ELSEVIER

Journal of Organometallic Chemistry 579 (1999) 97–105

Journal of Organometallic Chemistry

Cyclometallated compounds. XIII. Cyclopalladation of 2-phenoxypyridine and structurally-related compounds

Duncan J. de Geest, Brendan J. O'Keefe, Peter J. Steel *

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received 30 October 1998

Abstract

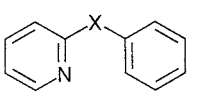
2-Phenoxypyridine and 2-phenylsulfanylpyridine are cyclopalladated readily by palladium acetate to give six-membered metallocycles. Extension to the three isomeric bis(2-pyridyloxy)benzenes leads to a new series of doubly-cyclopalladated compounds. In contrast, 3-6-diphenoxypyridazine and 4-6-diphenoxypyrimidine only undergo monopalladation, whilst their sulfur analogues are resistant to cyclopalladation. All cyclometallated compounds are converted to their acetylacetonate derivatives and the X-ray crystal structure of one of these is described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclometallation reactions; Palladium complexes; Acetylacetonate complexes; Crystal structure

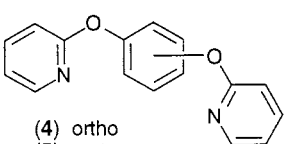
1. Introduction

Cyclopalladated compounds have attracted renewed interest in recent years as metallomesogens [1]. In particular, acetylacetonate (acac) derivatives of various cyclopalladated ligands, including doubly-metallated examples, have been the subject of several recent studies [2]. The vast majority of cyclopalladated compounds contain a five-membered metallocycle [3]. However, six-membered palladocycles are known, as exemplified by the cyclopalladation of 2-benzylpyridine (**1**) [4], in a less facile reaction than that of 2-phenylpyridine, which produces a five-membered ring.

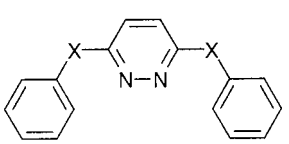
Since cyclopalladation of such ligands is well known to proceed via an electrophilic substitution process [5], it was felt that replacement of the methylene spacer of **1** by an oxygen, or sulfur, atom would activate the phenyl ring towards electrophilic substitution, thereby promoting the formation of a six-membered palladocycle. We thus report the cyclopalladation reactions of 2-phenoxypyridine (**2**) and 2-phenylsulfanylpyridine (**3**). Furthermore, we have incorporated these structural motifs into ligands potentially capable of undergoing double cyclopalladations and report the reactions of the three isomeric bis(2-pyridyloxy)benzenes (**4**–**6**) and the pyridazine and pyrimidine derivatives (**7**–**10**). All the cyclopalladated compounds have been converted to their acac derivatives and the structure of one of these has been determined by single crystal X-ray crystallography.



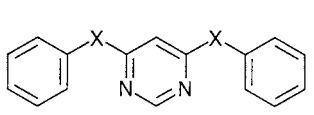
(1) X = CH_2
(2) X = O
(3) X = S



(4) ortho
(5) meta
(6) para



(7) X = O
(8) X = S



(9) X = O
(10) X = S

* Corresponding author. Tel.: +64-3-3642432; fax: +64-3-3642110.

E-mail address: p.steel@chem.canterbury.ac.nz (P.J. Steel)

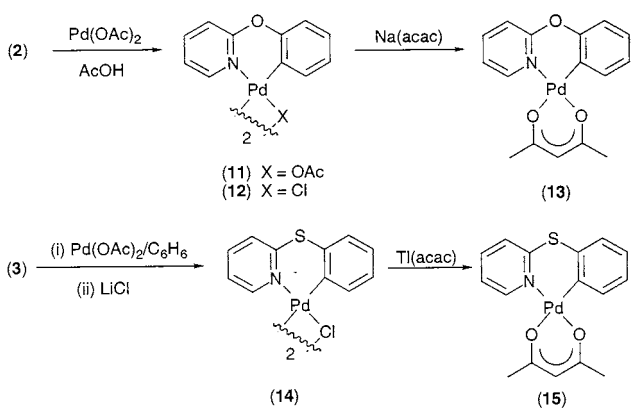
PII: S0022-328X(98)01203-0

2. Results and discussion

Cyclopalladations are usually carried out by reaction of the ligand with either lithium tetrachloropalladate or palladium acetate. Upon reaction with lithium tetrachloropalladate in methanol, 2-phenoxypyridine (**2**) gave a coordination complex, rather than a cyclopalladated compound [6]. However, reaction with palladium acetate in acetic acid at room temperature proceeded smoothly to give the acetate-bridged cyclopalladated dimer **11**, in 69% yield. Ligand metathesis of **11** with excess lithium chloride gave the chloro-bridged dimer, **12**, in good yield, and this, in turn, was converted to the mononuclear acac complex, **13**, by reaction with sodium acac (Scheme 1).

Complete assignment of the ^{1}H-NMR spectrum of **13** was complicated by the overlap of the resonances for H-5, H-4′ and H-5′. This problem was overcome conveniently by the use of 1D-TOCSY experiments, which enable the resolution of signals within isolated spin systems [7]. Thus, irradiation of the doublet at 8.81 ppm (assigned to H-6) provided the entry into the pyridyl ring spin system, allowing the assignment of the triplet at 7.08 ppm to H-5. Similarly, irradiations of the signals due to H6′ (6.98 ppm) and H3′ (7.62 ppm), with short mixing times, resulted in magnetisation transfer only to the adjacent protons H-5′ and H4′, respectively. The ^{13}C-NMR spectrum of **13** was assigned subsequently by means of an HMQC experiment (see Section 4).

Reaction of the corresponding thioether, **3**, with palladium acetate in acetic acid at room temperature, or under reflux, failed to produce the desired acetate-bridged dimer. However, reaction with palladium acetate in benzene, under conditions described recently for the cyclopalladation of primary and secondary benzylamines [8], successfully induced cyclopalladation, to give, following acetate–chloride exchange, a chloro-bridged dimer **14**, in reasonable yield. Subsequent ligand exchange of **14** with thallium acac gave the monomeric palladium acac complex, **15**, albeit in rather poor yield (Scheme 1). The ^{1}H- and ^{13}C-NMR spectra were assigned completely by a combination of one- and two-dimensional NMR techniques.

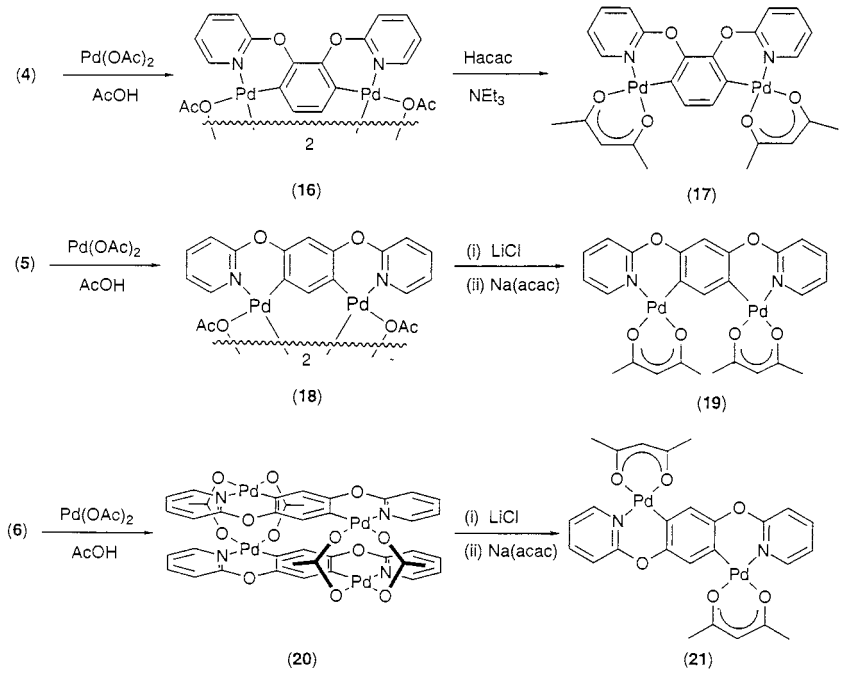


Scheme 1.

Having established that both **2** and **3** can be cyclopalladated with the formation of six-membered metallocyclic rings, consideration was given to the incorporation of two of these structural motifs within individual ligands, which would, therefore, be potentially capable of undergoing double cyclopalladation reactions. Doubly cyclopalladated compounds have been the subject of much study in recent years [9,10], with particular interest in compounds containing a doubly-palladated benzene ring [11]. The three isomeric bis(2-pyridyloxy)benzenes (**4**–**6**) are each potentially capable of undergoing such double metallations of a benzene ring. We have described previously the synthesis and coordination chemistry of these three ligands [12,13] and have now examined their cyclopalladation chemistry.

Reaction of 1,2-bis(2-pyridyloxy)benzene (**4**) with two equivalents of palladium acetate in refluxing acetic acid gave a product, in 67% yield, within which the central benzene ring is doubly metallated. Whereas single-metallation reactions using palladium acetate lead to acetate-bridged dimeric products [14], the products resulting from double-metallation of a ligand are represented usually as polymeric species. However, we have shown recently that this is not necessarily so and that tetranuclear molecular structures can be formed [14]. In the present example, we believe that the product, **16**, exists as a tetranuclear dimer with the two ligand components being bridged by four acetate ligands (Scheme 2). Direct ligand exchange of **16** with acetylacetone, in the presence of triethylamine, gave the dipalladium acac complex, **17**, in 72% yield. The FAB mass spectrum of this compound showed a strong cluster of peaks centred around $m/z = 674$ a.m.u., with the correct isotopic distribution for two palladium atoms. The ^{1}H- and ^{13}C-NMR spectra were completely assigned by a combination of one- and two-dimensional techniques (see Section 4).

Whereas the *ortho* isomer (**4**) can only undergo cyclometallation in the 3- and 6-positions, the *meta* isomer (**5**) has two possible modes of reaction: either single metallation in the 2-position, with tridentate coordination involving both of the pyridyl rings, or double metallation in the 4- and 6-positions. For related compounds, both modes of reaction are known [15]. In the event, reaction of the *meta* isomer, **5**, with two equivalents of palladium acetate in acetic acid, at room temperature, gave the 4,6-dicyclopalladated complex, **18**, in modest yield. Again, we believe that this complex is a tetranuclear dimer with four bridging acetate ligands. The cleft-shaped topology of such a species would be similar to that of a doubly-cyclopalladated product



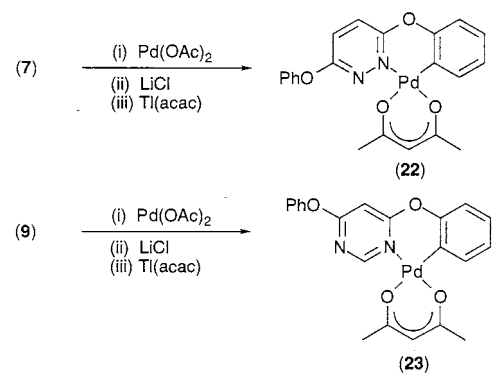
Scheme 2.

from reaction of 1,3-bis(1-ethylbenzimidazol-2-yl)-benzene, which has recently been crystallographically characterised [16]. Ligand metathesis of **18** with excess lithium chloride gave the corresponding chloro-bridged complex in 74% yield, and this was, in turn, converted into the dipalladium acac complex **19**. This compound was characterised fully by elemental analysis, mass spectrometry, infrared and NMR spectroscopy (see Section 4).

Reaction of the *para*-isomer **6** with two equivalents of palladium acetate in acetic acid, at room temperature, gave a doubly-palladated complex. This ligand can also undergo double metallation to give two possible regioisomers, depending upon whether it reacts in the 2- and 3-positions or the 2- and 5-positions. By analogy with our recently reported product from the double palladation of 1,4-bis(benzothiazol-2-yl)benzene [14], we believe that this complex has the box-shaped tetranuclear structure (**20**) shown in Scheme 2, with palladation occurring in the 2- and 5-positions, for steric reasons. This is supported by the FAB mass spectrum which shows a highest-mass cluster of peaks centred around 1186 a.m.u., with a Pd_4 isotopic distribution. Ligand metathesis of **20** with excess lithium chloride gave a chloro-bridged complex, in 92% yield, which in turn was converted into the monomeric dipalladium acac complex, **21**. This complex is insoluble in common NMR solvents.

This series of doubly-cyclopalladated complexes represents the first examples of double cyclopalladation with the formation of two six-membered rings, unsupported by additional donor groups [15]. Within this series, the binucleating ligands have utilised a phenyl ring as the central component, with two appended heterocycles. An alternative approach to new doubly-cyclopalladated compounds would be to use a heterocycle as the central component with two attached phenoxy groups. This is the case with the four ligands (**7–10**), containing central pyridazine and pyrimidine cores with two suitably placed phenoxy or phenylsulfanyl substituents. Previously, we have shown that diazines with two directly attached phenyl rings can be made to undergo double cyclopalladations [17].

The two pyridazine derivatives, (**7**) and (**8**), were prepared from 3,6-dichloropyridazine according to literature procedures [18,19]. Reaction of the pyridazine bis-ether, **7**, with one equivalent of palladium acetate in benzene gave the acetate-bridged dimer, [Pd(**7**–H)$OAc]_2$, which, after metathesis to the corresponding chloride and acac exchange, gave the mononuclear



Scheme 3.

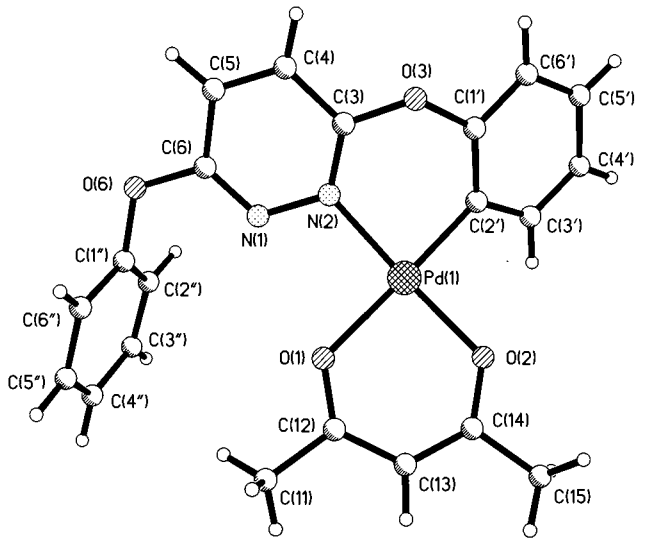


Fig. 1. Perspective view and atom labelling of one of the two independent molecules of **22**. Selected bond lengths (Å) and angles (°) for the Pd1 [and Pd1A] molecule: Pd1–C2′ 1.972(3) [1.974(3)], Pd1–N2 2.012(2) [2.006(2)], Pd–O1 2.080(2) [2.076(2)], Pd–O2 2.032(2) [2.018(2)]; C2′–Pd1–N2 87.3(2) [87.6(1)], O1–Pd1–O2 91.66(8) [91.92(7)], C3–O3–C1′ 119.5(2) [120.7(2)].

complex **22**, in good yield (Scheme 3). This monopalladated complex was again characterised fully by standard NMR techniques. A number of attempts were made to doubly-metallate **7** with palladium acetate (in a variety of solvents and under a range of reaction conditions), but these invariably gave only the singly-cyclopalladated product. This is despite the fact that a pyridazine subunit is well-known to act as a good bridging component in the formation of binuclear metal coordination complexes [20]. Furthermore, all attempts to react the sulfur analogue (**8**) with palladium acetate, in either acetic acid or benzene, failed to produce even a singly-cyclopalladated product. In view of these findings, it was decided to perform a single crystal X-ray structure determination of **22**, in order to examine its exact structure in more detail.

The cyclopalladated acac complex of 3,6-diphenoxypyridazine crystallises in the orthorhombic space group $P2_12_12_1$, with two independent molecules of **22** in the asymmetric unit. Fig. 1 shows a perspective view and atom labelling of the structure of one of the molecules, with selected interatomic distances and angles. The two independent molecules have similar bonding geometries, but differ in the conformations of the non-metallated phenoxy substituents. Specifically, the phenoxy and pyridazine ring meanplanes are inclined at an angle of 72.7° in the molecule shown but at an angle of 63.7° in the other molecule in the asymmetric unit.

The four phenyl and two pyridazine rings are each essentially planar, with the maximum displacement from the plane being 0.023(4) Å for C1′A. The six-membered metallocycles each exist in a shallow boat conformation: Pd1 and O3 are 0.640(2) and 0.368(3) Å, respectively, above the meanplane defined by N2, C3, C1′ and C2′; and Pd1A and O3A are 0.656(2) and 0.347(3) Å, respectively, above the meanplane defined by N2A, C3A, C1′A and C2′A. The cyclometallated phenyl ring is inclined to the pyridazine ring at an angle of 38.6° in one molecule and at 37.0° in the other.

The palladium atoms have approximately square planar coordination to the CNO_2 donor set (Fig. 1) and the Pd–C, Pd–N bond lengths are similar to those in related cyclopalladated complexes which incorporate a nitrogen donor in a five-membered metallocycle [21]. The geometries of the two acetylacetonate subunits are very similar to those that have been determined for related structures [21]. Of particular note is the difference in the Pd–O bond lengths, with those *trans* to carbon being significantly longer than those *trans* to nitrogen, this variation being consistent with those seen in related structures and a reflection of the different *trans* influences of carbanion and nitrogen donors [21]. This complex represents the first example of a crystallographically characterised structure incorporating a bidentate ligand with a nitrogen donor in a six-membered metallocycle formed from palladation of an aryl ring. Other related structures incorporate tridentate metallated ligands [22], or result from aliphatic palladation [23], or both [24].

A significant feature of the structure is the highly encumbered environment of the non-coordinated nitrogen (N1) of the pyridazine ring (Fig. 1). In order to undergo double cyclometallation the corresponding nitrogen in the monopalladated intermediate must first coordinate to a second palladium atom. We reasoned that this was a probable explanation for the resistance of **7** towards double metallation and therefore felt more optimistic that the pyrimidine analogues, (**9**) and (**10**), would be more amenable to double metallation. Thus, these two new ligands were synthesised, in yields of 89 and 47%, from 4,6-dichloropyrimidine, by reaction with two equivalents of phenoxide and thiophenoxide, respectively.

Despite our optimism that double metallation might occur, these two ligands behaved similarly to their pyridazine analogues. Thus, the diphenoxy derivative (**9**) reacted with palladium acetate in benzene to give, after conversion to the chloride derivative and ligand exchange, the mononuclear acac derivative **23**, the NMR spectra of which were assigned fully (Scheme 3). Once again, all attempts to induce double palladation proved unsuccessful, as did attempts to cyclometallate the sulfur analogue **10**.

3. Concluding comments

In this study we have shown that 2-phenoxypyridine (**2**) and its sulfur analogue (**3**) readily undergo cyclopalladation to produce complexes containing six-membered metallocycles. Furthermore, all three bis(2-pyridyloxy)benzenes (**4**–**6**) have been doubly-cyclometallated. Such compounds are of considerable topical interest [9–11] and these represent the first examples of doubly cyclometallated compounds with two six-membered metallocycles. In contrast, the diphenoxy-pyridazine (**7**) and -pyrimidine (**9**) only undergo monometallation, whilst their sulfur analogues, (**8**) and (**10**) are resistant to cyclopalladation. In all cases, the cyclometallated products have been converted to their acac derivatives, as such compounds have been shown recently to be interesting metallomesogens [2].

Some years ago, we reported a detailed study of the ^{1}H- and ^{13}C-NMR spectra of a series of 19 acac complexes of various cyclometallated ligands [25]. We showed that cyclopalladation leads to consistent changes in certain chemical shifts for the complexes, relative to those of the starting ligand. We showed subsequently that these parameters can be diagnostically useful for distinguishing the regioselectivity of cyclopalladation reactions for ligands that could potentially react at either of two sites [17]. In the present work, and in related studies [6,9], we have extended our sample of cyclopalladated Pd(acac) complexes to over 45 such compounds, thereby refining these parameters.

Fig. 2 shows the average induced changes in chemical shift of the proton and carbon-13 signals resulting from the introduction of the Pd(acac) substituent into the ortho position of a phenyl ring of 45 nitrogen-containing ligands. These values now reveal that the most reliably diagnostic parameters correspond to H4′ in the ^{1}H-NMR spectra, which consistently experiences a 0.25 ppm upfield shift, and C5′ in the ^{13}C-NMR spectra, which consistently moves upfield by 4.2 ppm.

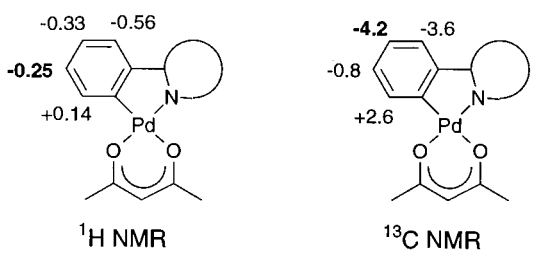


Fig. 2. Mean Pd(acac) induced chemical shift changes for 45 *N*-ligands.

4. Experimental

4.1. Ligand preparations and NMR spectra

2-Phenoxypyridine (**2**) was prepared by the reaction of phenol with 2-bromopyridine in the presence of anhydrous potassium carbonate, as previously reported [26]. Mp 41.5–43.5°C. ^{1}H-NMR ($CDCl_3$): δ 6.90 (d, 1H, H-3), 6.99 (t, 1H, H-5), 7.14 (d, 2H, H-2′ and H-6′), 7.20 (t, 1H, H-4′), 7.40 (t, 2H, H-3′ and H-5′), 7.68 (t, 1H, H-4), 8.20 (d, 1H, H-6). ^{13}C-NMR ($CDCl_3$): δ 111.47 (C-3), 118.41 (C-5), 121.12 (C-2′ and C-6′), 124.62 (C-4′), 129.65 (C-3′ and C-5′), 139.36 (C-4), 147.74 (C-6), 154.11 (C-1′), 163.72 (C-2).

2-Phenylsulfanylpyridine (**3**) was prepared by the reaction of thiophenol with 2-chloropyridine in the presence of triethylamine, as previously described [27]. ^{1}H-NMR ($CDCl_3$): δ 6.87 (d, 1H, H-3), 6.98 (t, 1H, H-5), 7.41 (m, 3H, H-3′, H-4′ and H-5′), 7.42 (t, 1H, H-4), 7.59 (d, 2H, H-2′ and H-6′), 8.41 (d, 1H, H-6). ^{13}C-NMR ($CDCl_3$): δ 119.77 (C-5), 121.20 (C-3), 128.98 (C-4′), 129.52 (C-3′ and C-5′), 130.88 (C-1′), 134.83 (C-2′ and C-6′), 136.61 (C-4), 149.44 (C-6), 161.40 (C-2).

The three isomeric bis(2-pyridyloxy)benzenes (**4**–**6**) were prepared from reactions of 2-bromopyridine with the appropriate dihydroxybenzene, as previously described [12,13] **4**: ^{1}H-NMR ($CDCl_3$) δ: 6.70 (d, 2H, H3′), 6.90 (t, 2H, H5′), 7.28 (s, 4H, H3-6), 7.56, (t, 2H, H4′), 8.10 (d, 2H, H6′). ^{13}C-NMR ($CDCl_3$) δ: 110.73 (C3′), 118.17 (C5′), 123.60 (C3,6), 125.73 (C4,5), 138.96 (C4′), 145.66 (C1,2), 147.31 (C6′), 163.06 (C2′). **5**: ^{1}H-NMR ($CDCl_3$) δ: 6.93 (d, 2H, H3′), 6.96 (s, 1H, H2), 6.99 (dd, 2H, H4,6), 7.00 (t, 2H, H5′), 7.40 (t, 1H, H5), 7.68 (t, 2H, H4′), 8.21 (d, 2H, H6′). ^{13}C-NMR ($CDCl_3$) δ: 111.48 (C3′), 113.88 (C2), 116.81 (C4,6), 118.56 (C5′), 129.92 (C4), 139.26 (C4′), 147.53 (C6′), 154.98 (C1,3), 163.07 (C2′). **6**: ^{1}H-NMR ($CDCl_3$) δ: 6.94 (d, 2H, H3′), 7.00 (t, 2H, H5′), 7.17 (s, 4H, H2,3,5,6), 7.69 (t, 2H, H4′), 8.21 (d, 2H, H6′). ^{13}C-NMR ($CDCl_3$) δ: 111.38 (C3′), 118.44 (C5′), 122.32 (C2,3,5,6), 139.41 (C4′), 147.63 (C6′), 150.58 (C1,4), 163.73 (C2′).

3,6-Diphenoxypyridazine (**7**) was prepared by the reaction of two equivalents of sodium phenoxide with 3,6-dichloropyridazine as previously reported [18]. Mp 141.5-142°C (lit. [18] 140-141°C). ^{1}H-NMR ($CDCl_3$): δ 7.17 (br t, 2H, H-4′ and H-4″), 7.18 (br d, 4H, H-2′, H-6′, H-2″ and H-6″), 7.19 (br s, 2H, H-4 and H-5), 7.36 (br t, 4H, H-3′, H-5′, H-3″ and H-5″). ^{13}C-NMR ($CDCl_3$): δ 120.97 (C-2′, C-6′, C-2″ and C-6″), 121.75 (C-4 and C-5), 125.02 (C-4′ and C-4″), 129.56 (C-3′, C-5′, C-3″ and C-5″), 153.52 (C-1′ and C-1″), 162.96 (C-3 and C-6).

3,6-Bis(phenylsulfanyl)pyridazine (**8**) was prepared by the reaction of sodium thiophenoxide with 3,6-dichloropyridazine in ethanol as previously reported

[19]. Mp 79.5-80.5°C (lit. [19] 78°C). ^{1}H-NMR ($CDCl_3$): δ 6.82 (s, 2H, H-4 and H-5), 7.40 (m, 6H, H-3′, H-4′, H-5′, H-3″, H-4″ and H-5″), 7.57 (m, 4H, H-2′, H-6′, H-2″ and H-6″). ^{13}C-NMR ($CDCl_3$): δ 125.39 (C-4 and C-5), 129.26 (C-1′ and C-1″), 129.55 (C-4′ and C-4″), 129.79 (C-3′, C-5′, C-3″ and C-5″), 134.95 (C-2′, C-6′, C-2″ and C-6″), 162.20 (C-3 and C-6).

4,6-Diphenoxypyrimidine (**9**): A mixture of phenol (2.88 g, 3.1 mmol), potassium carbonate (2.81 g, 2.0 mmol) and 4,6-dichloropyrimidine (1.53 g, 1.0 mmol) was heated at 160°C for 1 h after which it was allowed to cool to room temperature. Water (10 cm^3) and aqueous potassium hydroxide (0.13 mol dm^{-3}, 30 cm^3) were added and the suspension ultrasonicated to break up the solid. The mixture was filtered and the solid washed with water (50 cm^3), then dried under reduced pressure to give **9** in 89% yield. Mp 109–109.5°C. Anal. Calc. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60; Found: C, 72.55; H, 4.42; N, 10.61%. Calc. for $C_{16}H_{12}N_2O_2$: M^+, 264.0899; Found (EI): M^+, 264.0897. IR (KBr pellet): ν_{max} 1606, 1579, 1562, 1489, 1456, 1382, 1240, 1219, 1207, 1152, 820, 763, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.29 (s, 1H, H-5), 7.16 (d, 4H, H-2′, H-6′, H-2″ and H-6″), 7.28 (t, 2H, H-4′ and H-4″), 7.44 (t, 4H, H-3′, H-5′, H-3″ and H-5″), 8.45 (s, 1H, H-2). ^{13}C-NMR ($CDCl_3$): δ 92.11 (C-5), 121.48 (C-2′, C-6′, C-2″ and C-6′), 125.90 (C-4′ and C-4″), 129.87 (C-3′, C-5′, C-3″ and C-5″), 152.43 (C-1′ and C-1″), 158.42 (C-2), 171.61 (C-4 and C-6).

4,6-Bis(phenylsulfanyl)pyrimidine (**10**): Thiophenol (2.1 cm^3, 2.0 mmol) was added to a freshly prepared solution of sodium ethoxide (0.52 g sodium, 2.3 mmol) in ethanol (20 cm^3) and to the resultant solution was added 4,6-dichloropyrimidine (1.5 g, 1.0 mmol) dissolved in ethanol (20 cm^3). The reaction mixture was stirred under reflux for 1 day after which it was allowed to cool to room temperature and the precipitate of sodium chloride removed by filtration. The filtrate was chilled and the precipitate filtered off to give **10**. The filtrate was stripped of solvent and the residue taken up in water (50 cm^3). Aqueous sodium hydroxide (8 mol dm^{-3}, 5 cm^3) was added and the solution extracted with chloroform (3×25 cm^3). The organic extracts were combined, dried over magnesium sulfate and the solvent removed under reduced pressure to give a residue which crystallised upon standing overnight. The supernatant was removed and the solid recrystallised from ethanol to give additional **10**. Total yield 47%. Mp 116.5–117°C. Anal. Calc. for $C_{16}H_{12}N_2S_2$: C, 64.83; H, 4.08; N, 9.45; Found: C, 64.53; H, 3.91; N, 9.44%. Calc. for $C_{16}H_{12}N_2S_2$: M^+, 296.0442; Found (EI): M^+, 296.0443. IR (KBr pellet): ν_{max} 1530, 1494, 1474, 1427, 1281, 1082, 802, 748, 689 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.03 (s, 1H, H-5), 7.31 (t, 4H, H-3′, H-5′, H-3″ and H-5″), 7.36 (t, 2H, H-4′ and H-4″), 7.41 (d, 4H, H-2′, H-6′, H-2″ and H-6″), 8.62 (s, 1H, H-2). ^{13}C-NMR ($CDCl_3$): δ 111.91 (C-5), 127.28 (C-1′ and C-1″), 129.76 (C-3′, C-5′, C-3″ and C-5″), 129.97 (C-4′ and C-4″), 135.50 (C-2′, C-6′, C-2″ and C-6′), 156.70 (C-2), 172.20 (C-4 and C-6).

4.2. Cyclopalladation reactions

4.2.1. General procedures

Method A: A solution containing the ligand and one or two equivalents of palladium acetate in glacial acetic acid was stirred at room temperature for 24 h. The acetic acid was then removed under reduced pressure. The resultant μ-acetato complex was then converted to the μ-chloro complex by stirring with an acetone/water (60/40, v/v) solution containing excess lithium chloride (four equivalents) for up to four days. The resultant precipitate was filtered off and washed with acetone then with ether.

Method B: A solution containing the ligand and one or two equivalents of palladium acetate in glacial acetic acid was refluxed for 17 h. The acetato palladium complex was extracted by Soxhlet extraction with chloroform. An acetone solution of the acetato palladium complex and an excess of acetylacetone and triethylamine was stirred for 16 h. The acetone was then removed under reduced pressure. The residue was suspended in water and the acac complex was filtered off.

Method C: A solution containing the ligand and one or two equivalents of palladium acetate in benzene was degassed by passing a stream of nitrogen through it for 5 min and then heated at 60°C under an atmosphere of nitrogen for 24 h. The benzene was then removed under reduced pressure and the residue taken up in chloroform and filtered. The filtrate was stripped of solvent under reduced pressure and the residue stirred with an acetone/water (60/40, v/v) solution containing excess lithium chloride (four equivalents) for up to 4 days. The resultant μ-chloro palladium complex was filtered off and washed with acetone then with ether.

Method D: Excess acetylacetone was added to a freshly prepared solution of sodium methoxide in methanol and the resultant solution of sodium acac was added to a suspension of the μ-chloro palladium complex in methanol and the mixture stirred for one to four days. The precipitated acac complex was filtered off and washed with methanol and then with ether.

Method E: The chloro-bridged dimer was added to a solution of two equivalents of thallium acac in dichloromethane and the resultant solution stirred for 24 h. The precipitate of thallium chloride was filtered off using a plug of anhydrous magnesium sulfate and the dichloromethane removed from the filtrate under reduced pressure. The residue was taken up in chloroform and vapour diffusion of petroleum ether into this solution gave the acac complex, which was filtered off and washed with pentane.

*4.2.2. Cyclopalladation of 2-phenoxypyridine (**2**)*

Method A gave [Pd(**2**-H)OAc]$_2$, **11**, in 69% yield. Mp 226-228°C. Anal. Calc. for $C_{26}H_{22}N_2O_2Pd_2$: C, 46.52; H, 3.03; N, 4.17; Found: C, 46.24; H, 3.10; N, 4.14%. IR (KBr pellet): ν_{max} 1610, 1583, 1568, 1478, 1454, 1422, 1327, 1298, 1181, 775, 756 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.12 (s, 3H, CH_3COO), 6.62 (d, 1H, H-6′), 6.63 (t, 1H, H-5), 6.66 (t, 1H, H-4′), 6.82 (d, 1H, H-3′), 6.86 (t, 1H, H-5′), 6.88 (d, 1H, H-3), 7.55 (t, 1H, 4), 8.02 (d, 1H, H-6). ^{13}C-NMR ($CDCl_3$): δ 24.53 (CH_3COO), 114.29 (C-3), 115.18 (C-6′), 117.80 (C-5), 123.06 (C-4′), 124.90 (C-5′), 134.08 (C-3′), 139.80 (C-4), 148.82 (C-6), 149.30 (C-1′), 157.30 (C-2), 181.16 (CH_3COO). Ligand exchange gave[Pd(**2**-H)Cl]$_2$, **12**, in 69% yield. Mp > 300°C. Anal. Calc. for $C_{22}H_{16}N_2O_2Cl_2Pd_2$: C, 42.34; H, 2.58; N, 4.49: Cl, 11.36; Found: C, 42.49; H, 2.23; N, 4.27; Cl, 11.27%. IR (KBr pellet): ν_{max} 1610, 1577, 1480, 1454, 1437, 1424, 1313, 1302, 1184, 770, 749, 731 cm^{-1}. This complex is insoluble in common NMR solvents.

Method D then gave Pd(**2**-H)(acac), **13**, in 43% yield. Mp 133-135°C. Anal. Calc. for $C_{16}H_{15}NO_3Pd$: C, 51.15; H, 4.02; N, 3.73; Found: C, 50.89; H, 3.72; N, 3.84%. IR (KBr pellet): ν_{max} 1612, 1595, 1577, 1528, 1479, 1441, 1426, 1406, 1314, 1300, 761, 749, 732 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.04 (s, 3H, acac–CH_3), 2.09 (s, 3H, acac–CH_3), 5.42 (s, 1H, acac–CH), 6.98 (d, 1H, H-6′), 7.06 (t, 1H, H-4′), 7.08 (t, 1H, H-5), 7.12 (t, 1H, H-5′), 7.22 (d, 1H, H-3), 7.62 (d, 1H, H-3′), 7.82 (t, 1H, H-4), 8.81 (d, 1H, H-6). ^{13}C-NMR ($CDCl_3$): δ 27.58 and 27.95 (acac–CH_3), 100.39 (acac–CH), 114.91 (C-3), 115.47 (C-6′), 118.53 (C-5), 123.68 (C-4′), 125.65 (C-5′), 133.83 (C-3′), 140.27 (C-4), 148.22 (C-6), 187.02 and 188.12 (acac–CO).

*4.2.3. Cyclopalladation of 2-phenylsulfanylpyridine (**3**)*

Method C gave [Pd(**3**-H)Cl]$_2$, **14**, in 47% yield. IR (KBr pellet): ν_{max} 1587, 1551, 1458, 1431, 1421, 1157, 1020, 762, 746 cm^{-1}. This complex is insoluble in common NMR solvents.

Method E then gave Pd(**3**-H)(acac), **15**, in 20% yield. Mp 199–200°C (dec.). Anal. Calc. for $C_{16}H_{15}NO_2SPd$: C, 49.05; H, 3.86; N, 3.58; Found: C, 48.81; H, 4.02; N, 3.55%. IR (KBr pellet): ν_{max} 1592, 1559, 1511, 1420, 1394, 774, 745, 612 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.00 (s, 3H, acac–CH_3), 2.05 (s, 3H, acac–CH_3), 5.42 (s, 1H, acac–CH), 7.01 (t, 1H, H-5′), 7.07 (t, 1H, H-4′), 7.17 (t, 1H, H-5), 7.30 (d, 1H, H-6′), 7.44 (d, 1H, H-3′), 7.66 (t, 1H, H-4), 7.73 (d, 1H, H-3), 8.81 (d, 1H, H-6). ^{13}C-NMR ($CDCl_3$): δ 27.52 and 27.98 (acac–CH_3), 100.34 (acac–CH), 121.56 (C-5), 124.64 (C-5′), 125.82 (C-3), 126.02 (C-4′), 126.83 (C-6′), 131.75 (C-2′), 135.75 (C-3′), 137.32 (C-4), 145.63 (C-1′), 153.77 (C-6), 158.68 (C-2), 186.57 and 187.92 (acac–CO).

*4.2.4. Cyclopalladation of 1,2-bis(2-pyridyloxy)benzene (**4**)*

Method B gave [Pd$_2$(**4**-2H)(OAc)$_2$]$_2$, **16**, in 67% yield. Mp > 215°C (dec.). IR (KBr pellet): ν_{max} 1578, 1475, 1420, 1375, 1298, 928, 772 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.04 (s, 3H, CH_3COO), 2.22 (s, 3H, CH_3COO), 6.36 (s, 2H, H-4, H-5), 6.71 (t, 2H, H-5′), 7.07 (d, 2H, H-3′), 7.57 (t, 2H, H-4′), 8.38 (d, 2H, H-6′). Ligand exchange gave Pd$_2$(**4**–2H)(acac)$_2$, **17**, in 72% yield. The solid was recrystallised by diffusion of pentane into a chloroform solution of **17**. Mp > 215°C (dec.). Anal. Calc. for $C_{26}H_{24}N_2O_6Pd_2 \cdot CHCl_3$: C, 40.91; H, 3.18; N, 3.53; Found: C, 40.85; H, 2.84; N, 3.64%. Calc. for $C_{26}H_{24}N_2O_6^{106}Pd^{108}Pd$: M$^+$, 673.9705; Found (FAB): M$^+$, 673.9708. IR (KBr pellet): ν_{max} 1614, 1583, 1514, 1431, 1394, 1367, 1294, 1022, 924, 772 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.03 (s, 6H, acac–CH_3), 2.08 (s, 6H, acac–CH_3), 5.41 (s, 2H, acac-CH), 7.08 (t, 2H, H-5′), 7.24 (s, 2H, H-4, H-5), 7.35 (d, 2H, H-3′), 7.83 (t, 2H, H-4′), 8.80 (d, 2H, H-6′). ^{13}C-NMR ($CDCl_3$): 27.57 and 27.94 (acac–CH_3), 100.29 (acac–CH), 115.06 (C-3′), 118.61 (C-5′), 119.12 (C-3, C-6), 127.90 (C-4, C-5), 137.25 (C-1, C-2), 140.10 (C-4′), 148.44 (C-6′), 158.19 (C-2′), 187.15 and 187.79 (acac–CO).

*4.2.5. Cyclopalladation of 1,3-bis(2-pyridyloxy)benzene (**5**)*

Method A gave [Pd$_2$(**5**–2H)(OAc)$_2$]$_2$, **18**, in 36% yield. Mp > 220°C (dec.). IR (KBr pellet): ν_{max} 1612, 1566, 1477, 1421, 1294, 1242, 1123, 1028, 984, 777, 689 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.97 (s, 3H, CH_3COO), 2.20 (s, 3H, CH_3COO), 6.13 (s, 1H, H-2), 6.47 (s, 1H, H-5), 6.69 (t, 2H, H-5′), 6.90 (d, 2H, H-3′), 7.66 (t, 2H, H-4′), 8.06 (d, 2H, H-6′). Ligand exchange gave [Pd$_2$(**5**-2H)Cl$_2$]$_2$ in 74% yield. Mp > 240°C (dec.). IR (KBr pellet): ν_{max} 1611, 1570, 1474, 1421, 1294, 1242, 1123, 982, 777 cm^{-1}. Method D then gave Pd$_2$(**5**–2H)(acac)$_2$, **19**, in 52% yield. The solid was recrystallised by diffusion of pentane into a chloroform solution of **19**. Mp 158–160°C. Anal. Calc. for $C_{26}H_{24}N_2O_6Pd_2.CHCl_3$: C, 40.91; H, 3.18; N, 3.53; Found: C, 40.50; H, 2.93; N, 3.54%. Calc. for $C_{26}H_{24}N_2O_6^{106}Pd^{108}Pd$: M$^+$, 673.9705; Found (FAB): M$^+$, 673.9687. IR (KBr pellet): ν_{max} 1587, 1510, 1475, 1394, 1292, 1113, 984, 779, 746 cm^{-1}. ^{1}H-NMR (CDCl3): 2.02 (s, 6H, acac–CH_3), 2.09 (s, 6H, acac–CH_3), 5.40 (s, 2H, acac–CH), 6.70 (s, 1H, H-2), 7.05 (t, 2H, H-5′), 7.17 (d, 2H, H-3′), 7.67 (s, 1H, H-5), 7.82 (t, 2H, H-4′), 8.78 (d, 2H, H6′). ^{13}C-NMR ($CDCl_3$): 27.65 and 27.93 (acac–CH_3), 100.18 (acac–CH), 102.98 (C-2), 114.70 (C-3′), 118.43 (C-5′), 136.91 (C-5), 140.02 (C-4′), 148.52 (C-6′), 187.12 and 187.65 (acac–CO).

4.2.6. Cyclopalladation of 1,4-bis(2-pyridyloxy)benzene (6)

Method A gave $[Pd_2(\mathbf{6}-2H)(OAc)_2]_2$, **20**, in 27% yield. Mp > 210°C (dec.). IR (KBr pellet): ν_{max} 1582, 1479, 1427 1337, 1296, 1242, 1140, 899, 758, 673 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.06 (s, 3H, CH_3COO), 2.31 (s, 3H, CH_3COO), 6.22 (s, 2H, H-3, H-6), 6.63 (t, 2H, H-5′), 6.88 (d, 2H, H3′), 7.53 (t, 2H, H-4′), 8.19 (d, 2H, H-6′). Ligand exchange gave $[Pd_2(\mathbf{6}-2H)Cl_2]_2$ in 92% yield. Mp > 230°C (dec.). IR (KBr pellet): ν_{max} 1611, 1591, 1508, 1477, 1423, 1292, 1138, 1107, 893, 789 cm^{-1}. Method D then gave $Pd_2(\mathbf{6}-2H)(acac)_2$, **21**, in 94% yield. Mp > 220°C (dec.). Anal. Calc. for $C_{26}H_{24}N_2O_6Pd_2$: C, 46.38; H, 3.59; N, 4.16; Found: C, 46.12; H, 3.46; N, 4.25%. IR (KBr pellet): ν_{max} 1589, 1508, 1481, 1398, 1292, 1128, 1113, 1020, 893, 795, 771, 617 cm^{-1}. This complex is insoluble in common NMR solvents.

4.2.7. Cyclopalladation of 3,6-diphenoxypyridazine (7)

Method C gave [Pd(**7**-H)OAc]$_2$ [^{1}H-NMR ($CDCl_3$): δ 1.68 (s, 3H, CH_3COO), 6.70 (d, 1H, H-6′), 6.83 (t, 1H, H-4′), 6.91 (t, 1H, H-5′), 6.95 (d, 3H, H-5, H-2″ and H-6″), 7.11 (d, 1H, H-4), 7.16 (t, 1H, H-4″), 7.17 (d, 1H, H-3′), 7.33 (t, 2H, H-3″ and H-5“). ^{13}C-NMR ($CDCl_3$): δ 23.99 (CH_3COO), 114.56 (C-6′), 120.22 (C-2″ and C-6″), 123.20 (C-4′), 123.26 (C-5), 124.78 (C-5′), 124.89 (C-4), 125.02 (C-4″), 129.55 (C-3″ and C-5″), 134.99 (C-3′), 180.01 (CH_3COO)] followed by [Pd(**7**-H)Cl]$_2$, in 63% overall yield. IR (KBr pellet): ν_{max} 1491, 1441, 1425, 1418, 1279, 1180, 1163, 1111, 883, 764, 750, 689 cm^{-1}. This complex is insoluble in common NMR solvents.

Method E then gave, in 87% yield, Pd(**7**–H)(acac), **22**, as pale yellow crystals suitable for single crystal X-ray structure determination. Mp 186–188°C. Anal. Calc. for $C_{21}H_{18}N_2O_4Pd$: C, 53.80; H, 3.87; N, 5.98; Found: C, 53.70; H, 3.84; N, 5.94%. IR (KBr pellet): ν_{max} 1593, 1570, 1514, 1458, 1443, 1420, 1394, 1269, 1190, 1163, 754 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.90 (s, 3H, acac–CH_3), 2.03 (s, 3H, acac–CH_3), 5.34 (s, 1H, acac–CH), 6.96 (m, 1H, H-6′), 7.07 (m, 1H, H-5′), 7.10 (m, 1H, H-4′), 7.21 (m, 1H, H-4″), 7.36 (d, 1H, H-5), 7.41 (m, 4H, H-2″, H-3″, H-5″ and H-6″), 7.44 (d, 1H, H-4), 7.60 (m, 1H, H-3'). ^{13}C-NMR ($CDCl_3$): δ 27.30 and 27.63 (acac–CH_3), 100.08 (acac–CH), 115.13 (C-6'), 120.58 (C-2′), 120.88 (C-2″ and C-6″), 123.58 (C-5), 124.34 (C-5′), 125.32 (C-4″), 125.54 (C-4′), 125.60 (C-4), 129.48 (C-3″ and C-5″), 134.32 (C-3′), 150.86 (C-1′), 152.87 (C-1″), 156.81 (C-3), 160.82 (C-6), 185.84 and 188.45 (acac–CO).

4.2.8. Cyclopalladation of 4,6-diphenoxypyrimidine (9)

Method C gave [Pd(**9**-H)OAc]$_2$ [^{1}H-NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3COO), 6.23 (s, 1H, H-5), 6.71 (d, 1H, H-6′), 6.84 (t, 1H, H-4′), 6.97 (d, 1H, H-3′), 7.02 (t, 1H, H-5′), 7.04 (d, 2H, H-2″ and H-6″), 7.32 (t, 1H, H-4″), 7.47 (t, 2H, H-3″ and H-5″), 8.38 (s, 1H, H-2)] followed by [Pd(**9**–H)Cl]$_2$, in 37% overall yield. Mp 244–245°C (dec.). Anal. Calc. for $C_{32}H_{22}N_4O_4Cl_2Pd_2$: C, 47.34; H, 2.74; N, 6.91; Found: C, 47.44; H, 2.80; N, 6.97%. IR (KBr pellet): ν_{max} 1611, 1585, 1572, 1547, 1491, 1468, 1454, 1431, 1408, 1244, 1198, 758 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.62 (s, 1H, H-5), 6.92 (d, 1H, H-6′), 6.95 (t, 1H, H-4′), 7.08 (t, 1H, H-5′), 7.14 (d, 2H, H-2″ and H-6″), 7.34 (t, 1H, H-4″), 7.41 (d, 1H, H-3′), 7.47 (t, 2H, H-3″ and H-5″), 8.93 (s, 1H, H-2). ^{13}C-NMR ($CDCl_3$): δ 94.62 (C-5), 116.48 (C-6′), 121.32 (C-2″ and C-6″), 124.85 (C-4′), 126.30 (C-4″), 126.63 (C-5′), 130.10 (C-3″ and C-5″), 136.80 (C-3″), 160.00 (C-2).

Method E then gave Pd(**9**-H)(acac), **23**, in 62% yield. Mp 202–206°C (dec.). Anal. Calc. for $C_{21}H_{18}N_2O_4Pd$: C, 53.80; H, 3.87; N, 5.98; Found: C, 53.81; H, 4.16; N, 5.88%. IR (KBr pellet): ν_{max} 1611, 1585, 1548, 1509, 1490. 1471, 1456, 1432, 1394, 1309, 1241, 1227, 1196, 749 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.90 (s, 3H, acac–CH_3), 2.09 (s, 3H, acac–CH_3), 5.42 (s, 1H, acac–CH), 6.57 (s, 1H, H-5), 6.94 (d, 1H, H-6′), 7.10 (br t, 2H, H-4′ and H-5′), 7.17 (d, 2H, H-2″ and H-6″), 7.34 (t, 1H, H-4″), 7.49 (t, 2H, H-3″ and H-5″), 7.65 (d, 1H, H-3′), 9.19 (s, 1H, H-2). ^{13}C-NMR ($CDCl_3$): δ 27.56 and 27.71 (acac–CH_3), 93.97 (C-5), 100.44 (acac–CH), 115.53 (C-6′), 119.12 (C-2′), 121.39 (C-2″ and C-6″), 124.27 (C-4′), 125.86 (C-4″), 126.52 (C-5′), 130.12 (C-3″ and C-5″), 133.70 (C-3′), 145.05 (C-1′), 152.08 (C-1″), 158.91 (C-2), 187.00 and 188.13 (acac–CO).

4.3. X-ray crystallography

All measurements were made with a Siemens CCD area detector using graphite monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation. Intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved by direct methods using SHELXS [28], and refined on F^2 using all data by full-matrix least-squares procedures with SHELXS-96 [29]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The function minimised was $\Sigma\, w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.0413P^2]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

Crystal data for **22** at −130°C: $C_{21}H_{18}N_2O_4Pd$, $M_r = 468.8$, $0.53 \times 0.35 \times 0.13$ mm, orthorhombic, space group $P2_12_12_1$, $a = 13.0994(3)$, $b = 14.4413(4)$, $c = 20.1011(4)$ Å, $V = 3902.6(2)$ Å^3, $F(000) = 1888$, $Z = 8$, $D_c = 1.64$ g cm^{-3}, $\mu(Mo-K_\alpha) = 1.48$ mm^{-1}, $2\theta_{max} = 53°$, 509 parameters, $S = 1.07$, $wR_2 = 0.0503$ for all 7048 unique data, $R = 0.0223$ for 6837 data with $F_o > 4\sigma(F_o)$.

References

[1] (a) D.W. Bruce, J. Chem. Soc. Dalton Trans. (1993) 2983. (b) J. Buey, P. Espinet, J. Organomet. Chem. 507 (1996) 137, and Refs. therein. (c) A.T. Ionescu, D. Pucci, N. Scaramuzza, C. Versace, A.G. Petrov, R. Bartolino, J. Chem. Phys. 103 (1995) 5144. (d) P. Espinet, M.A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215.

[2] (a) D.P. Lydon, J.P. Rourke, Chem. Commun. (1997) 1741. (b) D.P. Lydon, G.W.V. Cave J.P. Rourke, J. Mater. Chem. 7(1997) 403. (c) G.W.V. Cave, D.P. Lydon; J.P. Rourke, J. Organomet. Chem. 555 (1998) 81, and Refs. therein.

[3] (a) I. Omae, J. Organomet. Chem. Library 18 (1986). (b) I. Omae, Coord. Chem. Rev. 83 (1988) 137.

[4] (a) K. Hiraki, Y. Fuchita, K. Takechi, Inorg. Chem. 20 (1981) 4316. (b) K. Hiraki, Y. Fuchita, Inorg. Synth. 26 (1989) 208.

[5] A.D. Ryabov, Chem. Rev. 90 (1990) 403.

[6] D.J. de Geest; P.J. Steel, unpublished results, 1996.

[7] (a) L. Braunschweiler; R. R. Ernst, J. Magn. Reson. 53 (1983) 521. (b) D.G. Davis, A. Bax, J. Am. Chem. Soc. 107 (1985) 7197. (c) H. Kessler, S. Mronga, G. Gemmecker, Magn. Reson. Chem. 29 (1991) 527.

[8] Y. Fuchita, H. Tsuchiya, A. Miyafuji, Inorg. Chim. Acta 233 (1995) 91.

[9] D.J. de Geest and P.J. Steel, Inorg. Chem. Comm. 1 (1998) 358, and Refs. therein.

[10] (a) P. Espinet, G. Garcia, F.J. Herrero, Y. Jeannin; M. Philoche-Levisalles, Inorg. Chem. 28 (1989) 4207. (b) G.B. Caygill, R.M. Hartshorn, P.J. Steel, J. Organomet. Chem. 382 (1990) 455. (c) G.B. Caygill, P.J. Steel, J. Organomet. Chem. 395 (1990) 359. (d) A. Jouaiti, M. Geoffroy, G. Bernardinelli, Tetrahedron Lett. 34 (1993) 3413. (e) K. Selvakumar, S. Vancheesan, Polyhedron 15 (1996) 2535. (f) J.M. Vila, M. Gayoso, M. Lopez Torres, J.J. Fernandez, A. Fernandez, J.M. Ortigueira, N.A. Bailey, H. Adams, J. Organomet. Chem. 511 (1996) 129. (g) C. Lopez, R. Bosque, J. Organomet. Chem. 524, (1996) 247.

[11] (a) S. Trofimenko, J. Am. Chem. Soc. 93 (1971) 1808. (b) I.G. Phillips, P.J. Steel, J. Organomet. Chem. 410 (1991) 247. (c) S. Chakladar, P. Paul, K. Venkatsubramanian, K. Nag, J. Chem. Soc. Dalton Trans. (1991) 2669. (d) S. Chakladar, P. Paul, K. Nag, Polyhedron 10 (1991)1513. S. Chakladar, P. Paul, A.K. Mukherjee, S.K. Dutta, K.K. Nanda, D. Podder, K. Nag, J. Chem. Soc. Dalton Trans. (1992) 3119. (e) S.J. Loeb, G.K. Shimizu, J. Chem. Soc. Chem. Commun. (1993) 1395. (f) J.M. Vila, M. Gayoso, M.T. Pereira, M.L. Torres, J.J. Fernandez, A. Fernandez, J.M. Ortigueira, J. Organomet. Chem. 506 (1996) 165. (g) P. Steenwinkel, S.L. James, D.M. Grove, H. Kooijman, A.L. Spek, G. van Koten, Organometallics 16 (1997) 513.

[12] C.M. Hartshorn, P.J. Steel, J. Chem. Soc. Dalton Trans. (1998) 3927.

[13] C.M. Hartshorn, P.J. Steel, Inorg. Chem. 35 (1996) 6902.

[14] B.J. O'Keefe, P.J. Steel, Organometallics 17 (1998) 3621, and Refs. therein.

[15] C.M. Hartshorn, P.J. Steel, Organometallics 17 (1998) 3487, and Refs. therein.

[16] R.C. Carina, A.F. Williams, G. Bernardinelli, J. Organomet. Chem. 548 (1997) 45.

[17] (a) G.B. Caygill, R.M. Hartshorn and P.J. Steel, J. Organomet. Chem. 382 (1990) 455. (b) P.J. Steel, G.B. Caygill, J. Organomet. Chem. 395 (1990) 359.

[18] J. Druey, K. Meier, K. Eichenberger, Helv. Chim. Acta 37 (1954) 121.

[19] T. Itai, H. Igeta, J. Pharm. Soc. Jpn. 74 (1954) 1195; Chem. Abstr., 49 (1955) 14768a.

[20] P.J. Steel, Coord. Chem. Rev. 106 (1990) 227.

[21] I.G. Phillips, P.J. Steel, J. Organomet. Chem. 410 (1991) 247, and Refs. therein.

[22] (a) G. Minghetti, M.A. Cinellu, G. Chelucci, S. Gladiali, J. Organomet. Chem. 307 (1986) 107. (b) A.J. Canty, N.J. Minchin, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1987) 1477. (c) S. Tollari, G. Palmisano, F. Demartin, M. Grassi, S. Magnaghi, S. Cenini, J. Organomet. Chem. 488 (1995) 79. (d) C.-W. Chan, D.M.P. Mingos, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (1995) 2469. (e) C.-W. Chan, D.M.P. Mingos, A.J.P. White, D.J. Williams, Chem. Commun. (1996) 81.

[23] (a) G.R. Newkome, W.E. Puckett, V.K. Gupta, F.R. Fronczek, Organometallics 2 (1983) 1247. (b) J. Albert, J. Granell, J. Sales, X. Solans, M. Font-Altaba, Organometallics 5 (1986) 2567. (c) J. Barro, J. Granell, D. Sainz, J. Sales, J. Organomet. Chem. 456 (1993) 147. (d) J. Albert, M. Gomez, J. Granell, J. Sales, X. Solans, Organometallics 9 (1990) 1405. (e) W. Klaui, H. Hamers, M. Pfeffer, A. de Cian, J. Fischer, J. Organomet. Chem. 394 (1990) 213. (f) J. Barker, N.D. Cameron, M. Kilner, M.M. Mahmoud, S.C. Wallwork, J. Chem. Soc. Dalton Trans. (1991) 3435. (g) R. Bosque, J. Granell, J. Sales, M. Font-Bardía, X. Solans, J. Organomet. Chem. 453 (1993) 147. (h) G. De Munno, M. Ghedini, F. Neve, Inorg. Chim. Acta 239 (1995) 155.

[24] (a) G.R. Newkome, G.E. Kiefer, Y.A. Frere, M. Onishi, V.K. Gupta, F.R. Fronczek, Organometallics 5 (1986) 348. (b) P.L. Alsters, P.F. Engel, M.P. Hogerheide, M. Copijn, A.L. Spek, G. van Koten, Organometallics, 12 (1993) 1831. (c) A. Yoneda, G.R. Newkome, Y. Morimoto, Y. Higuchi, N. Yasuoka, Acta Cryst. C49 (1993) 476. (d) A. Yoneda, T. Hakushi, G.R. Newkome, Y. Morimoto, N. Yasuoka, Chem. Lett. (1994) 175. (e) J. Vicente, I. Saura-Llamas, M.G. Palin, P.G. Jones, J. Chem. Soc. Dalton Trans. (1995) 2535. (f) A. Macchioni, P.S. Pregosin, P.F. Engel, S. Mecking, M. Pfeffer, J.-C. Daran, J. Vaissermann, Organometallics 14 (1995) 1637.

[25] P.J. Steel, G.B. Caygill, J. Organomet. Chem. 327 (1987) 101.

[26] R.R. Renshaw, R.C. Conn, J. Am. Chem. Soc. 59 (1937) 297.

[27] L.G.S. Brooker, G.H. Keyes, R.H. Sprague, R.H. Van Dyke, E. Van Lare, G. Van Zandt, F.L. White, J. Am. Chem. Soc. 73 (1951) 5326.

[28] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[29] G.M. Sheldrick, SHELXL-96, University of Göttingen, 1996.