Organometallics **1999,** *18,* 3337−3341

Divergent Behavior of Palladium(II) and Platinum(II) in the Metalation of 1,3-Di(2-pyridyl)benzene

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Received February 22, 1999

1,3-Di(2-pyridyl)benzene undergoes regioselective orthometalation with $Pd(OAc)_2$ on the central aryl ring, giving rise to a dimeric complex in which four acetate units act as bridges between two doubly metalated ligands and each pyridine ligand coordinates to a different metal atom. The reaction with chloride-containing Pd(II) complexes does not lead to C−H activation but to coordination complexes without Pd−C bonds. Cycloplatination of 1,3-di(2-pyridyl)benzene takes place at C-2 of the benzene ring, generating a terdentate ligand. This behavior is the same as that previously observed for Ru and Os. Both orthometalated complexes have been structurally characterized by X-ray diffraction.

Introduction

There has been an increasing interest in the preparation and study of complexes containing terdentate ligands which include one metal−carbon bond, especially for the platinum metals.[1] The variety of coordinating atoms (X) that can be used along with the possibility of having two types of coordinating structures, i.e., X−C−X and C−X−X, allow one to obtain complexes with different properties. For instance, photoinduced electron transfer has been observed in Ru and Os complexes derived from pyridyl-substituted arenes,[2] and certain Pd complexes display nematic phases.[3] The development of new catalysts is of course of main interest, and in this sense Pd complexes have been shown to be the most active and versatile. Complexes with terdentate ligands containing a Pd−C bond have shown catalytic activity in some C−C forming reactions in which the intermediacy of Pd(IV) intermediates has been invoked.[4] In addition, certain Pd(II) metallacycles have been demonstrated to catalyze Heck reactions, cross-couplings, and related processes.[5−8]

Metalation reactions are key steps in some metal-catalyzed reactions.[9,10] Therefore, studies on regioselectivity could shed light on the mechanism of these important processes.[11] As part of a project directed toward the synthesis of new catalysts, we decided to examine the metalation of 1,3-di(2-pyridyl)benzene (**1**) with Pd(II) and Pt(II).[12] In this study, we have found that ligand **1** undergoes regioselective monometalation at the more hindered position (C-2) with Pt(II), while Pd(II) leads to dimetalation of the central ring at C-4 and C-6.

Results and Discussion

Cyclometalation Studies. Ligand **1**[13] was best prepared by using an approach recently developed for the preparation of pyridine-based ligands based on the Stille coupling reaction.[14] Thus, reaction between (2-pyridyl)trialkylstannanes **2** or **3** and 1,4-dibromoben-

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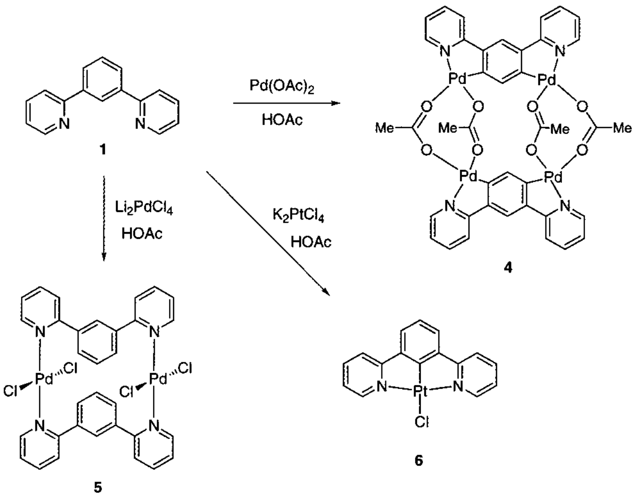
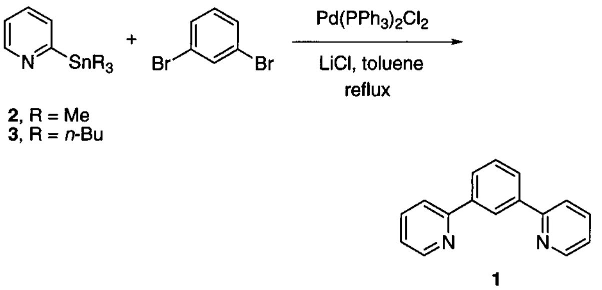
10.1021/om990125g CCC: $18.00
Publication on Web 07/20/1999

Scheme 1



zene in toluene in the presence of $Pd(PPh_3)_2Cl_2$ (ca. 8%) and LiCl afforded **1** in 83% yield (eq 1).



(1)

Reaction of **1** with $Pd(OAc)_2$ in HOAc led cleanly to the dimeric dipalladated complex **4** in 54% yield (Scheme 1). The existence of the doubly metalated ligand was evidenced by the presence of two broad singlets at 7.61 and 7.27 ppm in the ^{1}H NMR spectrum (DMSO-d_6) which correspond to the 1,2,4,5-tetrasubsituted aromatic ring. The IR spectrum showed two strong bands at 1573 and 1410 cm^{-1} typical of bridging acetate ligands. Two different signals in the ^{13}C{^{1}H} NMR spectrum at 180.31 and 179.03 ppm for the carboxylate, as well as methyl groups at 25.05 and 24.58 ppm, evidenced the existence of inequivalent acetates. X-ray diffraction of a single crystal obtained by slow diffusion of EtOH into a DMSO solution of **4** confirmed the existence of two monomeric dipalladated units bonded by four bridging acetate ligands (Scheme 1, Figures1 and 2). Only a few examples of this type of double cyclopalladation on an arene ring have been reported.[4,15] Usually, a 1,3-difunctionalized benzene ring with coordinating substituents yields monometalated complexes in position 2.[1,2,16,17]

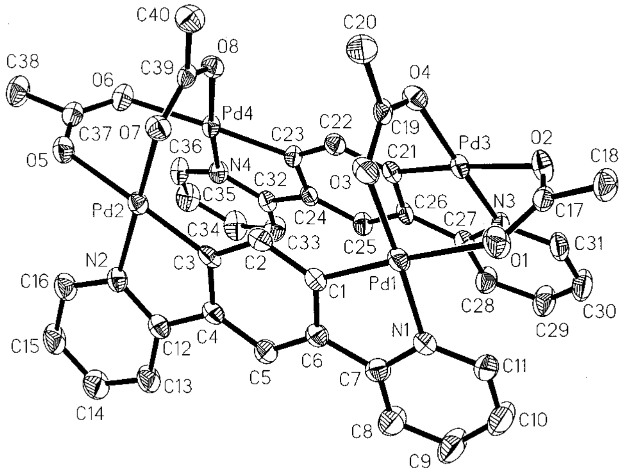


Figure 1. ORTEP plot of **4** with the labeling scheme (50% probability level).

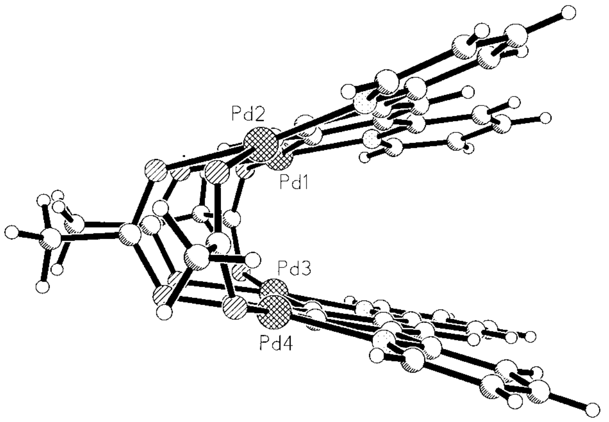


Figure 2. View of **4** showing the open book structure.

When ligand **1** was allowed to react with $[Pd(MeCN)_4](BF_4)_2$ in MeCN at 45 °C, a new complex was obtained whose ^{1}H NMR spectrum (DMSO-d_6) was very complicated probably due the coexistence of different species formed by coordination with the solvent. The addition of NaOAc to the DMSO-d_6 solution gave rise to a spectrum superimposable to that of **4**, indicating that $[Pd(MeCN)_4](BF_4)_2$ also yields the double palladation

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compound. On the other hand, treatment of ligand **1** with a HOAc solution of Li_2PdCl_4 gave a coordination complex corresponding to the formula $Pd(\mathbf{1})Cl_2$ (**5**), isolated in almost quantitative yield. The $^{13}C\{^1H\}$ NMR spectrum (DMSO-d_6) of **5** showed nine signals, which indicates that the complex has two equivalent pyridine rings. The highest shift observed in the ^1H NMR spectrum corresponds to the pyridine H-5 hydrogen (0.36 ppm downfield) due to the coordination with Pd(II). The FAB-MS spectrum obtained from crystals isolated from a DMSO solution shows peaks corresponding to the fragments $[Pd(\mathbf{1})]$ and $[Pd(\mathbf{1})Cl]$ as well as the higher fragments $[Pd_2(\mathbf{1})_2Cl]$ and $[Pd(\mathbf{1})_2H]$. A peak at *m*/*z* 489 may correspond to $Pd(\mathbf{1})(DMSO)Cl_2$. These data and the fact that if the central aryl ring is not metalated both pyridine moieties of one ligand cannot coordinate to a single Pd atom support the structure **5** shown in Scheme 1.

Treatment of complex **5** with different bases commonly used to induce C−H activation (MeOH−NaOAc, DMF−K_2CO_3, DMF−NaOAc) did not give rise to any cyclopalladated complex. A possible explanation for this lack of reactivity toward C−H activation is that the necessary Cl dissociation from Pd to permit the orthopalladation does not take place. The change in the reactivity of Pd complexes due to Cl coordination has been observed in the cyclopalladation of 2-aldimines derived from 8-methylquinolines.[18] We tried to perform the palladation reaction with other Pd(II)−chloride complexes which contained a lesser proportion of Cl as compared to Li_2PdCl_4. Thus, the palladation of **1** with $Pd(MeCN)_2Cl_2$, $Pd(COD)Cl_2$, and 1:1 mixtures of these complexes with $Pd(OAc)_2$ was assayed. However, in these experiments, complex mixtures of different species were obtained as shown by ^1H NMR, and cyclopalladated complexes could not be isolated.

On the other hand, treatment of **1** with K_2PtCl_4 in HOAc under reflux conditions for 3 days afforded the cycloplatinated complex **6** in 78% yield (Scheme 1).[19] The structure of **6** was determined on the basis of its ^1H and $^{13}C\{^1H\}$ NMR spectra (DMSO-d_6) which show the absence of H-2 of the benzene ring. Elemental analysis and the FAB mass spectrum also supported the monomeric structure **6**. A single crystal suitable for X-ray diffraction was grown by diffusion of EtOH into a DMSO solution, confirming the proposed platinated structure (Figure 3), analogous to that observed for the metalation of ligand **1** with Ru(II) and Os(II).[2]

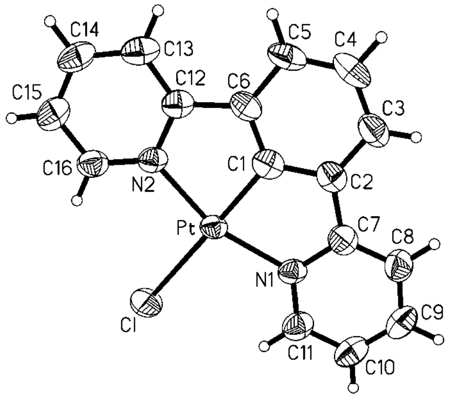

Figure 3. ORTEP plot of **6** with the labeling scheme (50% probability level).

The formation of the double palladation complex **4** must take place through a first C−H activation directed by coordination of *only one* of the pyridine rings to Pd. This would give rise to a more electron-rich aryl ring, which would be more reactive toward a second palladation.[14] Complex **4** remained unchanged when it was treated with 1 equiv of ligand **1** in refluxing HOAc to try to obtain an analogue of complex **6**. If such a complex were thermodynamically more stable, it could have been formed since orthopalladation has been shown to be reversible when performed in HOAc.[20] Thus, these results suggest that such a complex with a single Pd−C bond is not the most stable species under the mentioned conditions. On the other hand, when the reaction between $Pd(OAc)_2$ and **1** was performed in deuterated acetic acid (DOAc), no incorporation of deuterium into the aryl ring took place, which demonstrates that palladation at C-2 of the central benzene does not precede the formation of **4**. Complex **4** is the single species observed under all the conditions assayed. In the case of Pt (as well as for Os and Ru)[2] the activation of the more hindered position may arise from the need for having both N atoms coordinated to the metal before the C−H activation takes place. The different behavior of Pd(II) and Pt(II) in this case contrasts with the results obtained for the metalation of other N- or P-containing 1,3-disubstituted benzene ligands in which C−H activation takes place at C-2 for a series of metal atoms.[1b,15]

X-ray Crystal Structure of the Double Palladation Complex 4·EtOH. An ORTEP diagram of **4** is shown in Figure 1. Crystallographic data are listed in Table 1, and significant bond distances and angles are in Table 2. The molecular structure of complex **4**·EtOH contains two dipalladated ligands **1** bridged by four acetate molecules. The acetate-bridged dimer shows the usual open book or cleft structure where the angle between both dimetalated ligand planes is 26.3° (see Figure 3). The palladium coordination sites are essentially square-planar for the palladium atoms Pd(1), Pd(3), and Pd(4). However, a distorted square-planar coordination geometry has been found for the palladium atom Pd(2): the angle between the planes O(5)−Pd(2)−O(7) and N(2)−Pd(2)−C(3) is 8.4°. The Pd(1)−Pd(3) and Pd(2)−Pd(4) distances are significantly different [2.8460(5) and 2.9548(6) Å, respectively] the angle between the distances Pd(1)−Pd(2) and Pd(3)−Pd(4) being 3.2°. The Pd−C bond lengths [mean value 1.959(5) Å] are in the range observed for related dipalladated complexes (1.94−1.98 Å).[15a,b] The Pd−N distances are similar to those observed for Pd−terpyridine complexes[21] and for structurally related palladacycles with N-sp^2 bonded ligands.[14a,b] The Pd−O distances trans to carbon bond lengths [mean value

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Table 1. Crystal Data for Complexes 4·EtOH and 6

	4·EtOH	**6**
molecular formula	$C_{42}H_{38}N_4O_9Pd_4$	$C_{16}H_{11}ClN_2Pt$
source	Et_2O/DMSO vapor diffusion	EtOH/DMSO vapor diffusion
crystal habit	orange prisms	bright yellow needles
crystal system	orthorhombic	monoclinic
a, Å	19.716(2)	8.8985(4)
b, Å	15.347(1)	16.7545(9)
c, Å	26.779(2)	9.0451(7)
β, deg		92.154(5)
V, Å^3	8103.3(10)	1347.58(14)
Z	8	4
λ (Å)	0.71073	1.54178
T (K)	173(2)	296(2)
radiation used	Mo Kα	Cu Kα
monochromator	graphite	graphite
space group	*Pbca*	$P2_1/n$
crystal size, mm	0.40 × 0.32 × 0.30	0.40 × 0.10 × 0.10
μ, mm^{-1}	1.808	2.1203
abs correction	ψ scans	
max/min transmission, %	0.75/0.69	
diffractometer	Siemens P4	Siemens P4
scan method	ω scans	ω scans
2θ range, deg	6.1−50.0	5.3−57.2
reciprocal lattice segment	$-h, -k, -l$	$-h, -k, \pm l$
no. of rflns measd	8822	2341
no. of indep rflns	7130	1785
R_{int}	0.0281	0.0630
R1[a]	0.0366	0.0343
wR2[b]	0.0975	0.0943

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4·EtOH

Pd(1)−C(1)	1.959(5)	Pd(1)−N(1)	2.007(4)
Pd(1)−O(3)	2.063(4)	Pd(1)−O(1)	2.182(3)
Pd(2)−N(2)	2.004(4)	Pd(2)−C(3)	1.956(5)
Pd(2)−O(7)	2.054(3)	Pd(2)−O(5)	2.159(4)
Pd(3)−C(21)	1.960(5)	Pd(3)−N(3)	1.997(4)
Pd(3)−O(4)	2.047(4)	Pd(3)−O(2)	2.138(3)
Pd(4)−C(23)	1.963(5)	Pd(4)−N(4)	2.002(4)
Pd(4)−O(8)	2.057(3)	Pd(4)−O(6)	2.137(3)
O(1)−C(17)	1.265(6)	O(2)−C(17)	1.243(6)
O(3)−C(19)	1.248(6)	O(4)−C(19)	1.264(6)
O(5)−C(37)	1.256(6)	O(6)−C(37)	1.251(6)
O(7)−C(39)	1.254(6)	O(8)−C(39)	1.263(6)
C(1)−Pd(1)−N(1)	81.2(2)	C(1)−Pd(1)−O(3)	96.2(2)
N(1)−Pd(1)−O(1)	97.4(2)	O(3)−Pd(1)−O(1)	85.2(2)
C(3)−Pd(2)−N(2)	82.0(2)	C(3)−Pd(2)−O(7)	94.4(2)
N(2)−Pd(2)−O(5)	94.2(2)	O(7)−Pd(2)−O(5)	89.87(14)
C(21)−Pd(3)−N(3)	82.1(2)	C(21)−Pd(3)−O(4)	95.9(2)
N(3)−Pd(3)−O(2)	94.9(2)	O(4)Pd(3)−O(2)	87.22(14)
C(23)−Pd(4)−N(4)	81.1(2)	C(23)−Pd(4)−O(8)	95.3(2)
N(4)−Pd(4)−O(6)	93.3(2)	O(8)−Pd(4)−O(6)	90.23(14)
C(7)−N(1)−Pd(1)	116.2(3)	C(12)−N(2)−Pd(2)	115.8(3)
C(27)−N(3)−Pd(3)	116.1(3)	C(32)−N(4)−Pd(4)	116.7(3)
C(6)−C(1)−Pd(1)	115.1(4)	C(4)−C(3)−Pd(2)	113.6(3)
C(26)−C(21)−Pd(3)	112.9(3)	C(24)−C(23)−Pd(4)	114.2(3)
O(2)−C(17)−O(1)	125.2(5)	O(3)−C(19)−O(4)	126.3(5)
O(6)−C(37)−O(5)	126.9(5)	O(7)−C(39)−O(8)	126.7(4)

2.154(4) Å] are longer than the Pd−O distances trans to nitrogen bond lengths [mean value 2.055(4) Å], as usually observed, as a consequence of a stronger trans influence of the aryl group.[15b]

X-ray Crystal Structure of the Cycloplatination Complex 6. An ORTEP diagram of **6** is shown in Figure 2. Crystallographic data are listed in Table 1, and significant bond distances and angles are in Table 3. X-ray diffraction studies confirmed the proposed monometalated structure with both nitrogen atoms coordinated to platinum. The platinum center is four-coordinated in an approximately square-planar NCNCl environment, all the atoms of the molecule being essentially coplanar (mean deviation 0.028 Å). At the platinum center the chloride ligand is trans to the carbon atom. The Pt−C(1) bond distance [1.907(8) Å] lies in the range observed for Pt complexes of related N, C, N terdentate ligands (1.90−1.94 Å), which have been shown to exhibit shorter distances than those found in other orthoplatination complexes.[22] The Pt−N(1) and Pt−N(2) bond distances [2.041(6) and 2.033(6) Å] are shorter than those observed in related complexes containing N(sp^3)−C−N(sp^3) ligands. The main deviations from ideal sp^2 geometry in the N, C, N chelate system are the angles C(1)−C(2)−C(7) and C(1)−C(6)−C(12) [111.9(7)°, 112.2(7)°]; the small “bite” angle of the ligand [C(1)−Pt−N(1) 80.9(3)° and C(1)−Pt−N(2) 80.1(3)°] could explain these features. The C(1)−Pt−Cl axis is almost linear [179.0(2)°], whereas N(1)−Pt−N(2) is more distorted at 161.1(2)°, probably as a consequence of chelate ring strain.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

Pt−C(1)	1.907(8)	Pt−N(1)	2.041(6)
Pt−N(2)	2.033(6)	Pt−Cl	2.417(2)
N(1)−Pt−Cl	99.8(2)	N(2)−Pt−Cl	99.1(2)
N(1)−Pt−C(1)	80.9(3)	N(2)−Pt−C(1)	80.1(3)
C(1)−Pt−Cl	179.0(2)	N(1)−Pt−N(2)	161.1(2)
Pt−N(1)−C(7)	114.6(5)	Pt−N(2)−C(12)	114.5(5)
Pt−C(1)−C(2)	118.5(6)	Pt−C(1)−C(6)	119.8(6)
C(1)−C(2)−C(7)	111.9(7)	C(1)−C(6)−C(12)	112.2(7)

Conclusion

The orthometalation reaction of 1,3-di(2-pyridyl)-benzene with $Pd(OAc)_2$ or K_2PtCl_4 yields structurally different complexes. In the case of Pd, a double metalation takes place on the aryl ring, giving rise to a dimeric complex in which four acetate units act as bridges between two doubly metalated ligands. Each N coordinates to a different metal atom. The reaction with chloride-containing Pd(II) complexes does not lead to C−H activation but to coordination complexes without Pd−C bonds. On the other hand, cycloplatination takes place in position 2 of the benzene ring, generating a terdentate ligand. This behavior is the same as that previously observed for Ru and Os. The structure of both orthometalation complexes has been determined by X-ray diffraction. The details depending on the nature of the metal that control the mono- or dimetalation deserve further studies.

Experimental Section

General Procedures. All reactions (but not the subsequent workup) were carried out under an atmosphere of Ar. MeCN and CH_2Cl_2 were dried by standard methods. HOAc (synthetic grade) was used as received. $Pd(COD)Cl_2$ was prepared from $PdCl_2$,[23] and $[Pd(MeCN)_4](BF_4)_2$ was synthesized by reaction of $Pd(MeCN)_2Cl_2$[24] with $AgBF_4$ in MeCN.[25]

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1,3-Di(2-pyridyl)benzene (1). A mixture of 1,3-dibromopyridine (1.07 g, 4.52 mmol), (2-pyridyl)tri-*n*-butylstannane (**2**) or (2-pyridyl)trimethylstannane (**3**) (13.6 mmol), $Pd(PPh_3)_2Cl_2$ (254 mg, 0.36 mmol), and LiCl (1.92 g, 45.2 mmol) in toluene was heated under reflux conditions for 3 days. After cooling to 23 °C a saturated KF solution (15 mL) was added, and the mixture was stirred for 30 min. The solid residue formed was filtered off. CH_2Cl_2 (200 mL) and a 5% $NaHCO_3$ solution (150 mL) were added to the filtrate. The organic phase was separated and dried (Na_2SO_4), and the solvent was evaporated. The crude product was chromatographed (silica gel; hexanes−Et_2O, 4:1 to neat Et_2O) to give **1** as a light yellow oil (75−83%):[12] ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (dm, $J = 4.8$ Hz, 2H), 8.65 (t, $J = 1.8$ Hz, 1H), 8.06 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.81 (br d, $J = 7.5$ Hz, 2H), 7.74 (tm, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.23 (ddm, $J = 7.5, 4.8$ Hz, 2H); ^1H NMR (200 MHz, DMSO-d_6) δ 8.81 (t, $J = 1.8$ Hz, 1H), 8.69 (br d, $J = 4.5$ Hz, 2H), 8.13 (dd, $J = 7.7, 1.5$ Hz, 2H), 8.06 (br d, $J = 7.7$ Hz, 2H), 7.90 (td, $J = 7.7, 1.5$ Hz, 2H), 7.61 (t, $J = 7.7$ Hz, 1H), 7.37 (ddd, $J = 7.2, 4.6, 1.0$ Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT) δ 156.77 (C), 149.32 (CH), 139.55 (C), 136.48 (CH), 128.92 (CH), 127.14 (CH), 125.22 (CH), 121.98 (CH), 120.36 (CH).

$Pd_4(1\text{-}H_2)_2(OAc)_4$ (4). A mixture of **1** (108 mg, 0.46 mmol), $Pd(OAc)_2$ (95 mg, 0.42 mmol), and HOAc (7 mL) was heated under reflux conditions for 4.5 h. After being cooled to 23 °C the bright yellow precipitate was filtered and washed with HOAc and Et_2O to give **4** (64 mg, 54%). A lower yield (42%) was obtained when the reaction was carried out at 50 °C for 15 h: ^1H NMR (300 MHz, DMSO-d_6) δ 7.92 (dd, $J = 5.7, 1.2$ Hz, 4H), 7.69 (m, 4H), 7.61 (br d, $J = 7.4$ Hz, 4H), 7.27 (s, 2H), 6.92 (ddd, $J = 7.2, 5.8, 1.4$ Hz, 4H), 6.42 (s, 2H), 2.14 (s, 6H), 2.08 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6; DEPT) δ 180.31 (C), 179.03 (C), 164.67 (C), 155.96 (C), 148.39 (CH), 140.40 (C), 138.71 (CH), 137.86 (CH), 121.69 (CH), 118.00 (CH), 117.31 (CH), 25.05 (CH_3), 24.58 (CH_3); IR (KBr) (selected bands, cm^{-1}) 1573, 1410; FAB-MS *m/z* 1122.0 (M^+), 1063.0 [$(M - AcO)^+$], 2185.9 [$(2M - AcO)^+$]. Anal. Calcd for $C_{40}H_{32}N_4O_8Pd_4$: C, 42.80; H, 2.87; N, 4.99. Found: C, 42.45; H, 2.93; N, 4.72.

$Pd(1)Cl_2$ (5). Li_2PdCl_4 was prepared in situ by heating under reflux a suspension of $PdCl_2$ (79 mg, 0.45 mmol) and LiCl (60 mg, 1.42 mmol) in MeOH (10 mL) for 1.5 h to give a dark brown solution. The solvent was evaporated, and the resulting oil was dissolved in HOAc (10 mL). Ligand **1** (130 mg, 0.56 mmol) was added, and a white precipitate immediately appeared. The mixture was heated at 60 °C for 16 h. After being cooled to 23 °C, the light yellow precipitate was filtered and washed with HOAc, MeOH, and Et_2O (181 mg, quantitative). An analytical sample was obtained after suspension of the complex in MeOH, sonication, and filtration: ^1H NMR (300 MHz, DMSO-d_6) δ 8.80 (br d, $J = 5.5$ Hz, 2H), 8.73 (t, $J = 2.0$ Hz, 1H), 8.35−8.15 (m, 6H), 7.75 (t, $J = 7.8$ Hz, 1H), 7.66 (td, $J = 7.0, 2.0$ Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6; DEPT) δ 153.31 (C), 146.46 (CH), 142.10 (CH), 135.99 (C), 130.19 (CH), 129.50 (CH), 126.68 (CH), 124.69 (CH), 123.45 (CH); FAB-MS (DMSO) *m/z* 711 ([$Pd_2(\mathbf{1})_2Cl]^+$), 569.1 ([$Pd(\mathbf{1}_2)-H]^+$), 489.0 ([$Pd(\mathbf{1})(DMSO)Cl_2]^+$) 373.0 ([$Pd(\mathbf{1})Cl]^+$), 337.0 ([$Pd(\mathbf{1})-H^+$]). Anal. Calcd for $C_{16}H_{12}N_2Cl_2Pd\cdot 2H_2O$: C, 43.13; H, 3.62; N, 6.29. Found: C, 43.45; H, 3.23; N, 6.02.

Pt(1-H)Cl (6). A mixture of **1** (45 mg, 0.194 mmol), K_2PtCl_4 (80 mg, 0.193 mmol), and HOAc (5 mL) was heated at 110−115 °C (reflux). The progress of the reaction was monitored taking small aliquots and treating them with H_2O. The appearance of a red color indicated the presence of unreacted K_2PtCl_4. After 3 days the starting Pt salt was completely consumed and the mixture was allowed to cool to 23 °C. The resulting bright yellow complex was filtered off and washed with MeOH, H_2O, EtOH, and Et_2O (39 mg). The filtrate was evaporated to dryness and suspended in EtOH (5 mL), giving rise to an additional precipitate, which was filtered off and washed with EtOH and Et_2O (30 mg). Combined yield: 78%. An analytical sample of the corresponding dihydrate was prepared by diffusion of Et_2O into a DMSO solution (the solvents were not dry. H_2O in the complex was detected by ^1H NMR): ^1H NMR (300 MHz, DMSO-d_6) δ 9.07 [dd, $J = 5.5, 0.9$ Hz, $J(^1H-^{195}Pt) = 105.1$ Hz, 2H], 8.17 (td, $J = 7.7, 1.6$ Hz, 2H), 8.07 (br d, $J = 7.6$ Hz, 2H), 7.70 (d, $J = 7.7$ Hz, 2H), 7.52 (ddd, $J = 7.4, 5.8, 1.6$ Hz, 2H), 7.23 (t, $J = 7.7$ Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ 166.73 [$J(^{13}C-^{195}Pt) = 113$ Hz], 161.19, 151.41, 140.65 [$J(^{13}C-^{195}Pt) = 83$ Hz], 140.60, 125.09 [$J(^{13}C-^{195}Pt) = 36.4$ Hz], 124.28 [$J(^{13}C-^{195}Pt) = 30.5$ Hz], 123.28, 120.62 [$J(^{13}C-^{195}Pt) = 46.2$ Hz]. FAB-MS *m/z* 461.9 (M^+), 425.9 [$(M - HCl)^+$], 886.9 [$(2M - Cl)^+$]. Anal. Calcd for $C_{16}H_{11}N_2ClPt\cdot 2H_2O$: C, 38.60; H, 3.04; N, 5.63. Found: C, 38.27; H, 2.94; N, 5.50.

X-ray Structure Determinations. A crystal of **4**·EtOH was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 62 accurately centered reflections ($9.4° < 2\theta < 24.8°$). The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL 93).[26] The methyl group of the ethanol molecule is disordered over two sites (81 and 19% occupancy). Hydrogen atoms were included using a riding model or as rigid methyl groups. Hydrogen atoms for the disordered solvent were not considered. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0366, for 526 parameters and 433 restraints to local symmetry, and U components of neighboring light atoms. Maximum $\Delta/\sigma = 0.002$, maximum $\Delta\rho = 0.92$ e Å^{-3}. For compound **6** the determination of the cell constants and the data collection were performed on a Siemens P4 diffractometer (see Table 1). Unit cell constants were determined using 73 accurately centered reflections ($5.28° < 2\theta < 47.47°$). The structure was solved by the heavy atom method and refined anisotropically on F^2 (program SHELXTL 93).[25] Hydrogen atoms were included using a riding model. The final $R(F)$ [$I > 2\sigma(I)$] was 0.0343, for 182 parameters. Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 2.15$ e Å^{-3} (the largest difference peak is at 1.34 Å from the platinum atom).

Acknowledgment. We are grateful to the DGICYT (Project PB97-0002-C01-01) for support of this research. We acknowledge Johnson Matthey PLC for a generous loan of $PdCl_2$. We also thank César J. Pastor and Ivan Shmytko (permanent address: Institute of Solid State Physics, Chernogolovka Moscow distr. 149432, Russia) of the SIdI (UAM) for the resolution of the crystal structure of **6**.

Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and bond angles for complexes **4**·EtOH and **6.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM990125G

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