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Exo- and *endo*-cyclopalladated compounds of *N*-benzylideneamines. Synthesis and X-ray structure of $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N\text{-}2',4',6'\text{-}Me_3C_6H_2)\text{-}3,5\text{-}Me_2C_6H_2\}Br]_2$

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Abstract

The action of $Pd(AcO)_2$ on the imines $C_6R_mH_{5-m}CH{=}N(CH_2)_pC_6R'_nH_{5-n}$ has been studied. Five-membered *endo*-metallacycles were obtained from the imines **1a** (R = 4-Cl, $p = 0$, R′ = 2′,4′,6′-Me_3) and **1b** (R = 2-Cl, $p = 0$, R′ = 2′,4′,6′-Me_3), by activation of a C(aromatic)–H bond and from the imine **1c** (R = 2,6-Cl_2, $p = 0$, R′ = 2′,4′,6′-Me_3), by oxidative addition of the *ortho* C–Cl bonds to Pd^0 formed *in situ*. Six-membered *endo*-metallacycles were obtained from the imine **1d** (R = 2,4,6-Me_3, $p = 0$, R′ = 2′,4′,6′-Me_3) by activation of a C(aliphatic)–H bond. Imines **1e** (R = 2,6-Cl_2, $p = 1$, R′ = 2′-Me) and **1f** (R = 2,6-Cl_2, $p = 1$, R′ = 2′-Cl afforded five-membered *exo*-metallacycles, but the formation, in low yield, of the *endo*-compounds by oxidative addition of the *ortho* C–Cl bonds was also observed. These results show the strong tendency of imines to form *endo*-cyclic compounds. Complexes $[PdBr(C\frown N)(PPh_3)]$ can be obtained by the action of PPh_3 on the new cyclometallated compounds prepared. $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N\text{-}2',4',6'\text{-}Me_3C_6H_2)\text{-}3,5\text{-}Me_2C_6H_2\}Br]_2$ crystallizes in the monoclinic space group $C2/c$ with $a = 19.333(3)$; $b = 13.511(2)$; $c = 14.092(2)$ Å, $\beta = 96.94(2)$ and $Z = 4$. The *endo* six-membered ring displays a half-skew-chair conformation, with the palladium atom out of the plane (0.937 Å) defined by the other atoms.

1. Introduction

Cyclopalladation is one of the classic ways to activate C–H bonds in heterosubstituted organic molecules. The factors that influence the ease and manner of cyclopalladation reactions are not throughly understood but the following mechanism is widely accepted: (i) initial coordination of the ligand to the metal, and (ii) electrophilic attack of Pd^{II} on the C–H bond [1]. Moreover, there is a strong preference for five-membered cyclometallated compounds, and also preferential activation of C(aromatic)–H bonds compared to C(aliphatic)–H bonds, but recently, a few six-membered cyclopalladated compounds have been prepared by activation of C(aliphatic)–H bonds [2].

Schiff bases are suitable for the study of cyclometallation reactions since they can undergo metallation on different carbon atoms (polyfunctional). We have shown that imines have a strong tendency to form *endo*-cyclic cyclometallated compounds (when the C=N bond is part of the metallacycle). This *endo* effect is so strong that the action of $Pd(AcO)_2$ on the imine 2,4,6-$Me_3C_6H_2CH{=}N{-}CH_2C_6H_5$, in refluxing acetic acid, affords the cyclometallated compound $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}NCH_2C_6H_5)3,5\text{-}Me_2C_6H_2\}AcO]_2$, where the activation of a C(aliphatic)–H bond with formation of a six-membered *endo*-metallacycle takes place in preference to the activation of a C(aromatic)–H bond and formation of a five-membered *exo*-metallacycle [2c]. Furthermore, the five-membered *exo*-metallacycle $[Pd\{2\text{-}(CH_2N{=}CH\text{-}2',4',6'\text{-}(CH_3)_3C_6H_2)C_6H_3\}(AcO)]_2$ isomerizes to the six-membered metallacycle $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}NCH_2C_6H_5)3,5\text{-}(Me)_2C_6H_2\}AcO]_2$ [3].

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This *endo* effect is not restricted to cyclopalladation reactions. Recently it has been shown that oxidative addition of *ortho*-halogenated imines to palladium(0) complexes affords preferentially the *endo* metallacycles [4]. The reaction between $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and *N*-benzylideneamines shows that the *endo* effect is also important for platinum compounds [5]. Moreover, the selective activation of C–F bonds with formation of *endo* compounds takes place even in the presence of weaker C–H, C–Cl or C–Br bonds, when $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ reacts with $C_6F_5CH{=}NCH_2(2\text{-}XC_6H_4)$ [6].

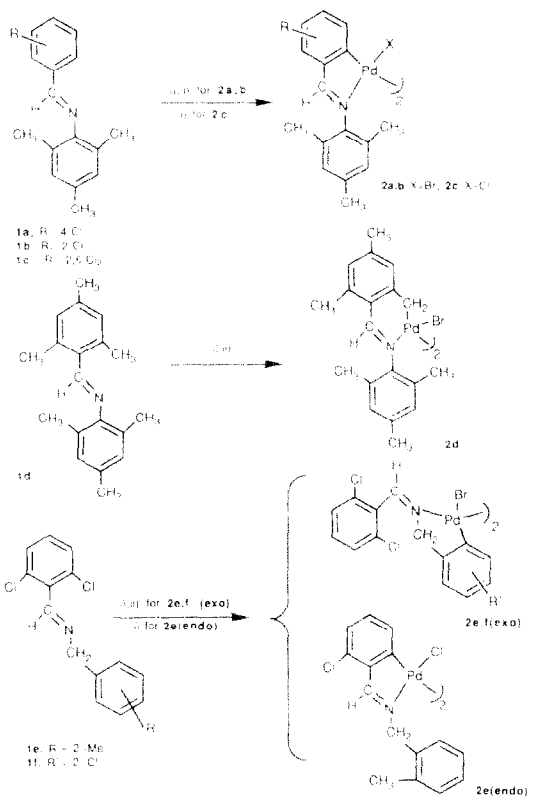
In order to obtain additional information on the factors that influence the ease and mode of cyclometallation reactions we report here the action of $Pd(AcO)_2$ on the *N*-benzylideneamines **1a–f**, in which, in principle, different metallacycles might be obtained.

Cyclopalladation reactions usually afford dinuclear compounds [Pd(C^N)X] [1], but there is also evidence for the formation of trinuclear and even polynuclear species [7,8]. The characterization of such compounds is not easy and very often they are treated with phosphines or amines to afford mononuclear complexes, which are easily characterizable.

The molecular structure of such dinuclear or polynuclear compounds has not been extensively investigated. X-Ray diffraction studies of some acetato- and chloro-bridged complexes have been reported [9], and there is also one bromo-bridged cyclometallated complex, whose crystal structure has been determinated [10]. Here we report the X-ray crystal structure of the bromo-bridged complex $[Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N\text{-}2',4',6'\text{-}Me_3C_6H_2)\text{-}3,5\text{-}Me_2C_6H_2\}Br]_2$.

2. Results and discussion

Imines **1a–f** were treated with $Pd(AcO)_2$, in a 2:1 ratio, in anhydrous acetic acid under reflux. Subsequent treatment of the residues with LiBr in ethanol afforded the bromo-bridged cyclometallated compounds **2** (see Scheme 1). Five-membered *endo*-metallacycles were obtained from the imines **1a,b** by activation of a C(aromatic)–H bond. These imines might also afford a five-membered *exo*-metallacycle by activation of a C(aliphatic)–H bond, but their formation was not observed. Imine **1c**, with two chlorine substituents in the *ortho* positions of the benzal ring, gave the five-membered *endo*-metallacycle, and no five-membered *exo*-metallacycle was observed. The formation of the *endo*-cyclic compound with this imine can be explained by oxidative addition of one of the *ortho* C–Cl bonds to palladium(0), formed by reduction *in situ* of Pd^{II} by the imine. This is a well known process, and has been proposed to occur in the catalytic arylation from olefines and organic halides [11]. The six-membered *endo*-metallacycle was obtained from the imine **1d** by activation of a C(aliphatic)–H bond in preference to the formation of a five-membered *exo*-metallacycle, also by activation of a C(aliphatic)–H bond. This shows that the size of the metallacycle is not the decisive factor in the cyclometallation reactions of imines, and that the *endo* effect is important in deciding the metallation position. The formation of five-membered *exo*-metallacycles was observed from the imines **1e** and **1f**. A small quantity of the *endo*-cyclic compounds was also obtained, by oxidative addition of the *ortho* C–Cl bonds of these imines to Pd^0 formed *in situ*, and it was possible to isolate and purify the *endo*-derivative **2e**. The *exo*-compounds obtained contain the imine in the *Z* form (see below) although either isomer, *E* or *Z*, can give *exo*-derivatives. As the free imine is in the *E* form, *E*–*Z* isomerization occurs during the cyclometallation reaction.



Scheme 1. (i) $Pd(AcO)_2$, in refluxing acetic acid. (ii) LiBr, EtOH, room temperature.

2.1. Reaction with PPh_3

The action of PPh_3 on the cyclometallated compounds **2** $[PdBr(C^N)]_2$, in a 2:1 molar ratio was studied to obtain more soluble easily characterizable mononuclear complexes. Compounds **3** [PdBr(C^N)-

(PPh_3)] were obtained in good yields in all cases. The $^{31}P\{^1H\}$ NMR spectra (Table 1) show that the phosphine is *trans* to the imine nitrogen. ^1H NMR spectra of these compounds also confirm this arrangement (see below).

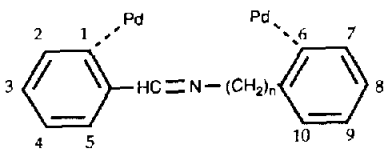
2.2. Proton NMR spectra

Proton NMR spectra (Table 1) afford conclusive evidence of the palladation position. In compounds containing PPh_3, the aromatic protons of the palladated aromatic ring in the five-membered metallacy-

TABLE 1. Proton [a] and ^{31}P [b] NMR data

Compound	Aromatic	HC=N, aliphatic	^{31}P
2a	7.18 (d (1H), ^3J(HH) = 8.3, H_5) 7.0–6.90 (br m (4H), H_2, H_4, H_7, H_9)	7.73 (s (1H), HC=N) 2.33–2.23 (br m (9H), Me_6, Me_8, Me_{10})	
3a	7.80–7.30 (br m (16H), H_5, PPh_3) 6.95 (dd (1H), ^4J(HH) = 7.9, ^4J(HH) = 1.9, H_4) 6.86 (s (2H), H_7, H_9) 6.30 (dd (1H), ^4J(HP) = 5.9, ^4J(HH) = 1.9 H_2)	8.05 (d (1H), ^4J(HP) = 7.5, HC=N) 2.32 (s (6H), Me_6, Me_{10}) 2.26 (s (3H), Me_8)	40.98
2b	7.0–6.70 (br m (5H), H_2, H_3, H_4, H_7, H_9)	8.15 (s (1H), HC=N) 2.35–2.20 (br m (9H), Me_6, Me_8, Me_{10})	
3b, 3c	8.00–7.20 (br m (15H), PPh_3) 6.90 (d (1H), ^3J(HH) = 7.4, H_4) 6.85 (s (2H), H_7, H_9) 6.55 (t (1H), ^3J(HH) = 7.4, H_3) 6.34 (t (1H), ^3J(HH) = ^4J(HP) = 7.4, H_2)	8.60 (d (1H), ^4J(HP) = 7.4, HC=N) 2.36 (s (6H), Me_6, Me_{10}) 2.27 (s (3H), Me_8)	42.18(s)
2d	7.0 (s (1H), H_4) 6.90 (s (2H), H_7, H_9) 6.81 (s (1H), H_2)	7.79 (s (1H), HC=N) 3.28 (s (2H), CH_2–Pd) 2.41 (s (3H), Me_5) 2.35–2.20 (br s (9H), Me_6, Me_8, Me_{10}) 2.17 (s (3H), Me_3)	
3d	7.70–7.20 (br m (15H), PPh_3) 6.94 (s (2H), H_7, H_9) 6.71 (s (1H), H_4 5.68 (s (1H), H_2)	8.05 (d (1H), ^4J(HP) = 12.4, HC=N) 2.92 (d (2H), ^3J(HP) = 11.9, CH_2–Pd) 2.57 (s (6H), Me_6, Me_{10}) 2.33 (s (3H), Me_8) 2.29 (s (3H), Me_5) 2.09 (s (3H), Me_3)	36.89(s)
3e (*exo*)	7.70–7.20 (br m (18H), H_2, H_3, H_4, PPh_3) 6.70–6.55 (br m (1H), H_9) 6.35–6.25 (br m (2H), H_7, H_8)	9.77 (d (1H), ^4J(HP) = 5.22, HC=N) 4.86 (br s (2H), CH_2–N) 2.07 (s (3H), Me_{10})	42.61(s)
3e (*endo*)	7.80–7.20 (br m (18H), H_7, H_8, H_9, PPh_3) 6.75 (d (1H), ^3J(HH) = 7.1 H_6) 6.60 (s (1H), ^3J(HH) = 7.3, H_4) 6.40 (t (1H), ^3J(HH) = 7.3, H_3) 6.25 (t (1H), ^3J(HH) = ^4J(HP) = 7.4, H_2)	8.00 (d (1H), ^4J(HP) = 7.5, HC=N) 5.40 (br s (2H), CH_2–N) 2.35 (s (3H), Me_{10})	42.8(s)
2f	7.50–6.80 (br m (6H), H_2, H_3, H_4, H_7, H_8, H_9)	9.05 (br s (1H), HC=N) 4.87 (s (2H), CH_2–N)	
3f	7.70–7.20 (br m (18H), H_2, H_3, H_4, PPh_3) 6.70–6.55 (br m (1H), H_9) 6.40–6.30 (br m (2H), H_7, H_8)	9.73 (br m (1H), HC=N) 5.04 (br s (2H), CH_2–N)	41.98(s)

[a] In $CDCl_3$; chemical shifts in ppm with respect to internal $SiMe_4$; coupling constants in Hz; numbering as in figure. [b] In $ClCl_3$; chemical shift in ppm with respect to 85% H_3PO_4.



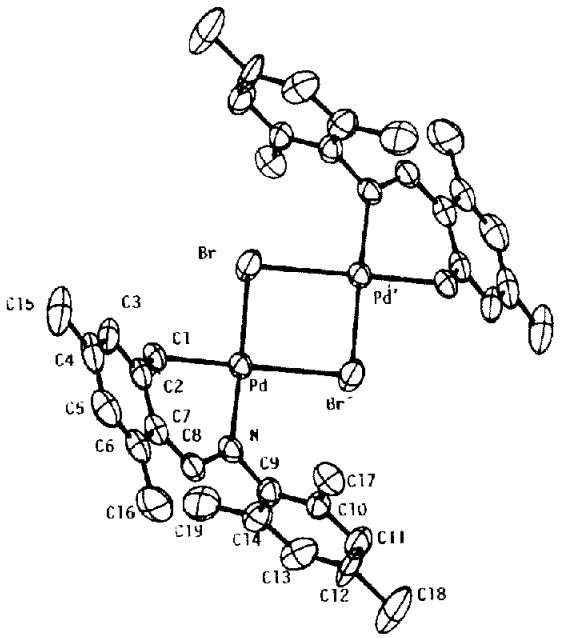


Fig. 1. Molecular structure of **2d**.

cles **3a,b,c,e,f** and those of the palladated benzylic unit in the six-membered metallacycle **3d**, resonate at high field. This could be caused by a phosphine phenyl ring, suggesting a *cis* arrangement of the phosphine and the metallated carbon atom and, in consequence, a *trans* arrangement of phosphorus and nitrogen atoms.

The chemical shift of methyne protons is useful for the structural characterization of cyclopalladated complexes. This signal appears shifted to high field (0.3–1.2 ppm) relative to that of the free imine in the *endo*-derivatives [12], and also in the *exo*-metallacycles, if the imine adopts the *E*-form [4]. However, in the *exo*-metallacycles with the imine in the *Z* form, the methyne proton resonates downfield [3,13]. The shift can be explained by the paramagnetic anisotropy of the metal [14], showing a close approach of Pd and H atoms, or by a weak three-centre four-electron interaction C–H · · · M, different from an agostic interaction [15]. The methyne proton resonance is shifted downfield in the new *exo*-metallacycles, showing that the imine is in the *Z* form.

TABLE 3. Bond distances (Å) for **2d**

Br–Pd	2.450(1)	C(7)–C(6)	1.406(10)
Br'–Pd	2.639(1)	C(16)–C(6)	1.505(16)
N–Pd	2.050(5)	C(8)–C(7)	1.423(10)
C(1)–Pd	2.021(7)	C(10)–C(9)	1.388(10)
C(8)–N	1.298(8)	C(14)–C(9)	1.390(11)
C(9)–N	1.436(9)	C(11)–C(10)	1.383(11)
C(2)–C(1)	1.500(11)	C(17)–C(10)	1.498(11)
C(3)–C(2)	1.413(11)	C(12)–C(11)	1.360(15)
C(7)–C(2)	1.417(11)	C(13)–C(12)	1.400(15)
C(4)–C(3)	1.411(13)	C(18)–C(12)	1.542(12)
C(5)–C(4)	1.387(16)	C(14)–C(13)	1.404(11)
C(15)–C(4)	1.505(12)	C(19)–C(14)	1.518(13)
C(6)–C(5)	1.368(13)		

2.3. *Molecular structure of* **2d**

The crystal structure of **2d** has been determined (Fig. 1). Crystallographic data and selected bond lengths and angles are listed in Tables 2–4, and atomic coordinates for non-hydrogen atoms are given in Table 5.

TABLE 2. Summary of crystallographic data for **2d**

Formula	$C_{38}H_{44}Br_2N_2Pd_2$
Mol wt	901.4
System	monoclinic
Space group	C2/c
a (Å)	19.333(3)
b (Å)	13.511(2)
c (Å)	14.092(2)
β (°)	96.94(2)
V (Å^3)	3654(1)
d_{calc} (g cm^{-3})	1.638
Z	4
F(000)	1792.0
Crystal size (mm^3)	0.07×0.07×0.1
μ(Mo Kα) (cm^{-1})	33.09
λ(Mo Kα) (Å)	0.71069
T (°C)	25
Reflections collected	2678
R	0.052
R_w	0.056

TABLE 4. Bond angles (°) for **2d**

Br'–Pd–Br	86.3(1)	C(16)–C(6)–C(5)	119.2(8)
N–Pd–Br	177.2(2)	C(16)–C(6)–C(7)	121.0(8)
N–Pd–Br'	96.2(2)	C(6)–C(7)–C(2)	119.7(7)
C(1)–Pd–Br	92.0(2)	C(8)–C(7)–C(2)	120.5(7)
C(1)–Pd–Br'	176.9(2)	C(8)–C(7)–C(6)	119.7(7)
C(1)–Pd–N	85.6(3)	C(7)–C(8)–N	124.3(7)
PD–BR–Pd'	93.7(1)	C(10)–C(9)–N	117.4(7)
C(8)–N–Pd	126.2(5)	C(14)–C(9)–N	119.9(7)
C(9)–N–Pd	116.9(4)	C(14)–C(9)–C(10)	122.6(7)
C(9)–N–C(8)	116.9(6)	C(11)–C(10)–C(9)	118.0(8)
C(2)–C(1)–Pd	111.3(5)	C(17)–C(10)–C(9)	121.0(7)
C(3)–C(2)–C(1)	119.6(8)	C(17)–C(10)–C(11)	121.0(8)
C(7)–C(2)–C(1)	121.3(7)	C(12)–C(11)–C(10)	121.4(9)
C(7)–C(2)–C(3)	119.1(7)	C(13)–C(12)–C(11)	120.5(8)
C(4)–C(3)–C(2)	120.3(9)	C(18)–C(12)–C(11)	121.4(11)
C(5)–C(4)–C(3)	118.5(8)	C(18)–C(12)–C(13)	118.1(12)
C(15)–C(4)–C(3)	119.5(11)	C(14)–C(13)–C(12)	119.8(9)
C(15)–C(4)–C(5)	122.0(9)	C(13)–C(14)–C(9)	117.6(8)
C(6)–C(5)–C(4)	122.5(8)	C(19)–C(14)–C(9)	121.0(7)
C(7)–C(6)–C(5)	119.8(8)	C(19)–C(14)–C(13)	121.3(8)

TABLE 5. Final atomic coordinates ($\times 10^4$) of **2d** ($B_{eq} = 8\pi^2/3\Sigma U_{ij} a_i^* a_j^* a_i a_j$)

	x	y	z	B_{eq}
Pd	26723(3)	32228(4)	11258(3)	2.80(2)
Br	28454(5)	14970(6)	6743(6)	4.34(4)
N	2567(3)	4659(4)	1555(4)	2.96(23)
C(1)	3030(5)	2948(6)	2508(5)	3.77(31)
C(2)	3617(4)	3630(6)	2861(5)	3.60(32)
C(3)	4247(5)	3232(7)	3317(5)	4.34(36)
C(4)	4792(4)	3865(10)	3696(5)	4.94(44)
C(5)	4682(5)	4879(9)	3652(6)	4.90(44)
C(6)	4082(5)	5288(7)	3203(5)	4.18(36)
C(7)	3541(4)	4671(6)	2792(5)	3.39(30)
C(8)	2942(4)	5097(6)	2260(5)	3.25(28)
C(9)	2035(4)	5241(5)	1017(5)	3.26(28)
C(10)	2234(4)	5836(5)	294(5)	3.82(32)
C(11)	1719(6)	6351(6)	−269(6)	4.63(41)
C(12)	1038(6)	6279(7)	−127(7)	5.55(47)
C(13)	839(5)	5680(7)	604(8)	5.01(43)
C(14)	1347(4)	5163(6)	1206(6)	4.06(34)
C(15)	5464(5)	3426(10)	4162(7)	6.63(55)
C(16)	4025(7)	6397(9)	3123(9)	5.95(55)
C(17)	2983(5)	5919(8)	130(6)	5.16(44)
C(18)	465(8)	6857(9)	−752(10)	8.21(69)
C(19)	1155(5)	4538(8)	2030(8)	5.71(51)

The crystal structure consists of discrete molecules separated by van der Waals' distances. The complex is a centrosymmetric palladium dimer with two asymmetrically bridging bromine atoms. The two cyclopalladated ligands are *transoid* around the Pd_2Br_2 unit, as observed in analogous cyclopalladated dimers [9,10]. The asymmetry within the bridges arises from the different *trans* groups; the Pd–Br bond *trans* to a benzylic carbon is longer (2.639(1) Å) than that *trans* to nitrogen (2.450(1) Å), consistent with relatively large and small *trans* influences for benzylic carbon and imine nitrogen, respectively. The Pd_2Br_2 is planar, in contrast to some chloro-bridged cyclopalladated compounds, in which this ring is folded [9b,f].

The palladium atom is square-planar coordinated to benzylic carbon, imine nitrogen and the two bridging bromine atoms. The coordination plane shows some tetrahedral distortion, the deviations from the mean plane being +0.033, +0.038, −0.033 and −0.047 Å for Br, N, Br′ and Cl, respectively. The angles between adjacent atoms in the coordination sphere lie in the range 96.2(2) (N–Pd–Br′) to 85.6(3)° (N–Pd–Cl). The smallest of these angles is that between the nitrogen and carbon atoms of the chelated ligand. The palladium-ligand distances are similar to those found for the analogous six-membered cyclometallated compound [Pd{1-CH_2-2-(CH=N-C_6H_5)-3,5-$(CH_3)_2C_6H_2$}-Br(PPh_3)] [2c] and [Pd{1-CH_2-2-(CH=N-C_6H_5)-3,5-$Me_2C_6H_2$}(2,4-lutidine)(PPh_3)]ClO_4 [16], except that Pd–N bond which is shorter in **2d** (2.050(5) Å) than in the above cyclopalladated compounds (2.138(4) and 2.119(7) Å respectively), but the relative *trans* influences of PPh_3 and bromine may explain this.

The six-membered metallacycle adopts a half-skew-chair conformation, with the palladium atom out of the plane (0.937 Å) defined by the other atoms. The six-membered metallacycle also adopts a half-skew-chair conformation in [Pd{1-CH_2-2-(CH=N-C_6H_5)-3,5-$Me_2C_6H_2$}Br(PPh_3)] and [Pd{1-CH_2-2-(CH=N-C_6H_5)-3,5-$Mc_2C_6H_2$}(2,4-lutidine)(PPh_3)]ClO_4, with the palladium atom out of the plane defined by the other atoms (1.325 and 1.086 Å respectively [2c,16].

3. Conclusion

The results described confirm the strong tendency of imines to form *endo*-cyclic compounds. This tendency (*endo* effect) is so strong that the oxidative addition to Pd^0, formed by reduction of the palladium(II) salts by imines forms *endo*-cyclic compounds by activation of a C–Cl bond in preference to *exo*-cyclic compounds. Furthermore, the activation of C(aliphatic)–H bonds with formation of five-membered *exo*-metallacycles was not observed, in sharp contrast with the easy preparation of six-membered *endo*-metallacycles with C(aliphatic)–Pd bonds. Cyclometallation reactions of analogous imines derived from methyl *ortho* substituted anilines show that only *endo*-cyclic cyclometallated compounds are formed [17].

There is no clear explanation for this *endo* effect [3]. The bond distances and bond angles of analogous *endo*- and *exo*-cyclometallated compounds are similar [18] and in consequence it is not easy to relate the stability of such complexes to their structures. Recent mechanistic studies of the formation of cyclometallated platinum compounds of *N*-benzylidencamines show that the entropy could be responsible for the favoured formation of *endo*-compounds [5]. Mechanistic studies of the cyclometallation of *ortho*-arylphenoxide ligands at Group 5 metal atoms suggest that rotation of the aryl ring to be metallated into a coplanar conformation in which the C–H bond about to be activated is being brought close to the metal contributes to cyclometallation reactions [19]. The strong tendency of imines to form *endo*-cyclic compounds may be related to restricted rotation around the C=N bond, which favours the approach of the C–X bond to be metallated to the coordination plane, previous to the metallation.

4. Experimental details

Routine NMR spectra were obtained on a Bruker WP 80SY spectrometer (^1H, 80.13 MHz; $^{31}P\{^1H\}$, 32.8).

^{1}H spectra (200 MHz) were obtained on a Varian XL-200 spectrometer. IR spectra were recorded as KBr discs on a Perkin-Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

4.1. Materials and synthesis

Solvents were dried and distilled before use. Imines were prepared by literature procedures [20].

4.1.1. Compounds **2a,b,d,f**

A stirred suspension of $Pd(AcO)_2$ (1 mmol, 224 mg) in anhydrous acetic acid (30 ml) was treated with an excess of imine **1a, 1b, 1d** or **1f** (2 mmol) and the mixture was refluxed for 3 h (**1a, 1f**) or for 2 h (**1b, 1d**). The solution was filtered to eliminate the small amount of black palladium formed. The filtrate was concentrated *in vacuo* and the residue was dissolved in ethanol and treated with an excess of LiBr (2 mmol, 173 mg) at room temperature for 1 h. The solids obtained were filtered and recrystallized from chloroform/methanol, to afford compounds **2**, as yellow solids, in 60–90% yield.

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-5-ClC$_6$H$_3$}Br]$_2$ (2a). Yield 708 mg (80%). Anal. Found: C, 43.7; H, 3.4; N, 3.2. $C_{32}H_{30}Br_2Cl_2N_2Pd_2$ calcd.: C, 43.37; H, 3.42; N, 3.16%.

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-3-ClC$_6$H$_3$}Br]$_2$ (2b). Yield 532 mg (60%). Anal. Found: C, 43.4; H, 3.3; N, 3.0. $C_{32}H_{30}Br_2Cl_2N_2Pd_2$ calcd.: C, 43.37; H, 3.42; N, 3.16%.

[Pd{1-CH$_2$-2-(CH=N-2',4',6'-Me$_3$C$_6$H$_2$)-3,5-Me$_2$C$_6$H$_2$}Br]$_2$ (2d). Yield 766 mg (85%). Anal. Found: C, 50.7; H, 4.8; N, 3.0. $C_{38}H_{44}Br_2N_2Pd_2$ calcd.: C, 50.62; H, 4.93; N, 3.11%.

[Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)-3-ClC$_6$H$_3$}Br]$_2$ (2f(exo)). Yield 628 mg (65%). Anal. Found: C, 34.8; H, 1.7; N, 2.8. $C_{28}H_{18}Br_2Cl_6N_2Pd_2$ calcd.: C, 34.75; H, 1.88; N, 2.89%.

4.1.2. Compounds **2c, 2e(exo), 2e(endo)**

A stirred suspension of $Pd(AcO)_2$ (1 mmol, 224 mg) in anhydrous acetic acid (30 ml) was treated with an excess of imine **1c** or **1e** (2 mmol) and the mixture was heated under reflux for 2 h (**1c**) or for 30 min (**1e**). The solution was filtered and the solid obtained was recrystallized from chloroform/methanol to afford **2c** or **2e**(*endo*). Compound **2e**(*exo*) was obtained from the solution, by concentration *in vacuo* and reaction of the residue obtained with an excess of LiBr (2 mmol, 174 mg) in ethanol, at room temperature for 1 h. The solid obtained was filtered and recrystallized from chloroform/methanol to afford **2e**(*exo*).

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-3-ClC$_6$H$_3$}Cl]$_2$ (2c). Yield 200 mg (25%). Anal. Found: C, 48.3; H, 3.8; N, 3.4. $C_{32}H_{30}Cl_4N_2Pd_2$ calcd.: C, 48.21; H, 3.80; N, 3.51%.

[Pd(2-{HC=NCH$_2$-(2'-MeC$_6$H$_4$)}-3-ClC$_6$H$_3$)Cl]$_2$ (2e(endo)). Yield 55 mg (7%). Anal. Found: C, 46.5; H, 3.2; N, 3.5. $C_{30}H_{26}Cl_4N_2Pd_2$ calcd.: C, 46.84; H, 3.41; N, 3.64%.

[Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)-3-MeC$_6$H$_3$}Br]$_2$ (2e(exo)). Yield 510 mg (55%). Anal. Found: C, 38.6; H, 2.7; N, 3.1. $C_{30}H_{24}Br_2Cl_4N_2Pd_2$ calcd.: C, 38.87; H, 2.61; N, 3.02%.

4.1.3. [PdBr(C^N)PPh$_3$] (3a–f)

A stirred suspension of **2** (0.5 mmol) in acetone (30 ml) was treated with PPh_3 (1 mmol, 262 mg) and, if the cyclometallated starting material was **2c** or **2e**(*endo*), LiBr (2 mmol, 174 mg) was added to the reaction mixture. The mixture was heated under reflux for 1 h, and then filtered. The filtered solution was concentrated *in vacuo* and the solid obtained after addition of ether was recrystallized from chloroform/methanol to afford **3** in 80–90% yield.

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-5-ClC$_6$H$_3$}Br(PPh$_3$)] (3a). Yield 634 mg (90%). Anal. Found: C, 57.6; H, 4.3; N, 1.8. $C_{34}H_{30}BrClNPPd$ calcd.: C, 57.89; H, 4.29; N, 1.98%.

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-3-ClC$_6$H$_3$}Br(PPh$_3$)] (3b). Yield 600 mg (85%). Anal. Found: C, 57.6; H, 4.3; N, 1.9. $C_{34}H_{30}BrClNPPd$ calcd.: C, 57.89; H, 4.29; N, 1.98%.

[Pd{2-(HC=N-2',4',6'-Me$_3$C$_6$H$_2$)-3-ClC$_6$H$_3$}Br(PPh$_3$)] (3c). Yield 565 mg (80%). Anal. Found: C, 57.7; H, 4.4; N, 2.0. $C_{34}H_{30}BrClNPPd$ calcd.: C, 57.89; H, 4.29; N, 1.98%.

[Pd{1-CH$_2$-2-(CH=N-2',4',6'-Me$_3$C$_6$H$_2$)-3,5-Me$_2$C$_6$H$_2$}Br(PPh$_3$)] (3d). Yield 606 mg (85%). Anal. Found: C, 62.3; H, 5.2; N, 1.8. $C_{37}H_{37}BrNPPd$ calcd.: C, 62.32; H, 5.24; N, 1.96%.

[Pd(2-{HC=NCH$_2$-(2'-MeC$_6$H$_4$)-3-ClC$_6$H$_3$})Br(PPh$_3$)] (3e(endo)). Yield 550 mg (80%). Anal. Found: C, 57.6; H, 4.0; N, 1.9. $C_{33}H_{28}BrClNPPd$ calcd.: C, 57.33; H, 4.09; N, 2.02%.

[Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)-3-MeC$_6$H$_3$}Br(PPh$_3$)] (3e(exo)). Yield 540 mg (75%). Anal. Found: C, 54.8; H, 3.5; N, 1.9. $C_{33}H_{27}BrCl_2NPPd$ calcd.: C, 54.61; H, 3.76; N, 1.93%.

[Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)-3-ClC$_6$H$_3$}Br(PPh$_3$)] (3f(exo)). Yield 595 mg (80%). Anal. Found: C, 51.5; H, 3.2; N, 1.8. $C_{32}H_{24}BrCl_3NPPd$ calcd.: C, 51.50; H, 3.25; N, 1.88%.

4.2. Data collection

A prismatic crystal ($0.07 \times 0.07 \times 0.1$ mm^3) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($12 \leq \theta \leq 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω–2θ scan technique; 5805 reflections were measured in the range $2 \leq \theta \leq 30$. R_{int} (on F) = 0.009, 2678 of which were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls, but significant intensity decay was not observed. Lorentz polarization, but not absorbtion, corrections were made.

4.3. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [21] for crystal structure determination and refined by the full-matrix least-squares method, with the SHELX76 computer program [22]. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = (\sigma^2(F_o) + 0.0044|F_o|^2)^{-1}$. f, f' and f'' were taken from International Tables of X-Ray Crystallography [23]. The positions of 15 H atoms was computed and the remainder were located from a difference synthesis, all refined with an overall isotropic temperature factor using a riding model for computed hydrogen atoms. The final R factor was 0.052 (R_w = 0.056) for all reflections observed. The number of refined parameters was 221. Max. shift/e.s.d. = 0.06, Maximum and minimum peaks in final difference synthesis were 0.3 and -0.3 e Å^{-3}, respectively.

5. Supplementary material available

Tables of hydrogen coordinates, structure factors and thermal parameters are available from the authors.

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