)–P(1)–C(21)	112.45(8)	C(14)–P(1)–C(20)	110.57(9)
C(1)–N(1)–C(9)	116.95(14)	C(6)–N(1)–C(7)	116.64(17)

It is likely that the imines **2a**–**c** are intermediates in the formation of the phospholium salts since treatment of the salicylaldehyde-derived iminophosphine, **2c**, with excess sulfuric acid in methanol gave rise to the salt **3c** (pathway c). The formation of neutral [1,3]azaphospholidines by condensation of β-amino secondary phosphines with aldehydes and ketones is well known [17], as is formation of a stable five-membered thiazole ring via the condensation of 2-(diphenylphosphino)benzaldehyde with 2-aminobenzenethiol [18]. Although 2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salts have been synthesized by P-alkylation of the corresponding azaphospholines [19], we are not aware of any reports of direct preparation from an amino-containing tertiary phosphine and a carbonyl compound.

In our attempts to synthesize the potentially tridentate pyridyl-functionalized iminophosphine **2i**, 2-(diphenylphosphino)aniline (**1**) was reacted with pyridine-2-carboxyaldehyde in the presence of formic acid. Surprisingly, this reaction did not produce the desired iminophosphine but instead gave the aminophosphine oxide **4** (Scheme 2). The $^{31}P\{^1H\}$-NMR spectrum of **4** contains a single resonance at δ 37.4 ppm, the down-field shift relative to that expected for an iminophosphine clearly indicating formation of phosphine oxide. The identity of **4** was unequivocally confirmed by a single-crystal X-ray crystal structure determination of its palladium dichloride derivative, **5**,

prepared by slow addition of a dichloromethane solution of **4** into a dichloromethane solution of [(cycloocta-1,5-diene)$PdCl_2$], at room temperature. The ^{1}H-NMR spectrum of **5** contains an AB multiplet at δ 4.57 and 4.49 ppm ($J = 16.5$ Hz) that corresponds to the diastereotopic methylene protons and a high-field multiplet at δ 10.7 ppm, which belongs to the N–H proton. A perspective view of the molecular structure of **5** is shown in Fig. 3 and a selection of relevant bond lengths and angles is listed in Table 3. The X-ray structure of a dichloromethane solvate clearly shows that **5** coordinates in a bidentate manner as an N_2-donor forming a puckered five-membered chelate ring. The coordination sphere at Pd(1) is close to square planar, the largest deviation of Cl(1), Cl(2), N(1) and N(2) from their mean plane being 0.100 Å. The difference between the palladium–chlorine bond lengths Pd(1)–Cl(1) [2.3028(7) Å)] and Pd(1)–Cl(2) [(2.2894(6) Å] of 0.0134 Å reflects the stronger *trans* influence of the pyridyl group compared with the secondary amine. As a result, Pd(1)–N(1) [2.032(2) Å] is significantly shorter than Pd(1)–N(2) [2.0557(18) Å], both of which are in the range previously reported for pyridyl-amine complexes of palladium. The natural bite angle of 81.98(8)° for N(1)–Pd(1)–N(2) is smaller than the ideal value of 90° and is similar to that of 80.82(9)° reported for the related pyridyl-amine complex [$PdLCl_2$] (where L = *trans*,*trans*-1-methyl-2-pyridin-2-yl-pyrrolidine-3,4-dicarboxylic acid dimethyl ester) [20]. While the Cl(1)–Pd(1)–Cl(2) angle is close to 90° [91.48(2)°] the remaining *cis* angles N(2)–Pd(1)–Cl(1) [93.29(6)°] and N(1)–Pd(1)–Cl(2) [93.63(6)°] are both greater than 90°.



Scheme 2.

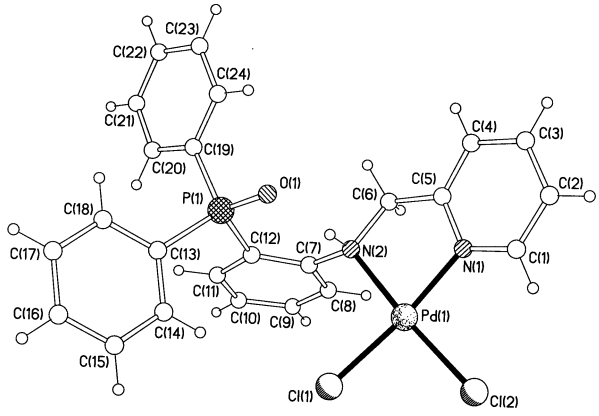
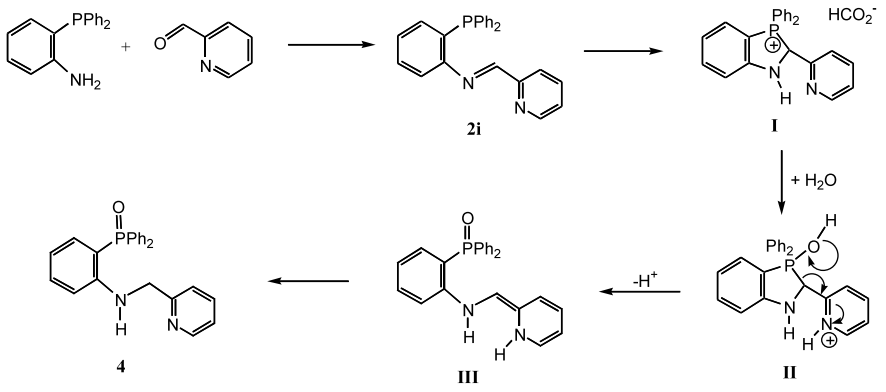


Fig. 3. Molecular structure of [Pd{2-$Ph_2P(O)C_6H_4NHCH_2Ph$}-Cl_2·CH_2Cl_2 (**5**). The CH_2Cl_2 molecule of crystallization has been omitted.

Table 3
Selected bond distances (Å) and angles (°) for **5**

Bond lengths	
Pd(1)–N(1)	2.032(2)
Pd(1)–N(2)	2.0557(28)
Pd(1)–Cl(1)	2.3028(7)
Pd(1)–Cl(2)	2.2894(6)
N(1)–C(5)	1.356(3)
N(2)–C(6)	1.497(3)
P(1)–O(1)	1.4975(19)
Bond angles	
N(1)–Pd(1)–N(2)	81.98(8)
Cl(1)–Pd(1)–Cl(2)	91.48(2)
N(1)–Pd(1)–Cl(2)	93.63(36)
N(2)–Pd(1)–Cl(1)	93.29(6)
N(1)–Pd(1)–Cl(1)	172.06(6)
N(2)–Pd(1)–Cl(2)	174.24(6)
C(6)–N(2)–C(7)	112.36(17)
Pd(1)–N(2)–C(7)	116.57(14)
C(1)–N(1)–C(5)	119.0(2)
Pd(1)–N(2)–C(6)	108.09(13)
Pd(1)–N(1)–C(5)	114.18(15)
Pd(1)–N(1)–C(1)	125.67(17)

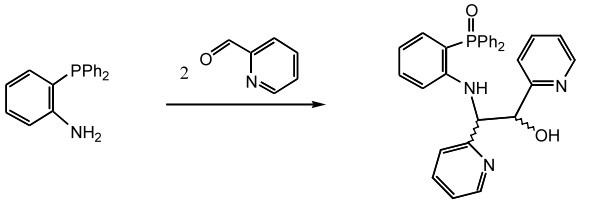
Although the mechanism of alkaline hydrolysis of phosphonium salts is well understood [21,22], hydrolysis under acidic conditions has received much less attention. Uchida has reported the observation of ligand coupling products on acid treatment of phosphonium salts containing at least two 2-pyridyl groups on phosphorus [23]. The C–P bond of aryl phosphonic acids and esters possessing electron donating groups in *ortho* or *para* positions is known to be susceptible to acid cleavage [24]. A mechanism leading to the unexpected phosphine oxide product is proposed in Scheme 3. Formation of the azaphospholium species **I** from the imine **2i** may be followed by nucleophilic attack at phosphorus by water (liberated from the aldehyde during imine formation) to give the P(**V**) intermediate **II,** which is protonated at the pyridine nitrogen. Cleavage of the benzylic C–P bond concomitant with formation of the P=O is assisted by the electron withdrawing effect of the protonated pyridine, which acts as an electron sink. The resulting 2-alkylidene-1,2-dihydropyridine **III** tautomerises to give the product **4**. Interestingly, Vrieze has prepared a hemilabile ligand that contains phosphine, imine and pyridyl donor groups, *N*-(2-(diphenylphosphino)benzylidene)(2-(2-pyridyl)ethyl) amine, by the condensation of 2-(diphenylphosphino)benzaldehyde with 2-(2-aminoethyl)pyridine [25]. This iminophosphine is stable with respect to the corre-



Scheme 3.

sponding phosphine oxide since the cyclization to give an azaphospholium salt cannot occur.

In an attempt to prevent formation of phosphine oxide **4** the condensation of 2-(diphenylphosphino)aniline with pyridine-2-carboxaldehyde was conducted in toluene, in the absence of acid. The condensation of 2-(diphenylphosphino)aniline with pyridine-2-carboxaldehyde in the absence of acid did not give the desired pyridyl iminophosphine, **2i**, but instead resulted in addition of two equivalents of aldehyde to give a diastereoisomeric mixture of 1,2-dipyridin-2-yl-2-(*o*-diphenylphosphinoyl)phenylamino-ethanol (**6**). Fortunately, X-ray quality crystals of one of the diastereoisomers of **6** slowly deposited from the reaction mixture upon prolonged standing at room temperature. The ^{1}H-NMR spectrum of this product clearly did not correspond to either **4** or the desired pyridyl iminophosphine and a single-crystal X-ray structure determination was undertaken in order to unequivocally establish its formulation. A perspective view of the molecular structure of **6**, together with the atomic numbering scheme, is shown in Fig. 4 and a selection of relevant bond lengths and angles is listed in Table 4. Molecules of **6** are linked to give centrosymmetric dimers in the crystal structure, through hydrogen bonds between the hydroxy group of one molecule and the phosphine oxide of the other [O(1)···O(2′) 2.646 Å, with an angle of 178° at H]. The amido hydrogen atom is not involved in hydrogen bonding (Eq. (1)).



(1)

6

A mechanism accounting for the formation of **6** is proposed in Scheme 4. In the absence of an acid, the azaphospholium species **I** does not form and instead 1,2-H migration affords the stabilized zwitterionic intermediate **IV**. Alternatively, **I** may be formed by protonation using the water produced in the imine formation and then subsequent deprotonation by the resulting hydroxide ion would give rise to **IV**. Intermediate **IV** readily undergoes addition to the carbonyl carbon of

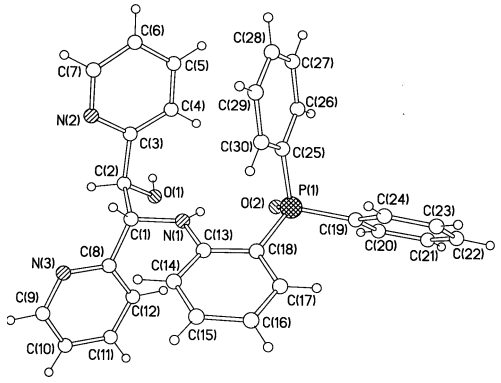
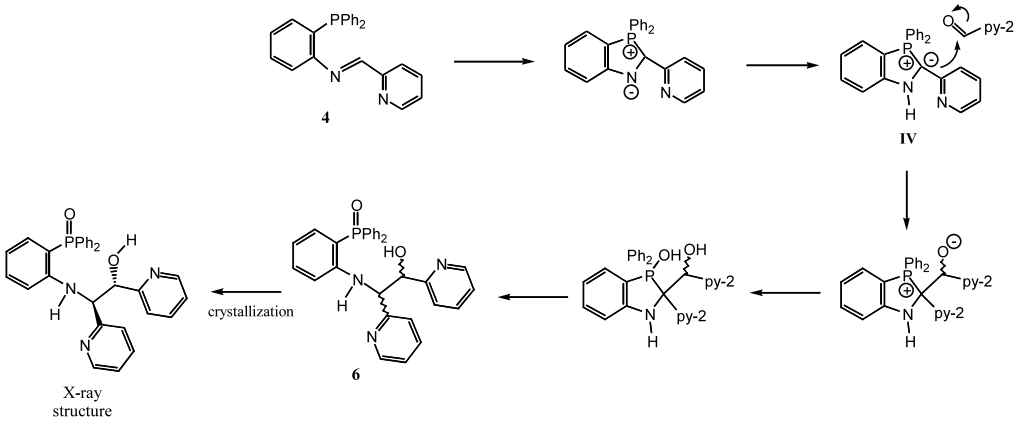


Fig. 4. Molecular structure of the 1,2-dipyridin-2-yl-2-(*o*-diphenylphosphinoyl)phenylamino-ethanol (**6**).

Table 4
Selected bond distances (Å) and angles (°) for **6**

Bond lengths	
N(1)–C(1)	1.455(2)
N(1)–C(13)	1.368(2)
C(1)–C(2)	1.529(2)
C(2)–O(1)	1.418(2)
P(1)–O(2)	1.4964(12)
Bond angles	
C(1)–N(1)–C(13)	123.12(14)
C(1)–C(2)–C(3)	110.48(14)
C(1)–C(2)–O(1)	106.46(13)
C(3)–C(2)–O(1)	114.38(15)
O(2)–P(1)–C(25)	112.89(8)
O(2)–P(1)–C(19)	110.89(7)
O(2)–P(1)–C(18)	112.24(7)
C(18)–P(1)–C(25)	105.97(8)
C(18)–P(1)–C(19)	109.68(7)
C(19)–P(1)–C(25)	104.80(8)



Scheme 4.

another molecule of pyridine-2-carboxaldehyde, in much the same manner that one aldehyde molecule adds to the carbonyl carbon atom of another in the cyanide mediated benzoin condensation i.e. the electron withdrawing power of the pyridyl group facilitates loss of the proton in much the same manner as the CN^- increases the acidity of the aldehyde C–H [26].

Since template reactions involving condensation between a carbonyl compound and a metal coordinated primary amine have been used extensively for the stereospecific synthesis of complex macrocyclic ligands [27], it seemed reasonable to believe that this strategy could be used to prepare pyridyl iminophosphine **2i**. Indeed, we have successfully prepared the target iminophosphine via a template reaction involving condensation of the 2-(diphenylphosphino)aniline complex $[Ni(2\text{-}PPh_2C_6H_4NH_2)_2][NO_3]_2$ with pyridine-2-carboxaldehyde, according to Eq. (2). Addition of pyridine-2-carboxaldehyde to a dichloromethane solution of $[Ni(2\text{-}PPh_2C_6H_4NH_2)_2][NO_3]_2$ resulted in the rapid appearance of a deep purple coloration. After stirring overnight, X-ray quality crystals of **7** were obtained by slow diffusion of diethyl ether into the reaction mixture, at room temperature. The molecular structure of **7** is shown in Fig. 5, a selection of bond lengths and angles is listed in Table 4 and crystal data is provided in Table 1. The structure is based on a distorted octahedron and the two iminophosphines adopt a meridional configuration with the two phosphorus donors and the two pyridyl nitrogen donors *cis* and the two imino N-donors *trans*. The coordinated iminophosphine forms a five-membered ring by P,N chelation and another by N,N chelation. The distortion from octahedral geometry is clearly evident from the N–Ni(1)–P and N–Ni(1)–N angles. The P(1)–Ni(1)–N(1) and P(2)–Ni(1)–N(3) angles of 81.91(10) and 81.19(10)°, respectively, and the N(1)–Ni(1)–N(2) and N(3)–Ni(1)–N(4) angles of 78.98(13) and 79.28(13)°, respectively, within the ligand are significantly less than the ideal value of 90°. The small natural bite angle of the iminophosphine manifests itself in an expansion of the *cis* angles between the ligands, namely, P(1)–Ni(1)–N(3) [100.55(9)°] and P(2)–Ni(1)–N(1) [97.75(10)°], which are substantially greater than the ideal value of 90°. The angle formed by the two imine nitrogen atoms is N(1)–Ni(1)–N(3) is 177.48(13)° while the two remaining *trans* angles P(1)–Ni(1)–N(2) [157.53(10)°] and P(2)–Ni(1)–N(4) [158.21(10)°] are considerably smaller, the compression presumably resulting from the less than 90° bite angles associated with the five-membered chelate rings. The sum of the angles at N(3) [359.9°] and N(1) [359.9°] together with the short N(3)–C(31) and N(1)–C(7) bond distances of 1.274(5) and 1.276(5) Å, respectively, are consistent with sp^2-hybridization and characteristic of a coordinated imine. The C–N bond lengths of coordinated iminophosphines can range from 1.25 to 1.442 Å.

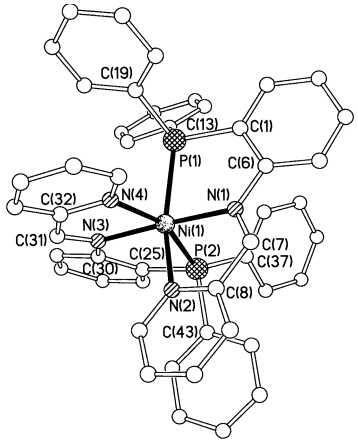


Fig. 5. Molecular structure of $[Ni\{2\text{-}Ph_2PC_6H_4N{=}C(H)C_5H_4\text{-}N\}_2][NO_3]_2{\cdot}5CH_2Cl_2$ (**7**). Hydrogen atoms and the CH_2Cl_2 molecules of crystallization have been omitted. Key atoms are labeled.

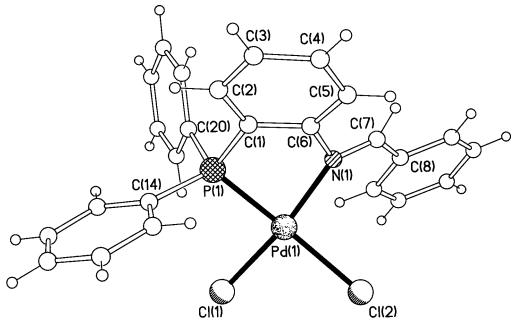


Fig. 6. Molecular structure of [Pd{2-$PPh_2C_6H_4N$=C(H)Ph}-Cl_2]·0.5CH_2Cl_2 (**8a**). The solvent molecule has been omitted.

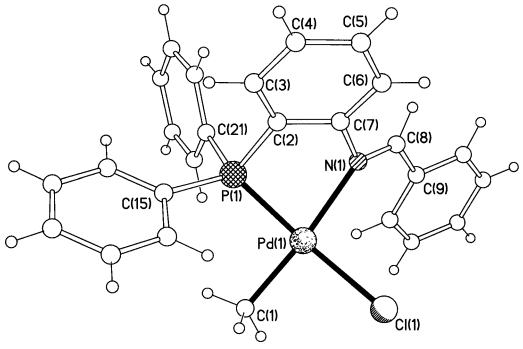
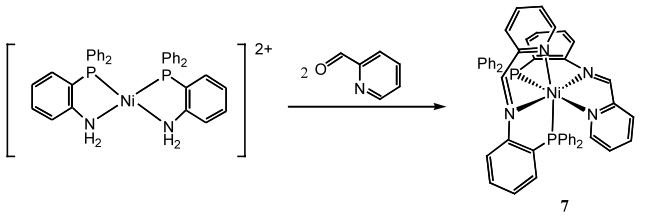


Fig. 7. Molecular structure of [Pd{2-$PPh_2C_6H_4N$=C(H)Ph}ClMe] (**8b**).

Table 5
Selected bond distances (Å) and angles (°) for **7**

Bond lengths	
Ni(1)–N(1)	2.045(3)
Ni(1)–N(2)	2.117(3)
Ni(1)–N(3)	2.056(3)
Ni(1)–N(4)	2.079(3)
Ni(1)–P(1)	2.3795(11)
Ni(1)–P(2)	2.4090(12)
N(1)–C(7)	1.276(5)
N(3)–C(31)	1.274(5)
Bond angles	
P(1)–Ni(1)–N(2)	157.53(10)
P(2)–Ni(1)–N(4)	158.21(10)
N(1)–Ni(1)–N(3)	177.48(13)
P(1)–Ni(1)–N(1)	81.91(10)
P(1)–Ni(1)–N(4)	89.70(9)
P(1)–Ni(1)–N(3)	100.55(9)
P(2)–Ni(1)–N(3)	81.19(10)
P(2)–Ni(1)–N(1)	97.75(10)
P(2)–Ni(1)–N(2)	90.90(9)
P(2)–Ni(1)–P(1)	103.35(4)
N(2)–Ni(1)–N(3)	98.72(13)
N(1)–Ni(1)–N(4)	101.36(13)
N(3)–Ni(1)–N(4)	79.28(13)
N(2)–Ni(1)–N(4)	82.62(13)
N(1)–Ni(1)–N(2)	78.98(13)



(2)

3.2. Iminophosphine coordination chemistry

Dropwise addition of a dichloromethane solution of iminophosphine **2a** into a dichloromethane solution of [(cycloocta-1,5-diene)PdClX] (X = Cl, Me) resulted in near quantitative formation of [Pd{2-$Ph_2PC_6H_4$-N=C(H)Ph}ClX] (X = Cl, **8a**; X = Me, **8b**). The $^{31}P\{^1H\}$-NMR spectrum of **8a** contains a singlet at δ 35.6 ppm and that of **8b** a singlet at δ 36.1 ppm, the latter being consistent with the formation of a single coordination isomer, most likely that with the methyl *trans* to the imino-nitrogen atom. A high-field doublet at δ 1.49 ppm (J_{PH} = 7.5 Hz) in the ^{1}H-NMR spectrum of **8b** corresponds to the palladium-bound methyl and a broad singlet at δ 8.59 ppm belongs to the imine N–H. The magnitude of this coupling is consistent with a *cis* arrangement of methyl and phosphorus in the coordination sphere of palladium [28], as would be expected for two groups exhibiting a large *trans* influence [29]. Both compounds are air stable for prolonged periods, in the solid state and in solution, and dissolve readily in polar solvents. Single-crystal X-ray structure determinations of **8a** and **8b** have been undertaken to obtain precise details of the structures and to compare with that of [Pd{2-$Ph_2PC_6H_4N$=C(H)Ph}PhI], which has recently appeared in the literature. The molecular structures of **8a** and **8b** are shown in Figs. 6 and 7, respectively, and a selection of bond lengths and angles for both compounds is listed in Tables 5 and 6. Since the structures of both compounds are based on palladium complexes of iminophosphines and are clearly related they will be discussed in parallel. In both cases the coordination sphere around Pd(1) is close to square planar, as indicated by the dihedral angles of 12.1 and 15.9°, for **8a** and **8b**, respectively, between the planes containing P(1)Pd(1)N(1) and Cl(1)Pd(1)X. The natural bite angles of 82.10(6)° (**8a**) and 80.65(8)° (**8b**) are similar to those reported for related complexes including [Pd{2-$Ph_2PC_6H_4N$=C(H)Ph}PhI] [80.3(2)°] and [Pd_2(2.2′-bis{*N*-[(2-diphenylphosphino)phenyl] formimidoyl}biphenyl)Cl_2Me_2] [79.70(11)°] [7,30] and significantly smaller than the ideal value of 90°. The Pd–Cl bond *trans* to phosphorus [2.3866(6) Å] in **8a** is significantly longer than that *trans* to nitrogen [2.2859(6) Å] and reflects the stronger *trans* influence of the diphenylphosphino group compared with an imine. The molecular structure of **8b** clearly shows that the methyl

group occupies the site *trans* the imine nitrogen [N(1)–Pd(1)–C(1) = 173.96(14)°]. The difference of 0.133 Å between the Pd(1)–N(1) bond lengths in **8a** [Pd(1)–N(1) = 2.053(2) Å] and **8b** [Pd(1)–N(1) = 2.196(3) Å] reflects the much greater *trans* influence of methyl compared with chloride. Not surprisingly, the Pd–P bond lengths in **8a** [Pd(1)–P(1) = 2.2104(6) Å] and **8b** [Pd(1)–P(1) = 2.2004(10) Å] are similar as a result of both being *trans* to chloride. The Pd–Cl bond *trans* to phosphorus in **8a** [Pd(1)–Cl(2) = 2.3866(6) Å] is similar in length to the comparable bond in **8b** [Pd(1)–Cl(1) = 2.3834(9) Å], both of which are within the range expected for palladium complexes of iminophosphines including [Pd{2-$PPh_2C_6H_4C(H)$=$NC_6H_3Pr^i_2$}MeCl] [2.3734(11) Å], [Pd{2-(diphenylphosphino)-benzylidene-S(−)-α-methylbenzylamine}ClX] [X = Cl, 2.370(2) Å; X = Me, 2.371(3) Å] and [$Pd_2(L^1H)Cl_2Me_2$] [2.3837(9) Å] (L^1H = 1,3-bis[(2-(diphenylphosphino)benzylidene)-amino]-propan-2-ol) [5,31,32].

Table 6
Selected bond distances (Å) and angles (°) for **8a** and **8b**

8a		**8b**	
Bond lengths			
Pd(1)–P(1)	2.2104(6)	Pd(1)–P(1)	2.2004(10)
Pd(1)–N(1)	2.063(2)	Pd(1)–N(1)	2.196(3)
Pd(1)–Cl(1)	2.2859(6)	Pd(1)–Cl(1)	2.3834(9)
Pd(1)–Cl(2)	2.3866(6)	Pd(1)–C(1)	2.028(3)
N(1)–C(7)	1.297(3)	N(1)–C(8)	1.281(4)
Bond angles			
P(1)–Pd(1)–N(1)	82.10(6)	P(1)–Pd(1)–N(1)	80.65(8)
Cl(1)–Pd(1)–Cl(2)	91.68(2)	Cl(1)–Pd(1)–C(1)	89.92(12)
P(1)–Pd(1)–Cl(1)	90.89(2)	P(1)–Pd(1)–C(1)	93.82(12)
N(1)–Pd(1)–Cl(2)	95.95(6)	N(1)–Pd(1)–Cl(1)	96.06(8)
N(1)–Pd(1)–Cl(1)	172.01(6)	N(1)–Pd(1)–C(1)	173.96(14)
P(1)–Pd(1)–Cl(2)	168.32(2)	P(1)–Pd(1)–Cl(1)	163.98(3)
C(6)–N(1)–C(7)	117.1(2)	C(7)–N(1)–C(8)	118.3(3)
Pd(1)–N(1)–C(6)	113.15(15)	Pd(1)–N(1)–C(7)	108.7(2)
Pd(1)–N(1)–C(7)	129.57(18)	Pd(1)–N(1)–C(8)	132.8(2)

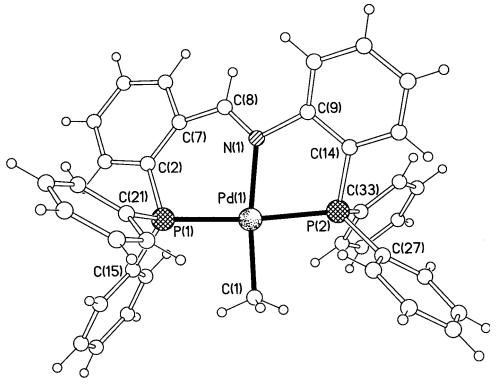


Fig. 8. Molecular structure of [Pd{2-$PPh_2C_6H_4N$=$C(H)C_6H_4$-2-PPh_2}CH_3][Cl]·$2CH_2Cl_2$ (**9b**). Solvent molecule, chloride anion and disorder are omitted.

The terdentate iminophosphine **2d** was reacted with [(cyclocta-1,5-diene)PdClMe] in dichloromethane. After stirring overnight the cationic palladium complex [Pd{2-$PPh_2C_6H_4N$=$C(H)C_6H_4PPh_2$}Me]$^+$ (**9a**) was isolated as its [$SnMe_3Cl_2$]$^-$, salt by crystallization from a dichloromethane solution layered with hexane. The $^{31}P\{^1H\}$-NMR spectrum of **9a** contains two signals which appear as an AB quartet at δ 38.4 and 31.4 (J_{PP} = 392.1 Hz), as expected for terdentate coordination of **2d**, and the magnitude of $^2J_{PP}$ is consistent with a *trans* arrangement of diphenylphosphino groups [33]. The presence of two high-field signals, a triplet at δ 0.53 (J_{PH} = 6.1 Hz) and a singlet at δ 0.69 ppm, the latter flanked by satellite peaks, provided the first indication that the palladium complex was not formed as its chloride salt. Moreover, the 1:3 intensity of these high-field signals strongly suggests that the counterion is in fact [$SnMe_3Cl_2$]$^-$, which is most likely formed by abstraction of chloride from [Pd{2-$PPh_2C_6H_4N$=$C(H)C_6H_4PPh_2$}Me][Cl] by $SnMe_3Cl$, which is present in the reaction mixture as a byproduct formed during the preparation of [(cyclocta-1,5-diene)PdMeCl] via selective methylation of [(cyclocta-1,5-diene)$PdCl_2$] with tetramethyltin [12]. Treatment of a dichloromethane solution of [Pd{2-$PPh_2C_6H_4N$=$C(H)C_6H_4PPh_2$}-Me][$SnMe_3Cl_2$] with a slight excess of [PPN][Cl] resulted in clean and quantitative anion exchange to give [Pd(2-$PPh_2C_6H_4N$=$C(H)C_6H_4PPh_2$)Me][Cl] (**9b**). This formulation is supported by elemental analysis, as well as ^{1}H-NMR spectroscopy, which shows the disappearance of the high-field singlet associated with the [$SnMe_3Cl_2$] anion. A single-crystal X-ray structure determination of **9b** has been undertaken to provide precise details on the mode of coordination of **2d**. A perspective view of the molecular structure is shown in Fig. 8 and a selection of bond lengths and angles is listed in Table 7, while crystal data is provided in Table 1. The molecular structure clearly reveals that **2d** coordinates in a terdentate manner, forming a five-membered ring by chelating P(2)N(1) and a six-membered ring by chelating P(2)N(1). There is two fold disorder of orientation of the ligand, equivalent to exchange of N(1) and C(8); both disorder components have essentially the same geometry, and only one is presented here. The coordination sphere around palladium is close to square-planar, as indicated by a root-mean square deviation of the coordinating atoms of 0.100 Å from their mean plane. The Pd–P bond lengths [Pd(1)–P(1) = 2.2648(14) Å, Pd(1)–P(2) = 2.2742(14) Å] are in the range expected for palladium complexes with a *trans* arrangement of diphenylphosphino groups such as [Pd{1,8-bis(diphenylphosphino)-3,6-dioxaoctane}Cl_2] [34] and [Pd{1,11-bis(diphenylphosphinomethyl)benzo-[*c*]phenanthrene}Cl_2] [35]. The Pd(1)–N(1) bond length of 2.136(9) Å is similar to that of 2.063(2) Å in [Pd{2-$PPh_2C_6H_4N$=$C(H)Ph$}Cl_2] and 2.020(3) Å in [Pd{2-

Table 7
Selected bond distances (Å) and angles (°) for **9b**

Bond lengths	
Pd(1)–P(1)	2.2648(14)
Pd(1)–P(2)	2.2742(14)
Pd(1)–N(1)	2.136(9)
Pd(1)–C(1)	2.052(6)
N(1)–C(8)	1.264(16)
Bond angles	
P(1)–Pd(1)–P(2)	173.63(6)
P(1)–Pd(1)–N(1)	94.4(3)
P(2)–Pd(1)–N(1)	80.1(3)
C(1)–Pd(1)–P(1)	93.24(17)
C(1)–Pd(1)–P(2)	92.62(17)
N(1)–Pd(1)–C(1)	169.2(3)
C(8)–N(1)–C(9)	113.7(8)
Pd(1)–N(1)–C(8)	127.8(8)
Pd(1)–N(1)–C(9)	118.4(6)

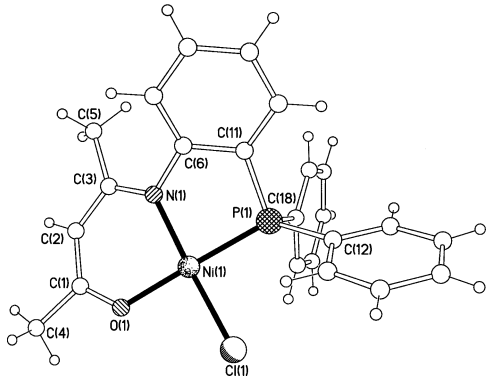
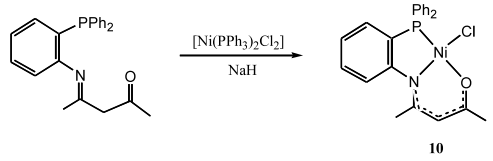


Fig. 9. Molecular structure of one of the two independent molecules of [Ni{2-$PPh_2C_6H_4$NC(Me)C(H)C(Me)O}Cl] (**10**).

$PPh_2C_6H_4N$–C(H)C_6H_4-4-Cl-2-O}Cl_2]. The P(1)Pd(1)-N(1) bite angle of 94.4(3)° is significantly larger than that of 80.1(3)° for P(2)Pd(1)N(1) and is similar to those previously reported for related compounds including [$Pd_2(L^1)(OAc)_2$][BF_4] [95.36(17)°] and [$Pd_2(L^1)$-Me_2][BF_4] [94.47(11)° and 93.78(11)°] (L^1H = 1,3-bis[(2-(diphenylphosphino)benzylidene)amino]-propan-2-ol) and [Pd{*N*-(2-(diphenylphosphino)benzylidene)(2-(2-pyridyl)ethyl)amine}Me][CF_3SO_3] [91.87(13)°]. While P–Pd–N bite angles in palladium complexes of iminophosphines that form six-membered chelate rings are generally larger than those that form five-membered rings, the latter appear to be extremely flexible and cover a broad range (84–95°). The *trans* angles P(1)Pd(1)P(2) 173.63(6)° and N(1)Pd(1)C(1) 169.2(3)° are slightly less than 180°, such distortions being common in platinum group complexes of P_2N ligands coordinated in a terdentate manner [36].

Addition of NaH to a dichloromethane solution containing [$NiCl_2(PPh_3)_2$] and 2-$Ph_2PC_6H_4$N=C(Me)-CH_2C(O)Me resulted in a dramatic color change from green to deep amber with the formation of the phosphino–ketoiminate complex [Ni{2-$Ph_2PC_6H_4$N=C-(Me)CHC(O)Me}Cl] (**10**), according to Eq. (3). The $^{31}P\{^1H\}$-NMR spectrum of **10** contains a sharp singlet at δ 22.7 ppm, in the region characteristic of a coordinated diphenylphosphino group. In the ^{1}H-NMR spectrum two singlets at δ 1.84 and 1.94 ppm, each of intensity 3H, correspond to the two methyl substituents of the ketoiminate fragment and a singlet at δ 4.94 ppm, intensity 1H, belongs to the methine proton. The formulation shown in Eq. (3) is also supported by elemental analysis and EIMS, where the parent molecular ion gives rise to the most abundant peak in the mass spectrum.



(3)

10

Since platinum group complexes of terdentate ligands containing three different donor groups are relatively rare [37] a single-crystal X-ray structure determination of **10** was undertaken to confirm the mode of binding and to provide precise structural details of the metal's coordination environment. A perspective view of one of the two independent molecules is shown in Fig. 9 and a selection of relevant bond lengths and angles is listed in Table 8 and crystal data is provided in Table 1. The molecular structure reveals that **10** coordinates in a terdentate manner, as a monobasic ligand, and forms a distorted square-planar complex, as evidenced by the dihedral angle of 9.5° between the planes containing Ni(1)O(1)N(1) and Ni(1)P(1)Cl(1) (6.5° for the second molecule). The Ni–Cl bond length of 2.171(2) Å is similar to those reported for related nickel complexes such as [Ni{2-$PPh_2C_5H_4$N=C(H)C_6H_4-2-O}Cl] [2.187(1) Å], [Ni{2-$PPh_2C_6H_4$C(H)=NC_6H_4-2-O}Cl] [2.148(3) Å] and [Ni{$Ph_2PC_6H_4$NC(H)C_6H_3-5-Br-2-O}Cl] [2.1857(8) Å], reported earlier by Parr and coworkers [38]. The Ni···O(1) six-membered chelate ring is somewhat distorted from planar, Ni(1) being displaced by 0.475 Å from the plane containing the remaining five atoms (0.587 Å for the second molecule). The ketoiminate nitrogen atom N(1) is close to planar (sum of angles = 359.7°) and the N(1)–C(3) bond distance of 1.335(9) Å is comparable to the C–N distances of 1.311(3) and 1.321(5) Å in the iminophosphine complex [Ni{2-$PPh_2C_6H_4$N=C(H)C_6H_4O}Cl] [38] and the ketoiminate complex [Zr{CH_3C(NPh)CH(O)CH_3}$_2Cl_2$] [39], respectively. The bond length pattern within the six-membered ring system suggests significant delocalization of bonding electron density as evidenced by a difference of only 0.026 Å in the C(1)–C(2) [1.389(12) Å] and C(2)–C(3) [1.415(11) Å] bond lengths, which is signifi-

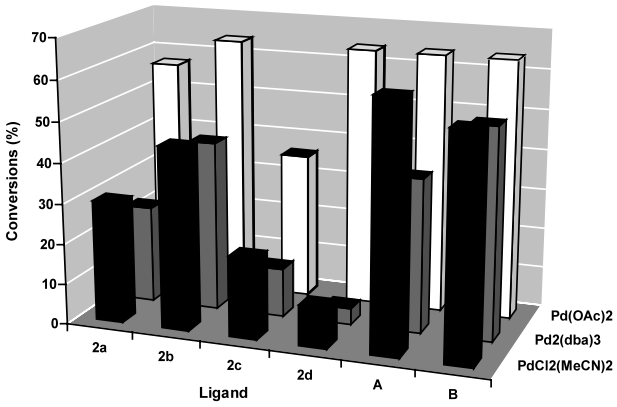
cantly smaller than the comparable difference in [Ti{CH_3(O)CHC(NCH_2CH_2O)}Cl_2(THF)] (0.071 Å) [40]. The Ni–O bond length of 1.877(5) Å is similar to those reported for Ni(II) complexes of related iminophosphine ligands including [Ni{2-$PPh_2C_6H_4N$=C(H)-2-C_6H_4-2-O}Cl] [1.863(25) Å] and [Ni{2-$PPh_2C_6H_4CH$=NC_6H_4-2-O}Cl] [1.875(51) Å], and similarly, the Ni–N bond length of 1.882(7) Å is comparable to those of 1.89(2) and 1.900(7) Å in the same two compounds, respectively [38].

3.3. Catalysis

Recent reports of the use of bidentate iminophosphines in platinum group catalyzed reactions including the palladium catalyzed Heck arylation, the copolymerization of ethylene with carbon monoxide and the ruthenium catalyzed hydrogen transfer reduction of ketones prompted us to evaluate the efficiency of iminophosphines **2a**–**h** in the Suzuki cross coupling reaction and the hydrosilylation of ketones. The Suzuki reaction is a powerful method for the formation of $C(sp^2)$–$C(sp^2)$ bonds which offers immense potential in organic synthesis [41]. Preliminary studies have been restricted to coupling of the electronically activated substrate 4-bromoacetophenone with phenyl boronic acid (Eq. (4)) by catalysts based on mixtures of **2a**–**i** and [$Pd_2(OAc)_6$], [$Pd_2(dba)_3$] and [$Pd(MeCN)_2Cl_2$]. The results are summarized in Charts 1 and 2, the former containing conversion using catalysts based on aprotic iminophosphines **2a**–**d** and the latter contain conversions obtained using monobasic terdentate phosphines **2f**–**g** and the amino-diphosphines **2g**. Cross coupling reactions were carried out in dioxane by combining the palladium precursor, iminophosphine and substrates and heating at 70 °C for 2 h and the extent of reaction monitored by GC. Herrman [42] and Bedford [43] have recently shown that palladacycles **11** and **12**, formed from tris(2-tolyl)phosphine (**A**) and tris(2,4-di-*tert*-butylphenyl)phosphite (**B**), respectively, are highly active for the Suzuki cross coupling reaction, giving TON in excess of 10^6. Thus, catalyst mixtures generated from tris(2-tolyl)phosphine (**A**) and tris(2,4-di-*tert*-butylphenyl)phosphite (**B**) and a variety of palladium sources have been used as standards under our reaction conditions.

Table 8
Selected bond distances (Å) and angles (°) for **10**

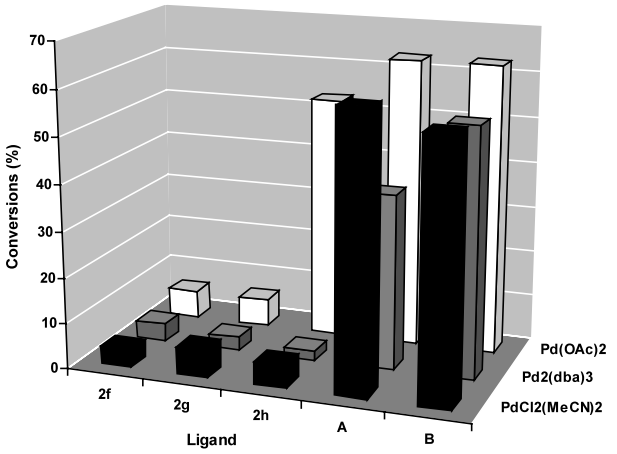
Molecule **a**		Molecule **b**	
Bond lengths			
Ni(1)–P(1)	2.142(2)	Ni(2)–P(2)	2.130(2)
Ni(1)–N(1)	1.882(7)	Ni(2)–N(2)	1.892(6)
Ni(1)–O(1)	1.877(5)	Ni(2)–O(2)	1.880(6)
Ni(1)–Cl(1)	2.171(2)	Ni(2)–Cl(2)	2.179(2)
N(1)–C(3)	1.335(9)	N(2)–C(26)	1.337(10)
O(1)–C(1)	1.264(9)	O(2)–C(24)	1.279(9)
C(1)–C(2)	1.389(12)	C(24)–C(25)	1.387(12)
C(2)–C(3)	1.415(11)	C(25)–C(26)	1.371(12)
Bond angles			
P(1)–Ni(1)–Cl(1)	91.54(9)	P(2)–Ni(2)–Cl(2)	89.23(9)
P(1)–Ni(1)–N(1)	85.7(2)	P(2)–Ni(2)–N(2)	85.8(2)
N(1)–Ni(1)–O(1)	95.0(3)	N(2)–Ni(2)–O(2)	93.8(3)
O(1)–Ni(1)–Cl(1)	88.25(18)	O(2)–Ni(2)–Cl(2)	91.02(18)
N(1)–Ni(1)–Cl(1)	175.8(2)	N(2)–Ni(2)–Cl(2)	174.9(2)
P(1)–Ni(1)–O(1)	170.81(18)	P(2)–Ni(2)–O(2)	174.06(19)
C(3)–N(1)–C(6)	119.5(7)	C(26)–N(2)–C(29)	122.0(7)
Ni(1)–N(1)–C(3)	123.2(6)	Ni(2)–N(2)–C(26)	119.3(6)
Ni(1)–N(1)–C(6)	117.0(5)	Ni(2)–N(2)–C(29)	117.7(5)
Ni(1)–O(1)–C(1)	123.8(5)	Ni(2)–O(2)–C(24)	123.8(6)



A = tris(2-tolyl)phosphine

B = tris(2,4-di-*tert*-butylphenyl)phosphite

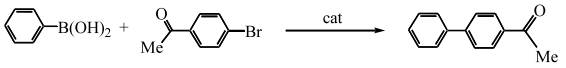
Chart 1. Conversion in the Suzuki coupling reaction between bromobenzene and phenylboronic acid. (A) Tris(2-tolyl)phosphine. (B) Tris(2,4-di-tert-butylphenyl)phosphite.



A = tris(2-tolyl)phosphine

B = tris(2,4-di-*tert*-butylphenyl)phosphite

Chart 2. Conversion in the Suzuki coupling reaction between bromobenzene and phenylboronic acid. (A) Tris(2-tolyl)phosphine. (B) Tris(2,4-di-tert-butylphenyl)phosphite.



(4)

Comparison of Charts 1 and 2 reveals a clear distinction between the performance of catalysts formed from **2a** to **d** and these based on **2f**–**g**. Firstly, catalyst mixtures of **2a**–**d** are more efficient at cross coupling than their monobasic counterparts **2f**–**h**, which consistently resulted in less than 8% conversion. In the case of catalysts based on **2a**–**d** there is a marked dependence of catalyst efficiency on the metal precursor, those formed using $[Pd_2(OAc)_6]$ consistently giving higher conversions than those formed using $[Pd_2(dba)_3]$ and $[PdCl_2(MeCN)_2]$. The efficiency of palladium catalyzed Suzuki coupling reactions is known to depend on the palladium source, as well as a number of other variables including additives, solvent, temperatures and base [42]. The dependence of catalyst efficiency on the palladium source is clearly evident in the conversions based on the amino-diphosphine **2h**, which ranged from 2% using $[Pd_2(dba)_3]$ to 53% using $[Pd_2(OAc)_6]$. Incorporation of an additional hard protic donor such as OH clearly deactivates the catalyst (Chart 2, entries **2f**–**g**), which could be due to formation of an adduct via interaction of boron with the oxygen donor. Further studies are required to investigate and determine the origin of catalyst deactivation. Encouragingly, under our conditions, the efficiency of the $Pd_2(OAc)_6$/**2a**–**d** catalyzed Suzuki couplings compare favorably with those of the standards.

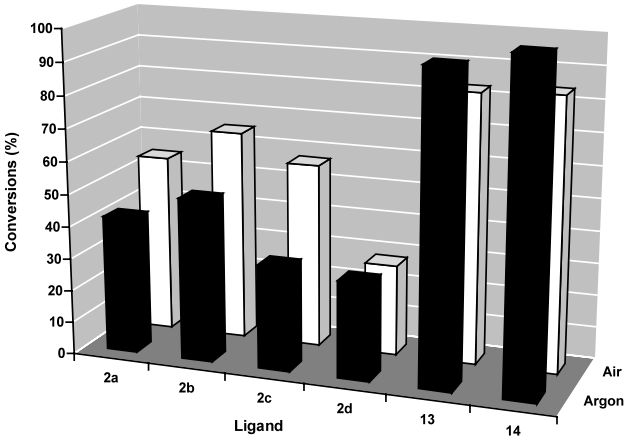


Chart 3. Conversion in the hydrosilylation of acetophenone.

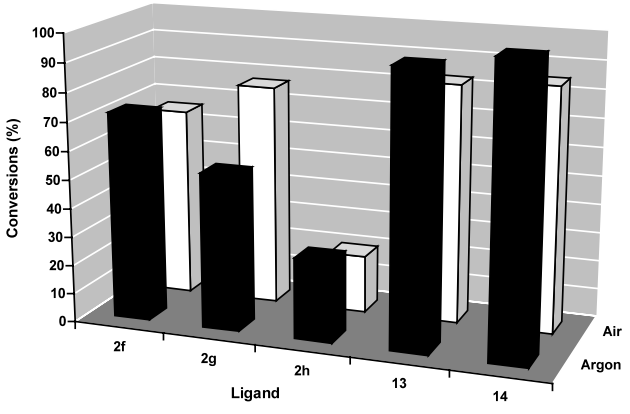
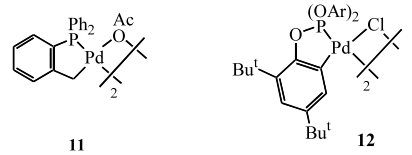


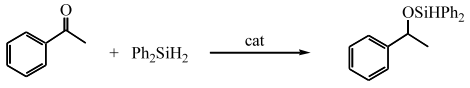
Chart 4. Conversion in the hydrosilylation of acetophenone.



11 **12**

Ar = 2-MeC_6H_4 Ar = 2,4-$Bu^t{}_2C_6H_3$

Feringa and coworkers have recently reported that the dinuclear rhodium complex $[Rh_2L^1(CO)_2][BF_4]$, where L^1H corresponds to 1,3-bis[(2-(diphenylphosphino)benzylidene)amino]propan-2-ol) is an effective catalyst for the hydrosilylation of acetophenone [32], the addition of one of the Si–H bonds of Ph_2SiH_2 to the carbonyl carbon to give the corresponding silyl ether which can be hydrolyzed to 1-phenylethanol (Eq. (5)). Hydrosilylation reactions were carried out in a multiwell reactor running Crabtree's (**13**) and Wilkinson's (**14**) catalysts in parallel as standards and the extent of reaction monitored by GC. As shown in Charts 3 and 4 mixtures of $[Ir(COD)Cl]_2$ and iminophosphines **2a**–**h** catalyze the room temperature hydrosilylation of acetophenone, with conversions reaching 74% after 18 h. The most effective catalysts are those based on the monobasic terdentate iminophosphines **2f**–**g** while those based on the amino-diphosphines **2i** resulted in poor conversions ($< 30\%$). Notably, there are only minor differences in the extent of conversion between reactions conducted under argon and in air.



(5)

4. Conclusions

Acid catalyzed condensation of 2-(diphenylphosphino)aniline has been used to prepare a range of neutral and monobasic bi- and terdentate iminophosphines. In the presence of a stoichiometric amount of acid, 2-(diphenylphosphino)aniline reacts with benzaldehyde, acetophenone and salicylaldehyde to give the corresponding 2,3-dihydro-1*H*-benzo[1,3]azaphosphol-3-ium salts. The acid catalyzed reaction between 2-(diphenylphosphino)aniline and pyridine-2-carboxaldehyde does not give the corresponding pyridyl iminophosphine but affords *N*-(pyridin-2-ylmethyl)-2-diphenylphosphinoylaniline. In the absence of acid, 2-(diphenylphosphino)aniline reacts with two equivalents

of aldehyde to give 1,2-dipyridin-2-yl-2-(*o*-diphenylphosphinoyl)phenylamino-ethanol (**6**), in an unusual transformation. The desired pyridyl iminophosphine has been successfully prepared via a template reaction involving condensation of $[Ni(2\text{-}Ph_2PC_6H_4NH_2)_2][NO_3]_2$ with pyridine-2-carboxaldehyde. Mixtures of **2a**–**h** form catalysts that are active for the Suzuki cross coupling reaction between 4-bromoacetophenone and bromobenzene, the conversion depending on the palladium source with $[Pd_2(OAc)]_6$ forming the most efficient catalysts. Under our conditions catalysts formed from iminophosphines **2a**–**d** and palladium acetate gave the highest conversions, which compared favorably with those obtained with the standards, catalyst mixtures generated by combining tris(2-tolyl)phosphine and tris(2,4-di-*tert*-butylphenyl)phosphite with $[Pd_2(OAc)_6]$ and $[PdCl_2(MeCN)_2]$ respectively. In contrast, catalysts formed from monobasic iminophosphines **2f**–**g** gave very low conversions. Iminophosphines **2a**–**h** and $[Ir(COD)Cl]_2$ also catalyze the hydrosilylation of acetophenone, the conversions obtained in air and under argon being similar. The results of our preliminary catalytic studies are encouraging and the effectiveness of these and related iminophosphines in a range of palladium-catalyzed reactions, the synthesis of chiral versions and their applications in asymmetric transformations are currently underway.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 174928 (**3b**), 174929 (**3c**), 174930 (**5**), 174931 (**6**), 174932 (**7**), 174933 (**8a**), 174934 (**8b**), 174935 (**9b**) 174936 (**10**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or http://www.ccdc.cam.ac.uk).

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