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Cyclometallated compounds

V *. Double cyclopalladation of diphenyl pyrazines and related ligands

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Abstract

2,3-Diphenylpyrazine and four structurally related ligands have each been singly and doubly cyclopalladated and the products characterised by ^{1}H and ^{13}C NMR studies of their acetylacetonate complexes. The structure of a doubly cyclometallated Pd(acac) complex of 2,3-diphenylpyrazine has been determined by an X-ray diffraction study ($R = 0.039$). A strong steric interaction between the two cyclopalladated phenyl rings is relieved by twisting; the two chelate ring mean-planes are mutually inclined at an angle of 19.6(5)°.

Introduction

The study of binuclear complexes containing bridging heterocyclic ligands has been the subject of much recent attention [1]. For example, 2,3-di(2-pyridyl)pyrazine forms both homo- and hetero-bimetallic complexes of type **1** in which the possibility exists for communication between the two metals via the π-system of the pyrazine ring [2,3]. By changing the ligand it is possible to vary the distance between the metals and accordingly the propensity for transfer of energy or electrons, or for magnetic interaction between the two metal centres [4].

We are currently studying doubly cyclometallated complexes in which chelating pyridine rings of binucleating ligands are replaced by phenyl rings that are capable of undergoing cyclometallation. Whereas cyclometallated complexes **2** of 2-phenylpyridine are well studied [5] analogues of 2,2′-bipyridine complexes **3**, relatively few examples of the double cyclometallation of a single ligand are known [6,7]. Recently we described [8] the preparation of complexes of type **4** [M = Pd(acac)], which were

* For part IV see ref. 8.

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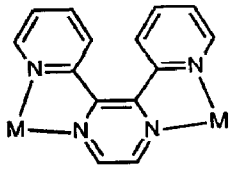
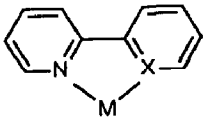
formed by the double cyclopalladation of 4,6-diphenylpyrimidine and are analogues of 4,6-di(2-pyridyl)pyrimidine complexes **5**. As an extension of this work we now report a study of the cyclopalladation reactions of 2,3-diphenylpyrazine and related ligands, which was carried out in the hope of producing cyclopalladated analogues of complexes of type **1**. The isomeric ligand 2,5-diphenylpyrazine has previously [6] been doubly cyclopalladated to form a complex **6** related to the well studied, 2,5-di(2-pyridyl)pyrazine complexes **7** [2,9].

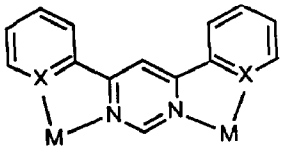


(1)



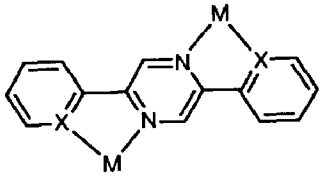
(2) X = C

(3) X = N



(4) X = C

(5) X = N



(6) X = C

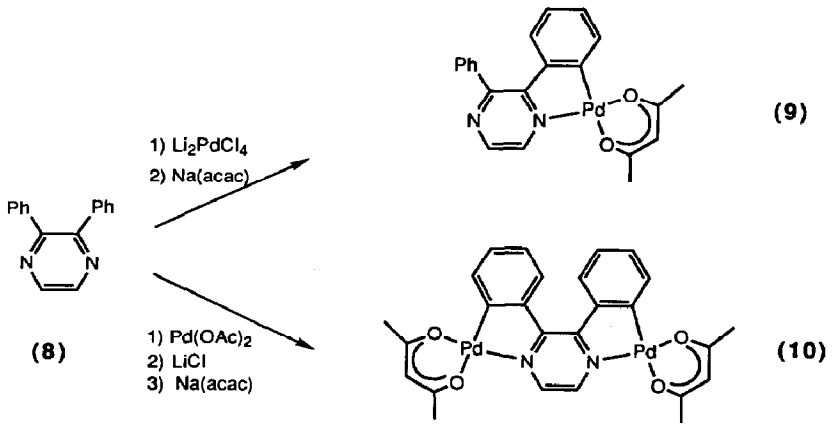
(7) X = N

Results and discussion

Cyclometallation reactions

The ligands employed in this work were either commercially available or were prepared by published procedures. Cyclopalladation was effected by reaction with either lithium tetrachloropalladate or palladium acetate, followed by acetate halide exchange, to produce chloro-bridged dimers that were then converted in acetylacetonate monomers by ligand exchange with sodium acetylacetonate. The change in out-of-plane aromatic C–H deformation pattern in the infrared spectrum was used to monitor the reaction. The structures of the products were readily determined by NMR spectroscopy by comparison with the spectra of the starting ligands and by use of the known [10] ^{1}H and ^{13}C NMR substituent effects induced by Pd(acac). All ^{1}H and ^{13}C NMR spectra of the starting ligands and cyclopalladated acetylacetonate complexes were definitively assigned by a combination of one- and two-dimensional techniques by use of methods previously described [10]. This revealed some incorrect literature assignments for the NMR spectra of the starting ligands. Full assignments of the spectra are given in the Experimental Section.

Reaction of 2,3-diphenylpyrazine (**8**) with lithium tetrachloropalladate, followed by sodium acetylacetonate exchange, gave the mono-cyclopalladated product **9** in 80% yield (Scheme 1). NMR and IR spectroscopy clearly indicated the presence of

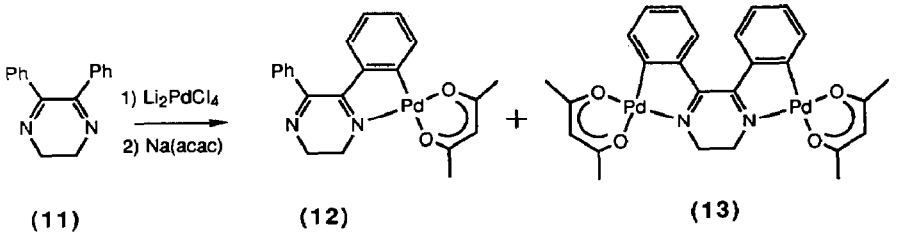


Scheme 1

one orthopalladated phenyl ring and one unsubstituted phenyl ring. Reaction of **8** with two equivalents of palladium acetate followed by chloride and acetylacetonate ligand exchange gave the dipalladated product **10** in 60% yield. The structure of **10** followed from the symmetrical nature of the NMR spectra and the characteristic pattern for an orthopalladated phenyl ring. Cyclometallation of **8** has been previously [11] carried out by reaction with methylmanganese(I) pentacarbonyl; however only mono-cyclomanganation was achieved.

A notable feature of the ^{1}H NMR spectra of **9** and **10** is the large difference in chemical shifts of the protons in the palladated phenyl ring. In particular the signal for H(3) appears at 6.64 ppm in the mono-palladated product **9** and at 7.94 ppm in the dipalladated product **10**, compared with 7.46 ppm in the starting ligand **8**. These large chemical shift differences can be explained by the relative orientations of the phenyl rings. Cyclopalladation constrains the metallated phenyl ring to lie approximately coplanar with the pyrazine ring. Thus in the mono-palladated product **9**, two of the rings will be approximately coplanar, whilst the third (unsubstituted) phenyl ring will, for steric reasons, lie approximately orthogonal to the plane of the other rings [12]. As a result H(3) will lie directly above the shielding plane of the unsubstituted phenyl ring, thereby accounting for the relatively high field position (6.64 ppm) of this proton. Similar upfield shifts have previously been observed in the spectra of cyclopalladated triphenyl-pyrazoles [13] and -pyrimidines [8]. In the doubly cyclopalladated product, however, the three aromatic rings are expected to be approximately coplanar, and as a result H(3) will lie in the deshielding region of the other (cyclopalladated) ring. This proton is therefore shifted downfield to 7.94 ppm.

Complex **10** therefore represents a carbon analogue of complexes of type **1** of the well studied [2,3] ligand 2,3-bis(2-pyridyl)pyrazine. Inspection of molecular models indicates that in **10** there is a large steric interaction between the H(3) protons of the two palladated phenyl rings. This steric interaction would be expected to be relieved by twisting of the rings, such that the two phenyl rings will not be mutually coplanar. Indeed such twisting has been detected [14] in NMR studies of platinum complexes **1** (M = Pt) of the dipyridyl ligand. In order to examine the extent of



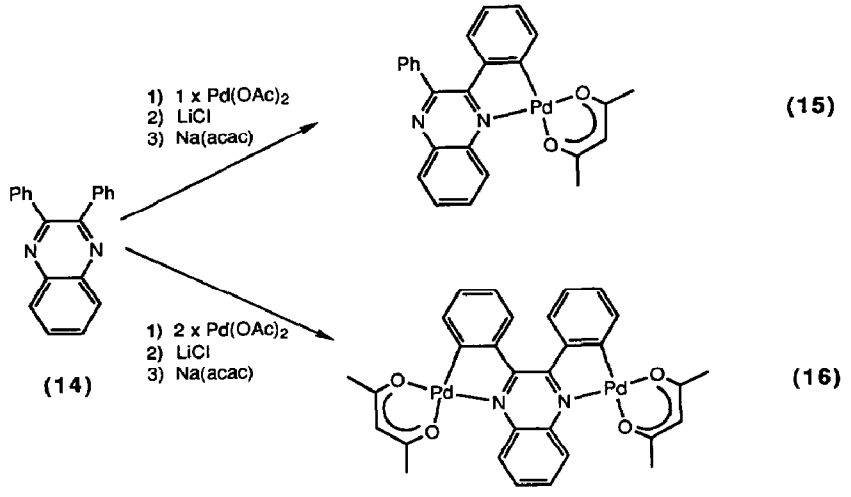
(11) (12) (13)

Scheme 2

twisting and to confirm the structure an crystal structure determination was carried out on **10** as described below. This confirmed the double cyclopalladation of **8**.

Encouraged by this successful double cyclopalladation we then examined the reactions of a number of structurally related ligands. Since 5,6-dihydro-2,3-di(2-pyridyl)pyrazine is also known to be good a chelating ligand [15], the corresponding diphenyl analogue **11** was examined. Reaction of **11** with two equivalents of lithium tetrachloropalladate followed by acetylacetonate exchange gave a mixture of the mono-palladated product **12**, and the dipalladated product **13** in a ratio of 2 : 1 (Scheme 2). Although these two products were not separated, structure identification and complete assignments of their ^{1}H and ^{13}C NMR spectra were achieved by a combination of one and two dimensional NMR techniques. Attempts to purify the mixture resulted in oxidation of the dihydropyrazine ring to give **9**, which was also isolated from the mother liquor of the crude reaction product. The double cyclopalladation of **11** but not **8** on reaction with lithium tetrachloropalladate is probably attributable to the greater flexibility of the dihydropyrazine ring than that which is possible in the planar aromatic pyrazine ring in **8**.

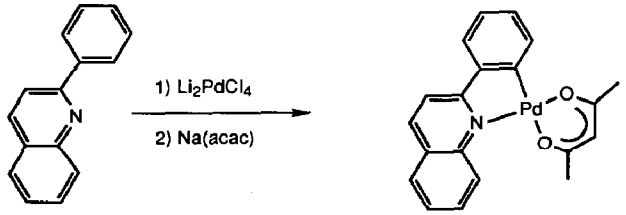
2,3-Diphenylquinoxaline (**14**) was not treated with lithium tetrachloropalladate owing to the low solubility of the ligand in methanol. However reaction occurred cleanly with palladium acetate (Scheme 3). Thus reaction of **14** with one equivalent of palladium acetate, followed by ligand exchange, gave the mono-palladated



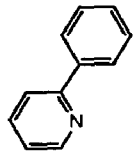
(14) (15) (16)

Scheme 3

product **15**, while reaction with two equivalents gave the dipalladated product **16**. Since the ^{1}H NMR spectrum of **15** was relatively complex, the model compound **17** was prepared from 2-phenylquinoline via the known [16] chloro-bridged cyclopalladated intermediate. The ^{1}H and ^{13}C NMR spectra of **17** were fully assigned by the procedures previously reported [10], and this allowed an assessment of the Pd(acac)-induced substituent shifts in the benzo ring of the quinoline and hence of the quinoxaline. This in turn led to a complete assignment of both the ^{1}H and ^{13}C NMR spectra of the products **15** and **16** (see Experimental Section). As with **9** and **10**, there are large differences in the ^{1}H NMR chemical shifts of the cyclopalladated phenyl ring protons in the mono-palladated products **9** and **15** relative to those for the dipalladated products **10** and **16**. The dipalladated product **16** is a carbon analogue of binuclear complexes of the corresponding dipyridyl ligand, which have been the subject of extensive study [12,17].



(17)



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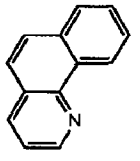
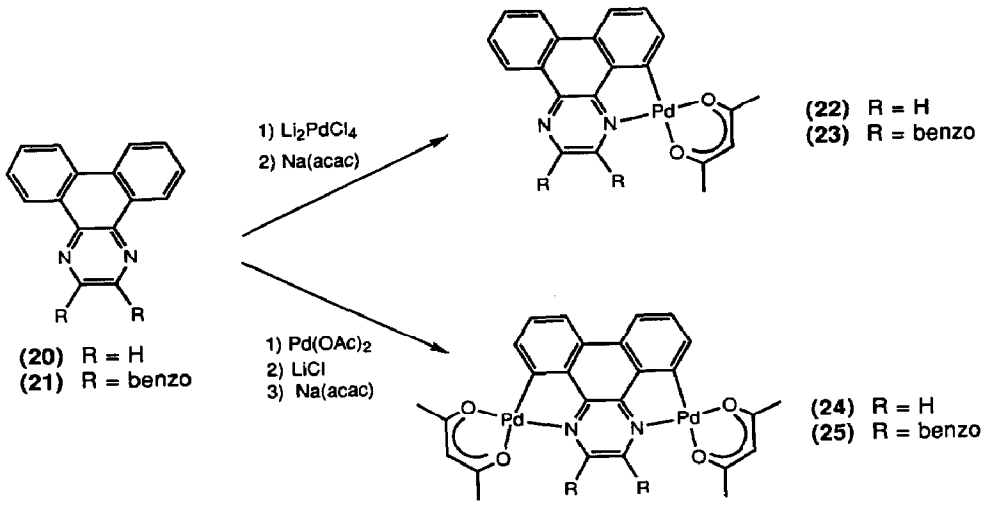


(19)

The above reactions all involve cyclopalladation of freely-rotating phenyl rings, as is the case with 2-phenylpyridine (**18**). Since benzo[*h*]quinoline (**19**) is more readily cyclometallated than 2-phenylpyridine owing to the fact that the required coplanar geometry is already present in the starting ligand, it was expected that the two planar fused ligands 1,4-diazatriphenylene (**20**) and dibenzo[*a*,*c*]phenazine (**21**) would readily undergo double cyclopalladation. Indeed this proved to be the case (Scheme 4). Thus reaction of 1,4-diazatriphenylene (**20**) with one equivalent of lithium tetrachloropalladate gave, after ligand exchange, the mono-palladated product **22** in 90% yield, while reaction with two equivalents of palladium acetate gave **24** in 80% yield. The dipalladated product **24** was, however, not soluble in common NMR solvents. Similarly, dibenzo[*a*,*c*]phenazine (**21**) gave the benzo analogues **23** and **25**, both of which were fully characterised by NMR spectroscopy. Again these dipalladated compounds represent carbon analogues of the corresponding dipyridyl ligands, whose ruthenium complexes have been the subject of much study [18].

The relative ease with which both mono- and di-cyclopalladated complexes of the above ligands can be prepared suggests the possibility of the preparation of heterobimetallic complexes. In such binuclear complexes there might be expected to



Scheme 4

be electronic and magnetic communication between the two different metals. Attempts to prepare heterodicyclometallated complexes of the above ligands are currently in progress [19].

X-ray crystal structure of ***10***

In order to confirm the structure of the doubly cyclopalladated product from 2,3-diphenylpyrazine, and to determine the extent of twisting of the phenyl rings, a single crystal X-ray analysis was carried out. Figure 1 shows a minimum overlap view of the structure and includes the atom labelling. Tables 1 and 2 list bond

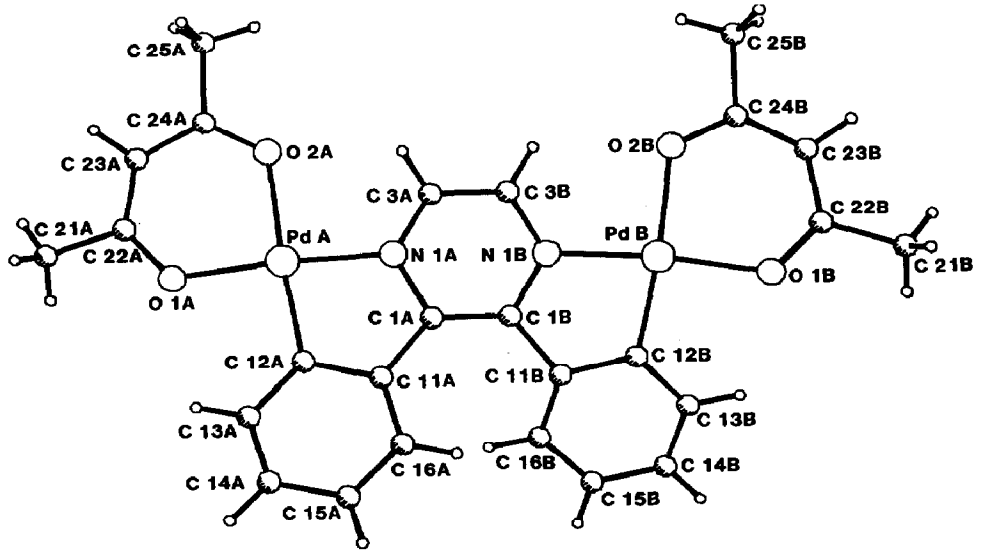


Fig. 1. Perspective view and atom labelling of the X-ray structure of **10**.

Table 1

Bond lengths [a] (Å) in **10**

Pd–N(1)	2.002(5)		2.004(5)
Pd–C(12)	1.956(7)		1.957(8)
Pd–O(1)	2.021(4)		2.008(5)
Pd–O(2)	2.082(5)		2.080(5)
C(1)–N(1)	1.356(10)		1.382(9)
N(1)–C(3)	1.348(9)		1.317(10)
C(1A)–C(1B)		1.407(9)	
C(3A)–C(3B)		1.390(9)	
C(1)–C(11)	1.486(9)		1.454(11)
C(11)–C(12)	1.411(10)		1.427(9)
C(11)–C(16)	1.392(11)		1.404(12)
C(12)–C(13)	1.388(10)		1.403(12)
C(13)–C(14)	1.382(12)		1.380(14)
C(14)–C(15)	1.380(11)		1.415(11)
C(15)–C(16)	1.389(10)		1.374(13)
O(1)–C(22)	1.273(10)		1.283(9)
O(2)–C(24)	1.276(9)		1.276(8)
C(21)–C(22)	1.512(10)		1.498(12)
C(22)–C(23)	1.385(11)		1.375(12)
C(23)–C(24)	1.392(10)		1.395(12)
C(24)–C(25)	1.514(12)		1.504(13)

[a] The first value refers to atoms labelled A and the second to atoms labelled B.

lengths and angles, respectively. The structure is confirmed as **10**, in which the ligand acts in a bis-bidentate binucleating mode. The intramolecular Pd–Pd distance is 6.725(1) Å (cf. 5.937(2) Å in **4** [M = Pd(acac)] [8]).

The coordination geometry at the palladium atoms and the geometry of the acetylacetonate ligands is similar to that in **4** [M = Pd(acac)]. Except for a small twisting to relieve an interaction between the acetylacetonate ligands, the molecule **4** [M = Pd(acac)] was found [8] to be nearly planar (rms deviation from mean plane for non-hydrogen atoms = 0.087 Å). In contrast, however, the molecule **10** is far from planar (rms deviation = 0.556 Å) owing to the strong steric interaction between the phenyl rings. This results in a significant twisting of the rings, as shown in Fig. 2.

This type of twisting has been the subject of much discussion [12,14,20,21], particularly for binuclear complexes **1** of the corresponding dipyridyl ligand. As mentioned above, such twisting has previously [14] been detected by variable temperature NMR studies of octahedral platinum(IV) complexes of the dipyridyl ligand **1** [M = Pt]. However, no X-ray structures of binuclear complexes of type **1** have been reported; the structure of a mononuclear ruthenium(II) complex of a related ligand has been reported [12]. It has been stated [20], however, that molecular models suggest that for the complex **1** [M = $Ru(bpy)_2$] twisting could result in an angle of 35–40° between the planes of the chelate rings. In the complex **10** this angle is only 19.6(5)°; the C(11A)–C(1A)–C(1B)–C(11B) torsional angle is 18(1)°.

This twisting also imposes strain on the pyrazine ring, which is significantly non-planar (for example C(1B) lies 0.15 Å above the mean plane; cf. the pyrimidine ring of **4** [M = Pd(acac)], where the maximum deviation from the mean plane is

Table 2

Bond angles [a] (°) in **10**

N(1)–Pd–C(12)	80.8(2)	81.6(3)
N(1)–Pd–O(1)	173.2(2)	174.0(2)
C(12)–Pd–O(1)	93.2(2)	92.9(3)
N(1)–Pd–O(2)	94.1(2)	93.1(2)
C(12)–Pd–O(2)	172.9(2)	170.3(3)
O(1)–Pd–O(2)	92.2(2)	92.7(2)
Pd–N(1)–C(1)	116.6(4)	115.8(5)
Pd–N(1)–C(3)	122.9(5)	123.1(4)
C(1)–N(1)–C(3)	120.5(6)	121.0(6)
N(1)–C(1)–C(1)	119.1(6)	117.4(7)
N(1)–C(1)–C(11)	111.9(6)	112.3(6)
C(1)–C(1)–C(11)	129.0(7)	130.1(6)
N(1)–C(3)–C(3)	119.6(7)	120.3(6)
C(1)–C(11)–C(12)	113.4(6)	114.6(7)
C(1)–C(11)–C(16)	125.6(6)	125.1(6)
C(12)–C(11)–C(16)	120.4(6)	119.4(7)
Pd–C(12)–C(11)	115.7(5)	114.5(6)
Pd–C(21)–C(13)	125.3(6)	125.8(5)
C(11)–C(12)–C(13)	118.4(7)	118.5(7)
C(12)–C(13)–C(14)	120.8(7)	121.1(7)
C(13)–C(14)–C(15)	120.5(7)	120.1(9)
C(14)–C(15)–C(16)	120.0(8)	119.6(9)
C(11)–C(16)–C(15)	119.7(7)	121.0(7)
Pd–O(1)–C(22)	123.7(4)	123.3(5)
Pd–O(2)–C(24)	123.0(4)	122.9(6)
O(1)–C(22)–C(21)	114.8(7)	114.1(7)
O(1)–C(22)–C(23)	127.2(6)	127.1(7)
C(21)–C(22)–C(23)	117.9(7)	118.8(7)
C(22)–C(23)–C(24)	127.9(8)	128.7(7)
O(2)–C(24)–C(23)	125.6(7)	125.0(8)
O(2)–C(24)–C(25)	115.6(6)	115.6(7)
C(23)–C(24)–C(25)	118.7(7)	119.4(7)

[a] The first value refers to angles subtended at atoms labelled A and the second to atoms labelled B.

< 0.02 Å [8]). The two phenyl rings are each inclined to the pyrazine ring at an angle of approximately 23° and are mutually inclined at 46°. However, the potential C_2 symmetry of the complex is destroyed by other torsional interactions

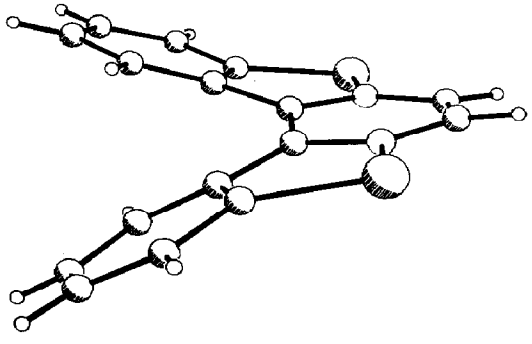


Fig. 2. View of **10** showing the ring twisting. Acac ligands omitted for clarity.

(for example, the two phenyl ring mean planes are inclined to the molecular mean plane at angles of 20.5 and 25.8°). The molecular packing is similar to that in **4** [M = Pd(acac)] [8].

Experimental

Infrared spectra were recorded with a Shimadzu IR 27G spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL300 spectrometer for $CDCl_3$ solutions with Me_4Si as internal standard. Definitive assignments of NMR spectra were made by a combination of one- and two-dimensional techniques by use of methods described in ref. 10.

Preparation and spectra of ligands

*2,3-Dihydro-5,6-diphenylpyrazine (**11**)* was prepared from benzil and ethylenediamine. M.p. 165–166°C (lit. [22]: 161.5–162.5°C). ^1H NMR; δ 3.69 (s), H(2,3)); 7.24 (m, 5,6-*meta*); 7.30 (m, 5,6-*para*); 7.40 (m, 5,6-*ortho*). ^{13}C NMR: δ 45.8 (C(2,3)); 127.8 (5,6-*ortho*); 128.1 (5,6-*meta*); 129.6 (5,6-*para*); 137.7 (5,6-*ipso*); 160.2 (C(5,6)).

*2,3-Diphenylpyrazine (**8**)* was prepared from **11** by treatment with two equivalents of alcoholic ferric chloride. The mixture was heated gently for 1 h then diluted with water and extracted with ether. After drying of the extract ($MgSO_4$) and removal of the ether, the residue was recrystallised twice from acetone, M.p. 119–120°C (lit. [23]: 118–119°C). ^1H NMR: δ 7.30 (m, 2,3-*meta* and *para*); 7.45 (m, 2,3-*ortho*); 8.60 (s, H(5,6)). ^{13}C NMR: δ 128.2 (2,3-*ortho*); 128.6 (2,3-*meta*); 129.6 (2,3-*para*); 138.6 (2,3-*ipso*); 142.0 (C(5,6)); 152.8 (C(2,3)).

*2,3-Diphenylquinoxaline (**14**)* was prepared from benzil and *ortho*-phenylenediamine. M.p. 125°C (lit. [24]: 126°C). ^1H NMR: δ 7.34 (m, 2,3-*meta* and *para*); 7.53 (m, 2,3-*ortho*); 7.77 (dd, $^3J_{6,5}$ 6.3 Hz, $^4J_{6,8}$ 3.4 Hz, H(6,7)); 8.19 (dd, $^3J_{5,6}$ 6.4 Hz, $^4J_{5,7}$ 3.5 Hz, H(5,8)). ^{13}C NMR: δ 128.2 (2,3-*meta*); 128.8 (2,3-*para*); 129.2 (C(5,8)); 129.8 (2,3-*ortho*); 129.9 (C(6,7)); 139.1 (2,3-*ipso*); 141.2 (C(4a,8a)); 153.4 (C(2,3)).

2-Phenylquinoline was obtained commercially (Aldrich). ^1H NMR: δ 7.44 (m, *para*); 7.49 (m, *meta*); 7.52 (m, H(6)); 7.71 (td, $^3J_{7,6} = {}^3J_{7,8}$ 7.0 Hz, $^4J_{7,5}$ 1.5 Hz, H(7)); 7.79 (dd, $^3J_{5,6}$ 8.1 Hz, $^4J_{5,7}$ 1.6 Hz, H(5)); 7.83 (d, $^3J_{3,4}$ 8.6 Hz, H(3)); 8.16 (dd, $^3J_{4,3}$ 8.5 Hz, $^5J_{4,8}$ 1.4 Hz, H(4)); 8.16 (m, *ortho* and H(8)). ^{13}C NMR: δ 118.9 (C(8)); 126.2 (C(6)); 127.1 (C(4a)); 127.4 (C(5)); 127.5 (*ortho*); 128.8 (*meta*); 129.3 (*para*); 129.6 (C(7)); 127.9 (C(8)); 139.6 (*ipso*); 148.2 (C(8a)); 157.3 (C(2)).

*Dibenzo[f,h]quinoxaline (**20**)* was prepared from 9,10-phenanthraquinone and ethylenediamine, and recrystallised from ethanol. M.p. 178–180°C (lit. [25]: 180.5°C). ^1H NMR: δ 7.68 (td, $^3J_{6,5} = {}^3J_{6,7}$ 7.1 Hz, $^4J_{6,8}$ 1.5 Hz, H(6,11)); 7.73 (td, $^3J_{7,6} = {}^3J_{7,8}$ 7.1 Hz, $^4J_{7,5}$ 1.8 Hz, H(7,10)); 8.53 (dd, $^3J_{8,7}$ 7.7 Hz, $^4J_{8,6}$ 1.7 Hz, H(8,9)); 8.83 (s, H(2,3)); 9.14 (dd, $^3J_{5,6}$ 7.2 Hz, $^4J_{5,7}$ 2.2 Hz, H(5,12)). ^{13}C NMR: δ 122.6 (C(8,9)); 125.3 (C(5,12)); 127.6 (C(6,11)); 129.5 (C(7,10)); 129.8 (C(4b,12a)); 131.3 (C(8a,8b)); 141.3 (C(4a,12b)); 143.4 (C(2,3)).

*Dibenzo[a,c]phenazine (**21**)* was prepared from 9,10-phenanthraquinone and *ortho*-phenylenediamine. M.p. 215°C (lit. [25]: 223–224°C). ^1H NMR: δ 7.72 (td, $^3J_{8,7} = {}^3J_{8,9}$ 7.1 Hz, $^4J_{8,10}$ 1.4 Hz, H(8,13)); 7.77 (td, $^3J_{9,8} = {}^3J_{9,10}$ 7.2 Hz, $^4J_{9,7}$ 1.6 Hz, H(9,12)); 7.83 (dd, $^3J_{3,2}$ 6.5 Hz, $^4J_{3,5}$ 3.4 Hz, H(3,4)); 8.30 (dd, $^3J_{2,3}$ 6.5 Hz, $^4J_{2,4}$ 3.5

Hz, H(2,5)); 8.52 (dd, $^3J_{10,9}$ 7.8 Hz, $^4J_{10,8}$ 1.5 Hz, H(10,11)); 9.37 (dd, $^3J_{7,8}$ 7.7 Hz, $^4J_{7,9}$ 1.8 Hz, H(7,14)). ^{13}C NMR: δ 122.9 (C(10,11)); 126.2 (C(7,14)); 127.9 (C(8,13)); 129.4 (C(2,5)); 129.7 (C(3,4)); 130.3 (C(9,12)).

Preparation and spectra of complexes

General procedure. (a) Reaction with lithium tetrachloropalladate: A solution of one equivalent of palladium chloride and three equivalents of lithium chloride in methanol was refluxed for 2 h and then filtered. The filtrate was then added to a methanol solution of the ligand and the resulting solution stirred for 1–4 days. The resulting precipitate of the di-μ-chloro dipalladium complex was filtered off and washed with methanol. The chloro-bridged dimer was then added to a methanol solution of sodium methoxide and an excess of acetylacetone and the mixture stirred for 24 h. The precipitated acetylacetonate complex was filtered off, washed with methanol, and, if necessary, recrystallised from dichloromethane/petroleum ether.

(b) Reaction with palladium acetate: A solution containing one or two equivalents of palladium acetate and the ligand in glacial acetic acid was refluxed for one hour. After cooling, the acetic acid was removed under reduced pressure at room temperature. The resulting μ-diacetato dipalladium complex was then converted in the μ-dichloro species by stirring with an acetone/water (60/40) solution containing excess lithium chloride (four equivalents) for up to four days. The resulting precipitate was then washed with acetone. The chloro-bridged dimer was then treated as above with sodium acetylacetonate in methanol to give the acetylacetonato-palladium complex.

Reaction of 2,3-diphenylpyrazine (**8**) with lithium tetrachloropalladate and subsequent ligand exchange with sodium acetylacetonate gave, in 80% yield, acetylacetonato[2-(3-phenylpyrazin-2-yl)phenyl-C^1,N^1]palladium(II) (**9**). M.p. 194–195 °C. ^{1}H NMR: δ 2.10 and 2.15 (acac-CH_3); 5.43 (acac-CH); 6.64 (H(3)); 6.75 (H(4)); 7.10 (H(5)); 7.54 (3′-*ortho, meta and para*); 7.62 (H(6)); 8.48 (H(5′)); 8.85 (H(6′)). ^{13}C NMR: δ 27.7 and 28.1 (acac-CH_3); 100.8 (acac-CH); 124.2 (C(4)); 127.3 (C(3)); 128.7 (3′-*meta*); 129.1 (3′-*ortho*); 129.5 (C(5)); 129.7 (3′-*para*); 131.2 (C(6)); 139.9 (C(6′)); 141.0 (C(5′)). Found: C, 55.4; H, 3.8; N, 6.1. $C_{21}H_{18}N_2O_2Pd \cdot H_2O$ calc.: C, 55.5; H, 4.4; N, 6.2%.

Reaction of 2,3-diphenylpyrazine (**8**) with two equivalents of palladium acetate, as described above, gave in 60% yield, μ-(2,3-diphenylpyrazine-$C^2,N^1 : N^4,C^{2'}$)bis-[acetylacetonato]dipalladium(II) (**10**). M.p. 328 °C (dec.). IR: ν(KBr) 755 and 720 cm^{-1} (C_6H_4 and $C_4H_2N_2$). ^{1}H NMR: δ 2.06 and 2.14 (acac-CH_3); 5.43 (acac-CH); 7.02 (H(4)); 7.22 (H(5)); 7.65 (H(6)); 7.94 (H(3)); 8.61 (H(4′,5′)). ^{13}C NMR: δ 27.6 and 28.1 (acac-CH_3); 100.9 (acac-CH); 123.9 (C(4)); 126.8 (C(3)); 130.5 (C(5)); 131.7 (C(6)); 138.5 (C(4′,5′)) 142.8 (C(2)); 156.4 (C(2′,3′)); 158.3 (C(1)); 187.1 and 188.7 (acac-CO). Found: C, 48.4; H, 3.9; N, 4.3. $C_{26}H_{24}N_2O_4Pd_2$ calc.: C, 48.7; H, 3.8; N, 4.4%.

2,3-Dihydro-5,6-diphenylpyrazine (**11**) was treated with two equivalents of lithium tetrachloropalladate and the product treated with sodium acetylacetonate. NMR analysis of the product showed it to consist of a 2/1 mixture of acetylacetonato[2-(2,3-dihydro-5-phenylpyrazin-6-yl)phenyl-C^1,N^2]palladium(II) (**12**) [^{1}H NMR: δ 2.05 and 2.11 (acac-CH_3); 3.86 (H(2′,3′); 5.42 (acac-CH); 6.45 (H(3)); 6.74 (H(4));

7.13 (H(5)); 7.41 (5-*meta*); 7.50 (5-*para*); 7.56 (5-*ortho*); 7.60 (H(6)). ^{13}C NMR: δ 27.6 and 28.0 (acac-CH_3); 44.5 (C(6′)); 45.8 (C(5′)); 123.5 (C(4)); 128.0 (5-*ortho*); 128.4 (5-*meta*); 128.9 (C(3)); 130.2 (C(5)); 130.6 (5-*para*); 131.3 (C(6))] and μ-[2,3-dihydro-5,6-diphenylpyrazine-$C^1,N^{4'}:N^{1'},C^1$]bis(acetylacetonato)dipalladium(II) (**13**) [^{1}H NMR: δ 2.03 and 2.12 (acac-CH_3); 3.54 (H(2′,3′(ax.))); 4.44 (H(2′,3′(eq.))); 5.42 (acac-CH); 7.02 (H(4)); 7.25 (H(5)); 7.34 (H(3)); 7.66 (H(6)). ^{13}C NMR: δ 27.6 and 28.0 (acac-CH_3); 46.7 (C(2′,3′)), 100.8 (acac-CH); 123.8 (C(4)); 129.6 (C(3)); 130.9 (C(5)); 131.6 (C(6))]. Attempts to separate the mixture resulted in oxidation of the dihydropyrazine to the previously prepared complex **9**.

Reaction of 2,3-diphenylquinoxaline (**14**) with one equivalent of palladium acetate as described above gave, in low yield, acetylacetonato[2-(3-phenylquinoxalin-2-yl)phenyl-$C^1,N^{1'}$]palladium(II) (**15**). M.p. 228°C (dec.). ^{1}H NMR: δ 2.11 and 2.16 (acac-CH_3); 5.51 (acac-CH); 6.68 (H(3)); 6.76 (H(4)); 7.08 (H(5)); 7.55 (3′-*meta* and *para*); 7.69 (H(6)); 7.72 (H(7′)); 7.73 (3′-*ortho*); 7.74 H(6′)); 8.08 (H(5′)); 9.28 (H(8′)). ^{13}C NMR: δ 27.8 and 28.2 (acac-CH_3); 100.2 (acac-CH); 124.3 (C(4)); 126.8 (C(8′)); 129.0 (5C) (C(3), C(5), 3′-*meta* and C(5′)); 129.2 (3′-*ortho*); 129.8 (3′-*para*); 130.0 (C(6′)); 130.7 (C(6)); 130.8 (C(7′)). Found: C, 61.4; H, 4.2; N, 5.5. $C_{25}H_{20}N_2O_2Pd$ calc.: C, 61.7; H, 4.1; N, 5.8%.

Reaction of 2,3-diphenylquinoxaline (**14**) with two equivalents of palladium acetate gave, in 40% yield, μ-(2,3-diphenylquinoxaline-$C^2,N^1:N^{4'},C^2$)bis[acetylacetonato]dipalladium(II) (**16**). M.p. 272°C (dec.). ^{1}H NMR: δ 2.09 and 2.17 (acac-CH_3); 5.50 (acac-CH); 6.99 (H(4)); 7.19 (H(5)); 7.67 (H(6′,7′)); 7.69 (H(6)); 7.81 (H(3)); 9.26 (H(5′,8′)). ^{13}C NMR: δ 27.8 and 28.1 (acac-CH_3); 100.2 (acac-CH); 124.3 (C(4)); 126.6 (C(5′,8′)); 128.7 (C(3)); 130.0 (C(5)); 130.6 (C(6′,7′)); 131.0 (C(6)); 140.9 (C(4a,8a)); 145.2 (C(2)); 156.6 (C(2′,3′)); 158.9 (C(1)); 186.9 and 188.4 (acac-CO). Found: C, 50.8; H, 3.8; N, 3.8. $C_{30}H_{26}N_2O_4Pd_2 \cdot H_2O$ calc.: C, 50.8; H, 4.0; N, 3.9%.

2-Phenylquinoline was treated with lithium tetrachloropalladate to give the previously described [16] μ-dichloro cyclopalladated complex, which after sodium acetylacetonate exchange, gave acetylacetonato[2-(quinolin-2′-yl)phenyl-C^1,N$^{1'}$]palladium(II) (**17**) in 50% overall yield. M.p. 203–207°C (dec). ^{1}H NMR: δ 2.09 and 2.13 (acac-CH_3); 5.46 (acac-CH); 7.14 (H(4)); 7.19 (H(5)); 7.50 (H(6)); 7.52 (H(3)); 7.69 (H(6)); 7.72 (H(7′)); 7.74 (H(5′)); 7.79 (H(3′)); 8.21 (H(4′)); 9.46 (H(8′)). ^{13}C NMR: δ 27.9 and 28.2 (acac-CH_3); 99.6 (acac-CH); 116.5 (C(3′)); 124.4 (C(3)); 124.8 (C(4)); 126.4 (C(6′)); 127.0 (C(8′)); 127.6 (C(5′)); 129.0 (C(5)); 130.7 (C(6)); 130.8 (C(7′)); 139.1 (C(4′)); 186.8 and 188.0 (acac-CO). Found: C, 58.4; H, 3.9; N, 3.4. $C_{20}H_{17}NO_2Pd$ calc.: C, 58.6; H, 4.2; N, 3.4%.

Dibenzo[*f*,*h*]quinoxaline (**20**) was treated with lithium tetrachloropalladate to give, in 90% yield after sodium acetylacetonate exchange, acetylacetonato[dibenzo-[*f*,*h*]quinoxalin-5-yl-C^5,N^4]palladium(II) (**22**). M.p. 287–289°C (dec.). ^{1}H NMR: δ 2.10 and 2.16 (acac-CH_3); 5.47 (acac-CH); 7.56 (H(7)); 7.67 (H(6)); 7.74 (H(11)); 7.8 (H(10)); 8.14 (H(8)); 8.53 (H(9)); 8.79 (H(2)); 8.84 (H(3)); 9.07 (H(12)). ^{13}C NMR: δ 100.8 (acac-CH); 118.2 (C(8)); 123.4 (C(9)); 125.2 (C(12)); 127.5 (C(11)); 129.67 (C(10); 129.72 (C(7)); 130.3 (C(6)); 140.2 (C(3)); 143.2 (C(2)). Found C, 55.1; H, 3.6; N, 5.8. $C_{21}H_{16}N_2O_2Pd \cdot H_2O$ calc.: C, 55.7; H, 4.0; N, 6.2%.

Dibenzo[*f*,*h*]quinoxaline (**20**) was treated with two equivalents of palladium acetate as described above to give, in 80% yield, μ-(dibenzo[*f*,*h*]quinoxaline-$C^{12},N^1:N^4,C^5$)bis[acetylacetonato]dipalladium(II) (**24**). M.p. > 350°C (dec.). IR

Table 3

Crystal data and details of data collection and refinement for **10**.

Formula	$C_{26}H_{24}N_2O_4Pd_2$
Molecular weight	641.3
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.021(3)
b (Å)	20.262(8)
c (Å)	13.350(4)
β (°)	107.47(2)
V (Å^3)	2328(1)
D_c (g cm^{-3})	1.830
Z	4
F (000)	1272
μ (cm^{-1})	15.4
Radiation	Mo-K_α
Wavelength (Å)	0.71069
Temperature (°C)	−100
Crystal dimensions (mm)	0.76×0.10×0.02
Scan mode	ω
2θ range (°)	3–50
Unique reflections	4093
Observed reflections ($I > 3\sigma(I)$)	2600
Number of parameters	307
R	0.039
R_w	0.043

ν(KBr) 755 cm^{-1} (C_6H_3). Insoluble in common NMR solvents. Found: C, 48.8; H, 3.5; N, 4.5. $C_{26}H_{22}N_2O_4Pd_2$ calc.: C, 48.9; H, 3.5; N, 4.4%.

Dibenzo[*a*,*c*]phenazine (**21**) was treated with lithium tetrachloropalladate to give, in 50% yield, acetylacetonato[dibenzo[*a*,*c*]phenazin-7-yl-C^2,N^6]palladium(II) (**23**). M.p. 253°C (dec.). ^{1}H NMR: δ 2.07 and 2.13 (acac-CH_3); 5.46 (acac-CH); 7.37 (H(9)); 7.56 (H(8)); 7.66 (H(13)); 7.8 (3H) (H(3), H(4) and H(12)); 7.96 (H(10)); 8.25 (H(1)); 8.34 (H(11)); 9.19 (H(14)); 9.71 (H(5)). ^{13}C NMR: δ 100.0 (acac-CH); 118.5, 123.1, 126.0, 126.1, 127.7, 129.1, 129.3, 129.5, 129.7, 130.6, 130.9. Found: C, 61.7; H, 3.5; N, 6.0. $C_{25}H_{18}N_2O_2Pd$ calc.: C, 61.9; H, 3.7; N, 5.8%.

Reaction of dibenzo[*a*,*c*]phenazine (**21**) and palladium acetate, as described above, gave in 45% yield μ-(dibenzo[*a*,*c*]phenazine-C^{14},N^1 : N^6,C^7)bis-(acetylacetonato)dipalladium(II) (**25**). M.p. 305–309°C (dec.). ^{1}H NMR: δ 2.19 and 2.20 (acac-CH_3); 5.54 (acac-CH); 7.45 (H(9,12)); 7.65 (H(8,13)); 7.80 (H(3,4)); 7.93 (H(10,11)), 9.81 (H(2,5)). Not sufficiently soluble to obtain ^{13}C NMR data. Found: C, 50.1; H, 3.4; N, 3.8. $C_{30}H_{24}N_2O_4Pd_2 \cdot H_2O$ calc.: C, 50.9; H, 3.7; N, 4.0%.

Crystallography

Table 3 lists crystal data and details of data collection and refinement for **10**. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo-K_α radiation. Cell parameters were determined by least-squares refinement, the setting angles of 22 accurately centred reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections

Table 4

Atom coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) for **10**

Atom	x	y	z	U_{eq} [a]
Pd(A)	−741(1)	5331(1)	3080(2)	23(1)
Pd(B)	5815(1)	4123(1)	6448(1)	26(1)
N(1A)	1171(7)	4991(3)	4150(5)	24(2)
N(1B)	3888(7)	4534(3)	5490(4)	23(2)
C(1A)	1785(8)	4424(4)	3910(5)	23(2)
C(1B)	3278(9)	4230(3)	4527(5)	24(2)
C(3A)	1862(8)	5310(4)	5056(5)	24(2)
C(3B)	3189(8)	5044(4)	5760(6)	21(2)
C(11A)	689(8)	4076(4)	3008(5)	24(2)
C(11B)	4339(9)	3747(4)	4316(6)	26(3)
C(12A)	−606(8)	4463(4)	2470(5)	22(2)
C(12B)	5622(9)	3579(4)	5204(6)	28(3)
C(13A)	−1759(10)	4175(4)	1656(6)	36(3)
C(13B)	6761(10)	3150(4)	5058(7)	36(3)
C(14A)	−1669(10)	3518(4)	1402(7)	39(3)
C(14B)	6699(10)	2925(4)	4071(7)	42(3)
C(15A)	−440(9)	3132(4)	1966(6)	33(3)
C(15B)	5495(10)	3139(4)	3181(7)	40(3)
C(16A)	741(9)	3408(4)	2777(6)	30(3)
C(16B)	4330(9)	3534(4)	3313(6)	32(3)
O(1A)	−2604(6)	5603(3)	1876(4)	28(2)
O(1B)	7692(6)	3627(3)	7312(4)	36(2)
O(2A)	−827(6)	6194(3)	3906(4)	30(2)
O(2B)	6025(6)	4835(3)	7605(4)	33(2)
C(21A)	−4686(10)	6247(5)	874(6)	42(3)
C(21B)	9878(10)	3374(5)	8720(7)	46(3)
C(22A)	−3367(9)	6132(4)	1868(6)	30(3)
C(22B)	8546(9)	3824(4)	8215(6)	33(3)
C(23A)	−3085(9)	6610(4)	2645(6)	33(3)
C(23B)	8336(9)	4380(4)	8747(6)	35(3)
C(24A)	−1915(10)	6619(4)	3602(6)	31(3)
C(24B)	7174(10)	4858(4)	8440(6)	37(3)
C(25A)	−1872(11)	7182(4)	4355(7)	39(3)
C(25B)	7230(11)	5451(5)	9129(6)	46(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

were monitored at regular intervals and found to show no significant change. The intensities were corrected for Lorentz and polarization effects but not for absorption. The space group was deduced from systematic absences.

The structure was solved by conventional direct methods, and refined by blocked cascade least-squares procedures. All non-hydrogen atoms were refined with anisotopic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. The function minimized was $\Sigma w(|F_o| - |F_o|)^2$, with $w = [\sigma^2(F_o)]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [26]

Final atom coordinates are listed in Table 4. Tables of structure factors, hydrogen atom coordinates, anisotropic thermal parameters, and equations of mean-planes are available from P.J.S.

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