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C–Br versus C–H bond activation in palladium(II) cyclopalladated compounds. Crystal and molecular structure of [Pd{$C_6H_4C(H)=NCy$}(MeCOCHCOMe)]

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

Treatment of *N*-(2-bromobenzylidene)cyclohexylamine, 2-$BrC_6H_4C(H)=NCy$ (**a**), with tris(dibenzylideneacetone)palladium(0) in refluxing benzene gave the cyclometallated compound [Pd{$C_6H_4C(H)=NCy$}(Br)]$_2$ (**1**). Treatment of **1** with thallium acetylacetonate gave the mononuclear cyclometallated compound [Pd{$C_6H_4C(H)=NCy$}(MeCOCHCOMe)] (**2**). Reaction of **a** with palladium(II) acetate in refluxing acetic acid gave the dinuclear Pd(II) compound [Pd{2-$BrC_6H_3C(H)=NCy$}(O_2CMe)]$_2$ (**3**). Treatment of **3** with aqueous sodium chloride gave the dimer complex [Pd{2-$BrC_6H_3C(H)=NCy$}(Cl)]$_2$ (**4**). Reaction of **4** with tertiary phosphines gave the cyclometallated complexes [Pd{2-$BrC_6H_3C(H)=NCy$}(L)] (**5**: L = PPh_3; **6**: L = $PEtPh_2$; **7**: L = $PMePh_2$), with the phosphine ligand *trans* to the imine nitrogen atom. Treatment of 2-Br–4,5-$(MeO)_2C_6H_2C(H)=NCH_2CH_2NMe_2$ (**b**), with palladium(II) chloride in refluxing octane or with tris(dibenzylideneacetone)palladium(0) gave [Pd{4,5-$(MeO)_2C_6H_2C(H)=NCH_2CH_2NMe_2$}(X)] (**8**: X = Cl; **16**: X = Br, respectively) and with the ligand as [C, N, N] terdentate. Treatment of **8** with tertiary phosphines gave [Pd{4,5-$(MeO)_2C_6H_2C(H)=NCH_2CH_2NMe_2$}(Cl)(L)] (**9**: L = PPh_3; **10**: L = $PEtPh_2$; **11**: L = $PMePh_2$). Reaction of 1,4-{2-Br–4,5-$(MeO)_2C_6H_2C(H)=N$}$_2C_6H_4$ (**c**), with $PdCl_2$, $Li_2[PdCl_4]$ or $K_2[PdCl_4]$ gave the tetranuclear compound [1,4-{Pd[4,5-$(MeO)_2C_6H_2C(H)=N$](Cl)}$_2C_6H_4$]$_2$ (**12**), which when treated with tertiary phosphines gave the dinuclear species **13**–**15**. The molecular structure of **2** has been determined by X-ray crystallography.

Keywords: Palladium(II) cyclopalladated compounds; Crystal and molecular structures; X-ray crystallography

1. Introduction

The chemistry of cyclometallated compounds [1,2] is a thoroughly developed area of organometallic chemistry and abundant articles and reviews have been published related to their syntheses, reactivity and fruitful applications, such as their use as active catalysts [3,4], as intermediates in the synthesis of new organometallic and organic compounds [5–7], in the preparation of optically active components [8,9], and as species with specific antitumor activity [10,11], among others.

Our interest in this field has mainly dealt with Pd(II) compounds, i.e. derivatives of differently substituted [*C*,*N*] Schiff bases [12,13], ferrocenylimines [14], or substituted imidazoles [15], as well as derivatives of [*C*,*N*,*X*] (X = N, O, S) terdentate ligands [16–18]. Metallation of the organic substrate may be achieved through activation of a C–H bond by electrophilic attack of Pd(II) pertaining to salts such as palladium(II) chloride, palladium(II) acetate or potassium tetrachloropalladate; and also by activation of C–X bonds, which

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supplies a means to reach the metallated compound in an oxidative addition reaction of the ligand with Pd(0) reagents such as $[Pd_2(dba)_3]$ [19]. In the former case, substitution of a metallation site by, e.g. Me, MeO groups or halogens, hinders C–Pd bond formation and the metal is directed towards a remaining C–H bond in the ligand, whereas in the latter, metallation proceeds via the C–X carbon atom, as opposed to the C–H bond.

In the present paper, we report our more recent findings related to cyclometallated Pd(II) compounds derived from 2-bromobenzylideneimines, where formation of the C–Pd bond seems to depend on the remainder substituents of the phenyl ring. Thus, $2\text{-}BrC_6H_4C(H){=}NCy$ follows the expected metallation pattern upon treatment with Pd(0) or Pd(II), whereas $2\text{-}Br\text{–}4,5\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2NMe_2$ and $1,4\text{-}\{2\text{-}Br\text{–}4,5\text{-}(MeO)_2C_6H_2C(H){=}N\}_2C_6H_4$ exhibit C–Pd bonds at the C2 carbon atom when treated with Pd(II), instead of the expected C(6)–Pd bonds.

2. Results and discussion

2.1. Cyclometallated compounds

The Schiff base ligands **a**, **b** and **c** were prepared by reaction of 2-bromobenzaldehyde or 2-bromo-4,5-dimethoxybenzaldehyde with cyclohexylamine, *N*,*N*-dimethylethylendiamine or 1,4-phenylenediamine as appropriate (see Section 4). The IR spectra showed the $\nu(C{=}N)$ stretch at 1638, **a**, 1635, **b**, and 1596, **c**, cm^{-1} and the *H*C=N resonance at δ 8.66, **a**, and 8.54, **b**, and 8.78, **c**. The oxidative adition reaction of *N*-(2-bromobenzylidene)cyclohexylamine, $2\text{-}BrC_6H_4C(H){=}NCy$, with tris(dibenzylideneacetone)palladium(0) in benzene gave the Pd(II) compound $[Pd\{C_6H_4C(H){=}NCy\}(Br)]_2$ (**1**), which was fully characterized. Although owing to its poor solubility in the more common organic solvents the final product was not obtained pure; we were able to identify the corresponding signals in the ^1H-NMR spectrum (see Table 1). To fully assert this was compound **1**, we reacted the crude product with thallium acetylacetonate which gave the very soluble species $[Pd\{C_6H_4C(H){=}NCy\}(MeCOCHCOMe)]$ (**2**), as a yellow solid for which full ^1H- and ^{13}C-NMR were obtained (see Section 4 and Table 1). The shift of the $\nu(C{=}N)$ stretch in the IR spectrum toward lower wavenumbers, 1609 cm^{-1}, and the shift of the HC=N resonance to lower frequency in the ^1H-NMR spectrum, δ 7.92, as compared to their values in the spectra of the non-coordinated ligand, were in agreement with palladium coordination to the nitrogen atom [20–22]. Four distinct resonances were assigned to the phenyl ring protons, δ 7.51 (H6), 7.23 (H3), 7.14 (H5) and 7.04 (H4), corroborating metallation of the aromatic ring at the C2 position, with removal of the bromine atom. The $^{13}C\{^1H\}$-NMR for **2** showed resonances at δ 171.0 (C=N), 157.0 (C2) and 146.1 (C1) shifted to higher frequency, also confirming metallation of the organic ligand [19]. There was no noticeable quadrupolar broadening of these resonances with the ^{105}Pd (22% natural abundance, $I = 5/2$) nucleus. The crystal structure of compound **2** has been determined by X-ray crystallography (vide infra). We and others have shown that treatment of the related ligand, $2\text{-}ClC_6H_4C(H){=}NCH_2CH_2NMe_2$, with Pd(II) salts such as palladium(II) acetate or $Li_2[PdCl_4]$ did not produce activation of the C–H or C–Cl bonds; only reduction to Pd(0) was observed [19,23]. However, in the present case reaction of ligand **a** with palladium(II) acetate in boiling acetic acid yielded the dinuclear cyclometallated complex with acetate-bridging ligands $[Pd\{2\text{-}BrC_6H_3C(H){=}NCy\}(O_2CMe)]_2$ (**3**), after C–H activation at the C6 atom, which was fully characterized (see Section 4 and Table 1). The $\Delta\nu$ value for the asymmetric and symmetric $\nu(COO)$ stretching modes was consistent with bridging acetate ligands [24]. In contrast to complex **2**, only three aromatic proton resonances were assigned at δ 7.11 (H3), 6.99 (H5) and 6.83 (H4), in accordance with metallation of the C6 carbon atom. Compound **3** was converted to the chloro-bridged species $[Pd\{2\text{-}BrC_6H_3C(H){=}NCy\}(Cl)]_2$ (**4**), after a simple metathesis reaction by treatment of **3** in acetone with aqueous sodium chloride. In contrast to compound **1**, the dinuclear species **4** was obtained pure and complete analytical data are given (see Section 4). The IR spectrum showed the absence of the acetate bands and the presence two $\nu(Pd\text{–}Cl)$ stretches at 316 and 247 cm^{-1}, consistent with an asymmetric Pd_2Cl_2 bridging unit [25]. However, attempts to make compound **4** by direct metallation of ligand **a** with palladium(II) chloride or $Li_2[PdCl_4]$ failed, and only a residue of black palladium metal was obtained. Reaction of **4** with tertiary phosphines gave the cyclometallated complexes $[Pd\{2\text{-}BrC_6H_3C(H){=}NCy\}(Cl)(L)]$ (**5**: $L = PPh_3$; **6**: $L = PEtPh_2$; **7**: $L = PMePh_2$). Compounds **5**–**7** were air-stable solids which have been fully characterized by elemental analysis (C, H, N) and by IR and ^1H- and ^{31}P-NMR spectroscopy (see Section 4 and Table 1). In the ^1H-NMR spectra the *H*C=N resonance showed coupling to the phosphorus nucleus with *J*(PH) ca. 8.5 Hz. In the $^{31}P\{^1H\}$ spectra the resonance of the coordinated phosphine was a singlet at δ 39.1, **5**; 36.9, **6**; 24.4, **7**; in agreement with a phosphorus *trans* to nitrogen arrangement [26–28].

In view of the peculiar behavior of ligand **a**, as opposed to the Schiff base $2\text{-}ClC_6H_4C(H){=}NCH_2CH_2NMe_2$, where only oxidative addition was possible, we tested other species with C–Br bonds in the C2 position in order to study their behavior towards Pd(II) salts, namely $2\text{-}Br\text{–}4,5\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2NMe_2$ (**b**), and $1,4\text{-}\{2\text{-}Br\text{–}4,5\text{-}(MeO)_2\text{-}$

Table 1
^{31}P [a]- and ^{1}H [b]-NMR data [c,d]

Compound	^{31}P	Aromatic	Others
1		7.51 [d, J(HH) = 7.5, 1H, H^{6}] 7.22 [dd, J(HH) = 7.2, 1.9, 1H, H^{5}] 7.03 [m, 2H, H^{3}, H^{4}]	7.88 [s, 1H, HC=N]
2		7.51 [dd, J(HH) = 7.5, 1.1, 1H, H^{6}] 7.23 [dd, J(HH) = 7.5, 1.5, 1H, H^{3}] 7.14 [td, J(HH) = 7.5, 1.5, 1H, H^{5}] 7.04 [td, J(HH) = 7.5, 1.1, 1H, H^{4}]	7.92 [s, 1H, HC=N] 5.36 [s, 1H, acac] 2.06 [s, 3H, Me] 1.99 [s, 3H, Me]
3		7.11 [dd, J(HH) = 7.8, 1.1, 1H, H^{3}] 6.99 [dd, J(HH) = 7.8, 1.1, 1H, H^{5}] 6.83 [t, J(HH) = 7.8, 1H, H^{4}]	7.68 [d, 1H, HC=N, 1.5 [e]] 2.16 [s, 6H, MeCOO]
4		7.32 [dd, J(HH) = 7.2, 1.0, 1H, H^{3}] 7.14 [dd, J(HH) = 7.2, 1.0, 1H, H^{5}] 7.14 [t, J(HH) = 7.2, 1H, H^{4}]	8.17 [d, 1H, HC=N, 1.1 [e]]
5	39.1s	6.98 [dd, J(HH) = 6.5, 1.1, 1H, H^{3}] 6.30 [m, 2H, H^{4}, H^{5}]	8.59 [d, 1H, HC=N, 8.6 [f]]
6	36.9s	6.97 [dd, J(HH) = 6.8, 1.9, 1H, H^{3}] 6.39 [m, 2H, H^{4}, H^{5}]	8.54 [d, 1H, HC=N, 8.5 [f]]
7	24.4s	6.99 [dd, J(HH) = 7.8, 1.2, 1H, H^{3}] 6.34 [m, 2H, H^{4}, H^{5}]	8.54 [dd, 1H, HC=N, 8.5 [f], 1.2 [e]]
8		7.27 [s, 1H, H^{6}] 6.88 [s, 1H, H^{3}]	7.92 [s, 1H, HC=N] 3.97 [s, 3H, MeO] 3.86 [m, 2H, CH$_2$] 3.84 [s, 3H, MeO] 2.97 [m, 2H, CH$_2$] 2.75 [s, 6H, NMe$_2$]
9	20.9s	7.04 [s, 1H, H^{6}] 6.95 [s, 1H, H^{3}]	7.61 [s, 1H, HC=N] 3.94 [s, 3H, MeO] 3.90 [s, 3H, MeO] 3.82 [m, 2H, CH$_2$] 2.66 [m, 2H, CH$_2$] 2.36 [s, 6H, NMe$_2$]
10	17.3s	7.06 [s, 1H, H^{6}] 6.90 [s, 1H, H^{3}]	7.59 [s, 1H, HC=N] 3.91 [s, 3H, MeO] 3.87 [s, 3H, MeO] 3.83 [m, 2H, CH$_2$] 2.61 [m, 2H, CH$_2$] 2.37 [s, 6H, NMe$_2$]
11	14.7s	7.09 [s, 1H, H^{6}] 6.94 [s, 1H, H^{3}]	7.64 [s, 1H, HC=N] 3.94 [s, 3H, MeO] 3.90 [s, 3H, MeO] 3.96 [m, 2H, CH$_2$] 2.62 [m, 2H, CH$_2$] 2.39 [s, 6H, NMe$_2$]
12		7.77 [s, 1H, H^{6}] 7.00 [s, 1H, H^{3}] 7.30 [s, 4H, C$_6$H$_4$]	8.77 [s, 1H, HC=N] 4.53 [s, 3H, MeO] 4.49 [s, 3H, MeO]
13	18.0s	7.72 [s, 1H, H^{6}] 7.00 [s, 1H, H^{3}] 7.20 [s, 4H, C$_6$H$_4$]	8.72 [s, 1H, HC=N] 3.94 [s, 3H, MeO] 3.89 [s, 3H, MeO]
14	16.5s	7.70 [s, 1H, H^{6}] 6.73 [s, 1H, H^{3}] 7.31 [s, 4H, C$_6$H$_4$]	8.78 [s, 1H, HC=N] 3.95 [s, 3H, MeO] 3.91 [s, 3H, MeO]
15	13.2s	7.80 [s, 1H, H^{6}] 6.75 [s, 1H, H^{3}] 7.33 [s, 4H, C$_6$H$_4$]	8.80 [s, 1H, HC=N] 3.99 [s, 3H, MeO] 3.94 [s, 3H, MeO]
16		7.49 [s, 1H, H^{6}]	7.81 [s, 1H, HC=N]

Table 1 (*Continued*)

Compound	^{31}P	Aromatic	Others
		6.78 [s, 1H, H^3]	3.95 [s, 3H, MeO] 3.85 [m, 2H, CH_2] 3.80 [s, 3H, MeO] 2.93 [m, 2H, CH_2] 2.70 [s, 6H, NMe_2]

[a] In $CDCl_3$. Measured at 100.6 MHz (ca. 20 °C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4.

[b] In $CDCl_3$, unless otherwise stated. Measured at 250 MHz (ca. 20 °C); chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$.

[c] Coupling constants in Hz.

[d] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; m, multiplet.

[e] $J(HH^5)$.

[f] $J(PH)$.

$C_6H_2C(H){=}N\}_2C_6H_4$ (**c**). Thus, treatment of **b** and **c** with palladium(II) chloride in boiling octane gave $[Pd\{4,5\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2NMe_2\}(Cl)]$ (**8**), and $[1,4\text{-}\{Pd[4,5\text{-}(MeO)_2C_6H_2C(H){=}N](Cl)\}_2C_6H_4]_2$ (**12**) [29], as air-stable solids, which were fully characterized (see Section 4 and Table 1). The ^1H-NMR spectra showed two singlet resonances at δ 7.49, 6.78, **8**, and 7.77, 7.00, **12**, assigned to the H6 and H3 protons, respectively; the N*Me*$_2$ resonance in **8** was shifted to higher frequency upon coordination of the amine nitrogen atom to the metal. The $^{13}C\{^1H\}$-NMR spectra showed the shift of the C2 carbon resonance towards higher frequency by ca. 19 ppm in both cases, in accordance with metallation of the C2 atom, whereas the C6 resonance was only slightly shifted by ca. 5, **8**, and 3, **12**, ppm (see Section 4). Therefore, both ligands, **b** and **c**, are bonded to the metal atom through the C2 carbon, leaving the C(6)–H bond unreacted; and ligand **8** is [C, N, N] terdentate. The different behavior of ligands **a** and **b**, **c** could stem from steric hindrance due to the C(5)–MeO group, in **b** and **c**, which impedes approach of the palladium atom, as we have observed earlier [13]. Treatment of ligand **b** with tris(dibenzylideneacetone)palladium(0), in an oxidative addition reaction, gave $[Pd\{4,5\text{-}(MeO)_2C_6H_2C(H){=}NCH_2CH_2\text{-}NMe_2\}(Br)]$ (**16**), in good yield, where metallation is through the C(2) carbon atom as expected; the ^1H-NMR spectrum is similar to that for **8** (see Section 4). Reaction of ligand **c** with $Li_2[PdCl_4]$ or $K_2[PdCl_4]$ also produced **12**. Treatment of **8** and **12** with tertiary phosphines gave compounds $[Pd\{4,5\text{-}(MeO)_2\text{-}C_6H_2C(H){=}NCH_2CH_2NMe_2\}(Cl)(L)]$ and $[1,4\text{-}\{Pd[4,5\text{-}(MeO)_2C_6H_2C(H){=}N](Cl)(L)\}_2C_6H_4]$, respectively (**9**, **13**: L = PPh_3; **10**, **14**: L = $PEtPh_2$; **11**, **15**: L = $PMePh_2$), as air-stable solids which were fully characterized (see Section 4 and Table 1). The ^1H-NMR spectra showed the HC=N and H3 resonances were not coupled to the phosphorus nucleus pointing towards a *trans* P–Pd–C disposition, as opposed to compounds **5**–**7** where a *trans* P–Pd–N geometry was observed. This was confirmed by the higher ν(Pd–Cl) values found for **9**–**11** and **13**–**15**, with respect to **5**–**7**, in agreement with the lower *trans* influence of the nitrogen atom as compared to the phenyl carbon atom; and in **13**–**15**, the C(4)–MeO resonance was not shifted towards lower frequency as would be expected in the case of a *trans* P–Pd–N arrangement, due to the shielding effects of the phosphine phenyl rings [30]. In the $^{31}P\{^1H\}$ spectrum of **9**–**11** and **13**–**15** the resonance of the coordinated phosphine was a singlet shifted to lower frequency ca. 20 ppm, as compared to the value found in compounds **5**–**7**, in accordance with the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [31]. These findings were in agreement with a phosphorus *trans* to carbon arrangement, as opposed to the results shown for compounds **5**–**7** and to others observed earlier, for which a *trans* P–Pd–N geometry seems to be the more common disposition for the entering phosphine [26,28,32]. Although the novel term *transfobia* has been introduced by Vicente et al. to describe the restricted coordination of mutually *trans* phosphines and phenyl carbon atoms [33,34], this is clearly not the case for compounds **9**–**11** and **13**–**15**.

2.2. Molecular structure of complex 2

Suitable crystals of the title compound were grown by slow evaporation of a dichloromethane–*n*-hexane solution of the complex. The numbering scheme is shown in Fig. 1. Crystallographic data and selected bond lengths and angles are listed in Tables 2 and 3. The crystal structure consists of discrete dinuclear molecules separated by normal van der Waals distances.

The coordination sphere around the palladium atom consists of an *ortho* carbon of the phenyl ring, the C=N nitrogen atom, and two oxygen atoms from the 2,4-pentanedionate group. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, in the range 81.30(14)–94.17(11)°, with the more noticeable distortions in the 'bite' angle C(1)–Pd(1)–N(1) 81.30(14)° consequent upon chelation. The sum of angles at palladium is 360.1°. This is reflected in the somewhat large value of

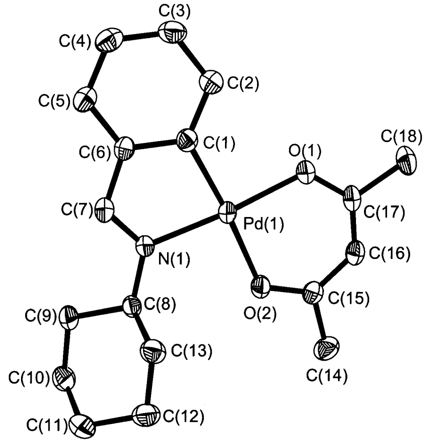


Fig. 1. Molecular structure of compound [Pd{$C_6H_4C(H)$=NCy}(MeCOCHCOMe)] (**2**), with labelling scheme (30% probability level). Hydrogen atoms have been omitted for clarity.

Table 2
Crystallographic data for complex **2**

Chemical formula	$C_{18}H_{23}NO_2Pd$
Formula weight	391.77
T (°C)	293(2)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.2710(10)
b (Å)	10.4090(10)
c (Å)	19.870(2)
V (Å^3)	1710.7(3)
Z	4
μ (mm^{-1})	1.091
Collected reflections	3183
Unique reflections	2924 [R_{int} = 0.0201]
R_1 [a]	0.0337
wR_2 [b]	0.0896
Absolute structure parameter	0.04(5)
Largest difference peak and hole (e Å^{-3})	1.045 and −1.430

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, [$F > 4\sigma(F)$].
[b] $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, all data.

the C(2)–C(1)–Pd(1) angle of 128.2(3)°. The palladium–carbon bond length [Pd(1)–C(1) = 1.967(4) Å], is shorter than the predicted value of 2.081 Å, based on the sum of covalent radii for carbon(sp^2) and palladium, 0.771 and 1.31 Å, respectively, suggesting some degree of multiple-bond character in the Pd–C(aryl) linkage, as has been observed before [16,19,35]. The palladium–nitrogen bond length [Pd(1)–N(1) = 2.022(3) Å is in good agreement with the predicted value of 2.01 Å, based on the sum of covalent radii for nitrogen(sp^2) and palladium, 0.701 and 1.31 Å, respectively [36].

The Pd–O distances [Pd(1)–O(1) 2.013(2) and Pd(1)–O(2) 2.077(3) Å] are within the expected values for Pd–O single-bonds. The stronger *trans* influence of the phenyl carbon as compared to the imine nitrogen atom, is put forward by the lengthening of the palladium–oxygen distances *trans* to carbon [Pd(1)–O(1) = 2.077(3), Pd(1)–O(2) = 2.013(2) Å].

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths			
Pd(1)–C(1)	1.967(4)	Pd(1)–N(1)	2.022(3)
Pd(1)–O(1)	2.013(2)	Pd(1)–O(2)	2.077(3)
C(1)–C(6)	1.408(5)	C(6)–C(7)	1.451(5)
N(1)–C(7)	1.287(5)	O(1)–C(17)	1.297(5)
O(2)–C(15)	1.287(5)		
Bond angles			
C(1)–Pd(1)–N(1)	81.30(14)	C(1)–Pd(1)–O(1)	92.40(14)
O(1)–Pd(1)–N(1)	173.06(13)	C(1)–Pd(1)–O(2)	175.11(13)
O(1)–Pd(1)–O(2)	92.22(11)	N(1)–Pd(1)–O(2)	94.17(11)
C(6)–C(1)–Pd(1)	113.4(3)	C(1)–C(6)–C(7)	113.8(3)
N(1)–C(7)–C(6)	116.5(3)	C(7)–N(1)–Pd(1)	114.9(2)

The aromatic (plane 1) and 2,4-pentanedionate (plane 2) rings are planar (mean deviation from the least-squares plane 0.0025 and 0.0143 Å, respectively) and almost coplanar with the five-membered cyclometallated ring (plane 3; mean deviation 0.0086 Å) (angles between planes: 1/2 = 6.2, 1/3 = 2.5, 2/3 = 4.9°). The geometry around the palladium atom is also planar (mean deviation of 0.0333 Å).

3. Conclusions

The three ligands, all possessing a bromine atom bonded to the C2 phenyl carbon, seem to show different behavior when treated with Pd(0) or Pd(II) reagents. Ligands **a** and **b** produce the expected products when treated with Pd(0) in an oxidative addition reaction. However, ligands **a**, **b** and **c** react differently towards Pd(II) salts. Thus, whilst **a** is metallated at the C6 carbon atom, **b** and **c** are metallated at the C2 carbon, with loss of the bromine atom, possibly due to steric hindrance of a methoxy group. Another interesting feature of the compounds stems from the comparison of the coordination mode of the phosphine ligand. In compounds **5**–**7**, a *trans*-N–Pd–P geometry was found in accordance with the *transfobia* effect, whereas for compounds **9**–**11** and **13**–**15**, a *trans*-C–Pd–P disposition was observed.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out in an atmosphere of dry Ar. Solvents were purified by standard methods [37]. Chemicals were reagent grade. $Pd_2(dba)_3$ and the phosphines PPh_3, $PEtPh_2$ and $PMePPh_2$ were purchased from Aldrich Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo–Erba Elemental Analyser, Model 1108. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$) and were recorded on Bruker WM250, AMX-300 and AC-200 spectrometers. All chemical shifts were reported downfield from standards.

The syntheses of the Schiff bases $2\text{-}BrC_6H_4C(H)=NCy$ (**a**), $2\text{-}Br\text{–}4,5\text{-}(MeO)_2C_6H_2C(H)=NCH_2CH_2NMe_2$ (**b**), and $1,4\text{-}\{2\text{-}Br\text{–}4,5\text{-}(MeO)_2C_6H_2C(H)=N\}_2C_6H_4$ (**c**), were performed by heating a $CHCl_3$ solution of the appropriate quantities of 2-bromobenzaldehyde or 2-bromo-4,5-dimethoxybenzaldehyde, and cyclohexylamine, *N*,*N*-dimethylethylendiamine or 1,4-phenylenediamine, as appropriate, in a Dean–Stark apparatus under reflux. The ligands were characterized by their IR and NMR spectra. IR spectra: **a**, ν(C=N), 1638s; **b**, ν(C=N), 1635s; **c**: ν(C=N), 1596m cm^{-1}. ^1H-NMR spectra: **a**, 8.66 [s, 1H, HC=N], 8.01 [dd, $J(HH) = 7.5$, 1.9, 1H, H^6], 7.55 [dd, $J(HH) = 8.2$, 1.5, 1H, H^3], 7.29 [m, 2H, H^3, H^4]; **b**, 8.54 [s, 1H, HC=N], 7.53 [s, 1H, H^2], 6.97 [s, 1H, H^5], 3.90 [s, 3H, MeO], 3.88 [s, 3H, MeO], 3.75 [m, $N = 11$, 2H, $N(CH_2)_2N$], 2.65 [m, $N = 11$, 2H, $N(CH_2)_2N$], 2.31 [s, 6H, NMe_2]; **c**, 8.78 [s, 1H, HC=N], 7.77 [s, 1H, H^6], 7.30 [s, 4H, C_6H_4], 7.05 [s, 1H, H^3]; 3.98 [s, 3H, MeO]; 3.94 [s, 3H, MeO].

$^{13}C\{^1H\}$-NMR spectra: **a**, phenyl: 125.3 (C1), 135.4 (C2), 128.0, 129.3, 131.9, 133.3 (C3, C4, C5, C6). Cy group: 25.1 (C9, C11), 26.0 (C10), 34.8 (C8, C12), 70.3 (C7). Others: 158.1 (C=N). **b**, phenyl: 151.9 (C5), 149.0 (C4), 127.3 (C2), 116.9 (C1), 115.3 (C6), 110.4 (C3). Others: 160.9 (C=N), 60.4, 59.0 (MeO), 56.5, 56.4 (NCH_2), 46.1 (Me_2). **c**, phenyl: 152.3 (C5), 148.3 (C4), 131.5 (C2), 121.6 (C_6H_4), 110.7 (C1), 117.3 (C8), 112.9 (C6), 110.2 (C3). Others: 149.3 (C=N), 56.5 (MeO).

4.2. Synthesis of [Pd{$C_6H_4C(H)=NCy$}(Br)]$_2$ (**1**)

$2\text{-}BrC_6H_4C(H)=NCy$ (116 mg, 437 mmol) and tris(dibenzylideneacetone)dipalladium(0) (200 mg, 218 mmol) were added to 25 cm^3 of dry C_6H_6 to give a dark-red solution which was heated under reflux for 4 h, after which a dark suspension resulted. After cooling to room temperature (r.t.) the product was filtered off to give a solid slightly unpurified with Pd(0). Due to its poor solubility the crude product was used without further purification. IR (KBr): ν(C=N), 1608s cm^{-1}.

4.3. Synthesis of [Pd{$C_6H_4C(H)=NCy$}(acac-*O*,*O*)] (**2**)

To a suspension of **1** (40 mg, 0.05 mmol) in $CHCl_3$ (20 cm^3), thallium-2,4-pentanedionate (33 mg, 0.11 mmol) was added and the mixture stirred at r.t. for 4 h. The resulting mixture was filtered over celite, concentrated in vacuo, and recrystallized from $CH_2Cl_2\text{–}C_6H_{14}$ to give the required complex as a yellow solid in 89% yield. Anal. Found: C, 55.1; H, 5.6; N, 3.4. $C_{18}H_{23}NO_2Pd$ requires: C, 55.2; H, 5.9; N, 3.6%. IR: ν(C=N) 1609s, ν(C–O) 1580s, 1515s cm^{-1}. $^{13}C\{^1H\}$-NMR data, phenyl: 157.0 (C2), 146.1 (C1), 128.7, 129.6, 130.5, 131.1 (C3, C4, C5, C6). Cy group: 25.9 (C9, C11), 26.4 (C10), 32.7 (C8, C12), 66.9 (C7). Others: 171.0 (C=N), acac: 28.0 (Me), 28.4 (Me), 100.5 (CH).

4.4. Synthesis of [Pd{$2\text{-}BrC_6H_3C(H)=NCy$}($O_2CMe$)]$_2$ (**3**)

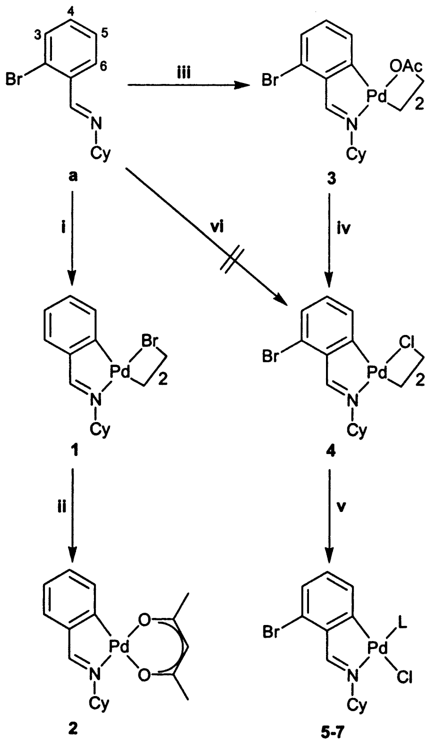
A mixture of $2\text{-}BrC_6H_4C(H)=NCy$ (300 mg, 1.13 mmol) and palladium(II) acetate (230 mg, 1.02 mmol) in glacial AcOH (40 cm^3) was refluxed under dry dinitrogen for 3 h. After cooling the mixture to r.t. the AcOH was removed under vacuum. The residue was treated with water and extracted with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give orange oil. This was chromatographed on a column packed with silica gel. Elution with CH_2Cl_2–EtOH (1%) removed unchanged starting material. Elution with CH_2Cl_2–EtOH (4%) afforded the final product as an orange powder after concentration in 67% yield. Anal. Found: C, 41.7; H, 4.1; N, 3.3. $C_{30}H_{36}Br_2N_2O_4Pd_2$ requires: C, 41.8; H, 4.2; N, 3.3%. IR: ν(C=N) 1609s, ν_{as}(COO) 1581s, ν_s(COO) 1406m cm^{-1}.

4.5. Synthesis of [Pd{$2\text{-}BrC_6H_3C(H)=NCy$}(Cl)]$_2$ (**4**)

An aq. solution of NaCl (ca. 10^{-2} M) was added dropwise to a solution of **3** (290 mg, 0.36 mmol) in C_3H_6O. The product immediately precipitated out as a yellow solid. After stirring for 16 h the solid was filtered off and dried in vacuo. Yield: 0.087 g, 89%. Anal. Found: C, 38.3; H, 3.5; N, 3.2. $C_{26}H_{30}Br_2Cl_2N_2Pd_2$ requires: C, 38.4; H, 3.7; N, 3.4%. IR: ν(C=N) 1607s, ν(Pd–Cl) 316w, 247w cm^{-1}.

4.6. Synthesis of [Pd{$2\text{-}BrC_6H_3C(H)=NCy$}($PPh_3$)] (**5**)

To a suspension of the cyclometallated halide-bridged complex **4** (100 mg, 0.12 mmol) in 15 cm^3 of CH_2Cl_2, PPh_3 (60 mg, 0.24 mmol) was added. The mixture was stirred for 8 h, after which the white solid formed was filtered off and recrystallized from $CH_2Cl_2\text{–}C_6H_{14}$. Yield: 70%. Anal. Found: C, 55.3; H, 4.4; N, 2.0. $C_{31}H_{30}BrClNPPd$ requires: C, 55.6; H, 4.5; N, 2.1%. IR: ν(C=N) 1617m, ν(Pd–Cl) 310w cm^{-1} (Scheme 1).



Scheme 1. (i) $[Pd_2(dba)_3]$/benzene, reflux; (ii) Tl(acac)/$CHCl_3$, stir; (iii) $PdAcO)_2$/AcOH, reflux; (iv) NaCl/Me_2CO/water; (v) L/acetone, stir [L = PPh_3 (**5**); $PEtPh_2$ (**6**); $PMePh_2$ (**7**)]; (vi) $PdCl_2$/octane, reflux; $Li_2[PdCl_4]$/MeOH/r.t.

*4.7. Synthesis of [Pd{2-BrC$_6$H$_3$C(H)=NCy}(PEtPh$_2$)] (**6**)*

To a suspension of the cyclometallated halide-bridged complex **4** (20 mg, 0.03 mmol) in 25 cm^3 of dry THF, $PEtPh_2$ (10 mg, 0.05 mmol) was added and the mixture was refluxed under nitrogen for 6 h. Removal of the solvent in vacuo gave a solid which was recrystallized from CH_2Cl_2–C_6H_{14}. Yield: 80%. Anal. Found: C, 52.1; H, 4.8; N, 2.3. $C_{27}H_{30}BrClNPPd$ requires: C, 52.2; H, 4.9; N, 2.3%. IR: ν(C=N) 1628m, ν(Pd–Cl) 308w cm^{-1}.

Compound **7** was obtained following a similar procedure.

4.8. Synthesis of [Pd{2-BrC$_6$H$_3$C(H)=NCy}(PMePh$_2$)] (7)

Yield: 70%. Anal. Found: C, 51.3; H, 4.6; N, 5.5. $C_{26}H_{28}BrClNPPd$ requires: C, 51.4; H, 4.7; N, 2.3%. IR: ν(C=N) 1620m, ν(Pd–Cl) 300w cm^{-1}.

*4.9. Synthesis of [Pd{4,5-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Cl)] (**8**)*

To a solution of 3,4-$(MeO)_2C_6H_2C(H)$=NCy (200 mg, 0.63 mmol) in dry *n*-octane (40 cm^3) palladium(II) chloride (101 mg, 0.57 mmol) was added. The mixture was heated to reflux for 10 h. After cooling to r.t. the solution was filtered through celite to remove the small amount of black Pd formed. The solution was concentrated until a yellow crystalline precipitate appeared. The solid was filtered off and washed with *n*-C_6H_{14}. Yield: 63%. Anal. Found: C, 41.2; H, 5.0; N, 7.3. $C_{13}H_{19}ClN_2O_2Pd$ requires: C, 41.4; H, 5.1; N, 7.4%. IR: ν(C=N) 1607m, ν(Pd–Cl) 339w cm^{-1}. $^{13}C\{^1H\}$-NMR spectra, phenyl: 152.0 (C5), 150.3 (C4), 149.2 (C2), 143.8 (C1), 121.4 (C6), 112.6 (C3). Others: 174.5 (C=N), 64.7 (NCH_2), 56.4, 56.1 (MeO), 55.4 (CH_2NMe_2), 49.1, 48.7 (Me_2).

*4.10. Synthesis of [Pd{4,5-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Cl)(PPh$_3$)] (**9**)*

PPh_3 (30 mg, 0.12 mmol) was added to a solution of **8** (40 mg, 0.12 mmol) in C_3H_6O (15 cm^3). The mixture was stirred for 6 h, the solvent removed and the product recrystallized from CH_2Cl_2–C_6H_{14} to give the desired complex as an orange solid. Yield: 69%. Anal. Found: C, 58.0; H, 5.5; N, 4.3. $C_{31}H_{34}ClN_2O_2PPd$ requires: C, 58.2; H, 5.4; N, 4.4%. IR: ν(C=N) 1591m, ν(Pd–Cl) 332w cm^{-1} (Scheme 2).

Compounds **10** and **11** were obtained following a procedure similar to **9**.

*4.11. Synthesis of [Pd{4,5-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Cl)(PEtPh$_2$)] (**10**)*

Yield: 82%. Anal. Found: C, 54.7; H, 5.8; N, 4.6. $C_{27}H_{34}ClN_2O_2PPd$ requires: C, 54.8; H, 5.8; N, 4.7%. IR: ν(C=N) 1591m, ν(Pd–Cl) 341w cm^{-1}.

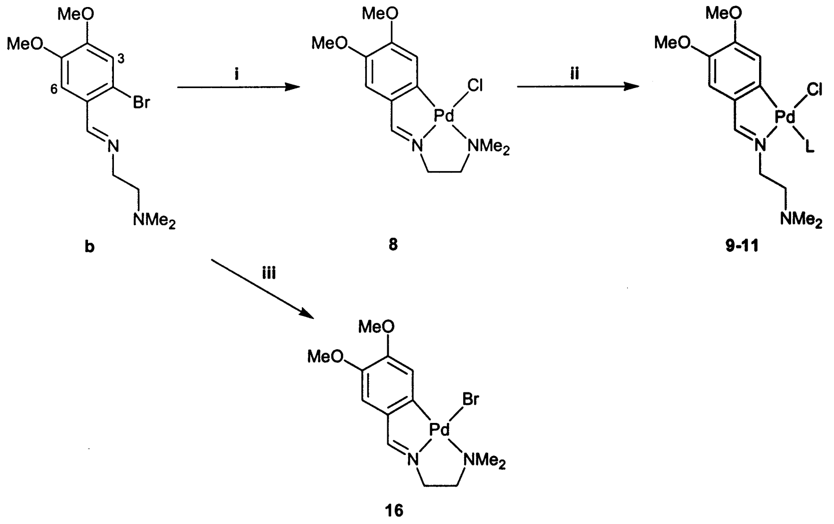
*4.12. Synthesis of [Pd{4,5-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$CH$_2$NMe$_2$}(Cl)(PMePh$_2$)] (**11**)*

Yield: 74%. Anal. Found: C, 54.0; H, 5.8; N, 4.6. $C_{26}H_{34}ClN_2O_2PPd$ requires: C, 53.9; H, 5.9; N, 4.8%. IR: ν(C=N) 1589m, ν(Pd–Cl) 333w cm^{-1}.

*4.13. Synthesis of [1,4-{Pd[4,5-(MeO)$_2$C$_6$H$_2$C(H)=N](Cl)}$_2$C$_6$H$_4$}]$_2$ (**12**)*

4.13.1. Method 1

To a solution of 1,4-{2-Br–4,5-$(MeO)_2C_6H_2C(H)$=N}$_2C_6H_4$ (520 mg, 1.93 mmol) in dry *n*-octane (40 cm^3), palladium(II) chloride (300 mg, 1.69 mmol) was added under Ar. The mixture was heated to reflux for 10 h. After cooling to r.t. the solution was filtered through celite to remove the small amount of black Pd formed. The solution was concentrated until a yellow solid appeared, which was filtered off and washed with *n*-C_6H_{14}. Yield: 79%. Anal. Found: C, 41.8; H, 3.1; N, 4.0. $C_{48}H_{44}Cl_4N_4O_8Pd_4$ requires: C, 42.0; H, 3.2; N, 4.1%. IR: ν(C=N) 1589m, ν(Pd–Cl) 339, 267w cm^{-1}.



Scheme 2. (i) $PdCl_2$/octane, reflux; (ii) L/acetone, stir [L = PPh_3 (**9**); $PEtPh_2$ (**10**); $PMePh_2$ (**11**)]; (iii) $[Pd_2(dba)_3]$/benzene, reflux.

$^{13}C\{^1H\}$-NMR spectra, phenyl: 152.7 (C5), 150.3 (C2), 149.2 (C4), 127.6 (C1), 122.5 (C_6H_4), 118.5 (C8), 115.8 (C6), 110.9 (C3). Others: 158.7 (C=N), 56.7 (MeO).

4.13.2. Method 2

Palladium(II) chloride (200 mg, 1.13 mmol) and LiCl (100 mg, 2.36 mmol) were added in MeOH and the resulting mixture was stirred until a dark red color appeared. Then AcONa (500 mg, 6.1 mmol) and 1,4-$\{2\text{-Br}-4,5\text{-}(MeO)_2C_6H_2C(H)=N\}_2C_6H_4$ (350 mg, 0.87 mmol) were added. The resulting mixture was stirred for 48 h, after which the precipitate formed was filtered off and washed with MeOH. The final solid was boiled in EtOH, filtered hot, cooled to r.t. and separated and dried in vacuo.

4.13.3. Method 3

To a mixture of water (6 cm^3)–EtOH (40 cm^3) $K_2[PdCl_4]$ (200 mg, 0.61 mmol) and $\{2\text{-Br}-4,5\text{-}(MeO)_2C_6H_2C(H)=N\}_2C_6H_4$ (340 mg, 0.85 mmol) were added. The mixture was stirred for 24 h. The resulting solid was filtered off, washed with absolute EtOH and dried in vacuo.

4.14. Synthesis of $[1,4\text{-}\{Pd[4,5\text{-}(MeO)_2C_6H_2C(H)=N](Cl)(PPh_3)\}_2C_6H_4]$ (**13**)

PPh_3 (150 mg, 0.58 mmol) was added to a solution of **12** (200 mg, 0.15 mmol) in C_3H_6O (15 cm^3). The mixture was stirred for 8 h, the solvent removed and the product recrystallized from CH_2Cl_2–C_6H_{14} to give the desired complex as a pale yellow solid. Yield: 83%. Anal. Found: C, 59.4; H, 4.4; N, 2.2. $C_{60}H_{52}Cl_2N_2O_4P_2Pd_2$ requires: C, 59.5; H, 4.3; N, 2.3%. IR: ν(C=N) 1591m, ν(Pd–Cl) 320w cm^{-1} (Scheme 3).

Compounds **14** and **15** were obtained following a procedure similar to **13**.

4.15. Synthesis of $[1,4\text{-}\{Pd[4,5\text{-}(MeO)_2C_6H_2C(H)=N](Cl)(PEtPh_2)\}_2C_6H_4]$ (**14**)

Yield: 81%. Anal. Found: C, 55.9; H, 4.5; N, 2.4. $C_{52}H_{52}Cl_2N_2O_4P_2Pd_2$ requires: C, 56.0; H, 4.7; N, 2.5%. IR: ν(C=N) 1590m, ν(Pd–Cl) 324w cm^{-1}.

4.16. Synthesis of $[1,4\text{-}\{Pd[4,5\text{-}(MeO)_2C_6H_2C(H)=N](Cl)(PMePh_2)\}_2C_6H_4]$ (**15**)

Yield: 76%. Anal. Found: C, 55.2; H, 4.3; N, 2.5. $C_{50}H_{48}Cl_2N_2O_4P_2Pd_2$ requires: C, 55.3; H, 4.5; N, 2.6%. IR: ν(C=N) 1590m, ν(Pd–Cl) 332w cm^{-1}.

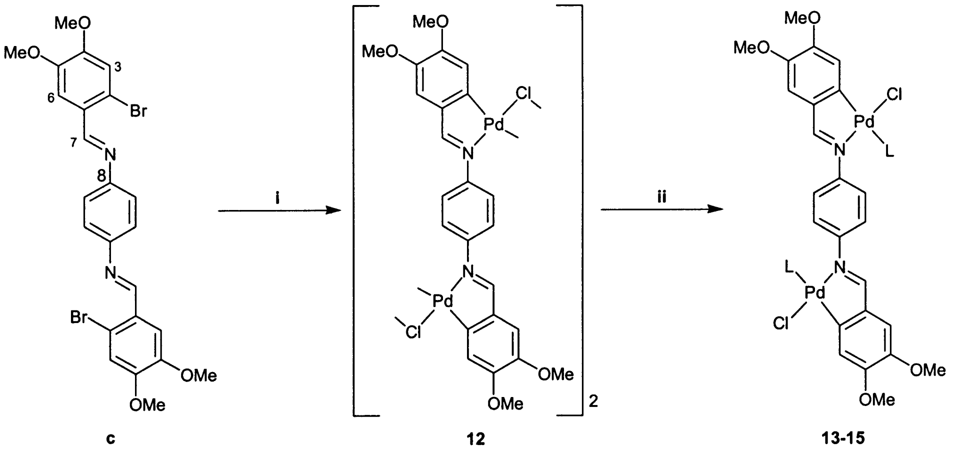
Compound **16** was obtained following a similar procedure to that described for **2**.

4.17. Synthesis of $[Pd\{4,5\text{-}(MeO)_2C_6H_2C(H)=NCH_2CH_2NMe_2\}(Br)]$ (**16**)

Yield: 63%. Anal. Found: C, 37.5; H, 4.6; N, 6.7. $C_{13}H_{19}BrN_2O_2Pd$ requires: C, 37.0; H, 4.5; N, 6.6%. IR: ν(C=N) 1619m cm^{-1}. $^{13}C\{^1H\}$-NMR spectra, phenyl: 152.1 (C5), 150.6 (C4), 146.0 (C2), 141.1 (C1), 120.7 (C6), 111.3 (C3). Others: 171.6 (C=N), 64.1 (NCH_2), 56.6, 56.4 (MeO); 53.2 (CH_2NMe_2), 48.8, 48.4 (Me_2).

4.18. X-ray crystallographic study

Three-dimensional, r.t. X-ray data were collected in the θ range 2.67–30.40° in a Enraf–Nonius CAD4 diffractometer by the ω–2θ scan method. Of the 3183 reflections measured, all of which were corrected from Lp effects and for absorption by semi-empirical methods



Scheme 3. (i) $PdCl_2$/octane, reflux; $Li_2[PdCl_4]$/MeOH/r.t.; $K_2[PdCl_4]$/MeOH/r.t.; (ii) L/acetone, stir [L = PPh_3 (**13**); $PEtPh_2$ (**14**); $PMePh_2$ (**15**)].

(minimum and maximum transmission coefficients 0.677 and 0.719), 2631 independent reflections exceeded the significance level $|F|/\sigma|F| > 2.0$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R_1 = 0.0337$ ($wR_2 = 0.0896$ for 2924 unique data, 202 parameters) with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [38].

5. Supplementary data

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 187370 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033); e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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