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New bulky phosphinopyridine ligands. P~N~C Tridentates in palladium complexes

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The sterically bulky pyridinyl phosphine (**P~N**) ligands have been prepared from the phosphinylation of 2,4-di-*tert*-butyl-6-methylpyridine. Due to the steric hindrance, substitution reaction of these **P~N** ligands with (COD)PdMeCl yields the chloro-bridged dipalladium species $[(\mathbf{P\sim N})_2Pd_2Me_2Cl_2]$, in which the **P~N** ligand acts as a monodentate. Treatment of these dimeric palladium compounds with $AgBF_4$ in the presence of acetonitrile gives the corresponding C–H activation metal complex $[(\mathbf{P\sim N\sim C})Pd(CH_3CN)]BF_4$. Both spectral and X-ray single-crystal characterization of these palladium complexes are presented.

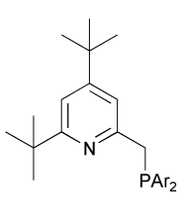
Introduction

There is considerable current interest in the design of mixed donor phosphine–amine ligands because of their potential importance in the catalysis of organic transformations[1] and also in polymerization.[2] This interest is based on the modification of the auxiliary ligand to fine-tune the property of catalysts for better control. Due to the soft and hard nature of phosphorus and nitrogen donors, respectively, study of phosphine–imine bidentates on either coordination or metal catalyzed organic transformations has received much attention.[3–33] Among these known P~N bidentates, few are known as sterically bulky ones.[29] In this work, we present the preparation of new bulky P~N ligands and their coordination behavior toward palladium(II) ions.

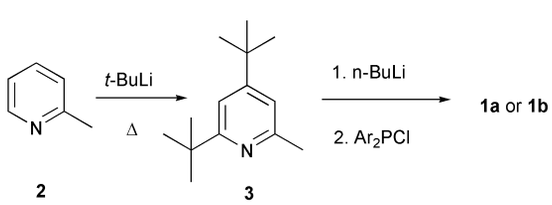
Results and discussion

Ligand synthesis

Synthesis of the desired phosphine ligands is summarized in Scheme 1. Starting with picoline **2**, nucleophilic aromatic substitution with an excess of *tert*-butyllithium provided the di-*tert*-butyl substituted picoline **3**.[34] Deprotonation followed by the treatment with diarylchlorophosphine yielded the corresponding pyridine based phosphine **1a** and **1b**, respectively. These ligands are air-sensitive compounds, which were handled under an inert atmosphere of nitrogen with standard inert atmosphere techniques. Characterization of these new **P~N** bidentates was performed by spectroscopic methods. In addition to the characteristic shifts for the substituents on ^{1}H NMR spectra, all ligands exhibit singlets in their ^{31}P NMR spectra and all shifts appear around −17 to 30 ppm relative to 85% H_3PO_4 in the typical range for diarylalkylphosphines.



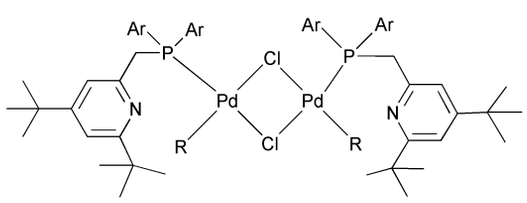
1a Ar = 2,4,6-$(Me)_3C_6H_2$
1b Ar = 2-MeC_6H_4



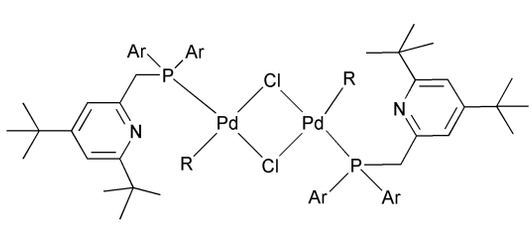
Scheme 1 Preparation of **P~N** ligands.

Palladium complexes with 1

Substitution reaction of [(COD)PdMeCl] with an equimolar amount of **1a**,**b** resulted in the formation of the corresponding complex immediately. A positive coordination chemical shift on ^{31}P NMR clearly indicates the coordination of the phosphorus donor toward the palladium center (Table 1). The downfield shift of ^{1}H NMR signals of CH_2P implies the possibility of the chelation of **P~N** donors. However, the shifts of *tert*-butyl groups appears not to significantly change, suggesting a free donor pyridinyl nitrogen atom. This observation was verified by X-ray single crystal analysis. Instead of a bidentate, the **P~N** ligand behaves in a monodentate mode with only the phosphine coordinated to the metal center. However, ligands **1a** and **1b** provide the corresponding complexes **4a** and **4b** in different stereochemistry (see below). The ^{1}H signal for Pd–CH_3 of **4a** shows P–H coupling (3.1 Hz), but this is not seen in **4b** for unknown reasons.



4a Ar = 2,4,6-$(Me)_3C_6H_2$-, R = Me
5a Ar = 2,4,6-$(Me)_3C_6H_2$-, R = MeCO



4b Ar = 2-MeC_6H_4-, R = Me
5b Ar = 2-MeC_6H_4-, R = MeCO

As shown in Fig. 1 and 2, chloro-bridged palladium ions with the nitrogen donor uncoordinated appear in both complexes **4a**,**b**. All metal centers are typically square planar in both com-

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Table 1 Selected spectral data of ligands and palladium complexes

Compound	^{1}H NMR [a]			^{31}P NMR
	CH_2P	Bu^t	Pd–CH_3 or Pd–$COCH_3$	
1a	3.99 (d, J = 2.1)	1.25, 1.05		−17.0
1b	4.03 (d, J = 2.4)	1.28, 1.17		−19.3
4a	4.19 (d, J = 11.4)	1.20, 1.16	1.43 (d, J = 3.1)	27.0
4b	4.14 (d, J = 10.1)	1.20, 1.15	0.53	31.5
5a	4.24 (d, J = 11.6)	1.24, 1.04	2.04	16.5
5b	4.05 (d, J = 9.9)	1.28, 1.25	1.56	21.9

[a] In $CDCl_3$ except for **1b** (in CD_3COCD_3).

Table 2 Selected bond distances (Å) and angles (°) for **4a**, **4b** and **5b**

Complex	**4a**	**4b**	**5b**
Pd(1)–P(1)	2.2630(9)	2.2279(9)	2.291(1)
Pd(1A)–P(1A)	2.269(1)	2.2279(9)	2.291(1)
Pd(1)–Cl(1)	2.465(1)	2.3931(9)	2.428(1)
Pd(1A)–Cl(1A)	2.039(4)	2.3931(9)	2.428(1)
Pd(1)–C(1)	2.034(4)	2.033(4)	1.968(5)
Pd(1A)–C(1A)	2.039(4)	2.033(4)	1.968(5)
Pd(1)–Cl(1A)	2.391(1)	2.481(1)	2.539(1)
Pd(1A)–Cl(1)	2.490(1)	2.481(1)	2.539(1)
P(1)–C(19)	1.887(4)	1.858(4)	1.848(4)
C(1)–Pd(1)–P(1)	90.2(1)	91.1(1)	89.8(2)
C(1A)–Pd(1A)–P(1A)	90.3(1)	91.1(1)	
C(1)–Pd(1)–Cl(1)	171.2(1)	89.6(1)	85.1(2)
C(1A)–Pd(1A)–Cl(1A)	86.9(2)	89.6(1)	
Pd(1)–Cl(1)–Pd(1A)	93.63(3)	93.60(3)	95.84(4)
Pd(1)–Cl(1A)–Pd(1A)	98.10(4)	93.60(3)	

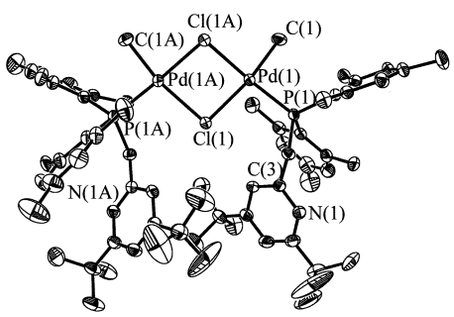


Fig. 1 ORTEP plot of complex **4a**.

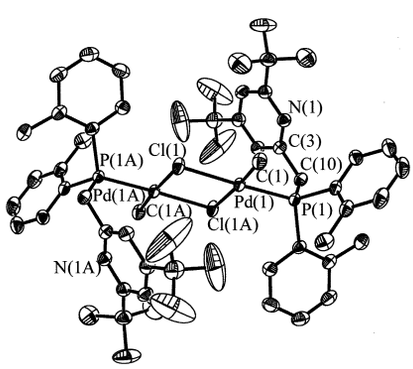


Fig. 2 Molecular structure of complex **4b**.

plexes with slight distortions as evidenced by the bond angles slightly deviating from 90°. Selected bond distances and bond angles are listed in Table 2. All bond distances and bond angles lie within the normal range even for **4a** with the bulky substituents being in *cis* arrangement. Distances of Pd–Cl bonds *trans* to carbon ligands appear to be longer than those *trans* to phosphine. The bulky pyridinyl groups appeared to be staggered to each other in Fig. 1, which it is believed is due to the crystal packing. In fact the ^{1}H NMR shifts of the *tert*-butyl groups remain the same as for the free ligands. Interestingly, complex **4a** was formed in a sterically congested fashion with the two bulky dimesitylphosphino groups positioned *cis* to each other, whereas the less steric bulky phosphino groups are in *trans* form for **4b**. In either instance, only one single isomer was formed out of the two possibilities. This outcome is similar to that in $[Pd_2(\mu\text{-}Cl)_2Me_2(PPh_2Me)]$ reported by Ladipo and Anderson.[35]

Treatment of **4a** and **4b** with carbon monoxide provided the corresponding chloro-bridged dipalladium acetyl complexes **5a** and **5b**, respectively, as evidenced by spectral data. ^{31}P NMR spectra of the carbonylated products shift to upper field relative to the starting materials, as typically observed for related species. ^{1}H NMR signals at 2.04 ppm for **5a** and 1.56 ppm for **5b** as well as the IR absorptions at 1730 cm^{-1} for **5a** and 1720 cm^{-1} for **5b** clearly illustrate the formation of the acetyl palladium complexes.

In the carbonylation reaction, there is no indication of the formation of any mononuclear species. Crystals suitable for X-ray analysis of complex **5b** were obtained. Fig. 3 shows its ORTEP drawing and selected bond distances and angles are also summarized in Table 2. Basically the structural framework is similar to that of **4b** except the replacement of methyl by the acetyl group. It is also noticed that the stereorelationship of the two acetyl groups remains *trans* as in **4b**.

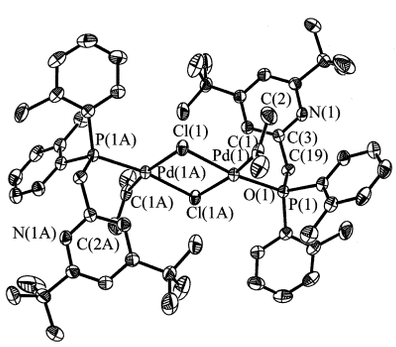


Fig. 3 ORTEP drawing of the palladium acetyl complex **5b**.

It has been illustrated that the related **P~N** ligand [2-(Ph_2-PCH_2)C_5H_4N] shows a chelating **P~N** nature with palladium ions.[36] Apparently, ligands designed in this work act as monodenate towards [(COD)PdMeCl] due to the steric hindrance of the *tert*-butyl group.

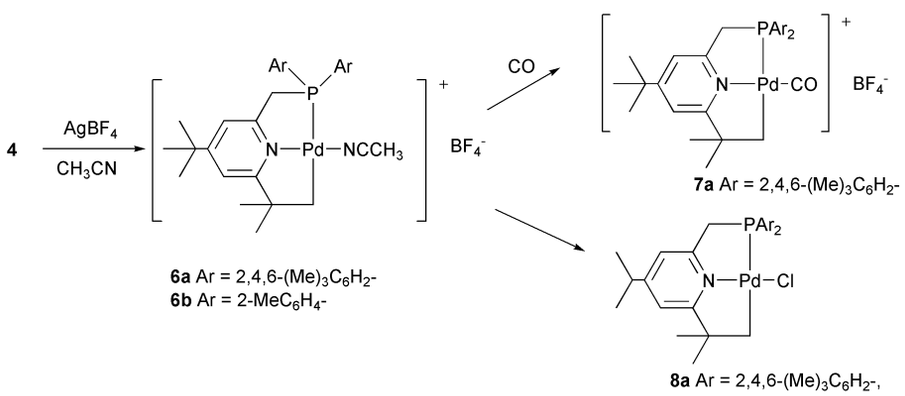
Intramolecular C–H activation

Treatment of **4a** with silver tetrafluoroborate in acetonitrile at room temperature gave an unexpected result. A new resonance at 2.83 (d, J_{PH} = 3.3 Hz, 2H) appears with the vanishing of the *ortho tert*-butyl group in the ^{1}H NMR spectrum, indicating the formation of a metallated CH_2 group. Complex **4b** behaves similarly (Scheme 2). Although both ^{1}H and ^{13}C NMR spectra give unambiguously the structural determination for the C–H

Table 3 Crystal data for **4a**, **4b**, **5b** and **6b**[a]

Complex	**4a**	**4b**	**5b**	**6b**
Formula	$C_{66}H_{94}Cl_2N_2P_2Pd_2$	$C_{29}H_{39}$ ClNPPd	$C_{60}H_{78}Cl_2N_2O_2P_2Pd_2$	$C_{30}H_{38}BF_4N_2PPd$
M_w	1261.07	574.43	1204.88	650.80
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	11.5490(1)	9.7940(1)	12.3940(2)	9.4710(2)
b/Å	16.1300(1)	12.2410(1)	16.7220(3)	12.1480(3)
c/Å	17.9020(2)	13.1120(2)	15.0540(2)	14.1510(4)
α/°	94.554(1)	75.428(1)	90	104.090(1)
β/°	101.601(1)	72.473(1)	106.559(1)	94.389(1)
γ/°	91.325(1)	72.846(1)	90	103.300(1)
V/Å^3	3253.83(5)	1409.27(3)	2990.58(8)	1521.56(7)
Z	2	2	2	2
D_c/Mg m^{-3}	1.287	1.354	1.338	1.420
F(000)	1320	596	1248	668
Crystal size/mm	0.25 × 0.20 × 0.15	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.15	0.15 × 0.20 × 0.25
θ range/°	2.16–25.00	2.20–25.00	1.71–25.00	2.00–25.00
Reflns. collected	21494	9383	14733	21100
Independent reflns. (R_{int})	11445 (0.0299)	4972 (0.0211)	5266 (0.0485)	5334 (0.0383)
R_1 [$I > 2\sigma(I)$]	0.0437	0.0408	0.0436	0.0498
wR_2	0.1219	0.1297	0.1097	0.1486

[a] Refinement method: full-matrix least squares on F^2.



Scheme 2 C–H Activation and ligand substitution reactions.

activation product, an X-ray diffraction study of **6b** further confirmed the proposed structure. An ORTEP view of **6b** is shown in Fig. 4. The crystal data for complex **6b** are summarized in Table 3. As expected, the palladium center displays a slightly distorted square-planar geometry with phosphorus, nitrogen as well as carbon donors from ligand **1b** and acetonitrile. All bond distances and bond angles lie within normal ranges. The Pd–C(9) bond length [2.041(4) Å] is slightly longer by about 0.04 Å than that of the related species **10** reported by Minghetti and coworkers.[37] Presumably this is due to the *trans* influence of phosphorus *versus* nitrogen donors. As for the angles C(9)–Pd(1)–N(1) [80.9(2)°] and N(1)–Pd(1)–P(1) [83.71(9)°], deviation from 90° indicate these chelating rings have a high strain energy.

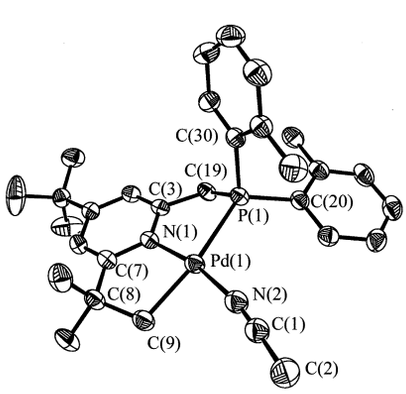
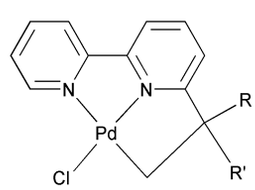


Fig. 4 ORTEP plot of **6b**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.390(1), Pd(1)–C(9) 2.041(4), Pd(1)–N(1) 1.996(3), Pd(1)–N(2) 2.014(4); C(9)–Pd(1)–P(1) 164.1(1); N(1)–Pd(1)–N(2) 169.2(1), N(1)–Pd(1)–C(9) 80.9(2), N(2)–Pd(1)–C(9) 88.6(2), N(1)–Pd(1)–P(1) 83.71(9).



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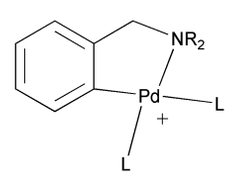
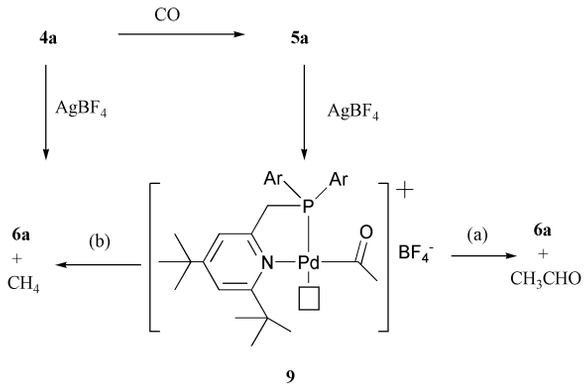


11

Concerning the C–H activation, reaction of **5a** with $AgBF_4$ gave a similar result, but accompanied with the formation of methane and acetaldehyde as evidenced by the NMR spectrum. Apparently the abstraction of chloride from the palladium complexes readily generates the free coordination sites, which allows the coordination of nitrogen and C–H activation to take place. Upon the treatment of **5a** with $AgBF_4$, the tricoordinated species **9** was the possible intermediate (Scheme 3), which then underwent either C–H activation and reductive elimination of acetaldehyde (path a) or the de-insertion of carbonyl group followed by C–H activation and reductive elimination of methane (path b).

In fact, the C–H activation reaction depends on the reaction temperature. Fig. 5 shows variable-temperature ^{1}H NMR spectra for the reaction of complex **4a** with an equimolar amount of $AgBF_4$ in CD_3CN. At −30 °C, the *tert*-butyl groups



Scheme 3

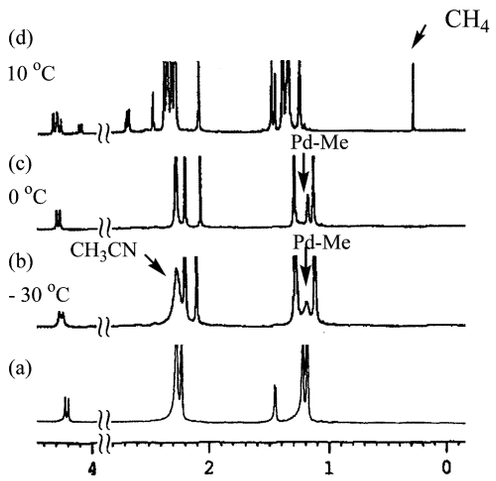


Fig. 5 (a) Partial ^{1}H NMR spectrum of **4a** and partial ^{1}H NMR spectra upon addition of $AgBF_4$ to **4a** in the presence of CH_3CN at (b) −30 °C, (c) 0 °C and (d) 10 °C.

remain intact with the signal of Pd–CH_3 up-field shifted relative to the chloro-bridged species (Fig. 5(b)). As the temperature increases, the signal of the Pd–CH_3 becomes sharper as the exchange of actonitrile becomes faster. (Fig. 5(c)) Above 0 °C, C–H activation takes place as evidenced by the decrease in the Pd–CH_3 signal intensity and the appearance of a new signal corresponding to methane (Fig. 5(d)). This observation suggests that the removal of chloride ligand readily helps the coordination of the pyridinyl nitrogen donor toward the palladium center at lower temperature and the C–H activation takes place above 0 °C to form **6a**.

The coordinating acetonitrile of **6** is easily substituted by carbon monoxide and chloride to yield the corresponding complexes **7a** and **8a** (Scheme 2). However, migratory insertion of CO does not occur in these complexes even at elevated temperature or pressure. This is quite unlike the behaviour of the palladium complex **11** reported by Herrmann and coworkers,[38] presumably due to the stable fused five-membered chelating rings.

In summary, the *tert*-butyl group at the α position of the pyridine ring hinders the coordination of the nitrogen donor towards the metal center. However, C–H activation of the *tert*-butyl group readily occurs to relieve the steric interaction, which allows the **P~N** ligand to become a **P~C~N** tridentate. The catalytic activity of these palladium complexes are currently under investigation.

Experimental

General information

All reactions, manipulations and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or d_6-acetone on either a Bruker AC-E 200 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^{1}H and ^{13}C NMR spectra and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Due to the complication of the aromatic region, only chemical shifts of non-aromatic carbons are reported. IR spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pallets, unless otherwise noted.

Ligand 1a

To a THF solution (10 mL) of compound **3** (1.3 g, 6.3 mmol) was slowly added a hexane solution of *n*-butyllithium (2.5 M, 2.53 mL, 6.3 mmol) at ice-cold temperature. After stirring for 1 h, a solution of bis(2,4,6-trimethylphenyl)chlorophosphine (1.67 M in 3.83 mL THF, 6.4 mmol) was added to the above solution at −78 °C. The reaction mixture was stirred at room temperature for 3 h. Upon concentration, the residue was extracted with pentane and the extracts were filtrated through Celite. The filtrate was concentrated to give a light yellow viscous liquid, which was dissolved in methanol. The desired phosphine was crystallized as a white solid (1.79 g, 60%): mp 129–130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.96 (s, 1H, py-H^5), 6.65 (s, 4H, Ar-H), 6.24 (s, 1H, py-H^3), 3.99 (d, J = 2.08 Hz, 2H, CH_2), 2.16 (s, 6H, Ar–CH_3), 2.10 (s, 12H, Ar–CH_3), 1.25 (s, 9H, Bu^t), 1.05 (s, 9H, Bu^t). ^{31}P NMR: δ −17. ^{13}C NMR: δ 168.0, 158.9, 156.3 (d, J = 6.6 Hz), 141.8 (d, J = 13.6 Hz), 137.1, 132.9 (d, J = 24.8 Hz), 129.6, 118.2 (d, J = 6.1 Hz), 112.6, 37.9 (d, J = 20.9 Hz, py–CH$_2$), 38.3, 34.3, 34.2 (d, J = 16.6 Hz), 29.9, 22.8 (d, J = 13.0 Hz), 20.7. HR-FAB MS: calc. for $C_{32}H_{44}PN$: m/z 473.3211. Found: 473.3212. Anal. Calc. for $C_{32}H_{44}NP$: C, 81.84; H, 9.36; N, 2.96. Found: C, 81.29; H, 9.60; N, 2.97%.

Ligand 1b

To a THF solution of **5** (1.1 g, 5.3 mmol) was added a 1.6 M hexane solution of *n*-butyllithium (3.4 mL, 5.3 mmol) at ice-cold temperature. After stirring for 1 h, (*o*-Tol)$_2$PCl (1.33 g, 5.4 mmol) in THF (5 mL) was added to the above mixture at −78 °C. The resulting mixture was warmed to room temperature and stirred for another 5 h. After concentration, the residue was distilled under vacuum to give the desired product as a viscous liquid (0.98 g, 45%). ^{1}H NMR (d_6-acetone, 400 MHz): δ 7.46–7.42 (m, 2H, Ar-H), 7.26–7.23 (m, 7H, Ar-H), 6.60 (s, 1H, py-H^3), 4.03 (d, J = 2.4 Hz, 2H, py–CH_2), 2.35 (s, 6H, CH_3), 1.28 (s, 9H, Bu^t), 1.17 (s, 9H, Bu^t). ^{31}P NMR (d_6-acetone, 161.9 MHz): δ −19.3. HR-FAB MS: calc. for $C_{28}H_{36}PN$: m/z 417.2585. Found (M + 1): 418.2337.

Complex 4a

A mixture of (COD)PdMeCl (0.177 g, 0.67 mmol) and ligand **1a** (0.317 g, 0.67 mmol) in dichloromethane (15 mL) was stirred at ambient temperature for 1 h. Upon concentration and washed with hexane, the chloro-bridged palladium complex was obtained as a yellow solid (0.39 g, 92%). ^{1}H NMR (d_6-acetone, 400 MHz): δ 7.12 (s, 2H, py-H^5), 7.06 (s, 2H, py-H^3), 6.77 (s, 8H, Ar-H), 4.19 (d, J = 11.4 Hz, 4H, CH_2), 2.25 (s, 16H, Ar–CH_3), 2.21 (s, 12H, Ar–CH_3), 1.43 (d, J = 3.1, 6H, Pd–CH_3), 1.20 (s, 18H, Bu^t), 1.16 (s, 18H, Bu^t). ^{31}P NMR (d_6-acetone, 161.9 MHz): δ 27. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.2, 160.1, 152.4, 140.9 (d, J = 9.9 Hz), 130.9 (d, J = 8.8 Hz), 126.7, 126.3, 119.2 (d, J = 5.5 Hz), 114.6 (d, J = 2.9 Hz), 40.4 (d, J = 20.6 Hz, py–CH$_2$), 37.5, 34.7, 30.4, 30.1, 22.2 (d, J = 10.1 Hz), 20.7, 5.7 (Pd–CH_3). Anal. Calc. for $C_{66}H_{94}N_2$-

$Cl_2P_2Pd_2$: C, 62.86; H, 7.51; N, 2.13. Found: C, 63.99; H, 7.71; N, 2.13%.

Complex 4b

The procedure for the preparation of this complex is essentially similar to that for **4a**. Yellow solid (97%): mp 188–189 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93–7.91 (m, 2H, Ar-H), 7.26–7.23 (m, 10H, Ar-H), 6.35 (s, 1H, py-H^3), 6.77 (s, 4H, Ar-H), 4.14 (d, J = 10.1 Hz, 2H, CH_2), 2.52 (s, 6H, CH_3), 1.20 (s, 9H, Bu^t), 1.15 (s, 9H, Bu^t), 0.53 (s, 3H, Pd–CH_3). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 31.5. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.8, 159.7, 153.6 (d, J = 5.7 Hz), 141.9 (d, J = 8.8 Hz), 135.3 (d, J = 11.3 Hz), 131.3 (d, J = 8.2 Hz), 130.2, 128.6 (d, J = 46 Hz), 125.1 (d, J = 10.5 Hz), 119.5 (d, J = 4.4 Hz), 113.2, 37.4, 36.7 (d, J = 24.9 Hz, py–CH_2), 34.6 (d, J = 5.5 Hz), 30.6, 30.1, 23.1 (d, J = 7.5 Hz), 22.6, 6.55 (Pd–CH_3). Anal. Calc. for $C_{58}H_{78}N_2Cl_2P_2Pd_2$: C, 60.63; H, 6.81; N, 2.44. Found: C, 60.63; H, 7.31; N, 2.23%. FAB MS: m/z = 1132.5 ($C_{58}H_{78}Cl_2N_2P_2Pd_2 - CH_3$).

Complex 5a

A solution of **4a** (0.50 g, 0.39 mmol) in dichloromethane (5 mL) was bubbled with carbon monoxide for 30 min. The reaction mixture was passed through Celite and diethyl ether was added to the filtrate, which gave the complex **5a** as a yellow precipitate (0.52 g, 98%): mp 168–169 °C (decomp.). IR (KBr): 1730 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 1H, py-H^5), 7.04 (s, 1H, py-H^3), 6.73 (d, J = 2.9 Hz, 4H, Ar-H), 4.24 (d, J = 11.6 Hz, 2H, CH_2), 2.19 (s, 6H, Ar–CH_3), 2.13 (s, 12H, Ar–CH_3), 2.04 (s, 3H, $COCH_3$), 1.24 (s, 9H, Bu^t), 1.04 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 16.5. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.7 (C=O), 168.7, 160.6, 153.0, 140.8 (d, J = 9.8 Hz), 131.0 (d, J = 8.2 Hz), 126.0 (d, J = 40.5 Hz), 119.6 (d, J = 5.7 Hz), 114.4 (d, J = 3.4 Hz), 37.2, 37.1 (d, J = 19.7 Hz, py–CH_2), 34.9 (d, J = 19.7 Hz), 34.8, 30.5, 29.7, 22.4 (d, J = 7.4 Hz), 20.7. FAB MS: m/z = 1228.4 ($C_{68}H_{94}N_2Cl_2P_2Pd_2O_2 - C_2H_6O_2$). Anal. Calc. for $C_{68}H_{94}N_2Cl_2P_2Pd_2O_2$: C, 62.01; H, 7.19; N, 2.13. Found: C, 61.56; H, 7.90; N, 1.69%.

Complex 5b

The procedure for the preparation of this complex is essentially similar to that for **5a**. Yellow solid (97%): mp 172–174 °C (decomp.). IR (KBr): 1720 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (br, 2H, Ar-H^5), 7.44 (s, 1H, py-H^3), 7.26 (t, J = 14.8 Hz, 2H, Ar-H), 7.16–7.08 (m, 5H, Ar-H, py-H^3), 4.05 (d, J = 9.9 Hz, 2H, CH_2), 2.45 (s, 6H, Ar–CH_3), 1.56 (s, 3H, $COCH_3$), 1.28 (s, 9H, Bu^t), 1.25 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 21.9. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 219.5 (C=O), 168.0, 160.5, 153.9 (d, J = 5.6 Hz), 142.2 (d, J = 8.5 Hz), 131.3 (d, J = 7.7 Hz), 130.6, 129.0, 128.6, 125.6 (d, J = 10.9 Hz), 120.3 (d, J = 4.2 Hz), 113.7, 37.5, 36.8 (d, J = 20.78 Hz, py–CH_2), 35.0, 30.8, 30.2, 22.9 (d, J = 7.6 Hz). Anal. Calc. for $C_{60}H_{78}Cl_2N_2O_2P_2Pd_2$: C, 59.81; H, 6.52; N, 2.32. Found: C, 59.85; H, 6.21; N, 2.08%. FAB MS: m/z 1125.3 ($C_{60}H_{78}Cl_2N_2O_2P_2Pd_2 - CH_3OCl$).

Complex 6a

A solution of **4a** (0.50 g, 0.15 mmol) in dichloromethane (5 mL) was added to a suspension of $AgBF_4$ (62.0 mg, 0.15 mmol) in dichloromethane (5 mL) at room temperature. After stirring for 1 h, the reaction mixture was passed through Celite to remove the silver salt. The filtrate was concentrated to a small volume of solution. Diethyl ether was added to the solution and the palladium complex was obtained as a yellow precipitate (191 mg, 97%): mp 173–174 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (s, 1H, py-H^5), 7.05 (s, 1H, py-H^3), 6.84 (d, J = 3.1 Hz, 4H, Ar-H), 4.21 (d, J = 9.6 Hz, 2H, CH_2), 2.59 (d, J = 8.4 Hz, 2H, CH_2–Pd), 2.38 (s, 3H, $NCCH_3$), 2.23 (s, 18H, Ar–CH_3), 1.39 (s, 6H, CH_3), 1.30 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 1.1. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.7, 165.4, 160.8 (d, J = 10.7 Hz), 140.3 (d, J = 9.9 Hz), 131.0 (d, J = 6.9 Hz), 127.8, 127.5, 124.2, 119.2 (d, J = 9.4 Hz), 116.8, 52.6 (d, J = 6 Hz), 48.7 (d, J = 42.4 Hz, py–CH_2), 35.6, 31.86 (d, J = 5.8 Hz), 30.3, 23.4 (d, J = 9.5 Hz), 20.8, 3.1 (CH_3CN). HR-FAB MS: Calc. for $C_{34}H_{46}BF_4N_2PPd - CH_3CNBF_4$: m/z = 578.2168. Found: 578.2152. Anal. Calc. for $C_{34}H_{46}BF_4N_2PPd$: C, 57.76; H, 6.89; N, 3.75. Found: C, 58.05; H, 6.56; N, 3.96%.

Complex 6b

The procedure for the preparation of this complex is essentially similar to that for **6a**. Yellow solid (97%): mp: 169–173 °C (decomp.). ^{1}H NMR (d_6-acetone, 400 MHz): δ 7.87 (s, 1H, py-H^5), 7.49–7.44 (m, 4H, Ar-H), 7.42–7.28 (m, 5H, Ar-H), 4.30 (d, J = 8.8 Hz, 2H, py–CH_2), 2.92 (d, J = 8.2 Hz, 2H, CH_2–Pd), 2.67 (s, 3H, $NCCH_3$), 2.55 (s, 6 H, Ar–CH_3), 1.38 (s, 6H, CH_3), 1.36 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 6.9. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.6, 163.4, 158.9 (d, J = 8.8 Hz), 141.8 (d, J = 14.3 Hz), 131.8, 131.7 (d, J = 14.9 Hz), 128.3, 127.9, 127.0 (d, J = 7.9 Hz), 125.5, 119.4, 117.2, 52.6 (d, J = 5.5 Hz), 49.7 (d, J = 31.2 Hz, py–CH_2), 35.7, 31.8 (d, J = 6.0 Hz), 31.6, 22.6, 21.7 (d, J = 11.8 Hz), 3.4 (CH_3CN). Anal. Calc. for $C_{32}H_{43}NPPdCl$: C, 62.54; H, 7.05; N, 2.28. Found: C, 62.88; H, 6.64; N, 2.31%. HR-FAB MS: Calc. for $C_{30}H_{38}BF_4N_2PPd - CH_3CNBF_4$) m/z = 522.1542. Found: 522.1550.

Complex 7a

A solution of **6a** (0.30 g, 0.48 mmol) in dichloromethane (3 mL) was bubbled with carbon monoxide at ambient temperature for 10 min. The reaction mixture was filtered through Celite and the filtrate was evaporated to a small volume. Upon the addition of diethyl ether, a yellow precipitate was obtained, filtered off, and washed with diethyl ether to give the analytically pure sample as a yellow solid (0.24 g, 82%). IR (KBr): 2099 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H, py-H^5), 7.20 (s, 1H, py-H^3), 6.89 (d, J = 11.4 Hz, 4H, Ar-H^{3,5}), 4.76 (d, J = 11.5 Hz, 2H, py–CH_2), 2.83 (d, J = 3.3 Hz, 2H, Pd–CH_2), 2.27 (s, 18H, Ar–CH_3), 1.49 (s, 6H, CH_3), 1.38 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 5.7. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.5 (C=O), 175.1, 168.2, 161.7 (d, J = 9.5 Hz), 141.2, 140.3, 131.4 (d, J = 8.0 Hz), 125.6 (d, J = 38.6 Hz), 121.3 (d, J = 10.0 Hz), 54.1 (d, J = 5.5 Hz), 49.0 (d, J = 70.2 Hz), 43.1 (d, J = 26.5 Hz), 36.1, 32.4 (d, J = 5.8 Hz), 23.7 (d, J = 9.4 Hz), 20.8. HR-FAB MS: Calc. for $C_{33}H_{43}PNPdOBF_4 - BF_4$: m/z = 606.2117. Found: 606.2122.

Complex 8a

To a mixture of **6a** (0.10 g, 0.14 mmol) and Et_4NCl (13.9 mg, 0.16 mmol) was added acetonitrile (3 mL). The resulting solution was stirred at room temperature for 3 h. Upon filtration through Celite, diethyl ether was added to the filtate to precipitate the desired complex out of the solution. Filtration gave the **8a** as a light yellow solid (61 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12 (d, J = 1.4 Hz, 1H, py-H^5), 6.99 (d, J = 1.7 Hz, 1H, py-H^3), 6.76 (d, J = 3.0 Hz, 4H, Ar-H), 4.02 (d, J = 8.4 Hz, 2H, CH_2), 2.63 (d, J = 9.2 Hz, 2H, CH_2–Pd), 2.31 (s, 12H, Ar–CH_3), 2.20 (s, 6H, Ar–CH_3), 1.37 (s, 6H, CH_3), 1.30 (s, 9H, Bu^t). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 0.51. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.0 (d, J = 7.9 Hz), 162.9, 159.8 (d, J = 10.3 Hz), 140.5 (d, J = 10.4 Hz), 139.0, 130.4 (d, J = 6.3 Hz), 129.9 (d, J = 19.3 Hz), 117.9 (d, J = 7.5 Hz), 116.1, 52.8 (d, J = 5.6 Hz), 48.0 (d, J = 96.6 Hz, py–CH_2), 43.2 (d, J = 17.2 Hz), 35.3, 31.7 (d, J = 6.2 Hz), 30.4, 23.8 (d, J = 9.1 Hz), 20.8. HR-FAB MS: Calc. for $C_{32}H_{43}NPPdCl$: m/z 613.1856. Found: 613.1863. Anal. Calc. for $C_{32}H_{43}NPPdCl$: C, 62.54; H, 7.05; N, 2.28. Found: C, 62.88; H, 6.64; N, 2.31%.

Crystallography

Crystals suitable for X-ray determination were obtained for **4a**, **4b**, **5b** and **6b** by slow diffusion of diethyl ether into a dichloromethane solution at room temperature. Cell parameters were determined either by a Siemens SMART CCD diffractometer. Crystal data of complexes **4a**, **4b**, **5b** and **6b** are listed in Table 3 and their ORTEP plots are shown in Figs. 1–4, respectively (labels of phenyl groups are omitted for clarity).

CCDC reference numbers 199587–199590.

See http://www.rsc.org/suppdata/dt/b2/b212169g/ for crystallographic data in CIF or other electronic format.

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