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### New palladium(II) cyclometallated compounds derived from *trans*cinnamalylideneimines via C–H activation of an sp<sup>2</sup>-aliphatic carbon atom

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Dedicated to Professor Joachim Strähle on the occasion of his 65th birthday.

#### Abstract

Treatment of the Schiff-base ligands  $C_6H_5C(H)=C(R)C(H)=NCy$  (R = H, a; R = Me, b) with Pd(OAc)<sub>2</sub> gave the acetato-bridged dinuclear compounds [Pd{ $C_6H_5C=C(R)C(H)=NCy$ }( $O_2CMe$ )]<sub>2</sub> (R = H, 1a; R = Me, 1b) after C–H activation of the aliphatic carbon atom. Reaction of 1a and 1b with aqueous sodium chloride gave the dinuclear chloro-bridged compounds [Pd{ $C_6H_5C=C(R)C(H)=NCy$ }(X)]<sub>2</sub> (R = H, 2a; R = Me, 2b), which could also be prepared by treatment of the ligands with Li<sub>2</sub>[PdCl<sub>4</sub>] in methanol. Reaction of 1a with aqueous sodium bromide or iodide gave the halide-bridged species [Pd{ $C_6H_5C=C(H)C(H)=NCy$ }(X)]<sub>2</sub> (X = Br, 3a; X = I, 4a). Treatment of 1a and 1b with Tl(acac), Tl( $C_5H_5$ ) or PPh<sub>3</sub>, as appropriate, gave the mononuclear complexes [Pd{ $C_6H_5C=C(R)C(H)=NCy$ }(acac)], (R = H, 5a; R = Me, 3b) [Pd{ $C_6H_5C=C(H)C(Me)=NCy$ }( $C_5H_5$ )] (4b) and [Pd{ $C_6H_5C=C(H)C(Me)=NCy$ }(PPh<sub>3</sub>)] (5b).

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### 1. Introduction

In the past years, increasing attention has been dedicated to cyclometallated compounds [1–6] in view of their ever growing chemistry and of the many applications they present, such as their use in organic and organometallic synthesis [7], in optical resolution [8], in the synthesis of new metal mesogenic compounds [9], in biologically active compounds [10,11], in catalytic materials [12], and to promote unusual coordination environments [13], to name but a few. Numerous factors are involved in the synthesis and stability of cyclometallated compounds, among which the nature of the ligand, the number and type of donor atoms, the metal, and ring size should be emphasized [2]. In particular,

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compounds prepared by direct metallation of an organic moiety by palladium as the metal atom, i.e. the palladacycles, are among the most abundant, especially when the metallated carbon atom, bearing sp<sup>2</sup>-hybridization, is part of an aromatic ring. In addition to the abundant examples in the literature, we have dealt with complexes derived from potentially [C, N, X], (X = O, S,N) terdentate ligands, such as semicarbazones [14,15], thiosemicarbazones [16,17] or Schiff-bases [18,19], as well as imidazoles [20] and ferrocenylimines [21]. Nevertheless, Schiff-base palladacycles where metallation is directly produced at an aliphatic sp<sup>2</sup>-carbon atom are scarce, and to the best of our knowledge the examples that are known are derived from insertion reactions of a previously metallated aromatic carbon atom [22]. More recently, activation of the C=N bond in imines has been achieved by platinum(II) [23], and addition of an Au-X bond across a styryl double bond [24] has been reported,

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although in both cases the C-H bond remains after metal linkage to the carbon atom.

Our aim was to prepare palladacycles by activation of a non-aromatic C–H bond, with displacement of the hydrogen atom, for which purpose, we chose Schiff-base ligands derived from *trans*-cinnamaldehyde and  $\alpha$ methyl-*trans*-cinnamaldehyde; accordingly, the four ligand atoms which conform the metallacycle when an aryl carbon is metallated, Fig. 1(a), would now be part of an aliphatic chain as in Fig. 1(b).

Consequently, herein, we report the synthesis of cyclopalladated complexes derived from  $C_6H_5C(H) = C(H)C(H) = NCy$  and  $C_6H_5C(H) = C(Me)C(H) = NCy$  with palladium(II) salts and the reactivity of the resulting compounds.

### 2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR spectroscopy (data in the Section 3) and by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (see Table 1). The ligands were prepared by reaction of *trans*-cinnamaldehyde or  $\alpha$ -methyl-*trans*cinnamaldehye and cyclohexylamine as appropriate; they showed the characteristic v(C=N) stretch in the IR spectra. The <sup>1</sup>H NMR spectrum for ligand **a** showed an ABX pattern for the H7-H9 protons (H7, H8, AB part,  $\delta$  6.91; H9, X part,  $\delta$  8.04), whilst for ligand **b**, two singlets were assigned to the H7,  $\delta$  6.78, and H9,  $\delta$  8.02, protons (see Table 1). In both spectra the H9 proton was shifted to higher frequency due to the deshielding effect of the C=N double bond. From the ligands new cyclometallated compounds were obtained which are shown in Schemes 1 and 2. Preparative details, characterizing microanalytical data, IR and NMR data are in the Section 3 and in Table 1.



Fig. 1. Metallacycle ligand atoms with  $C(sp^2)_{aromatic}$  (a) and  $C(sp^2)_{aliphatic}$  (b) carbons.



Scheme 1. (i) Li<sub>2</sub>[PdCl<sub>4</sub>], MeOH; (ii) Pd(OAc)<sub>2</sub>, AcOH; (iii) NaCl, acetone/water; (iv) NaX, acetone/water.



Scheme 2. (i) TICp, chloroform; (ii) Tl(acac), chloroform; (iii) PPh<sub>3</sub>, acetone/water; (iv) PPhEt<sub>2</sub>, acetone/water.

Reaction of the Schiff-base ligands  $C_6H_5C(H) = C(H)C(H) = NCy$  (a) and  $C_6H_5C(H) = C(Me)C(H) = NCy$  (b) with palladium(II) acetate in glacial acetic acid, gave the dinuclear cyclometallated complexes [Pd{ $C_6H_5C$ =

Table 1					
<sup>31</sup> P <sup>a</sup> and	$^{1}\mathrm{H}$	b	NMR	data	c,d

Compound	<sup>31</sup> P	Aliphatic	Aromatic
a		8.04[t,1H, H <sup>9</sup> ]; 6.91[m, 2H, H <sup>7</sup> , H <sup>8</sup> ]	7.48-7.27 [m, 5H, H <sup>2</sup> -H <sup>6</sup> ]
1a		7.93[d, 2H, ${}^{3}J(HH) = 13.6$ , H <sup>9</sup> ]; 6.77[d, 2H, ${}^{3}J(HH) = 13.6$ , H <sup>8</sup> ]; 2.4[s, 3H,	7.94[dd, 2H, ${}^{3}J(HH) = 8.1$ ,]; ${}^{4}J(HH) = 1.5$ , H <sup>2</sup> ,
		O <sub>2</sub> CMe]	$H^{6}$ ]; 7.57–7.30 [m, 3H, $H^{3}-H^{5}$ ]
2a		8.03[d, 2H, ${}^{3}J(HH) = 13.7, H^{9}$ ]; 6.78[d, 2H, ${}^{3}J(HH) = 13.7, H^{8}$ ]	7.94[d, 2H, ${}^{3}J(HH) = 6.7, H^{2}, H^{6}$ ]; 7.59–7.35 [m,
			$3H, H^3 - H^5$ ]
3a		$8.02[d, 2H, {}^{3}J(HH) = 13.6, H^{9}]; 6.78[d, 2H, {}^{3}J(HH) = 13.6, H^{8}]$	7.94[d, 2H, ${}^{3}J(HH) = 7.0, H^{2}, H^{6}$ ]; 7.47–7.40 [m,
			$3H, H^3 - H^5$ ]
4a		8.05[d, 2H, ${}^{3}J(HH) = 13.4$ , H <sup>9</sup> ]; 6.60[d, 2H, ${}^{3}J(HH) = 13.4$ , H <sup>8</sup> ]	7.95[d, 2H, ${}^{3}J(HH) = 7.5, H^{2}, H^{6}$ ]; 7.52–7.38 [m,
			$3H, H^3 - H^5$ ]
5a		$8.02[d, 2H, {}^{3}J(HH) = 13.6, H^{9}]; 6.78[d, 2H, {}^{3}J(HH) = 13.6, H^{8}]; 5.30[s, 1H,$	7.94[dd, 2H, ${}^{3}J(HH) = 8.2$ , ${}^{3}J(HH) = 1.5$ , $H^{2}$ ,
		CH(acac)]; 2.17[s, 3H, Me(acac)]; 2.09[s, 3H, Me(acac)]	$H^{6}$ ]; 7.53–7.35 [m, 3H, $H^{3}-H^{5}$ ]
b		8.02[s,1H, H <sup>9</sup> ]; 6.78[s,1H, H <sup>7</sup> ]; 2.15[s, 3H, Me(C8)]	$7.42-7.28[m, 5H, H^2-H^6]$
1b		7.95[s, 1H, H <sup>9</sup> ]; 2.17[s, 3H, Me(C8)]; 1.94[s, 3H, O <sub>2</sub> CMe]	$7.90-7.20[m, 5H, H^2-H^6]$
2b		7.69[s, 2H, H <sup>9</sup> ]; 3.00[s, 3H, Me(C8)]	$7.56-7.09[m, 5H, H^2-H^6]$
3b		7.69[s, 1H, H <sup>9</sup> ]; 5.45[s, 1H, CH(acac)]; 3.00[s, 3H, Me(C8)]; 2.20[s, 3H,	$7.54-6.91[m, 5H, H^2-H^6]$
		Me(acac)]; 2.13[s, 3H, Me(acac)]	
4b		7.68[s, 1H, H <sup>9</sup> ]; 5.30[s, 5H, C <sub>5</sub> H <sub>5</sub> ]; 3.00[s, 3H, Me(C8)]	$7.61-6.91[m, 5H, H^2-H^6]$
5b 2	21.44s	7.65[s, 1H, H <sup>9</sup> ]; 3.00[s, 3H, Me(C8)]	$7.59-6.80[m, 5H, H^2-H^6]$

<sup>a</sup> In CDCl<sub>3</sub>. Measured at 100.6 MHz (approximately 20 °C); chemical shifts ( $\delta$ ) in ppm (±0.1) to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> In CDCl<sub>3</sub>, unless otherwise stated. Measured at 250 MHz (aproximately 20 °C); chemical shifts ( $\delta$ ) in ppm ( $\pm$ 0.01) to high frequency of SiMe<sub>4</sub>. <sup>c</sup> Coupling constants in Hz.

<sup>d</sup> s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.

 $C(H)C(H)=NCy\{(O_2CMe)\}_2$  (1a) and  $[Pd\{C_6H_5C=$  $C(Me)C(H)=NCy\{(O_2CMe)\}_2$  (1b), respectively, which were fully characterized. The IR spectra of 1a and 1b showed the v(C=N) stretch at 1610 and 1608 cm<sup>-1</sup>, respectively, shifted to lower wavenumbers (as compared with the free ligand) due to N-coordination of the imine [25,26]. The IR spectra also showed strong bands assigned to the symmetric and asymmetric v(COO)vibrations, in agreement with those expected for bridging acetate ligands [27] (see Section 3). Only one singlet resonance was assigned to the 2 equiv. methyl acetate groups, in each spectrum, in accordance with the presence of the anti isomer for both 1a and 1b. Metallation of the ligand through the aliphatic carbon atom C7 is clear for 1a, from the absence of the ABX system of the aliphatic chain, which was substituted by an AB pattern with  ${}^{3}J(HH)$  approximately 13 Hz; whereas for 1b, the H7 singlet was absent and only one singlet resonance appeared which was assigned to H9 (see Table 1). The resonance corresponding to the C(H)=N proton in the <sup>1</sup>H NMR spectra was only slightly shifted by approximately 0.1 ppm to lower frequency consequent upon coordination of the imine group to the palladium atom via the lone pair of the nitrogen atom [28].

The reaction of **1a** and **1b** with aqueous sodium chloride gave the chloro-bridged complexes  $[Pd\{C_6H_5C=C(H)C(H)=NCy\}(Cl)]_2$  (**2a**) and  $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(Cl)]_2$  (**2b**), respectively, and reaction of **1a** with aqueous sodium bromide or iodide gave the halide-bridged complexes  $[Pd\{C_6H_5C=$  C(H)C(H)=NCy}(X)]<sub>2</sub>, (X = Br, **3a**; X = I, **4a**), which were fully characterized (see Table 1, Section 3). The IR spectra showed the absence of the acetate bands, and for **2a** and **2b**, the appearance of two  $\nu$ (Pd–Cl) bands, consistent with an asymmetric Pd<sub>2</sub>Cl<sub>2</sub> bridging unit [29]. Alternatively, compounds **2a** and **2b** could be made by treatment of **a** and **b** with Li<sub>2</sub>[PdCl<sub>4</sub>] in methanol in good yield (see Section 3).

Reaction of **2b** with PPh<sub>3</sub> in a 1:2 molar ratio gave the mononuclear cyclometallated complex [Pd{C<sub>6</sub>H<sub>5</sub>C=  $C(H)C(Me)=NCy\{(Cl)(PPh_3)\}$  (5b), in a typical bridgesplitting reaction. In the <sup>1</sup>H NMR spectrum the C(H)= N resonance was a singlet, hence not showing coupling to the phosphorus nucleus; and in the  ${}^{31}P{}^{1}H$  spectrum the resonance of the coordinated phosphine was a singlet at  $\delta$  21.44. Although triphenylphosphine tends to adopt a trans to nitrogen disposition, these findings are in agreement with a phosphorus trans to carbon geometry. For a phosphorus trans to nitrogen arrangement greater  $\delta$ -values would be expected for the phosphorus resonance [30,31], in accordance with the higher trans influence of the carbon atom with respect to the C=N nitrogen atom [32], as well as coupling of the C(H)=N resonance to the <sup>31</sup>P nucleus. Further proof stems from the v(Pd-Cl) band in the IR spectrum. The value of 350  $\text{cm}^{-1}$  is in accordance with the chlorine atom trans to nitrogen, as a trans to carbon geometry would give a band at lower wavenumbers [29]. In the present case, we suggest that steric hindrance of the C7phenyl ring with the phosphine ligand prevents the latter to occupy the *trans* to nitrogen coordination site.

Reaction of **2b** with larger quantities of PPh<sub>3</sub>, 1:4 molar ratio or greater, did not produce opening of the metallated ring, nor did compound **2b** react with more basic phosphines such as PPhEt<sub>2</sub> (see Scheme 2).

Treatment of **2a** or **2b** with thallium cyclopentadienyl or with thallium acetylacetonate gave the monuclear compounds [Pd{C<sub>6</sub>H<sub>5</sub>C=C(H)-C(Me)=NCy}(acac)] (**3b**) and [Pd{C<sub>6</sub>H<sub>5</sub>C=C(H)C(H)=NCy}(acac)] (**5a**) and complex [Pd{C<sub>6</sub>H<sub>5</sub>C=C(H)C(Me)=NCy}(C<sub>5</sub>H<sub>5</sub>)] (**4b**), as air-stable solids which were fully characterized (see Section 3). The <sup>1</sup>H NMR spectra showed singlet resonances at  $\delta$  5.30 (**5a**),  $\delta$  5.45 (**3b**);  $\delta$  2.17 (**5a**),  $\delta$ 2.20 (**3b**) and  $\delta$  2.09 (**5a**),  $\delta$  2.13 (**3b**), assigned to the *CH* and to the 2 inequiv. C–Me groups, respectively. In the <sup>1</sup>H NMR spectra of **4b** a singlet resonance was assigned to the 5 equiv. protons of the C<sub>5</sub>H<sub>5</sub> ring.

Also noticeable in the <sup>1</sup>H NMR spectra of compounds 1a-5a were the resonances of the H2 and H6 phenyl ring protons, which appeared separated from the multiplet ascribed to the H3-H5 proton signals and shifted towards lower field, at approximately  $\delta$  7.94, due to the deshielding effect of the C=N double bond (see Table 1). For compounds 1b-5b a multiplet was observed for the H2-H6 phenyl ring protons; however, the signal for **1b** expanded as far as  $\delta$  7.90, whereas for **2b–5b** the lowest value for the multiplet was  $\delta$  7.61 (in **4b**). This seems to indicate that the C=N group does not affect protons H2 and H6 in 2b-5b, which could be due to rotation of the phenyl ring away from the coplanarity of the metallated ring. Further evidence for this assumption was the Me(C8) resonance, for which values of  $\delta$  2.17 (1b) and  $\delta$  3.00 (2b–5b) were found; the former datum close to the one observed in the <sup>1</sup>H NMR spectrum of the free ligand **b**,  $\delta$  2.15. We also tentatively suggest that the aforementioned rotation of the aromatic ring brings the Me(C8) group closer to the deshielding region of the phenyl ring and the corresponding resonance is thus shifted to lower field. Presently, we are in the process of studying related compounds which will enable us to gather further data in order shed new light regarding the precise disposition of the phenyl ring as well as other interesting properties of these complexes.

### 3. Experimental

All reactions were carried out in an atmosphere of dry nitrogen. Solvents were purified by standard methods [33]. Chemicals were reagent grade. Palladium(II) acetate was purchased from Alfa Products, thallium acetylacetonate, thallium cyclopentadienyl, *trans*-cinnamaldehyde and  $\alpha$ -methyl-*trans*-cinnamaldehyde, and the phosphines PPh<sub>3</sub> and PEt<sub>2</sub>Ph were purchased form Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of

Santiago using a Carlo-Erba Elemental Analyzer, Model 1108. IR spectra were recorded as KBr pellets on a Perkin–Elmer 1330 and on a Mattson (Servicio de Espectroscopía of the University of Santiago) spectrophotometers. NMR spectra were obtained as CDCl<sub>3</sub> or  $(CD_3)_2CO$  solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}) and were recorded on Bruker WM-250, AMX-300 and AC-200 spectrometers. All chemical shifts were reported downfield from the standards.

The synthesis of  $C_6H_5C(H)=C(R)C(H)=NCy$  (R = H, Me) was performed by heating a chloroform solution of the appropriate quantities of *trans*-cinnamaldehyde or of  $\alpha$ -methyl-*trans*-cinnamaldehyde and cyclohexylamine in a Dean–Stark apparatus under reflux.

3.1.1.  $C_6H_5C(H) = C(H)C(H) = NCy(a)$ 

 $C_{15}H_{19}N$  (213.3): Calc. C, 84.4; H, 9.0; N, 6.6. Found: C, 84.0; H, 8.9; N, 6.5%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1622m (C= N).

3.1.2.  $C_6H_5C(H) = C(Me)C(H) = NCy(b)$ 

 $C_{16}H_{21}N$  (227.4): Calc. C, 84.5; H, 9.3; N, 6.2. Found: C, 84.3; H, 9.1; N, 6.0%. IR (KBr  $\nu$  cm<sup>-1</sup>): 1620m (C= N).

### 3.2. Preparation of the complexes

# 3.2.1. Synthesis of $[Pd\{C_6H_5C=C(H)C(H)=NCy\}(O_2CMe)]_2$ (1a)

A mixture of  $C_6H_5C=C(H)C(H)=NCy$  (310 mg, 1.45) mmol) and palladium(II) acetate (300 mg, 1.34 mmol) in glacial acetic acid (40 cm<sup>3</sup>) was refluxed under dry dinitrogen for 3 h. After cooling the mixture to room temperature (r.t.) the acetic acid was removed under vacuum. The residue was treated with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give an orange oil. This was chromatographed on a column packed with silica-gel. Elution with dichloromethane removed unchanged starting material. Elution with dichloromethaneethanol(0.5%) afforded the final product as a yellow powder after concentration. Yield: 389 mg, 77%. C<sub>34</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>Pd<sub>2</sub> (775.5): Calc. C, 54.0; H, 5.6; N, 3.7. Found: C, 53.9; H, 5.5; N, 3.6%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1600m (C=N), 1585s (v<sub>as</sub>COO), 1410s (v<sub>s</sub>COO).

Compound **1b** was prepared similarly.

## 3.2.2. Synthesis of $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(O_2CMe)]_2$ (**1b**)

Yield: 393 mg, 75%. C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>Pd<sub>2</sub> (783.6): Calc. C, 55.2; H, 5.9, N, 3.6. Found: C, 55.0; H, 5.8; N, 3.4%. IR

(KBr v cm<sup>-1</sup>): 1605m (C=N), 1575s ( $v_{as}$ COO), 1410s ( $v_{s}$ COO).

3.2.3. Synthesis of  $[Pd\{C_6H_5C=C(H)C(H)=NCy\}(Cl)]_2$  (2a)

3.2.3.1. Method 1. An aqueous solution of NaCl (approximately  $10^{-2}$  M) was added dropwise to a solution of **1a** (58 mg, 0.07 mmol) in acetone. The product immediately precipitated out as a yellow solid. After stirring for 10 h the solid was filtered off and dried in vacuo. Yield: 47 mg, 87%. C<sub>30</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>2</sub>Pd<sub>2</sub> (708.37): Calc. C, 50.9; H, 5.1; N, 4.0. Found: C, 50.7; H, 5.0; N, 3.9%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1600m (C=N), 286m, 230m (Pd–Cl).

3.2.3.2. Method 2. To a stirred solution of lithium tetrachloropalladate in methanol (30 cm<sup>3</sup>), prepared in situ from 210 mg (1.18 mmol) of palladium(II) chloride and 100 mg (2.33 mmol) of lithium chloride, 240 mg (1.13 mmol) of the Schiff-base  $C_6H_5C(H)=C(H)C(H)=$  NCy (a) were added. The mixture was stirred for 48 h at r.t. The precipitate was filtered off and washed with methanol. Yield: 239 mg, 80%.

Compounds 3a, 4a, (Section 3.2.3.1) and 2b, were prepared similarly.

3.2.4.  $[Pd\{C_6H_5C=C(H)C(H)=NCy\}(Br)]_2$  (**3a**) Yield: 43 mg, 82%.  $C_{30}H_{36}Br_2N_2Pd_2$  (797.3): Calc. C, 45.2; H, 4.6; N, 3.5. Found: C, 45.0; H, 4.4; N, 3.4%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1603m (C=N).

3.2.5.  $[Pd\{C_6H_5C=C(H)C(H)=NCy\}(I)]_2$  (4a)

Yield: 45 mg, 79%.  $C_{30}H_{36}I_2N_2Pd_2$  (891.3): Calc. C, 40.4; H, 4.1; N, 3.1. Found: C, 40.1; H, 4.0; N, 2.9%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1605m (C=N).

3.2.6.  $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(Cl)]_2$  (2b)

Yield: 45 mg, 75% (Section 3.2.3.1); 243 mg, 78% (Section 3.2.3.2).  $C_{32}H_{40}Cl_2N_2Pd_2$  (736.4): Calc. C, 52.2; H, 5.5; N, 3.8. Found: C, 52.0; H, 5.3; N, 3.7%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1611m (C=N), 287m, 238m (Pd–Cl).

## 3.2.7. Synthesis of $[Pd\{C_6H_5C=C(H)C(H)=NC_8\}(acac-O,O)]$ (5a)

To a suspension of **2a** (50 mg, 0.07 mmol) in chloroform (25 cm<sup>3</sup>), thallium-2,4-pentanedionate (4 mg, 0.014 mmol) was added and the mixture stirred at r.t. for 4 h. The resulting mixture was filtered over celite, concentrated in vacuo, and recrystallised from dichloromethane-hexane to give the required complex as a yellow solid. Yield: 50 mg, 85%. C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub>Pd (417.8): Calc. C, 57.5; H, 6.0; N, 3.4. Found: C, 57.2; H, 5.9; N, 3.2%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1604m (C=N), 1580m, 1515m (C-O).

Compound 3b was prepared similarly.

3.2.8.  $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(acac-O,O)]$ (3b)

Yield: 48 mg, 82%.  $C_{21}H_{27}NO_2Pd$  (431.9): Calc. C, 58.4; H, 6.3; N, 3.2. Found: C, 58.1; H, 6.1; N, 3.1%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1603m (C=N), 1582m, 1514m (C–O).

Compound **4b** was prepared in a similar fashion to **5a** but using  $Tl(C_5H_5)$ .

3.2.9.  $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(C_5H_5)]$  (4b)

Yield: 44 mg, 81%.  $C_{21}H_{25}NPd$  (397.9): Calc. C, 63.4; H, 6.3; N, 3.5. Found: C, 63.3; H, 6.2; N, 3.3%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1607m (C=N).

# 3.2.10. Synthesis of $[Pd\{C_6H_5C=C(Me)C(H)=NCy\}(Cl)(PPh_3)]$ (5b)

To a suspension of the cyclometallated halide-bridged complex (**2b**) (100 mg, 0.13 mmol) in 15 cm<sup>3</sup> of dichloromethane, PPh<sub>3</sub> (68 mg, 0.26 mmol) was added. The mixture was stirred for 8 h, after which the white solid formed was filtered off and recrystallized from dichloromethane-hexane. Yield: 125 mg, 73%. C<sub>34</sub>H<sub>35</sub>CINPPd (630.5): Calc. C, 64.8; H, 5.6; N, 2.2. Found: C, 64.7; H, 5.3; N, 2.1%. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1617m (C=N), 350m (Pd-Cl).

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