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PAPER

N–H bond activation by palladium(II) and copper(I) complexes featuring a reactive bidentate PN-ligand†‡

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The first examples of reactivity at the backbone of a bidentate PN-ligand **L1H** relevant to N–H activation are described, leading to novel Pd^{II} and Cu^{I} amido complexes. Activation of the PN-ligand backbone led to selective dearomatization of the pyridyl ring structure. In the case of Pd^{II}, the intermediate could be efficiently stabilized using PMe_3. Selective N–H bond cleavage of *e.g.* trifluorosulfonylamide resulted in facile formation of mononuclear metal–amido species **2** and **4**, which have been crystallographically characterized. Hydrogen-bonding dimerization is observed in these solid state structures. The results obtained with these structurally versatile and reactive scaffolds likely open up new avenues in cooperative catalysis.

Introduction

In biological systems, cooperative substrate activation by earth-abundant metals, often in combination with protein-based ligands or other organic co-factors, is omnipresent.[1] Surprisingly, the combination of a first row transition metal and a 'reactive ligand' environment acting in concert has been scarcely exploited in a conceptual manner in synthetic chemistry,[2] which is in contrast to landmark examples for the heavier 2nd and 3rd row metals.[3]

The activation of N–H bonds by transition metals (and main group compounds) is of huge interest these days, because it could lead to the development of new catalytic routes to functionalize *e.g.* alkenes with amines.[4] Connected to this research area is the potential use of ammonia as an interesting substrate for homogeneous catalysis.[5] Selective N–H bond cleavage of NH_3 by transition metals is a big challenge and might represent one of the inherent limitations of this widely available compound. The development of complexes that may engage in efficient N–H activation and functionalization processes is therefore considered very relevant. One potential pathway for selective and productive N–H bond activation proceeds *via* a cooperative ligand–metal mechanism,[6] and this may provide a viable strategy to generate metal–amido species in a controlled manner and facilitate subsequent intra- and intermolecular reactions.[7]

Understanding the fundamental reactivity of metal complexes featuring a solitary amido group (*i.e.* where the amido is not a donor integrated in a ligand scaffold) is of relevance to several elementary catalytic processes.[8] Palladium amido species have recently been studied extensively to understand C–N bond formation *via* reductive elimination[9] in the context of *e.g.* *N*-amination of aryl halides[10] and aza-Wacker aminations,[11] but facile and general preparative methods to obtain these amido species are still relatively scarce. Also copper–amido species have been implied in various functionalization reactions,[12] but despite recent reports on reactive Cu^{I} precursors (featuring NHC-ligands), Cu^{I}–amide complexes are rare.[13] Furthermore, to date no Pd– or Cu–amido species have been prepared using a reactive or cooperative ligand approach, to the best of our knowledge.[14]

Notably, a bifunctional activation mode might enable facile intra- rather than intermolecular hydroaddition pathways, which could ultimately enhance catalyst activity and selectivity pronouncedly, even with cheap, earth-abundant transition metals. We therefore started a program to explore metal–ligand bifunctional reactivity with *inter alia* first row metals, initially focusing on tridentate 'pincer'[15,16] PNP ligands[17] that display cooperative behaviour by deprotonation (Scheme 1).[18,19] Strikingly, the coordination chemistry of copper with any 'pincer' ligand is still relatively unexplored.[20] To allow for more structural versatility as well as steric accessibility and to enhance reactivity of the (first row) transition metal with incoming exogenous substrates such as amines, we herein report our results on cooperative N–H activation by Pd and Cu complexes with bidentate PN analogues of these lutidine-derived PNP ligands. Although extensively studied in the last decade,[21] the potential cooperative character of these PN ligands[22] or related P^{V}-phosphorane structures[23] and their application in specific bond activation processes has hardly been exploited to date.

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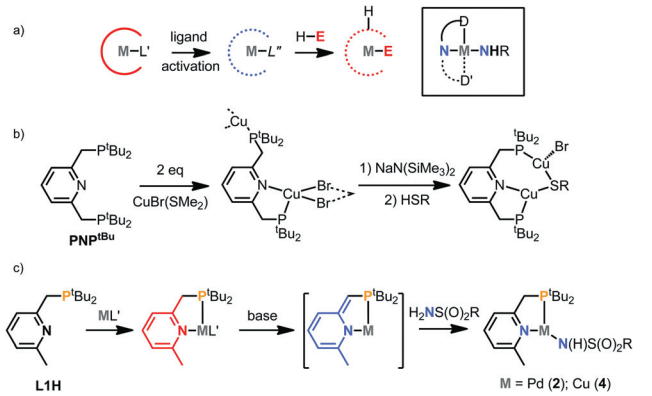
‡Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis



Scheme 1 (a) General concept of cooperative activation of H–E bonds, particularly to desirable metal–amides, (b) precedent[18] for Cu^{I}(PNP) reactivity and (c) current work with a *second generation* cooperative ligand system.

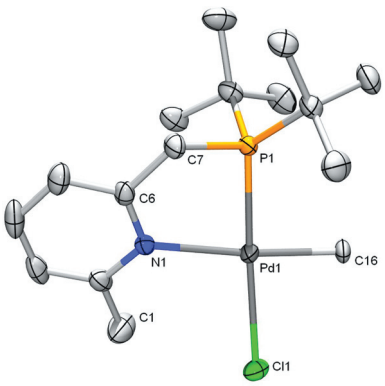


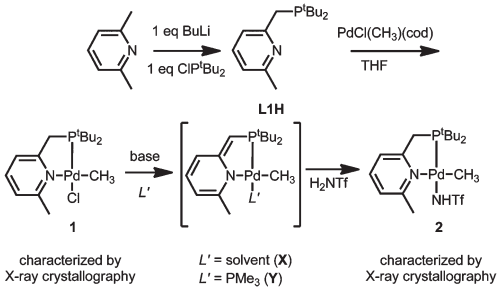
Fig. 1 ORTEP plot (50% probability displacement ellipsoids) of complex **1**, Pd(CH_3)Cl(**L1H**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles and torsion angles (°): Pd1–P1 2.2216(5); Pd1–N1 2.2474(16); Pd1–Cl1 2.3906(5); Pd1–C16 2.0679(18); P1–C7 1.834(2); C6–C7 1.497(3); P1–Pd1–N1 82.80(4); P1–Pd1–Cl1 170.637(19); P1–Pd1–C16 93.22(6); N1–Pd1–C16 173.19(7); P1–C7–C6–N1 26.3(2); Pd1–P1–C7–C6 −38.34(15); Pd1–N1–C6–C7 1.5(2).

Results and discussion

Synthesis of ligand L1H and Pd complex 1, Pd(CH_3)(Cl)(L1H)

Ligand **L1H**, 2-(di-*tert*-butylphosphino)methyl-6-methyl-pyridine, was prepared, following a modified literature procedure starting from 2,6-lutidine, in a one-pot two-step reaction and with an overall yield of 70%. The corresponding ^{31}P NMR spectrum showed a singlet at δ 34.9 (C_6D_6) for **L1H**. Reaction of this potentially bidentate PN ligand with PdCl(CH_3)(cod) (cod = 1,5-cyclooctadiene) yielded a yellow solid that was fully characterized as Pd(CH_3)(Cl)(**L1H**), complex **1**. X-ray crystallography of single crystals obtained *via* slow diffusion of hexane into a concentrated solution of dichloromethane resulted in the molecular structure depicted in Fig. 1.

The palladium atom displays a slightly distorted square planar geometry, with angles P1–Pd1–N1 and P1–Pd1–Cl1 of 82.80(4) and 170.637(19)°, respectively. The Pd1–P1 (2.2216(5) Å), Pd1–N1 (2.2474(16) Å) and Pd1–C16 (2.0679(18) Å) bond lengths are all within the expected ranges.[24] The methyl ligand is located *cis* to the phosphine donor (in agreement with the doublet observed in the ^{1}H NMR spectrum at δ 1.04 ($^2J_{PH}$ = 1.6 Hz) and the pyridine is strongly coordinated, as also confirmed by the IR spectrum, showing bands at 1572 and 1600 cm^{-1}.



Scheme 2 Preparative route to ligand **L1H**, Pd(CH_3)(Cl)(**L1H**)-complex **1** and related amido-species **2**.

Synthesis and characterization of Pd–amido species 2

Activation of this palladium complex by deprotonation–dearomatization of the methylene CH_2-group using a strong base generated a red homogeneous solution. The relative instability of this intermediate compared to starting compound **1** precluded its full characterization. However, preliminary spectroscopic data (δ(^{31}P) 66 ppm and δ(^{1}H) 3.12 ppm (d, $^2J_{P–H}$ = 8.8 Hz) for the –CH spacer) provide support for selective dearomatization of the ligand backbone, in agreement with reported data for related PNP-based systems,[14,17,24] with likely formation of a solvent-stabilized Pd(**L1**)(CH_3)-species **X** (Scheme 2).

Further investigation of the species formed upon dearomatization of the ligand backbone whilst coordinated to Pd showed that this intermediate could be stabilized by addition of a neutral co-ligand such as PMe_3. *In situ* addition of trimethylphosphine during the deprotonation of Pd-complex **1** yielded a dark-red solution. The ^{31}P NMR spectrum showed two doublets at δ 68.8 and −23.2 for the P^{t}Bu$_2$ and PMe_3 respectively, both with a coupling constant $^2J_{P–P}$ of 439 Hz, indicative of mutual *trans* disposition. The ^{1}H NMR spectrum nicely showed a doublet ($^2J_{P–H}$ = 7.6 Hz) at δ 3.37 for the –CH spacer and a doublet-of-doublets ($^3J_{P1–H}$ = 9.6 Hz; $^3J_{P2–H}$ = 3.6 Hz) at δ 0.56 for the Me-ligand at the Pd center. The formation of this species **Y** as Pd(CH_3)(**L1**)(PMe_3) was also confirmed by FAB-MS spectrometry, showing the molecular ion peak at *m*/*z* 448.1522.

Addition of one molar equiv. of H_2NTf (trifluoromethanesulfonamide)[25] to either the initial complex **X** or derivative **Y** led to an immediate color change from red to yellow-brown. The ^{31}P NMR spectrum of the resultant brown solid displayed one singlet at δ 75.2, and all expected signals in the ^{1}H NMR spectrum. A doublet ($^2J_{P–H}$ = 10.0 Hz) at δ 3.80 is nicely shown in the ^{1}H NMR spectrum for the –CH_2 spacer of the ligand arm and a singlet for the NH moiety at δ 3.15. Two signals indicative of formation of the amido-species were distinctly observed by FAB-MS, at *m*/*z* 505.0529 [M − Me] and 372.1089 [M − NHTf]. The IR spectrum displayed two peaks at ν 1600

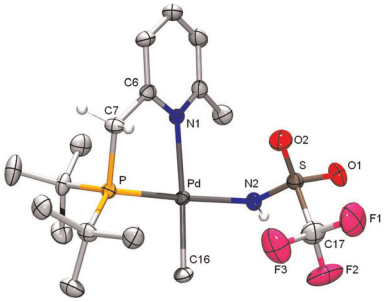


Fig. 2 ORTEP plot (50% probability displacement ellipsoids) of complex **2**, Pd(CH_3)(NHTf)(**L1H**). Hydrogen atoms have been omitted for clarity, except for those at C7 and N2. Selected bond lengths (Å), angles and torsion angles (°): Pd1–P1 2.2232(10); Pd1–N1 2.191(3); Pd1–N2 2.108(3); Pd1–C16 2.042(4); P1–C7 1.850(4); C6–C7 1.500(6); N2–S1 1.540(4); P1–Pd1–N1 82.28(9); P1–Pd1–N2 170.03(10); N1–Pd1–C16 175.92(15); P1–C7–C6–N1 −18.4(5); Pd1–P1–C7–C6 35.7(3); Pd1–N1–C6–C7 −10.9(4).

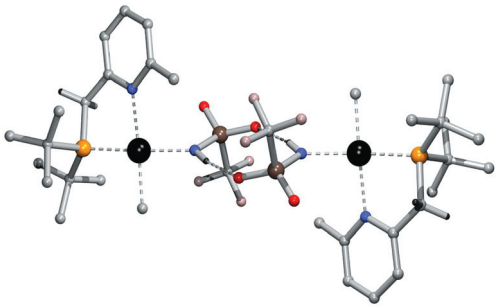
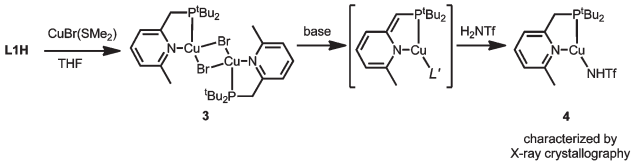


Fig. 3 Dimeric H-bonded structure of complex **2**, with a Pd···Pd [1 − *x*, 1 − *y*, 1 − *z*] distance of 8.4216(6) Å.



Scheme 3 Preparative route to [Cu(μ-Br)(**L1H**)]$_2$ **3** and Cu^{I}–amido complex **4**, obtained *via* cooperative N–H activation.

and 1564 cm^{-1}, suggestive of rearomatization of the pyridine moiety.[18a] The analogous *p*-toluenesulfonamide (NHTs) complex **2A** could also be prepared in a similar smooth fashion, as indicated by the spectroscopic and mass spectrometric data (see the experimental section).

We also have preliminary indications that *e.g.* 2,3,4,5,6-pentafluoroaniline (H_2NAr^{F5}) can be activated in a similar manner, judging from NMR spectroscopic data (*i.e.* $\delta(^{31}P)$ 67.4, $\delta(^{1}H)$ 3.04 (–N*H*Ar)) as well as consistent MS data for derivatives of the resulting Pd(CH_3)($HNAr^{F5}$)(**L1H**) species ([M − CH_3]$^+$ peak at *m*/*z* 539.0872). This suggests that the potential substrate scope for subsequent (catalytic) transformations involving N–H activation using a bifunctional mechanism may be quite broad.

Single crystals of complex **2**, suitable for X-ray crystallographic analysis, were grown by slow diffusion of pentane into a concentrated CH_2Cl_2 solution (Fig. 2). The molecular structure reveals a slightly distorted square planar geometry around the palladium atom, with angles P–Pd–N1 and P–Pd–N2 of 82.28(9) and 170.03(10)°, respectively. There are marginal changes for complex **2** compared to complex **1** with respect to the Pd1–P1 (2.2232(10) Å) and Pd1–C16 (2.042(4) Å) bond lengths, but the Pd1–N1 bond length (2.191(3) Å) is significantly smaller.

The Pd1–N2 bond length of 2.108(3) Å is typical for a palladium–sulfonamide bond.[26] Substitution of the halide co-ligand has occurred with retention of configuration around the palladium center, as the amide is coordinated *trans* to the phosphine donor. The amide nitrogen is trigonal planar [angle sum 359(4)°]. The aromaticity of the heterocycle is restored (C7) and the C6–C7 bond length of 1.500(6) Å is in the range for a C–C single bond. The solid state structure of this complex reveals intermolecular hydrogen bonding of two sulfonamide units to generate a dimeric conformation (Fig. 3).

Synthesis and characterization of Cu–amido species 4

Starting from complex **3**, [Cu(μ-Br)(**L1H**)]$_2$,[27] activation of the ligand backbone using KO^{t}Bu resulted in a characteristic color-change from light-yellow to deep-orange, concomitant with dearomatization of the pyridine ring (Scheme 3).[18b,c] *In situ* addition of DCl to this activated complex yielded a yellow solution, which displayed a broad signal at δ 40.1 in the ^{31}P NMR spectrum. Both the ^{1}H and ^{2}H NMR spectra displayed a multiplet at δ 3.80 for the –C*HD* (methylene) spacer, illustrating selective reversibility of the deprotonation process, also for Cu^{I}.

Analogously to the Pd case, addition of H_2NTf to this neutral copper(I) complex yielded a broad signal at δ 31.9 in the ^{31}P NMR spectrum. Also ^{1}H and ^{13}C NMR spectroscopic data were in accord with formulation of the resulting species as complex **4**, Cu(NHTf)(**L1H**). The pyridine ring has undergone rearomatization, with a doublet at δ 3.45 (J_{P-H} = 5.6 Hz) observable for the methylene spacer of the backbone. FAB-MS confirmed formation of Cu-complex **4**, since both the molecular ion peak [M + H] (*m*/*z* 462.0780) and the fragment peak [M − NHTf] (*m*/*z* 314.1277) were present. Rearomatization of the pyridine complex is also suggested by the bands at ν 1595 and 1572 cm^{-1} in the IR spectrum. The related NHTs-derived complex **4A** was also successfully prepared, as can be deduced from the spectroscopic data (*e.g.* $\delta(^{31}P)$ 35.3).

Single crystals of **4** were grown by slow evaporation of a concentrated CH_2Cl_2 solution of the yellow Cu–NHTf complex. The resulting molecular structure as obtained by X-ray crystal structure determination is depicted in Fig. 4. The copper center is in a highly distorted trigonal planar geometry (in-between the traditional Y-shape and the less common T-shape),[18a] as indicated by ∠P–Cu–N2 (87.48(5)°) and ∠P–Cu–N2 (151.37(5)°). The Cu–P and Cu–N distances are in accord with previous Cu(PNP) complexes[17] and related copper(I)–phosphine complexes.[28] From the long Cu–O2 distance of 3.2357(18) Å and the S–O–Cu angle of only 69.40(7)°, we can exclude κ^2-*N*,*O*-bonding of the trifluorosulfonamide fragment.[29] The C7 carbon bears two H atoms and the amido nitrogen only one, showing that activation of an N–H bond of H_2NTf can occur using this Cu(**L1H**) complex. In the solid state, complex **4** forms a centrosymmetric dimer through intermolecular H-bonding interactions of the N–H and S═O groups, as depicted in Fig. 5, with an intermolecular Cu···Cu distance of 7.9744(5) Å.

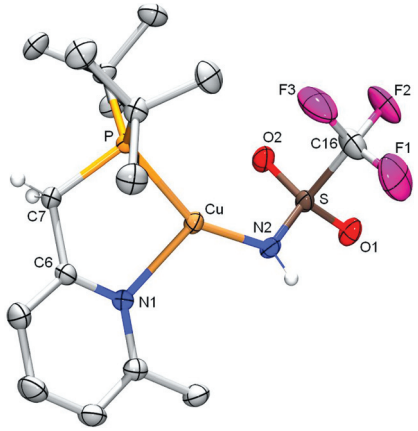


Fig. 4 ORTEP plot (50% probability displacement ellipsoids) of complex **4**, Cu(NHTf)(**L1H**). All hydrogen atoms, except for those located on C7 and N2, have been omitted for clarity. Selected bond lengths (Å), angles and torsion angles (°): Cu1–P1 2.1980(5); Cu1–N1 2.1694(14); Cu1–N2 1.9124(16); P1–C7 1.8467(17); N2–S1 1.5416(15); P1–Cu1–N1 87.48(5); P1–Cu1–N2 151.37(5); N1–Cu1–N2 121.13(6); Cu1–N2–S1 123.20(10); P1–C7–C6–N1 −36.6(2); Cu1–P1–C7–C6 32.52(13); Cu1–N1–C6–C7 19.25(19).

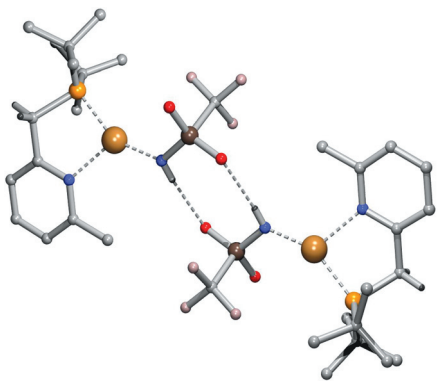


Fig. 5 Dimeric H-bonded structure of complex **4**, with a Cu···Cu [1 − *x*, 1 − *y*, 1 − *z*] distance of 7.9744(5) Å.

Conclusions

In summary, we have shown the improved synthesis of the (electron-rich) dialkylphosphinopyridine framework **L1H** and its coordination as a bidentate PN-ligand to $Pd(CH_3)(Cl)(cod)$, including a crystal structure for compound $Pd(CH_3)(Cl)$(**L1H**). Using a dearomatization–reprotonation strategy, utilizing the reactive backbone of **L1H**, selective activation of N–H bonds resulted in the formation of Pd^{II} or Cu^{I} metal–amido species. Although the exact mechanism of the N–H bond activation is still under investigation, the combined data as well as literature precedent on related tridentate analogues[14a,f,17] suggest a metal–ligand bifunctional pathway. It remains to be seen whether there are significant limitations in the *N*-based substrate scope in combination with first-row metals, given the working hypothesis of cooperative N–H bond rupture (on tri- as well as bidentate reactive ligand scaffolds), which implies coordination of the substrate to the metal center, resulting in efficient pre-activation of the N–H bond and subsequent proton-transfer.[30]

The solid state structures of complexes **2** and **4** show H-bonding interactions between the triflic amide N–H and S═O fragments, which leads to dimerization. The relative open and modular coordination sphere of these hybrid bidentate PN-ligands, especially compared to their rigid tridentate PNP analogues, brings about new avenues for stoichiometric and catalytic studies involving *e.g.* intra- and intermolecular amination reactions, including but not limited to the hydroamidation of alkynes.[31]

Experimental section

General

Solvents were either distilled over suitable drying agents or dried using an MBraun SPS (Solvent Purification System). All experiments were carried out under an inert-gas atmosphere using standard Schlenk techniques. The chemicals used were commercially available and used without further purification, unless described otherwise. The ^{1}H, $^{1}H\{^{31}P\}$, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 400, 162 and 100 MHz, respectively, on a Bruker AV400 spectrometer. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as a matrix. IR spectra (ATR) were recorded with a Bruker Alpha-p FT-IR spectrometer. $Pd(CH_3)Cl(1,5\text{-cod})$ was synthesized according to a literature procedure.[32]

Ligand L1H, 2-((di-*tert*-butylphosphino)methyl)-6-methylpyridine. This is an improved procedure, modified from two literature procedures.[33] Freshly distilled 2,6-lutidine (3.0 mL, 25.8 mmol) was dissolved in diethyl ether (35 mL) and then cooled to 0 °C, whereafter *n*-butyllithium (2.5 M solution in THF) (10.4 mL, 26.0 mmol) was added dropwise. The yellow-orange solution was stirred for 1 h at 0 °C and then cooled to −78 °C. Subsequently, di-*tert*-butylchlorophosphine (5.0 mL, 26.0 mmol) was added and the mixture stirred for an additional hour at −78 °C. After this, the yellow reaction mixture was allowed to warm up to room temperature and stirred for 18 h to give an orange suspension. The suspension was quenched with degassed water (40 mL) and extracted with diethyl ether (3 × 30 mL). The ether fractions were combined and dried over Na_2SO_4. Evaporation of the solvent gave a yellow-white oil. The remaining di-*tert*-butylchlorophosphine was removed *via* flash chromatography over basic alumina (10 : 1 hexane–ether), yielding the product as a white solid (4.59 g, 70.2%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.37 (d, J_H = 8 Hz, 1H, pyH), 7.20 (t, J_H = 7.6 Hz, 1H, pyH), 6.68 (d, J_H = 7.2 Hz, 1H, pyH), 3.21 (d, J_{PH} = 2.4 Hz, 2H, CH_2), 2.54 (s, 3H, CH_3), 1.23 (d, J_{PH} = 10.8 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, C_6D_6, ppm): δ 34.9 (s). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ 161.7 (d, J_{PC} = 14.4 Hz, pyC), 157.2 (s, pyC), 135.6 (s, pyCH), 120.6 (d, J_{PC} = 9.6 Hz, pyCH), 119.3 (s, pyCH), 32.0 (d, J_{PC} = 25.3 Hz, CH_2), 31.5 (d, J_{PC} = 23.8 Hz, ^{t}Bu-C), 29.5 (d, J_{PC} = 13.7 Hz, ^{t}Bu-CH_3), 24.3 (s, CH_3). HR-MS (FAB) ($C_{15}H_{26}NP$): *m*/*z* calcd, 252.1881; found, 252.1884. IR (ATR, cm^{-1}): 1592 (m), 1577 (m).

Complex 1, $Pd(CH_3)Cl(L1H)$. Adaptation of a literature procedure.[34] **L1H** (180.5 mg, 0.72 mmol) and $Pd(CH_3)Cl(1,5\text{-cod})$

(190.4 mg, 0.72 mmol) were dissolved in dichloromethane (5 mL) and the mixture was stirred at room temperature for 18 h. Then, the light-yellow solution was concentrated to approximately 0.5 mL and diethyl ether (10 mL) was added under vigorous stirring. The precipitate was collected by cannula-filtration and washed with diethyl ether (3 × 5 mL). The product was obtained as an off-white powder (277.8 mg, 94.8%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (t, J_H = 8 Hz, 1H, pyH), 7.17 (d, J_H = 8 Hz, 1H, pyH), 7.09 (d, J_H = 7.6 Hz, 1H, pyH), 3.51 (d, J_{PH} = 10 Hz, 2H, CH_2), 3.16 (s, 3H, CH_3), 1.33 (d, J_{PH} = 14 Hz, 18H, ^{t}Bu-H), 1.04 (d, J_{PdH} = 1.6 Hz, 3H, Pd-CH_3). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): δ 72.8 (s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.5 (s, pyC), 158.2 (d, J_{PC} = 2.4 Hz, pyC), 137.8 (s, pyCH), 123.9 (s, pyCH), 119.9 (d, J_{PC} = 7.5 Hz, pyCH), 35.6 (d, J_{PC} = 16.6 Hz, ^{t}Bu-C), 35.2 (d, J_{PC} = 20.2 Hz, CH_2), 29.4 (d, J_{PC} = 4 Hz, ^{t}Bu-CH_3), 27.5 (s, CH_3), −8.6 (s, Pd-CH_3). HR-MS (FAB) ($C_{16}H_{29}ClNPPd$): *m/z* calcd, 407.0761, 372.1079 (M − Cl); found, 372.1076 (M − Cl). IR (ATR, cm^{-1}): 1600 (m), 1572 (m).

Complex Y, Pd(CH_3)(L1)(PMe_3). To a suspension of complex **1** (47.3 mg, 0.116 mmol) in THF was added KO^{t}Bu (1 M solution in THF) (0.12 mL, 0.116 mmol) at room temperature and the mixture, which became red immediately, was stirred for 5 min. Then, trimethylphosphine (1 M solution in toluene) (0.12 mL, 0.116 mmol) was added and the color of the solution changed to dark-red. The reaction was left stirring for 2 h before the solvent was removed *in vacuo*. The product was obtained as a red powder (44.8 mg, 86.2 %). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 6.60 (ddd, J_H = 8.8 Hz, J_H = 6.4 Hz, J_{PH} = 2.4 Hz, 1H, pyH), 6.26 (d, J_H = 8.8 Hz, 1H, pyH), 5.56 (d, J_H = 6.4 Hz, 1H, pyH), 3.37 (d, J_H = 7.6 Hz, 1H, CH), 2.09 (s, 3H, CH_3), 1.42 (d, J_{PH} = 13.2 Hz, 18H, ^{t}Bu-H), 0.77 (d, J_{PH} = 8.0 Hz, 9H, P(CH_3)$_3$), 0.56 (dd, J_{P1H} = 3.6 Hz, J_{P2H} = 9.6, 3H, Pd-CH_3). ^{31}P NMR (162 MHz, C_6D_6, ppm): δ 68.8 (d, $^2J_{PP}$ = 439 Hz, P1), −23.2 (d, $^2J_{PP}$ = 439 Hz, P2). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ 172.8 (d, J_{PC} = 23.2 Hz, 1C, pyC), 154.2 (s, 1C, pyC), 132.9 (s, 1C, pyCH), 111.9 (d, J_{PC} = 19.3 Hz, 1C, pyCH), 102.4 (s, 1C, pyCH), 36.7 (d, J_{PC} = 22.7 Hz, 2C, ^{t}Bu-C), 32.3 (s, 1C, CH), 29.4 (d, J_{PC} = 6.7 Hz, 2C, ^{t}Bu-CH_3), 27.5 (s, 1C, CH_3), 13.6 (d, J_{PC} = 26.8 Hz, 3C, P(CH_3)$_3$), −13.3 (d, J_{PC} = 12.1 Hz, 1C, Pd-CH_3). HR-MS (FAB) ($C_{16}H_{29}ClNPPd$): *m/z* calcd, 448.1522; found, 448.1522.

Complex 2, Pd(CH_3)(NHTf)(L1H). To a suspension of complex **1** (63.8 mg, 0.16 mmol) in THF (15 mL) was added KO^{t}Bu (1 M solution in THF) (0.16 mL, 0.16 mmol) at room temperature and the mixture, which became dark red immediately, was stirred for 5 min. Then, triflic amine (23.3 mg, 0.16 mmol) was added and the color of the mixture changed to yellowish brown. The reaction was left stirring for 2 h before the solvent was removed *in vacuo*. After addition of toluene (10 mL), the solution was filtered and evaporated. The product was obtained as a sand-brown powder (30.0 mg, 36.8%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 7.75 (t, J_H = 7.6 Hz, 1H, pyH), 7.44 (d, J_H = 7.6 Hz, 1H, pyH), 7.23 (d, J_H = 7.6 Hz, 1H, pyH), 3.80 (d, J_{PH} = 10.0 Hz, 2H, CH_2), 2.99 (s, 3H, CH_3), 2.23 (s, 1H, NH), 1.34 (d, J_{PH} = 13.6 Hz, 18H, ^{t}Bu-H), 0.68 (d, J_{PH} = 1.6 Hz, 3H, Pd-CH_3). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 75.2 (s). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, ppm): δ 161.2 (s, 1C, pyC), 159.1 (s, 1C, pyC), 138.1 (s, 1C, pyCH), 123.4 (s, 1C, pyCH), 120.5 (d, J_{PC} = 10.4 Hz, 1C, pyCH), 35.1 (d, J_{PC} = 23.9 Hz, 2C, ^{t}Bu-C), 34.5 (d, J_{PC} = 29.5 Hz, 1C, CH_2), 28.6 (d, J_{PC} = 5.9 Hz, 6C, ^{t}Bu-CH_3), 26.0 (s, 1C, CH_3), −10.7 (s, 1C, Pd-CH_3). HR-MS (FAB) ($C_{17}H_{30}F_3N_2O_2PPdS$): *m/z* calcd, 520.0753, 505.0524 (M − NHTf), 372.1072 (M − Cl); found, 505.0529 (M − NHTf), 372.1089 (M − Cl). IR (ATR, cm^{-1}): 1600 (m), 1564 (m).

Complex 2A, Pd(CH_3)(NHTs)(L1H). This product is synthesized in the manner as complex **2** from complex **1** (69.4 mg, 0.17 mmol), KO^{t}Bu (1 M solution in THF) (0.17 mL, 0.17 mmol) and tosyl amine (29.2 mg, 0.17 mmol), and is obtained as a sand-brown powder (78.3 mg, 84.8%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 7.72 (t, J_H = 7.6 Hz, 1H, pyH), 7.62 (d, J_H = 8 Hz, 2H, TsH), 7.41 (d, J_H = 9.2 Hz, 1H, pyH), 7.17 (d, J_H = 7.2 Hz, 1H, pyH), 7.10 (d, J_H = 8 Hz, 2H, TsH), 3.69 (d, J_{PH} = 9.6 Hz, 2H, CH_2), 3.11 (s, 3H, CH_3), 2.31 (s, 3H, TsCH_3), 2.23 (s, 1H, NH), 1.21 (d, J_{PH} = 13.2 Hz, 18H, ^{t}Bu-H), 0.36 (d, J_{PH} = 2.4 Hz, 3H, Pd-CH_3). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 73.5 (s). HR-MS (FAB) ($C_{23}H_{37}N_2O_2PPdS$): *m/z* calcd, 542.1348, 527.1113 (M − Me), 372.1072 (M − NHTs); found, 527.1121 (M − Me), 372.1075 (M − NHTs). IR (ATR, cm^{-1}): 1601 (m), 1576 (m).

Complex 2B, Pd(CH_3)($NHAr^{F5}$)(L1H). To a suspension of complex **1** (44.4 mg, 0.109 mmol) in THF was added KO^{t}Bu (1 M solution in THF) (0.11 mL, 0.109 mmol) at room temperature and the mixture, which became red immediately, was stirred for 5 min. Then, 2,3,4,5,6-pentafluoroaniline (H_2NAr^{F5}) (20 mg, 0.109 mmol) was added and the reaction was left stirring for 0.5 h before the solvent was removed *in vacuo*. The product was obtained as an orange powder (45.2 mg, 74.8 %). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 6.74 (t, J_H = 7.6 Hz, 1H, pyH), 6.32 (d, J_H = 7.6 Hz, 1H, pyH), 6.28 (d, J_H = 7.6 Hz, 1H, pyH), 3.04 (br s, 1H, NH), 2.84 (s, 3H, CH_3), 2.77 (d, J_{PH} = 9.6 Hz, 2H, CH_2), 0.97 (d, J_{PH} = 3.2 Hz, 3H, Pd-CH_3), 0.89 (d, J_{PH} = 13.2 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, C_6D_6, ppm): δ 67.4 (s). ^{13}C NMR (100 MHz, C_6D_6, ppm): δ 161.8 (s, 1C, pyC), 158.9 (s, 1C, pyC), 140.4 (s, 2C, aniline-CF), 139.6 (s, 2C, aniline-CF), 138.0 (s, 1C, aniline-CF), 137.2 (s, 1C, aniline-C), 136.9 (s, 1C, pyCH), 123.2 (s, 1C, pyCH), 119.5 (d, J_{PC} = 7.4 Hz, 1C, pyCH), 34.2 (d, J_{PC} = 18.4 Hz, 1C, CH_2), 33.9 (d, J_{PC} = 15.7 Hz, 2C, ^{t}Bu-C), 28.7 (d, J_{PC} = 4.4 Hz, 6C, ^{t}Bu-CH_3), 24.9 (s, 1C, CH_3), −9.1 (s, 1C, Pd-CH_3). ^{19}F NMR (282 MHz, C_6D_6, ppm): δ −166.8 (m), −169.7 (m), −190.2 (m). HR-MS (FAB) ($C_{22}H_{30}F_5N_2PPd$): *m/z* calcd, 554.1102, 539.0875 (M − Me), 372.1072 (M − H_2NAr^{F5}); found, 539.0872 (M − Me), 372.1403 (M − H_2NAr^{F5}). IR (ATR, cm^{-1}): 1601 (m), 1573 (m).

Complex 3, $[CuBr(L1H)]_2$. This product is prepared by using a literature procedure.[27] A solution of **L1H** (458.5 mg, 1.82 mmol) in Et_2O (10 mL) was added to a suspension of $CuBrSMe_2$ (374.9 mg, 1.82 mmol) in Et_2O (20 mL) by a cannula at room temperature. The light yellow solution was stirred for 16 h before all volatiles were removed *in vacuo* and the product was obtained as a light-yellow powder in quantitative yield (716.7 mg, 99.5%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm):

δ 7.70 (t, J_H = 7.6 Hz, 1H, pyH), 7.36 (d, J_H = 7.2 Hz, 1H, pyH), 7.20 (d, J_H = 6.8 Hz, 1H, pyH), 3.39 (d, J_{PH} = 7.6 Hz, 2H, CH_2), 2.98 (s, 3H, CH_3), 1.31 (d, J_{PH} = 12.8 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 26.6 (br s). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, ppm): δ 159.9 (d, J_{PC} = 17.1 Hz, pyC), 138.7 (s, pyCH), 134.5 (s, pyC), 122.8 (s, pyCH), 122.5 (s, pyCH), 33.5 (d, J_{PC} = 7.8 Hz, ^{t}Bu-C), 31.1 (d, J_{PC} = 11 Hz, CH_2), 28.2 (d, J_{CH} = 10.8 Hz, ^{t}Bu-CH_3), 26.3 (s, CH_3). HR-MS (FAB) ($C_{30}H_{52}Br_2Cu_2N_2P_2$): *m/z* calcd, 790.0530; found, 790.0530. IR (ATR, cm^{-1}): 1593 (m), 1572 (m).

Complex 4, Cu(NHTf)(L1H). To a suspension of complex **3** (32.4 mg, 0.04 mmol) in diethyl ether (30 mL) was added KO^{t}Bu (1 M solution in THF) (0.08 mL, 0.08 mmol) at room temperature and the mixture, which became orange immediately, was stirred for 5 min. Then, triflic amine (12.2 mg, 0.08 mmol) was added and the color of the mixture changed to yellow-brown. The reaction was left stirring for 2 h before the solvent was removed *in vacuo* to leave the product as a pale yellow solid (26.4 mg, 70.0%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 7.75 (t, J_H = 7.6 Hz, 1H, pyH), 7.42 (d, J_H = 7.6 Hz, 1H, pyH), 7.42 (d, J_H = 8 Hz, 1H, pyH), 3.45 (d, J_{PH} = 8 Hz, 2H, CH_2), 2.77 (s, 3H, CH_3), 2.46 (s, 1H, NH), 1.29 (d, J_{PH} = 13.6 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 31.9 (s). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, ppm): δ 159.0 (d, J_{PC} = 2.1 Hz, 1C, pyC), 158.1 (d, J_{PC} = 2.3 Hz, 1C, pyC), 138.1 (s, 1C, pyCH), 122.0 (d, J_{PC} = 3.8 Hz, 1C, pyCH), 121.8 (d, J_{PC} = 2.5 Hz, 1C, pyCH), 120.0 (s, 1C, CF_3), 32.1 (d, J_{PC} = 11.1 Hz, 2C, ^{t}Bu-C), 29.7 (d, J_{PC} = 16.2 Hz, 1C, CH_2), 28.5 (s, 6C, ^{t}Bu-CH_3), 24.5 (s, 1C, CH_3). HR-MS (FAB) ($C_{16}H_{27}CuF_3N_2O_2PS$): *m/z* calcd, 462.0779, 314.1099 (M − NHTf); found, 462.0780, 314.1277 (M − NHTf). IR (ATR, cm^{-1}): 1595 (m), 1572 (m).

Complex 4A, Cu(NHTs)(L1H). This product was synthesized in the same manner as complex **4** from complex **3** (96.6 mg, 0.12 mmol), KO^{t}Bu (1 M solution in THF) (0.24 mL, 0.24 mmol) and tosyl amine (41.8 mg, 0.24 mmol), and was obtained as a pale brown powder (63.5 mg, 53.6%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 7.82 (d, J_H = 8 Hz, 1H, TsH), 7.64 (t, J_H = 7.6 Hz, 1H, pyH), 7.32 (d, J_H = 7.6 Hz, 1H, pyH), 7.18 (d, J_H = 8 Hz, 1H, TsH), 7.12 (d, J_H = 8 Hz, 1H, pyH), 3.26 (d, J_{PH} = 5.6 Hz, 2H, CH_2), 2.56 (s, 3H, CH_3), 2.45 (s, 1H, NH), 2.34 (s, 3H, $TsCH_3$), 1.21 (d, J_{PH} = 12.4 Hz, 18H, ^{t}Bu-H). ^{31}P NMR (162 MHz, $(CD_3)_2CO$, ppm): δ 35.3 (br s). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, ppm): δ 159.3 (s, pyC), 157.7 (s, pyC), 138.5 (s, TsC), 137.3 (s, pyCH), 128.0 (s, TsCH), 125.6 (s, TsCH), 121.4 (d, J_{PC} = 5.2 Hz, pyCH), 121.0 (s, pyCH), 31.9 (d, J_{PC} = 2.6 Hz, ^{t}Bu-C), 30.1 (d, J_{PC} = 5.2 Hz, CH_2), 28.7 (J_{PC} = 9.4 Hz, ^{t}Bu-CH_3), 24.0 (s, CH_3), 20.1 (s, $TsCH_3$). IR (ATR, cm^{-1}): 1590 (m), 1576 (m).

X-ray crystallography. X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K. Intensity data were integrated with the Saint software.[35] Absorption correction and scaling was performed with SADABS or TWINABS.[36] The structures were solved with direct methods using the program SHELXS-97[37] and refined with SHELXL-97[37] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions (complex **1**) or located in difference Fourier maps (complexes **2** and **4**). C–H hydrogen atoms were refined with a riding model, N–H hydrogen atoms were refined freely with isotropic displacement parameters. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[38]

Details for complex 1. $C_{16}H_{29}ClNPPd$, Fw = 408.22, yellow block, 0.26 × 0.18 × 0.08 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 10.0545(3), b = 15.8268(5), c = 11.3903(4) Å, β = 91.6010 (10)°, V = 1811.84(10) Å^3, Z = 4, D_x = 1.497 g cm^{-3}, μ = 1.25 mm^{-1}. 49 119 Reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 4161 Reflections were unique (R_{int} = 0.022), of which 3706 were observed [$I > 2\sigma(I)$]. 189 Parameters were refined with no restraints. Minor disorder between chlorine and methyl has been ignored. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0206/0.0475. R_1/wR_2 [all refl.]: 0.0263/0.0508. S = 1.108. Residual electron density between −0.35 and 0.48 e Å^{-3}. CCDC 861127.

Details for complex 2. $C_{17}H_{30}F_3N_2O_2PPdS$, Fw = 520.86, brown plate, 0.50 × 0.40 × 0.15 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 9.8419(3), b = 10.8652(3), c = 11.6779(4) Å, α = 109.9870(15), β = 99.6665(15), γ = 101.8868(15)°, V = 1109.16(6) Å^3, Z = 2, D_x = 1.560 g cm^{-3}, μ = 1.04 mm^{-1}. The crystal was cracked into two fragments related by a rotation of 7.1° about an arbitrary axis. This was taken into account during the integration, which resulted in a file in HKLF5 format.[39] 36 399 Reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 5033 Reflections were unique (R_{int} = 0.050), of which 4207 were observed [$I > 2\sigma(I)$]. 257 Parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0432/0.1061. R_1/wR_2 [all refl.]: 0.0579/0.1148. S = 1.067. Residual electron density between −1.03 and 1.74 e Å^{-3}. CCDC 861128.

Details for complex 4. $C_{16}H_{27}CuF_3N_2O_2PS$, Fw = 462.97, green plate, 0.28 × 0.16 × 0.06 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 10.6306(5), b = 10.8516(5), c = 11.2839(5) Å, α = 110.4196(13), β = 93.6403(14), γ = 117.9401(12)°, V = 1036.42(8) Å^3, Z = 2, D_x = 1.484 g cm^{-3}, μ = 1.27 mm^{-1}. The crystal was cracked into two fragments related by a rotation of 6.1° about an arbitrary axis. This was taken into account during the integration, which resulted in a file in HKLF5 format.[39] 38 810 Reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. 4715 Reflections were unique (R_{int} = 0.035), of which 3863 were observed [$I > 2\sigma(I)$]. 247 Parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0269/0.0606. R_1/wR_2 [all refl.]: 0.0417/0.0650. S = 1.016. Residual electron density between −0.24 and 0.45 e Å^{-3}. CCDC 861129.

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