Polyhedron 29 (2010) 601–605

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Firsts lysidinyl- and lysidinium-triphosphines Pd(II) complexes

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ARTICLE INFO

Article history:
Available online 5 August 2009

Keywords:
Triphosphine
Synthesis of polyphosphines
Imidazoline
Imidazole
Palladium complexes

ABSTRACT

The preparation of first lysidinyl-triphosphine ligand (named *Triphosline*) is described in three steps which are first a Michael type addition of imidazolidine (or *lysidine*) to diethylvinylphosphonate, second a phosphonate reduction with $LiAlH_4$ and third an anti-Markovnikov radical addition of the primary phosphine to diphenylvinylphosphine. The *Triphosline* behaves as a tridentate P-coordinating ligand in palladium(II) complexes. The dangling *lysidine* function is then cleanly and totally alkylated by methyl iodide to lead to a new kind of lysidinium-triphosphine complexes. Subsequent anion exchange with $TlPF_6$ affords the first example of a chloride free lysidinium-triphosphine palladium complex which has been fully characterized by spectroscopic and analytical methods.

1. Introduction

The development of efficient continuous-flow catalytic systems represents a major challenge in modern homogenous catalysis. However, it requires a perfect immobilization, 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]. For example, the association of a nonvolatile solvent such as imidazolium salts with supercritical carbon dioxide has given very good results in Rh catalyzed olefin hydroformylation [2] or in Ni catalyzed styrene hydrovinylation in continuous-flow conditions [3]. Nevertheless, the performances of catalytic processes can become even better by introduction on the coordinated phosphines of a cationic imidazolium fragment which strongly decreases the metal–phosphine leaching in the mobile phase [4]. For example, an imidazolium monophosphine salt was recently successfully employed in palladium alkynylation, platinum hydrogenation and rhodium hydroformylation catalysis in ionic liquids without metal leaching into the organic layer [5,6]. In the same manner, addition of an imidazolium fragment to a diphosphine has decreased the rhodium leaching in asymmetric hydrogenation of phenylethenamine to traces level [4]. Additionally, multi-phosphines, specially the $[PhP(CH_2CH_2PPh_2)_2]$ ligand, offer advantages over mono- or di-phosphines in homogeneous catalysis. Indeed, the simultaneous coordination of three phosphorus atoms increases significantly the immobilizing behavior of such ligand as well as the nucleophilic character of the metal centre. This favors the C–H bond oxidative addition to rhenium catalysts in cyclooctane dehydrogenation [7] and to rhodium catalysts in aldehydes decarbonylation [8] or increases the M–H bond reactivity towards weakly polar carbonyl functions [9]. Imidazolium-triphosphines are thus very appealing to perform the above catalysis in continuous-flow conditions using an ionic liquid and we have previously reported a synthetic method opening the access to such unprecedented ligands [10], see Scheme 1.

However, in this previous work, we described only partial N-alkylation reactions of imidazolyl-triphosphines despite the use of different alkylating reagents [10]. Nevertheless, we emphasize that complete conversion of neutral N-heterocycles to imidazolium fragments is absolutely essential to render the related tridentate ligand totally insoluble in an extracting mobile phase and, therefore, to maintain the active species stable for a long period of time in the ionic liquid phase. We thus report now the solvation of this problem of partial N-alkylation by the replacement of the imidazole by a stronger nucleophile like an imidazoline.

2. Results and discussion

The procedure we have developed in the case of ligands **1a,b** [10] was thus applied to the 2-methylimidazoline **2** (also named *lysidine*), see Scheme 2.

According to this procedure, the lysidinyl-phosphine **3** was successfully prepared by a one pot synthesis including a Michael type addition of **2** to diethylvinylphosphonate followed by the reduction of the phosphonate function of the intermediate lysidinyl-phosphonate with $LiAlH_4$. The functionalized primary phosphine **3** was obtained in a moderate yield of 32%, identical to those found for the analogous ligands **1a,b**. The presence of the PH_2 group is confirmed in the phosphorus NMR spectrum by the existence of a triplet of quintuplets at $\delta = -149.70$ ppm which is very similar to $\delta = -136.17$ and -137.60 ppm found respectively for **1a** and

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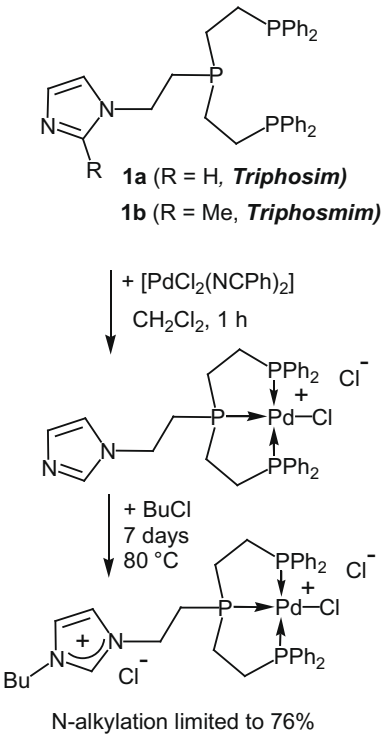
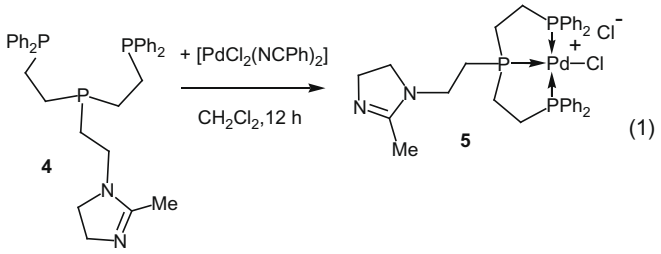
doi:10.1016/j.poly.2009.07.055



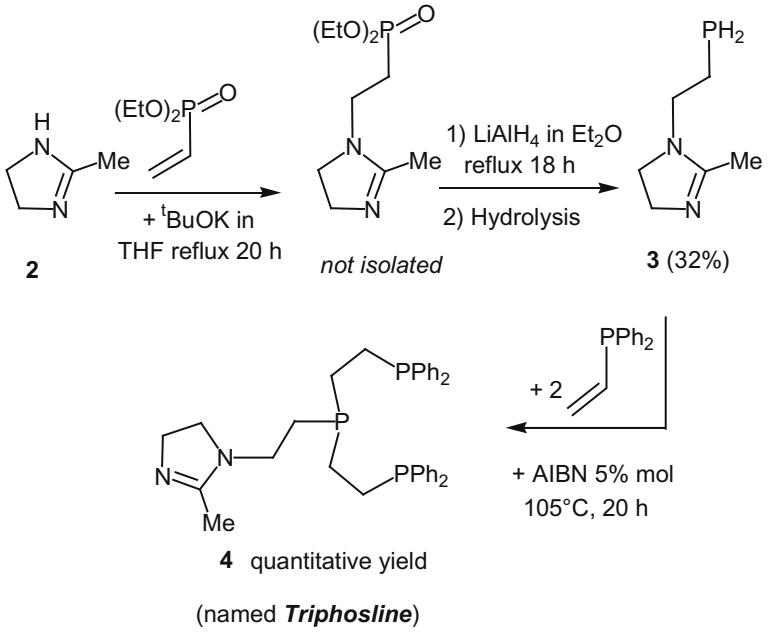
Scheme 1.

1b and with a typical high phosphorus–hydrogen coupling constant of 195 Hz [10]. Addition of two equivalents of diphenylvinylphosphine and 5% of AIBN to the air-sensitive ligand **3** followed by heating at 105 °C for 20 h led to the new functionalized triphosphine ligand **4** (named *Triphosline*) in quantitative yield. Its proton-decoupled phosphorus NMR spectrum confirms unambiguously the formation of the two PCH_2CH_2P units by the unique presence of a doublet at $\delta = -13.00$ ppm for the terminal P-atoms and a triplet at $\delta = -25.38$ ppm for the internal P-atom with a ^2J(P,P) coupling constant of 27 Hz.

The further addition of a stoechiometric amount of ligand **4** to $[PdCl_2(NCPh)_2]$ in CH_2Cl_2 solution led to the air stable cationic palladium complex **5** (see Eq. (1)) which is characterized by a triplet at $\delta = 110.81$ ppm and a doublet at $\delta = 47.17$ ppm with a ^2J(P,P) coupling constant of ca. 7 Hz and a 1:2 integration-ratio in its proton-decoupled phosphorus NMR spectrum. The phosphorus chemical shifts as well as the phosphorus–phosphorus coupling constant are very close to those reported in the literature for analogous unmodified- and modified-triphosphine cationic complexes $[PdCl(P_3)]Cl$ with P_3 = *Triphos*, *Trisphosim* or *Triphosmim* [10,11]. The molecular structure of **5** was definitely confirmed by a positive-mode electrospray ionization mass-spectrum which showed the molecular peaks of the expected cationic palladium complex (see Section 4 for details).



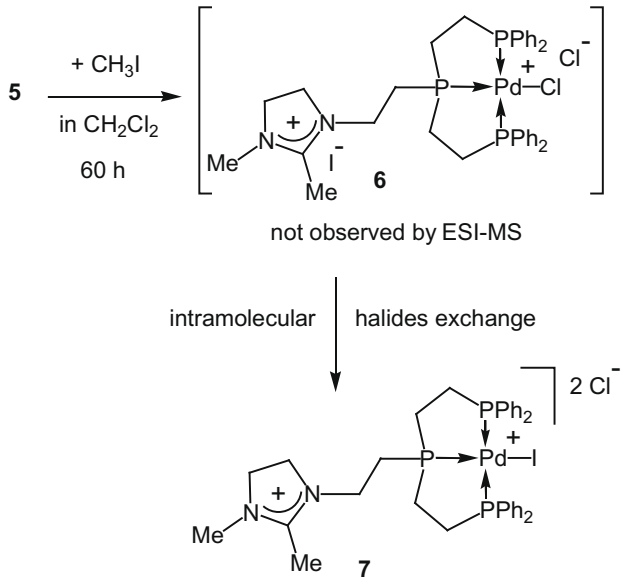
Since imidazoles are known to undergo a complete alkylation reaction after two days in refluxing BuCl [12], we have applied similar conditions to complex **5**. As imidazolines are stronger nucleophiles than imidazoles due to their nitrogen lone pair which cannot be delocalized on the N-heterocycle, we indeed anticipated that such procedure would lead to a complete alkylation of **5**. In this case however, a mixture of several complexes was observed in proton-decoupled phosphorus NMR, resulting likely from a decomposition of **5** in such reaction conditions whereas a clean but incomplete alkylation reaction was previously observed with its analogous *Trisphosim* palladium complex [10]. The same reaction performed in neat boiling EtBr led also, after three days, to a mixture of palladium complexes which could unfortunately not be clearly identified due to their insolubility in common organic solvents. Nevertheless, we finally succeeded to perform a



Scheme 2.

quantitative alkylation reaction without formation of any decomposition product by using a CH_3I/CH_2Cl_2 mixture, as shown by the presence of new signals at $\delta = 109.25$ and 46.78 ppm in the proton-decoupled phosphorus NMR spectrum of the crude, corresponding to the internal and external P-atoms, respectively. Besides, the presence of the N-methyl group is confirmed by a new signal at $\delta = 42.2$ ppm in the proton-decoupled carbon NMR spectrum, thus suggesting the presence of the alkylated derivative **6** (see Scheme 3). Since the phosphorus, proton and carbon chemical shifts of compounds **5** and **6** are practically the same, an additional characterization experiment was investigated in order to confirm unambiguously the formation of this new cationic palladium complex.

Interestingly, a positive-mode electrospray ionization mass analysis of complex **6** was performed but did not show the expected molecular peak at *m/z* 362.06 for the dicationic palladium species $[M–Cl–I]^{2+}$ but another signal at *m/z* 408.05. This signal has been unambiguously assigned through simulation as the dicationic species $[M–2Cl]^{2+}$ which subsequently contains a Pd–I covalent bond instead of a Pd–Cl as anticipated in **6** (see Scheme 3).



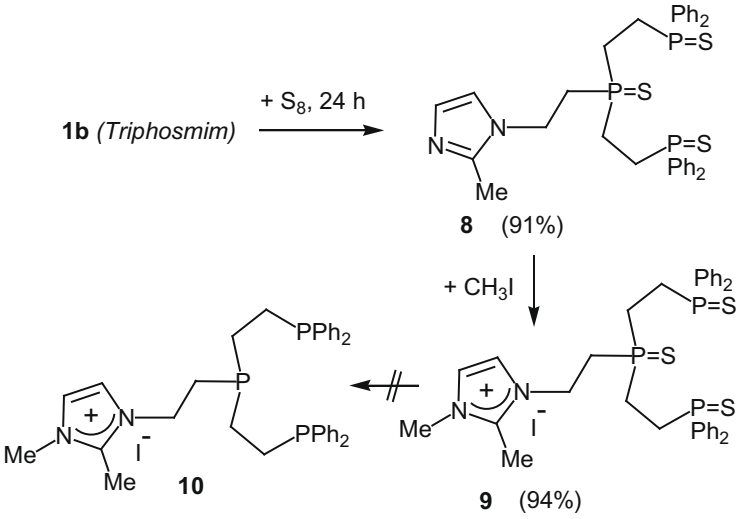
Scheme 3.

Although this substitution of the chloride by the iodide anionic ligand was quite unexpected, it can be rationalized in terms of lower electronegativity and thus better σ-donor character of the iodide and has been previously reported for a similar complex containing the *Triphos* ligand by simple addition of KI to the complex [PdCl(*Triphos*)]Cl [13].

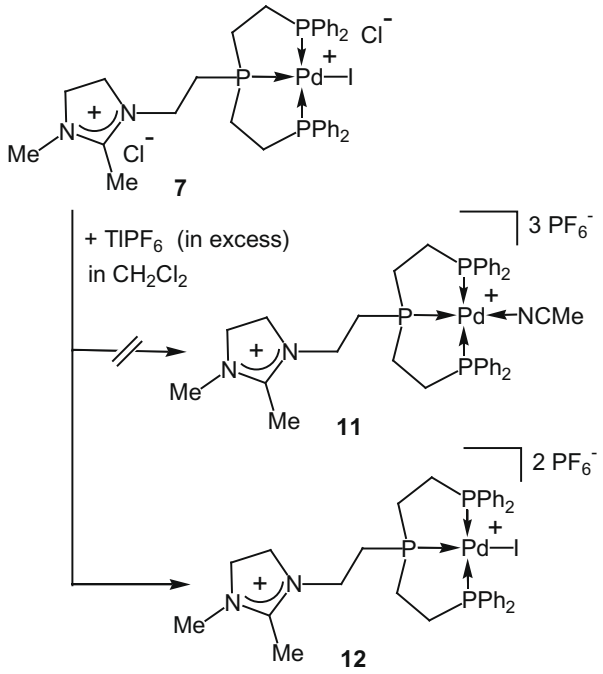
It is noteworthy that apart from the above strategy consisting in protecting the phosphorus atoms through coordination to a transition metal in order to obtain the imidazolium- or imidazolinium-triphosphine complexes, we also wished to obtain the free ligand and therefore we explored a more direct synthetic method. Since it is well known that the nitrogen atom is a better nucleophile center than the phosphorus atom, the direct alkylation reaction of imidazole-phosphine ligands should take place preferentially on the imidazole moiety. However, in order to avoid the formation of any mixture, our alternative synthesis consisted in protecting the phosphorus atoms by oxidation prior to the alkylation reaction, followed by a P^V-atoms reduction to release the phosphine functions. We indeed found that the addition of an excess of molecular sulfur to ligand **1b** [10] led to the complete formation of pure trisulfide ligand **8** after 1 day at room temperature, see Scheme 4.

The further addition of methyl iodide in large excess allowed the convert quantitatively ligand **8** to the expected compound **9** (see Scheme 4) after 3 days. Unfortunately, all attempts to deprotect the phosphorus atoms using either HMPT, $LiAlH_4$ in refluxing THF for 4 days or fresh Raney Ni in refluxing acetonitrile for 1 day remained unsuccessful.

Finally, the conversion of complex **7** to the corresponding halide free palladium complex was investigated. Three equivalents of $AgNO_3$ or AgOTf were added to this complex in a CH_2Cl_2/MeOH solution but this treatment unfortunately led to a mixture of palladium complexes as shown by the existence of several signals in the related proton-decoupled phosphorus NMR spectra of the crude products. Nonetheless, when $TlPF_6$ was used in a CH_2Cl_2/CH_3CN mixture, a selective and complete formation of a new palladium complex was detected by the presence of only two new signals at $\delta = 115.04$ and 49.16 ppm, respectively for the internal and external P-atoms in addition to the PF_6 signal. It is worth to mention that the corresponding mass spectrum, recorded using the electrospray technique, is unconsistent with the expected complex **11** as it is identical to the one obtained for the starting complex **7**. Indeed, the formation of **12** was instead observed as determined from NMR and elemental analysis data (see Section 4). This latter observation is likely the consequence of a selectivity in the halide



Scheme 4.



Scheme 5.

abstraction reaction induced by a strong covalent character of the Pd–I bond (See Scheme 5). Other halide abstracting reagents and/or other strategies are currently in progress in our group in order to get totally halide-free lysidinium-triphosphine palladium complexes which would be better suitable for further studies in homogeneous catalysis.

3. Conclusion

In this paper, we have described the preparation of the first lysidinyl-triphosphine (*Triphosline*) in three steps comprising an addition of 2-methylimidazoline to vinylphosphonate followed by a reduction of the P^V-atom to primary phosphine and its addition of diphenylvinylphosphine. With the aim to get the related lysidinium-triphosphine salts for further studies in homogenous catalysis, we have clearly shown that the higher nucleophilic character of the *lysidine* fragment compared to imidazole, together with a prior coordination to a palladium(II) complex, allows to perform a clean N-alkylation reaction using methyl iodide. Since the new cationic functionalized triphosphines thus obtained are very appealing as a new family of immobilizing ligands in transition metal catalysis due to the simultaneous presence of three strongly coordinating P-centers and a stable cationic fragment, we are currently investigating the catalytic properties of their metal complexes in our laboratory.

4. Experimental section

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 NMR measurements (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) were carried out with a Bruker Avance 300 spectrometer at room temperature in $CDCl_3$ solution. The peak positions are reported with positive shifts in ppm downfield of TMS as calculated from the residual solvent peaks (^{1}H and ^{13}C{^{1}H}) or downfield of external 85% H_3PO_4 in water (^{31}P). Electrospray mass-spectra of palladium complexes were performed on Bruker micrOTOF-Q instrument. Elemental analyses were carried out by the analytical service in our laboratory with a Fisons Instruments EA1108 analyzer. The commercial compounds CH_3I, S_8, 2-methylimidazoline (also named *lysidine*), diphenylvinylphosphine, diethylvinylphosphonate, $LiAlH_4$, AIBN [2,2-azobis(2-methyl-propionitrile)], $AgNO_3$, $TlPF_6$ and $[PdCl_2(NCPh)_2]$ were used as received. The *Triphosmim* **1a** and *Triphosmim* **1b** ligands have been prepared according to the procedure described in the literature [10].

4.2. Synthesis of ligands and complexes

4.2.1. Synthesis of 2-methyl-1-(2-phosphinoethyl)-imidazoline ***3***

A mixture of 2-methylimidazoline or *lysidine* (1.485 g, 17.66 mmol), diethylvinylphosphonate (2.889 g, 17.61 mmol) and 30 mL of THF was treated with ^{t}BuOK (0.286 g, 2.55 mmol) and heated in refluxing THF for 21 h. The solvent was removed under vacuum 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 $LiAlH_4$ (1.266 g, 33.3 mmol) were rapidly added. A strong gas evolution was immediately observed with an increase of the temperature. When the exothermic reaction was subsided, the Et_2O mixture was refluxed for 19 h. The grey suspension was cooled down to room temperature and hydrolyzed by 15 mL of deoxygenated water. The organic phase was separated and the aqueous solution was extracted twice with 20 mL of Et_2O. The combined organic layers were dried over K_2SO_4 and filtered. Evaporation of the solvent led to a colorless viscous oil which was dried under vacuum for 2 h at room temperature (0.819 g, 32%). ^{1}H NMR δ ($CDCl_3$) = 3.59 (t, 2H, $C^{(4/5)}H_2$–N, J(H,H) = 9.5 Hz), 3.20 (t, 2H, $C^{(5/4)}H_2$–N, J(H,H) = 9.5 Hz), 3.16 (m, 2H, CH_2N), 2.56 (dt, 2H, PH_2, J(P,H) = 195 Hz, ^3J(H,H) = 7.8 Hz), 1.86 (s, 3H, CH_3), 1.62 (m, 2H, CH_2P). ^{13}C{^{1}H} NMR δ ($CDCl_3$) = 163.90 (s, 1C, NCN), 51.94 (s, 1C, CH_2(N=C)), 49.71 (s, 1C, CH_2(N–C)), 49.50 (s, 1C, CH_2N), 14.37 (s, 1C, CH_3), 13.52 (d, 1C, CH_2P, J(P,C) = 10.7 Hz). ^{31}P{^{1}H} NMR δ = −149.70 (s, 1P), ^{31}P NMR δ ($CDCl_3$) = −149.70 (tquint., 1P, J(P,H) = 195 Hz, ^2J(P,H) = ^3J(P,H) = 5.5 Hz).

4.2.2. Synthesis of 1-{2-[Bis-(2-diphenylphosphinoethyl)-phosphino]-ethyl}-2-methylimidazoline ***4*** *named Triphosline*

A mixture of ligand **7** (0.136 g, 0.943 mmol), diphenylvinylphosphine (0.418 g, 1.97 mmol) and AIBN (9 mg, 0.05 mmol, equivalent to 5% mol/mol) was heated at 105 °C for 22 h. Ligand **4** was purified by heating at 180 °C under vacuum for 1 h and obtained as a yellow-orange waxy oil (0.536 g, quantitative yield). ^{1}H NMR δ ($CDCl_3$) = 7.33–7.18 (m, 20H aromatics), 3.53 (t, 2H, $C^{(4/5)}H_2$–N, J(H,H) = 9.7 Hz), 3.12 (t, 2H, $C^{(5/4)}H_2$–N, J(H,H) = 9.7 Hz), 2.99 (m, 2H, CH_2N), 1.96 (m, 4H, CH_2PPh_2), 1.75 (s, 3H, CH_3), 1.41 (m, 6H, $P(CH_2)_3$). ^{13}C{^{1}H} NMR δ ($CDCl_3$) = 164.35 (s, 1C, NCN), 138.13–128.44 (m, 24C, aromatics), 51.09 (s, 1C, CH_2(N=C)), 49.72 (s, 1C, CH_2(N–C)), 44.30 (d, 1C, CH_2N, ^2J(P,C) = 21.8 Hz), 25.88 (d, 1C, $CH_2P(CH_2)_2$, J(P,C) = 16.7 Hz), 23.66 (t, 2C, CH_2PCH_2–CH_2, J(P,C) = ^2J(P′,C) = 15 Hz with P and P′ respectively for $CH_2P(CH_2)_2$ and CH_2PPh_2, similar to *Triphosmim* ligand [10]), 21.99 (t, 2C, CH_2PPh_2, J(P′,C) = ^2J(P,C) = 15 Hz), 14.18 (s, 1C, CH_3). ^{31}P{^{1}H} NMR δ ($CDCl_3$) = −13.00 (d, 2P, ^2J(P,P) = 26.9 Hz), −25.38 (t, 1P, ^2J(P,P) = 27.0 Hz).

4.2.3. Synthesis of palladium(II) complex ***5***

To a red suspension of $[PdCl_2(NCPh)_2]$ (0.228 g, 0.594 mmol) in 5 mL of CH_2Cl_2 was slowly added a solution of ligand **4** (0.338 g, 0.594 mmol) in 5 mL of CH_2Cl_2. An orange suspension was immediately formed which became a clear orange solution after about 15 min at room temperature. After stirring for 12 h at this

temperature, the solution was filtered over Celite® and the solvent was removed under vacuum. An orange powder was obtained which was washed twice with 10 mL of Et_2O and dried under vacuum at room temperature for 5 h (0.418 g, 94%). ^{1}H NMR δ ($CDCl_3$) = 7.91–.22 (m, 20H aromatics), 3.44 (m, 4H, $C^{(4+5)}H_2$–N), 3.36–2.40 (m, 12H, 5 CH_2P plus CH_2N), 1.69 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) = 165.13 (s, 1C, NCN), 133.16–127.61 (m, 24C, aromatics), 50.19 (s, 1C, CH_2(N=C)), 48.80 (s, 1C, CH_2(N–C)), 44.47 (s, br, 1C, CH_2N), 29.57 (s, br, 3C, $P(CH_2)_3$), 27.59 (s, br, 2C, CH_2PPh_2), 12.59 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) = 110.81 (t, 1P, ^2J(P,P) = 6.8 Hz), 47.17 (d, 2P, ^2J(P,P) = 6.8 Hz). ESI-MS (positive mode, CH_2Cl_2) found for $C_{34}H_{39}N_2P_3PdCl_2$ (744.073) *m/z* = 709.114 $[M-Cl]^+$ and *m/z* = 354.562 $[M+H-Cl]^{2+}$. Simulated: *m/z* = 709.105 and *m/z* = 354.552. *Anal.* Calc. for $C_{34}H_{39}N_2P_3PdCl_2$: C, 54.74; H, 5.27; N, 3.75. Found: C, 54.67; H, 5.56; N, 3.91%.

4.2.4. Synthesis of palladium(II) complex **7**

To a solution of complex **5** (0.090 g, 0.121 mmol) in 6 mL of CH_2Cl_2 was added CH_3I (0.3 mL, 3.20 mmol). The resulting clear orange solution was stirred for 60 h. It is worth to note that an orange suspension started to appear after about 12 h. The solvent was removed under vacuum and an orange powder was obtained which was dried under vacuum at room temperature for 2 h (0.107 g, quantitative yield). ^{1}H NMR δ (CD_3CN) = 7.90–7.24 (m, 20H aromatics), 3.62–2.61 (m, 19H, CH_3N plus 5 PCH_2 plus $N(CH_2)_3$), 1.74 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR δ (CD_3CN) = 166.89 (s, 1C, NCN), 134.14–128.03 (m, 24C, aromatics), 49.53 (s, 1C, $C^{(4/5)}H_2$–N), 48.21 (s, 1C, $C^{(5/4)}H_2$–N), 46.69 (s, br, 1C, CH_2N), 42.21 (s, br, 1C, CH_3N), 31.82 (s, br, 3C, $P(CH_2)_3$), 26.48 (s, br, 2C, CH_2PPh_2), 12.06 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR δ (CD_3CN) = 109.25 (s, br, 1P), 46.78 (s, br, 2P). ESI-MS (positive mode, CH_2Cl_2) found for $C_{35}H_{42}N_2P_3PdCl_2I$ (866.001) *m/z* = 408.0515 $[M-2Cl]^{2+}$, simulated: 408.0321. *Anal.* Calc. for $C_{35}H_{42}N_2P_3PdCl_2I$: C, 64.20; H, 6.01; N, 4.28. Found: C, 63.86; H, 6.24; N, 4.37%.

4.2.5. Synthesis of ***8*** *(Triphosmim trisulfide)*

To a mixture of ligand *Triphosmim* **1b** (0.270 g, 0.476 mmol) and S_8 (0.055 g, 1.71 mmol) were added 10 mL of dichloromethane. The resulting colorless solution was stirred at room temperature for 24 h. Evaporation of solvent led to a white powder which was dried under vacuum for 1 h (0.287 g, 91%). ^{1}H NMR δ $CDCl_3$ = 7.76–7.19 (m, 20H aromatics), 6.73 (s, 1H, =CHN), 6.72 (s, 1H, =CH′N), 4.15 (m, 2H, CH_2N), 2.48 (m, 4H, CH_2PPh_2), 2.15 (s, 3H, CH_3), 2.13 (m, 4H, $CH_2P(CH_2)_2$), 1.92 (m, 2H, $CH_2P(CH_2)_2$). $^{13}C\{^1H\}$ NMR δ $CDCl_3$ = 143.39 (s, 1C, NCN), 131.01–117.84 (m, 24C aromatics plus 2C from =CHN), 38.66 (s, 1C, CH_2N), 30.93 (d, 1C, $CH_2P(CH_2)_2$, *J*(P,C) = 48 Hz), 25.11 (d, 2C, CH_2PCH_2–CH_2, *J*(P,C) = 54 Hz), 23.40 (d, 2C, CH_2PPh_2, *J*(P,C) = 50 Hz), 12.22 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR δ $CDCl_3$ = 50.18 (part B of AA′B spin system, 1P, $P_{internal}$, $^2J(P^A,P^B)$ = 54 Hz and $^2J(P^{A'},P^B)$ = 57 Hz), 44.33 (part A of AA′B spin system, 1P, $P^A{}_{terminal}$, $^2J(P^A,P^B)$ = 54 Hz and part A′ of AA′B spin system, 1P, $P^{A'}{}_{terminal}$, $^2J(P^{A'},P^B)$ = 57 Hz). *Anal.* Calc. for $C_{34}H_{37}N_2P_3S_3$ (M = 662.79): C, 61.61; H, 5.63; N, 4.22. Found: C, 60.94; H, 5.51; N, 4.12%.

4.2.6. Synthesis of ***9*** *(Imidazolium–Triphosmim trisulfide iodide salt)*

To a solution of **8** (1.000 g, 1.509 mmol) in 10 mL of CH_2Cl_2 was added CH_3I (2 mL, 21.35 mmol). The resulting solution was stirred for 3 days at room temperature. The solvent was removed under vacuum, leaving a yellow powder which was washed twice with 10 mL of Et_2O and dried under vacuum for 2 h (1.143 g, 94%). ^{1}H NMR δ ($CDCl_3$) = 7.89–7.21 (m, 20H aromatics plus 2H from =CH′N), 4.51 (m, 2H, CH_2N), 3.71 (s, 3H, N–CH_3), 2.80 (m, 4H, CH_2PPh_2), 2.71 (s, 3H, CH_3C), 2.60 (m, 2H, $CH_2P(CH_2)_2$), 2.01 (m, 4H, $CH_2P(CH_2)_2$). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) = 143.33 (s, 1C, NCN), 130.94–120.80 (m, 24C aromatics plus 2C from =CHN), 41.89 (s, 1C, CH_2N), 35.30 (s, 1C, N–CH_3), 29.92 (d, 1C, $CH_2P(CH_2)_2$, *J*(P,C) = 48 Hz), 24.70 (d, 2C, CH_2PCH_2–CH_2, *J*(P,C) = 52 Hz), 23.41 (d, 2C, CH_2PPh_2, *J*(P,C) = 50 Hz), 11.09 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR δ ($CDCl_3$) = 51.47 (part B of AA′B spin system, 1P, $P_{internal}$, $^2J(P^A,P^B)$ = 54 Hz and $^2J(P^{A'},P^B)$ = 57 Hz), 45.00 (part A of AA′B spin system, 1P, $P^A{}_{terminal}$, $^2J(P^A,P^B)$ = 54 Hz and part A′ of AA′B spin system, 1P, $P^{A'}{}_{terminal}$, $^2J(P^{A'},P^B)$ = 57 Hz). *Anal.* Calc. for $C_{35}H_{40}N_2P_3S_3I$ (M = 804.73): C, 52.24; H, 5.01; N, 3.48. Found: C, 52.66; H, 4.86; N, 3.39%.

4.2.7. Synthesis of palladium(II) complex ***12***

To a mixture of **7** (0.123 g, 0.139 mmol) and thallium hexafluorophosphate (0.148 g, 0.424 mmol) were added 7 mL of dichloromethane. The deep orange suspension was stirred at room temperature for 3 h and then filtered. Evaporation of the solvent led to an orange powder which was washed with Et_2O and dried under vacuum (0.139 g, 91%). ^{1}H NMR δ (DMSO) = 7.92–7.52 (m, 20H, aromatics), 3.88 (s, 3H, CH_3N), 3.81–2.74 (m, 16H, $N(CH_2)_3$ plus 5 PCH_2), 2.19 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR δ (DMSO) = 167.00 (s, 1C, NCN), 134.65–129.84 (m, 24C, aromatics), 50.43 (s, 1C, $C^{(4/5)}H_2$–N), 49.43 (s, 1C, $C^{(5/4)}H_2$–N), 47.42 (s, 1C, CH_2N), 42.29 (s, 1C, CH_3–N), 36.68 (s, 3C, $P(CH_2)_3$), 34.34 (s, 2C, CH_2PPh_2), 11.25 (s, 1C, CH_3). $^{31}P\{^1H\}$ NMR δ (DMSO) = 115.04 (t, 1P, ^2J(P,P) = 4.9 Hz), 49.16 (d, 2P, ^2J(P,P) = 4.9 Hz), −144.18 (hept., 1P, *J*(P,F) = 711 Hz). ESI-MS (positive mode, CH_2Cl_2/MeOH) found for $C_{35}H_{42}N_2P_5PdF_{12}I$ (1105.99) *m/z* = 408.0309 $[M-2PF_6]^{2+}$, simulated: 408.0321. *Anal.* Calc. for $C_{35}H_{42}N_2P_5PdF_{12}I$: C, 37.97; H, 3.83; N, 2.53. Found: C, 37.54; H, 3.69; N, 2.66%.

Acknowledgments

We wish to acknowledge the Ministère de l'Enseignement Supérieur et de la Recherche, the Université de Bourgogne, the Centre National de la Recherche Scientifique and the Conseil Régional de Bourgogne for support of this work. We also thank Miss M.-J. Penouilh (Université de Bourgogne) for her technical assistance and discussion in the electrospray analyses of palladium complexes.

References

[1] M. Picquet, S. Stutzmann, I. Tkatchenko, I. Tommasi, J. Zimmermann, P. Wasserscheid, Green Chem. 5 (2003) 153.
[2] D.J. Cole-Hamilton, Science 299 (2003) 1702.
[3] A. Bösmann, G. Franciò, E. Janssen, M. Solinas, W. Leitner, P. Wasserscheid, Angew. Chem., Int. Ed. Engl. 40 (2001) 2697.
[4] S.-G. Lee, Y.J. Zhang, J.Y. Piao, C.E. Song, J.H. Choi, J. Hong, Chem. Commun. (2003) 2624.
[5] E. Fayad, S. Saleh, M. Azouri, J.-C. Hierso, J. Andrieu, M. Picquet, Adv. Synth. Catal. 351 (2009) 1621.
[6] K.W. Kottsieper, O. Stelzer, P. Wasserscheid, J. Mol. Catal. A 175 (2001) 285.
[7] D. Michos, X.-L. Luo, J.W. Faller, R.H. Crabtree, Inorg. Chem. 32 (1993) 1370.
[8] C.M. Beck, S.E. Rathmill, Y.J. Park, J. Chen, R.H. Crabtree, L.M. Liable-Sands, A.L. Rheingold, Organometallics 18 (1999) 5311.
[9] M.C. van Engelen, H.T. Teunissen, J.G. de Vries, C.J. Elsevier, J. Mol. Catal. A: Chem. 206 (2003) 185.
[10] J. Andrieu, M. Azouri, Inorg. Chim. Acta 360 (2007) 131.
[11] D. Fernández, M.I. García-Seijo, P. Sevillano, A. Castiñeiras, M.E. García-Fernández, Inorg. Chim. Acta 358 (2005) 2575.
[12] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.
[13] D. Fernández, P. Sevillano, M.I. García-Seijo, A. Castiñeiras, L. Jánosi, Z. Berente, L. Kollár, M.E. García-Fernández, Inorg. Chem. Acta 312 (2001) 40.