

Reactivity of functionalised cyclometallated complexes of palladium(II). Crystal and molecular structure of [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PEtPh₂)]

José M. Vila ^{a,*}, M. Teresa Pereira ^a, Juan M. Ortigueira ^a, Margarita López Torres ^a, Alfonso Castiñeiras ^a, D. Lata ^a, Jesús J. Fernández ^b, Alberto Fernández ^b

^a Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

^b Departamento de Química Fundamental e Industrial, Universidad de La Coruña, 15071 La Coruña, Spain

Received 5 August 1997

Abstract

Treatment of the cyclometallated complexes [Pd{3-(CHO)C₆H₃C(H)=NCy}(X)]₂ [X = Cl (**1**), Br (**2**), I (**3**)] with tertiary monophosphines in a complex/phosphine 1:2 or 1:4 molar ratio afforded the halide-bridged cleaved [Pd{3-(CHO)C₆H₃C(H)=NCy}(X)(L)] (**6–17**) and non-cyclometallated complexes [Pd{3-(CHO)C₆H₃C(H)=NCy}(X)(L)₂] (**18–23**) (X = Cl, Br or I; L = PPh₃, PEtPh₂, PEt₂Ph or PMePh₂), respectively. Reaction of **6–17** with cyclohexylamine in a complex/amine 1:1 or 1:2 molar ratio gave [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(X)(L)] (**24–28**) and the non-cyclometallated [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(X)(L)(NH₂Cy)] (**29–32**) complexes, respectively. Compounds **18**, **19** and **22** gave [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(X)(PR₃)₂] (**33–35**) with two uncoordinated C=N groups, when treated with cyclohexylamine. Other reaction routes are also discussed. The complexes were characterised by their elemental analysis (C, H, N) and by IR and ³¹P{¹H} and ¹H-NMR data, and [Pd{3-(CHO)(C₆H₃C(H)=NCy)(Br)(PEtPh₂)] (**12**) was characterised crystallographically. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclometallated; Palladium; Phosphine complexes

1. Introduction

Activation of aryl C–H bonds to give cyclometallated complexes is very important in organometallic chemistry [1–6]. Bidentate nitrogen-donor ligands may undergo double cyclometallation to produce compounds with two σM–C bonds and with coordination of each nitrogen atom to one of the metal centres [7–11]. However, we have reported that when the aryl ring is substituted with two C=N double bonds, as in the case of Schiff bases derived from dialdehydes (e.g. terephthalaldehyde and isophthalaldehyde) mono- or dicyclometallated compounds were obtained [12,13]; thus, the organic ligand may undergo cleavage of one C=N

double bond in the metallation process.

One of the very important reactions of cyclometallated compounds is the cleavage of halide bridged complexes by neutral or anionic reagents. We have shown the reactions of halide-bridged complexes derived from *N,N*-isophthalylidenebis(cyclohexylamine) with anionic reagents (thallium acetilacetate and thallium cyclopentadienyl) and with cyclohexylamine [13]. We considered that complexation of tertiary phosphines to the palladium atom could be carried out together with reaction of the dinuclear species with cyclohexylamine, which should give regeneration of the C=N double bond and/or coordination of the amine moiety, and this is what we have done. Although we have previously studied the reactivity of the halide-bridged complexes derived from a similar ligand (*N,N*-

* Corresponding author.

terephthalylidenebis-cyclohexylamine) with monophosphines, no crystallographic evidence was provided for mononuclear cyclometallated complexes with the formyl functionality on the metallated aryl ring. We have now been able to obtain suitable crystals for the X-ray analysis of one such compound.

2. Results and discussion

2.1. Crystal structure of

$[Pd\{3-(CHO)C_6H_3C(H)=NCy\}(Br)(PEtPh_2)]$ (**12**)

Suitable crystals of the title compound were grown from slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 1. Crystal data are given in Table 1. Fractional coordinates and isotropic thermal parameters are listed in Table 2, while selected bond lengths and bond angles with estimated standard deviations are listed in Table 3.

The molecule comprises a palladium(II) to which is bonded a chelated *N*-(3-formylbenzylidene)cyclohexylamine- C^2,N group, to a bromine atom and to an ethyldiphenylphosphine ligand. The palladium atom adopts a square-planar geometry as expected for Pd^{2+} . The donor atoms of the chelating Schiff base occupying *cis* sites, with a somewhat reduced bond angle C(1)–Pd(1)–N(1) of $80.9(2)^\circ$, consequent upon chelation. This is reflected in the value of the C(2)–C(1)–Pd(1), $132.0(3)^\circ$, angle. The sum of angles at palladium is 360.49° . The Pd–C bond length [Pd(1)–C(1), $2.017(4)$ Å] is shorter than the expected

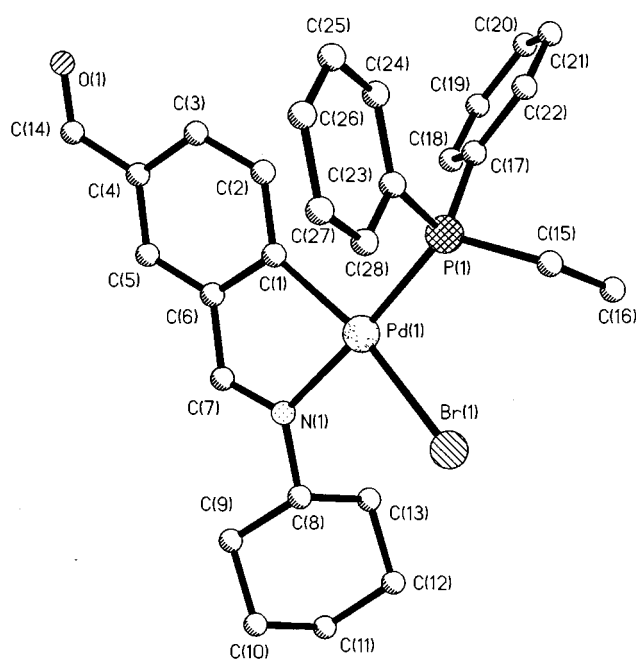


Fig. 1. Molecular structure of $[Pd\{3-(CHO)C_6H_3C(H)=NCy\}(Br)(PEtPh_2)]$ **12**.

Table 1

Crystal data for compound 12

Empirical formula	$C_{28}H_{31}BrNOPd$
Formula weight	614.82
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
<i>a</i> (Å)	8.663(1)
<i>b</i> (Å)	12.212(1)
<i>c</i> (Å)	24.954(4)
α ($^\circ$)	90
β ($^\circ$)	93.902(7)
γ ($^\circ$)	90
Volume	2634.0 (6) Å ³
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	1.550
Absorption coefficient (mm ⁻¹)	2.303
<i>F</i> (000)	1240
θ range for data collection	3.05–30.01 $^\circ$
Index ranges	0 < <i>h</i> < 12, 0 < <i>k</i> < 17, –34 < <i>l</i> < 34
Reflections collected	8061
Independent reflections	7605 (R_{int} = 0.0772)
Data/restraints/parameters	7604/0/293
GOF on F^2	1.014
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0550$, $wR_2 = 0.1094$
<i>R</i> indices (all data)	$R_1 = 0.1366$, $wR_2 = 0.1373$
Largest difference peak and hole (e Å ⁻³)	0.935 and –1.228

value of 2.081 Å based on the sum of the covalent radii for carbon and palladium, 0.771 and 1.31 Å, respectively [14]. This is consistent with those found in related complexes where partial multiple-bond character of the Pd–C bond was assumed [15–17]. The Pd–N bond length [Pd(1)–N(1), $2.128(4)$ Å] is longer than the expected value of 2.01 Å calculated from the covalent radii of N(sp²) 0.70 Å and palladium 1.31 Å. This lengthening reflects the *trans* influence of the phosphine ligand. The Pd–P bond length Pd(1)–P(1), 2.266 Å is shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å [14], as has been found earlier [16]. The Pd–Br bond length Pd(1)–Br(1), 2.495 Å is somewhat longer than the sum of the covalent radii (2.45 Å), consistent with the *trans*-influence of the C(phenyl) atom.

The aromatic ring of the Schiff base is planar (r.m.s. 0.0033 Å) and approximately coplanar (2.7°) with the adjacent five-membered cyclometallated ring (r.m.s. 0.0179 Å). The geometry around the palladium atom is planar (r.m.s. 0.1134 Å), from which the displacement of palladium is only -0.0635 Å.

2.2. Reactions with tertiary monophosphines and cyclohexylamine

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterised by elemental

analysis and by IR spectroscopy (data in Section 4) and by ^1H and $^{31}\text{P}\{^1\text{H}\}$ (Table 4) and ^{13}C -NMR spectroscopy.

In a previous paper [13] we reported the reactions of compounds **1–3** with cyclohexylamine, steps **i** and **iii**; however, step **ii** was not described then, and it has been included here to further complete Scheme 1. Thus, treatment of compound **4** ($\text{X} = \text{Cl}$) with cyclohexylamine under reflux gave compound **5** ($\text{X} = \text{Cl}$), with regeneration of the $\text{C}=\text{N}$ double bond (for characterisation of **4** and **5**, and for the corresponding bromine and iodine analogues, for which step **ii** also could be effected, see reference [13]).

Treatment of the halide-bridged complexes $[\{\text{Pd}[\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{X})\}_2]$ [$\text{X} = \text{Cl}$ (**1**), $\text{X} = \text{Br}$ (**2**), $\text{X} = \text{I}$ (**3**)] with tertiary monophosphines in a dimer/phosphine 1:2 molar ratio gave the cyclometallated monomer compounds $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Cl})(\text{L})]$ (L: **6**, PPh_3 ; **7**, PEt_2Ph ; **8**, PEtPh_2 ; **9**, PMePh_2), $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Br})(\text{L})]$ (L: **10**, PPh_3 ; **11**,

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12**

Atom	x	y	z	U (eq)
Pd(1)	-11(1)	-16(1)	1239(1)	33(1)
Br(1)	1737(1)	1281(1)	1761(1)	61(1)
P(1)	907(1)	-1463(1)	1733(1)	34(1)
O(1)	-3881(6)	-3380(4)	-742(2)	85(2)
N(1)	-1076(4)	1243(3)	755(2)	37(1)
C(1)	-1181(5)	-954(4)	684(2)	31(1)
C(2)	-1250(5)	-2083(4)	609(2)	36(1)
C(3)	-2043(5)	-2548(4)	168(2)	38(1)
C(4)	-2822(6)	-1909(4)	-225(2)	41(1)
C(5)	-2761(6)	-778(4)	-162(2)	45(1)
C(6)	-1959(6)	-306(4)	279(2)	37(1)
C(7)	-1855(6)	870(4)	349(2)	41(1)
C(8)	-978(6)	2429(4)	870(2)	38(1)
C(9)	-1590(7)	3167(4)	410(2)	48(1)
C(10)	-1322(9)	4359(5)	582(3)	71(2)
C(11)	-2125(9)	4631(5)	1080(3)	74(2)
C(12)	-1596(8)	3857(5)	1539(3)	66(2)
C(13)	-1821(7)	2664(4)	1365(2)	51(1)
C(14)	-3720(7)	-2423(5)	-677(2)	59(2)
C(15)	2142(6)	-1217(4)	2351(2)	45(1)
C(16)	1325(8)	-760(5)	2818(2)	68(2)
C(17)	-540(5)	-2402(4)	1976(2)	37(1)
C(18)	-2111(6)	-2166(5)	1892(2)	46(1)
C(19)	-3188(7)	-2844(6)	2115(2)	60(2)
C(20)	-2703(7)	-3733(6)	2412(2)	63(2)
C(21)	-1160(7)	-3960(5)	2495(2)	55(2)
C(22)	-82(6)	-3313(4)	2276(2)	47(1)
C(23)	2240(5)	-2249(4)	1350(2)	36(1)
C(24)	2128(6)	-3365(4)	1243(2)	47(1)
C(25)	3238(7)	-3884(5)	948(2)	59(2)
C(26)	4428(7)	-3284(6)	759(2)	62(2)
C(27)	4544(7)	-2175(5)	861(2)	60(2)
C(28)	3457(6)	-1666(5)	1151(2)	47(1)

U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

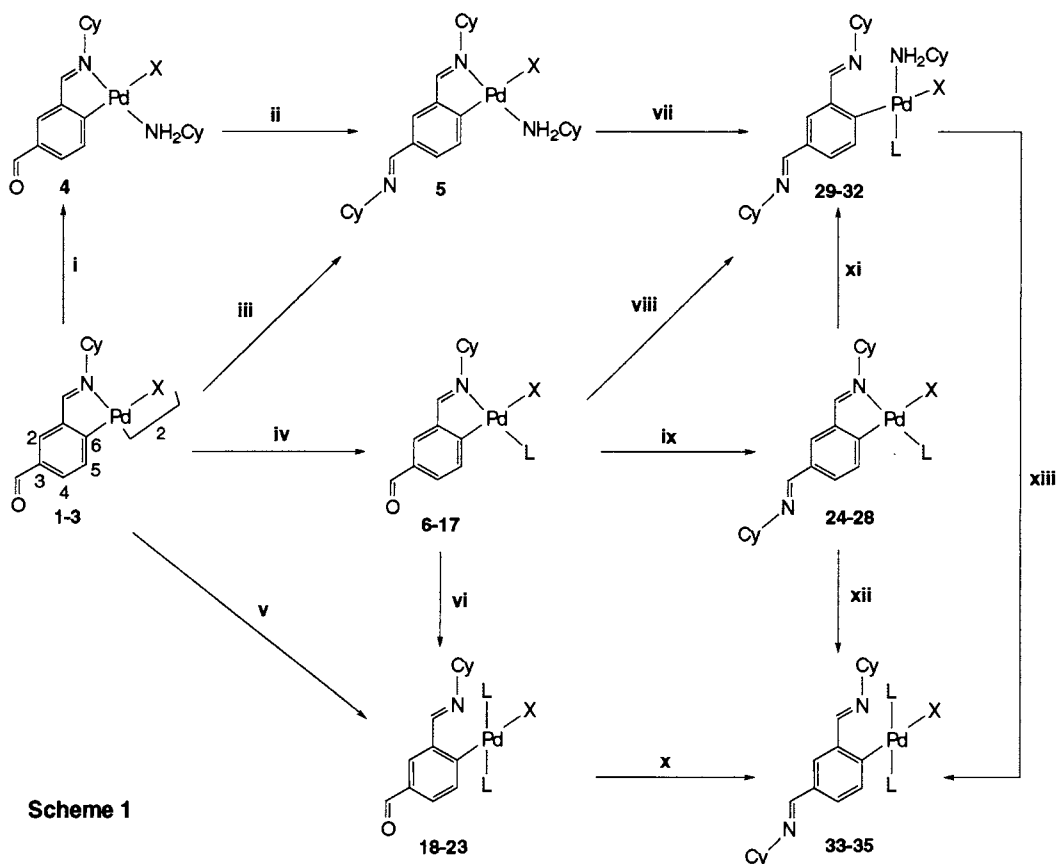
Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for **12**

Bond lengths (\AA)			
Pd(1)–C(1)	2.017(4)	Pd(1)–N(1)	2.128(4)
Pd(1)–P(1)	2.2665(13)	Pd(1)–Br(1)	2.4953(7)
N(1)–C(8)	1.478(6)	N(1)–C(7)	1.264(6)
C(1)–C(6)	1.416(6)	P(1)–C(23)	1.821(5)
C(6)–C(7)	1.449(7)	P(1)–C(17)	1.832(5)
P(1)–C(15)	1.841(5)		
Bond angles ($^\circ$)			
C(1)–Pd(1)–N(1)	80.9(2)	C(1)–Pd(1)–P(1)	94.13(13)
N(1)–Pd(1)–P(1)	174.17(11)	C(1)–Pd(1)–Br(1)	167.79(13)
N(1)–Pd(1)–Br(1)	93.53(10)	P(1)–Pd(1)–Br(1)	91.93(4)
C(23)–P(1)–C(17)	108.4(2)	C(23)–P(1)–C(15)	99.9(2)
C(17)–P(1)–C(15)	101.3(2)	C(23)–P(1)–Pd(1)	109.8(2)
C(17)–P(1)–Pd(1)	116.4(2)	C(15)–P(1)–Pd(1)	119.4(2)
C(7)–N(1)–C(8)	122.0(4)	C(7)–N(1)–Pd(1)	112.5(3)
C(8)–N(1)–Pd(1)	125.5(3)	C(2)–C(1)–C(6)	116.3(4)
C(2)–C(1)–Pd(1)	132.0(3)	C(6)–C(1)–Pd(1)	111.4(3)
C(5)–C(6)–C(7)	122.0(4)	C(1)–C(6)–C(7)	116.5(4)
N(1)–C(7)–C(6)	118.6(4)		

PEt_2Ph ; **12**, PEtPh_2 ; **13**, PMePh_2) and $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{I})(\text{L})]$ (L: **14**, PPh_3 ; **15**, PEt_2Ph ; **16**, PEtPh_2 ; **17**, PMePh_2), respectively, as pure air-stable solids, which were fully characterised (see Section 4 and Table 4).

Reaction of the halide-bridged complexes **1–3** with tertiary monophosphines in a dimer/phosphine 1:4 molar ratio gave the non-cyclometallated monomer compounds $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Cl})(\text{L})_2]$ (L: **18**, PPh_3 ; **19**, PMePh_2), $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Br})(\text{L})_2]$ (L: **20**, PPh_3 ; **21**, PMePh_2) and $[\text{Pd}\{\text{3}-(\text{CHO})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{I})(\text{PR}_3)_2]$ (L: **22**, PPh_3 ; **23**, PMePh_2) respectively, which were fully characterised (see Section 4 and Table 4). The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra confirmed the *trans* geometry of the phosphine ligands, with a singlet resonance in each case, this is also confirmed by the weak intensity of the band at 550 cm^{-1} in the IR spectra [18]. These complexes can also be obtained by reaction of the appropriate cyclometallated monomer compounds (**6–17**) with the corresponding monophosphine in a complex/phosphine 1:1 molar ratio. The reactivity of compounds **6–17** was also tested against cyclohexylamine by refluxing them with the amine to produce compounds where regeneration of the $\text{C}=\text{N}$ double bond from the formyl group was achieved: mononuclear cyclometallated complexes **24–28** (complex/cyclohexylamine 1:1 molar ratio) $[\text{Pd}\{\text{3}-(\text{CyC}(\text{H})=\text{N})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Cl})(\text{L})]$ (L: **24**, PPh_3 ; **25**, PEt_2Ph ; **26**, PEtPh_2 ; **27**, PMePh_2), respectively, and $[\text{Pd}\{\text{3}-(\text{CyC}(\text{H})=\text{N})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{I})(\text{PPh}_3)]$ (**28**), and mononuclear non-cyclometallated complexes **29–32** (monomer/cyclohexylamine 1:2 molar ratio) $[\text{Pd}\{\text{3}-(\text{CyC}(\text{H})=\text{N})\text{C}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{Cl})(\text{L})-(\text{NH}_2\text{Cy})]$ (L: **29**, PPh_3 ; **30**, PEtPh_2 ; **31**, PMePh_2), re-



Scheme 1. (i) CyNH_2 (2 mol), chloroform, reflux; (ii) CyNH_2 (1 mol), chloroform, reflux; (iii) CyNH_2 (4 mol), chloroform, reflux; (iv) PR_3 (1:2 molar ratio), aqueous acetone, stir at r.t.; (v) PR_3 (1:4 molar ratio), aqueous acetone, stir at r.t.; (vi) PR_3 (1:1 molar ratio), aqueous acetone, stir at r.t.; (vii) PR_3 (1:1 molar ratio), aqueous acetone, stir at r.t.; (viii) CyNH_2 (2 mol), chloroform, reflux; (ix) CyNH_2 (1 mol), chloroform, reflux; (x) CyNH_2 (1 mol), chloroform, reflux; (xi) CyNH_2 (1 mol), chloroform, reflux; (xii) PR_3 (1:1 molar ratio), aqueous acetone, stir at r.t.; (xiii) PR_3 (1:1 molar ratio), aqueous acetone, stir at r.t..

spectively, and $[\text{Pd}\{3\text{-(CyC(H)=N)C}_6\text{H}_3\text{C(H)=NCy}\}\text{(Br)(PPh}_3\text{)(NH}_2\text{Cy)}]$ (**32**); which also show an uncoordinated C=N double bond; the amine cleaves the Pd-N bond to give compounds where the palladium atom is bonded to four different ligands. The HC=N and H5 resonances are not coupled to phosphorus, which is evidence for the twisting of the metallated Schiff base out of the palladium(II) coordination plane [15]; the organic ligand is monodentate through the phenyl carbon atom. Ring opening of the chelate ring was also brought about by treating **24–28** with equimolar amounts of cyclohexylamine; alternatively, type **5** compounds could be treated with equimolar amounts of the appropriate phosphine to yield compounds **29–32** (see Section 4).

Treatment of **24–28** with the appropriate phosphine in a complex/phosphine 1:1 molar ratio gave the mononuclear non-cyclometallated compounds $[\text{Pd}\{3\text{-(CyNC(H)C}_6\text{H}_3\text{C(H)=NCy}\}\text{(Cl)(L)}_2]$ (L: **33**, PPh_3 ; **34**, PMePh_2) and $[\text{Pd}\{3\text{-(CyNC(H)C}_6\text{H}_3\text{C(H)=NCy}\}\text{(I)(PPh}_3\text{)}_2]$ (**35**) with two uncoordinated C=N groups each, and with two mutually *trans* phosphine ligands which were fully characterised (see Section 4 and Table 4).

The compounds could also be made from **18–23** by treatment with equimolar amounts of cyclohexylamine under reflux, or from **29–32**, by reaction with the corresponding phosphine at room temperature (r.t.) (see Section 4). Attempts to obtain **33–35** from **6–17** by successive reaction with the amine and the phosphine in a 'one pot' process, were unsuccessful.

3. Conclusions

Although Schiff base cyclometallated palladium(II) complexes with a phosphine ligand bonded to the metal atom are known, the structure of compound **12** is the first example where the metallated ring is functionalised by a free formyl group. The presence of the formyl group renders versatile reaction routes; the order with which the ligands are added to the coordination sphere of the palladium atom and with which the second C=N double bond is regenerated, may be varied. This gives different approaches to the synthesis of many of the compounds described.

Table 4
³¹P-NMR^a and ¹H-NMR^b data^{c,d}

Compound	³¹ P	Aromatic	Others
6	21.5s	7.71[d, 1H, H ² , 1.9 ^e] 6.98[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.59[ddd, 1H, H ⁵ , 8.0 ^f , 5.9 ^h , 0.9 ^g]	9.75[s, 1H, HC=O] 8.24[dd, 1H, HC=N, 8.6 ^h , 0.9 ^g]
7	32.5s	7.71[d, 1H, H ² , 1.9 ^e] 7.15[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.62[ddd, 1H, H ⁵ , 8.0 ^f , 5.7 ^h , 1.0 ^g]	9.78[s, 1H, HC=O] 8.17[dd, 1H, HC=N, 8.2 ^h , 1.0 ^g]
8	34.6s	7.71[d, 1H, H ² , 1.9 ^e] 7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.66[ddd, 1H, H ⁵ , 8.0 ^f , 5.7 ^h , 1.0 ^g]	9.76[s, 1H, HC=O] 8.19[dd, 1H, HC=N, 8.4 ^h , 1.0 ^g]
9	21.9s	7.72[d, 1H, H ² , 1.8 ^e] 7.05[dd, 1H, H ⁴ , 7.9 ^f , 1.8 ^e] 6.59[ddd, 1H, H ⁵ , 7.9 ^f , 6.0 ^h , 0.9 ^g]	9.76[s, 1H, HC=O] 8.19[dd, 1H, HC=N, 8.7 ^h , 0.9 ^g]
10	20.4s	7.71[d, 1H, H ² , 1.8 ^e] 7.00[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e] 6.58[dd, 1H, H ⁵ , 8.0 ^f , 6.2 ^h]	9.76[s, 1H, HC=O] 8.26[d, 1H, HC=N, 8.6 ^h]
11	32.9s	7.71[d, 1H, H ² , 1.5 ^e] 7.16[dd, 1H, H ⁴ , 7.9 ^f , 1.5 ^e] 6.61[dd, 1H, H ⁵ , 7.9 ^f , 6.0 ^h]	9.78[s, 1H, HC=O] 8.18[d, 1H, HC=N, 7.9 ^h]
12	35.0s	7.71[d, 1H, H ² , 1.8 ^e] 7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e] 6.62[dd, 1H, H ⁵ , 8.0 ^f , 6.0 ^h]	9.76[s, 1H, HC=O] 8.22[d, 1H, HC=N, 8.3 ^h]
13	22.0s	7.71[d, 1H, H ² , 1.8 ^e] 7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e] 6.57[d, 1H, H ⁵ , 8.0 ^h]	9.76[s, 1H, HC=O] 8.21[d, 1H, HC=N, 7.9 ^h]
14	20.7s	7.71[d, 1H, H ² , 1.4 ^e] 7.00[dd, 1H, H ⁴ , 7.5 ^f , 1.4 ^e] 6.54[t, 1H, H ⁵ , 7.5 ^f , 7.5 ^h]	9.76[s, 1H, HC=O] 8.32[d, 1H, HC=N, 8.1 ^h]
15	34.6s	7.71[d, 1H, H ² , 1.9 ^e] 7.18[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.61[ddd, 1H, H ⁵ , 8.0 ^f , 6.0 ^h , 0.9 ^g]	9.79[s, 1H, HC=O] 8.24[dd, 1H, HC=N, 8.0 ^h , 0.9 ^g]
16	36.2s	7.71[d, 1H, H ² , 1.9 ^e] 7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.54[ddd, 1H, H ⁵ , 8.0 ^f , 6.3 ^h , 1.0 ^g]	9.76[s, 1H, HC=O] 8.27[dd, 1H, HC=N, 8.2 ^h , 1.0 ^g]
17	22.0s	7.71[d, 1H, H ² , 1.9 ^e] 7.07[dd, 1H, H ⁴ , 7.4 ^f , 1.9 ^e] 6.53[dd, 1H, H ⁵ , 7.4 ^f , 7.0 ^h]	9.76[s, 1H, HC=O] 8.27[d, 1H, HC=N, 8.0 ^h]
18 ^l	22.0s	6.98[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.62[d, 1H, H ⁵ , 8.0 ^h]	9.76[s, 1H, HC=O] 8.26[s, 1H, HC=N]
19 ^l	4.0s	7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.4 ^e] 7.18[d, 1H, H ⁵ , 8.0 ^h]	9.70[s, 1H, HC=O] 8.42[s, 1H, HC=N]
20 ^l	21.5s	6.97[dd, 1H, H ⁴ , 8.0 ^f , 1.9 ^e] 6.65[d, 1H, H ⁵ , 8.0 ^h]	9.74[s, 1H, HC=O] 8.33[s, 1H, HC=N]
21 ^l	3.6s	7.05[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e]	9.68[s, 1H, HC=O] 8.43[s, 1H, HC=N]
22 ^l	20.8s	6.95[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e] 6.65[d, 1H, H ⁵ , 8.0 ^h]	9.73[s, 1H, HC=O] 8.44[s, 1H, HC=N]
23 ^l	2.4s	7.05[dd, 1H, H ⁴ , 7.9 ^f , 1.9 ^e]	9.67[s, 1H, HC=O] 8.35[s, 1H, HC=N]
24 ^l	40.8s	6.80[dd, 1H, H ⁴ , 8.0 ^f , 2.0 ^e] 6.45[dd, 1H, H ⁵ , 8.0 ^f , 5.7 ^h]	8.19[d, 1H, HC=N, 7.8 ^h] 8.08[s, 1H, HC=N]
25	32.4s	7.66[d, 1H, H ² , 1.8 ^e] 7.00[dd, 1H, H ⁴ , 8.0 ^f , 1.8 ^e] 6.48[dd, 1H, H ⁵ , 8.0 ^f , 5.8 ^h]	8.13[d, 1H, HC=N, 9.4 ^h] 8.11[s, 1H, HC=N]

Table 4 (continued)

Compound	³¹ P	Aromatic	Others
26	34.6s	7.64[d, 1H, H ² , 1.6 ^e] 6.87[dd, 1H, H ⁴ , 8.0 ^f , 1.6 ^e] 6.51[dd, 1H, H ⁵ , 8.0 ^f , 5.5 ^h]	8.14[d, 1H, HC=N, 8.0 ^h] 8.08[s, 1H, HC=N ^j]
27 ^l	22.0s	6.90[d, 1H, H ⁴ , 8.0 ^f] 6.47[dd, 1H, H ⁵ , 8.0 ^f , 5.6 ^h]	8.16[d, 1H, HC=N, 7.8 ^h] 8.10[s, 1H, HC=N ^j]
28 ^l	41.0s	6.81[dd, 1H, H ⁴ , 7.9 ^f , 2.0 ^e] 6.38[dd, 1H, H ⁵ , 7.9 ^f , 5.8 ^h]	8.25[d, 1H, HC=N, 8 ^h] 8.06[s, 1H, HC=N ^j]
29 ^l	27.2s	6.81[dd, 1H, H ⁴ , 8.0 ^f , 2.0 ^e] 6.44[d, 1H, H ⁵ , 8.0 ^f]	8.21[s, 1H, HC=N] 8.07[s, 1H, HC=N ^j]
30 ^l	34.5s	6.87[d, 1H, H ⁴ , 7.9 ^f] 6.51[d, 1H, H ⁵ , 7.9 ^f]	8.13[s, 1H, HC=N] 8.07[s, 1H, HC=N ^j]
31 ^l	21.9s	6.88[dd, 1H, H ⁴ , 7.9 ^f , 1.9 ^e] 6.45[d, 1H, H ⁵ , 7.9 ^f]	8.15[s, 1H, HC=N] 8.07[s, 1H, HC=N ^j]
32 ^l	40.7s	6.81[dd, 1H, H ⁴ , 8.0 ^f , 2.0 ^e] 6.42[d, 1H, H ⁵ , 8.0 ^f]	8.21[s, 1H, HC=N] 8.07[s, 1H, HC=N ^j]
33 ^l	27.3s	6.80[dd, 1H, H ⁴ , 7.9 ^f , 1.9 ^e] 6.43[d, 1H, H ⁵ , 7.9 ^f]	8.26[s, 1H, HC=N] 8.09[s, 1H, HC=N ^j]
34 ^l	6.3s	7.11[dd, 1H, H ⁴ , 7.9 ^f , 1.9 ^e] 7.00[d, 1H, H ⁵ , 7.9 ^f]	8.39[s, 1H, HC=N] 8.09[s, 1H, HC=N ^j]
35 ^l	27.4s	6.82[dd, 1H, H ⁴ , 8.1 ^f , 2.0 ^e] 6.43[d, 1H, H ⁵ , 8.1 ^f]	8.29[s, 1H, HC=N] 8.06[s, 1H, HC=N ^j]

^a In CDCl₃. Measured at 100.6 MHz (ca. ± 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H₃PO₄. ^b In CDCl₃, unless otherwise stated. Measured at 250 MHz (ca. ± 20°C); chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe₄. ^c Coupling constants in Hz. ^d s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet. ^e ⁴J(HH). ^f ³J(HH). ^g ⁵J(HH). ^h ⁴J(PH). ⁱ Occluded by the phosphine resonances. ^j C=N group bonded to C3.

4. Experimental details

4.1. Materials and instrumentation

The synthesis of complexes **1–5** has been reported previously [13]. Solvents were purified by standard methods [19]. Chemicals were reagent grade. Cyclohexylamine and the phosphines PPh₃, PEtPh₂, PEt₂Ph and PMePh₂ were purchased from Aldrich. 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 or polythene discs on a Perkin-Elmer 1330 and on a Mattson (Servicio de Espectroscopía of the University of Santiago) spectrophotometers. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe₄ (¹H, ¹³C) or 85% H₃PO₄ (³¹P{¹H}) and were recorded on Bruker WM-250, AMX-300 and AMX-500 spectrometers. All chemical shifts were reported downfield from the standards.

4.2. Preparations

4.2.1. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PPh₃)] **6**

A sample of PPh₃ (44 mg, 0.17 mmol) was added to a solution of **1** (60 mg, 0.08 mmol) in acetone (15 cm³).

The mixture was stirred for 4 h at r.t. and the resulting precipitate was filtered off and the product recrystallised from dichloromethane/hexane as a yellow solid. Yield 75%. Anal. Found: C, 61.8; H, 5.3; N, 2.1. C₃₂H₃₁NOPdPCL requires: C, 62.2; H, 5.1; N, 2.3. IR: ν(C=N), 1622m cm⁻¹; ν(Pd-Cl), 302m cm⁻¹.

The following compounds were made analogously:

4.2.2. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PEt₂Ph)] **7**

Yield 75%. Anal. Found: C, 55.2; H, 6.4; N, 2.9. C₂₄H₃₁NOPdPCL requires: C, 55.2; H, 6.0; N, 2.7. IR: ν(C=N), 1620m cm⁻¹; ν(Pd-Cl), 302m cm⁻¹.

4.2.3. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PEtPh₂)] **8**

Yield 78%. Anal. Found: C, 57.0; H, 5.5; N, 2.5. C₂₈H₃₁NOPdPCL·0.33 CH₂Cl₂ requires: C, 56.8; H, 5.3; N, 2.3. IR: ν(C=N), 1622m cm⁻¹; ν(Pd-Cl), 301m cm⁻¹.

4.2.4. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PMePh₂)] **9**

Yield 75%. Anal. Found: C, 58.3; H, 5.4; N, 2.8. C₂₇H₂₉NOPdPCL requires: C, 58.3; H, 5.3; N, 2.5. IR: ν(C=N), 1615m cm⁻¹; ν(Pd-Cl), 299m cm⁻¹.

4.2.5. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PPh₃)] 10

Yield 75%. Anal. Found: C, 57.4; H, 4.5; N, 1.9. C₃₂H₃₁NOPdPBr requires: C, 58.0; H, 4.7; N, 2.1. IR: $\nu(\text{C}=\text{N})$, 1625m cm⁻¹.

4.2.6. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PEt₂Ph)] 11

Yield 68%. Anal. Found: C, 51.2; H, 5.8; N, 2.0. C₂₄H₃₁NOPdPBr requires: C, 50.9; H, 5.5; N, 2.5. IR: $\nu(\text{C}=\text{N})$, 1615m cm⁻¹.

4.2.7. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PEtPh₂)] 12

Yield 75%. Anal. Found: C, 54.3; H, 5.1; N, 2.4. C₂₈H₃₁NOPdPBr requires: C, 54.7; H, 5.0; N, 2.3. IR: $\nu(\text{C}=\text{N})$, 1615m cm⁻¹.

4.2.8. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PMePh₂)] 13

Yield 70%. Anal. Found: C, 54.5; H, 4.8; N, 2.8. C₂₇H₂₉NOPdPBr requires: C, 54.0; H, 4.9; N, 2.3. IR: $\nu(\text{C}=\text{N})$, 1615m cm⁻¹.

4.2.9. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PPh₃)] 14

Yield 70%. Anal. Found: C, 54.4; H, 4.8; N, 2.1. C₃₂H₃₁NOPdPI requires: C, 54.1; H, 4.4; N, 2.0. IR: $\nu(\text{C}=\text{N})$, 1620m cm⁻¹.

4.2.10. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PEt₂Ph)] 15

Yield 70%. Anal. Found: C, 46.8; H, 5.0; N, 2.2. C₂₄H₃₁NOPdPI requires: C, 47.0; H, 5.1; N, 2.3. IR: $\nu(\text{C}=\text{N})$, 1618m cm⁻¹.

4.2.11. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PEtPh₂)] 16

Yield 70%. Anal. Found: C, 50.8; H, 4.7; N, 2.2. C₂₈H₃₁NOPdPI requires: C, 50.8; H, 4.7; N, 2.1. IR: $\nu(\text{C}=\text{N})$, 1622m cm⁻¹.

4.2.12. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PMePh₂)] 17

Yield 73%. Anal. Found: C, 48.9; H, 4.4; N, 2.4. C₂₇H₂₉NOPdPI·0.33CH₂Cl₂ requires: C, 48.6; H, 4.4; N, 2.6. IR: $\nu(\text{C}=\text{N})$, 1620m cm⁻¹.

4.2.13. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PPh₃)₂] 18

4.2.13.1. Method a. The complex was synthesised following a similar procedure to that of **6** but using a dimer/phosphine 1:4 molar ratio. Yield 68%. Anal. Found: C, 65.4; H, 5.5; N, 1.8. C₅₀H₄₆NOPdP₂Cl·0.5CH₂Cl₂ requires: C, 65.7; H, 5.1; N, 1.5. IR: $\nu(\text{C}=\text{N})$, 1625m cm⁻¹; $\nu(\text{Pd}-\text{Cl})$, 290m cm⁻¹.

4.2.13.2. Method b. A sample of PPh₃ (21.2 mg, 0.08 mmol) was added to a solution of **6** (50 mg, 0.08 mmol) in acetone (15 cm³). The mixture was stirred for 4 h at r.t. and the resulting precipitate was filtered off and the product recrystallised from dichloromethane/hexane as a yellow solid.

The following compounds were made similarly:

4.2.14. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Cl)(PMePh₂)₂] 19

Yield 70%. Anal. Found: C, 64.0; H, 6.0; N, 2.0. C₄₀H₄₂NOPdP₂Cl requires: C, 63.5; H, 5.6; N, 1.9. IR: $\nu(\text{C}=\text{N})$, 1625m cm⁻¹; $\nu(\text{Pd}-\text{Cl})$, 294m cm⁻¹.

4.2.15. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PPh₃)₂] 20

Yield 65%. Anal. Found: C, 61.4; H, 4.8; N, 1.6. C₅₀H₄₆NOPdP₂Br·0.5CHCl₃ requires: C, 61.6; H, 4.8; N, 1.4. IR: $\nu(\text{C}=\text{N})$, 1625m cm⁻¹.

4.2.16. [Pd{3-(CHO)C₆H₃C(H)=NCy}(Br)(PMePh₂)₂] 21

Yield 65%. Anal. Found: C, 60.5; H, 5.6; N, 1.4. C₄₀H₄₂NOPdP₂Br requires: C, 60.0; H, 5.3; N, 1.8. IR: $\nu(\text{C}=\text{N})$, 1630m cm⁻¹.

4.2.17. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PPh₃)₂] 22

Yield 60%. Anal. Found: C, 61.8; H, 4.7; N, 1.3. C₅₀H₄₆NOPdP₂I requires: C, 61.8; H, 4.8; N, 1.4. IR: $\nu(\text{C}=\text{N})$, 1625m cm⁻¹.

4.2.18. [Pd{3-(CHO)C₆H₃C(H)=NCy}(I)(PMePh₂)₂] 23

Yield 76%. Anal. Found: C, 57.2; H, 5.5; N, 2.0. C₄₀H₄₂NOPdP₂I requires: C, 56.7; H, 5.0; N, 1.7. IR: $\nu(\text{C}=\text{N})$, 1630m cm⁻¹.

4.2.19. [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(Cl)(PPh₃)₂] 24

A mixture of **6** (50 mg, 0.08 mmol) and cyclohexylamine (9 mg, 0.09 mmol) in chloroform (25 cm³) was heated under reflux for 8 h in a Dean–Stark apparatus. After cooling to r.t., the solution was evaporated under reduced pressure and the required product was isolated from dichloromethane/hexane as a yellow solid. Yield 88%. Anal. Found: C, 59.2; H, 6.0; N, 3.2. C₃₈H₄₂N₂PdP₂Cl·CH₂Cl₂ requires: C, 59.7; H, 5.7; N, 3.6. IR: $\nu(\text{C}=\text{N})$, 1638h,m, 1620m cm⁻¹; $\nu(\text{Pd}-\text{Cl})$, 275m cm⁻¹.

The following compounds were made analogously:

4.2.20. [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(Cl)-(PEt₂Ph)] 25

Yield 83%. Anal. Found: C, 54.7; H, 6.7; N, 3.8. C₃₀H₄₂N₂PdP₂Cl·CHCl₃ requires: C, 55.2; H, 6.5; N, 4.2. IR: $\nu(\text{C}=\text{N})$, 1640sh,m, 1620sh,m cm⁻¹; $\nu(\text{Pd}-\text{Cl})$, 275m cm⁻¹.

4.2.21. [Pd{3-(CyC(H)=N)C₆H₃C(H)=NCy}(Cl)-(PEtPh₂)] 26

Yield 78%. Anal. Found: C, 59.6; H, 6.3; N, 3.7. C₃₄H₄₂N₂PdP₂Cl·0.5CH₂Cl₂ requires: C, 60.0; H, 6.2; N, 4.0. IR: $\nu(\text{C}=\text{N})$, 1638m, 1620m cm⁻¹; $\nu(\text{Pd}-\text{Cl})$, 271m cm⁻¹.

4.2.22. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PMePh_2)]$ **27**

Yield 70%. Anal. Found: C, 57.5; H, 6.2; N, 3.8. $C_{33}H_{40}N_2PdP_2Cl \cdot 0.5CHCl_3$ requires: C, 57.7; H, 5.9; N, 4.0. IR: $\nu(C=N)$, 1638m, 1620m cm^{-1} ; $\nu(Pd-Cl)$, 271m cm^{-1} .

4.2.23. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(I)(PPh_3)]$ **28**

Yield 80%. Anal. Found: C, 58.0; H, 6.0; N, 4.0. $C_{38}H_{42}N_2PdPI$ requires: C, 57.7; H, 5.4; N, 3.5. IR: $\nu(C=N)$, 1632m, 1618m cm^{-1} .

4.2.24. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PPh_3)(NH_2Cy)]$ **29**

4.2.24.1. *Method a.* The complex was synthesised following a similar procedure to that of **24** but using a monomer/cyclohexylamine 1:2 ratio. Yield 55%. Anal. Found: C, 63.3; H, 6.5; N, 4.8. $C_{44}H_{55}N_3PdP_2Cl \cdot 0.5CH_2Cl_2$ requires: C, 63.5; H, 6.7; N, 5.0. IR: $\nu(C=N)$, 1630sh,m, 1620m cm^{-1} ; $\nu(Pd-Cl)$, 273m cm^{-1} .

4.2.24.2. *Method b.* To a solution of **24** (30 mg, 0.043 mmol) in $CHCl_3$ $CyNH_2$ (4.3 mg, 0.043 mmol) was added in a cyclometallated complex/amine 1:1 molar ratio. The solution was heated under reflux for 8 h in a Dean–Stark apparatus. After cooling to r.t., the solution was evaporated under reduced pressure and the required product was isolated from dichloromethane/hexane.

4.2.24.3. *Method c.* A sample of PPh_3 (9.78 mg, 0.04 mmol) was added to a solution of **5** (20 mg, 0.04 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h at r.t. and the resulting precipitate was filtered off and the product recrystallised from dichloromethane/hexane.

The following compounds were prepared similarly:

4.2.25. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PEtPh_2)(NH_2Cy)]$ **30**

Yield 40%. Anal. Found: C, 60.4; H, 6.8; N, 5.0. $C_{40}H_{55}N_3PdP_2Cl \cdot 0.5CHCl_3$ requires: C, 60.1; H, 6.8; N, 5.2. IR: $\nu(C=N)$, 1635m, 1618m cm^{-1} ; $\nu(Pd-Cl)$, 272m cm^{-1} .

4.2.26. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PMePh_2)(NH_2Cy)]$ **31**

Yield 60%. Anal. Found: C, 63.0; H, 7.0; N, 5.4. $C_{39}H_{53}N_3PdP_2Cl$ requires: C, 63.6; H, 7.3; N, 5.7. IR: $\nu(C=N)$, 1635sh,m, 1620m cm^{-1} ; $\nu(Pd-Cl)$, 270m cm^{-1} .

4.2.27. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Br)(PPh_3)-(NH_2Cy)]$ **32**

Yield 65%. Anal. Found: C, 54.0; H, 5.5; N, 4.0. $C_{44}H_{55}N_3PdPBr \cdot 1.5CHCl_3$ requires: C, 54.3; H, 5.7; N, 4.2. IR: $\nu(C=N)$, 1635m, 1618m cm^{-1} .

4.2.28. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PPh_3)_2]$ **33**

4.2.28.1. *Method a.* The complex was synthesised following a similar procedure to that of **24**. Yield 70%. Anal. Found: C, 58.2; H, 5.4; N, 2.4. $C_{56}H_{57}N_2PdP_2Cl \cdot 2CHCl_3$ requires: C, 58.0; H, 5.0; N, 2.3. IR: $\nu(C=N)$, 1637m cm^{-1} ; $\nu(Pd-Cl)$, 291m cm^{-1} .

4.2.28.2. *Method b.* A sample of PPh_3 (11.2 mg, 0.04 mmol) was added to a solution of **24** (30 mg, 0.04 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h at r.t. and the resulting precipitate was filtered off and the product recrystallised from chloroform/hexane.

4.2.28.3. *Method c.* A sample of PPh_3 (6.75 mg, 0.025 mmol) was added to a solution of **29** (20 mg, 0.025 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h at r.t. and the resulting precipitate was filtered off and the product recrystallised from chloroform/hexane.

Compounds **34** and **35** were prepared similarly:

4.2.29. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(Cl)-(PMePh_2)_2]$ **34**

Yield 76%. Anal. Found: C, 62.6; H, 6.3; N, 3.3. $C_{46}H_{53}N_2PdP_2Cl \cdot 0.5CHCl_3$ requires: C, 62.2; H, 6.0; N, 3.1. IR: $\nu(C=N)$, 1636m cm^{-1} ; $\nu(Pd-Cl)$, 275m cm^{-1} .

4.2.30. $[Pd\{3-(CyC(H)=N)C_6H_3C(H)=NCy\}(I)(PPh_3)_2]$ **35**

Yield 75%. Anal. Found: C, 63.8; H, 5.7; N, 2.5. $C_{56}H_{57}N_2PdP_2I$ requires: C, 63.9; H, 5.5; N, 2.7. IR: $\nu(C=N)$, 1638sh,m, 1622m cm^{-1} .

4.3. Single-crystal X-ray diffraction analysis

A prismatic yellow crystal of dimensions $0.15 \times 0.25 \times 0.40$ mm of **12** was mounted on a glass fiber in a Enraf-Nonius CAD4 diffractometer for data collection. Unit cell parameters were determined from least-squares on setting angles of 25 reflections with $8.45 < \theta < 11.90^\circ$. Data were collected at r.t. by the $\omega/2\theta$ scan technique using graphite monochromatised Mo-K $_{\alpha}$ ($\lambda = 0.71093$ Å) radiation. A total of 8061 reflections were measured with $\theta_{max} = 30.01^\circ$; 7605 unique reflections; $R_{int} = 0.0772$; 4260 reflections were considered observed on the criterion $I > 2\sigma(I)$ and corrected for Lorentz and polarisation effects. An empirical absorption correction was also made. A summary of the

crystal data, experimental details and refinement results is shown in Table 1.

The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares procedure. A weighting scheme $w = 1/[s^2 (F_o^2) + (0.0555P)^2 + 1.3320P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Computations were performed by means of VAX-SDP [20], SHELXS86 [21], and SCHAKAL [22] programs on a DEX MICROVAXII computer. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [23].

Acknowledgements

We wish to thank the Ministerio de Educación y Ciencia (DGICYT) (Proyecto No. PB92-0376) for financial support.

References

- [1] S. Trofimenko, *Inorg. Chem.* 12 (1973) 1215.
- [2] I. Omae, *Coord. Chem. Rev.* 79 (1979) 287.
- [3] I. Omae, *Coord. Chem. Rev.* 28 (1979) 97.
- [4] E.C. Constable, *Polyhedron* 3 (1984) 1037.
- [5] I. Omae, *Organometallic Intramolecular-Coordination Compounds*, Elsevier, Amsterdam, 1986.
- [6] G.R. Newkome, W.E. Puckett, W.K. Gupta, G.E. Kiefer, *Chem. Rev.* 86 (1986) 451.
- [7] R.M. Ceder, J. Sales, X. Solans, M. Font-Altaba, *J. Chem. Soc. Dalton Trans.* (1986) 1351.
- [8] G.B. Cayhill, P.J. Steel, *J. Organomet. Chem.* 395 (1990) 375.
- [9] G.B. Cayhill, P.J. Steel, *J. Organomet. Chem.* 395 (1990) 359.
- [10] J.L. Casas, E. Gayoso, J.M. Vila, M.T. Pereira, M. Gayoso, *Synth. React. Inorg. Met. Org. Chem.* 21 (1991) 263.
- [11] (a) J.M. Vila, M.T. Pereira, M. Gayoso, M.C. Rodríguez, J.M. Ortigueira, M. Thornton-Pett, *J. Organomet. Chem.* 426 (1992) 267; (b) J.M. Vila, M.T. Pereira, M. Gayoso, M.C. Rodríguez, J.M. Ortigueira, J.J. Fernández, M. López Torres, *J. Organomet. Chem.* 479 (1994) 37.
- [12] J.M. Vila, M. Gayoso, M.T. Pereira, M. López Torres, G. Alonso, J.J. Fernández, *J. Organomet. Chem.* 445 (1993) 287.
- [13] J.M. Vila, M. Gayoso, M.T. Pereira, M. López Torres, J.J. Fernández, A. Fernández, J.M. Ortigueira, *J. Organomet. Chem.* 506 (1996) 165.
- [14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, 1960.
- [15] J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernández, M. Thornton-Pett, *J. Organomet. Chem.* 401 (1991) 385 and references therein.
- [16] J.M. Vila, M. Gayoso, M. López Torres, et al., *J. Organomet. Chem.* 511 (1996) 129.
- [17] J. Selbin, K. Abboud, S.F. Watkins, M.A. Gutiérrez, F.R. Fronczek, *J. Organomet. Chem.* 241 (1983) 259.
- [18] S. H. Mastin, *Inorg. Chem.* 13 (1974) 1003.
- [19] D.D. Perrin, W.L.F. Armarego, D.P. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Oxford, Pergamon, 1983.
- [20] B.A. Frenz & Associates, *Structure determination package, SDP/VAX 2.2*, College Station, TX, USA, and Enraf-Nonius, Delft, Netherlands, 1985.
- [21] G.M. Sheldrick, *SHELXTL*, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 5.1), University of Gottingen, Germany, 1985.
- [22] E. Keller, *SCHAKAL*. Program for plotting molecular and crystal structures, University of Freiburg, Germany, 1988.
- [23] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974.