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Palladium(II) complexes of 3,3′-, 5,5′-, and 7,7′-dimethyl-2,2′-biindazole

Ana C. Albéniz [a], Juan C. Cuevas [b], Pablo Espinet *[a], Javier de Mendoza *[b], and Pilar Prados [b]

[a] *Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005-Valladolid (Spain)*
[b] *Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid (Spain)*

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Abstract

Palladium-chelate complexes of the type $[PdX_2(L–L)]$ [X = Cl; L–L = 3,3′- (**1**), 5,5′- (**2**), or 7,7′-dimethyl-2,2′-biindazole (**3**) have been prepared, but are too insoluble for structural studies. When $X = C_6F_5$ the position of the methyl substituents is critical; thus, **3** is unable to give the corresponding complex due to severe methyl–C_6F_5 interactions, **2** gives a planar complex, and **1** gives a non-planar (likely helicene-type) complex due to methyl–methyl interaction, as shown by ^{19}F NMR spectroscopy. $[Pd(C_6F_5)X(L–L)]$ [X = Br; L–L = **1**] is also non-planar.

Introduction

Ligands containing the N–C–C–N′ moiety, such as 2,2′-bipyridine [1] and *ortho*-phenanthroline [2], have been much used as powerful chelating agents, and some of their platinum(II) and palladium(II) complexes display interesting anti-tumor properties [3]. Furthermore, the ability of these complexes to undergo cyclometallation and to activate remote carbon sites has given rise to much interest [4].

A type of ligand of special interest is represented by *N,N′*-biazoles in which the two aromatic rings are linked by a $N_{sp^2}–N_{sp^2}$ bond, the orthogonal conformation around this bond being the most stable [5]. The presence of substituents at certain positions may cause additional hindrance to the rotation around the N–N bond, so new coordination features could be expected for these ligands.

This is the case for the 3,3′-dimethyl derivative of 2,2′-biindazole (**1**), for which we have previously shown the operation of an unusual coordination mode leading to a $ZnCl_2$ complex of 2:2 stoichiometry [6]. We report here our studies on Pd^{II} complexation by **1**, the 5,5′-dimethyl isomer (**2**), and the frontally hindered 7,7′-dimethyl isomer (**3**).

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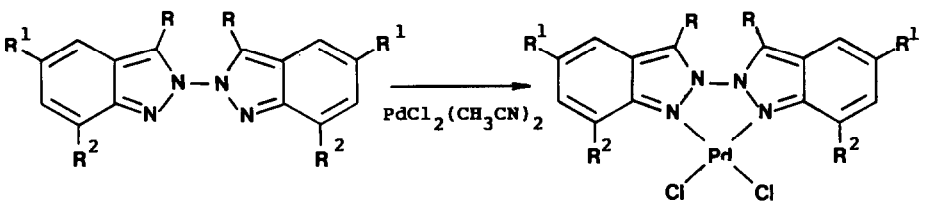
Results and discussion

The palladium complexes **4–6** were prepared by reaction of **1–3** [3] with either $[PdCl_2(CH_3N)_2]$ in acetonitrile at room temperature or palladium(II) chloride in refluxing ethanol (Scheme 1). Analytical data revealed 1:1 stoichiometries in all cases. The far-infrared spectra of **4–6** showed two N–Pd stretching absorptions (C_{2v}, $A_1 + B_1$) at ca. 303 and 280 cm^{-1}, in good agreement with those found for bipyridine complexes [8]. Moreover, Pd–Cl stretching absorption bands, along with the corresponding shoulders, were found at ca. 350 cm^{-1}, confirming the presence of two stretching vibrations, as expected for *cis*-square-planar geometries.

Because of the extreme insolubility of the complexes in all the common solvents, we were unable either to obtain crystals for X-ray diffraction studies or to read further spectroscopic data that could provide information on the coordination features of the ligands. Therefore, we undertook the preparation of the corresponding *cis*-bis(pentafluorophenyl)palladium(II) complexes, which we expected to be more soluble. In the case of 7,7′-dimethyl-2,2′-biindazole (**3**), inspection of CPK molecular models indicated a very crowded structure for the *cis*-bis(pentafluorophenyl) complex, and in keeping with this the reaction of **3** with *cis*-$[Pd(C_6F_5)_2(THF)_2]$ [9] failed to give any complex, and the free ligand was recovered unchanged.

In contrast, ligands **1** and **2** gave the 1:1 complexes **7** and **8** on reaction with *cis*-$[Pd(C_6F_5)_2(THF)_2]$ (Scheme 2). The IR spectra of **7** and **8** showed two bands at

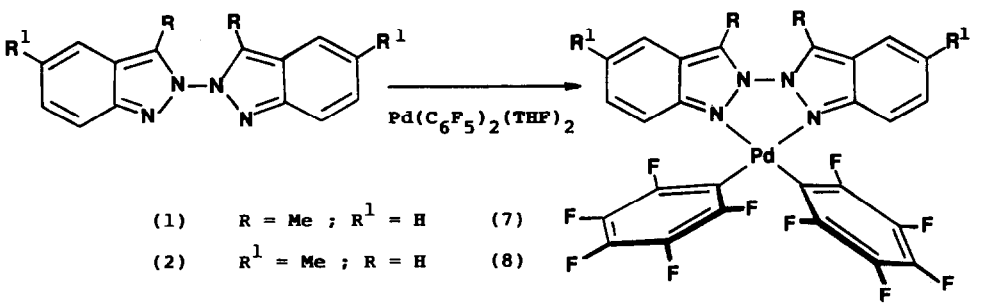


(1) R = Me ; R^1, R^2 = H (4)

(2) R^1 = Me ; R, R^2 = H (5)

(3) R^2 = Me ; R, R^1 = H (6)

Scheme 1



(1) R = Me ; R^1 = H (7)

(2) R^1 = Me ; R = H (8)

Scheme 2

Table 1

^{1}H NMR spectra (200 MHz)

Compd.	Solvent	H-3,3′	H-4,4′	H-5,5′	H-6,6′	H-7,7′	CH_3
1	$CDCl_3$	–	7.65	7.16	7.41	7.69	2.49
7	$CDCl_3$	–	7.57	6.86	6.52	5.54	3.10
9	$CDCl_3$	–	7.44	6.9–7.1	6.9–7.1	7.77	3.10
			7.32	6.9–7.1	6.69	5.91	2.92
2	acetone-d_6	8.78	7.57	–	7.30	7.59	2.42
8	acetone-d_6	9.65	7.72	–	7.29	6.39	2.40

795 and 780 cm^{-1}, corresponding to the two modes of C_6F_5–X vibration [10], in accord with their expected *cis* stereochemistry.

As expected, complexes **7** and **8** were found to be much more soluble in common organic solvents than their dichloro analogues, and ^{1}H NMR spectra could be recorded (Table 1). Comparison of the spectrum of **7** with that of the parent ligand **1** showed two important features: a downfield shift (δ +0.6 ppm) for the methyl group signal and upfield shifts for the four aromatic signals, especially H-6 (δ 0.9 ppm) and H-7 (δ 2.1 ppm).

The downfield shift of the CH_3-3 signals of **7** (and the corresponding effect observed for H-3 in **8**, see Table 1) is due to the change in the biindazolyl ligand from an almost orthogonal to a quasi-planar conformation upon complexation. On the other hand, the upfield shifts of H-7 and H-7′ (also observed in **8**) reveal their close proximity to the C_6F_5 ligands that lie almost perpendicular to these protons.

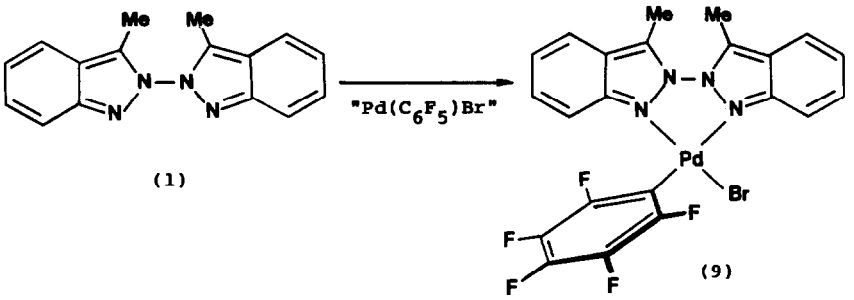
In the complexes derived from ligand **1**, the steric interaction between the two methyl groups prevents the chelating ligand from adopting a planar conformation. This was nicely confirmed by analysis of the ^{19}F NMR spectra of complexes **7** and **8** (Table 2), taking into account the fact that C_6F_5 groups are not free to rotate about the Pd–C bond in these complexes [11]. Whereas the spectrum of the unhindered complex **8** showed only three signals in a 2 : 2 : 1 ratio, revealing that the coordination plane is a plane of symmetry, the corresponding spectrum of **7** showed well-separated signals for each of the five fluorine atoms in the two equivalent C_6F_5 ligands, as expected if the two halves of each C_6F_5 group are inequivalent.

This same effect was encountered with the "mixed" complex **9**, which has one C_6F_5 group and one Br ligand on the Pd atom (Scheme 3). Again, the ^{19}F NMR spectrum showed five distinct signals, confirming the lack of a symmetry plane. Furthermore, since this complex also lacks a C_2 axis, both halves of the biindazole **1** are inequivalent, as revealed by the splitting of all the signals in the ^{1}H NMR

Table 2

^{19}F NMR Spectra (188.2 MHz)

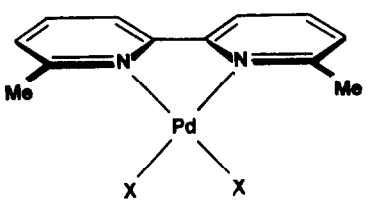
Compd.	Solvent	$F_{o,o'}$	$F_{m,m'}$	F_p
7	$CDCl_3$	−114.15	−164.16	−161.02
		−118.53	−164.68	
8	acetone-d_6	−114.15	−163.56	−160.41
9	$CDCl_3$	−114.49	−164.34	−160.40
		−122.23	−164.46	



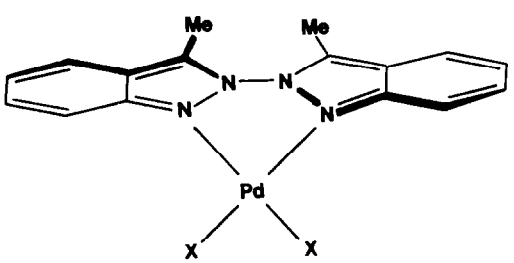
Scheme 3

spectrum. The H-7 proton, close to the C_6F_5 ring, showed an upfield shift similar to that observed for complexes **7** and **8**, whereas H-7′, close to the bromine atom, was relatively unaffected (Table 1).

It has been reported that the related ligands 6,6′-dimethyl-2,2′-bipyridine [12] and 2,9-dimethyl-1,10-phenanthroline [13], unlike their corresponding unsubstituted analogues, do not give planar palladium complexes, but the aromatic rings are tilted away from their expected geometries, and the ligand itself is "bowed" away from the perfect planarity. In other words, both nitrogen atoms are above the coordination plane of the palladium, so that both methyl substituents can lie under this plane and reduce the unfavourable methyl–chlorine interaction (Fig. 1a).



(a)



(b)

Fig. 1. The two possible types of deviation from planarity for $[PdX_2(L–L)]$ ligands.

In the case of ligand **3**, which is similar to the above-mentioned substituted bipyridine or phenanthroline, the dichloropalladium derivative could not be studied because of its insolubility, whereas the corresponding bis(pentafluorophenyl) derivative could not be made, suggesting that the methyl–pentafluorophenyl interactions are too severe for this complex to form.

For ligand **2**, which has both methyl substituents far apart from the palladium atom and from each other, the spectroscopic data for the complex showed that it is either planar or planar-averaged on the NMR time scale.

Finally, for ligand **1**, the NMR spectra of both complexes **7** and **9** showed that they are not planar. The origin of this non-planarity is evidently not related to the ligand–palladium coordination features, since this effect was not observed for ligand **2**, but rather to the unfavourable methyl–methyl intraligand interaction when this coordinates as a chelating ligand. The most likely way for the ligand to reduce this interaction is by a twisting of both indazole moieties about the N–N bond, so that their coordinated nitrogen atoms lie on different sides of the coordination plane (Fig. 1b).

In summary, both interligand interactions (as in the substituted bipyridines and phenanthrolines, and likely in ligand 3) and intraligand interactions (as in the case of ligand **1**) can prevent the coordinated ligands from adopting a planar conformation. Whereas in the former case complexes of the type $[PdX_2(L–L)]$ are non chiral, in the latter case helicene-type chiral molecules must be formed [14].

Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WP 200 SY instrument, operating at 200 MHz. For the ^{19}F NMR spectra, a Varian XL-200 instrument, operating at 188.2 MHz, was employed. Mass spectra were recorded on a Hewlett–Packard 5985. FT-IR spectra of compounds **4–6** were registered on a Nicolet 60-SX instrument. For the remaining compounds, a Perkin–Elmer 599 was used. Solvents were purified by standard procedures. The synthesis of biindazolyl ligands has been described previously [7].

Preparation of palladium(II) complexes; general procedures

Method A: A solution of dichloro-bis(acetonitrile)palladium (0.4 mmol) in acetonitrile (20 ml) was added to one of the biindazole (0.4 mmol) in the same solvent (30 ml). The mixture was stirred at room temperature for 5 hours, and the yellow solid was filtered off.

Method B: A mixture of biindazole (0.4 mmol) and palladium chloride (0.4 mmol) in ethanol (35 ml) was refluxed for one day. The yellow solid was filtered off.

Dichloro-(3,3'-dimethyl-2,2'-biindazole)palladium (4). Yield 75% (method A) and 60% (method B). Dark yellow solid. M.p. > 300 °C (Found: C, 43.85; H, 3.49; N, 12.54. $C_{16}H_{14}N_4Cl_2Pd$ calc: C, 43.79; H, 3.19; N, 12.77%.) IR (KBr) 1620 (m), 1531 (m), 1473 (m), 1429 (w), 1356 (m), 1339 (m), 1326 (m), 1248 (m), 1163 (m), 927 (w), 740 (s), 624 (w), and 436 (w) cm^{-1}.

Dichloro-(5,5'-dimethyl-2,2'-biindazole)palladium (5). Yield 72% (method A). Yellow powder. M.p. > 300 °C. IR (KBr) 1530 (m), 1441 (m), 1337 (m), 1318 (w), 1269 (m), 1242 (m), 1061 (s), 1021 (m), 971 (m), 863 (w), 180 (s), 737 (w), 572 (w), 484 (m), and 429 (m) cm^{-1}.

Dichloro-(7,7′-dimethyl-2,2′-biindazole)palladium (6). Yield 45% (method A). Yellow. M.p. > 300 °C (Found: C, 43.41; H, 3.21, N, 12.82. $C_{16}H_{14}N_4Cl_2Pd$ calc: C, 43.79; H, 3.19; N, 12.77%.) IR (KBr) 1626 (m), 1546 (m), 1538 (m), 1382 (m), 1362 (m), 1258 (m), 1054 (m), 946 (w), 801 (m), and 749 (s) cm^{-1}.

Bis(pentafluorophenyl)-(3,3′-dimethyl-2,2′-biindazole)palladium (7). $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ [9a,15] (0.094 g, 0.062 mmol) was added to a solution of silver perchlorate (0.026 g, 0.124 mmol) in THF (30 ml), as in the procedure described by Usón et al. [9c]. The mixture was stirred in the dark for 30 min. Silver bromide was filtered off and the solvent evaporated. The residue was extracted with ether (40 ml), and the insoluble tetrabutylammonium perchlorate was removed. 3,3′-Dimethyl-2,2′-biindazole (0.032 g, 0.124 mmol) was then added to the filtered solution, and the mixture was stirred for 3 hours. Concentration of the solution afforded **7** in 62% yield (0.054 g). Yellow powder. M.p. > 300 °C. Further evaporation afforded some additional **7** (0.006 g) (Found: C, 48.04; H, 2.93; N, 7.71. $C_{28}H_{14}N_4F_{10}Pd$ calc: C, 47.85; H, 2.01; N, 7.97%). IR (Nujol) 1630 (m), 1525 (m), 1490 (s), 1240 (w), 1150 (w), 1120 (w), 1060 (s), 955 (s), 930 (m), 850 (w), 795 (s), 780 (s), 740 (s), 730 (s), and 720 (s) cm^{-1}.

Bis(pentafluorophenyl)-(5,5′-dimethyl-2,2′-biindazole)palladium (8). This complex was obtained in 62% yield by the procedure described for **7**. Yellow solid. M.p. > 300 °C (Found: C, 47.97; H, 2.35; N, 7.80. $C_{28}H_{14}N_4F_{10}Pd$ calc: C, 47.85; H, 2.01; N, 7.97%.) IR (Nujol) 1495 (m), 1370 (m), 1360 (m), 1235 (w), 1070 (m), 1050 (m), 1005 (w), 955 (s), 800 (s), 790 (w), 780 (m), 730 (s), and 720 (s) cm^{-1}.

Bromo(pentafluorophenyl)-(3,3′-dimethyl-2,2′-biindazole)palladium (9). A mixture of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ [16] (0.076 g, 0.056 mmol), silver perchlorate (0.023 g, 0.112 mmol), and 3,3′-dimethyl-2,2′-biindazole (**1**) (0.029 g, 0.112 mmol) in dichloromethane (40 ml) was stirred in the dark at room temperature for 5 hours. The resulting yellow precipitate was filtered off and the yellow filtrate was evaporated to dryness. The residue was triturated with ethanol (2 ml) to give **9** in 26% yield. Pale yellow solid. M.p. > 300 °C (Found: C, 43.23; H, 2.47; N, 9.02. $C_{22}H_{14}N_4F_5BrPd$ calc: C, 42.92; H, 2.29; N, 9.10%) IR (Nujol) 1625 (m), 1525 (w), 1495 (s), 1245 (w), 1160 (w), 1150 (w), 1060 (s), 960 (s), 920 (w), 795 (m), 740 (s), 730 (s), and 720 (s) cm^{-1}.

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