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N-Heterocyclic Carbenes

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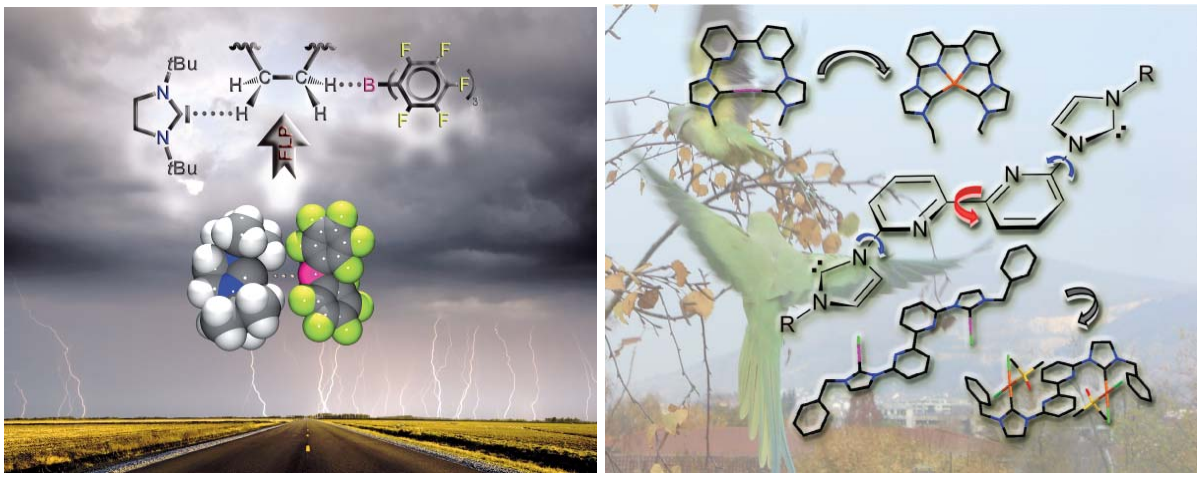

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Synthesis and characterization of Pd^{II}-methyl complexes with *N*-heterocyclic carbene-amine ligands†

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A number of palladium(II) complexes with a heteroditopic NHC-amine ligand and their precursor silver(I) carbene complexes have been efficiently prepared and their structural features have been investigated. The heteroditopic coordination of this ligand class was unequivocally shown by NMR-spectroscopy and X-ray crystallographic analysis. The neutral and cationic *cis*-methyl-palladium(NHC) complexes are not prone to reductive elimination, which is normally a major degenerative pathway for this type of complex. In contrast, under carbon monoxide atmosphere rapid reductive elimination of the acyl-imidazolium salt was observed.

Introduction

Research in the area of *N*-heterocyclic carbenes (NHC) has taken a great flight in the past decade since the isolation of the first stable carbene in 1991.[1] This ligand class is nowadays able to compete with the ubiquitous phosphane ligands. As more and more unique characteristics were uncovered, the attention directed to these versatile and relatively robust ligands is fully justified. Their use as coordination compounds and as ligands in organometallic chemistry and homogeneous catalysis is well documented, and the understanding of their chemistry is increasing steadily.[2]

Combining strong and weak donors in one ligand may, by virtue of the differentiation in relative *trans*-influences and effects, lead to interesting reactivity of its transition metal complexes. Such heteroditopic ligands may also lend stability to resting states of catalytically active complexes, at the same time ensuring temporary stabilization of active pre-catalysts. The NHC function is usually strongly bound to the metal, whereas a second, weaker donor moiety can dissociate in a reversible fashion, opening up a coordination site for substrate binding and activation.

We have recently communicated the synthesis, characterization and catalytic activity of a class of palladium(0) complexes with such heteroditopic NHC-amine ligands.[3] We now report the corresponding complexes of carbene-amine ligands with divalent palladium (Fig. 1).

It has been shown that the zero valent palladium compounds [Pd(NHC-N)] are excellent catalysts for selective transfer semi-hydrogenation of alkynes to *cis*-alkenes. A special feature of these catalysts is that they contain an internal amine base, thereby obviating the need to add a stoichiometric amount of base, as was needed for simple Pd-NHC catalysts with simple carbene ligands lacking the tethered amine function. Furthermore, we are interested in the possible degeneration of the NHC-complexes by reductive elimination of hydrocarbyl-species where the alkyl group would be *cis* or *trans* relative to the coordinated NHC carbon. This degenerative pathway has been well documented by Cavell and others[4] and constitutes a potential disadvantage of the use of NHCs in catalysis. To prevent reductive elimination from occurring in such cases, biscarbene ligands or carbenes bearing a strong secondary donor have been employed.[2g] In our system, only a weakly coordinating secondary amine donor is present. In this fashion, we expect to stabilize the complex while still being able to retain activity in for example transfer and insertion reactions, as well as hydrosilylation. The synthesis and reactivity of the complexes and possible pathways for catalyst deactivation are investigated.

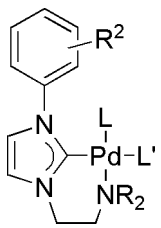

Fig. 1 General structure of the reported complexes.

Results and discussion

Indirect synthesis of neutral Pd^{II}-complexes

The synthetic route to the imidazolium ligand precursors and their corresponding silver(I) complexes has been previously reported[3] and a series of bis(carbene)silver complexes **1–3** was synthesized in (near) quantitative yields for the ligands with *ortho*-substituents on the *N*-aryl groups and yields of 76% for **2** and **3** (Scheme 1). The disappearance of the imidazolium proton at C-2 in the ^{1}H NMR is indicative for the formation of the Ag(NHC) complexes, as is the shift of the signal for C-2 in the ^{13}C NMR. For all complexes, a downfield shift of about 40 ppm is observed, resulting

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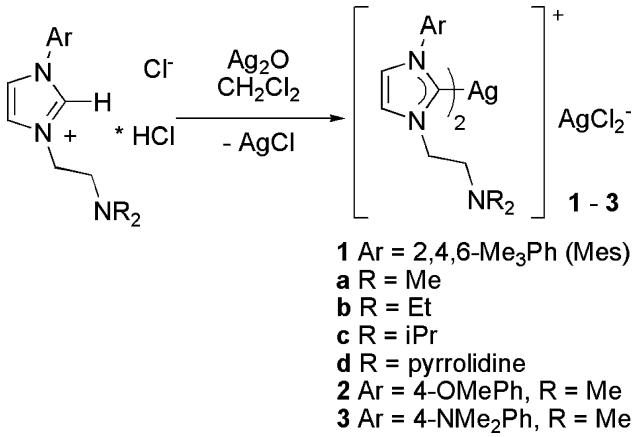
† CCDC reference numbers 726754 and 726755. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b906817a



Scheme 1 Synthesis of bis(NHC) silver complexes.

in a characteristic signal around 180 ppm. In mass spectrometry, signals for mono- or bis(carbene)silver species are observed for **1–3**.

As the exact structure of the silver-adducts cannot be completely established with only NMR and mass spectrometry, X-ray analysis of a single crystal usually provides valuable additional information.[5]

Hence, we grew X-ray quality crystals of **1c** by slow diffusion of pentane into a dichloromethane solution of the complex (Fig. 2). Two cationic bis(NHC)Ag units are found in the unit cell, with the complex anion $Ag_2Cl_4^{2-}$ located on an inversion center. The bis-carbene-silver(I) complex has a nearly linear geometry around silver, with an C–Ag–C angle of 169.80(11)°. The silver–carbene distances are equal within experimental error and amount to 2.073(3) and 2.072(3) Å, which are rather short Ag–C distances for complexes with this geometry.[6] The ligands are arranged in an anti-parallel fashion, with the two carbene-rings disposed in an almost co-planar arrangement. The mesityl-rings are twisted with respect to the carbene-rings, the planes making angles of 77.6(4)° and 79.9(4)° for the two cases. There is no interaction of the amine-donor with the silver-ion, neither is there any argentophilic interaction between the cationic and anionic parts of the complex.

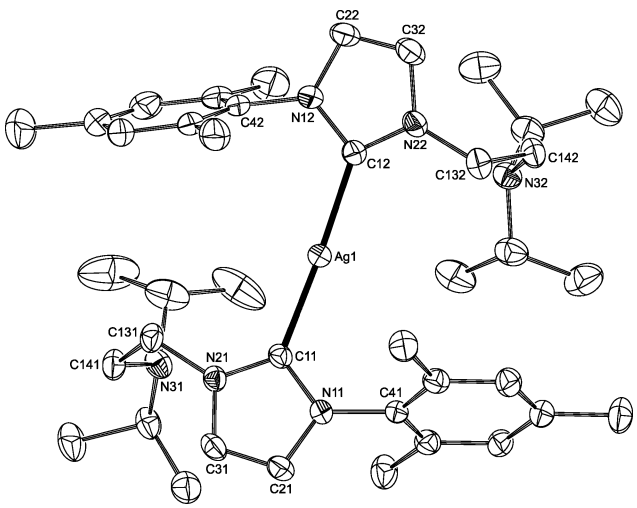
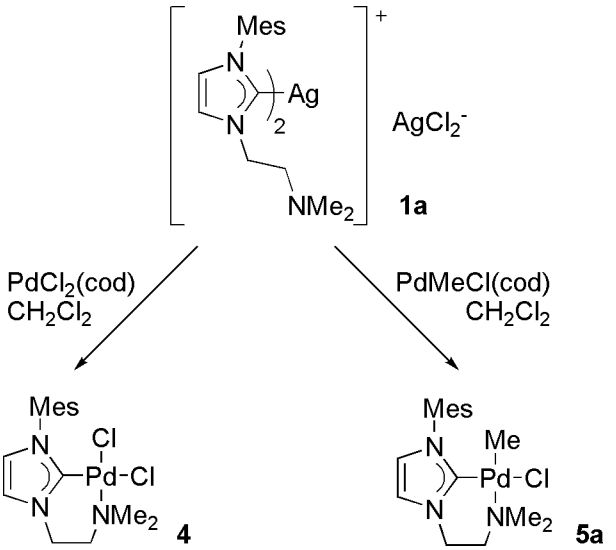


Fig. 2 Displacement ellipsoid plot of the cationic portion of **1c** (50% probability). Hydrogen atoms and $\frac{1}{2}[Ag_2Cl_4]^{2-}$ anion are omitted for clarity.

The transmetallation of **1a** to divalent palladium precursors was carried out smoothly and the products were obtained in high yields and purity. Previously we reported the palladium dichloride complex **4**[3], in addition to which the palladium methylchloride complex **5a** has now been synthesized (Scheme 2).



Scheme 2 Synthesis of neutral Pd^{II} complexes from **1a**.

Complexes **4** and **5a** have a characteristic signal in the ^{13}C NMR for the carbenic carbon at 175 and 171 ppm, respectively. Proof of the coordination of the nitrogen-donor function has been obtained from the resonances for the amino methyl-groups, for which a downfield shift is observed in the ^{1}H NMR. The signals for the hydrogens of the ethylene tether group clearly reveal an AA'BB' second order pattern in the ^{1}H NMR, confirming the diastereotopicity of these protons. In the latter complex, the heteroditopicity of the NHC-amine ligand was unequivocally proved by the formation of only one of the possible geometrical isomers, as indicated by ^{1}H and ^{13}C NMR. Upon coordination of the carbene ligand, a large low-frequency shift is observed for the PdMe signal. A shift of –0.15 ppm is observed in the ^{1}H NMR and at –12 ppm in the ^{13}C NMR. Due to the difference in *trans*-influence of the carbene and the amine-donor, we anticipated the chloride to be in a position *trans* to the NHC.

Our expectations were confirmed by X-ray analysis of **5a**, crystals of which were grown by slow evaporation of a dichloromethane solution (Fig. 3).

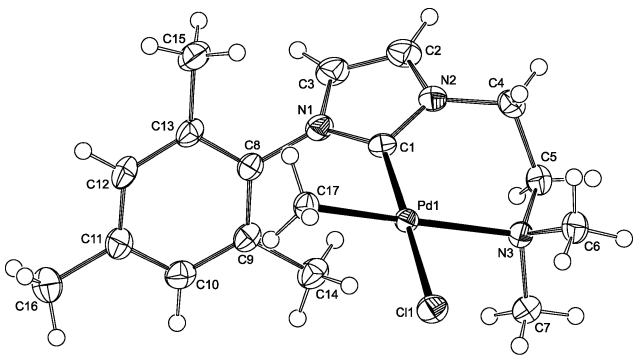


Fig. 3 Displacement ellipsoid plot of **5a** (50% probability).

The chloride, being best acceptor ligand, is found *trans* to the NHC moiety, just as the methyl and amine are in mutual *trans* positions. The flexible linker of the bidentate ligand allows for a nearly perfect square planar geometry of the complex, with angles deviating no more than 3° from the ideal 90°. The chelate ring itself forms a twist-boat. The NHC is twisted by 37.5(2)° with respect to the coordination plane and makes an angle of 67.2(3)° with the mesityl-ring. The carbene-palladium distance is 1.991(2) Å, which is expected for a palladium(II)–NHC bond. The bond length of the methyl ligand to palladium is 2.046(2) Å, which is quite short compared to related structures.[7] We attribute this to the weak donor character of the amine in the *trans* position. The distance between the amine nitrogen and palladium is 2.2600(2) Å. In comparison with other divalent palladium complexes with amine donors this is quite long[8], reflecting the large electron density imparted on the palladium by the NHC-ligand.

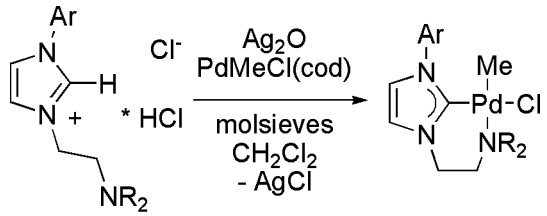
The thermal stability of the complex is remarkable because the carbene and the methyl are in *cis* position relative to one another. Together with the tilted geometry of the carbene with respect to the coordination plane, this would be expected to facilitate reductive elimination of the methylimidazolium salt.[4] Apparently, the amine donor provides already enough stabilization to prevent this degenerative pathway from being accessible at room temperature. To probe the sensitivity towards reductive elimination at higher temperatures, an NMR study at higher temperatures was performed. It appeared that **5a** remained stable up to at least 353 K in CD_2Cl_2[9], which is quite striking. In earlier work, these *cis* species were often found to decompose at room temperature or below in dichloromethane.[4] Until now, recourse had to be taken to the use of biscarbenes or bidentate ligands bearing a strong donor besides the carbene, in order to lend greater stability to these *cis*-bis(hydrocarbyl) transition metal complexes[7], whereas our system features only a weakly coordinating secondary donor. The ease with which the amine is, nevertheless, able to dissociate might very well prove an important feature in catalytic applications where a metal center with low coordination number is required.

Direct synthesis of Pd^{II}(NHCN̂)MeCl complexes

Theoretically, the most time- and cost-efficient method to synthesize complexes bearing NHC-ligands is by direct complexation, *i.e.* deprotonation of the imidazolium salt by a strong base followed by *in situ* complexation to the desired metal. However, previous research has shown that this route does not yield the products in satisfactory yields for our ligands.[3] The two-step method described here gives the product in high yields and purities without the need for stringent reaction conditions.

We have focused on a protocol that combines these good results with the short reaction times generally associated with the direct complexation. The *in situ* formation of the bis(NHC)silver complex followed by addition of the metal precursor is well documented, but we felt that this is in principle still a two-step process.

We were satisfied to find that when imidazolium salt, silver(I) oxide and palladium methyl chloride cyclooctadiene were suspended in dry dichloromethane and stirred overnight, complex **5a** could be obtained in reasonable yield. Optimization revealed that the use of activated molecular sieves brings about yields that are comparable to those obtained with the optimized two-step process. The reaction times and use of solvents are significantly decreased, making this process as a whole much more efficient. To explore the versatility of this protocol, various imidazolium salts were used as ligand precursors, resulting in complexes **5–10** (Scheme 3).



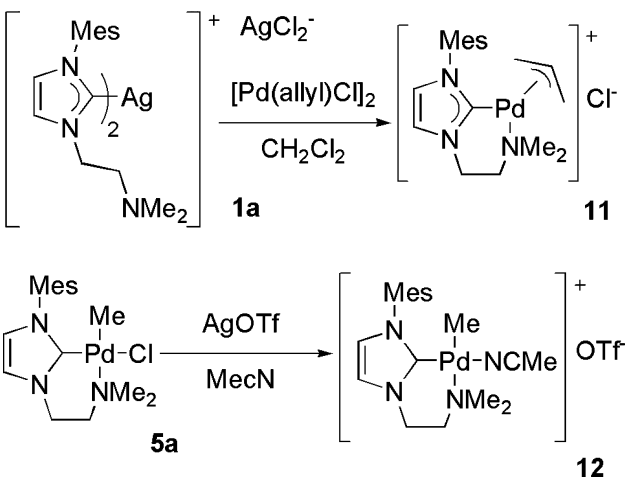
5 Ar =Mes
a R = Me
b R = Et
c R = iPr
d R = pyrrolidine
6 Ar = 4-OMePh, R = Me
7 Ar = 4-NMe_2Ph, R = Me
8 Ar = Ph, R = Me
9 Ar = 4-AcPh, R = Me
10 Ar = 4-CF_3Ph, R = Me

Scheme 3 Direct synthesis of Pd^{II}MeCl(NHC) complexes.

Results were generally very good, with yields ranging from 65 to 95%. In all cases, the formation of only the *cis*-methyl NHC-complex was observed. Only in the case of the diisopropyl-substituted amine, the product **5c** was not obtained pure. In all likelihood, the secondary donor introduces too much bulk near the metal-center, leading to the formation of side products and concomitant decomposition.

Synthesis and reactivity of cationic Pd^{II} complexes

In addition to the neutral complexes, we were interested in the synthesis and reactivity of cationic palladium-carbene species. Two different cationic complexes were synthesized, by transmetallation from **1a** to $[Pd(allyl)Cl]_2$ and by halide abstraction with silver(I) triflate from **5a** (Scheme 4).



1a **11**

5a **12**

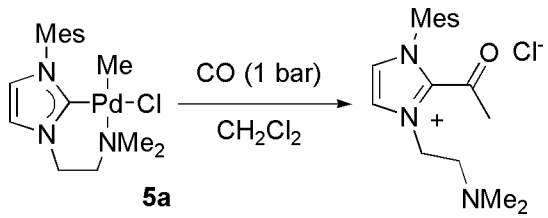
Scheme 4 Synthesis of cationic complexes.

Complex **11** was smoothly formed in a yield of 83%, and the heteroditopicity was reflected in the spectroscopic behaviour of the

allyl-ligand, for which five unique signals in the ^{1}H NMR and 3 signals in the ^{13}C NMR were observed. The signal for the carbene carbon is found at 176 ppm in the ^{13}C NMR. Additionally, a broadening and splitting of the ortho-methyl groups on the mesityl N-substituent is observed in NMR.

Another way to make reductive elimination a more realistic option is to synthesize the cationic methylpalladium complex by halide abstraction with silver. Starting from an acetonitrile solution of **5a**, immediate precipitation of silver(I) chloride was observed on addition of silver(I) triflate. The solvent-complex **12** was obtained in a reasonable yield of 52% and high purity. For these cationic complexes, decomposition was still not observed, even after prolonged standing in dichloromethane solution. This is again in contrast with earlier studies, which indicated that reductive elimination occurred more readily from cationic complexes.[4]

In contrast, when complex **5a** in dichloromethane was subjected to a carbon monoxide atmosphere, rapid deposition of palladium black was observed. Analysis of the reaction mixture revealed the complete disappearance of the palladium-methyl signal in the ^{1}H NMR and the appearance of a new signal at 2.8 ppm, suggesting the formation of an acylimidazolium salt[4e] (Scheme 5). A possible pathway for this degenerative process is exchange of the chloride anion for CO, followed by migratory insertion and isomerisation to the cationic *cis*-acyl carbene complex, from which reductive elimination takes place. However, none of these intermediates were observed in the reaction mixture. Another possible scenario is decoordination of the amine donor. In this case the methyl and carbon monoxide ligands would end up in mutual *trans* positions. In a complex with this geometry, formation of the acyl and concomitant reductive elimination is only possible after isomerization. A third possibility is CO-insertion from a 5-coordinate species.[10] To the best of our knowledge, palladium complexes bearing both NHC and acyl ligands have not been isolated.[4e]



Scheme 5 Decomposition of **5a** under influence of CO with potential reaction product.

The reactivity of NHC-bearing complexes does not necessarily have implications for catalysis[4], but the facile decomposition in presence of CO does not bode well for application in for example CO/alkene copolymerization.

Conclusions

We have synthesized a series of neutral and cationic palladium(II) complexes with heteroditopic NHC-amine ligands, with various substituents on the ligand aryl-groups and the amine, as well as the other ligands on palladium. The complexes were prepared *via* two routes: (a) initial formation of the bis(NHC)silver(I) complexes followed by transmetallation and (b) direct complexation in a one-pot procedure, which efficiently gives the desired product in yields comparable to the two-step process. A high (thermal) stability towards reductive elimination was observed for the neutral and cationic methylpalladium complexes. This is remarkable because the *cis*-geometry of the complex in combination with the tilted conformation of the carbene normally favours a degenerative pathway. This resilience is induced by the weak secondary donor. However, the decomposition under influence of carbon monoxide proved to be a facile process. X-Ray analysis of a representative (NHC)palladium(II) methylchloride complex was performed, which unequivocally proved the heteroditopicity of the ligand.

Future research will exploit the striking stability of these complexes, their reactivity and application in catalysis.

Experimental

All reactions involving air- or moisture-sensitive compounds were carried out under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard methods.[11] palladium(II) methyl chloride cyclooctadiene was prepared according to a literature procedure.[12] NMR measurements were performed on a Varian Mercury300 spectrometer (^{1}H: 300.13 MHz, ^{13}C 75.47 MHz), and Bruker DRX300 spectrometer (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz). ^{13}C NMR spectra were measured with ^{1}H decoupling. Positive chemical shifts (δ) are denoted for high-frequency shifts relative to the external TMS reference. HRMS measurements were performed on a JEOL JMS SX/SX102A four sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high resolution FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used.

General procedure for the synthesis of bis(NHC)silver(I) complexes

A procedure from the literature[13] was modified as follows: silver(I) oxide (1.0 equivalent) and the imidazolium salt (1.0 equivalent) were suspended in dichloromethane to 0.2 M and stirred overnight at room temperature. The reaction mixture was then filtered over a pad of Celite, which was washed with 10 mL dichloromethane. The filtrate was then concentrated.

Bis[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-mesityl)imidazol-2-ylidene] silver(I) dichloride (1a). The product (0.75 g, quantitative yield) was obtained as a pale oil. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.34 (d, ^{3}J (HH) = 1.8 Hz, 1 H, CH), 6.99 (s, 2 H, aryl-H), 6.94 (d, ^{3}J (HH) = 1.8 Hz, 1 H, CH), 4.22 (t, ^{3}J (HH) = 6 Hz, 2 H, N-CH_2), 2.69 (t, ^{3}J (HH) = 6 Hz, 2 H, Im-CH_2), 2.34 (s, 3 H, *p*-aryl-CH_3), 2.25 (s, 6 H, *o*-aryl-CH_3), 1.96 (s, 6 H, N(CH_3)$_2$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 181.8 (NCN), 140.0 (*p*-aryl-C), 136.4 (*i*-aryl-C), 135.2 (*o*-aryl-C), 129.9 (*m*-aryl-C), 123.0 (CH), 121.5 (CH), 59.3 (CH_2), 50.5 (CH_2), 45.5 (N(CH_3)$_2$), 22.3 (*p*-aryl-CH_3), 18.7 (*o*-aryl-CH_3). MS(FAB+): m/z = 623.2840 for $C_{32}H_{46}N_6Ag$ [$(NHC)_2Ag$]$^{+}$.

Bis[(1-(2-*N*,*N*-diethylamino)-ethylene-3-mesityl))imidazol-2-ylidene] silver(I) dichloride (1b). The product (487 mg, 95%) was obtained as greyish crystals. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.32 (d, ^{3}J (HH) = 1.5 Hz, 1 H, CH), 6.97 (s, 2 H, aryl-CH), 6.92 (d, ^{3}J (HH) = 1.5 Hz, 1 H, CH), 4.17 (bm, 2 H, N-CH_2), 2.77 (bm, 2 H, Im-CH_2), 2.50 (q, ^{3}J (HH) = 6.9 Hz, 4 H,

2 CH_2), 2.34 (s, 3 H, *p*-aryl-CH_3), 1.95 (s, 6 H, *o*-aryl-CH_3), 0.94 (t, ^3J (HH) = 6.9 Hz, 6 H, 2 CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 181.3 (NCN), 139.7 (*p*-aryl-C), 136.2 (*i*-aryl-C), 135.3 (*o*-aryl-C), 129.6 (*m*-aryl-C), 122.9 (CH), 122.4 (CH), 54.6 (CH_2), 51.2 (CH_2), 47.8 ($N(CH_2)_2$), 21.3 (*p*-aryl-CH_3), 17.8 (*o*-aryl-CH_3), 12.5 (CH_3). MS(FAB+): m/z = 392.1256 for $C_{18}H_{27}N_3Ag$ [M – Cl]$^+$.

Bis[(1-(2-*N*,*N*-diisopropylamino)-ethylene-3-mesityl)imidazol-2-ylidene] silver(I) dichloride (1c). The product (236 mg, quantitative yield) was obtained as colourless crystals. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.23 (d, ^3J (HH) = 1.7 Hz, 1 H, CH), 6.99 (s, 2 H, aryl-H), 6.91 (d, ^3J (HH) = 1.7 Hz, 1 H, CH), 4.14 (bs, 2 H, N-CH_2), 3.02 (septet, ^3J (HH) = 6.6 Hz, 2 H, ^{i}Pr-CH), 2.85 (bs, 2 H, Im-CH_2), 2.34 (s, 6 H, *p*-aryl-CH_3), 1.96 (bs, 6 H, *o*-aryl-CH_3), 0.95 (d, ^3J (HH) = 6.6 Hz, 12 H, ^{i}Pr-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 182.3 (NCN), 139.8 (*p*-aryl-C), 136.1 (*i*-aryl-C), 135.5 (*o*-aryl-C), 129.0 (*m*-aryl-C), 123.1 (CH), 122.1 (CH), 54.7 (CH_2), 48.5 (CH_2), 46.7 ($N(CH)_2$), 21.5 (*p*-aryl-CH_3), 21.0 (CH_3), 17.8 (*o*-aryl-CH_3). MS(FAB+): m/z = 420.1411 for $C_{20}H_{29}N_3Ag$ [M – Cl]$^+$.

Bis[(1-(2-*N*-pyrrolidinyl)-ethylene-3-mesityl)imidazol-2-ylidene] silver(I) dichloride (1d). The product (246 mg, 92%) was obtained as a sticky yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.35 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 7.02 (s, 2 H, aryl-CH), 6.96 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 4.30 (t, ^3J (HH) = 6.0 Hz, 2 H, CH_2), 2.93 (t, ^3J (HH) = 6.0 Hz, 2 H CH_2), 2.58 (m, ^3J (HH) = 2.4 Hz, 4 H, pyrrolidinyl), 2.37 (s, 3 H, *p*-aryl-CH_3), 1.99 (s, 6 H, *o*-aryl-CH_3), 1.77 (m, ^3J (HH) = 1.8 Hz, 4 H, pyrrolidinyl). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 181.3 (NCN), 140.0 (*p*-aryl-C), 136.2 (*o*-aryl-C), 137.2 (*i*-aryl-C), 129.7 (*m*-aryl-C), 122.7 (CH), 122.1 (CH), 57.1 (pyrrolidinyl), 54.7 (CH_2), 51.6 (CH_2), 24.1 (pyrrolidinyl), 21.3 (*p*-aryl-CH_3), 17.9 (*o*-aryl-CH_3). MS(FAB+): m/z = 673.3149 for $C_{36}H_{50}N_6Ag$ [$(NHC)_2Ag$]$^+$.

Bis[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-methoxyphenyl)) imidazol-2-ylidene] silver(I) dichloride (2). The product (284 mg, 76%) was obtained as a brown/green oil. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.49 (m, 2 H, aryl-H), 7.31 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.24 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.03 (m, 2 H, aryl-H), 4.26 (t, ^3J (HH) = 6 Hz, 2 H, N-CH_2), 3.87 (s, 3 H, OCH_3), 2.72 (t, ^3J (HH) = 6 Hz, 2 H, Im-CH_2), 2.29 (s, 6 H, N-Me). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 179.8 (NCN), 160.4 (*p*-aryl-C), 133.7 (*i*-aryl-C), 126.0 (*o*-aryl-C), 122.4 (CH), 122.1 (CH), 115.1 (*m*-aryl-C), 60.4 (OCH_3), 56.1 (CH_2), 50.5 (CH_2), 45.7 ($N(CH_3)_2$). MS(FAB+): m/z = 352.0572 for $C_{14}H_{19}N_3OAg$ [M – Cl]$^+$.

Bis[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-*N*,*N*-dimethylphenyl))imidazol-2-ylidene] silver(I) dichloride (3). The product (180 mg, 76%) was obtained as a brown solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.39 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 7.28 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 7.21 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 6.78 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 4.24 (t, ^3J (HH) = 9 Hz, 2 H, N-CH_2), 3.01 (s, 6 H, aryl-$N(CH_3)_2$), 2.71 (d, ^3J (HH) = 9 Hz, 2 H, Im-CH_2), 2.29 (s, 6 H, $N(CH_3)_2$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 179.5 (NCN), 151.1 (*p*-aryl-C), 129.7 (*i*-aryl-C), 125.4 (*o*-aryl-C), 122.3 (CH), 122.1 (CH), 112.7 (*m*-aryl-C), 60.5 (CH_2), 50.5 (CH_2), 45.9 ($N(CH_3)_2$), 40.8 (aryl-$N(CH_3)_2$). MS(FAB+): m/z = 365.0893 for $C_{15}H_{22}N_4Ag$ [M – Cl]$^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-mesityl)imidazol-2-ylidene] palladium(II) methyl chloride (5a). A procedure from the literature[13] was modified as follows: palladium(II) methyl chloride cyclooctadiene (1.0 equivalent) and bis(imidazol-2-ylidene) silver complex (0.5 equivalent) were suspended in dry dichloromethane to 0.1 M and stirred at room temperature for 2 h under an atmosphere of dry nitrogen. The reaction mixture was then filtered over a pad of Celite, which was washed with 10 mL dry dichloromethane. The solution was concentrated and the residue was then washed three times with 10 mL dry diethyl ether. The product (126 mg, 86%) was obtained as an off-white microcrystalline solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.09 (d, ^3J (HH) = 2 Hz, 1 H, CH), 6.96 (s, 2 H, aryl-CH), 6.79 (d, ^3J (HH) = 2 Hz, 1 H, CH), 4.19 (m, 2 H, N-CH_2), 2.63 (s, 6 H, $N(CH_3)_2$), 2.42 (m, 2 H, Im-CH_2), 2.31 (s, 3 H, *p*-aryl-CH_3), 2.18 (s, 6 H, *o*-aryl-CH_3), –0.16 (s, 3 H, $PdCH_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 170.9 (NCN), 139.1 (*p*-aryl-C), 136.6 (*i*-aryl-C), 134.9 (*o*-aryl-C), 129.4 (*m*-aryl-C), 123.1 (CH), 121.2 (CH), 63.3 (CH_2), 49.4 (CH_2, $N(CH_3)_2$), 21.2 (*p*-aryl-CH_3), 18.8 (*o*-aryl-CH_3), –12.2 (Pd-CH_3). MS(FAB+): m/z = 378.1170 for $C_{17}H_{26}N_3Pd$ [M – Cl]$^+$.

General procedure for the one-pot synthesis of palladium(II) methyl chloride NHC complexes

Imidazolium salt, silver(I) oxide (1.0 equivalent) and palladium methyl chloride cyclooctadiene (1.0 equivalent) were suspended in dry dichloromethane and stirred with activated molecular sieves overnight at room temperature under an atmosphere of dry nitrogen. The reaction mixture was then filtered over a pad of Celite, which was washed with 10 mL dry dichloromethane. The filtrate was then concentrated and washed three times with 10 mL dry diethyl ether.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-mesityl)imidazol-2-ylidene] palladium(II) methyl chloride (5a). The product (183 mg, 81%) was obtained as an off-white microcrystalline solid.

[(1-(2-*N*,*N*-diethylamino)-ethylene-3-mesityl)imidazol-2-ylidene] palladium(II) methyl chloride (5b). The product (128 mg, 92%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.06 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 6.98 (s, 2 H, aryl-H), 6.80 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 4.25 (m, 2 H, CH_2), 3.40–2.80 (2 broad multiplets, 4 H, CH_2), 2.66 (m, 2 H, CH_2), 2.35 (s, 3 H, *p*-aryl-CH_3), 2.17 (s, 6 H, *o*-aryl-CH_3), 1.26 (t, ^3J (HH) = 7.2 Hz, 6 H, CH_3), –0.05 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 169.7 (NCN), 139.2 (*p*-aryl-C), 136.6 (*i*-aryl-C), 135.1 (*m*-aryl-C), 129.3 (*o*-aryl-C), 123.3 (CH), 120.8 (CH), 53.4 (CH_2), 52.8 ($N(CH_2)_2$), 50.7 (CH_2), 21.2 (*p*-aryl-CH_3), 18.8 (*o*-aryl-CH_3), 11.4 (CH_3), –11.7 (Pd-CH_3). MS(FAB+): m/z = 406.1486 for $C_{19}H_{30}N_3Pd$ [M – Cl]$^+$.

[(1-(2-*N*-pyrrolidinyl)-ethylene-3-mesityl)imidazol-2-ylidene] palladium(II) methyl chloride (5d). The product (0.068 g, 66%) was obtained as a white powder. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.05 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.00 (s, 2 H, aryl-CH), 6.84 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 4.22 (m, 2 H, CH_2), 3.79 (m, 2 H, CH, pyrrolidinyl), 2.71 (m, 2 H, CH, pyrrolidinyl), 2.44 (m, 2 H, CH_2), 2.35 (s, 3 H, *p*-aryl-CH_3), 2.22 (s, 6 H, *o*-aryl-CH_3), 1.80 (m, 4 H, CH_2, pyrrolidinyl), –0.13 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 170.0 (NCN), 139.3 (*p*-aryl-C), 137.3 (*i*-aryl-C), 134.8 (*o*-aryl-C), 129.6 (aryl-CH),

123.2 (CH), 120.9 (CH), 58.6 (pyrrolidinyl), 57.4 (CH_2), 51.1 (CH_2), 22.3, (pyrrolidinyl), 21.4 (*p*-aryl-CH_3), 18.9 (*o*-aryl-CH_3), –12.5 (Pd-CH_3). MS(FAB+): m/z = 404.1327 for $C_{19}H_{28}N_3Pd$ $[M - Cl]^+$.

(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-methoxy) phenyl)-imidazol-2-ylidene] palladium(II) methyl chloride (6). The product (161 mg, 76%) was obtained as a pale yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.61 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 7.13 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.04 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.00 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 4.20 (m, 2 H, CH_2), 2.70 (s, 6 H, CH_3), 2.48 (m, 2 H, CH_2), –0.09 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 169.8 (NCN), 159.8 (*p*-aryl-C), 133.8 (*i*-aryl-C), 126.9 (*o*-aryl-C), 122.6 (CH), 121.5 (CH), 114.2 (*m*-aryl-C), 63.0 (CH_2), 55.9 (OCH_3), 49.6 (CH_2), 49.4 ($N(CH_3)_2$), –8.2 (Pd-CH_3). MS(FAB+): m/z = 366.0808 for $C_{15}H_{22}N_3OPd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-*N*,*N*-dimethyl) phenyl)imidazol-2-ylidene] palladium(II) methyl chloride (7). The product (163 mg, 95%) was obtained as a brown solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.48 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 7.07 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 7.00 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 6.74 (d, ^3J (HH) = 9 Hz, 2 H, aryl-H), 4.17 (m, 2 H, N-CH_2), 2.98 (s, 6 H, aryl-$N(CH_3)_2$), 2.67 (s, 6 H, $N(CH_3)_2$), 2.44 (m, 2 H, Im-CH_2), –0.09 (s, 3 H, $PdCH_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 169.2 (NCN), 150.6 (*p*-aryl-C), 130.0 (*i*-aryl-C), 126.4 (*o*-aryl-C), 122.7 (CH), 121.2 (CH), 111.9 (*m*-aryl-C), 63.1 (CH_2), 49.5 (CH_2), 48.8 ($N(CH_3)_2$), 40.7 (aryl-$N(CH_3)_2$), –8.5 (Pd-CH_3). MS(FAB+): m/z = 379.1125 for $C_{16}H_{25}N_4Pd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-phenyl)imidazol-2-ylidene] palladium(II) methyl chloride (8). The product (156 mg, 80%) was obtained as off-white crystals. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.75–7.70 (m, 2 H, Ph), 7.54–7.50 (m, 3 H, Ph), 7.18 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 7.09 (d, ^3J (HH) = 1.8 Hz, 1 H, CH), 4.22 (m, 2 H, N-CH_2), 2.71 (s, 6 H, $N(CH_3)_2$), 2.50 (m, 2 H, Im-CH_2), –0.11 (s, 3 H, $PdCH_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 170.1 (NCN), 140.8, 130.1, 128.7, 126.9 (Ph), 125.0 (CH), 122.3 (CH), 63.1 (CH_2), 49.7 (CH_2), 48.5 ($N(CH_3)_2$), –8.1 (Pd-CH_3). MS(FAB+): m/z = 336.0697 for $C_{14}H_{20}N_3Pd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-acetyl)phenyl) imidazol-2-ylidene] palladium(II) methyl chloride (9). The product (73 mg, 66%) was obtained as a pale yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 8.09 (d, ^3J (HH) = 8.7 Hz, 2 H, aryl-H), 7.89 (d, ^3J (HH) = 8.7 Hz, 2 H, aryl-H), 7.23 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.11 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 4.23 (m, 2 H, CH_2), 2.73 (s, 6 H, CH_3), 2.62 (s, 3 H, acetyl-CH_3), 2.52 (m, 2 H, CH_2), –0.09 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 197.2 (CO), 170.9 (NCN), 144.0 (*p*-aryl-C), 136.9 (*i*-aryl-C), 129.3 (*o*-aryl-C), 125.8 (*m*-aryl-C), 122.3 (CH), 122.0 (CH), 62.9 (CH_2), 49.7 (CH_2), 46.5 ($N(CH_3)_2$), 27.0 (CO-CH_3), –7.2 (Pd-CH_3). MS(FAB+): m/z = 378.0809 for $C_{16}H_{22}N_3OPd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-(4-trifluoromethyl) phenyl)imidazol-2-ylidene] palladium(II) methyl chloride (10). The product (107 mg, 69%) was obtained as an off-white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.94 (d, ^3J (HH) = 9.6 Hz, 2 H, aryl-H), 7.78 (d, ^3J (HH) = 9.6 Hz, 2 H, aryl-H), 7.21 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 7.11 (d, ^3J (HH) = 2.1 Hz, 1 H, CH), 4.24 (m, 2 H, CH_2), 2.73 (s, 6 H, CH_3), 5.24 (m, 2 H, CH_2), –0.10 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 171.0 (NCN), 143.4 (*p*-aryl-C), 130.3 (CF_3), 127.9 (*i*-aryl-C), 126.4, 126.1 (*o*- and *m*-aryl-C), 122.3 (CH), 122.0 (CH), 62.8 (CH_2), 49.7 (CH_2), 49.4 ($N(CH_3)_2$), –7.3 (Pd-CH_3). MS(FAB+): m/z = 404.0577 for $C_{15}H_{19}F_3N_3Pd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-mesityl)imidazol-2-ylidene palladium(II) allyl] chloride (11). Palladium(II) allyl chloride dimer (68.5 mg, 0.19 mmol) and bis(imidazol-2-ylidene) silver complex (157 mg, 1.0 equivalent) were suspended in 10 mL dry dichloromethane and stirred at room temperature for 2 h under an atmosphere of dry nitrogen. The reaction mixture was then filtered over a pad of Celite, which was washed with 10 mL dry dichloromethane. The solution was concentrated and the residue was washed three times with 10 mL dry diethyl ether. The product (136 mg, 83%) was obtained as a yellow sticky solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.57 (d, ^{3}(HH) = 1.8 Hz, 1 H, CH), 7.00, (s, 2 H, aryl-H), 6.97 (d, ^{3}(HH) = 1.8 Hz, 1 H, CH), 5.23 (m, 1 H, allyl), 4.64–4.34 (broad multiplet, 2 H, CH_2), 4.05 (d, ^{3}(HH) = 7.8 Hz, 1H, allyl), 3.19 (d, ^{3}(HH) = 13.8 Hz, 1 H, allyl), 2.91 (m, 2 H, CH_2), 2.78 (s, 6 H, CH_3), 2.65 (broad multiplet, 1 H, allyl), 2.35 (s, 3 H, *p*-aryl-CH_3), 2.07 (broad singlet, 3 H, *o*-aryl-CH_3), 1.99 (broad singlet, 3 H, *o*-aryl-CH_3), 1.78 (broad doublet, ^{3}(HH) = 11.4 Hz, 1 H, allyl). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 176.1 (NCN), 139.9 (*p*-aryl-C), 136.9 (*i*-aryl-C), 135.7 (*o*-aryl-C), 135.3 (*o*-aryl-C), 129.4 (*m*-aryl-C). 129.3 (*m*-aryl-C), 123.3 (CH), 122.4 (CH), 118.6 (allyl), 74.4 (allyl), 62.8 (CH_2), 51.7 (CH_2), 48.6 (allyl), 48.5 (NMe_2), 21.2 (*p*-aryl-CH_3), 18.3 (*o*-aryl-CH_3), 18.1 (*o*-aryl-CH_3). MS(FAB+): m/z = 404.1332 for $C_{19}H_{28}N_3Pd$ $[M - Cl]^+$.

[(1-(2-*N*,*N*-dimethylamino)-ethylene-3-mesityl)imidazol-2-ylidene palladium(II) methyl acetonitrile] trifluoromethane sulfonate (12). To a solution of **5a** (134 mg, 0.32 mmol) in 20 mL dry acetonitrile was added silver(I) trifluoromethane sulfonate (1.1 equivalent) and the immediately formed white suspension was stirred for 20 min at room temperature under an atmosphere of dry nitrogen. The reaction mixture was then filtered over a pad of Celite, which was washed with 10 mL dry dichloromethane. The solution was then concentrated under reduced pressure. The product (97 mg, 52%) was obtained as a grey sticky solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ/ppm: 7.30 (d, ^{3}(HH) = 2.1 Hz, 1 H, CH), 7.00, (s, 2 H, aryl-H), 6.91 (d, ^{3}(HH) = 2.1 Hz, 1 H, CH), 4.30 (m, 2 H, CH_2), 2.62 (s, 6 H, CH_3), 2.56 (m, 2 H, CH_2), 2.35 (s, 3 H, *p*-aryl-CH_3), 2.32 (broad singlet, 3 H, MeCN), 2.16 (s, 6 H, *o*-aryl-CH_3), –0.13 (s, 3 H, Pd-CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ/ppm: 165.4 (NCN), 139.6 (*p*-aryl-C), 136.0 (*i*-aryl-C), 134.8 (or-aryl-C), 129.5 (*m*-aryl-C), 124.1 (CH), 122.5 (CH), 120.0 (CN), 62.9 (CH_2), 50.1 (NMe_2), 49.4 (CH_2), 21.2 (*p*-aryl-CH_3), 18.7 (*o*-aryl-CH_3), 3.5 (Me-CN), –11.2 (Pd-Me). The signal for the triflate was not observed. MS(FAB+): m/z = 419.1440 for $C_{19}H_{29}N_4Pd$ $[M - OTf]^+$.

X-Ray crystal structure determinations

Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å)

at a temperature of 150 K. Integration of the intensities was performed with the programs EvalCCD[14] (compound **1c**) or HKL2000[15] (compound **5a**). The programs SADABS or TWINABS[16] were used for absorption correction and scaling. The structures were solved with Direct Methods using the program SHELXS-97.[17] Refinement was performed with SHELXL-97 against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions (compound **1c**) or located in difference Fourier maps (compound **5a**) and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[18]

Crystallographic data for 1c. $[C_{40}H_{62}AgN_6][Ag_2Cl_4]_{\frac{1}{2}}$, FW = 913.60 g mol^{-1}, yellow block, $0.48 \times 0.45 \times 0.15$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 11.2826(3)$, $b = 13.6358(3)$, $c = 15.4197(4)$ Å, $\alpha = 83.075(1)$, $\beta = 77.757(1)$, $\gamma = 69.874(1)°$, $V = 2173.83(10)$ Å^3, $Z = 2$, $D_x = 1.396$ g cm^{-3}, $\mu = 1.057$ mm^{-1}. 33 419 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.61$ Å^{-1}. The crystal consisted of two fragments with arbitrary orientation with respect to each other (2.6° approximately about the vector uvw = [1.93, –5.00, –0.13]). The integration was therefore performed on the basis of two orientation matrices. Absorption correction range 0.70–0.85. 8097 reflections were unique ($R_{int} = 0.025$), of which 7103 were observed [$I > 2\sigma(I)$]. 466 parameters were refined with no restraints on the basis of the non-overlapping reflections of the first crystal fragment and the overlapping reflections of both fragments using a HKLF5 file.[19] R_1/wR_2 [$I > 2\sigma(I)$]: 0.0323/0.0673. R_1/wR_2 [all reflections]: 0.0422/0.0738. $S = 1.109$. Batch scale factor 0.152(2). Residual electron density between –1.52 and 1.26 e Å^{-3}.

Crystallographic data for 5a. $C_{17}H_{26}ClN_3Pd$, FW = 414.26, colourless block, $0.21 \times 0.21 \times 0.12$ mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 13.1723(1)$, $b = 11.1113(2)$, $c = 14.7333(2)$ Å, $\beta = 121.8193(6)°$, $V = 1832.31(5)$ Å^3, $Z = 4$, $D_x = 1.502$ g cm^{-3}, $\mu = 1.159$ mm^{-1}. 18 520 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. Absorption correction range 0.51–0.87. 4158 reflections were unique ($R_{int} = 0.043$), of which 3450 were observed [$I > 2\sigma(I)$]. 205 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0280/0.0643. R_1/wR_2 [all reflections]: 0.0398/0.0687. $S = 1.070$. Residual electron density between –0.75 and 0.74 e Å^{-3}.

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