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Reactivity of cyclometallated compounds of N-benzylideneamines. Synthesis and X-ray crystal structure of $[\overline{\mathrm{Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N}}\mathrm{\text{-}C_6H_5)\text{-}3,5\text{-}(CH_3)_2C_6H_2\}\ (2,4\text{-}Me_2C_5H_3N)]ClO_4}$

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Abstract

The action of $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dpe) on the cyclometallated compounds $[\{\mathrm{Pd}(\widehat{\mathrm{CN}})\mathrm{Br}\}_2]$ ($\widehat{\mathrm{CN}}$ = $\mathrm{2\text{-}(HC{=}NC_6H_5)\text{-}5\text{-}ClC_6H_3}$ **1a**, $\mathrm{2\text{-}(CH_2N{=}CH\text{-}2',6'\text{-}Cl_2C_6H_3)C_6H_4}$ **1b**, or $\mathrm{1\text{-}CH_2\text{-}2\text{-}(CH{=}N\text{-}C_6H_5)\text{-}3,5\text{-}(CH_3)_2C_6H_2}$ **1c**) in a 2:1 molar ratio, gives the novel neutral species $[\mathrm{Pd}(\widehat{\mathrm{CN}})\mathrm{Br(dpe)}]$ (**2a,b**) or the ionic compound $[\underline{\mathrm{Pd}(\widehat{\mathrm{CN}}}\mathrm{)(dpe)]Br}$ (**3c**). The action of dpe on compound **1** in a 1:1 molar ratio gives the dinuclear cyclometallated compound **4**, in which two palladium atoms are bridged by the diphosphine. The ionic compounds $[\underline{\mathrm{Pd}(\widehat{\mathrm{CN}}}\mathrm{)(lut)(PPh_3)]ClO_4}$ **6** (lut = 2,4-lutidine) were obtained by reaction between $\mathrm{AgClO_4}$ and acetone solutions of the cyclometallated compounds $[\underline{\mathrm{PdBr}(\widehat{\mathrm{CN}}}\mathrm{)PPh_3}]$, and subsequent addition of 2,4-lutidine. $[\overline{\mathrm{Pd\{1\text{-}CH_2\text{-}2\text{-}(CH{=}N}}\mathrm{\text{-}C_6H_5)\text{-}3,5\text{-}(CH_3)_2C_6H_2\}(2,4\text{-}lut)]ClO_4}$ crystallizes in the orthorhombic space group *Pcab* with a = 16.331(3) Å; b = 18.885(3) Å; c = 24.702(4) Å, and Z = 8. The *endo* six-membered ring displays a half-skew-chair conformation, with the palladium atom out of the plane (1.086 Å) defined by the other atoms.

1. Introduction

The preparation of cyclometallated compounds of transition elements and their use in regiospecific organic synthesis have attracted much attention in recent years [1,2], but the factors that influence the stability and lability of such compounds are not throughly understood. Cyclometallation of polyfunctional ligands (that can give different metallacycles) [3] or ligand exchange reactions [4] have been used to evaluate the relative stability of cyclometallated species.

The action of dpe, 1,2-bis(diphenylphosphino)-ethane, on cyclometallated compounds derived from azines, can lead to ionic compounds, retaining the Pd–N bond, or to neutral compounds, if this Pd–N bond is broken [5]. Moreover, in spite of the strong tendency of dpe to chelate this diphosphine can also act as a bridging ligand [6]. These reactions could also provide information about the stability of cyclometallated compounds. We describe the reaction of three cyclometallated compounds with dpe in different proportions. The starting cyclometallated compounds were selected for their different structural features and allow us to compare the effect of various factors, such as the size of the metallacycle (five- or six-membered ring), the nature of the metallated carbon atom (aliphatic or aromatic) and the nature of the metallacycle (*endo*, if it contains the C=N double bond or *exo* if it does not).

We also describe the preparation of ionic cyclometallated compounds by using $\mathrm{AgClO_4}$ and 2,4-lutidine. Cyclometallated ionic compounds show interesting reactivity and are good intermediates for regioselective organic synthesis [7]. Furthermore, recent attempts to develop new synthetic approaches to late transition-metal amide complexes have focused on the addition of nucleophiles to cationic *ortho*-metallated imine

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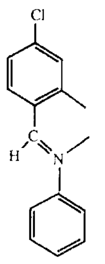

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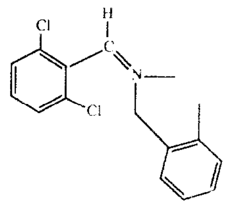

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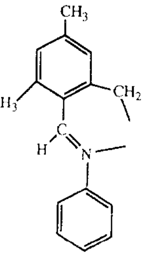


c

compounds [8]. Dinuclear derivatives with a single bridging halide ligand have also been obtained from cyclometallated ionic compounds [9].

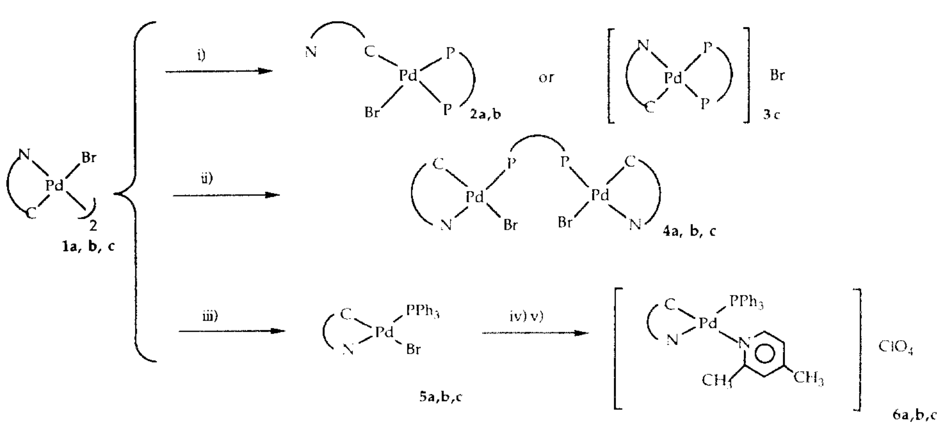
2. Results and discussion

2.1. Synthesis and characterization

The action of dpe on the cyclometallated compounds $[\{Pd(\widehat{CN})Br\}_2]$, $\widehat{CN}$ = 2-(HC=NC_6H_5)-5-ClC_6H_3 (**1a**), 2-(CH_2N=CH-2′,6′-$Cl_2C_6H_3$)C_6H_4 (**1b**) and 1-CH_2-2-(CH=N-C_6H_5)-3,5-$(CH_3)_2C_6H_2$ (**1c**), in a 2:1 molar ratio, gave the novel neutral species [Pd($\widehat{CN}$)Br(dpe)] (**2a,b**) or the ionic compound [Pd($\widehat{CN}$)(dpe)]Br (**3c**) (see Scheme 1), depending on the cyclometallated starting material.

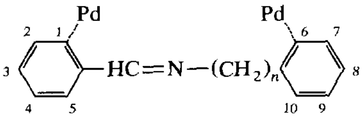
The $^{31}P\{^1H\}$ NMR spectra (see Table 1) show the inequivalence of the phosphorus atoms, consistent with a chelating diphosphine. The values of the molar conductivities in acetone (see Experimental details) show that **3c** is a 1:1 electrolyte and that **2a** and **2b** are non-electrolytes. Dpe [5] reacts with cyclometallated benzalazines to give neutral compounds, breaking the Pd–N bond; ionic compounds, keeping the Pd–N bond, were only obtained if a less coordinating anion such as perchlorate was present. These results show that the Pd–N bond in **1c** is strong, because the cyclometallated ionic compound is obtained even in the absence of perchlorate. The strength of the Pd–N bond in **1c** may be related to the high stability of this six-membered *endo*-metallacycle with a palladium-C(aliphatic) bond. Results obtained from other reactions of cyclometallated compounds, such as cyclometallation of polyfunctional ligands [3] or ligand exchange reactions, [4] are consistent with this.

The reaction between dpe and the cyclometallated compound **1a** affords a considerable amount of $[PdBr_2(dpe)]$ and, in consequence, the yield of **2a** is low. If PPh_3 is used instead of dpe in the reaction with the same cyclometallated starting material, the amount of $[PdBr_2(PPh_3)_2]$ formed is very low. This shows that dpe breaks the Pd–C bond of the cyclometallated compound **1a**. The higher reactivity of the Pd–C bond in the *endo*-compound **1a**, compared to the *exo*-derivative **1b**, differs from the results obtained from other reactions of cyclometallated compounds such as cyclometallation of polyfunctional ligands [3] or ligand exchange reactions [4] but is consistent with the stability of dinuclear compounds **4** (see below).



Scheme 1. (i) dpe, 2:1 ratio, refluxing acetone for 1 h; (ii) dpe, 1:1 ratio, refluxing acetone for 2 h; (iii) PPh_3, 2:1 ratio, refluxing chloroform for 1 h; (iv) $AgClO_4$ in acetone, room temperature for 1 h; (v) 2,4-lutidine, refluxing acetone for 3 h.

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



Compound	aromatic	HC=N, aliphatic	^{31}P
2a	7.80–7.00 (br m, 25H, H_6-H_{10}, dpe) 6.95 (dd, 1H, $^3J(HH) = 7.0$, $^4J(HH) = 1.5$ H_4) 6.70 (br m, 4H, H_2, H_5)	8.45 (d, 1H, $^5J(HP) = 5$, HC=N) 2.75–2.20 (br m, 4H, CH_2-P)	49.99 ($^3J(PP) = 26.5$) 37.99 ($^3J(PP) = 26.5$)
2b	8.00–7.20 (br m, 24H, H_2, H_3, H_4, HC=N dpe) 7.20–6.60 (br m, 4H, H_7–H_{10})	HC=N [c] 4.60 (s, 2H, CH_2-N) 2.90–2.50 (br m, 4H, CH_2-P)	61.15 (d, $^3J(PP) = 26.9$) 43.93 (d, $^3J(PP) = 26.9$)
3c	7.20–7.80 (br m, 25H, H_6–H_{10}, dpe) 6.82 (s, 1H, H_2) 5.53 (s, 1H, H_4)	8.3 (d, 1H, $^4J(HP) = 7.5$, HC=N) 3.10 (br m, 2H, CH_2-Pd) 2.80–2.25 (br m, CH_2-P) 2.45 (s, 3H, Me_5) 2.06 (s, 3H, Me_3)	56.38 (d, $^3J(PP) = 29.5$) 38.54 ($^3J(PP) = 29.5$)
4b	8.00–7.20 (br m, 23H, H_2, H_3, H_4, dpe) 6.80 (br m, 2H, H_7, H_8) 6.50 (br m, 2H, H_5,H_6)	9.50 (br m, 1H, HC=N) 4.90 (s, 2H, CH_2-N) 3.05 (s, 4H, CH_2-P)	37.68 (s)
4c	7.60–7.05 (br m, 25H, H_6-H_{10}, dpe) 6.65 (s, 1H, H_4) 5.50 (s, 1H, H_2)	8.30 (br m, HC=N) 2.80 (s, 2H, CH_2-Pd) 2.70 (s, 2H, CH_2-P) 2.32 (s, 3H, Me_5) 1.98 (s, 3H, Me_3)	35.45 (s)
6a	8.30 (d, 1H, $^3J(HH) = 6.8$, lut) 7.70–6.90 (br m, 22H, H_6–H_{10}, PPh_3, lut) 6.70 (d, 1H, $^3J(HH) = 6.4$ H_5) 6.45 (br d, 1H, H_4) 6.30 (dd, 1H, $^3J(HP) = 5.9$, $^4J(HH) = 1.8$ H_2)	8.05 (d, 1H, $^4J(HP) = 5.5$, HC=N) 2.40 (s, 3H, lut) 2.10 (s, 3H, lut)	41.23 (s)
6b	8.25 (d, 1H, $^3J(HH) = 7.0$ lut) 7.70–7.20 (br m, 20H, H_2, H_3, H_4, PPh_3, lut) 6.90 (br m, 2H, H_9, H_{10}) 6.50 (br m, 2H, H_7, H_8)	HC=N [c] 5.0 (s, 2H, CH_2N) 2.74 (s, 3H, lut) 2.26 (s, 3H, lut)	41.46 (s)
6c	8.30 (d, 1H lut) 7.60–6.75 (br m, 22H, H_6–H_{10}, PPh_3, lut) 6.55 (s, 1H, H_4) 6.12 (s, 1H, H_2)	7.85 (br s, 1H, HC=N) 3.30 (br s, 2H, CH_2-Pd) 2.47 (s, 3H, lut) 2.31 (s, 3H, Me_5) 2.21 (s, 3H, lut) 2.07 (s, 3H, Me_3)	35.53 (s)

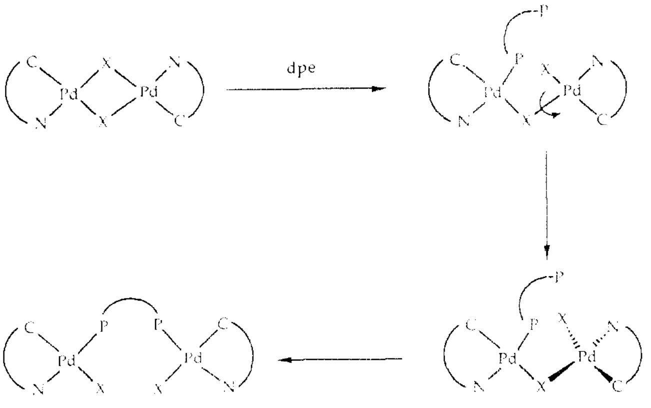
[a] In $CDCl_3$; chemical shifts in ppm with respect to internal $SiMe_4$; coupling constants in Hz; numbering as in figure. [b] In $CHCl_3$; chemical shift in ppm with respect to 85% H_3PO_4. [c] Not visible: resonance under aromatic protons.

Cyclometallation reactions often afford di- or polynuclear compounds that are characterized by their reaction with phosphines [1]. Our results show that the phosphine used in this halogen-bridge splitting reaction is important, and that dpe is not suitable for characterizing cyclopalladated compounds.

The action of dpe on compound **1** in a 1:1 ratio gives the neutral compound **4**. The ^{31}P $\{^1H\}$ NMR spectra (see Table 1) show the equivalence of the phosphorus atoms and suggest a dinuclear cyclometallated structure in which the two palladium atoms are bridged by the diphosphine. The chemical shifts show that phosphorus atoms are *trans* to the nitrogen atoms. The ^1H NMR spectra corroborate this (see below). This confirms that the attack of the diphosphine takes place *trans* to nitrogen, as has been proposed to explain the difference of behaviour between PPh_3 and dpe when they react with cyclometallated benzalazine compounds [5].

The dinuclear compounds **4** are more unstable than the mononuclear species **2** and **3**. It was not possible to isolate complex **4a**, although the ^{31}P $\{^1H\}$ NMR spectrum shows its formation ($\delta = 37.2$ s). **4b** is clearly more stable than **4a**, and its acetone or chloroform solutions may be heated under reflux for 1 h without detectable decomposition. Compound **4c** is the most stable, and its acetone or chloroform solution may be heated under reflux for several hours without decomposition.

Dpe usually chelates [10]. The relatively easy prepa-



Scheme 2. Proposed mechanism for dpe attack on cyclopalladated compounds.

ration of these dinuclear cyclometallated species with bridging dpe is remarkable. Another cyclometallated compound has been reported with this bridging ligand [6]. The preparation of such species can be explained by the dinuclear structure of the cyclometallated starting materials and by the stability of the metallacycles. When one of the phosphorus atoms attacks the cyclometallated compound, breaking one of the Pd–X–Pd bridging bonds, there is another Pd–X–Pd bond keeping the other palladium atom in a suitable position to be attacked by the second phosphorus atom of the dpe (see Scheme 2). The diphosphines 1,1-bis(diphenylphosphino)methane and 1,1-bis(diphenylphosphino)-ethene and cyclometallated compounds of *N*-benzylidenecyclohexylamines also give dinuclear cyclometallated compounds in which the two palladium atoms are bridged by a diphosphine, but these complexes also contain a bridging halide ligand and are, in consequence, ionic [11]. The different behaviour of dpe compared to these diphosphines may be related with the bigger bite of dpe.

The action of $AgClO_4$ on acetone solutions of the cyclometallated compounds $[\underline{PdBr(C^\frown N})PPh_3]$ precipitates AgBr. Subsequent addition of 2,4-lutidine to the filtered solutions leads to the ionic compounds $[\underline{Pd(C^\frown N})(lut)(PPh_3)]ClO_4$ **6a,b,c** in good yield in all cases. The $^{31}P\{^1H\}$ NMR spectra show that the phosphines are *trans* to the imine nitrogens. The ^1H NMR spectra and the X-ray structure of **6c** confirm this arrangement (see below).

2.2. Proton NMR spectra

Proton NMR spectra (Table 1) confirm the Pd–C bonds in all the new compounds obtained. The aromatic proton signals of the metallated ring in **3c**, **4** and **6**, which contain Pd–N bonds, are shifted to high fields. This must be caused by a phosphine phenyl ring, consistent with a *cis* arrangement of the phosphine and the metallated ring, and thus a *trans* disposition of phosphorus and nitrogen atoms.

The chemical shifts of methyne protons appear at high field, shifted (0.3–1.3 ppm) relative to those of the free imine in the *endo* derivatives [12]. In the *exo* metallacycles the imine can adopt the *E* or the *Z* form. In compounds with the imine in the *Z* form, the imine hydrogen is low-field shifted relative to the corresponding free imine [13]. This down-field shift can be explained by the paramagnetic anisotropy of the metal [14], with a close approach of Pd and H atoms in the *Z* form adopted by the coordinated imine. In the *exo* compounds with the imine in the *E* form, this proton resonates very near to the position in the free imine, showing that the proton is not under the influence of the metal [15].

The signal assigned to the methinic proton resonates at $\delta = 9.5$ in the *exo*cyclic cyclometallated compound **4b**, consistent with the *Z* form adopted by the ligand but, surprisingly, the methinic proton in **6b** is under the aromatic signals, high-field shifted. This seems to indicate that the imine could adopt the *E* form in this compound. However, since the imine is in the *Z* form in the starting cyclometallated compound **5b** [13] and since the *E*–*Z* isomerization of metallated imines seems to need acetic acid to take place [15], it is difficult to accept that the imine is in the E form in **6b**. The anomalous shift of methinic hydrogen in **6b** can be explained by the presence of the lutidine *ortho* methyl group, which prevents the methinic hydrogen from being near to the palladium atom. Moreover the ring current of lutidine can shift the methinic hydrogen signal to high fields.

The *ortho* methyl group of the lutidine appears at $\delta = 2.4$–2.7 in compounds **6**. In spite of the proximity of the palladium atom (see X-ray structure of **6c**) these protons do not undergo an important low-field shift. The presence of the phenyl groups of PPh_3 *cis* to lutidine, can explain this.

2.3. Molecular structure of **6c**

The crystal structure of **6c** has been determined (Fig. 1). Crystallographic data, selected bond lengths and bond angles are listed in Tables 2, 3 and 4, and atomic coordinates for non-hydrogen atoms in Table 5.

The crystal structure consists of discrete molecules separated by van der Waals distances. The palladium atom is in a square-planar environment, coordinated to phosphorus, carbon, imine and lutidine nitrogen atoms. The coordination plane shows some tetrahedral distortion, the deviation from the mean plane being +0.067, +0.081, −0.074 and −0.087 Å for P, N1, N2 and C1 respectively. The phosphine molecule is *trans* to imine nitrogen. The angles between adjacent atoms in the

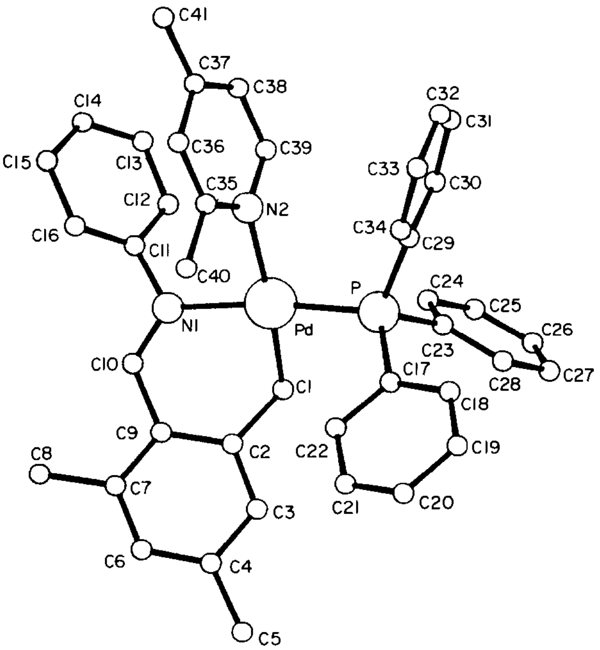


Fig. 1. Molecular structure of **6c**.

TABLE 2. Summary of crystallographic data for **6c**

Formula	$C_{41}H_{40}ClN_2O_4PPd$
Mol. wt.	797.61
System	orthorhombic
Space group	*Pcab*
a	16.331(3) Å
b	18.885(3) Å
c	24.702(4) Å
V	7618(4) Å^3
d_{calc}	1.390 g cm^{-3}
Z	8
F(000)	3280.0
Cryst. size	0.1 mm × 0.1 mm × 0.2 mm
μ(Mo-Kα)	6.35 cm^{-1}
λ(Mo-Kα)	0.71069 Å
T,	25°C
Reflections coll	4138
R	0.055
R_w	0.064

coordination sphere lie in the range 96.3(2)° (P–Pd–N2) to 83.5(3)° (N1–Pd–C). The smallest of these angles is that between the coordinated nitrogen and carbon atoms of the chelate ring.

The palladium donor distances are shorter than those found for the very similar six-membered cyclometallated compound $[\overline{\mathrm{Pd}\{1\text{-}\mathrm{CH_2}\text{-}2\text{-}(\mathrm{CH{=}N}}\text{-}\mathrm{C_6H_5})\text{-}3,5\text{-}(\mathrm{CH_3})_2\mathrm{C_6H_2}\}\mathrm{Br}(\mathrm{PPh_3})]$ [3c]. This may be related to the ionic nature of **6c**, which renders the palladium atom more acid. The six-membered metallacycle adopts a half-skew-chair conformation, with the palladium atom out of the plane (1.086 Å) defined by the other atoms and is *endo*, because the C=N bond is contained in the metallacycle. This conformation is also adopted by the metallacycle in the neutral compound $[\overline{\mathrm{Pd}\{1\text{-}\mathrm{CH_2}\text{-}2\text{-}(\mathrm{CH{=}N}}\text{-}\mathrm{C_6H_5})\text{-}3,5\text{-}(\mathrm{CH_3})_2\mathrm{C_6H_2}\}\mathrm{Br}(\mathrm{PPh_3})]$, the

TABLE 3. Bond distances (Å) for **6c**

P–Pd	2.244(2)	C(16)–C(15)	1.440(18)
N(1)–Pd	2.119(7)	C(18)–C(17)	1.378(12)
N(2)–Pd	2.163(6)	C(22)–C(17)	1.399(10)
C(1)–Pd	2.027(7)	C(19)–C(18)	1.372(13)
C(17)–P	1.814(7)	C(20)–C(19)	1.410(14)
C(23)–P	1.829(7)	C(21)–C(20)	1.325(15)
C(29)–P	1.809(7)	C(22)–C(21)	1.412(11)
C(10)–N(1)	1.286(11)	C(24)–C(23)	1.355(10)
C(11)–N(1)	1.441(10)	C(28)–C(23)	1.365(12)
C(35)–N(2)	1.341(10)	C(25)–C(24)	1.406(11)
C(39)–N(2)	1.348(9)	C(26)–C(25)	1.311(15)
C(2)–C(1)	1.507(10)	C(27)–C(26)	1.454(16)
C(3)–C(2)	1.388(11)	C(28)–C(27)	1.386(13)
C(9)–C(2)	1.395(12)	C(30)–C(29)	1.391(10)
C(4)–C(3)	1.411(12)	C(34)–C(29)	1.343(11)
C(5)–C(4)	1.516(14)	C(31)–C(30)	1.400(12)
C(6)–C(4)	1.368(15)	C(32)–C(31)	1.353(16)
C(7)–C(6)	1.369(13)	C(33)–C(32)	1.346(15)
C(8)–C(7)	1.504(15)	C(34)–C(33)	1.402(14)
C(9)–C(7)	1.410(11)	C(36)–C(35)	1.371(12)
C(10)–C(9)	1.482(12)	C(40)–C(35)	1.487(12)
C(12)–C(11)	1.394(12)	C(37)–C(36)	1.402(14)
C(16)–C(11)	1.334(13)	C(38)–C(37)	1.360(16)
C(13)–C(12)	1.361(14)	C(41)–C(37)	1.491(14)
C(14)–C(13)	1.315(18)	C(39)–C(38)	1.409(11)
C(15)–C(14)	1.373(20)		

metal atom being 1.325 Å out of the plane defined by the other atoms [3c].

The dihedral angle between the lutidine ring and the coordination plane is 80.3° and, in consequence, the *ortho* methyl group occupies an apical site in the coordination compound. The same arrangement has been found in the *ortho*-palladated oxime complexes $[\overline{PdCl(C_6H_4C(Me)=NOH)}\ (L)]$, L = 2-MeC_5H_4N or $2,4,6\text{-Me}_3C_5H_2N$, in which the dihedral angles between the palladium and pyridine planes are 84.1° and 81.4° respectively [16]. The oxime cyclopalladated compound $[\overline{PdCl(C_6H_4C(Me)=NOH)}(2\text{-MeC}_5H_4N)]$ show a rather strong interaction between a hydrogen of the *ortho* methyl group and palladium [16], but in **6c** the distance between the palladium atom and the lutidine *ortho* methyl carbon atom is 3.232(7) Å, suggesting only a slight interaction between the two atoms. The presence of the bulky PPh_3 *cis* to the amine may hinder this interaction in **6c**.

TABLE 4. Bond angles (deg) for **6c**

N(1)–Pd–P	173.1(2)	C(14)–C(13)–C(12)	119.9(11)
N(2)–Pd–P	96.3(2)	C(15)–C(14)–C(13)	121.0(12)
N(2)–Pd–N(1)	89.8(2)	C(16)–C(15)–C(14)	120.0(12)
C(1)–Pd–P	90.6(2)	C(15)–C(16)–C(11)	117.3(10)
C(1)–Pd–N(1)	83.5(3)	C(18)–C(17)–P	123.9(6)
C(1)–Pd–N(2)	171.5(3)	C(22)–C(17)–P	118.4(6)
C(17)–P–Pd	113.6(3)	C(22)–C(17)–C(18)	117.8(6)
C(23)–P–Pd	112.7(2)	C(19)–C(18)–C(17)	122.4(8)
C(23)–P–C(17)	106.8(3)	C(20)–C(19)–C(18)	119.2(9)
C(29)–P–Pd	113.9(2)	C(21)–C(20)–C(19)	119.4(8)
C(29)–P–C(17)	104.5(3)	C(22)–C(21)–C(20)	122.1(8)
C(29)–P–C(23)	104.5(3)	C(21)–C(22)–C(17)	119.1(8)
C(10)–N(1)–Pd	123.9(6)	C(24)–C(23)–P	118.0(6)
C(11)–N(1)–Pd	118.2(5)	C(28)–C(23)–P	123.3(6)
C(11)–N(1)–C(10)	117.9(7)	C(28)–C(23)–C(24)	118.5(7)
C(35)–N(2)–Pd	121.7(5)	C(25)–C(24)–C(23)	120.7(8)
C(39)–N(2)–Pd	117.2(5)	C(26)–C(25)–C(24)	122.6(9)
C(39)–N(2)–C(35)	120.1(6)	C(27)–C(26)–C(25)	117.7(8)
C(2)–C(1)–Pd	111.5(5)	C(28)–C(27)–C(26)	118.5(10)
C(3)–C(2)–C(1)	118.9(7)	C(27)–C(28)–C(23)	122.0(9)
C(9)–C(2)–C(1)	122.0(7)	C(30)–C(29)–P	120.2(5)
C(9)–C(2)–C(3)	119.0(7)	C(34)–C(29)–P	122.3(6)
C(4)–C(3)–C(2)	120.8(8)	C(34)–C(29)–C(30)	117.3(7)
C(5)–C(4)–C(3)	117.2(9)	C(31)–C(30)–C(29)	120.4(8)
C(6)–C(4)–C(3)	118.7(8)	C(32)–C(31)–C(30)	120.4(9)
C(6)–C(4)–C(5)	124.0(9)	C(33)–C(32)–C(31)	119.7(10)
C(7)–C(6)–C(4)	122.1(8)	C(34)–C(33)–C(32)	119.8(10)
C(8)–C(7)–C(6)	119.7(9)	C(33)–C(34)–C(29)	122.2(8)
C(9)–C(7)–C(6)	119.2(8)	C(36)–C(35)–N(2)	121.4(7)
C(9)–C(7)–C(8)	121.0(8)	C(40)–C(35)–N(2)	117.9(6)
C(7)–C(9)–C(2)	120.1(7)	C(40)–C(35)–C(36)	120.6(8)
C(10)–C(9)–C(2)	120.9(7)	C(37)–C(36)–C(35)	120.4(9)
C(10)–C(9)–C(7)	119.1(7)	C(38)–C(37)–C(36)	117.2(9)
C(9)–C(10)–N(1)	123.9(8)	C(41)–C(37)–C(36)	121.4(10)
C(12)–C(11)–N(1)	116.9(7)	C(41)–C(37)–C(38)	121.3(9)
C(16)–C(11)–N(1)	122.5(8)	C(39)–C(38)–C(37)	121.2(8)
C(16)–C(11)–C(12)	120.6(9)	C(38)–C(39)–N(2)	119.6(8)
C(13)–C(12)–C(11)	121.0(9)		

TABLE 5. Final atomic coordinates ($\times 10^4$) of **6c** ($B_{eq} = 8\pi^2/3\Sigma U_{ij}a_i^*a_j^*a_ia_j$)

	x	y	z	B_{eq}
Pd	18488(3)	5829(2)	11498(2)	3.52(3)
P	17263(9)	3886(9)	20424(9)	3.56(8)
N(1)	1809(4)	760(3)	303(3)	4.55(32)
N(2)	3009(3)	1133(3)	1191(2)	4.36(29)
C(1)	824(4)	7(4)	1006(3)	4.62(36)
C(2)	167(4)	450(4)	743(4)	4.49(39)
C(3)	−621(5)	428(4)	953(4)	5.09(40)
C(4)	−1265(5)	801(5)	702(5)	5.80(48)
C(5)	−2099(6)	768(6)	969(5)	7.87(62)
C(6)	−1096(5)	1195(5)	250(4)	6.22(51)
C(7)	−329(5)	1222(4)	28(4)	5.68(46)
C(8)	−179(8)	1669(6)	−466(5)	8.57(69)
C(9)	316(4)	849(4)	278(4)	4.68(37)
C(10)	1146(5)	882(4)	37(4)	5.37(43)
C(11)	2571(5)	767(4)	9(3)	5.32(43)
C(12)	3061(5)	164(5)	50(4)	5.77(47)
C(13)	3814(7)	140(6)	−186(4)	7.60(61)
C(14)	4060(8)	666(7)	−495(6)	9.56(77)
C(15)	3596(9)	1267(8)	−552(5)	10.28(88)
C(16)	2817(8)	1323(5)	−281(5)	8.69(67)
C(17)	894(4)	878(3)	2353(3)	3.66(33)
C(18)	769(5)	918(5)	2904(4)	5.36(46)
C(19)	117(6)	1273(5)	3126(4)	6.69(52)
C(20)	−450(5)	1608(5)	2779(4)	5.90(49)
C(21)	−327(5)	1593(4)	2249(4)	5.28(44)
C(22)	352(4)	1245(3)	2017(3)	4.18(33)
C(23)	1564(4)	−546(3)	2205(3)	3.95(31)
C(24)	1861(5)	−1038(4)	1856(4)	5.45(40)
C(25)	1742(6)	−1764(4)	1954(4)	6.44(48)
C(26)	1330(6)	−2001(5)	2372(5)	7.75(56)
C(27)	998(7)	−1483(5)	2748(5)	9.83(67)
C(28)	1123(6)	−771(4)	2642(4)	7.32(53)
C(29)	2622(4)	635(3)	2429(3)	4.43(33)
C(30)	3282(4)	173(4)	2469(4)	5.59(42)
C(31)	4014(5)	392(6)	2711(4)	7.71(57)
C(32)	4088(6)	1056(6)	2911(4)	7.69(58)
C(33)	3442(7)	1498(6)	2896(5)	8.28(61)
C(34)	2714(5)	1284(4)	2644(4)	6.59(48)
C(35)	3060(4)	1836(4)	1127(3)	4.89(37)
C(36)	3795(6)	2162(5)	1028(4)	6.34(48)
C(37)	4519(6)	1765(6)	1002(4)	6.41(52)
C(38)	4456(5)	1055(6)	1082(3)	6.10(49)
C(39)	3693(4)	734(5)	1185(3)	5.22(40)
C(40)	2286(6)	2252(5)	1131(4)	7.31(53)
C(41)	5321(6)	2103(7)	876(5)	10.21(73)
Cl	1618(1)	3244(1)	−685(1)	6.59(12)
O(1)	2458(9)	3444(7)	−653(6)	7.82(10)
O(2)	6411(9)	1079(8)	−953(6)	17.90(14)
O(3)	4092(20)	−1414(17)	504(13)	16.49(31)
O(4)	1595(11)	3022(11)	−145(9)	11.32(16)
O(3)′	6661(10)	2332(9)	−1063(6)	16.74(14)
O(4)′	6117(15)	2301(15)	−1041(10)	28.91(32)

3. Experimental section

CAUTION. Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Routine NMR spectra were obtained on a Bruker WP 80SY (^{1}H, 80.13 MHz; ^{31}P{^{1}H}, 32.8 MHz). 200 MHz ^{1}H spectra were obtained on a Varian XL-200 spectrometer. IR spectra were recorded as KBr disks on a Perkin Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC). The molar conductivities in anhydrous acetone (10^{-4} M) at 20°C correspond to non-electrolytes for the neutral compounds (1–5 ohm^{-1} cm^2 mol^{-1}) and to 1:1 electrolytes for ionic compounds (110–130 ohm^{-1} cm^2 mol^{-1}).

3.1. Materials and synthesis

Solvents were dried and distilled before use. Cyclometallated compounds **1** and **5** were prepared by literature procedures [12b,13,3d].

3.1.1. Compounds 2a,b

A stirred suspension of **1** (0.3 mmol) in acetone (30 ml) was treated with dpe (0.6 mmol, 220 mg) and the mixture was heated under reflux for 1 h. The precipitate was washed with acetone and recrystallized from chloroform–methanol to afford compounds **2a,b**.

3.1.1.1. [Pd{2-(HC=NC$_6$H$_5$)-5-ClC$_6$H$_3$}(dpe)-Br](2a). Yield 90 mg (35%); mp: 184–88°C dec. Anal. Found: C, 58.7; H, 4.2; N, 1.6. $C_{39}H_{33}BrClNP_2Pd$ calc.: C, 58.59; H, 4.17; N, 1.75%.

3.1.1.2. [Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)-C$_6$H$_4$}(dpe)Br] (2b). Yield 180 mg (70%); mp: 165–70°C dec. Anal. Found: C, 56.8; H, 4.1; N, 1.6. $C_{40}H_{34}BrCl_2NP_2Pd$ calc.: C, 56.66; H, 4.05; H, 1.65%.

3.1.2. [Pd{1-CH$_2$-2-(CH=N-C$_6$H$_5$)-3,5-(CH$_3$)$_2$-C$_6$H$_2$}(dpe)]Br (3c)

A stirred suspension of **1** (0.3 mmol) in acetone (30 ml) was treated with dpe (0.6 mmol, 220 mg) and the mixture was heated under reflux for 1 h. The solution was filtered, the filtrate was concentrated *in vacuo*, and the solid obtained was recrystallized from chloroform–methanol. Compound **2c** was obtained in 75% yield (185 mg); mp: 190–98°C dec. Anal. Found: C, 62.5; H, 5.0; N, 1.7. $C_{42}H_{40}BrNP_2Pd$ calc.: C, 62.50; H, 5.00; N, 1.73%. Molar conductivity: 114 ohm^{-1} cm^2 mol^{-1}.

3.1.3. Compounds 4b,c

Stirred suspensions of compound **1** (0.25 mmol) were treated with dpe (0.25 mmol, 92 mg) in refluxing acetone (30 ml) for 2 h and then filtered. The precipitate was washed with acetone and recrystallized from chloroform to afford compounds **4b,c**.

3.1.3.1. [Pd$_2${2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)C$_6$H$_4$}$_2$-Br$_2$(μ-dpe)] (4b). Yield 130 mg (40%); mp: 165–70°C dec. Anal. Found: C, 48.8; H, 3.3; N, 2.2. $C_{54}H_{44}Br_2Cl_4N_2P_2Pd_2$ calc.: C, 49.99; H, 3.42; N, 2.16%

3.1.3.2. [Pd$_2${1-CH$_2$-2-(CH=N-C$_6$H$_5$)-3,5-(CH$_3$)$_2$-C$_6$H$_2$}$_2$Br$_2$ (μ-dpe)] (4c). Yield 150 mg (50%); mp: 225–30°C dec. Anal. Found: C, 57.3; H, 4.5; N, 2.2. $C_{58}H_{56}Br_2N_2P_2Pd_2$ calc.: C, 57.46; H, 4.65; N, 2.30%.

3.1.4. Compounds 6a,b,c

A stirred solution of compound **5** (0.4 mmol) in acetone (50 ml) was treated with $AgClO_4$ (0.4 mmol, 83 mg), 1 h at room temperature, and the precipitated AgBr was filtered off. 2,4-lutidine (0.4 mmol, 43 mg) was added to the filtrate and the mixture was heated under reflux for 3 h. The resulting solutions were concentrated *in vacuo* and the solid obtained was recrystallized from chloroform–ether to afford compounds **6a,b,c**.

3.1.4.1. [Pd{2-(HC=NC$_6$H$_5$)-5-ClC$_6$H$_3$}(PPh$_3$)(2,4-lut)]ClO$_4$ (6a). Yield 205 mg (65%); mp: 178–84°C dec. Anal. Found: C, 57.0; H, 4.0; N, 3.4. $C_{38}H_{33}Cl_2N_2O_4PPd$ calc.: C, 57.76; H, 4.21; N, 3.55%. Molar conductivity: 110 ohm^{-1} cm^2 mol^{-1}.

3.1.4.2. [Pd{2-(CH$_2$N=CH-2',6'-Cl$_2$C$_6$H$_3$)C$_6$H$_4$}-(PPh$_3$)(2,4-lut)] ClO$_4$ (6b). Yield 200 mg (60%); mp: 176–80°C dec. Anal. Found: C, 55.6; H, 4.1; N, 3.8. $C_{39}H_{34}Cl_3N_2O_4PPd$ calc.: C, 55.86; H, 4.00; N, 3.34%. Molar conductivity: 104 ohm^{-1} cm^2 mol^{-1}.

3.1.4.3. [Pd{1-CH$_2$-2-(CH=N-C$_6$H$_5$)-3,5(CH$_3$)$_2$-C$_6$H$_2$}(PPh$_3$)(2,3-lut)]ClO$_4$ (6c). Yield 225 mg (70%); mp: 285–90°C dec. Anal. Found: C, 60.9; H, 4.9; N, 3.4. $C_{41}H_{40}ClN_2O_4PPd$ calc.: C, 61.73; H, 5.06; N, 3.51%. Molar conductivity: 128 ohm^{-1} cm^2 mol^{-1}.

3.2. Data collection

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf Nonius CAD4 diffractometer. Unit cell parameters were determined from automic centering of 25 reflections ($16 \leqslant \theta \leqslant 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$-scan technique. 8837 reflections were measured in the range $2 \leqslant \theta \leqslant 30°$, 4138 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Corrections were applied for Lorentz-polarization but not for absorption.

3.3. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [17] and refined by full-matrix least-squares method, with the SHELX76 computer program [18] for crystal structure determination. The function minimized was $\Sigma w[|F_o|-|F_c|]^2$, where $w = (\sigma^2(F_o) + 0.0019|F_o|^2)^{-1}$. f, f' and f'' were taken from *International Tables of X-Ray Crystallography* [19]. Disorder among some atoms of perchlorate ion was treated by assigning appropriate occupancy factors according to the height of the Fourier synthesis. The position of all H atoms was computed and refined with an overall isotropic temperature factor using a riding model and the remaining non-oxygen atoms were computed anisotropically. The final R factor was 0.055 ($R_w = 0.064$) for all observed reflections. The number of refined parameters was 442. Max. shift/esd = 0.1, The maximum and minimum peaks in final difference synthesis were 0.3 e Å^{-3} and −0.3 e Å^{-3}, respectively.

4. Supplementary material available

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

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