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Palladium(II) coordination and cyclometallated complexes derived from 3- and 5-aryl-substituted pyrazoles

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Abstract

Palladium(II) coordination complexes of nine 3- or 5-arylpyrazoles (phenyl, 2-bromophenyl, or 3-methoxyphenyl), as well as of 3,5-diphenylpyrazole, are reported. A *cis–trans* mixture of $[PdL_2Cl_2]$ isomers is found in the case of 3-aryl-1-methylpyrazoles, the *cis*-isomers being transformed into *trans* by heating. Only *trans* isomers are isolated with the other ligands. Cyclopalladation of 3-aryl-1-methylpyrazoles can be performed with palladium(II) acetate, and the resultant μ-acetate bridged dimers can be transformed into μ-chloro bridged dimers or acetylacetonate monomers. The structures of the complexes have been characterized by ^{1}H- and ^{13}C-NMR spectroscopy.

Introduction

Despite the extensive work on the coordination chemistry of pyrazole (Pz), few complexes derived from unsymmetrically substituted pyrazoles have been described [1]. Structural modifications of the parent ligand might result in new ligands and complexes of interest in metalloenzyme modelling, a field where pyrazole can successfully replace imidazole [2]. On the other hand, the study of cyclometallated compounds constitutes an area of recent increased interest [3,4]. Surprisingly few organometallic compounds of unsymmetrically substituted pyrazoles have been reported so far [5,6].

As a part of a study of metallation reactions with *C*-substituted pyrazoles [7], we report here the preparation of complexes of several 3- and 5-arylpyrazoles and the first example of cyclopalladated complexes from 3-arylpyrazoles.

Results and discussion

Complexes

When pyrazoles **1a–d** or 1-methyl-5-substituted pyrazoles **2a–c** were treated with lithium tetrachloropalladate or palladium(II) chloride the corresponding Pd^{II}

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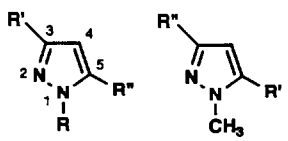
complexes **4a–d** (R = H) and **5a–c** (R = CH_3) of $[PdCl_2L_2]$ stoichiometry and *trans* stereochemistry were obtained readily. The *trans* stereochemistry was deduced from the IR spectra, which showed only one ν(Pd–Cl) band. The ^{1}H-NMR spectra (Table 1) showed low-field shifts for the protons nearest to the coordination centre (Pz-3). The deshielding effect of Pd^{II} has already been reported for other ligands [8,9]. For **1a–d**, the annular tautomerism allows the metal to coordinate to either ring nitrogen atom (the tautomers are equivalent in the case of the unsymmetrically substituted pyrazole **1d**). Thus, two different regioisomeric complexes might be formed. However, the ^{1}H-NMR spectra for all complexes, unsubstituted (**4a–c**) and 1-methyl-5-substituted (**5a–c**), are very similar, suggesting a great structural similarity (R″ = Aryl) between them. The steric interaction between the aryl groups and the chlorine atoms on the metal coordination sphere shifts the reaction equilibria towards the less hindered isomer.



1 R = H **3**

2 R = CH_3

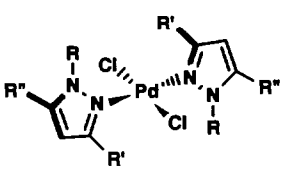
a R′ = H ; R″ = C_6H_5

b R′ = H ; R″ = 3-MeO-C_6H_4

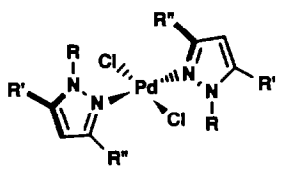
c R′ = H ; R″ = 2-Br-C_6H_4

d R′ = C_6H_5 ; R″ = C_6H_5

In contrast, complexes derived from 1-methyl-3-substituted pyrazoles **3a–c** give *cis/trans* mixtures **6a–c** $[PdCl_2L_2]$, the ratio of stereoisomers, depending on the palladium salt ($PdCl_2$ or K_2PdCl_4) and the reaction temperature is shown in Table 2. Use of $PdCl_2$ at room temperature favours *cis* stereoisomers, whereas less soluble *trans* stereoisomers were isolated at reflux temperature, with $K_2[PdCl_4]$. Moreover, *trans* isomers precipitated slowly from solutions of *cis* isomers. *Cis* and *trans* Pt^{II} complexes of pyrazole have been reported [10], but for a Pd^{II} *cis* to *trans* isomerization has been suggested only from an imidazole complex [11]. The *trans* complexes are always less soluble than their *cis* counterparts. A *cis–trans* mixture was also obtained for the complex **6d**, derived from the symmetrical pyrazole **2d**.

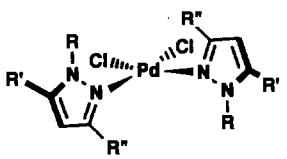


4a-d 5a-c



6a-d

trans



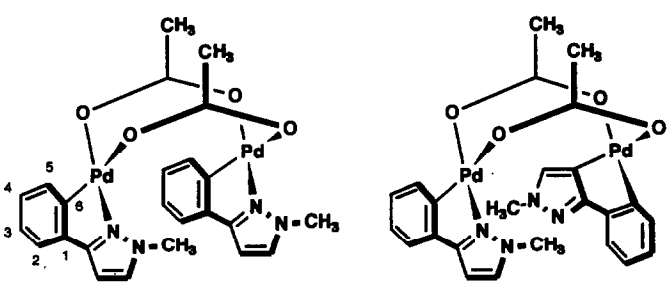
cis **6a-d**

The *trans* structures were confirmed by the resemblance of their ^{1}H-NMR spectra to those for the *trans* complexes **4a–d**, **5a–c**, previously discussed. For the assignment of the *cis* structures, IR spectroscopy [two ν(Pd–Cl) bands] was employed. Moreover, in the case of **6c**, chemical correlation was performed with a model complex of *cis* geometry prepared by reaction with $Na_2[Pd(oxalate)_2]$ (Scheme 1).

Table 1 shows that *cis* and *trans* complexes derived from 1-methyl-3-substituted pyrazoles **3a–c** have quite different ^{1}H-NMR spectra. For instance, signals are shifted both upfield and downfield, with respect to those of the free bases. The effect, which reaches a maximum for the N–CH_3 signals ($\delta_{cis} = -0.4$ ppm; $\delta_{trans} = +0.5$ ppm), is due to the different effects of both pyrazole rings. In the *cis* complexes both heterocycles are closer and their methyl groups are shielded by the neighbouring aromatic ring. This was confirmed by the observation of a NOE enhancement (8.4%) of the phenyl ring signals upon irradiation of the methyl group of the *cis* complex of pyrazole **3a**. On the other hand, variable temperature NMR experiments showed no significant differences, revealing a small rotational barrier around the Pd–N bonds.

Cyclometallation reactions

Cyclometallation of 1-phenylpyrazole derivatives takes place readily with $PdCl_2$ [12]. In contrast, all our attempts to metallate *C*-arylpyrazoles **3a–d** with $PdCl_2$ or $K_2[PdCl_4]$ were unsuccessful, even at high temperatures and with prolonged reaction times. Thus, *C*-arylpyrazoles appear to be less reactive than their *N*-aryl analogues. Assuming an aromatic electrophilic substitution mechanism for the metallation reaction [13], this distinction may be accounted for by the deactivating effect of the Pd^{II} coordination to the pyrazole nucleus, which affects the nucleophilicity of the conjugated *C*-substituent more than that of the less-conjugated *N*-substituent. To achieve cyclopalladation, refluxing acetic acid with the more reactive $Pd(OAc)_2$ was therefore necessary, producing acetate-bridged dimers **7a–d** $[LPdOAc]_2$, respectively (formula **7a** shown). The dimers were then trans-



syn **7a** *anti*

Table 1

^{1}H-NMR Spectra of bases and Pd^{II} coordination complexes [a]

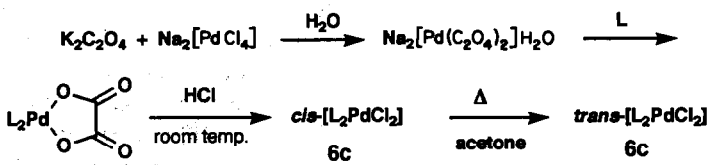
Compound	H-2	H-3	H-4	H-5	H-6	Pz-3[Pz-5]	Pz-4	N-H[N-CH_3]	OCH_3
1a	7.75	7.34	7.34	7.34	7.75	7.55	6.59	[b]	
trans-**4a**	7.50 (−0.25)	7.50 (0.16)	7.50 (0.16)	7.50 (0.16)	7.50 (−0.25)	8.01 (0.46)	6.47 (−0.12)	11.85	
1b	7.28		6.82	7.28	7.28	7.55	6.57	[b]	3.83
trans-**4b**	7.00 (−0.28)		6.90 (0.08)	7.31 (0.03)	7.05 (−0.23)	7.93 (0.38)	6.48 (−0.09)	11.90	3.72 (−0.11)
1c		7.58	7.18	7.30	7.66	7.55	6.69	7.72	
trans-**4c**		7.45 (−0.13)	7.42 (0.24)	7.32 (0.02)	7.61 (−0.05)	8.19 (0.64)	6.62 (−0.07)	10.09 (−2.37)	
1d	7.72	7.38	7.38	7.38	7.72		6.82	[b]	
trans-**4d**	7.81 (0.09)	7.52 (0.14)	7.51 (0.13)	7.51 (0.13)	7.81 (0.09)		6.12 (−0.70)	12.20	
2a	7.43	7.43	7.43	7.43	7.43	7.53	6.30	3.89	
trans-**5a**	7.45 (0.02)	7.45 (0.02)	7.45 (0.02)	7.45 (0.02)	7.45 (0.02)	7.81 (0.28)	6.40 (0.10)	4.47 (0.58)	
2b	7.01		6.94	7.37	6.94	7.51	6.30	3.89	3.89
trans-**5b**	6.88 (−0.13)		6.98 (0.04)	7.40 (0.03)	7.01 (0.07)	7.81 (0.30)	6.38 (0.08)	4.45 (0.56)	3.84 (−0.05)
2c		7.30	7.30	7.30	7.62	7.47	7.20	3.65	
trans-**5c**		7.31 (0.01)	7.43 (0.13)	7.40 (0.10)	7.72 (0.10)	7.84 (0.37)	6.38 (−0.82)	4.30 (0.65)	
3a	7.81	7.30	7.30	7.30	7.81	7.30	6.52	3.93	
cis-**6a**	7.76 (−0.05)	7.52 (0.22)	7.52 (0.22)	7.52 (0.22)	7.76 (−0.05)	7.01 (−0.29)	6.04 (−0.48)	3.47 (−0.46)	
trans-**6a**	8.41 (0.60)	7.67 (0.37)	7.67 (0.37)	7.67 (0.37)	8.41 (0.60)	7.41 (0.11)	6.40 (−0.12)	4.46 (0.53)	
3b	7.33		6.84	7.33	7.33	7.36	6.51	3.95	3.85
cis-**6b**	6.69 (−0.64)		7.10 (0.26)	7.47 (0.14)	7.29 (−0.04)	7.12 (−0.24)	6.12 (−0.39)	3.57 (−0.38)	4.02 (0.17)
trans-**6b**	8.04 (0.71)		7.06 (0.22)	7.51 (0.18)	7.80 (0.47)	7.44 (0.08)	6.39 (−0.12)	4.38 (0.43)	3.92 (0.07)
3c		7.67	7.18	7.35	7.71	7.41	6.74	3.97	
cis-**6c**		7.75 (0.08)	7.44 (0.26)	7.71 (0.36)	8.33 (0.62)	7.30 (−0.11)	6.34 (−0.40)	3.46 (−0.51)	
trans-**6c** [c]									
3d	7.83	7.40	7.40	7.40	7.83		6.59	3.88	
cis-**6d**	8.03 (0.20)	7.46 (0.06)	7.20 (0.20)	7.46 (0.06)	8.03 (0.20)		6.18 (−0.41)	3.54 (−0.34)	
trans-**6d**	8.40 (0.57)	7.47 (0.07)	7.47 (0.07)	7.47 (0.07)	8.40 (0.57)		6.43 (−0.16)	4.37 (0.49)	

[a] 200 MHz, solvent $CDCl_3$. Values in parentheses correspond to $\Delta\delta = \delta_{complex} - \delta_{ligand}$. [b] Not observed. [c] Not soluble in $CDCl_3$.

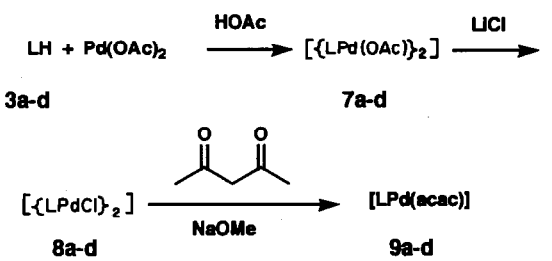
Table 2

Ratio of *cis / trans* isomers (yield, %) in the synthesis of coordination complexes from 1,3-disubstituted pyrazoles.

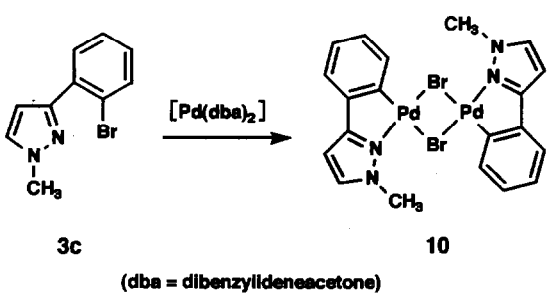
Complex	$PdCl_2$ (25°C)	$PdCl_2$ (60°C)	$Na_2[PdCl_4]$ (25°C)	$Na_2[PdCl_4]$ (60°C)
6a	1:0 (80–85)	0:1 (75–80)	–	0:1 (75–80)
6b	5:1 (75–80)	0:1 (70–75)	9:1 (2–5)	0:1 (70–75)
6c	5:2 (80–85)	0:1 (70–75)	–	0:1 (70–75)
6d	2:1 (80–85)	0:1 (70–74)	4:1 (1–2)	0:1 (70–74)



Scheme 1



Scheme 2



Scheme 3

formed into new chloro-bridged dimers **8a–d** by ligand exchange with lithium chloride and finally into acetylacetonate monomers **9a–d** by treatment with sodium acetylacetonate (Scheme 2). Compound **10**, a bromo-bridged analogue of **8a**, was obtained by oxidative coordination of **3c** with $Pd(dba)_2$ [14] (Scheme 3).

Acetate-bridged dimers can exist as either *syn* or *anti* isomers. Two acetate resonances should be present in a *syn* isomer, whereas only one signal should appear in an *anti* complex. The ^{1}H-NMR spectra of dimers **7a–d** (Table 3), showing a sharp methyl signal for the μ-acetate groups (at *ca.* 2.0 ppm), strongly suggest the exclusive formation of the *anti* isomer. This is in good agreement with the *anti* structures proposed for other cyclopalladated acetate-bridged compounds with a Pd–C_{sp^2} bond [15]. The shielding experienced by all aromatic protons, which attains a maximum for aryl H-2 [16*], is much greater than that observed for monomeric complexes **9a–d**, showing that it is caused mainly by the parallel arrangement of the aromatic rings in the dimers. The aromatic part of the spectra of the monomeric complexes showed, as expected, two double doublets for H-2 and H-5, the most deshielded being assigned to H-5 because of its close proximity to the acetylacetonate oxygens, as reported for other cyclometallated phenylpyrazoles [17]. The assignment of the ^{13}C-NMR spectra of these compounds was made by DEPT and heteronuclear 2D correlation experiments. The carbon atom C-6 attached to palladium was deshielded in all cases (18.7 to 21.5 ppm), in good agreement with the values found by Hartwell [18] and Clark [19] for quaternary carbons bound to palladium (20–28 ppm).

Experimental

Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker WP 200 SY spectrometer, mass spectra on a Hewlett–Packard 5985 (70 eV, EI mode), and IR spectra on a Nicolet 5DX (FT) instrument. Abbreviations used are as follows: s, singlet; d, doublet, t, triplet, q, quartet, m, multiplet, br, broad. Elemental analyses were carried out on a Perkin–Elmer 2400 THM aparatus.

Merck 230–400 mesh silica gel and DC-Alufolien 60 were used for flash and analytical chromatography, respectively. Thin layer plates were examined under UV light. Most chemicals were purchased from Aldrich, and used as received without purification. Organic solvents were purified by standard procedures. 3(5)-Phenylpyrazole (**1a**), 3(5)-(2-bromophenyl)pyrazole (**1c**), 3,5-diphenylpyrazole (**1d**), 1-methyl-5-phenylpyrazole (**2a**), and 1-methyl-3-phenylpyrazole (**3a**), were prepared as described in the literature [20,21].

Preparation of bases

General procedure. To a freshly prepared slurry of sodium methoxide (0.085 mol) were added in one portion the corresponding acetophenone (0.085 mol) and ethyl formate (0.128 mol) in 50 ml of toluene. The compact slurry which formed was stirred for 4 h and then filtered. The resultant solid was washed with hot toluene and then with hexane, air dried, and added to 50 ml of methanol. A solution of hydrazine dihydrochloride (or methylhydrazine) (0.085 mol) in 50 ml of

* Reference number with asterisk indicates a note in the list of references.

Table 3

^{1}H-NMR Spectra of bases and Pd^{II} cyclometallated acetate and acetylacetonate complexes [a,b]

Compound	H-2	H-3	H-4	H-5	Pz-4	Pz-5	N-CH_3	Other [c]
3a	7.81	7.30	7.30	7.30	6.52	7.30	3.93	
7a	6.85 (−0.96)	6.85 (−0.45)	6.85 (−0.45)	6.85 (−0.45)	5.92 (−0.60)	6.60 (−0.70)	3.20 (−0.73)	2.15
9a	7.23 (−0.58)	7.05 (−0.25)	7.05 (−0.25)	7.50 (0.20)	6.39 (−0.13)	7.30 (0.00)	4.13 (0.20)	1.99, 2.11, 5.41
3b [d]	7.33		6.84	7.33	6.51	7.36	3.95	
7b [d]	6.51 (−0.82)		6.47 (−0.37)	6.80 (−0.53)	5.95 (−0.56)	6.68 (−0.68)	3.22 (−0.73)	2.16
9b [d]	6.82 (−0.51)		6.67 (−0.17)	7.36 (−0.03)	6.33 (−0.18)	7.23 (−0.13)	4.06 (0.11)	2.02, 2.06, 5.37
3c		7.67	7.18	7.35	6.74	7.41	3.97	
7c		6.93 (−0.74)	6.67 (−0.51)	7.13 (−0.22)	6.79 (0.05)	6.71 (−0.70)	3.26 (−0.71)	2.16
9c		7.25 (−0.42)	6.80 (−0.38)	7.52 (0.17)	7.30 (0.56)	7.00 (−0.41)	4.12 (0.15)	1.98, 2.09, 5.40
3d	7.83	7.40	7.40	7.40	6.59		3.88	
7d	6.80 (−1.03)	6.80 (−0.60)	6.80 (−0.60)	6.80 (−0.60)	5.98 (−0.61)		3.15 (−0.73)	2.11
9d	7.24 (−0.59)	7.06 (−0.34)	7.06 (−0.34)	7.53 (0.13)	6.45 (−0.14)		4.08 (0.20)	2.05, 2.11, 5.41

[a] 200 MHz, solvent $CDCl_3$. Values in parentheses correspond to $\Delta\delta = \delta_{complex} - \delta_{ligand}$. [b] Chloro-bridged complexes were not soluble in $CDCl_3$ and are not included. [c] Acetate or acetylacetonate signals. [d] OCH_3 signals: (**3b**) 3.85; (**7b**) 3.75 (−0.10); (**9b**) 3.79 (−0.06).

water was added, and the mixture was heated under reflux for 12 h. The product was extracted with dichloromethane. Solvent was evaporated and the residue was purified by column chromatography.

*3(5)-(3-Methoxyphenyl)pyrazole (**1b**).* Obtained from 3-methoxyacetophenone. Elution with dichlorometane-methanol 95:5 gave **1b**, yield 75%, m.p. 84–85°C. IR (Nujol): 3.250, 850, 805, and 692 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.55 (d, J 2.2 Hz, 1H, Pz-5), 7.32–7.20 (m, 3H, H-1, H-3 and H-6), 6.83 (ddd, J 7.0 Hz, J 1.5 Hz, J 1.8 Hz, 1H, H-5), 6.55 (d, J 2.2 Hz, 1H, Pz-4). ^{13}C-NMR ($CDCl_3$): δ 159.8 (C-4), 149.3 (Pz-3), 133.4 (C-2), 133.0 (Pz-5), 129.7 (C-6), 118.4 (C-1), 113.7 (C-5), 11.0 (C-3), 102.6 (Pz-4), 55.0 (OCH_3).

*3-(3-Methoxyphenyl)-1-methylpyrazole (**3b**) and 5-(3-methoxyphenyl)-1-methylpyrazole (**2b**).* Reaction of 3-methoxyacetophenone with ethyl formate and methylhydrazine as above gave a 60:40 mixture of **3b** and **2b**. The isomers were partially separated by flash chromatography. Elution with dichloromethane–ether 7:1 gave first **3b**, yield 47%, oil. IR (neat): 1521, 871, 759, and 689 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.40–7.28 (m, 4H, Pz-5, H-1, H-3, H-6), 6.90–6.80 (m, 1H, H-5), 6.51 (d, J 2.4 Hz, 1H, Pz-4), 3.95 (s, 3H, NCH_3), 3.85 (s, 3H, OCH_3). ^{13}C-NMR ($CDCl_3$): δ 159.7 (C-4), 151.2 (Pz-3), 134.8 (C-2), 131.2 (Pz-5), 129.4 (C-6), 117.9 (C-1), 113.4 (C-5), 110.4 (C-3), 102.8 (Pz-4), 55.1 (OCH_3), 38.8 (NCH_3). Further elution afforded **2b**, yield 31%, oil. IR (neat): 1520, 781, 760, and 689 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.51 (d, J 1.8 Hz, 1 H, Pz-3), 7.37 (dd, J 7.7 Hz, J 7.4 Hz, 1H, H-6), 7.01 (dd, J 1.0 Hz, J 1.4 Hz, 1H, H-3), 7.00–6.90 (m, 2H, H-5, H-1), 6.30 (d, J 1.8 Hz, 1H, Pz-4), 3.89 and 3.84 (s, 6H, OCH_3, NCH_3). ^{13}C-NMR ($CDCl_3$): δ 159.2 (C-4), 142.9 (Pz-5), 138.0 (Pz-3), 131.6 (C-2), 129.3 (C-6), 120.7 (C-1), 114.7 and 113.4 (C-5 and C-3), 105.6 (Pz-4), 54.8 (OCH_3), 37.1 (NCH_3).

*3-(2-Bromophenyl)-1-methylpyrazole (**3c**) and 5-(2-bromophenyl)-1-methylpyrazole (**2c**).* These isomers were synthesized in a 60:40 ratio (51% yield) by methylation of 3(5)-(2-bromophenyl)pyrazole (**1c**) with methyl iodide (potassium hydroxide, acetonitrile). The isomers were partially separated by chromatography. Elution with dichloromethane-hexane 4:1 gave first **3c**, oil. ^{1}H-NMR ($CDCl_3$): δ 7.71 (dd, J 1.8 Hz, J 7.8 Hz, 1H, H-1), 7.66 (dd, J 1.7 Hz, J 8.5 Hz, 1H, H-4), 7.41 (d, J 2.2 Hz, 1H, Pz-5), 7.35 (ddd, J 1.7 Hz, J 7.8 Hz, J 7.8 Hz, 1H, H-6), 7.18 (ddd, J 1.8 Hz, J 7.8 Hz, J 8.5 Hz, 1H, H-5), 6.75 (d, J 2.2 Hz, 1H, Pz-4), 3.87 (s, 3H, NCH_3). ^{13}C-NMR ($CDCl_3$): δ 149.8 (Pz-3), 134.1 (C-2), 133.0 (C-4), 130.6 (C-1) 129.9 (Pz-5) 128.5 (C-5), 126.9 (C-6), 121.4 (C-3), 106.4 (Pz-4), 38.4 (NCH_3). Further elution afforded **2c**, oil. ^{1}H-NMR ($CDCl_3$): δ 7.63 (m, 1H, H-1), 7.48 (d, J 2.0 Hz, 1H, Pz-3), 7.37–7.19 (m, 3H, H-4, H-5, H-6), 6.20 (d, J 2.0 Hz, 1H, Pz-4), 3.65 (s, 3H, NCH_3). ^{13}C-NMR ($CDCl_3$): δ 141.6 (Pz-5), 138.0 (Pz-3), 132.7 (C-1), 131.8 (C-2), 131.8 (C-4), 130.4 (C-5), 127.1 (C-6), 124.1 (C-3), 106.6 (Pz-4), 36.7 (NCH_3).

*3,5-Diphenyl-1-methylpyrazol (**2d**).* This compound was synthesized by methylation of 3,5-diphenylpyrazole (**1d**) with methyl iodide. The product was purified by flash chromatography. Eluent dichloromethane–methanol 97:3, yield 72%, m.p. 47–49°C. IR (Nujol): 1550, 725, and 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.84 (dd, J 8.1 Hz, J 1.6 Hz, 2H, H-2, H-6), 7.43–7.27 (m, 8H, H-2′, H-6′, H-3, H-3′, H-4, H-4′, H-5, H-5′), 6.58 (s, 1H, Pz-4), 3.88 (s, 3H, NCH_3). ^{13}C-NMR ($CDCl_3$): δ 150.3 (Pz-3), 144.9 (Pz-5), 133.3 (C-1), 130.5 (C-1′), 128.6 and 128.5 (C-2′, C-3, C-3′), 128.4 (C-4′), 127.5 (C-4), 125.4 (C-2), 103.1 (Pz-4), 37.4 (NCH_3).

Preparation of addition complexes

A. General method for complexes ***4a–d, 5a–c.*** To a solution of palladium(II), chloride or sodium tetrachloropalladate (0.5 mmol) in 5 ml of methanol was added 1 mmol of the corresponding arylpyrazole. The mixture was stirred for 12 h at room temperature and the precipitate was filtered and washed with cold methanol. The yellow solid was recrystallized from dichloromethane–hexane. Yields were *ca.* 80%.

trans-*Dichloro[bis(5-phenylpyrazole)]palladium(II)* ***(4a).*** M.p. 208–210°C. IR (Nujol): 3285, 1500, and 361 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 144.7 (Pz-5), 142.9 (Pz-3), 129.7 (C-4), 129.0 (C-3, C-5), 127.3 (C-1), 125.7 (C-2, C-4), 103.7 (Pz-4). Anal. Found: C, 44.87; H, 3.21; N, 11.34. $C_{18}H_{16}Cl_2N_4Pd.H_2O$ calc.: C, 44.68; H, 3.31; N, 11.58%.

trans-*Dichloro{bis[5-(3-methoxyphenyl)pyrazole]}palladium(II)* ***(4b).*** M.p. 190–193°C IR (Nujol): 3200, 1500, and 354 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 160.1 (C-4), 144.8 (Pz-5), 143.1 (Pz-3), 130.2 (C-6), 128.4 (C-2), 118.2 (C-1), 115.7 (C-5), 111.0 (C-3), 103.7 (Pz-4), 55.5 (OCH_3). Anal. Found: C, 45.62; H, 3.60; N, 10.95. $C_{20}H_{20}Cl_2N_4O_2Pd$ calc.: C, 45.68; H, 3.80; N, 10.66%.

trans-*Dichloro{bis[5-(2-bromophenyl)pyrazole]}palladium(II)* ***(4c).*** M.p. 213–215°C IR (Nujol): 3100, 1530, 749, and 369 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 143.6, (Pz-5), 142.4 (Pz-3), 134.3 (C-4), 131.1 (C-5), 130.8 (C-1), 128.5 (C-2), 129.0 (C-6), 120.0 (C-3), 107.2 (Pz-4). Found: C, 34.38; H, 2.05; N, 8.78. $C_{18}H_{14}Br_2Cl_2N_4Pd$ calc.: C, 34.66; H, 2.25; N, 8.99%.

trans-*Dichloro[bis(3,5-diphenylpyrazole)]palladium(II)* ***(4d).*** M.p. 278–283°C (dec). IR (Nujol): 3198, 1566, and 360 cm^{-1}. Anal. Found: C, 57.92; H, 3.79; N, 8.90. $C_{30}H_{24}Cl_2N_4Pd$ calc.: C, 58.30; H, 3.88; N, 9.07%.

trans-*Dichloro[bis(1-methyl-5-phenylpyrazole)] palladium(II)* ***(5a).*** M.p. 215°C (dec). IR (Nujol): 1530 and 357 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 147.5 (Pz-5), 142.1 (Pz-3), 129.6 (C-1), 128.9 (C-2, C-6, C-3, C-5, C-4), 108.0 (Pz-4), 39.1 (NCH_3). Anal. Found: C, 48.27; H, 3.97; N, 11.24. $C_{20}H_{20}Cl_2N_4Pd$ calc.: C, 48.64; H, 4.05; N, 11.35%.

trans-*Dichloro{bis[5-(3-methoxyphenyl)-1-methylpyrazole]}palladium(II)* ***(5b).*** M.p. 252–255°C. IR (Nujol): 1520 and 362 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 159.8 (C-4), 147.4 (Pz-5), 142.0 (Pz-3), 130.0 (C-6), 121.3 (C-1), 115.3 (C-5), 114.6 (C-3), 108.0 (Pz-4), 55.4 (OCH_3), 39.1 (NCH_3). Anal. Found: C, 46.20; H, 3.98; N, 9.54. $C_{22}H_{24}Cl_2N_4O_2Pd.H_2O$ calc.: C, 46.20; H, 4.20; N, 9.80%.

trans-*Dichloro{bis[5-(2-bromophenyl)-1-methylpyrazole]}palladium(II)* ***(5c).*** M.p. 231–232°C. IR (Nujol): 1505, 755, and 356 cm^{-1}. ^{13}C-NMR ($CDCl_3$): 145.7 (Pz-5), 141.8 (Pz-3), 133.2 (C-1), 131.9 (C-4), 131.5 (C-5), 130.2 (C-2), 127.6 (C-6), 124.2 (C-3), 108.8 (Pz-4), 38.7 (NCH_3). Anal. Found: C, 36.78; H, 2.53; N, 8.65. $C_{20}H_{18}Br_2Cl_2N_4Pd$ calc.: C, 36.85; H, 2.76; N, 8.60%.

B. General method for preparation of cis *complexes.* To a suspension of palladium(II) chloride (0.5 mmol) in methanol (5 ml) was added 1 mmol of the arylpyrazole. The mixture was stirred for 12 h at room temperature and the solid was filtered and washed with cold methanol. The yellow-orange solid was recrystallized from dichloromethane-hexane, yielding *ca.* 75% of pure *cis*-isomers.

C. General method for preparation of trans *complexes.* To a solution of sodium tetrachloropalladate (0.5 mmol) in methanol (5 ml) was added 1 mmol of the arylpyrazole. The mixture was heated under reflux with stirring for 12 h. The

precipitate was filtered and washed with methanol. The yellow solid was recrystallized from dichloromethane. Yields were *ca.* 70%.

cis-*Dichloro[bis(1-methyl-3-phenylpyrazole)]palladium(II)* (cis-***6a***). M.p. 228–230°C (dec). IR (Nujol): 1500, 343, and 322 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 154.3 (Pz-3), 134.0 (C-1), 132.0 (Pz-5), 129.5, 129.3 (C-2, C-6, C-3, C-5, C-4), 106.8 (Pz-4), 39.6 (N-CH_3). Anal. Found: C, 46.90 H 4.33; N, 10.54. $C_{20}H_{20}Cl_2N_4Pd.H_2O$ calc.: C, 46.94; H, 4.33; N, 10.95%.

trans-*Dichloro[bis(1-methyl-3-phenylpyrazole)]palladium(II)* (trans-***6a***). M.p. 225°C (dec). IR (Nujol): 1510 and 355 cm^{-1}. Anal. Found: C, 47.30; H, 4.31; N, 10.38. $C_{20}H_{20}Cl_2N_4Pd.H_2O$ calc.: C, 46.94; H, 4.33; N, 10.95%.

cis-*Dichloro{bis[3-(3-methoxyphenyl)-1-methylpyrazole]}palladium(II)* (cis-***6b***). M.p. 260–262°C. IR (Nujol): 1505, 345, and 320 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 160.0 (C-4), 154.3 (Pz-3), 134.8 (C-2), 134.4 (Pz-5), 129.5 (C-6), 121.8 (C-1), 116.2 (C-5), 114.1 (C-3), 156.7 (Pz-4), 56.0 (OCH_3), 39.5 (NCH_3). Anal. Found: C, 46.06; H, 4.19; N, 9.70. $C_{22}H_{24}Cl_2N_4O_2Pd.H_2O$ calc.: C, 46.20; H, 4.55; N, 9.80%.

trans-*Dichloro{bis[3-(3-methoxyphenyl)-1-methylpyrazole]}palladium(II)* (trans-***6b***). M.p. 243–250°C (dec). IR (Nujol): 1500 and 355 cm^{-1}. Anal. Found: C, 47.36; H, 4.07; N, 9.85. $C_{22}H_{24}Cl_2N_4O_2Pd.H_2O$ calc.: C, 46.20; H, 4.55; N, 9.80%.

cis-*Dichloro{bis[3-(2-bromophenyl)-1-methylpyrazole]}palladium(II)* (cis-***6c***). M.p. 288°C (dec). IR (Nujol): 1508, 758, 349, and 335 cm^{-1}. Anal. Found: C, 36.74; H, 2.50; N, 8.64. $C_{20}H_{18}Br_2Cl_2N_4Pd$ calc.: C, 36.85; H, 2.76; N, 8.60%.

trans-*dichloro{bis[3-(2-bromophenyl)-1-methylpyrazole]}palladium(II)* (trans-***6c***). M.p. 293°C (dec). IR (Nujol): 1508, 760 cm^{-1}, and 347 cm^{-1}. Anal. Found: C, 36.06; H, 2.50; N, 8.36. $C_{20}H_{18}Br_2Cl_2N_4Pd$ calc.: C, 36.85; H, 2.76; N, 8.60%.

cis-*Dichloro[bis(3,5-diphenyl-1-methylpyrazole)]palladium(II)* (cis-***6d***). M.p. 228–230°C (dec). IR (Nujol): 1550, 764, 698, 342, and 336 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 153.5 (Pz-3), 147.6 (Pz-5), 134.2 (C-1), 132.2 (C-1'), 129.6 and 129.5 (C-2, C-6, C-3, C-5, C-4), 129.2, 128.8 and 128.6 (C-2', C-6', C-3', C-5', C-4'), 107.1 (Pz-4), 38.1 (NCH_3). Anal. Found: C, 59,23; H, 4.10; N, 8.50. $C_{32}H_{28}Cl_2N_4Pd$ calc.: C, 59.49; H, 4.34; N, 8.67%.

trans-*Dichloro[bis(3,5-diphenyl-1-methylpyrazole)]palladium(II)* (trans-***6d***). M.p. 290–293°C. IR (Nujol): 1550, 710, 695, and 353 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 153.8 (Pz-3), 148.2 (Pz-5), 137.4 (C-1), 132.3 (C-1'), 129.5 and 129.0 (C-2, C-6, C-3, C-5, C-4), 128.9, 128.6 and 128.4 (C-2', C-6', C-3', C5', C-4'), 107.3 (Pz-4), 38.8 (NCH_3). Anal. Found: C, 59.56; H, 4.21; N, 8.46. C, 59.49; H, 4.34; N, 8.67%.

Oxalate{bis[3-(2-bromophenyl)-1-methylpyrazole]}palladium(II). Potassium oxalate (70 mg) was added to a suspension of palladium(II) chloride (0.1 mmol) in 8 ml of water, and the mixture was stirred for 12 h. To the clear yellow solution was added base **3c** (0.2 mmol) and the mixture was stirred again for 12 h. The solid product was filtered, washed with water, ethanol and diethylether and dried *in vacuo* at room temperature. The complex was recrystallized from dichloromethane/hexane. Yield 60%. M.p. 270°C (dec). IR (Nujol): 1510, 1710, 1680, 1375, 1240, 810, and 750 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.79 (d, *J* 9.0 Hz, 2H, H-4), 7.68–7.41 (m, 6H, H-1, H-5, H-6), 7.30 (d, *J* 2.6 Hz, 2H, Pz-5), 6.30 (d, *J* 2.6 Hz, 2H, Pz-4). Anal. Found: C, 38.23; H, 2.39; N, 8.09, $C_{22}H_{18}Br_2N_4O_2Pd.H_2O$ calc.: C, 38.47; H, 2.91; N, 8.16%.

Preparation of cyclometallated complexes

A. General method for acetate-bridged dimers. A solution of equimolar quantities of palladium(II) acetate and the base in dry acetic acid was heated at 100°C for 3 h. After removal of most of the acetic acid under vacuum, the residue was dissolved in dichloromethane and washed with 10% aqueous sodium bicarbonate. The mixture was filtered through Celite, and the organic layer was dried over $MgSO_4$ and evaporated to give the crude complex which was recrystallized from dichloromethane-hexane. Yield was *ca.* 75%.

*Di-μ-acetate-bis[(1-methylpyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (7a).* M.p. 190°C (dec). IR (Nujol): 1590, 1420, and 750 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 181.1 (CO), 157.7 (Pz-3), 143.8 (C-2), 137.5 (C-1), 132.0 (Pz-5), 130.6 (C-3), 124.8 (C-4(5)), 123.6 (C-5(4)), 121.2 (C-6), 99.6 (Pz-4), 37.3 (NCH_3), 24.6 ($COCH_3$). MS *m/z*: 322 ($M^+/2$), 263, 158. Anal. Found: C, 44.90; H, 4.00; N, 8.75. $C_{24}H_{24}N_4O_2Pd_2$ calc.: C, 44.66; H, 3.72; N, 8.68%.

*Di-μ-acetate-bis[4-methoxy(1-methylpyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (7b).* M.p. 186–191°C (dec). IR (Nujol): 1590, 1500, 1430, 860, and 830 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 181.1 (CO), 157.4 (Pz-3), 156.8 (C-5), 137.8 (C-1), 133.4 (C-2), 131.8 (Pz-5), 131.0 (C-3), 110.1 (C-4), 107.6 (C-6), 99.7 (Pz-4), 55.3 (OCH_3), 37.5 (NCH_3), 24.5 ($COCH_3$). MS *m/z*: 352 ($M^+/2$); 293; 188. Anal. Found: C, 44.22; H, 3.57; N, 7.84. $C_{26}H_{28}N_4O_6Pd_2$ calc.: C, 44.26; H, 3.97; N, 7.94%.

*Di-μ-acetate-bis[3-bromo(1-methylpyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (7c).* M.p. 228°C (dec). ^{13}C-NMR ($CDCl_3$): δ 181.4 (CO), 156.8 (Pz-3), 147.1 (C-2), 136.0 (C-1), 131.4 (Pz-5), 129.7 (C-5), 129.0 (C-3), 125.5 (C-4), 116.0 (C-6), 105.1 (Pz-4), 37.9 (NCH_3), 24.6 ($COCH_3$). MS *m/z*: 804 (M^+); 402; 359; 343; 156. Anal. Found: C, 35.45; H, 2.54; N, 6.54. $C_{24}H_{22}Br_2N_4O_4Pd_2$ calc.: C, 35.88; H, 2.74; N, 6.98%.

*Di-μ-acetate-bis[(1-methyl-5-phenyl-pyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (7d).* M.p. 230–240°C (dec). IR (Nujol): 1568, 1510, and 1420 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 181.4 (CO), 157.1 (Pz-3), 144.8 (Pz-5), 144.6 (C-2), 137.8 (C-1), 131.1 (C-3), 129.0, 128.8 and 128.4 (C-1′ to C-6′), 125.2 (C-4(5)), 124.1 (C-5(4)), 121.4 (C-6), 99.6 (Pz-4), 36.3 (NCH_3), 24.7 ($COCH_3$). MS *m/z*: 398 ($M^+/2$); 339; 234. Anal. Found: C, 54.25; H, 3.93; N, 7.18. $C_{36}H_{32}N_4O_4Pd_2$ calc.: C, 54.22; H, 4.02; N, 7.03%.

B. General method for chloro-bridged dimers. To a solution of the acetate-bridged complex (1 mmol) in 5 ml of acetone was added lithium chloride (3 mmol) in 1 ml of water. The mixture was stirred at room temperature for 12 h. The solid was filtered and washed with acetone-water 1:1. Yields were *ca.* 85%.

*Di-μ-chloro-bis[(1-methylpyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (8a).* M.p. 250°C. IR (Nujol): 1510, 745, 360, and 350 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.80 (br s, 2H, Pz-5), 7.68 (br s, 2H, H-3), 7.24 (d, *J* 7.1 Hz, 2H, H-6), 6.98 (dd, *J* 7.1 Hz, 2H, H-5), 6.80 (dd, *J* 7.1 Hz, 2H, H-4), 6.62 (br s, 2H, Pz-4), 4.00 (s, 6H, NCH_3). Anal. Found: C, 38.07; H, 3.43; N, 8.23: $C_{20}H_{18}Cl_2N_4Pd_2.H_2O$ calc.: C, 38.97; H, 3.24, N, 9.09%.

*Di-μ-chloro-bis[4-methoxy(1-methylpyrazol-3-yl)phenyl-*C,N*]dipalladium(II) (8b).* M.p. 252–255°C (dec). IR (Nujol) 1520, 865, 800, 351, and 277 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.83 (br s, 2H, Pz-5), 7.55 (br s, 2H, H-3), 7.03 (br s, 2H, H-6), 6.70 (br s, 2H, Pz-4), 6.48 (br s, 2H, H-4), 4.00 (br s, 6H, NCH_3), 3.75 (s, 6H, OCH_3). Anal. Found: C, 39.76; 3.24; N, 8.25. $C_{22}H_{22}Cl_2N_4O_2Pd_2$ calc.: C, 40.13; H, 3.15; N, 8.02%.

Di-μ-chloro-bis[3-bromo(1-methylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(8c)***. M.p. 246°C (dec). ^{1}H-NMR (DMSO-d_6): δ 7.94 (d, *J* 2.5 Hz, 2H, Pz-5), 7.71 (d, *J* 7.1 Hz, 2H, H-3), 7.23 (d, *J* 7.7 Hz, 2H, H-5), 7.05 (d, *J* 2.5 Hz, 2H, Pz-4), 6.70 (dd, *J* 7.7 Hz, *J* 7.1 Hz, 2H, H-4), 3.95 (s, 6H, NCH_3). Anal. Found: C, 32.07; H, 1.96; N, 7.32. $C_{20}H_{16}N_4Br_2Cl_2Pd_2$ calc: C, 31.76; H, 2.12; N, 7.41%.

Di-μ-chloro-bis[(1-methyl-5-phenylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(8d)*** M.p. 246–249°C (dec). IR (Nujol): 1510, 350, and 293 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.70 (br s, 2H, H-3), 7.65–7.50 (m, 10H, H-2′ to H-6′), 7.32 (d, *J* 7.0 Hz, 2H, H-6), 7.00 (dd, *J* 7.0 Hz, *J* 7.0 Hz, 2H, H-5), 6.82 (dd, *J* 7.0 Hz, *J* 7.0 Hz, 2H, H-4), 6.82 (s, 2H, Pz-4), 3.90 (s, 6H, NCH_3). Anal. Found: C, 49.96; H, 3.63; N, 7.23. $C_{32}H_{26}Cl_2N_4Pd_2.H_2O$ calc.: C, 50.01; H, 3.64; N, 7.29%.

Di-μ-bromo-bis[(1-methylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(10)***. To a suspension of [Pd(dba)$_2$] (0.13 mmol) in benzene (20 ml) was added pyrazole **3c** (0.12 mmol) dissolved in benzene (5 ml). The mixture was stirred and heated at 60°C under argon until the reddish-purple colour changed to green. The precipitated product was filtered and washed with hot benzene to give complex **10** (yield 91%). M.p. 240°C (dec). ^{1}H-NMR (DMSO-d_6): δ 7.84 (d, *J* 2.8 Hz, 2H, Pz-5), 7.81 (d, *J* 7.3 Hz, 2H, H-3), 6.95 (dd, *J* 7.3 Hz, *J* 7.3 Hz, 2H, H-5), 6.72 (dd, *J* 7.3 Hz, *J* 7.3 Hz, 2H, H-4), 6.66 (d, *J* 2.8 Hz, 2H, Pz-4), 3.92 (s, 6H, NCH_3). Anal. Found: C, 33.83; H, 2.63; N, 7.65. $C_{20}H_{18}Br_2N_4Pd_2.H_2O$ calc.: C, 34.06; H, 2.84; N, 7.95%.

C. General method for acetylacetonate complexes. The chloro-bridged dimer (1 mmol) was added to a methanol solution containing sodium methoxide (3 mmol) and acetylacetone (3 mmol). The resultant mixture was stirred at room temperature for 24 h. The product was filtered and recrystallized from dichloromethane-hexane. Yields were *ca.* 70%.

Acetylacetonato[(1-methylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(9a)***. M.p. 168–170°C. IR (Nujol): 1578, 1516, 1510, and 746 cm^{-1}. Anal. Found: C, 49.43; H, 4.63; N, 7.63. $C_{15}H_{16}N_2O_2Pd$ calc.: C, 49.67; H, 4.41; N, 7.72%.

Acetylacetonato[4-methoxy(1-methylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(9b)***. M.p. 160°C (dec). IR Nujol): 1580, 1510, 1500, 865, and 840 cm^{-1}. MS. *m/z*: 392 (M^+); 349; 293; 187. Anal. Found: C, 48.61; H, 4.26; N, 7.08. $C_{16}H_{18}N_2O_3Pd$ calc.: C, 48.93; H, 4.58; N, 7.13%.

Acetylacetonato[3-bromo(1-methylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(9c)***. M.p. 184–186°C. MS *m/z*: 442 (M^+); 399; 343; 156. Anal. Found: C, 40.47; H, 3.07; N, 6.43. $C_{15}H_{14}Br_2N_2O_2Pd$ calc.: C, 40.79; H, 3.40; N, 6.38%.

Acetylacetonato[(1-methyl-5-phenylpyrazol-3-yl)phenyl-C,N]dipalladium(II) ***(9d)***. M.p. 212–214°C. IR (Nujol) 1582, 1530, 752, 730, and 701 cm^{-1}. Anal. Found: C, 56.80; H, 4.33; N, 6.53. $C_{21}H_{20}N_2O_2Pd$ calc.: C, 57.48; H, 4.56; N, 6.38%.

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