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Bis(N-heterocyclic carbene) Dipalladium Complexes: Synthesis, Solid-State Conformational Studies and Solution Behaviour

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New palladium(II) bis(N-heterocyclic carbene) (NHC) complexes have been prepared via metallomacrocyclic Ag^I ligand transfer agents. Reaction of 1,4-bis(3-isopropylimidazolium)xylene (**1a**) hexafluorophosphate with Ag_2O gives a Ag^I macrocyclic NHC complex in which two silver ions are sandwiched between two dipodal ligands (**2a**). The NHC moieties adopt a *cisoid* conformation relative to one another. Upon transfer to palladium to give $[\{PdCl_2(MeCN)\}_2$(bis-NHC)] (**3a**) the NHC ligands in the complexes adopt a mixture of *cisoid* and *transoid* conformers in the solid state, which have been characterized by X-ray crystallography. In CD_3CN solution the *cisoid* and *transoid* conformers interconvert and exhibit resonances for a single averaged form. DFT calculations indicate an interconversion barrier of 56 kJ mol^{-1}. In $CDCl_3$ solution two different isomers are observed which have been assigned to isomers of a chloride-bridged dimer (**4a**) following dissociation of the acetonitrile ligands.

Introduction

N-heterocyclic carbene (NHC) metal complexes have been the focus of intense research over the past decade, due to their ability to generate robust and versatile catalyst precursors that offer complementary properties to phosphane congeners, in some cases showing superior efficacy.[1–3] NHC ligands offer structural diversity via modification of substituents, particularly at the N-atoms, enabling control of reactivity. Palladium(II)–NHC complexes have been found to be highly active in C–C cross-coupling reactions, such as Heck and Suzuki–Miyaura,[4–7] and also in polymerization reactions.[8] Furthermore, palladium complexes of the type Pd(pyridine)Cl_2(NHC) and $PdCl_2(NHC)_2$ have been found to exhibit potent anticancer activity.[9]

Various bis-NHC ligands have been reported, which are usually linked by alkenic chains[7,10–13] or an N-donor such as a pyridyl derivative or amine,[14–16] and tend to form chelating complexes with metals. NHC ligands containing a xylylene-bridge are surprisingly rare. Those reported to date either possess one carbene donor,[9] two carbene donors,[17,18] or form part of a cyclophane.[19,20] Tripodal arene-anchored NHC ligands, in which the imidazolium moieties are in the 1-, 3- and 5-positions, have also been reported, though these are unusual and tripodal NHCs linked by a carbon or nitrogen atom tend to dominate this class.[21,22] There are very few reports of bis-NHC complexes in which the carbene moieties are linked by an arene group devoid of an N-donor.[23] This is possibly due to the instability of the imidazolium precursors towards strong bases traditionally used for deprotonation (e.g. *t*BuOK).

In recent years, silver(I) complexes of NHCs as carbene transfer reagents have been the subject of intense study, due to their superior stability over many free carbenes.[24,25] In this paper we report the synthesis of new palladium complexes containing bis-NHC ligands, via silver(I) macrocycles. The new complexes show distinct dynamic behaviour in different solvents, which has been probed in solution and in the solid state. DFT calculations complement the findings.

Results and Discussion

A convenient method for the formation of NHCs involves deprotonation of an imidazolium salt precursor.[26] Reaction of 1,4-bis(bromomethyl)benzene and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene with the appropriate *N*-substituted imidazole in dichloromethane at room temperature affords the diimidazolium salts **1a**, **1b**, and **1c** in high yields. Treatment of the diimidazolium bromide salts with NH_4PF_6 or NH_4BF_4 in methanol affords the diimidazolium hexafluorophosphate or tetrafluoroborate salts

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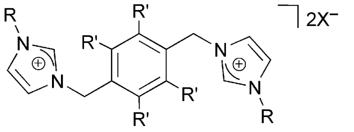
(Figure 1). The characteristic proton resonances observed in the ^{1}H NMR spectra are the imidazolium N(CH)N proton at 8.7–9.4 ppm, and the splitting of the backbone $N(CH)_2N$ protons into two doublets.



X = Br, PF_6, BF_4

1a R = *i*Pr, R' = H
1b R = Me, R' = H
1c R = Me, R' = Me

Figure 1. Diimidazolium salts.

Colourless crystals of **1b**$(PF_6)_2$ were grown via slow evaporation of a saturated acetonitrile solution, in a drybox, at room temperature and the compound was characterised by X-ray crystallography. The imidazolium moieties in the structure adopt a *transoid* position relative to one another and interact with the PF_6^- anions via CH···F interactions (Figure 2).

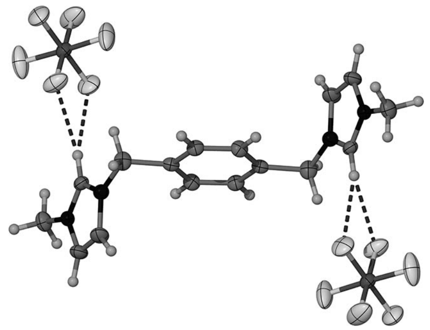


Figure 2. X-ray crystal structure of the diimidazolium salt **1b**$(PF_6)_2$ (30% ellipsoids).

Attempts to deprotonate the imidazolium precursors using traditionally used strong bases [e.g. *t*BuOK, KH, $LiN(SiMe_3)_2$] led to decomposition, possibly as a result of the base reacting with the acidic benzylic methylene groups.[27,28] The imidazolium salts were treated with $Pd(OAc)_2$, which itself acts as a base, in an attempt to synthesise Pd^{II} bis-NHC complexes. Although NMR spectroscopy suggested NHC complexes to have formed, the resonances were broad and the products difficult to purify, presumably due to the formation of polymeric Pd^{II}–NHC complexes.

An effective route for the generation of NHCs is the reaction of an imidazolium salt with a silver base to form the Ag^I–NHC compound.[24] The carbene can then be transmetallated to a transition metal to generate the desired "M–NHC" complex. Reaction of the imidazolium salts **1a**$(PF_6)_2$, **1b**$(BF_4)_2$ and **1c**$(PF_6)_2$ with Ag_2O in DMSO at 75 °C affords the silver complexes **2a**$(PF_6)_2$, **2b**$(BF_4)_2$ and **2c**$(PF_6)_2$, respectively (Figure 3). The absence of the N(CH)N imidazolium proton in the ^{1}H NMR spectra, and the appearance of a Ag–C resonance at δ = 206.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum for **2b**$(BF_4)_2$, indicates that the reaction has reached completion. The ^{1}H NMR spectrum of **2c**$(PF_6)_2$ in both [D$_6$]DMSO and CD_3CN exhibits relatively broad resonances, suggesting fluxional behaviour in solution. A ^{13}C NMR spectrum of this silver complex was unobtainable, possibly due to the broadness of the resonances and its relatively low solubility. The compounds are all air and moisture stable and relatively light stable. [D$_6$]DMSO NMR samples kept for one week showed no sign of decomposition in the ^{1}H NMR spectra, although a slight darkening of the solutions did occur.

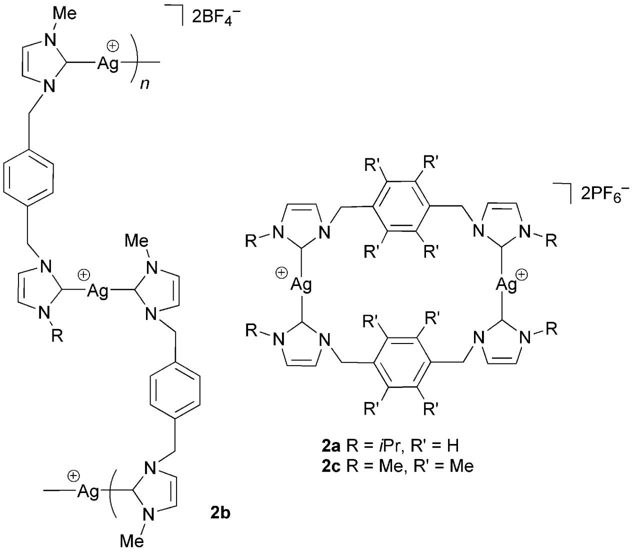


Figure 3. Ag^I–NHC compounds.

Colourless crystals of **2a**$(PF_6)_2$ and **2c**$(PF_6)_2$ were grown by the slow evaporation of saturated dichloromethane solutions at room temperature and characterised by X-ray crystallography. The structures reveal metallomacrocyclic dimers, in which two silver(I) ions are bridged by two bis-NHC ligands (Figure 4). Although the Ag atoms are coplanar with the ring, the distances between them (8.92 Å for **2a**$(PF_6)_2$ and 8.50 Å for **2c**$(PF_6)_2$) are too large for any Ag···Ag interactions.[29,30] The C–Ag–C bond in **2c** is slightly bent (C–Ag–C 169.3°), presumably due to steric effects from the benzylic methyl groups. The aromatic rings adopt an offset π-π-stacking arrangement and there is essentially no free space in the centre of the rings. Contamination with X^-/AgX_2^- species does not occur which is a problem more commonly observed when the imidazolium bromide or chloride precursors are employed.[24] The Ag–C distances 2.089(2) and 2.091(2) Å (**2b**) and 2.089(2) and 2.094(2) Å (**2c**) are comparable to those reported in the literature.[31–33,20]

Colourless crystals of **2b**$(BF_4)_2$ were grown by the slow evaporation of a saturated acetonitrile solution at room temperature. The structure reveals an interesting coordination polymer. As in previous structures, Ag^I ions are bridged by two NHC ligands, though the second NHC of each ligand coordinates to different Ag^I ions to form a continuous one-dimensional chain (Figure 5). BF_4^- anions and acetonitrile molecules occupy the space in between the

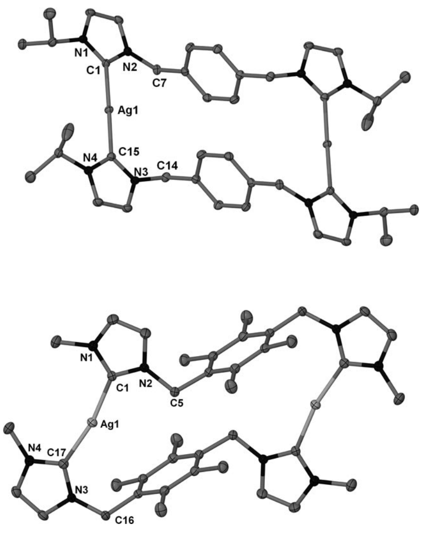


Figure 4. X-ray molecular structures of the metallomacrocyclic dications **2a** (top) and **2c** (bottom) (50% ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: (**2a**) Ag(1)–C(1) 2.0906(18), Ag(1)–C(15) 2.0886(18); C(1)–Ag(1)–C(15) 178.76(7), C(1)–N(2)–C(7) 123.46(17). (**2c**) Ag(1)–C(1) 2.0893(18), Ag(1)–C(17) 2.0940(19); C(1)–Ag(1)–C(17) 169.33(7), C(1)–N(2)–C(5) 124.15(15).

chains and there are negligible π–π-stacking interactions. The Ag–C distances, 2.072(7) and 2.067(6) Å, are relatively short compared to the mean value of Ag–C (NHC) distances in the Cambridge Structural Database (CSD) of 2.108 Å.[31–33,20] Although the distance between the Ag atoms of 5.41 Å is shorter than in **2a** and **2c**, it remains too large for Ag···Ag interactions.[29,30]

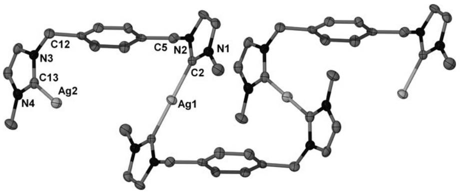


Figure 5. X-ray molecular structure of the metallopolymer **2b** (50% ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: Ag(1)–C(2) 2.072(5), Ag(2)–C(13) 2.067(5), C(2)–Ag(1)–C(2) 180.0, C(13)–Ag(2)–C(13) 180.000, C(2)–N(2)–C(5) 124.3(4).

Using the Ag^I–NHC compounds we have successfully transferred the bis-NHC ligands on to palladium(II). Reaction of **2a**$(PF_6)_2$ with four equivalents of $PdCl_2(MeCN)_2$ in DMSO at room temperature, followed by filtration through Celite™ and removal of the solvent in vacuo affords a compound showing a complex ^{1}H NMR spectrum in $CDCl_3$ solution. The spectrum simplifies in CD_3CN solution. Recrystallisation from acetonitrile gives [{$PdCl_2(MeCN)$}$_2$-(bis-NHC)] **3a**. It is likely that the crude mixture prior to recrystallisation is undergoing exchange processes in solution, for example between monomers, dimers and polymers, of which there is precedence for in the literature (Figure 6).[34] This may be promoted by the presence of residual $PdCl_2(MeCN)_2$ or ligand from the reaction. A mass spectrum recorded in dichloromethane prior to recrystallisation shows a signal at *m*/*z* 681.9 attributable to **3a**, and also a signal at *m*/*z* 1316.9 attributable to the chloride-bridged dimer **4a**. Recrystallisation from acetonitrile/diethyl ether selectively precipitates **3a**.

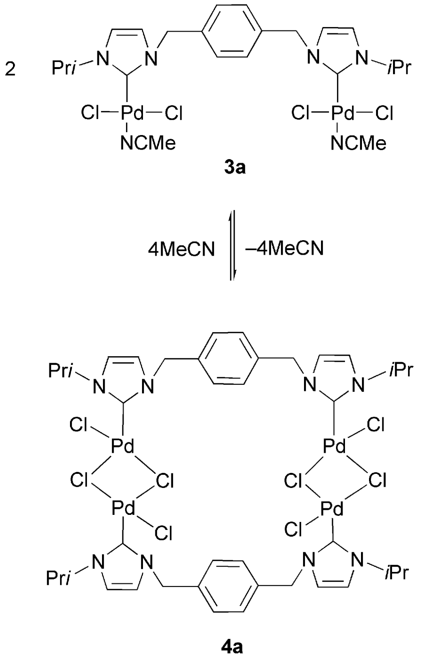


Figure 6. Proposed dynamic processes of complex **3a** in solution.

The preparation of **3a** can also be achieved using dichloromethane as the reaction solvent. Following a reaction at room temperature and filtration through Celite™ a yellow solid was precipitated by adding *n*-hexane. The ^{1}H NMR spectra following recrystallisation are identical to that obtained from the reaction in DMSO.

Colourless crystals of formula [{$PdCl_2(MeCN)$}$_2$(μ-**1a**-2 H)] were grown via diffusion of diethyl ether into an acetonitrile solution of **3a**. The structure shows a bis-NHC complex containing two palladium(II) centres (Figure 7). The coordination geometry around the palladium(II) centres is essentially square planar with one carbene, two chloride ligands and one acetonitrile ligand *trans* to the NHC. The imidazolium moieties adopt a *transoid* arrangement with respect to one another with the Pd–C(NHC) bond length being 1.948(2) Å, which is relatively short when compared to chelating bis-NHC complexes.[14,19,35,36] The Pd-C(NHC) bond length is, however, comparable to those in which the palladium(II) centre possesses only one NHC donor.[37,38] The shortest intermolecular contacts in the structure are CH···Cl interactions involving the acetonitrile solvent molecules, aryl rings and methylene groups, with the H···Cl distances in the region of 2.9 Å. Metal-coordinated chloride is known to be a good hydrogen-bond acceptor.[39–41]

A second crystal structure was also obtained via diffusion of diethyl ether into an acetonitrile solution of the complex. The structure shows a bis-NHC containing two palladium(II) centres, with the environment around each palladium being identical to the previous structure (Fig-

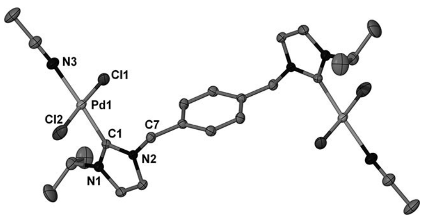


Figure 7. X-ray molecular structure of *transoid*-**3a** (50% ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: Pd(1)–Cl(1) 2.2995(6), Pd(1)–Cl(2) 2.2964(6), Pd(1)–C(1) 1.9481(18), Pd(1)–N(3) 2.0826(18); N(2)–C(7)–C(8) 111.95(15).

ure 8). The imidazolium moieties, however, are disposed in a mutually *cisoid* orientation with respect to the aromatic ring face. The Pd–C(NHC) bond length of 1.944(5) Å is comparable to the *transoid* conformer. The structure packs in an interesting $Z' = 2$ arrangement with the isopropyl group of one molecule entering the C-shaped cup of the other, where it forms a particularly short imidazole CH···Cl hydrogen bond, H···Cl 2.66 Å.[42] It is possible that the isolation of pure crystalline conformers of either conformer is highly dependent on the crystallisation conditions. This is likely to be concentration dependent as both conformers crystallise from acetonitrile/diethyl ether in different ratios, depending upon the amount of sample in solution.

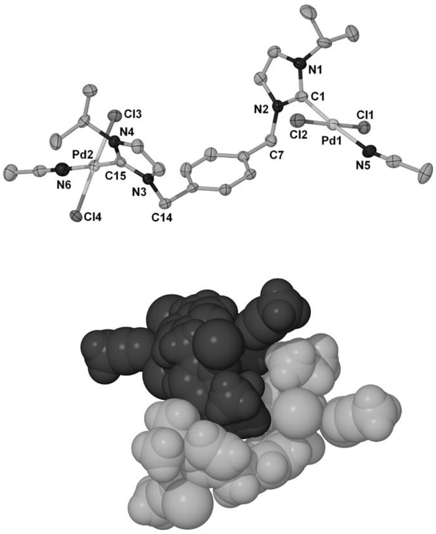


Figure 8. (top) X-ray molecular structure of *cisoid*-**3a** (50% ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: Pd(1)–Cl(1) 2.3031(14), Pd(1)–Cl(2) 2.3144(15), Pd(1)–C(1) 1.944(5), Pd(1)–N(5) 2.088(5); N(2)–C(7)–C(8) 113.3(4). (bottom) Space filling diagram showing the crystal packing in *cisoid*-3a (the two independent molecules are shown in different colours).

The ^{1}H NMR spectrum of crystals of both isomers of **3a** in CD_3CN exhibits resonances attributable to a single species, with the Ar-H and CH_2 resonances existing as singlets (Figure 9). It is likely that the interconversion between *cisoid* and *transoid* conformers is relatively fast on the NMR timescale, hence resonances for an averaged species are observed in the ^{1}H NMR spectrum. The mass spectrum of **3a** recorded in acetonitrile displays a major signal at *m*/*z* 681.7 attributable to [**3a** – Cl – MeCN]$^+$. There are no signals that indicate the presence of the chloride-bridged dimer **4a**.

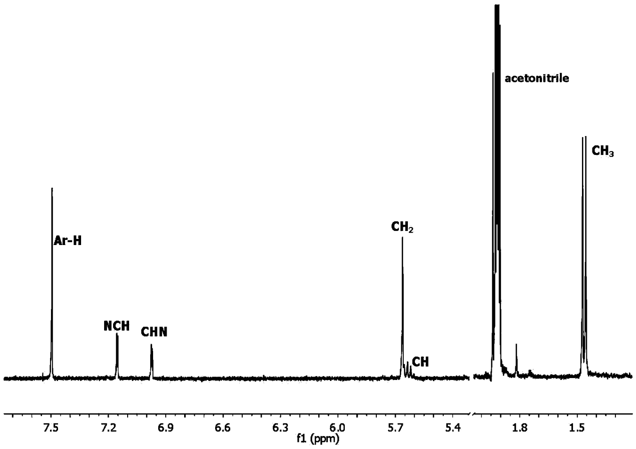


Figure 9. ^{1}H NMR spectrum of **3a** in CD_3CN.

The ^{1}H NMR spectrum of crystals of **3a** in $CDCl_3$, from which the *transoid* crystal structure had been obtained, exhibits sets of resonances attributable to two NHC complexes (Figure 10a). We assign these two sets of resonances to two isomers of the chloride-bridged dimer, **4x** and **4y** (Figure 11). Multiplets at δ = 5.58 ppm and 5.44 ppm suggest the presence of two different *i*Pr CH environments, and two pairs of geminal doublets in the CH_2 region (δ = 5.7 ppm to 5.1 ppm) with coupling constants of 13.8 Hz indicate that, in addition to two different CH_2 environments, the CH_2 protons are diastereotopic and magnetically inequivalent. The aromatic region exhibits two singlets, two doublets each with a coupling constant of 8.4 Hz, and four doublets each with a smaller coupling constant of 1.4 Hz. The doublets possessing the smaller coupling constant are likely to be due to $N(CH)_2N$, as these protons exhibit coupling constants of 1.6 Hz in the Ag–NHC **2a**$(PF_6)_2$. The remaining aromatic region resonances suggest that two dif-

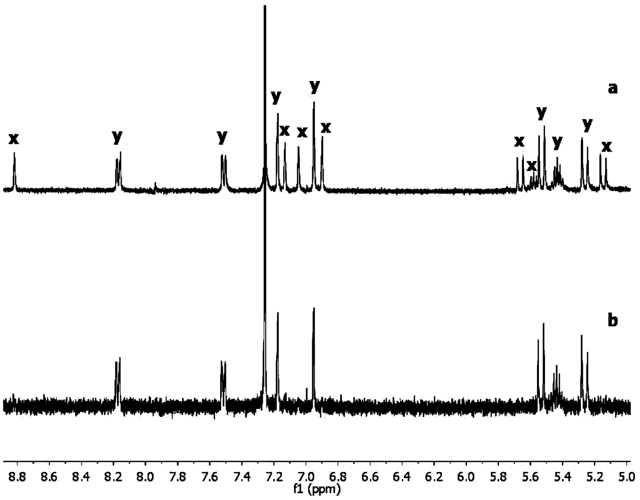


Figure 10. ^{1}H NMR spectrum of (a) an equilibrium mixture of two isomers of **4a** and (b) one isomer of **4a**.

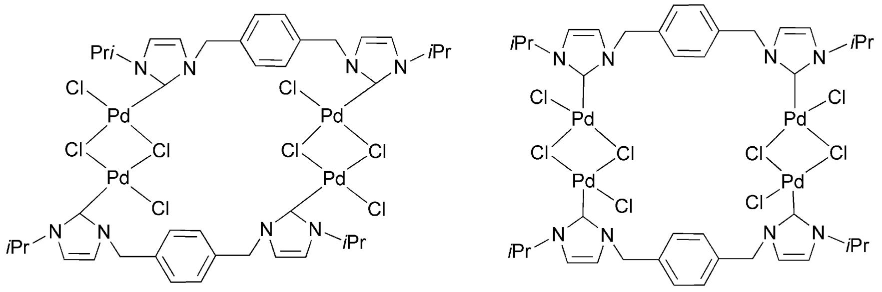


Figure 11. Two potential isomers of **4a** differing in the relative orientations of the terminal chloride ligands.

ferent species are present and that the CH protons of the aromatic ring are inequivalent in $CDCl_3$ solution. The ^1H NMR spectrum also exhibits two doublets, each with a coupling constant of 6.7 Hz, attributable to *i*Pr CH_3 protons. A resonance at $\delta = 1.99$ ppm, attributable to acetonitrile, integrates to two acetonitrile molecules for each bis-NHC ligand, though it is unclear from the ^1H NMR spectrum if this is coordinated to palladium or has dissociated in solution. The ^1H NMR spectrum of crystals of **3a** in $CDCl_3$, from which the *cisoid* crystal structure had been obtained, indicates the presence of only one of the products, as shown in Figure 10 (b), (resonances labelled "**y**" in Figure 10, (a)]. The sample equilibrates over a period of a few hours to give an **x**:**y** ratio of 2:3.

The two different species observed in $CDCl_3$ solution are unlikely to be the *cisoid* and *transoid* conformers of **3a** identified in the solid state. Rotation around the CH_2 bond between the two different conformers is likely to be relatively fast in solution, hence they would not be observed independently on the NMR timescale, as indicated in the ^1H NMR spectrum recorded in CD_3CN. The lability of acetonitrile ligands coordinated to palladium gives rise to dynamic processes in solution, which is known to occur in chloroform in other reported systems, and gives **4a** in our system (Figure 6).[34] Crystals of **3a** were dissolved in chloroform and subjected to ES^+ mass spectrometry. A signal at *m*/*z* 1318.7 corresponds to $[\mathbf{4a} - Cl]^+$. 10 μL of acetonitrile was added to the mass spectrometry sample which was again subjected to ES^+ mass spectrometry. There was no longer evidence for **4a**, and signals at *m*/*z* 681.7, corresponding to $[\mathbf{3a} - Cl - MeCN]^+$, and *m*/*z* 641.0, corresponding to $[\mathbf{3a} - Cl - 2MeCN]^+$, indicate that **4a** has been cleaved by acetonitrile to give **3a**. A search of the CSD reveals that the non-bridging chloride atoms in chloride-bridged palladium dimers are generally *trans* to one another. As there are four palladium centres in **4a**, there are two likely isomers as shown in Figure 11. Interconversion between the two is likely to be slow, hence both species are observed on the NMR timescale.

Evidence for the similarity of the two species **4x** and **4y** comes from the ^1H DOSY NMR spectrum of the mixture which shows that the two species have a very similar diffusion coefficient, ruling out the possibility of different size species such as one being a dimer of type **4a** with the second being **3a**.

5 μL of CD_3CN was added to an NMR sample of the recrystallised product in $CDCl_3$. The major resonances in the ^1H NMR spectrum are attributable to the single species **3a** observed in pure CD_3CN, with both isomers of **4a** exhibiting minor resonances. Addition of a further 5 μL of CD_3CN results in full conversion to **3a**. A similar single species was also obtained upon addition of pyridine to a $CDCl_3$ sample of **4a**, indicating that pyridine is also able to cleave **4a** to give$[\{PdCl_2(pyridine)\}_2(bis\text{-}NHC)]$. A sample of **3a** was dissolved in chloroform and subjected to vacuum. This was repeated several times to ensure removal of all the solvent. Elemental analysis on the resulting yellow powder is consistent with the acetonitrile ligands being removed from the palladium centres to form **4a**.

In order to confirm the relative stabilities of the *cisoid* and *transoid* conformers of **3a**, and verify that their interconversion is unlikely to be observed on the NMR timescale, we undertook DFT calculations (using the B3LYP functional) on both forms and modelled the interconversion of one into the other. Geometry optimization was performed using the Stuttgart-Dresden (SDD) pseudo-potential basis on the palladium, and the 6-31G(d) basis on all other atoms. The effects of implicit solvent were included using the polarisable continuum model (PCM), using DMSO as a dielectric medium. *Cisoid* and *transoid* geometries were confirmed as minima on the potential energy surface by computation of the analytical Hessian and observing that they were positive definite. The calculations identified that the *cisoid* and *transoid* forms lie very close in energy to each other. The *cisoid* compound has a much higher dipole moment than the *transoid* system, however (2.578 vs. 0.024 D), and hence explicit solvation effects may make it slightly more stable in solution. A series of energy calculations were also undertaken by varying the aryl-CH_2 dihedral angle in 15 degree increments as shown in Figure 12. The transition-state geometry for the interconversion was not fully optimized but this dihedral scan provides an upper limit to the energy barrier as 56 kJ mol^{-1}. This barrier corresponds to a rate constant of approximately 1000 s^{-1} and a reaction half-life of about 1 ms, hence it is unlikely that the two conformers will be seen separately using solution state NMR spectroscopy. This is further evidence that the two species seen in $CDCl_3$ are **4a** as opposed to **3a**.

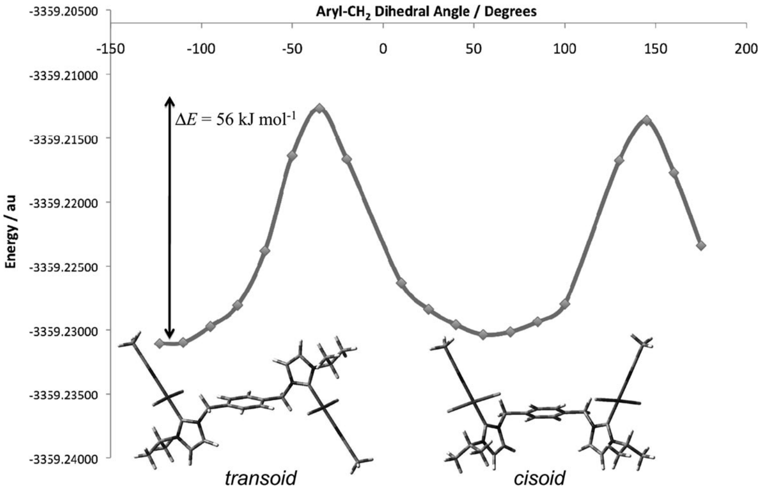


Figure 12. One-dimensional DFT potential energy scan along aryl-CH$_2$ dihedral angle, showing upper barrier between *transoid* and *cisoid* minima.

The synthetic experiments were repeated using **2b**(BF_4)$_2$ and **2c**(PF_6)$_2$ with $PdCl_2(MeCN)_2$ in dichloromethane to give [{$PdCl_2(MeCN)$}$_2$(bis-NHC)] complexes **3b** and **3c**. After precipitation of **3b** from dichloromethane by adding *n*-hexane and recrystallisation from acetonitrile the ^{1}H NMR spectrum in $CDCl_3$ exhibits resonances attributable to two isomers (**4b**), with the shifts and coupling patterns being similar to those of **4x** and **4y** in Figure 10, (a). In addition there are minor resonances attributable to a single species assigned to **3b**, likely as a result of residual acetonitrile from the recrystallisation process. Addition of 5 µL of CD_3CN to the $CDCl_3$ solution results in almost full conversion to **3b**. Yellow crystals of **3b** were grown via diffusion of diethyl ether into an acetonitrile solution. The structure shows a bis-NHC containing two palladium(II) centres, with the environment around each palladium being identical to the previous Pd–NHC structures (Figure 13). The imidazolium moieties are disposed in a mutually *transoid* orientation with respect to the aromatic ring face. An ^{1}H NMR spectrum of the *transoid* crystals in $CDCl_3$ shows resonances due to two isomers of **4b**, and in CD_3CN shows resonances attributable to a single species **3b**.

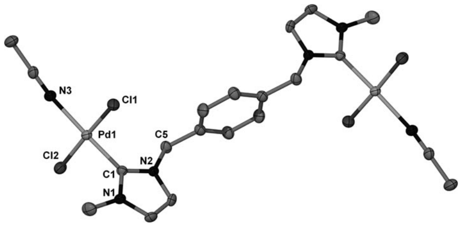


Figure 13. X-ray molecular structure of *transoid*-**3b** (50 % ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: Pd(1)–Cl(1) 2.2967(10), Pd(1)–Cl(2) 2.2930(10), Pd(1)–C(1) 1.949(3), Pd(1)–N(3) 2.085(3); N(2)–C(5)–C(6) 114.1(3).

After precipitation of **3c** from dichloromethane using *n*-hexane the ^{1}H NMR spectrum in $CDCl_3$ exhibits resonances attributable to one isomer, with the shifts being similar to those of **4x** in Figure 10, (a). Over one week in solution only one isomer of **4c** remains, as determined by ^{1}H NMR spectroscopy. Isomerisation does not occur in $CDCl_3$ solution, presumably due to steric effects from the aromatic ring methyl groups. Addition of 5 µL of CD_3CN to the $CDCl_3$ solution results in resonances attributable to a single species assigned to **3c**, though **4c** dominates. Addition of a further 5 µL of CD_3CN results in further conversion to **3c**, with **4c** still dominating. Full conversion to **3c** is achieved upon addition of excess CD_3CN. Yellow crystals of **3c** were grown via diffusion of diethyl ether into an acetonitrile solution. The structure shows a bis-NHC containing two palladium(II) centres, with the environment around each palladium being identical to the previous Pd–NHC structures (Figure 14). It forms a co-crystal with $Pd_2(MeCN)_2$ which is likely due to residual $Pd_2(MeCN)_2$ from the reaction mixture. The imidazolium moieties are disposed in a mutually *transoid* orientation with respect to the aromatic ring face. An ^{1}H NMR spectrum of the crystals in $CDCl_3$ shows resonances due to two isomers. It appears that the initial reaction in dichloromethane results in a single isomer of the chloride-bridged dimer **4c**, which is unable to isomer-

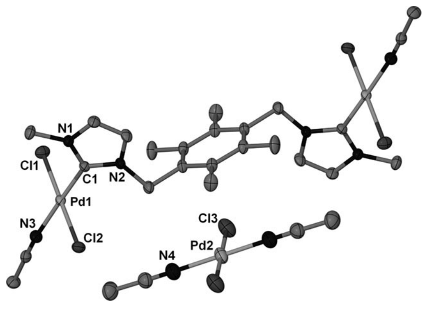


Figure 14. X-ray molecular structure of *transoid*-**3c** (50 % ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] with estimated standard deviations: Pd(1)–Cl(1) 2.2960(10), Pd(1)–Cl(2) 2.2975(10), Pd(1)–C(1) 1.959(4), Pd(1)–N(3) 2.085(3); N(2)–C(5)–C(6) 112.4(3).

ise in chloroform. Recrystallisation from acetonitrile results in cleavage of the chloride-bridged dimer, allowing it to redimerise to form two isomers.

Conclusions

Imidazolium salts **1a**, **1b** and **1c** were prepared in high yields from the reaction of α,α′-dibromo-*p*-xylene with the appropriate imidazole derivative. Silver(I) oxide was used to deprotonate the imidazolium protons and form macrocyclic Ag^{I}–NHC dimers and a coordination polymer. These bis-NHC ligands can be transferred on to palladium to give dipalladium(II) complexes in which one ligand bears two square-planar (NHC)Pd(MeCN)Cl_2 centres. The complexes exist as two different conformers in the solid state and interconvert by single bond rotation at room temperature in acetonitrile solution. DFT calculations indicate an interconverion barrier for **3a** of 56 kJ mol^{-1}, which is consistent with the relatively fast rate of interconversion in acetonitrile. In chloroform, however, the acetonitrile ligands dissociate from the palladium centres to form two isomers of the chloride-bridged dimer **4a**, as confirmed from ^{1}H NMR spectroscopy and mass spectrometry experiments. Isomerisation is slow on the NMR timescale hence both isomers are observed in $CDCl_3$. The Ag-transfer reagents may provide a route for the addition of these bis-NHC ligands, and other similar ligands, on to different transition metal centres. The bridging mode of the ligand is likely to result in interesting and novel metal complexes, leading to potential new catalysts and/or metal-organic frameworks. Catalytic studies are currently being conducted using the bis-NHC dipalladium complexes, and investigations concerning the addition of the bis-NHC ligands on to other transition metal centres are being explored.

Experimental Section

General: All manipulations were carried out using standard glovebox and Schlenk line techniques. Solvents were purified and degassed by standard procedures. 1-Isoproylimidazole was prepared using literature procedure.[27] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker 400 MHz or Varian 400 MHz NMR spectrometer. X-ray diffraction data were collected with Bruker diffractometers equipped with either a SMART 1K or SMART 6K CCD area detectors and Oxford Cryostream N_2 cooling devices, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Gaussian03 was used for the DFT calculations.

Synthesis of 1a(Br)$_2$: A dichloromethane solution (20 mL) of 1-isopropylimidazole (2.48 g, 22.5 mmol) was added to a dichloromethane solution (60 mL) of 1,4-bis(bromomethyl)benzene (2.64 g, 10.0 mmol). The solution was stirred at room temperature for 18 h, resulting in a white precipitate. The solid was filtered, washed with dichloromethane (2 × 20 mL) and dried in vacuo; yield 3.79 g (78 %).

Synthesis of 1b(Br)$_2$: A dichloromethane solution (20 mL) of 1-methylimidazole (1.85 g, 22.5 mmol) was added to a dichloromethane solution (60 mL) of 1,4-bis(bromomethyl)benzene (2.64 g, 10.0 mmol) . The solution was stirred at room temperature for 18 h, resulting in a white precipitate. The solid was filtered and washed with dichloromethane (2 × 20 mL) and dried in vacuo; yield 3.20 g (75 %).

Synthesis of 1c(Br)$_2$: To a dichloromethane solution (60 mL) of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.20 g, 10.0 mmol) was added a dichloromethane solution (20 mL) of 1-methylimidazole (1.85 g, 22.5 mmol). The solution was stirred at room temperature for 18 h, resulting in a white precipitate. The solid was filtered and washed with dichloromethane (2 × 20 mL) and dried in vacuo; yield 3.46 g (81 %).

Synthesis of 1a(PF$_6$)$_2$: NH_4PF_6 (3.00 g, 18.4 mmol) was added to a methanol solution (50 mL) of **1a**(Br)$_2$ (1.97 g, 4.6 mmol) resulting in a white precipitate. The mixture was stirred at room temperature for 1 h and the solid was filtered, washed with methanol (2 × 20 mL) and dried in vacuo; yield 2.35 g (83 %). ^{1}H NMR ([D$_6$]-DMSO, 400 MHz): δ = 9.37 [s, 2 H, N(CH)N], 7.92 [d, $^3J_{HH}$ = 1.7 Hz, 2 H, N(CH)$_2$N], 7.79 [d, $^3J_{HH}$ = 1.7 Hz, 2 H, N(CH)$_2$N], 7.47 (s, 4 H, Ar-H), 5.40 (s, 4 H, CH$_2$), 4.63 (m, 2 H, CH), 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.6 MHz): δ = 135.3 (q), 135.0 [N(CH)N], 128.9 (Ar), 122.6 [N(CH)$_2$N], 121.1 [N(CH)$_2$N], 52.4 (CH), 51.5 (CH$_2$), 22.2 (CH$_3$) ppm. MS ES$^+$ (MeCN): *m*/*z* (%) = 469.3 (100) [M – PF$_6$]$^+$, 323.3 (32) [M – 2PF$_6$ – H]$^+$. $C_{20}H_{28}F_{12}N_4P_2$ (614.39): calcd. C 39.10, H 4.59, N 9.12; found C 39.31, H 4.57, N 8.84.

Synthesis of 1b(BF$_4$)$_2$: NH_4BF_4 (1.93 g, 18.4 mmol) was added to a methanol solution (50 mL) of **1b**(Br)$_2$ (1.97 g, 4.6 mmol) resulting in a white precipitate. The mixture was stirred at room temperature for 1 h and the solid was filtered, washed with methanol (2 × 20 mL) and dried in vacuo. Colorless crystals of **1b**(PF$_6$)$_2$ (prepared through reaction with NH_4PF_6) were grown by slow evaporation of a saturated acetonitrile solution; yield 1.85 g (91 %). ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 9.20 [s, 2 H, N(CH)N], 7.75 [d, $^3J_{HH}$ = 1.8 Hz, 2 H, N(CH)$_2$N], 7.71 [d, $^3J_{HH}$ = 1.8 Hz, 2 H, N(CH)$_2$N], 7.46 (s, 4 H, Ar-H), 5.42 (s, 4 H, CH$_2$), 3.85 (s, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.6 MHz): δ = 137.2 (q), 135.9 [N(CH)N], 129.4 (Ar), 124.5 [N(CH)$_2$N], 122.8 [N(CH)$_2$N], 51.9 (CH$_2$), 36.4 (CH$_3$) ppm. MS ES$^+$ (MeCN): *m*/*z* (%) = 355.2 (78) [M – BF$_4$]$^+$, 267.2 (100) [M – 2BF$_4$ – H]$^+$. $C_{16}H_{20}F_{12}N_4P_2$ (558.29): calcd. C 34.42, H 3.61, N 10.04; found C 34.86, H 3.60, N 10.27.

Crystal Data: $C_{16}H_{20}F_{12}N_4P_2$, M = 558.30, colourless block, 0.20 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 6.079(4), b = 12.540(8), c = 15.047(10) Å, β = 92.89(3)°, V = 1145.6(13) Å^3, Z = 2, D_c = 1.619 g/cm^3, F(000) = 564, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 58.5°, 18775 reflections collected, 3097 unique (R_{int} = 0.1266). Final GooF = 0.982, R_1 = 0.0655, wR_2 = 0.1453, R indices based on 1172 reflections with $I > 2\sigma(I)$ (refinement on F^2), 163 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.299 mm^{-1}.

Synthesis of 1c(PF$_6$)$_2$: NH_4PF_6 (1.63 g, 10.0 mmol) was added to a methanol solution (50 mL) of **1c**(Br)$_2$ (1.22 g, 2.5 mmol) resulting in a white precipitate. The mixture was stirred at room temperature for 1 h and the solid was filtered, washed with methanol (2 × 20 mL) and dried in vacuo; yield 1.45 g (94 %). ^{1}H NMR ([D$_6$]-DMSO, 400 MHz): δ = 8.76 [s, 2 H, N(CH)N], 7.72 [d, J_{HH} = 1.6 Hz, 2 H, N(CH)$_2$N], 7.56 [d, $^3J_{HH}$ = 1.6 Hz, 2 H, N(CH)$_2$N], 5.53 (s, 4 H, CH$_2$), 3.82 (s, 6 H, CH$_3$), 2.24 (s, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.6 MHz): δ = 135.9 (q), 135.2 [N(CH)N], 130.7 (Ar), 123.8 [N(CH)$_2$N], 122.1 [N(CH)$_2$N], 47.8 (CH$_2$), 35.9 (CH$_3$), 16.4 (CH$_3$) ppm. MS ES$^+$(MeCN): *m*/*z* (%) = 469.3 (100) [M – PF$_6$]$^+$, 162.2 (40) [M – 2PF$_6$]$^{2+}$. $C_{20}H_{28}F_{12}N_4P_2$

(614.39): calcd. C 39.10, H 4.59, N 9.12; found C 39.04, H 4.59, N 8.67.

Synthesis of 2a(PF$_6$)$_2$: Dimethyl sulfoxide (100 mL) was added to a mixture of **1a**(PF$_6$)$_2$ (0.888 g, 1.44 mmol) and Ag$_2$O (0.348 g, 1.50 mmol). The mixture was stirred at 75 °C, in the dark, for 48 h. After cooling the mixture was filtered through Celite™ and water (100 mL) was added to the filtrate. The resulting pale brown precipitate was filtered and washed with diethyl ether (3 × 20 mL), affording the product as an air-stable off-white powder. Colorless crystals were grown by slow evaporation of a dichloromethane solution; yield 0.348 g (42%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.64 [d, $^3J_{HH}$ = 1.6 Hz, 2 H, N(CH)$_2$N], 7.56 [d, $^3J_{HH}$ = 1.6 Hz, 2 H, N(CH)$_2$N], 7.12 (s, 4 H, Ar-H), 5.30 (s, 4 H, CH$_2$), 4.71 (m, 2 H, CH), 1.46 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO): Ag-C not observed, δ = 137.5 (q), 128.1 (Ar), 122.8 [N(CH)$_2$N], 119.8 [N(CH)$_2$N], 54.4 (CH), 54.0 (CH$_2$), 23.9 (CH$_3$) ppm. $C_{40}H_{52}Ag_2F_{12}N_8P_2$ (1150.56): calcd. C 41.11, H 4.66, N 9.59; found C 41.00, H 4.69, N 9.31.

Crystal Data: $C_{40}H_{52}Ag_2F_{12}N_8P_2$, M = 1150.58, colourless block, 0.30 × 0.20 × 0.20 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 20.3327(14), b = 11.7934(8), c = 21.9604(16) Å, β = 116.319(2)°, V = 4720.1(6) Å^3, Z = 4, D_c = 1.619 g/cm^3, F(000) = 2320, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 58.3°, 39998 reflections collected, 6357 unique (R_{int} = 0.0310). Final GooF = 1.006, R_1 = 0.0269, wR_2 = 0.0670, R indices based on 5349 reflections with $I > 2\sigma(I)$ (refinement on F^2), 293 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.984 mm^{-1}.

Synthesis of 2b(BF$_4$)$_2$: Dimethyl sulfoxide (100 mL) was added to a mixture of **1b**(BF$_4$)$_2$ (0.636 g, 1.44 mmol) and Ag$_2$O (0.348 g, 1.50 mmol). The mixture was stirred at 75 °C, in the dark, for 48 h. After cooling the mixture was filtered through Celite™ and water (100 mL) was added to the filtrate. The resulting pale brown precipitate was filtered and washed with diethyl ether (3 × 20 mL), affording the product as an air-stable off-white powder. Colorless crystals were grown by slow evaporation of a saturated acetonitrile solution; yield 0.193 g (29%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.55 [d, $^3J_{HH}$ = 1.6 Hz, 2 H, N(CH)$_2$N], 7.47 [d, $^3J_{HH}$ = 1.6 Hz, 2 H, N(CH)$_2$N], 7.14 (s, 4 H, Ar-H), 5.31 (s, 4 H, CH$_2$), 3.86 (s, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]DMSO): δ = 206.9 (Ag-C), 137.6 (q), 128.1 (Ar), 124.0 [N(CH)$_2$N], 122.7 [N(CH)$_2$N], 54.0 (CH$_2$), 31.14 (CH$_3$) ppm. $C_{32}H_{36}Ag_2F_{12}N_8P_2$ (1038.35): calcd. C 37.01, H 3.49, N 10.79; found C 36.61, H 3.26, N 10.37.

Crystal Data: $C_{18}H_{21}AgBF_4N_5$, M = 502.08, colourless block, 0.20 × 0.20 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 10.8090(7), b = 10.9374(7), c = 10.9522(7) Å, α = 116.892(2), β = 107.461(2), γ = 101.406(2)°, V = 1013.41(11) Å^3, Z = 2, D_c = 1.645 g/cm^3, F(000) = 504, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 58.4°, 17107 reflections collected, 5475 unique (R$_{int}$ = 0.0847). Final GooF = 1.021, $R1$ = 0.0561, $wR2$ = 0.1261, R indices based on 3244 reflections with I $> 2\sigma(I)$ (refinement on F^2), 268 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.044 mm^{-1}.

Synthesis of 2c(PF$_6$)$_2$: Dimethyl sulfoxide (100 mL) was added to a mixture of **1c**(PF$_6$)$_2$ (0.890 g, 1.44 mmol) and Ag$_2$O (0.348 g, 1.50 mmol). The mixture was stirred at 75 °C, in the dark, for 48 h. After cooling the mixture was filtered through Celite™ and water (100 mL) was added to the filtrate. The resulting pale brown precipitate was filtered and washed with diethyl ether (3 × 20 mL), affording the product as an air-stable off-white powder. Colorless crystals were grown by slow evaporation of a dichloromethane solution; yield 0.300 g (36%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.55 [d, $^3J_{HH}$ = 1.2 Hz, 2 H, N(CH)$_2$N], 7.46 [d, $^3J_{HH}$ = 1.2 Hz, 2 H, N(CH)$_2$N], 5.50 (s, 4 H, CH$_2$), 3.67 (s, 6 H, CH$_3$), 2.20 (s, 12 H, CH$_3$) ppm. $C_{40}H_{52}Ag_2F_{12}N_8P_2$ (1186.59): calcd. C 40.49, H 4.76, N 9.44; found C 40.54, H 4.46, N 9.31.

Crystal Data: $C_{42}H_{56}Ag_2Cl_4F_{12}N_8P_2$, M = 1320.43, colourless block, 0.20 × 0.20 × 0.20 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 10.8548(7), b = 11.2177(16), c = 12.6787(12) Å, α = 101.890(5), β = 113.490(6), γ = 106.412(4)°, V = 1265.98(6) Å^3, Z = 1, D_c = 1.732 g/cm^3, F(000) = 664, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 58.3°, 21573 reflections collected, 6819 unique (R_{int} = 0.0258). Final GooF = 1.055, R_1 = 0.0283, wR_2 = 0.0711, R indices based on 6063 reflections with $I > 2\sigma(I)$ (refinement on F^2), 322 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.133 mm^{-1}.

Synthesis of 3a: Dichloromethane (20 mL) was added to a mixture of **2a**(PF$_6$)$_2$ (0.1 g, 0.0866 mmol) and PdCl$_2$(MeCN)$_2$ (0.1348 g, 0.5196 mmol). The mixture was stirred at room temperature, in the dark, for 18 h. The mixture was filtered through Celite™. The filtrate was reduced in vacuo to 5 mL and *n*-hexane (10 mL) was added resulting in a yellow precipitate. This was filtered and washed with *n*-hexane. The yellow precipitate was recrystallised from acetonitrile/diethyl ether. Yellow (*cis*) and pale yellow (*trans*) crystals were grown by diffusion of diethyl ether into an acetonitrile solution; yield 0.099 g (75%). ^{1}H NMR (400 MHz, CD$_3$CN): δ = 7.52 (s, 4 H, Ar-H), 7.18 [d, $^3J_{HH}$ = 2.2 Hz, 2 H, N(CH)$_2$N], 7.00 [d, $^3J_{HH}$ = 2.2 Hz, 2 H, N(CH)$_2$N], 5.69 (s, 4 H, CH$_2$), 5.66 (m, 2 H, CH), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD$_3$CN): Pd-C not observed, δ = 136.8 (q), 128.6 (Ar), 122.1 [N(CH)$_2$N], 119.3 [N(CH)$_2$N], 53.6 (CH), 52.9 (CH$_2$), 21.7 (CH$_3$) ppm. MS ES$^+$ (CH$_3$CN): m/z (%) = 681.7 (100) [**3a** – MeCN – Cl]$^+$. $C_{24}H_{32}Cl_4N_6Pd_2 \cdot CH_3CN$ (800.26): calcd. C 39.02, H 4.41, N 12.25; found C 38.93, H 4.40, N 12.48.[43].

Crystal Data for *transoid*-3a: $C_{28}H_{38}Cl_4N_8Pd_2$, M = 841.26, yellow block, 0.20 × 0.20 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 7.8645(6), b = 8.1376(6), c = 14.0277(10) Å, α = 89.584(2), β = 89.011(2), γ = 86.601(2)°, V = 896.02(11) Å^3, Z = 1, D_c = 1.559 g/cm^3, F(000) = 422, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 273(2) K, $2\theta_{max}$ = 58.3°, 15218 reflections collected, 4823 unique (R_{int} = 0.0281). Final GooF = 1.040, R_1 = 0.0264, wR_2 = 0.0625, R indices based on 4159 reflections with $I > 2\sigma(I)$ (refinement on F^2), 194 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.332 mm^{-1}.

Crystal Data for *cisoid*-3a: $C_{24}H_{32}Cl_4N_6Pd_2$, M = 759.16, yellow block, 0.20 × 0.20 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 13.9665(19), b = 14.613(2), c = 17.494(2) Å, α = 107.169(6), β = 90.903(5), γ = 116.882(4)°, V = 2995.7(7) Å^3, Z = 4, D_c = 1.683 g/cm^3, F(000) = 1512, SMART 6k, Mo-K_α radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 58.5°, 51297 reflections collected, 16239 unique (R_{int} = 0.0877). Final GooF = 0.970, R_1 = 0.0528, wR_2 = 0.1019, R indices based on 9252 reflections with $I > 2\sigma(I)$ (refinement on F^2), 661 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.582 mm^{-1}.

Data for 4a: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.82 [s, Ar-H (x)], 8.17 [d, $^3J_{HH}$ = 8.4 Hz, Ar-H (y)], 7.52 [d, $^3J_{HH}$ = 8.4 Hz, Ar-H (y)], 7.18 (d, $^3J_{HH}$ = 1.4 Hz, N(CH)$_2$N (y)), 7.13 (d, $^3J_{HH}$ = 1.4 Hz, N(CH)$_2$N (x)), 7.05 [s, Ar-H (x)], 6.95 [d, $^3J_{HH}$ = 1.4 Hz, N(CH)$_2$N (y)], 6.90 [d, $^3J_{HH}$ = 1.4 Hz, N(CH)$_2$N (x)], 5.66 [d, $^3J_{HH}$ = 13.8 Hz, CH$_2$ (x)], 5.58 [m, CH (x)], 5.54 [d, $^3J_{HH}$ = 13.8 Hz, CH$_2$ (y)], 5.44 [m, CH (y)], 5.26 [d, $^3J_{HH}$ = 13.8 Hz, CH$_2$ (y)], 5.15 [d, $^3J_{HH}$ = 13.8 Hz, CH$_2$ (x)], 1.99 (s, MeCN), 1.47 (d, $^3J_{HH}$ = 6.7 Hz, CH$_3$), 1.42 (d, $^3J_{HH}$ = 6.7 Hz, CH$_3$) ppm. MS ES$^+$(CHCl$_3$): m/z (%) = 1316.7 (18) [**4a** – Cl]$^+$, 641.0 (15) [4 – 2Cl]$^{2+}$.

$C_{40}H_{52}Cl_8N_8Pd_4{\cdot}4H_2O$ (1426.26): calcd. C 33.68, H 4.24, N 7.86; found C 33.88, H 3.79, N 7.97.[43]

CCDC-713109 [for **1b**(PF_6)$_2$], -713110 [for **2b**(BF_4)$_2$], -713111 [for **2a**(PF_6)$_2$], -713112 [for **2c**(PF_6)$_2$], -713113 (for *transoid*-**3b**), -713114 (for *cisoid*-**3a**), -713115 (for *transoid*-**3a**), -713116 (for *transoid*-**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Additional ^{1}H NMR and DOSY spectra, experimental details and Cartesian coordinates for the calculated structures.

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[43] Leaving **3** to dry further in an attempt to remove excess acetonitrile results in the measured carbon and nitrogen values becoming lower than calculated. This is likely due to the labile nature of the acetonitrile ligands on palladium. Due to the hygroscopic nature of **4** (gained weight upon leaving in air) it was not possible to obtain an accurate elemental anlysis without the presence of water molecules.

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