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5-Methylquinoxaline as a versatile mono-, bi- and tridentate ligand in Palladium(II) chemistry. Crystal structures of *trans*-[Pd(OAc)$_2$(*N*1-C$_8$H$_5$N$_2$Me-5)$_2$] and [Pd(OAc)(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(PPh$_3$)]

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Abstract

To study the potential coordination versatility of 5-methylquinoxaline, the preparation of complexes which contain it as a mono-, bi- or tridentate ligand was carried out. On reaction with [Pd(OAc)$_2$]$_3$ it coordinates to the metal through its less sterically blocked nitrogen atom (N(1), distal to the Me group) to give *trans*-[Pd(OAc)$_2$(*N*1-C$_8$H$_5$N$_2$Me-5)$_2$] (**1**). Reflux of **1**, or a mixture of [Pd(OAc)$_2$]$_3$ and 5-methylquinoxaline, in glacial acetic acid gave the cyclometallated acetate-bridged dimer [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(μ-OAc)]$_2$ (**2**). Complex **2** reacted with: (i) LiCl to give [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(μ-Cl)]$_2$ (**3**); (ii) PPh$_3$ to give [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(OAc)(PPh$_3$)] (**4**); (iii) PR$_3$ and LiCl to give [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)Cl(PR$_3$)] [R = Ph (**5**), Me (**6**), Et (**7**)]; (iv) Tl(acac) to give [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(*O*,*O*-acac)] (**8**); and (v) 2,2′-bipyridine (bpy)–NaClO$_4$·H$_2$O to give [Pd(*C*,*N*4-CH$_2$C$_8$H$_5$N$_2$-5)(bpy)]ClO$_4$ (**9**). Complex **5** reacted with [PdCl$_2$(NCPh)$_2$] in a 2:1 molar ratio to form the *C*,*N*4,*N*1-coordinated tripalladium derivative [PdCl$_2${PdCl(*C*,*N*4,*N*1-CH$_2$C$_8$H$_5$N$_2$-5)(PPh$_3$)}$_2$] (**10**). By contrast, when this reaction was carried out with an excess or equimolecular amount of PdCl$_2$(NCPh)$_2$] compound **3** was obtained together with [PdCl(μ-Cl)(PPh$_3$)]$_2$. We present evidence for formation of novel multimetallic species of the type [Pd(*C*,*N*4,*N*1-CH$_2$C$_8$H$_5$N$_2$-5)(PR$_3$)]$_n$X$_n$ by reaction of **5** or **6** with TlOTf (OTf = O$_3$SCF$_3$), AgClO$_4$ or TlClO$_4$. The crystal structures of **1** and **4**·2CHCl$_3$ were determined by X-ray diffraction studies. They conclusively prove that Pd is coordinated to N(1) in **1** and to N(4) in **4**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclometallation; Methylquinoxaline; Palladium; X-ray diffraction

1. Introduction

The chemistry of organometallic polymers in which the metals are connected by π-conjugated molecular frameworks has developed markedly during the last years as a consequence of their potential applications [1–4]. In this respect, there has been some interest in the use of N-containing bi- and triheteroaromatic compounds to form polymeric structures in which these ligands link between the metal atoms through N–metal bonds. For example, there have been described Cu, Ag, Ru or Rh containing polymers of quinoxaline- [5–7] or phenazine-based [8–11] ligands. However, while many N-coordinated derivatives containing this type of heterocycle are known, their organometallic chemistry has not been investigated in depth. The aim of our work is the synthesis of multimetallic complexes containing C–metal bonds as well as N–metal bonds, and the use of the new species as building blocks for the formation of chains and polymers. For this reason, we have decided to explore the coordination properties of 5-

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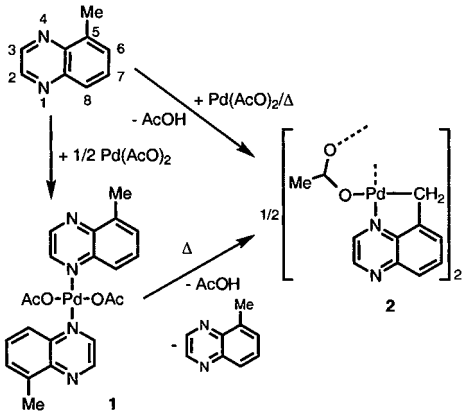
methylquinoxaline, which can act as a mono- or bidentate *N*-donor, and also, via deprotonation of the methyl substituent, as a *C*,*N*4-chelating ligand. It is, therefore, a potentially versatile ligand.

There have been described Pd(II) and Pt(II) bis-cyclometallated derivatives of 2,3-diphenylquinoxaline, 2,3-diphenylpyrazine [12], and evidence has been given of polymers containing 2-(2′-pyridyl)quinoxaline [13]. Although, there exists a wide number of complexes containing the mono-nitrogen analogue 8-methylquinoline [14–22], to our knowledge, there are no metal derivatives of 5-methylquinoxaline. In this paper, we present its reactivity towards Pd(II), and describe complexes which contain it as a mono-, bi- or tridentate ligand. Of particular interest are the cyclometallation product of 5-methylquinoxaline **2** and its isolated precursor, the coordination complex **1**. Usually, the donor atom bonded in the precursor (for example, E) helps the cyclometallation process by bringing together the metal and carbon atoms. As a consequence of this, E usually remains bonded to the metal after cyclometallation. In addition, the carbon atom involved in the cyclometallated complex is that which is properly placed with respect to E in the precursor: (i) to allow approach of the metal to the C–H bond to be activated; and (ii) to result in a five- or six-membered ring metalacycle [23,24]. Neither of these conditions are met in the process we describe: the nitrogen atom coordinated to palladium in complex **1** (N(1)) is different from that in complex **2** (N(4)) and N(1) is not properly placed to assist the C–H activation.

2. Results and discussion

To facilitate discussion of the coordination chemistry of the ambidentate ligand 5-methylquinoxaline, we will refer to the nitrogen atoms using the numbering scheme adopted for this heterocycle (see Scheme 1), i.e. N(1) for the nitrogen atom most distant to the methyl substituent and N(4) for the closest one.



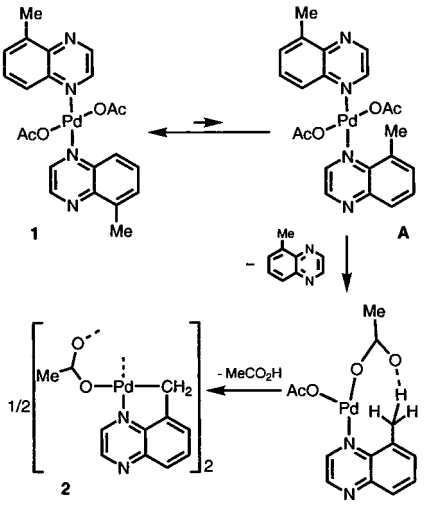
Scheme 1.

2.1. Synthesis of mono- and dinuclear complexes

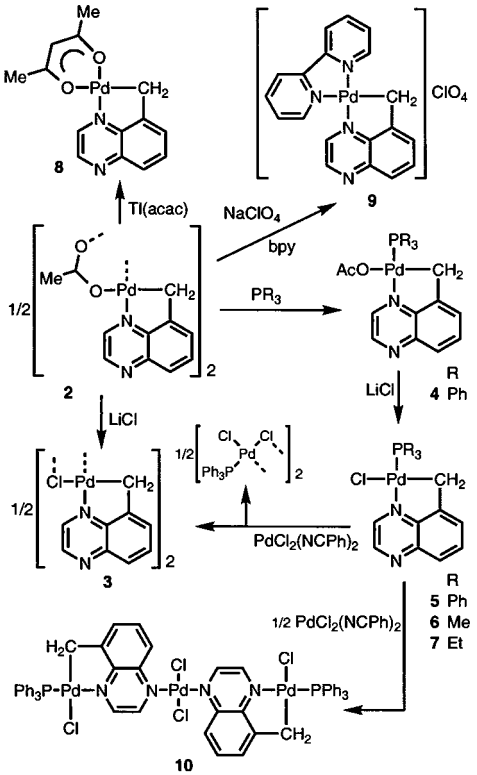
5-Methylquinoxaline coordinates readily to palladium through N(1) which is the less sterically blocked nitrogen atom. Thus, reaction of six equivalents of the free ligand with $[Pd(OAc)_2]_3$ in acetone at room temperature gives complex *trans*-$[Pd(OAc)_2(N1\text{-}C_8H_5N_2Me\text{-}5)_2]$ (**1**) in quantitative yield (Scheme 1).

The reaction of 5-methylquinoxaline with $[Pd(OAc)_2]_3$ in acetone (3:1 or 3:2, 24 h, room temperature) gave no cyclometallated species (as shown by ^{1}H-NMR spectroscopy). Instead, an intractable mixture of compounds was obtained, in which complex **1** could be identified as one of the components. This behavior contrasts with that of 8-methylquinoline which yields the analogous cyclometallated compound, $[Pd(\mu\text{-}OAc)_2(C,N4\text{-}CH_2C_9H_6N\text{-}8)]_2$, by smooth reaction with palladium acetate in methanol, chloroform or dichloromethane at room temperature [18]. Because of the marked influence of the nature of the solvent on cyclometallation reactions [23], we successfully attempted the same reaction in glacial acetic acid. Thus, by reacting 5-methylquinoxaline and $[Pd(OAc)_2]_3$ in 3:1 molar ratio at reflux for 1 h we obtained the cyclometallated acetate-bridged dimer $[Pd(\mu\text{-}OAc)(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)]_2$ (**2**) (Scheme 1). When the same reaction was carried out at room temperature, a mixture of **1** and unreacted starting materials was obtained (as shown by ^{1}H-NMR spectroscopy). Complex **2** could also be obtained by refluxing a solution of **1** in acetic acid. The direct method is, however, more convenient.

Although the use of acetic acid as the solvent for cyclometallation reactions has been shown to favor cyclometallation of electron-poor aromatic rings [23,25,26], it is difficult to use the same arguments to justify the success in the present case. In our opinion, the influence of N(1) on the methyl group in 5-methylquinoxaline is not responsible for the different behavior of this ligand with respect to 8-methylquinoline. The difference could be in the preference of palladium to coordinate to N(1), less sterically congested than N(4), as shown by the high yield synthesis of **1**. We believe that the ratio between N(4)–Pd- and N(1)–Pd-coordinated species in acetic acid is not null, as it probably is in acetone, and that, once some N(4)–Pd-coordinated complex is formed, palladation of the methyl group could occur as in the case of 8-methylquinoline. In Scheme 2, we suggest a possible reaction pathway which would involve rearrangement of one quinoxaline ligand in **1** to its N(4)-coordinated mode to give complex **A**, followed by dissociation of the remaining N(1)-bound ligand to give a 14-electron intermediate, which would undergo the C–H activation. The necessity of this reactive intermediate as a precursor for cyclopalladation has been previously postulated [18,23,25,27–33]. Formation of **2** requires that the equilibrium between **1** and **A** displaces to the right.



Scheme 2.



Scheme 3.

In general, when species which are possible intermediates prior to cyclometallation, are isolated at low temperature, they are complexes bonded to the ligand through the same atom as in the final cyclopalladated complex [23,24]. The present example, where formation of complex **1** is first observed, is therefore unusual. However, if we accept the reaction pathway depicted in Scheme 2, the required conditions are met by the intermediate **A**.

The reaction of 5-methylquinoxaline and $[Pd(OAc)_2]_3$ in acetonitrile also leads to complex **2** but the reaction is much slower and more complicated than in acetic acid. Although this solvent is, for these reasons, less convenient from a synthetic point of view, the study of this reaction has allowed us to gain some evidence about the intermediate **A** (deduced by ^{1}H-NMR spectroscopy). Thus, when both reagents are refluxed in acetonitrile, the yellow suspension of complex **1**, formed shortly after mixing the reagents, became a brown mixture after 3 h. After removal of Pd metal, the mixture consisted of ca. 60% unreacted starting materials, 5% complex **1**, 25% complex **2**, and 10% of a new species that could be the intermediate **A**. Fractional precipitation did not allow us to resolve the mixture, but confirmed that the ^{1}H-NMR signals assigned to **A** should correspond to a unique species, because their integral ratios remained constant after each precipitation. In addition, its ^{1}H-NMR data suggest that it contains two types of 5-methylquinoxaline ligands (see below). Shorter reaction times (e.g. 1 h) gave mainly compound **1**, while refluxing for longer periods did not improve the yield of complex **2** or **A**, but gave decomposition to a greater extent. Although conclusive evidence as to the structure of **A**, or of its possible conversion into **2**, could not be obtained, the above data allow us to suggest that **A** could be a N(4)–Pd-coordinated intermediate formed prior to cyclometallation.

Substitution of the acetato bridges by chloride was achieved by reacting **2** with excess LiCl in acetone to give compound $[Pd(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)(\mu\text{-}Cl)]_2$ (**3**). In addition, triphenylphosphine splits the acetato bridges in complex **2** to give the monomeric species $[Pd(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)(OAc)(PPh_3)]$ (**4**) quantitatively. Complex **4** could also be obtained in one step by reacting 5-methylquinoxaline and $[Pd(OAc)_2]_3$, followed by addition of PPh_3. Treatment of **4** with LiCl yielded the chloro derivative $[Pd(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)(PPh_3)Cl]$ (**5**). Analogous phosphine complexes $[PdCl(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)(PR_3)]$ [R = Me (**6**), Et (**7**)] were prepared by similar methods (Scheme 3). Splitting of the acetato bridges in dimer **2** or **3** was not achieved by 5-methylquinoxaline (1:2) after 24 h reaction in acetone.

Substitution of the acetato ligands in **2** by acetylacetonate (acac) to give $[Pd(O,O\text{-acac})(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)]$ (**8**) or 2,2′-bipyridine (bpy) to give $[Pd(C,N4\text{-}CH_2C_8H_5N_2\text{-}5)(bpy)]$ (**9**) was achieved by reacting it with Tl(acac) or a 1:1 mixture of bpy and $NaClO_4{\cdot}H_2O$, respectively (Scheme 3).

2.2. Attempts to prepare polynuclear complexes

With the aim of preparing multimetallic derivatives of 5-methylquinoxaline, we made several attempts to

coordinate the two nitrogen atoms of the ligand with varying results. Thus, N(1)-coordination of the quinoxaline ligand in complex [PdCl(*C*,*N*4-$CH_2C_8H_5N_2$-5)(PPh_3)] (**5**) did not take place when this was reacted with excess (1:1.3 or 1:2) or an equimolecular amount of [$PdCl_2(NCPh)_2$] (dichloromethane, room temperature, 3–5 h). Instead, we obtained the poorly soluble chloride-bridged dimer [Pd(μ-Cl)(*C*,*N*4-$CH_2C_8H_5N_2$-5)]$_2$ (**3**) together with *trans*-[PdCl(μ-Cl)(PPh_3)]$_2$ (Scheme 3), as confirmed by spectroscopic data and the X-ray study of single crystals of the latter which grew from the mixture.[4] Although this compound was reported some time ago [34], its X-ray crystal structure has not been described previously. Cyclopalladated complexes analogous to **5** are known to undergo solvolysis in AcOH at 80 °C in the presence of LiCl to afford the corresponding non-palladated ligand and [PdCl(μ-Cl)(PPh_3)]$_2$ [35]. Formation of complex **3** was also detected, by ^{1}H-NMR spectroscopy, when **6**, **7** or **8** were reacted with excess [$PdCl_2(NCPh)_2$] [1:1.3 (**6**), 1:2 (**7**, **8**)].

However, when the reaction between **5** and [$PdCl_2(NCPh)_2$] was carried out in a 2:1 molar ratio, the *bis*-*C*,*N*4,*N*1-coordinated tripalladium derivative [$PdCl_2${PdCl(*C*,*N*4,*N*1-$CH_2C_8H_5N_2$-5)(PPh_3)}$_2$] (**10**) was obtained in quantitative yield (Scheme 3). Although a number of triangular tripalladium complexes with quinoline-based ligands have been described [19], to our knowledge, there are no linear tripalladium derivatives containing heterocyclic ligands. The only fully characterized dipalladated quinoxaline-based ligand reported [12] coordinates two Pd atoms via double cyclometallation.

We did not succeed in the synthesis of mixed-metal Pt(II)–Pd(II) derivatives. For example, complex **5** did not react with [$PtCl_2L_2$] [L = NCPh (2:1)], SMe_2 (2:1) (room temperature, acetone, 16 h) or [$PtCl_2$(COD)] [COD = 1,5-cyclooctadiene (2:1), room temperature, dichloromethane, 22 h].

In order to prepare polymeric species of the type [Pd(*C*,*N*4,*N*1-$CH_2C_8H_5N_2$-5)(PR_3)]$_n$$X_n$, we reacted **6** with $AgClO_4$ in acetone. Immediate precipitation of a pale yellow solid was observed. Upon evaporation of the solvent in vacuum, removal of AgCl formed in the reaction was possible by extracting the residue with DMSO. Filtration and concentration of the extracts gave a yellow solid, whose infrared spectrum in Nujol emulsion showed two bands at ca. 1100 and 620 cm^{-1}, indicating the ionically bonded perchlorate. Also, the Pd–Cl band that appears at 270 cm^{-1} in **6** was not present in the reaction product. The above data, together with the insolubility of the product in a variety of organic solvents such as acetone, chloroform, dichloromethane, toluene or nitromethane, suggests that it consists of multimetallic species of general formula [Pd(*C*,*N*4,*N*1-$CH_2C_8H_5N_2$-5)(PR_3)]$_n$(ClO_4)$_n$. Unfortunately, its poor solubility also prevented further purification and an analytically pure sample was not obtained. The solid was moderately soluble in DMSO and its ^{1}H-NMR spectrum could be obtained, which indicated that *N*(1)-coordination does not persist in solution, since the expected downfield shift for the aromatic hydrogens was not observed (see below). In fact, both its ^{1}H- and ^{31}P-NMR spectra resembled those of the starting complex **6**, therefore suggesting the formation of a monomeric compound of related nature, i.e. a solvento complex [Pd(*C*,*N*4-$C_8H_5N_2CH_2$-5)(DMSO)(PMe_3)](ClO_4). However, after precipitation of the compound from a DMSO solution, no significant amounts of sulfur were found in the elemental analysis, indicating that coordination of DMSO does not occur in the solid material. Other related method of preparation, e.g. reaction of **5** with Tl(CF_3SO_3) or AgX (X = ClO_4, CF_3SO_3) in acetone, gave comparable results.

It has been reported that complexes containing 2-(2′-pyridyl)quinoxaline (L) as a bidentate chelating ligand, [PtX_2L] (X = Cl, Br), undergo thermal decomposition to insoluble polymers ($PtCl_2L_{0.5}$–$PtBr_2L_{0.25}$), where L acts as a tridentate bridging ligand [13]. Vibrational spectroscopic studies have been used to prove the polymeric nature of these compounds. For example while a single sharp band at 965–970 cm^{-1} is present in the IR spectrum of the starting materials, this splits into a triplet when both quinoxaline nitrogens participate in coordination. Although thermogravimetric evidence of formation of analogous Pd polymers was found, they were too unstable to be isolated. In the IR spectra of our complexes, only very weak ligand bands are found in the region 940–980 cm^{-1}, which do not allow clear assignments. However, in one case (the product of the reaction of **5** with $AgClO_4$), a weak but distinct triplet at 950 cm^{-1}, corresponding closely to the above data, was observed in place of a singlet in the starting compound (**5**).

2.3. Structures of complexes

^{1}H- and ^{31}P-NMR data for the isolated complexes are presented in Table 1. In the ^{1}H-NMR spectra, the set of signals corresponding to H6, H7 and H8, consists of one apparent triplet (H7) and two apparent doublets, occurring within the range 6.81–10 ppm. However, when the ligand is bound through N(1) (complexes **1**

[4] X-ray crystallographic data (excluding structure factors) for *trans*-[PdCl(μ-Cl)(PPh_3)]$_2$ have been deposited with the Cambridge Crystallographic Data Centre as a Private Communication, J. Vicente, M.C. Lagunas, E. Bleuel and M. Ramírez de Arellano, CCDC-100877, 1997. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

and **10**), the signal corresponding to H8 (Scheme 1) undergoes a large downfield shift ($\delta = 9.91$–9.43 ppm) with respect to that in the other complexes where N(1) is not coordinated ($\delta < 8$ ppm), as might be expected. Another two doublets, corresponding to H2 and H3, are located in the interval 8.46–9.84 ppm for both N(4)- and N(1)-coordinated complexes and therefore they do not provide additional information about which nitrogen atom binds to the metal.

The resonances assigned to the intermediate compound **A** (see above) are consistent with the presence of two types of 5-methylquinoxaline ligands since two sets of H2, H3 protons are found [9.5 (d, 1H), 8.9 ('t', 2H), and 8.7 (d, 1H) ppm, $^3J(HH) = 2$ Hz]. One of the ligands should coordinate to Pd(II) via N(1), as deduced by the presence of a doublet at 9.3 ppm [$^3J(HH) = 7$ Hz], typical for H8 of N(1)-bound quinoxaline. Other aromatic protons of **A** could not be assigned because they overlap with a multiplet at 7.5–8 ppm due to other products in the mixture.

The values of the $^3J(HH)$ coupling constants, similar for both coordination types, are 2 and 7–8 Hz for $^3J(H2H3)$ and $^3J(H6H7) = {}^3J(H7H8)$, respectively. In tripalladium compound **10** we observe, when compared to the parent complex **5**, the expected downfield shift for H8, together with a less $|\delta H2 - \delta H3|$ value, which is in agreement with both nitrogen atoms in the ligand being bound to palladium.

The ^{1}H- and ^{31}P-NMR spectra of complexes **1**, **4**–**7**, and **10** show only one set of signals, suggesting that only one isomer is obtained. For N(1)-coordinated species **1** and **10**, we expect that the thermodynamically stable *trans* isomers are isolated [36]. This has been confirmed by the crystal structure of complex **1** (see Fig. 1), and by the IR spectrum of **10**, which gives one ν(MCl) stretching band at 360 cm^{-1}, as expected for a *trans*-$PdCl_2$ group [37]. Complex **10** also contains one stretching band due to Pd–Cl *trans* to *C* at 279 cm^{-1}, similar to that found in **5**. We propose an *anti* disposition of the quinoxaline moieties in **10**, by analogy with the structure of **1** (Fig. 1). Attempts to obtain single crystals of complex **10**, suitable for X-ray diffraction studies, were unfruitful.

The CH_2 groups in the phosphine derivatives **4**–**7**, and **10** appear as doublets with $^3J(PH)$ values of 2–4 Hz, which are in agreement with their *cis* position with

Table 1
^{1}H- and ^{31}P-NMR data of complexes **1**–**10** [a]

Complex	^{1}H-NMR				$^{31}P\{^1H\}$-NMR
	H2, H3	H6, H7, H8	CH_2–Me	Other signals	
1	8.93 d, 9.65 d (2 [b])	7.78 d, 8.02 t, 9.91 d (8 [b])	2.83 s	OAc: 1.51 s	
2	8.46 d, 8.77 d (2 [b])	6.81 d, 7.21 t, 7.36 d (7 [b])	2.55 d, 3.60 d (14 [c])	OAc: 2.15 s	
3 [d,e]	9.19 s	7.76 d, 7.87 t, 7.95 d (8 [b])	3.68 s		
4	8.77 m, 8.99 m	7.67 t, 7.89 d (8 [b]) [f]	2.85 d (4 [g])	OAc: 1.66 s; PPh_3: 7.45 m, 7.78 m	33.4 s
5	9.03 m, 9.66 br s	7.36 d, 7.63 t, 7.89 d (8 [b])	2.88 d (3 [g])	PPh_3: 7.45 m, 7.81 mh	33.9 s
6	9.38 br s, 8.97 br s	7.60 d, 7.69 t, 7.88 d (7 [b])	3.15 br s	PMe_3: 1.60 d (11 [h])	−4.9 s
7 [d]	9.01 br s, 9.47 br s	7.63 d, 7.73 't', 7.91 d (7 [b])	3.13 d (2 [g])	PEt_3: 1.25 dt, Me (25 [g]); 1.97 quint, CH_2 (12 [i])	28.9 s
8 [d]	8.88 s	7.65 d, 7.73 t, 7.87 d (8 [b])	3.65 s	acac: 2.01 s, 2.05 s, Me; 5.35 s CH	
9 [d,e]	7.56–8.98 m (includes bipy)	3.76 s			
10	9.52 m, 9.84 m	7.56 d, 7.97 t, 9.43 d (8 [b])	2.86 d (3 [g])	PPh_3: 7.47 m, 7.80 m	33.9 s

[a] Spectra recorded in a Varian Unity 300 in $CDCl_3$ at r.t., unless stated otherwise; δ in ppm rel. to $SiMe_4$ (^{1}H) or H_3PO_4 ($^{31}P\{^1H\}$); *J* in brackets in Hz.
[b] $^3J(HH)$.
[c] $^2J(HH)$.
[d] ^{1}H-NMR recorded in a Bruker AC200.
[e] In DMSO-d_6.
[f] One doublet hidden by PPh_3 multiplet at 7.45 ppm.
[g] $^3J(PH)$.
[h] $^2J(PH)$.
[i] $^2J(PH) = {}^3J(HH)$.

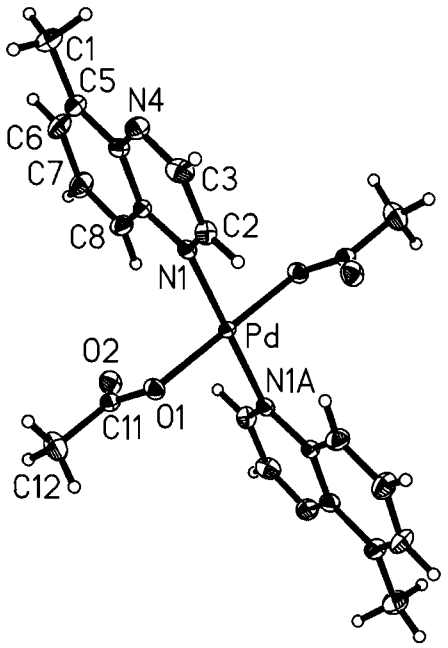


Fig. 1. Ellipsoid plot of **1** with the labelling scheme (50% probability level).

Table 2
Crystal data for compounds **1** and **4**·2CHCl$_3$

	1	**4**·2CHCl$_3$
Empirical formula	$C_{22}H_{22}N_4O_4Pd$	$C_{31}H_{27}Cl_6N_2O_2PPd$
M	512.84	809.62
Space group	$P21/n$	$P\bar{1}$
a (Å)	10.695(2)	10.0978(12)
b (Å)	7.9424(12)	11.2837(12)
c (Å)	12.689(2)	15.681(2)
α (°)	90.00	73.914(10)
β (°)	101.048(7)	83.932(8)
γ (°)	90.00	74.800(8)
V (Å^3)	1057.8(3)	1655.6(3)
Z	2	2
λ (Å)	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.610	1.624
$F(000)$	520	812
μ (mm^{-1})	0.914	1.125
No. reflections/parameters	1859/144	5755/418
$R(F)$ [a]	0.033	0.022
$R_w(F^2)$ [b]	0.085	0.055

[a] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma I$.

[b] $R_w(F_2) = \{\Sigma\,[w(F_o^2-F_c^2)^2]/\Sigma\,[w(F_o^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2)+(aP)^2+bP$, where $P = (2F_o^2+F_c^2)/3$ and a and b are constants set by the program.

respect to the PR_3 ligand [18]. This is the expected geometry according to the well-known transphobia between P- and C-donor ligands [38] and is as observed in the crystal structure of compound **4**·2CHCl$_3$.

Compounds **8** and **9** have ^{1}H-NMR spectra consistent with the presence of bpy and acac ligands, respectively. The IR spectrum of **9** shows two bands at 1573 and 1510 cm^{-1}, typical of chelating acac ligands [37].

It has been established that dinuclear palladium complexes like **2** and **3** adopt a dimeric *trans* geometry in the solid state [33,39–42]. While the structures found for the chloride-bridged dimers show that the Pd_2Cl_2 ring is usually planar [43], for the acetato bridged derivatives, is known that the $Pd_2(\mu\text{-}COO)_2$ ring exhibits a non-planar open-book structure. The ^{1}H-NMR spectra corresponding to CH_2 protons in **2** (two doublets) and **3** (a singlet) agree with these expectations. Compound **2** shows, in its IR spectrum, asymmetric and symmetric C–O stretching frequencies at 1560 and 1415 cm^{-1}, respectively, in agreement with the presence of one type of bridging acetate, and, therefore, with the expected dimeric *trans* conformation [39]. When an analytically pure sample of **2** was dissolved in $CDCl_3$, its ^{1}H-NMR spectrum consisted mainly ($>90\%$) of the *trans* isomer, as deduced by comparison of our data (Table 1) with those given for the 8-methylquinoline analogue *trans*-{Pd(μ-OAc)(*C*,*N*4-$C_9H_6NCH_2$-8)}$_2$ [18]. However, a number of smaller peaks which could not be fully resolved were also present in the spectrum, possibly due to the *cis* isomer. The ^{1}H-NMR spectrum of **3** shows that only one isomer, presumably *trans*, was formed. Its IR spectrum showed two bands at 317 and 237 cm^{-1}, which correspond well with the frequencies, which have been attributed to bridging ν(PdCl) vibrations in related complexes [40].

The crystal structure of **1** (see Tables 2, 3 and Fig. 1) consists of mononuclear units with the palladium atom lying on an inversion center, thus presenting a *trans* square-planar coordination geometry. In the crystal structure, the 5-methylquinoxaline groups are monocoordinated to the palladium atom through the nitrogen atom opposite to the methyl group [N(1)] and perpendicular to the palladium coordination plane (89.0°). The Pd–N(1) distance of 2.034(3) Å is comparable to that found in a μ-pyrazine Pd(II) dimer [2.050(3) Å] [44]. The acetate groups are bonded to palladium in a terminal mode and its main plane [O(1)–O(2)–C(11)–C(12)] forms a 13° angle to the palladium coordination plane. The Pd–O(1) bond length of 2.008(3) Å is similar to that found in other *trans*-acetato-Pd(II)

Table 3
Selected bond lengths (Å) and angles (°) for compound **1**

Bond lengths			
Pd–O(1)	2.008(3)	O(1)–C(10)	1.297(5)
N(2)–C(8)	1.303(5)	N(1)–C(1)	1.381(5)
Pd–N(1)	2.035(3)	O(2)–C(10)	1.214(5)
N(2)–C(2)	1.366(5)	C(10)–C(11)	1.519(6)
N(1)–C(7)	1.316(5)		
Bond angles			
O(1)–Pd–O(1)	180.0	O(1)A–Pd–N(1)	90.03(12)
O(2)–C(10)–O(1)	125.6(4)	O(1)–C(10)–C(11)	112.3(3)
O(1)–Pd–N(1)	89.97(12)	C(10)–O(1)–Pd	117.4(2)
O(2)–C(10)–C(11)	122.1(4)		

complexes [45,46]. A weak intramolecular C(8)–H(8)···O(2) hydrogen bond could possibly exist [C(8)···O(2) 3.300(5), H(8)···O(2) 2.54 Å C(8)–H(8)···O(2) 136.9°].

Crystallographic data and selected bond lengths and angles for compound **4**·2$CHCl_3$ are given in Tables 2 and 4, respectively. The crystal structure of **4**·2$CHCl_3$ (see Fig. 2) shows a mononuclear square planar palladium complex (mean deviation 0.031 Å). The 5-methylquinoxaline group is bonded to the palladium centre through both the N(4) and the C(1) atoms and is coplanar to the palladium coordination plane (mean deviation 0.038 Å). The dihedral angle between the quinoxaline and C(1)–Pd–N(4) planes (3.7°) shows the slight puckering of the five-membered ring. The same dihedral angles for related 8-methylquinoline derivatives lie in the range of 1.5–19.5° [19]. The quinoxaline chelated ligand bite angle [N(4)–Pd–C(1): 83.44 (7)°] and the bond lengths and angles observed for the cyclopalladated five-membered ring Pd–C(1)–C(5)–C(10)–N(4), are similar to the values observed in related quinoxaline compounds [19]. The acetate ligand is bonded to palladium in a terminal mode and *trans* to the C(1) atom while the PPh_3 is *trans* to the N(4) atom. The Pd–O(1) bond distance of 2.126(1) Å lies within the range found for other Pd(II) complexes containing terminal acetate ligands *trans* to carbon (2.090–2.143 Å) [47,48]. The longer Pd–O bond length found for acetate ligands *trans* to carbon than *trans* to oxygen could be due to the greater *trans* influence of the carbon. Both chloroform molecules act as hydrogen bond donor to O(2) thus, making a strong [C(99)···O(2) 3.089(3) Å, H(99)···O(2) 2.09 Å, C(99)–H(99)···O(2) 174.2°] and a weak [C(98)···O(2) 3.209(3), H(98)···O(2) 2.31 Å, C(98)–H(98)···O(2) 148.7°] hydrogen bond.

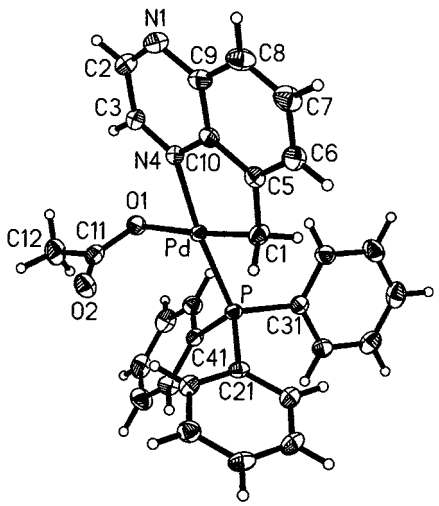


Fig. 2. Ellipsoid plot of **4** with the labelling scheme (50% probability level).

3. Experimental

3.1. General

The C, H and N analyses, conductance measurements, IR and NMR spectra and m.p. determinations were carried out as described elsewhere [49]. ^{1}H- and ^{31}P-NMR data of complexes **1**–**10** are presented in Table 1.

3.2. Preparation of *trans*-[Pd(OAc)$_2$(N1-$C_8H_5N_2Me$-5)$_2$] (**1**)

To a solution of $[Pd(OAc)_2]_3$ (88.3 mg, 0.13 mmol) in C_3H_6O (10 cm^3) was added 5-methylquinoxaline (0.1 cm^3, 0.79 mmol). The resulting orange solution was stirred for ca. 1 h, until an abundant yellow precipitate was formed. The solid was filtered and recrystallized from CH_2Cl_2–Et_2O to give **1** as a yellow solid. Yield: 189.2 mg, 94%. M.p. 211 °C (dec.). ν_{max} (cm^{-1}) (CO) 1615, 1300. Anal. Calc. for $C_{22}H_{22}N_4O_4Pd$: C, 51.53; H, 4.32; N, 10.92. Found: C, 51.52; H, 4.43; N, 10.78%.

3.3. Preparation of [Pd(μ-OAc)(C,N4-$CH_2C_8H_5N_2$-5)]$_2$ (**2**)

To a suspension of $[Pd(OAc)_2]_3$ (353 mg, 0.52 mmol) in glacial AcOH (20 cm^3) was added 5-methylquinoxaline (0.20 cm^3, 1.54 mmol). The reaction mixture was heated to reflux for 1 h and it was filtered through Celite when cold. The solvent was evaporated under reduced pressure on a steam bath to give an orange residue, which was washed with Et_2O and then recrystallized from CH_2Cl_2–Et_2O yielding complex **2** as a red solid. Yield: 389 mg, 82%. M.p. 193 °C (dec.). ν_{max} (cm^{-1}) (CO) 1560, 1415. Anal. Calc. $C_{22}H_{20}N_4O_4Pd_2$: C, 42.81; H, 3.27; N, 9.08. Found: C, 42.59; H, 3.20; N, 8.81%.

3.4. Preparation of [Pd(μ-Cl)(C,N4-$CH_2C_8H_5N_2$-5)]$_2$ (**3**)

A suspension of complex **2** (150 mg, 0.24 mmol) and LiCl (41.2 mg, 0.97 mmol) in C_3H_6O (20 cm^3) was stirred for 0.5 h. The resulting orange solution was brought to dryness, and the solid residue was washed by stirring it for 10 min in 20 cm^3 of water. The solid was filtered off, washed with C_3H_6O (10 cm^3) and Et_2O (10 cm^3), and dried in vacuum to give **3** as an orange solid. Yield: 130 mg, 94%. M.p. 234 °C (dec.). ν_{max} (cm^{-1}) (PdCl) 317, 237. Anal. Calc. for $C_{18}H_{14}Cl_2N_4Pd_2$: C, 37.92; H, 2.48; N, 9.83. Found: C, 37.38; H, 2.38; N, 9.46%.

3.5. Preparation of [Pd(OAc)(C,N4-$CH_2C_8H_5N_2$-5)(PPh_3)] (**4**)

Complex **2** was prepared as above but it was not isolated. When excess of AcOH was eliminated, **2** was dissolved in C_3H_6O (30 cm^3) and ca. 60% excess PPh_3 (525 mg, 2.00 mmol) was added to it. The resulting solution was stirred for 2 h, and the solvent was removed in vacuum to ca. 2 cm^3. Addition of Et_2O gave a suspension which was filtered off and the solid dried in vacuum to give **4** as a yellow solid. Yield: 763 mg, 85%. M.p. 166 °C (dec.). ν_{max} (cm^{-1}) (CO) 1595, 1312. Anal. Calc. for $C_{29}H_{25}N_2O_2PPd$: C, 61.01; H, 4.41; N, 4.91. Found: C, 61.01; H, 4.51; N, 5.26%.

3.6. Preparation of [PdCl(C,N4-$CH_2C_8H_5N_2$-5)(PPh_3)] (**5**)

A suspension of complex **4** (656 mg, 1.15 mmol) and LiCl (244 mg, 5.75 mmol) in C_3H_6O (20 cm^3) was stirred for 4 h. The solvent was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2 (40 cm^3). The extract was filtered through Celite and the filtrate was concentrated to dryness. The resulting yellow oil was stirred with Et_2O to form a solid, which was filtered and dried in vacuum to give **5** as a yellow solid. Yield: 565 mg, 90%. M.p. 224 °C (dec.). ν_{max} (cm^{-1}) (PdCl) 279. Anal. Calc. for $C_{27}H_{22}ClN_2PPd$: C, 59.25; H, 4.05; N, 5.12. Found: C, 59.32; H, 3.97; N, 4.97%.

3.7. Preparation of [PdCl(C,N4-$CH_2C_8H_5N_2$-5)(PR_3)] [R = Me (**6**), Et (**7**)]

To a suspension of complex **2** (R = Me, 184 mg, 0.27 mmol; R = Et, 150 mg, 0.24 mmol) in C_3H_6O was added excess PR_3 under N_2 atmosphere (R = Me, 0.55 mmol in 20 cm^3 of C_3H_6O added via a dropping funnel over 30 min; R = Et, 0.58 mmol). The resulting orange solution was stirred for 30 min, and then treated with LiCl (R = Me, 115 mg, 2.72 mmol; R = Et, 52.5 mg, 1.21 mmol). The reaction mixture was stirred at room temperature (r.t.) (R = Me, 2 h; R = Et, 14 h), the solvent was removed in vacuum and the yellow residue was extracted with CH_2Cl_2. The extract was filtered through Celite and the solvent was evaporated to ca. 2 ml. Addition of C_5H_{12} yielded compound **6** (Yield: 146.5 mg, 75%. M.p. 199 °C (dec.). ν_{max} (cm^{-1} (PdCl) 270) or **7** (Yield: 133 mg, 68%. M.p. 137 °C. ν_{max} (cm^{-1} (PdCl) 296) as a yellow solid. Complex **6**: Anal. Calc. for $C_{12}H_{16}ClN_2PPd$: C, 39.91; H, 4.47; N, 7.76. Found: C, 40.08; H, 4.34; N, 7.42%. Complex **7**: Anal. Calc. for $C_{15}H_{22}ClN_2PPd$: C, 44.69; H, 5.50; N, 6.95. Found: C, 45.36; H, 5.67; N, 6.83%.

3.8. Preparation of [Pd(O,O-acac)(C,N4-$CH_2C_8H_5N_2$-5) (**8**)

To a suspension of complex **2** (150 mg, 0.24 mmol) in C_3H_6O (20 cm^3) was added Tl(acac) (148 mg, 0.49 mmol). The resulting suspension was stirred for 4 h and then filtered through Celite. The orange filtrate was brought to dryness and C_5H_{12} was added to give complex **8** as an orange solid. Yield: 124 mg, 73%. M.p. 191 °C (dec.). ν_{max} (cm^{-1}) (acac: CC + CO) = 1573, 1510. Anal. Calc. for $C_{14}H_{14}N_2O_2Pd$: C, 48.23; H, 4.05; N, 8.03. Found: C, 48.11; H, 3.81; N, 7.82%.

3.9. Preparation of [Pd(C,N4-$CH_2C_8H_5N_2$-5)(bpy)]ClO_4 (**9**)

To a suspension of complex **2** (216.7 mg, 0.35 mmol) in C_3H_6O (25 cm^3) was added bpy (124 mg, 0.79 mmol). The reaction mixture was stirred for 2 h and the solvent was removed in vacuum to given an orange solid, which was suspended in Et_2O, filtered off and washed with C_5H_{12}. This solid was dissolved in MeOH (20 cm^3) and excess $NaClO_4 \cdot H_2O$ (327 mg, 2.31 mmol) was added, resulting in the immediate formation of a yellow precipitate. The solid was filtered off and washed first with MeOH (3 × 10 cm^3) and then with C_5H_{12} (2 × 5 cm^3) to give **9** as a yellow solid. Yield: 250.2 mg, 70%. M.p. 247 °C (dec.). Λ_M (Ω mol cm^{-2}) (5×10^{-4} M in nitromethane) 81. Anal. Calc. for $C_{19}H_{15}ClN_4O_4Pd$: C, 45.17; H, 2.99; N, 11.09. Found: C, 44.81; H, 2.81; N, 10.80%.

3.10. Preparation of [$PdCl_2${PdCl(C,N4,N1-$CH_2C_8H_5N_2$-5)(PPh_3)}$_2$] (**10**)

To a solution of complex **5** (155 mg, 0.28 mmol) in CH_2Cl_2 (20 cm^3) was added [$PdCl_2(NCPh)_2$] (54.3 mg, 0.14 mmol). After stirring for 22 h the solvent was evaporated to ca. 2 cm^3 and Et_2O was added to give a suspension which was filtered off and the solid dried in vacuum to give **10** as an orange solid. Yield: 168.6 mg, 94%. M.p. 197 °C (dec.). ν_{max} (cm^{-1}) (PdCl) = 360, 279 cm^{-1}. Anal. Calc. for $C_{54}H_{44}Cl_4N_4P_2Pd_3$: C, 50.99; H, 3.49; N, 4.40. Found: C, 50.51; H, 3.23; N, 4.30%.

3.11. Crystal structures determination of complexes **1** and **4·2CHCl$_3$**

A pale yellow plate of 0.31 × 0.30 × 0.15 mm, obtained by slow evaporation of a solution of **1** in CH_2Cl_2, was used to collect 2529 reflections at 173 K on a Siemens P4 diffractometer (Mo–K_α radiation, $2\theta_{max}$ 50°, 1859 unique, $R_{int} = 0.030$) as summarized in Table 2. The orientation matrix was refined from setting angles of 65 reflections in the 2θ range 10–25°. An absorption correction based on ψ-scans was applied,

Table 4
Selected bond lengths (Å) and angles (°) for compound **4**·2$CHCl_3$

Bond lengths			
Pd–C(1)	2.004(2)	C(1)–C(5)	1.510(3)
Pd–N(4)	2.0747(16)	N(4)–C(10)	1.374(3)
Pd–O(1)	2.1257(14)	C(5)–C(10)	1.409(3)
Pd–P	2.2340(6)		
Bond angles			
C(1)–Pd–N(4)	83.43(7)	C(3)–N(4)–Pd	128.56(14)
N(4)–Pd–O(1)	90.76(6)	C(10)–N(4)–Pd	113.09(13)
C(1)–Pd–P	89.42(6)	C(6)–C(5)–C(1)	125.23(19)
O(1)–Pd–P	96.45(4)	C(10)–C(5)–C(1)	117.90(17)
C(5)–C(1)–Pd	108.53(13)	N(4)–C(10)–C(5)	116.94(17)
C(3)–N(4)–C(10)	118.22(17)		

with transmission factors 0.707–0.811. The structure was solved by the heavy atom method and refined anisotropically on all F^2 data using SHELXL-97 (G.M. Sheldrick, University of Göttingen). Hydrogen atoms for the methyl group were refined using a rigid model and the others riding. **4**·2$CHCl_3$: a yellow 0.58 × 0.40 × 0.18 mm tablet of **4**·2$CHCl_3$, obtained by slow evaporation of a solution of the complex in $CHCl_3$, was mounted in inert oil on a glass fiber and transferred to a Siemens P4 diffractometer. A set of 8190 reflections (Mo–K_α radiation, $2\theta_{max}$ 50°, 5755 unique, R_{int} = 0.009) was collected at 173 K. Unit cell parameters were determined from a least-squares fit of 63 accurately centred reflections ($23 < 2\theta < 25$). An absorption correction based on ψ-scans was applied, with transmission factors 0.716–0.919. The structure was solved by the heavy atom method and refined anisotropically on all F^2 data using SHELXL-97 (G.M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or as rigid methyl groups. One of the $CHCl_3$ molecules is disordered over two sites (62 and 38% refined occupancy). Table 2 gives crystallographic data and Tables 3 and 4 selected bond lengths and angles for compounds **1** and **4**·2CHC_3, respectively.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 160146 and 160147 for complexes **1** and **4**·2$CHCl_3$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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