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Synthesis of mixed *N*,*N*′-(Ar,Ar′-diaryl)iminoisoindolines for applications in palladacycle formations

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ABSTRACT

The synthesis of *N*,*N*′-(Ar,Ar′-diaryl)iminoisoindolines containing different aryl groups bound to the two nitrogen atoms is described. The iminoisoindolines were obtained by a three component, one-pot reaction of phthalaldehyde with 1 equivalent *p*-NO_2-aniline and 1 equivalent *p*-R-aniline, where R = H, Me, MeO or ^{i}Pr, resulting in formation of non-symmetrically substituted (mixed) iminoisoindolines, 1-*p*-nitrophenylimino-2-*p*-R-phenylisoindoline (R = H (**1**), Me (**2**), MeO (**3**), and ^{i}Pr (**4**)), as analytically pure precipitates requiring no further purification. Only one isomer precipitates from solution wherein the nitro group resides exclusively at the imine position while the more electron donating substituent ends up on the isoindoline ring position. Further reaction with $Pd(OAc)_2$ in dichloromethane at room temperature results in formation of six-membered [C,N] dinuclear cyclopalladated complexes with the general formula [(Ar,Ar′-diaryliminoisoindoline)Pd{μ-OAc}]$_2$.

1. Introduction

Carbon–carbon (C–C) coupling reactions are among the most important transformations in organic synthesis. Palladium based catalysts, in particular palladacycles, have been found to be superior catalytic systems in this regard due to their ease of preparation, air and moisture stability, low loading and high activity. Palladacycles have been known since the 1960s but were not used for C–C coupling reactions until 1995 and have rapidly emerged as being among the most active catalysts known for a large variety of coupling reactions [1,2]. There is a large diversity of palladacycles reported in the literature, the most common of which are palladacycles incorporating [C,P] and [C,N] metallacyclic formations [3]. The Pd–C bonds in palladacycles are most commonly formed by intramolecular C–H activation in the *ortho* position of a proximal aryl group to form the metal–carbon bond usually resulting in five- or six-membered ring palladacycles. Several palladacycles are even commercially available; most notably the diimine-based Nájera catalyst [4], the amine-based Indolese catalyst [5] and Bedford's phosphite-based catalyst [6].

While *N*,*N*′-diaryliminoisoindolines were first synthesized in 1910, few applications have been found for this subclass of indolines, either as ligands or as organic substrates [7]. For example, a SciFinder structure search reveals only 19 independent references in the last 100 years [8]. One possible reason for the dearth of interest in diaryliminoisoindolines is simply that they have not been found as a subunit of any natural product.

We recently reported the synthesis of a series of air and moisture stable *N*,*N*′-diaryliminoisoindoline-based palladacycles (Fig. 1) [9]. The corresponding palladacycles also required only one synthetic step and precipitate from solution as analytically pure solids. These complexes were found to be active pre-catalysts in the activation of aryl chlorides for the formation of biphenyls and cinnamates in the Suzuki and the Heck coupling reactions [9]. We further reported that with 1-*p*-nitrophenylimino-2-*p*-nitrophenylisoindoline (R = R′ = NO_2; Fig. 1), there was no reaction with palladium(II) acetate and thus no formation of the corresponding palladacycle. This is likely due to the electron withdrawing/deactivating effects of the nitro substituent inhibiting both imine coordination and *ortho*-palladation. Intrigued by this result, we decided to investigate the synthesis of mixed *N*,*N*′-(Ar,Ar′-diaryl)iminoisoindolines ligands containing different aryl groups bound to the two nitrogen atoms (R ≠ R′, Fig. 1) wherein the aryl groups of the mixed diaryliminoisoindoline would contain alternatively one nitro group and one neutral or electron donating group in the *para* positions. Herein we report the synthesis and characterization of a series of mixed (*N*,*N*′)-Ar,Ar′-diaryliminoisoindolines and subsequent formation of the corresponding air and moisture stable iminoisoindoline-based palladacycles in a simple two-step protocol. Their applications in Mizoroki–Heck coupling reactions were also investigated.

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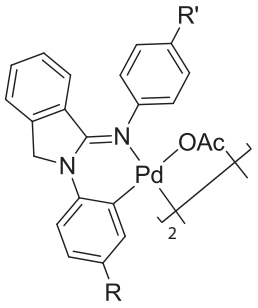


Fig. 1. Mixed iminoisoindoline-based palladacycles where R ≠ R′.

2. Results and discussion

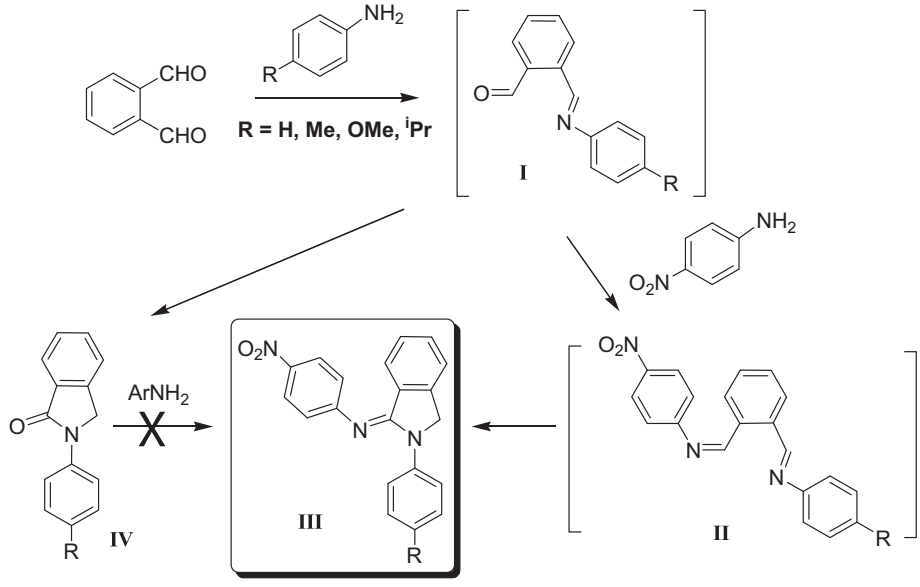
2.1. Ligand Synthesis

As we have previously reported, the diaryliminoisoindoline, 1-*p*-nitrophenylimino-2-*p*-nitrophenylisoindoline (R = R′ = NO_2; Fig. 1), did not react with palladium(II) acetate to form the corresponding palladacycle which is likely due to the highly electron withdrawing nature of the nitro substituents inhibiting *ortho*-palladation [9]. We envisioned that substitution of the nitro group of the aryl ring bound directly to the isoindoline skeleton with more electron donating substituents would allow for C–H activation and subsequent palladacycle formation. As with the previously reported symmetrically substituted iminoisoindolines, the non-symmetrically substituted ligands proved remarkably easy to synthesize. The one pot reaction of phthalaldehyde with equimolar amounts of *p*-NO_2-aniline and *p*-R-aniline (R = H, Me, MeO or ^{i}Pr) results in successful formation of non-symmetrically substituted iminoisoindoline ligands (R = H (**1**), Me (**2**), MeO (**3**), and ^{i}Pr (**4**)) in 40–55% yield as shown in Schemes 1 and 2. In all cases, the nitro group resides exclusively at the imine position while the more electron donating substituent ends up on the isoindoline ring position. The desired compounds precipitated out of solution as analytically pure solids. The mixed iminoisoindolines are all previously unreported except for **3** [10]. Compounds **1**–**4** were characterized by ^{1}H and ^{13}C NMR, mass spectrometry, elemental analysis and IR spectroscopy. ^{1}H NMR spectra show a characteristic singlet for the CH_2 moiety of the isoindoline ring of **1**–**4** at ~5 ppm and the C=N stretching frequency in the IR spectra appears at ~1645 cm^{-1}.

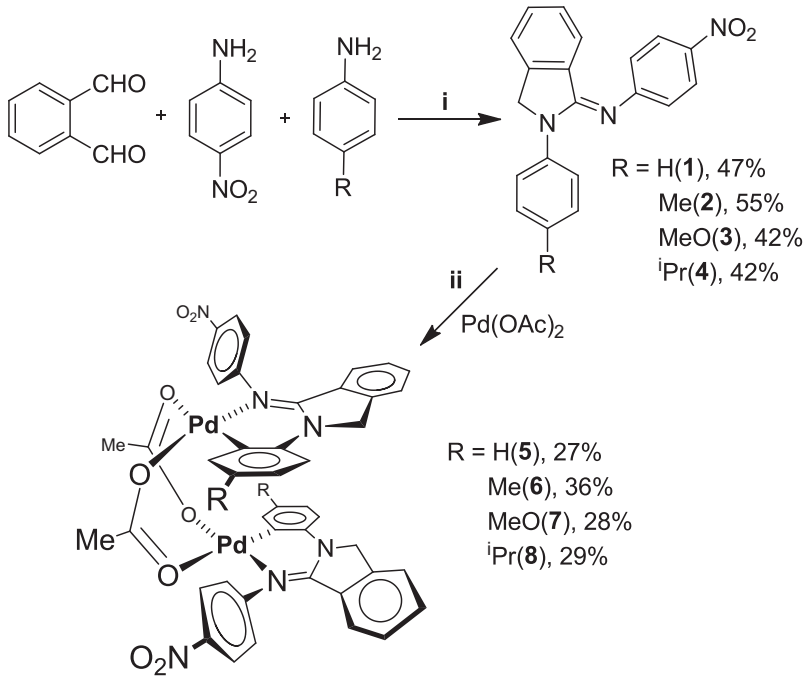
The mixed Ar,Ar′-diaryliminoisoindoline synthesis likely proceeds first via reaction of phthalaldehyde with one equivalent of the more electron donating aniline resulting in formation of an imino-aldehyde **I** (Scheme 1). The resulting imino-aldehyde can then undergo a slower second condensation reaction with *p*-NO_2-aniline forming a transient γ-diimine **II**. The γ-diimine then undergoes intramolecular cyclization initiated by the more electron donating imine resulting in formation of the corresponding iminoisoindoline **III** with the NO_2 moiety residing exclusively on the imine position. We have previously shown that the γ-diimine intermediate **II** can only be isolated providing the aryl groups are sufficiently bulky to inhibit intramolecular cyclization [11]. A competing side reaction also occurs where intramolecular cyclization of the transient imino-aldehyde species results in formation of the corresponding isoindolinone **IV** which limits the overall yield of the mixed iminoisoindoline ligands. The presence of the isoindolinone was confirmed by MS analysis of the filtrate. Fortuitously, under the reaction conditions employed, the isoindolinone remains in solution while the desired iminoisoindoline precipitates out as a yellow powder. The isoindolinone does not further react with $ArNH_2$ (Scheme 1).

Unlike the diaryliminoisoindolines, the corresponding *N*-arylisoindolinones have found widespread application in the pharmaceutical industry with many examples being commercially available including the isoindolinones from Scheme 1 [12]. Recent publications by the groups of Pan as well as Alajarín and Sánchez-Andrada provide mechanistic details into the formation of isoindolinones from phthaldehyde [13,14].

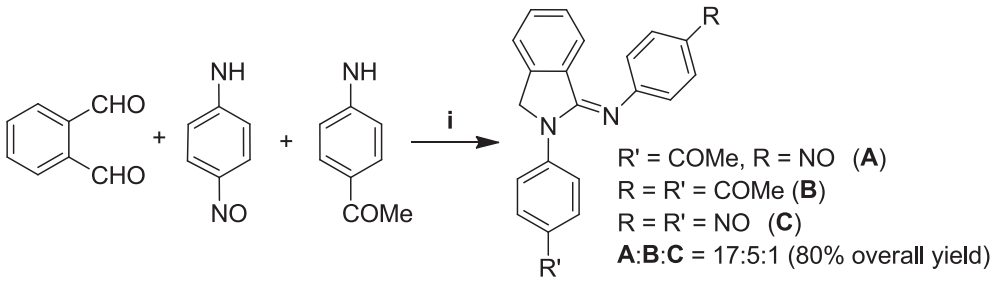
When the reaction is carried out with two different anilines both bearing electron withdrawing groups in the *para* position (specifically NO_2 and COMe), the resulting iminoisoindoline precipitates as a mixture of three compounds: 1-*p*-nitrophenylimino-2-*p*-acetylphenylisoindoline (**A**), 1-*p*-acetylphenylimino-2-*p*-acetylphenylisoindoline (**B**) and 1-*p*-nitrophenylimino-2-*p*-nitrophenylisoindoline (**C**) in the ratio 17:5:1, respectively as shown in Scheme 3 in 80% overall yield. Compounds **A**–**C** were identified by mass spectrometry as well as ^{1}H and ^{13}C NMR spectroscopy. Compounds **B** and **C** have been previously reported [9,10], while characterization of **A** is herein reported. Thus it appears that in order to facilitate isolation of a mixed iminoisoindoline in a one-pot



Scheme 1. Synthesis of mixed Ar,Ar′-diaryliminoisoindolines.



Scheme 2. Preparation of mixed-iminoisoindoline ligands and their corresponding palladacycles. (i) methanol:ether (1:1) as solvent, formic acid, room temperature, 12 h. (ii) CH_2Cl_2 as solvent, room temperature, 12 h.



Scheme 3. Synthesis of mixed iminoisoindoline ligands from two substituted anilines which both contain electron withdrawing groups. (i) Methanol:ether (1:1) as solvent, formic acid, room temperature, 12 h.

synthesis, a significant difference in the electron donating ability of the two *para*-substituted anilines must be employed, consistent with the proposed mechanism in Scheme 1.

2.2. Synthesis of [(mixed-iminoisoindoline)Pd{-OAc}]$_2$ palladacycles

Reaction of $Pd(OAc)_2$ in dichloromethane at room temperature, with one equivalent of the respective mixed-iminoisoindoline **1**–**4** resulted in formation of acetato-bridged, dinuclear palladacyclic complexes **5**–**8** as analytically pure yellow solids of the general formula, [(iminoisoindoline)Pd(μ-OAc)]$_2$ (Scheme 2). As mentioned earlier, no palladacycle was obtained from reaction of 1-*p*-nitrophenylimino-2-*p*-nitrophenylisoindoline (**C**) and $Pd(OAc)_2$. Substitution of one nitro group on the ring position of **C** with a more electron donating substituent results in successful formation of air and moisture stable mixed-iminoisoindoline palladacycles **5**–**8**.

Palladacycles **5**–**8** were characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis. Crystal structures were also obtained for all palladacycles to further confirm the coordination environment around the metal centers.

In the IR spectra of complexes **5**–**8**, the signals for the C=N bond vibrations were shifted to lower wavenumber compared to those of the free iminoisoindoline ($\Delta\lambda \sim 35\ cm^{-1}$) consistent with the formation of a Pd–N bond in the cyclopalladated complexes. Elemental analyses for all complexes indicate the presence of the anion acetate in the structure.

Dinuclear palladacycles in which the two palladium centers are linked by two bridging acetato groups can exhibit *anti*- and *syn*-conformations [9,15]. In this case, NMR data allows for easy differentiation between the *anti*- and *syn*-conformations where the *anti*-isomer exhibits overall C_2 symmetry and the *syn*-isomer is C_s symmetric. A characteristic indication of cyclopalladation in complexes **5**–**8** is the observed ^{1}H NMR resonance for the CH_2 protons of the iminoisoindoline ring. The ligands (**1**–**4**) show a singlet corresponding to the two methylene protons at ~5 ppm. Upon cyclopalladation, these methylene protons become diastereotopic in the *anti*-isomer resulting in formation of two doublets at ~4.6 and ~3.5 ppm, where each doublet corresponds to one proton per ligand. In all four complexes only the *anti*-isomers were obtained due to steric effects. The ESI-Q-TOF mass spectra of complexes **5**–**8** all showed a distinct signal which was assigned to their respective molecular cation $[M-OAc]^+$.

X-ray diffraction studies were undertaken and the crystal structures of palladacycles **5**–**8** were determined. Complex **5** co-crystallized with one molecule of chloroform, the solvent of crystallization, while **6** had two unsymmetrical molecules along with water and dichloromethane in the unit cell. This latter complex was crystallized under air from dichloromethane which had not been previously

dried. As expected, all four complexes crystallized exclusively as the *anti*-isomers, unambiguously confirming the presence of six-membered [C,N] palladacycles. *Anti*-configurations are also observed in the crystal structures of most previously reported acetato-bridged dinuclear palladacycles [10]. The two palladium atoms are bridged by two acetate ligands with each palladium center having a chelating [C,N]-bound iminoisoindoline ligand forming the palladacycle. The dinuclear acetato-bridged complexes adopt a characteristic closed-book conformation where the two [C,N]-bound iminoisoindoline ligands stack on top of one another. As expected, the coordination geometry about the palladium atoms in all four structures is approximately square planar with the sum of the angles around the palladium atoms for all four complexes being 360 ± 1°. The Pd–Pd distances were found to be 3.1109(6) Å for **5**, 2.9856(6) Å for **6**, 3.0449(6) Å for **7** and 3.0453(4) Å for **8** which are consistent with previously reported acetato-bridged dinuclear palladacycles [10]. The Pd–C and Pd–N bond lengths of complexes **5**–**8** were all essentially identical (within esd) at 1.97(1) Å and 2.01(1) Å, respectively. The Pd–O distances of the two acetate ligands differ by about 0.10 Å for **5**–**8** (for example, in **6**, Pd(1)–O(1) is 2.137 Å while Pd(1)–O(3) is 2.063 Å), indicative of the stronger trans-influence of the metallated carbon compared to that of the imine nitrogen.

ORTEP plots for **5**–**8** are shown in Figs. 2–5 with bond distances and angles indicated in their respective captions. Crystallographic data and refinement parameters are summarized in Table 1.

2.3. Applications of [(mixed-iminoisoindoline)Pd{-OAc}]$_2$ palladacycles in Mizoroki–Heck coupling reactions

We have previously shown that (diaryliminoisoindoline)Pd{μ-OAc}]$_2$ palladacycles bearing electron-donating aryl groups are effective pre-catalysts in the activation of aryl chlorides for the formation of biphenyls and cinnamates in the Suzuki–Miyaura and the Mizoroki–Heck coupling reactions [9]. For example, in the Heck

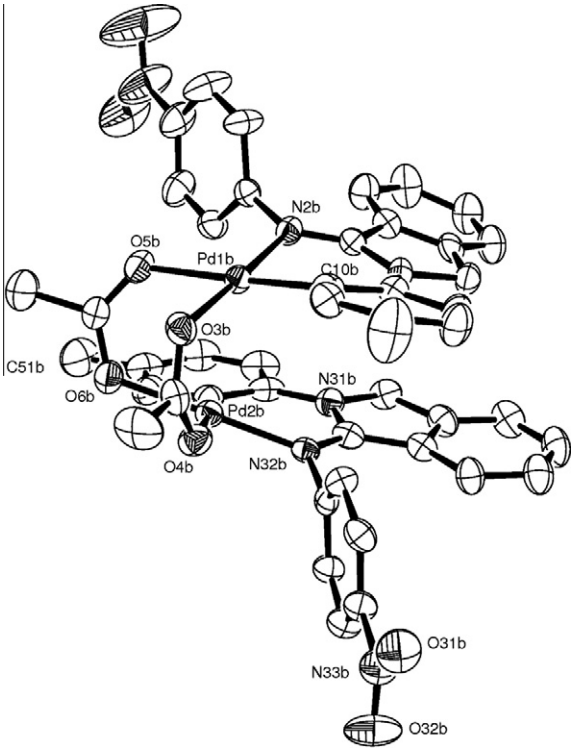


Fig. 3. ORTEP plot of **6** (view of molecule B) at the 30% probability level. Hydrogen atoms, molecule A and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1B)–C(10B) = 1.968(6), Pd(1B)–N(2B) = 2.004(5), Pd(1B)–O(3B) = 2.058(4), Pd(1B)–O(1B) = 2.140(4), Pd(1B)···Pd(2B) = 2.9856(6), C(10B)–Pd(1B)–N(2B) = 89.0(2), C(10B)–Pd(1B)-O(3B) = 91.5(2), N(2B)–Pd(1B)–O(5B) = 178.25(18), N(2B)–Pd(1B)–O(1B) = 93.70(18), O(3B)–Pd(1B)–O(1B) = 85.62(17).

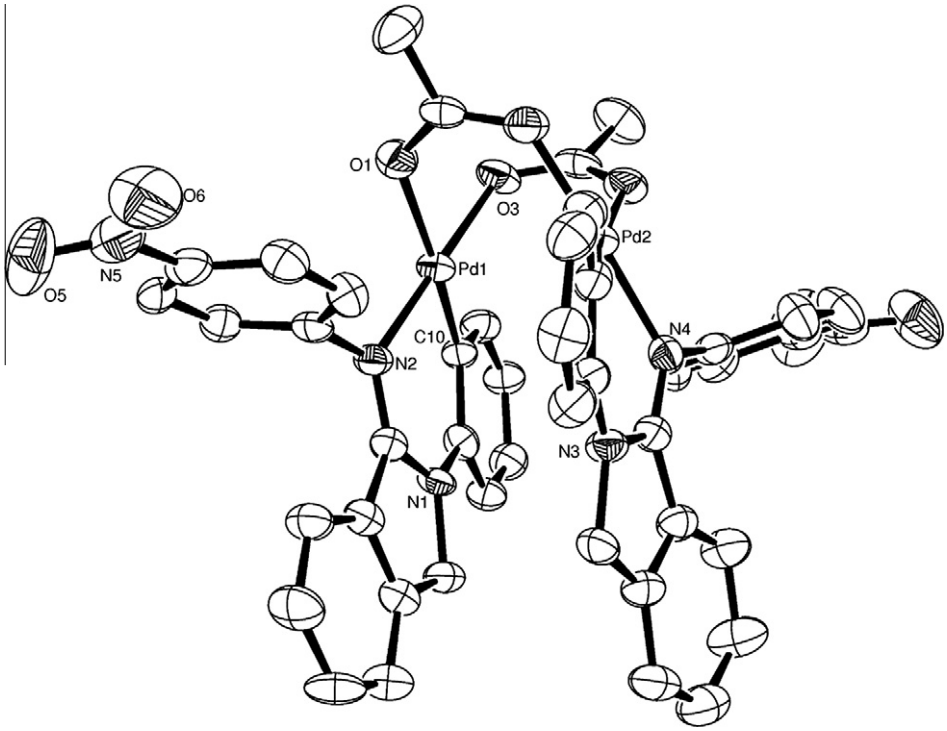


Fig. 2. ORTEP plot of **5** at the 50% probability level. The hydrogen atoms and $CHCl_3$ molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(10) = 1.967(6), Pd(1)–N(2) = 2.006(5), Pd(1)–O(3) = 2.063(5), Pd(1)–O(1) = 2.138(4), Pd(1)···Pd(2) = 3.1109(6), C(10)–Pd(1)–N(2) = 89.6(2), C(10)-Pd(1)–O(3) = 90.6(2), N(2)–Pd(1)–O(1) = 94.05(19), N(2)–Pd(1)–O(3) = 179.34(18), O(3)–Pd(1)–O(1) = 85.75(18).

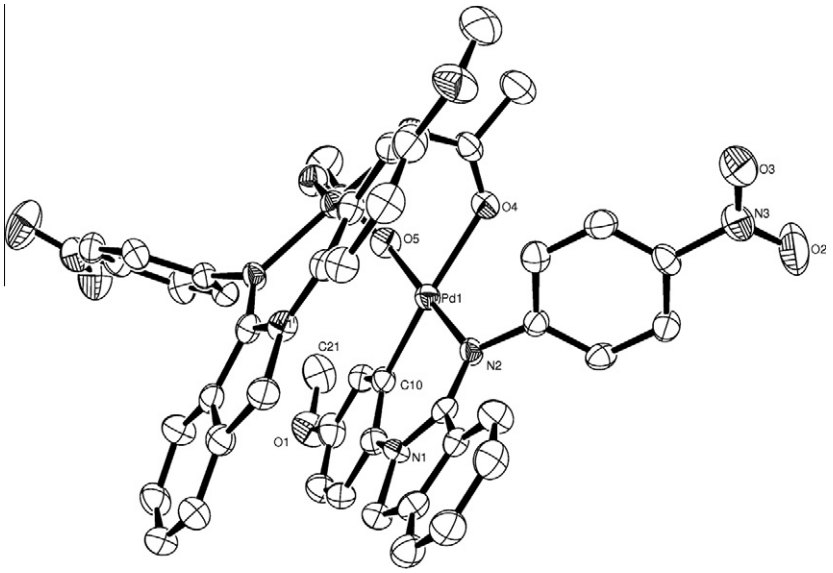


Fig. 4. ORTEP plot of **7** at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(10) = 1.974(6), Pd(1)–N(2) = 2.011(5), Pd(1)–O(3) = 2.060(4), Pd(1)–O(1) = 2.137(4), Pd(1)···Pd(2) = 3.0444(9), C(10)–Pd(1)–N(2) = 89.7(2), C(10)–Pd(1)–O(3) = 91.5(2), N(2)–Pd(1)-O(1) = 95.89(17), N(2)–Pd(1)–O(3) = 178.48(18), O(3)–Pd(1)–O(1) = 82.99(17).

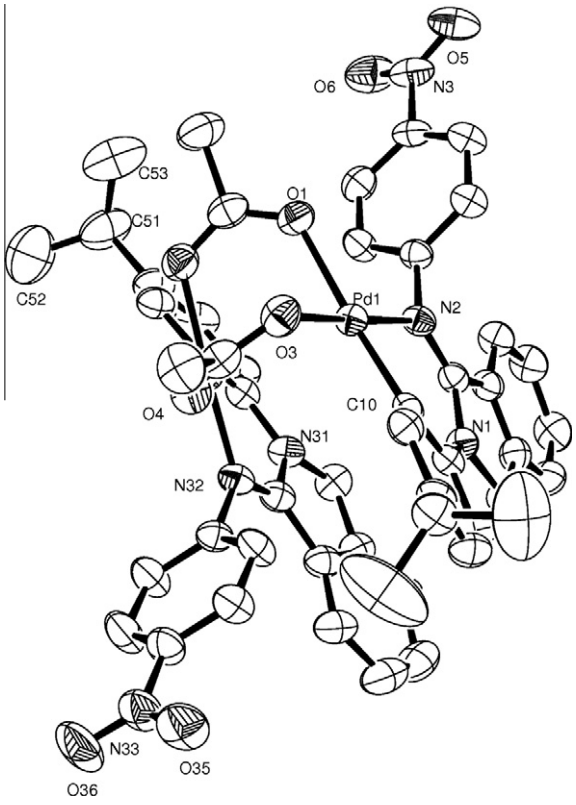


Fig. 5. ORTEP plot of **8** at the 30% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(10) = 1.964(4), Pd(1)–N(2) = 2.012(3), Pd(1)–O(3) = 2.057(3), Pd(1)–O(1) = 2.133(3), Pd(1)···Pd(2) = 3.0453(3), C(10)–Pd(1)–N(2) = 89.92(15), C(10)–Pd(1)–O(3) = 90.29(14), N(2)–Pd(1)–O(5) = 178.18(14), N(2)–Pd(1)–O(1) = 93.11(12), O(3)–Pd(1)–O(1) = 86.50(12).

reaction, using 1 mol% of catalyst in the presence of 2 equivalents of Cs_2CO_3 as base in DMA at 145 °C, the coupling of *p*-chlorobenzaldehyde with butylacrylate produced the corresponding cinnamate in up to 60% yields, while the analogous reaction with *p*-bromobenzaldehyde yields turnover numbers of up to 1000. We were interested in investigating the effect of incorporating a more electron withdrawing aryl group on the imino nitrogen position of the iminoisoindoline anticipating that weakening the N–Pd bond might lead to a more active a catalyst. On the other hand, this could also lead to an increased rate of catalyst decomposition. Unfortunately, it is the latter case which dominates catalytic activity with yields of only 15% exhibited for palladacycles **5** and **8** using *p*-chlorobenzaldehyde under the same conditions as stated above along with rapid precipitation of palladium black (Scheme 4). The activity for the analogous Mizoroki–Heck reaction with bromobenzaldehyde yielded turnover numbers of only 35. Repeating the reactions at 80 °C resulted in no observable coupling product.

3. Conclusion

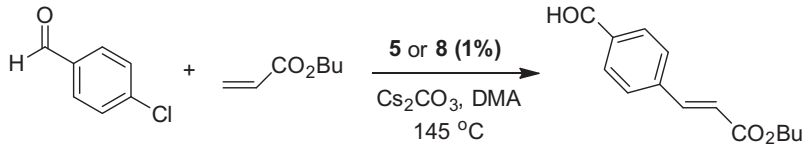
N,N′-(Ar,Ar′-diaryl)iminoisoindolines containing different aryl groups on the two nitrogen atoms were obtained by a three-component, one-pot reaction from inexpensive, commercially available starting materials. The aryl groups were chosen to maximize the difference in electron donating character of the substituents. This not only favors formation of the desired mixed iminoisoindolines, wherein the more electron withdrawing substituted aryl groups reside exclusively on the imine position, but promotes C_{aryl}–H activation to form air and moisture stable palladacyclic complexes in a simple two step reaction. This is in contrast to the electron-poor iminoisoindoline, 1-*p*-nitrophenylimino-2-*p*-nitrophenylisoindoline, which does not undergo *ortho*-palladation.

4. Experimental

Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.23). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. High resolution mass spectra (HRMS) were measured on an Applied Biosystem QSTAR® XL MS/MS system (ESI-QTOF). $Pd(OAc)_2$ was purchased from PMO Pty Ltd, Australia.

Table 1
Crystal data and refinement parameters for complexes **5**·$CHCl_3$, **6**·$1.5H_2O$·$0.75CH_2Cl_2$, **7** and **8**.

	5·$CHCl_3$	**6**·$1.5H_2O$·$0.75CH_2Cl_2$	**7**	**8**
Formula	$C_{44}H_{35}Cl_3N_6O_8Pd_2$	$C_{187}H_{170}Cl_6N_{24}O_{38}Pd_8$	$C_{46}H_{38}N_6O_{10}Pd_2$	$C_{50}H_{46}N_6O_8Pd_2$
Formula weight	1106.94	4425.37	1047.62	1071.77
Color	pale yellow	yellow	orange	yellow
Crystal size (mm^3)	0.12 × 0.10 × 0.09	0.12 × 0.10 × 0.10	0.15 × 0.13 × 0.05	0.20 × 0.18 × 0.10
Crystal system	Triclinic	Orthorhombic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P21\ 21\ 2$	$P41\ 21\ 2$	$P21/c$
a (Å)	11.7500(4)	20.4831(3)	9.2363(13)	12.7855(2)
b (Å)	12.0285(6)	21.2390(3)	9.2363(13)	17.2702(4)
c (Å)	17.2210(8)	23.8327(3)	47.882(10)	23.0660(5)
α (°)	107.308(2)	90	90	90
β (°)	109.238(3)	90	90	120.0295(14)
γ (°)	91.590(3)	90	90	90
Z	2	2	4	4
ρ_{calc} ($Mg\,m^{-3}$)	1.692	1.418	1.704	1.429
T (K)	173(2)	173(2)	173(2)	173(2)
Collected/individual reflections	27459/7655	101049/18295	27158/3605	47210/9856
R_{int}	0.1114	0.0890	0.1095	0.0947
$F(000)$	1108	4468	2112	2176
θ Range (°)	2.39–25.10	2.20–25.03	1.70–25.03	2.16–26.10
Final R_1 ($I > 2\sigma I$)	$R_1 = 0.0618$, $wR_2 = 0.1475$	$R_1 = 0.0444$, $wR_2 = 0.1032$	$R_1 = 0.0477$, $wR_2 = 0.0956$	$R_1 = 0.0495$, $wR_2 = 0.1182$
R_1 (all data)	$R_1 = 0.0861$, $wR_2 = 0.1652$	$R_1 = 0.0526$, $wR_2 = 0.1077$	$R_1 = 0.0634$, $wR_2 = 0.1142$	$R_1 = 0.0631$, $wR_2 = 0.1256$



Scheme 4. Mizoroki–Heck cross-coupling of *p*-chlorobenzaldehyde with butyl acrylate.

Aniline, *p*-toluidine, *p*-anisidine and *p*-isopropylaniline were purchased from the Sigma–Aldrich Chemical Company and used as received except for aniline which was distilled prior to use. Phthalaldehyde was purchased from Alfa Aesar and used as received.

4.1. General procedure for the synthesis for ligands A and **1–4**

A Schlenk flask was charged with equimolar amounts of the corresponding two substituted anilines in 30 mL methanol:ether (1:1) solvent mixture. Stoichiometric amounts of phthalaldehyde and 0.05 mL of formic acid were then added. The initially homogeneous solution was stirred at room temperature for 12 h, over which time the product gradually precipitated from solution. The resultant suspension was then filtered and the precipitate washed with cold methanol, and dried under vacuum to obtain the desired product as a white or yellow solid.

4.1.1. 1-p-Nitrophenylimino-2-phenylisoindoline (**1**)

Compound **1** was obtained as a yellow powder in 47% yield (576 mg) from *p*-NO_2-aniline (517 mg, 3.74 mmol), aniline (349 mg, 3.74 mmol) and phthalaldehyde (502 mg, 3.74 mmol). ^1H NMR ($CDCl_3$): δ 8.16 (d, J = 9.3, 2H, Ar), 7.80 (d, J = 7.4, 2H, Ar), 7.46 (m, 2H), 7.38 (m, 2H), 7.15 (m, 2H), 7.02 (d, J = 8.8, 2H), 6.93 (m, 1H), 4.99(s, 2H, CH_2). $^{13}C\{H\}$NMR ($CDCl_3$): δ 157.5 ($C_{C=N}$), 153.1 (C_{Ar}), 142.7(C_{Ar}), 140.8(C_{Ar}), 140.7(C_{Ar}), 131.6(C_{Ar}), 131.3(CH_{Ar}), 129.3(CH_{Ar}), 128.0(CH_{Ar}), 125.9(CH_{Ar}), 125.4(CH_{Ar}), 124.6(CH_{Ar}), 123.2(CH_{Ar}), 121.8(CH_{Ar}), 121.3(CH_{Ar}), 54.1(CH_2). *Anal.* Calc. for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 72.78; H, 4.53; N, 12.57%. FT-IR (KBr, cm^{-1}): 1654 (C=N), 1590, 1589, 1498, 1469. HRMS *m/z* calcd. for $C_{20}H_{15}N_3O_2$: 329.1164 [M], found: 328.1096 $[M-H]^+$.

4.1.2. 1-p-Nitrophenylimino-2-p-methylphenylisoindoline (**2**)

Compound **2** was obtained as a yellow powder in 55% yield (711 mg) from *p*-NO_2-aniline (517 mg, 3.74 mmol), *p*-toluidine (401 mg, 3.74 mmol) and phthalaldehyde (502 mg, 3.74 mmol). ^1H NMR ($CDCl_3$): δ 8.14 (d, J = 8.7, 2H, Ar), 7.63 (d, J = 7.7, 2H, Ar), 7.46 (m, 2H), 7.17 (m, 3H), 7.00 (d, J = 8.7, 2H), 6.95 (m, 1H), 4.99 (s, 2H, CH_2), 2.32 (s, 3H, Ar-CH_3. $^{13}C\{H\}$NMR ($CDCl_3$): δ 157.7 ($C_{C=N}$), 153.2(C_{Ar}), 142.6(C_{Ar}), 140.8(C_{Ar}), 138.2(C_{Ar}), 134.6(C_{Ar}), 131.7(CH_{Ar}), 131.1(CH_{Ar}), 129.9(CH_{Ar}), 127.9(CH_{Ar}), 125.8(CH_{Ar}), 125.4(CH_{Ar}), 123.2(CH_{Ar}), 121.9(CH_{Ar}), 121.8(CH_{Ar}), 121.3(CH_{Ar}), 54.3(CH_2), 21.1 (Ar-CH_3). *Anal.* Calc. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.26; H, 4.69; N, 11.99%. FT-IR (KBr, cm^{-1}): 1646 (C=N), 1612, 1584, 1512. HRMS *m/z* calcd. for $C_{21}H_{17}N_3O_2$: 343.1321 [M], found: 342.1244 $[M-H]^+$.

4.1.3. 1-p-Nitrophenylimino-2-p-methoxyphenylisoindoline (**3**)

Compound **3** was obtained as a yellow powder in 42% yield (568 mg) from *p*-NO_2-aniline (521 mg, 3.77 mmol), *p*-anisidine (464 mg, 3.74 mmol) and phthalaldehyde (506 mg, 3.77 mmol). ^1H NMR ($CDCl_3$): δ 8.12 (d, J = 8.7, 2H, Ar), 7.61 (d, J = 8.3, 2H, Ar), 7.46 (m, 2H, Ar), 7.18 (m, 1H, Ar), 6.98 (m, 3H, Ar), 6.90 (d, J = 8.8, 2H, Ar), 4.93 (s, 2H, CH_2), 3.78 (s, 3H, Ar-OCH_3). $^{13}C\{H\}$NMR ($CDCl_3$): δ 157.8 ($C_{C=N}$), 157.0(C_{Ar}), 153.4(C_{Ar}), 142.5(C_{Ar}), 140.8(C_{Ar}), 133.7(C_{Ar}), 131.8(C_{Ar}), 131.1(CH_{Ar}), 127.9(CH_{Ar}), 125.8(CH_{Ar}), 125.3(CH_{Ar}), 123.8(CH_{Ar}), 123.2(CH_{Ar}), 121.8(CH_{Ar}), 114.5(CH_{Ar}), 55.7(Ar-OCH_3), 54.8(CH_2). *Anal.* Calc. for $C_{21}H_{15}N_3O_2$: C, 70.18; H, 4.77; N, 11.69. Found: C, 70.25; H, 4.77; N, 11.58%. FT-IR (KBr, cm^{-1}): 1643 (C=N), 1581, 1510, 1467. HRMS *m/z* calcd. for $C_{21}H_{15}N_3O_2$: 359.1270 [M], found: 359.1259 [M].

4.1.4. 1-p-Nitrophenylimino-2-p-isopropylphenylisoindoline (**4**)

Compound **4** was obtained as a yellow powder in 42% yield (580 mg) from *p*-NO_2-aniline (516 mg, 3.73 mmol), *p*-^{i}Pr-aniline

(505 mg, 3.73 mmol) and phthalaldehyde (502 mg, 3.74 mmol). ^{1}H NMR ($CDCl_3$): δ 8.12 (d, J = 8.4, 2H, Ar), 7.65 (d, J = 6.6, 2H, Ar), 7.46 (m, 2H), 7.20 (m, 3H), 6.99 (m, 3H), 4.96 (s, 2H, CH_2), 2.88(sept, J = 6.9, 1H, $CH(CH_3)_2$), 1.22 (d, J = 6.9, 6H, $CH(CH_3)_2$). ^{13}C{H}NMR ($CDCl_3$): δ 157.7 ($C_{C=N}$), 153.2(C_{Ar}), 145.6(C_{Ar}), 142.6(C_{Ar}), 140.8(C_{Ar}), 138.4(C_{Ar}), 131.8(CH_{Ar}), 131.1(CH_{Ar}), 127.9(CH_{Ar}), 127 .2(CH_{Ar}), 125.8(CH_{Ar}), 125.3(CH_{Ar}), 123.2(CH_{Ar}), 121.9(CH_{Ar}), 121.8(CH_{Ar}), 54.4(CH_2), 33.9 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$). *Anal.* Calc. for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.70; N, 11.31. Found: C, 73.98; H, 5.52; N, 11.23%. FT-IR (KBr, cm^{-1}): 1642 (C=N), 1609, 1583, 1509. HRMS m/z calcd. for $C_{23}H_{21}N_3O_2$: 371.1634 [M], found: 370.1544 $[M-H]^+$.

4.1.5. 1-p-Nitrophenylimino-2-p-acetylphenylisoindoline (**A**)

Compound **A** was obtained as a yellow powder in 59% yield (820.0 mg) from p-NO_2-aniline (517 mg, 3.74 mmol), p-COMe-aniline (506 mg, 3.74 mmol) and phthalaldehyde (502 mg, 3.74 mmol). ^{1}H NMR ($CDCl_3$): δ 8.23 (d, J = 8.5, 2H, Ar), 8.06 (d, J = 8.6, 2H, Ar), 8.01 (d, J = 8.6, 2H, Ar), 7.49 (m, 2H, Ar), 7.14 (m, 1H, Ar), 7.06 (d, J = 8.6, 2H, Ar), 6.81 (d, J = 7.9, 1H, Ar), 5.03 (s, 2H, CH_2), 2.58 (s, 3H, $-COCH_3$). ^{13}C NMR ($CDCl_3$): δ 196.9 (C_{COMe}), 156.5 ($C_{C=N}$), 152.7(C_{Ar}), 144.9(C_{Ar}), 143.0(C_{Ar}), 140.1(C_{Ar}), 132.1(C_{Ar}), 131.5(CH_{Ar}), 130.1(C_{Ar}), 129.6(CH_{Ar}), 128.0(CH_{Ar}), 126.0(CH_{Ar}), 125.5(CH_{Ar}), 123.2(CH_{Ar}), 121.2(CH_{Ar}), 118.9(CH_{Ar}), 53.1 (CH_2), 26.5 ($COCH_3$). HRMS m/z calcd. for $C_{22}H_{17}N_3O_3$: 371.1270 [M], found: 370.1189 $[M-H]^+$.

4.2. General synthesis for palladacycles **5**–**8**

A Schlenk flask was charged with equimolar amounts of iminoisoindoline (**1**–**4**) and $Pd(OAc)_2$ in dichloromethane (30 mL) to form red homogeneous solution. After 12 h of stirring at room temperature under dinitrogen, the reaction mixture was filtered through Celite to remove palladium black. The filtrate was concentrated and then ether (30 mL) added to precipitate the desired palladacycles. The resulting precipitates of palladacycles (**5**–**8**) were filtered, washed with cold ether (3 × 10 mL) then dried under vacuum. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation from a 50:50 dichloromethane/hexane solution under air.

4.2.1. Bis(-acetato)bis(1-p-nitrophenylimino-2-phenylisoindoline) dipalladium(**II**) (**5**)

Complex **5** was obtained as a yellow powder in 27% yield (205 mg) from **1** (252 mg, 0.765 mmol) and $Pd(OAc)_2$ (206 mg, 0.918 mmol). ^{1}H NMR ($CDCl_3$): δ 8.08 (d, J = 8.4, 2H, Ar), 7.68 (d, J = 7.1, 2H, Ar), 7.55 (m, 4H, Ar), 7.35 (d, J = 7.5, 2H, Ar), 7.05 (m, 8H, Ar), 6.26 (d, J = 7.3, 2H, Ar), 5.79 (m, 8H, Ar), 4.65 (d, J = 17.2, 2H, CH_2), 3.27 (d, J = 17.2, 2H, CH_2), 1.66 (s, 6H, acetate); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 180.1 ($C_{acetate}$), 152.0, ($C_{C=N}$), 151.4(C_{Ar}), 145.7(C_{Ar}), 141.0(C_{Ar}), 136.7 (C_{Ar}) 136.7(CH_{Ar}), 135.7(C_{Ar}), 131.9(CH_{Ar}), 130.3(C_{Ar}), 128.9(CH_{Ar}), 128.7(CH_{Ar}), 127.0(CH_{Ar}), 126.7(CH_{Ar}), 125.6(CH_{Ar}), 124.8(CH_{Ar}), 124.1(CH_{Ar}), 123.1(CH_{Ar}), 122.8(CH_{Ar}), 122.6(CH_{Ar}), 112.5(CH_{Ar}), 53.1(CH_2), 24.7($CH_{3acetate}$). *Anal.* Calc. for $C_{44}H_{34}N_6O_8Pd_2$: C, 53.51; H, 3.47; N, 8.51. Found: C, 52.56; H, 3.40; N, 7.76%; FT-IR (KBr, cm^{-1}) 1618 (C=N), 1562, 1520. HRMS m/z calcd. for $C_{44}H_{34}N_6O_8Pd_2$ 987.6162 [M], 929.0379 $[M-OAc]^+$; found 929.0390 $[M-OAc]^+$.

4.2.2. Bis(-acetato)bis(1-p-nitrophenylimino-2-p-methylphenyliso indoline)dipalladium(**II**) (**6**)

Complex **6** was obtained as a yellow powder in 36% yield (270 mg) from **2** (254 mg, 0.740 mmol) and $Pd(OAc)_2$ (197 mg, 0.878 mmol). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, J = 8.6, 2H, Ar), 7.66 (d, J = 8.8, 2H, Ar), 7.52 (m, 2H, Ar), 7.38 (d, J = 7.5, 2H, Ar), 7.33 (d, J = 7.5, 2H, Ar), 7.11 (m, 4H, Ar), 6.83 (d, J = 7.9, 2H, Ar), 6.16 (d, J = 8.2, 2H), 5.82 (m, 4H, Ar), 4.61 (d, J = 17.3, 2H, CH_2), 3.31 (d, J = 17.3, 2H, CH_2), 2.38 (s, 6H, Ar-CH_3), 1.68 (s, 6H, acetate); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 180.0 ($C_{acetate}$), 152.2, ($C_{C=N}$), 151.1(C_{Ar}), 145.6(C_{Ar}), 141.0(C_{Ar}), 136.9 (CH_{Ar}) 136.7(CH_{Ar}), 133.5(C_{Ar}), 133.1(C_{Ar}), 132.5(C_{Ar}), 131.7(CH_{Ar}), 130.4(CH_{Ar}), 129.1(CH_{Ar}), 128.6 (CH_{Ar}), 127.2 (CH_{Ar}), 126.5(CH_{Ar}), 126.2(CH_{Ar}), 124.8(CH_{Ar}), 123.9(CH_{Ar}), 122.6(CH_{Ar}), 121.9(C_{Ar}), 112.3(CH_{Ar}), 53.1(CH_2), 24.8 ($-CH_3$, $_{Acetate}$), 21.2 (Ar-CH_3). *Anal.* Calc. for $C_{46}H_{38}N_6O_{10}Pd_2$: C, 54.40; H, 3.77; N, 8.27. Found: C, 54.37; H, 3.41; N, 8.00%; FT-IR (KBr, cm^{-1}) 1619 (C=N), 1605, 1576, 1576. HRMS m/z calcd. for $C_{46}H_{38}N_6O_8Pd_2$ 1014.0821 [M], 957.0692 $[M-OAc]^+$; found 957.0651 $[M-OAc]^+$.

4.2.3. Bis(-acetato)bis(1-p-nitrophenylimino-2-p-methoxyphenyliso indoline)dipalladium(**II**) (**7**)

Complex **7** was obtained as a yellow powder in 28% yield (207 mg) from **3** (254 mg, 0.707 mmol) and $Pd(OAc)_2$ (190 mg, 0.846 mmol). ^{1}H NMR ($CDCl_3$): δ 8.09 (d, J = 8.0, 2H, Ar), 7.69 (d, J = 7.7, 2H, Ar), 7.52 (m, 2H, Ar), 7.32 (d, J = 7.5, 2H, Ar), 7.17 (m, 2H, Ar), 7.10 (m, 4H, Ar), 6.62 (d, J = 8.7, 2H, Ar), 6.21 (d, J = 8.8, 2H, Ar), 5.91 (d, J = 8.5, 2H, Ar), 5.83 (d, J = 8.2, 2H, Ar), 4.61 (d, J = 17.2, 2H, CH_2), 3.22 (s, 6H, Ar-OCH_3), 3.22 (d, J = 17.2, 2H, CH_2), 1.69 (s, 6H, acetate); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 180.0($C_{acetate}$), 154.6($C_{C=N}$), 152.2(C_{Ar}), 151.0(C_{Ar}), 145.7(C_{Ar}), 141.0 (C_{Ar}) 131.6(CH_{Ar}), 130.5(C_{Ar}), 129.1(C_{Ar}), 128.6(CH_{Ar}), 126.4(CH_{Ar}), 125.8(C_{Ar}), 124.0(CH_{Ar}), 122.6(CH_{Ar}), 122.6(CH_{Ar}), 119.3(CH_{Ar}), 113.1(CH_{Ar}), 112.7(CH_{Ar}), 55.8($C_{Ar\text{-}OMe}$), 53.2(CH_2), 24.5($C_{Me,\ Acetate}$). *Anal.* Calc. for $C_{46}H_{38}N_6O_{10}Pd_2$: C, 52.74; H, 3.66; N, 8.02. Found: C, 51.90; H, 3.59; N, 7.79%; FT-IR (KBr, cm^{-1}) 1612 (C=N), 1602, 1575. HRMS m/z calcd. for $C_{46}H_{38}N_6O_{10}Pd_2$ 1046.0719 [M], 989.0590 $[M-OAc]^+$; found 989.0615 $[M-OAc]^+$.

4.2.4. Bis(-acetato)bis(1-p-nitrophenylimino-2-p-isopropylphenyliso indoline)dipalladium(**II**) (**8**)

Complex **8** was obtained as a yellow powder in 29% yield (212 mg) from **4** (254 mg, 0.684 mmol) and $Pd(OAc)_2$ (184 mg, 0.821 mmol). ^{1}H NMR ($CDCl_3$): δ 8.05 (d, J = 8.6, 2H, Ar), 7.62 (d, J = 8.8, 2H, Ar), 7.53(m, 2H, Ar), 7.47 (s, 2H, Ar), 7.27 (d, J = 7.5, 2H, Ar), 7.11 (m, 2H, Ar), 7.05 (d, J = 8.6, 2H, Ar), 6.95 (d, J = 8.2, 2H, Ar), 6.22 (d, J = 8.2, 2H, Ar), 5.82 (m, 4H, Ar), 4.54 (d, J = 17.3, 2H, CH_2), 2.95 (sept, J = 6.9, 2H, $CH(CH_3)_2$), 2.90 (d, J = 17.3, 2H, CH_2), 1.73 (s, 6H, acetate), 1.36 (d, J = 6.9, 6H, $CH(CH_3)_2$), 1.34 (d, J = 6.9, 6H, CH ($CH_3)_2$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 180.1 ($C_{acetate}$), 152.1, ($C_{C=N}$), 151.3(C_{Ar}), 145.6(C_{Ar}), 143.9(C_{Ar}), 141.2(C_{Ar}), 134.2(CH_{Ar}), 133 .8(C_{Ar}), 131.7(CH_{Ar}), 130.4(C_{Ar}), 129.0(CH_{Ar}), 128.6(CH_{Ar}), 127.0(CH_{Ar}), 126.5(CH_{Ar}), 124.7(CH_{Ar}), 124.2(C_{Ar}), 124.0(CH_{Ar}), 122 .8(CH_{Ar}), 122.8(CH_{Ar}), 112.3(CH_{Ar}), 52.9(CH_2), 34.1($CH(CH_3)_2$), 24.8($-CH_3$, acetate), 24.6($CH(CH_3)_2$), 24.5($CH(CH_3)_2$). *Anal.* Calc. for $C_{50}H_{46}N_6O_8Pd_2$: C, 56.03; H, 4.33; N, 7.84. Found: C, 55.65; H, 4.29; N, 7.93%; FT-IR (KBr, cm^{-1}) 1614 (C=N), 1604, 1575, 1514. HRMS m/z calcd. for $C_{50}H_{46}N_6O_8Pd_2$ 1070.1447 [M], 1013.1318 $[M-OAc]^+$; found 1013.1316 $[M-OAc]^+$.

4.3. General procedure for the Mizoroki–Heck coupling reactions

In a typical experiment, an oven-dried 25 mL vial equipped with a stir bar and septum was charged with 1 mol % catalyst and base (2.0 mmol). Under nitrogen, DMA (3 mL), aryl halide (1.0 mmol) and n-butylacrylate (2.0 mmol) were added via syringe. The flask was then placed in a pre-heated sand bath at 145 °C. After 24 h the vial was removed from the sand bath and water (20 mL) added followed by extraction with ether (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, filtered and the internal standard (dodecahydrotriphenylene) was added. Solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. Yields were determined by ^{1}H NMR against dodecahydrotriphenylene as the internal standard [16].

4.4. X-ray structure determinations

Data were collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program [17]. Cell refinement and data reductions used the programs DENZO and SCALEPACK [18] SIR97 [19] was used to solve the structures and SHELXL97 [20] was used to refine the structures. ORTEP-3 for Windows [21] was used for molecular graphics and PLATON [22] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

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Appendix A. Supplementary material

CCDC 766977, 766978, 766979 and 766980 contain the supplementary crystallographic data for complexes **5**·CHCl3, **6**·H2O·CH2Cl2, **7** and **8**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.054.

References

[1] W.A. Herrmann, C. Brossmer, K. Ofele, C.-P. Reisinger, T. Priermeier, M. Beller, M.H. Fischer, Angew. Chem., Int. Ed. Engl. 34 (1995) 1844.
[2] (a) J. Dupont, C.S. Consorti, J. Spencer, J. Chem. Rev. 105 (2005) 2527;
(b) J. Tsuji, Palladium Reagents and Catalysts, Wiley, New York, 2004;
(c) A. de Meijere, P.J. Diederich (Eds.), Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH, Weinheim, 2004.;
(d) E. Negishi, A. de Mejere, Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley-VCH, Weinheim, 2002.;
(e) J. Dupont, M. Pfeffer (Eds.), Palladacycles: Synthesis, Characterization and Applications, Wiley-VCH, Weinheim, 2008.;
(f) J. Spencer, B.Z. Chowdhry, A.I. Mallet, R.P. Rathnam, T. Adatia, A. Bashall, F. Rominger, Tetrahedron 64 (2008) 6082;
(g) V. Montoya, J. Pons, V. Branchadell, J. Garcia-Anton, X. Solans, M. Font-Bardia, J. Ros, Organometallics 27 (2008) 1084;
(h) M. Guerrero, J. Pons, J. Ros, J. Organomet. Chem. 695 (2010) 1957.
[3] For reviews on palladacycles, see: (a) R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283;
(b) V. Farina, Adv. Synth. Catal. 346 (2004) 1553;
(c) I.P. Beletskaya, A.V. Cheprakov, J. Organomet. Chem. 689 (2004) 4055;
(d) W.A. Herrmann, K. Ofele, D. von Preysing, S.K. Schneider, J. Organomet. Chem. 687 (2003) 229;
(e) E. Alacid, D.A. Alonso, L. Botella, C. Nájera, M.C. Pacheco, Chem. Rec. 6 (2006) 117;
(f) J. Vicente, I. Saura-Llamas, Comments Inorg. Chem. 28 (2007) 39;
(g) D.A. Albison, R.B. Bedford, P.N. Scully, Tetrahedron Lett. 39 (1998) 9793;
(h) G. Aragay, J. Pons, J. García-Antón, X. Solans, M. Font-Bardia, J. Ros, J. Organomet. Chem. 693 (2008) 3396.
[4] (a) D.A. Alonso, L. Botella, C. Nájera, C. Pacheco, Synthesis (2004) 1713;
(b) E. Alacida, C. Nájera, Adv. Synth. Catal. 348 (2006) 2085.
[5] A. Schnyder, A.F. Indolese, M. Studer, H.-U. Blaser, Angew. Chem., Int. Ed. 41 (2002) 3668.
[6] D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, Chem. Commun. (1998) 2095.
[7] J. Thiele, J. Schneider, Justus Liebigs Ann. Chem. 369 (1910) 287.
[8] SCIFINDER, Version: 2007, Search Performed May 11, 2011.
[9] (a) J.M. Chitanda, D.E. Prokopchuk, J.W. Quail, S.R. Foley, Dalton Trans. (2008) 6023;
(b) J.M. Chitanda, J.W. Quail, S.R. Foley, J. Organomet. Chem. 694 (2009) 1542.
[10] I. Takahashi, K. Nishiuchi, R. Miyamoto, M. Hatanaka, H. Uchida, K. Isa, A. Sakushima, S. Hosoi, Lett. Org. Chem. 2 (2005) 40.
[11] J.M. Chitanda, D.E. Prokopchuk, J.W. Quail, S.R. Foley, Organometallics 27 (2008) 2337.
[12] (a) P. Zuman, Chem. Rev. 104 (2004) 3217;
(b) T. Tsuritani, S. Kii, A. Akao, K. Sato, N. Nonoyama, T. Mase, N. Yasuda, Synlett 5 (2006) 801;
(c) U. Ghosh, R. Bhattacharyya, A. Keche, Tetrahedron 66 (2010) 2148.
[13] (a) J. Wan, B. Wu, Y. Pan, Tetrahedron 63 (2007) 9338;
(b) J. Wan, J. Zhou, H. Mao, Y. Pan, A. Wu, Tetrahedron 64 (2008) 11115.
[14] M. Alajarín, P. Sánchez-Andrada, C. López-Leonardo, Á. Álvarez, J. Org. Chem. 70 (2005) 7617.
[15] (a) A.D. Tanase, G.D. Frey, E. Herdtweck, S.D. Hoffmann, W.A. Herrmann, J. Organomet. Chem. 692 (2007) 3316;
(b) F. Tjosaas, A. Fiksdahl, J. Organomet. Chem. 692 (2007) 5429;
(c) S.F. Kirsch, L.E. Overman, J. Org. Chem. 70 (2005) 2859;
(d) J. Vicente, I. Saura-Llamas, J. Cuadrado, M.C. Ramirez de Arellano, Organometallics 22 (2003) 5513;
(e) B. Teijido, A. Fernández, M. López-Torres, S. Castro-Juiz, A. Suárez, J.M. Ortigueira, J.M. Vila, J.J. Fernández, J. Organomet. Chem. 598 (2000) 71;
(f) M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357.
[16] T.A.P. Paulose, J.A. Olson, J.W. Quail, S.R. Foley, J. Organomet. Chem. 693 (2008) 3405.
[17] Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 1998.
[18] Z. Otwinowski, W. Minor, Methods in Enzymology, in: C.W. Carter, R.M. Sweet (Eds.), Macromolecular Crystallography, Part A, vol. 276, Academic Press, London, 1997, pp. 307–326.
[19] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[20] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
[21] L.J.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[22] A.L. Spek, PLATON, University of Utrecht, The Netherlands, 2001.