

# Cyclopalladation of 6-Substituted-2,2'-bipyridines. Metalation of Unactivated Methyl Groups vs Aromatic C–H Activation

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6-Alkyl-2,2'-bipyridines, HL, ( $N_2C_{10}H_7R$ ;  $R = CH_2Me$ ,  $HL^{et}$ ;  $CHMe_2$ ,  $HL^{ip}$ ;  $CMe_3$ ,  $HL^{tb}$ ,  $CH_2-CMe_3$ ,  $HL^{np}$ ,  $CMe_2Ph$ ,  $HL^{dm}$ ) react with  $Na_2[PdCl_4]$  to give either 1:1 adducts  $[Pd(HL)Cl_2]$  ( $HL^{et}$ ,  $HL^{ip}$ ,  $HL^{np}$ ) or cyclometalated complexes  $[Pd(L)Cl]$  ( $HL^{tb}$ ,  $HL^{dm}$ ). Reaction of palladium(II) acetate, followed by exchange with LiCl, affords a series of cyclopalladated species  $[Pd(L)Cl]$  where L is a terdentate anionic N–N–C ligand which originates from HL through direct activation of a  $C(sp^3)–H$  or a  $C(sp^2)–H$  bond. The structures of  $[Pd(L^{tb})Cl]$  and  $[Pd(L^{np})Cl]$ , which contain a [5,5] or a [5,6] fused ring system, respectively, have been determined by X-ray diffraction and are compared. In the case of the ligand  $HL^{ip}$ , three different cyclometalated species have been isolated,  $[Pd(L)Cl]$ ,  $[Pd(L)Cl]_2$ , and  $[Pd\{N_2C_{10}H_7[CH(CH_2OC(O)CH_3)(CH_2)]\}Cl]$ , the latter one arising from activation of both methyl groups of the substituent. The isolation of two  $[Pd(L^{dm})Cl]$  species (compounds **8** and **9**), having an aromatic or an aliphatic carbon–metal bond, respectively, is an example of isomerism, still rare in organometallic chemistry.

## Introduction

Cyclopalladation of N donor ligands has been studied for many years:<sup>1</sup> it is a common belief that five-membered rings and activation of  $C(sp^2)–H$  bonds are preferred.<sup>1,2</sup> Accordingly, very many species having  $C_{aromatic}–metal$  bonds and five-membered rings can be found in the literature. Although a number of derivatives containing nitrogen ligands and  $C(sp^3)–Pd$  bonds are known, those derived from activation of simple alkyls to give  $Pd–CH_2$  bonds are still a minority.<sup>2b,3</sup>

Recently there has been an increasing interest in species containing terdentate anionic ligands, the sequence of donor atoms being either  $N–N–C^4$  or  $N–C–N$ ,<sup>5</sup> owing to their potential in several fields. Their properties have often been compared with those of the classical N,N,N coordination species.

In the last years we have studied the behavior of a series of 6-substituted 2,2'-bipyridines with  $Pd(II)$ ,<sup>6</sup>  $Pt(II)$ ,<sup>7</sup>  $Au(III)$ ,<sup>8</sup> and  $Rh(III)$ <sup>9</sup> ions and characterized cyclometalated species with terdentate N,N,C anions.

In this paper we report the synthesis of new adducts and metalated species of palladium, the latter having both  $M–CH_2$  and  $M–Ar$  bonds, and show that the nature of the substituent on the 2,2'-bipyridine is crucial in driving the reactivity of the ligand, often in unpre-

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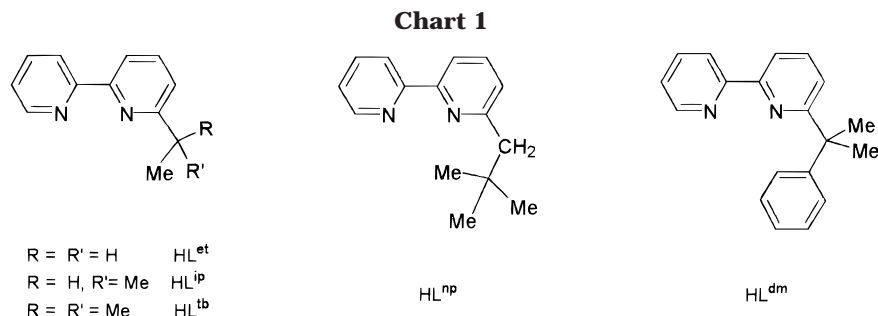
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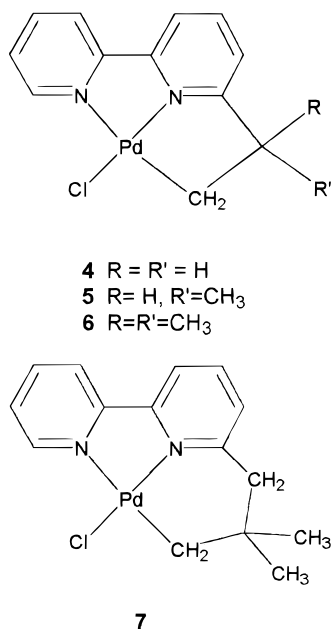
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dictable ways: even subtle differences can play a role in the outcome of the reaction.

Noteworthy is the behavior of  $HL^{dm}$ , able to give both aromatic and aliphatic C–H activation under the same experimental conditions. In two cases ( $HL^{ip}$  and  $HL^{dm}$ ) a stereogenic carbon atom,  $\beta$  to the metal atom, is directly generated by metalation.

The structures of compounds **6** and **7** in the solid state were solved by X-ray diffraction to compare the five- vs the six-membered C,N ring. A brief report of part of this work has been previously given.<sup>10</sup>



## Results and Discussion

The ligands HL (see Chart 1) were obtained as previously described.<sup>11</sup>

Our purpose in this study was to evaluate the influence of the substituents on the behavior of the ligands:

(6) (a) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107. (b) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A. *Gazz. Chim. Ital.* **1992**, *122*, 455.

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$HL^{et}$ ,  $HL^{ip}$ , and  $HL^{tb}$ , should be able to give five-membered cyclometalated species, and  $HL^{np}$  a less common six-membered ring. In principle, activation of a methyl or a phenyl group to give a five- or a six-membered ring, respectively, should be possible for  $HL^{dm}$ .

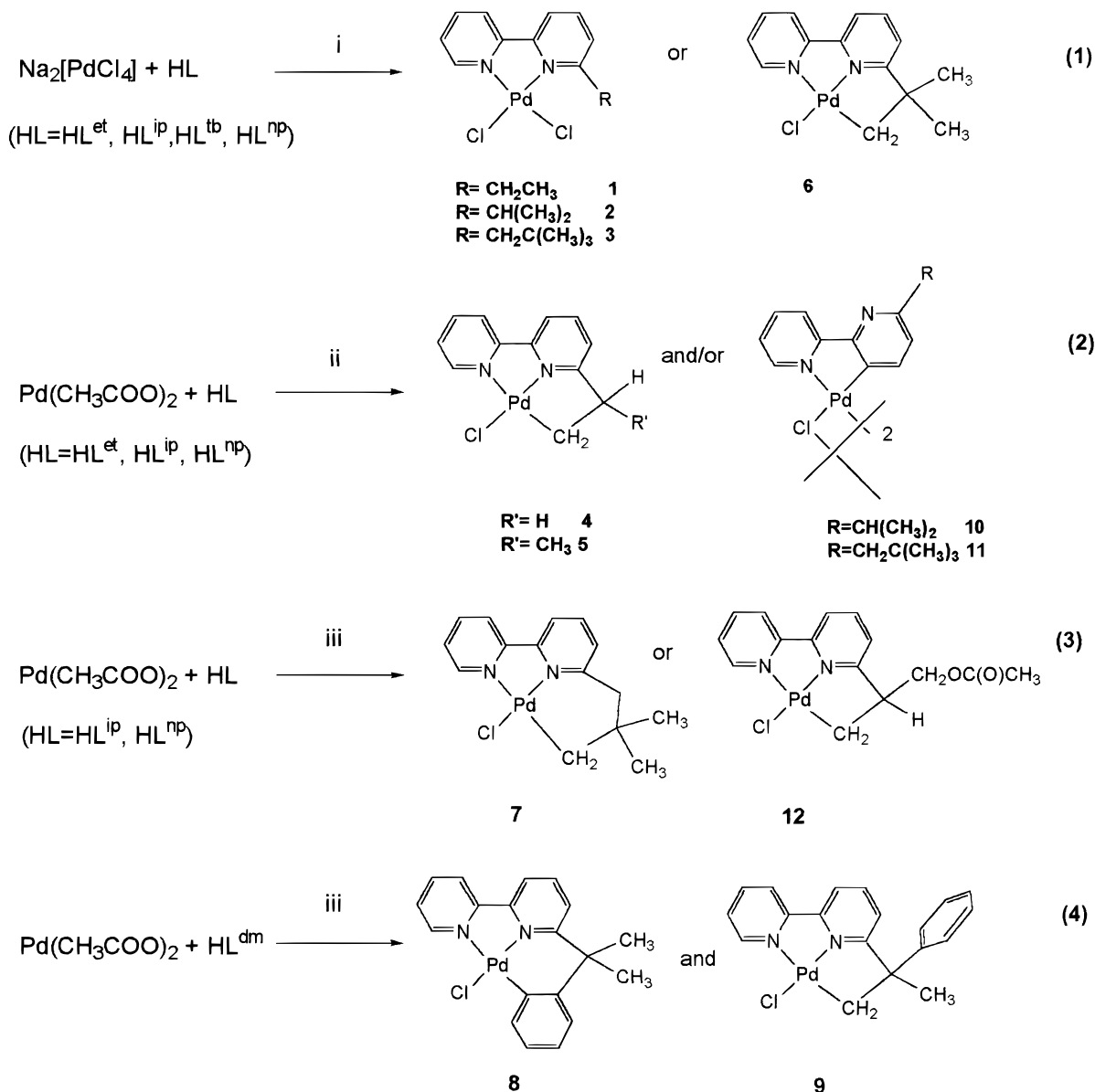
The behavior of the various ligands toward Pd(II) salts is summarized in Scheme 1. Striking differences are observed in their reactivity so that almost each of them has a peculiar behavior.

The reaction of  $Na_2[PdCl_4]$  with HL in aqueous HCl (Scheme 1, eq 1) affords adducts or cyclometalated derivatives depending on the ligand. Pure 1:1 adducts  $[Pd(HL^{et})Cl_2]$  (**1**),  $[Pd(HL^{ip})Cl_2]$  (**2**), and  $[Pd(HL^{np})Cl_2]$  (**3**) were obtained in good yields (>85%) both at room temperature and in refluxing conditions. The behavior of  $HL^{tb}$  is different: in this case we were unable to isolate the adduct. The metalated complex  $[Pd(L^{tb})Cl]$  (**6**) was obtained even at room temperature. The easy C–H activation of the *tert*-butyl group has been previously reported and commented on.<sup>9</sup> With the other alkyl-substituted ligands,  $HL^{et}$ ,  $HL^{ip}$ , and  $HL^{np}$ , even at reflux temperature no cyclometalated complex was obtained. Compounds **1–3** are characterized by correct elemental analyses and FAB mass spectra which show the  $M - Cl$  and  $M - 2Cl$  peaks. In the  $^1H$  NMR spectra the resonances of the protons on the substituents at C(6), as well as of H(6'), are strongly deshielded, as usually observed when a chlorine atom is in proximity of a proton.<sup>12</sup>

Different routes were envisaged for the synthesis of the metalated species  $[Pd(L^{et})Cl]$  (**4**),  $[Pd(L^{ip})Cl]$  (**5**),  $[Pd(L^{tb})Cl]$  (**6**), and  $[Pd(L^{np})Cl]$  (**7**), as shown in Scheme 1. Apart from compound **6**, which can be obtained also from  $Na_2[PdCl_4]$ , the other complexes were achieved only by reaction of Pd(II)acetate, in refluxing benzene (**4** and **5**) or acetic acid (**7**), followed by treatment with LiCl in  $H_2O$ /acetone. Owing to the rather vigorous conditions, these reactions are quite complex, giving often a mixture of metalated species, some of which were identified and will be described below. In the case of  $HL^{et}$ , complex **4** was isolated in very low yield (ca. 2%). The reaction afforded a mixture of products that have proved difficult to separate. The amount of **4** that we isolated in pure form upon a very slow crystallization was considerably less than the amounts actually formed during the reaction (ca. 30%). Several attempts to improve the yield have been carried out, but even

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Scheme 1<sup>a</sup>

<sup>a</sup> (i)  $\text{H}_2\text{O}/\text{HCl}$ , rt or  $\Delta$ , see text; (ii) (a) benzene,  $\Delta$ ; (b)  $\text{H}_2\text{O}/\text{acetone}$ ,  $\text{LiCl}$ ; (iii) (a)  $\text{CH}_3\text{COOH}$ , rt; (b)  $\text{H}_2\text{O}/\text{acetone}$ ,  $\text{LiCl}$ .

reaction of the adduct **1** with sodium acetate in refluxing methanol was unsuccessful, despite the easy conversion of **2** into the metalated compound **5** under the same conditions.

In this context it is worth noting that in some cases the reaction can be reversed, as shown by the conversion of the metalated compound **7** into the adduct **3** in aqueous  $\text{HCl}$  (see Experimental Section). This can account for the unsuccessful isolation of **7** under conditions i in Scheme 1.

The metalation in compounds **5–7** is easily confirmed by the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which give unambiguous evidence for the presence of a metalated  $\text{CH}_2$  group (see Table 1). The  $\text{H}(6')$  proton is strongly deshielded only in compound **7** ( $\Delta\delta$  ca. 0.5 ppm), having a [5,6] fused ring system: in compounds **4–6**, the resonances are slightly deshielded ( $\Delta\delta$  ca. 0.1–0.2 ppm). In complex **5**, because of the stereogenic carbon the hydrogen atoms of the  $\text{M}-\text{CH}_2$  group are diastereotopic ( $\delta$  2.43 dd, 2.90 dd). In the aromatic region all the signals are deshielded with respect to the free ligands except for  $\text{H}(3)$  and  $\text{H}(3')$ ,

which are, on the contrary, strongly shielded ( $\Delta\delta$  = ca. 0.4–0.5 ppm). Complexes having a stereogenic carbon atom arising from metalation are not unprecedented but are still rare.<sup>3a,b,9,13</sup>

Two of these complexes, **6** and **7**, have been studied in depth and fully characterized both in solution, by  $^1\text{H}$ ,  $^{13}\text{C}$ , 2D COSY, and  $^1\text{H}-^{13}\text{C}$  HETCOR NMR experiments (Table 2), and in the solid state by an X-ray diffraction study, to compare in detail a five-membered with a six-membered cyclometalated ring.

The structure of **6** consists of the packing of three crystallographically independent  $[\text{Pd}(\text{L}^{\text{tb}})\text{Cl}]$  molecules (labeled molecules A, B, and C, respectively) in the asymmetric unit of space group  $P1$ . Principal bond lengths and angles for the three molecules are reported in Table 3. An ORTEP<sup>14</sup> view of molecule A is shown in

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Table 1. Proton and <sup>31</sup>P NMR Data<sup>a</sup>

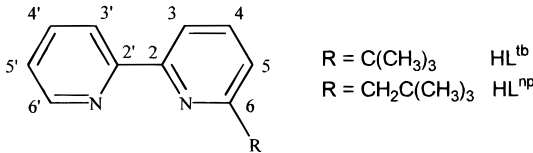
compound		CH <sub>3</sub>	CH <sub>2</sub>	CH	H(6')	other aromatics	<sup>31</sup> P
[Pd(HL <sup>ct</sup> )Cl <sub>2</sub> ]	<b>1</b>	1.42 [t, 3H] (7.6)	3.66 [q, 2H] (7.6)		9.28 [dd, 1H]	7.37–8.12 [m, 6H]	
[Pd(HL <sup>ip</sup> )Cl <sub>2</sub> ]	<b>2</b>	1.32 [d, 6H] (6.9)		4.63 [m, 1H] (6.9)	9.19 [ddd, 1H]	7.37–8.21 [m, 6H]	
[Pd(HL <sup>np</sup> )Cl <sub>2</sub> ]	<b>3</b>	1.07 [s, 9H]	3.84 [s, 2H]		9.22 [dd, 1H]	7.35–8.15 [m, 6H]	
[Pd(L <sup>ct</sup> )Cl]	<b>4</b>		2.79 [t, 2H] (6.6)		8.80 [ddd, 1H]	7.42–8.02 [m, 6H]	
			3.25 [t, 2H] (6.6)				
[Pd(L <sup>ip</sup> )Cl]	<b>5</b>	1.41 [d, 3H] (7.1)	2.43 [dd, 1H] (6.1, 9.8)	3.43 [m, 1H]	8.78 [ddd, 1H]	7.35–8.05 [m, 6H]	
			2.90 [dd, 1H] (6.9, 9.8)				
[Pd(L <sup>ib</sup> )Cl]	<b>6</b>	1.43 [s, 6H]	2.53 [s, 2H]		8.75 [dm, 1H]	7.25–8.01 [m, 6H]	
[Pd(L <sup>np</sup> )Cl]	<b>7</b>	1.06 [s, 6H]	2.22 [s, 2H]		9.22 [d, 1H]	7.35–8.05 [m, 6H]	
			2.94 [s, 2H]				
[Pd(L <sup>dm</sup> )Cl] (C <sub>sp</sub> <sup>2</sup> -Pd)	<b>8</b>	2.15 [s, 6H]			9.27 [ddd, 1H]	6.84–8.05 [m, 6H]	
[Pd(L <sup>dm</sup> )Cl] (C <sub>sp</sub> <sup>3</sup> -Pd)	<b>9</b>	1.89 [s, 3H]	2.86 [1H] (9.8)		8.90 [dt, 1H]	6.96–8.02 [m, 6H]	
			3.12 [1H] (9.8)				
[Pd{C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> CH-CH <sub>2</sub> OC(O)CH <sub>3</sub> CH <sub>2</sub> }Cl]	<b>12</b>	2.06 [s, 3H]	2.47 [1H] (4.6, 10.3)	3.55 m [1H]	8.80 [ddd, 1H]	7.46–8.05 [m, 6H]	
			2.77 [1H] (7.1, 10.3)				
			4.33 [1H] (7.7, 11.1)				
			4.38 [1H] (5.9, 11.1)				
[Pd(L <sup>ib</sup> )(PPh <sub>3</sub> )](BF <sub>4</sub> )	<b>14</b>	1.38 [s, 6H]	2.16 [d, 2H] {4.4}			7.11–8.66 [m, 22H]	34.00
[Pd <sub>2</sub> (L <sup>ib</sup> ) <sub>2</sub> (μ-dppe)](BF <sub>4</sub> ) <sub>2</sub>	<b>15</b>	1.32 [s, 12H]	2.06, 2.64			7.18–8.35 [m, 34H]	28.77

<sup>a</sup> Spectra recorded at room temperature in CDCl<sub>3</sub>, chemical shifts in ppm from internal TMS (<sup>1</sup>H) and external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P); coupling constants are given in hertz: J(H–H) in parentheses, J(P–H) in curly brackets; s = singlet, d = doublet, br = broad, m = multiplet, dd = double doublet, t = triplet.

Table 2. Proton and <sup>13</sup>C NMR Data for HL<sup>ib</sup>, HL<sup>np</sup>, **6**, and **7**<sup>a</sup>

	HL <sup>ib</sup>	Pd(L <sup>ib</sup> )Cl, <b>6</b>	HL <sup>np</sup>	Pd(L <sup>np</sup> )Cl, <b>7</b>
<sup>1</sup> H CH <sub>3</sub>	1.43 s	1.43 s	1.01 s	1.06 s
CH <sub>2</sub> -Pd		2.53 s		2.25 s
CH <sub>2</sub>			2.76 s	2.94 s
H(6')	8.66 ddd	8.75 ddd	8.66 ddd	9.22 ddd
H(5')	7.28 m	7.58 m	7.27 m	7.53 m
H(4')	7.81 td	8.08 td	7.79 td	7.95 overlap
H(3')	8.54 dt	8.02 dt	8.44 dt	8.03 dd
H(3)	8.21 dd	7.86 dd	8.22 dd	7.95 dd
H(4)	7.74 t	7.95 t	7.69 t	7.93 t
H(5)	7.36 dd	7.28 dd	7.11 dd	7.39 dd
<sup>13</sup> C CH <sub>3</sub>	30.2	31.1	29.65	28.9
CH <sub>2</sub> -Pd		34.9		32.8
CH <sub>2</sub>			51.9	54.9
C(CH <sub>3</sub> ) <sub>3</sub>			32.0	32.9
C(6')	148.8	149.1	149.0	149.3
C(5')	123.3	127.0	123.4	126.1
C(4')	136.6	138.9	136.8	138.3
C(3')	121.0	121.6	121.2	121.1
C(3)	117.5	119.5	118.0	119.6
C(4)	136.9	138.1	136.4	138.0
C(5)	118.9	123.2	124.6	127.8
C(6)	168.3	177.5	159.7	161.5
C(2), C(2')	154.3, 156.7	154.7, 153.3	155.0, 156.8	153.2, 156.5

<sup>a</sup> Assignments based on <sup>1</sup>H–<sup>1</sup>H COSY and <sup>1</sup>H–<sup>13</sup>C HETCOR experiments, room temperature, solvent CDCl<sub>3</sub>, chemical shifts in ppm from internal TMS.



**Table 4. Average Bond Distances (Å) and Angles (deg) for Complexes [M(L<sup>tb</sup>)Cl] (M = Pd, Pt)**

	M = Pd <sup>a</sup>	M = Pt <sup>b</sup>
M–Cl	2.312	2.300
M–N(1)	2.146	2.114
M–N(2)	1.966	1.948
M–C(12)	2.012	2.003
C1–M–N(1)	100.3	98.6
C1–M–N(2)	177.2	178.3
C1–M–C(12)	97.8	97.8
N(1)–M–N(2)	79.0	79.9
N(1)–M–C(12)	161.5	163.4
N(2)–M–C(12)	82.8	83.6

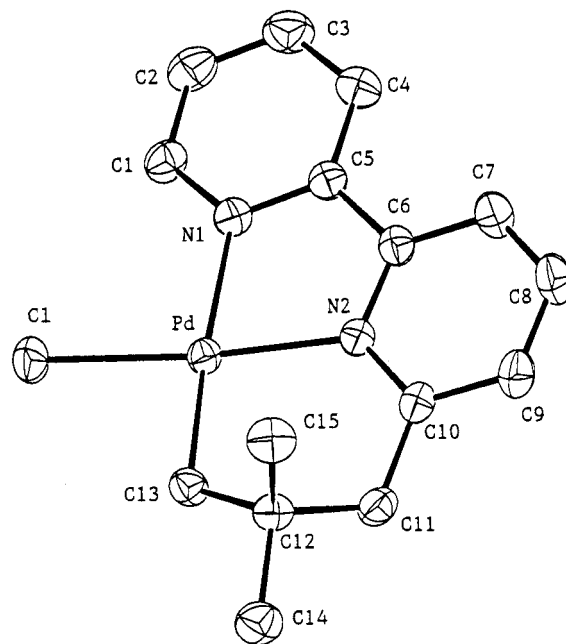
<sup>a</sup> This work, average of three. <sup>b</sup> Reference 7b, average of two.

sponding best plane of +0.059(2) Å for N(2) and –0.053 Å for C(6) in molecule A, +0.052(2) Å for N(2) and –0.039(1) Å for Pd in molecule B, and +0.041(2) Å for N(2) and –0.041(3) Å for C(6) in molecule C. In the Pd–N(2)–C(10)–C(11)–C(12) pentaatomic ring the quasi planarity is limited to atoms Pd, N(2), C(10), and C(12), with atom C(11) displaced from their best plane of +0.374(3), +0.421(3), and +0.352(3) Å in molecules A, B, and C, respectively. The two pyridinic rings are planar and are twisted with respect to each other by 8.8(4)°, 3.4(1.1)°, and 7.4(5)° in molecules A, B, and C, respectively. Since direct comparison of analogous Pt(II) and Pd(II) organometallic complexes is still rare,<sup>15</sup> Table 4 lists the average bond parameters for the present complex and for the analogous Pt(II) derivative, [Pt(L<sup>tb</sup>)Cl].<sup>7b</sup> It is to be noted that the two complexes are not isomorphous since the Pt(II) derivative crystallizes in monoclinic space group *P*2<sub>1</sub>/*c* with two crystallographically independent molecules in the asymmetric unit. An inspection of Table 4 shows that bond lengths involving platinum are always shorter than corresponding bond lengths involving palladium, thus suggesting that the covalent radius of Pt(II) is slightly shorter than that of Pd(II). The amount of the shortening, averaged on the M–Cl, M–N, and M–C distances reported in Table 4, is 0.018 Å. It must be observed that no similar regularity had been found in previous reports.<sup>15,16</sup> The slight differences between corresponding angles in the Pd and Pt derivatives (see Table 4) may be due both to the different corresponding bond lengths and to packing forces. In the present palladium derivative there are five rather short Cl···H contacts, in the range 2.69–2.80 Å, that suggest the possibility of weak intermolecular hydrogen bonds.

The structure of **7** consists of the packing of [Pd(L<sup>np</sup>)Cl] molecules with normal van der Waals contacts (but see later for a possible weak hydrogen bond). Principal bond lengths and angles are reported in Table 5. An ORTEP view of the molecule is shown in Figure 2. The palladium atom displays a square-planar coordination

**Table 5. Principal Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compound 7, [Pd(L<sup>np</sup>)Cl]**

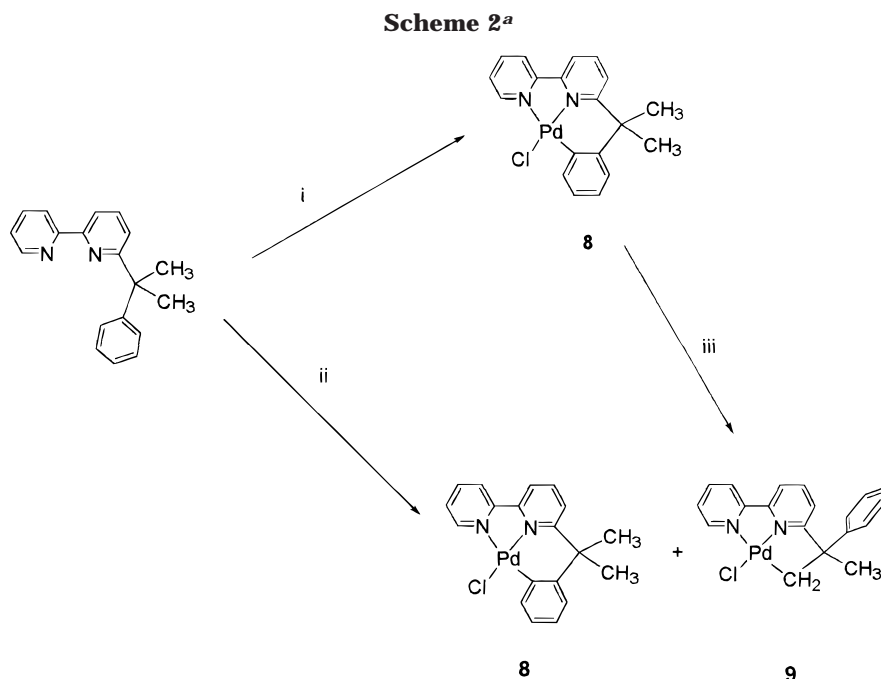
Pd–Cl	2.314(1)	Pd–N(1)	2.138(2)
Pd–N(2)	2.046(2)	Pd–C(13)	2.022(3)
Cl–Pd–N(1)	96.3(1)	Cl–Pd–N(2)	174.4(1)
Cl–Pd–C(13)	88.1(1)	N(1)–Pd–N(2)	79.1(1)
N(1)–Pd–C(13)	175.6(1)	N(2)–Pd–C(13)	96.5(1)

**Figure 2.** ORTEP view of compound **7**. Thermal ellipsoids as in Figure 1.

with a very slight square-pyramidal distortion, maximum distances from the best plane being +0.034(2) Å for N(2) and –0.0289(1) Å for Pd. The Pd–N(1)–C(5)–C(6)–N(2) pentaatomic ring is quasi planar, with maximum distances from the best plane of +0.053(3) Å for C(6) and –0.066(2) Å for N(2). The Pd–N(2)–C(10)–C(11)–C(12)–C(13) six-membered ring is in an irregular conformation, which does not approach any of the common ones (chair, boat, or twisted boat). Actually, the Pd, N(2), C(10), and C(13) atoms are essentially coplanar, maximum deviations from their best plane being +0.018(2) and –0.012(3) Å for N(2) and C(10), respectively, with atoms C(11) and C(12) lying –0.345(3) and +0.443(3) Å below and above the best plane, respectively. The two pyridinic rings are planar and are twisted 6.0(6)° with respect to each other. Bond lengths and angles involving the palladium atom can be compared with the corresponding parameters observed in compound **6**, [Pd(L<sup>tb</sup>)Cl]. Thus, the Pd–Cl, Pd–N(1), and Pd–C bond lengths in the two compounds are very similar: the three values observed in **7**, 2.314(1), 2.138(2), and 2.022(3) Å, respectively, are very close to the average values found in **6**, 2.312, 2.146, and 2.012 Å, respectively. Instead, the Pd–N(2) distance found in **7**, 2.046(2) Å, is markedly longer than the average Pd–N(2) bond length found in **6**, 1.966 Å. We can consider the 2.046(2) value found in **7** as the normal one, and the 1.966 Å value found in **6** as imposed by the presence of the two 5,5' fused rings, which usually display a rather short "central" metal–ligand distance: compare for instance 1.948 Å in [Pt(L<sup>tb</sup>)Cl],<sup>7b</sup> 1.976(5) Å in cation [Au(L<sup>tb</sup>)Cl]<sup>+</sup>,<sup>8b</sup> and 1.960(4) Å in [Pd(L)Cl] (HL = 6 phenyl-

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<sup>a</sup> (i)  $\text{Na}_2[\text{PdCl}_4]$ ,  $\text{H}_2\text{O}/\text{HCl}$ ,  $\Delta$ ; (ii) (a)  $\text{Pd}(\text{CH}_3\text{COO})_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\Delta$ , (b) acetone/ $\text{H}_2\text{O}$ ,  $\text{LiCl}$ ; (iii)  $\text{CH}_3\text{COOH}$ , reflux temperature.

2,2'-bipyridine).<sup>17</sup> With the obvious exception of the  $\text{N}(1)\text{--Pd--N}(2)$  angle ( $79.1(1)^\circ$  in **7** and  $79.0^\circ$  in **6**), angles at the metal atom are different in the two complexes (see Tables 3 and 5). This is due to the different bites of the  $\text{L}^{\text{th}}$  and  $\text{L}^{\text{np}}$  ligands: the former, which forms a five-membered ring, imposes a  $\text{N}(2)\text{--Pd--C}$  angle of  $82.8^\circ$ , whereas the latter, which forms a six-membered ring, imposes a  $\text{N}(2)\text{--Pd--C}$  angle of  $96.5(1)^\circ$ . The deviation from the ideal value of  $90^\circ$  is approximately the same in the two rings, but in different directions. As already discussed, this difference in bond angles does not induce marked differences in the planarity of the two metal coordination planes. Also in compound **7** there is the possibility of a weak intermolecular hydrogen bond, suggested by a rather short  $\text{Cl}\cdots\text{H}$  contact of  $2.79 \text{ \AA}$ .

**Aliphatic vs Aromatic Activation.** Among the ligands employed,  $\text{HL}^{\text{dm}}$  is peculiar, as both aromatic and aliphatic C–H activation are possible. Recently we have reported that aliphatic C–H activation can be achieved by reaction with  $\text{RhCl}_3$  to give the octahedral species  $[\text{Rh}(\text{L}^{\text{dm}})\text{Cl}_2(\text{CH}_3\text{CN})]$ .<sup>9</sup> In the case of palladium(II) two isomers  $[\text{Pd}(\text{L})\text{Cl}]$  ( $\text{C}_{\text{sp}^2}\text{--Pd}$ ), **8**, and ( $\text{C}_{\text{sp}^3}\text{--Pd}$ ), **9**, have been obtained. Compounds **8** and **9** as obtained from palladium(II) acetate under the same experimental conditions (see Scheme 2) can be separated taking advantage of the different solubility in chlorinated solvents. In our experience species with aromatic C–M bonds are usually much less soluble in common organic solvents than those with aliphatic C–M bonds. Compound **8** is converted almost quantitatively into **9** in refluxing acetic acid. This behavior is reminiscent of the isomerization of cyclopalladated derivatives of *N*-methylbenzylideneamines described by Sales and co-workers<sup>18</sup> as an example of intramolecular exchange reaction. In acid media the driving force of the isomerization is

likely to be the different behavior of the two metalated species toward acetolysis.

In solution complexes **8** and **9** have been studied mainly by means of  $^1\text{H}$  NMR spectroscopy. In complex **8**, which is likely to adopt a boatlike conformation,<sup>6a</sup> the six-membered ring is fluxional, on the NMR time scale, as shown by the equivalence of the  $\text{CH}_3$  groups ( $\delta$  2.15, s, 6H). The  $^1\text{H}$  NMR spectrum of **9**, which contains a stereogenic carbon, shows only one methyl group ( $\delta$  1.89 s, 3H), an AB system ( $\text{CH}_2$ ) ( $\delta_{\text{A}}$  2.86,  $\delta_{\text{B}}$  3.12,  $J_{\text{AB}} = 9.8 \text{ Hz}$ ), and 12 aromatic protons. In the IR spectrum an absorption at ca.  $700 \text{ cm}^{-1}$ , not observed in the spectrum of **8**, confirms the presence of a monosubstituted phenyl ring.

Examples of aliphatic C–H activation preferred to an aromatic one are extremely rare.<sup>2b,18,19</sup> In our case the two processes also imply five- vs six-member ring formation, to give [5,5] or [5,6] fused rings, so that different factors should be taken into account.

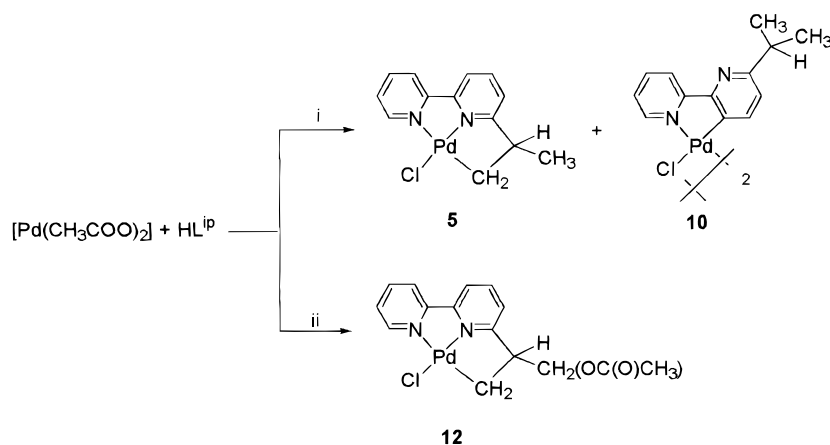
**“Roll Over” Metalation.** As previously mentioned, the reaction of the alkyl-substituted ligands with palladium(II) acetate often gives more metalated species (Scheme 3). Thus the reaction of  $\text{HL}^{\text{tp}}$  and  $\text{HL}^{\text{np}}$  in refluxing benzene, followed by exchange with  $\text{LiCl}$ , besides the terdentate-bound species **5** and **7** gives the uncommon metalated compounds  $[\text{Pd}(\text{L})\text{Cl}]_2$  **10** and **11**, respectively. The compounds arising from activation of the C(3)–H bond of the substituted pyridine are an example of “roll over” metalation. As far as we know, only two complexes of this type, namely, an iridium<sup>20</sup> and a platinum<sup>21</sup> derivative, have been previously reported.

The structure of compound **10**, solved by X-ray determination, has been recently reported by us.<sup>22</sup> The

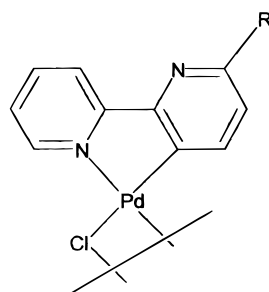
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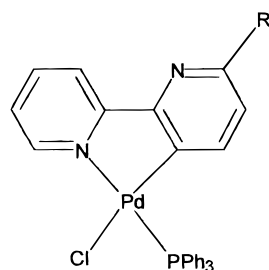
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Scheme 3<sup>a</sup>

<sup>a</sup> (i) (a) benzene, reflux, (b)  $\text{H}_2\text{O}/\text{acetone}$ ,  $\text{LiCl}$ ; (ii) (a)  $\text{CH}_3\text{COOH}$  rt; (b)  $\text{H}_2\text{O}/\text{acetone}$ ,  $\text{LiCl}$ .



R =  $\text{CH}(\text{CH}_3)_2$  **10**  
 R =  $\text{CH}_2\text{C}(\text{CH}_3)_3$  **11**



**10a**  
**11a**

dimeric compounds **10** and **11** can be split by  $\text{PPh}_3$  to give mononuclear species  $[\text{Pd}(\text{L})(\text{PPh}_3)\text{Cl}]$  (P trans to N), **10a** and **11a**.

In the case of  $\text{HL}^{\text{et}}$  a mixture of **4** and  $[\text{Pd}(\text{L}^{\text{et}})\text{Cl}]_2$  was obtained in solution.  $[\text{Pd}(\text{L}^{\text{et}})\text{Cl}]_2$  was not isolated, but in the aromatic region of the  $^1\text{H}$  NMR spectrum, a typical AB system indicates roll over metalation.

In the case of  $\text{HL}^{\text{b}}$  only complex **6** was detected in solution: this can be due to the strong tendency of  $\text{HL}^{\text{b}}$  to give the terdentate-bound cyclometalated species and to the difficulty of obtaining an adduct likely due to the presence of the bulky substituent.

Reaction of **10a** and **11a** with  $(18\text{-crown-6})\cdot\text{HBF}_4\cdot\text{H}_2\text{O}$ <sup>23</sup> or  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ , respectively, gives the cationic species  $[\text{Pd}(\text{L})(\text{PPh}_3)\text{Cl}]\cdot\text{HBF}_4$  (L =  $\text{HL}^{\text{ip}}$ , **10b**;  $\text{HL}^{\text{b}}$ , **11b**) characterized on the basis of spectroscopic (IR and NMR) and analytical data. The  $^1\text{H}$  NMR spectra, in particular, show the presence of a strongly deshielded NH proton ( $\delta$  13.18, **10b** broad; 13.06, **11b** broad).

**Reactivity of  $\text{HL}^{\text{ip}}$ .** In this series of ligands the behavior of  $\text{HL}^{\text{ip}}$  is much more complicated than that of the other ligands. Indeed by reaction with  $\text{Pd}(\text{II})$  acetate three different species were obtained, as reported in Scheme 3, originating from different C–H activations.

The cyclometalated species **12** was obtained from palladium acetate, in acetic acid, followed by treatment with  $\text{LiCl}$  in  $\text{H}_2\text{O}/\text{acetone}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show in the aliphatic region the disappearance of the signals of the two methyl groups of the isopropyl substituent. The  $^1\text{H}$  NMR spectrum shows a complicated situation consistent with a  $-\text{CH}(\text{CH}_2\text{X})\text{CH}_2-\text{Pd}$  system, originated by a double  $\text{C}_{\text{aliphatic}}-\text{H}$  activation. In agreement, the  $^{13}\text{C}$  NMR spectrum shows the presence of one CH, two  $\text{CH}_2$ , and one  $\text{CH}_3$  carbon atom (APT experiments).

On the whole, analytical and spectroscopic data are consistent with the formula  $[\text{Pd}\{\text{C}_{10}\text{H}_7\text{N}_2-[\text{CH}(\text{CH}_2)(\text{CH}_2\text{OC}(\text{O})\text{CH}_3)]\}\text{Cl}]$ , where a hydrogen atom of a methyl group has been substituted by an acetato group.<sup>24</sup>

In the attempt to gain insight into the reaction pathway, we reacted either the adduct or the N,N,C cyclometalated species with acetic acid or sodium acetate. In both cases the  $^1\text{H}$  NMR spectra provided no evidence of the formation of complex **12**. Although several pathways may be envisaged, the mechanism likely involves an equilibrium between a cyclometalated and a hydrido-olefinic species ( $\beta$ -hydrogen transfer), a nucleophilic attack of an acetato on the olefin, followed by a second metalation of a methyl group.

**Reactivity of Complex 6 with CO,  $\text{PPh}_3$ , and dppe.** The reactivity of complex **6** with CO has been studied in ethanol solution. Up to 70 °C and 70 atm no reaction occurs. Only under more severe conditions (100

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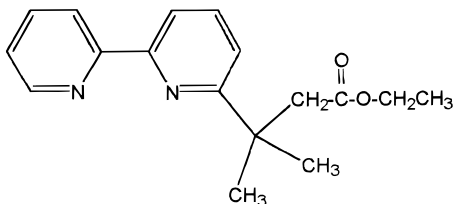
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(24) 2D  $^{13}\text{C}-^1\text{H}$  inverse correlation spectra (HMQC for  $^1J_{\text{CH}}$  spin couplings, and HMBC, for long-range C–H correlations): Lucchini, V. Personal communication.

atm, 100 °C) is the extrusion of palladium and formation of two organic species identified via GCMS as the ligand HL<sup>th</sup> (80%) and 3-methyl-3-[6-(2,2'-dipiridyl)]ethylbutanoate, **13** (20%), observed. Compound **13** is an ex-

**13**

pected reaction product, likely generated by nucleophilic attack of an ethylate to an acyclic intermediate formed by insertion of CO into the Pd–C bond. The formation of the ligand, HL<sup>th</sup>, is not unprecedented.<sup>25</sup>

Reaction of **6** with PPh<sub>3</sub> does not require displacement of the chloride by silver salts, in contrast with the behavior observed for the cyclometalated species derived from 6-benzyl-substituted 2,2'-bipyridines but in line with what is observed for the analogous platinum(II) derivatives.<sup>7b</sup> In the presence of BF<sub>4</sub><sup>−</sup>, the cationic species [Pd(L<sup>th</sup>)(PPh<sub>3</sub>)]<sup>+</sup>, **14**, was isolated in fairly good yield. In the <sup>1</sup>H NMR spectrum the signals of the H(6) (hidden by other aromatic signals) and of the CH<sub>2</sub>–Pd (δ 2.21, <sup>3</sup>J<sub>P–H</sub> = 29.2 Hz) protons are shielded, as expected owing to the PPh<sub>3</sub> ligand in their proximity.

The reaction of **6** with the potentially bidentate ligand Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, dppe, has been investigated in order to study the robustness of the terdentate ligand. With a 1/1 Pd/dppe molar ratio an unstable crude product is formed which turns into complex **15** upon recrystallization. With the appropriate Pd/dppe ratio (2/1) the reaction to give complex **15**, i.e., a species with bridging dppe, is straightforward.

### Experimental Section

The bipyridines HL were prepared according to literature methods.<sup>11</sup> Na<sub>2</sub>[PdCl<sub>4</sub>] (29.15% Pd) and Pd(CH<sub>3</sub>COO)<sub>2</sub> (47.4% Pd) were obtained from Johnson Matthey and Engelhard, respectively. All the solvents were purified before use according to standard methods. Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. The neutral complexes **1–9** and **12** are nonconducting in acetone. Infrared spectra were recorded with a Perkin-Elmer 983 using Nujol mulls. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9, 75.4, and 121.4 MHz, respectively, and are collected in Tables 1 and 2. Chemical shifts are given in ppm relative to internal TMS (<sup>1</sup>H, <sup>13</sup>C) and external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). The 2D experiments were performed by means of standard pulse sequences. The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

**Preparations. [Pd(HL)Cl<sub>2</sub>] [HL = HL<sup>et</sup> (**1**), HL<sup>ip</sup> (**2**), HL<sup>np</sup> (**3**)].** (a) To a solution of Na<sub>2</sub>[PdCl<sub>4</sub>] (365.0 mg, 1.00 mmol) in water (40 mL) were added 1.00 mmol of HL (184.2, 198.3, and 226.3 mg for HL<sup>et</sup>, HL<sup>ip</sup>, and HL<sup>np</sup>, respectively)

and 3 mL of 2 M HCl. The mixture was stirred for 16, 1, or 5 h, respectively. The precipitate formed was filtered off and washed with water, ethanol, and diethyl ether. The crude obtained was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample.

**1:** orange, yield 93%, mp 227 °C. Found: C, 40.10; H, 3.54; N, 7.48 (calcd for C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>Pd: C, 39.87; H, 3.35; N, 7.75). FAB mass spectrum: *m/z* 325 [M – Cl], 290 [M – 2Cl]. IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1596 s, 1564 m, 342 s.

**2:** orange, yield 82%, mp 250 °C. Found: C, 41.38; H, 3.72; N, 7.18 (calcd for C<sub>13</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>Pd: C, 41.57; H, 3.76; N, 7.46). FAB mass spectrum: *m/z* 339 [M – Cl], 304 [M – 2Cl], 713 [M<sub>2</sub> – Cl]. IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1597 s, 1563 m, 337 s, 303 m.

**3:** orange-yellow, yield 98%, mp 248 °C (dec). Found: C, 44.65; H, 4.65; N, 7.38 (calcd for C<sub>15</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Pd: C, 44.64; H, 4.50; N, 6.94). FAB mass spectrum: *m/z* 367 [M – Cl], 332 [M – 2Cl]. IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1600 s, 1560 w, 340 s.

**[Pd(L<sup>et</sup>)Cl], **4**.** A mixture containing HL<sup>et</sup> (377.7 mg, 2.05 mmol) and Pd(CH<sub>3</sub>COO)<sub>2</sub> (460.2 mg, 2.05 mmol) in benzene (50 mL) was refluxed under stirring for 15 h, then filtered and evaporated to dryness. The crude obtained was treated with 1/3 water/acetone (40 mL) containing an excess of LiCl and stirred for 4 days, then evaporated to dryness and crystallized from CH<sub>2</sub>Cl<sub>2</sub>. Yield: ca. 2%, mp 223–224 °C (dec). Found: C, 44.02; H, 3.38; N, 8.60 (calcd for C<sub>12</sub>H<sub>11</sub>ClN<sub>2</sub>Pd: C, 44.33; H, 3.41; N, 8.62). FAB mass spectrum: *m/z* 324 [M<sup>+</sup>], 289 [M – Cl].

**[Pd(L<sup>ip</sup>)Cl], **5**.** (a) A mixture containing **2** (50.0 mg, 0.133 mmol) and sodium acetate (12.8 mg) in MeOH (15 mL) was refluxed for 15 min, then filtered and evaporated to dryness. The crude obtained was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample in almost quantitative yield.

(b) [Pd(L<sup>ip</sup>)Cl] **5** and [Pd(L<sup>ip</sup>)Cl]<sub>2</sub> **10**: A solution of HL<sup>ip</sup> (297.4 mg, 1.50 mmol) and Pd(CH<sub>3</sub>COO)<sub>2</sub> (336.7, 1.50 mmol) in benzene (40 mL) was refluxed for 7 h, then filtered, evaporated to dryness, and treated with 1/3 water/acetone (40 mL) containing an excess of LiCl. The mixture was stirred for 6 days. The precipitate formed was filtered and crystallized from CH<sub>2</sub>Cl<sub>2</sub> to give [Pd(L<sup>ip</sup>)Cl]<sub>2</sub>, **10**, as a yellow solid (yield ca. 25%). The filtrate consisted of a mixture of compounds **5** and **10** in a 2/1 ratio (NMR criterion). Pure **5** was obtained by chromatography on a column of silica gel (60 mesh) using a benzene/acetone mixture (3/2) as eluent.

**5:** yield 10%; mp 205 °C (dec). Found: C, 45.71; H, 3.64; N, 8.09 (calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>ClPd: C, 46.04; H, 3.86; N, 8.26). IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1591 s, 1558 m.

**[Pd(L<sup>th</sup>)Cl], **6**.** To a solution of Na<sub>2</sub>[PdCl<sub>4</sub>] (365.0 mg, 1.00 mmol) in water (50 mL) were added HL<sup>th</sup> (212.3 mg, 1.00 mmol) and 5 mL of 2 M HCl. The mixture was stirred at room temperature for 3 h. The precipitate formed was filtered off, washed with water, ethanol, and diethyl ether, and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid. Yield: 92%, mp 181 °C. Found: C, 48.08; H, 4.24; N, 7.55 (calcd for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>Pd: C, 47.62; H, 4.28; N, 7.93). IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1600 s, 1560 m.

**[Pd(L<sup>np</sup>)Cl], **7**.** To a solution of [Pd(CH<sub>3</sub>COO)<sub>2</sub>] (224.5 mg, 1.00 mmol) in acetic acid (25 mL) was added 226.3 mg of HL<sup>np</sup> (1.00 mmol). The solution was stirred at room temperature for 1 day, then evaporated to dryness and treated with 1/2 water/acetone (30 mL) containing an excess of LiCl. The suspension was stirred for 3 days. The yellow precipitate formed was filtered off, washed with diethyl ether, and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid. Yield: 33%, mp 254 °C (dec). Found: C, 48.84; H, 4.51; N, 7.39 (calcd for C<sub>15</sub>H<sub>17</sub>ClN<sub>2</sub>Pd: C, 49.07; H, 4.67; N, 7.63). FAB mass spectrum, *m/z*: 366 [M<sup>+</sup>], 331 [M – Cl]. IR (Nujol) *ν*<sub>max</sub>/cm<sup>−1</sup>: 1600 s, 1560 w, 780 s, 320 s.

**Reaction of **7** with HCl.** To a suspension of **7** (100.0 mg, 0.272 mmol) in water (10 mL) was added 2 mL of 2 N HCl. The mixture was refluxed for 5 h, then evaporated to dryness.

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The crude obtained was crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give complex **3** in almost quantitative yield (NMR criterion).

**[Pd(L<sup>dm</sup>)Cl] (C<sub>sp</sub><sup>2</sup>-Pd), **8**.** To a solution of  $\text{Na}_2[\text{PdCl}_4]$  (1.095 g, 3.00 mmol) in water (30 mL) were added HL<sup>dm</sup> (0.823 g, 3.00 mmol) and 10 mL of 2 M HCl. The mixture was heated in a water bath until the solution was colorless. The yellow precipitate formed was filtered off, washed with water, ethanol, and diethyl ether, and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample as a yellow solid. Yield: 80%, mp 244 °C. Found: C, 55.41; H, 4.54; N, 6.51 (calcd for  $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{Pd}$ : C, 54.96; H, 4.13; N, 6.75). FAB mass spectrum,  $m/z$ : 414 [M<sup>+</sup>], 379 [M - Cl]. IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1592 s, 1563 m, 1552 m, 346 s, 331 s.

**[Pd(L<sup>dm</sup>)Cl] (C<sub>sp</sub><sup>3</sup>-Pd), **9**.** (a) A suspension of **8** (103.8 mg, 0.25 mmol) in acetic acid (20 mL) was refluxed for 1 h. The solution obtained was evaporated to dryness. The crude obtained was crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give **9** in almost quantitative yield.

(b) To a solution of  $\text{Pd}(\text{CH}_3\text{COO})_2$  (112.2 mg, 0.50 mmol) in acetic acid (10 mL) was added 137.2 mg of HL<sup>dm</sup> (0.50 mmol) in the same solvent (3 mL). The mixture was stirred for 20 h. After addition of water the organometallic compounds were extracted with  $\text{CH}_2\text{Cl}_2$ , dried with  $\text{Na}_2\text{SO}_4$ , neutralized with  $\text{K}_2\text{CO}_3$ , filtered, and evaporated to dryness. The crude obtained was treated with a water/acetone mixture (1/2, 15 mL) and an excess of LiCl, stirred for 2 day, then evaporated to dryness and crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . The product obtained was a mixture of compounds **8** and **9** (ca. 1/1, NMR criterion). Pure **9** (yield 20%) was obtained by extraction with a mixture  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  (2/1) and precipitation with  $\text{Et}_2\text{O}$ . Mp: 187–189 °C. Found: C, 53.35 H, 4.11 N, 6.67 (calcd for  $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{Pd}$ -0.25  $\text{CH}_2\text{Cl}_2$ : C, 52.98; H, 4.04; N, 6.42). FAB mass spectrum,  $m/z$ : 793 [M<sub>2</sub> - Cl], 414 [M<sup>+</sup>], 379 [M - Cl]. IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1593 s, 1556 m, 702 s, 336 m.

**[Pd(L)(PPh<sub>3</sub>)Cl]·HBF<sub>4</sub> (L = L<sup>ip</sup> (**10b**), L<sup>np</sup> (**11b**)).** To a solution of the relevant  $[\text{Pd}(\text{L})(\text{PPh}_3)\text{Cl}]$  (**10a**, 23.5 mg, 0.039 mmol; **11a**, 25.2 mg, 0.04 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added under vigorous stirring a 5% excess of 18-crown-6·HBF<sub>4</sub>·H<sub>2</sub>O. The solution was stirred for 6 h, then filtered and evaporated to small volume. The precipitate formed after addition of diethyl ether was filtered and washed with diethyl ether to give the analytical sample as a cream solid in almost quantitative yield.

Compounds **11b** can be obtained also by reaction of **11a** with HBF<sub>4</sub>·Et<sub>2</sub>O.

**10b**: mp158–160 °C (dec). Found: C, 52.10 H, 4.13 N, 3.79 (calcd for  $\text{C}_{31}\text{H}_{29}\text{BClF}_4\text{N}_2\text{PPd}\cdot\text{H}_2\text{O}$ : C, 52.64; H, 4.39; N, 3.96). IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3520 br, 1626 s, 1604 m, 1558 m, 1060 vs br, 331w, 302w.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone): 122  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.32 (CH<sub>3</sub>), 3.66 CH-CH<sub>3</sub>, 6.84 (H<sub>5</sub>), 7.33 (H<sub>4</sub>), 7.66 (H<sub>5'</sub>), 8.28 (H<sub>4'</sub>), 8.82 (H<sub>3'</sub>), 9.76 (H<sub>6'</sub>), 7.76 (H<sub>ortho</sub>), 7.45 (H<sub>meta</sub>), 7.55 (H<sub>para</sub>), 13.18, broad (NH). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  42.03.

**11b**: mp155–160 °C (dec). Found: C, 53.45 H, 4.88 N, 3.68 (calcd for  $\text{C}_{33}\text{H}_{33}\text{BClF}_4\text{N}_2\text{PPd}\cdot\text{H}_2\text{O}$ : C, 53.90; H, 4.76; N, 3.68). IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3540 s vbr, 1626 s, 1603 m, 1556 m, 1050 s br, 706s, 693 s, 355 w, 286 w.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone): 116  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  0.96 (CH<sub>3</sub>), 2.96 (CH<sub>2</sub>), 6.73 (H<sub>5</sub>), 7.29 (H<sub>4</sub>), 7.66 (H<sub>5'</sub>), 8.27 (H<sub>4'</sub>), 8.78 (H<sub>3'</sub>), 9.75 (H<sub>6'</sub>), 7.76 (H<sub>ortho</sub>), 7.45 (H<sub>meta</sub>), 7.55 (H<sub>para</sub>), 13.06, broad (NH). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  41.61.

**[Pd{C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>CH(CH<sub>2</sub>OC(O)CH<sub>3</sub>)CH<sub>2</sub>}Cl], **12**.** A solution of HL<sup>ip</sup> (198.3 mg, 1.00 mmol) and  $\text{Pd}(\text{CH}_3\text{COO})_2$  (224.5 mg, 1.00 mmol) in acetic acid (30 mL) was stirred for 4 days at room temperature, then evaporated to dryness. The crude obtained was treated with 1/2 water/acetone (30 mL) containing an excess of LiCl and stirred for 3 days, then evaporated to dryness and crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical product. Yield: 45%, mp 174 °C (dec). Found: C, 44.98; H, 3.65; N, 6.93 (calcd for  $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_2\text{Pd}$ : C, 45.36; H, 3.81; N, 7.05). FAB mass spectrum  $m/z$ : 361 [M - Cl] 757

Table 6. Crystallographic Data

	6	7
formula	$\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{Pd}$	$\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{Pd}$
<i>M</i>	353.1	367.2
color	yellow	yellow
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> /Å	9.289(2)	9.104(2)
<i>b</i> /Å	11.404(2)	11.219(1)
<i>c</i> /Å	20.046(4)	14.709(1)
$\alpha/\text{deg}$	83.81(2)	
$\beta/\text{deg}$	86.49(2)	102.07(2)
$\gamma/\text{deg}$	87.14(2)	
<i>U</i> /Å <sup>3</sup>	2105.2(8)	1469.1(4)
<i>T</i> /K	293	293
<i>Z</i>	6	4
<i>F</i> (000)	1056	736
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.671	1.660
crystal dimens/mm	$0.34 \times 0.39 \times 0.45$	$0.17 \times 0.23 \times 0.51$
$\mu$ (Mo K $\alpha$ )/cm <sup>-1</sup>	14.8	14.2
min., max. transmsn	0.92–1.00	0.89–1.00
factors		
scan mode	$\omega$	$\omega$
$\omega$ -scan width	$1.1 + 0.35 \tan \theta$	$1.4 + 0.35 \tan \theta$
$\theta$ -range	3–27	3–27
reciprocal space explored	$+h, \pm k, \pm l$	$+h, +k, \pm l$
no. of measd rflns	9139	3187
no. of unique obsd rflns	7393	2518
with $I > 3\sigma(I)$		
final <i>R</i> and <i>R'</i> indices <sup>a</sup>	0.021, 0.034	0.023, 0.030
no. of variables	487	172
goodness of fit <sup>b</sup>	1.35	1.45

<sup>a</sup>  $R = [\sum(|F_o - kF_c|)/\sum F_o]$ ,  $R' = [\sum w(F_o - kF_c)^2/\sum wF_o^2]^{1/2}$ . <sup>b</sup> GOF =  $[\sum w(F_o - kF_c)^2/(N_o - N_v)]^{1/2}$ , where  $w = 4F_o^2/[\sigma(F_o^2)]^2$ .  $\sigma(F_o^2) = [\sigma^2(F_o^2) + (P F_o^2)^2]^{1/2}$ ,  $N_o$  is the number of observations,  $N_v$  is the number of variables, and  $P$ , the ignorance factor, = 0.04 for **6** and 0.03 for **7**.

[2M - Cl], 302 [M - Cl-CH<sub>3</sub>COO]. <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  19.14 (CH<sub>2</sub>-Pd), 20.88 (CH<sub>3</sub>), 54.04 (CH), 66.92 (CH<sub>2</sub>-O), 119.35, 121.24, 123.81, 126.78, 137.30, 138.57 (aromatic CH), 149.24 (C<sub>6'</sub>), 153.25, 154.25 (C<sub>2</sub>, C<sub>2'</sub>), 170.39, 170.66 (C(2), CO). IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1725 s, 1592 s, 1557 w, 328 m.

**Reaction between 6 and CO.** A solution of complex **6** (50.1 mg, 0.142 mmol) in EtOH (30 mL) was placed in a stainless steel autoclave, pressurized with CO (100 atm), heated at 100 °C, and stirred for 6 h. Metallic palladium was formed. After filtration, the solution was evaporated to dryness, solubilized with  $\text{CH}_2\text{Cl}_2$ , treated with  $\text{K}_2\text{CO}_3$ , then filtered and evaporated to dryness. The oil obtained was analyzed by GCMS. Two products were identified: HL<sup>th</sup> (80%) and 3-methyl-3-[6-(2,2'-dipiridyl)]ethylbutanoate, **13** (20%). GCMS: HL<sup>th</sup>,  $m/z$ : 212 (25%, M<sup>+</sup>), 197 (100%, M - CH<sub>3</sub>), 155 (40%, M - C(CH<sub>3</sub>)<sub>3</sub>). **13**,  $m/z$ : 284 (10%, M<sup>+</sup>), 211 (100%, M - CH<sub>3</sub>CH<sub>2</sub>OC(O)), 197, 155.

**[Pd(L<sup>th</sup>)(PPh<sub>3</sub>)] [BF<sub>4</sub>], **14**.** To a solution of **6** (50.2 mg, 0.142 mmol) in acetone (15 mL) was added under vigorous stirring 42.0 mg of PPh<sub>3</sub> (0.16 mmol). To the resulting colorless solution was added 100 mg of NaBF<sub>4</sub>, and the mixture was stirred for 1 h, then evaporated to dryness and the residue crystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample as a white solid. Yield: 82%, mp 254–257 °C. Found: C, 57.30; H, 4.67; N, 4.28 (calcd for  $\text{C}_{32}\text{H}_{30}\text{BF}_4\text{N}_2\text{PPd}$ : C, 57.64; H, 4.53; N, 4.20). FAB mass spectrum,  $m/z$ : 579 [M<sup>+</sup>], 317 [M - PPh<sub>3</sub>]. IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1594 s, 1561 m, 1060 vs (br), 697 s.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone): 156  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

**[Pd<sub>2</sub>(L<sup>th</sup>)<sub>2</sub>(μ-dppe)] [BF<sub>4</sub>]<sub>2</sub>, **15**.** To a solution of **6** (176.6 mg, 0.50 mmol) in acetone (20 mL) were added under vigorous stirring 99.6 mg of dppe (0.25 mmol) and 200 mg of NaBF<sub>4</sub>. The mixture was stirred for 1 h, then evaporated to dryness and the residue recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample as a white solid. Yield: 80%, mp > 280 °C. Found: C, 54.16; H, 4.85; N, 4.51 (calcd for  $\text{C}_{54}\text{H}_{54}\text{B}_2\text{F}_8\text{N}_4\text{P}_2$ -

Pd<sub>2</sub>: C, 53.72; H, 4.51; N, 4.64). IR (Nujol)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1594 s, 1565 m, 1060 vs (br), 699 s.  $\Lambda_{\text{M}}$  ( $5 \times 10^{-4}$  M, acetone): 280  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

#### X-ray Data Collections and Structure Determinations.

Crystal data and other experimental details are summarized in Table 6. Crystals of **6** and **7** were mounted on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrixes were obtained from the least-squares refinement of 25 reflections in the range  $2^\circ < \theta < 23^\circ$ . A periodic monitoring of the three standard reflections did not reveal any crystal decay for either **6** or **7**. The diffracted intensities were corrected for Lorentz, polarization, and absorption effects (empirical correction).<sup>26</sup> The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package<sup>27</sup> and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref 28.

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The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function  $\sum w(F_o - k|F_c|)^2$ . Anisotropic thermal factors were refined for all the non-hydrogen atoms of both **6** and **7**. All the hydrogen atoms were placed in their ideal positions ( $\text{C-H} = 0.97 \text{ \AA}$ ,  $B$  1.15 times that of the carbon atom to which they are attached) and not refined. The final Fourier maps showed maximum residuals of 0.33(5)  $\text{e \AA}^{-3}$  at 0.90  $\text{\AA}$  from PdA in **6** and 0.78(6)  $\text{e \AA}^{-3}$  at 1.41  $\text{\AA}$  from Cl in **7**. The atomic coordinates of the structure models have been deposited with the CCDC.

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**Supporting Information Available:** X-ray structural information on compounds **6** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0002390

(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.