Organo-palladium(II) complexes bearing unsymmetrical $N,N,N$-pincer ligands: synthesis, structures and oxidatively induced coupling reactions†

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The 2-(2-anilino)-6-irnine-pyridines, 2-(C$_6$H$_4$-2'-NH$_2$)-6-(CMe=NC$_6$H$_4$N (Ar = 4-i-PrC$_6$H$_4$ (H1La), 2,6-i-Pr$_2$C$_6$H$_5$ (H1Lb)), have been synthesised via sequential Stille cross-coupling, deprotection and condensation steps from 6-tritylstannyl-2-(2-methyl-1,3-dioxolan-2-yl)pyridine and 2-bromonitrobenzene. The palladium(II) acetate $N,N,N$-pincer complexes, [(2-(C$_6$H$_4$-2'-NH)$_6$-(CMe=NC$_6$H$_4$N)Pd(OAc)] (Ar = 4-i-PrC$_6$H$_4$ (1a), 2,6-i-Pr$_2$C$_6$H$_5$ (1b)), can be prepared by reacting H1L with Pd(OAc)$_2$ or, in the case of 1a, more conveniently by the template reaction of ketone 2-(C$_6$H$_4$-2'-NH$_2$)-6-(CMe=O)-C$_6$H$_4$N, Pd(OAc)$_2$ and 4-isopropylaniline; ready conversion of 1 to their chloride analogues, [(2-(C$_6$H$_4$-2'-NH)$_6$-(CMe=NC$_6$H$_4$N)PdCl] (Ar = 4-i-PrC$_6$H$_4$ (2a), 2,6-i-Pr$_2$C$_6$H$_5$ (2b)), has been demonstrated. The phenyl-containing complexes, [(2-(C$_6$H$_4$-2'-NH)$_6$-(CMe=NC$_6$H$_4$N)PdPh] (Ar = 4-i-PrC$_6$H$_4$ (3a), 2,6-i-Pr$_2$C$_6$H$_5$ (3b)), can be obtained by treating H1L with (PPh$_3$)$_2$PdPh(Br) in the presence of NaH or with regard to 3a, by the salt elimination reaction of 2a with phenyllithium. Reaction of 2a with silver tetrafluoroborate or triflate in the presence of acetonitrile allows access to cationic [(2-(C$_6$H$_4$-2'-NH)$_6$-(CMe=NI(4-i-PrC$_6$H$_4$C$_6$H$_4$N)Pd(NC$_6$H$_4$)][X] (X = BF$_4$ (4), X = O$_2$SCF$_3$ (5)], respectively; the pyridine analogue of 5, [(2-(C$_6$H$_4$-2'-NH)$_6$-(CMe=N(4-i-PrC$_6$H$_4$C$_6$H$_4$N)Pd(NC$_6$H$_4$)][O$_2$SCF$_3$] (5), is also reported. Oxidation of phenyl-containing 3a with one equivalent of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor™) in acetonitrile at low temperature leads to a new palladium species that slowly decomposes to give 4 and biphényl; biphényl formation is also observed upon reaction of 3a with XeF$_2$. However, no such oxidatively induced coupling occurs when using 3b. Single crystal X-ray diffraction studies have been performed on H1Lb, 1a, 1b, 2a, 2b, 3a, 3b and 5.

Introduction

Recent years have seen a surge of interest in oxidatively induced coupling reactions involving Pd(II) and Pd(IV) intermediates due, in part, to their potential to promote transformations inaccessible using the conventional low valent Pd(0)/(II) cycle.1–3 For example, the historically challenging arene-fluoride bond forming reaction has become a reality with both types of high valent intermediate isolated and/or proposed in reaction pathways derived from Pd(II) species.4 Central to these developments have been reagents such as Selectfluor™ [1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)] and xenon difluoride that can oxidise the metal centre as a two electron oxidant (from Pd(II) to Pd(IV))4,5 or as a one electron oxidant (from Pd(II) to Pd(III))6,7 and moreover provide a source of F (e.g., as F or F). In cases where these types of oxidant deliver a fluorine atom direct to the metal centre, selective C–F reductive elimination from the high valent organo–metal intermediate can be challenging as alternative (and potentially desirable) degradation pathways can prove competitive.3d Sanford, for example, has reported that the Pd(IV) mono-aryl complex, [(4,4-t-Bu$_2$biPy)Pd(Ar)-(F)$_2$(FHF)] (Ar = 4-FC$_6$H$_4$), only undergoes selective C$_{aryl}$–F reductive elimination when heated in the presence of excess oxidant, otherwise competitive Ar–Ar coupling occurs through a process described as σ-aryl exchange between metal centres.3 Indeed this type of intermolecular Ar–Ar coupling involving palladium mono-aryl species has some precedent in Pd(II) and
Pd(II) chemistry involving complexes bearing a variety of multidentate ligands.

Given the apparent variation in coupling events that can occur from a high valent organo-Pd species,1–7 we have been interested in exploring the influence of a supporting multidentate ligand on the oxidatively induced reaction pathway. Herein, we report the reactivity of a family of N,N,N-pincer bearing Pd(II) mono-phenyl complexes of the type, \( [[2-(C_6H_4-2-NH)]_3C_5H_3N}Pd\) \( \) (Ar = aryl \( \) (Scheme 1);10 as an additional point of interest the effects that steric variation (Ar = 4-i-PrC\(_6\)H\(_4\), 2,6-i-Pr\(_2\)C\(_6\)H\(_3\)) has on the reactivity, will be investigated. Furthermore, we report the full synthetic details for the preparation of the novel pro-ligands (HL1) and their palladium(II) acetate (1), chloride (2) and phenyl (3) derivatives.

**Results and discussion**

**Preparation of pro-ligand HL1**

The 2-(2′-aniline)-6-imine-pyridines, 2-(C\(_6\)H\(_4\)-2′-NH\(_2\))-6-(CMe=NAr)C\(_5\)H\(_3\)N \( \) (Ar = 4-i-PrC\(_6\)H\(_4\) \( \) (HL1a), 2,6-i-Pr\(_2\)C\(_6\)H\(_3\) \( \) (HL1b)), have been prepared in reasonable yield via sequential Stille coupling, deprotection and condensation reactions from 6-tri-butylstannyl-2-(2-methyl-1,3-dioxolan-2-yl)pyridine and 2-bromo-nitrobenzene (Scheme 1). For both HL1a and HL1b, the condensation step proved sluggish in alcoholic media but proceeded more effectively by running the reaction in the neat aniline at high temperature; nevertheless problems encountered in the work-up of HL1a resulted in its isolation in only a modest yield (see later for a higher yielding template approach to HL1a). The precursor ketone and the two N,N,N-pro-ligands, HL1a and HL1b, have been characterised using a combination of electrospray mass spectrometry, IR, \(^1\)H NMR and \(^{13}\)C NMR spectroscopy (see Experimental section).

Compounds, HL1a, and HL1b, both display protonated molecular ions peaks in their electrospray mass spectra and downfield shifted signals for the amino protons (range: \( \delta 5.72–5.79 \) \( \) ) in their \(^1\)H NMR spectra. Characteristic imine stretching frequencies of ca. 1638 cm\(^{-1}\) \( \) are seen in their IR spectra as are higher wavenumber bands corresponding to the N–H stretches. Further confirmation of the composition of HL1b was achieved in the form of a single crystal X-ray determination.

A perspective view of HL1b is depicted in Fig. 2; selected bond distances and angles are listed in Table 1. The structure consists of a central pyridine ring that is substituted at its 2-position by a phenyl-2′-amine group and at the 6-position by a trans-configured N-arylimine unit \( [\text{C}(7)\text{–N}(1) 1.277(3) \text{ Å}] \). The pyridine nitrogen atoms adopt a cis configuration with respect to the neighbouring aniline nitrogen (tors: \( N(2)\text{–C}(13)\text{–C}(14)\text{–C}(15) \) 8.1°) as a result of a hydrogen-bonding interaction between one of the amino hydrogen atoms and the pyridine nitrogen \( [N(3)\text{–N}(2) 2.675 \text{ Å}] \); a similar arrangement has been reported for a related quinolinyl-substituted aniline.11

**Palladium(II) complexes of L1**

Interaction of HL1b with Pd(OAc)\(_2\) at 60 °C in toluene gave on work-up, \( [[2-(C_6H_4-2-NH)]_3C_5H_3N}Pd\) \( \) (Ar = 4-i-PrC\(_6\)H\(_4\) \( \) (Scheme 2). While \( [[2-(C_6H_4-2-NH)]_3C_5H_3N}Pd\) \( \) (Ar = 4-i-PrC\(_6\)H\(_4\)) \( \) (1b), in good yield (Scheme 2). While \( [[2-(C_6H_4-2-NH)]_3C_5H_3N}Pd\) \( \) (Ar = 4-i-PrC\(_6\)H\(_4\)) \( \) (1a) could also be made by this route, it was more conveniently prepared by the template reaction of ketone 2-(C\(_6\)H\(_4\)-2-NH\(_2\))-6-(CMe=NAr)C\(_5\)H\(_3\)N \( \) (Pd(OAc)\(_2\)) and 4-isopropylaniline. Compounds 1a can be readily converted to their chloride analogues, \( [[2-(C_6H_4-2-NH)]_3C_5H_3N}PdCl\) \( \) (Ar = 4-i-PrC\(_6\)H\(_4\)) \( \) (2a), 2,6-i-Pr\(_2\)C\(_6\)H\(_3\) \( \) (2b), by treatment of a dichloromethane solution of 1 with aqueous sodium chloride. All four complexes are air stable and have been characterised using a combination of FAB mass spectrometry, IR and NMR (\(^1\)H and \(^{13}\)C) spectroscopy and elemental analyses (see Experimental section). In addition, crystals of each complex have been the subject of single crystal X-ray diffraction studies.

![Scheme 1](Image)
Views of acetate-containing 1a and 1b are given in Fig. 3 and 4; selected bond distances and angles are collected for both structures in Table 2. There are two independent molecules for 1b in the unit cell (A and B) which differ most noticeably in the relative inclination of neighbouring pyridyl and anilido ring planes (vide infra). The structures of 1a and 1b are similar consisting of a four-coordinate palladium centre bound by a tridentate monoanionic 2-(2′-anilido)-6-imine-pyridine ligand and a monodentate O-bound acetate, but contrast in the nature of the hydrogen bonding involving the acetate ligand. In 1a, a water molecule present within the unit cell links the palladium-acetate units to form a hydrogen-bonded network [O(1)acetate⋯O(3)water 2.837, O(3)water⋯O(2A)acetate 2.877 Å], while in 1b the hydrogen bonding is intramolecular in origin involving the pendant acetate oxygen and the anilido proton [N(3)⋯O(2)acetate 2.799, 2.889 Å]. Within the N,N,N-ligand there are both 5- and 6-membered chelate rings with the bite angle for the 6-membered ring being more compatible with the square planar geometrical requirements of the palladium(II) centre [N(3)⋯Pd(1)⋯N(2)6-membered: 93.7(2) (1a), 92.2(3)A, 93.6(2)B (1b) vs. N(2)⋯Pd(1)⋯N(1)5-membered 82.2(2) (1a), 82.6(3)A, 82.1(2)B° (1b)]. In both cases some twisting of the anilido unit with respect to the adjacent pyridyl plane is apparent [tors. N(2)⋯C(13)⋯C(14)⋯C(15) 3.6(4) (1a), 4.9(4)A, 9.0(5)B° (1b)]. For a given complex, the Pd–Nimine bond distance is the longest of the three metal–ligand interactions involving the N,N,N-ligand followed by the Pd–Npyridine distance and then by the Pd–Nanilido distance which is best exemplified for 1a

Table 1 Selected bond distances (Å) and angles (°) for H1L1b

| Bond lengths | 1b          |
|--------------|-------------|
| C(15)–N(3)   | 1.366(4)    |
| C(7)–N(1)    | 1.277(3)    |
| C(7)–C(8)    | 1.504(4)    |
| C(7)–C(14)   | 1.477(4)    |
| C(7)–C(9)    | 1.482(4)    |

| Bond angles   | 1b          |
|---------------|-------------|
| C(7)–C(8)–N(1) | 125.3(2)   |
| C(9)–C(7)–N(1) | 116.4(3)   |

Reagents and conditions: (i) Pd(OAc)2, toluene, 60 °C; (ii) NaCl(aq.), CH2Cl2, RT.
Table 2  Selected bond distances (Å) and angles (°) for 1a and 1b

| Bond lengths           | 1a             | Molecule A | Molecule B |
|------------------------|-----------------|------------|------------|
| Pd(1)–N(1)             | 2.014(6)        | 2.017(8)   | 2.019(8)   |
| Pd(1)–N(2)             | 1.963(5)        | 1.970(9)   | 1.977(7)   |
| Pd(1)–N(3)             | 1.932(5)        | 1.920(9)   | 1.922(8)   |
| Pd(1)–O(1)             | 2.036(5)        | 2.011(8)   | 2.021(7)   |
| Bond angles            |                 |            |            |
| N(1)–Pd(1)–N(2)        | 82.2(2)         | 82.6(3)    | 82.1(2)    |
| N(1)–Pd(1)–N(3)        | 174.6(3)        | 174.3(3)   | 174.4(2)   |
| N(1)–Pd(1)–O(1)        | 93.8(2)         | 89.6(3)    | 93.8(2)    |
| N(2)–Pd(1)–N(3)        | 93.7(2)         | 92.3(2)    | 93.6(2)    |
| N(3)–Pd(1)–O(1)        | 90.3(2)         | 95.6(3)    | 90.5(2)    |

Table 3  Selected bond distances (Å) and angles (°) for 2a and 2b

| Bond lengths           | 2a             | Molecule A | Molecule B |
|------------------------|-----------------|------------|------------|
| Pd(1)–N(1)             | 2.022(5)        | 2.035(6)   | 2.025(3)   |
| Pd(1)–N(2)             | 1.976(5)        | 1.984(5)   | 1.987(3)   |
| Pd(1)–N(3)             | 1.934(5)        | 1.931(6)   | 1.927(3)   |
| Pd(1)–Cl(1)            | 2.297(18)       | 2.293(18)  | 2.312(3)   |
| Bond angles            |                 |            |            |
| N(1)–Pd(1)–N(2)        | 81.6(2)         | 82.3(3)    | 82.01(13)  |
| N(1)–Pd(1)–N(3)        | 174.4(2)        | 174.0(2)   | 173.63(13) |
| N(1)–Pd(1)–Cl(1)       | 93.1(2)         | 92.3(1)    | 91.91(13)  |
| N(2)–Pd(1)–Cl(1)       | 178.2(17)       | 175.39(15) | 179.27(9)  |
| N(3)–Pd(1)–Cl(1)       | 88.54(16)       | 89.14(17)  | 88.47(10)  |

Replacing a chloride for an O-bound acetate has little effect on the trans Pd–N-pyridine distance [1.976(5)Å, 1.984(5)Å (2a), 1.987(3)Å (2b) vs. 1.963(5)Å (1a), 1.970(9)Å 1.977(7)Å (1b)]. Unlike 1b, the anilido NH proton is not involved in any intra- or intermolecular contacts of note.

Complexes 1a, 1b, 2a and 2b, all display molecular ion peaks in their FAB mass spectra along with fragmentation peaks corresponding to the loss of an acetate or a chloride, respectively. In their IR spectra the imine stretching frequencies are shifted between 28 and 35 cm⁻¹ to lower wavenumber in comparison with the corresponding free HL1, characteristic of imine-nitrogen coordination.12 In 1b and 2b two distinct doublets are seen for the isopropyl methyl groups in their ¹H NMR spectra consistent with some restricted rotation about the N-2,6-disopropylphenyl bond in solution. The acetate methyl groups in 1 can be seen at δ ca. 1.5 in their ¹H NMR spectra with the MeC(O)O carbon atoms observable at δ ca. 177.1 in their ¹3C NMR spectra. The anilido NH proton in 2 is observable at a similar chemical shift (ca. δ 5.8) to that seen in free HL1, but in acetate-containing 1 there is some variation with that observed in 1b being more downfield (δ 5.60 (1a), 7.39 (1b)) this is likely to be due to the influence of the intramolecular NH···Oacetate hydrogen bonding seen in 1b (see Fig. 4). As with related monodentate acetate complexes, 1a and 1b both show strong bands assignable to the symmetric and asymmetric ν(CO)O vibrations.16

Their phenyl derivatives, [(2-[C₆H₄-2'-NH]-6-[CMe=NR]-CH₃)N]Pd(OAc) [Ar = 4-i-PrC₆H₄] and [2-[C₆H₄-2'-NH]-6-[CMe=NR]-CH₃]PdPh [Ar = 4-i-PrC₆H₄] could be readily accessed by treatment of HL1 with NaH followed by (PPh₃)₃PdPh(Br) (Scheme 3). Alternatively, 3a can be prepared by treating chloride 2a with phenyl lithium; a related salt elimination approach to make 3b has not proved possible. In the case of 2a, chloride abstraction with both silver tetrafluoroborate and triflate in acetonitrile proved facile affording [2-[C₆H₄-2'-NH]-6-[CMe=NR]-CH₃]Pd(NCMe)X [X = BF₄ (4), X = O₂SCF₃ (5)] in high yield (Scheme 3). Monophenyl 3a and 3b are air and water stable, whereas 4 and 5 proved hygroscopic on prolonged standing. All four complexes

Fig. 5  Molecular structure of 2b including a partial atom numbering scheme. All hydrogen atoms, apart from H3, have been omitted for clarity.
have been characterised using a combination of FAB mass spectrometry, IR and NMR (1H and 13C) spectroscopy and elemental analyses (see Experimental section).

The mass spectra of 3a and 3b exhibit molecular ions while 4 and 5 display peaks corresponding to their cationic units. As with 1 and 2, all four complexes exhibit ν(C=N)imine stretches at lower wavenumber (typically by 35 cm⁻¹) when compared with HL1, supporting coordination of L1 to the metal centre. The imine methyl resonances are seen between δ 2.2 and 2.5 in their 1H NMR spectra, while signals for the imine carbon fall between δ 170.5 and 174.8 in their 13C spectra. Signals attributable to [BF₄]⁻ and [O₃SCF₃]⁻ counterions could also be seen in the 19F NMR spectra of 4 and 5. In addition, crystals of 3a, 3b and the pyridine analogue of 5, [(2-(C₆H₄-2'-NH)-6-(CMe₃)NPy)[Pd(N(Me)₃)₂][O₃SCF₃] (5'), have been the subject of single crystal X-ray diffraction studies.

As a representative of the mono-phenyl pair of structures, a view of the molecular structure of 3a is depicted in Fig. 6; selected bond distances and angles are listed in Table 4 for both 3a and 3b. As with 1 and 2, 2-(2'-anilido)-6-imine-pyridine ligand acts a tridentate ligand with the σ-phenyl ligand now occupying the fourth coordination site to complete a distorted square planar geometry. The phenyl ligand in both structures is tilted with respect to the trans-pyridine unit of the N,N,N-ligand and most noticeably for 3a, presumably as a consequence of the variation in steric hindrance imposed by the N-aryl groups [tors. C(13)-N(2)-C(23)-C(24) 46.4(4) (3a), 41.4(4)° (3b)]. When compared to 1 and 2, the presence of a σ-phenyl group in 3 results in an elongation of the trans Pd–N₃pyridine distance [Pd–N(2) 2.066(6) (3a), 2.069(2) (3b) vs. 1.963(5)] Å] and 1.974(8)Å (1), 1.980(5)Å (2a), 1.987(3)Å (2b)] Å, an observation attributable to the strong trans-influence exhibited by the aryl group. In contrast, the exterior nitrogen-palladium distances remain similar in length to those seen in 1 and 2. To accommodate the increased Pd–N₃pyridine distance, there is increased twisting of the ligand backbone which is most apparent in 3b [tors. N(2)-C(13)-C(14)-C(15) 25.2(4) and N(1)-C(7)-C(9)-N(2) 13.7(4)°]. As with chloride-containing 2, the anilido NH proton shows no notable intra- or inter-molecular contacts of note.

Unfortunately cationic 4 and 5 were not amenable to forming crystals suitable for an X-ray determination. To overcome this practical issue, small amounts of pyridine were added to a solution of 5 in chloroform and hexane slowly diffused forming single crystals of [(2-(C₆H₄-2'-NH)-6-(CMe₃)NPy)[Pd(N(Me)₃)₂][O₃SCF₃] (5'). The molecular structure of the cationic unit 5' is depicted in Fig. 7; selected bond distances and angles are listed in Table 5. As with a number of the structures reported in this study, two independent molecules (A and B) were present in the unit cell which, in this case, differ most noticeably in the inclination of the N-aryl groups. The structure of 5' consists of a palladium(n) cationic unit charge balanced by a non-coordinating triflate counterion. Within the distorted square planar cationic

![Fig. 6](image_url) Molecular structure of 3a including a partial atom numbering scheme. All hydrogen atoms, apart from H3, have been omitted for clarity.
unit, the 2-(2’anilido)-6-imine-pyridine ligand acts a tridentate ligand and an N-bound pyridine fills the fourth coordination site. Similar to phenyl-bound 3, the monodentate hetero-aromatic in 5’ is not co-planar with the trans-pyridine unit of the tridentate ligand. Instead it adopts a tilted configuration comparable with those seen in trans-Pd greater than that for the aryl group in 3a.

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Table 5 Selected bond distances (Å) and angles (°) for 5’

| Bond lengths          | Molecule A | Molecule B |
|-----------------------|------------|------------|
| Pd(1)–N(1)            | 2.049(12)  | 2.034(12)  |
| Pd(1)–N(2)            | 1.992(11)  | 1.932(11)  |
| Pd(1)–N(3)            | 1.937(11)  | 1.962(11)  |
| Pd(1)–N(4)            | 2.010(11)  | 2.015(11)  |
| C(7)–N(1)             | 1.276(16)  | 1.279(16)  |
| C(15)–N(3)            | 1.336(15)  | 1.316(16)  |
| Bond angles           |            |            |
| Range S–O (triflate)  | 1.424(11)–1.485(10) |

To investigate the reaction further and potentially observe any possible intermediates, a reaction involving an equimolar ratio of 3a and Selectfluor was undertaken in CD3CN at a series of lower temperatures and the reaction monitored by 1H and 19F NMR spectroscopy (Scheme 4). At 15 minutes at room temperature the 19F NMR spectrum revealed full consumption of Selectfluor and a new peak at δ −181 attributable to the formation of hydrogen fluoride.4 The 1H NMR spectrum contained signals consistent with biphenyl, the salt [[2-(C6H4-2-NH)6-CMe3-N-6-(C6H5-N)=N][BF4]] (4) (vide supra) and 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium tetrafluoroborate, the Selectfluor degradation product. In addition, there were signals present attributable to another palladium species that slowly reduced in intensity over time.

When the reaction was carried out at −40 °C, full consumption of Selectfluor was again evident from the 19F NMR spectrum which also contained a peak attributable to HF, albeit temperature shifted (δ −172). In the 1H NMR spectrum full conversion of 3a to a single palladium species was observed with the aromatic/pyridyl region integrating to sixteen protons; no peaks assignable to biphenyl nor 4 could be identified. As the reaction mixture was warmed to 0 °C, only sharpening of the 1H NMR spectrum was observed with peaks that clearly match those observed for the decomposing palladium species seen at room temperature (Fig. S9 in ESI†). In the 19F NMR spectrum a 1 : 8 ratio between the HF signal (δ −174) and the BF4 peak (δ −152) accounts for all the fluorine introduced from the Selectfluor (Fig. S10 in ESI†). On warming to room temperature, decomposition of the palladium intermediate ensued generating biphenyl and 4; full conversion being
Conclusions

A new family of imino-based monoanionic \( N,N,N \) pincer ligands have been developed that can support neutral palladium(II) complexes and are capable of forming 1:1 complexes with Selectfluor. A subsequent oxidative coupling reaction between the palladium(II) complexes and selectfluor (Selectfluor™) was also explored at a range of different temperatures. However, despite consumption of 2-bromonitrobenzene and formation of biphenyl, fluorobenzene nor the corresponding palladium(II) intermediate were observed. Unfortunately, further attempts to fully characterise the high valent palladium intermediate were unsuccessful.

The 1:1 reaction of 2,6-diisopropylphenyl-containing \( 3b \) with Selectfluor was also explored at a range of different temperatures. However, despite consumption of 2-bromonitrobenzene and formation of biphenyl, fluorobenzene nor could any characterisable palladium species be identified. It is unclear as to the origin of these differences in reactivity between \( 3a \) and \( 3b \) towards Selectfluor.

Experimental

General

All operations, unless otherwise stated, were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk and cannula techniques or in a nitrogen purged glove box. Operations involving a Microwave were performed on a CEM Discover Explorer Hybrid instrument. Solvents were distilled under nitrogen from appropriate drying agents or were employed directly from a Solvent Purification System (Innovative Technology, Inc.). The electrospray (ESI) mass spectra were recorded using a micromass Quattro LC mass spectrometer with acetonitrile or methanol as the matrix. FAB spectra were recorded using a micromass Quattra LC mass spectrometer with acetonitrile or methanol as the matrix. The infrared spectra were recorded using a Kratos Concept spectrometer with NBA as matrix or on a Perkin-Elmer Spectrum One FTIR spectrometer with a universal ATR sampling accessory (Universal ATR sampling accessory). The NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13 MHz (\( ^{1}H \)), 376.46 MHz (\( ^{19}F \)) and 100.61 MHz (\( ^{13}C \)) or a Bruker Avance III 500 spectrometer at 125 MHz (\( ^{13}C \)), at ambient temperature unless otherwise stated; chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in hertz (Hz). Melting points (mp) were measured on a Gallenkamp melting point apparatus (model MFB-595) in open capillary tubes and were uncorrected. Elemental analyses were performed at the Science and Technical Support Unit, London Metropolitan University.

Synthesis of 2-(2-methyl-1,3-dioxolan-2-yl)-6-(2-nitrophenyl)pyridine

A 25 mL microwave vial was loaded with 2-bromonitrobenzene (0.536 g, 2.70 mmol), 6-tributylstannyl-2-(2-methyl-1,3-dioxolan-2-yl)pyridine (1.226 g, 2.70 mmol), \( \text{Pd(OAc)}_2 \) (0.025 g, 0.11 mmol) and triphenylphosphine (0.058 g, 0.22 mmol) and the contents dissolved in benzene (13 mL). The system was then sealed and stirred for 30 s in a microwave before heating to 100 °C (with 100 W power and 10 bar pressure limits) for 1 h. The resulting dark brown reaction mixture was concentrated under reduced pressure to yield a dark brown oil. This oil was then dried on to a silica column and eluted with a 70:30 mixture of petroleum ether (40-60 °C) and ethyl acetate affording 2-(2-methyl-1,3-dioxolan-2-yl)-6-(2-nitrophenyl)pyridine as a yellow oil (0.517 g, 67%) along with trace amounts of the homocoupled by-product 6,6'-bis(2-methyl-1,3-dioxolan-2-yl)-2,2'-bipyrindine. \(^{1}H\) NMR (400 MHz, CDCl3): \( \delta \) 1.66 (s, 3H, CH₃), 3.84 (m, 2H, O-CH₂-CH₂-O), 4.02 (m, 2H, O-CH₂-CH₂-O), 2.37 (dd, \( \text{J}_{HH} \) 7.8, \( \text{J}_{HH} \) 1.0, 1H, Ar-H), 7.42-7.46 (m, 1H, Ar-H), 7.50 (dd, \( \text{J}_{HH} \) 7.5, \( \text{J}_{HH} \) 0.9, 1H, Ar-H), 7.54-7.57 (m, 2H, Ar-H), 7.74 (dd, \( \text{J}_{HH} \) 7.8, \( \text{J}_{HH} \) 7.9, Ar-H), 7.78 (dd, \( \text{J}_{HH} \) 8.0, \( \text{J}_{HH} \) 8.1, 1H, Ar-H). \(^{13}C\) NMR (100 MHz, CDCl₃): \( \delta \) 24.9 (CH₃), 65.0 (CH₃), 65.1 (CH₃), 108.6 (C), 118.7 (C), 121.7 (C), 124.4 (C), 129.1 (C), 131.1 (CH), 135.3 (C), 137.5 (CH), 149.8 (C), 154.9 (C), 161.1 (C). IR (cm⁻¹): 1587 (C=N)pyridine, 1530 (NO₂)asymm, 1369 (NO₂)symm HRMS (TOFMS, ASAP): calcd for C₇H₅N₂O₄ [M + H]⁺ 287.1032, found 287.1034.

Synthesis of 1-(6-(2-aminophenyl)pyridine-2-yl)ethanone

2-(2-Methyl-1,3-dioxolan-2-yl)-6-(2-nitrophenyl)pyridine (1.040 g, 3.6 mmol) and SnCl₂·2H₂O (8.220 g, 36.0 mmol) were suspended in benzene (34 mL) and sonicated for 2 h, whereupon a bright yellow slurry was obtained. This slurry was concentrated under reduced pressure and partitioned between 1 M NaOH (100 mL) and CHCl₃ (100 mL) until a bright yellow organic phase was observed. The organic phase was separated and the aqueous phase was neutralised with K₂CO₃, the organic phase separated and the aqueous
phase washed with dichloromethane (2 \times 30 \text{ mL}). The combined organic extracts were washed with water (1 \times 30 \text{ mL}) and brine (1 \times 30 \text{ mL}) and then filtered through Celite layered with magnesium sulphate. The filtrate was concentrated under reduced pressure to afford 1-(6-(2-aminophenyl)pyridin-2-yl)-ethanone as a brown/yellow oil which slowly solidifies (0.68 g, 89%). Mp: 95–98 °C. 1H NMR (400 MHz, CDCl3): δ 2.73 (s, 3H, MeC=O), 5.77 (br, s, 2H, NH2), 6.82 (m, 2H, Ar-H), 7.22 (dd, JHH 7.3, JHH 8.1, 1.6, 1H, Ar-H), 7.56 (dd, JHH 7.8, JHH 1.5, 1H, Ar-H), 7.85–7.95 (m, 3H, Py-H). 13C{1H} NMR (100 MHz, CDCl3): δ 26.1 (MeC=O), 117.4, 118.0, 119.0 (CH), 121.3 (C), 125.7 (CH), 129.6 (CH), 130.5 (CH), 137.9 (CH), 146.5 (C), 151.7 (C), 158.7 (C), 199.4 (CO). IR (cm⁻¹): 3456, 3363 (NH), 1695 (C=O)ketone, 1585 (C=N)pyridine. EIMS: m/z 213 [M + H]⁺. HRMS (FAB): calecd for C13H12N3O [M + H]⁺ 213.10246, found 213.10252.

**Synthesis of 2-(C6H4-2-NH)-6-(CMe=N=Ar)C6H5N (HL1)**

(a) Ar = 4-i-PrC6H4 (HL1a). To a round bottomed flask equipped with stir bar was added 1-(6-(2-aminophenyl)pyridin-2-yl)ethanone (0.500 g, 2.4 mmol) and 4-isopropylaniline (0.690 g, 6.9 mmol), 4-isopropylaniline (0.660 g, 4.9 mmol) and toluene (70 mL). The reaction vessel was stirred and heated to 80 °C for 3 h. The resultant green/brown solution was evaporated and the resultant solid dissolved in the minimum volume of chloroform before hexane was added to precipitate 1a as a green/brown solid (1.45 g, 89%). Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of 1a in CHCl₃ at room temperature. Mp: >260 °C. 1H NMR (400 MHz, CDCl₃): δ 1.22 (d, JHH 6.9, 6H, CHMe₂), 1.53 (s, 3H, –OC(O)Me), 2.33 (s, 3H, MeC=N), 2.98 (sept, JHH 6.9, 1H, CHMe₂), 5.60 (br, s, 1H, NH), 6.42 (dd, JHH 6.6, 8.5, 1.2, 1H, Ar-H), 6.86 (dd, JHH 8.5, JHH 1.2, 1H, Ar-H), 7.02 (dd, JHH 6.6, JHH 7.9, 1H, Ar-H), 7.23 (d, JHH 8.3, 2H, Ar-H), 7.59 (dd, JHH 7.4, 1.0, 1H, Py-H), 7.89 (d, JHH 8.0, 1H, Ar-H), 7.99 (dd, JHH 7.4, JHH 8.8, 1H, Py-H), 8.56 (d, JHH 8.8, 1H, Py-H). 13C{1H} NMR (100 MHz, CDCl₃): δ 16.3 (MeC=N), 21.9 (MeCO₂), 22.9 (CHMe₂), 32.9 (CHMe₂), 111.8 (CH), 112.9 (C), 119.7 (CH), 121.5 (CH), 122.0 (CH), 125.4 (CH), 125.6 (CH), 128.3 (CH), 129.1 (CH), 133.5 (CH), 141.7 (C), 146.9 (C), 148.5 (C), 148.8 (C), 152.7 (C), 169.5 (MeC=N), 177.0 (MeCO₂). IR (cm⁻¹): 1600 (C=N)pyridine, 1367 (COO)pyridine FABMS: m/z 493 [M⁺], 433 [M – OAc]⁻. Anal Calc. for (C24H25N3O2Pd): C, 58.36; H, 5.10; N, 8.51. Found: C, 58.26; H, 5.23; N, 8.51%.

(b) Ar = 2,6-i-PrC6H4 (HL1b). Employing a similar procedure to that described for HL1a, a Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with Pd(OAc)₂ (0.740 g, 3.3 mmol), 1-(6-(2-aminophenyl)pyridin-2-yl)ethanone (0.690 g, 0.81 mmol), 4-isopropylaniline (0.660 g, 4.9 mmol) and toluene (70 mL). The reaction vessel was stirred and heated to 80 °C for 3 h. The resultant green/brown solution was evaporated and the resultant solid dissolved in the minimum volume of chloroform before hexane was added to precipitate 1b as a green/brown solid (1.45 g, 89%). Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of 1b in CHCl₃ at room temperature. Mp: >260 °C. 1H NMR (400 MHz, CDCl₃): δ 1.14 (d, JHH 6.8, 6H, CHMe₂), 1.39 (d, JHH 6.9, 6H, Ar-H), 2.71 (dd, JHH 7.3, JHH 8.0, 1H, Ar-H), 7.21 (dd, JHH 7.3, JHH 8.0, 1H, Ar-H), 7.59 (dd, JHH 8.0, JHH 1.5, 1H, Ar-H), 7.78 (dd, JHH 8.0, 1H, Py-H), 7.90 (dd, JHH 7.9, JHH 7.9, 1H, Py-H), 8.26 (dd, JHH 7.8, JHH 0.9, 1H, Py-H). 13C{1H} NMR (100 MHz, CDCl₃): δ 7.5 (MeC=N), 22.9 (CHMe₂), 23.2 (CHMe₂), 28.3 (CHMe₂), 117.6, 118.2 (CH), 118.8 (C), 122.2 (CH), 123.0 (CH), 123.4 (CH), 123.7 (CH), 129.6 (CH), 130.1 (CH), 135.8 (C), 137.6 (CH), 146.1 (C), 146.3 (C), 154.5 (C), 158.2 (C), 165.0 (MeC=N). IR (cm⁻¹): 3451, 3282 (br, NH), 1642 (C=N)pyridine. EIMS: m/z 372 [M + H]⁺. HRMS (FAB): calecd for C24H23N4O [M + H]⁺ 372.24322, found 372.24310.
Synthesis of [(2-(C6H5-C2H4)-6-(C-Me=N=Ar))PdCl] (2) 

(a) Ar = 4-i-PrC6H4 (2a). A round bottomed flask equipped with stir bar and open to the air was loaded with 1a (0.595 g, 1.20 mmol), dichloromethane (5 mL) and brine (5 mL). The reaction mixture was stirred rapidly for 1 h at room temperature whereupon both phases were diluted and the aqueous layer removed via a separating funnel. The organic phase was washed with water (2 × 20 mL) and concentrated to a smaller volume under reduced pressure. The dark green solution was filtered through a Celite plug and the plug washed thoroughly with dichloromethane. All volatiles were removed under reduced pressure affording 2a as a dark brown solid (0.56 g, 99%). Single crystals suitable an X-ray determination were grown by diffusion of hexane into a solution of 2a in chloroform at room temperature. Mp: >260 °C. 1H NMR (400 MHz, CDCl3): δ 1.23 (d, JHH 6.9, 6H, CHMe2), 2.28 (s, 3H, MeC=C=N), 2.89 (sept, JHH 6.9, 1H, CHMe2), 5.59 (br s, 1H, NH), 6.43 (ddd, JHH 6.1, JHH 8.0, JHH 1.20, 1H, Ar–H), 6.81 (dd, JHH 8.6, JHH 1.0, 1H, Ar–H), 6.99–7.03 (m, 5H, Ar–H), 7.19 (d, JHH 8.2, 2H, Ar–H), 7.55 (dd, JHH 7.5, JHH 0.9, 1H, Py–H), 7.73–7.79 (m, 2H, Py–H/Ar–H), 8.30 (d, JHH 8.7, 1H, Py–H). 13C{1H} NMR (125 MHz, CDCl3): δ 17.0 (CH=C=N), 22.9 (CHMe2), 32.7 (CHMe2), 112.1 (CH), 112.8 (C), 119.7 (CH), 121.6 (CH), 122.3 (CH), 125.1 (CH), 125.5 (CH), 128.2 (CH), 129.5 (CH), 133.4 (CH), 142.9 (C), 146.6 (C), 148.4 (C), 153.1 (C), 171.0 (MeC=C=N). IR (cm−1): 1603 (C=NNImine), 1576 (C=Npyridine). FABMS: m/z 469 [M]+, 434 [M–Cl]+. Anal Calc. for (C24H18Cl2N2Pd)Cl: C, 56.18; H, 4.71; N, 8.93. Found: C, 56.11; H, 4.69; N, 9.00%.

(b) Ar = 2,6-i-i-PrC6H4 (2b). Employing a similar procedure to that described for 2a using 1b (0.544 g, 1.02 mmol) gave 2b as a dark green solid (0.520 g, 99%). Single crystals suitable an X-ray diffraction study could be grown by slow diffusion of hexane into a chloroform solution of 2b at room temperature. Mp: >260 °C. 1H NMR (400 MHz, CDCl3): δ 1.05 (d, JHH 6.9, 6H, CHMe2), 1.35 (d, JHH 6.9, 6H, CHMe2), 2.28 (s, 3H, MeC=C=N), 2.99 (sept, JHH 6.9, 2H, CHMe2), 5.91 (br s, 1H, NH), 6.49 (ddd, JHH 8.5, JHH 8.5, JHH 7.3, 1H, Ar–H), 6.92 (ddd, JHH 8.6, JHH 1.2, 1H, Ar–H), 7.06 (ddd, JHH 8.2, JHH 8.2, JHH 6.5, JHH 1.4, Ar–H), 7.19 (m, 2H, Ar–H), 7.28 (dd, JHH 8.7, JHH 8.5, JHH 8.5, 1H, Ar–H), 7.77 (dd, JHH 7.3, JHH 1.1, 1H, Py–H), 7.92 (dd, JHH 8.6, JHH 1.5, 1H, Ar–H), 8.06 (dd, JHH 8.8, JHH 8.4, 1H, Ar–H), 8.63 (d, JHH 8.6, 1H, Py–H). 13C{1H} NMR (125 MHz, CDCl3): δ 18.0 (MeC=C=N), 23.7 (CHMe2), 23.8 (CHMe2), 28.7 (CHMe2), 113.6 (CH), 113.8 (C), 121.3 (CH), 122.1 (CH), 123.6 (CH), 127.2 (CH), 128.1 (CH), 129.1 (CH), 130.9 (CH), 134.1 (CH), 139.7 (C), 141.6 (C), 150.0 (C), 150.3 (C), 153.7 (C), 172.1 (MeC=C=N). IR (cm−1): 1608 (C=NNImine), 1577 (C=Npyridine). FABMS: m/z 511 [M + H]+, 475 [M–Cl]+. Anal Calc. for (C22H14Cl2N2Pd)Cl: C, 58.60; H, 5.51; N, 8.20. Found: C, 58.49; H, 5.35; N, 8.26%.

Synthesis of [(2-(C6H5-C2H4)-6-(C-Me=N=Ar))PdCl2] (3)

(a) Ar = 4-i-PrC6H4 (3a). A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with 2a (0.208 g, 0.44 mmol) and THF (20 mL). The reaction mixture was stirred and cooled to −78 °C for 15 min. A solution of PhLi (861 µL, 1.55 mmol, 1.8 M in n-BuLi) was added to the mixture, and the solution slowly warmed to room temperature. All volatiles were removed under reduced pressure and the resultant green solid redissolved in dichloromethane (20 mL) and washed with water (2 × 20 mL) and brine (10 mL). Following drying over anhydrous magnesium sulphate and filtration, the resulting green solution was concentrated to a smaller volume (ca. 5 mL) and hexane added to precipitate 3a as a green solid (0.161 g, 71%). Single crystals suitable for an X-ray determination were obtained by slow diffusion of hexane into a solution of 3a in chloroform at room temperature. 1H NMR (400 MHz, CDCl3): δ 1.19 (d, JHH 6.9, 6H, CHMe2), 2.46 (s, 3H, MeC=C=N), 2.80 (sept, JHH 6.9, 1H, CH=CH), 5.48 (br s, 1H, NH), 6.44 (ddd, JHH 6.5, JHH 8.0, JHH 1.1, 1H, Ar–H), 6.65 (d, JHH 8.4, 2H, Ar–H), 6.73–6.75 (m, 3H, Ar–H), 6.90 (ddd, JHH 8.6, JHH 1.3, 1H, Ar–H), 6.95 (d, JHH 8.4, 2H, Ar–H), 7.05 (ddd, JHH 6.6, JHH 8.1, JHH 1.4, 1H, Ar–H), 7.07–7.09 (m, 2H, Ar–H), 7.82 (d, JHH 7.1, 1H, Py–H), 7.98 (dd, JHH 8.5, JHH 1.3, 1H, Ar–H), 8.05 (dd, JHH 7.5, JHH 8.6, 1H, Ar–H), 8.58 (d, JHH 8.8, 1H, Py–H). 13C{1H} NMR (100 MHz, CDCl3): δ 18.3 (MeC=C=N), 24.0 (CHMe2), 33.7 (CHMe2), 111.9 (CH), 114.0 (C), 121.3 (CH), 122.2 (CH), 122.6 (CH), 122.9 (CH), 125.9 (CH), 126.0 (CH), 126.1 (CH), 129.9 (CH), 130.0 (CH), 134.2 (CH), 135.9 (CH), 145.1, 146.9, 152.0, 152.1, 153.1, 158.5 (C), 170.5 (MeC=C=N). IR (cm−1): 1602 (C=NNImine), 1574 (C=Npyridine). FABMS: m/z 511 [M]+. Anal Calc. for (C22H12N2Pd2)Cl2: C, 62.40; H, 5.61; N, 7.80. Found: C, 62.04; H, 5.33; N, 8.16%.

(b) Ar = 2,6-i-i-PrC6H4 (3b). A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with 2b (0.100 g, 0.13 mmol), NaH (0.052 g, 2.20 mmol) and THF (10 mL). The resulting slurry was stirred and heated to reflux for 72 h before being allowed to cool to room temperature. The reaction mixture was transferred by cannula filtration to a second Schlenk flask containing [{PPh3}2PdPhBr] (0.100 g, 0.13 mmol) and the contents stirred and heated to
reflux for a further 72 h. On cooling to room temperature, the resulting green solution was concentrated under reduced pressure and re-dissolved in chloroform (10 mL) before being filtered through a Celite plug. All volatiles were removed under reduced pressure and the resulting residue triturated with hexane (3 × 20 mL) and 3b collected as a green solid (0.067 g, 93%). Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a solution of 3b in chloroform at room temperature. 1H NMR (400 MHz, CD3CN): δ 0.90 (d, 3JHH 6.7, 6H, CHMe2), 0.95 (d, 3JHH 6.8, 6H, CHMe2), 2.32 (s, 3H, MeC=N), 2.94 (sept, 3JHH 6.8, 2H, CHMe2), 6.40 (dd, 3JHH 8.1, 3JHH 1.3, 1H, Ar–H), 6.66–6.73 (m, 3H, Ar–H), 6.84 (dd, 3JHH 8.4, 3JHH 1.2, 1H, Ar–H), 6.88–6.93 (m, 2H, Ar–H), 6.99 (dddd, 3JHH 8.3, 3JHH 6.6, 1JHH 1.6, 1H, Ar–H), 6.99 (d, 3JHH 7.8, 2H, Ar–H), 7.12 (dd, 3JHH 7.7, 3JHH 7.7, 1H, Ar–H), 7.80 (dd, 3JHH 7.5, 3JHH 1.0, 1H, Py–H), 7.91 (dd, 3JHH 8.6, 3JHH 1.4, 1H, Ar–H), 8.02 (dd, 3JHH 8.8, 3JHH 7.5, 1H, Py–H), 8.55 (d, 3JHH 8.7, 1H, Py–H). 13C[1H] NMR (100 MHz, CD3CN): δ 19.3 (MeC=N), 22.9 (CHMe2), 24.2 (CHMe2), 28.2 (CHMe2), 112.1 (CH), 114.5 (C), 121.3 (C), 122.5 (CH), 123.8 (CH3), 125.8 (CH), 126.5 (CH), 127.1 (CH), 130.0 (CH), 130.1 (CH), 134.3 (CH), 135.9 (CH), 139.5 (CH), 142.9 (C), 151.5 (C), 152.4 (C), 153.2 (C), 155.5 (C), 172.1 (MeC=N). IR (cm⁻¹): 1605 (C=N)min, 1571 (C=N)pyridine. FABMS: m/z 553 [M + H⁺].

Synthesis of [(2-{C(H2)2}-2-N)·6-(CM(C=N)—4-Pr(Ph4)Pd)](NCMe)(X) [14] and 5
(a) X = BF₄⁻ (4). A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen and loaded with 2a (0.200 g, 0.426 mmol), AgBF₄ (0.083 g, 0.426 mmol) and MeCN (20 mL). The reaction mixture was stirred at room temperature for 12 h, at which point the suspension was allowed to settle and the solution transferred by cannula filtration into another Schlenk flask. All volatiles were removed under reduced pressure to afford 4 as a dark green solid (0.233 g, 97%). Mp: >260 °C. 1H NMR (400 MHz, CD3CN): δ 1.21 (d, 3JHH 6.9, 3H, CHMe2), 2.27 (s, 3H, CH2C=N), 2.93 (sept, 3JHH 6.9, 1H, CHMe2), 6.60 (dd, 3JHH 7.5, 3JHH 7.5, 1H, Ar–H), 6.98 (d, 3JHH 8.4, 1H, Ar–H), 7.04 (d, 3JHH 7.8, 2H, Ar–H), 7.10 (dd, 3JHH 7.6, 3JHH 7.8, 1H, Ar–H), 7.34 (d, 3JHH 8.0, 2H, Ar–H), 7.83 (d, 3JHH 7.5, 1H, Py–H), 7.89 (d, 3JHH 8.0, 1H, Ar–H), 8.08 (dd, 3JHH 8.0, 3JHH 8.0, 1H, Py–H), 8.53 (d, 3JHH 8.6, 1H, Py–H), the coordinated CH3CN ligand was not observed due to rapid exchange with bulk CD3CN. 13C[1H] NMR (100 MHz, CD3CN): δ 17.0 (CH2C=N), 22.9 (CHMe2), 33.3 (CHMe2), 115.3 (CH), 117.0 (C), 119.6 (CH), 122.3 (CH), 124.9 (CH), 126.9 (CH), 129.7 (CH), 131.0 (CH), 136.7 (CH), 142.8 (C), 146.7 (C), 148.8 (C), 149.3 (C), 154.8 (C), 174.7 (MeC=N), C(SO3F) not observed. 19F¹H NMR (375 MHz, CD3CN): δ −79 [O₃SCF₃]. IR (cm⁻¹): 1602 (C=N)min, 1570 (C=N)pyridine. ESIMS (+ve): m/z 475 [M – O₂SCF³⁻]; ESIMS (−ve): m/z 419 [O₃SCF₃⁻]. Anal Calc. for (C₅₂H₂₅N₄O₃F₃PdS·CH₂Cl₂): C, 43.99; H, 3.83; N, 7.89. Found: C, 44.13; H, 3.78; N, 7.60%.

Reaction of 3a with Selectfluor in NMR tube at reduced temperatures
(a) −40 to 0 °C. Complex 3a (0.005 g, 0.0098 mmol) and Selectfluor™ (0.0035 g, 0.0098 mmol) were loaded into a Young’s NMR tube open to the air and then cooled to −100 °C before acetonitrile-d₃ was added and the system sealed. The NMR tube was inserted into a 400 MHz NMR spectrometer pre-cooled to −40 °C and the ¹F and ¹H NMR spectra were recorded at −40 °C and then at 0 °C intervals up to 0 °C. At −40 °C, ¹H NMR (400 MHz, CD3CN): δ 1.16 (d, 3JHH 6.8, 6H, CHMe2), 2.40 (s, 3H, MeC=N), 2.82 (sept, 3JHH 6.8, 1H, CHMe2), 6.70 (d, 3JHH 8.5, 2H, Ar–H), 6.72–6.77 (m, 2H, Ar–H), 6.84–6.86 (m, 2H, Ar–H), 7.04 (d, 3JHH 8.4, 2H, Ar–H), 7.36–7.43 (m, 2H, Ar–H), 7.47–7.55 (m, 2H, Ar–H), 7.86 (dd, 3JHH 7.7, 3JHH 1.9, 1H, Ar–H), 8.17 (m, 1H, Ar–H), 8.40 (m, 2H, Ar–H). ¹F¹H NMR (375 MHz, CD3CN): δ −152 (BF₄⁻), −172 (HF). At −30 °C, ¹H NMR δ no change. ¹F¹H NMR: δ −152 (BF₄⁻), −172 (HF). At −20 °C, ¹H NMR δ no change. ¹F¹H NMR: δ −152 (BF₄⁻), −173 (HF). At −10 °C, ¹H NMR δ no change. ¹F¹H NMR: δ −152 (BF₄⁻), −173 (HF). At 0 °C: ¹H NMR δ no change. ¹F¹H NMR: δ −152 (BF₄⁻), −174 (1H, HF).

(b) 0 °C to room temperature. The reaction mixture prepared in (a) was further warmed to room temperature and the ¹H NMR spectrum recorded periodically. After 48 h, complete conversion to 4 (data as reported for 4 above) and biphenyl was observed. ¹F¹H NMR δ −152 (BF₄⁻), −181 (HF).

Crystallographic studies
Data for HLi₁b, 1a, 1b, 2a, 2b, 3a, 3b and 5 were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 6. The data were corrected for Lorentz and polarization effects and empiri-
| Complex | HL1b | 1a | 1b | 2a |
|---------|------|----|----|----|
| Formula | \(\text{C}_{25}\text{H}_{29}\text{Cl}_4\text{N}_3\text{Pd}\) | \(\text{C}_{25}\text{H}_{29}\text{Cl}_4\text{N}_3\text{Pd}\) | \(\text{C}_{28}\text{H}_{26}\text{F}_3\text{N}_4\text{O}_3\text{Pd}\) | \(\text{C}_{28}\text{H}_{26}\text{Cl}_4\text{N}_3\text{Pd}\) |
| Crystal size (mm\(^3\)) | 0.26 × 0.12 × 0.05 | 0.27 × 0.05 × 0.04 | 0.23 × 0.20 × 0.04 | 0.96–1.00 Å |
| Temperature (K) | 150(2) | 150(2) | 150(2) | 150(2) |
| Crystal system | Orthorhombic | Triclinic | Triclinic | Monoclinic |
| Space group | \(\text{P}2_1\text{ca}\) | \(\text{P}1\) | \(\text{P}1\) | \(\text{P}2(1)/\text{n}\) |
| \(a\) (Å) | 12.906(10) | 12.848(10) | 12.848(10) | 12.848(10) |
| \(b\) (Å) | 8.308(6) | 8.308(6) | 8.308(6) | 8.308(6) |
| \(c\) (Å) | 39.43(3) | 39.43(3) | 39.43(3) | 39.43(3) |
| \(\alpha\) (°) | 90 | 90 | 90 | 90 |
| \(\beta\) (°) | 90 | 90 | 90 | 90 |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 |
| \(U (\text{Å}^3)\) | 4228(5) | 4228(5) | 4228(5) | 4228(5) |
| \(Z\) | 2 | 2 | 2 | 2 |
| \(D_\text{c}\) (Mg m\(^{-3}\)) | 1.167 | 1.167 | 1.167 | 1.167 |
| \(f(000)\) | 640 | 640 | 640 | 640 |
| \(\mu(\text{Mo-K}_{\alpha})\) (mm\(^{-1}\)) | 0.069 | 0.069 | 0.069 | 0.069 |
| Reflected reflections | 28 600 | 28 600 | 28 600 | 28 600 |
| Independent reflections | 10 332 | 10 332 | 10 332 | 10 332 |
| \(R_{\text{int}}\) | 0.2201 | 0.2201 | 0.2201 | 0.2201 |
| Restraints/parameters | 20 319 | 20 319 | 20 319 | 20 319 |
| Final R indices \((I > 2\sigma(I))\) | \(R_1 = 0.0628\) | \(R_1 = 0.0683\) | \(R_1 = 0.0873\) | \(R_1 = 0.0582\) |
| \(wR_{2}\) | 0.1155 | 0.1067 | 0.1788 | 0.0914 |
| Goodness of fit on \(F^2\) (all data) | 0.871 | 0.861 | 0.848 | 0.890 |

Table 6 Crystallographic and data processing parameters for HL1b, 1a, 1b, 2a, 3a, 3b and 5a

- **Calculation absorption corrections applied.** Structure solution by direct methods and structure refinement based on full-matrix least-squares on \(F^2\) employed SHELXTL version 6.10. Hydrogen atoms were included in calculated positions (C–H = 0.96–1.00 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 \(U_{eq}(C)\) for methyl H atoms and 1.2 \(U_{eq}(C)\) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.
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