Bisimino-functionalized dibenzo[a,c]acridines as highly conjugated pincer frameworks for palladium(II): synthesis, characterization and catalytic performance in Heck coupling†

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A new pair of highly conjugated ligands, 10-[1-(arylimino)ethyl]-14-[(arylimino)methyl]dibenzo[a,c]acridine (aryl = 2,6-Me₂Ph **L1**, 2,6-Et₂Ph **L2**) incorporating both aldimine and ketimine units, have been prepared by a straightforward sequence of organic transformations from phenanthrene-9,10-dione. Cyclopalladation occurs readily at ambient temperature on treating **L1** or **L2** with PdCl₂(NCCH₃)₂ in aprotic solvents to afford exclusively (N_{ketimine}NC)Pd(II) chloride pincer complexes **Pd1** or **Pd2**, respectively. By contrast in methanol, **Pd1** or **Pd2** are isolated as the minor product with aldehyde-containing **Pd3** or **Pd4** as the major one, the result of hydrolysis of the pendant aldimine units in **Pd1** and **Pd2**, respectively. All the ligands and palladium complexes have been characterized by FT-IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis; the molecular structures for **L1**, **Pd1**, **Pd2**, **Pd3** and **Pd4** are also reported. Using low catalyst loadings (0.0005 – 0.002 mol%) and elevated temperatures (140 – 200 °C), **Pd1** – **Pd4** are able to efficiently mediate the coupling of haloarenes with vinyl-containing substrates with turnover numbers as high as 174000; the effects of steric/electronic variation within the substrate and NNC-pincer complex on catalyst performance are examined.

Introduction

Palladium complexes bearing neutral and monoanionic pincer ligands have established themselves as a powerful tool for a wide range of organic transformations such as the aldol reaction, Michael addition, allylation of aldehydes and imines as well as a range of cross-coupling reactions.^{1–4} With regard to Heck-type coupling, numerous pincer catalysts have been developed incorporating two neutral donors and an anionic aryl-C donor within the terdentate ligand set. In particular those based on symmetrical EC¹E type (E = neutral donor) (**A**, Chart 1)⁵ framework have been at the forefront of research while those involving unsymmetrical ligand frames such as EC¹E' (**B**, Chart 1)⁶ and EEC¹ (**C**, Chart 1)⁷ have also started to emerge as efficient catalysts for this transformation. The presence of a Pd-C σ-bond as the central or exterior donor no doubt imparts the complex with a high level of thermal stability and tolerance of many functional groups, hence

inhibiting facile deactivation pathways and thus leading to highly productive catalysts.⁸ Indeed, pincer complexes have proved exceptional in determining this necessary balance between stability and reactivity.⁹ Consequently, it can be viewed that an ideal pincer catalyst would deliver high turnover numbers, while allowing low catalyst loading and exhibiting good thermal stability.¹⁰ Furthermore, it needs to be amenable to rational design, allowing for systematic tuning of the ligand to enable subtle control over the catalytic properties of the central metal atom.

With a view to enhancing the thermal stability further of an NNC-type palladium pincer complex, we have been interested in developing a means of increasing the conjugation of the ligand backbone through the introduction of suitably fused arene and heteroarene rings. In this report we devise an

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Chart 1. Monoanionic pincer frameworks reported (**A – C**) along with our current work; E and E' refer to neutral donors.

implement a synthetic approach to develop novel bisimino-functionalized benzo[a,c]acridines that are conducive to ready steric and electronic variation (see Chart 1). Owing to the planarity of the pentacyclic skeleton, cyclopalladation proceeds efficiently generating NNC complexes which have been used in the coupling of haloarenes to vinyl-containing substrates. Full synthetic details are reported as is an in depth discussion of the catalytic evaluation of the complexes and substrate scope.

Results and Discussion

Synthesis of **L1** and **L2**

Ligands **L1** and **L2** have been prepared using a six step procedure in reasonable overall yield from commercially available phenanthrene-9,10-dione (Scheme 1). The intermediate compound, 10-ethyl-14-methyldibenzo[a,c]acridine (**2**), has been previously reported using a rather cumbersome low yielding route.¹¹ We have found that **2** can be more conveniently prepared by firstly treating phenanthrene-9,10-dione with a slight excess of 2,6-diethylaniline in the presence of *para*-toluenesulfonic acid to form spiro-[7-ethyl-3-methylindoline-2,10-phenanthren-9-one] (**1**) and then completing the heterocyclization by heating **1** at reflux in 1,2-dichlorobenzene. Mono-bromination at both the ethyl and methyl groups in **2** with two equivalents of *N*-bromosuccinimide (NBS) in carbon tetrachloride gave **3** in near quantitative yield.¹² Substitution of the two bromide groups in **3** for OH groups to give **4** occurred readily by using a silver nitrate assisted hydrolysis in acetone/water (3:1 ratio),¹² which when followed by a pyridinium chlorochromate (PCC) oxidation afforded the mixed aldehyde-ketone **5** in excellent yield.¹³ Finally, the target ligands, 10-[1-(arylimino)ethyl]-14-[(arylimino)methyl]dibenzo[a,c]acridine (aryl = 2,6-Me₂Ph **L1**, 2,6-Et₂Ph **L2**), could be obtained by the Schiff base

condensation of **5** with either 2,6-dimethylaniline or 2,6-diethylaniline in toluene, respectively in reasonable yield.^{14,15} All organic compounds have been characterized by ¹H, ¹³C NMR, IR spectroscopy, HR mass spectrometry or elemental analysis.

It is noteworthy that the formation of **1** was unexpected and, to the knowledge of the authors, has not been observed as a product (*ca.* 38%) in the condensation reaction of phenanthrene-9,10-dione with 2,6-substituted anilines; only small quantities of the expected mono- and bis-imine derivatives of phenanthrene-9,10-dione could be detected under these conditions.^{16,17} The thermally driven rearrangement and ring closing steps involved in the formation of **2** (70%) from **1** are likely mediated by a combination of the relief in ring strain in **1** and the thermodynamic stability of the highly conjugated aromatic **2**. A proposed mechanism for the formation of **2** is depicted in Scheme 2 highlighting the role of acid and involving the elimination of water. Further confirmation of the structures of **1** and **2** was provided in the form of single crystal X-ray structures (see ESI).

The ¹H NMR spectra of **L1** and **L2** recorded in CDCl₃ feature prominent singlets for their -CH=N protons at δ 8.84_{av.} and -CMe=N protons at δ 2.51_{av.}, while the ¹³C NMR spectra show -C=N peaks at δ 171.5_{av.} (ketimine) and δ 163.4_{av.} (aldimine) for **L1** and for **L2**. In their ToF mass spectra peaks corresponding to their protonated molecular ions are seen for each. In addition, the structure of **L1** has been the subject of a single X-ray diffraction study. Suitable crystals for the study were grown by layering a dichloromethane solution of **L1** with heptane. A view of **L1** is shown in Figure 1; selected bond distances and angles are collected in the figure caption.

The structure consists of a slightly twisted dibenzo[a,c]acridine polycycle based on five fused aromatic rings. At the C15- and C20-carbons of the dibenzo[a,c]acridine are located the aldimine and ketimine units, respectively, with the ketimine fragment positioned on the same side as the acridine nitrogen. The two imino C-N bond distances are quite typical

Scheme 1. Reagents and conditions: (a) p-TsOH, toluene, reflux, 12 h; (b) p-TsOH, 1,2-dichlorobenzene, reflux, 12 h; (c) NBS, dibenzoyl peroxide, CCl₄, reflux, 6 h; (d) AgNO₃, acetone/water, 50 °C, 6 h; (e) PCC, CH₂Cl₂, molecular sieves, RT, 6 h.

Scheme 2. Proposed mechanism for the formation of **2** from **1**.

for C=N double bond distances and are indeed similar to one another [C32-N2 1.274(2); C22-N3 1.271(2) Å]. The *N*-aryl ring of the aldimine unit is oriented towards orthogonality with respect to the heterocyclic ring, N1-C12-C13-C15-C16-C21, with a dihedral angle of *ca.* 77.53°, whilst the *N*-aryl ring of the ketimine adopts a shallower angle of *ca.* 32.85°.

Synthesis of NNC Pd pincer complexes

With a view to preparing organo-palladium complexes based on **L1** or **L2**, we envisaged that, due to the presence of more than one nitrogen-based directing group, two sites for C_{aryl}-H activation on the dibenzo[*a,c*]acridine could conceivably occur, namely at the C₂-position or the C₁₁-position (see Scheme 3 for numbering system). To explore these possibilities, **L1** and **L2** were treated with PdCl₂(NCMe)₂ under different reaction conditions (Table 1). Hence, the equimolar reaction of **L1** or **L2**

a mixture of methanol/toluene at 50 °C, two types of complexes were isolable for each namely **Pd1**/**Pd3** or **Pd2**/**Pd4**, respectively.¹⁸ Indeed, **Pd3** and **Pd4** were formed as the major products while **Pd1** and **Pd2** the minor ones. Addition of sodium bicarbonate to the reaction of **L1** with PdCl₂(NCMe)₂ in toluene gave some modest increase in the yield of **Pd1**. Complexes **Pd1**, **Pd2**, **Pd3** and **Pd4** were characterized by ¹H NMR, ¹³C NMR, FT-IR spectroscopy, ESI mass spectrometry and by elemental analysis. In addition, all four complexes were the subject of single crystal X-ray diffraction studies.

Single crystals of **Pd1** and **Pd2** were grown by layering chloroform solutions of the complex with heptane. The molecular structures of both are similar and will be discussed together. As a representative example a view of **Pd1** is depicted in Figure 2; selected bond distances and angles are listed in Table 2. Each structure reveals a mononuclear species in which the palladium(II) center occupies a tridentate cavity within the ligand frame with the ketimine nitrogen, the acridine nitrogen and an aryl carbon serving as the donor atoms. The geometry of the palladium can be best described as distorted square planar with a chloride ligand filling the fourth coordination site. Within the NNC-palladium unit both five- and six-membered chelate rings are present with the carbon donor incorporated into the smaller metallacycle. Due to the constraints of the NNC ligand the C1-Pd1-N2 angles are less than the desired 180°: 167.25(19)° for **Pd1**, 167.09(13)° for **Pd2**. The Pd(1)-C(1) bond distances in **Pd1** [1.979(5) Å] and **Pd2** [1.986(3) Å], are comparable with those found in related NNC pincer complexes¹⁹ and are the shortest of the three NNC contacts to palladium; this reflects the ionic contribution to the Pd-C bond. Little significant bond variation is seen between the bound C=N_{ketimine} bond length and the C=N_{aldimine} bond lengths in either structure and indeed similar to that found in **L1**. Some puckering of the six-membered chelate ring is apparent with the bound C=N_{ketimine} unit some way of co-planar with the pyridine plane (dihedral angle = 30.1° **Pd1**, 34.6° **Pd2**); the corresponding angle for the pendant aldimine is close to 45° (dihedral angle = 44.8° **Pd1**, 43.8° **Pd2**). For both complexes the *N*-aryl rings are inclined towards perpendicular (**Pd1** 88.28°, 85.59°; **Pd2** 81.63°, 89.44°) with respect to the C1-N1-N2-C11 coordination plane, presumably to minimize steric interactions.

Figure 1. ORTEP diagram of **L1** with the thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)-C(12) 1.324(2), N(1)-C(21) 1.353(2), N(3)-C(22) 1.271(2), N(3)-C(24) 1.427(2), C(32)-N(2) 1.274(2), N(2)-C(33) 1.426(2), C(11)-C(10) 1.405(2), C(10)-C(9) 1.378(3), C(12)-N(1)-C(21) 119.07(14), C(32)-N(2)-C(33) 117.86(14), C(22)-N(3)-C(24) 121.21(15), N(3)-C(22)-C(20) 116.38(15), N(3)-C(22)-C(23) 125.38(16), C(9)-C(10)-C(11) 120.63(18).

with PdCl₂(NCCH₃)₂ in aprotic solvents such as dichloromethane or toluene at room temperature gave **Pd1** and **Pd2**, respectively, as the only isolable product in reasonable yield (Scheme 3). However, on reacting **L1** or **L2** in

The ^1H NMR spectra of **Pd1** and **Pd2** are supportive of their solid state structures being maintained in solution. The presence of only 16 protons in the aromatic region is

Scheme 3. Synthesis of NNC-Pd pincer complexes: (a) dichloromethane or toluene, RT; (b) toluene, NaHCO₃ (cat.), 60 °C, 6 h; (c) methanol/toluene, 50 °C, 6 h

the chemical shift of the pendant $\text{CH}=\text{N}$ remains relatively unchanged. Surprisingly, no discernible difference in $\nu(\text{C}=\text{N})_{\text{imine}}$ stretching frequency in the IR spectrum could be observed for the two types of imine. The ESI mass spectra for each complex recorded in acetonitrile show strong $[\text{M}-\text{Cl}]^+$ peaks as their MeCN adducts.

aldehyde group is linked to the *para*-position of the pyridine unit rather than an aldimine group. The presence of the aldehyde on the back of the ligand frame has little effect on the NNC bond parameters with the Pd-N_{imine} distance again the longest [**Pd3** 2.111(2) Å, **Pd4** 2.1276 (16) Å] and the Pd-C distance the shortest [**Pd3** 1.978(3) Å, **Pd4** 1.9834 (19) Å]. As with the aldimine unit in **Pd1** and **Pd2**, the aldehyde unit is tilted with regard to the pyridine plane (dihedral angle = 42.1° **Pd3**, 54.8° **Pd4**).

Figure 2. ORTEP diagram of **Pd1** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity.

Crystals of **Pd3** and **Pd4** suitable for the X-ray determination were grown by layering dichloromethane solutions with heptane at room temperature. A perspective view of representative **Pd4** is given in Figure 3; selective bond lengths and bond angles for **Pd3** and **Pd4** are collected alongside **Pd1** and **Pd2** in Table 2. The structures closely resemble **Pd1** and **Pd2** with the main difference being that an

Figure 3. ORTEP diagram of **Pd4** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity.

The presence of the aldehyde groups is further confirmed in the ^1H NMR spectra for **Pd3** and **Pd4** with downfield signals for the $-\text{CHO}$ protons visible at δ 10.63 and δ 10.62 respectively, while in the ^{13}C NMR spectra the $-\text{CHO}$ carbons appear at δ

Method

Table 1. Reaction condition effects on product formation

Entry	Ligand	Solvent	Base	Temp. (°C)	Product 1 (%)	Product 2 (%)
1	L1	Dichloromethane	-	25	Pd1 (42)	-
2	L2	Dichloromethane	-	25	Pd2 (38)	-
3	L1	Toluene	-	25	Pd1 (36)	-
4	L2	Toluene	-	25	Pd2 (30)	-
5	L1	Toluene	NaHCO ₃ (cat.)	60	Pd1 (52)	-
6	L1	Methanol/Toluene	-	50	Pd1 (12)	Pd3 (46)
7	L2	Methanol/Toluene	-	50	Pd2 (15)	Pd4 (41)

193.2 and 192.1 ppm. In the IR spectra bands corresponding to both $\nu(\text{C}=\text{O})_{\text{aldehyde}}$ and $\nu(\text{C}=\text{N})_{\text{imine}}$ at 1697 and 1614 cm^{-1} , respectively are clearly observable for both. As with **Pd1** and **Pd2** the ESI mass spectrum for each complex recorded in acetonitrile show strong $[\text{M}-\text{Cl}]^+$ peaks as their MeCN adducts.

The preferential C-H activation of the C₂-H proton (see Scheme 3 for numbering system) of the dibenzo[a,c]acridine unit over the C₁₁-H position is likely due to the extra chelate ring stability afforded when **Pd1** and **Pd2** are formed. Attempts to react **Pd1** or **Pd2** with a further equivalent of $\text{PdCl}_2(\text{NMe}_2)_2$, with a view to initiating a second C-H activation, were

unsuccessful. It is assumed the C-H activation step to form **Pd1** or **Pd2** follows an AMLA type mechanism with a chloride ligand acting as the intramolecular base.²⁰ Nevertheless the ready activation of this C-H bond at room temperature with palladium(II) chloride is worthy of note and it seems likely that this is made more facile by the close and fixed proximity of the aryl-H bond that is imposed by the conjugated ligand framework. With regard to the unexpected formation of **Pd3** and **Pd4**, it would seem likely that the use of protic MeOH as solvent is initiating the hydrolysis of the corresponding aldimine groups.

Table 2. Selected bond lengths (Å) and angles (°) for **Pd1**, **Pd2**, **Pd3** and **Pd4**.

	Pd1	Pd2	Pd3	Pd4
Pd(1)-C(1)	1.979(5)	1.986(3)	1.978(3)	1.9834(19)
Pd(1)-N(1)	2.028(4)	2.027(3)	2.027(2)	2.0254(16)
Pd(1)-N(2)	2.123(4)	2.115(3)	2.111(2)	2.1276(16)
Pd(1)-Cl(1)	2.3100(17)	2.3009(9)	2.3039(8)	2.3030(8)
C(32)-N(3) _{aldimine}	1.264(7)	1.275(4)	-	-
C(22)-N(2) _{ketimine}	1.294(7)	1.281(4)	-	-
C(32)-O(1) _{aldehyde}	-	-	1.205(4)	1.207(2)
C(1)-Pd(1)-N(1)	82.38(19)	82.98(13)	82.94(10)	82.96(7)
N(1)-Pd(1)-N(2)	90.44(17)	89.57(10)	91.55(8)	91.11(6)
C(1)-Pd(1)-N(2)	167.25(19)	167.09(13)	170.18(10)	166.88(7)
N(1)-Pd(1)-Cl(1)	173.29(12)	173.55(8)	172.84(6)	170.39(4)
C(1)-Pd(1)-Cl(1)	93.17(16)	92.48(11)	92.05(8)	92.80(6)
N(2)-Pd(1)-Cl(1)	94.83(13)	95.71(8)	94.11(6)	94.73(5)

Heck coupling reactions

To probe the capacity of NNC pincer complexes **Pd1** – **Pd4** to mediate a range of Heck-type coupling reactions, we initially explored the use of **Pd1** to establish the most suitable conditions for the coupling of bromobenzene with styrene. Using a 0.002 mol% catalyst loading we explored the effect of base, solvent, temperature and reaction duration on the conversion to stilbene; the results are collected in Table 3.

On inspection of the data, the most suitable reaction parameters were found when the coupling was performed in dimethylformamide (DMF) at 140 °C in the presence of Na₂CO₃ for eight hours resulting in a 67% conversion to stilbene (Table 3, entry 11). Some other solvents such as dimethylacetamide (DMA) (entries 1-6, Table 3), toluene (entry 10, Table 3) and acetonitrile (entry 12, Table 3) were also examined under similar conditions but these all proved less effective. Likewise,

a variety of different bases such as K_2CO_3 (entry 7, Table 3), $NaHCO_3$ (entry 8, Table 3) and $NaOH$ (entry 9, Table 3) were screened but these again gave less promising results. Notably, the high temperature of 140 °C proved vital as performing the reactions at temperatures below 120 °C gave no conversion (entries 1-3, Table 3).

As expected, using more activated arenes led to higher conversions. For example with iodobenzene 90% conversion

Table 3. Optimization of reaction conditions using **Pd1** as catalyst^a

Entry	Base	Solvent	Temp. (°C)	Time (h)	Conv. (%) ^b	TON ^c
1	Na_2CO_3	DMA	60	8	0	0
2	Na_2CO_3	DMA	100	8	0	0
3	Na_2CO_3	DMA	120	8	0	0
4	Na_2CO_3	DMA	140	4	21	10500
5	Na_2CO_3	DMA	140	8	29	14500
6	Na_2CO_3	DMA	140	12	41	20500
7	K_2CO_3	DMA	140	8	6	3000
8	$NaHCO_3$	DMA	140	8	21	10500
9	$NaOH$	DMA	140	8	6	3000
10	Na_2CO_3	Toluene	100	8	0	0
11	Na_2CO_3	DMF	140	8	67	33500
12	Na_2CO_3	CH_3CN	60	8	0	0
13 ^d	Na_2CO_3	DMF	140	8	90	45000
14 ^d	Na_2CO_3	DMF	200	8	88	44000
15 ^e	Na_2CO_3	DMF	140	8	87	174000

^a Reaction conditions: 4×10^{-5} mmol **Pd1**, 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol base, 4.0 mL solution. ^b Determined by GC. ^c TON: mol stilbene/mol Pd. ^d 2.0 mmol iodobenzene used in place of bromobenzene. ^e 2.5×10^{-6} mmol **Pd1** (0.0005 mol%), 2.0 mmol iodobenzene used in place of bromobenzene.

(entry 13, Table 3) was achieved, while with 4-iodotoluene close to quantitative conversion was noted (Table S1a). Prolonging the reaction time gave only modest improvements in the conversion (Table S1b). Most notably, **Pd1** allowed 88% conversion to stilbene even at 200 °C (entry 14, Table 3) which highlights the exceptional balance between thermal stability and reactivity displayed by this catalyst.^{9, 10} Reducing the catalyst loading from 0.002 to 0.0005 mol%, showed only a slight drop in conversion (87%, TON = 174000) (Table 3, entry 15). Compared with previous reports that show similarly high conversions in Heck reactions, **Pd1** is at the lower end of the range in terms of catalyst loading; its high thermal robustness represents a notable advantage.^{6e, 7b, 7c, 7d}

To examine the role of electronic and steric effects on the catalytic efficiency, **Pd2**, **Pd3** and **Pd4** were additionally evaluated under the optimized reaction conditions established for **Pd1**; the results are compiled in Table 4. Several points emerge from examining the data. Firstly, both aldehyde-containing complexes **Pd3** and **Pd4** (entries 3 and 4 respectively) gave improved catalytic efficiency when compared with their imine counterparts **Pd1** and **Pd2**, respectively. Secondly, the more sterically protected **Pd2** gave a lower conversion to stilbene (entry 2, Table 4) compared to **Pd1**. Thirdly, the use of palladium(II) chloride alone gave only 20% conversion; albeit at higher catalyst loading. These

observations highlight the role of the ligand in influencing catalytic performance. Both steric and electronic factors present within the ligand frame further affect turnover with a combination of good electron withdrawing groups and less sterically hindered aryl groups leading to optimal performance.

On the basis of the encouraging results obtained for the Heck coupling of bromobenzene with styrene, we decided to explore the potential of **Pd3** for the coupling reaction of other haloarenes with styrene and *N-tert*-butylacrylamide; the results are documented in Table 5. Under similar conditions (*viz.*, 0.002 mol% of catalyst, 8 h reaction at 140 °C, DMF as solvent and Na_2CO_3 as base), **Pd3** showed a broad substrate scope with respect to the haloarenes employed (Table 5). In all the reactions involving styrene (entries 1-5, 7-9), good to very good TON values were observed²¹ with the iodoarenes the best. However 2,6-dimethylbromobenzene appeared the least active substrate (entry 6) which can be attributed to the

Table 4. Heck reaction of bromobenzene with styrene catalyzed by **Pd1** – **Pd4**^a

Entry	Complex	Conversion (%) ^b	TON ^c
1	Pd1	67	33500
2	Pd2	62	31000
3	Pd3	70	35000
4	Pd4	66	33000
5 ^d	PdCl ₂	20	200

^a Reaction conditions: 4×10^{-5} mmol complex, 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol Na₂CO₃, 4.0 mL DMF, 140 °C for 8 h. ^b Determined by GC. ^c TON: mol stilbene/mol Pd; ^d 2×10^{-3} mmol Pd.

Table 5. Heck reaction of aryl halides with styrene and *N*-*tert*-butylacrylamide using **Pd3** as catalyst^a

$\text{Ar}-\text{X} + \text{vinyl substrate} \xrightarrow[\text{Na}_2\text{CO}_3, \text{DMF}, 140^\circ\text{C}]{\text{Pd3 (0.002 mol\%)}} \text{Ar}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5 \text{ or } \text{Ar}-\text{CH}=\text{CH}-\text{C}(=\text{O})\text{NH}-\text{Bu}^t$					
Entry	Ar-X	Vinyl substrate	Conv. (%)	Yield (%)	TON ^d
1		styrene	49	38	24500
2		styrene	60	51	30000
3		styrene	45	36	24500
4		styrene	78	70	39000
5		styrene	50	44	25000
6		styrene	19	12	9500
7		styrene	42	35	21000
8		styrene	97	90	45000
9		styrene	97	91	48500
10			50	41	25000
11			78	70	34000
12			43	30	21500
13			55	40	27500
14			57	45	28500
15			94	87	47000
16			>99	93	49500

Method

^a Reaction conditions: 4×10^{-5} mmol **Pd3**, 2.0 mmol Ar-X, 2.4 mmol styrene or *N*-*tert*-butylacrylamide, 2.2 mmol Na_2CO_3 , 4.0 mL DMF, 140 °C for 8 h. ^b Determined by GC. ^c Isolated yield, their ^1H and ^{13}C NMR spectra were compared with literature reports.²⁵⁻²⁷ ^d TON: mol product/mol Pd.

detrimental effect of the *ortho*-methyl substituents due to their steric properties, similar observations have been seen elsewhere.^{22,23} No negative effects on conversion were observed with either electron withdrawing (-CN) or donating (-NH₂) groups positioned on the *ortho*-position of the bromoarenes, in fact some conversion rates were improved (entries 3 and 7). Meanwhile electron donating groups on the *para*-position enhanced the coupling reaction (entries 1,4,8,9). Using *N*-*tert*-butylacrylamide as the vinyl substrate with **Pd3** also resulted in good to excellent conversions albeit with a narrower range of turnover numbers (entries 10-16). 4-Iodotoluene gave the highest activity (essentially quantitative conversion) of all the reactions screened (entry 16) and slightly higher than observed when styrene was employed as the vinyl-containing substrate (entry 8), an observation that has been noted previously.²⁴

Conclusions

In summary, we have reported the synthesis of two highly conjugated mixed aldimine-ketimine ligands, **L1** and **L2**, based on the dibenzo[a,c]acridine motif by a series of simple steps including heterocyclization of an unusual spirocycle. $\text{N}_{\text{ketimine}}\text{NC}$ -palladium pincer complexes, **Pd1** and **Pd2**, are readily accessible at room temperature on reaction of **L1** or **L2** with $\text{PdCl}_2(\text{NCMe})_2$ in aprotic solvents while the introduction of methanol leads to hydrolysis of the non-coordinated aldimine unit in **Pd1** and **Pd2** to give aldehyde-containing **Pd3** and **Pd4**. All four complexes display good to very good performance for the metal-mediated coupling of bromobenzene with styrene at elevated temperatures (*ca.* 140 °C) with **Pd3** the standout performer. The effectiveness of **Pd3** to catalyze the coupling of a series of electronically and sterically distinct bromobenzenes with styrene and *N*-*tert*-butylacrylamide has also shown the general applicability of this NNC pincer complex. Further studies are underway to determine the scope of these thermally robust ligand frames to support other metal-mediated catalytic processes.

Experimental

General Consideration: All manipulations of ligands were carried out under an open air atmosphere while those

involving complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled under nitrogen from appropriate drying agents immediately prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 400 MHz spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) at ambient temperature using TMS as an internal standard; δ values were given in ppm and *J* values in Hz. Fourier Transform IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was performed using an HPMOD 1106 microanalyzer. GC measurements were performed on a VARIAN CP-3800 GC containing a chrompack capillary column (cp-sil 5 CB). The electrospray (ESI) mass spectra for the complexes and the high resolution mass spectra (MALDI ToF) for all new organic compounds were measured using Bruker 9.4T Solarix (FT-ICR-MS) instrument. Phenanthrene-9,10-dione, 2,6-diethylaniline, 2,6-dimethylaniline, the haloarenes, styrene and *N*-*tert*-butylacrylamide were purchased from Aldrich and Acros and used without further purification. $\text{PdCl}_2(\text{NCCH}_3)_2$ was prepared using the literature method.²⁸ Other general reagents were purchased from Aldrich, Acros or local suppliers.

Synthesis of pincer Ligands

Preparation of spiro-[7-ethyl-3-methylindoline-2,10-phenanthrene-9-one] (1)

To a solution of phenanthrene-9,10-dione (10.00 g, 48.03 mmol) and *p*-toluenesulfonic acid (1.83 g, 20 mol%) in dry toluene (200 mL) was added dropwise 2,6-diethylaniline (14.34 g, 96.06 mmol) and the reaction mixture stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was concentrated on the rotary evaporator and purified by silica gel column chromatography using petroleum ether/ethyl acetate (125/1) as the eluent to give **1** as a yellow crystalline solid (6.23 g, 38%). The mono-imine¹⁶ and bis-imine^{16,17} derivatives of phenanthrene-9,10-dione were discarded. Mp: 118-119 °C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.97 (d, *J* = 8 Hz, 1H, Ph-*H*), 7.90-7.87 (m, 2H, Ph-*H*), 7.79 (d, *J* = 7.6 Hz, 1H, Ph-*H*), 7.69 (t, *J* = 8 Hz, 1H, Ph-*H*), 7.43-7.30 (m, 3H, Ph-*H*), 7.03 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 6.81-6.73 (m, 2H, Ph-*H*), 4.64 (s, 1H, NH), 3.46 (q, *J* = 7.2 Hz, 1H, CH), 2.75-2.69 (m, 2H, CH₂), 1.38 (t, *J* = 7.8 Hz, 3H, CH₃), 0.98 (d, *J* = 7.2 Hz, 3H, CH₃). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 201.4, 152.7, 148.7, 143.0, 137.6, 134.7, 131.4, 130.8, 130.7, 129.5, 128.7, 128.1, 127.4, 127.2, 127.0, 126.3, 124.2, 123.1, 121.1, 120.5, 54.7, 24.5, 17.6, 13.6. FT-IR (KBr, cm^{-1}): 3070 (w), 2964 (s), 2927 (w), 2870 (w), 1676 (v(-C=O) s), 1596 (s), 1478 (s), 1478 (s), 1393 (m), 1267 (w), 1064 (m), 987 (w), 898 (m), 733 (s). HRMS (MALDI) (*m/z*) calcd for $\text{C}_{24}\text{H}_{21}\text{NO}$ [*M* + *H*]⁺ 340.17014; found 340.16953.

Preparation of 10-ethyl-14-methyldibenzo[a,c]acridine (2)

A solution of **1** (5.00 g, 14.74 mmol) and *p*-toluenesulfonic acid (0.56 g, 20 mol%) in dichlorobenzene (40 mL) was stirred and heated to reflux for 12 h. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (250/1) as the eluent, yielding **2** as a white solid (3.31 g, 70%). Mp: 100–101 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 9.68–9.44 (m, 1H, Ph-*H*), 8.55 (d, *J* = 8 Hz, 1H, Ph-*H*), 8.48–8.45 (m, 1H, Ph-*H*), 8.30 (d, *J* = 8 Hz, 1H, Ph-*H*), 8.09 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 7.71–7.69 (m, 2H, Ph-*H*), 7.63 (t, *J* = 6.8 Hz, 2H, Ph-*H*), 7.55 (t, *J* = 7.2 Hz, 2H, Ph-*H*), 3.60–3.55 (m, 2H, CH₂), 3.28 (s, 3H, CH₃), 1.54 (t, *J* = 7.6 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 146.6, 144.7, 143.7, 140.8, 132.3, 132.2, 131.6, 130.6, 130.1, 129.4, 128.0, 127.9, 127.6, 127.6, 126.7, 126.1, 126.0, 123.7, 123.4, 122.5, 122.4, 25.4, 20.4, 15.5. FT-IR (KBr, cm⁻¹): 3066 (w), 2963 (s), 2935 (m), 2880 (w), 1424 (m), 1398 (s), 1352 (m), 793 (s), 753 (s). HRMS (MALDI) (*m/z*) calcd for C₂₄H₁₉N [M + H]⁺ 322.15957; found 322.15902.

Preparation of 10-(1-bromoethyl)-14-(bromomethyl)dibenzo[*a,c*]acridine (**3**)

2 (3.00 g, 9.34 mmol), N-bromosuccinimide (3.32 g, 18.68 mmol) and dibenzoyl peroxide (0.23 g, 10 mol%) were suspended in CCl₄ (100 mL). The suspension was stirred and heated to reflux in a vessel open to the air for 6 h. On completion of the reaction, the mixture was filtered whilst hot. The filtrate was collected and the solvent removed under reduced pressure. The residue was recrystallized from dichloromethane and heptane forming **3** as a light yellow solid (4.25 g, 95%). Mp: 174–175 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 9.42 (s, 1H, Ph-*H*), 8.82 (d, *J* = 7.6 Hz, 1H, Ph-*H*), 8.58 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 8.47 (d, *J* = 7.6 Hz, 2H, Ph-*H*), 8.10 (d, *J* = 6.0 Hz, 1H, Ph-*H*), 7.78–7.67 (m, 5H, Ph-*H*), 7.05 (q, *J* = 7.2 Hz, 1H, CH), 5.37 (s, 2H, CH₂), 2.32 (broad singlet, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 147.5, 141.8, 137.6, 132.2, 132.2, 131.5, 130.3, 130.2, 128.8, 128.7, 128.4, 127.5, 127.2, 126.9, 126.7, 126.2, 124.7, 124.1, 122.6, 44.3, 31.9, 26.4. FT-IR (KBr, cm⁻¹): 3069 (w), 3031 (w), 2971 (m), 1374 (s), 1348 (s), 789 (s), 764 (m), 748 (s). HRMS (MALDI) (*m/z*) calcd for C₂₄H₁₇Br₂N [M + H]⁺ 477.98060; found 477.98005.

10-(1-hydroxyethyl)-14-(hydroxymethyl)dibenzo[*a,c*]acridine (**4**)

3 (1.00 g, 2.10 mmol) was added to a solution of silver nitrate (1.25 g, 7.34 mmol, 3.5 equiv.) in 100 mL of 70% aqueous acetone at 50 °C, and the resultant suspension was stirred for 50 °C for 3 h. On completion of the reaction, the mixture was filtered through sintered glass, diluted with water (50 mL) and extracted with dichloromethane (3 × 30 mL). The combined dichloromethane extracts were washed twice with water, dried over anhydrous MgSO₄ and concentrated under reduced pressure to give **4** as a brown powder (0.71 g, 96%). No further purification was performed. Mp: 177–178 °C. ¹H NMR (400 MHz, DMSO, TMS): δ 9.24 (s, 1H, Ph-*H*), 8.87 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 8.75 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 8.69 (d, *J* = 6.8 Hz, 1H, Ph-*H*), 8.45 (d, *J* = 8.4 Hz, 1H, Ph-*H*), 8.00 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 7.80–7.71 (m, 5H, Ph-*H*), 6.22–6.19 (m, 2H, CH₂), 5.38 (d, *J* = 4.4 Hz, 1H, OH), 5.29 (t, *J* = 4.4 Hz, 2H, OH, CH), 1.63 (s, 3H, CH₃).

¹³C NMR (100 MHz, DMSO, TMS): δ 145.6, 145.2, 142.8, 141.9, 131.6, 130.7, 130.3, 130.2, 129.9, 128.5, 128.4, 128.1, 127.0, 126.8, 126.3, 125.6, 125.0, 123.7, 123.5, 123.0, 122.7, 64.3, 58.9, 25.8. FT-IR (KBr, cm⁻¹): 3226 (broad, OH), 3074 (w), 2963 (w), 2921 (w), 1706 (s), 1550 (s), 1278 (w), 760 (s), 730 (s). HRMS (MALDI) (*m/z*) calcd for C₂₄H₁₉NO₂ [M + H]⁺ 354.14940; found 354.14885.

Preparation of 10-acetyl-14-formyldibenzo[*a,c*]acridine (**5**)

Pyridinium chlorochromate (1.13 g, 5.25 mmol) was added to solution of **4** (1.0 g, 2.83 mmol) in dichloromethane (50 mL) at 0 °C. Crushed molecular sieves (1 g) were also added to adsorb sticky by-products. The mixture was stirred for 6 h at ambient temperature. On completion of the reaction (as monitored by TLC), the mixture was filtered through a silica plug. The filtrate was diluted by the addition of water (50 mL) and extracted with dichloromethane (3 × 15 mL). The combined extracts were dried over anhydrous magnesium sulfate and, following solvent evaporation, the residue was recrystallized from dichloromethane and heptane affording **5** as a yellow solid (0.89 g, 90%). Mp: 196–197 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 10.58 (s, 1H, CHO), 9.31–9.28 (m, 1H, Ph-*H*), 9.03–8.99 (m, 1H, Ph-*H*), 8.67 (d, *J* = 10.4 Hz, 1H, Ph-*H*), 8.58–8.55 (m, 1H, Ph-*H*), 8.12–8.10 (m, 1H, Ph-*H*), 7.93–7.90 (m, 1H, Ph-*H*), 7.87–7.73 (m, 5H, Ph-*H*), 3.14 (s, 1H, CH₃). ¹³C NMR (100 MHz, DMSO, TMS): δ 202.5, 194.9, 149.5, 147.3, 143.4, 139.2, 136.9, 131.7, 131.3, 130.9, 130.9, 130.1, 129.6, 129.5, 128.6, 127.8, 127.7, 127.3, 126.0, 125.6, 124.3, 123.3, 123.2, 121.6. FT-IR (KBr, cm⁻¹): 3075 (w), 2855 (w), 1682 (v(C=O) m), 1391 (s), 1344 (m), 797 (s), 760 (m), 739 (s). HRMS (MALDI) (*m/z*) calcd for C₂₄H₁₅NO₂ [M + H]⁺ 350.11810; found 350.11755.

Preparation of 10-[1-(2,6-dimethylphenylimino)ethyl]-14-[(2,6-dimethylphenylimino)methyl]dibenzo[*a,c*]acridine (**L1**)

To a mixture of **5** (0.85 g, 2.43 mmol) and catalytic amount of *p*-toluenesulfonic acid (0.13 g, 10 mol%) in dry toluene (30 mL) was added dropwise 2,6-dimethylaniline (0.74 g, 6.08 mmol). The mixture was stirred and heated to reflux for 12 h. On cooling to room temperature, all volatiles were removed under reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate (125:1, v/v) as the eluent affording **L1** as a deep yellow powder (0.60 g, 45%). Mp: 195–196 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 9.69 (d, *J* = 8.8 Hz, 1H, Ph-*H*), 9.33 (d, *J* = 7.6 Hz, 1H, Ph-*H*), 8.84 (s, 1H, CH=N), 8.59 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 8.52 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 8.22 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 8.17 (d, *J* = 8.0 Hz, 1H, Ph-*H*), 7.82–7.686 (m, 4H, Ph-*H*), 7.53 (t, *J* = 8.0 Hz, 1H, Ph-*H*), 7.18 (t, *J* = 6.4 Hz, 4H, Ph-*H*), 7.08–6.99 (m, 2H, Ph-*H*), 2.52 (s, 3H, CH₃C=N), 2.37 (s, 12H, 4 × CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 171.5, 163.7, 151.0, 148.8, 147.4, 145.4, 141.6, 135.3, 132.1, 131.8, 131.2, 130.0, 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0, 127.6, 127.0, 126.6, 126.3, 126.0, 124.5, 124.4, 124.2, 123.9, 123.0, 122.7, 31.9, 28.9, 23.4, 22.7, 18.5, 18.1, 17.5, 14.0. FT-IR (KBr, cm⁻¹): 2959 (w), 2918 (w), 2855 (m), 1646 (v(HC=N) s), 1628 (v(CH₃C=N) s), 1375 (s), 1347 (s), 1292 (m), 1202 (m), 854 (s), 797 (s), 768 (s). Anal. Calcd for C₄₀H₃₃N₃ (555): N, 7.56; C, 86.45; H, 5.99. Found: N, 7.61; C, 86.38; H, 6.09. HRMS (MALDI) (*m/z*) calcd for C₄₄H₃₃N₃ [M + H]⁺ 556.27527; found 556.27472..

Preparation of 10-[1-(2,6-diethylphenylimino)ethyl]-14-[(2,6-diethylphenylimino)methyl]dibenzo[a,c]acridine (**L2**)

L2 was prepared using a similar procedure and molar ratios to that described for **L1** affording a deep yellow solid (0.61 g, 41%). Mp: 207–208 °C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 9.76 (d, J = 8.4 Hz, 1H, Ph-H), 9.34 (d, J = 8.0 Hz, 1H, Ph-H), 8.83 (s, 1H, CH=N), 8.59 (d, J = 8.0 Hz, 1H, Ph-H), 8.52 (d, J = 7.6 Hz, 1H, Ph-H), 8.19 (d, J = 8.0 Hz, 1H, Ph-H), 8.13 (d, J = 8.0 Hz, 1H, Ph-H), 7.82–7.76 (m, 2H, Ph-H), 7.73–7.68 (m, 2H, Ph-H), 7.51 (t, J = 8.0 Hz, 1H, Ph-H), 7.23–7.21 (m, 4H, Ph-H), 7.17–7.13 (m, 2H, Ph-H), 2.88–2.69 (m, 8H, $4 \times \text{CH}_2$), 2.52 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 1.34 (t, J = 7.6 Hz, 6H, $2 \times \text{CH}_3$), 1.26 (t, J = 7.6 Hz, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 171.4, 163.3, 149.9, 147.8, 147.5, 145.4, 141.8, 134.8, 133.3, 132.2, 132.0, 131.9, 131.8, 131.2, 130.0, 129.0, 128.8, 128.2, 128.1, 127.7, 127.1, 126.7, 126.6, 126.4, 125.9, 124.8, 124.3, 123.9, 123.3, 12.7, 53.4, 24.6, 23.6, 15.2, 14.0. FT-IR (KBr, cm^{-1}): 2963 (w), 2925 (w), 2866 (m), 1652 (v(HC=N) s), 1620 (v($\text{CH}_3\text{C}=\text{N}$) s), 1456 (w), 1347 (s), 1290 (m), 1256 (m), 856 (s), 799 (s), 766 (s). Anal. Calcd for $\text{C}_{44}\text{H}_{41}\text{N}_3$ (611): N, 6.87; C, 86.38; H, 6.75. Found: N, 6.76; C, 86.07; H, 6.86. HRMS (MALDI) (m/z) calcd for $\text{C}_{44}\text{H}_{41}\text{N}_3$ [$\text{M} + \text{H}$] $^+$ 612.33787; found 612.33732.

Synthesis of NNC pincer complexes

a) Typical procedure in either toluene or dichloromethane solution: Equimolar amounts of **L1** (0.200 g, 0.36 mmol) and $\text{PdCl}_2(\text{NCCH}_3)_2$ (0.093 g, 0.036 mmol) were added to either dichloromethane (10 mL) or toluene solution (10 mL) and the reaction mixture stirred for 10 h at ambient temperature. The resultant precipitate was collected by filtration, washed with diethyl ether and heptane. The respective yields are given in Table 1.

b) Typical procedure in toluene solution along with base: To a solution of **L1** (0.200 g, 0.36 mmol) in toluene (25 mL), was added $\text{PdCl}_2(\text{NCCH}_3)_2$ (0.093 g, 0.36 mmol) under a nitrogen atmosphere. A catalytic amount of NaHCO_3 was also added and the reaction mixture stirred and heated at 60 °C for 6 h. On cooling to room temperature, all volatiles were removed under reduced pressure. The residue was re-dissolved in CH_2Cl_2 (20 mL) and filtered to remove any insoluble material. Following filtration, the filtrate was concentrated and the residue recrystallized from heptane to give **Pd1** as an orange solid (0.130 g, 52%).

c) Typical procedure in methanol solution: $\text{PdCl}_2(\text{NCCH}_3)_2$ (0.093 g, 0.36 mmol) was added to a solution of **L1** (0.200 g, 0.36 mmol) in a mixture of methanol/toluene (10 mL/15 mL) under a nitrogen atmosphere. After stirring and heating the reaction mixture at 50 °C for 6 h, all volatiles were removed under reduced pressure. The resultant residue was purified by a short column of silica gel. Elution with petroleum ether/ethyl acetate (100/1) firstly afforded **Pd1** as an orange solid on rotary evaporation. **Pd3** could then be collected using petroleum ether/ethyl acetate 50/1 as an orange solid on evaporation. The respective yields are given in Table 1.

Pd1: Based on either of the procedures described in a), b) and c), **Pd1** was obtained as an orange solid in the corresponding yield given in Table 1. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 9.75

(d, J = 8.4 Hz, 1H, Ph-H), 8.83 (s, 1H, CH=N), 8.48 (d, J = 8.0 Hz, 1H, Ph-H), 8.41 (d, J = 7.6 Hz, 1H, Ph-H), 8.19 (d, J = 7.2 Hz, 1H, Ph-H), 8.03–7.98 (m, 2H, Ph-H), 7.78 (t, J = 8.4 Hz, 1H, Ph-H), 7.71 (t, J = 7.2 Hz, 1H, Ph-H), 7.50–7.42 (m, 2H, Ph-H), 7.21–7.11 (m, 6H, Ph-H), 2.40 (s, 6H, $2 \times \text{CH}_3$), 2.37 (s, 6H, $2 \times \text{CH}_3$), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 169.4, 162.3, 156.7, 150.3, 148.6, 141.5, 140.2, 137.2, 136.6, 133.4, 132.6, 132.5, 132.2, 131.5, 131.2, 130.0, 128.8, 128.1, 127.9, 126.9, 126.6, 126.5, 126.4, 125.7, 125.1, 124.3, 118.3, 53.3, 52.9, 23.0, 18.9, 18.5. FT-IR (KBr, cm^{-1}): 2961 (w), 2914 (w), 2850 (w), 1618 (v(HC=N), ($\text{CH}_3\text{C}=\text{N}$) broad), 1588 (m), 1567 (m), 1368 (m), 1268 (m), 1235 (m), 1186 (w), 849 (w), 756 (m), 698 (s). ESI MS (MeCN): m/z 701 [$\text{M}-\text{Cl}+\text{MeCN}$]. Anal. Calcd for $\text{C}_{40}\text{H}_{32}\text{N}_3\text{PdCl}$ (695): N, 6.03; C, 68.97; H, 4.63. Found: N, 6.11; C, 68.91; H, 4.55.

Pd2: Based on either of the procedures outlined in a) and c), **Pd2** was obtained as an orange solid in the corresponding yield given in Table 1. ^1H NMR (400 MHz, CD_2Cl_2 , TMS): δ 9.78 (d, J = 8.4 Hz, 1H, Ph-H), 8.81 (s, 1H, CH=N), 8.5 (d, J = 8.0 Hz, 1H, Ph-H), 8.43 (d, J = 8.0 Hz, 1H, Ph-H), 8.05–8.01 (m, 3H, Ph-H), 7.79 (t, J = 8.4 Hz, 1H, Ph-H), 7.72 (t, J = 7.6 Hz, 1H, Ph-H), 7.49 (t, J = 7.6 Hz, 1H, Ph-H), 7.41 (t, J = 7.6 Hz, 1H, Ph-H), 7.23–7.14 (m, 6H, Ph-H), 2.97–2.88 (m, 2H, CH_2), 2.7–2.6 (m, 6H, $3 \times \text{CH}_2$), 2.3 (s, 3H, CH_3), 1.29–1.21 (m, 12H, $4 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CD_2Cl_2 , TMS): δ 170.3, 162.1, 149.3, 147.8, 140.3, 137.6, 136.4, 133.4, 133.3, 132.6, 132.6, 131.4, 131.0, 130.1, 127.3, 126.7, 126.6, 125.7, 125.4, 125.3, 124.2, 118.3, 24.5, 24.5, 23.7, 15.2, 13.3. FT-IR (KBr, cm^{-1}): 2961 (w), 2927 (w), 2869 (w), 1612 (v(HC=N), ($\text{CH}_3\text{C}=\text{N}$) broad), 1564 (v($\text{CH}_3\text{C}=\text{N}$) w), 1350 (w), 1269 (s), 1239 (s), 1177 (m), 857 (w), 759 (s), 709 (s). ESI MS (MeCN): m/z 757 [$\text{M}-\text{Cl}+\text{MeCN}$]. Anal. Calcd for $\text{C}_{44}\text{H}_{40}\text{N}_3\text{PdCl}$ (751): N, 5.36; C, 70.21; H, 5.58. Found: N, 5.28; C, 70.91; H, 5.55.

Pd3: Based on the procedure outlined in c), **Pd3** was obtained as an orange solid in the yield given in Table 1. ^1H NMR (400 MHz, CD_2Cl_2 , TMS): δ 10.63 (s, 1H, CHO), 8.88 (d, J = 8.0 Hz, 1H, Ph-H), 8.57 (d, J = 8.0 Hz, 1H, Ph-H), 8.44 (d, J = 7.6 Hz, 1H, Ph-H), 8.05 (t, J = 7.6 Hz, 2H, Ph-H), 7.88–7.78 (m, 3H, Ph-H), 7.69 (t, J = 7.6 Hz, 1H, Ph-H), 7.43 (t, J = 7.6 Hz, 1H, Ph-H), 7.17 (t, J = 7.6 Hz, 3H, Ph-H), 2.33 (s, 6H, $2 \times \text{CH}_3$), 2.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2 , TMS): δ 193.1, 169.9, 156.8, 148.8, 138.3, 137.9, 133.1, 132.9, 132.5, 132.1, 130.8, 129.8, 128.7, 128.1, 127.9, 127.2, 126.7, 125.5, 125.3, 124.3, 123.6, 118.5, 29.3, 22.9, 18.5. FT-IR (KBr, cm^{-1}): 2973 (m), 2916 (w), 2851 (w), 1696 (v(C=O) s), 1614 (v(C=N) s), 1567 (w), 1349 (w), 1265 (m), 1190 (m), 1050 (m), 853 (w), 754 (s), 724 (s). ESI MS (MeCN): m/z 598 [$\text{M}-\text{Cl}+\text{MeCN}$]. Anal. Calcd for $\text{C}_{32}\text{H}_{23}\text{N}_2\text{OPdCl}$ (593): N, 4.72; C, 64.77; H, 3.91. Found: N, 4.72; C, 64.91; H, 4.90.

Pd4: Based on the procedure outlined in c), **Pd4** was obtained as an orange solid in the yield given in Table 1. NMR (400 MHz, CD_2Cl_2 , TMS): δ 10.62 (s, 1H, CHO), 8.87 (d, J = 8.0 Hz, 1H, Ph-H), 8.55 (d, J = 8.0 Hz, 1H, Ph-H), 8.43 (d, J = 7.6 Hz, 1H, Ph-H), 8.04 (d, J = 7.6 Hz, 2H, Ph-H), 7.86–7.77 (m, 3H, Ph-H), 7.68 (d, J = 7.6 Hz, 1H, Ph-H), 7.41 (d, J = 7.6 Hz, 1H, Ph-H), 7.20 (s, 3H, Ph-H), 2.94–2.85 (m, 2H, CH_2), 2.6–2.56 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.28–1.24 (m, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz,

CD₂Cl₂, TMS): δ 193.2, 170.2, 156.9, 147.7, 141.2, 140.0, 138.3, 138.0, 136.4, 133.3, 132.8, 132.0, 131.4, 131.2, 131.2, 130.8, 127.5, 127.1, 126.6, 125.8, 124.3, 123.7, 118.5, 24.5, 23.6, 13.2. FT-IR (KBr, cm⁻¹): 2962 (w), 2912 (w), 2839 (w), 1689 (v(C=O) s), 1611 (v(C=N) s), 1584 (m), 1346 (m), 1265 (w), 1178 (m), 1096 (s), 854 (m), 755 (s), 724 (m). ESI MS (MeCN): m/z 626 [M-Cl+MeCN]. Anal. Calcd for C₃₄H₂₇N₂OPdCl (620): N, 4.51; C, 65.71; H, 4.38 Found: N, 4.52; C, 65.91; H, 4.38.

General procedure for Heck reaction

The Heck coupling reactions of haloarenes with styrene or *N*-*tert*-butylacrylamide were carried out in the presence of catalytic amounts of the palladium pincer complex. In a typical procedure (entry 11, Table 3) a mixture of bromobenzene (0.21 mL, 2.0 mmol), styrene (0.25 mL, 2.2 mmol), DMF (4 mL), anhydrous Na₂CO₃ (0.22 g, 2.1 mmol) was loaded into an oven dried Schlenk flask under a nitrogen atmosphere. **Pd1** (100 μ L, 4×10^{-5} mmol, 2×10^{-3} mol%), taken from a 4×10^{-4} M stock solution in DMF (10 mL), was added to the Schlenk flask *via* syringe and the reaction mixture stirred and heated at 140 °C. After the desired reaction time, the mixture was allowed to cool to room temperature, diluted with water and ethyl acetate. The organic layers were combined, washed with brine and then dried over anhydrous MgSO₄. All volatiles were removed under reduced pressure and the residue purified by

flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent affording stilbene (0.24 g, 67%).

X-Ray structure determination

X-ray data were collected with a Rigaku MM007-HF Saturn 724 + CCD diffractometer using Mo K α radiation (λ = 0.71073 Å), employing a confocal mirror monochromator as a radiation source for **L1** whilst graphite-monochromator as a radiation source was employed for complexes **Pd1**, **Pd2**, **Pd3** and **Pd4**. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were determined by direct methods and refined by full-matrix least squares on F^2 . All the hydrogen atoms were placed in calculated positions. The molecular structure determination and their refinement were performed by the SHELXL-97 package.²⁹ The disorder behavior of two ethyl groups in complex **Pd2** was also processed by the SHELXL-97 software. During the structure refinement, free solvent (chloroform) was squeezed (**Pd2**) with PLATON software.³⁰ Details of the crystal data and structure refinements for all five structures are shown in Table 6.

Table 6. Crystal data and structure refinements for **L1**, **Pd1**, **Pd2**, **Pd3** and **Pd4**

L1	Pd1 ·2CHCl ₃	Pd2	Pd3 ·CH ₂ Cl ₂	Pd4
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Empirical formula	C ₄₀ H ₃₃ N ₃	C ₄₂ H ₃₄ N ₃ PdCl ₇	C ₄₄ H ₄₀ N ₃ PdCl	C ₃₃ H ₂₅ N ₂ OPdCl ₃	C ₃₄ H ₂₇ N ₂ OPdCl
Formula weight	555.69	935.29	751.63	678.30	621.43
Temperature/K	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic,	Triclinic	trigonal	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> ¹	<i>R</i> ³	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
a/Å	11.910(2)	10.641(2)	36.490(5)	11.611(2)	14.187(3)
b/Å	32.793(7)	10.978(2)	36.490(5)	19.188(4)	12.380(3)
c/Å	9.4655(19)	17.744(3)	21.305(4)	13.466(3)	14.674(3)
Alpha/°	90	100.04(3)	90.00	90.00	90.00
Beta/°	113.37(3)	106.43(3)	90.00	113.15(3)	92.59(3)
Gamma/°	90	93.41(3)	120.00	90.00	90.00
Volume/Å ³	3393.6(12)	1944.7(6)	24568(7)	2758.5(10)	2574.7(9)
Z	4	2	18	25	4
D _{calcd} /(g·cm ⁻³)	1.088	1.597	0.916	2.782	1.603
μ/mm ⁻¹	0.064	0.994	0.412	4.624	0.857
F(000)	1176	944	6984	2125	1264
Crystal size/mm	0.23 × 0.14 × 0.10	0.54 × 0.38 × 0.12	0.33 × 0.33 × 0.30	0.32 × 0.21 × 0.12	0.20 × 0.19 × 0.11
θ Range (°)	1.96 to 27.50	1.22 to 27.47	2.24 to 54.82	4.48 to 54.96	3.9 to 54.98
Limiting indices	-15 ≤ h ≤ 15 -42 ≤ k ≤ 42 -11 ≤ l ≤ 12	-13 ≤ h ≤ 13 -14 ≤ k ≤ 1 -23 ≤ l ≤ 23	-47 ≤ h ≤ 47 -47 ≤ k ≤ 47 -27 ≤ l ≤ 27	-14 ≤ h ≤ 15 -24 ≤ k ≤ 24 -17 ≤ l ≤ 17	-18 ≤ h ≤ 18 -16 ≤ k ≤ 16 -19 ≤ l ≤ 19
No. of rflns collected	23288	24363	102155	19114	32464
No. unique rflns	7780	8870	12432	6237	5894
R(int)	0.0518	0.0370	0.0899	0.0262	0.0422
No. of params	393	483	469	364	355
Completeness to θ	99.6	99.5	100	98.8	99.7
Goodness of fit on F ²	1.047	1.024	1.072	1.107	1.084
Final R indices [I > 2σ(I)]	R1 = 0.0633 wR2 = 0.1406	R1 = 0.0765 wR2 = 0.2212	R1 = 0.0652, wR2 = 0.2055	R1 = 0.0369, wR2 = 0.0834	R1 = 0.0281, wR2 = 0.0705
R indices (all data)	R1 = 0.0814 wR2 = 0.1510	R1 = 0.0811, wR2 = 0.2352	R1 = 0.0755, wR2 = 0.2162	R1 = 0.0392, wR2 = 0.0850	R1 = 0.0286, wR2 = 0.0708
Largest diff. peak, and hole/(e Å ⁻³)	0.219/-0.164	1.946/-2.206	0.72/-0.92	1.02/-0.84	0.64/-0.58

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