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Cyclometallated compounds

IV*. Cyclopalladation of phenylpyrimidines and X-ray structure of a doubly cyclopalladated derivative of 4,6-diphenylpyrimidine

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Abstract

Seven phenylpyrimidines have been cyclopalladated with lithium tetrachloropalladate and the products characterised by ^{1}H and ^{13}C NMR studies of their acetylacetonate complexes. 6-Methyl-2,4-diphenylpyrimidine and 2,4,6-triphenylpyrimidine undergo preferential metallation of the 2-phenyl ring. 4-(*para*-Nitrophenyl)-6-phenylpyrimidine is selectively monopalladated in the unsubstituted phenyl ring. 4,6-Diphenylpyrimidine has been doubly cyclopalladated, and an X-ray crystal structure of its acetylacetonate complex refined to an R value of 0.053.

Introduction

The chemistry of cyclometallated compounds has been extensively studied during the past two decades [1–5]. Cyclometallation of 2-phenylpyridine [6], for example, results in the formation of complexes **1**, which differ from the well-studied 2,2′-bipyridine complexes **2** by replacement of one nitrogen donor with a carbon σ-donor. Thus natural extension of the exhaustive studies [7] of the $Ru(bpy)_3^{2+}$ cation have been to the synthesis, spectroscopic, and physicochemical studies of cyclometallated analogues [8–11].

Another area of active research in recent years has been the study of homo- and hetero-bimetallic complexes containing binucleating ligands such as 2,2′-bipyrimidine (**3**) and 3,6-bis(2′-pyridyl)pyridazine (**4**) [12–17]. However, surprisingly few cyclometallated analogues of such binucleating ligands have been reported. 2,2′-Bipyridine itself can act as a binucleating ligand after double cyclometallation, as has been demonstrated by the report of a complex of type **5** formed from the "roll-over"

* For part III see ref. 33.

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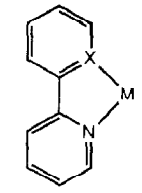

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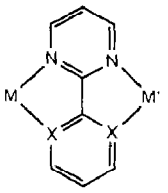
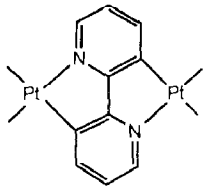
(2) X = N



(3) X=N
(6) X=C



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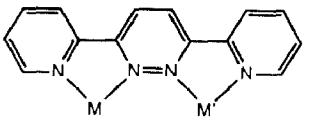

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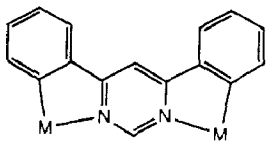


(7)

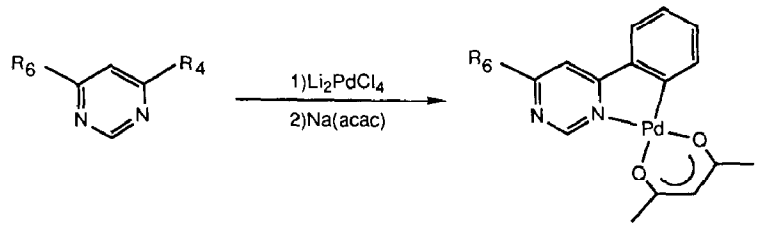
rearrangement of diaryl(2,2′-bipyridine)platinum(II) complexes [18]. Other ligands which have been doubly cyclometallated include azobenzene [19–21], tetraethyl α,α'-xylene diamines [22], 2,5-diphenylpyrazine [23], and a number of benzalazines [24–26].

We are currently undertaking an extensive study of the metallation reactions of ligands which are potentially capable of undergoing multiple cyclometallation. Particular emphasis is being given to analogues of well-studied binucleating ligands in which a chelating pyridine ring is replaced by a phenyl ring capable of undergoing cyclometallation. In this context we now report our results for the cyclopalladation reactions of several phenylpyrimidines. 2-Phenylpyrimidines are potentially capable of forming complexes of type **6**, isomeric with **5** and carbon analogues of **3**. Similarly, 4,6-diphenylpyrimidine could produce complexes of type **7**, which are carbon analogues of binuclear complexes of 4,6-bis(2′-pyridyl)pyrimidine [27].

Results and discussion

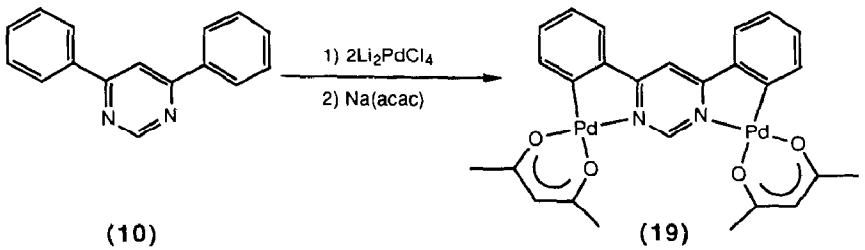
Cyclometallation reactions

The seven phenylpyrimidines **8–14** were each treated with lithium tetrachloropalladate to produce cyclopalladated chloro-bridged dimers. Infrared spectroscopy was used to confirm that cyclopalladation had occurred by utilizing the change in out-of-plane C–H deformation pattern from a monosubstituted benzene in the starting ligand to an *ortho*-disubstituted benzene ring in the product. The chloro-bridged dimers were then converted into acetylacetonate monomers by ligand exchange with sodium acetylacetonate. The structures of the products were readily determined by NMR spectroscopy by comparison with the spectra of the starting pyrimidines and by use of the known [28] ^{1}H and ^{13}C NMR shifts induced by Pd(acac). All the ^{1}H and ^{13}C NMR spectra of the starting pyrimidines and cyclopalladated acetylacetonate complexes were definitively assigned by a combination of one- and two-dimensional techniques by use of methods previously described [28]. Full assignments of the spectra are given in the Experimental section.



(8) R_4 = Ph , R_6 = H
(9) R_4= Me , R_6 = Ph
(10) R_4 = R_6 = Ph
(11) R_4 = p-NO_2-Ph , R_6 = Ph

(15) R_6 = H
(16) R_6 = Me
(17) R_6 =Ph
(18) R_6 = p-NO_2-Ph



(10) (19)

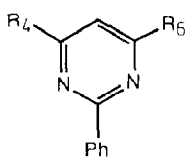
Reaction of 4-phenylpyrimidine (**8**) and 4-methyl-6-phenylpyrimidine (**9**) with lithium tetrachloropalladate and subsequent ligand exchange gave the monopalladated complexes **15** and **16**, respectively. In these cases there is no possibility of double cyclometallation. 4-Phenylpyrimidine has been previously cyclometallated with manganese(I) methylpentacarbonyl [29]. Similarly, reaction of 4,6-diphenylpyrimidine (**10**) with one equivalent of lithium tetrachloropalladate and ligand exchange gave the mono-palladated complex **17**, the NMR spectra of which clearly showed the presence of one *ortho*-disubstituted benzene ring and one monosubstituted benzene. Reaction of the mono-*para*-nitro derivative **11** gave only the complex **18**, with none of the product that would result from cyclopalladation of the nitrophenyl ring. This result is consistent with the generally accepted mechanism for cyclopalladation [30] in which the rate-determining step involves electrophilic attack by palladium on the phenyl ring. The electron-withdrawing effect of the nitro group is therefore sufficient to prevent cyclopalladation of one ring.

Reaction of 4,6-diphenylpyrimidine (**10**) with two equivalents of lithium tetrachloropalladate and subsequent ligand exchange gave in moderate yield a product which is insoluble in common NMR solvents. Infrared spectroscopy suggested that this was a doubly cyclopalladated product, and an X-ray crystal structure, described below, showed this to be the symmetrically dipalladated compound **19**. Thus after double cyclopalladation the ligand acts as a binucleating ligand for two palladium atoms which are geometrically arranged in a similar way to the metal atoms in complexes of the binucleating ligands 4,6-bis(2′-pyridyl)pyrimidine [27] and 4,6-bis(3,5-dimethylpyrazol-1-yl)pyrimidine [31]. Furthermore, the relative ease with which both mono- and dicyclopalladated complexes of **10** are prepared suggests the

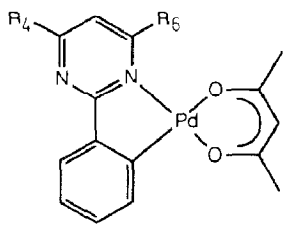
possibility of the preparation of heterobimetallic complexes. Recent reports have shown that related diimine ligands containing π electrons facilitate electronic and magnetic communication between metals in such binuclear complexes [12–17]. Attempts at the preparation of heterobicyclometallated complexes of **10** are currently underway.

4,6-Dimethyl-2-phenylpyrimidine (**12**) reacted with one equivalent of lithium tetrachloropalladate to give a product of stoichiometry $Pd(\mathbf{12})_2Cl_2$. Infrared spectroscopy indicated that cyclopalladation had not occurred, and hence the structure was assigned as a *trans*-dichlorobis(pyrimidine) complex in which **12** acts as a monodentate ligand. The *trans* geometry is that expected for square planar complexes of palladium with monodentate ligands. However, reaction of **12** with excess lithium tetrachloropalladate and ligand exchange gave the monocyclopalladated complex **20**, the structure of which was confirmed by NMR. An important feature of the ^1H NMR spectrum of **20** is the 0.28 ppm downfield shift of the C(6) methyl protons in **20** relative to their position in the starting ligand **12**. These protons lie close in space to an oxygen atom of the acetylacetonate ligand in **20**. No evidence for double cyclopalladation of **12** (to give a complex of type **6**) was detected after prolonged reaction with lithium tetrachloropalladate, or after reaction with palladium acetylacetonate in refluxing toluene.

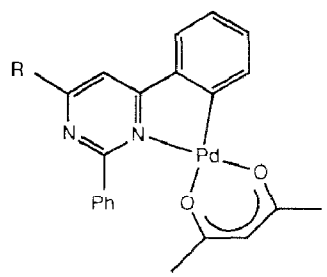
Reaction of 2,4-diphenyl-6-methylpyrimidine (**13**) with lithium tetrachloropalladate and subsequent ligand exchange gave a single product containing one cyclopalladated phenyl ring. Three isomeric structures **21**–**23** are possible for this product. The ^1H NMR spectrum clearly indicated that the 2-phenyl ring had undergone cyclopalladation. In particular, the existence of a doublet at 7.99 ppm for a proton in the cyclopalladated phenyl ring indicated that this proton is deshielded by a nitrogen lone pair, a situation found in structures **21** and **22** but not in **23**. Furthermore, the chemical shift of the *ortho* protons of the non-metallated phenyl ring (8.22 ppm) is similar to that for the 4-phenyl *ortho* protons in the starting ligand **13** (8.19 ppm; cf. 2-phenyl *ortho* protons at 8.58 ppm). Distinction between the two remaining possible structures **21** and **22** was made on the basis of the chemical shift of the methyl protons, which are shifted 0.30 ppm downfield in the complex from their position in the starting ligand. Thus, as in **20**, the methyl group must be spacially proximate to the acetylacetonate ligand and hence the structure of the reaction product is **21**.



(**12**) $R_6 = R_4 = Me$
(**13**) $R_6 = Ph$, $R_4 = Me$
(**14**) $R_6 = R_4 = Ph$



(**20**) $R_6 = R_4 = Me$
(**21**) $R_6 = Ph$, $R_4 = Me$
(**22**) $R_6 = Me$, $R_4 = Ph$
(**24**) $R_6 = R_4 = Pn$



(**23**) R = Me
(**25**) R = Ph

Table 1

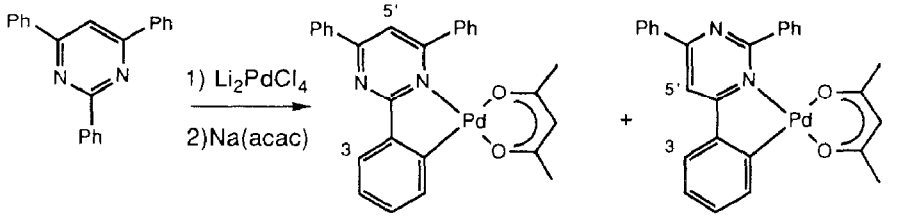
Selected ^{1}H and ^{13}C NMR chemical shifts for **24** and **25**

	24		**25**	
	Calc.	Obs.	Calc.	Obs.
H(3)	8.14	8.06	7.73	7.70
H(5′)	7.59	7.59	7.83	7.92
ortho-H's	8.29	8.28	8.29	8.25
	8.09	8.00	8.53	8.37
C(3)	127.0	126.9	124.3	124.0
C(5′)	111.0	114.0	107.0	106.7
ortho-C's	128.8	128.8	130.0	130.1
	127.4	127.4	127.5	127.3

Thus 2,4-diphenyl-6-methylpyrimidine (**13**) undergoes selective cyclopalladation of the 2-phenyl ring and with selective coordination to N(1) rather than N(3). The preference for reaction of the 2-phenyl ring can be explained as follows. In the cyclopalladated products the metallated phenyl ring and the pyrimidine ring are constrained, by the chelate ring, to lie coplanar. Metallation of the 4-phenyl ring to produce **23** would therefore result in a strong steric interaction between H(5) of the pyrimidine ring and H(3) of the metallated phenyl ring. This is similar to the well-studied steric interactions between *ortho* hydrogens in biphenyl derivatives. In contrast, metallation of the 2-phenyl ring does not result in such an interaction since H(3) of the phenyl ring interacts only with a nitrogen lone pair, a much more energetically favourable situation [32]. Furthermore, the nitrogen atom (N(1)) between the methyl and phenyl substituents in **13** is likely to be both more basic and more sterically accessible for coordination to a metal than that (N(3)) between the two phenyl rings. If N(1) is to act as the nitrogen donor then cyclopalladation can only produce **21**.

Reaction of 2,4,6-triphenylpyrimidine (**14**) with lithium tetrachloropalladate and subsequent ligand exchange gave a mixture of the two possible monocyclopalladated complexes in a ratio of ca. 2/1. Attempts to separate these two isomers by chromatography and fractional crystallisation were not successful, but distinction between the two isomers was possible, by means of NMR studies on a solution of the mixture. In particular, comparison of the observed chemical shifts with those predicted on the basis of the spectra for **15–21** and of structurally related cyclopalladated phenylpyrazoles [33] and the known shift effects induced by Pd(acac) [28] led to a clear distinction (Table 1) between the two products **24** and **25**. Full assignments of both the ^{1}H and ^{13}C NMR spectra of the mixture were made by a detailed series of one- and two-dimensional NMR experiments and are given in the Experimental Section. A notable feature in the ^{1}H NMR spectrum of the mixture was the relatively high field position of one of the acetylacetonate methyl groups in each complex (1.23 ppm in **24**; 1.27 ppm in **25**; cf. normal [28] value ca. 2.1 ppm). This can be accounted for in terms of the fact that the non-metallated phenyl ring adjacent to the coordinated nitrogen in **24** and **25** will lie orthogonal to the plane of the pyrimidine ring in order to minimise steric interactions. As a consequence the proximate *cis*-methyl group of the acetylacetonate ligand will lie over the shielding plane of this phenyl ring. A similar upfield shift is found for a structurally related triphenylpyrazole complex [33].

Thus, cyclopalladation of 2,4,6-triphenylpyrimidine (**14**) leads to a mixture of two mono-palladated isomers **24** and **25** which differ only in the transposition of a nitrogen atom and a C–H group, and so it is perhaps not surprising that attempts to separate the two isomers were not successful. It is noteworthy that the ratio of the products is the reverse of the statistical ratio of the number of phenyl rings in the starting material. That is, preferential metallation of the 2-phenyl ring occurs, as was observed for **13**. However, in **14** the two nitrogens are equivalent, and hence the selectivity for 2-phenyl metallation is attributed solely to the existence of the steric ortho interactions discussed above.



(14) **(24)** [70 %] **(25)** [30 %]

X-ray crystal structure of ***19***

In order to confirm the suspected doubly cyclopalladated structure of the product from 4,6-diphenylpyrimidine a single crystal X-ray analysis was carried out.

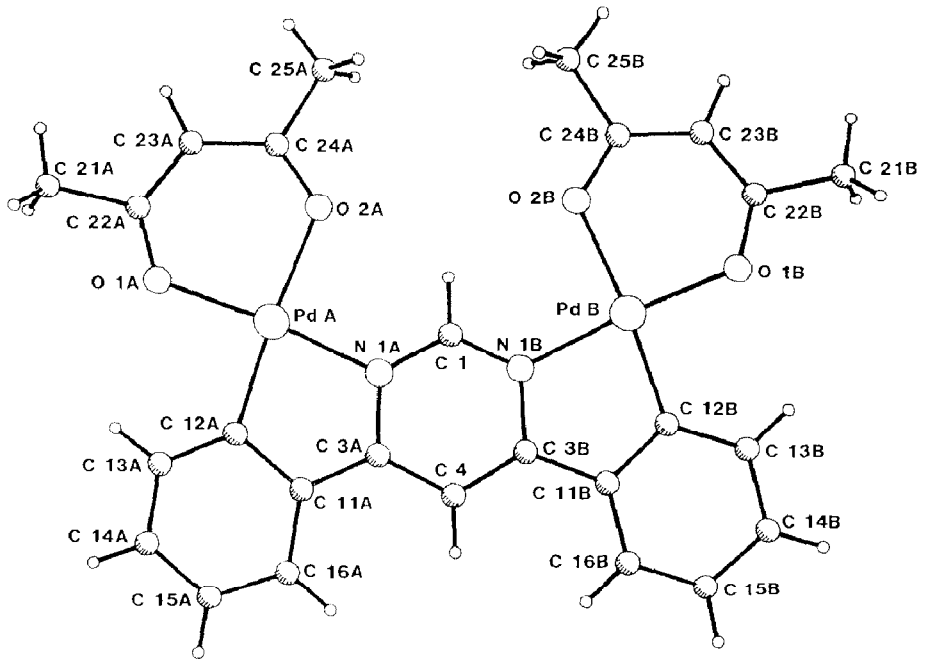


Fig. 1. Perspective view and atom labelling of the X-ray structure of **19**.

Table 2

Bond lengths [a] (Å) for **19**

Pd–N(1)	2.007(10)	2.006(10)
Pd–C(12)	1.967(12)	1.965(12)
Pd–O(1)	2.006(9)	1.991(9)
Pd–O(2)	2.084(9)	2.069(8)
C(1)–N(1)	1.319(16)	1.313(15)
N(1)–C(3)	1.376(16)	1.390(15)
C(3)–C(4)	1.399(18)	1.409(17)
C(3)–C(11)	1.413(18)	1.437(17)
C(11)–C(12)	1.433(17)	1.405(18)
C(11)–C(16)	1.415(18)	1.373(18)
C(12)–C(13)	1.368(18)	1.393(19)
C(13)–C(14)	1.365(20)	1.406(20)
C(14)–C(15)	1.375(20)	1.402(21)
C(15)–C(16)	1.386(20)	1.363(19)
O(1)–C(22)	1.249(18)	1.262(16)
O(2)–C(24)	1.271(15)	1.285(16)
C(21)–C(22)	1.511(21)	1.507(20)
C(22)–C(23)	1.395(20)	1.359(20)
C(23)–C(24)	1.403(18)	1.410(20)
C(24)–C(25)	1.516(19)	1.509(20)

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

Figure 1 shows a minimum overlap view of the structure and includes the atom labelling. Tables 2 and 3 list bond lengths and angles, respectively. The structure is confirmed as **19**, in which the ligand acts as a bis-bidentate binucleating ligand. The intramolecular Pd–Pd distance is 5.937(2) Å.

The coordination about each palladium atom is square planar, the maximum deviation from the meanplanes described by the palladium and their four coordinated atoms being < 0.05(1) Å. The Pd–C and Pd–N bond lengths are similar to those in related cyclopalladated complexes which incorporate an internal nitrogen

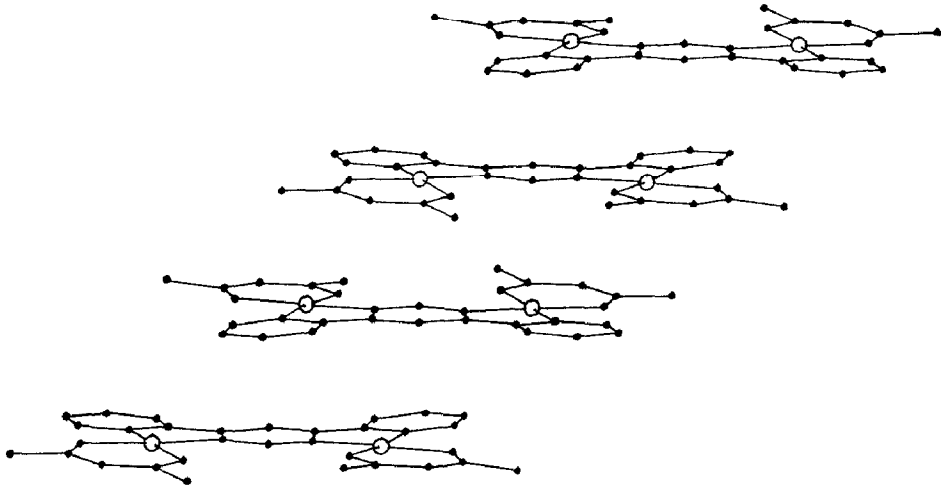


Fig. 2. Molecular packing diagram for **19**.

Table 3

Bond angles (°) for **19**

N(1)–Pd–C(12)	82.6(4)		81.8(5)
N(1)–Pd–O(1)	174.9(4)		174.8(4)
C(12)–Pd–O(1)	92.5(4)		93.1(5)
N(1)–Pd–O(2)	92.5(4)		92.7(4)
C(12)–Pd–O(2)	174.2(4)		173.9(4)
O(1)–Pd–O(2)	92.4(4)		92.5(4)
N(1A)–C(1)–N(1B)		125.4(11)	
C(3A)–C(4)–C(3B)		121.1(11)	
Pd–N(1)–C(1)	125.9(8)		126.9(8)
Pd–N(1)–C(3)	113.9(8)		114.2(7)
C(1)–N(1)–C(3)	120.1(11)		119.0(10)
N(1)–C(3)–C(4)	117.0(12)		117.4(10)
N(1)–C(3)–C(11)	114.9(11)		114.5(10)
C(4)–C(3)–C(11)	128.1(11)		128.1(11)
C(3)–C(11)–C(12)	116.1(11)		114.7(11)
C(3)–C(11)–C(16)	123.3(12)		125.5(12)
C(12)–C(11)–C(16)	120.5(11)		119.9(12)
Pd–C(12)–C(11)	112.3(8)		114.9(9)
Pd–C(12)–C(13)	130.0(9)		126.6(10)
C(11)–C(12)–C(13)	117.7(11)		118.5(11)
C(12)–C(13)–C(14)	122.0(13)		121.2(13)
C(13)–C(14)–C(15)	120.6(13)		118.4(13)
C(14)–C(15)–C(16)	121.3(13)		119.9(13)
C(11)–C(16)–C(15)	117.9(12)		122.0(13)
Pd–O(1)–C(22)	124.0(9)		124.6(8)
Pd–O(2)–C(24)	123.3(8)		123.2(8)
O(1)–C(22)–C(21)	117.3(13)		115.0(12)
O(1)–C(22)–C(23)	127.4(13)		127.0(13)
C(21)–C(22)–C(23)	115.3(12)		118.1(12)
C(22)–C(23)–C(24)	127.9(12)		128.7(13)
O(2)–C(24)–C(23)	124.7(12)		124.1(12)
O(2)–C(24)–C(25)	114.0(11)		114.6(11)
C(23)–C(24)–C(25)	121.2(11)		121.3(12)

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

donor [1–4,24,33–40]. The geometry of the acetylacetonate ligands is similar to that in other Pd(acac) complexes [33,40–43]. The different *trans* influences [33–40] of carbon and nitrogen are reflected in the unequal Pd–O bond lengths, with those *trans* of carbon significantly longer than those *trans* to nitrogen.

Comparable bonding geometry within the two halves of the complex is similar. However, the potential C_{2V} symmetry of the complex is destroyed in the solid state by small torsional distortions. For example, although all three aromatic rings are planar to within 0.02 Å, the mean planes through the two phenyl rings are inclined to the pyrimidine meanplane at angles of 4.7 and 1.5° and are mutually inclined at an angle of 6.1°. Similarly, a small interaction between the acetylacetonate ligands is relieved by twisting with C(25A) lying 0.17(2) Å above and C(25B) 0.18(2) Å below the overall mean plane through the complex.

As shown in Fig. 2 the molecules of the complex stack in layers separated by ca. 3.4. Å. The molecular packing suggests the existence of an electronic interaction

between the palladium d_{z^2} orbitals and the π electrons of the pyrimidine rings in adjacent molecules.

Experimental

Infrared spectra were recorded with a Shimadzu IR 27G spectrophotomer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL300 spectrometer for $CDCl_3$ solutions with Me_4Si as internal standard. Definite assignments of NMR spectra were made by a combination of one- and two-dimensional techniques as described in ref. 28. Mass spectra were recorded with a Kratos MS80RFA spectrometer.

Preparation and spectra of ligands

4-Phenylpyrimidine (**8**) was obtained commercially (Aldrich). ^1H NMR δ 7.52, m, 4-*meta* and 4-*para*; 7.71, dd, $^3J_{5,6}$ 5.4, $^5J_{5,2}$ 1.4 Hz, H(5); 8.09, m, 4-*ortho*; 8.76, d, $^3J_{6,5}$ 5.4 Hz, H(6); 9.27, d, $^5J_{2,5}$ 1.4 Hz, H(2). ^{13}C NMR δ 117.0, C5; 127.1, 4-*ortho*; 129.0, 4-*meta*; 131.0, 4-*para*; 136.4, 4-*ipso*; 157.4, C(6); 159.0, C2; 163.9, C(4).

4-Methyl-6-phenylpyrimidine (**9**) was prepared from benzoylacetone and formamide as previously described [44]. ^1H NMR δ 2.59, s, 4-CH_3; 7.50, m, 6-*meta* and 6-*para*; 7.58, d, $^5J_{5,2}$ 1.2 Hz, H(5); 8.07, m, 6-*ortho*; 9.14, d, $^5J_{2,5}$ 1.2 Hz, H(2). ^{13}C NMR δ 24.4, 4-CH_3; 116.4, C(5); 127.0, 6-*ortho*; 128.8, 6-*meta*; 130.7, 6-*para*; 136.6, 6-*ipso*; 158.5, C(2); 163.6, C6; 167.3, C(4).

4,6-Diphenylpyrimidine (**10**) was prepared from dibenzoylmethane and formamide. m.p. 95–97 °C; lit. [44] m.p. 102–103 °C. ^1H NMR δ 7.54, m, 4,6-*meta* and 4,6-*para*; 8.10, d, $^5J_{5,2}$ 1.3 Hz, H(5); 8.15, m, 4,6-*ortho*; 9.32, d, $^5J_{2,5}$ 1.3 Hz, H(2). ^{13}C NMR δ 112.8, C(5); 127.1, 4,6-*ortho*; 128.9, 4,6-*meta*; 130.8, 4,6-*para*; 136.9, 4.6-*ipso*; 159.1, C(2); 164.6, C(4) and C(6).

4-(*para*-Nitrophenyl)-6-phenylpyrimidine (**11**) was prepared from *para*-nitrodibenzoylmethane [45] and formamide. m.p. 153–155 °C; lit. [44] m.p. 157–159 °C. ^1H NMR δ 7.57, m, 6-*meta* and 6-*para*; 8.17, d, $^5J_{5,2}$ 1.3 Hz, H(5); 8.18, m, 6-*ortho*; 8.34, d, J 9.1 Hz, 4-*ortho*; 8.40, d, J 9.1 Hz, 4-*meta*; 9.38, d, $^5J_{2,5}$ 1.3 Hz, H(2). ^{13}C NMR δ 113.4, C(5); 124.2, 4-*meta*; 127.3, 6-*ortho*; 128.2, 4-*ortho*; 129.2, 6-*meta*; 131.4, 6-*para*; 159.4, C(2); 162.3 and 165.5, C(4) and C(6).

4,6-Dimethyl-2-phenylpyrimidine (**12**) was prepared from acetylacetone, benzamidine hydrochloride and aqueous potassium carbonate as previously described [46]. m.p. 79–81 °C; lit. [46] m.p. 81–83 °C. ^1H NMR δ 2.53, s, 4,6-CH_3; 6.92, s, H(5); 7.46, m, 2-*meta* and 2-*para*; 8.43, m, 2-*ortho*. ^{13}C NMR δ 24.2, 4,6-CH_3; 117.9, C(5); 128.1, 2-*ortho*; 128.3, 2-*meta*; 130.1, 2-*para*; 138.0, 2-*ipso*; 164.0, C(2); 166.6, C(4) and C(6).

2,4-Diphenyl-6-methylpyrimidine (**13**) was prepared by a similar reaction of benzoylacetone. m.p. 93–94 °C; lit. [47] m.p. 93–94 °C. ^1H NMR δ 2.63, s, 6-CH_3; 7.44, s, H(5); 7.50, m, 2-*meta*, 2-*para*, 4-*meta* and 4-*para*; 8.19, m, 4-*ortho*; 8.58, m, 2-*ortho*. ^{13}C NMR δ 24.7, 6-CH_3; 113.9, C(5); 127.1, 4-*ortho*; 128.2, 2-*ortho*; 128.3, 2-*meta*; 128.7, 4-*meta*; 130.3 and 130.5, 2-*para* and 4-*para*; 137.1, 4-*ipso*; 138.0, 2-*ipso*; 163.5, C(4); 164.1, C(2); 167.6, C(6).

2,4,6-Triphenylpyrimidine (**14**) was prepared from dibenzoylmethane, benzaldehyde and ammonium acetate as previously described [48]. ^1H NMR δ 7.53, m, 2-*meta*, 2-*para*, 4,6-*meta* and 4,6-*para*; 8.01, s, H(5); 8.29, m, 4,6-*ortho*. 8.73, m, 2-*ortho*. ^{13}C NMR δ 110.2, C(5); 127.2, 4,6-*ortho*; 128.3, 2-*ortho*; 128.4, 2-*meta*;

128.8, 4,6-*meta*; 130.5, 2-*para*; 130.7, 4,6-*para*; 137.5, 4,6-*ipso*; 138.1, 2-*ipso*; 164.4, C(2); 164.6, C(4) and C(6).

Preparation and spectra of complexes

General procedure: 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 added to a methanol solution of the ligand and the resulting solution stirred for 1–4 days. The precipitate of the di-μ-chlorodipalladium complex was filtered off and washed with methanol. The chloro-bridged dimer was then added to a methanol solution containing sodium methoxide and an excess 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.

Reaction of 4-phenylpyrimidine (**8**) with lithium tetrachloropalladate gave di-μ-chlorobis[2-(pyrimidin-4-yl)phenyl-C^1,N^3]dipalladium(II) in 96% yield. m.p. > 350 °C. ν(KBr) 745 cm^{-1} (1,2-C_6H_4). Ligand exchange with sodium acetylacetonate gave acetylacetonato[2-(pyrimidin-4-yl)phenyl-C^1,N^3]palladium(II) (**15**) in 65% yield. m.p. 253 °C. ^{1}H NMR δ 2.07 and 2.11, acac-CH_3; 5.42, acac-CH; 7.14, H(4); 7.26, H(5); 7.50, H(3); 7.53, H(5′); 7.63, H(6); 8.73, H(6′); 9.35, H(2′). ^{13}C NMR δ 27.6 and 28.0, acac-CH_3; 100.7, acac-CH; 114.1, C(5′); 124.5, C(3); 124.9, C(4); 131.2, C(5); 131.8, C(6); 157.5, C(2′); 158.1, C(6′); 186.7 and 188.5, acac-CO. Found: C, 50.2; H, 4.0; N, 7.5. $C_{15}H_{14}N_2O_2Pd$ calc.: C, 50.0; H, 3.9; N, 7.8%.

Reaction of 4-methyl-6-phenylpyrimidine (**9**) with lithium tetrachloropalladate gave di-μ-chlorobis[2-(6-methylpyrimidin-4-yl)phenyl-C^1,N^3]dipalladium(II) in 92% yield. m.p. > 300 °C. ν(KBr) 740 cm^{-1} (1,2-C_6H_4). Ligand exchange with sodium acetylacetonate gave acetylacetonato[2-(6-methylpyrimidin-4-yl)phenyl-C^1,N^3]palladium(II) (**16**) in 60% yield. m.p. 245 °C (dec). ^{1}H NMR δ 2.06 and 2.11, acac-CH_3; 2.63, 6′-CH_3; 5.41, acac-CH; 7.13, H(4); 7.25, H(5); 7.40, H(5′); 7.50, H(3); 7.62, H(6); 9.20, H(2′). ^{13}C NMR δ 24.7, 6′-CH_3; 27.6 and 27.9, acac-CH_3; 100.5 acac-CH; 113.2, C(5′); 123.9, C(3); 124.6, C(4); 130.7, C(5); 131.6, C(6); 156.5, C(2′); 186.4 and 188.2, acac-CO. M^+ 376.0260, $C_{16}H_{16}N_2O_2{}^{108}Pd$, calc. M^+ 376.0251. Found: C, 49.7; H, 4.2. $C_{16}H_{16}N_2O_2Pd.1/2H_2O$ calc.: C, 50.1; H, 4.4%.

Reaction of 4,6-diphenylpyrimidine (**10**) with one equivalent of lithium tetrachloropalladate gave di-μ-chlorobis[2-(6-phenylpyrimidin-4-yl)phenyl-C^1,N^3]dipalladium(II) in 95% yield. m.p. > 350 °C. ν(KBr) 755 and 695 (C_6H_5), 750 cm^{-1} (1,2-C_6H_4). Found: C, 48.7; H, 3.0; N, 6.9. $[C_{16}H_{11}N_2ClPd.H_2O]_2$ calc.: C, 49.1; H, 3.3; N, 7.2%. Ligand exchange with sodium acetylacetonate gave acetylacetonato[2-(6-phenylpyrimidin-4-yl)phenyl-C^1,N^3]palladium(II) (**17**) in 70% yield. m.p. 203–205 °C. ^{1}H NMR δ 2.07 and 2.11, acac-CH_3; 5.43, acac-CH; 7.16, H(4); 7.27, H(5); 7.56, 6′-*meta*; 7.57, 6′-*para*; 7.62, H(3); 7.65, H(6); 7.92, H(5′); 8.16, 6′-*ortho*; 9.36, H(2′). ^{13}C NMR δ 27.7 and 28.1, acac-CH_3; 100.6, acac-CH; 109.4, C(5′); 124.1, C(3); 124.7, C(4); 127.4, 6′-*ortho*; 129.1, 6′-*meta*; 130.9, C(5); 131.7, 6′-*para*; 131.8, C(6); 157.0, C(2′); 186.5 and 188.3, acac-CO. Found: C, 56.6; H, 3.9; N, 6.7. $C_{21}H_{18}N_2O_2Pd \cdot 1/2H_2O$ calc.: C, 56.6; H, 4.3; N, 6.3%. Reaction of **10** with two equivalents of lithium tetrachloropalladate gave the doubly metallated chloro-bridged polymer in 70% yield. m.p. > 300 °C. ν(KBr) 740 cm^{-1} (1,2-C_6H_4). Found: C, 37.6; H, 1.8; N, 5.2. $[C_{16}H_{10}N_2Cl_2Pd_2]_n$ calc.: C, 37.4; H, 2.0; N, 5.5%. Ligand exchange with sodium acetylacetonate gave μ-(4,6-diphenylpyrimidine-$C^2,N^1:N^3,C^2$)bis[(ace-

tylacetonato)palladium(II)] (**19**) in 88% yield. m.p. 270 °C (dec.). Insoluble in common NMR solvents. Found: C, 48.2; H, 3.8; N, 4.4. $C_{26}H_{24}N_2O_4Pd_2$ calc.: C, 48.7; H, 3.8; N, 4.3%.

Reaction of 4-(*para*-nitrophenyl)-6-phenylpyrimidine (**11**) with lithium tetrachloropalladate and subsequent ligand exchange gave acetylacetonato[2-(6-*para*-nitrophenylpyrimidin-4-yl)phenyl-C^1,N^3]palladium(II) (**18**) in 50% yield. m.p. 268–270 °C (dec). ^{1}H NMR δ 2.09 and 2.12, acac-CH_3; 5.44, acac-CH; 7.19, H(4); 7.31, H(5); 7.64, H(3); 7.67, H(6); 7.97, H(5′); 8.35, 6′-*ortho*; 8.40, 6′-*meta*; 9.43, H(2′). ^{13}C NMR δ 27.6 and 28.0, acac-CH_3; 100.8, acac-CH; 110.2, C(5′); 124.3, 6′-*meta*; 124.5, C(3); 125.0, C(4); 128.5, 6′-*ortho*; 131.6, C(5); 132.0, C(6); 157.4, C(2′). Found: C, 51.8; H, 3.6; N, 8.4. $C_{21}H_{17}N_3O_4Pd$ calc.: C, 52.4; H, 3.6; N, 8.7%.

Reaction of 4,6-dimethyl-2-phenylpyrimidine (**12**) with one equivalent of lithium tetrachloropalladate gave *trans*-bis(4,6-dimethyl-2-phenylpyrimidine)-dichloropalladium(II) in 90% yield. m.p. > 350 °C. ν(KBr) 697 and 762 cm^{-1} (C_6H_5). ^{1}H NMR δ 2.52, 4-CH_3; 2.64, 6-CH_3; 6.98, H(5); 7.61, 2-*meta*; 7.63, 2-*para*; 8.06, 2-*ortho*. ^{13}C NMR δ 23.8, 4-CH_3; 26.2, 6-CH_3; 120.1, C(5); 128.2, 2-*meta*; 129.6, 2-*para*; 130.4, 2-*ortho*; 139.5, 2-*ipso*; 168.3, 168.8 and 168.9, C(2), C(4) and C(6). Found: C, 52.3; H, 4.5; N, 10.0. $C_{24}H_{24}N_4Cl_2Pd$ calc.: C, 52.8; H, 4.4; N, 10.3%.

Reaction with excess lithium tetrachloropalladate gave di-μ-chlorobis[2-(4,6-dimethylpyrimidin-2-yl)phenyl-C^1,N^1]dipalladium(II) in 48% yield. m.p. > 300 °C. ν(KBr) 752 cm^{-1} (1,2-C_6H_4). Found: C, 42.8; H, 3.4; N, 8.1. $C_{24}H_{22}N_4Cl_2Pd_2 \cdot H_2O$ calc.: 43.1; H, 3.6; N, 8.4%. Ligand exchange gave acetylacetonato[2-(4,6-dimethylpyrimidin-2-yl)phenyl-C^1,N^1]palladium(II) (**20**) in 60% yield. m.p. 152 °C. ^{1}H NMR δ 1.97 and 2.10, acac-CH_3; 2.52, 4′-CH_3; 2.81, 6′-CH_3; 5.40, acac-CH; 6.79, H(5′); 7.12, H(4); 7.20, H(5); 7.61, H(6); 7.81, H(3). ^{13}C NMR δ 24.0 and 24.1, 4′-CH_3 and 6′-CH_3; 27.8 and 27.9, acac-CH_3; 99.8, acac-CH; 118.7, C(5′); 124.9, C(4); 126.7, C(3); 129.6, C(6); 130.0, C(5); 186.2 and 187.7, acac-CO. Found: C, 50.6, H, 4.5; N, 7.1. $C_{17}H_{18}N_2O_2Pd \cdot H_2O$ calc.: C, 50.2; H, 4.9; N, 6.9%.

Reaction of 2,4-diphenyl-6-methylpyrimidine (**13**) with lithium tetrachlorpalladate gave di-μ-chlorobis[2-(6-methyl-4-phenylpyrimidin-2-yl)-phenyl-C^1,N^1]palladium(II) in 76% yield. m.p. 330 °C (dec). ν(KBr) 697 and 758 (C_6H_5), 755 cm^{-1} (1,2-C_6H_4). Found: C, 51.5; H, 3.3; N, 7.0. $C_{34}H_{26}N_4Cl_2Pd_2 \cdot H_2O$ calc.: C, 51.5; H, 3.6; N, 7.1%. Ligand exchange gave acetylacetonato[2-(6-methyl-4-phenylpyrimidin-2-yl)phenyl-C^1,N^1]palladium(II) (**21**) in 94% yield. m.p. 220 °C. ^{1}H NMR δ 2.00 and 2.12, acac-CH_3; 2.93, 6′-CH_3; 5.42, acac-CH; 7.17, H(4); 7.24, H(5); 7.35, H(5′); 7.54, 4′-*meta*; 7.55, 4′-*para*; 7.65, H(6); 7.99, H(3); 8.22, 4′-*ortho*. ^{13}C NMR δ 24.4, 6′-CH_3; 27.6 and 27.8, acac-CH_3; 99.7, acac-CH; 114.3, C(5′); 124.8, C(4); 126.8, C(3); 127.3, 4′-*ortho*; 128.8, 4′-*meta*; 129.5, C(6); 130.0, C(5); 131.4, 4′-*para*; 186.0 and 187.6, acac-CO. Found: C, 57.8; H, 4.5; N, 6.6. $C_{22}H_{20}N_2O_2Pd$ calc.: C, 58.6, H, 4.5; N, 6.2%.

Reaction of 2,4,6-triphenylpyrimidine (**14**) with lithium tetrachloropalladate and subsequent ligand exchange gave, in 55% yield, a 2/1 mixture of acetylacetonato[2-(4,6-diphenylpyrimidin-2-yl)phenyl-C^1,N^1]palladium(II) (**24**). ^{1}H NMR δ 1.23 and 2.02, acac-CH_3; 5.13, acac-CH; 7.22, H(4); 7.28, H(5); 7.47, 6′-*para*; 7.48, 6′-*meta*; 7.56, 4′-*meta* and 4′-*para*; 7.59, H(5′); 7.65, H(6); 8.00, 6′-*ortho*; 8.06, H(3); 8.28, 4′-*ortho*. ^{13}C NMR δ 26.7 and 27.4, acac-CH_3; 99.5, acac-CH; 114.0, C(5′); 124.8, C(4); 126.9, C(3); 127.4, 4′-*ortho*; 127.7, 6′-*meta*; 128.8, 6′-*ortho*; 128.9, 4′-*meta*;

129.9, C(6); 130.0, 6′-*para*; 130.1, C(5); 131.6, 4′-*para*; 185.0 and 187.1, acac-CO; and acetylacetonato[2-(2,6-diphenylpyrimidin-4-yl)phenyl-C^1,N^3]palladium(II) (**25**). ^{1}H NMR δ 1.27 and 2.03, acac-CH_3; 5.15, acac-CH; 7.21, H(4); 7.28, H(5); 7.45, 2′-*meta* and 2′-*para*; 7.56, 6′-*meta* and 6′-*para*; 7.67, H(6); 7.70, H(3); 7.92, H(5′); 8.25, 6′-*ortho*; 8.37, 2′-*ortho*. ^{13}C NMR δ 26.7 and 27.4, acac-CH_3; 99.6, acac-CH; 106.7, C(5′); 124.0, C(3); 124.7, C(4); 127.2, 2′-*meta*; 127.3, 6′-*ortho*; 128.8, 6′-*meta*; 129.9, C(6); 130.1, 2′-*ortho*; 130.2, C(5); 131.1 and 131.5, 2′-*para* and 6′-*para*, m.p. (for the mixture) 220–225 °C. Found: C, 61.9; H, 4.1; N, 5.4. $C_{27}H_{22}N_2O_2Pd \cdot 1/2H_2O$ calc.: C, 62.1; H, 4.4; N, 5.5%.

Crystallography

Table 4 lists crystal data and X-ray experimental details for **19**. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo-K_α radiation. Cell parameters were determined by least squared refinement, the setting angles of 25 accurately centred reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects but not for absorption. The space group followed from systematic absences.

The structure was solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. All non-hydrogen atoms were

Table 4

Crystal data and details of X-ray study of **19**

Formula	$C_{26}H_{24}N_2O_4Pd_2$
Molecular weight	641.3
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.652(3)
b (Å)	13.610(5)
c (Å)	18.034(6)
β (°)	90.64(3)
V (Å^3)	2369(1)
D_c (g cm^{-3})	1.798
Z	4
$F(000)$	1272
μ (cm^{-1})	15.2
Radiation	Mo-K_α
Wavelength (Å)	0.71069
Temperature (°C)	20
Crystal dimensions (mm)	$0.69 \times 0.05 \times 0.02$
Scan mode	$\theta/2\theta$
2θ range (°)	4–48
Unique reflections	3726
Observed reflections ($I > 3\sigma(I)$)	1904
Number of parameters	307
g	0.0017
R	0.053
wR	0.064

Table 5

Atom coordinates ($\times 10^4$) and temperature factors [a] ($Å^2 \times 10^3$) for **19**

Atom	x	y	z	U
Pd(A)	517(1)	6348(1)	5498(1)	36(1)
Pd(B)	4852(1)	4223(1)	3826(1)	37(1)
C(1)	2697(13)	5141(9)	4777(7)	36(4)
N(1A)	1838(10)	5231(7)	5337(5)	36(4)
N(1B)	3530(10)	4394(7)	4667(5)	31(3)
C(3A)	1734(15)	4491(9)	5853(7)	42(5)
C(3B)	3535(12)	3622(9)	5171(7)	34(4)
C(4)	2626(13)	3688(8)	5775(6)	37(4)
C(11A)	756(13)	4661(9)	6416(7)	37(4)
C(11B)	4479(13)	2841(9)	4999(7)	38(5)
C(12A)	−56(12)	5537(8)	6343(7)	32(4)
C(12B)	5224(14)	2977(9)	4342(7)	40(5)
C(13A)	−1077(15)	5693(10)	6850(7)	50(5)
C(13B)	6174(14)	2259(10)	4136(8)	47(5)
C(14A)	−1332(15)	5044(11)	7409(8)	53(5)
C(14B)	6357(16)	1400(11)	4559(8)	56(6)
C(15A)	−548(15)	4206(10)	7487(8)	56(6)
C(15B)	5573(15)	1285(9)	5203(8)	53(5)
C(16A)	507(15)	3990(10)	6999(7)	47(5)
C(16B)	4685(15)	2008(9)	5416(8)	50(5)
O(1A)	−823(9)	7420(7)	5751(5)	50(4)
O(1B)	6193(9)	3929(7)	3025(5)	51(3)
O(2A)	1164(10)	7075(6)	4545(5)	46(3)
O(2B)	4397(9)	5593(6)	3391(5)	42(3)
C(21A)	−1895(15)	8978(10)	5706(8)	58(6)
C(21B)	7584(17)	4142(12)	1984(8)	69(7)
C(22B)	−938(16)	8204(11)	5397(8)	53(6)
C(22B)	6497(14)	4513(10)	2508(7)	43(5)
C(23A)	−271(14)	8461(9)	4742(7)	46(5)
C(23B)	5960(15)	5423(11)	2387(7)	54(5)
C(24A)	718(14)	7917(9)	4353(7)	44(5)
C(24B)	4963(14)	5934(10)	2803(7)	47(5)
C(25A)	1289(16)	8281(10)	3623(7)	57(6)
C(25B)	4519(16)	6962(10)	2597(8)	57(6)

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

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 $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [49].

Final atom coordinates are listed in Table 5. Tabulations of structure factors, hydrogen atom coordinates, anisotropic thermal parameters and equations of mean planes are available from P.J.S.

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