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Palladium(II) complexes featuring a mixed Phosphine-Pyridine-Iminophosphorane pincer ligand : synthesis and reactivity

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An original mixed ligand (labelled **L**) of formula PPh_2-CH_2-Pyr-CH_2-N=PPh_3 combining a pyridine core with a phosphine and an iminophosphorane was synthesised. Its coordination to palladium(II) centers was studied. With $[Pd(COD)Cl_2]$ a cationic complex [**L**PdCl](Cl) **1**, where L is coordinated in pincer mode was obtained. Chloride abstraction with silver salt in presence of pyridine generated the dicationic complex $[\mathbf{L}Pd(py)](BF_4)_2$ (**2**). When reacting with a base such as potassium hexamethyldisilazane (KHMDS), **1** gave the neutral complex **3** [**L***PdCl] where the benzylic position alpha to the phosphine was selectively deprotonated, which induced a dearomatisation of the pyridine ring. A similar complex [**L***Pd(CH_3)] (**4**) was obtained upon reaction of $[Pd(CH_3)_2(TMEDA)]$ and **L** via the departure of methane. Neutral complexes with deprotonated ligand such as **3** yielded in presence of deuterated methanol the corresponding deuterated complex, showing that, with this ligand, the protonation is reversible. Finally, upon attempting to dealkylate complex **4** using $B(C_6F_5)$, an unexpected cationic borated complex **5** resulting from the formation of a C-B bond in benzylic position with restoration of the aromatic character of the pyridine was isolated. Interestingly when the metal is introduced after the ligand has interacted with the borane reagent another palladium complex formed, namely [**L**PdMe][$MeB(C_6F_5)_3$], coming from methyl abstraction.

Introduction

Since the first report by Shaw et coll. in 1976,[1] pincer ligands[2] has gained much interest in coordination chemistry and play now an important role in organometallic reactions and catalysis,[3] or in the development of switches,[4] and sensors.[3a,5] They are generally compatible with a wide range of metals, offer a high degree of synthetic tunability allowing variation of the central donor atom as well as the nature of the two ancillary coordination sites. Various phosphorous groups were incorporated in such ligands such as phosphonites,[6] phosphaalkenes,[7] phosphines,[8] or aminophosphines[9] affording pincers with divergent electronic properties from strong electron accepting to good electron donating ones. Studies on anionic phosphine pincer ligands have focused on (PCP) derivatives (**A**, Fig. 1) associating two phosphines and an arylic central carbon, [8,10] nevertheless many variations of the pivotal donor were also proposed (N^-, Si^-, P^-, **B**; Fig. 1).[11] Neutral derivatives featuring a central pyridine ring have also received considerable attention,[12] especially the PNP derivatives (**C**, Fig. 1) evidencing cooperative reactivity with the metal (through a switch between aromatised/dearomatised pyridine) allowing efficient catalytic and stoichiometric reactions.[3c,13] Interestingly, with PNN ligands, where one phosphine is replaced by an amine, the hemilability of the amine may influence the course of the reaction.[3c,14] Following our studies on iminophosphorane (P=N) ligands[15] where the nitrogen behaves as a strong σ and π donor, we were interested in developing pincer iminophosphorane ligands.[16] More precisely, as mixed phosphine-iminophosphorane ligands have already been used with success in coordination chemistry and catalysis,[17] we set out to synthesise a mixed tridentate ligand combining phosphine, iminophosphorane and a central pyridine core. In this paper, we described the synthesis of ligand **L** (Fig. 1), its coordination to palladium(II) centers, as well as the formation of [**L***PdR] (R = Me, Cl) complexes, featuring a deprotonated ligands, which were reacted with methanol and borane.

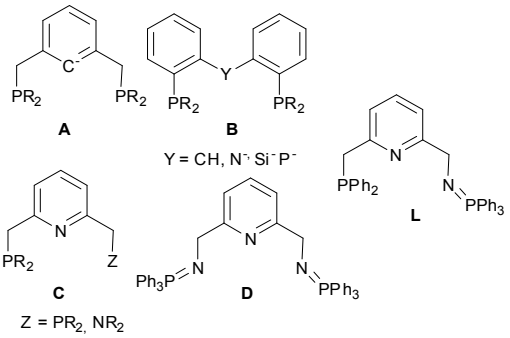

Figure 1: Pincer phosphine and/or iminophosphorane ligands

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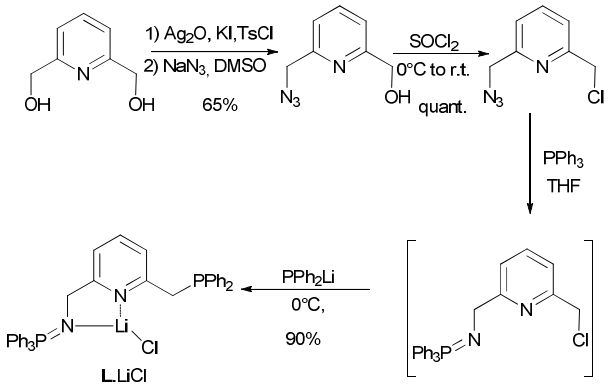
† Electronic Supplementary Information (ESI) available: [Crystallographic data for **1, 2, 3, 5** (CCDC 1414327-1414330) and some NMR spectra]. See DOI: 10.1039/x0xx00000x

Results and discussion

Ligand synthesis

Following the synthesis of the tridentate pincer bis-iminophosphorane pyridine ligand we recently published (**D**, Fig. 1),[18] we chose lutidine diol as starting material. Its efficient dessymetrisation is crucial to develop an efficient preparation of **L**. After having attempted several pathways, 2-(azidomethyl)-6-(hydroxymethyl)pyridine was identified as a key intermediate. Its synthesis from 2,6-bis(hydroxymethyl)pyridine was first realised by a selective bromination[19] followed by an azidation nevertheless better yields were obtained going through a mono-tosylated intermediate[20] (Scheme 1). After substitution of the tosyl group by the azide, the hydroxyl was replaced by a chloride. The iminophosphorane was then formed by a Staudinger reaction with triphenylphosphine. Then, the phosphine group was introduced by a nucleophilic substitution of the chloride with PPh_2Li. First, the iminophosphorane intermediate was isolated but better yield was obtained when both reactions were conducted in the same pot without isolation of the intermediate iminophosphorane. Indeed this last step was conveniently followed by *in situ* $^{31}P\{^1H]$ NMR, the formation of the iminophosphorane was evidenced by a singlet at δ= 6.7 ppm in diethyl ether, its transformation to the phosphine-iminophosphorane adduct gave rise to two singlets at 7.7 and -12 ppm corresponding respectively to the iminophosphorane and the phosphine groups. **L** was obtained as a lithium chloride adduct by precipitation from the reaction mixture. **L**.LiCl was isolated as a white powder in 91% yield. The presence of the lithium was confirmed by ^{7}Li NMR showing a singlet at -0.5 ppm in THF-d_8, the elemental analysis corroborates a 1:1 stoechiometry.

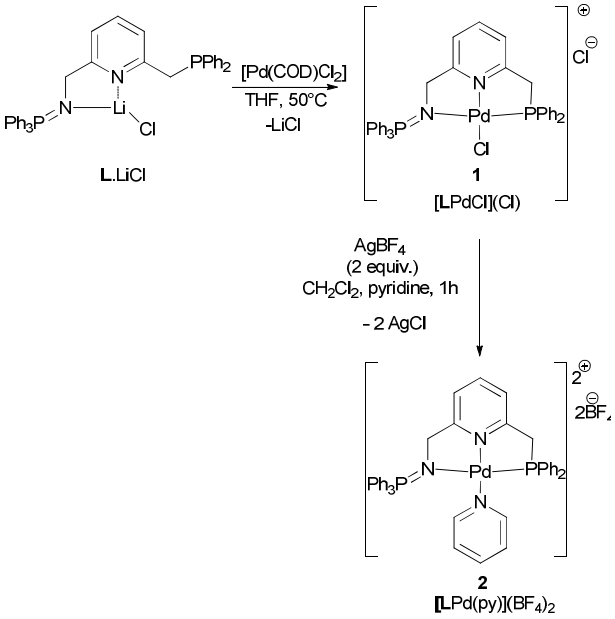


Scheme 1: Synthesis of **L**.LiCl

Two types of benzylic protons were observed in the ^{1}H NMR spectrum: one doublet at δ= 4.32 ($J_{P,H}$= 15Hz) and a singlet at 3.55 ppm. They were respectively assigned to the CH_2 alpha to the iminophosphorane and the phosphine groups thanks to 2D ^{1}H-^{31}P correlation. The absence of coupling between the methylene protons and the phosphorus of the phosphine has been already observed for a biphosphine PNP ligand.[21] NMR data seem to indicate that the lithium is only coordinated by the two nitrogen atoms, and therefore should be stabilised as a dimer (omitted for clarity in Scheme 1) in non-coordinating solvent and in the solid-state while a solvated monomer is more likely in coordinating solvents. This was confirmed by DOSY ^{1}H NMR studies (see Figure S5 and S6 in supplementary information) which depicted a 1.5 fold increase of the hydrodynamic volume between THF and chloroform.

Palladium complexes

First coordination of **L** was realised by mixing **L**.LiCl and $[Pd(COD)Cl_2]$ in THF (Scheme 2). After 2h reaction at 50°C, the resulting complex was isolated as a yellow solid in 80% yield after filtration. The coordination to the metal induced a large deshielding of the phosphorus nuclei appearing as two doublets ($^3J_{P,P}$ = 10.5 Hz) at 35.1 ppm and 33.9. They respectively correlate with a doublet at 4.93 ($J_{P,H}$ = 13.0 Hz) and a doublet of doublets at 4.60 ($J_{P,H}$ = 6.5 Hz, $J_{H,H}$ = 2.0 Hz) in the ^{31}P-^{1}H 2D NMR spectrum. After analysis of the ^{13}C NMR spectrum, the former was assigned to the benzylic protons on the phosphine arm and the latter to those of the iminophosphorane arm.



Scheme 2: Formation of complexes **1** and **2**

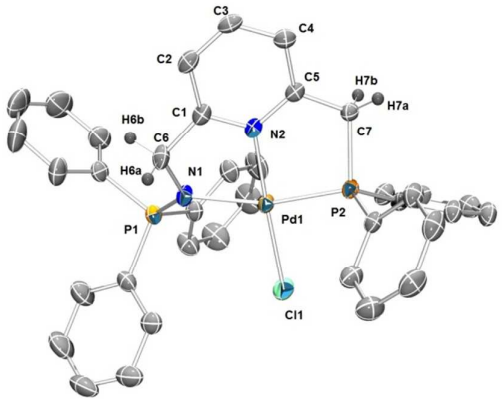
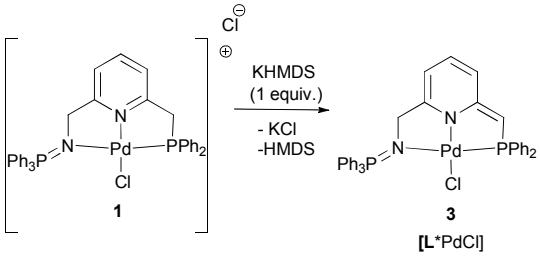


Figure 2: ORTEP of the solid-state structure of **1** with 50% probability thermal ellipsoids. Most Hydrogen atoms, one non-coordinating chloride and one benzonitrile solvent molecule were omitted for clarity. Selected bond lengths [Å] and angles (deg): N1-P1 1,603(2), N1-Pd1 2,110(2), P2-Pd1 2,2112(7), N2-Pd1 1,998(2), Cl1-Pd1 2,2953(7) ; N1-Pd1-P2 164,23(6), N2-Pd1-Cl1 175,95(6), N1-Pd1-N2 80,2(1), P2-Pd1-N2 84,04(6), N1-Pd1-Cl1 99,9(2), P2-Pd1-Cl1 93,19(3).

Therefore, the replacement of lithium by palladium induces a large deshielding only for the protons in the vicinity of the phosphine ($\Delta\delta\approx$1.4 ppm from 3.55 to 4.93 ppm) which is in agreement with the presence of a free phosphine in **L**.LiCl (as proposed above). Definitive evidence concerning the structure of **1** (Figure 2) was given by X-ray diffraction analysis performed on crystals obtained by gas diffusion of diethyl ether in acetonitrile/benzonitrile solution of **1**. As expected for a d^8 metal, the geometry around the metal is square planar, (distance from Pd to the mean coordination plane : 0.03 Å). The P-Pd and the N2-Pd bond lengths are rather short in **1** (2.2112(7) and 1.998(2) Å respectively) compared to those measured in the corresponding (di-tertbutylphosphinomethyl)pyridine (^{tBu}PNP)[22] adduct (2.2961(1) and 2.0430(12) Å) which is probably due to the lower steric hindrance generated by the two phenyl rings. Conversely, the N1-Pd1-P2 angle of 164.23(6)° is more acute than in the phosphine analogue (P-Pd-Pd: 168.729(2)°).

Chloride ligand was easily abstracted from **1** using 2 equivalents of silver tetrafluoroborate in dichloromethane in presence of pyridine (Scheme 2). The same type of complex was formed in presence of other 2-electron ligands such as acetonitrile or trimethylphosphine.‡ The dicationic complex [**L**Pd(py)]$(BF_4)_2$ **2** was isolated after filtration of the salts as a yellow solid in 60 % yield. This behaviour contrasts with that observed by Milstein et coll.[22] who reported that for [(^{tBu}PNP)PdCl](Cl) only the outer-sphere chloride could be abstracted. Complex **2** was characterised by multinuclear NMR spectroscopy in CD_2Cl_2. In $^{31}P\{^1H\}$ spectrum an AB system was observed with doublets at 37.1 and 36.9 ppm ($J_{P,P}$ = 10.5 Hz) which are very close to those described for **1**. Cationisation has more influence on ^{1}H chemical shifts since in **2** the benzylic protons near the phosphine are shielded by 0.46 ppm compared to **1** (4.47 ($J_{P,H}$ = 12.5 Hz) *vs* 4.93 ppm). Pyridine gives well defined signals at 9.26 and 8.86 ppm which are largely deshielded compared to free pyridine which suggest that this ligand is not labile at the NMR time scale in dichloromethane. The presence of non coordinated tetrafluoroborate anion was evidenced by a singlet at -151.4 ppm in ^{19}F NMR. The structure was confirmed by X-ray analysis of single crystals obtained by diffusion of pentane into dichloromethane solution (see supporting information, Fig. S1). It is highly similar to that obtained for **1**, with a slight contraction of the coordination sphere. The pyridine is perpendicular to the pyridine ring of the tridentate ligand to minimise steric hindrance. Other parameters do not deserve further comments.

As **L** should, as its phosphine analogue, exhibit a cooperative behaviour via the deprotonation of a benzylic proton and dearomatisation of the central pyridine, this reaction was realised by addition of one equivalent of KHMDS (potassium hexamethyldisilazane) to a THF solution of complex **1** (Scheme 3).§ The solution darkened rapidly, nevertheless not much change was observed in the *in situ* $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showing two doublets at 34.8 and 32.9 ($^3J_{P,P}$ = 11.5 Hz). Petroleum ether was added in order to induce the precipitation of the complex and remove the amine by-product. Then complex [**L***PdCl] (**3**) was extracted from the precipitate with CH_2Cl_2. **3** was obtained as a pale brown solid in a fair yield of 43% (which is explained by a moderate solubility of **3** in petroleum ether).



Scheme 3: Deprotonation of 1

^{1}H NMR spectroscopy confirms the deprotonation since two types of benzylic protons are observed: one doublet at 3.26 ppm ($J_{P,H}$ = 3.5 Hz) corresponding to one proton and another at 4.10 ($J_{P,H}$ = 7.5 Hz) corresponding to 2 protons. 2D-NMR confirms that deprotonation occurred selectively on the phosphine arm. The loss of aromaticity of the N-heterocycle was also obvious with 3 signals at 6.57, 6.23, 5.28 ppm, it has also much impact on the resonances of the carbon atoms. Indeed C5 is deshielded by 10 ppm whereas C4, C3, C2 are shielded by respectively 25, 10, 24, and 4 ppm compared to complex **1**. The chemical shift variations observed are similar to those reported by Milstein and coworkers for the (^{tBu}PNP) complexes.[22] It is accompanied by an increase of the carbon-phosphorus coupling constants for C4 to C7, which is in agreement with a deprotonation at C7. This was further confirmed by X-ray analysis (Figure 3) realised on single crystals formed by diffusion of pentane into saturated dichloromethane solution of **3** at -40°C.

Not much change was observed in the geometry around the metal, the coordination bonds do not experience more than 0.7% variation. On the contrary, the C_7-C_5 bond shortens from 1.494(3) Å in **1** to 1.38(1) Å in the neutral complex. This change

is accompanied by a modification of the bond lengths within the heterocyclic ring which resembles much more to a diene fragment with short C1-C2 and C3-C4 bonds (1.37(1) and 1.34(1) Å respectively) and longer C2-C3 and C4-C5 ones (1.43(1) and 1.44(1)). Concomitantly the N2C5 bond elongates slightly from 1.359(3) Å in the cationic to 1.389(3) Å in the neutral complex. On the contrary C5-C7 and C7-P2 bonds shorten from 1.494(3) and 1.834(3) to 1.38(1) and 1.742(1) Å respectively. The N-heterocyclic ring remains planar (C4-C3-C2-C1 at 0.2°). Moreover the formation of the delocalised π-system induces a planarisation of the metallacyclopentane incorporating the phosphine arm. Indeed, the dihedral angles N1-C6-C1-N2 and P2-C7-C5-N2 were measured at 19.4° and 25.4° [**L**PdCl](Cl) *vs* 26.2° and 5.8° in [**L***PdCl] respectively. A similar observation was made by Milstein and coll. for the phosphine analogue.[22] Interestingly, **3** is to the best of our knowledge the first X-ray characterised complex featuring a dearomatised (PNN) ligand.

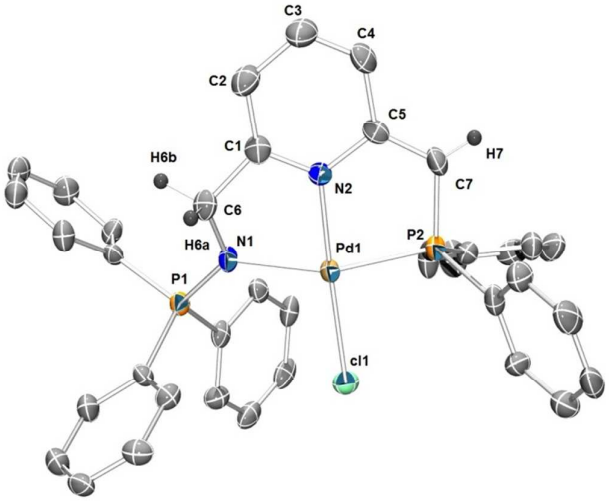
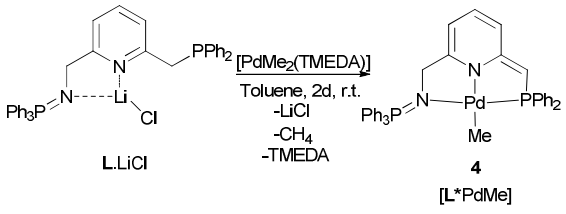


Figure 3: ORTEP of the solid-state structure of [**L***PdCl] **3** with 50% probability thermal ellipsoids. Most hydrogen atoms were omitted for clarity. Hydrogen atoms H_7, H_{6a}, and H_{6b} were refined isotropically. Selected bond lengths [Å] and angles (deg): N1-P1 1,595(5), N1-Pd1 2,124(5), P2-Pd1 2,218(2), N2-Pd1 1,994(5), Cl1-Pd1 2,313(2), C7-P2 1,742(7), N2-C1 1,358(8), C1-C2 1,37(1), C2-C3 1,43(1), C3-C4 1,34(1), C4-C5 1,44(1), C5-N2 1,389(8), C1-C6 1,50(1), C5-C7 1,38(1), C7-H7 0,87(8), C6-H6A 0,90(7), C6-H6B 1,08(7); N1-Pd1-P2 161,8(1), N2-Pd1-Cl1 176,1(2), N1-Pd1-N2 79,8(2), P2-Pd1-N2 84,4(2), N1-Pd1-Cl1 102,8(1), P2-Pd1-Cl1 93,46(6).

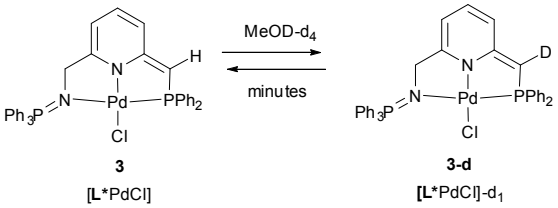


Scheme 4: Formation of [**L***PdMe](**4**)

As the isolated yield of **3** is relatively low while the reaction is rapid and quantitative as attested by *in situ* NMR, we thought to access to such complex from a metal precursor incorporating an internal base. We chose [$PdMe_2$(TMEDA)] (TMEDA= tetramethylethylenediamine) which should give access to [**L***PdMe] (**4**) with methane as the sole side product (Scheme 4). Mixing ligand **L** and this precursor in toluene at room temperature led to the precipitation of the lithium salt. After filtration and overnight standing, crystals formed from a red solution exhibiting two doublets in $^{31}P\{^1H\}$ spectroscopy at 33.7 and 29.0 ppm ($^3J_{P,P}$ = 8.5 Hz). [23] Monitoring this reaction in THF-d_8 showed that the appearance of these doublets is accompanied by the evolution of methane, as attested by the presence of a singlet at 0.19 ppm in ^1H NMR spectrum. Signals at 6.40, 6.08, and 5.23 ppm confirm the dearomatisation of the pyridine ring. The presence of two doublets at 4.12 ($J_{P,H}$ = 7.5 Hz) and 3.17 ($J_{P,H}$ = 3.0 Hz) ppm corresponding respectively to two and one protons as well as one doublet at -0.80 ppm ($J_{P,H}$ = 2.0 Hz) with an integration of 3 corroborates the formation of complex [**L***PdMe] (**4**) which was isolated in 56% yield. Noteworthy attempts to accelerate the reaction by heating, led to the formation of a metallic deposit on the wall of the schlenk as well as the formation of ethane as attested by the presence of a signal at 0.85 ppm in ^1H NMR spectrum. Therefore this reaction involves intermediates that are not thermally stable and can eliminate ethane to form Pd^0. Low quality single crystals were grown from THF solution, the crystallographic data (presented as supporting information) only allow to confirm the connectivity.

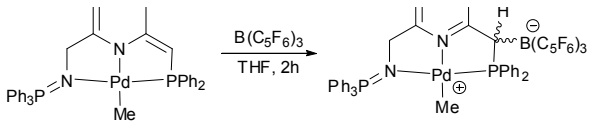
Reactivity of 2 and 3 featuring L* ligand

Upon reaction with protic substrate (of general formula EH) such complexes with dearomatised pyridine generally get protonated on the benzylic position together with transfer of the E moiety on the metal.[3c,13a] When complex [**L***PdCl] reacted with a slight excess of deuterated methanol, the signal of H_7 had almost totally disappeared in the ^1H NMR spectrum within the short time required to perform the measurement (see Figure S3) whereas the rest of the spectrum as well as the $^{31}P\{^1H\}$ one remained unchanged. Thus, the protonation took place but is reversible and only the excess of the methanol allowed the total deuteration (Scheme 5). For the (^{tBu}PNP) analogue examined by Milstein et coll.[22] the equilibrium between the dearomatised and aromatised form is shifted to the cationic complex by a large excess methanol. In that case, the neutral complex is favored at room temperature and the cationic one below 243 K. In our case, no change was observed with the temperature.



Scheme 5: Reactivity of [**L***PdCl](**3**) with deuterated methanol

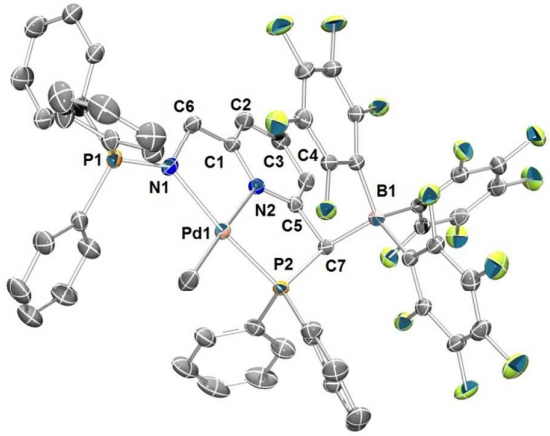
When reacting [**L***PdMe] (**4**) with $B(C_6F_5)$ to achieve the demethylation, the expected cationic complex was not observed. Instead, the reaction afforded a new product labeled **5** exhibiting one doublet at 31.1 ppm ($^3J_{P,P}$ = 7.5 Hz) and one doublet of doublet at 47.1 ($^3J_{P,P}$ = 7.5 Hz and 23.0 Hz) in the $^{31}P\{^1H\}$ spectrum in toluene. In ^1H NMR and ^{11}B spectra, signals corresponding to $MeB(C_6F_5)_3$ (the demethylation side product) were not seen (δ_H = 0.50 ppm, δ_B = -14.8 ppm).[24] Moreover, a doublet at -0.26 ($J_{P,H}$ = 1.5 Hz) attests the presence of a coordinated methyl group. An AMX system of two doublets of doublets at 4.08 and 3.79 ppm each corresponding to one proton were also observed. It simplified to a AM system ($|^2J_{H,H}|$ = 17.0 Hz) upon decoupling of phosphorous nucleus, therefore these are two diastereopic protons which do not exhibit the same coupling to phosphorus. This clearly evidenced a loss of planar symmetry in the formed complex **5**. This is corroborated by HSQC ^1H-^{13}C spectrum (Figure S4) where these 2 signals correlate with the same carbon, with a phase showing they correspond to CH_2. In addition, the proton at C7 is highly deshielded appearing at 6.63 ppm (*vs* 3.5 ppm in **4**) and correlates with a CH carbon resonating at 48.1 ppm.[25] Only one signal of the pyridine is shielded at 5.62 ppm, whereas the two others are in agreement with an aromatised pyridine ring. Finally the ^{11}B spectrum evidenced a singlet at -10.5 ppm which indicated an alkylborane species. All these data suggest the formation of a zwitterionic complex resulting from the boration at the benzylic position (Scheme 6).[26] This is agreement with the results of elemental analysis and was further confirmed by X-ray analysis (Figure 4a).



Scheme 6: Formation of **5**

5 adopts a distorted square planar geometry around the palladium (N2-N1-P1-Pd1 -28.77°), the loss of planarity compared to **1** may be ascribed to the steric hindrance brought by the boron fragment. This also induces an elongation of the C5-C7 and C7-P2 bonds from respectively 1.494(3) and 1.834(3) Å in **1** to 1.515(3) and 1.868(2) Å. The coordination sphere of the palladium, nevertheless, does not differ much from that of **1**, except that Pd1-N1 is slightly elongated in **5** (2.130(2) *vs* 2.110(2) Å) and the N1-Pd1-N2 angle is a bit more acute (159.68(6) *vs* 164.23(6)°). The pyridine is aromatised since the inner ring C-C bond lengths are comparable to those observed in **1** at around 1.38 Å. Concerning the formed alkyl-borane, the C7-B1 bond was measured at 1.710(3) Å which is a high value compared to the average C-$B(C_6F_5)_3$ bond lengths recorded by the CCDC (1.667 Å). Interestingly two π–π interactions are present in this structure, between fluorinated rings and respectively the central pyridine and one phenyl group (figure 4b).

a)



b)

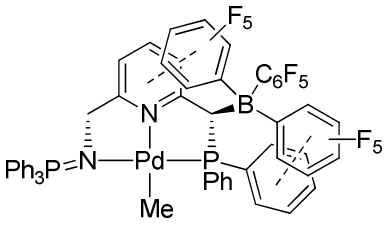


Figure 4 a) ORTEP of the solid-state structure of **5** with 50% probability thermal ellipsoids. Most hydrogen atoms were omitted for clarity, hydrogen atoms H_{6a}, H_{6b} and H_7 were refined isotropically. Selected bond lengths [Å] and angles (deg): N1-P1 1,597(2), N1-Pd1 2,136(2), P2-Pd1 2,2078(6), N2-Pd1 2,073(2), C38-Pd1 2,056(2), C5-C7 1,515(3), C7-P2 1,868(2), C7-B1 1,710(3), C7-H7 0,94(3) ; N1-Pd1-P2 159,60(6), N2-Pd1-C38 177,6(1), N1-Pd1-N2 80,11(7), P2-Pd1-N2 81,95(5), N1-Pd1-C38 101,9(1), P2-Pd1-C38 95,81(7), P2-C7-B1 122,9(1), C5-C7-B1 108,0(2), B1-C7-H7 104(2).b) Schematic representation of π–π interactions.

Milstein and coll described the reaction of [(^{tBu}PNP*)Ru(H)(CO)] with pinacolborane yielding, after loss of H_2, a complex with a dearomatised ligand where the vinylic position is substituted by the pinacolborane.[27] DFT calculations have pointed towards an intermediate with an aromatic pyridine and the borane at the benzylic position resembling the isolated complex **5**. Interestingly to form **5** the ligand has to be dearomatised. Indeed, reacting $B(C_6F_5)_3$ with the ligand **L**.LiCl gave a Lewis pair observed *in situ* (δ_P = 25.7 and -17.6 ppm for the iminophosphorane and the phosphine respectively in C_6D_6). Then addition of [$PdMe_2$(TMEDA)] to this solution led to the formation of a new complex characterised by two doublets ($^3J_{P,P}$ = 7.5 Hz) in ^{31}P NMR at 34.1 and 29.7 pm. ^{11}B and ^{19}F spectra showed the presence of $MeB(C_6F_5)$ anion. ^1H NMR spectroscopy reveals an aromatic pyridine, one methyl group on the palladium, and two doublets for the benzylic protons at 4.29 ($J_{P,H}$ = 7.0 Hz) and 3.63 ppm ($J_{P,H}$ = 12.0 Hz). Therefore in that case, a cationic complex [**L**PdMe][$MeB(C_6F_5)_3$] resulting from methyl abstraction by the borane was formed.

Conclusion

In conclusion, an unprecedented mixed phosphine-iminophosphorane ligand exhibiting a central pyridine moiety was synthesised and coordinated to Pd^{II} yielding a cationic complex or a neutral one if the metallic precursor incorporates a basic ligand (we used [$PdMe_2$(TMEDA)]). In that latter case, the selective deprotonation at the benzylic position alpha to the phosphine is observed. A similar complex is obtained when reacting cationic complex **1** [**L**PdCl](Cl) with a base. Those neutral complexes can be protonated by methanol but the protonation is reversible as demonstrated upon reaction with deuterated methanol. Finally an original complex resulting from the selective boration at the benzylic position was isolated and characterised. Indeed reaction of [**L***PdMe] with $B(C_6F_5)_3$ formed the cationic complex **5**, whereas adding the palladium precursor to a mixture of **L** and $B(C_6F_5)_3$ resulted in methyl abstraction. This evidences that the formation of the C-B bond requires the presence of a deprotonated ligand **L***. Thus the behaviour of **L** differs from that observed with the (^{tBu}PNN) ligand developed by Milstein, which encourages us to pursue further its coordination study to other metals such as ruthenium(II).

Experimental part

Synthesis

All reactions were conducted under an atmosphere of dry nitrogen, or argon, using standard Schlenk and glovebox techniques. Solvents and reagents were obtained from commercial sources. Tetrahydrofuran, diethyl ether, toluene and petroleum ether were dried with an MBraun MB-SPS 800 solvent purification system. Pentane was distilled from CaH_2, under dry nitrogen. CD_3CN and CD_2Cl_2 were distilled from CaH_2, under dry nitrogen, other deuterated solvents were used as received and stored over molecular sieves. Unless otherwise stated reagents were used without further purification. [$PdMe_2$(TMEDA)][28] and 2-(azidomethyl)-6-(hydroxymethyl) pyridine[20] were prepared following literature procedure.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Av300 spectrometer operating at 300 MHz for ^{1}H, 116.6 MHz for ^{7}Li, 96.3 MHz for ^{11}B, 75.5 MHz for ^{13}C, 282.2 MHz for ^{19}F and 121.5 MHz for ^{31}P. Solvent peaks were used as internal references for ^{1}H and ^{13}C chemical shifts (ppm). ^{31}P peaks were referenced to external 85% H_3PO_4. The following abbreviations are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Labelling of atoms is indicated in Figure 5. Index py and Ar were used to indicated signals corresponding to coordinated pyridine and aryl ring (when non discernable) respectively. Mass spectrometry experiments were carried out by Dr. S. Bourcier in the positive mode with a QTOF Premier instrument equipped with a Z-spray electrospray source (Waters, Saint Quentin-en-Yvelines, France). Ion source parameters were adjusted as followed: the cone voltage (Vcone) was ranged from 20 to 80 V while the capillary voltage was set to 2.6 kV. Typical values for the other source parameters were 2 V for the extraction cone and 2.4 V for the ion guide. Source and desolvation temperatures were set to 80 °C and 250 °C, respectively. Nitrogen was used as both nebulizing and desolvation gas. Gas flows were ranged from 10 L.h-1 to 100 L.h-1. Solution was introduced with a flow of 10µLmin-1. For MS/MS analysis, argon was used as collision gas at a flow rate of 0.28 mL min-1 corresponding to a pressure of ca. 4 10-3 mBar. Elemental analyzes were determined by Mr. S. Boyer at the London Metropolitan University.

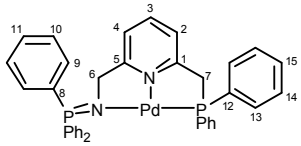


Figure 5: Labelling scheme

2-(azidomethyl)-6-(chloromethyl)pyridine $SOCl_2$ was slowly added at 0°C (10 mL) to 2-(azidomethyl)-6-(hydroxymethyl)pyridine (1.26 g, 7.68 mmol) in CH_2Cl_2 (5 mL) under stirring. The mixture was stirred for 1h30 while the ice bath gently warms. The mixture was quenched and neutralised by the slow addition of a saturated Na_2CO_3 solution resulting in a vigorous gas evolution. The mixture was then extracted with 3x40 mL of EtOAc, dried with $MgSO_4$. The evaporation of all volatiles gaves the title compound as a clear oil in nearly quantitative yield (1.39 g, 7.61 mmol, 99%). ^{1}H ($CDCl_3$) δ 7.77 (t, *J* = 8.0 Hz, 1H, H_3), 7.45 (d, *J* = 8.0 Hz, 1H, H_2), 7.30 (d, *J* = 8.0 Hz, 1H, H_4), 4.67 (s, 2H, H_7), 4.49 (s, 2H, H_6). ^{13}C ($CDCl_3$) δ 156.8 (C_1), 155.4 (C_5), 138.2 (C_3), 122.1 (C_2), 121.3 (C_4), 55.5 (C_7), 46.6 (C_7).[29]

L.LiCl. In a Schlenk flask, PPh_3 (2.0 g, 7.61 mmol) was dissolved in Et_2O (20 mL), and a solution of 2-(azidomethyl)-6-(chloromethyl)pyridine **(**1.26 g, 7.61 mmol) in Et_2O (5 mL) was then added via canula resulting in a small nitrogen evolution. The mixture was stirred under a nitrogen flow for 1 h and then closed and stirred overnight. The completion of the Staudinger reaction was then checked by ^{31}P NMR (singlet at 6.7 ppm). THF (15 mL) was added. In another Schlenk flask, $HPPh_2$ (1.32 mL, 7.58 mmol) was dissolved in THF (40 mL), the flask was cooled to -78°C and 1.6M BuLi solution (4.8 mL, 7.68 mmol) was added dropwise. The red mixture of the anion was stirred for 5 min at -78°C and then at 0°C for 15 min. Both Schlenk flasks were then cooled to 0°C and the mixture of the phosphide was added via a canula to the iminophosphorane derivative within about 20 min (*ca.* 1 drop/second). The mixture was then stirred at 0°C for 1h. The final mixture may present a deep blue coloration which can be quenched by the addition of 4-5 drops of TMSCl. Solvents were then evaporated until *ca.* 5 mL and pentane (30 mL) was then added. The mixture was sonicated for 5 min leading to the formation of a white powder. The powder was filtered under nitrogen and washed with pentane (3x30 mL) to yield the **L**.LiCl as a white powder in 91% yield (4.195 g, 6.89 mmol). ^{31}P{^{1}H} (THF-d^8) δ 7.7 (br s, N=PPh_3), -12.0 (s, PPh_2); ^{7}Li (THF-d^8) δ -0.5 (s, LiCl); ^{1}H (THF- d^8) δ 7.83-7.62 (m, 6H, H_9), 7.61 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, H_4), 7.56-7.37 (m, 13H, $H_{10,11,13}$), 7.36 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, H_3), 7.27-7.17 (m, 6H, $H_{14,15}$), 6.73 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, H_2), 4.32 (d, $^3J_{P,H}$

= 15.0, 2H, H_6), 3.55 (s, 2H, H_7); ^{13}C (THF- d^8) δ 165.9 (C_5, $J_{P,C}$ not visible), 157.1 (d, $^2J_{P,C}$ = 8.5 Hz, C_1), 140.2 (d, $^1J_{P,C}$ = 17.0 Hz, C_{12}), 136.3 (s, C_3), 133.6 (d, $^2J_{P,C}$ = 19.0 Hz, C_{13}), 133.3 (d, $^2J_{P,C}$ = 9.0 Hz, C_9), 132.8 (d, $^1J_{P,C}$ ~ 100 Hz, C_8), 131.8 (s, C_{11}), 128.9 (d, $^3J_{P,C}$ = 12.0 Hz, C_{10}), 128.8 (d, $^3J_{P,C}$ = 6.5 Hz, C_{14}), 128.7 (s, C_{15}), 120.8 (d, $^3J_{P,C}$ = 6.5 Hz, C_2), 119.0 (s, C_4), 51.4 (s, C_6), 39.1 (d, $^1J_{P,C}$ = 17.0 Hz, C_7). Calcd for $C_{37}H_{32}ClLiN_2P_2$: C, 72.97; H, 5.30; N, 4.60. Found: C, 72.84; H, 5.38; N, 4.50.

[LPdCl](Cl) 1. In a Schlenk flask, [$PdCl_2$(COD)] (544 mg, 1.91 mmol) was suspended in THF (25 mL) and **L**·LiCl (1.16g, 1.91 mmol) added as a solid, THF (5 mL) was added to clean the walls of the Schlenk. The mixture was sonicated for 1 min and stirred at 50°C for 2 h. After cooling to room temperature a yellow precipitate was formed. The precipitate was filtered under nitrogen and washed with THF (2x10 mL) and Et_2O (2x10 mL) and finally dried under high vacuum for 2 h to yield [**L**PdCl](Cl) (**1**) as a pale-yellow powder (1.136 g, 1.25 mmol, 80%). $^{31}P\{^1H\}$ (CD_2Cl_2) δ 35.1 (d, $^3J_{P,P}$= 10.5 Hz, PPh_2), 33.9 (d, $^3J_{P,P}$ = 10.5 Hz, N=PPh_3); ^1H (CD_2Cl_2) δ 8.26 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H_2), 8.06-7.79 (m, 11H, $H_{3,9,13}$), 7.78-7.66 (m, 3H, H_{11}), 7.66-7.44 (m, 12H, $H_{10,14,15}$), 7.20 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H_4), 4.93 (d, $^2J_{P,H}$ = 13.0 Hz, 2H, H_7), 4.60 (dd, $J_{P,H}$ = 6.5, 2.0 Hz, 2H, H_6); ^{13}C (CD_2Cl_2) δ 166.1 (d, $^3J_{P,C}$ = 19.0 Hz, C_5), 160.4 (d, $^2J_{P,C}$ = 3.5 Hz, C_1), 140.6 (s, C_3), 134.3 (d, $^2J_{P,C}$ = 10.0 Hz, C_9), 133.7 (d, $^2J_{P,C}$ = 11.5 Hz, C_{13}), 133.6 (s, C_{11}), 132.7 (d, $^4J_{P,C}$ = 3.0 Hz, C_{15}), 129.6 (d, $^3J_{P,C}$ = 11.9 Hz, C_{14}), 129.2 (d, $^3J_{P,C}$ = 12.5 Hz, C_{10}), 127.7 (d, $^1J_{P,C}$ = 56.0 Hz, C_{12}), 126.3 (d, $^1J_{P,C}$ = 101.5 Hz, C_8), 123.7 (d, $^3J_{P,C}$ = 14.0 Hz, C_2), 120.2 (s, C_4), 59.8 (s, C_6), 45.1 (d, $^1J_{P,C}$ = 34.0 Hz, C_7). Calcd for $C_{37}H_{32}Cl_2N_2P_2Pd$: C, 59.74; H, 4.34; N, 3.77. Found: C, 59.85; H, 4.35; N, 3.81.

[LPd(py)]$(BF_4)_2$ 2. In a Schlenk flask, [**L**PdCl](Cl) (100 mg, 0.13 mmol) and $AgBF_4$ (52.3 mg, 0.27 mmol) were stirred for 1 hour in a mixture of dichloromethane (5 mL) and pyridine (1 mL). The silver chloride salt was filtered and Et_2O (20 mL) was added leading to the precipitation of a yellowish solid. The precipitate was filtered and washed with Et_2O (10 mL). After drying under vacuum, [**L**Pd(py)]$(BF_4)_2$ **2** (72.1 mg, 60%) was isolated.$^{31}P\{^1H\}$ (CD_2Cl_2) δ 37.1 (d, $^3J_{P,P}$ = 10.5 Hz, N=P), 36.9 (d, $^3J_{P,P}$ = 10.5 Hz, PPh_2); ^1H NMR (CD_2Cl_2) δ 9.27 (dd, $J_{H,H}$ = 6.5, 1.5 Hz, 1H, H_{py}), 8.76 (dd, $J_{H,H}$ = 6.5, 1.5 Hz, 1H, H_{py}), 7.98 – 7.47 (m, 30H, $H_{3,4,9,10,11,13,14,15,py}$), 7.22 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H_2), 4.63 (dd, $J_{P,H}$ = 6.0, 2.5 Hz, 2H, H_6), 4.47 (d, $^2J_{P,H}$ = 12.5 Hz, 2H, H_7); ^{13}C NMR (CD_2Cl_2) δ 166.6 (d, $^4J_{P,C}$ *ca.* 17 Hz, C_5), 159.7 (d, $^3J_{P,C}$ = 3.7 Hz, C_1), (152.2 (s, C_{py})), 152.0 (s, C_{py}), 140.7 (s, C_3), 140.5 (s, C_{py}), 140.3 (s, C_{py}), 134.3 (d, $^2J_{P,C}$ = 9.4 Hz, C_9), 133.7 (d, $^4J_{P,C}$ = 2.7 Hz, C_{11}), 133.4 (d, $^2J_{P,C}$ = 11.0 Hz, C_{13}), 133.0 (d, $^4J_{P,C}$ = 2.8 Hz, C_{15}), 129.7 (d, $^3J_{P,C}$ = 11.5 Hz, C_{14}), 129.3 (d, $^3J_{P,C}$ = 12.0 Hz, C_{10}), 127.6 (d, $^1J_{P,C}$ = 43.0 Hz, C_{12}), 127.1 (s, C_{py}), 126.2 (d, $^1J_{P,C}$ = 103.0 Hz, C_8), 122.5 (d, $^3J_{P,C}$ = 14.0 Hz, C_2), 120.4 (s, C_4), 59.85 (s, C_6), 45.1 (d, $^1J_{P,C}$ = 33.0 Hz, C_7); ^{19}F (CD_2Cl_2) δ – 151.4 (s, BF_4). MS (ES+) ($C_{37}H_{32}N_2P_2Pd^{2+}$): calculated m/z: 336.06, found: 336.06.

[L*PdCl] 3. THF (5 mL) was added to a Schlenk flask containing [**L**PdCl](Cl) **1** (75.1 mg, 0.1 mmol) and KHMDS (20.2 mg, 0.1 mmol). The mixture turned dark within seconds and was stirred for an extra hour. Then, petroleum ether (20 mL) was added, resulting in the precipitation of the complex. After filtration under nitrogen, the obtained solid was washed with petroleum ether (2x10 mL). The product was then was extracted from the precipitate using of dichloromethane (2x10 mL).[30] The solvent was then evaporated under vacuum and the product dried under high vacuum to furnish [**L***PdCl] **3** as a brown solid in 43 % yield (30.2 mg). $^{31}P\{^1H\}$ (THF-d^8) δ 34.8 (d, $^3J_{P,P}$= 11.5 Hz, PPh_2), 32.9 (d, $^3J_{P,P}$ = 11.5 Hz, N=PPh_3); ^1H (THF-d^8) δ 7.94-7.83 (m, 6H, H_9), 7.83-7.75 (m, 4H, H_{13}), 7.64-7.55 (m, 3H, H_{11}), 7.54-7.45 (m, 6H, H_{10}), 7.33-7.18 (m, 6H, $H_{14,15}$), 6.53 (ddd, $^3J_{H,H}$ = 9.0, 6.5 Hz, $J_{P,H}$ = 2.4 Hz, 1H, H_3), 6.19 (d, $^3J_{H,H}$ = 9.0 Hz, 1H, H_4), 5.25 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, H_2), 4.06 (d, $^3J_{P,H}$ = 7.5 Hz, 2H, H_6), 3.23 (d, $^2J_{P,H}$ = 3.5 Hz, 1H, H_7). ^{13}C (THF-d^8) δ 170.8 (d, $^2J_{P,C}$ = 16.0 Hz, C_1), 162.8 (d, $^3J_{P,C}$ = 18.0 Hz, C_5), 137.7 (d, $^1J_{P,C}$ = 58.0 Hz, C_{12}), 134.8 (d, $^2J_{P,C}$ = 9.5 Hz, C_9), 133.9 (s, C_3), 133.3 (d, $^2J_{P,C}$ = 11.0 Hz, C_{13}), 133.3 (d, $^4J_{P,C}$ = 3.0 Hz, C_{11}), 129.6 (d, $^4J_{P,C}$ = 3.0 Hz, C_{15}), 128.9 (d, $^3J_{P,C}$ = 12.5 Hz, C_{10}), 128.5 (d, $^1J_{P,C}$ = 99.5 Hz, C_8), 128.1 (d, $^3J_{P,C}$ = 11.1 Hz, C_{14}), 111.8 (d, $^4J_{P,C}$ = 23.0 Hz, C_2), 96.6 (s, C_4), 59.7 (d, $^1J_{P,C}$ = 74.5 Hz, C_7), 58.5 (d, $^2J_{P,C}$ = 2.5 Hz, C_6).

[L*PdMe] 4. In a Schlenk flask, toluene (7.5 mL) was added to **L.**LiCl (240.9 mg, 0.40 mmol) [$PdMe_2$(TMEDA)] (100 mg, 0.40 mmol). The mixture was stirred at room temperature for 30 minutes and filtered. The filtrate was kept at room temperature overnight without stirring resulting in the formation of an orange micro-crystalline material and a dark-red solution. The mixture was purged and back filled with nitrogen and kept without stirring for 2 extra days. After that, the Schlenk was cooled to -20°C for 2 hours. While cold, the mixture was filtered and the solid was washed with Et_2O (2x5 mL), petroleum ether (2x5 mL) and finally dried under high vacuum to yield [**L***PdMe] **4** (152 mg, 0.22 mmol, 56 %). $^{31}P\{^1H\}$ (THF-d^8) δ 33.7 (d, $^3J_{P,P}$ = 8.5 Hz, N=PPh_3), 29.0 (d, $^3J_{P,P}$ = 8.5 Hz, PPh_2); ^1H NMR (THF-d^8) δ 7.86 (dd, $J_{P,H}$ = 11.7, J_{HH} = 7.5 Hz, 6H, H_9), 7.79-7.56 (m, 7H, $H_{11,13}$), 7.55-7.36 (m, 6H, H_{10}), 7.26-7.14 (m, 6H, $H_{14,15}$), 6.45 (dd, $^3J_{H,H}$ = 8.5, 7.0 Hz, 1H, H_3), 6.04 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H_4), 5.19 (d, $^3J_{H,H}$ = 7.0 Hz, 1H, H_2), 4.08 (d, $^3J_{P,H}$ = 8.0, 2H, H_6), 3.13 (d, $^2J_{P,H}$ = 3.5 Hz, 2H, H_7), -0.83 (d, $^3J_{P,H}$ *ca.* 2 Hz, 3H, CH_3). **4** is poorly soluble in THF-d^8 and slowly decomposes in CD_2Cl_2 therefore no ^{13}C NMR could be recorded. Calcd for $C_{38}H_{34}N_2P_2Pd$: C, 66.43; H, 4.99; N, 4.08. Found: C, 66.38; H, 5.06; N, 3.95.

[LPdMe(B(C_6F_5)$_3$)] 5. In a glove-box, [**L***PdMe] **(**30 mg, 44 μmol) and B(C_6F_5)$_3$ (22.4 mg, 44 μmol) were suspended in toluene (3 mL). After 3 hours of stirring the mixture turned clear and was checked in $^{31}P\{^1H\}$ probing the disappearance of the starting material. The volatiles were then removed under vacuum. The solid was then suspended in pentane (3 mL), filtered, then the solid was washed with Et_2O (1 mL) and pentane (2x3 mL) to give an off-white solid which was dried under high vacuum to furnish [**L**PdMe(B(C_6F_5)$_3$)] **5** (39.2 mg , 33 μmol, 75 %). $^{31}P\{^1H\}$ (Tol-d^8) δ 47.1 (dd, *J* = 23.0, 7.5 Hz, PPh_2), 31.1 (d, $^3J_{P,P}$ = 7.5 Hz, N=P); ^{11}B (Tol-d^8) δ -10.5 (s, $\nu_{1/2}$ = 27 Hz); ^1H NMR (Tol-d^8) δ 8.06-7.80 (m, 2H, H_{Ar}), 7.62-7.47 (m, *ca.* 10H, $H_{3,Ar}$), 7.21-6.72 (m, *ca.* 14H, H_{Ar}), 6.62 (m, 2H, $H_{3,7}$), 5.59 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, H_2), 4.08 (dd , $^2J_{H,H}$ = 17.0 Hz, $^3J_{P,H}$ = 2.5 Hz, 1H, H_{6a}) ; 3.79 (dd , $^2J_{H,H}$ = 17.0 Hz, $^3J_{P,H}$ = 10.5 Hz, 1H, H_{6b}), -0.26 (d, $^3J_{P,H}$ *ca.* 1.5 Hz, 3H, CH_3).[31] ^{13}C (Tol-d^8) δ 165.9 (s, C_5),

160.5 (d, $^{3}J_{P,C}$ = 19.5 Hz, C_1), 136.2 (s, C_3), 121.0 (bm, C_4), 115.9 (s, C_2), 59.7 (s, C_6), 48.5 (br s, C_6, only visible in HMBC), -3.5 (d, $^{2}J_{P,C}$ = 4.5 Hz, CH_3). Calcd for $C_{56}H_{34}BF_{15}N_2P_2Pd$: C, 56.09; H, 2.86; N, 2.34. Found: C, 55.90; H, 2.93; N, 2.42.

[LPdMe][MeB(C_6F_5)$_3$)] In a glove box, **L**.LiCl (44.6 mg, 73 µmol) and B(C_6F_5)$_3$ (37.5 mg, 73 µmol) were stirred in toluene (3 mL) for 20 minutes, then [$PdMe_2$(TMEDA)] (18.5 mg, 73 µmol) was added as a solid leading to the immediate formation of a yellow solution. The mixture was stirred for 1 hour and the solvent was evaporated under vacuum leading to the formation of a red oil. Petroleum ether (5 mL) was added, and the mixture stirred for 1 h. Upon standing a red oil decanted. The solvent was carefully removed with a Pasteur pipette and the operation was repeated, finally the resulting red oil was dried under high vacuum overnight leading to **[LPdMe][MeB(C_6F_5)$_3$)]**.(toluene)$_3$ as a red oil (80 mg, 66 µmol, 73 %). Last molecules of toluene cannot be removed by high vacuum overnight. The ratio 1:3 was determined by ^{1}H NMR spectroscopy. $^{31}P\{^{1}H\}$ (C_6D_6) δ 34.1 (d, $^{3}J_{P,P}$ = 7.3 Hz, PPh_2), 29.7 (d, $^{3}J_{P,P}$ = 7.5 Hz, N=P); ^{1}H NMR (C_6D_6) δ 7.65-7.50 (m, 9H, $H_{9,11}$), 7.45-7.29 (m, 6H, $H_{13,15}$), 7.27-7.05 (m, 10H, $H_{10,14}$), 7.01 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1H, H_3), 6.73 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H, H_4), 6.25 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H, H_2), 4.29 (d, $^{3}J_{P,H}$ = 7.0 Hz, 2H, H_6), 3.63 (d, $^{2}J_{P,H}$ = 12.0 Hz, 2H, H_7), 1.30 (br s., 3H, CH_3-B), -0.26 (d, $^{3}J_{P,H}$ = 2.4 Hz, 3H, CH_3-Pd). ^{13}C (C_6D_6) δ 162.4 (dd, $^{3}J_{P,C}$ = 18.5 Hz, C_1), 155.7 (d, $^{2}J_{P,C}$ = 4.0 Hz, C_5), 138.5 (s, C_3), 133.6 (d, $^{2}J_{P,C}$ = 9.5 Hz, C_{13}), 133.4 (d, $^{4}J_{P,C}$ = 3.0 Hz, C_{11}), 132.9 (d, $^{2}J_{P,C}$ = 12.5 Hz, C_9), 131.9 (d, $^{4}J_{P,C}$ = 2.5 Hz, C_{15}), 129.7 (d, $^{1}J_{P,C}$ = 51.4 Hz, C_{12}), 129.4 (d, $^{3}J_{P,C}$ = 11.0 Hz, C_{10}), 129.1 (d, $^{3}J_{P,C}$ = 12.3 Hz, C_{14}), 126.6 (d, $^{1}J_{P,C}$ = 100.0 Hz, C_8), 120.8 (d, $^{3}J_{P,C}$ = 11.5 Hz, C_4), 119.2 (s, C_2), 59.5 (s, C_6), 45.8 (d, $^{1}J_{P,C}$ = 33.0 Hz, C_7), -5.2 (d, $^{3}J_{P,C}$ = 6.5 Hz, CH_3-Pd). Signals of the counter anion MeB(C_6F_5)$_3$ were also visible as very broad doublets separated by $^{1}J_{CF}$ of about 240 Hz at respectively 149, 138 and 136 ppm, the CH_3-B appears as a very broad singlet and can be located by HSQC at 11.3 ppm in the ^{13}C spectrum. ^{19}F (C_6D_6) δ -128.0 (d, $^{3}J_{F,F}$ = 21 Hz, 6F, *o*-F), -160.9 (t, $^{3}J_{F,F}$ = 21 Hz, 3F, *p*-F), -163.2 (t, $^{3}J_{F,F}$ = 21 Hz, 6F, *m*-F); ^{11}B NMR (C_6D_6) δ -13.8 (br s., $\nu_{1/2}$ *ca.* 150 Hz).

X-ray analysis

Data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo-κ (λ=0.71069Å) X-ray source and a graphite monochromator. The crystal structure was solved using SIR 97 [32] and Shelxl-97 or Shelxl-2013 [33] ORTEP drawings were made using ORTEP III for Windows.[34] Structures for **1**, **2**, **4**, **5** were deposited under CCDC numbers 1414327-1414330.

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Notes and references

‡ Addition of a slight excess of MeCN or PMe_3 to a CH_2Cl_2 solution of [LPd]$(BF_4)_2$ lead to the formation of [**L**Pd(MeCN)]$(BF_4)_2$ ($^{31}P\{^{1}H\}$ (CD_2Cl_2) δ 43.8 (d, $^{3}J_{P,P}$ = 10.0 Hz, PPh_2), 39.8 (d, $^{3}J_{P,P}$ = 10.0 Hz, N=P); 1H (CD_2Cl_2) δ 8.06-7.51 (m, 27H, $H_{9\text{-}11,13\text{-}15,PY}$), 7.24 (d, J = 8.0 Hz, 1H, H_2), 4.67 (m, 4H, $H_{6,7}$), 1.50 (s, 3H, MeCN) or [**L**Pd(PMe_3)]$(BF_4)_2$ ($^{31}P\{^{1}H\}$ (CD_2Cl_2) δ 44.8 (dd, $^{2}J_{P,P}$ = 29.0 Hz, $^{3}J_{P,P}$ = 13.5 Hz, PPh_2), 42.7 (d, $^{3}J_{P,P}$ = 13.5 Hz, N=P), -4.6 (d, $^{2}J_{P,P}$ = 29.0 Hz, PMe_3); ^{1}H (CD_2Cl_2) δ 8.24-7.99 (m, 10H, $H_{9,13}$), 7.93-7.52 (m, 16H, $H_{10,11,14,15,3}$), 7.40 (d, J = 8.0 Hz, 1H, H_4), 6.79 (d, J = 8.0 Hz, 1H, H_2), 4.84 (m, 4H, $H_{6,7}$), 0.57 (d, J = 11.5 Hz, 9H, PMe_3).

§ The deprotonation of **2** was attempted in the same conditions, unfortunately the very low solubility of the formed complex hampers its characterization.

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