Journal of Organometallic Chemistry, 445 (1993) 287–294

JOM 23125

Cyclometallated complexes of Pd^{II} and Mn^{I} with *N,N*-terephthalylidenebis(cyclohexylamine)

José M. Vila, Miguel Gayoso, M[a]. Teresa Pereira, Margarita López, Gabino Alonso and Jesús J. Fernández

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

(Received June 4, 1992)

Abstract

Treatment of *N,N*-terephthalylidenebis(cyclohexylamine), 1,4-(CyN=CH)$_2$C$_6$H$_4$ (Cy = cyclohexyl) with palladium(II) acetate in glacial acetic acid gave the monocyclometallated dimer complex [{Pd[4-(CHO)C$_6$H$_3$CH=NCy](O$_2$CMe)}$_2$] (**1**) which was shown to have a free formyl group on each phenyl ring by IR and ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy. Treatment of 1,4-(CyN=CH)$_2$C$_6$H$_4$ with [MnMe(CO)$_5$] in octane gave the doubly cyclometallated complex [(OC)$_4$MnN(Cy)=C(H)CC$_6$H$_2$C(H)=N(Cy)Mn(CO)$_4$] (**2**). Reaction of **1** with aqueous sodium chloride, bromide or iodide gave the monocyclometallated dimer complexes [{Pd[4-(CHO)C$_6$H$_3$C(H)=NCy](X)}$_2$] [X = Cl (**3**), Br (**4**), or I (**5**)]. Complexes **1**, **3** and **4** react with amines to give the corresponding cyclometallated dimer complexes [Pd{4-(CyN=CH)C$_6$H$_3$C(H)=NCy}(O$_2$CMe)]$_2$ (**6**) and [{Pd[4-(CyN=CH)C$_6$H$_3$C(H)=NR](X)}$_2$] [X = Cl (**7**), X = Br (**8**) R = Cy; X = Cl, R = 2,4,6-Me$_3$C$_6$H$_2$ (**9**)] with an uncoordinated C=N group on each phenyl ring. Treatment of **3**, **4** or **5** with thallium acetylacetonate gave the cyclometallated monomer compound [Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}(CH$_3$COCHCOCH$_3$)] (**10**) with a chelating 2,4-pentanedionate group. Treatment of **3**, **4** or **5** with tertiary phosphines in a dimer/phosphine 1:2 or 1:4 molar ratio afforded the cyclometallated [Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}(X)(L)] (**11–18**) and non-cyclometallated [Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}(X)(L)$_2$] (**25–31**) (X = Cl, Br, or I; L = PPh$_3$, PPh$_2$Et, PPhEt$_2$, or PPh$_2$Me). Reaction of **11–13** with cyclohexylamine (L = PPh$_3$) gave the non-cyclometallated compounds [Pd{4-(CyN=CH)C$_6$H$_3$C(H)=NCy}(X)(PPh$_3$)(NH$_2$Cy)] (**19–21**) with two uncoordinated C=N groups whereas reaction of **14–18** with cyclohexylamine (L = PPh$_2$Et, PPhEt$_2$, or PPh$_2$Me) gave the cyclometallated compounds [Pd{4-(CyN=CH)C$_6$H$_3$C(H)=NCy}(X)(L)] (**22–24**). Compounds **25** and **29** gave [Pd{4-(CyN=CH)C$_6$H$_3$C(H)=NCy}(Cl)(L)$_2$] (**32,33**) (L = PPh$_3$, or PPh$_2$Et) when treated with cyclohexylamine. IR and ^{1}H, ^{13}C and ^{31}P NMR data are discussed.

1. Introduction

Cyclometallated complexes have been the subject of much attention in recent years [1,2]. We have been investigating the cyclometallation of ligands with one nitrogen-donor atom such as Schiff bases [3,4] and phenylimidazoles [5], and more recently that of ligands with two nitrogen-donor atoms such as bis(benzylidene)hydrazones [6] and bis(benzylidene)phenylenediamines [7]. One feature of diimine ligands of type **I** derived from terephthalaldehydes is the possibility of double metallation of a phenyl ring to give species of types **II** and **III**.

We felt it might be possible to induce double cyclometallation in **I** (R = Cy, **a** throughout the text) as we have done previously in other diimines [6,7] with double metallation in this case taking place on a single phenyl ring; this kind of metallation has been achieved before [8] and a doubly metallated dioxime derivative has been made recently [9]. However, the spectroscopic data for the compounds synthesized so far in our laboratory suggest that double metallation has not been produced and instead palladation at only one carbon atom is achieved. This produces an *ortho*-palladated Schiff base with a formyl group in the *meta* position to the M–C σ-bond; such a ligand system is hitherto unknown. In this paper we describe the synthesis and characterization of mono-palladated acetato- and halide-bridged dimer complexes and the study of some

Correspondence to: Dr. J.M. Vila.

0022-328X/93/$6.00

© 1993 – Elsevier Sequoia S.A. All rights reserved

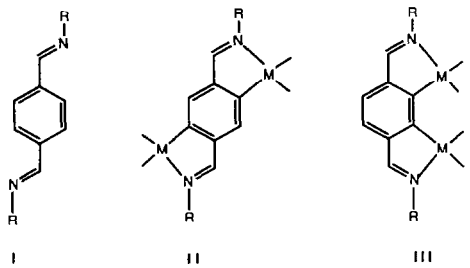


Fig. 1.

of their reactions with: (a) amines, to give dimer species with an uncoordinated C=N group; (b) (for the halide-bridged complexes) bridge splitting reactants, such as thallium acetylacetonate and tertiary phosphines, to give the corresponding monomeric complexes. Further reactions of type (a) with the monomeric complexes have also been carried out.

We hoped that different experimental conditions would give a doubly cyclometallated derivative of **a**. Although double metallation with palladium was not successful, in non-acidic media using Mn^{I} double metallation of **a** was possible.

2. Results and discussion

Treatment of *N,N*-terephthalylidenebis(cyclohexylamine), 1,4-$(CyN{=}CH)_2C_6H_4$ with an appropriate amount of palladium(II) acetate in glacial acetic acid under reflux gave the acetato-bridged cyclometallated dimer complex **1** in 60% yield (details in the Experimental section). The reaction did not produce the hoped-for complex of type **II** or of type **III**, with a doubly cyclometallated ligand; instead the dimer species **1** with a formyl group in *meta* position to the Pd–C σ-bond was obtained. The complex was characterized by elemental analysis (C, H and N), IR and NMR spectroscopy. The ^{1}H NMR spectrum (see Table 2) shows a doublet at δ 7.34 assigned to the H3 proton and the resonances of the H5 and H6 protons (AB spin system) as a doublet of doublets (H5, also coupled to H3) and a doublet (H6) at δ 7.52 and δ 7.20, respectively; ^3J[H(5)H6)] = 7.6 Hz, ^4J[H(3)H(5)] = 1.5 Hz. Singlets at δ 9.94 (1H), and δ 7.56 (1H) were assigned to the *H*C=O and *H*C=N proton resonances, respectively. A singlet at δ 2.20 was assigned to the two equivalent methyl groups, MeCOO, suggesting that the ligands are in a *trans* disposition [10]. The ^{13}C-{^{1}H} NMR spectrum (see Table 3) confirmed the assigned structure with resonances at δ 192.1 (HC=O), δ 181.4 (COO) and δ 167.6 (C=N); the last is shifted towards higher frequency compared to the free donor by *ca.* 10 ppm. The resonance for C2 is shifted towards higher frequency by *ca.* 30 ppm compared to the free donor, confirming that metallation has occurred [11]. The C1 resonance is also shifted towards higher frequency upon metallation. There was no noticeable quadrupolar broadening of these resonances by coupling with the ^{105}Pd (22.2% natural abundance, $I = 5/2$) nucleus.

The other phenyl and cyclohexyl resonances were assigned accordingly (data in Table 3). The singlet resonance at δ 24.3 was assigned to the methyl acetate carbon atoms, consistent with a *trans* geometry of the cyclometallated moieties (*vide supra*). The IR spectrum shows a carbonyl stretch at 1690 cm^{-1}; also assigned are ν(C=N) at 1605 cm^{-1} and ν_{as}(COO) and ν_s(COO) at 1576 and 1420 cm^{-1}, respectively; the last two are consistent with bridging acetate ligands [12]. Coordination of the metal to the C=N nitrogen atom is shown by the shift of the IR ν(C=N) stretching vibration to lower wave numbers [13,14] and by the upfield shift of the *H*C=N proton resonance in the ^{1}H NMR spectrum [15].

On the basis of the experimental results, one would be inclined to believe that mono-cyclometallation takes place, the unbound C=N double bond being cleaved during column chromatography on silica gel to produce a formyl group. This would be contrary to other experimental results which show that metallation of a phenyl ring promotes a second metallation of the same ring [8]. However, we propose that, rather surprisingly, one C=N double bond is cleaved in the acidic reaction medium whereas the other C=N bond is involved in the cyclometallated ring. Attempts to cyclometallate the ligand through the C=O group failed.

We then heated the free donor in glacial acetic acid under reflux for 4 h and we obtained a mixture in which the major product (as shown by ^{1}H NMR) is compound **b** where one C=N bond was cleaved; also present were cyclohexylamine and terephthalaldehyde. We were not successful in isolating **b** from the mixture. The ^{1}H NMR spectrum is in agreement with the assigned formula for **b**.

Thus, singlet resonances at δ 9.94 (1H) and δ 8.28 (1H) are assigned to the *H*C=O and *H*C=N protons, respectively. An apparent triplet, typical of an AA′XX′ spin system, is assigned to the C_6H_4 protons. The cyclohexyl resonances appear *ca.* δ 3.2 and δ 1.5. The

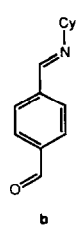


Fig. 2.

IR spectrum shows a carbonyl stretch at 1690 cm^{-1} and a C=N stretch at 1635 cm^{-1}.

We thought that in a non-acidic medium, where cleavage of the C=N double bond would be negligible, the ligand would be doubly cyclometallated. Thus, treatment of 1,4-$(CyN{=}CH)_2C_6H_4$ with the appropri-

TABLE 1. Microanalytical, colour, yield and IR data

		Colour	Yield (%)	Analytical data, found (calc.)(%)			IR data (cm^{-1}) [a]		
				C	H	N	ν(C=O) [b]	ν(C=N) [c]	ν(Pd–Cl)
1		Orange	75	50.4(50.6)	5.0(5.0)	3.3(3.7)	1690s	1605sh,m	
2		Yellow	52	53.6(53.5)	4.2(4.2)	4.0(4.5)	1982m 1960m 1915s	1600m	
3		Yellow	85	47.3(47.2)	4.7(4.5)	3.7(3.9)	1695vs	1607s	285m 240m
4	CH_2Cl_2	Dark yellow	85	38.8(39.3)	3.9(3.9)	2.9(3.2)	1695s	1609m	
5	$1.5CH_2Cl_2$	Dark yellow	93	34.4(34.6)	3.3(3.4)	2.8(2.7)	1690s	1605m	
6		Orange	91	57.0(57.3)	6.4(6.6)	6.1(6.1)		1630m 1605m	
7		Orange	89	54.4(54.9)	6.7(6.2)	5.9(6.4)		1625sh,m 1608m	280m 257m
8	$2.5CHCl_3$	Orange	85	40.8(40.5)	4.8(4.5)	4.1(4.4)		1635sh,m 1610m	
9	$1.5CHCl_3$	Dark yellow	63	50.5(50.6)	5.1(5.0)	5.0(5.0)		1615sh,m 1605m	305m 260m
10		Yellow	85	51.8(52.0)	5.6(5.5)	3.1(3.0)	1689vs	1605sh,m	
11	$1.5CH_2Cl_2$	Yellow	81	59.0(59.1)	4.9(4.9)	2.3(2.1)	1692s	1619m	309m
12		Light yellow	80	58.3(58.0)	4.8(4.7)	2.0(2.1)	1685s	1614m	
13	$0.25CHCl_3$	Yellow	87	52.4(52.4)	4.4(4.3)	1.9(1.9)	1685s	1615m	
14	$0.5CHCl_3$	Light yellow	75	52.6(52.1)	5.9(5.7)	2.3(2.5)	1690vs	1620m	285m
15	$CHCl_3$	Orange	60	43.9(43.8)	5.2(4.7)	2.0(2.0)	1685s	1615m	
16		Yellow	73	47.3(47.0)	5.0(5.1)	2.0(2.3)	1680s	1608m	
17		Light yellow	72	58.9(59.0)	5.4(5.5)	2.5(2.5)	1680s	1612m	315m
18		Yellow	75	58.8(58.3)	5.5(5.3)	2.8(2.5)	1692vs	1615m	289m
19	$2CHCl_3$	Yellow	71	53.3(53.3)	4.9(5.4)	3.5(4.0)		1632m 1615m	280m
20	$1.5CH_2Cl_2$	Orange	80	56.8(56.3)	6.5(6.0)	4.0(4.3)		1635m 1615m	
21	$CHCl_3$	Yellow	69	54.0(53.5)	6.0(5.6)	4.2(4.2)		1630m 1610m	
22	$0.5CHCl_3$	Yellow	74	54.7(55.2)	6.7(6.5)	3.8(4.2)		1640sh,m 1620m	270m
23		Yellow	67	53.2(53.9)	5.4(5.6)	3.3(3.7)		1635sh,m 1620m	275m
24	$0.33CH_2Cl_2$	Yellow	65	60.1(60.6)	6.2(5.9)	4.2(4.3)		1630sh,m 1620m	302m
25		White	78	68.4(68.2)	4.8(5.3)	1.5(1.6)	1681s	1621m	292m
26	$CHCl_3$	Orange	92	59.0(58.6)	4.8(4.5)	1.3(1.3)	1685m	1621m	
27	$1.5CHCl_3$	Yellow	90	54.4(53.7)	4.0(4.4)	1.0(1.2)	1687s	1628m	
28	$0.5CHCl_3$	Light yellow	58	55.0(55.4)	6.9(6.4)	1.9(1.9)	1683vs	1615m	285m
29	CH_2Cl_2	Pale yellow	63	59.0(59.4)	5.5(5.6)	1.6(1.6)	1685vs	1615sh,m	290m
30	$0.33CH_2Cl_2$	Yellow	80	59.3(59.3)	6.0(5.5)	1.6(1.6)	1684vs	1622m	
31		Yellow	66	57.5(57.6)	5.3(5.3)	1.7(1.6)	1685vs	1627m	
32	$0.5CHCl_3$	Yellow	93	66.4(66.4)	5.4(5.7)	2.8(2.7)		1635m 1622m	304m
33	$CHCl_3$	Yellow	90	60.2(59.7)	6.4(5.9)	3.0(2.8)		1620m 1610sh,m	320m

[a] vs, very strong; s, strong; m, medium; sh, shoulder.
[b] ν(C=O) values (in cm^{-1}): **b**, 1690.
[c] ν(C=N) values (in cm^{-1}): **a**, 1638; **b**, 1635.
[d] ν(COO) values (in cm^{-1}): **1**, ν_{as}(COO) 1576s; ν_s(COO) 1420s; **6**, ν_{as}(COO) 1570s; ν_s(COO) 1410s.
[e] 2,4-Pentanedionate: ν(C ⋯ C) 1580s; ν(C ⋯ O) 1514s.

ate amount of $[MnMe(CO)_5]$ in boiling octane gave the doubly cyclometallated complex **2** in 52% yield (details in the Experimental section and microanalytical data in Table 1). The ^1H NMR spectrum (data in Table 2) showed two singlets at δ 8.40 and δ 8.09 assigned to the *H*C=N (2H) and C_6H_2 (2H) resonances, respec-

TABLE 2. ^1H [a,b] and $^{31}P\{^1H\}$ [c] NMR data for the complexes [d]

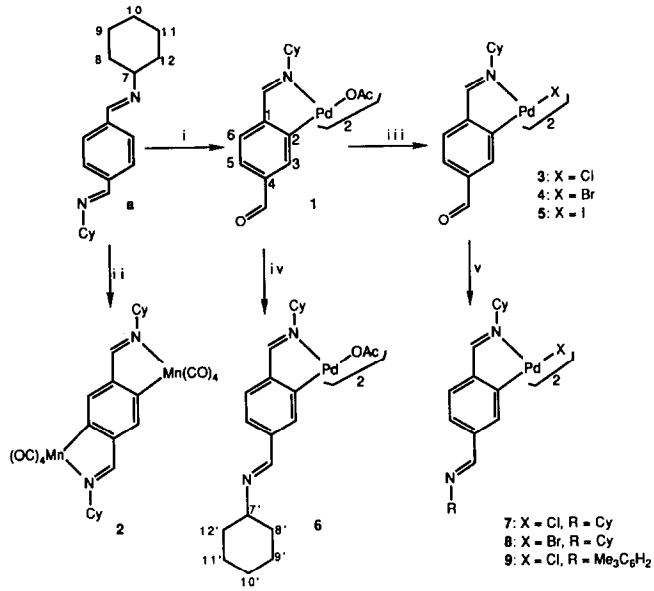
	δ(HC=O)	δ(HC=N)	δ(H(3))	δ(H(5))	δ(H(6))	δ(P)	^4J(PH) [e]	^4J[PH(3)]
1 [f]	9.94s	7.56s	7.34d ^3J[H(3)H(5)] = 1.5	7.52dd ^3J[H(5)H(6)] = 7.6	7.20			
2		8.40s	8.09s		8.09s			
3	9.97s	7.95s	7.87d ^3J[H(3)H(5)] = 1.3	7.60d ^3J[H(5)H(6)] = 7.6	7.35			
4	9.98s	8.05s	7.99s	7.60d ^3J[H(5)H(6)] = 7.5	7.38d			
5	9.96s	8.07s	8.00s	7.62d ^3J[H(5)H(6)] = 7.6	7.40d			
6 [f]		8.20s 7.86s	7.21d ^3J[H(3)H(5)] = 1.2	7.37dd ^3J[H(5)H(6)] = 7.7	7.24d			
7		7.97s 7.81s	6.93s	7.58d ^3J[H(5)H(6)] = 7.8	7.18d			
8		8.05s 7.81s	7.19s	7.60d ^3J[H(5)H(6)] = 7.7	7.37d			
9 [g]		8.18s 7.87s	6.87s	7.59d ^3J[H(5)H(6)] = 7.8	7.43d			
10 [h]	9.98s	7.97s	7.94d ^3J[H(3)H(5)] = 1.5	7.53dd ^3J[H(5)H(6)] = 7.7	7.33d			
11 [i]	9.15s	8.22d	6.73dd ^3J[H(3)H(5)] = 1.1			39.3s	8.5	5.9
12 [i]	9.17s	8.22d	6.80d			39.8s	8.0	5.4
13 [i]	9.18s	8.25d	6.79dd ^3J[H(3)H(5)] = 1.1			39.7s	7.7	6.3
14 [i]	9.38s	8.14d	6.87d			32.1s	7.9	6.6
15 [i]	9.38s	8.15d	6.87d			33.5s	7.3	5.4
16 [i]	9.38s	8.13d	6.86dd ^3J[H(3)H(5)] = 1.1			34.4s	7.6	5.7
17 [i]	9.23s	8.15d	6.86d			34.3s	8.2	5.8
18 [i]	9.20s	8.15d	6.74dd ^3J[H(3)H(5)] = 1.1			34.5s	8.5	7.0
19 [i]		8.12s	6.62s			39.5s		
20 [i]		8.16s	6.64s			39.4s		
21 [i]	8.19s	6.65s				39.8s		
22 [i]		8.05d	6.87d			31.6s	8.1	6.3
23 [i]		8.16d	6.85d			34.1s	8.0	6.5
24 [i]		8.06d	6.63d			35.0s	8.1	5.5
25 [i]	9.16s	8.21s	6.79s			27.5s		
26 [i]	9.17s	8.38s	6.83s			27.5s		
27 [i]	9.18s	8.69s	6.85s			27.4s		
28 [i]	9.57s	8.45s	7.11s			9.8s		
29 [i]	9.24s	8.18s	6.87s			10.5s		
30 [i]	9.33s	8.56s	7.04s			12.7s		
31 [i]	9.37s	8.54s	7.04s			16.5s		
32 [i]		8.16s	6.81s			27.3s		
33 [i]		8.10s	6.84s			12.0		

[a] Data for the free ligand: δ 8.32 (2H, s, *H*C=N); δ 7.74 (4H, s, C_6H_4).
[b] In $CDCl_3$. Measured at 250 MHz (*ca.* +20°C). Chemical shifts (δ) in ppm ($\pm$0.01 ppm) relative to high frequency of $SiMe_4$; coupling constants in Hz ($\pm$0.1 Hz).
[c] In $CDCl_3$. Measured at 100.6 MHz (*ca.* +20°C). Chemical shifts (δ) in ppm ($\pm$0.1 ppm) relative to high frequency of 85% H_3PO_4.
[d] s, singlet; d, doublet; dd, doublet of doublets.
[e] Coupling of phosphorus to the *H*C=N proton.
[f] **1** δ 2.20 (6H, s, CH_3COO); **16** δ 2.17 (6H, s, CH_3COO).
[g] δ 6.77 (2H, s, MeC_6H_2).
[h] 2,4-Pentanedionate δ 5.36 (1H, s, C*H*); δ 2.12 (3H, s, CH_3); δ 2.07 (3H, s, CH_3).
[i] The H(5) and H(6) resonances are obscured by the phosphine resonances.

tively. The carbon-13 NMR spectrum (data in Table 3) was in agreement with the assigned structure **2**. The carbonyl resonances were at δ 213.1 (due to the two mutually *trans* carbonyls) and at δ 193.6 and δ 191.6 ppm. The IR spectrum shows the ν(C=O) bands at 1960, 1922, and 1915 cm^{-1}.

Treatment of **1** with aqueous NaX (X = Cl, Br, or I) gave the chloro (**3**), bromo (**4**), or iodo-bridged (**5**) complexes, respectively (details in the Experimental section). They have been fully characterized by elemental microanalysis (C, H, and N), and by IR and NMR spectroscopy (data in Tables 1–3). We have effected the regeneration of the second C=N double bond in complexes **1**, **3** and **4** which gave the monocyclometallated complexes of ligand **a**. Thus, reaction of the acetato-bridged, **1**, or of the halide-bridged complexes, **3** and **4**, with cyclohexylamine in boiling chloroform for 3 h gave **6–8**, respectively (see Experimental section and Tables 1–3). The IR spectrum showed two ν(C=N) bands at 1630, 1605 cm^{-1} (**6**), 1625, 1608 cm^{-1} (**7**) and 1635, 1610 cm^{-1} (**8**); the second in each case corresponds to the C=N moiety bonded to the metal atom [13,14]. The ^1H NMR spectrum shows two singlet resonances for each compound at δ 8.20, δ 7.86 (**6**), δ 7.97, δ 7.81 (**7**), δ 8.05, δ 7.81 (**8**); the first (higher frequency) in each case is assigned to the free *H*C=N proton and the second (lower frequency) to the *H*C=N proton of the cyclometallated ring [15]. The remaining resonances have been assigned accordingly (data in Table 2).

Other amines may be used to give analogous monocyclometallated complexes. Thus, treatment of **3** with 2,4,6-trimethylaniline gives complex **9** in good yield



Scheme 1. (i) $Pd(OAc)_2$, glacial acetic acid, reflux; (ii) $[MnMe(CO)_5]$, octane, reflux; (iii) NaX (X = Cl, Br, or I) in aqueous acetone; (iv) $CyNH_2$, chloroform, reflux; (v) $CyNH_2$ or $Me_3C_6H_2NH_2$, chloroform, reflux.

(see Experimental section and Tables 1 and 2). This species contains a metallated asymmetric Schiff base ligand. Treatment of **9** with $LiAlH_4$ should provide a new synthetic route to asymmetric diimines which we are currently investigating.

2.1. Bridge-splitting reactions

Reaction of the halide-bridged complexes with thallium 2,4-pentanedionate gave the soluble complex **10**

TABLE 3. $^{13}C\{^1H\}$ NMR data for the free base and selected complexes [a]

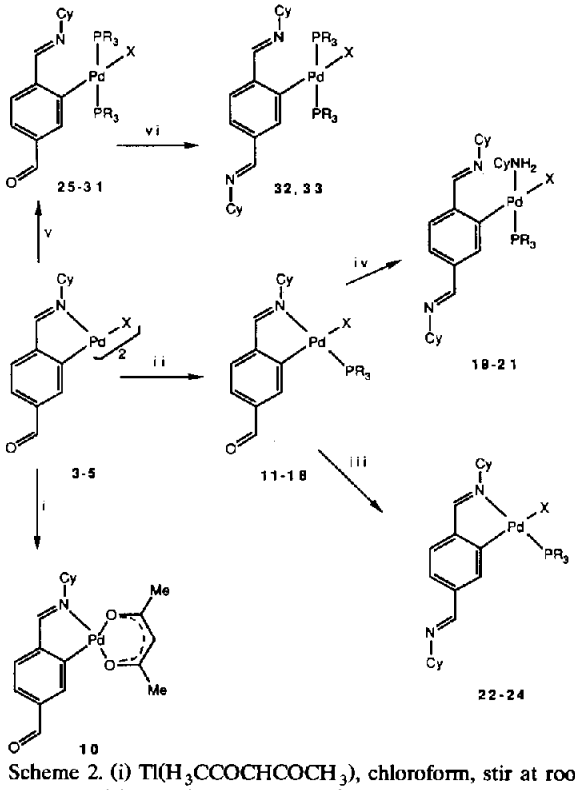
Compound	CHO	CO	C=N	C_1	C_2	C_3	C_4	C_5	C_6	CH_3	C_7	C_8,C_{12}	C_9, C_{11}	C_{10}
a			158.5	138.3	128.3		138.3	128.3			69.9	34.3	24.7	25.6
1	192.1	181.4 [b]	167.6	151.9	159.8	132.7	135.3	128.8	126.4	24.3	65.5	34.4	25.3	30.1
2		213.1 [c]	172.2	142.7	182.4	130.2					72.8	33.5	25.2	29.6
		193.6 [c]												
		191.6 [c]												
3	192.3		167.4	155.3	151.9	135.3	132.9	126.4	125.3		65.5	34.5	24.3	25.4
4	192.3		170.1	152.4	154.7	136.0	136.7	127.4	125.4		67.5	33.3	25.3	25.4
5	192.4		170.7	157.3	153.2	136.8	139.7	127.8	125.4		65.2	33.6	25.2	25.5
6		181.0 [b]	167.5	153.4	149.8	132.1	135.8	127.0	124.0	23.3	64.3	35.4	24.9	25.4
			158.5								54.3	34.2	24.5	25.1
7			170.6	154.8	150.7	131.8	135.2	127.4	125.4		64.3	34.9	25.0	25.6
			158.4								54.9	33.2		25.3
10 [e]	193.0	188.1 [d]	170.0	157.4	151.9	132.6	135.3	126.4	124.9	27.8	66.7	32.2	25.3	
		186.5 [d]								27.4				

[a] In $CDCl_3$. 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] Data for the COO groups.
[c] Data for the mutually *trans* carbonyl groups.
[d] Data for the 2,4-pentanedionate carbonyl carbon atoms.
[e] 2,4-Pentanedionate methylene carbon: δ 100.4 ppm.

as an air-stable solid, which was fully characterized (see Experimental section and Tables 1–3). The ^{1}H NMR spectrum shows singlets at δ 9.98 and δ 7.97 assigned to the *H*C=O and *H*C=N proton resonances, respectively. Singlet resonances at δ 5.36 and at δ 2.12, δ 2.07 are assigned to the C*H* and to the two inequivalent Me groups, respectively. The ^{13}C-{^{1}H} spectrum shows two carbonyl and two methyl-carbon resonances at δ 188.1, 186.5, and δ 27.8, 27.4, respectively, as expected of a 2,4-pentanedionate bonded to a square planar palladium(II) compound, indicating the non-equivalence of the two coordination sites.

Reaction of the halide-bridged complexes, **3–5**, with the appropriate amount of tertiary phosphines gave the mono-cyclometallated (**11–18**) and non-cyclometallated monomer compounds **25–31**. Thus, treatment of **3**, **4** or **5** with triphenylphosphine, diethylphenylphosphine, ethyldiphenylphosphine or with methyldiphenylphosphine in a dimer/phosphine 1:2 molar ratio gave the cyclometallated complexes, L = PPh_3: **11**, X = Cl, **12**, X = Br and **13**, X = I; L = PEt_2Ph: **14**, X = Cl, **15**, X = Br and **16**, X = I; L = $PEtPh_2$: **17**, X = Cl; L = $PMePh_2$: **18**, X = Cl (see Experimental section and Tables 1 and 2). They have been fully characterized. In particular, the ^{1}H NMR spectra show a shift of the *H*C=O resonance to lower frequency by *ca.* 0.6–0.8 ppm, in relation to the parent dimer complex, due to the shielding of the phosphine phenyl ring; this places the phosphine ligand *trans* to the nitrogen atom [16].

We effected the reaction of the monomer complexes with cyclohexylamine in order to regenerate the C=N double bond from the formyl group. With a monomer/cyclohexylamine 1:1 molar ratio a mixture of products was obtained, which we were unable to separate; an excess of amine gave similar results. However, when a 1:2 molar ratio was used, the C=N double bond was formed, but the amine cleaves the Pd–N bond to give the non-cyclometallated monomer compounds, formulated as **19**, **20**, and **21** (L = PPh_3) with a palladium atom bonded to four different ligands (details in the Experimental section and Tables 1 and 2). The ^{1}H NMR spectrum showed singlet resonances at: (a) δ 8.12 (**19**), δ 8.16 (**20**) and δ 8.19 (**21**) assigned to the *H*C=N proton (*ortho* to the Pd–C bond); (b) δ 6.62 (**19**), δ 6.64 (**20**) and δ 6.65 (**21**) assigned to the *H*3 proton. Since there is no Pd–N bond, the metallated ring can rotate about the Pd–C vector so that its plane is at 90° to the palladium coordination plane and coupling of this proton to the ^{31}P nucleus is absent [3]. The *H*C=N proton resonance (*meta* to the Pd–C bond) is shielded by the phosphine phenyl ring and is therefore shifted towards lower frequency; the signal is obscured by the phenyl proton resonances. The phosphorus resonance in the ^{31}P-{^{1}H} NMR spectrum is not



Scheme 2. (i) $Tl(H_3CCOCHCOCH_3)$, chloroform, stir at room temperature; (ii) PR_3 (1:2 molar ratio), aqueous acetone, stir at room temperature; (iii) $CyNH_2$, chloroform, reflux; (iv) $CyNH_2$, chloroform, reflux; (v) PR_3 (1:4 molar ratio), aqueous acetone, stir at room temperature; (vi) $CyNH_2$, chloroform, reflux. See text for X and PR_3 ligands.

significantly shifted on moving from complexes **11–13** to **19–21** (Table 2) suggesting that the phosphine is *trans* to the cyclohexylamine ligand. A C–Pd–PPh_3 *trans* geometry would shift the phosphorus resonance to lower frequency; this is based on the assumption that a ligand of greater *trans* influence shifts the ^{31}P resonance of the phosphorus nucleus *trans* to it to lower frequency [17].

When the tertiary phosphine is PEt_2Ph (X = Cl, **22**), $PEtPh_2$ (X = Cl, **23**), or $PMePh_2$ (X = Cl, **24**) the reaction proceeds without cleavage of the Pd–N bond. The complexes have been fully characterized (Tables 1 and 2). The ^{1}H NMR spectrum shows doublets at δ 8.05 (**22**), δ 8.16 (**23**) and δ 8.06 (**24**) assigned to the *H*C=N proton of the cyclometallated ring [^4J(PH) = 8.1 (**22**), 8.0 (**23**) and 8.1 Hz (**24**)]. Doublets at δ 6.87 (**22**) δ 6.85 (**23**) and δ 6.63 (**24**) are assigned to the *H*3 proton with ^4J(PH) = 6.3 (**22**), 6.5 (**23**) and 5.5 Hz (**24**). The free *H*C=N resonance is obscured by the phosphine proton resonances for reasons given earlier. The above results led us to correlate the reaction pathways (iii and iv in Scheme 2) with the different labilizations of the Pd–N bond caused by the different *trans* influence of the

phosphines bonded to the metal atom in **11–18**. On the basis of π-acceptor properties, it may be that triphenylphosphine exerts a stronger *trans* influence than the mixed aryl/alkyl phosphines, hence producing compounds **19–21**, as opposed to compounds **22–24**. These reactions are being investigated with a greater variety of phosphines and of amines in iii and iv.

Treatment of **3**, **4** or **5** with tertiary phosphines in a dimer/phosphine molar ratio of 1:4 gave the non-cyclometallated complexes, L = PPh_3: **25**, X = Cl; **26**, X = Br; **27**, X = I, L = PEt_2Ph: **28**, X = Cl, L = $PEtPh_2$: **29**, X = Cl; **30**, X = Br; **31**, X = I; which have been fully characterized (see Experimental section and Tables 1 and 2). The ^1H NMR spectra show singlet resonances at δ 9.16 (**25**), δ 9.17 (**26**), δ 9.18 (**27**), δ 9.57 (**28**), δ 9.24 (**29**), δ 9.33 (**30**) and δ 9.37 (**31**) assigned to the *H*C=O proton; they are shifted towards lower frequency (*vide supra*). The remaining proton resonances have been assigned unequivocally (Table 2). The *H*C=N and *H*3 resonances show no coupling to the ^{31}P nucleus as expected (*vide supra*). The IR spectrum shows carbonyl stretches at *ca.* 1680 cm^{-1}. The ^{31}P-{^1H} NMR spectra show a singlet (Table 2) for the phosphorus resonance, indicating that the two phosphine ligands are *trans*. This is confirmed by the weak intensity of the band at *ca.* 550 cm^{-1} in the IR spectrum [17]. These complexes may undergo reaction with primary amines to regenerate the C=N double bond. As an example, we treated complexes **25** and **29** with cyclohexylamine in boiling chloroform to give the compounds formulated as **32** (L = PPh_3, X = Cl) and **33** (L = $PEtPh_2$, X = Cl) (see Experimental section). They have been fully characterized by elemental microanalysis (C, H and N) and by IR, ^{31}P-{^1H} and ^1H NMR spectroscopy (Tables 1 and 2). Treatment of compound **25** with a twofold excess of cyclohexylamine did not give compound **19**.

3. Experimental details

Solvents were purified by the standard methods [19]. Chemicals were reagent grade. Palladium(II) acetate was purchased from Aldrich-Chemie. Microanalyses were carried out by Mr. J. Ulloa in the Servicio de Análisis Elemental of the University of Santiago using a Carlo–Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin–Elmer 1330 spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P-{^1H}), and were recorded on a Bruker WM-250 spectrometer. $MnMe(CO)_5$ was prepared as described in the literature [20].

The synthesis of 1,4-$(CyN{=}CH)_2C_6H_4$ was performed by heating a chloroform solution of the appropriate quantities of terephthalaldehyde and cyclohexylamine in a Dean–Stark apparatus under reflux.

3.1. Preparation of $[\{\overline{Pd[4\text{-}(CHO)C_6H_3C(H){=}N}Cy]\text{-}(O_2CMe)\}_2]$ (1)

1,4-$(CyN{=}CH)_2C_6H_4$ (0.350 g, 1.559 mmol) and palladium(II) acetate (0.242 g, 0.816 mmol) were added to 40 ml of glacial acetic acid to give an orange solution, which was heated under reflux under dry dinitrogen for 4 h. After cooling to room temperature, the acetic acid was removed under vacuum. The residue was diluted with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulphate, filtered, and concentrated *in vacuo* to give a dark orange solid. This was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (1%) afforded the final product as an orange solid after concentration. Yield: 75%

3.2. Preparation of $[(OC)_4\overline{MnN(Cy){=}C(H)C_6H_2C\text{-}(H){=}N(Cy)}Mn(CO)_4]$ (2)

A mixture of $[MnMe(CO)_5]$ (0.1 g, 0.476 mmol) and 1,4-$(CyN{=}CH)_2C_6H_4$ was added to 25 ml of octane to give a clear solution, which was heated under reflux under dry dinitrogen for 4 h. After cooling to room temperature, an orange precipitate appeared. This was filtered off and column chromatographed on a column packed with silica gel. Elution with chloroform gave the final product as a yellow solid after concentration. Yield: 52%.

3.3. Preparation of $[\{\overline{Pd[4\text{-}(CHO)C_6H_3C(H){=}N}Cy]\text{-}Cl\}_2]$ (3)

An aqueous solution of NaCl (*ca.* 10^{-2} M) was added dropwise to a solution of **1** (0.100 g, 0.131 mmol) in acetone (5 ml). The product immediately precipitated as a yellow solid. After stirring for 0.5 h, the solid was filtered off and the required product was isolated from dichloromethane/hexane as a yellow solid. Yield: 85%.

Compounds **4** and **5** were prepared similarly.

3.4. Preparation of $[\{\overline{Pd[4\text{-}(CyN{=}CH)C_6H_3C(H){=}N}Cy]O_2CMe\}_2]$ (6)

A mixture of **1** (25 mg, 0.033 mmol) and cyclohexylamine (6.5 mg, 0.066 mmol) in chloroform (25 ml) was heated under reflux under dry dinitrogen for 4 h in a Dean–Stark apparatus. After cooling to room temperature, the solution was evaporated to low bulk under reduced pressure. Addition of hexane gave the required product as an orange solid. Yield: 91%.

Compounds **7–9** were made analogously; for compound **7**, 2,4,6-trimethylaniline was used.

3.5. Preparation of $[\overline{Pd\{4\text{-}(CHO)C_6H_3C(H)=N}Cy\}\text{-}(H_3CCOCHCOCH_3)]$ (10)

To a suspension of **2** (0.08 g, 0.11 mmol) in dichloromethane, thallium 2,4-pentanedionate (0.068 g, 0.22 mmol) was added and the mixture stirred at room temperature for 1 h. The resulting solution was chromatographed on a column packed with silica gel. Elution with dichloromethane/chloroform (3:1) afforded the desired complex which was recrystallized from dichloromethane/hexane to give a yellow solid. Yield: 85%.

3.6. Preparation of $[\overline{Pd\{4\text{-}(CHO)C_6H_3C(H)=N}Cy\}\text{-}Cl(PPh_3)]$ (11)

PPh_3 (15 mg, 0.056 mmol) was added to a suspension of **2** (20 mg, 0.028 mmol) in acetone (5 ml). The mixture was stirred for 2 h at room temperature and the resulting precipitate was filtered off and the product recrystallized from dichloromethane/hexane. Yield: 81%.

Compounds **12–18** were prepared similarly and separated from dichloromethane/hexane or chloroform/hexane.

3.7. Preparation of $[Pd\{4\text{-}(CyN=CH)C_6H_3C(H)=NCy\}\text{-}(Cl)(PPh_3)(NH_2Cy)]$ (19)

The complex was synthesized following a similar procedure to that for **6**. Compounds **20–24** and **32–33** were made similarly and the final product recrystallized from dichloromethane/hexane or chloroform/hexane.

3.8. Preparation of $[Pd\{4\text{-}(CHO)C_6H_3C(H)=NCy\}\text{-}(Cl)(PPh_3)_2]$ (25)

The complex was synthesized following a similar procedure to that of **11** but using a dimer/phosphine ratio of 1:4. Yield: 78%.

Compounds **26–31** were made similarly but the reaction mixture was heated under reflux for 1 h. The final product was recrystallized from chloroform/hexane or dichloromethane/hexane, as appropriate.

Acknowledgements

We wish to thank the Ministerio de Educación y Ciencia (DGICYT, proyecto no. PS90-0198) for support and the Xunta de Galicia for grants to M.L. and to J.J.F.

References

1 I. Omae, *Coord. Chem. Rev.*, *53* (1984) 261.
2 V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev.*, *5* (1988) 250.
3 J. M. Vila, M. Gayoso, M. T. Pereira, A. Romar, J. J. Fernández and M. Thornton-Pett, *J. Organomet. Chem.*, *401* (1991) 385.
4 M. T. Pereira, J. M. Vila, A. Suárez, E. Gayoso and M. Gayoso, *Gazz. Chim. Ital.*, *118* (1988) 783.
5 A. Suárez, J. M. Vila, M. T. Pereira, E. Gayoso and M. Gayoso, *J. Organomet. Chem.*, *335* (1987) 359.
6 J. L. Casas, E. Gayoso, J. M. Vila, M. T. Pereira and M. Gayoso, *Synth. React. Inorg. Met.-Org. Chem.*, *21* (1991) 263.
7 J. M. Vila, M. T. Pereira, M. Gayoso, M. C. Rodríguez, J. M. Ortigueira and M. Thornton-Pett, *J. Organomet. Chem.*, *426* (1992) 267.
8 S. Trofimenko, *Inorg. Chem.*, *12* (1973) 247.
9 I. G. Phillips and P. J. Steel, *J. Organomet. Chem.*, *410* (1991) 247.
10 J. Selbin, K. Abboud, S. F. Watkins, M. A. Gutiérrez and F. R. Fronczek, *J. Organomet. Chem.*, *241* (1983) 259.
11 J. Granell, D. Sáinz, J. Sales, X. Soláns and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, (1986) 1785.
12 K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, 4th edition, Wiley–Interscience, New York, 1986.
13 H. Onoue and I. Moritani, *J. Organomet. Chem.*, *43* (1972) 431.
14 H. Onoue, K. Minami and K. Nakagawa, *Bull. Chem. Soc. Jpn.*, *43* (1970) 3480.
15 Y. Ustynyuk, V. A. Chertov and J. V. Barinov, *J. Organomet. Chem.*, *29* (1971) C53.
16 J. M. Vila, A. Suárez, M. T. Pereira, E. Gayoso and M. Gayoso, *Polyhedron*, *6* (1987) 1003.
17 P. S. Pregosin and R. W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, in: P. Diehl, E. Fluck and R. Kosfeld (eds.), NMR 16, Springer, Berlin, 1979.
18 S. H. Mastin, *Inorg. Chem.*, *13* (1974) 1003.
19 D. D. Perrin, W. L. F. Armarego and D. P. Perrin, *Purification of Laboratory Chemicals*, 2nd edition, Pergamon, Oxford, 1983.
20 R. B. King, *Organometallic Syntheses*, Academic Press, New York, 1965, p. 147.