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Synthesis of the first imidazolyl-triphosphines containing a *Triphos* unit

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Abstract

Since biphasic liquid–liquid continuous-flow catalytic processes often require the use of cationic phosphine ligands for the metal sequestration in the polar phase, we have prepared the first imidazolyl triphosphines, named *Triphosim* and *Triphosmim*. These ligands contain the *Triphos* unit [-P($CH_2CH_2PPh_2$)] which is linked to the imidazole fragment and have been obtained in three steps from imidazole (or 2-methylimidazole), diethylvinylphosphonate and diphenylvinylphosphine with global yields of 42–48%. The *Triphosim* ligand adopts a tridentate P-coordination mode in a palladium dichloride complex and the reaction of the dangling imidazole function with alkyl halides leads to a new kind of imidazolium-phosphine complexes.

Keywords: Triphosphine; Imidazole; Imidazolium; Synthesis of polyphosphines; Tridentate ligand

1. Introduction

The development of efficient continuous-flow catalytic systems represents a major challenge in modern homogeneous catalysis. However, it requires a perfect immobilisation, or sequestration, of the catalytic species in one liquid phase while the organic products are continuously extracted from the catalytic medium by a mobile phase [1,2]. For example, the association of a nonvolatile solvent such as imidazolium salts with supercritical carbon dioxide has given very good results in Rh catalysed olefins hydroformylation [3,4] or in Ni catalysed styrene hydrovinylation in continous-flow conditions [5]. Nevertheless, the efficiency of the catalytic processes can still be increased by introduction of a cationic imidazolium fragment on the coordinated phosphines, which strongly decreases the metal-phosphine leaching in the mobile phase [6]. For example, imidazolium monophosphines salts obtained from the neutral bis(1-imidazolylethyl)phosphines were employed in hydroformylation of 1-octene and no Rh catalyst leaching from the [BMIM](PF_6) ionic phase to the organic layer was observed [7]. In the same manner, the presence of an imidazolium fragment on a chiral 1,4-diphosphine has allowed the rhodium leaching in asymmetric hydrogenation of N-acetylphenylethenamine to decrease from 2% to less than 1 ppm [6]. On the other hand, chelating polydentate phosphines, especially the *Triphos* ligand [$PhP(CH_2CH_2PPh_2)_2$], offer advantages over mono or diphosphines in homogeneous catalysis. Indeed, the higher nucleophilic character of the metal centre due to the presence of three coordinated phosphorus atoms (i) favours the C–H bond oxidative addition and subsequently increases the catalytic activity of rhenium catalysts in cyclooctane dehydrogenation [8] or of rhodium catalysts in aldehydes decarbonylation [9] or (ii) increases the reactivity of the metal-hydride bond towards the weak polar carbonyl function of an ester [10].

Imidazolyl- or imidazolium-triphosphines are thus very appealing to perform the above catalyses in continuous-flow conditions and we decided to investigate the elaboration of a synthetic method allowing the open access to such unprecedently described ligands, see Scheme 1.

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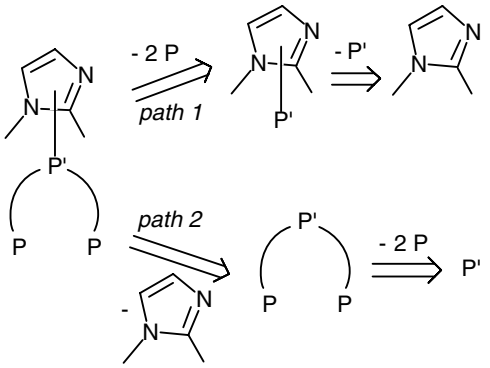


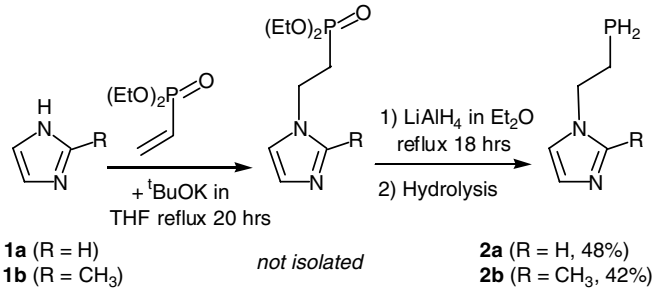
Scheme 1.

2. Results and discussion

Scheme 1 shows two possible pathways for the preparation of triphosphines bearing an imidazole moiety (or an imidazolium group, omitted for the sake of clarity). In contrast to the di- or tri-phosphines which are rather difficult to functionalise [11–13], many syntheses of polyphosphines from monophosphines ligands are well known and some examples are given below. Besides, in the last years, different preparations of imidazolyl or imidazolium mono- [7,14,15] and di-phosphines [7,15–17] have been described. This literature examination drove us to choose path 1 (Scheme 1) to elaborate the first triphosphine imidazole ligands.

The vinylphosphonate esters are interesting building blocks in the synthesis of polyphosphines ligands since the vinyl function can react with P–H bonds of primary (or secondary) phosphines under specific conditions. Moreover, their phosphonate function can easily be reduced to primary or secondary phosphines with $LiAlH_4$ [18]. By analogy with the Michael type addition, we wished to extend the reactivity from the P–H bond to the N–H bond of imidazoles. We have thus applied the procedure described for the preparation of $Ph_2P(CH_2)_2PH_2$ (from Ph_2PH and $CH_2{=}CHP(=O)(OEt)_2$ [18]) to imidazole **1a** and 2-methylimidazole **1b** (see Scheme 2). Both ligands **2a** and **2b** are obtained in good yields. The presence of the PH_2 group is confirmed by the existence of a triplet at −136.17 and −137.60 ppm with a $J(P,H) = 193$ Hz, respectively, for **2a** and **2b** in their phosphorus-proton coupled NMR spectra.

The above functional primary phosphines **2a** and **2b** are excellent starting materials in the construction of polyphosphines ligands. Indeed, it was reported that the P–H bond from aryl primary (or secondary) phosphines leads to the PCH_2CH_2P unit by a base-catalysed addition to the C=C double bond of vinylphosphines, phenyllithium and the more efficient ^{t}BuOK [19] being the most common catalysts to perform this reaction. It is also interesting to note that a less basic organic catalyst like NEt_3 can also be efficient in this addition reaction, provided that the P–H bond is previously activated by a platinum coordination, although the

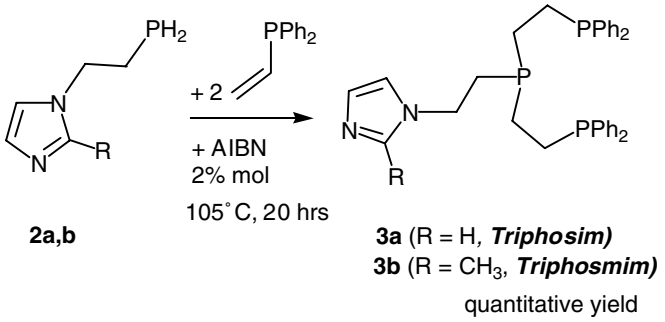


Scheme 2.

reaction does not lead then to free triphosphine ligand [20]. We thus applied a similar procedure to the primary phosphine **2b** in the presence of diphenylvinylphosphine and a catalytic amount of ^{t}BuOK (10 mol%) and heating under THF or toluene reflux for 20 h. The $^{31}P\{^1H\}$ NMR spectra of the crude product in C_6D_6 reveals the expected ligand **3b** with an unsatisfying conversion of 60%. Thus, an alternate synthetic method has been attempted, based on the anti-Markovnikov radical addition of primary phosphines to vinyl derivatives. Indeed, the addition of phenylphosphine to terminal fluorous olefins can be catalysed by AIBN at about 80 °C to lead to the corresponding dialkyl-phenylphosphine in good to excellent yields [21]. We used similar conditions to achieve our transformation of ligand **2** into **3** with only 2 mol% of AIBN per mol of diphenylvinylphosphine, see Scheme 3.

The analysis of NMR phosphorus spectra of the crude products obtained from **2a** and **2b** after reaction at 105 °C for 20 h shows a complete and selective conversion to the corresponding imidazolyl- and methylimidazolyl-triphosphine ligands **3a** and **3b**, which have been named, respectively, *Triphosim* and *Triphosmim* (see Scheme 3) due to their very close analogy with the *Triphos* ligand $[PhP(CH_2CH_2PPh_2)_2]$. Their $^{31}P\{^1H\}$ NMR spectra confirm unambiguously the formation of the two PCH_2CH_2P units by the presence of a doublet at $\delta = -0.11$ ppm for the terminal P in both **3a** and **3b** and a triplet at $\delta = -12.63$ ppm and −12.83 ppm for the internal P of **3a** and **3b**, respectively, with a $^2J(P,P)$ coupling constant of 27 Hz.

The further addition of an equimolar amount of ligand **3a** to $[PdCl_2(NCPh)_2]$ leads to the air stable complex **4a**

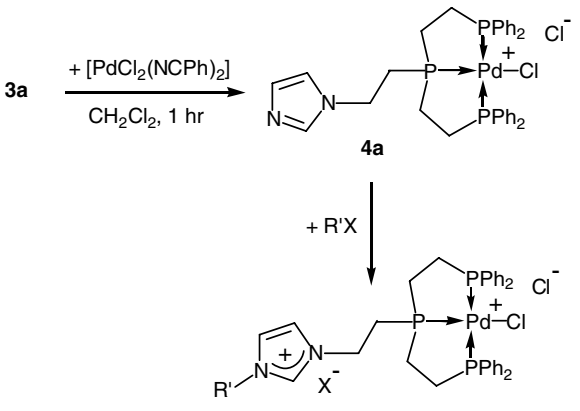


Scheme 3.

(see Scheme 4), which is characterised by a triplet at $\delta = 106.56$ ppm and a doublet at $\delta = 45.96$ ppm with a $^2J(P,P) = 7$ Hz in a 1:2 ratio in its $^{31}P\{^1H\}$ NMR spectrum. The phosphorus chemical shifts as well as the phosphorus-phosphorus coupling constant of **4a** are very similar to those reported in the literature for its analogous triphosphine cationic complex [PdCl(*Triphos*)]Cl with a triplet at $\delta = 109.6$ ppm and a doublet at $\delta = 44.3$ ppm with $^2J(P,P) = 9.4$ Hz [22] and are comparable to other cationic triphosphine metal complexes like $[NiCl(Triphos)]^+$, $[PtCl(Triphos)]^+$ or $[Rh(CO)(Triphos)]^+$ [9,22,23]. Moreover, the tridentate chelating behaviour of triphosphine has clearly been proved by X-ray structure analysis of complexes [PtCl(*Triphos*)]Cl and [NiCl(*Triphos*)](BPh_4) in which the square-planar geometry around the metal centers is slightly distorted with both P–M–P angles of 84° instead of 90° as expected [22,23]. Therefore, ligand **3a** in palladium complex **4a** acts as a tridentate chelating ligand with a dangling imidazole fragment, available for a further functionalisation. We have, therefore, investigated N-alkylation reactions of **4a** with different alkylating reagents and preliminary results are given hereafter.

Since imidazoles can undergo a complete alkylation reaction after 2 days of refluxing in BuCl [24], we have applied similar conditions with complex **4a**. In this case, a conversion of only 36% is obtained which has been increased to 76% by prolonging the heating period up to 7 days. In neat boiling EtBr, complex **4a** is also partially transformed to the related imidazolium-triphosphine complex after 2 days (See Scheme 4).

Both corresponding N-alkylated products **5a** and **6a** were characterized by the presence of new triplets in the phosphorus NMR spectra recorded in $CDCl_3$, at 102.93 ppm with $^2J(P,P) = 9.3$ Hz for **5a** and at 104.83 ppm with $^2J(P,P) = 7$ Hz for **6a**, and new doublets at 45.32 ppm with $^2J(P,P) = 8.5$ Hz for **5a** and at 45.88 ppm with $^2J(P,P) = 7$ Hz for **6a**, respectively. Since our lower conversion rates could be due to the steric hindrance of the triphos fragment in complex **4a** and/or to the weak solubility of complex **4a** in these solvents, we have then used stronger alkylating reagents. Unfortunately, the reaction between a solution of complex **4a** in CH_2Cl_2 and the methyliodide, or the Meerwein salt [$(CH_3)_3O^+$,BF_4^-], led to a mixture of palladium complexes which are not yet identified. Optimisation of the N-alkylation reactions is subsequently under investigation as, to the best of our knowledge, complexes **5a** and **6a** represent the first triphosphine-metal compounds bearing a cationic fragment in the ligand backbone. Such functionalisation should significantly increase their solubility and retention in polar ionic solvents (vs. for example $scCO_2$) and subsequently render this kind of complexes very promising for the biphasic homogeneous catalyses.



5a (R' = Bu, X= Cl, 76% after 7 days at 80°C)

6a (R' = Et, X= Br, 79% after 2 days at 40°C)

Scheme 4.

3. Conclusions

We report in this paper the synthesis of the first *Triphos* ligands bearing an imidazolyl moiety and the reactivity of the related palladium complex toward different N-alkylating reagents. Since the corresponding imidazolium-triphosphines complexes are partially formed, their purification and their complete characterization are currently being investigated. However, other synthetic routes are also being examined to avoid the use of transition metal as phosphorus protecting group. On the other hand, we are also examining the coordination properties of imidazolium-*Triphosim* as a source of new tetradentate assembling ligands as well as the potential of the N-alkylated *Triphosmim* ligands in the development of new continuous-flow catalytic processes.

4. Experimental

4.1. General procedures and instrumentation

All manipulations were carried out under purified argon using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use by standard methods. Standard pressure NMR measurements (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) were carried out with a Bruker Avance 300 spectrometer at room temperature. Complete assignment was achieved by use of DEPT and HMQC experiments. The peak positions are reported with positive shifts in ppm downfield of TMS as calculated from the residual solvent peaks (^1H and $^{13}C\{^1H\}$) or downfield of external 85% H_3PO_4 in water (^{31}P). Elemental analyses were carried out by the analytical service of the L.S.E.O. with a Fisons Instruments EA1108 analyser. The commercial compounds imidazole **1a**, 2-methylimidazole **1b**, diphenylvinylphosphine, diethyl vinylphosphonate, 1-chlorobutane, bromoethane, $LiAlH_4$, ^{t}BuOK, AIBN (2,2′-azobis(2-methyl-propionitrile)), CH_3I, [$(CH_3)_3O^+(BF_4^-)$] and [$PdCl_2(NCPh)_2$] were used as received.

4.2. Syntheses of compounds

4.2.1. Synthesis of 1-(2-phosphino-ethyl)-imidazole (**2a**)

A mixture of imidazole (1.327 g, 19.49 mmol), diethyl vinyl phosphonate (3.20 g, 19.49 mmol) and 30 mL of THF was treated with ^{t}BuOK (0.249 g, 2.21 mmol) and heated under THF reflux for 20 h. The solvent was removed in vacuo and the yellow residue obtained was dried for 1 h at 70 °C. The residue was then cooled at 0 °C and 90 mL of Et_2O and $LiAlH_4$ (1.31 g, 34.5 mmol) was rapidly added. A strong gas evolution was immediately observed with an increase of the temperature. When the exothermic reaction was subsided, the mixture was boiled under Et_2O reflux for 18 h. The gray suspension was cooled down to room temperature and hydrolysed by 15 mL of deoxygenated water. The organic phase was separated and the aqueous solution was extracted twice with 25 mL of Et_2O. All organic phases were dried over K_2SO_4 and filtered. Evaporation of solvent led to a colourless viscous oil which was dried for 2 h at room temperature (1.20 g, 48%). ^{1}H NMR δ (C_6D_6, 300.13 MHz) = 7.22 (s, 1H, NCHN), 7.09 (s, 1H, =CHN), 6.38 (s, 1H, =CH′N), 3.12 (m, 2H, CH_2N), 2.09 (dt, 2H, PH_2, J(P,H) = 193 Hz, ^2J(H,H) = 4.8 Hz), 1.07 (m, 2H, CH_2P). ^{13}C{^{1}H} δ NMR (C_6D_6, 75.47 MHz) = 135.69 (s, 1C, NCHN), 128.63 (s, 1C, =CHN), 116.80 (s, 1C, =C′HN), 47.55 (s, 1C, CH_2N), 14.93 (d, 1C, CH_2P, J(P,C) = 13.5 Hz). ^{31}P{^{1}H} NMR δ (C_6D_6, 121.49 MHz) = −136.17 (s, 1P), ^{31}P NMR δ (C_6D_6, 121.49 MHz) = −137.76 (t, 1P, J(P,H) = 193 Hz).

4.2.2. Synthesis of 2-methyl-1-(2-phosphino-ethyl)-imidazole (**2b**)

Ligand **2b** was prepared in an analogous manner to that above given for **2a**, starting from 2-methylimidazole **1b** (1.60 g, 19.49 mmol) and was obtained as a colourless viscous oil (1.18 g, 42%). ^{1}H NMR δ (C_6D_6, 300.13 MHz) = 7.03 (s, 1H, =CHN), 6.37 (s, 1H, =CH′N), 3.12 (m, 2H, CH_2N), 2.15 (dt, 2H, PH_2, J(P,H) = 193 Hz, ^2J(H,H) = 7.6 Hz), 1.97 (s, 3H, CH_3N), 1.12 (m, 2H, CH_2P). ^{13}C{^{1}H} NMR δ (C_6D_6, 75.47 MHz) = 142.35 (s, 1C, NCN), 129.97 (s, 1C, =CHN), 116.49 (s, 1C, =C′HN), 46.62 (s, 1C, CH_2N), 14.46 (d, 1C, CH_2P, J(P,C) = 13.6 Hz), 11.48 (s, 1C, CH_3N). ^{31}P{^{1}H} NMR δ (C_6D_6, 121.49 MHz) = −137.60 (s, 1P), ^{31}P NMR δ (C_6D_6, 121.49 MHz) = −137.60 (t, 1P, J(P,H) = 193 Hz).

4.2.3. Synthesis of 1-{2-[bis-(2-diphenylphosphino-ethyl)-phosphino]-ethyl}-imidazole (**3a**) (Triphosim)

A mixture of ligand **2a** (0.160 g, 1.249 mmol), diphenylvinylphosphine (0.531 g, 2.502 mmol) and AIBN (8 mg, 0.049 mmol, 2% mol) was heated at 105 °C for 22 h. Ligand **3a** was purified by heating at 180 °C in vacuo for 2 h and obtained as a yellow waxy oil (0.691 g, quantitative yield). ^{1}H NMR δ (C_6D_6, 300.13 MHz) = 7.52–7.10 (m, 20 H aromatics plus 2H, from =CHN and NCHN), 6.47 (s, 1H, =CH′N), 3.26 (m, 2H, CH_2N), 2.05 (m, 4H, CH_2PPh_2), 1.41 (m, 4H, $CH_2P(CH_2)_2$), 1.26 (m, 2H, $CH_2P(CH_2)_2$). ^{13}C{^{1}H} NMR δ (C_6D_6, 75.47 MHz) = 139.20–118.24 (m, 12C, aromatics plus 2C from =CHN and 1C from NCHN), 43.74 (d, 1C, CH_2N, ^2J(P,C) = 22.6 Hz), 28.45 (d, 1C, $CH_2P(CH_2)_2$, J(P,C) = 18.9 Hz), 23.96 (t, 2C, CH_2PCH_2–CH_2, J(P,C) = ^2J(P′,C) = 14 Hz with P and P′, respectively for $CH_2P(CH_2)_2$ and CH_2PPh_2, similar to *Triphos* ligand [25]), 22.02 (t, 2C, CH_2PPh_2, J(P′,C) = ^2J(P,C) = 16 Hz). ^{31}P{^{1}H} NMR δ (C_6D_6, 121.49 MHz) = −0.11 (d, 2P, J(P,P) = 26.7 Hz), −12.63 (t, 1P, J(P,P) = 26.7 Hz).

4.2.4. Synthesis of 1-{2-[bis-(2-diphenylphosphino-ethyl)-phosphino]-ethyl}-2-methyl-imidazole (**3b**) (Triphosmim)

A mixture of ligand **2b** (0.335 g, 2.357 mmol), diphenylvinylphosphine (1.001 g, 4.712 mmol) and AIBN (15 mg, 0.091 mmol equivalent to 2% mol/mol) was heated at 105 °C for 20 h. Ligand **3b** was purified by heating at 180 °C in vacuo for 2 h and obtained as a yellow waxy oil (1.335 g, quantitative yield). ^{1}H NMR δ (C_6D_6, 300.13 MHz) = 7.51–7.10 (m, 20 H aromatics plus 1H from =CHN), 6.50 (s, 1H, =CH′N), 3.33 (m, 2H, CH_2N), 2.15 (s, 3H, CH_3), 2.08 (m, 4H, CH_2PPh_2), 1.45 (m, 4H, $CH_2P(CH_2)_2$), 1.29 (m, 2H, $CH_2P(CH_2)_2$). ^{13}C{^{1}H} NMR δ (C_6D_6, 75.47 MHz) = 143.70 (s, 1C, NCHN), 139.19–118.35 (m, 12C, aromatics plus 2C from =CHN), 43.19 (d, 1C, CH_2N, ^2J(P,C) = 23.4 Hz), 28.53 (d, 1C, $CH_2P(CH_2)_2$, J(P,C) = 18.1 Hz), 24.22 (t, 2C, CH_2PCH_2–CH_2, J(P,C) = ^2J(P′,C) = 14 Hz with P and P′, respectively for $CH_2P(CH_2)_2$ and CH_2PPh_2, similar to *Triphos* ligand [25]), 22.46 (t, 2C, CH_2PPh_2, J(P′,C) = ^2J(P,C) = 16 Hz), 13.19 (s, 1C, CH_3). ^{31}P{^{1}H} NMR δ (C_6D_6, 121.49 MHz) = −0.11 (d, 2P, ^2J(P,P) = 26.7 Hz), −12.83 (t, 1P, ^2J(P,P) = 26.7 Hz).

4.2.5. Synthesis of Pd(II) complex (**4a**)

To a red suspension of [$PdCl_2(NCPh)_2$] (0.167 mg, 0.434 mmol) in 10 mL of CH_2Cl_2 was slowly added a solution of ligand **3a** (0.240 g, 0.434 mmol) in 10 mL of CH_2Cl_2. A white suspended solution was immediately formed which became a clear yellow orange solution after about 15 min. After stirring for 1 h, the solution was filtered over Celite and the solvent was removed in vacuo. A yellow orange powder was obtained which was washed twice with 10 mL of Et_2O and dried in vacuo at 50 °C for 2 h (0.273 g, 86%). ^{1}H NMR δ ($CDCl_3$, 300.13 MHz) = 8.51–6.82 (m, 20 H aromatics plus 2H from =CHN and =CH′N), 4.70 (m, br, 2H, CH_2N), 3.26 (m, br, 4H, CH_2PPh_2), 3.02 (m, br, 4H, $CH_2P(CH_2)_2$), 2.13 (m, br, 2H, $CH_2P(CH_2)_2$). ^{13}C{^{1}H} NMR δ ($CDCl_3$, 75.47 MHz) = 138.24–129.23 (m, 12C, aromatics plus 2C from =CHN and 1C from NCHN), 44.01 (s, br, 1C, CH_2N), 29.95 (s, br, 1C, $CH_2P(CH_2)_2$), 26.60 (s, br, 4C, $P(CH_2)_2P$). ^{31}P{^{1}H} NMR δ ($CDCl_3$, 121.49 MHz) = 110.66 (s, br, 1P), 50.79 (s, br, 2P). ^{31}P{^{1}H} NMR δ (CH_2Cl_2/C_6D_6, 121.49 MHz) = 106.56 (t, 1P, ^2J(P,P) = 7 Hz), 45.96 (d, 2P, ^2J(P,P) = 7 Hz). $C_{33}H_{35}N_2P_3PdCl_2$ requires: C, 54.30; H, 4.83, N 3.83. Found: C, 54.07; H, 4.97; N, 3.52%

*4.2.6. Synthesis of imidazolium Pd(II) salt (**5a**)*

A suspension of complex **4a** (46 mg, 0.063 mmol) in 20 mL of neat 1-chlorobutane was refluxed for 7 days. The solvent was removed in vacuo and a conversion of 76% was found in the NMR spectra of the crude product. ^{1}H NMR δ ($CDCl_3$, 300.13 MHz) = 9.10 (s, 1H, NCHN), 7.93–7.02 (m, 20 H aromatics plus 2H from =CHN and =CH′N), 5.28 (m, br, 2H, CH_2N), 4.03 (t, 2H, CH_2N, butyl fragment), 3.46 (m, br, 4H, CH_2PPh_2), 3.27 (m, br, 4H, $CH_2P(CH_2)_2$), 2.11 (m, br, 2H, $CH_2P(CH_2)_2$), 1.70 (m, 2H, NCH_2CH_2, butyl fragment), 1.40 (m, 2H, $N(CH_2)_2CH_2$), 0.87 (t, 3H, $N(CH_2)_2CH_3$). ^{13}C{^{1}H} NMR 137.36–120.43 (m, 12C, aromatics plus 2C from =CHN and 1C from NCHN), 49.86 (s, br, 1C, CH_2N, butyl fragment), 44.01 (s, br, 1C, CH_2N), 31.87 (s, br, 1C, NCH_2CH_2, butyl fragment), 29.46 (m, br, 3C, $CH_2P(CH_2)_2$), 20.00 (m, br, 2C, $Ph_2P(CH_2)_2$), 19.51 (m, 1C, $N(CH_2)_2CH_2$), 13.35 (s, 1C, $N(CH_2)_2CH_3$). ^{31}P{^{1}H} NMR δ ($CDCl_3$, 121.49 MHz) = 102.93 (t, 1P, ^{2}J(P,P) = 9.3 Hz), 45.32 (s, br, 2P, ^{2}J(P,P) = 9.3 Hz).

*4.2.7. Synthesis of imidazolium Pd(II) salt (**6a**)*

A suspension of complex **4a** (64 mg, 0.088 mmol) in 15 mL of neat bromoethane was refluxed for 2 days. The solvent was removed in vacuo and a conversion of 79% was found in the NMR spectra of the crude product. ^{1}H NMR δ ($CDCl_3$, 300.13 MHz) = 8.81 (s, 1H, NCHN), 7.93–7.02 (m, 20 H aromatics plus 2H from =CHN and =CH′N), 5.16 (m, br, 2H, CH_2N), 4.11 (q, 2H, NCH_2CH_3), 3.38 (m, br, 8H, $P(CH_2\text{-}CH_2)_2PPh_2$), 2.08 (m, br, 2H, $CH_2P(CH_2)_2$), 1.46 (t, 3H, NCH_2CH_3). ^{13}C{^{1}H} NMR 135.56–119.57 (m, 12C, aromatics plus 2C from =CHN and 1C from NCHN), 44.32 (s, br, 1C, NCH_2CH_3), 43.02 (s, br, 1C, CH_2N), 29.96 (m, br, 3C, $CH_2P(CH_2)_2$), 24.56 (m, br, 2C, $Ph_2P(CH_2)_2$), 14.24 (s, 1C, NCH_2CH_3). ^{31}P{^{1}H} NMR δ ($CDCl_3$, 121.49 MHz) = 104.83 (t, 1P, ^{2}J(P,P) = 7 Hz), 45.88 (s, br, 2P, ^{2}J(P,P) = 7 Hz).

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