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Synthesis and characterization of cyclometallated complexes of palladium(II) and manganese(I) with bidentate Schiff bases ☆

José M. Vila *, Miguel Gayoso, M[a], Teresa Pereira, Margarita López Torres, Jesús J. Fernández, Alberto Fernández, Juan M. Ortigueira

Department of Inorganic Chemistry, University of Santiago, E-15706 Santiago de Compostela, Spain

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Abstract

Treatment of *N,N*-isophthalylidenebis(cyclohexylamine), 1,3-(CyN=CH)$_2$C$_6$H$_4$ (**L^2**) (Cy = cyclohexyl) with palladium(II) acetate in glacial acetic acid gave after column chromatography the monocyclometallated dimer complex [{Pd[3-(CHO)C$_6$H$_3$C(H)=NCy](O$_2$CMe)}$_2$] (**1**) with a free formyl group on each phenyl ring, and a mixture of **1** with the doubly cyclometallated complex [Pd{3-(CyN=CH)C$_6$H$_3$C(H)=NCy}(O$_2$CMe)] (**2**). Treatment of **1** with cyclohexylamine gave the corresponding dimer complex [{Pd[3-(CyN=CH)C$_6$H$_3$C(H)=NCy](O$_2$CMe)}$_2$] (**17**) with an uncoordinated C=N group on each phenyl ring. Treatment of **1** and **2** with aqueous NaX gave the dimer complexes [{Pd[3-(CHO)C$_6$H$_3$C(H)=NCy](X)}$_2$] (**3**: X = Cl; **4**: X = Br; **5**: X = I) and a mixture of **3**, **4** or **5** with the doubly cyclometallated complex [Pd{3-(CyN=CH)C$_6$H$_3$C(H)=NCy}(X)] (**6**: X = Cl; **7**: X = Br; **8**: X = I), respectively. The dicyclometallated iodo complex **8** was isolated pure. Treatment of **3**, **4** or **5** with cyclohexylamine in a 1 : 2 or 1 : 4 molar ratio gave the cyclometallated complexes [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}(X)(NH$_2$Cy)] (**9**: X = Cl; **10**: X = Br; **11**: X = I) and [Pd{3-(CyN=CH)C$_6$H$_3$C(H)=NCy}(X)(NH$_2$Cy)] (**12**: X = Cl; **13**: X = Br; **14**: X = I), respectively; the last three compounds each contain an uncoordinated C=N group. The corresponding bromo and iodo analogues were made similarly. Treatment of **3**, **4** or **5** with thallium cyclopentadienyl or thallium acetylacetonate gave the mononuclear complexes [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}(C$_5$H$_5$)] (**15**) and [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}(H$_3$CCOCHCOCH$_3$)] (**16**), respectively. Treatment of **L^2** with MnMe(CO)$_5$ in a 1 : 1 molar ratio gave the monocyclometallated complex [(OC)$_4$Mn{3-(CHO)C$_6$H$_3$C(H)=NCy}] (**18**) by cleavage of one C=N bond, whereas treatment of **L^2** with MnMe(CO)$_5$ in a 1 : 1.2 molar ratio produced a mixture of the doubly cyclometallated complex **19** and the monocyclometallated complex **20** without cleavage of the C=N bond. Treatment of *N,N*-terephthalylidenebis(cyclohexylamine), 1,4-(CyN=CH)$_2$C$_6$H$_4$ (**L^1**) (Cy = cyclohexyl), with MnMe(CO)$_5$ in a 1 : 1.2 molar ratio gave a mixture of the monocyclometallated compound [(OC)$_4$Mn{4-(CHO)C$_6$H$_3$C(H)=NCy}] (**22**) and the monocyclometallated compound [(OC)$_4$Mn{4-(CyN=CH)C$_6$H$_3$C(H)=NCy}] (**23**); compound **22** was isolated in a pure state.

Keywords: Palladium; Manganese; Schiff bases; Cyclometallation; Carbonyl; Diimine

1. Introduction

Cyclometallation is an important process in organometallic chemistry and reviews dealing with cyclometallated compounds are available [1]. Organic ligands that may enter into cyclometallation reactions are numerous and varied; nitrogen-donor ligands are the most widely involved [2], but ligands bearing phosphorus [3], arsenic [4], oxygen [5a] or sulphur [5a,b] donor atoms have also been used. Bidentate nitrogen-donor ligands may undergo double cyclometallation to produce compounds with two σ-M–C bonds and with coordination of each nitrogen atom to one of the metal centres. As examples, *N,N,N′,N′*-tetraethyl-*p*-xylene-α,α'-diamines [6], azines [7], diphenylpyrimidines [8], diphenylpyrazines [9], benzylidenehydrazones [10] and bis(*N*-benzylidene)-1,4-phenylenediamines [11] always give doubly cyclometallated complexes. However, when Schiff bases derived from dialdehydes such as terephthalaldehyde were used in cyclometallation reactions, mono- or dicyclometallated compounds were obtained. We previously reported that the bidentate Schiff

☆ Dedicated to Professor Bernard L. Shaw on the occasion of his 65th birthday.

* Corresponding author.

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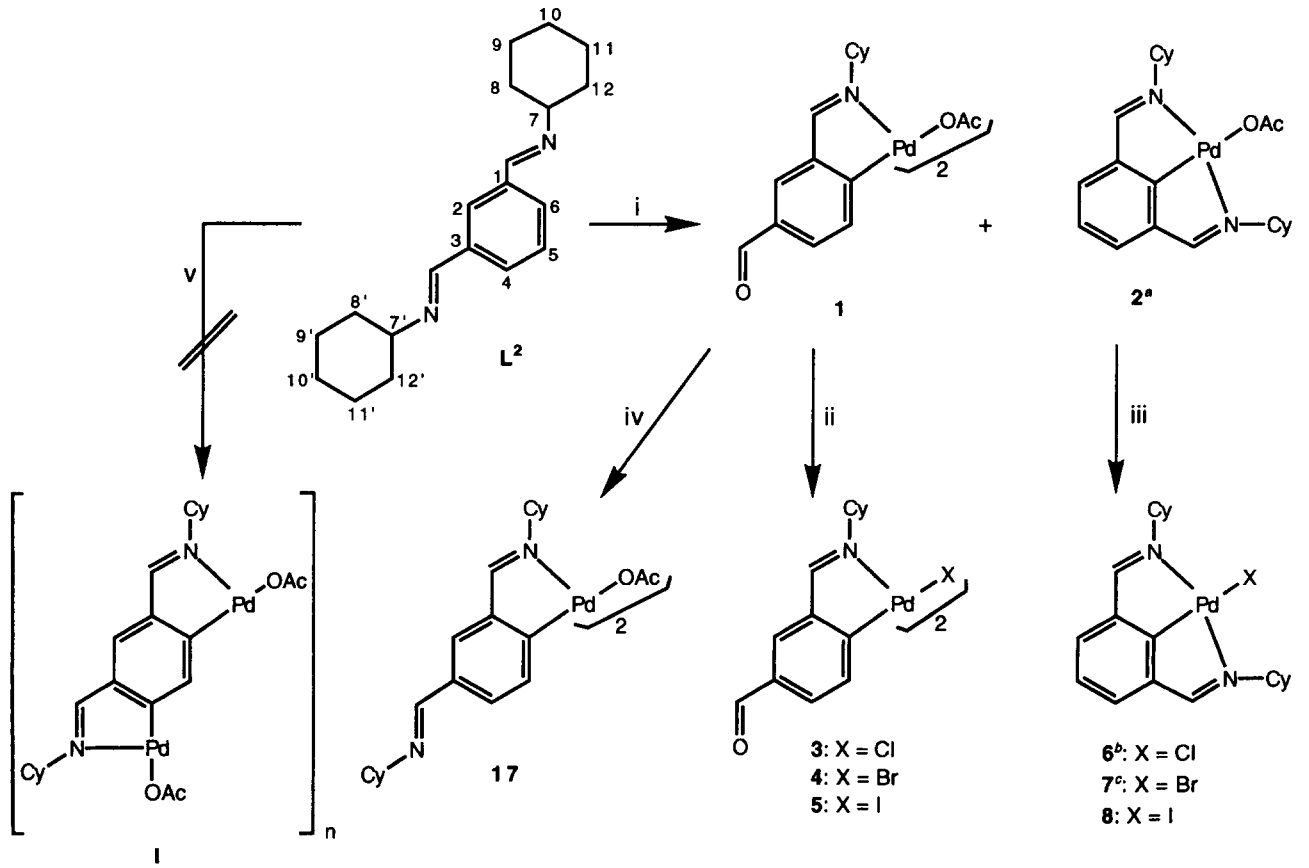
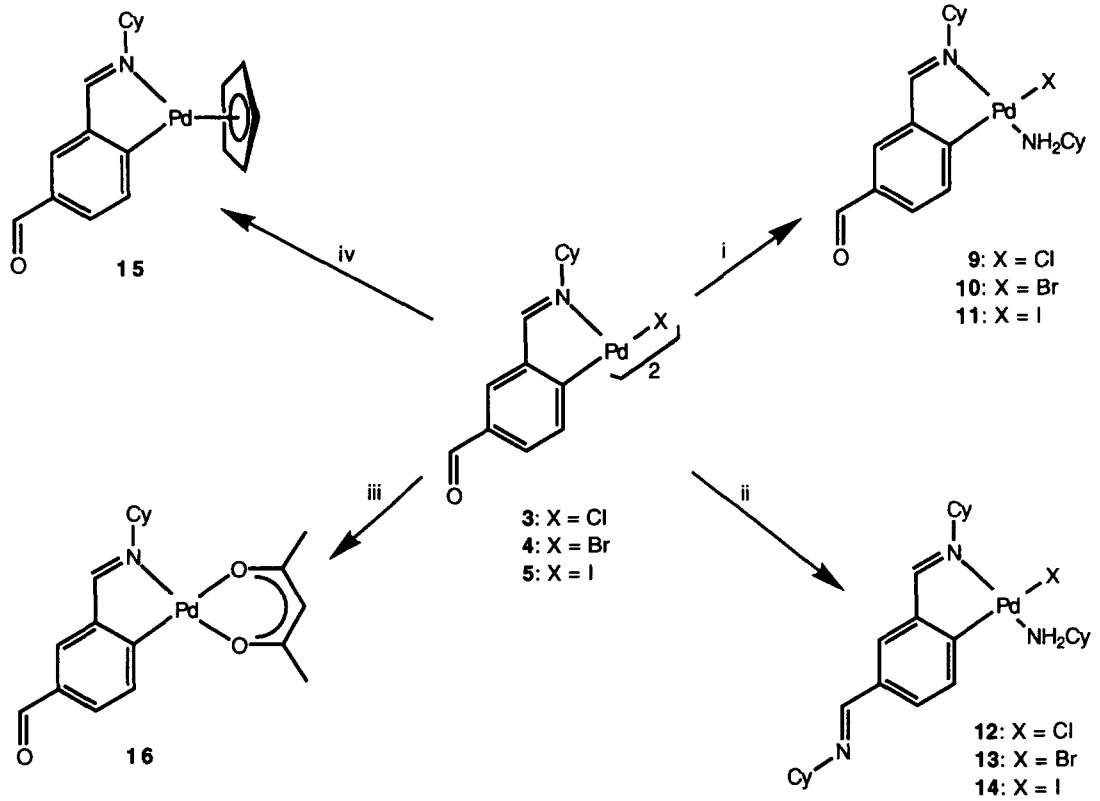
base *N*,*N*-terephthalylidenebis(cyclohexylamine), 1,4-(CyN=CH)$_2$C$_6$H$_4$ (**L^1**), reacts with palladium(II) acetate to give a monocyclometallated dimer complex with a free formyl group on each phenyl ring [12]. Thus, the organic ligand undergoes cleavage of one of the C=N double bonds in the metallation process. The C=N double bond could be regenerated by treatment of the cyclometallated complexes with primary amines to produce compounds with a coordinated C=N group and an uncoordinated C=N group. We expected that in a non-acidic medium cleavage of the C=N double bond would be negligible and that the ligand would be doubly cyclometallated and double cyclometallation was in fact achieved by use of MnMe(CO)$_5$ in boiling octane.

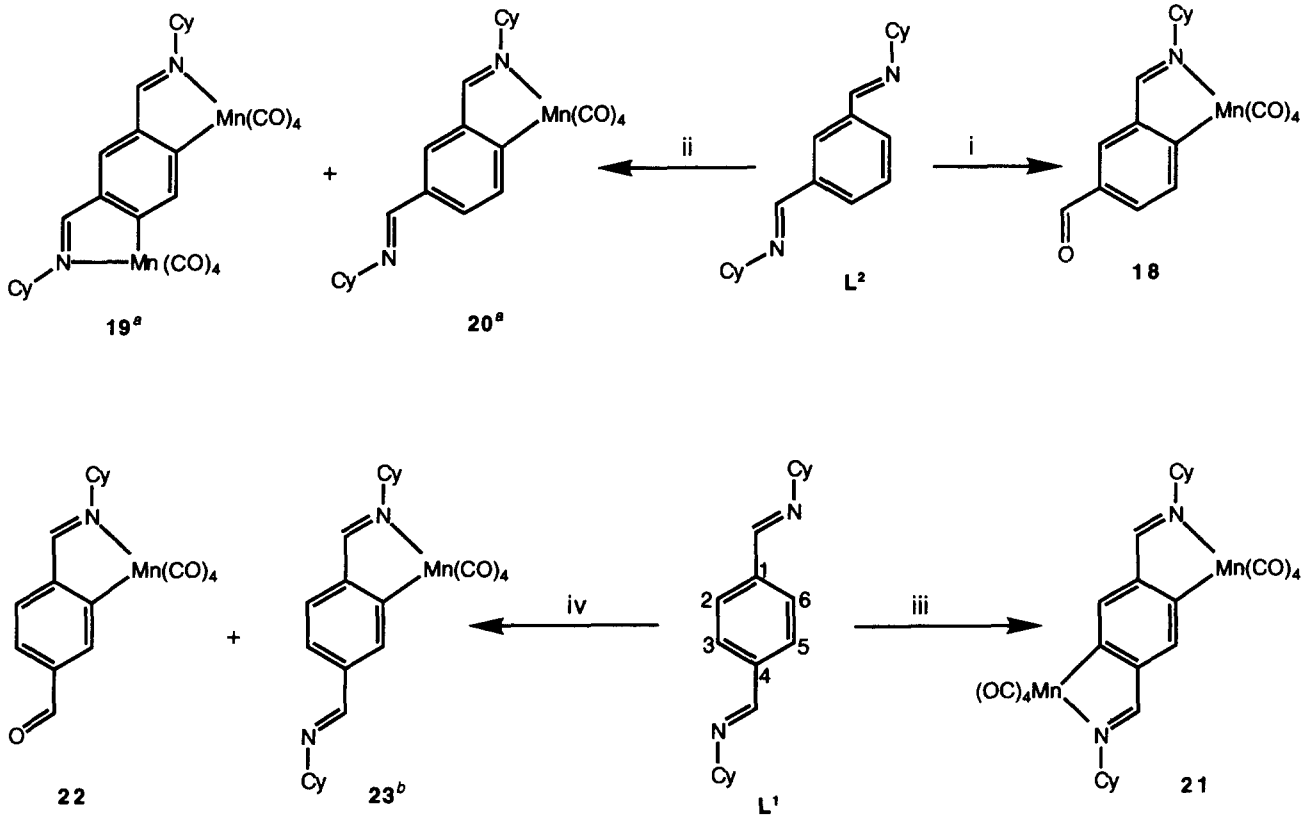
Previous studies on the related ligands 2,6-dialdiminobenzenes [13] have shown that these may be doubly cyclometallated by Pd(II) to give complexes with the palladium atom bonded to the C-3 and to the C-5 carbon atoms; no C=N bond cleavage was reported. In view of the different behaviour of this ligand, we decided to study the behaviour of the similar ligand *N*,*N*-isophthalylidenebis(cyclohexylamine), 1,3-(CyN=CH)$_2$C$_6$H$_4$ (**L^2**), towards Pd(II) and Mn(I). However, we hoped that under the conditions we had used earlier [12] we would be able to produce new cyclometallated complexes, which would show a behaviour of ligand **L^2** towards cyclometallation with palladium(II) acetate different from that found for the related dialdiminobenzenes. As described below, for the Pd(II) complexes this proved to be the case. Furthermore, a second cyclometallated complex was obtained in low yield in the metallation of ligand **L^2**, and this has only one σ-Pd–C bond and two coordinated Pd–N bonds. We now report the reaction of ligand **L^2** with palladium(II) acetate in glacial acetic acid to give a monopalladated dinuclear acetato-bridged complex with a free formyl group along with a monopalladated mononuclear complex with both nitrogen-donor atoms bonded to the metal atom. Subsequent reactions of this and other related complexes are also reported. We have also studied the reaction of **L^2** with MnMe(CO)$_5$ under the conditions we used previously [12], and we found that even in a non-acidic medium different compounds can be obtained when the molar ratio of the reactants is varied. The results led us also to re-examine the reaction 1,4-(CyN=CH)$_2$C$_6$H$_4$ with MnMe(CO)$_5$.



Scheme 1. (i) Pd(OAc)$_2$, glacial acetic acid, reflux; (ii) NaX (X = Cl, Br, I) in aqueous acetone; (iii) NaX (X = Cl, Br, I) in aqueous acetone; (iv) CyNH$_2$ (2 mol), chloroform, stir at room temperature; (v) Pd(OAc)$_2$, glacial acetic acid, reflux. [a] Isolated as a mixture of **1** + **2**. [b] Isolated as a mixture of **3** + **6**. [c] Isolated as a mixture of **4** + **7**.



Scheme 2. (i) $CyNH_2$ (2 mol), chloroform, stir at room temperature; (ii) $CyNH_2$ (4 mol), chloroform, stir at room temperature; (iii) $Tl(H_3CCOCHCOCH_3)$, stir at room temperature; (iv) $Tl(C_5H_5)$, chloroform, reflux.



Scheme 3. (i) $[MnMe(CO)_5]$, 1 : 1 molar ratio; (ii) $[MnMe(CO)_5]$–L^2, 1 : 1.2 molar ratio; (iii) $[MnMe(CO)_5]$, 1 : 2 molar ratio; (iv) $[MnMe(CO)_5]$–L^1, 1 : 1.2 molar ratio. [a] Isolated as a mixture of **19** + **20**. [b] Isolated as a mixture of **22** + **23**.

Table 1
Proton NMR data [a]

Compound	δ(HC=O)	δ(HC=N)	Aromatics	Others
L^1		8.23 (2H, s)	7.69 (4H, s, H^2, H^3, H^5, H^6)	3.13 (2H, m, H^7, $H^{7'}$)
L^2		8.29 (2H, s)	7.36 (1H, t, 7.6 [d,e], H^5)	3.14 (2H, m, H^7, $H^{7'}$)
			7.73 (2H, dd, 7.6 [d,e], 1.7 [b,c], H^4, H^6)	
			8.00 (1H, t, 1.7 [b,c], H^2)	
1	9.88 (2H, s)	7.59 (2H, s)	7.30 (2H, d, 7.9 [d], H^5)	3.00 (2H, m, H^7)
			7.45 (2H, d, 1.7 [b], H^2)	2.16 (6H, s, O_2CMe)
			7.52 (2H, dd, 7.9 [d], 1.7 [b], H^4)	
2		7.98 (2H, s)	7.05 (1H, t, 7.6 [d,e], H^5)	
			7.16 (2H, d, 7.6 [d,e], H^4, H^6)	
3	9.90 (2H, s)	7.96 (2H, s)	7.53 (2H, dd, 8.0 [d], 1.7 [b], H^4)	3.75 (2H, m, H^7)
			7.63 (2H, d, 8.0 [d], H^5)	
			7.75 (2H, d, 1.7 [b], H^2)	
4	9.91 (2H, s)	8.00 (2H, s)	7.52 (2H, dd, 7.9 [d], 1.8 [b], H^4)	3.95 (2H, m, H^7)
			7.73 (2H, d, 1.8 [b], H^2)	
			7.81 (2H, d, 7.9 [d], H^5)	
5	9.91 (2H, s)	8.02 (2H, s)	7.44 (2H, dd, 7.5 [d], 1.8 [b], H^4)	4.05 (2H, m, H^7)
			7.70 (2H, d, 1.8 [b], H^2)	
			7.85 (2H, d, 7.5 [d], H^5)	
6		8.00 (2H, s)	7.05 (2H, d, 7.5 [d,e], H^4, H^6)	3.87 (2H, m, H^7, $H^{7'}$)
			7.21 (1H, t, 7.5 [d,e], H^5)	
7		8.02 (2H, s)	7.08 (2H, d, 7.3 [d,e], H^4, H^6)	3.9 (2H, m, H^7, $H^{7'}$)
			7.21 (1H, t, 7.3 [d,e], H^5)	
8		8.02 (2H, s)	7.09 (2H, d, 7.4 [d,e], H^4, H^6)	4.25 (2H, m, H^7, $H^{7'}$)
			7.22 (1H, t, 7.4 [d,e], H^5)	
9	9.84 (1H, s)	7.89 (1H, s)	7.00 (1H, d, 7.8 [d], H^5)	4.07 (1H, m, H^7)
			7.54 (1H, dd, 7.8 [d], 1.7 [b], H^4)	
			7.68 (1H, d, 1.7 [b], H^2)	
10	9.58 (1H, s)	7.95 (1H, s)	7.02 (1H, d, 7.9 [d], H^5)	4.31 (1H, m, H^7)
			7.63 (1H, dd, 7.9 [d], 1.6 [b], H^4)	
			7.75 (1H, d, 1.6 [b], H^2)	
11	9.91 (1H, s)	7.83 (1H, s)	6.88 (1H, d, 7.8 [d], H^5)	
			7.31 (1H, d, 7.8 [d], H^4)	
			7.65 (1H, s, H^2)	
12		7.76 (1H, s)	6.93 (1H, d, 7.8 [d], H^5)	3.92 (1H, m, $H^{7'}$)
		8.18 (1H, s)	7.35 (1H, d, 7.8 [d], H^4)	3.15 (1H, m, H^7)
			7.63 (1H, s, H^2)	
13		7.86 (1H, s)	6.86 (1H, d, 7.5 [d], H^5)	4.19 (1H, m, $H^{7'}$)
		8.23 (1H, s)	7.41 (1H, d, 7.5 [d], H^4)	3.04 (1H, m, H^7)
			7.69 (1H, s, H^2)	
14		7.89 (1H, s)	6.79 (1H, d, 7.9 [d], H^5)	4.20 (1H, m, $H^{7'}$)
		8.22 (1H, s)	7.44 (1H, dd, 7.9 [d], 1.5 [b], H^4)	3.05 (1H, m, H^7)
			7.68 (1H, d, 1.5 [b], H^2)	
15	9.87 (1H, s)	7.99 (1H, s)	7.32 (1H, dd, 7.9 [d], 1.9 [b], H^4)	5.84 (5H, s, C_5H_5)
			7.87 (1H, d, 1.9 [b], H^2)	
			7.91 (1H, d, 7.9 [d], H^5)	
16	9.91 (1H, s)	8.04 (1H, s)	7.62 (1H, dd, 7.9 [d], 1.9 [b], H^4)	5.41 (1H, s, CH) [h]
			7.73 (1H, d, 1.9 [b], H^2)	2.10 (3H, s, Me) [h]
			7.76 (1H, d, 7.9 [d], H^5)	2.02 (3H, s, Me) [h]
17		7.83 (1H, s)	6.88 (1H, d, 7.8 [d], H^5)	3.6 (1H, m, H^7)
		8.17 (1H, s)	7.31 (1H, d, 7.8 [d], H^4)	3.14 (1H, m, $H^{7'}$)
			7.65 (1H, s, H^2)	
18	9.96 (1H, s)	8.46 (1H, s)	7.68 (1H, d, 7.6 [d], H^5)	3.59 (1H, m, H^7)
			7.95 (1H, s, H^2)	
			8.22 (1H, d, 7.6 [d], H^4)	
19		8.30 (2H, s)	7.51 (1H, s, H^5)	3.59 (2H, m, H^7, $H^{7'}$)
			8.72 (1H, s, H^2)	
20		8.83 (1H, s)	7.22 (1H, d, 7.2 [d], H^5)	3.59 (1H, m, H^7)
			7.83 (1H, d, 7.2 [d], H^4)	3.14 (1H, m, $H^{7'}$)
			8.30 (1H, s, H^2)	
21		8.40 (2H, s)	8.09 (2H, s, H^2, H^5)	
22	9.96 (1H, s)	8.46 (1H, s)	7.69 (1H, dd, 7.5 [f], 1.4 [g], H^3)	3.54 (1H, m, H^7)
			7.95 (1H, d, 1.4 [g], H^5)	
			8.22 (1H, d, 7.5 [f], H^2)	

Table 1 (continued)

Compound	δ(HC=O)	δ(HC=N)	Aromatics	Others
23		8.32 (1H, s) 8.85 (1H, s)	7.22 (1H, d, 7.2 [f], H^2) 7.83 (1H, d, 7.2 [f], H^3) 8.32 (1H, s, H^5)	

[a] In $CDCl_3$. Measured at 250 MHz (ca. 20°C). Chemical shifts (δ) in ppm (±0.01 ppm) to high frequency of $SiMe_4$. Coupling constants in Hz. s, Singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.
[b] ^4J(H-2,H-4).
[c] ^4J(H-2,H-6).
[d] ^3J(H-4,H-5).
[e] ^3J(H-5,H-6).
[f] ^3J(H-2,H-3).
[g] ^4J(H-3,H-5).
[h] Data for the 2,4-pentanedionate ligand

2. Results and discussion

For ease of reading, the compounds and reactions are shown in Schemes 1, 2 and 3. The compounds described were characterized by elemental analysis and by IR spectroscopy (data are given in the Experimental section) and by ^1H (Table 1) and ^{13}C NMR (Table 2) spectroscopy.

2.1. Palladium(II) complexes

Treatment of *N,N*-isophthalylidenebis(cyclohexylamine), 1,3-$(CyN{=}CH)_2C_6H_4$ ($\mathbf{L^2}$), with palladium (II) acetate in glacial acetic acid gave the mono- and dicyclometallated complexes $[\{Pd[3\text{-}(CHO)C_6H_3C(H){=}NCy](O_2CMe)\}_2]$ (**1**) and $[Pd\{3\text{-}(CyN{=}CH)C_6H_3C(H){=}NCy\}(O_2CMe)]$ (**2**). Compound **1** was obtained pure in 65% yield but **2** was obtained only as a mixture of **1** + **2** in 15% yield (we were not able to separate **1** and **2** by fractional recrystallization or column chromatography). As we expected, under the conditions used, i.e. involving an acidic medium, ligand $\mathbf{L^2}$ did not undergo double metallation through the C-4 and C-6 positions (see Scheme 1), unlike the related 2,6-dialdiminobenzenes [13]; instead, $\mathbf{L^2}$ was metallated only through the C-6 carbon atom, with simultaneous cleavage of the C=N (C-3) bond to give **1**, which has a free formyl group on the C-3 position of each phenyl ring; we previously showed that similar bidentate Schiff base ligands undergo cleavage of one C=N double bond in an acidic reaction medium [12] prior to metallation, implying that only one C=N is involved in a cyclometallated ring. Interestingly, ligand $\mathbf{L^2}$ was also metallated at the C-2 position. However, in this case there was no cleavage of a C=N bond, the palladium atom being bonded to both imine nitrogen atoms. As shown before [14], if we assume that cyclometallation takes place in two steps, i.e. coordination of the donor atom to the metal followed by formation of the σ-M–C bond, it follows that coordination of the second nitrogen atom to palladium, in this case, is faster than cleavage of the C=N bond [15]. This is not possible when the C-6 carbon atom of $\mathbf{L^2}$ is palladated, or in the case of ligands we used earlier [12].

The ^1H NMR spectrum (Table 1) for **1** showed a doublet at δ7.45 assigned to H-2 and the resonances of the H-4 and H-5 protons (AB spin system) as a doublet of doublets (H-4, also coupled to H-2) and a doublet (H-5) at δ7.52 and δ7.05, respectively; ^3J(H-4, H-5) = 7.9 Hz, ^4J(H-2, H-4) = 1.7 Hz. Singlets at δ9.88 (2H) and at δ7.59 (2H) were assigned to the *H*C=O and *H*C=N proton resonances, respectively; the latter was shifted to lower frequency on palladium–nitrogen coordination [16]. A singlet at δ2.16 (6H) was assigned to the two equivalent methyl groups, *Me*COO, in accordance with a *trans* disposition of the organic ligands [17].

The ^{13}C NMR spectrum (Table 2) was also unequivocally assigned, showing resonances at δ191.3 (HC=O), δ181.3 (O_2CMe), δ167.8 (HC=N) and δ147.4 (C-6); the last two were shifted by ca. 9 and 17 ppm, respectively, from those for the free ligand, confirming that metallation had taken place [18]. The C-1 resonance, δ165.6, was also shifted towards higher frequency by ca. 28 ppm. There was no noticeable quadrupolar broadening of these resonances by coupling with the ^{105}Pd (22% natural abundance, $I = 5/2$) nucleus. The remaining phenyl and cyclohexyl resonances were also assigned (Table 2). The resonance at δ24.3 was assigned to the two equivalent O_2CMe carbon atoms, in accordance with a *trans* geometry of the organic ligands (see above).

The IR data (see Experimental) were in agreement with these findings: bands at 1695 and at 1605 cm^{-1} were ascribed to ν(C=O) and ν(C=N) stretches, respectively, the latter shifted towards lower wavenumbers, consistent with palladium coordination to the nitrogen atom [19,20]; also assigned were the ν_{as}(COO) and ν_s(COO) bands at 1570 and 1410 cm^{-1} expected for bridging acetate groups [21].

Treatment of **1** with cyclohexylamine in a 1:2 molar ratio gave $[\{Pd[3\text{-}(CyN{=}CH)C_6H_3C(H){=}NCy]$-

Table 2
$^{13}C-\{^1H\}$ NMR data [a]

Compound	δ_C
L[1]	128.3 (4C, C^2, C^3, C^5, C^6), 138.3 (2C, C^1, C^4), 158.5 (2C, C=N) Cy groups: 24.7 (4C, C^9, $C^{9'}$ C^{11}, $C^{11'}$), 25.6 (2C, C^{10}, $C^{10'}$), 34.3 (4C, C^8, $C^{8'}$ C^{12}, $C^{12'}$), 69.9 (2C, C^7, $C^{7'}$)
L[2]	128.1 (1C, C^5), 129.0 (1C, C^2), 130.0 (2C, C^4, C^6), 137.2 (2C, C^1, C^3), 158.5 (2C, C=N) Cy groups: 25.0 (4C, C^9, $C^{9'}$ C^{11}, $C^{11'}$), 25.9 (2C, C^{10}, $C^{10'}$), 34.6 (4C, C^8, $C^{8'}$, C^{12}, $C^{12'}$), 70.3 (2C, C^{10}, $C^{10'}$)
1	24.3 (2C, O_2CMe) 126.0 (2C, C^5), 130.5 (2C, C^4), 132.5 (2C, C^2), 133.2 (2C, C^3), 147.4 (2C, C^6), 165.6 (2C, C^1), 167.8 (2C, C=N), 181.3 (2C, O_2CMe), 191.3 (2C, C=O) Cy groups: 25.8 (4C, C^9, C^{11}), 33.2 (2C, C^{10}), 34.4 (4C, C^8, C^{12}), 65.3 (2C, C^7)
3	126.5 (2C, C^5), 126.9 (2C, C^4), 131.6 (2C, C^2), 133.8 (2C, C^3), 147.7 (2C, C^6), 169.7 (2C, C=N), 191.6 (2C, C=O) Cy groups: 25.5 (4C, C^9, C^{11}), 25.6 (2C, C^{10}), 33.3 (4C, C^8, C^{12}), 67.9 (2C, C^7)
4 [b]	127.7 (2C, C^5), 130.5 (2C, C^4), 132.9 (2C, C^3), 133.5 (2C, C^2), 148.9 (2C, C^6), 171.9 (2C, C=N), 192.6 (2C, C=O) Cy groups: 25.4 (4C, C^9, C^{11}), 25.5 (2C, C^{10}), 32.4 (4C, C^8, C^{12}), 64.2 (2C, C^7)
5 [b]	127.9 (2C, C^5), 131.0 (2C, C^4), 132.5 (2C, C^3), 143.9 (2C, C^2), 149.3 (2C, C^6), 163.6 (2C, C^1), 171.5 (2C, C=N), 192.6 (2C, C=O) Cy groups: 25.4 (4C, C^9, C^{11}), 25.5 (2C, C^{10}), 32.8 (4C, C^8, C^{12}), 63.2 (2C, C^7)
8	123.1 (1C, C^5), 125.4 (2C, C^4, C^6), 143.2 (1C, C^2), 168.4 (2C, C=N) Cy groups: 24.1 (4C, C^9, $C^{9'}$, C^{11}, $C^{11'}$), 24.5 (2C, C^{10}, $C^{10'}$), 32.5 (4C, C^8, $C^{8'}$, C^{12}, $C^{12'}$), 67.2 (2C, C^7)
9	126.3 (1C, C^5), 129.7 (1C, C^4), 135.0 (1C, C^2), 137.4 (1C, C^3), 147.7 (1C, C^6), 157.6 (1C, C^1), 168.1 (1C, C=N), 191.7, (1C, C=O) Cy groups: 24.8, 25.1, 25.5, 26.0, 31.3 (2C, C^8, C^{12}), 34.7 (2C, H_2NCy, C^2, C^6), 65.7 (1C, C^7)
12	126.2 (1C, C^5), 129.9 (1C, C^4), 131.3 (1C, C^2), 133.6 (1C, C^3), 148.7 (1C, C^6), 158.2 (1C, C=N), 159.0 (1C, C^1), 170.2 (1C, C=N–Pd) Cy groups: 25.2, 25.4, 25.5, 25.8, 26.0, 26.1, 33.6 (2C, C^8, C^{12}), 34.8 (2C, $C^{8'}$, $C^{12'}$), 36.7 (2C, H_2NCy, C^2, C^6), 55.3 (1C, H_2NCy, C^1), 65.4 (1C, C^7), 70.3 (1C, $C^{7'}$)
13	126.4 (1C, C^5), 129.9 (1C, C^4), 130.5 (1C, C^2), 133.8 (1C, C^3), 148.8 (1C, C^6), 158.1 (1C, C=N), 159.1 (1C, C^1), 170.5 (1C, C=N–Pd) Cy groups: 25.2, 25.5, 25.7, 26.0, 33.9 (2C, C^8, C^{12}), 34.8 (2C, $C^{8'}$, $C^{12'}$), 36.9 (2C, H_2NCy, C^2, C^6), 55.5 (1C, H_2NCy, C^1), 66.6 (1C, C^7), 70.3 (1C, $C^{7'}$)
14	126.5 (1C, C^5), 129.8 (1C, C^4), 129.9 (1C, C^2), 133.9 (1C, C^3), 148.9 (1C, C^6), 158.0 (1C, C=N), 159.5 (1C, C^1), 170.8 (1C, C=N–Pd) Cy groups: 25.2, 25.5, 25.6, 26.0, 34.1 (2C, C^8, C^{12}), 34.8 (2C, $C^{8'}$, $C^{12'}$), 36.9 (2C, H_2NCy, C^2, C^6), 56.0 (1C, H_2NCy, C^1) 68.6 (1C, C^7), 70.3 (1C, $C^{7'}$)
15	94.8 (5C, C_5H_5), 125.6 (1C, C^5), 128.1 (1C, C^4), 131.0 (1C, C^3), 140.5 (1C, C^2), 143.6 (1C, C^6), 163.1 (1C, C=N), 190.8 (1C, C=O) Cy groups: 23.8 (2C, C^9, C^{11}), 24.3 (1C, C^{10}), 34.1 (2C, C^8, C^{12}), 69.3 (1C, C^7)
16	26.5 [c] (1H, Me), 26.9 [c] (1H, Me), 99.3 [c] (1C, CH), 125.2 (1C, C^5), 129.7 (1C, C^4), 130.3 (1C, C^2), 132.4 (1C, C^3), 146.2 (1C, C^6), 155.6 (1C, C^1), 169.0 (1C, C=N), 185.4 [c] (1C, C–O), 187.1 [c] (1C, C–O), 190.8 (1C, C=O) Cy groups: 24.4 (1C, C^9, C^{11}), 24.7 (1C, C^{10}), 26.5 [c] (1C, Me), 26.9 [c] (1C, Me), 31.3 (2C, C^8, C^{12}), 65.6 (1C, C^7),
17	24.0 (2C, O_2CMe) 126.2 (2C, C^5), 129.8 (2C, C^4), 131.8 (2C, C^2), 133.4 (2C, C^3), 148.8 (2C, C^6), 157.9 (2C, C^1), 158.4 (2C, C=N), 169.8 (2C, C=N–Pd), 180.4 (2C, O_2CMe) Cy groups: 25.2, 25.5, 25.6, 26.0, 34.1 (4C, C^8, C^{12}), 34.8 (4C, $C^{8'}$, $C^{12'}$), 54.8 (2C, H_2NCy, C^1), 64.5 (2C, C^7), 70.3 (2C, $C^{7'}$)
18	127.9 (1C, C^5), 130.7 (2C, C^4), 133.5 (1C, C^3), 141.6 (1C, C^2), 148.3 (1C, C^6), 172.1 (1C, C=N), 192.1 (1C, C=O), 197.5 (1C, C≡O), 203.1 (1C, C≡O), 212.7 [d] (2C, C≡O) Cy groups: 25.3 (2C, C^9, C^{11}), 33.6 (2C, C^8, C^{12}), 72.5 (1C, C^7)
21	130.2 (2C, C^2, C^5), 142.7 (2C, C^1, C^4), 182.4 (2C, C^3, C^6), 172.2 (2C, C=N), 213.1 [d] (2C, C≡O), 193.6 (1C, C≡O), 191.6 (1C, C≡O) Cy groups: 25.3 (4C, C^9, C^{11}), 29.6, (2C, C^{10}), 33.5 (4C, C^8, C^{12}), 72.8 (2C, C^7)

$(O_2CMe)\}_2]$ (**17**), a dinuclear monocyclometallated complex of **1**, with regeneration of the C=N double bond. The ^{1}H NMR spectrum showed singlets at δ8.17 (1H, free C=N group) and δ7.83 (1H, coordinated C=N group); the remaining resonances were assigned accordingly (Table 1). The IR spectrum showed two ν(C=N) bands, at 1642 (non-coordinated C=N group) and 1615 (coordinated C=N group) cm^{-1}. As in the case of complex **2**, the ^{1}H NMR spectrum showed a singlet at δ7.98 (2H) assigned to the two equivalent *H*C=N protons; a doublet at δ7.16 (2H) and a triplet at δ7.05 (1H) were assigned to the H-4, H-6 and H-5 proton resonances, respectively.

Reaction of **1** with an aqueous solution of NaX (X = Cl, Br, I) gave the halide-bridged complexes $[\{Pd[3\text{-}(CHO)C_6H_3C(H)=NCy](X)\}_2]$ (**3**: X = Cl; **4**: X = Br; **5**: X = I), respectively, which were fully characterized (see Experimental section and Tables 1 and 2). Treatment of the mixture of **1** + **2** with aqueous NaX (X = Cl, Br, I) resulted in replacement of the acetato ligands by halide ligands, to give mixtures of $[Pd\{3\text{-}(CyN=CH)C_6H_3C(H)=NCy\}(X)]$ (**6**: X = Cl; **7**: X = Br; **8**: X = I) along with the corresponding halide-bridged complex **3**, **4** or **5**, respectively (see Scheme 1). Only in the case of compound **8** were we able to effect separation from the halide-bridged dimer, **5** (see Experimental section). The presence of **6** or **7** was unequivocally detected by ^{1}H NMR spectroscopy (Table 1); complex **8** was fully characterized by elemental analysis and by IR and ^{1}H and ^{13}C NMR spectroscopy (data in the Experimental section and in Tables 1 and 2), clearly showing coordination of both C=N groups to the palladium atom.

Although complexes similar to **2**, **6**, **7** and **8** have been described before for sp^3-N donor atoms [22a] and P-donor atoms [22b], to the best of our knowledge these are the first examples of cyclometallated complexes with two –C=N– groups of the same ligand simultaneously bonded to the metal centre, once again revealing the difference in the behaviour of $\mathbf{L^2}$ from that of the aforementioned 2,6-dialdiminobenzenes.

Treatment of the halide-bridged complexes **3**, **4** or **5** with cyclohexylamine did not produce the expected dimer compounds with two free C=N groups, analogous to **17**. Instead, two new types of complexes were produced: on the one hand, reaction of **3**, **4** or **5** with a 2 molar proportion of cyclohexylamine gave the mononuclear compounds $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}(X)(NH_2Cy)]$ (**9**: X = Cl; **10**: X = Br; **11**: X = I), respectively, containing a free formyl group (see Experimental section and Scheme 2); the ^{1}H NMR spectra showed singlet resonances for the *H*C=O and *H*C=N protons at δ9.84, δ7.89, **9**; δ9.58, δ 7.95, **10**; and δ9.91, δ7.83, **11**. The remaining proton resonances are included in Table 1. The IR spectra showed the ν(C=O) stretch at 1693 (**9**), 1692 (**10**) and 1692 cm^{-1} (**11**). On the other hand, reaction of **3**, **4** or **5** with a 4 molar proportion of cyclohexylamine gave the mononuclear compounds $[Pd\{3\text{-}(CyN=CH)C_6H_3C(H)=NCy\}(X)(NH_2Cy)]$ (**12**: X = Cl; **13**: X = Br; **14**: X = I), respectively, with regeneration of the C=N double bond (see Experimental section and Scheme 2); use of an excess of cyclohexylamine did not induce opening of the cyclometallated ring. The ^{1}H and ^{1C} NMR spectra showed singlet proton and carbon resonances for the free and the coordinated *H*C=N groups at δ8.18, δ158.2 and δ7.76, δ170.2, **12**; δ8.23, δ158.1 and δ7.86, δ170.5, **13**; and δ8.22, δ158.0 and δ7.89, δ170.8, **14**. The remaining resonances were assigned accordingly (Tables 1 and 2). The IR spectra showed the ν(C=N) stretches at 1641, 1615 (**12**), 1640, 1614 (**13**) and 1640, 1613 cm^{-1} (**14**).

Treatment of the halide-bridged complexes with thallium 2,4-pentanedionate or with thallium cyclopentadienyl gave the mononuclear complexes $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}(C_5H_5)]$ (**15**) and $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}(H_3CCOCHCOCH_3)]$ (**16**), respectively (Scheme 2), which were fully characterized (see Experimental section and Tables 1 and 2). The same products were obtained regardless of the halogen atom in the starting material. A singlet at δ5.84 (5H) in the ^{1}H NMR spectrum showed the equivalence of the five C*H* protons of the cyclopentadienyl ligand in complex **15**, and two carbonyl (δ185.4, δ187.1) and two methyl (δ26.4, δ26.9) resonances in the ^{13}C NMR spectrum showed the non-equivalence of the two coordination sites of the 2,4-pentadionate ligand in complex **16**.

2.2. Manganese(I) complexes

By the procedure we used previously [12], we carried out the cyclometallation of $\mathbf{L^2}$ in a non-acidic medium, i.e. octane, in the hope of obtaining a doubly cyclometallated complex of $\mathbf{L^2}$ with Mn(I). Thus, we heated a solution of $\mathbf{L^2}$ and $MnMe(CO)_5$ in a 1:2 molar ratio

Notes to Table 2

[a] In $CDCl_3$ unless stated otherwise. Measured at 62.8 MHz (ca. 20°C). Chemical shifts (δ) in ppm ($\pm$0.1 ppm) relative to high frequency of $SiMe_4$.

[b] In DMSO.

[c] Data for the 2,4-pentanedionate ligand.

[d] Data for the mutually *trans* carbonyl groups.

and obtained an inseparable mixture; this was probably a result of decomposition of the organic ligand, but we did not pursue it further. We then treated $\mathbf{L}^2$ with $MnMe(CO)_5$ in a 1 : 1 molar ratio and, contrary to our expectations, this did not produce the expected monocyclometallated complex **20** but instead gave the complex $[(OC)_4Mn\{3\text{-}(CHO)C_6H_3C(H)=NCy\}]$ (**18**) by cleavage of a C=N bond and formation of a free formyl group at C-3 (see Scheme 3). Complex **18** was fully characterized (see Experimental section and Tables 1 and 2). The ^1H NMR spectrum showed singlets at δ9.96 (1H) and δ8.46 (1H), assigned to the *HC*=O and *HC*=N resonances, respectively. The ^{13}C NMR spectrum showed singlets at δ192.1 and δ172.1 for the C=O and C=N resonances, respectively; the carbonyl resonances were at δ197.7 (1C, *trans* to N), δ203.1 (1C, *trans* to C-6) and δ212.7 (2C, mutually *trans* C≡O groups). The ν(C≡O) bands appeared at 1987, 1978 and 1933 cm^{-1}.

We then heated solutions of $\mathbf{L}^2$ and $MnMe(CO)_5$ in various molar ratios to no avail, and only in the case depicted in Scheme 3, reaction ii, were we able to identify any product complexes. Thus, reaction of $\mathbf{L}^2$ with $MnMe(CO)_5$ in a 1 : 1.2 molar ratio in boiling octane for 4 h gave a yellow solid, which was a mixture of **19** and **20**, from which neither complex could be isolated pure. However, the presence of complexes **19** and **20** was unambiguously established by ^1H NMR spectroscopy (Table 1). We previously prepared and characterized the doubly cyclometallated complex **21**, derived from the ligand 1,4-$(CyN=CH)_2C_6H_4$ ($\mathbf{L}^1$) (Scheme 3, reaction iii); but in view of the results described in the present paper, we decided to re-examine the chemistry of $\mathbf{L}^1$. We found that treatment of $\mathbf{L}^1$ with $MnMe(CO)_5$ in the manner described, i.e. with a 1 : 1.2 molar ratio in refluxing octane for 5 h, gave a yellow solid, which proved to be a mixture of **22** and **23** (see Scheme 3, reaction iv). This was chromatographed on a column of silica gel with dichloromethane as eluent to give a band which was shown to contain **23** as the major product along with some of complex **22**. ^1H NMR spectroscopy allowed us to establish unequivocally the presence of both compounds in the final mixture (Table 1). Further attempts to separate them failed, but most of **22** was eluted with dichloromethane–ethanol (1%) and the complex was isolated pure after concentration (see Experimental section). In the ^1H NMR spectrum, two singlets at δ9.96 and δ8.46 were assigned to the *HC*=O and *HC*=N resonances, respectively. The IR spectrum showed a band at 1691 cm^{-1} for ν(C=O) and a band at 1625 cm^{-1} for ν(C=N).

These findings illustrate the chemical versatility of ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ towards various metal salts in acidic and non-acidic reaction media. At present we are investigating new aspects of their chemistry and attempting to obtain heterodicyclometallated complexes through the uncoordinated C=N group, as well as bringing about bridge-splitting reactions with neutral ligands such as tertiary phosphines.

3. Experimental details

All reactions were carried out under dry nitrogen. Solvents were purified by standard methods [23]. Chemicals were of reagent grade. Palladium(II) acetate, thallium acetylacetonate and thallium cyclopentadienyl were purchased from Aldrich-Chemie. $MnMe(CO)_5$ was prepared as described previously [24]. Microanalyses were carried out at the Sevicio de Análisis Elemental at the University of Santiago using a Carlo Erba Model 1108 elemental analyser. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer Model 1330 spectrophotometer and on a Matson (Servicio de Espectroscopía of the University of Santiago) spectrophotometer. NMR spectra were obtained with $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C), and were recorded on a Bruker WM-250 spectrometer. All chemical shifts are reported downfield from the standards.

1,3-$(CyN=CH)_2C_6H_4$ ($\mathbf{L}^2$) was prepared by heating a chloroform solution of the appropriate quantities of isophthalaldehyde and cyclohexylamine in a Dean–Stark apparatus under reflux. The synthesis of 1,4-$(CyN=CH)_2C_6H_4$ was described previously [12].

3.1. Preparation of $[\{Pd[3\text{-}(CHO)C_6H_3C(H)=NCy]\text{-}(O_2CMe)\}_2]$ (1) and $[Pd\{3\text{-}(CyN=CH)C_6H_3\text{-}C(H)=NCy\}(O_2CMe)]$ (2)

An orange solution of 1,3-$(CyN=CH)_2C_6H_4$ (0.58 g, 1.9 mmol) and palladium(II) acetate (0.4 g, 1.78 mmol) in 45 cm^3 of glacial acetic acid was heated under reflux for 5 h, then allowed to cool to room temperature. The acetic acid was then removed under vacuum, water was added to the residue and the products were extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give an orange solid. This was chromatographed on a column of silica gel, with dichloromethane as eluent, to give a mixture of **1** and **2** as a yellow solid. Subsequent elution with dichloromethane–ethanol (1%) afforded product **1** as a bright yellow solid. Yield: 65% (**1**), 15% (**1** + **2**) (Found: **1**, C, 50.4; H, 5.00; N, 3.71. $C_{32}H_{38}N_2O_6Pd_2$ requires C, 50.61; H, 5.04; N, 3.69%). IR (for **1**): ν(C=O) 1695s, ν(C=N) 1605m, ν_{as}(COO) 1570s, ν_s(COO) 1410s cm^{-1}.

3.2. Preparation of $[\{Pd[3\text{-}(CHO)C_6H_3C(H)=NCy]\text{-}(Cl)\}_2]$ (3)

An aqueous solution of NaCl (ca. 10^{-2} M) was added dropwise to a solution of **1** (0.1 g, 0.13 mmol) in

acetone (5 cm^3). The product separated immediately as a yellow solid. After stirring for 1 h, the solid was filtered off recrystallized from dichloromethane–hexane as a yellow solid. Yield: 87%. (Found: C, 47.1; H, 4.55; N, 3.91. $C_{28}H_{32}N_2Cl_2O_2Pd_2$ requires C, 47.21; H, 4.53; N, 3.93%). IR: ν(C=O) 1690m, ν(C=N) 1615s, ν(Pd–Cl) 290m, 255m cm^{-1}.

The following compounds were made similarly: [{Pd[3-(CHO)C_6H_3C(H)=NCy](Br)}$_2$] (**4**) Yield: 85% (Found: C, 41.8; H, 4.0; N, 3.41. $C_{28}H_{32}N_2Br_2O_2Pd_2$ requires C, 41.97; H, 4.03; N, 3.5%). IR: ν(C=O) 1685s, ν(C=N) 1600m cm^{-1}. [{Pd[3-(CHO)C_6H_3C(H)=NCy](I}$_2$] (**5**). Yield: 83% (Found: C, 37.5; H, 3.55; N, 3.9. $C_{28}H_{32}N_2I_2O_2Pd_2$ requires C, 37.57; H, 3.60; N, 3.93%). IR: ν(C=O) 1690s, ν(C=N) 1615m cm^{-1}.

3.3. Preparation of [Pd{3-(CyN=CH)C_6H_3C(H)=NCy}(I)] (8)

An aqueous solution of NaI (ca. 10^{-2} M) was added dropwise to a solution of **1** and **2** in acetone. After stirring for 1 h, the precipitated solid was filtered off and chromatographed on silica gel, with dichloromethane an eluent, to give **8** as a yellow solid (Found: C, 45.52; H, 5.07; N, 5.12. $C_{20}H_{27}N_2IPd$ requires C, 45.43; H, 5.15; N, 5.30%). IR: ν(C=N) 1604m cm^{-1}.

3.4. Preparation of [Pd{3-(CHO)C_6H_3C(H)=NCy}(Cl)(NH_2Cy)] (9)

A mixture of **3** (50 mg, 0.07 mmol) and cyclohexylamine (14 mg, 0.15 mmol) in chloroform (25 cm^3) was heated under reflux for 4 h in a Dean–Stark apparatus and then allowed to cool to room temperature. The solution was evaporated to small volume under reduced pressure and hexane was added to give **9** as an orange solid in 73% yield (Found: C, 52.56; H, 6.3; N, 6.2. $C_{20}H_{29}N_2ClOPd$ requires C, 52.76; H, 6.42; N, 6.15%) IR: ν(C=O) 1693s, ν(C=N) 1605m cm^{-1}.

The same procedure was used to prepare [Pd{3-(CyN=CH)C_6H_3C(H)=NCy}(Cl)(NH_2Cy)] (**12**) in 70% yield from **3** (50 mg, 0.07 mmol) and cyclohexylamine (0.03 mg, 0.31 mmol) (Found: C, 58.4; H, 7.45; N, 7.74. $C_{26}H_{40}N_3ClPd$ requires C, 58.21; H, 7.51; N, 7.83%). IR: ν(C=N) 1641m, 1615m, ν(Pd–Cl) 306m cm^{-1}.

The following compounds were made analogously: [Pd{3-(CHO)C_6H_3C(H)=NCy}(Br)(NH_2Cy)] (**10**). Yield: 55% (Found: C, 48.2; H, 5.9; N, 5.73. $C_{20}H_{29}N_2BrOPd$ requires C, 48.07; H, 5.85; N, 5.61%). IR: ν(C=O) 1692s, ν(C=N) 1616m cm^{-1}. [Pd{3-(CHO)C_6H_3C(H)=NCy}(I)(NH_2Cy)] (**11**). Yield: 65% (Found: C, 43.82; H, 5.2; N, 4.95. $C_{20}H_{29}N_2IOPd$ requires C, 43.93; H, 5.35; N, 5.12%). IR: ν(C=O) 1692s, ν(C=N) 1614m cm^{-1}. [Pd{3-(CyN=CH)C_6H_3C(H)=NCy}(Br)(NH_2Cy)] (**13**). Yield: 50% (Found: C, 53.9; H, 6.73; N, 7.1. $C_{26}H_{40}N_3BrPd$ requires C, 53.75; H, 6.94; N, 7.23%). IR: ν(C=N) 1640m, 1614m cm^{-1}. [Pd{3-(CyN=CH)C_6H_3C(H)=NCy}(I)(NH_2Cy)] (**14**). Yield: 60% (Found: C, 49.5; H, 6.25; N, 6.43. $C_{26}H_{40}N_3IPd$ requires C, 49.73; H, 6.42; N, 6.69%). IR: ν(C=N) 1640m, 1613m cm^{-1}.

3.5. Preparation of [Pd{3-(CHO)C_6H_3C(H)=NCy}(C_5H_5)] (15)

To a suspension of **3** (50 mg, 0.07 mmol) in chloroform was added thallium cyclopentadienyl (39 mg, 0.15 mmol). The mixture was refluxed for 4 h and the resulting solution was chromatographed on silica gel, with chloroform as eluent, to give complex **15**, which was recrystallized from dichloromethane/hexane to give an orange solid in 85% yield (Found: C, 59.3; H, 5.2; N, 3.45. $C_{19}H_{21}NOPd$ requires C, 59.15; H, 5.49; N, 3.63%). IR: ν(C=O) 1685s, ν(C=N) 1600sh, m cm^{-1}.

3.6. Preparation of [Pd{3-(CHO)C_6H_3C(H)=NCy}($H_3CCOCHCOCH_3$)] (16)

To a suspension of **3** (50 mg, 0.07 mmol) in chloroform was added thallium-2,4-pentanedionate (45 mg, 0.15 mmol). The mixture was stirred at room temperature for 2 h and the mixture was then chromatographed on silica gel, with dichloromethane–chloroform (3 : 1) as eluent, to give a yellow solid, which was recrystallized from dichloromethane–hexane to give **16** as a yellow solid in 86% yield (Found: C, 54.2; H, 5.03; N, 3.1. $C_{19}H_{23}NO_3Pd$ requires C, 54.36; H, 5.22; N, 3.34%). IR: ν(C=O) 1690s, ν(C=N) 1605sh, m, ν(C–O) 1580s, 1515s cm^{-1}.

3.7. Preparation of [{Pd[3-(CyN=CH)C_6H_3C(H)=NCy](O$_2$CMe)}$_2$] (17)

By the procedure used for **9**, **17** was prepared from **1** (50 mg, 0.05 mmol) and cyclohexylamine (10 mg, 0.1 mmol) as a yellow solid in 65% yield (Found: C, 55.34; H, 6.28; N, 5.86. $C_{44}H_{60}N_4O_4Pd_2 \cdot 0.5CH_2Cl_2$ requires C, 55.54: H, 6.39: N, 5.82%). IR: ν(C=N) 1642, 1615m, ν_{as}(COO) 1570s, ν_s(COO) 1398s cm^{-1}.

3.8. Preparation of [(OC)$_4$Mn{3-(CHO)C_6H_3C(H)=NCy}] (18)

A solution of the ligand 1,3-(CyN=CH)$_2C_6H_4$ (L^2) (50 mg, 0.17 mmol) and [MnMe(CO)$_5$] (36 mg, 0.17 mmol) in octane (25 cm^3) was heated under reflux for 4 h. It was then allowed to cool to room temperature and the precipitate that appeared was filtered off and the

filtrate concentrated to give **18** as an orange solid in 54% yield (Found: C, 56.52; H, 4.06; N, 3.5. $C_{18}H_{16}NO_5Mn$ requires C, 56.71; H, 4.23; N, 3.67%). IR: ν(C≡O) 1987s, 1978sh, m, 1933s, ν(C=O) 1691m, ν(C=N) 1605m cm^{-1}.

3.9. Preparation of $[(OC)_4\overline{Mn\{4\text{-}(CHO)C_6H_3C(H)=NCy\}}]$ (22)

A solution of the ligand 1,4-$(CyN{=}CH)_2C_6H_4$ (L^1) (50 mg, 0.17 mmol) and $[MnMe(CO)_5]$ (36 mg, 0.17 mmol) in octane (25 cm^3) was heated under reflux for 5 h. It was then allowed to cool to room temperature and the yellow precipitate that formed was filtered off and chromatographed on silica gel, with dichloromethane–ethanol (1%) as eluent, to give **22** as a yellow solid in 54% yield (Found: C, 56.82; H, 4.37; N, 3.8. $C_{18}H_{16}NO_5Mn$ requires C, 56.71; H, 4.23; N, 3.67%). IR: ν(C≡O) 1985s, 1969sh,m, 1926s, ν(C=O) 1691m, ν(C=N) 1605m cm^{-1}.

Compound **21** was prepared as previously described [12].

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