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Phosphines with 2-imidazolium and *para*-phenyl-2-imidazolium moieties — synthesis and application in two-phase catalysis

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Abstract

Deprotonation of 1-*n*-butyl-3-methyl-imidazolium chloride or hexafluorophosphate with *n*-butyl lithium and subsequent reaction of the intermediate 2,3-dihydro-imidazol-2-ylidene with diphenylchlorophosphine affords the 2-imidazolium phosphines **3a** or **3b**. The phosphine **4** with a *para*-phenylene spacer between the imidazolyl moiety and the phosphorus atom has been obtained by Kosugi–Stille coupling between 2-tri-*n*-butyl-stannyl-1-methylimidazole and 4-fluoroiodobenzene followed by nucleophilic substitution of fluorine with PPh_2K. The X-ray structure of **4** (space group $P\bar{1}$) has been determined. Selective N-protonation or N-quaternization of **4** affords the corresponding imidazolium phosphines **5a–5c**. The ligands **3b** and **5c** have been tested in the biphasic Rh-catalyzed hydroformylation of 1-octene employing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as catalyst solvent.

Keywords: 2-Imidazolium phosphine; *para*-Phenyl-2-imidazolium phosphine; Metallation; Ionic liquids; Hydroformylation; ^{15}N-NMR spectroscopy

1. Introduction

The sustained interest in phosphines bearing 2-imidazolyl moieties (**A**) is mainly due to their interesting ligand properties. They may function as ambivalent P,N-donor systems capable of binding soft and hard transition metals via phosphorus [1] or nitrogen [2a], respectively. Tris(2-imidazolyl)-phosphines show tridentate N-coordination towards hard transition metals (**B**) [2]. Some of these Zn(II), Cu(I) and Fe(III) complexes have been considered as model compounds to mimic the catalytically active site in metallo enzymes like carbonic anhydrase [3a] or to provide benchmarks for the dimetal sites in hemocyanin [3b] or hemerythrin [3c]. In addition to their multidentate donor properties the ligands discussed above should be convertible into cations by N-protonation or N-alkylation of the 2-imidazolyl moieties. The resulting 2-imidazolium phosphines contain structural elements of ionic liquids ($\mathbf{C}^+\mathbf{X}^-$) [4], which have very recently been employed as 'designer solvents' [5] in novel two-phase catalytic reactions [6]. There are only very few reports on 2-imidazolium phosphines ($\mathbf{D}^+\mathbf{X}^-$) in the literature. They have been obtained by selective N-alkylation of the corresponding neutral phosphine [7] or by reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene with diphenylchlorophosphine [8a]. The 2,3-dihydro-1,3,4,5-tetraalkyl-imidazol-2-ylidenes have been obtained by reduction of the corresponding imidazole-2(3*H*) thiones with potassium [8b]. Reaction of chlorophosphines with imidazol-2-ylidenes, generated from the corresponding 2-imidazolium salt by deprotonation, have been reported by Zoller in a preliminary publication [9a], no experimental details are given, however. Due to the low CH-acidity of the imidazolium ions (e.g. $pK_a \approx 17$ for the 1,3,5-trimethyl derivative) strong bases are necessary for their deprotonation [9b].

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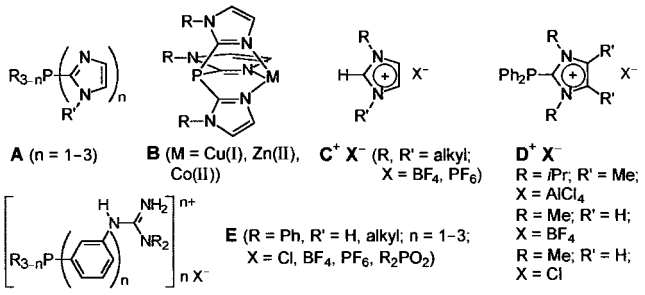


Chart 1.

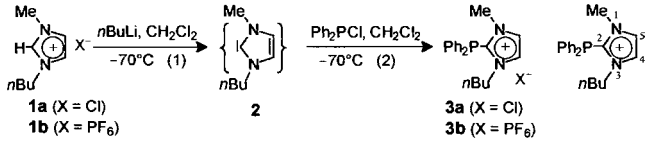
We report here on the synthesis of imidazolium phosphines of type $\mathbf{D}^{+}\mathbf{X}^{-}$ derived directly from commercially available ionic liquids and their application in catalysis. Imidazolium phosphines with a *para*-phenylene spacer unit between phosphorus and the imidazole unit will also be included in our studies. In contrast to the guanidininium phosphines (**E**) [10,11], which likewise contain amidinium type substituents, imidazolium phosphines have so far not been applied in homogeneous catalysis.

2. Synthesis of 2-imidazolium phosphines by metallation of 2-imidazolium salts and subsequent reaction with chlorophosphines

For the synthesis of 2-imidazolium phosphines the commercially available 1-*n*-butyl-3-methylimidazolium salts **1a** and **1b** ($[BMIM]^{+}Cl^{-}$ or $[BMIM]^{+}PF_6^{-}$), typically used as ionic liquids or their precursors, were employed as starting materials. The water content of **1a** and **1b** [12a] was determined by Karl Fischer titration [12b,c] and was found to be less than 0.01% [12d].

On lithiation of thoroughly dried **1a** or **1b** with *n*-BuLi in dichloromethane at -70 °C the intermediate **2** is formed in an easy manner (Eq. (1)). Reaction of **2** with the diphenylchlorophosphine Ph_2PCl gave the 2-imidazolium phosphines **3a** and **3b** in high yields (Eq. (2)). To the intermediate **2** the structure of a 2,3-dihydroimidazole-2-ylidene [13] is assigned. Stable carbenes have been obtained by deprotonation of substituted imidazolium salts with NaH [13a] or KNH_2 in liquid ammonia [13b] and in a more sophisticated manner by desulfurization of the corresponding imidazole-2-ylidene thiones with potassium metal [8b].

After removal of the solvent the lithium chloride formed was separated by filtration (**3a**) or extracted completely from the reaction mixture with water (**3b**). According to the elemental analysis, **3b** contained less than 0.1% LiCl. Using THF or ether as solvents for the synthesis of **3a** or **3b** gave only poor results probably due to the low solubilities of the *N*-butyl-*N*-methyl imidazolium salts **1a** and **1b** at low temperature. Under the conditions employed for the synthesis of **3a** or **3b** the intermediate carbene **2** did not react with di-*tert*-butylchlorophosphine, however. This is possibly due to steric hindrance of the reaction by the bulky *tert*-butyl groups and the alkyl groups in 1- and 3-position of the heterocyclic carbene.



(1)

In the $^{31}P\{^{1}H\}$-NMR spectra the 2-imidazolium phosphines **3a** or **3b** (dissolved in CD_2Cl_2) show singlets at $\delta = -27.3$ or -26.1, respectively, in a shift range typical for tertiary arylalkyl phosphines bearing C-bound heterocyclic substituents [14a,b]. Due to the unsymmetrical substitution of the imidazolium nitrogen atoms the protons of the imidazole ring are chemically different — two multiplet patterns being observed in the ^{1}H-NMR spectra. This is reflected in the $^{13}C\{^{1}H\}$-NMR spectra of **3a** or **3b**, respectively. Two resonances are observed for the olefinic carbon atoms C5 and C4 (**3a**: $\delta = 128.9$, 126.1; **3b**: $\delta = 127.5$, 125.2). The doublet at $\delta = 142.0$ ($^{1}J(PC) = 52.1$ Hz) (**3a**) or at $\delta = 142.7$ ($^{1}J(PC) = 53.9$ Hz) (**3b**) with a large P–C coupling corresponds to carbon atom C2. The complete assignment of the $^{13}C\{^{1}H\}$-NMR signals of the *N*-methyl group and the *N*-butyl group and those of the Ph_2P moiety has been supported by DEPT spectra, CH-COSY- and long range CH-COSY-NMR spectra and by comparison of their ^{13}C chemical shift values with the pertinent data of related compounds (e.g. Ph_3P [15a] and $\mathbf{C}^{+}PF_6^{-}$ ($CDCl_3$, C1 = 137, C3, C4 = 124–122 [15b]). In agreement with the structure proposed for **3b** the ^{15}N-NMR-INEPT spectrum shows two different resonances at $\delta = -185.8$ and -200.6.

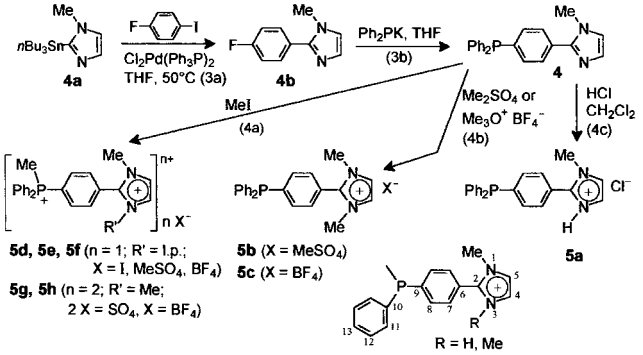
While the 2-imidazolium phosphine **3a** is hygroscopic and soluble in water, **3b** is less hygroscopic and almost insoluble in water. It shows a pronounced solubility in ionic liquids, e.g. $[BMIM]^{+}PF_6^{-}$ (310 g kg^{-1} at 45 °C). The NMR data of **1a** and **1b** as well as **3a** and **3b** are somewhat solvent dependent as indicated in Table 1 for selected carbon atoms and phosphorus as well as for the nitrogen atoms of the heterocyclic ring. Introduction of the Ph_2P group into the imidazolium salt **1a** or **1b** causes a significant lowfield shift of the ^{15}N resonances.

3. Synthesis of *para*-phenyl-2-imidazolyl and 2-imidazolium phosphines by Stille coupling and consecutive nucleophilic substitution

By introduction of a *para*-phenylene spacer group between the heterocyclic substituent and the phosphorus atom in ligands of type **3** derivatives of Ph_3P are obtained bearing the functional group in a position

where it does not influence the steric requirements of the P-donor center [10a].

For the synthesis of the neutral triphenylphosphine derivative **4** bearing a 2-(*N*-methyl-imidazolyl) substituent in *para*-position to phosphorus a two-step synthesis has been developed involving a Kosugi–Stille-type coupling [16] followed by a nucleophilic phosphination [17].



(2)

The starting material 2-(4-fluorophenyl)-1-methyl-imidazole (**4b**) was obtained in a high yield synthesis by reaction of 4-fluoroiodobenzene with 2-tributylstannyl-1-methyl-imidazole (**4a**) [18] using $(Ph_3P)_2PdCl_2$ as the catalyst (Eq. (3a)). This procedure is superior to the possible multistage synthesis of **4b** by N-alkylation of 2-(4-fluorophenyl)-1*H*-imidazole which is accessible by reaction of 4-fluorobenziminoethyl ether hydrochloride with aminoacetaldehyde diethylacetate [19].

Nucleophilic phosphination of **4b** with potassium diphenylphosphide in THF yields the tertiary phosphine **4** in 90% yield. (Eq. (3b)). It shows a ^{31}P-NMR resonance at $\delta = -4.4$, the chemical shift value being similar to that of Ph_3P (δ = -6.0 [14a,g]) or comparable to Ph_3P derivatives with polar substituents in *meta*- or *para*-position to phosphorus [14c–f]. For the vinylic hydrogen atoms an AB-type ^{1}H-NMR spectrum is observed. In agreement with the structure proposed for **4** 12 $^{13}C\{^1H\}$-NMR signals are observed, the assignment of which has been supported by DEPT-^{13}C-NMR spectra and by comparison with the ^{13}C chemical shift values of Ph_3P [15a] and *N*-methylimidazole [15c]. While the resonances at $\delta = 128.4$ and 124.3 may be assigned to the olefinic carbon atoms C4 and C5, the signal at $\delta = 148.4$ corresponds to carbon atom C2. For the *N*-methyl group a resonance at $\delta = 34.9$ is obtained in the $^{13}C\{^1H\}$-NMR spectrum. The resonances at $\delta =$ 138.1 ($^1J(PC) = 11.2$ Hz) and 140.2 ($^1J(PC) = 13.2$ Hz) may be assigned to the *ipso*-carbon atoms connected directly to the phosphorus atom.

The imidazolium phosphine **5a** was obtained in high purity by working up the crude reaction mixture with 2 M HCl in a two-phase system water–CH_2Cl_2 (Eq. (4c)). From the pK_a values of 2-phenylimidazole (6.48), 1-methylimidazole (7.32) and imidazole (7.12) [20a], a pK_a of ca. 6.8 may be estimated for the imidazole group of **4** comparable to that of *N*,*N*-diethylaniline (6.43) [20b] being about 3.7 units higher than that of PPh_3 [20c].

Formation of **5a** ($\delta = -3.7$) from the neutral phosphine **4** ($\delta = -4.4$) has little effect on the phosphorus chemical shift. For Ph_3P ($\delta = -6.0$ [14a,e]) the effect of protonation on δP is dependent on the solvent used; δP values of +5.0 to 7.0 are reported for the Ph_3PH^+ cation [14h]. The $^{13}C\{^1H\}$-NMR signals of the carbon atoms C2, C4 and C5 of the imidazole ring system and the *ipso*-carbon atom C6 are shifted to higher field, however, on protonation of **4** (**4/5a**: C2: 148.4/145.7, C4: 128.4/126.1, C5: 124.3/120.3 and C6: 131.6/123.5; for the notation of the C atoms see formula (2). These results indicate that protonation of **4** primarily occurs at the nitrogen atom. A similar high field protonation shift of the $^{13}C\{^1H\}$-NMR of the ring carbon atoms has been observed for unsubstituted imidazole [15a] supporting the interpretation of the chemical shift changes for **4** given above.

N-quaternization of **4** with methyliodide in a 1:1 stoichometric ratio gave mainly the phosphonium salt **5d** (δP = 23.3) (Eq. (4a)). However, using dimethylsulfate or trimethyloxonium tetrafluoroborate, the imidazolium salts **5b** or **5c**, respectively, are formed preferably (Eq. (4b)), (85–90%, $\delta = -4.7$ or -3.1).

Table 1
Selected NMR data of **1a**, **1b** and **3a**, **3b** in different solvents

	δP	δC2	δH2	δC4	δH4	δC5	δH5	δN
1b (neat)	−142.8[a]	135.8	7.98	122.0	7.02	123.4	6.98	−201.5, −214.0
1a (D_2O)		138.2	8.76	124.6	7.51	125.9	7.46	
1a (CD_2Cl_2)		136.8	10.14	121.4	7.30	123.0	7.45	−201.6, −214.5
3a (**1b**)[b]	−28.3	144.0 (50.9)[c]		127.6	7.75	129.8	7.03	
3a (CD_2Cl_2)	−27.3	142.0 (52.1)[c]		126.1	8.36	128.9	8.68	
3b (D_2O)	−27.8, −142.9[a]	143.0 (52.9)[c]		125.3	7.66	127.6	7.56	
3b (CD_2Cl_2)	−26.1, −143.1[a]	142.7 (53.9)[c]		125.2	7.65	127.5	7.59	−185.8, −200.6

[a] PF_6^- anions.
[b] Solvent: **1b**.
[c] Coupling constants ^1J(PC) in Hz.

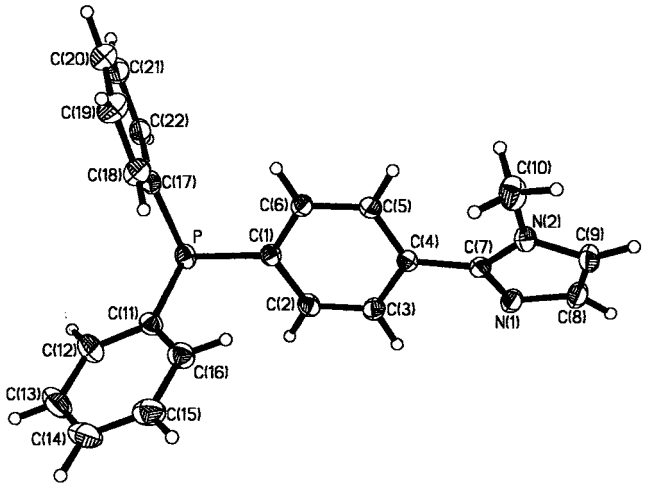


Fig. 1. A perspective drawing of **4** with 20% probability thermal ellipsoids for the non-hydrogen atoms

Table 2
Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths			
P–C(1)	1.828(2)	N(2)–C(7)	1.366(2)
P–C(11)	1.831(2)	N(2)–C(9)	1.371(2)
P–C(17)	1.829(2)	N(2)–C(10)	1.459(3)
N(1)–C(7)	1.323(2)	C(4)–C(7)	1.470(2)
N(1)–C(8)	1.368(2)	C(8)–C(9)	1.336(3)
Bond angles			
C(1)–P–C(11)	101.91(8)	C(5)–C(4)–C(7)	125.3(2)
C(1)–P–C(17)	102.50(8)	C(3)–C(4)–C(7)	117.0(2)
C(11)–P–C(17)	102.71(8)	N(1)–C(7)–N(2)	110.6(2)
C(7)–N(1)–C(8)	105.5(2)	N(1)–C(7)–C(4)	122.5(2)
C(7)–N(2)–C(9)	106.6(2)	N(2)–C(7)–C(4)	126.9(2)
C(7)–N(2)–C(10)	129.4(2)	N(1)–C(8)–C(9)	110.7(2)
C(9)–N(2)–C(10)	124.0(2)	N(2)–C(9)–C(8)	106.6(2)
C(3)–C(4)–C(3)	117.6(2)		

They could not be separated from the two side products showing resonances at $\delta = 22.4$ and 23.4, which are tentatively assigned to the phosphonium cations of the type **5e**, **5f** or **5g**, **5h**, respectively. The reactions depicted in Eqs. (4b) and (4c) reflect the higher nucleophilicity of the phosphorus atom in **4** as compared to more basic nitrogen atom. A similar behavior towards electrophiles has been found for the P,N-ligands $Ph_2P–(CH_2)_n–NMe_2$ ($n = 2$, 3) which even with MeI form the corresponding ammonium phosphines $[Ph_2P–(CH_2)_n–NMe_3]^+I^-$ as shown by Peiffer et al. [20e].

The $^{13}C\{^1H\}$-NMR spectrum of **5c** shows eight resonances in the δC range typical for aromatic carbon atoms which were assigned by means of DEPT-^{13}C-NMR spectra and by comparison of the pertinent data within the series **1a**, **1b**, **4b**, **4**, and **5a**. The signal at $\delta = 120.6$ corresponds to the equivalent carbon atoms C4 and C5, while the resonance at $\delta = 144.8$ may be assigned to C2 of the imidazolium group. The $^{13}C\{^1H\}$-NMR resonance of the N*Me* group appears at $\delta =$ 36.2. The $^{13}C\{^1H\}$-NMR signals at $\delta = 123.8$, 129.1 ($^3J(PC) = 7.2$ Hz), 134.3 ($^2J(PC) = 20.3$ Hz) and 135.9 ($^1J(PC) = 11.1$ Hz) are assigned to the carbon atoms C6–C9 of the *para*-phenylene spacer unit.

For the BF_4^- anion two resonances at $\delta = 152.75$ and 152.81 in the $^{19}F\{^1H\}$-NMR spectrum corresponding to the ^{10}B or ^{11}B isotopomer (^{10}B:I = 3, 19.9%; ^{11}B:I = 3/2, 80.1%) are observed, the latter showing a well resolved quartet splitting due to $^{11}B–^{19}F$ coupling ($^1J(BF) = 1.0$ Hz) [14i].

4. X-Ray-structure of 4

Crystals suitable for X-ray structural analysis were obtained by recrystallization of **4** from ethanol. The structure and numbering scheme for **4** is shown in Fig. 1, and selected bond lengths and angles are collected in Table 2. Intermolecular contacts are normal. The average P–C bond length (1.829(2) Å) and C–P–C bond angle (102.4(4)°) do not differ significantly from the corresponding values in Ph_3P [21,22] (P–C 1.831(1) Å, C–P–C 102.8(2)°).

The aromatic ring systems C(1)–C(6) (ring 1), C(11)–C(16) (ring 2) and C(17)–C(22) (ring 3), which are planar to within ± 0.02 Å, are inclined in a propeller-like fashion to the plane defined by the *ipso*-carbon atoms C(1), C(11) and C(17). As is evident from Fig. 1, the degree of inclination is different for each substituent, values for the corresponding interplanar angles being 41.8(1), 56.0(1) and 73.5(1)°.

The non-hydrogen atoms of the imidazolyl group are planar within experimental error, and this plane forms an interplanar angle of 24.5(1)° with ring 1. Coplanarity of these two groups is obstructed by repulsions between the N–CH_3 group and the proton at C(5). These repulsions result in an opening of the C(5)–C(4)–C(7), C(4)–C(7)–N(2) and C(7)–N(2)–C(10) bond angles by an average of 6(2)° with respect to the other exocylic angle on the same pivot atom (Table 2).

5. Rh-catalyzed hydroformylation of 1-octene employing imidazolium phosphines as ligands

In context with our ongoing interest in the application of aromatic phosphines with mesomeric cationic groups in homogeneous catalysis [10,11] we studied the Rh-catalyzed hydroformylation of 1-octene employing the imidazolium phosphines **3b** and **5c** as ligands. They were specially designed to be used in ionic liquid biphasic systems [23], which have been employed to circumvent problems arising from the low water solubility of longer chain olefins in aqueous biphasic hydroformylation reactions [24].

Imidazolium phosphines of type **3b** are capable of forming complexes with transition metals. This has very recently been shown by Kuhn et al. [25] for $\mathbf{D}^+Cl^-$ (R, R′ = *i*-Pr, Me) related to **3b**. With $PdCl_2$ and $PtCl_2$ these ligands form neutral complexes {[**D**]MCl_3} (M = Pd, Pt) in which the cationic phosphine $\mathbf{D}^+$ reveals triarylphosphine type properties as indicated by NMR and structural data.

In our hydroformylation experiments the active catalyst was prepared in-situ by mixing $Rh(CO)_2acac$ with two equivalents of the ligand in the ionic liquid $[BMIM]^+PF_6^-$. The reaction was carried out at 100 °C and 30 bar synthesis gas pressure (CO, H_2 = 1:1) for 1 h. The biphasic 1-octene hydroformylation under these conditions showed significantly higher turnover frequency (TOF) values with ligand **3b** (TOF 552 moles 1-octene converted per mole Rh and h, *n*:*i* ratio = 1.1) in comparison with ligand **5c** (TOF 51 moles 1-octene converted per mole Rh and h, *n*:*i* ratio = 2.8). These results are in good agreement with former experiments by Brasse et al. Investigating cationic phosphine ligands in Rh-catalyzed biphasic hydroformylation in ionic liquids these authors could demonstrate that close proximity of the positive charge to the phosphorus atom greatly enhances the catalytic activity [26]. In addition it should be noted that with both ligands no significant leaching of the Rh catalyst into the almost colorless organic layer was observed.

6. Experimental

For experimental details see Refs. [10a,10b]. $[BMIM]^+Cl^-$ (**1a**) and $[BMIM]^+PF_6^-$ (**1b**) have been obtained from Solvent Innovation GmbH, Cologne [27]. They have been dried by heating in vacuo (0.01 mbar) for 0.5–1 h at 100 °C. According to the results of a coulometric Karl Fischer titration with a Mitsubishi Moisture Meter, model CA-05, these samples of **1a** and **1b** contained less than 0.01% water. *N*-methylimidazole, *n*-Bu_3SnCl, Ph_2PCl and 4-fluoro-iodobenzene were obtained from Aldrich GmbH and Fluorochem, respectively, and used after distillation.

6.1. Preparation of *3a* and *3b*

6.1.1. Preparation of *3a*

To a solution of 2.68 g (15.34 mmol) of **1a** in 60 ml of CH_2Cl_2 (dried over P_4O_{10}) 6.55 g of a *n*-BuLi solution (15% in *n*-hexane, 15.34 mmol) were added at −78 °C within a period of 15 min. After stirring for 45 min the reaction mixture was charged with 3.38 g (15.34 mmol) of Ph_2PCl at this temperature over a time of 1 h. Thereafter the reaction mixture was warmed up gradually. The LiCl precipitated was filtered off using a cannula fitted with a Teflon filter. After removing the solvent in vacuo **3a** was obtained as waxy solid in quantitative yield.

Anal. Found: C, 65.47; H, 6.46; N, 7.42. Calc. for $C_{20}H_{24}ClN_2P{\cdot}0.5H_2O$ (MW 367.9): C, 65.30; H, 6.85; N, 7.62%. ^{1}H-NMR (CD_2Cl_2, δ ppm): 0.76 (t, 3H), 1.15 (sext., 2H), 1.59 (m, 2H), 3.62 (3H), 4.39 (m, 2H), 7.31 (m, 4H), 7.47 (m, 6H), 8.36 (m, 1H), 8.68 (m, 1H). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ ppm): 13.3, 19.5, 33.1 (J = 1.9 Hz), 37.9 (J = 4.8 Hz), 50.4 (J = 12.8 Hz), 126.1, 128.0 (J = 6.4 Hz), 128.9, 130.0 (J = 9.2 Hz), 130.9, 132.7 (J = 20.0 Hz), 142.0 (J = 52.1 Hz). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ ppm): −27.3.

6.1.2. Preparation of *3b*

A solution of 15.39 g of *n*-BuLi (15% in *n*-hexane, 36.0 mmol) was added at −78 °C within a period of 15 min to 10.24 g (36.0 mmol) of **1b** dissolved in 60 ml of CH_2Cl_2 (dried over P_4O_{10}). After stirring for 45 min the reaction mixture was charged within 20 min with 7.95 g (36.0 mmol) of Ph_2PCl at this temperature. The reaction mixture was warmed up gradually over night. Thereafter the solution was extracted with three aliquots of 20 ml of deaerated water. The organic phase was dried over Na_2SO_4. After evaporation of the solvent in vacuo the cream-colored solid obtained was dried in vacuo. Yield: 14.2 g (84%).

Anal. Found: C, 51.35; H, 5.02; F, 24.57; N, 5.96; P, 13.30. Calc. for $C_{20}H_{24}F_6N_2P_2$ (MW 468.4): C, 51.29; H, 5.16; F, 24.34; N, 5.98; P, 13.23%. ^{1}H-NMR (CD_2Cl_2, δ ppm): 0.80 (t, 3H), 1.18 (m, 2H), 1.60 (m, 2H), 3.54 (m, 3H), 4.29 (m, 2H), 7.39 (m, 4H), 7.54 (m, 6H), 7.59 (m, 1H), 7.65 (m, 1H). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, δ ppm): 13.1, 19.2, 32.6, 37.6 (J = 5.1 Hz), 50.3 (J = 12.2 Hz), 125.2, 127.5, 127.8 (J = 6.1 Hz), 130.0 (J = 7.1 Hz), 130.9, 132.7 (J = 20.4 Hz), 142.7 (J = 53.9 Hz). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ ppm): −26.1, −143.1 (PF_6^-, J(PF) = 711 Hz). $^{19}F\{^1H\}$-NMR (CD_2Cl_2, δ ppm): −72.8 (PF_6^-, J(PF) = 711 Hz). ^{15}N-NMR (CD_2Cl_2, δ ppm): −185.8, −200.6.

6.2. Preparation of *4b*, *4*, *5a* and *5c*

6.2.1. Synthesis of *4b*

A solution of 6.66 g (30.0 mmol) of 4-fluoro-iodobenzene and 11.11 g (30.0 mmol) of 2-(tris-*n*-butylstannyl)-1-methyl-imidazole and 0.42 g (2 mol%) of $(Ph_3P)_2PdCl_2$ in 25 ml of THF were heated under reflux for four days. The orange colored reaction mixture was evaported in vacuo. The remaining residue was suspended in 50 ml of ether and extracted with three aliquots of 40 ml of 2 M HCl. The aqueous phase was neutralized with 2 N NaOH until a pH value of 8–9 was reached and then extracted with three aliquots of 40 ml of ether. The collected organic extracts were dried over $MgSO_4$. After removal of the solvent **4b** was obtained as a colorless solid. Yield: 3.7 g (70%).

^{1}H-NMR ($CDCl_3$, δ ppm): 3.60 (3 H), 6.90 (1 H, d, J(HH) = 1.0 Hz), 7.00 (1 H, d, J(HH) = 1.0 Hz), 7.00–7.10 (m, 2H), 7.40–7.50 (m, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$, δ ppm): 34.0, 115.2 (d, ^2J(CF) = 21.4 Hz), 122.1, 126.6, 128.1, 130.2 (d, ^3J(CF) = 8.1 Hz), 146.5, 162.5 (d, ^1J(CF) = 249.2 Hz). ^{19}F{^{1}H}-NMR ($CDCl_3$, δ ppm): −113.0.

6.2.2. Synthesis of **4**

A 0.5 molar solution of 121.3 g of Ph_2PK (65.3 mmol) in THF was added in the course of 1 h to 11.5 g (65.3 mmol) of **4b**, dissolved in 120 ml of THF. After stirring the reaction mixture for 5 h at 40 °C the solvent was removed in vacuo. The residue was dissolved in 100 ml of CH_2Cl_2 and washed with three aliquots of water. The solvent was evaporated and the residue left was recrystallized from MeOH. Yield: 19.8 g (89%).

Anal. Found: C, 77.11; H, 5.59; N, 8.70. Calc. for $C_{22}H_{19}N_2P$ (MW 342.4): C, 77.18; H, 5.59; N, 8.18%. ^{1}H-NMR (CD_3OD, δ ppm): 3.90 (3H), 7.00 (d, 1H, J(HH) = 1.2 Hz.), 7.10 (d, 1H J(HH) = 1.2 Hz), 7.30–7.80 (m, 14H). ^{13}C{^{1}H}-NMR (CD_3OD, δ ppm): 34.9, 124.3, 128.4, 129.7, 129.8, 130.1, 131.6, 134.7 (J = 19.3 Hz), 134.8 (J = 20.3 Hz), 138.1 (J = 11.2 Hz), 140.2 (J = 13.2 Hz), 148.4. ^{31}P{^{1}H}-NMR (CD_3OD, δ ppm): −4.4.

Table 3
Crystal data and structure refinement parameters for **4**

Empirical formula	$C_{22}H_{19}N_2P$
Formula weight	342.4
Temperature (°C)	20
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.594(3)
b (Å)	10.389(3)
c (Å)	11.340(3)
α (°)	63.09(2)
β (°)	66.93(2)
γ (°)	76.15(2)
V (Å^3)	924.7(4)
Z	2
D_{calc} (g cm^{-3})	1.230
μ (mm^{-1})	0.154
Crystal size (mm)	0.36 × 0.34 × 0.26
θ Range (°)	2.13–25.05
Index ranges	$0 \le h \le 11$, $-12 \le k \le 12$, $-12 \le l \le 13$
Reflections collected	3509
Reflections observed [$I > 2\sigma(I)$]	2532
Unique reflections	3293 [R_{int} = 0.013]
Max/min transmission	0.9657, 0.9530
Parameters	246
R_1 (all data)	0.0499
wR_2 (all data)	0.1028
Goodness-of-fit on F^2	1.019
Largest difference peak and hole (e Å^{-3})	0.16 and −0.19

6.2.3. Synthesis of **5a**

The reaction mixture as obtained above from 1.53 g (8.7 mmol) of **4b** and 16.1 g of a 0.5 M Ph_2PK solution in THF (8.7 mmol) was evaporated and the residue was dissolved in 50 ml of CH_2Cl_2. The organic phase was treated with three aliquots of 2 M HCl. After removal of the organic phase in vacuo the remaining solid was recrystallized from 20 ml of EtOH. Yield: 1.48 g (45%).

Anal. Found: C, 69.69; H, 5.33; N, 7.63. Calc. for $C_{22}H_{20}ClN_2P$ (MW 378.8): C, 69.75; H, 5.32; N, 7.39%. ^{1}H-NMR (CD_3OD, δ ppm): 3.90 (3H), 7.00 (d, 1H J(HH) = 1.2 Hz.), 7.10 (d, 1H J(HH) = 1.2 Hz), 7.30–7.80 (m, 14H). ^{13}C{^{1}H}-NMR (CD_3OD, δ ppm): 34.9, 120.3, 123.5, 126.1, 129.7 (J = 6.1 Hz), 129.9 (J = 7.1 Hz), 130.5, 135.0 (J = 20.4 Hz), 137.1 (J = 11.2 Hz), 145.3 (J = 16.3 Hz), 145.7. ^{31}P{^{1}H}-NMR (CD_3OD, δ ppm): −3.7.

6.2.4. Synthesis of **5c**

To a solution of 1.0 g (2.9 mmol) of **4** in 30 ml of CH_2Cl_2 a suspension of 0.43 g (2.9 mmol) of Me_3O^+ BF_4^- in 10 ml of CH_2Cl_2 was added at −30 °C and the reaction mixture was stirred for 45 min. Thereafter all volatiles were removed in vacuo leaving 1.4 g of **5c** which according to ^{31}P{^{1}H}-NMR control contained small quantities of the starting material **4** (δP = −4.1, ca. 5%), as well as phosphonium salts of type **5e** and **5g** (δP = 23.4 and 22.4, respectively) both together about 7%. The starting material **4** could be removed by extraction with ether.

Anal. Found: C, 62.35; H, 4.47; N, 6.22. Calc. for $C_{23}H_{22}BF_4N_2P$ (MW 444.2): C, 62.19; H, 4.99; N, 6.31%. ^{1}H-NMR (CD_2Cl_2, δ ppm): 3.74 (6H), 7.38–7.75 (m, 16H). ^{13}C{^{1}H}-NMR (CD_2Cl_2, δ ppm): 36.2, 120.6, 123.8, 129.1 (J = 7.2 Hz), 129.8, 130.2 (J = 6.1 Hz), 134.3 (J = 20.3 Hz), 134.4 (J = 18.3 Hz), 135.9 (J = 11.1 Hz), 144.8, 145.2 (J = 17.3 Hz). ^{19}F{^{1}H}-NMR (CD_2Cl_2, δ ppm): 152.75 (^{10}B), 152.81 (^{11}B), (J = 1.0 Hz). ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ ppm): −3.1.

6.3. X-ray sructure analysis of **4**

A crystal of **4** was mounted on a glass fiber. X-ray data were collected on a Siemens P3 diffractometer equipped with graphite monochromator and employing Mo–K_α radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using all unique data with all non-hydrogen atoms anisotropic. Hydrogen atoms were positioned geometrically, only the torsional orientation of the methyl group being refined. Crystal data and refinement details are given in Table 3. The program SHELX-93 was used for the refinement [28].

6.4. Catalysis

In 6.0 g of $[BMIM]^+PF_6^-$ (**1b**) 0.04 mmol of the respective ligand and 0.02 mmol of $Rh(CO)_2acac$ was dissolved at 80 °C. The solution was transferred into a 75 ml steel autoclave with a dropping funnel and a magnetic stirring bar. The autoclave was pressurized with synthesis gas ($CO–H_2 = 1:1$) and heated to 100 °C. The pressure was then adjusted to 30 bar and the autoclave was stirred for 30 min for catalyst preformation. Thereafter a mixture of 2.5 g (22.3 mmol) of 1-octene and 0.7 g of dibutylether (internal standard) were added through the dropping funnel. After 1 h the autoclave was cooled to room temperature, depressurized and opened. The product was isolated by phase separation and analysed by GC (50 m Pona HP-FS column).

7. Supplementary material

Crystallographic data for the structural analysis have been deposited with the dditional crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153734 for compound **4**. Copies of this information data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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