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Cyclometallated nitrogen heterocycles

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Abstract

The cyclometallation of four different classes of nitrogen heterocycle (pyridazine, tetrazines, pyrazines and pyrimidines) by palladium and platinum has been studied. Pyridazines readily form singly and doubly cyclometallated compounds, whilst pyrazines only metallate once. Both tetrazines and pyrimidines readily metallate once and doubly metallated species have been identified in solution. The use of *trans*-cyclometallating reagents based on benzylamine and Schiff's base ligands was also studied: considerable promise was shown by a benzylamine compound.

Keywords: Cyclometallation; Nitrogen heterocycles; Bridging ligands

1. Introduction

Cyclometallation has proved to be a fertile area of research, both for mechanistic studies, and as a route into stable compounds. Conventionally, cyclometallation has involved one ligating group holding a metal centre close to a C–H bond and the subsequent closure of the ring via the formation of a carbon to metal bond [1]. Whilst some have adapted this reaction to activate bonds other than C–H (for example C–Si [2] or C–C bonds [3]), we have been investigating bringing about double cyclometallations with a single metal (generating ĈN̂C tridentate complexes) [4,5]. Others have followed Trofimenko's pioneering work of thirty years ago [6,7] using two ligating groups to hold two metal centres close to a single benzene ring, thus forming two metal to carbon bonds on the same aromatic ring. Trofimenko's original work concerned systems where the two metals on the metallated ring are *ortho*, *meta* and *para* to each other, whilst we [8] and others [9–12] have largely restricted our investigations to systems where the two metals are opposite (*para*) across a phenyl ring, though other arrangements have been studied [13–16]. A recent development has been the design of a ligand capable of undergoing a triple cyclopalladation, and the successful realisation of this aim [17]. We too have been investigating a number of different nitrogen containing heterocycles that are capable of multiple cyclometallation reactions, and it is the results concerning four of these systems that we report in this paper.

2. Results and discussion

2.1. Heterocycles

We chose to study four nitrogen containing heterocycles that would be capable of undergoing multiple cyclometallations (Fig. 1): 3,6-bis-(4-alkyloxyphenyl)pyridazines (**1**), 3,6-bis(4-alkyloxyphenyl)[1,2,4,5]tetrazines (**2**), 2,5-bis-(4-alkyloxyphenyl)pyrazines (**3**) and 1,4-bis-(5-alkyloxypyrimidin-2-yl)benzenes (**4**). A number of different alkyloxy groups were used, and there were no differences in the reactivity of the homologues. We have reported previously some of our results concerning pyridazines [18,19]. The synthesis of the

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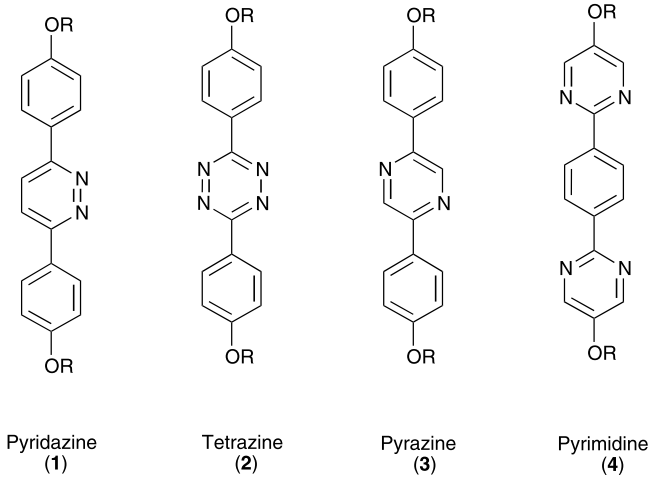


Fig. 1.

heterocycles has previously been reported though the yields might leave a little to be desired [20–22].

2.2. Pyridazines (*1*)

We have discussed the cyclometallation of pyridazines (**1**) previously [18], but it is salient to summarise our findings here (Scheme 1). Pyridazines are cleanly cyclopalladated once by palladium acetate in acetic acid, when one equivalent of palladium is used. Extended reaction temperatures and reaction times are necessary to bring about a second cyclopalladation with palladium acetate, but the compounds can be isolated. In contrast, the use of potassium tetrachloroplatinate results in exclusive double cycloplatination, even with one equivalent of platinum. We ascribed this difference to the presence of halide bridges which bring a second metal close to the organic framework, resulting in second cyclometallation that is quicker than the first.

2.3. Tetrazines (*2*)

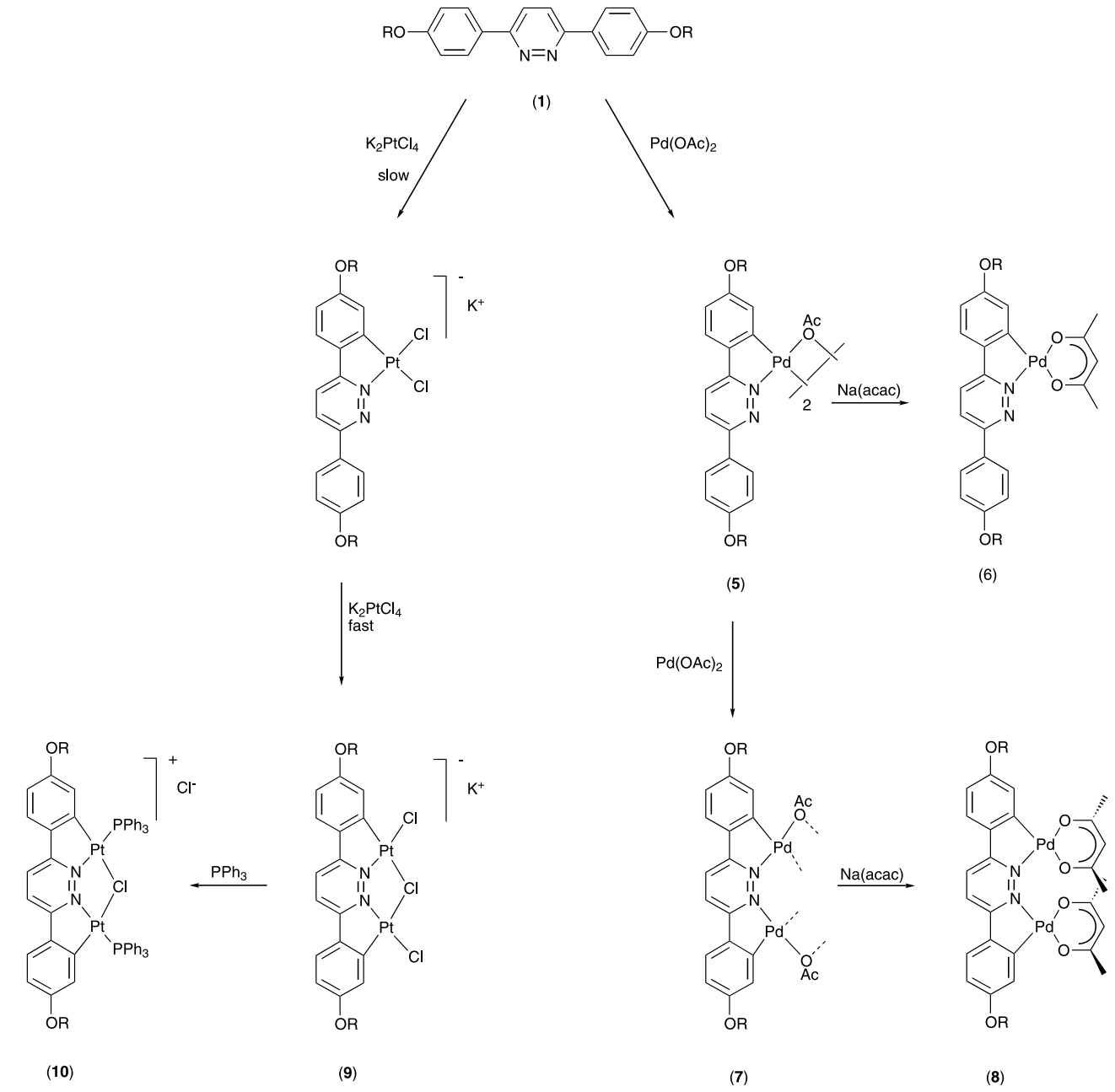
Tetrazines have the potential to be mono, di, tri and tetra-dentate, although by comparison with similar co-ordination complexes of 3,6-bis(2-pyrimidyl)-[1,2,4,5]tetrazine the formation of either tri- or tetra-nuclear compounds is highly unlikely [23]. While the mesomorphic properties of 3,6-disubstituted tetrazines have been studied [24,25] and the use of tetrazines as guest–host dyes for use in guest–host liquid crystal displays has previously been described [26,27], the mesomorphic properties of the tetrazines discussed here does not seem to have been reported in the literature before, we include full details here in the supporting information.

Tetrazines (**2**) react with one equivalent of palladium(II) acetate in acetic acid to give the brown–orange mono cyclopalladated compound, (**11**) (Scheme 2). By analogy with the work of others [10,28,29] these compounds are assumed to be dimers. These dimers were characterised by solution NMR and then cleaved by reaction with sodium acetylacetonate in tetrahydrofuran to give the monomeric compound **12**. Compounds (**12**) have been fully characterised. In contrast to the derivatives of the pyridazines [19] none of the tetrazine derivatives showed any mesomorphic behaviour, instead they decompose at temperatures in excess of 200 °C without melting. While the co-ordination compounds of a number of 3,6-substituted-[1,2,4,5]tetrazines have been reported [23] this would appear to be the first time such a cyclometallated tetrazine compound has been reported. In an attempt to doubly cyclometallate the tetrazines, they were reacted with two equivalents of palladium acetate in acetic acid, at elevated temperatures and for an extended time. No second cyclometallation was observed to take place.

We also tried to doubly cyclopalladate the tetrazines to form compounds **13** and **14**, using potassium tetrachloropalladate. While this did yield a small amount of a new compound, as identified by NMR, it was not clear which isomer was formed, either the *cis* metallated (**13**) or the *trans* metallated (**14**). The yield was very small, even when the reaction was carried out under a number of different reaction conditions; the other identified product being the monometallated chloride equivalent of **11**. The product had a distinctive NMR: only three peaks in the aromatic region, two doublets and a doublet of doublets, with both alkoxy chains being equivalent (all coupling constants and integrations appropriate for either structure). Even when vast excesses of palladium source was used the yield was never good, nor was triply or tetra cyclometallated product observed.

Cycloplatination reactions were also carried with tetrazines: one equivalent of potassium tetrachloroplatinate in acetic acid yielded an insoluble mono metallated derivative, assumed to be **15**, again this is in contrast to the case with pyridazines where no mono platination was observed. Subsequent reaction with triphenylphosphine gave the orange monomeric species **16**, whose structure was confirmed by good quality solution state NMR. The configuration of **16**, with the triphenylphosphine *trans* to the nitrogen of the tetrazine was inferred from the platinum satellite coupling constants in the ^{31}P-NMR of the compound: a coupling of 4336 Hz was observed which is typical of ^{1}J coupling *trans* to nitrogen. Attempts at double cycloplatination using two equivalents potassium tetrachloro platinate proved unsuccessful with only the monometallated species being formed.

The reason why these tetrazines will not readily undergo a second cyclometallation is, perhaps at first, not clear. The fact that pyridazines (**1**) will undergo a *cis* double cyclometallation rules out the possibility of it



Scheme 1.

being a totally steric effect. Some light is shed on the situation if we consider the following points:

The first cyclometallation of the tetrazines takes place as with the pyridazines, but at a substantially lower rate. This reduction in rate can be attributed to the presence of four electronegative nitrogens in a conjugated six member ring which results in the basicity of each individual N donor centre being very small with $pK_a < 0$: therefore they are poor nucleophiles. Although compared to the pyridazine the tetrazine ring is a poor σ-donor it is an excellent π acceptor due to the presence of an unusually low π*-orbital. Whilst this may result in a more thermodynamically stable mono cyclometallated product due to the presence of π-backbonding, it does hinder the formation of the di-metallated product. In addition, the central tetrazine ring is very electron withdrawing, this results in a lowering of the electron density in the phenyl rings in the 2 and 6 positions making them less susceptible to electrophilic attack and therefore cyclometallation. With the less active chloride based palladation source K_2PdCl_4, tetrazines were observed to undergo a second cyclometallation, but with unimpressive yields. Presumably this is similar to the effect we observed with pyridazines, where a chloride based platinum source resulted in high yields of a doubly metalled compound [18]. This would also imply

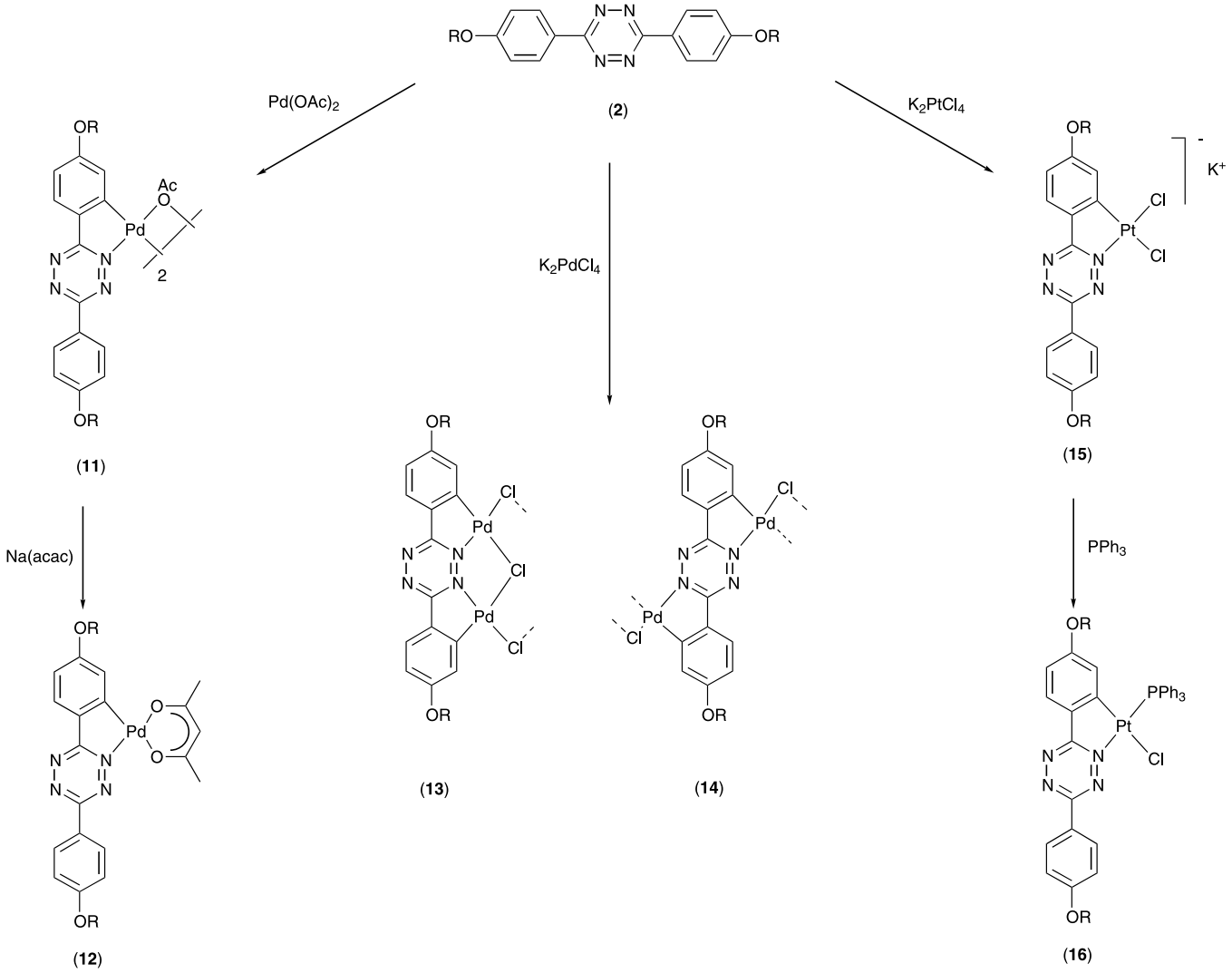
that the compound we produce here is the *cis* isomer **13** and not the *trans* isomer **14**. The absence of any sign of multiple cycloplatinations could just be due to the fact that platinations are that much less easy than palladations.

2.4. Pyrazines (*3*)

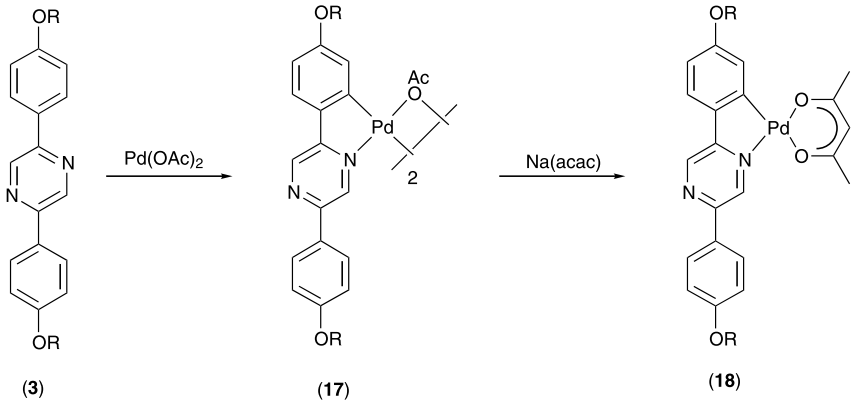
Pyrazines (**3**) are only capable of undergoing a *trans* dicyclometallation; when they were reacted with one equivalent of palladium acetate in acetic acid they yielded the monometallated dimer (**17**) (Scheme 3). These monometallated compounds were unambiguously characterised by ^{1}H-NMR, with the diagnostic doublet, doublet and doublet of doublets splitting pattern for the metallated ring and the protons of the central pyrazine ring rendered inequivalent, thus coupling to each other. The dimeric compound was cleaved by reaction with sodium acetylacetonate to give compound **18**, which was characterised by ^{1}H-NMR. Extended reaction times and elevated temperatures and other palladium sources did not lead to any doubly cyclometallated species. The lack of a second cyclometallation taking place must result entirely from electronic effects and not sterics, since there is no possibility of a sterically disfavoured *cis* dimetallation taking place. Although there is not the option for a *cis* dimetallation there is also no possibility of the first metallation holding a second metal atom close to the second co-ordination site via a bridging acetate or chlorine, thus promoting a second cyclometallation, as we proposed with the metallation of the pyridazines (**1**). Once again, the first co-ordination results in electron density being withdrawn from the pyrazine ring, resulting in the second nitrogen being a poorer nucleophile.

2.5. Pyrimidines (*4*)

Reaction of pyrimidines (**4**) with palladium acetate gave unexpected results. Rather than reacting cleanly



Scheme 2.

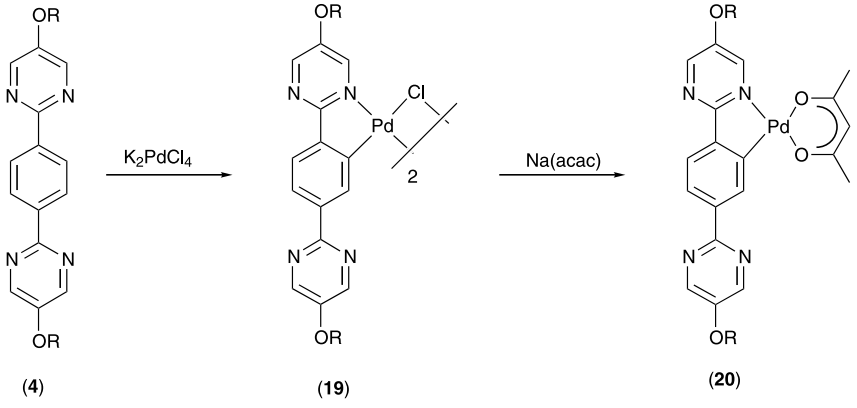


Scheme 3.

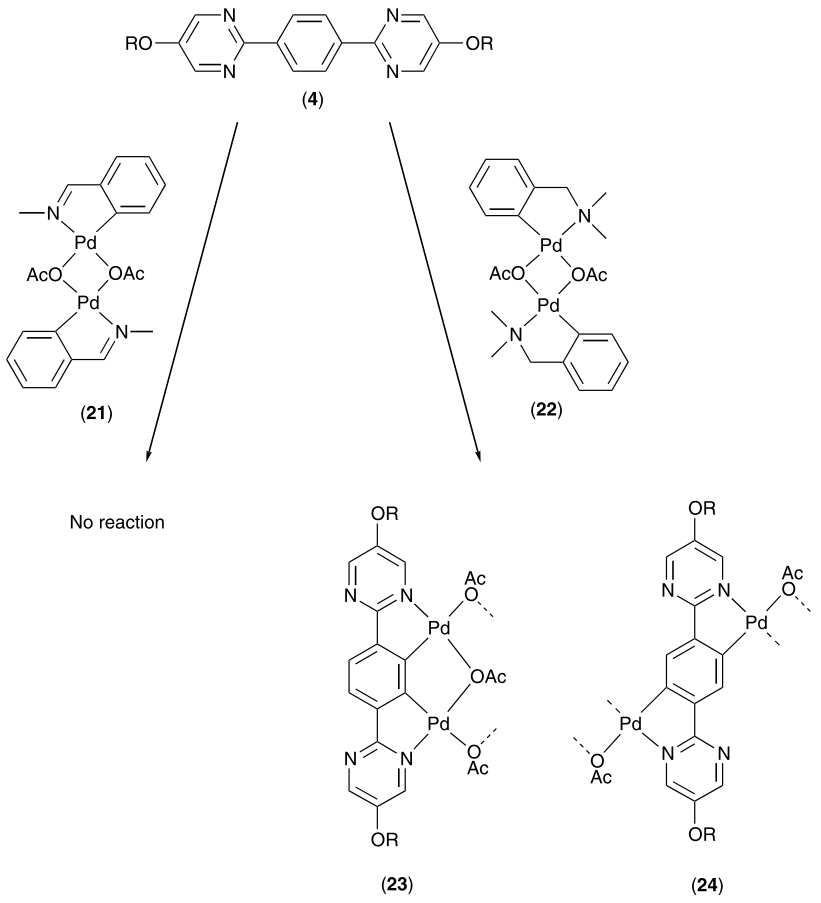
with one equivalent of palladium acetate to give only one compound with an unambiguous NMR spectrum comprising a singlet for the unmetallated ring, a pair of doublets for the metallated pyrimidine ring and the highly characteristic set of two doublets and a doublet of doublet for the central ring, the NMR spectra were in fact far more complicated. The ^{1}H-NMR showed a set of four singlets of equal intensity equally spaced and centred about 6.70 ppm, and five distinct sets of multiplets situated up field of this. Reaction of this mixture with sodium acetylacetonate, in an attempt to isolate some of the monometalated acetylacetonate derivatives proved unsuccessful. This line of synthesis was not pursued any further. However, pyrimidines do react cleanly with one equivalent of potassium tetrachloropalladate in acetic acid to give a yellow insoluble species, again by analogy with our work and others this is assumed to be the dimer (Scheme 4). Due to the insolubility of this material, no NMR data could be recorded. Subsequent reaction with acetylacetonate in tetrahydrofuran yields a monomeric species (**20**) which was fully characterised. Cyclometallation was clearly shown to have occurred at only one of the four possible positions.

Attempts at synthesising the di- tri- and tetra-metallated compounds proved unsuccessful both with potassium tetrachloro palladate and palladium acetate. Reaction with palladium chloride sources simply yielded the monometallated compound. This is presumably due to the lack of solubility of the monometallated derivative hindering the formation of a second metallocycle (this was the only case where a lack of solubility was an issue). When the more soluble acac complex **20** was reacted with a second equivalent of potassium tetrachloro palladate in acetic acid, rather than a second metallation occurring, the chloride (**19**) was simply reformed.

In an attempt to force a dimetallation reaction to take place we investigated the possibility of carrying out *trans*-cyclometallation [30] reactions with pyrimidines (**4**). Two palladium sources were synthesised as potential transmetallating agents. When the pyrimidines were mixed with one equivalent of the metallated Schiff's base compound **21** no reaction took place. If, however, the metallated *N*,*N*-dimethylbenzylamine (**22**) was reacted with the pyrimidine ligands then a small amount of what we believe to be a dimetallated pyrimidine compound **23** or **24** was identified by ^{1}H-NMR (Scheme 5). It is not clear which of the two possible isomers is formed, as the NMR spectrum for both will be very similar. In the aromatic region the NMR spectrum will essentially only comprise two doublets with small



Scheme 4.



Scheme 5.

coupling constants and a singlet; since the acetate groups are fluxional on the NMR timescale no difference will be seen in that region. By analogy with our previous work we might expect the *cis* (**23**) isomer to be favoured over the *trans* (**24**).

Attempts at reacting **23/24** further with either sodium acetylacetonate or triphenylphosphine gave untractable products.

2.6. Comparative reactivities

All of the ligands we have used underwent a single cyclometallation with monomeric compounds isolated as their acetylacetonate or PPh_3 derivatives. Differences in reactivity were observed in this cyclometallation reaction. In the case of pyridazines, a reaction of one equivalent of ligand with palladium acetate consumed all the ligand within 4 h. Pyrazines and pyrimidines reacted slower with all the ligand having been consumed within 24 h. In the case of cyclometallation of tetrazines the rate was even slower and there was still unreacted ligand present after reaction times of 24 h. However, these differences were not as pronounced as those in the reactivity when we attempted to doubly metallate the ligand.

The pyridazines were the only series of ligands to successfully undergo a double cyclometallation with isolable compounds in high yields. It might be expected that with pyridazines a second co-ordination would be less favourable than the first as, following the formation of the first σ-bond between a lone pair on nitrogen and the metal, the remaining nitrogen in the heterocycle is a less good σ-donor. In part this is simply due to the fact that the first co-ordination reduces the electron density in the donor ring, reducing its ability to co-ordinate, but pyridazines have an enhanced nucleophilicity of the first nitrogen as a result of the α-effect: two adjacent lone pairs on the nitrogens raise the HOMO of the ligand, thus making it a better nucleophile. With the pyridazines, we believe another factor that affects the second cyclometallation is the participation of the first metal with a bridging ligand holding a second metal close to the ligand thus assisting the second cyclometallation. The extreme manifestation of this effect is that a single cycloplatinated pyridazine derivative could not be isolated, and only doubly metallated derivatives were identified. When palladium acetate is used as the source of palladium the bridging group will be an acetate, resulting in a seven membered ring. Whilst this arrangement might assist in the second cyclometallation, the

steric and electronic requirements means that this second cyclometallation is kinetically disfavoured over another monocyclometallation on a different ligand—hence we can isolate 100% monocyclopalladated material from one equivalent of palladium acetate and pyridazine.

With pyrimidines and tetrazines there is also the potential to form the same sort of bridge as with pyridazines, but no second cyclometallation was observed with palladium acetate. The first cyclometallation of a pyrimidine results in an insoluble compound thus precluding the formation of any multiply cyclometallated species. The tetrazine ligands are very poor σ-donors and as such the formation of complexes is presumably unfavourable, even with the presence of a bridging ligand. As with the other ligands here, coordination of the first metal would reduce the capability of the remaining nitrogens in the tetrazine ring to form σ-bonds due to the reduction of electron density in the ring, thus it is not surprising that multiple cyclometallation is not favoured.

With pyrazines the second metallation will be less likely to take place than the first one because of the reduced σ-donor ability of the ligand after the coordination of the first metal, and also because there is no opportunity for any bridging ligands to hold a metal in close proximity to the second nitrogen.

The transcyclometallation reactions outlined in Scheme 5 show considerable promise, and allow us to propose an adaptation to van Koten's theory, where the driving force for the reaction is attributed to the differences in Pd-donor atom bond strength [30]. Our Schiff's base reagent **21** does not show any reactivity, whereas the benzylamine reagent **22** does: we propose that an additional factor that may tip the balance is the aromaticity of the metallocycles that are formed or destroyed. Thus, the five-membered aromatic palladocycle [31] in the Schiff's base reagent would be replaced by another five membered aromatic palladocycle in the product (energetically neutral) whereas the five membered non-aromatic palladocycle in the benzylamine reagent would be replaced by five membered aromatic palladocycle in the product (energetically favourable).

3. Conclusions

The four different nitrogen containing heterocycles that we studied here show very different reactivities towards the cyclopalladation and cycloplatination reactions. To a large extent these differences can be attributed to the differing ground state structures of the heterocycle, but there are additional factors at work here. In particular we have identified further examples of a first cyclometallated metal assisting a second cyclometallation, through the assistance of bridging ligands. Additional work with a *trans*-cyclometallation reagent shows considerable promise.

4. Experimental

4.1. General

All chemicals were used as supplied, unless noted otherwise. All heterocycles were synthesised via the published routes [20–22]. All elemental analyses were performed by Warwick Analytical Service.

4.2. Preparation of palladium(acetato)-3,6-bis(4-pentoxphenyl)[1,2,4,5]tetrazine (*11*)

Palladium acetate (0.025 g, $1.10 \times 10^{--4}$ mol) was added to a solution of 3,6-bis-(4-pentoxy-phenyl)-[1,2,4,5]tetrazine (0.051 g, $1.10 \times 10^{--4}$ mol) in acetic acid (15 ml) at 60 °C. The solution was stirred for 16 h and the solvent removed. The compound was washed with hexane, dissolved in chloroform and filtered through Celite. The chloroform was removed and the brown solid dried. Yield 0.04 g (4.02×10^{-3} mol, 73%).

δ_H (400 MHz, $CDCl_3$): 8.27 (2H, AA′XX′, unmetallated ring), 7.55 (1H, d, $^3J_{(HH)} = 8$ Hz, metallated ring), 7.00 (2H, AA′XX′, unmetallated ring), 6.40 (1H, dd, $^3J = 8$ Hz, $^4J = 4$ Hz, metallated ring), 6.35 (1H, d, $^4J =$ 4 Hz, metallated ring), 4.05 (2H, t, $^3J = 7$ Hz, OCH_2), 3.45 (2H, t, $^3J = 7$ Hz, OCH_2), 2.35 (3H, s, OAc), 2.10 (3H, s, OAc), 1.9 (12H, m, CH_2), 0.90 (6H, t, Me).

4.3. Preparation of palladium(acac)-[3,6-bis(4-pentoxphenyl)[1,2,4,5] tetrazine] (*12*)

Sodium acetylacetonate (0.005 g, 4.05×10^{-5} mol) was added to a solution of palladium(μ-acetato)-3,6-bis(4-pentoxphenyl)[1,2,4,5]tetrazine (0.02 g, 1.84×10^{-5} mol) in THF (25 ml). The mixture was stirred at room temperature (r.t.) for 4 h and the solvent removed under reduced pressure. The resulting solid was washed with hexane (5 ml) and diethyl ether (5 ml) and dried to yield an orange solid. Yield 0.015 g (2.57×10^{-5} mol, 70%).

δ_H (400 MHz, $CDCl_3$): 8.45 (2H, AA′XX′, unmetallated ring), 7.90 (1H, d, $^3J_{(HH)} = 7$ Hz, metallated ring), 7.20 (1H, d, $^4J_{(HH)} = 3$ Hz, metallated ring), 7.00 (2H, AA′XX′, unmetallated ring), 6.75 (1H, dd, $^3J_{(HH)} = 7$ Hz, $^4J_{(HH)} = 3$ Hz, metallated ring), 5.40 (1H, s, central acac), 4.05 (4H, m, OCH_2), 2.15 (3H, s, acac Me), 2.13 (3H, s, acac Me), 1.45 (12H, m, CH_2), 0.90 (6H, m, Me).

4.4. Preparation of di-palladium(chloro)-3,6-bis(4-pentoxphenyl)[1,2,4,5]tetrazine (**13**)/(**14**)

Potassium tetrachloropalladate (0.080 g, 2.46×10^{-4} mol) was added to a solution of 3,6-bis-(4-pentoxyphenyl)-[1,2,4,5]tetrazine (0.050 g, 1.23×10^{-4} mol) in acetic acid (15 ml) at 60 °C. The solution was stirred for 16 h and the solvent removed. The compound was washed with water, acetone and then dissolved in chloroform and filtered through Celite. The chloroform was removed and the brown solid dried under vacuum. Yield 0.0056 g (8.24×10^{-6} mol, 7%).

δ_H (400 MHz, $CDCl_3$): 8.42 (2H, d, $^3J_{(HH)} = 7$ Hz, metallated ring), 7.45 (2H, d, $^4J = 2$ Hz, metallated ring), 7.03 (2H, dd, $^3J = 7$ Hz, $^4J = 2$ Hz, metallated ring), 4.02 (4H, t, $^3J = 7$ Hz, OCH_2), 1.72 (4H, m, CH_2), 1.3 (8H, m, CH_2), 0.91 (6H, t, Me).

4.5. Preparation of platinum(chloro)-3,6-bis(4-pentoxphenyl)[1,2,4,5]tetrazine (**15**)

Potassium tetrachloroplatinate (0.10 g, 2.50×10^{-4} mol) was added to a solution of 3,6-bis-(4-pentoxyphenyl)-[1,2,4,5]tetrazine (0.10 g, 2.46×10^{-4} mol) in acetic acid (25 ml). The mixture was stirred under reflux for 48 h and the solvent removed to yield a brown solid, which was washed with hexane (5 ml) and diethyl ether (5 ml). The product proved insoluble in common NMR solvents and was used in the next step without further purification (0.052 g, 1.25×10^{-4} mol, 41%).

4.6. Preparation of [platinum (triphenylphosphine)(chloro){3,6-(4-pentyloxyphenyl)[1,2,4,5]tetrazine}] (**16**)

Triphenylphosphine (0.063 g, 2.4×10^{-4} mol) was added to **15** (0.041 g, 6×10^{-5} mol) in acetone (5 ml) and stirred for 10 min. The acetone was removed and the residue dissolved in chloroform:methanol 99:1 and filtered through a short column of silica. The solvent was removed yielding a very dark yellow solid (0.035 g, 6.08×10^{-5} mol, 77%).

$\delta_H\{^{31}P\}$ (400 MHz, $CDCl_3$): 8.45 (2H, AA′XX′, unmetallated ring), 8.05 (1H, d, $^3J_{(HH)} = 8$ Hz, metallated ring), 7.60–7.10 (15H, m, PPh_3), 6.90 (2H, AA′XX′, unmetallated ring), 6.60 (1H, dd $^3J_{(HH)} = 8$ Hz $^4J_{(HH)} = 5$ Hz, metallated ring), 6.20 (1H, d, $^4J_{(HH)} = 5$ Hz $^3J_{(PtH)} = 61$ Hz, metallated ring), 4.00 (2H, t, OCH_2), 2.90 (2H, t, OCH_2), 2.75 (4H, m, CH_2), 1.50–1.0 (8H, m, CH_2), 0.85 (3H, t, Me), 0.75 (3H, t, Me). $\delta_P\{^1H\}$ (161.92 MHz, $CDCl_3$): 37.66 (s, $^1J_{(Pt-P)} =$ 4336 Hz)

4.7. Preparation of palladium(μ-acetato)-2,5-bis(4-hexyloxyphenyl)pyrazine (**17**)

Palladium acetate (0.05 g, 2.22×10^{-4} mol) was added to a solution of 2,5-bis(4-hexyloxyphenyl)pyrazine (0.100 g, 2.17×10^{-4} mol) in acetic acid (25 ml) and stirred overnight at 60 °C. The solvent was removed under reduced pressure and the yellow residue washed with hexane (5 ml) and diethyl ether (5 ml). Yield 0.136 g (7.81×10^{-5} mol, 72%).

δ_H (400 MHz, $CDCl_3$): 8.35 (1H, d $^5J_{(HH)} = 1.5$ Hz, central ring), 8.15 (1H, d $^5J_{(HH)} = 1.5$ Hz, central ring), 7.60 (2H, AA'XX', unmetallated ring), 6.90 (2H, AA′XX′, unmetallated ring), 6.80 (1H, d $^3J_{(HH)} = 9$ Hz, metallated ring), 6.25 (1H, d $^4J_{(HH)} = 4$Hz, metallated ring), 6.05 (1H, dd $^3J_{(HH)} = 9$ Hz $^4J_{(HH)} = 4$ Hz, metallated ring), 3.95 (4H, m, OCH_2), 1.75 (4H, m, CH_2), 1.50 (6H, s, OAc), 1.45–1.10 (16H, m, CH_2), 0.85 (6H, m, Me).

4.8. Preparation of [palladium(acac){2,5-bis(4-hexyloxyphenyl)pyrazine] (**18**)

Sodium acac (0.0211 g, 7.6×10^{-4} mol) was added a solution of palladium(μ-acetato)-2,5-bis(4-hexyloxyphenyl)pyrazine (**17**) (0.1g, 8.00×10^{-5} mol) in acetone (15 ml) and stirred overnight at room temperature. The solvent was removed and the resulting yellow compound purified by column chromatography on silica, using $CHCl_3$:MeOH, 90:10 as an elutant. Yield 0.086 g (1.30×10^{-4} mol, 81%).

δ_H (400 MHz, $CDCl_3$): 8.85 (1H, s, central ring), 8.65 (1H, s, central ring), 7.85 (2H, AA′XX′, unmetallated ring), 7.30 (1H, d $^3J_{(HH)} = 8$Hz, metallated ring), 6.95 (2H, AA′XX′, unmetallated ring), 6.95 (1H, d $^4J_{(HH)} =$ 3Hz, metallated ring), 6.55 (1H, dd $^4J_{(HH)} = 3$Hz $^3J_{(HH)} = 8$ Hz, metallated ring), 5.30 (1H, s, central acac), 3.95 (4H, m, OCH_2), 2.00 (3H, s, acac Me), 2.01 (3H, s, acac Me), 1.70 (2H, m, CH_2), 1.3 (12H, m, CH_2), 0.90 (6H, m, Me).

4.9. Preparation of [palladium(dichloro){3,6-bis(4-octyloxyphenyl)pyrimidine}] (**19**)

Potassium tetrachloropalladate (0.071 g, 2.16×10^{-4} mol) was added to a stirred solution of 3,-6-bis(4-octyloxyphenyl)pyrimidine (0.10 g, 2.16×10^{-4} mol) in acetic acid (25 ml) at 60 °C and stirred overnight. The solvent was removed to yield a bright yellow sparingly soluble compound (0.083 g, 8.02×10^{-5} mol, 74%).

4.10. Preparation of [palladium(acac){3,6-bis(4-octyloxyphenyl)pyrimidine}] (**20**)

Sodium acetylacetonate (0.013 g, 1.06×10^{-4} mol) was added to a solution of palladium(dichloro){3,6-

bis(4-octyloxyphenyl)pyrimidine} (19) (0.05 g, 4.81×10^{-5} mol) in THF (25 ml) and stirred overnight. The solvent was removed under vacuum and the dark yellow solid dissolved in chloroform and filtered through Celite. The chloroform was removed under reduced pressure yielding (20) (0.048 g, 7.20×10^{-5} mol. 75%).

δ_H (400 MHz, $CDCl_3$): 8.60 (1H, d $^4J_{(HH)} = 4$ Hz, central ring), 8.45 (2H, s, non coordinating ring), 8.10 (1H, dd $^3J_{(HH)} = 8$ Hz $^4J_{(HH)} = 4$ Hz, central ring), 7.75 (1H, d $^3J_{(HH)} = 8$ Hz, central ring), 6.95 (2H, s, coordinating ring), 5.01 (1H, s, central acac), 4.10 (2H, t, $^3J_{(HH)} = 7$ Hz, OCH_2), 3.75 (2H, t, $^3J_{(HH)} = 7$ Hz, OCH_2), 2.25 (3H, s, acac Me), 2.20 (3H, s, acac Me), 1.85 (4H, m, CH_2), 1.3 (16H, m, CH_2), 0.90 (6H, m, Me).

FAB MS (NBA) $m/z = 695$ [M^+], 595 [largest, $M^+ -$ acac].

4.11. Preparation of [bis-palladium-bis(μ-acetato){1,4-bis-(5-alkoxy-pyrimidin-2-yl)-benzene}] (**23**)/(**24**)

Cyclometallated benzylamine (**22**) (0.12 g, 2.04×10^{-4} mol) was added to a solution of 1,4-bis-(5-octyloxy-pyrimidin-2-yl)-benzene (0.10 g, 2.04×10^{-4} mol) in acetic acid. The mixture was stirred overnight at 60 °C and the solvent removed. Products were not isolated, and the NMR spectrum run directly. The peaks listed below were present corresponding to a yield of about 20%, other expected peaks (the octyloxy chain) were obscured by unreacted pyrimidine.

δ_H (400 MHz, $CDCl_3$): 8.75 (2H, s, central ring), 7.10 (2H, d, $^4J_{(HH)} = 3$Hz), 6.90 (2H, d, $^4J_{(HH)} = 3$Hz), 3.90 (4H, t, $^3J_{(HH)} = 7$Hz, OCH_2).

5. Supplementary material

Full thermal behaviour of the homologous tetrazines and a discussion of this data is available as supporting information and is available from the author on request.

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