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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 $\text{PPh}_2\text{-CH}_2\text{-Pyr-CH}_2\text{-N=PPh}_3$, combining a pyridine core with phosphine and iminophosphorane, was synthesised. Its coordination with palladium(II) centers was studied. With $[\text{Pd}(\text{COD})\text{Cl}_2]$, a cationic complex $[\text{LPdCl}](\text{Cl})$ **1**, where **L** is coordinated in the pincer mode, was obtained. Chloride abstraction with silver salt in the presence of pyridine generated the dicationic complex $[\text{LPd}(\text{py})](\text{BF}_4)_2$ (**2**). When reacting with a base such as potassium hexamethyldisilazane (KHMDs), **1** gave the neutral complex **3** $[\text{L}^*\text{PdCl}]$, wherein the benzylic position alpha to phosphine was selectively deprotonated, which induced dearomatisation of the pyridine ring. A similar complex $[\text{L}^*\text{Pd}(\text{CH}_3)]$ (**4**) was obtained upon a reaction of $[\text{Pd}(\text{CH}_3)_2(\text{TMEDA})]$ and **L** via the departure of methane. Neutral complexes with the deprotonated ligand such as **3** yielded in the presence of deuterated methanol the corresponding deuterated complex, showing that the protonation is reversible with this ligand. Finally, upon attempting to dealkylate complex **4** using $\text{B}(\text{C}_6\text{F}_5)_3$, an unexpected zwitterionic borated complex **5**, resulting from the formation of a C–B bond in the benzylic position with restoration of the aromatic character of the pyridine, was isolated. Interestingly, when the metal was introduced after the ligand interacted with the borane reagent, another palladium complex formed, namely, $[\text{LPdMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, originating from methyl abstraction.

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Introduction

Since the first report by Shaw *et al.* in 1976,¹ pincer ligands² have gained considerable interest in coordination chemistry and now play 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 and offer a high degree of synthetic tunability, allowing variations 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 phosphalkenes,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 the (PCP) derivatives (**A**, Fig. 1), associating two phosphines and one aryl central carbon;^{8,10} nevertheless, many variations of the pivotal donor were also proposed (N^- , Si^- , P^- , **B**;

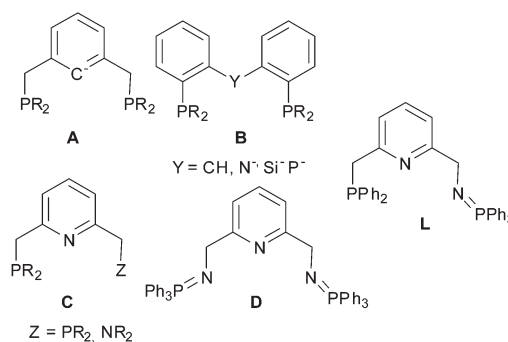


Fig. 1 Pincer phosphine and/or iminophosphorane ligands.

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 ($\text{P}=\text{N}$) ligands,¹⁵ wherein nitrogen behaves as a strong σ and π donor, we were interested in

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† Electronic supplementary information (ESI) available: Crystallographic data for **1**, **2**, **3**, **5** and some NMR spectra. CCDC 1414327–1414330. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02789f

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 study, we describe 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 ligand, which was reacted with methanol and borane.

Results and discussion

Ligand synthesis

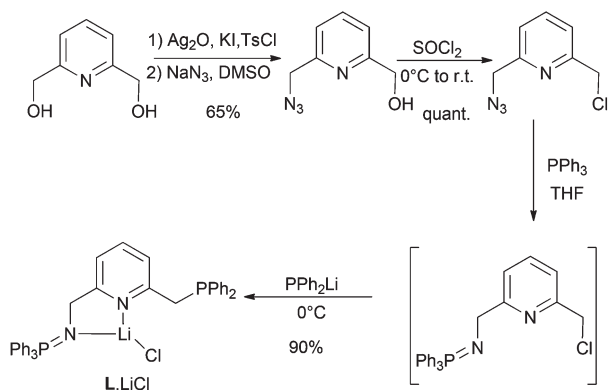
Based on the synthesis of the tridentate pincer bis-iminophosphorane pyridine ligand we recently published (**D**, Fig. 1),¹⁸ we chose lutidine diol as the starting material. Its efficient desymmetrization is crucial to the development of an efficient preparation of **L**. After having attempted several pathways, 2-(azidomethyl)-6-(hydroxymethyl)pyridine was identified as a key intermediate. Its synthesis from 2,6-bis(hydroxymethyl)pyridine was first realised by selective bromination¹⁹ followed by azidation; nevertheless better yields were obtained using a mono-tosylated intermediate²⁰ (Scheme 1). After substitution of the tosyl group by azide, hydroxyl was replaced by chloride. Iminophosphorane was then formed by a Staudinger reaction with triphenylphosphine. The phosphine group was then introduced by a nucleophilic substitution of chloride with PPh_2Li . First, the iminophosphorane intermediate was isolated; however, a better yield was obtained when both the reactions were conducted in the same pot without isolation of the intermediate iminophosphorane. Indeed, this last step was followed conveniently by *in situ* $^{31}P\{^1H\}$ NMR. The formation of iminophosphorane was evidenced by a singlet at $\delta = 6.7$ ppm in diethyl ether, its transformation to the phosphine–iminophosphorane adduct gave rise to two singlets at 7.7 and -12 ppm corresponding 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

lithium was confirmed by 7Li NMR showing a singlet at -0.5 ppm in THF- d_8 ; elemental analysis corroborated a 1 : 1 stoichiometry.

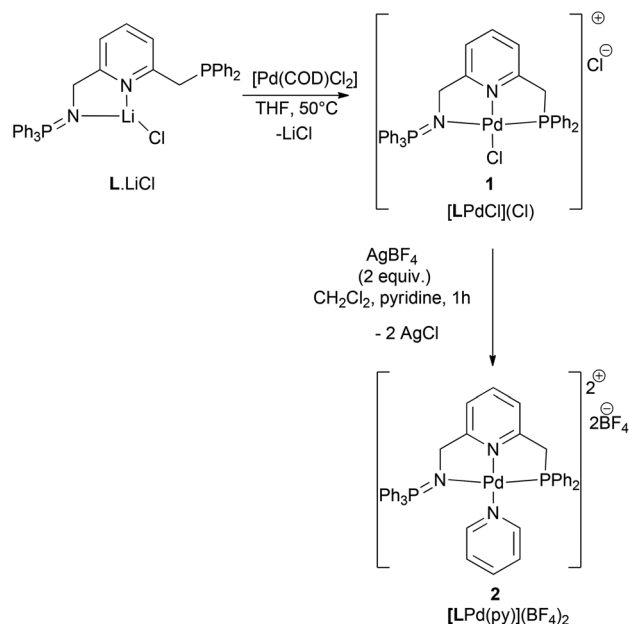
Two types of benzylic protons were observed in the 1H NMR spectrum: one doublet at $\delta = 4.32$ ($J_{P,H} = 15$ Hz) and a singlet at 3.55 ppm. They were respectively assigned to CH_2 alpha to iminophosphorane and phosphine groups thanks to a 2D 1H – ^{31}P correlation. The absence of coupling between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

Palladium complexes

First, the coordination of **L** was realised by mixing **L**·LiCl and $[Pd(COD)Cl_2]$ in THF (Scheme 2). After a 2 h reaction at 50 °C, the resulting complex was isolated as a yellow solid in 80% yield after filtration. The coordination to the metal induced large deshielding of the phosphorus nuclei appearing as two doublets ($^3J_{P,P} = 10.5$ Hz) at 35.1 and 33.9 ppm. They respectively correlated with a doublet at 4.93 ($^3J_{P,H} = 13.0$ Hz) and a doublet of doublets at 4.60 ($^3J_{P,H} = 6.5$ Hz, $^4J_{P,H} = 2.0$ Hz) in the ^{31}P – 1H 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 1 Synthesis of **L**·LiCl.



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

Therefore, the replacement of lithium with palladium induces large deshielding only for the protons in the vicinity of phosphine ($\Delta\delta = 1.4$ 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** (Fig. 2) was given by X-ray diffraction analysis performed on the crystals obtained by the gas diffusion of diethyl ether in an 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) compared to those measured in the corresponding (di-tertbutylphosphinomethyl)pyridine ($t^t\text{BuPNP}$)^{22a} adduct (2.2961(1) and 2.0430(12) Å), which is probably due to the lower steric hindrance generated by the two phenyl rings. In contrast, the N1-Pd1-P2 angle of 164.23(6)° is more acute than in the phosphine analogue (P-Pd-P: 168.729(2)°).

The 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 [LPd(py)](BF₄)₂ **2** was isolated after filtration of the salts as a

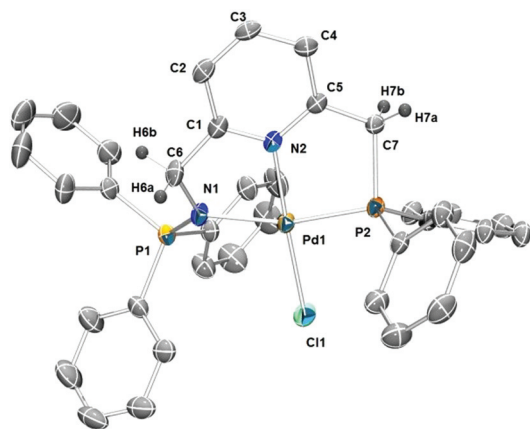


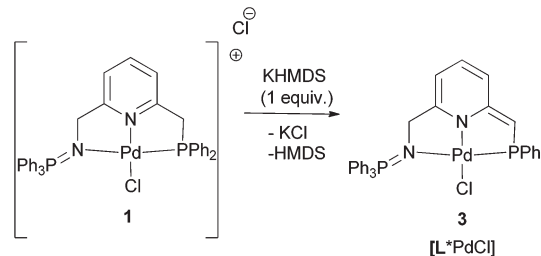
Fig. 2 ORTEP of the solid-state structure of **1** with 50% probability thermal ellipsoids. Most hydrogen atoms, one non-coordinating chloride and one benzonitrile solvent molecule were omitted for clarity. Selected bond lengths [Å] and angles (°): N1–P1 1.603(2), N1–Pd1 2.110(2), P2–Pd1 2.2112(7), N2–Pd1 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).

† Addition of a slight excess of MeCN or PMe₃ to a CH₂Cl₂ solution of [LPd](BF₄)₂ lead to the formation of [LPd(MeCN)](BF₄)₂ (³¹P{¹H} (CD₂Cl₂) δ 43.8 (d, ³J_{P,P} = 10.0 Hz, PPh₂), 39.8 (d, ³J_{P,P} = 10.0 Hz, N=P); ¹H (CD₂Cl₂) δ 8.06–7.51 (m, 27H, H_{9-11,13-15,py}), 7.24 (d, *J* = 8.0 Hz, 1H, H₂), 4.67 (m, 4H, H_{6,7}), 1.50 (s, 3H, MeCN) or [LPd(PMe₃)](BF₄)₂ (³¹P{¹H} (CD₂Cl₂) δ 44.8 (dd, ²J_{P,P} = 29.0 Hz, ³J_{P,P} = 13.5 Hz, PPh₂), 42.7 (d, ³J_{P,P} = 13.5 Hz, N=P), –4.6 (d, ²J_{P,P} = 29.0 Hz, PMe₃); ¹H (CD₂Cl₂) 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, H₄), 6.79 (d, *J* = 8.0 Hz, 1H, H₂), 4.84 (m, 4H, H_{6,7}), 0.57 (d, *J* = 11.5 Hz, 9H, PMe₃).

yellow solid in 60% yield. This behaviour contrasts with that observed by Milstein *et al.*^{22a} who reported that for [(^tBuPNP)PdCl](Cl), only the outer-sphere chloride could be abstracted. Complex **2** was characterised by multinuclear NMR spectroscopy in CD₂Cl₂. In the ³¹P{¹H} spectrum, an AB system was observed with doublets at 37.1 and 36.9 ppm (³J_{P,P} = 10.5 Hz), which are very close to those described for **1**. Cationisation has more influence on the ¹H chemical shifts because 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. This suggests 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 ¹⁹F NMR. The structure was confirmed by X-ray analysis of single crystals obtained by the diffusion of pentane into a dichloromethane solution (see ESI, Fig. S1†). It is very similar to that obtained for **1** with a slight contraction of the coordination sphere. Pyridine is perpendicular to the pyridine ring of the tridentate ligand to minimize steric hindrance. The 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 the addition of one equivalent of KHMDS (potassium hexamethyldisilazane) to a THF solution of complex **1** (Scheme 3).§ The solution darkened rapidly, but not much change was observed in the *in situ* ³¹P{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 to induce the precipitation of the complex and remove the amine by-product. The complex [L*PdCl] (**3**) was then extracted from the precipitate with CH₂Cl₂. **3** was obtained as a pale brown solid in a fair yield of 43% (which is explained by the moderate solubility of **3** in petroleum ether).

¹H NMR spectroscopy confirms the deprotonation because 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.

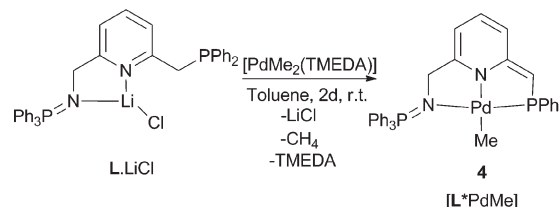


Scheme 3 Deprotonation of **1**.

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

2D-NMR confirms that deprotonation occurred selectively on the phosphine arm. The loss of aromaticity of N-heterocycle was also obvious with 3 signals at 6.57, 6.23 and 5.28 ppm, it has also considerable impact on the resonances of the carbon atoms. Indeed, C5 is deshielded by 10 ppm, whereas C4, C3, C2 and C1 are shielded by 12, 7, 24, and 4 ppm respectively, compared to complex **1**. The chemical shift variations observed were similar to those reported by Milstein^{22a} and van der Vlugt^{22b} for the (*t*^{Bu}PNP) complexes. This is accompanied by an increase in the carbon–phosphorus coupling constants for C4 to C7, which is in agreement with deprotonation at C7. This was further confirmed by X-ray analysis (Fig. 3) on the single crystals formed by the diffusion of pentane into a saturated dichloromethane solution of **3** at $-40\text{ }^{\circ}\text{C}$.

Not much change was observed in the geometry around the metal; moreover, the coordination bonds do not experience more than 0.7% variation. On the contrary, the C7–C5 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 N2–C5 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 deloca-



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

lised π -system induces a planarisation of metallacyclopentane incorporating the phosphine arm. Indeed, the dihedral angles for N1–C6–C1–N2 and P2–C7–C5–N2 were measured at 19.4° and 25.4° in [LPdCl](Cl) vs. 26.2° and 5.8° in [L*PdCl], respectively. A similar observation was made by Milstein *et al.* for the phosphine analogue.^{22a} Interestingly, **3** is to the best of our knowledge the first X-ray characterised complex featuring a dearomatised (PNN) ligand.

As the isolated yield of **3** is relatively low while the reaction is rapid and quantitative as attested by *in situ* NMR, we decided to access to such a complex from a metal precursor incorporating an internal base. We chose [PdMe₂(TMEDA)] (TMEDA = tetramethylethylenediamine), which should afford [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 ³¹P{¹H} NMR spectroscopy at 33.7 and 29.0 ppm (³J_{P,P} = 8.5 Hz).²³ Monitoring this reaction in THF-d₈ 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 the 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 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 flask, as well as the formation of ethane, as attested by the presence of a signal at 0.85 ppm in the ¹H NMR spectrum. Therefore, this reaction involves intermediates that are not thermally stable and can eliminate ethane to form Pd⁰. Low quality single crystals were grown from the THF solution, the crystallographic data (see ESI, Fig. S2†) only allow the confirmation of the connectivity.

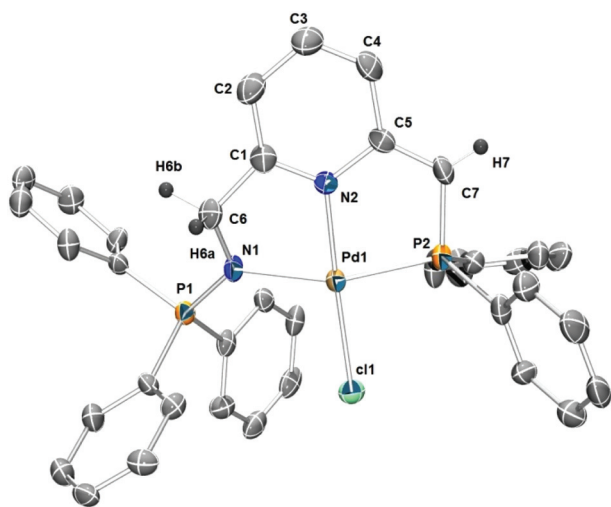


Fig. 3 ORTEP of the solid-state structure of [L*PdCl] **3** with 50% probability thermal ellipsoids. Most hydrogen atoms were omitted for clarity. Hydrogen atoms H₇, H_{6a}, and H_{6b} were refined isotropically. Selected bond lengths [Å] and angles ($^{\circ}$): N1–P1 1.595(5), N1–Pd1 2.124(5), P2–Pd1 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).

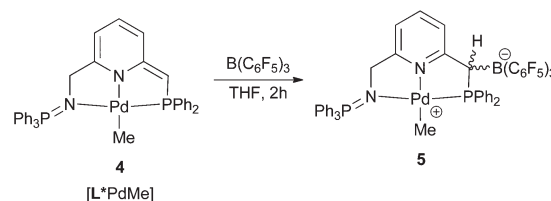
Reactivity of **3** and **4** featuring L* ligand

Upon reaction with a protic substrate (of general formula EH), such complexes with dearomatized pyridine generally become 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 H₇ had almost totally disappeared in the ¹H NMR spectrum

within the short time required to perform the measurement (see Fig. S3†), whereas the rest of the spectrum as well as the $^{31}\text{P}\{\text{H}\}$ one remained unchanged. Therefore, protonation took place but was reversible and only the excess of methanol allowed total deuteration (Scheme 5). For the ($^{t\text{Bu}}\text{PNP}$) analogue examined by Milstein *et al.*,^{22a} the equilibrium between the dearomatised and aromatised form was 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 temperature.

When reacting $[\text{L}^*\text{PdMe}]$ (**4**) with $\text{B}(\text{C}_6\text{F}_5)_3$ to achieve demethylation, the expected cationic complex was not observed. Instead, the reaction afforded a new product labeled **5**, exhibiting one doublet at 31.1 ppm ($^3J_{\text{P,P}} = 7.5$ Hz) and one doublet of doublets at 47.1 ($^3J_{\text{P,P}} = 7.5$ Hz and 23.0 Hz) in the $^{31}\text{P}\{\text{H}\}$ spectrum in toluene. In ^1H NMR and ^{11}B spectra, signals corresponding to $\text{MeB}(\text{C}_6\text{F}_5)_3$ (the demethylation side product) were not seen ($\delta_{\text{H}} = 0.50$ ppm, $\delta_{\text{B}} = -14.8$ ppm).²⁴ Moreover, a doublet at -0.26 ($J_{\text{P,H}} = 1.5$ 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. This was simplified to an AM system ($|^2J_{\text{H,H}}| = 17.0$ Hz) upon the decoupling of the phosphorus nuclei, therefore these are two diastereopic protons that do not exhibit the same coupling to phosphorus. This clearly evidenced a loss of planar symmetry in the formed complex **5**. This was corroborated by the HSQC ^1H - ^{13}C spectrum (Fig. S4†), wherein 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 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 boration at the benzylic position (Scheme 6).²⁶ This is in agreement with the results of elemental analysis and was further confirmed by X-ray analysis (Fig. 4a).

5 adopts a distorted square planar geometry around 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



Scheme 6 Formation of **5**.

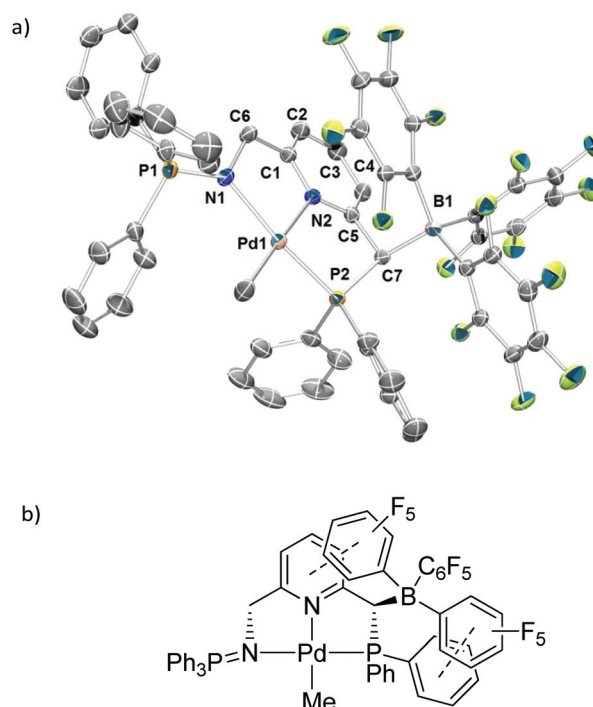
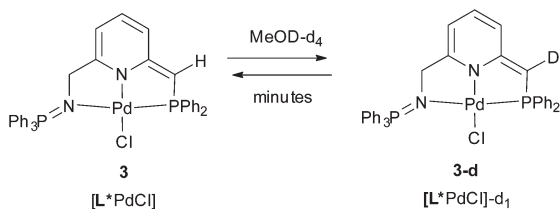


Fig. 4 (a) ORTEP of the solid-state structure of **5** with 50% probability thermal ellipsoids. Most hydrogen atoms were omitted for clarity, hydrogen atoms H_{6a} , H_{6b} and H_7 were refined isotropically. Selected bond lengths [Å] and angles ($^\circ$): N1–P1 1.597(2), N1–Pd1 2.136(2), P2–Pd1 2.2078(6), 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.

C5–C7 and C7–P2 bonds from 1.494(3) and 1.834(3) Å in **1** to 1.515(3) and 1.868(2) Å, respectively. The coordination sphere of 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–P2 angle is slightly more acute (159.68(6) *vs.* 164.23(6) $^\circ$). Pyridine is aromatised because the inner ring C–C bond lengths are comparable to those observed in **1** at around 1.38 Å. Regarding the alkyl-borane formed, 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



Scheme 5 Reactivity of $[\text{L}^*\text{PdCl}]$ (**3**) with deuterated methanol.

present in this structure between fluorinated rings and the central pyridine and one phenyl group (Fig. 4b). Interestingly, Iluc *et coll.* recently described similar C–B bond formations with $B(C_6F_5)_3$ on the anionic ligand of a palladium complex.²⁷

Milstein *et coll.* showed that the reaction of $[(^{tBu}PNN)Ru(H)(CO)]$ with pinacolborane yields, after loss of H_2 , a complex with a dearomatised ligand where the vinylic position is substituted by the pinacolborane.²⁸ DFT calculations pointed towards an intermediate with aromatic pyridine and 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* ($\delta_P = 25.7$ and -17.6 ppm for the iminophosphorane and the phosphine respectively in C_6D_6). The addition of $[PdMe_2(TMEDA)]$ to this solution then 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 ppm. The ^{11}B and ^{19}F spectra showed the presence of a $MeB(C_6F_5)_3$ anion. 1H NMR spectroscopy revealed 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 $[LPdMe][MeB(C_6F_5)_3]$ resulting from methyl abstraction by borane was formed.

Conclusion

In conclusion, an unprecedented mixed phosphine–iminophosphorane ligand exhibiting a central pyridine moiety was synthesised and coordinated with Pd^{II} , yielding a cationic complex or a neutral one if the metallic precursor incorporates a basic ligand (we used $[PdMe_2(TMEDA)]$). In the latter case, the selective deprotonation at the benzylic position alpha to phosphine was observed. A similar complex was obtained when reacting cationic complex **1** $[LPdCl](Cl)$ with a base. Those neutral complexes can be protonated by methanol but the protonation is reversible, as demonstrated by the 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 shows 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 with 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. The 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. The other deuterated solvents were used as received and stored over molecular sieves. Unless stated otherwise, the reagents were used without further purification. $[PdMe_2(TMEDA)]$ ²⁹ and 2-(azidomethyl)-6-(hydroxymethyl)pyridine²⁰ were prepared following the literature procedure.

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Av300 spectrometer operating at 300 MHz for 1H , 116.6 MHz for 7Li , 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 . The solvent peaks were used as the internal references for the 1H and ^{13}C chemical shifts (ppm). The ^{31}P peaks were referenced to external 85% H_3PO_4 . The following abbreviations are used: br, broad; s, singlet; d, doublet; t, triplet; and m, multiplet. Labelling of atoms is indicated in Fig. 5. Index py and Ar were used to indicate signals corresponding to coordinated pyridine and aryl ring (when non discernable). Mass spectrometry was 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). The ion source parameters were adjusted as follows: the cone voltage (V_{cone}) 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 the nebulizing and desolvation gas. The gas flows ranged from 10 L h^{-1} to 100 L h^{-1} . The solution was introduced with a flow of 10 μL min^{-1} . For MS/MS analysis, argon was used as the collision gas at a flow rate of 0.28 mL min^{-1} corresponding to a pressure of *ca.* 4×10^{-3} mBar. Elemental analyses were determined by Mr S. Boyer at the London Metropolitan University.

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 1 h and 30 min while the ice bath gently warmed. 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 3×40 mL of EtOAc and dried with $MgSO_4$. The evaporation of all volatiles gave the title compound as a clear oil in near quantitative yield (1.39 g, 7.61 mmol, 99%). 1H ($CDCl_3$) 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_6).³⁰

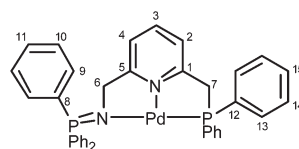


Fig. 5 Labelling scheme.

L-LiCl. In a Schlenk flask, PPh₃ (2.0 g, 7.61 mmol) was dissolved in Et₂O (20 mL), and a solution of 2-(azidomethyl)-6-(chloromethyl)pyridine (1.26 g, 7.61 mmol) in Et₂O (5 mL) was then added *via* a 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 ³¹P NMR (singlet at 6.7 ppm). THF (15 mL) was then added. In another Schlenk flask, HPPPh₂ (1.32 mL, 7.58 mmol) was dissolved in THF (40 mL), the flask was cooled to -78 °C and a 1.6 M 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 the Schlenk flasks were then cooled to 0 °C and the mixture of 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 1 h. The final mixture may present a deep blue coloration, which can be quenched by the addition of 4–5 drops of TMSCl. The 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 (3 × 30 mL) to yield L-LiCl as a white powder in 91% yield (4.195 g, 6.89 mmol). ³¹P{¹H} (THF-d⁸) δ 7.7 (br s, N=PPh₃), -12.0 (s, PPh₂); ⁷Li (THF-d⁸) δ -0.5 (s, LiCl); ¹H (THF-d⁸) δ 7.83–7.62 (m, 6H, H₉), 7.61 (d, ³J_{H,H} = 7.5 Hz, 1H, H₄), 7.56–7.37 (m, 13H, H_{10,11,13}), 7.36 (t, ³J_{H,H} = 7.5 Hz, 1H, H₃), 7.27–7.17 (m, 6H, H_{14,15}), 6.73 (d, ³J_{H,H} = 7.5 Hz, 1H, H₂), 4.32 (d, ³J_{P,H} = 15.0, 2H, H₆), 3.55 (s, 2H, H₇); ¹³C (THF-d⁸) δ 165.9 (C₅, J_{P,C} not visible), 157.1 (d, ²J_{P,C} = 8.5 Hz, C₁), 140.2 (d, ¹J_{P,C} = 17.0 Hz, C₁₂), 136.3 (s, C₃), 133.6 (d, ²J_{P,C} = 19.0 Hz, C₁₃), 133.3 (d, ²J_{P,C} = 9.0 Hz, C₉), 132.8 (d, ¹J_{P,C} ~ 100 Hz, C₈), 131.8 (s, C₁₁), 128.9 (d, ³J_{P,C} = 12.0 Hz, C₁₀), 128.8 (d, ³J_{P,C} = 6.5 Hz, C₁₄), 128.7 (s, C₁₅), 120.8 (d, ³J_{P,C} = 6.5 Hz, C₂), 119.0 (s, C₄), 51.4 (s, C₆), 39.1 (d, ¹J_{P,C} = 17.0 Hz, C₇). Calcd for C₃₇H₃₂ClLiN₂P₂: 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, [PdCl₂(COD)] (544 mg, 1.91 mmol) was suspended in THF (25 mL) and L-LiCl (1.16 g, 1.91 mmol) added as a solid, and THF (5 mL) was added to clean the walls of the Schlenk flask. 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 (2 × 10 mL) and Et₂O (2 × 10 mL) and finally dried under high vacuum for 2 h to yield [LPdCl](Cl) (1) as a pale-yellow powder (1.136 g, 1.25 mmol, 80%). ³¹P{¹H} (CD₂Cl₂) δ 35.1 (d, ³J_{P,P} = 10.5 Hz, PPh₂), 33.9 (d, ³J_{P,P} = 10.5 Hz, N=PPh₃); ¹H (CD₂Cl₂) δ 8.26 (d, ³J_{H,H} = 8.0 Hz, 1H, H₂), 8.06–7.79 (m, 11H, H_{3,9,13}), 7.78–7.66 (m, 3H, H₁₁), 7.66–7.44 (m, 12H, H_{10,14,15}), 7.20 (d, ³J_{H,H} = 8.0 Hz, 1H, H₄), 4.93 (d, ²J_{P,H} = 13.0 Hz, 2H, H₇), 4.60 (dd, J_{B,H} = 6.5, 2.0 Hz, 2H, H₆); ¹³C (CD₂Cl₂) δ 166.1 (d, ³J_{P,C} = 19.0 Hz, C₅), 160.4 (d, ²J_{P,C} = 3.5 Hz, C₁), 140.6 (s, C₃), 134.3 (d, ²J_{P,C} = 10.0 Hz, C₉), 133.7 (d, ²J_{P,C} = 11.5 Hz, C₁₃), 133.6 (s, C₁₁), 132.7 (d, ⁴J_{P,C} = 3.0 Hz, C₁₅), 129.6 (d, ³J_{P,C} = 11.9 Hz, C₁₄), 129.2 (d, ³J_{P,C} = 12.5 Hz, C₁₀), 127.7 (d, ¹J_{P,C} = 56.0 Hz, C₁₂), 126.3 (d, ¹J_{P,C} = 101.5 Hz, C₈), 123.7 (d,

³J_{P,C} = 14.0 Hz, C₂), 120.2 (s, C₄), 59.8 (s, C₆), 45.1 (d, ¹J_{P,C} = 34.0 Hz, C₇). Calcd for C₃₇H₃₂Cl₂N₂P₂Pd: C, 59.74; H, 4.34; N, 3.77. Found: C, 59.85; H, 4.35; N, 3.81.

[LPd(py)](BF₄)₂ 2. In a Schlenk flask, [LPdCl](Cl) (100 mg, 0.13 mmol) and AgBF₄ (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 Et₂O (20 mL) was added, leading to the precipitation of a yellowish solid. The precipitate was filtered and washed with Et₂O (10 mL). After drying under vacuum, [LPd(py)](BF₄)₂ 2 (72.1 mg, 60%) was isolated. ³¹P{¹H} (CD₂Cl₂) δ 37.1 (d, ³J_{P,P} = 10.5 Hz, N=P), 36.9 (d, ³J_{P,P} = 10.5 Hz, PPh₂); ¹H NMR (CD₂Cl₂) 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, H₂), 4.63 (dd, J_{B,H} = 6.0, 2.5 Hz, 2H, H₆), 4.47 (d, ²J_{P,H} = 12.5 Hz, 2H, H₇); ¹³C NMR (CD₂Cl₂) δ 166.6 (d, ⁴J_{P,C} *ca.* 17 Hz, C₅), 159.7 (d, ³J_{P,C} = 3.7 Hz, C₁), (152.2 (s, C_{py})), 152.0 (s, C_{py}), 140.7 (s, C₃), 140.5 (s, C_{py}), 140.3 (s, C_{py}), 134.3 (d, ²J_{P,C} = 9.4 Hz, C₉), 133.7 (d, ⁴J_{P,C} = 2.7 Hz, C₁₁), 133.4 (d, ²J_{P,C} = 11.0 Hz, C₁₃), 133.0 (d, ⁴J_{P,C} = 2.8 Hz, C₁₅), 129.7 (d, ³J_{P,C} = 11.5 Hz, C₁₄), 129.3 (d, ³J_{P,C} = 12.0 Hz, C₁₀), 127.6 (d, ¹J_{P,C} = 43.0 Hz, C₁₂), 127.1 (s, C_{py}), 126.2 (d, ¹J_{P,C} = 103.0 Hz, C₈), 122.5 (d, ³J_{P,C} = 14.0 Hz, C₂), 120.4 (s, C₄), 59.85 (s, C₆), 45.1 (d, ¹J_{P,C} = 33.0 Hz, C₇); ¹⁹F (CD₂Cl₂) δ -151.4 (s, BF₄). MS (ES+) (C₃₇H₃₂N₂P₂Pd²⁺): calculated *m/z*: 336.06, found: 336.06.

[L*PdCl] 3. THF (5 mL) was added to a Schlenk flask containing [LPdCl](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. Petroleum ether (20 mL) was then added, resulting in the precipitation of the complex. After filtration under nitrogen, the resulting solid was washed with petroleum ether (2 × 10 mL). The product was then extracted from the precipitate using dichloromethane (2 × 10 mL).³¹ 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). ³¹P{¹H} (THF-d⁸) δ 34.8 (d, ³J_{P,P} = 11.5 Hz, PPh₂), 32.9 (d, ³J_{P,P} = 11.5 Hz, N=PPh₃); ¹H (THF-d⁸) δ 7.94–7.83 (m, 6H, H₉), 7.83–7.75 (m, 4H, H₁₃), 7.64–7.55 (m, 3H, H₁₁), 7.54–7.45 (m, 6H, H₁₀), 7.33–7.18 (m, 6H, H_{14,15}), 6.53 (ddd, ³J_{H,H} = 9.0, 6.5 Hz, J_{B,H} = 2.4 Hz, 1H, H₃), 6.19 (d, ³J_{H,H} = 9.0 Hz, 1H, H₄), 5.25 (d, ³J_{H,H} = 6.5 Hz, 1H, H₂), 4.06 (d, ³J_{P,H} = 7.5 Hz, 2H, H₆), 3.23 (d, ²J_{P,H} = 3.5 Hz, 1H, H₇). ¹³C (THF-d⁸) δ 170.8 (d, ²J_{P,C} = 16.0 Hz, C₁), 162.8 (d, ³J_{P,C} = 18.0 Hz, C₅), 137.7 (d, ¹J_{P,C} = 58.0 Hz, C₁₂), 134.8 (d, ²J_{P,C} = 9.5 Hz, C₉), 133.9 (s, C₃), 133.3 (d, ²J_{P,C} = 11.0 Hz, C₁₃), 133.3 (d, ⁴J_{P,C} = 3.0 Hz, C₁₁), 129.6 (d, ⁴J_{P,C} = 3.0 Hz, C₁₅), 128.9 (d, ³J_{P,C} = 12.5 Hz, C₁₀), 128.5 (d, ¹J_{P,C} = 99.5 Hz, C₈), 128.1 (d, ³J_{P,C} = 11.1 Hz, C₁₄), 111.8 (d, ⁴J_{P,C} = 23.0 Hz, C₂), 96.6 (s, C₄), 59.7 (d, ¹J_{P,C} = 74.5 Hz, C₇), 58.5 (d, ²J_{P,C} = 2.5 Hz, C₆).

[L*PdMe] 4. In a Schlenk flask, toluene (7.5 mL) was added to L-LiCl (240.9 mg, 0.40 mmol) [PdMe₂(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. Furthermore, the Schlenk flask was cooled to $-20\text{ }^{\circ}\text{C}$ for 2 hours. After cooling, the mixture was filtered and the solid was washed with Et_2O ($2 \times 5\text{ mL}$), petroleum ether ($2 \times 5\text{ mL}$) and finally dried under high vacuum to yield $[\text{L}^*\text{PdMe}]$ **4** (152 mg, 0.22 mmol, 56%). $^{31}\text{P}\{^1\text{H}\}$ (THF- d^8) δ 33.7 (d, $^3J_{P,P} = 8.5\text{ Hz}$, $\text{N}=\text{PPh}_3$), 29.0 (d, $^3J_{P,P} = 8.5\text{ Hz}$, PPh_2); ^1H NMR (THF- d^8) δ 7.86 (dd, $J_{P,H} = 11.7$, $J_{H,H} = 7.5\text{ Hz}$, 6H, H_9), 7.79–7.56 (m, 7H, $\text{H}_{11,13}$), 7.55–7.36 (m, 6H, H_{10}), 7.26–7.14 (m, 6H, $\text{H}_{14,15}$), 6.45 (dd, $^3J_{H,H} = 8.5$, 7.0 Hz, 1H, H_3), 6.04 (d, $^3J_{H,H} = 8.5\text{ Hz}$, 1H, H_4), 5.19 (d, $^3J_{H,H} = 7.0\text{ Hz}$, 1H, H_2), 4.08 (d, $^3J_{P,H} = 8.0$, 2H, H_6), 3.13 (d, $^2J_{P,H} = 3.5\text{ Hz}$, 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 $\text{C}_{38}\text{H}_{34}\text{N}_2\text{P}_2\text{Pd}$: C, 66.43; H, 4.99; N, 4.08. Found: C, 66.38; H, 5.06; N, 3.95.

$[\text{LPdMe}(\text{B}(\text{C}_6\text{F}_5)_3)]$ **5**. In a glove-box, $[\text{L}^*\text{PdMe}]$ (30 mg, 44 μmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (22.4 mg, 44 μmol) were suspended in toluene (3 mL). After 3 hours of stirring, the mixture turned clear and was checked by $^{31}\text{P}\{^1\text{H}\}$ probing the disappearance of the starting material. The volatiles were then removed under vacuum. The solid was then suspended in pentane (3 mL), filtered, and the solid was then washed with Et_2O (1 mL) and pentane ($2 \times 3\text{ mL}$) to give an off-white solid, which was dried under high vacuum to furnish $[\text{LPdMe}(\text{B}(\text{C}_6\text{F}_5)_3)]$ **5** (39.2 mg, 33 μmol , 75%). $^{31}\text{P}\{^1\text{H}\}$ (Tol- d^8) δ 47.1 (dd, $J = 23.0$, 7.5 Hz, PPh_2), 31.1 (d, $^3J_{P,P} = 7.5\text{ Hz}$, $\text{N}=\text{P}$); ^{11}B (Tol- d^8) δ -10.5 (s, $\nu_{1/2} = 27\text{ Hz}$); ^1H NMR (Tol- d^8) δ 8.06–7.80 (m, 2H, H_{Ar}), 7.62–7.47 (m, ca. 10H, $\text{H}_{3,Ar}$), 7.21–6.72 (m, ca. 14H, H_{Ar}), 6.62 (m, 2H, $\text{H}_{3,7}$), 5.59 (d, $^3J_{H,H} = 8.0\text{ Hz}$, 1H, H_2), 4.08 (dd, $^2J_{H,H} = 17.0\text{ Hz}$, $^3J_{P,H} = 2.5\text{ Hz}$, 1H, H_{6a}); 3.79 (dd, $^2J_{H,H} = 17.0\text{ Hz}$, $^3J_{P,H} = 10.5\text{ Hz}$, 1H, H_{6b}), -0.26 (d, $^3J_{P,H}$ ca. 1.5 Hz, 3H, CH_3). ^{13}C (Tol- d^8) δ 165.9 (s, C_5), 160.5 (d, $^3J_{P,C} = 19.5\text{ Hz}$, 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, $^2J_{P,C} = 4.5\text{ Hz}$, CH_3). Calcd for $\text{C}_{56}\text{H}_{34}\text{BF}_{15}\text{N}_2\text{P}_2\text{Pd}$: C, 56.09; H, 2.86; N, 2.34. Found: C, 55.90; H, 2.93; N, 2.42.

$[\text{LPdMe}][\text{Me}(\text{B}(\text{C}_6\text{F}_5)_3)]$. In a glove box, $\text{L}\cdot\text{LiCl}$ (44.6 mg, 73 μmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (37.5 mg, 73 μmol) were stirred in toluene (3 mL) for 20 minutes. $[\text{PdMe}_2(\text{TMEDA})]$ (18.5 mg, 73 μmol) was then 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 removed carefully with a Pasteur pipette and the operation was repeated. Finally, the resulting red oil was dried overnight under high vacuum, leading to $[\text{LPdMe}][\text{Me}(\text{B}(\text{C}_6\text{F}_5)_3)]\cdot(\text{toluene})_3$ as a red oil (80 mg, 66 μmol , 73%). Remaining molecules of toluene cannot be removed by high vacuum overnight. The ratio 1:3 was determined by ^1H NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6) δ 34.1 (d, $^3J_{P,P} = 7.3\text{ Hz}$, PPh_2), 29.7 (d, $^3J_{P,P} = 7.5\text{ Hz}$, $\text{N}=\text{P}$); ^1H NMR (C_6D_6) δ 7.65–7.50 (m, 9H, $\text{H}_{9,11}$), 7.45–7.29 (m, 6H, $\text{H}_{13,15}$), 7.27–7.05 (m, 10H, $\text{H}_{10,14}$), 7.01 (t, $^3J_{H,H} = 8.0\text{ Hz}$, 1H, H_3), 6.73 (d, $^3J_{H,H} = 7.5\text{ Hz}$, 1H, H_4), 6.25 (d, $^3J_{H,H} = 8.0\text{ Hz}$, 1H, H_2), 4.29 (d, $^3J_{P,H} = 7.0\text{ Hz}$,

2H, H_6), 3.63 (d, $^2J_{P,H} = 12.0\text{ Hz}$, 2H, H_7), 1.30 (br s., 3H, $\text{CH}_3\text{-B}$), -0.26 (d, $^3J_{P,H} = 2.4\text{ Hz}$, 3H, $\text{CH}_3\text{-Pd}$). ^{13}C (C_6D_6) δ 162.4 (dd, $^3J_{P,C} = 18.5\text{ Hz}$, C_1), 155.7 (d, $^2J_{P,C} = 4.0\text{ Hz}$, C_5), 138.5 (s, C_3), 133.6 (d, $^2J_{P,C} = 9.5\text{ Hz}$, C_{13}), 133.4 (d, $^4J_{P,C} = 3.0\text{ Hz}$, C_{11}), 132.9 (d, $^2J_{P,C} = 12.5\text{ Hz}$, C_9), 131.9 (d, $^4J_{P,C} = 2.5\text{ Hz}$, C_{15}), 129.7 (d, $^1J_{P,C} = 51.4\text{ Hz}$, C_{12}), 129.4 (d, $^3J_{P,C} = 11.0\text{ Hz}$, C_{10}), 129.1 (d, $^3J_{P,C} = 12.3\text{ Hz}$, C_{14}), 126.6 (d, $^1J_{P,C} = 100.0\text{ Hz}$, C_8), 120.8 (d, $^3J_{P,C} = 11.5\text{ Hz}$, C_4), 119.2 (s, C_2), 59.5 (s, C_6), 45.8 (d, $^1J_{P,C} = 33.0\text{ Hz}$, C_7), -5.2 (d, $^3J_{P,C} = 6.5\text{ Hz}$, $\text{CH}_3\text{-Pd}$). Signals of the counter anion $\text{MeB}(\text{C}_6\text{F}_5)_3$ were also visible as very broad doublets separated by $^1J_{CF}$ of about 240 Hz at 149, 138 and 136 ppm, and the $\text{CH}_3\text{-B}$ 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, $^3J_{F,F} = 21\text{ Hz}$, 6F, *o*-F), -160.9 (t, $^3J_{F,F} = 21\text{ Hz}$, 3F, *p*-F), -163.2 (t, $^3J_{F,F} = 21\text{ Hz}$, 6F, *m*-F); ^{11}B NMR (C_6D_6) δ -13.8 (br s., $\nu_{1/2}$ ca. 150 Hz).

X-ray analysis

The data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo- κ ($\lambda = 0.71069\text{ \AA}$) X-ray source and a graphite monochromator. The crystal structure was solved using SIR 97,³³ and Shelxl-97 or Shelxl-2013³⁴ ORTEP drawings were made using ORTEP III for Windows.³⁵ The structures for **1**, **2**, **4**, and **5** were deposited under CCDC numbers 1414327–1414330.

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