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Novel O^N^N Pyrazolyl-imine and Imidazolyl-imine Pincer Palladium Complexes as Heck Coupling Catalysts

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ABSTRACT

Five pyrazolyl and imidazolyl compounds, 2,4-di-tert-butyl-6-[2-pyrazol-1-yl-ethylimino-methyl]-phenol (L1), 2,4-di-tert-butyl-6-{[2-(3,5-dimethyl-pyrazol-1-yl)-ethylimino]-methyl}-phenol (L2), 2,4-di-tert-butyl-6-{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (L3), 4-tert-butyl-2-{[2-(1H-imidazole-4-yl)-ethylimino]-methly}-phenol (L4) and 2-{[2-(1H-imidazole-4-yl)-ethylimino]-methly}-phenol (L5) were synthesized by condensation of the appropriate 2-hydroxybenzaldehyde and the corresponding alkylamine. Reactions of L1–L5 with either [Pd(NCMe)$_2$Cl$_2$] or [Pd(COD)MeCl] led to *in situ* deprotonation of the phenolic-OH proton to afford the pincer palladium complexes [Pd(L1)Cl] (1), [Pd(L1)Me] (2), [Pd(L2)Cl] (3), [Pd(L3)Cl] (4), [Pd(L4)Cl] (5) and [Pd(L5)Cl] (6). The tridentate coordination modes of the ligands were confirmed by the solid state structures of 1, 2, 3 and 4.H$_2$O. Complexes 1–6 catalyzed the Heck coupling reactions of iodobenzene and butylacrylate. In addition, complex 4 catalyzed the Heck coupling reaction of butyl acrylate and bromobenzene; giving conversions as high as 70 %.

KEYWORDS

Pincer palladium complexes, pyrazolyl-imine, imidazolyl imine, aryl halides, Heck coupling catalysts.

1. Introduction

Metal complexes that feature pincer ligands have gradually developed into a new class of coordination compounds since they were first reported by Moulton and Shaw in 1976.[1] A few years later, van Koten reported the first N^C^N pincer tin compounds[2] which subsequently led to the explosion of new pincer anchored metal complexes. Indeed, several articles and reviews have been written on the synthesis and catalytic applications of pincer metal complexes.[3] Such is the impact of pincer compounds that a recent issue of Dalton Transactions[3h] was devoted to their chemistry.

Milstein and coworkers were among the first groups to use pincer palladium complexes in Heck coupling reactions. The general form of pincer ligands involves two heteroatoms and a central ionic carbon. The heteroatoms are usually a combination of N[5] and P,[4,6] but there are recent examples of an N^N^N[7] ligand motif. In designing pincer compounds, the conventional approach has been to have a central carboanion[1–6] which is usually produced *via* the deprotonation of a central benzene ring. A new approach to the design of an anionic ligand is to use the N-H functionality in the backbone of the pincer, which is deprotanated with a base to produce an anion. Fryzuk pioneered this approach in 1992[8] to make P^N^P pincer compounds and this has been extended to synthesize N^N^N pincer compounds containing heterocycles like carbazoles,[9] pyrrole[10] and isoindoline.[11] The latter ligand design appears to be driven by the presence of an acidic proton that leads to the anion on deprotonation. We used this new method to design pincer precursors featuring a phenolic group, which yield O^N^N pincer ligands upon deprotonation. In doing so, we have combined an imine, pyrazole, and imidazole as nitrogen donor atoms to synthesize a series of pincer palladium complexes that display very good activities as catalysts in Heck coupling reactions.

There are several examples of imine[12] and pyrazolyl[13] palladium complexes that have been used as catalysts for Heck coupling reactions. On the other hand, imidazole palladium complexes are known to catalyze Suzuki coupling reactions.[14] We envisioned that a combination of these three nitrogen-donor atoms to form pincer palladium complexes would result in enhanced catalytic activity in Heck coupling reactions compared to other nitrogen-donor ligand stabilized palladium(0) catalysts.[12,13] Here we report the syntheses, structural characterization of new pyrazolyl-imine and imidazolyl-imine pincer palladium complexes, and their applications as Heck coupling catalysts.

2. Results and Discussion

Compounds **L1**–**L4** were prepared by the condensation of the appropriate 2-hydroxybenzaldehyde with either substituted 2-(pyrazol-1-yl)ethylamine or histamine dihydrochloride in methanol (Schemes 1 and 2). Compounds **L1**–**L4** were isolated as yellow solids in high yields (80–85 %). Compound **L5**[15] and the intermediate 2-(pyrazol-1-yl)ethylamines[16] were prepared following literature procedures.

Compounds **L1**–**L5** showed characteristic imine proton signals between 7.98 and 8.17 ppm. The signature signals of the ethylene linkers were recorded as triplets between 3.98 and 4.34 ppm, but only **L3** showed a peak for the phenolic proton at 13.82 ppm. This is consistent with hydrogen bonding between the hydroxyl group and the nitrogen atom of the imine group. Downfield shifts of the phenolic OH protons (16.8 ppm and 14.8 ppm) have been reported for 1-(2-hydroxy-3,5-dichlorophenyl)-2,5-diaza-6-methylnona-1-6-diene-8-one[17] and 2-[1-(2,6-diethylphenyl-

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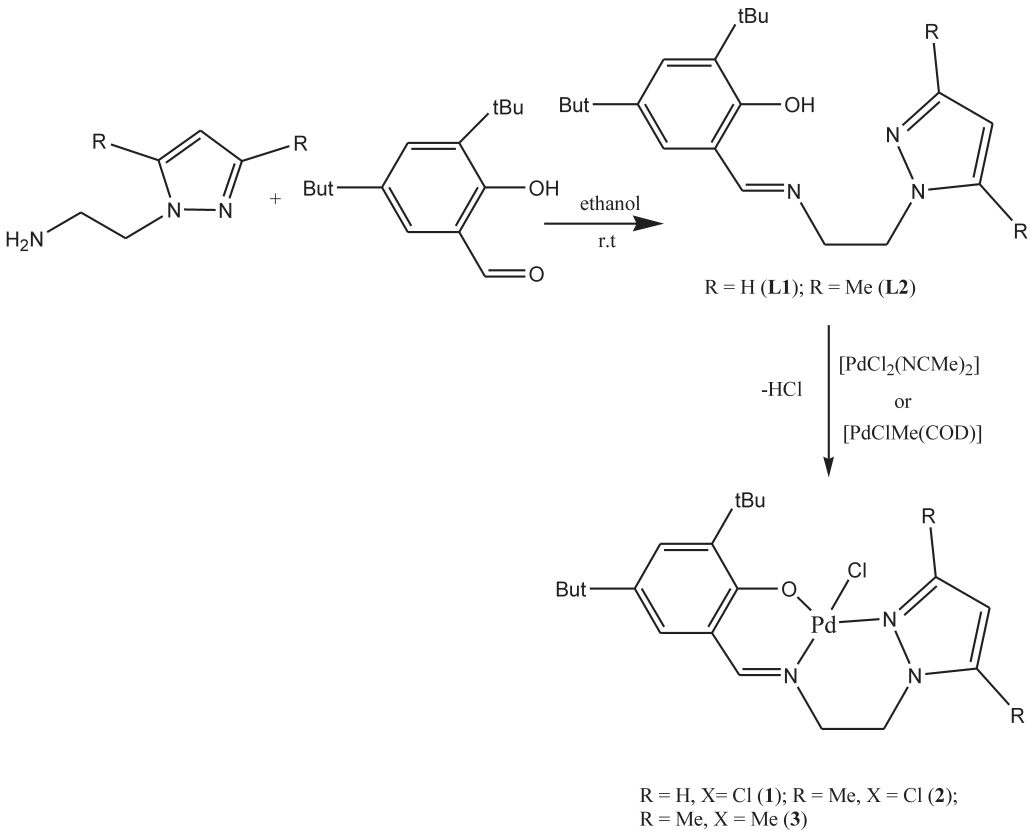
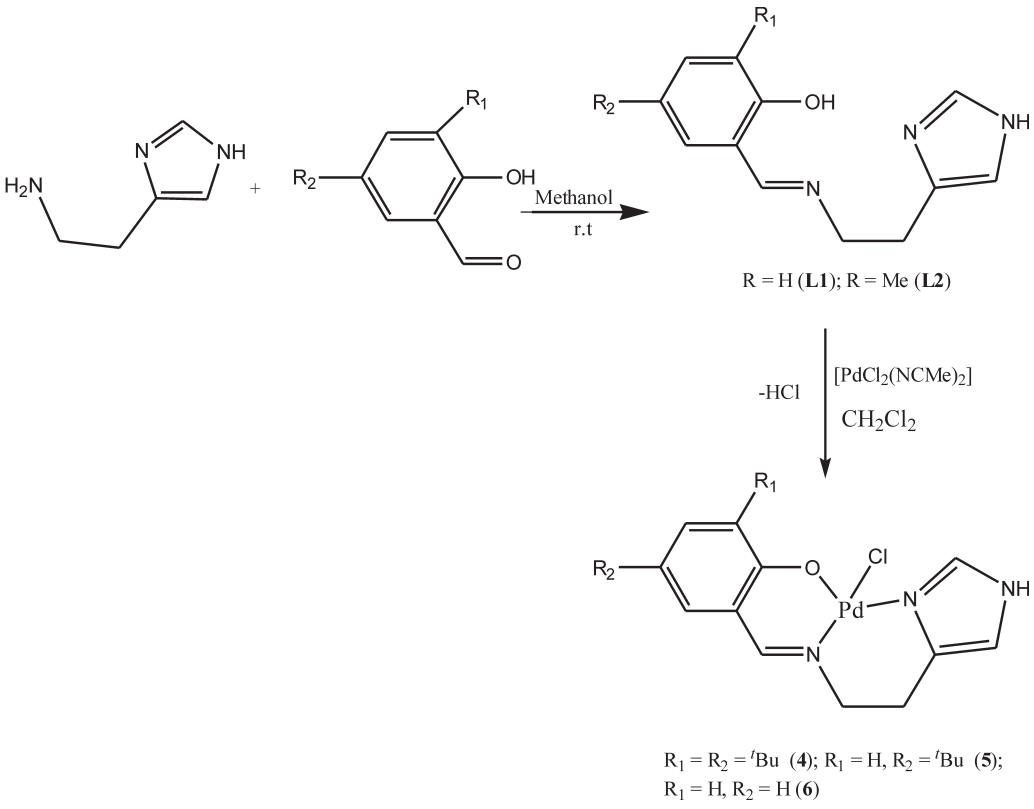


Scheme 1

imino) ethyl]-phenol, respectively.[18] High resolution mass spectral data of **L1**–**L4** confirmed the purity and the molecular ions of the compounds, while the solid state structure of **L2** confirmed the molecular structure of the compounds.

Reactions of **L1**–**L4** with equimolar amounts of $[PdCl_2(NCMe)_2]$ or [PdClMe(COD)] afforded the corresponding complexes **1**–**6** in moderate to high yields (Schemes 1 and 2). ^{1}H NMR spectra of the complexes generally showed downfield shifts of the signals in comparison to the ligand peaks. For example, the imine proton in complex **3** shifted to 8.35 ppm from 8.26 ppm in the



Scheme 2

Table 1 Crystal data and structure refinement parameters for compounds **L2**, **1–4**.

Parameter	**L2**	**1**	**2**	**3**	**4**
Formula	$C_{22}H_{33}N_3O$	$C_{20}H_{28}ClN_3OPd$	$C_{22}H_{32}ClN_3OPd$	$C_{23}H_{35}N_3OPd$	$C_{20}H_{28}ClN_3OPd.H_2O$
Formula weight	355.51	468.30	496.36	475.94	485.31
Temperature /K	100(2)	105(2)	100(2)	100(2)	100(1)
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	1.54178
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	C2/c	P1	Pbca	C2/c	$P2_1/_C$
a /Å	23.564(3)	9.7800(12)	10.0125(2)	32.225(3)	20.391(9)
b /Å	11.2784(13)	11.4862(14)	26.9810(6)	7.7754(6)	9.456(4)
c /Å	19.567(2)	18.809(2)	51.9073(12)	19.7596(16)	11.192(5)
α /°	90	95.528(2)	90	90	90
β /°	124.944(2)	92.533(2)	90	113.1390(10)	102.62(3)
γ /°	90	90.098(2)	90	90	90
Volume /Å^3	4262.6(9)	2101.0(4)	14022.6(5)	4552.7(6)	2105.8(16)
Z	8	4	24	8	4
D_{Calcd} /mg m^{-3})	1.108	1.481	1.411	1.389	1.531
Absorption coefficient /mm$^-$)	0.068	1.024	0.925	0.833	8.431
F(000)	1552	960	6144	1984	996
Final R indices (R1)	0.0564	0.0378	0.0690	0.0267	0.0254
R indices all data (R1)	0.0938	0.0601	0.1078	0.0372	0.0306
Reflections collected	21474	37866	189250	30401	25851
Completeness to theta (°)	98.6 % (29.57°)	95.7 % (30.04°)	99.8 % (26.04°)	99.7 % (28.32°)	97.3 % (67.00°)
Goodness of fit on F^2	1.019	1.051	1.065	1.088	1.035
Largest diff. peak and hole	0.411 and –0.261 e.Å^{-3}	2.923 and –0.567 e.Å^{-3}	2.107 and –3.132 e.Å^{-3}	1.316 and –0.366 e.Å^{-3}	0.967 and –0.341 e.Å^{-3}

corresponding **L3**, signifying palladium coordination to the imine nitrogen. Similar shifts were also observed for the other ligands (**L1**, **L2**, **L4** and **L5**) and their respective complexes (**1**, **2**, **4–6**). These chemical shifts are similar to those reported for palladium-coordinated imine and pyrazolyl nitrogen atoms by Kostas *et al*.[15] and Lee *et al*.[19] Mass spectral data for complexes **1–6** consistently showed the loss of one chloride. Determination of the solid state structures of **1–4** (*vide infra*) confirmed a concerted loss of HCl upon coordination of **L1–L5** to the palladium metal precursors (Schemes 1 and 2). The solid state structures also confirmed that all the ligands coordinate to the palladium atom in a tridentate fashion, giving the first examples of O^N^N pincer palladium complexes containing either pyrazole or imidazole. Remarkably, this is a rare example of pincer formation that does not require prior generation of an anionic ligand[3d,20] or high temperature activation.[21]

2.1. Molecular Structures of L2 and Complexes 1–4

Crystals suitable for single crystal X-ray analysis for **L2** were grown by slow evaporation of hexane at room temperature while single crystals suitable for X-ray analyses of complexes **1–4** were grown by slow diffusion of hexane into solutions of dichloromethane containing the complexes at –4 °C. Crystal data collection and refinement parameters for **L2**, complexes **1–4** are given in Table 1 while selected bond lengths and angles for the complexes are given in Table 2. The molecular structures of **L2** and complexes **1–4** are shown in Figs 1–5.

The coordination geometry around the metal centre in **1–4** can be regarded as slightly distorted square-planar with the X-Pd-X angles between the neighbouring ligands ranging between 84.79(6) 92.70(6)° (Table 2). The Pd-Cl, Pd-N1, Pd-N3 and Pd-O bond lengths for **1**, **2** and **4**.H_2O average to 2.319(13), 2.029(5), 1.988(9) and 1.964(12) Å, respectively. In **3**, atom N3 resides on the central metal opposite a methyl group, thus the Pd-N3 distance in **3** (2.0815(16) Å) is approximately 0.1 Å longer than the respective bonds in **1**, **2**, and **4**.H_2O. The difference is indicative of a stronger *trans*-effect of a Me group compared to a Cl ligand. Consequently, in complexes **1**, **2**, and **4**.H_2O the

Table 2 Selected bond lengths and angles for complexes **1**, **2**, **3** and **4.H$_2$O**. In the cases of **1** and **2** the values are averaged between the symmetry independent molecules.

	1 X = Cl(1)	**2** X = Cl(1)	**3** X = C(23)	**4.H$_2$O** X = Cl(1)
Bond lengths /Å				
Pd(1)-N(1)	2.035(2)	2.028(6)	2.0196(16)	2.023(2)
Pd(1)-N(3)	1.982(2)	1.985(5)	2.0815(16)	2.001(2)
Pd(1)-X	2.3197(8)	2.310(2)	2.0795(17)	2.3440(10)
Pd(1)-O(1)	1.952(2)	1.966(5)	1.9858(14)	1.9848(17)
Bond angles /°				
N(1)-Pd(1)-N(3)	92.70(6)	91.1(2)	91.96(6)	91.13(9)
N(3)-Pd(1)-X	174.80(7)	176.4(3)	172.24(6)	175.83(6)
N(1)-Pd(1)-X	90.89(8)	92.1(2)	92.29(7)	91.13(7)
N(1)-Pd(1)-O(1)	175.3(2)	176.0(2)	176.10(6)	175.41(8)
N(3)-Pd(1)-O(1)	91.30(7)	91.8(2)	91.24(6)	92.59(8)
X-Pd(1)-O(1)	85.29(10)	84.9(4)	84.79(6)	85.33(6)

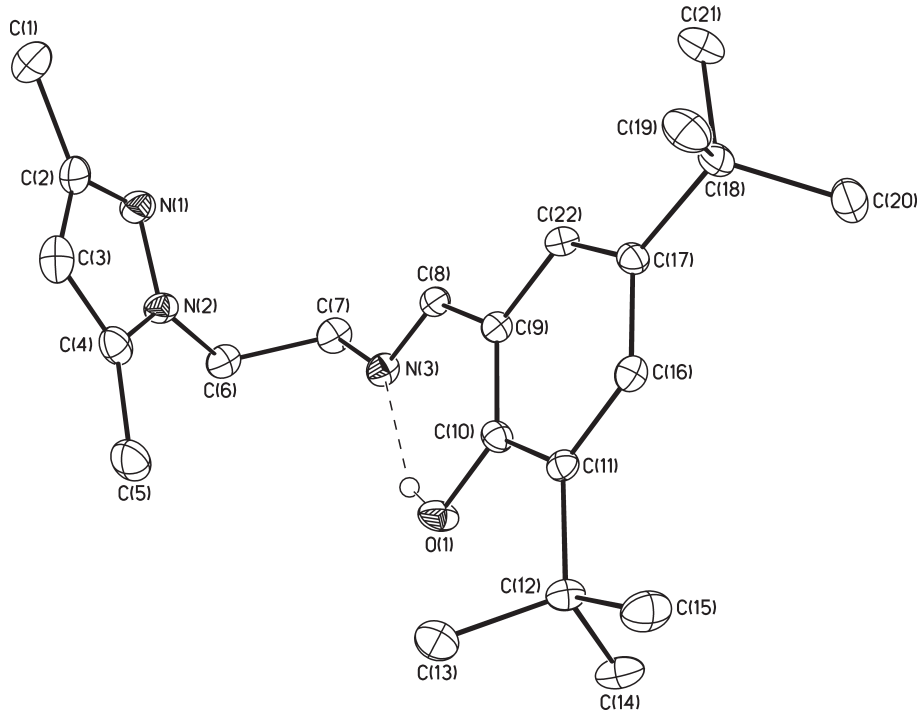


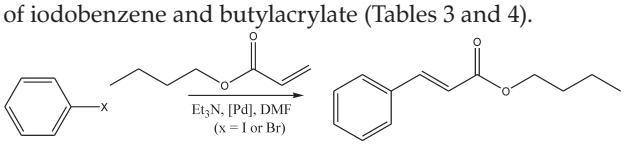
Figure 1 Molecular drawing of **L2** shown with 50 % probability ellipsoids. The hydrogen atoms attached to C atoms are omitted for clarity.

pyrazolyl or imidazolyl N1 atom is bonded to the Pd centre in a weaker manner than the imino nitrogen N3, whereas the opposite is observed in **3**. In all cases the bonds distances and angles fall in the usual ranges and agree well with literature data.[22] We note that **1** crystallizes with two symmetry independents molecules in the asymmetric unit, **2** with three molecules of which two have similar overall conformations, and **4** crystallizes as a hydrate.

The crystal structure of **L2** exhibits one intramolecular hydrogen bond of the type O-H...N. A Mogul[23] structural check confirmed that all bond distances and angles fall in the usual ranges for the corresponding parameters.

2.2. Heck Coupling Reactions

All the six complexes **1**–**6** prepared were investigated for their ability to catalyze the Heck coupling reactions of iodobenzene or bromobenzene with butylacrylate (Eq. 1). This was done to investigate catalytic activity of our pincer palladium complexes in this type of reaction relative to other pincer palladium complexes. All our complexes efficiently catalyzed the coupling of iodobenzene and butylacrylate (Tables 3 and 4).



(1)

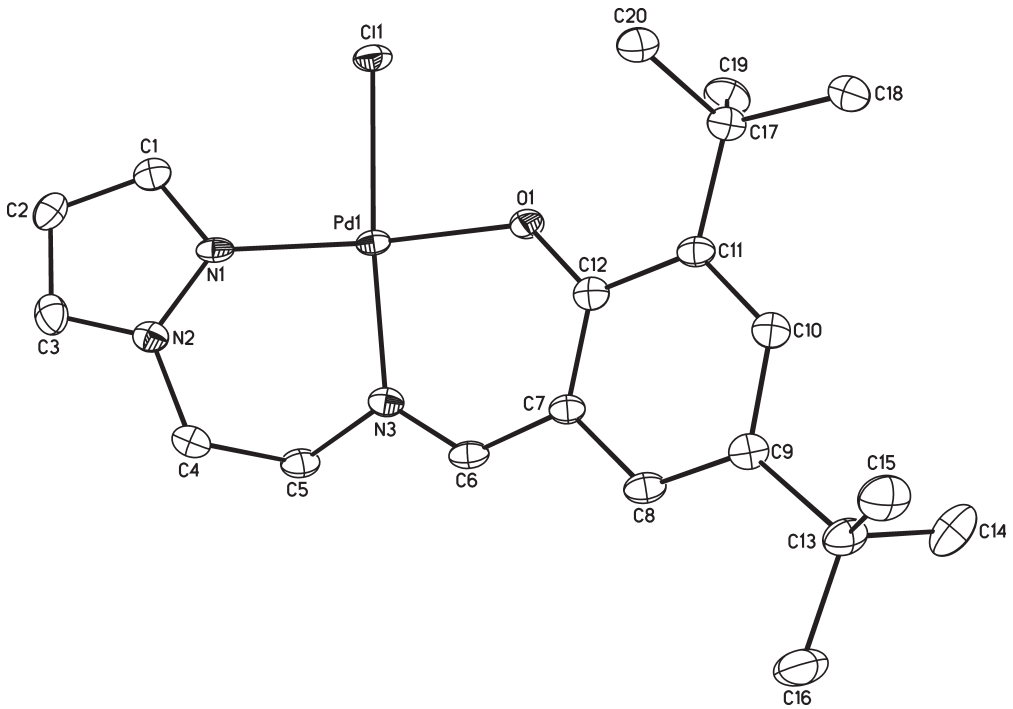


Figure 2 Molecular drawing of **1** shown with 50 % probability ellipsoids. The hydrogen atoms are omitted for clarity.

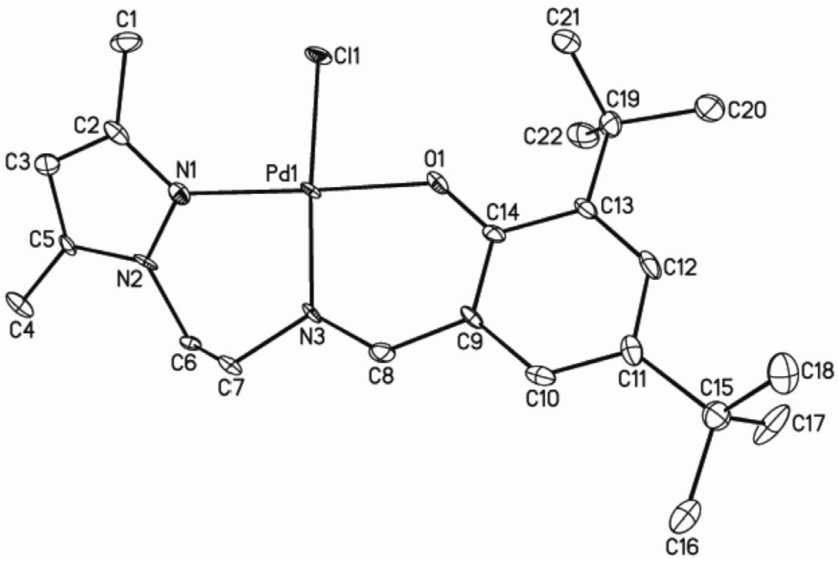


Figure 3 Molecular drawing of **2** shown with 50 % probability ellipsoids. The hydrogen atoms are omitted for clarity.

The pyrazolyl-imine complexes **1–3** catalyzed this reaction at 80 °C (Table 3), a temperature considered mild for Heck reactions. On the other hand, the imidazolyl-imine complexes, **4–6**, did not produce active catalysts at 80 °C, and only formed active catalysts above 110 °C (Table 4). It is generally accepted that prior to the formation of active species, palladium pre-catalysts first decompose to ligand-stabilized Pd(0)[1–5] species. It is therefore conceivable that the higher temperatures required for imidazolyl-imine complexes (**4–6**) to generate active species reflect the higher stabilities of complexes **4–6** compared to the pyrazolyl-imine analogues **1–3**. The differences in the stabilities of complexes **1–3** and **4–6** are further reflected in the conversion rates of their Heck coupling reactions. Whereas **1–3** attained conversions of 95 % within 1 h, complexes **5** and **6** attained such conversions only after 5 h, and complex **4** attained 87 % conversion after 24 h. In all cases the reactions led to the formation of the *trans* isomer of butylcinnamate as the only product as established by ^{1}H NMR analysis.

Table 3 Heck coupling reactions of iodobenzene and butylacrylate catalyzed by **1–3** [a]

Entry	Catalyst	Time /h	%Conv [b]
1	**1**	1	94
2	**1**	4	97
3	**1**	8	97
4	**1**	24	100
5	**2**	4	96
6	**3**	1	96
7	**3**	4	97
8	**3**	8	98
9	**3**	24	100

[a] Reaction conditions: amounts, butyl acrylate 0.9 mmol; iodobenzene, 0.9 mmol; base Et_3N, 0.9 mmol; [Pd] 0.1 mol%. Solvent, DMF (10 mL).
[b] Determined by GC.

The effect of catalyst loading is known to affect the efficiency of catalysts in Heck coupling reactions. We thus investigated the influence of catalyst loading using complexes **4–6** (Table 4) by varying the catalyst loadings from 0.05 to 0.2 mol%. Generally there was increase in conversions when catalyst loading was increased from 0.05 mol% to 0.1 mol% (Table 4), but an increase from 0.1 mol% to 0.2 mol% did not result in significant increase in percentage conversion. Reduced activity at higher catalyst concentrations has been reported by many researchers,[24] and is

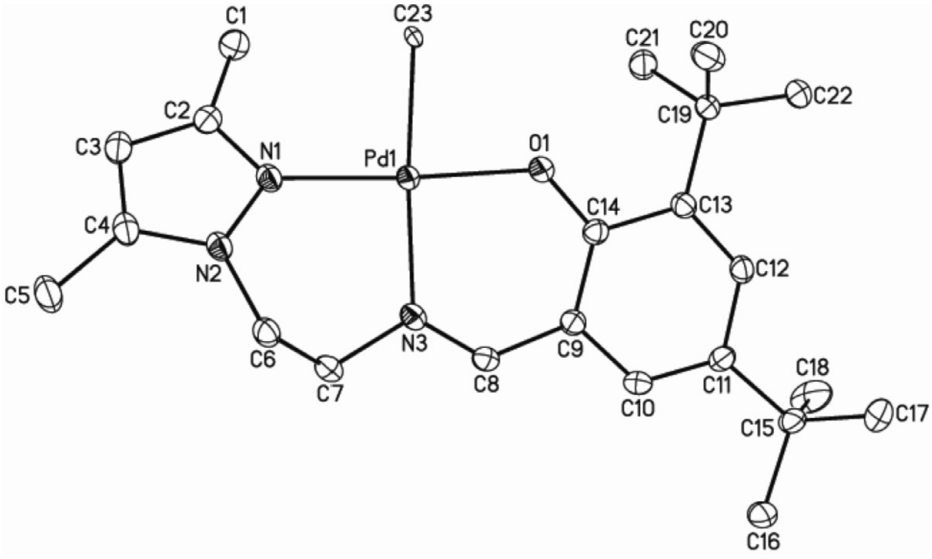


Figure 4 Molecular drawing of **3** shown with 50 % probability ellipsoids. The hydrogen atoms are omitted for clarity.

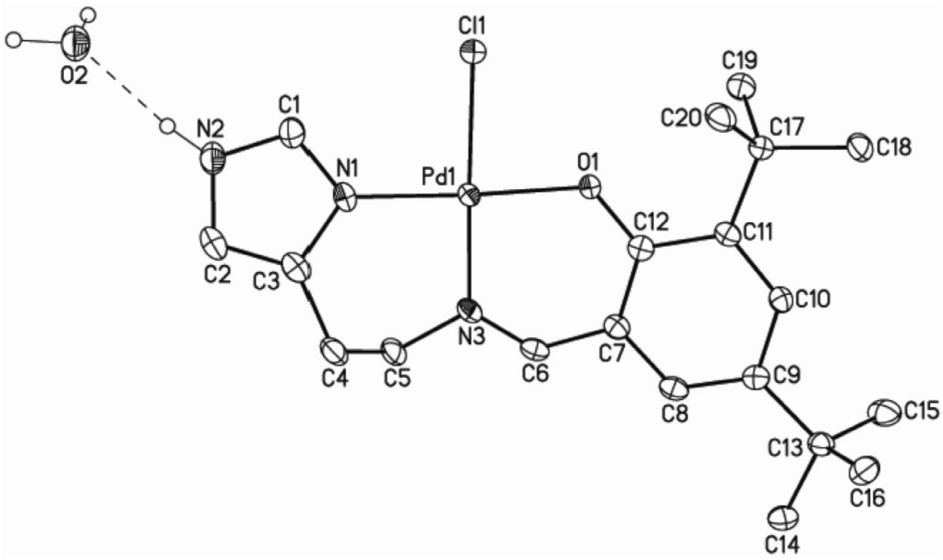


Figure 5 Molecular structure of complex **4**. Ellipsoids are drawn at 50 % probability level and hydrogen atoms residing on C atoms have been omitted for clarity.

believed to emanate from palladium nanoparticles aggregating to palladium black. Indeed, formation of appreciable amounts of palladium black was observed for reactions performed using 0.2 mol%. In a review of palladium cluster chemistry, Murahashi and Kurosawa[25] associated reduced catalytic activity with formation of palladium aggregates in solution that leads to fewer free binding sites available on the active palladium(0) species.

One of the greatest challenges in Heck coupling reactions is to design catalysts that can catalyze non-activated aryl bromides and aryl chlorides. These halides are cheaper than aryl iodides, but are extremely difficult to activate due to their stronger carbon-halide bonds. We tested our complexes for the coupling reactions of bromobenzene with butylacrylate. No activity was observed for the pyrazolyly-imine complexes **1**–**3**. The imidazolyl-imine complexes **4**–**6** were active, but **5** and **6** demonstrated very low activities; hence further studies were performed using only complex **4**. Complex **4** produced active catalyst for the coupling of bromobenzene and butylacrylate at 170 °C and at low catalyst loadings of 0.05 mol% (Table 5). Very good conversions were obtained in 24 h (60 %) and 48 h (70 %). These rates exceed those for other non-phosphine pincer palladium complexes used in the Heck coupling reactions of bromobenzene. For example, bis(azole) pincer palladium complexes reported by Luo *et. al.*[26] showed conversion of 25 % in 20 h. We believe complex **4** catalyzed bromobenzene coupling more efficiently than complexes **5** and **6** because it forms more stable Pd(0) species. This is consistent with the proposal by de Vries[27] that at higher temperatures, Pd(0) colloids produced would be stabilized by electron-rich ligands.

3. Conclusions

We have demonstrated that pyrazolyl-imine and imidazolyl-imine compounds featuring a phenolic group readily undergo deprotonation when reacted with palladium chloride substrates to produce O^N^N pincer palladium complexes. These pincer palladium complexes catalyze the Heck coupling of iodobenzene and butylacrylate in short reaction times and in some cases even at 80 °C. More significant is the ability of complex **4** to catalyze the coupling of bromobenzene. Complex **4** represents one of the few non-phosphine palladium complexes that catalyze the Heck coupling of bromobenzene.

Table 4 Heck coupling reactions of iodobenzene and butylacrylate catalyzed by **4–6.**

Entry	Catalyst	Time /h	[Pd] /mol%	Temp /°C	%Conv
1	**4**	1	0.05	80	0
2	**4**	5	0.05	110	0
3	**4**	24	0.05	110	87
4	**5**	24	0.05	110	75
5	**6**	24	0.05	110	89
6	**4**	24	0.05	140	88
7	**6**	24	0.05	140	95
8	**4**	5	0.1	110	95
9	**4**	5	0.2	110	95
10	**5**	5	0.05	110	75
11	**5**	5	0.1	110	90
12	**5**	5	0.2	110	97
13	**6**	5	0.1	110	92
14	**6**	5	0.2	110	95
15	**6**	15	0.2	110	95

[a] Reaction conditions: amounts, butylacrylate (10 mmol); iodobenzene (10 mmol); Et_3N (10 mmol). Solvent, DMF (10 mL).
[b] Determined by GC.

Table 5 Heck coupling reactions of bromobenzene and butylacrylate catalysed by **4**.

Entry	Catalyst	Time (h)	Temp (°C)	%Conv
1	**4**	5	170	0
2	**4**	15	170	40
3	**4**	24	170	60
4	**4**	48	170	70

[a]Reaction conditions: Amounts, butylacrylate (10 mmol); bromobenzene (10 mmol); Et_3N (10 mmol); [Pd] 0.05 mol%. Solvent, DMF (10 mL).
[b] Determined by GC.

4. Experimental

4.1. General Procedures

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Diethyl ether, tetrahydrofuran and hexane were dried and distilled over sodium with benzophenone as an indicator. CH_2Cl_2 was dried over P_2O_5. All other solvents were of analytical grade and were used as received. The materials: (3,5-di-tert-butyl-2-hydroxybenzaldehyde, bromoethylamine hydrobromide, 3,5-dimethylpyrazole, pyrazoles, tetrabutylammonium bromide, potassium carbonate, potassium hydroxide, 2-pyridine(carboxaldehyde), 3,5-di-tert-butyl-2-hydroxybenzaldehyde, 5-tert-butyl-2-hydroxybenzaldehyde and histamine dihydrochloride were obtained from Sigma-Aldrich and used as received. Ligands 2-{[2-(1H-imidazole-4-yl)-ethylimino]-methly}-phenol[15] (**L5**) and 2-(pyrazol-1-yl)-ethylamines[16] were synthesized according to literature procedures. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini-300 MHz instrument (^1H at 300MHz and $^{13}C\{^1H\}$ at 75.01 MHz) at room temperature. The chemical shifts are reported in δ (ppm) and referenced to residual protons of $CHCl_3$ for ^1H (δ 7.26) and $^{13}C\{^1H\}$ (δ 77.0). Coupling constants are measured in Hertz (Hz). Micro analyses were performed on a Vario Elementar III microcube CHNS analyser. High resolution mass spectra for the Schiff base ligands were recorded on a Waters API Q-TOF Ultima. Heck coupling products were quantified on a Varian 3900 gas chromatograph equipped with a flame ionization detector.

Synthesis of 2,4-di-tert-butyl-6-[2-pyrazol-1-yl-ethylimino-methyl]-phenol (L1)

To a solution of 2-pyrazol-1-yl-ethylamine (0.49 g, 4.27 mmol) in ethanol (50 mL) was added 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.00 g, 4.27 mmol) and the deep yellow solution stirred for 24 h at room temperature. After the reaction period, the solution was evaporated to give a yellow solid. Hexane (20 mL) was then added to induce precipitation to obtain the pure product as yellow solid. Yield = 1.16 g (83 %). ^1H NMR ($CDCl_3$): δ 1.16 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, C(CH_3)$_3$), 3.98 (t, 2H, $^3J_{HH}$ = 4.5 Hz, CH_2), 4.34 (t, 2H, $^3J_{HH}$ = 4.5 Hz, CH_2), 6.07 (t, 1H, $^3J_{HH}$ = 5.7 Hz, 4-pz*H*), 6.85 (s, 1H, 3-Ph*H*), 7.13 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 5-pz*H*), 7.24 (s, 1H, 5-Ph*H*), 7.42 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 3-pz*H*), 7.98 (s, 1H, N=C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.3, 31.4, 34.0, 35.0, 52.5, 59.1, 99.9, 105.4, 126.0, 127.2, 130.1, 139.8, 140.1, 157.9, 168.1. ESI-MS (HRMS): calculated $C_{20}H_{28}N_3O$ *m/z* 328.2397, found $C_{20}H_{29}N_3O$ *m/z* 328.2389 (M^+, 100 %).

Synthesis of 2,4-di-tert-butyl-6-{[2-(3,5-dimethyl-pyrazol-1-yl)-ethylimino]-methyl}-phenol (L2)

2-(3,5-dimethyl-pyrazol-1-yl)ethylamine (0.71 g, 5.11 mmol) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.19 g, 5.11 mmol). Yellow solid. Yield = 2.08 g (85 %). ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 2.16 (s, 3H, pz-CH_3), 2.22 (s, 3H, pz-CH_3), 3.98 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 4.27 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 5.70 (s, 1H, 4-pz*H*), 6.98 (s,1H, 3-Ph*H*), 7.36 (s, 1H, 5-Ph*H*), 8.12 (s, 1H, N=C*H*), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.9, 13.5, 29.3, 31.4, 48.7, 59.3, 104.8, 140.0, 136.5, 157.8, 168.0. ESI-MS (HRMS): calculated $C_{22}H_{33}N_3O$ *m/z* 356.2702, found $C_{22}H_{34}N_3O$ *m/z* 356.2708 (M^+, 100 %).

Synthesis of 2,4-di-tert-butyl-6-{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (L3)

To a solution of 3,5-di-tert-butylhydroxybenzaldehyde **1a** (2.00 g, 8.54 mmol) and histamine dihydrochloride (1.57 g, 8.54 mmol) in methanol (50 mL) was added $NaHCO_3$ (1.43 g, 17.07 mmol). Formic acid (six drops) was added to the reaction mixture as a catalyst. The reaction mixture was stirred under reflux for 24 h forming a yellow solution. The mixture was filtered and the solvent removed to obtain the product as yellow oil. CH_2Cl_2 was then added to dissolve the product leaving behind the salt formed during the condensation reaction. The solvent was then evaporated leaving a bright yellow solid as product. Yield: 2.75 g (98 %). ^1H NMR, ($CDCl_3$), δ 1.28 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 2.98 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 3.87 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 6.81 (s, 1H, 3-Ph*H*), 7.01 (d, 1H, $^3J_{HH}$ = 2.4 Hz, 5-im*H*), 7.37 (d, 1H, $^3J_{HH}$ = 2.4 Hz, 2-im*H*), 7.57 (s, 1H, 5-Ph*H*), 8.26 (s, 1H, C*H*=N), 13.82 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.7, 29.4, 31.4, 34.0, 34.9, 59.1, 117.1, 117.7, 125.8, 126.8, 134.6, 135.1, 136.6, 139.9, 158.1, 166.3. HRMS (ESI): calculated for $[M+H]^+$ 328.2390, found *m/z* 328.2389. IR (ATR) cm^{-1}: 1631 (s) ($\nu_{C=N}$).

Synthesis of 4-tert-butyl-2-{[2-(1H-imidazole-4-yl)-ethylimino]-methyl}-phenol (L4) Ligand

L4 was prepared according to the procedure described for **L3** using 4-tert-butyl-hydroxybenzaldehyde (0.73 g, 4.10 mmol) and histamine dihydrochloride (0.75 g, 4.10 mmol) to afford a bright yellow solid (0.78 g, 70 %). ^1H NMR, ($CDCl_3$): δ 1.25 (s, 9H, C(CH_3)$_3$), 2.92 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 3.83 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 6.78 (s, 1H, 5-im*H*), 6.84 (d, 1H, $^3J_{HH}$ = 8.7 Hz, 3-Ph*H*), 7.15 (d, 1H, $^3J_{HH}$ = 8.7 Hz, 2-Ph*H*), 7.31 (s, 1H, 5-Ph*H*), 7.52 (s, 1H, 2-im*H*), 8.23 (s, 1H, N=C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.6, 31.3, 33.8, 58.7, 116.5, 116.7, 117.7, 127.6, 129.7, 134.7, 135.1, 141.1, 159.2,165.6 HRMS (ESI): calculated for $[M+H]^+$ 272.1764, found *m/z* 272.1751. IR (ATR), (cm^{-1}): 1634 (s) ($\nu_{C=N}$).

Synthesis of [Pd(L1)Cl$_2$] (1)

To a yellow solution of **L1** (0.05 g, 10.24 mmol) (20 mL) was added [Pd(Cl_2NCMe)$_2$] (0.03 g, 10.24 mmol) and the solution changed colour within 5 min from yellow to dark orange and then to red. The red solution was then stirred for 4 h after which the solution was concentrated to about 10 mL and hexane (40 mL) added to precipitate a yellow solid. The solid was further recrystallized from a CH_2Cl_2-hexane mixture to afford single crystals suitable for X-ray analysis. Yield = 0.035 g (60 %). ^1H NMR ($CDCl_3$): δ 1.23 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 3.85 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2), 4.58 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2), 6.02 (t, 1H, $^3J_{HH}$ = 6.0 Hz, 4-pz*H*), 7.35 (s, 1H, 5-Ph*H*), 7.34 (d, 1H, $^3J_{HH}$ = 7.5 Hz, 5-pz*H*), 7.71 (s, 1H, 3-Ph*H*), 7.45 (d, 1H, $^3J_{HH}$ = 7.5 Hz, 3-pz*H*), 8.49 (s, 1H, N=C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.2, 31.1, 33.5, 35.1, 51.0, 54.9, 117.8, 127.9, 129.3, 131.1, 135.6, 141.3, 159.6, 162.6. MS (ESI): *m/z* (%) = 447 (20) (M^+). Anal. calc. for $C_{21}H_{31}N_3OPd.2C_2H_6OS$: C, 45.32; H, 6.12; N, 6.89. Found: C, 45.45; H, 6.08, N, 7.95.

Synthesis of [Pd(L2)Cl] (2)

Compound **2** was prepared following the procedure described for **1** using **L2** (0.50 g, 1.39 mmol) and $[PdCl_2(NCMe)_2]$ (0.36 g, 1.39 mmol). Recrystallization from a CH_2Cl_2-hexane mixture gave single crystals suitable for X-ray analysis. Yield = 0.42 g (54 %). ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9H, C(CH_3)$_3$), 1.46 (s, 9H, C(CH_3)$_3$), 2.26 (s, 3H, pz-CH_3), 2.58 (s, 3H, pz-CH_3), 3.68 (t, 2H, $^3J_{HH}$ = 6.3 Hz , CH_2), 4.58 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 5.87 (s, 1H, 4-pz*H*), 6.88 (s,1H, , 3-Ph*H*), 7.39 (s, 1H, 5-Ph*H*), 7.49 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.7, 16.0, 29.5, 31.2, 33.8, 35.7, 49.0, 57.5, 108.2, 118.5, 126.8, 130.9, 141.6, 136.9, 154.5, 161.8. MS (ESI): *m*/*z* (%) = 497 (80) (M^+). Anal. calc. for $C_{22}H_{32}ClN_3OPd$: C, 53.23; H, 6.50; N, 8.47. Found: C, 52.58; H, 6.80, N, 8.40.

Synthesis of [Pd(L2)Me] (3)

To a solution of [PdClMe(COD)] (0.10 g, 37.88 mmol) in diethyl ether (20 mL) was added a solution of **L2** (0.13 g, 37.88 mmol) in diethyl ether (20 mL) and the mixture stirred for 4 h. After the reaction period, the solvent was evaporated followed by recrystallization from a CH_2Cl_2-hexane mixture to give single crystals suitable for X-ray analysis. Yield = 0.37 g (54 %). ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 3H, Pd-CH_3), 1.20 (s, 9H, C(CH_3)$_3$), 1.25 (s, 9H, C(CH_3)$_3$), 2.24 (s, 3H, pz-CH_3), 2.51 (s, 3H, pz-CH_3), 3.60 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 4.59 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 5.87 (s, 1H, 4-pz*H*), 6.89 (s,1H, 3-Ph*H*), 7.39 (s, 1H, 5-Ph*H*), 7.50 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.7, 15.9, 29.5, 31.2, 33.8, 35.7, 49.0, 57.5, 108.2, 126.9, 130.9, 136.9, 141.6, 136.9, 154.9, 161.9. MS (ESI): *m*/*z* (%) = 475 (80) (M^+). Anal. calc. for $C_{23}H_{35}N_3OPd$: C, 54.59; H, 7.33; N, 8.83. Found: C, 54.28; H, 7.73, N, 8.51.

Synthesis of [Pd(L3)Cl] (4)

To a solution of $[PdCl_2(NCMe)_2]$ (0.67 mmol) in CH_2Cl_2 was added to a solution of **L3** (0.67 mmol) in CH_2Cl_2 and the resultant maroon solution was stirred for 16 h. After the reaction period, the solution was filtered and the crude product recrystallized from CH_2Cl_2-hexanes to give single crystals suitable for X-ray analysis (0.30 g, 96 %). ^{1}H NMR, ($CDCl_3$): δ 1.23 (s, 9H, C(CH_3)$_3$), 1.40 (s, 9H, C(CH_3)$_3$), 2.87 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 3.58 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 6.72 (s, 1H, 3-Ph*H*), 6.93 (d, 1H, $^3J_{HH}$ = 2.7 Hz, 2-im*H*), 7.35 (d, 1H, $^3J_{HH}$ = 2.7 Hz, 5-im*H*), 7.60 (s, 1H, 5-Ph*H*), 8.35 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.0, 29.5, 31.3, 33.8, 35.6, 58.8, 112.5, 117.9, 127.5, 130.6, 135.2, 136.7, 138.9, 140.1, 161.3, 161.8. Anal. calc. for $C_{20}H_{29}N_3ClOPd.0.5\ CH_2Cl_2$: C, 48.11; H, 5.91; N, 8.21. Found: C, 48.47; H, 5.78; N, 8.40 %. MS (ESI): *m*/*z* (%) = 471 (40) (M^+). IR (ATR) (cm^{-1}): 1613 (s) ($\nu_{C=N}$).

Synthesis of [Pd(L4)Cl] (5)

Compound **5** was prepared in a similar manner to complex **4** using $[PdCl_2(NCMe)_2]$ (0.69 mmol) and **L4** (0.69 mmol) to give **5** as an orange solid (0.16 g 57 %). ^{1}H NMR, (DMSO-d_6): δ 1.23 (s, 9H, C(CH_3)$_3$), 2.83 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 3.61 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2), 6.69 (d, 1H, $^3J_{HH}$ = 8.7 Hz, 2-ph*H*), 7.07 (s, 1H, 5-Ph*H*), 7.27 (d, 1H, $^3J_{HH}$ = 8.7 Hz, 3-Ph*H*), 7.36 (d, 1H, $^3J_{HH}$ = 2.7 Hz, 5-im*H*), 8.08 (d, 1H, $^3J_{HH}$ = 2.7 Hz, 2-im*H*), 8.22 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 26.2, 31.0, 33.3, 58.2, 113.1, 117.7, 119.0, 125.0, 130.0, 133.0, 135.0, 138.7, 159.2, 162. Anal. calc. for $C_{16}H_{20}N_3ClOPd.1.5\ CH_2Cl_2$: C, 38.95; H, 3.30; N, 7.79. Found: C, 38.85; H, 3.19; N, 7.93 %. MS (ESI): *m*/*z* (%) = 412 (20) (M^+), 376 (5) (M^+-Cl). IR (ATR) (cm^{-1}): 1618 (s) ($\nu_{C=N}$).

Synthesis of [Pd(L5)Cl] (6)

This compound was synthesized following the procedure described for complex **4** using $[PdCl_2(NCMe)_2]$ (0.96 mmol) and **L5** (0.96 mmol) to afford 6 as an orange solid (0.32 g 92 %). ^{1}H NMR, (DMSO-d_6): δ 2.84 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 3.59 (t, 2H, $^3J_{HH}$ = 6.3 Hz, CH_2), 6.56 (d, 1H, 3J_{HH} = 8.1 Hz, 2-Ph*H*), 6.73 (t, 1H, $^3J_{HH}$ = 8.7 Hz, 3-Ph*H*); 7.08 (s, 1H, C=C*H*), 7.27 (t, 1H, $^3J_{HH}$ = 8.7 Hz, 4-Ph*H*), 7.35 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 5-im*H*), 7.56 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 5-Ph*H*), 8.09 (s, 1H, 2-im*H*), 8.22 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 26.1, 58.2, 118.7, 113.1, 114.5, 119.3, 128.8, 134.9, 136.4, 138.7, 161.7, 163.1. Anal. calc. for $C_{12}H_{12}N_3ClOP$ d.CH_2Cl_2: C, 35.40; H, 3.20; N, 9.53. Found: C, 35.10; H, 3.51; N, 9.11 %. MS (ESI): *m*/*z* (%) = 356 (100) (M^+), 320 (20) (M^+-Cl). IR (ATR) (cm^{-1}): 1660 (s) ($\nu_{C=N}$).

4.2. Heck Coupling Reactions

A mixture of aryl halide (iodobenzene or bromobezene) (10 mmol), butyl acrylate (10 mmol) and triethylamine (10 mmol) in 20 mL of DMF was placed in a three-necked flask. The appropriate amount of catalyst was added and the mixture refluxed at the set temperature. Aliquots of the mixture (0.7 mL) were drawn periodically and were analyzed by GC. Percentage conversions were calculated based on the consumption of the aryl halide.

4.3. Single Crystal X-ray Crystallography

The crystal evaluation and data collection for **L2** and **1**–**3** were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation, the single-crystal diffraction experiment for 4 was conducted on a SMART APEX2 diffractometer with Cu K_α (λ = 1.54178 Å) radiation. The crystal-to-detector distance was optimized at 4.9 cm for **L2**, **1**, and **3**, to 6.29 cm for **2**, and to 4.03 cm for **4**. The rest of the structural determination was similar for all compounds and routine. A typical description is given here for **L2**. The initial cell constants were obtained from three series of T scans at different starting angles. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a predetermined resolution. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[28] A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

5. Supplementary Material

CCDC numbers: 836078, 836081, 836079, 836080 and 836077, contain the supplementary crystallographic data for **L2, 1, 2, 3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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