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N-Heterocyclic Carbenes

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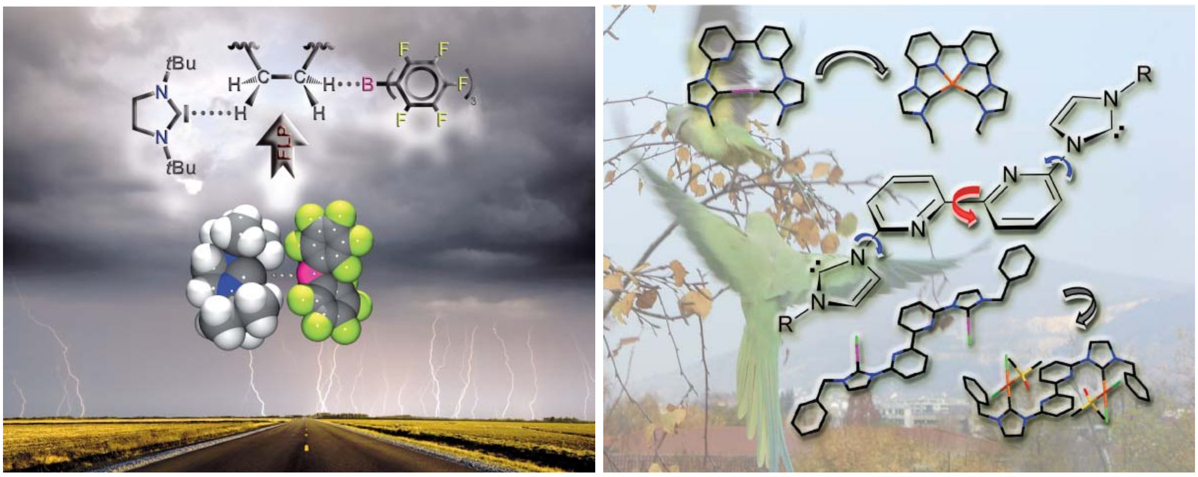

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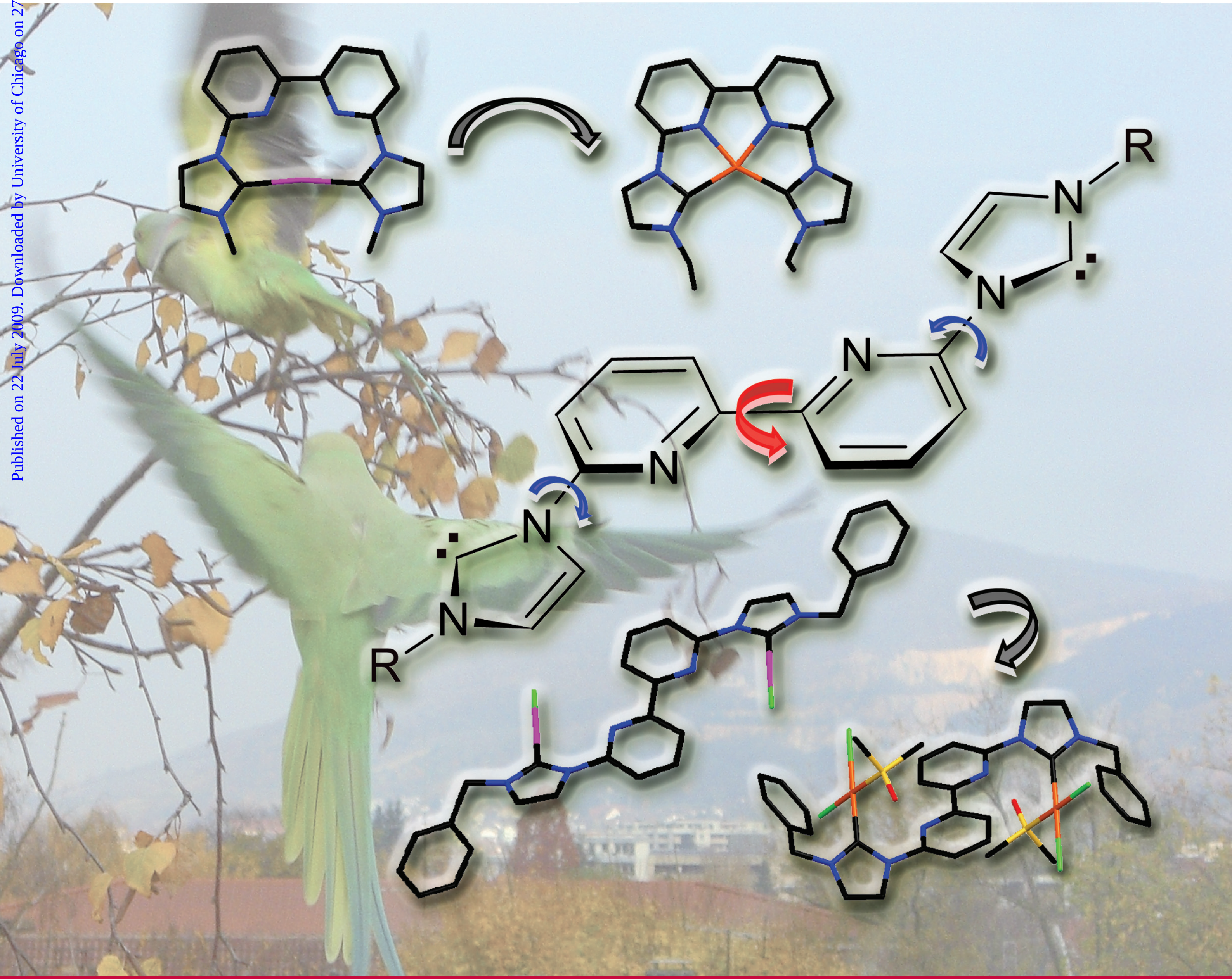

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Controlling the coordination modes of a new and highly flexible ligand bearing two *N*-heterocyclic carbene moieties at a bipyridine backbone†

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A new and highly flexible biscarbene ligand with two imidazolin-2-ylidene moieties in 6,6′-position of a 2,2′-bipyridine was prepared and structurally characterised by X-ray analysis. Various silver complexes were prepared from the imidazolium salts. Depending on the counterion, the coordination mode of the ligand can be mono- or bidentate. Pd complexes are feasible directly from the imidazolium salt using palladium(II)-acetate or *via* transmetallation from silver carbene complexes with [$PdCl_2(CH_3CN)_2$] or [$PdCl_2$(COD)]. Controlled by the structure of the silver complexes the biscarbenebipyridine ligand is a di- or tetracoordinating ligand forming mono- or dinuclear complexes. The high flexibility of this ligand is confirmed by transmetallation from silver to copper, which results in formation of a dinuclear copper complex with two bridging biscarbene ligands.

Introduction

Multidentate ligands containing *N*-heterocyclic carbene moieties are becoming increasingly popular as the electron donor properties of the ligand can be enhanced and certain geometric arrangements realised.[1] For tetradentate ligands containing NHC moieties very rigid backbones or macrocyclic systems[2] are used, so that the number of possible conformations is limited to only one or a few. If such steric restrictions are not imposed, the enhanced flexibility can lead to a variety of possible conformations, but still certain preferred conformers are observed.[3] Factors that control formation of different conformers are plenty including the metal precursor, counterion[4], base[5] and reaction conditions.[6] Bipyridines are among the most common ligands in transition metal chemistry partly due to their excellent properties in redox active complexes.

For multidentate NHCs the use of bipyridines is scarce, only a *pincer* ligand containing one imidazole moiety[7] and an anthracene based *pincer* ligand[8] are known to date. The use of bipyridine as a flexible backbone bearing two NHC moieties at the *ortho*-positions was not realised so far. This ligand is expected to show a rich coordination chemistry serving for mononuclear as well as dinuclear complexes in a bidentate as well as in a tetradentate fashion (Fig. 1). Our aim was to synthesise various late transition metal complexes with this new ligand and investigate the factors that control formation of preferred conformers.

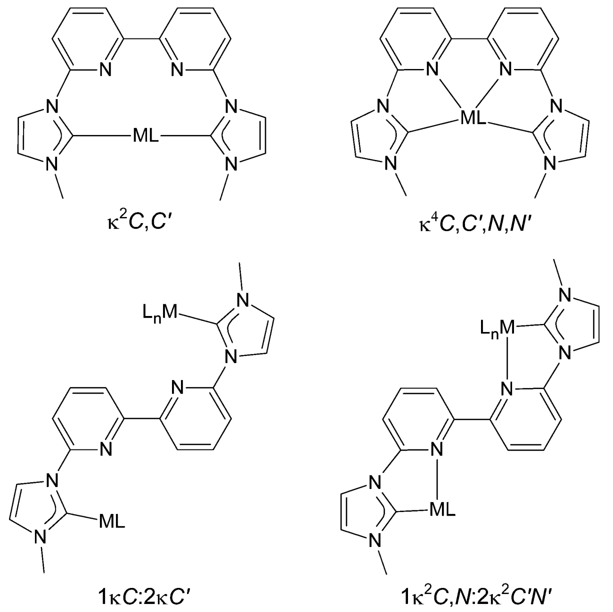

Fig. 1 Various possible coordination modes of a bisimidazolinylidenebipyridine ligand.

Results and discussion

Ligand synthesis

The strategy we used to synthesise the desired biscarbene ligand (Scheme 1) starts with an arylamination of 6,6′-dibromo-2,2′-bipyridine (**1**) with imidazole, followed by alkylation of bisimidazolylbipyridine **2** with various alkyl halides to give the imidazolium salts **3–7**. The free carbenes **8–10** are then obtained by deprotonation with base.

For arylamination we tested various palladium and copper catalysed variations. Palladium catalysed reactions with dppf or *in situ* generated NHC ligands gave no or only poor yields of the

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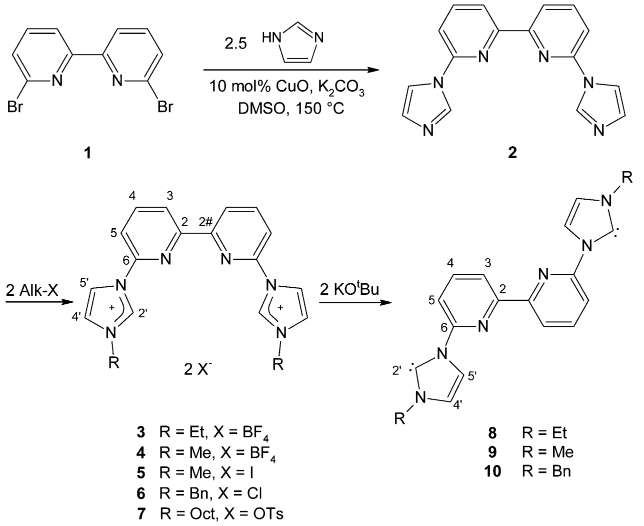


Scheme 1 Synthesis of the bipyridine derived bis(NHC) ligands **8–10**.

desired product **2** along with some monosubstituted bipyridine. However, the copper catalysed Ullmann coupling[9] provides the desired product **2** in almost quantitative yield. Subsequent alkylation with two equivalents of the highly reactive trialkyloxonium tetrafluoroborates (Meerwein's salts) as alkylating reagents in acetonitrile at temperatures from −35 °C to room temperature leads to the imidazolium salts **3** and **4** with the weakly coordinating tetrafluoroborate anion in up to 90% yield. Reaction of the bisimidazole **2** with benzyl chloride or methyl iodide in dimethylsulfoxide at 100 °C also proceeds well with good to excellent yields of the bisimidazolium salts **5** and **6**. Upon reaction with octyltosylate in acetonitrile under reflux only 25% of the product **7** were obtained.

All bisimidazolium salts **3–7** are white solids and almost insoluble in organic solvents like dichloromethane or tetrahydrofuran, but soluble in dimethylsulfoxide. In the ^1H-NMR spectrum formation of the bisimidazolium salts can be followed by the characteristic signal of the acidic imidazolium proton H2′ at 10.3 ppm, which is independent from the counterion. Only the signal of the benzyl substituted bisimidazolium chloride **6** is shifted to low field at 10.7 ppm. In the ^{13}C-NMR spectrum the characteristic imidazolium signal C2′ is found for all bisimidazolium salts between 135.1 and 135.9 ppm, a typical value for unsaturated imidazolium ions.[10] Imidazolium salts with *N*-alkyl substituents often have melting points below 100 °C and are therefore considered as Ionic Liquids.[11] However, the bisimidazolium salts **3–7** show very high melting points between 242 °C (**7**) and 299 °C (**5**).

The molecular structures of the bisimidazolium salts **3–6** were revealed by X-ray crystal structure analyses (see Fig. 2). As it can be expected, the nitrogen atoms of the bipyridine moiety point in opposite directions. This can be rationalised by the molecule avoiding nitrogen lone pair repulsion and minimalising the dipole moment. An $N_{pyridine}$-H interaction could be possible with the imidazolium protons H2′ or H5′ depending on the conformation. Indeed, the molecular structures of compounds **3–6** show a planar zig-zag like arrangement. While the molecular structures of **3**, **5** and **6** show the imidazole H2′ pointing to the same side as the $N_{pyridine}$ lone-pair, in the molecular structure of bisimidazolium salt **4** the imidazolium moieties are rotated by 180° around the $C6_{pyridine}$-$N1'_{imidazole}$ axis, so that the H5′ hydrogen points toward the $N_{pyridine}$ lone pairs. The molecular structures containing iodide (**5**) and tetrafluoroborate counterions (**3–4**) show no hydrogen bonds between the acidic H2′ and the counterion, while in case of chloride counterions a hydrogen bond is found between chloride and the imidazolium H2′ as well as between the chloride and the hydroxyl group of included ethanol.

Synthesis of the free carbenes worked well by deprotonation of the bisimidazolium salts **3–6** with a 20% excess of potassium *tert*-butoxide. The reaction was carried out by adding the base to a suspension of the bisimidazolium salts in toluene at −35 °C and

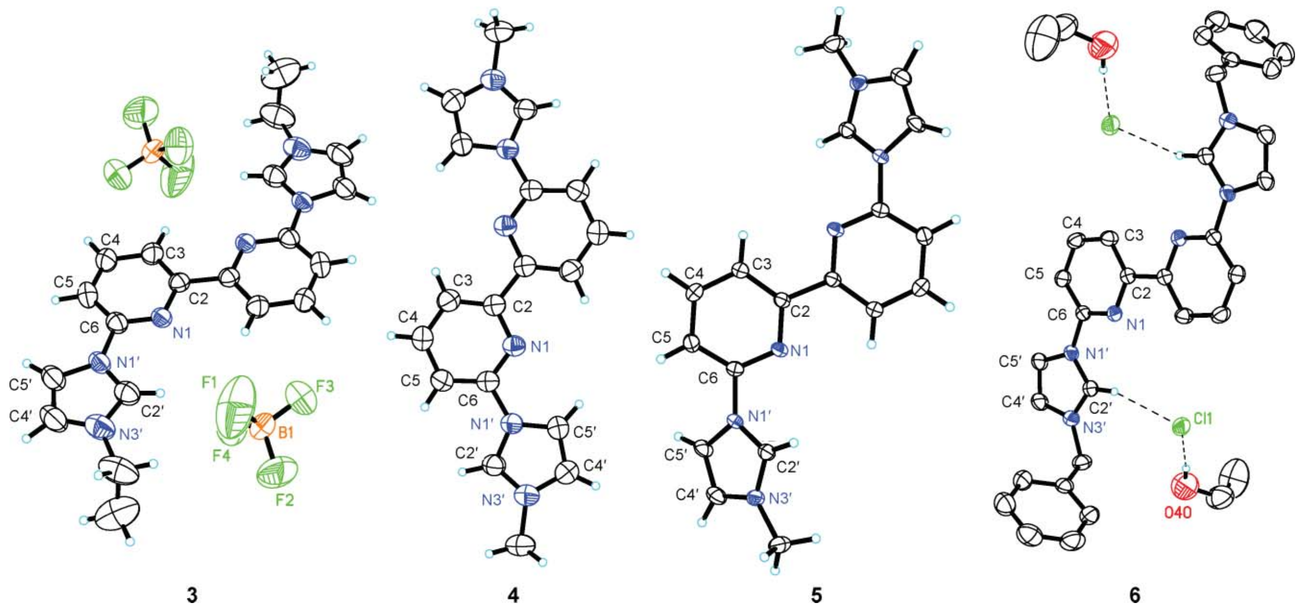


Fig. 2 Molecular structures of the bisimidazolium salts **3–6** showing 50% probability ellipsoids; hydrogen atoms in **6** except H2′ as well as the counterions in **4** (BF_4^-) and **5** (I^-) are omitted for clarity. For selected bond lengths and angles see Table 1.

Table 1 Selected bond distances (Å) and angles (°) for the imidazolium salts **3–6** and the carbene **8**. Atom labelling is defined in Scheme 1

	3	4		5	6	8
Bond distances		1st molecule	2nd molecule			
N1′-C2′	1.318(5)	1.340(4)	1.332(4)	1.333(4)	1.3427(19)	1.3799(17)/1.3763(18)
C2′-N3′	1.337(5)	1.320(4)	1.320(4)	1.318(4)	1.3264(19)	1.3541(18)/1.3574(18)
N1′-C5′	1.386(5)	1.385(4)	1.382(4)	1.392(4)	1.3869(19)	1.3954(17)/1.3911(17)
C5′-C4′	1.344(6)	1.338(4)	1.337(4)	1.349(5)	1.347(2)	1.3388(19)/1.341(2)
C4′-N3′	1.354(6)	1.377(4)	1.368(4)	1.369(4)	1.379(2)	1.3898(18)/1.3907(19)
Bond angles						
N1′-C2′-N3′	108.5(4)	109.0(3)	108.5(3)	108.6(3)	107.87(13)	101.41(11)/101.46(12)
N1′-C6-N1	113.6(3)	114.0(3)	113.6(3)	113.7(3)	113.98(12)	115.25(11)/115.44(11)
N1-C2-C2#	116.3(4)	115.9(3)	115.7(3)	115.6(3)	115.85(15)	116.00(11)/115.95(11)

stirring the reaction mixture for 6 hours at room temperature. As the product is soluble in toluene it can be easily separated from the inorganic salts by filtration providing the biscarbenes as an off-white (**8**) and a pale yellow (**9**) solid in moderate to good yields. The free biscarbenes do not show any decomposition during weeks, if stored under an inert atmosphere and they decompose only above 202 °C (**8**) and 265 °C (**9**). The same procedure was also used for generating biscarbene **10** *in situ* as an NMR experiment in THF-d_8. Stronger bases like lithium diisopropylamide and methyl lithium turned out to be less suitable, as an excess of base led to rapid decomposition of the carbenes in solution. Formation of the carbenes is indicated in the ^{13}C NMR spectrum by a characteristic low field shift of the carbene C2′ signals at 216.9 (**8**), 217.4 (**9**) and 217.5 ppm (**10**). Additional proof is provided by 2D ^{1}H,^{13}C multiple bond correlation spectroscopy (Fig. 3), showing cross peaks between the carbene signal and the proton signals of the CH_2 (**8**) and CH_3 (**9**) group as well as between the H5 signal of the pyridine ring in **8**. The chemical shift for the carbene carbon signal is typical for imidazolinylidenes showing the carbene signal between 210 and 220 ppm.[10]

By slow diffusion of pentane into a solution of carbene **8** in tetrahydrofuran we were able to obtain crystals suitable for X-ray structure analysis. Fig. 4 shows one of the rare examples of the molecular structure of a biscarbene.[12]

Biscarbene **8** adopts a planar zig-zag conformation with the pyridine rings rotated around the C2-C2# axis by 180° as it was already observed for the imidazolium salts **3–6**. Compared to the structure of its imidazolium salt **3** the imidazolinylidene rings of **8** are rotated by 180 ° around the N1′-C6 bond which is most likely due to a lone pair repulsion between the carbene and the nitrogen lone pair. The angle N1′-C2′-N3′ measures 101.4° (mean), a value that is expected on basis of the chemical shift–angle correlation we reported earlier.[13]

Carbene **8** is also identified by mass spectrometry (HR-EI$^+$) showing the molecule peak at $m/z = 344.1753$ (calcd. 344.17409). Fragmentation occurs on both ethyl groups as well as the imidazole rings.

Synthesis of carbene complexes with basic metal salts

Attempts to react the isolated carbene **8** with the precursors $[PdCl_2(COD)]$ and $[Pd(\mu\text{-}Cl)(C_3H_5)]_2$ in THF-d_8 did not lead to the desired complexes, although the free carbene gets consumed. We therefore decided to react the imidazolium salts with basic metal

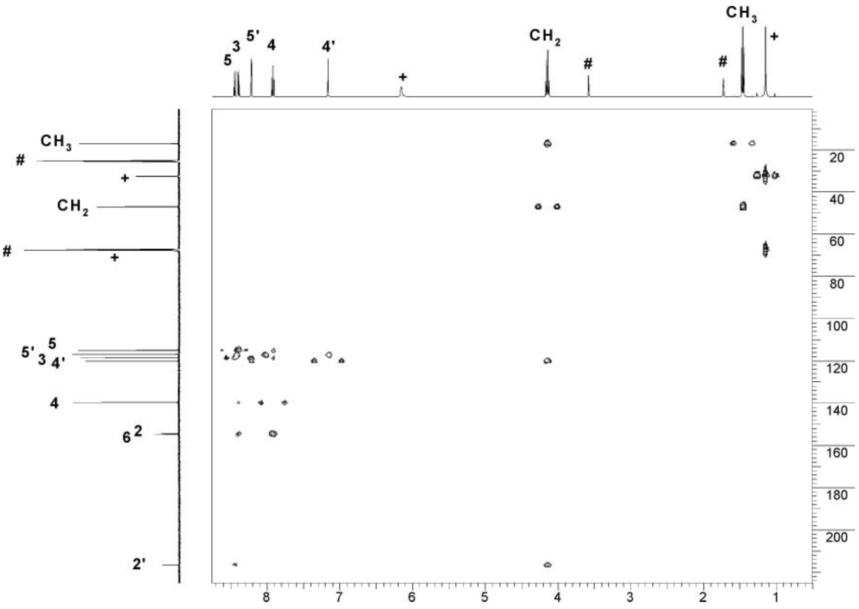


Fig. 3 ^{1}H,^{13}C HMBC spectrum of carbene **8** in THF-d_8 (#), (*t*-BuOH (+)).

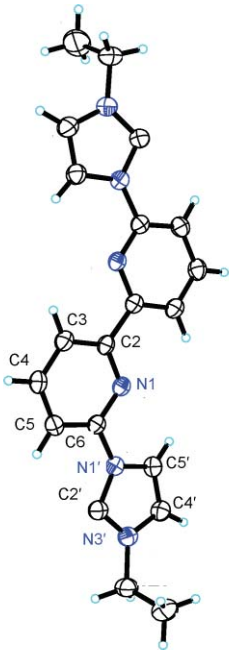


Fig. 4 Molecular structure of the biscarbene **8** showing 50% probability ellipsoids. For selected bond lengths and angles see Table 1.

salts to obtain the metal carbene complexes of silver, palladium and copper. It is well known that palladium(II)-acetate[14] and silver(I)-oxide[15,16] are suitable metal salts for the synthesis of the corresponding carbene complexes. The silver complexes could then be used as carbene transfer reagents.[15]

We monitored the reaction of imidazolium salt **3** with 1.3 equiv of silver(I)-oxide in dimethylsulfoxide-d_6 at 100 °C by NMR spectroscopy. After 2 h formation of a new signal set and of water (3.33 ppm) is observed (Fig. 5). During the course of the reaction, the signal intensities of the new complex **11** increase, while the signals of the starting material diminish. After 24 h the signals of the starting material are vanished as well as those of an intermediate (★) with a characteristic peak at 10.20 ppm (probably a monocarbenemonoimidazolium salt). Using the less basic silver carbonate as a starting material slows down the reaction rate and increases the reaction time to 1.5 days for full conversion. Identical spectra were obtained by synthesising the silver carbene complex **11** on a preparative scale in acetonitrile in 84% yield. The elemental analysis reveals the constitution $[Ag_2(\mathbf{8})(BF_4)_2]$. However more information is necessary to elucidate the structure of this complex.

The ^{13}C NMR spectrum confirms formation of a symmetric silver NHC complex with a single signal at 180.9 ppm which is a typical value for silver imidazolinylidene complexes,[10,16,17] however $^{107/109}Ag$-^{13}C coupling is not observed. The ^{109}Ag NMR spectrum shows only one singlet at 270.1 ppm. This value is lower than those observed for NHC complexes in the few ^{109}Ag-NMR spectra available for silver NHC complexes (597–727 ppm).[16] Free $AgBF_4$ can be excluded as it shows a ^{109}Ag NMR chemical shift of 173.0 ppm. Therefore both silver atoms are magnetically equivalent and bound to the carbene carbon or more likely show a fast exchange.[15a] The high resolution mass spectrometry shows a cationic fragment containing one ligand and only one silver atom using fast atom bombardment as well as electrospray as ionisation methods. Silver carbene complexes are known to aggregate by formation of d^{10}-d^{10} Ag-Ag interactions,[16,18] therefore the structure of complex **11** can be more complicated and still remains unresolved. The complex is best described as the overall formula $[Ag_2(\mathbf{8})(BF_4)_2]_n$ with $n = 1, 2$ or even higher (Scheme 2).

Reacting the imidazolium salt **4** with silver(I)-oxide in acetonitrile at 90 °C for two days leads to formation of the silver complex **12** (Scheme 2) in which one silver cation is coordinated by one ligand according to the mass spectrum (ESI^+). The signals of the aromatic protons in the ^1H NMR spectrum are identical to those of compound **11**. In the ^{13}C NMR spectrum the carbene signal is found at 183.5 ppm which is also similar to that of **11**; $^{107/109}Ag$-^{13}C coupling was not found in this case either. The ^{109}Ag NMR spectrum of **12** could not be obtained due to its poor solubility in DMSO-d_6. However, we were able to obtain light yellow needles

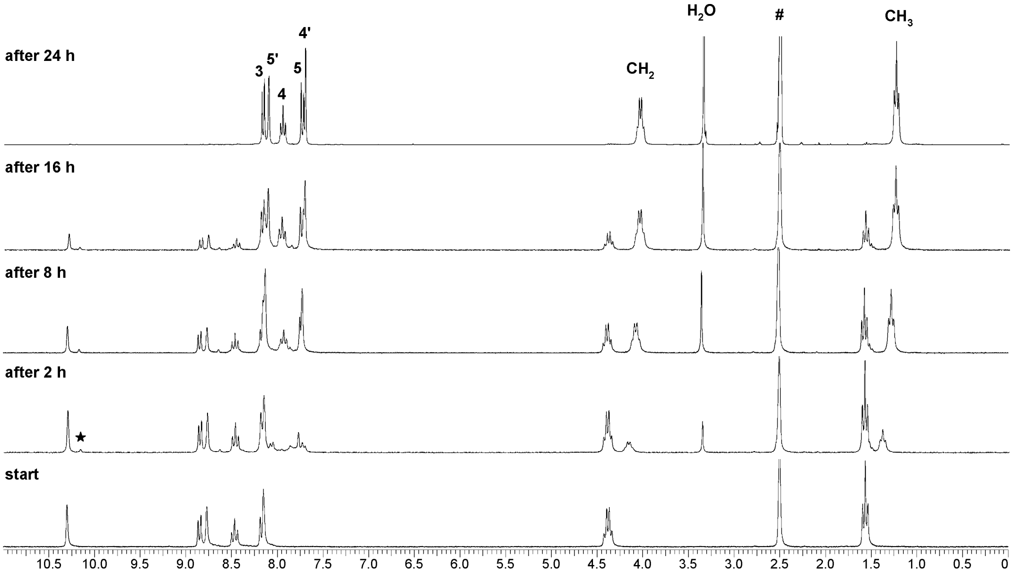
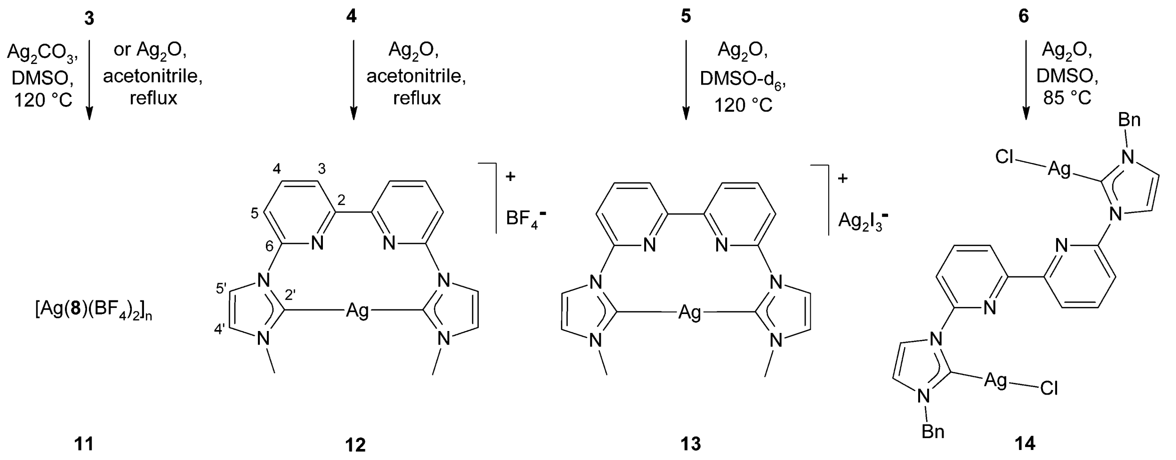


Fig. 5 Monitoring the reaction of imidazolium salt **3** with Ag_2O in DMSO-d_6 by ^1H NMR spectroscopy.



Scheme 2 Syntheses of silver biscarbene complexes **11–14** from the bisimidazolium salts **3–6**.

suitable for X-ray structure analysis by slow evaporation of a saturated solution of **12** in acetonitrile.

The molecular structure of **12** (Fig. 6) shows an almost planar mononuclear complex with the silver atom linearly coordinated by the two imidazolinylidene moieties (C2′-Ag-C2′# = 171.3(3)°). The mean silver-carbene distance is 2.14 Å, which is typical for Ag(NHC) complexes. Compared with the imidazolium salt, the N1′-C2′-N3′ angle at the carbene is more acute by about 5° (104.0° (mean)), but more opened compared to free imidazolinylidene **8** (101.4° (mean)). The tetrafluoroborate counterion does not show any close contacts with the cationic complex.

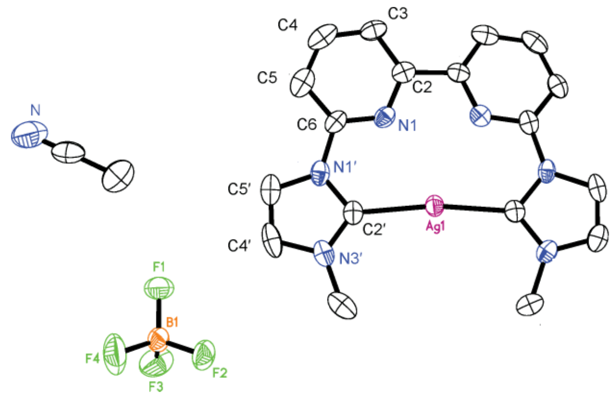


Fig. 6 Molecular structure of the silver biscarbene complex **12** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 2.

Starting from imidazolium iodide **5**, the similar silver complex **13** was obtained after prolonged heating with silver(I)-oxide at 100 °C in DMSO (Scheme 2). The product is even less soluble in DMSO than compound **12**, but this is somehow expected as imidazolium iodides are in general less soluble in organic solvents than imidazolium tetrafluoroborates. At room temperature the spectrum of **13** shows only broad peaks. However heating up to 100 °C results in a sharpening of the signals and an enhanced resolution. The signals in the ^{13}C NMR spectrum are almost identical to those of complex **12**, therefore structural similarities are expected. An X-ray structure analysis of compound **13** confirms the mononuclear cationic complex with a bidentate coordination of the biscarbene ligand (Fig. 7). More interesting however is the unusual structure of the polysilveriodide anion that forms a waffle iron-like ribbon consisting of tetrahedral coordinated silver atoms within one plane and the iodide anions oriented above and below this plane. The cation and the complex anion show weak Ag-I interactions. Due to the limited quality of the crystal this is only proof for the connectivity, discussing the bond lengths is not appropriate. Formation of oligomeric or polymeric silver(I)-iodide chains in DMSO is a well known phenomenon.[19] This explains also the even decreased solubility of compound **13** compared to its tetrafluoroborate **12** analogue.

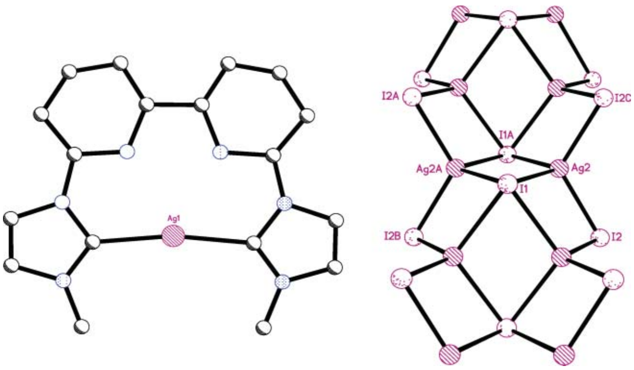


Fig. 7 Molecular structure of the silver biscarbene complex **13** showing the cation (left) and a fragment of the polysilveriodide anion $[(Ag_2I_3)^-]_n$ (right); hydrogen atoms are omitted for clarity. Due to the limited quality of the crystal only the connectivities can be discussed.

Reaction of the chloride containing imidazolium salt **6** with silver(I) oxide in DMSO is performed at 120 °C. The product complex **14** can be isolated in 80% yield by recrystallisation from DMSO.

The ^{1}H NMR spectrum at 22 °C shows only the signals of the benzyl and the imidazolinylidene moieties. The signals of the bipyridine protons are extremely broadened (7.0 to 8.8 ppm) and can only be recognized by integration of the baseline in that region. Heating up to 67 °C leads to a sharpening of the signals with the bipyridine signals being still broad. At this temperature the carbene carbon signal can be detected by a multiple bond correlation experiment showing a cross peak between the

Table 2 Selected bond distances (Å) and angles (°) for the silver, palladium and copper carbene complexes **12**, **14–15** and **17–18**. Atom labelling is defined in Scheme 1

	12	**14**	**15**	**17**	**18**	
Bond distances					1^{st} molecule	2^{nd} molecule
N1′-C2′/N1′#-C2′#	1.367(8)/1.388(8)	1.357(19)	1.388(2)/1.391(2)	1.356(3)	1.372(7)/1.371(7)	1.368(7)/1.373(7)
C2′-N3′/C2′#-N3′#	1.321(8)/1.348(8)	1.338(18)	1.334(3)/1.332(2)	1.340(3)	1.340 (8)/1.340(8)	1.336(8)/1.341(7)
N1′-C5′/N1′#-C5′#	1.375(9)/1.392(8)	1.37(2)	1.386(3)/1.385(3)	1.385(3)	1.390(7)/1.395(7)	1.382(8)/1.393(7)
C5′-C4′/C5′#-C4′#	1.336(11)/1.339(10)	1.33(2)	1.335(3)/1.337(3)	1.342(4)	1.318(10)/1.325(9)	1.327(11)/1.311(9)
C4′-N3′/C4′#-N3′#	1.397(9)/1.386(9)	1.38(2)	1.396(3)/1.392(2)	1.388(4)	1.391(8)/1.387(8)	1.388(9)/1.391(8)
C2′-M/C2′#-M	2.154(6)/2.124(6)	2.079(15)	2.044(2)/2.0458(18)	1.962(3)	1.932(6)/1.922(6)	1.916(6)/1.923(5)
N1-M/N1#-M(#)	—/—	—	1.9768(16)/1.9782(16)	—	2.246(5)/2.306(5)	2.314(4)/2.325(4)
M-Cl$_{trans}$/M-Cl$_{cis}$	—/—	2.307(4)	—/—	2.3518(8)/2.3212(7)	—/—	—/—
Pd-S	—	—	—	2.2229(7)	—	—
Bond angles						
N1′-C2′-N3′/N1′#-C2′#-N3′#	104.7(5)/103.4(5)	105.7(13)	104.00(17)/103.41(15)	105.1(2)	103.3(5)/103.4(5)	103.9(5)/103.7(5)
N1′-C6-N1/N1′#-C6′#-N1#	113.3(5)/113.3(5)	116.8(13)	111.23(17)/111.16(16)	114.8(2)	113.7(5)/113.7(5)	113.9(5)/114.8(5)
N1-C2-C2#/N1#-C2#-C2	113.7(5)/112.7(6)	116.4(17)	112.87(17)/112.38(18)	115.6(3)	115.0(5)/115.5(5)	116.0(5)/114.8(5)
C2′-M-C2′#/C2′-M#-C2′#	171.3(3)	—	121.54(7)	—	156.7(4)/158.2(4)	157.3(4)/160.6(3)
C2′-M-N1	—	—	79.56(8)	—	78.3(2)	77.6(2)
C2′#-M#-N1#	—	—	79.63(7)	—	77.7(2)	76.9(2)
N1-M-N1# or N1-M-N12/N1#-M#-N12#	—	—	79.33(7)	—	117.1(2)/110.4(2)	122.1(2)/124.3(2)

methylene protons and the carbene carbon at 5.48/184.5 ppm. In mass spectrometry, the electrospray as well as the laser induced field desorption ionisation method lead only to detection of a cationic fragment bearing one silver atom and the carbene ligand ($m/z = 577.2$). Single crystals suitable for X-ray structure analysis were obtained by recrystallisation from DMSO. The molecular structure of complex **14** exhibits a dinuclear complex with one carbene ligand (Fig. 8). Each silver atom is coordinated by one carbene moiety and one chloro ligand in a linear fashion. The bipyridine moiety is rotated by 180 °C, so that both NHC moieties are oriented in opposite directions. The Ag-C2′ bond length of 2.079(15) Å is shorter than in complex **12** (Ag-C2′ = 2.154(6) Å, Ag-C2′# = 2.124(6) Å) in which the silver atom is coordinated by two carbene atoms.

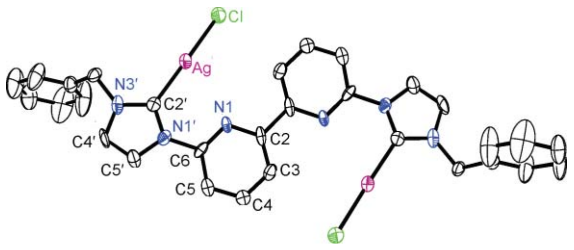
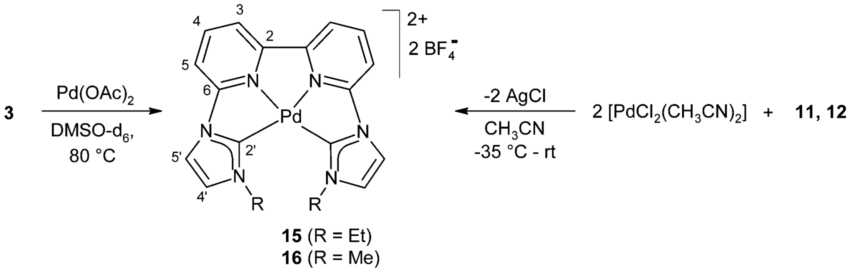


Fig. 8 Molecular structure of the silver biscarbene complex **14** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 2.

The various silver carbene complexes **11–14** demonstrate the flexibility of the biscarbene ligand. Imidazolium salt **4** with the weakly-coordinating tetrafluoroborate anion leads to a mononuclear complex with both carbene moieties coordinated to silver. Imidazolium salt **6** containing the well coordinating chloride anion leads to the dinuclear silver complex **14** with chloride ions coordinated to silver. Iodide takes in a special role: it coordinates very well with silver forming a polysilveriodide anion that behaves as a weakly coordinating counterion and therefore leads to a mononuclear silver complex **13** with both NHCs coordinated to the silver atom.

Synthesis of palladium complexes

To synthesise palladium complexes with the new biscarbenebipyridine ligand **8** we first chose a direct metallation of bisimidazolium salt **3** with basic palladium(II)-acetate (Scheme 3). Monitoring the reaction of **3** and palladium(II)-acetate in DMSO-d$_6$ at 80 °C shows formation of a new signal set along with some acetic acid.



Scheme 3 Synthesis of Pd complexes **15** and **16** bearing the biscarbene ligands **8** and **9**.

However, despite reaction for several days and addition of a second equivalent of palladium(II)-acetate full conversion of the starting material was not achieved. As Ag-NHC bonds are quite weak[20] we tried a transmetallation from silver to palladium according to Lin *et al.*[15] The transmetallation of silver complex **8** with [PdCl$_2$(COD)] or [PdCl$_2$(CH$_3$CN)$_2$] proceeds already at room temperature in acetonitrile with fast formation of a gray precipitate that is removed by filtration over Celite®. Addition of tetrahydrofuran and pentane to the filtrate leads to crystallisation of the product complex **15** as colourless crystals in a 72% isolated yield. The ^{1}H NMR spectrum shows formation of one signal set of a symmetric species. The signals shifted to low field in comparison to silver complex **8**. In the ^{13}C NMR spectrum formation of the carbene complex **15** is indicated by a carbene signal at 161.0 ppm, which is a typical value for imidazolinylidene palladium complexes and is shifted more than 20 ppm highfield compared to the signal of the silver carbene complex **8**. The mass spectra confirm formation of the mononuclear complex [Pd(Et$_2$NHC$_2^{\mathrm{Bipy}}$)](BF$_4$)$_2$ (**15**) with peaks at 537.0892 (HR-FAB$^+$) and 537.08113 (HR-ESI$^+$) (Calcd. [M − BF$_4^+$] m/z = 537.08080). Single crystals suitable for X-ray analysis were obtained by slow concentration of a saturated solution of **15** in acetonitrile. The molecular structure of the dicationic complex shows a distorted square planar coordinated palladium atom (Fig. 9a). Interestingly, the dication complex has both ethyl substituents oriented to the same side. Obviously steric hindrance is not pronounced.

The palladium carbene bond length (2.045 Å) is typical for NHC-palladium(II) complexes. The mean Pd-N distance (1.978 Å) is rather unusually short for bipyridine complexes (1.98–2.12 Å).[21] The N1-Pd-N1# as well as the N1-Pd-C2′ angle are about 79° while the C2′-Pd-C2′# angle measures 122° and thus is clearly opened up from the ideal 90°. Fig. 9b shows the overlay of the molecular structures of the silver complex **12** and the Pd complex **15**: The C2′-M-C2′# angle is changed from 171.3(3) (**12**) to 121.54(7)° (**15**). The N1′-C6-N1 angle becomes more acute, so that the carbene distance C2′-C2′# gets significantly shorter (3.569(3) (**15**), 4.266(3) Å (**12**)). This demonstrates nicely the high flexibility of our new biscarbene ligand.

Under the same conditions the Ag complex **12** bearing *N*-methyl substituents was reacted with [PdCl$_2$(CH$_3$CN)$_2$] and complex **16** was isolated (Scheme 3). The compound is less soluble than complex **15** and therefore the NMR spectra were recorded in DMSO-d$_6$. They show the same characteristic peaks as for complex **15**, especially the carbon carbene signal at 162.5 ppm. In mass spectrometry the [M − BF$_4$]$^+$ peak is detected at m/z = 509.2 (ESI$^+$).

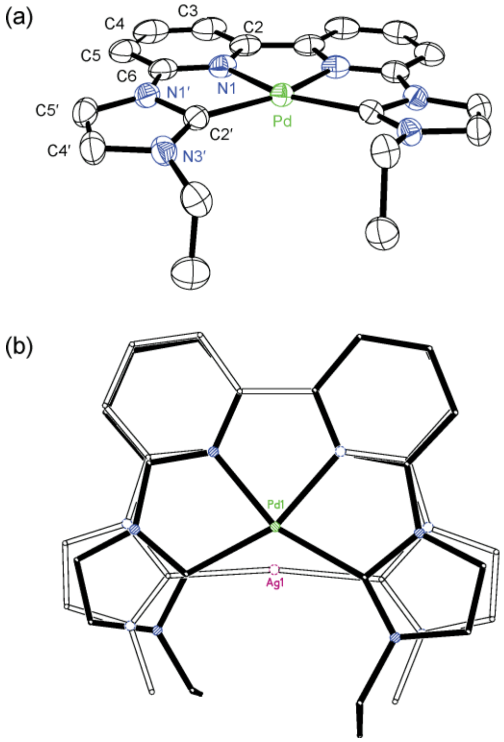
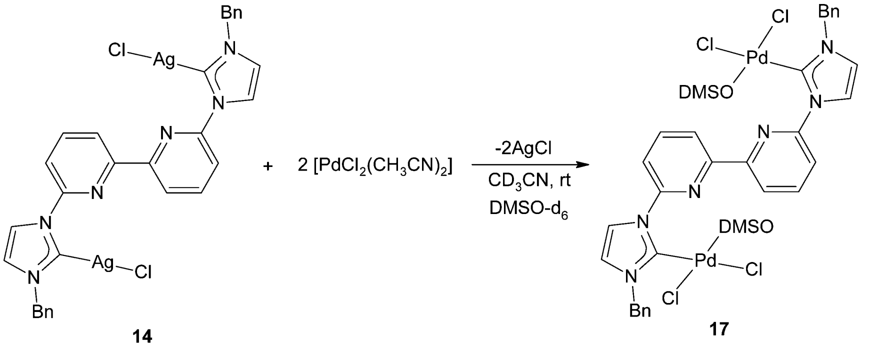


Fig. 9 (a) Molecular structure of the palladium biscarbene complex **15** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 2. (b) Overlay of the molecular structures of silver complex **12** (white) and palladium complex **15** (black).

A change of the bisimidazolium salt counterion leads to a change in the hapticity of the biscarbene ligand in the silver carbene complexes. This observation is also to be tested for transmetallation reactions of various silver complexes. We therefore reacted a suspension of the dinuclear silver complex **14** with [PdCl$_2$(CH$_3$CN)$_2$] at room temperature (Scheme 4). The transmetallation reaction is accompanied by formation of a grey solid. Because of the low solubility of the product **17**, the NMR analysis is carried out in DMSO-d$_6$, however, the signals are still broad multiplets between 5.89 and 8.41 ppm. From this saturated solution in DMSO-d$_6$ big yellow crystals suitable for X-ray structure analysis are formed after four weeks.



Scheme 4 Synthesis of the dinuclear Pd biscarbene complex **17**.

The molecular structure of **17** is the first example of a [Pd(NHC)(DMSO)] complex (Fig. 10). The dinuclear complex shows the two carbene moieties coordinated to two palladium dichloride fragments. Instead of a coordination of the bipyridine nitrogen, the fourth coordination site is occupied by DMSO that is coordinated *via* sulfur. The palladium carbene distance (1.962(3) Å) is smaller than in the Ag complex **14** (2.079(15) Å).

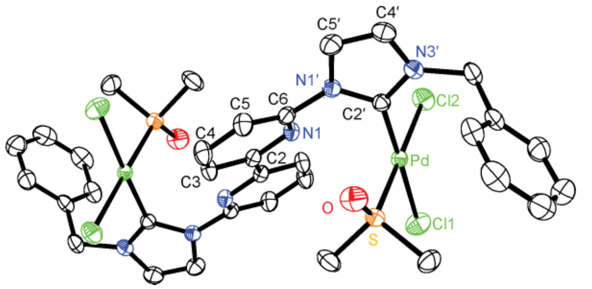


Fig. 10 Molecular structure of the dinuclear Pd biscarbene complex **17** showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 2.

Although such complexes had been postulated and observed by NMR spectroscopy,[22] the structural evidence was still missing.

We could show that the best way to synthesise palladium carbene complexes bearing our new biscarbene ligand is *via* transmetallation from its silver complex. With the weak coordinating tetrafluoroborate counterion the reaction leads to mononuclear complex **15** coordinated by the ligand in a tetradentate fashion. With chloride as a counterion the Pd-chloride bonds of the precursor stay intact and a dinuclear complex **17** with a bridging ligand in a monodentate fashion is formed.

Synthesis of copper complexes[15c]

In analogy to the reactivity with Ag_2O we reacted the imidazolium salt **3** with copper(I)-oxide in acetonitrile-d_3 at 110 °C in a sealed NMR tube (Scheme 5). After 16 h the spectrum shows formation of one new signal set along with some H_2O, after 7 days at 110 °C about 33% of the new complex has formed.

To avoid too long reaction times we tried the transmetallation route. Suspension of silver complex **11** with two equivalents of CuCl in acetonitrile at −35 °C led immediately to formation of a voluminous grey precipitate and a red solution. After filtration the orange-red filtrate was concentrated and the product precipitated by addition of pentane. After filtration 82% of product **18** were obtained as a copper-red solid. It is important to use the Ag-complex:Cu = 1:2 ratio. In the case of a 1:1 ratio only 50% of the silver complex are consumed.

The use of CuI instead of CuCl leads to the identical copper complex. The ^{1}H NMR spectrum of complex **18** is identical to that obtained by synthesis from the imidazolium salt **3** and copper(I)-oxide. Formation of carbene complex **18** is indicated by the signal of the carbene carbon at 185.0 ppm in the ^{13}C NMR spectrum. Mass spectrometry (HR-ESI) reveals a signal (53%) at m/z = 901.21149 that can be attributed to a dinuclear complex with two carbene ligands $[Cu_2(\mathbf{8})_2]BF_4^+$ (calc. m/z = 901.21215) and a signal (100%) at m/z = 407.10640 that is consistent with the fragment $[Cu_2(\mathbf{8})]^+$ (calc. m/z = 407.10400). Elucidation of the molecular structure of complex **18** was finally obtained by X-ray analysis. Single crystals were obtained by slow diffusion of diethylether into a saturated solution of **18** in acetonitrile. The molecular structure (Fig. 11) shows a dicationic copper complex consisting of two ligands and two copper atoms, each coordinated *via* one carbene and one pyridine moiety of both ligands forming a double helical arrangement. The copper atoms are coordinated distorted tetrahedral showing copper-carbene distances of Cu1-C2′ = 1.932(6) and Cu2-C2′# = 1.922(6) Å and copper-nitrogen distances of Cu1-N1 = 2.246(5) and Cu2-N1# = 2.306(5) Å. The torsion angle of the bipyridine unit is 51.9°. The unit cell contains a second independent molecule that shows similar bond lengths, however the bipyridine torsion angle of 37.4° is smaller by almost

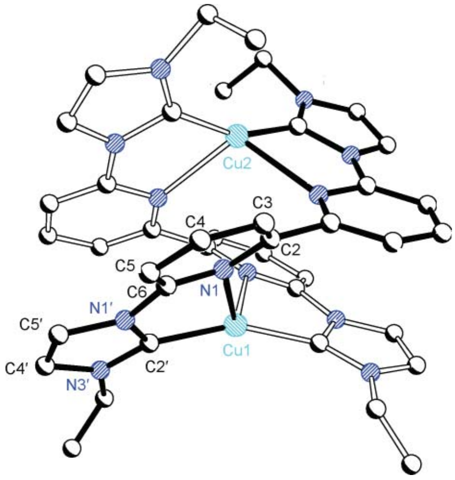
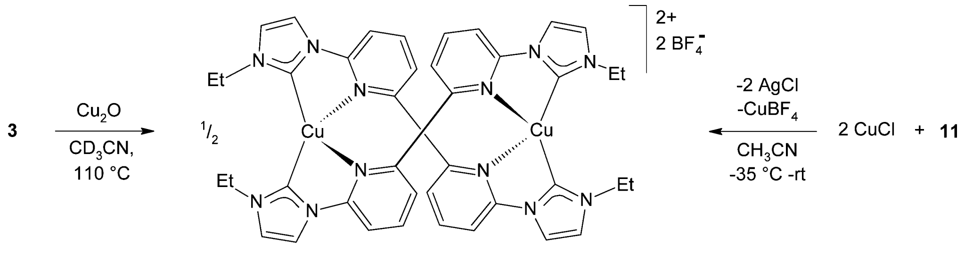


Fig. 11 View of the molecular structure of the dinuclear copper(I) biscarbene complex **18**; for clarity the two bridging ligands are drawn black and white and hydrogen atoms are omitted. For selected bond lengths and angles see Table 2.



18

Scheme 5 Synthesis of the dinuclear copper complex **18** with two bridging biscarbene ligands.

15° which leads to a significant shortening of the Cu-Cu distance (4.106(3) Å (1st molecule), 3.706(3) Å (2nd molecule)).

Conclusions

We showed that the new $R_2NHC_2^{bipy}$ ligand is highly flexible and can be prepared easily. Upon addition of base it forms thermally stable biscarbenes. Formation of palladium and copper complexes with this new ligand is however best achieved *via* transmetallation of the respective silver complexes. The silver complexes are obtained by reaction of the imidazolium salts with silver(I)-oxide. The nature of the imidazolium counterion determines the configuration of the silver complex. Weakly coordinating anions lead to a mononuclear biscarbene complex while the strongly coordinating chloride anion prefers dinuclear complexes. As iodide forms a polysilveriodide anion, it acts as a weakly coordinating anion. This principle is kept in the transmetallation to palladium and copper. With the tetrafluoroborate anion a mononuclear Pd complex with a η^4 coordination of the ligand is obtained, while transmetallation from the dinuclear silver carbene complex leads to a dinuclear Pd complex. Transmetallation of the tetrafluoroborate silver complex **8** with copper(I)-chloride leads, as expected, to a 1:1 ratio of ligand and metal, however a dinuclear complex with two bridging ligands is formed.

With the results presented above, it should now be possible to predict the ligand:metal ratio of transition metal complex with the $R_2NHC_2^{bipy}$ ligand or even the conformation.

Experimental

General methods

Unless otherwise noted all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or were performed in a nitrogen filled glove box. All solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purification. 6,6′-Dibromo-2,2′-bipyridine was synthesised according to literature.[23] ^{1}H, ^{13}C NMR and ^{109}Ag NMR spectra were recorded using a Bruker ARX 250, DRX 300, DRX 500 or DRX 600 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (2.49 ppm DMSO-d_6, 2.13 ppm toluene-d_8, 1.73 ppm THF-d_8). Assignments of ^{13}C NMR spectra were made with the aid of 2D correlation spectra. Unless otherwise noted, all NMR spectra were acquired at room temperature. Mass spectra were recorded on a Jeol JMS-700 with NBA (nitrobenzylalcohol) as matrix or a Bruker ApexQe hybrid 9.4 T FT-ICR instrument. Infrared spectra were recorded using a Bruker Equinox 55 FT-IR-spectrometer. Melting points were determined with a Büchi Melting Point B 540 apparatus. Elemental analyses were performed by Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

Synthesis of 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (2)[1]. A Schlenk tube was charged under nitrogen atmosphere with 6,6′-dibromo-2,2′-bipyridine (**1**) (3.76 g, 12.0 mmol), dried imidazole (2.03 g, 30.0 mmol), potassium carbonate (4.14 g, 30.0 mmol), copper(II) oxide (95.3 mg, 1.20 mmol) and 15 mL abs. DMSO. The suspension was stirred for 8 hours at 150 °C to give an off-white suspension. Upon cooling to room temperature a greenish solid precipitated. The solvent was removed under reduced pressure by slow distillation at 80 °C. Subsequent removal of all volatiles *in vacuo* gave a greenish solid. The purification of the crude product was achieved by repeated extraction with 500 mL of boiling ethanol. The precipitated solid was subsequently recrystallised from ethanol. The solid was filtered and dried *in vacuo* to yield 3.36 g (97%) of the product as a white fluffy solid. M.p. 254 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.17 (s, 2H, H-4′), 7.91 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-5), 8.15 (s br, 2H, H-5′), 8.19 (t, $^3J_{HH}$ = 8.0 Hz, 2H, H-4), 8.49 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-3), 8.76 (s, 2H, H-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 113.4 (C-5), 116.7 (C-5′), 119.0 (C-3), 130.2 (C-4′), 135.3 (C-2′), 141.0 (C-4), 148.3 (C-6), 153.3 (C-2); IR (KBr): ν = 3106 (w), 1590 (m), 1573 (s), 1504 (s), 1476 (s), 1449 (s), 1303 (s), 1271 (m), 1108 (w), 1053 (s), 744 (s) cm^{-1}; MS (EI)$^+$: *m/z* (%) 288.1 [M]$^+$ (100), 256.1 [M − $C_3H_3N_2$]$^+$ (21), 144.1 [M − $C_8H_6N_3$]$^+$ (6), 68.0 [$C_3H_3N_2$]$^+$ (62); elemental analysis calcd (%) for $C_{16}H_{12}N_6$: C 66.66, H 4.20, N 29.15; found: C 66.38, H 4.21, N 29.06.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-ethyl-1*H*-imidazolium) bistetrafluoroborate [$H_2(Et_2NHC_2^{bipy})$]$(BF_4)_2$ (3). Under an inert atmosphere a suspension of 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (**2**) (500 mg, 1.73 mmol) in 50 mL acetonitrile was cooled to −35 °C and triethyloxonium tetrafluoroborate (660 mg, 3.47 mmol) was added. The mixture was stirred at room temperature over night. The resulting white solid was filtered off and evaporation of the filtrate under reduced pressure led to further precipitation of the product **3**. The entire solid was collected, washed with acetone and dried *in vacuo* over night. Further purification was achieved by recrystallisation from ethanol to yield 570 mg (64%) of the product as a white solid. M.p. 266 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.55 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3), 4.36 (q, $^3J_{HH}$ = 7.4 Hz, 4H, CH_2), 8.13–8.16 (m, 2H, H-4′), 8.15 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-5), 8.45 (t, $^3J_{HH}$ = 8.0 Hz, 2H, H-4), 8.76–8.78 (m, 2H, H-5′), 8.83 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-3), 10.29 (s, 2H, H-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 15.0 (CH_3), 45.1 (CH_2), 115.0 (C-5), 119.4 (C-5′), 121.9 (C-3), 123.3 (C-4′), 135.1 (C-2′), 142.0 (C-4), 146.2 (C-6), 153.0 (C-2); IR (KBr): ν = 3123 (m), 3083 (s), 2986 (w), 1604 (m), 1566 (s), 1538 (s), 1448 (s), 1223 (s), 1084 (vs), 807 (m) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{20}H_{22}N_6BF_4$: *m/z* 433.19296; found *m/z* (%) 433.19282 [M − BF_4]$^+$ (100); calcd for $C_{18}H_{17}N_6$: *m/z* 317.15092; found *m/z* (%) 317.15096 [M − 2BF_4 − C_2H_5]$^+$ (50); calcd for $C_{16}H_{13}N_6$: *m/z* 289.11962; found *m/z* (%) 289.11971 [M − 2BF_4 − C_4H_9]$^+$ (5). Elemental analysis calcd for $C_{20}H_{22}N_6B_2F_8$: C 46.19, H 4.26, N 16.16; found; C 46.06, H 4.30, N 16.17. Crystals suitable for X-ray analysis were obtained from a concentrated ethanol solution.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-methyl-1*H*-imidazolium) bistetrafluoroborate [$H_2(Me_2NHC_2^{bipy})$]$(BF_4)_2$ (4). Under an inert atmosphere a suspension of 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (**2**) (2.00 g, 6.94 mmol) in 70 mL acetonitrile was cooled to −35 °C and trimethyloxonium tetrafluoroborate (2.05 g, 13.9 mmol) were added. The mixture was stirred at room temperature for 24 hours. The resulting white solid was filtered off. Slow evaporation of the filtrate solvent under reduced pressure led to further precipitation of the product **4**. The combined residue was collected, washed with acetone and dried *in vacuo* over night. Further purification was achieved by recrystallisation from acetonitrile/ethanol (1:1) to obtain 3.28 g (95%) of the product as a white solid. M.p. 265 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 4.02 (s, 6H, CH$_3$), 8.01–8.04 (m, 2H, H-4′), 8.14 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-5), 8.45 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-4), 8.70–8.73 (m, 2H, H-5′), 8.82 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, H-3), 10.28 (s, 2H, H-2′); ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d$_6$, 25 °C): δ = 36.4 (CH$_3$), 114.9 (C-5), 119.1 (C-5′), 121.9 (C-3), 124.9 (C-4′), 135.9 (C-2′), 142.1 (C-4), 146.2 (C-6), 152.9 (C-2); IR (KBr): ν = 3128 (m), 3077 (s), 2965 (w), 1602 (m), 1565 (s), 1539 (s), 1447 (s), 1231 (s), 1084 (vs br), 806 (s) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{18}H_{18}N_6BF_4$: *m/z* 405.162211; found *m/z* 405.16170 [M – BF$_4$]$^+$; elemental analysis calcd for $C_{18}H_{18}N_6B_2F_8$: C 43.94, H 3.69, N 17.08; found C 43.73, H 3.70, N 17.04. Crystals suitable for X-ray analysis were obtained from a concentrated ethanol/acetonitrile solution.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-methyl-1*H*-imidazolium) diiodide $[H_2(Me_2NHC_2^{bipy})]I_2$ (5). Methyl iodide (0.3 mL, 0.6 g, 4 mmol) was added by a syringe to a suspension of 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (**2**) (500 mg, 1.73 mmol) in 20 mL DMSO under an inert atmosphere. The mixture was heated to 100 °C for 24 h. After the removal of the solvent under reduced pressure by distillation a pale brown residue was obtained. Further purification was achieved by a two-fold recrystallisation from a water/ethanol mixture. After cooling to room temperature the precipitated solid was collected by filtration, washed with acetone (2 × 10 mL) and dried *in vacuo* to yield 699 mg (70%) of the product as a white solid. M.p. 299 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 4.02 (s, 6H, CH$_3$), 8.02 (t, $^{3,4}J_{HH}$ = 1.7 Hz, 2H, H-4′), 8.16 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-5), 8.45 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-4), 8.73 (t, $^{3,4}J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.83 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-3), 10.31 (s br, 2H, H-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 36.5 (CH$_3$), 114.9 (C-5), 119.2 (C-5′), 121.9 (C-3), 124.9 (C-4′), 135.9 (C-2′), 142.1 (C-4), 146.2 (C-6), 152.9 (C-2); IR (KBr): ν = 3081 (m), 2962 (w), 1603 (m), 1566 (s), 1537 (s), 1445 (s), 1274 (s), 1090 (w), 1068 (m), 970 (s) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{18}H_{18}N_6I$: *m/z* 473.09451; found: *m/z* 473.09485 [M – I]$^+$; elemental analysis calcd. for $C_{18}H_{18}N_6I_2\cdot H_2O$: C 36.63, H 3.42, N 14.24; found C 36.33, H 3.51, N 14.04. Crystals suitable for X-ray analysis were obtained upon recrystallisation from boiling water.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-benzyl-1*H*-imidazolium) dichloride $[H_2(Bn_2NHC_2^{bipy})]Cl_2$ (6). Degassed benzyl chloride (0.40 mL, 0.40 g, 3.5 mmol) was added to a suspension of 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (**2**) (500 mg, 1.73 mmol) in 10 mL DMSO under an inert atmosphere. The mixture was heated to 100 °C for 15 h. After the removal of the solvent under reduced pressure by distillation an off-white residue was obtained which was washed three times with 50 mL of ethanol and dried in vacuum for 3 h. Further purification was achieved by recrystallisation from ethanol. After filtration and drying of the white precipitate *in vacuo* 0.89 g (95%) of the product were obtained. M.p. 287 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 5.62 (s, 4H, CH$_2$), 7.38–7.50 (m, 6H, *m*/*p*-Ph), 7.53–7.60 (m, 4H, *o*-Ph), 8.11 (s br, 2H, H-4′), 8.21 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, H-5), 8.44 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-4), 8.80 (s br, 2H, H-5′), 8.87 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-3), 10.70 (s, 2H, H-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 52.5 (CH$_2$), 115.1 (C-5), 120.0 (C-5′), 122.0 (C-3), 123.6 (C-4′), 128.4 (*o*-Ph), 128.9 (*p*–Ph), 129.0 (*m*-Ph), 134.5 (*i*-Ph), 135.6 (C-2′), 142.0 (C-4), 146.2 (C-6), 152.9 (C-2); IR (KBr): ν = 3027 (m), 2972 (m), 1602 (m), 1565 (m), 1530 (s), 1446 (s), 1222 (s), 1116 (m), 806 (s), 769 (m), 724 (m), 710 (m) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{23}H_{19}N_6$: *m/z* 379.16657; found *m/z* (%) 379.16672 [M – Cl – BnCl]$^+$ (100); calcd for $C_{30}H_{26}N_6Cl$: *m/z* 505.19020; found *m/z* (%) 505.19038 [M – Cl]$^+$ (33); elemental analysis calcd for $C_{30}H_{26}N_6Cl_2{*}H_2O$: C 64.40, H 5.04, N 15.02; found: C 64.55, H 4.92, N 15.33. Crystals suitable for X-ray analysis were obtained by recrystallisation of a DMSO solution.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-octyl-1*H*-imidazolium) ditoluenesulfonate $[H_2(Oct_2NHC_2^{bipy})](OTs)_2$ (7). A 50 mL round-bottom flask was charged with 6,6′-di-1*H*-imidazol-1-yl-2,2′-bipyridine (**2**) (207 mg, 0.720 mmol), octyl toluenesulfonate (614 mg, 2.16 mmol) and 25 mL of abs. acetonitrile. The mixture was stirred under reflux for 2 d. Upon cooling down the reaction solution, a solid precipitated, which was filtered, washed with acetone and dried *in vacuo* for 6 h. After recrystallisation from ethanol and DMSO/water a white solid was obtained which was dried in vacuum over night to yield 155 mg (25%) of the product. M.p. 242 °C; ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ = 0.85 (t, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH$_3$), 1.20–1.40 (m, 20H, CH$_2$), 1.88–1.95 (m, 4H, CH$_2$), 2.27 (s, 6H, CH$_3$-OTs), 4.32 (t, $^{3}J_{HH}$ = 7.3 Hz, 4H, NCH$_2$), 7.09 (d, $^{3}J_{HH}$ = 7.9 Hz, 4H, *o*–OTs), 7.46 (d, $^{3}J_{HH}$ = 7.9 Hz, 4H, *m*-OTs), 8.12 (t, $^{3,4}J_{HH}$ = 1.8 Hz, 2H, H-4′), 8.16 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-5), 8.44 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-4), 8.77 (t, $^{3,4}J_{HH}$ = 1.8 Hz, 2H, H-5′), 8.84 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-3), 10.33 (s br, 2H, H-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 13.9 (CH$_3$), 20.7 (CH$_3$-OTs), 22.0 (CH$_2$), 25.5 (CH$_2$), 28.4 (CH$_2$), 28.5 (CH$_2$), 29.2 (CH$_2$), 31.1 (CH$_2$), 49.2 (NCH$_2$), 115.0 (C-5), 119.4 (C-5′), 121.9 (C-3), 123.6 (C-4′), 125.4 (*o*-OTs), 128.0 (*m*-OTs), 135.3 (C-2′), 137.5 (*p*-OTs), 142.0 (C-4), 145.8 (*i*-OTs), 146.2 (C-6), 152.9 (C-2); IR (KBr): ν = 3090 (m), 2957 (m), 2925 (s), 2855 (m), 1601 (m), 1565 (m), 1538 (m), 1469 (s), 1222 (vs), 1195 (vs), 1125 (s), 1070 (m), 1035 (s), 1012 (s), 816 (m), 800 (m), 681 (m), 567 (m) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{39}H_{53}N_6O_3S$: *m/z* 685.38944; found *m/z* (%) 685.38927 [M – OTs]$^+$ (100); calcd for $C_{24}H_{29}N_6$: *m/z* 401.24482; found *m/z* (%) 401.24487 [M – OTs – OctOTs]$^+$ (38); elemental analysis calcd for $C_{46}H_{60}N_6O_6S_2\cdot 0.3DMSO$: C 63.56, H 7.07, N 9.54; found: C 63.55, H 7.05, N 9.48.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-ethyl-1,3-dihydro-2*H*-imidazol-2-ylidene) $(Et_2NHC_2^{bipy})$ (8). $[H_2(Et_2NHC_2^{bipy})](BF_4)_2$ **3** (200 mg, 0.385 mmol) was suspended in 30 mL of toluene under an argon atmosphere and cooled to −35 °C. KO*t*-Bu (104 mg, 0.923 mmol) was added and the mixture was stirred at room temperature for 6 h. The yellow suspension was filtered by a syringe filter and the solvent evaporated *in vacuo*. The crude product was subsequently washed three times with 3 mL of pentane before it was dried in vacuum over night to yield 86.1 mg (65%) of the product as an off-white solid. M.p. 202 °C (dec.); ^{1}H NMR (300 MHz, thf-d$_8$): δ = 1.46 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH$_3$), 4.15 (q, $^{3}J_{HH}$ = 7.2 Hz, 4H, CH$_2$), 7.17 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, H-4′), 7.91 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H, H-4), 8.22 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H, H-5′), 8.40 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 0.9 Hz, 2H, H-3), 8.43 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, H-5); ^{13}C{^{1}H} NMR (75 MHz, thf-d$_8$): δ = 17.0 (CH$_3$), 46.8 (CH$_2$), 114.8 (C-5), 116.7 (C-5′), 118.4 (C-3), 119.9 (C-4′), 139.5 (C-4), 154.3 (C-2), 154.6 (C-6), 216.9 (C-2′); IR (KBr): ν = 3083 (w br), 2972 (m), 2934 (w), 2851 (w), 1679 (s), 1573 (vs), 1501 (m), 1443 (vs), 1261 (m), 1153 (w), 1109 (m), 1077 (m), 1015 (w), 808 (m), 792 (m) cm^{-1}; HR-MS (EI$^+$) calcd for $C_{20}H_{20}N_6$: *m/z* 344.17409 (%); found: *m/z* 344.1753 [M]$^+$ (100); calcd for $C_{18}H_{15}N_6$: *m/z* 315.13518 (%); found: *m/z* 315.1379 [M – Et]$^+$ (15); calcd for $C_{16}H_{12}N_6$: *m/z* 288.11183 (%); found *m/z* 288.125 [M – C_4H_8]$^+$ (65). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a tetrahydrofuran solution.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-methyl-1,3-dihydro-2*H*-imidazol-2-ylidene) ($Me_2NHC_2{}^{bipy}$) (9). [$H_2(Me_2NHC_2{}^{bipy})$]$(BF_4)_2$ **4** (200 mg, 0.406 mmol) was suspended in 30 mL of toluene under an argon atmosphere and cooled to –35 °C. KO*t*-Bu (109 mg, 0.976 mmol) was added and the mixture was stirred at room temperature for 5 h. The yellow suspension was filtered by a syringe filter and the solvent evaporated *in vacuo*. The crude product was subsequently washed three times with 3 mL of pentane before it was dried in vacuum for 19 h to yield 54.1 mg (42%) of the product as a yellow solid. M.p. 265 °C (dec.); ^{1}H NMR (300 MHz, thf-d_8): δ = 3.82 (s, 6H, CH_3), 7.12 (d, $^3J_{HH}$ = 1.8 Hz, 2H, H-4′), 7.92 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H-4), 8.22 (d, $^3J_{HH}$ = 1.8 Hz, 2H, H-5′), 8.39 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, H-3), 8.42 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, H-5) ^{13}C{^{1}H} NMR (75 MHz, thf-d_8): δ = 38.5 (CH_3), 115.1 (C-5), 117.0 (C-5′), 118.6 (C-3), 121.7 (C-4′), 139.8 (C-4), 154.3 (C-2), 154.7 (C-6), 217.4 (C-2′). IR (KBr): ν = 3094 (w br), 2963 (w), 2925 (w), 2852 (w), 1680 (s), 1573 (vs), 1447 (vs), 1427 (w), 1261 (m), 1153 (w), 1103 (m), 1015 (w), 808 (m), 738 (w) cm^{-1}; HR-MS (FAB$^+$) calcd for $C_{18}H_{17}N_6$: *m/z* 317.1512; found: *m/z* 317.1460 [M + H]$^+$.

Synthesis of 1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-benzyl-1,3-dihydro-2*H*-imidazol-2-ylidene) ($Bn_2NHC_2{}^{bipy}$) (10) as NMR experiment. Under nitrogen atmosphere [$H_2(Bn_2NHC_2{}^{bipy})$]Cl_2 **6** (20.0 mg, 36.9 μmol) was suspended in 0.5 mL of thf-d_8 and cooled to –35 °C. KO*t*-Bu (9.9 mg, 89 μmol) was added in one portion. After 6 h at room temperature no further deprotonation reaction could be monitored by ^{1}H nmr spectroscopy. ^{1}H NMR (500 MHz, thf-d_8): δ = 5.34 (s, 4H, CH_2), 7.08 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 7.22–7.26 (m, 2H, *p*-Ph), 7.33–7.34 (m, 4H, *m*-Ph), 7.35–7.36 (m, 4H, *o*-Ph), 7.94 (br t, $^3J_{HH}$ = 7.8 Hz, 2H, H-4), 8.25 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.42 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, H-3), 8.50 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.7 Hz, 2H, H-5), spectrum contains free *t*-BuOH: 1.15 (s, $C(CH_3)_3$), 3.41 (s, OH); ^{13}C{^{1}H} NMR (125 MHz, thf-d_8): δ = 56.0 (CH_2), 115.3 (C-5), 117.8 (C-5′), 118.9 (C-3), 120.9 (C-4′), 128.5 (*p*-Ph), 128.7 (*o*-Ph), 129.4 (*m*-Ph), 139.7 (*i*-Ph), 140.0 (C-4), 154.5 (C-2), 154.9 (C-6), 217.5 (C-2′), spectrum contains free *t*-BuOH: 31.9 ($C(CH_3)_3$), 67.8 ($C(CH_3)_3$); HR-MS (FAB$^+$) calcd for $C_{30}H_{25}N_6$: *m/z* 469.21300; found: *m/z* 469.2119 [M + H]$^+$.

Synthesis of [1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-ethyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ^{2}C^2)disilver(I)] ditetrafluoroborate [$Ag_2(Et_2NHC_2{}^{bipy})$]$(BF_4)_2$ (11). A Schlenk tube was charged under glovebox atmosphere with [$H_2(Et_2NHC_2{}^{bipy})$]$(BF_4)_2$ **3** (200 mg, 0.769 mmol), Ag_2O (98.0 mg, 0.846 mmol) and 10 mL of acetonitrile. The mixture was refluxed under stirring for 40 h. Reaction control was carried out by ^{1}H NMR spectroscopy in CD_3CN of a small probe and if necessary further Ag_2O was added. After complete conversion of **3** the solid was filtered off by a Whatman® syringe filter. The solvent was evaporated in vacuum and dried for 12 h to yield 238 mg (84%) of **11** as a light brown solid. M.p. 185 °C (dec.); ^{1}H NMR (500 MHz, CD_3CN): δ = 1.16 (t, $^3J_{HH}$ = 7.3 Hz, 6H, CH_3), 3.95 (q, $^3J_{HH}$ = 7.3 Hz, 4H, CH_2), 7.32 (d, $^3J_{HH}$ = 1.9 Hz, 2H, H-4′), 7.53 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-5), 7.65 (d, $^3J_{HH}$ = 1.9 Hz, 2H, H-5′), 7.94 (t, $^3J_{HH}$ = 8.1 Hz, 2H, H-4), 8.12 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-3); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.02 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.68 (d, $^3J_{HH}$ = 1.9 Hz, 2H, H-4′), 7.72 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H-5), 7.93 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H-4), 8.09 (d, $^3J_{HH}$ = 1.9 Hz, 2H, H-5′), 8.15 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H-3); ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ = 17.0 (CH_3), 48.5 (CH_2), 118.2 (C-5), 121.2 (C-5′), 123.7 (C-3/4′), 142.7 (C-4), 151.1 (C-6), 152.7 (C-2), 182.0 (C-2′); ^{13}C{^{1}H}.

NMR (75.47 MHz, DMSO-d_6): δ = 16.5 (CH_3), 47.0 (CH_2), 116.2 (C-5), 120.1 (C-5′), 121.6 (C-3), 122.9 (C-4′), 141.2 (C-4), 149.5 (C-6), 151.4 (C-2), 180.9 (C-2′); ^{109}Ag{^{1}H} NMR (23.27 MHz, DMSO-d_6): δ = 270.1; IR (KBr): ν = 3171 (w br), 3094 (w), 2981 (w br), 2919 (m), 1850 (w), 1658 (w), 1598 (s), 1573 (s), 1479 (s), 1463 (s), 1442 (vs), 1281 (m), 1262 (m), 1084 (vs br), 794 (s), 730 (m) cm^{-1}; HR-MS (FAB$^+$) calcd for $C_{20}H_{20}N_6Ag$: *m/z* 453.07949; found: *m/z* 453.0821 [M – AgB_2F_8]$^+$; HR-MS (ESI$^+$): calcd for $C_{20}H_{20}N_6Ag$: *m/z* 453.07949; found: *m/z* 453.07973 [M – AgB_2F_8]$^+$; elemental analysis calcd for $C_{20}H_{20}N_6Ag_2B_2F_8\cdot 0.5CH_3CN$: C 33.44, H 2.87, N 12.07; found: C 33.29, H 3.18, N 12.25.

Synthesis of [1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-ethyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ^2*C*,*C′*)disilver(I)]bistetrafluoroborate [$Ag_2(Et_2NHC_2{}^{bipy})$]$(BF_4)_2$ (11) with Ag_2CO_3 as NMR experiment. A Young® NMR tube was charged with [$H_2(Et_2NHC_2{}^{bipy})$]$(BF_4)_2$ **3** (15.0 mg, 28.8 μmol), Ag_2CO_3 (9.6 mg, 34 μmol) and 0.5 mL of DMSO-d_6 in glovebox atmosphere. The NMR tube was heated at 120 °C for 43 h. The reaction progress was monitored by ^{1}H NMR spectroscopy with a product:substrate ratio of 93:7).

^{1}H-NMR (250.13 MHz, 25 °C, DMSO-d_6): identical to spectrum of **11** prepared from Ag_2O (*vide supra*).

Synthesis of [L-2]-[1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ^2*C*,*C′*) silver(I)] tetrafluoroborate [$Ag(Me_2NHC_2{}^{bipy})$](BF_4) (12). A Schlenk tube was charged with [$H_2(Me_2NHC_2{}^{bipy})$]$(BF_4)_2$ **4** (200 mg, 0.407 mmol), Ag_2O (104 mg, 0.447 mmol) and 5 mL of acetonitrile under glovebox atmosphere. The mixture was refluxed for 35 h. Reaction control was carried out by ^{1}H NMR spectroscopy in CD_3CN of a small sample and if necessary further Ag_2O was added. After complete conversion of **3** the solid was filtered off over Celite®. The solvent was evaporated *in vacuo* and dried for 12 h to yield 132 mg (63%) of **12** as an off-white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.37 (s br, 6H, CH_3), 7.50 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-4′), 7.77 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H-5), 8.01 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H-4), 8.08 (d, $^3J_{HH}$ = 1.7 Hz, 2H, H-5′), 8.53 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H-3); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ = 38.9 (CH_3), 113.6 (C-5), 118.9 (C-5′), 120.6 (C-3), 123.5 (C-4′), 140.6 (C-4), 149.0 (C-6), 153.0 (C-2), 183.5 (C-2′); IR (KBr): ν = 3124 (w), 3094 (m), 2952 (w br), 2920 (m), 1599 (s), 1573 (s), 1481 (s), 1463 (s), 1442 (s), 1400 (m), 1348 (w), 1283 (m), 1239 (m), 1084 (vs br), 796 (m), 740 (m) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{18}H_{16}N_6{}^{107}Ag$: *m/z* 423.04819; found: *m/z* 423.04823 [M – BF_4]$^+$, calcd for $C_{36}H_{32}N_{12}{}^{107}Ag_2BF_4$: *m/z* 933.09984; found: *m/z* 933.09968 [2M – BF_4]$^+$; elemental analysis calcd for $C_{18}H_{16}N_6AgBF_4\cdot 0.20Ag_2O$: C 38.79; H 2.89, N 15.08; found: C 38.61, H 3.07, N 14.88. Crystals suitable for

X-ray analysis were obtained by slow evaporation of an acetonitrile solution.

Synthesis of [L-2]-[1,1′-(2,2′-bipyridin-6,6′-diyl)bis(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ²*C*,*C*′) silver(I)] (μ₂-iodo)bis(μ₂-iodo)-diargentate [Ag(Me$_2$NHC$_2$$^{\text{bipy}}$)][Ag$_2I_3$] (13) as NMR experiment. A Young® NMR tube was charged with [H$_2$(Me$_2$NHC$_2$$^{\text{bipy}}$)]I$_2$ **5** (20.0 mg, 35.0 μmol), Ag$_2$O (26.2 mg, 113 μmol) and 0.5 mL DMSO-d$_6$ under glovebox atmosphere. The NMR tube was heated at 120 °C for 3 d. Reaction control was carried out by ^{1}H NMR spectroscopy. ^{1}H NMR (300.13 MHz, DMSO-d$_6$, 100 °C): δ = 3.91 (s br, 6H, CH$_3$), 7.60 (s br, 2H, H-4′), 7.83 (d, ^3J(HH) = 8.1 Hz, 2H, H-5), 8.06–8.12 (m, 2H, H-3/4), 8.28 (s br, 2H, H-5′), the low solubility causes a poor resolution; ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d$_6$, 100 °C): δ = 38.8 (CH$_3$), 112.0 (C-5), 118.0 (C-5′), 118.8 (C-3), 119.4 (C-4′), 123.7 (C-4), 140.5 (C-6), 148.6 (C-2), 184.4 (C-2′); HR-MS (FAB$^+$) calcd for $C_{18}H_{16}N_6Ag$: calc. *m*/*z* 423.04819; found *m*/*z* 423.0522 [M − Ag$_2$I$_3$]$^+$. Crystals suitable for X-ray analysis were obtained by recrystallisation from boiling DMSO.

Synthesis of [L-2]-dichloro[μ-(2,2′bipyridin-6,6-diyl)bis(3-benzyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-1κ*C*:2κ*C*′)] disilver(I) [Ag$_2$Cl$_2$(μ-Bn$_2$NHC$_2$$^{\text{bipy}}$)] (14). A Schlenk tube was charged under glovebox atmosphere with [H$_2$(Bn$_2$NHC$_2$$^{\text{bipy}}$)]Cl$_2$ **6** (300 mg, 0.554 mmol), Ag$_2$O (167 mg, 0.720 mmol) and 8 mL of DMSO. The mixture was stirred at 85 °C for 4 d. After complete conversion the product solution was filtered at 90 °C over a Whatman® filter and the residue was extracted four times with 4 mL of DMSO. The solvent was removed under reduced pressure by distillation. The resulting brown solid was washed with acetonitrile and dried *in vacuo* over night. Further purification was achieved by recrystallisation from DMSO to yield 298 mg (71%) of the product as a light brown solid. M.p. 261 °C (dec.); ^{1}H NMR (600 MHz, DMSO-d$_6$, 67 °C): δ = 5.47 (s, 4H, CH$_2$), 7.29–7.37 (m, 10H, *o*/*m*/*p*-Ph), 7.50–8.50 (m, 6H, H-3/4/5), 7.78 (s br, 2H, H-4′), 8.28 (s br, 4H, H-5′); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d$_6$, 67 °C): δ = 55.5 (CH$_2$), 120.2 (C-5′), 123.4 (C-4′), 127.1 (*o*-Ph), 127.7 (*p*-Ph), 128.4 (*m*-Ph), 137.2 (*i*-Ph), 183.7 (C-2′), signals for C-2/3/4/5/6 are not observed; IR (KBr): ν = 3161 (w), 3122 (w), 3093 (w), 3028 (w), 2924 (w), 1594 (m), 1565 (s), 1442 (vs), 1412 (m), 1356 (m), 1281 (m) 1244 (m), 1082 (s), 1028 (s), 800 (s), 732 (s) cm^{-1}; MS (LIFDI): *m*/*z* (%) = 575.2 [M(^{107}Ag)]$^+$; 577.2 [M(^{109}Ag)]$^+$; MS (ESI$^+$): *m*/*z* (%) = 577.3 [M$^+$] (100); 485.3 [M$^+$ − Bn] (7); 379.4 [M$^+$ − Bn − Ag] (10), contains unidentified products at *m*/*z* = 361.3, 179.4; elemental analysis calcd for $C_{30}H_{24}N_6Ag_2Cl_2{\cdot}2H_2O$: C 45.54, H 3.57, N 10.62; found: C 45.35, H 3.17, N 10.48; Crystals suitable for X-ray analysis were obtained by recrystallisation from boiling DMSO.

[SP-4-3]-[1,1′-(2,2′-bipyridin-6,6′-diyl-κ²*N*,*N*′)bis(3-ethyl-1H-imidazol-1-yl-2(3*H*)-ylidene-κ²*C*,*C*′)palladium(II)]ditetrafluoroborate [Pd(Et$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$)$_2$ (15). A solution of [Ag$_2$(Et$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$)$_2$ **11** (100 mg, 136 μmol) in 5 mL of acetonitrile was cooled to −35 °C. [PdCl$_2$(COD)] (38.9 mg, 136 μmol) was added. Immediately a large amount of grey solid precipitated. The mixture was kept under nitrogen atmosphere at rt for 16 h without stirring. The solution was decanted and filtered over Celite®. The residue was extracted with 5 mL of acetonitrile. Evaporation of the solvent *in vacuo* yielded **15** as a pale brown solid which was dried *in vacuo* for 24 h. The crude product was dissolved in 5 mL of acetonitrile and the addition of 2 mL of thf and pentane causing a white precipitate to form. After 24 h without stirring, the residue was filtered, washed with pentane and dried *in vacuo* over night to yield 161 mg (72%) of the product as a colourless solid. M.p. 225 °C (dec.); ^{1}H NMR (300 MHz, CD$_3$CN): δ = 1.57 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 6H, CH$_3$), 4.38 (q, $^3J_{\text{HH}}$ = 7.3 Hz, 4H, CH$_2$), 7.49 (d, $^3J_{\text{HH}}$ = 2.3 Hz, 2H, H-4′), 7.93 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-5), 7.99 (d, $^3J_{\text{HH}}$ = 2.3 Hz, 2H, H-5′), 8.10 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-3), 8.45 (t, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-4); ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.54 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 6H, CH$_3$), 4.38 (q, $^3J_{\text{HH}}$ = 7.3 Hz, 4H, CH$_2$), 7.94 (d, $^3J_{\text{HH}}$ = 2.2 Hz, 2H, H-5′), 8.30 (d, $^3J_{\text{HH}}$ = 8.3 Hz, 2H, H-5), 8.45 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 2H, H-3), 8.57 (d, $^3J_{\text{HH}}$ = 2.2 Hz, 2H, H-4′), 8.65 (t, $^3J_{\text{HH}}$ = 8.3 Hz, 2H, H-4); ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN): δ = 17.0 (CH$_3$), 48.5 (CH$_2$), 115.5 (C-5), 120.8 (C-5′), 122.6 (C-3), 124.2 (C-4′), 147.4 (C-4), 152.6 (C-6), 156.1 (C-2), 163.1 (C-2′); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 16.1 (CH$_3$), 46.3 (CH$_2$), 114.2 (C-5), 119.9 (C-5′), 121.3 (C-3), 123.2 (C-4′), 146.1 (C-4), 150.8 (C-6), 154.4 (C-2), 161.0 (C-2′); IR (KBr): ν = 3169 (w), 3139 (w), 3116 (w), 3078 (w), 2986 (w br), 1658 (w), 1607 (m), 1580 (m), 1502 (s), 1477 (m), 1454 (m), 1346 (m), 1282 (m), 1225 (w), 1195 (w), 1084 (vs), 809 (m), 730 (m) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{20}H_{20}N_6PdBF_4$: *m*/*z* 537.08080; found: *m*/*z* 537.08113 [M − BF$_4$]$^+$; calcd for $\frac{1}{2}$($C_{20}H_{20}N_6Pd$): *m*/*z* 225.03867; found: *m*/*z* 225.03865, [M − 2BF$_4$]$^{2+}$; HR-MS (FAB$^+$) calcd for $C_{20}H_{20}N_6PdBF_4$: *m*/*z* 537.08080; found: *m*/*z* 537.0892 [M − BF$_4$]$^+$; elemental analysis calcd for $C_{20}H_{20}N_6PdB_2F_8{\cdot}0.5H_2O$: C 37.92, H 3.41, N 13.27; found: C 37.98, H 3.42, N 13.19; Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated acetonitrile solution.

Synthesis of [SP-4-3]-[1,1′-(2,2′-bipyridin-6,6′-diyl-κ²*N*,*N*′)-bis(3-ethyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ²*C*,*C*′)palladium(II)] ditetrafluoroborate [Pd(Et$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$)$_2$ (15) with Pd(OAc)$_2$ as NMR experiment. A Young® NMR tube was charged under glovebox atmosphere with [H$_2$(Et$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$)$_2$ **3** (10.0 mg, 28.8 μmol), palladium(II) acetate (6.5 mg, 29 μmol) and 0.5 mL of DMSO-d$_6$. The NMR tube was heated at 80 °C for 48 h. Reaction control was carried out by ^{1}H NMR spectroscopy.

Yield: product:substrate 2:1 (by ^{1}H NMR).

^{1}H-NMR (250.13 MHz, 25 °C, DMSO-d$_6$): identical to spectrum of **15** prepared by transmetallation (*vide supra*).

HR-MS (ESI$^+$) calcd for $C_{20}H_{20}N_6PdBF_4$: *m*/*z* 537.08080; found *m*/*z* 537.08113 [M − BF$_4$]$^+$.

Synthesis of [1,1′-(2,2′-bipyridin-6,6′-diyl-κ²*N*,*N*′)bis(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-κ²*C*,*C*′)palladium(II)] ditetrafluoroborate [Pd(Me$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$)$_2$ (16). A solution of [Ag(Me$_2$NHC$_2$$^{\text{bipy}}$)](BF$_4$) **12** (100 mg, 142 μmol) in 4 mL of acetonitrile was cooled to −35 °C. [PdCl$_2$(CH$_3$CN)$_2$] (36.8 mg, 142 μmol) was added. Immediately a large amount of grey solid precipitated. The mixture was kept under nitrogen atmosphere at rt for 16 h without stirring. The solution was decanted and after evaporation of the solvent the product was obtained as a pale brown solid which was dried *in vacuo* for 24 h.

^{1}H NMR (300.13 MHz, DMSO-d$_6$): δ = 4.15 (s, 6H, CH$_3$), 7.78 (d, $^3J_{\text{HH}}$ = 1.6 Hz, 2H, H-4′), 8.28 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-5), 8.42 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-3), 8.48 (d, $^3J_{\text{HH}}$ = 1.6 Hz, 2H, H-5′), 8.62 (t, $^3J_{\text{HH}}$ = 8.1 Hz, 2H, H-4), the spectrum contains impurities;

Table 3 Crystal data and structure refinement details for **3**, **4**, **5**, **6** and **8**[a]

	3	**4**[b]	**5**	**6**	**8**
empirical formula	$C_{24}H_{28}B_2F_8N_8$	$C_{18}H_{18}B_2F_8N_6$	$C_{18}H_{20}I_2N_6O$	$C_{34}H_{38}C_{12}N_6O_2$	$C_{20}H_{20}N_6$
formula weight	602.16	492.00	590.20	633.60	344.42
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$
Z	2	4	4	2	4
unit cell dimensions					
a (Å), α (°)	6.6257(14), 90.0	10.8786(3), 90,0	17.6632(3), 90.0	10.4027(1), 90.0	17.950(2), 90.0
b (Å), β (°)	18.518(4), 90.122(5)	16.5990(4), 108.443(1)	9.5519(1), 99.129(1)	11.8996(2), 96.115(1)	10.4863(13), 90.672(3)
c (Å), γ (°)	11.731(3), 90.0	12.5729(4), 90.0	12.7633(2), 90.0	13.3902(1), 90.0	9.6501(12), 90.0
volume (Å^3)	1439.3(5)	2153.73(10)	2126.11(5)	1648.11(3)	1816.3(4)
density (calculated) (g cm^{-3})	1.39	1.517	1.84	1.28	1.26
absorption coefficient (mm^{-1})	0.12	0.141	2.98	0.24	0.08
crystal colour	colourless	colourless	colourless	colourless	colourless
crystal shape	polyhedron	needle	polyhedron	polyhedron	polyhedron
theta range for data collection (°)	1.1 to 24.2	1.97 to 22.12	2.3 to 27.4	2.3 to 27.5	2.3 to 28.3
index ranges	$-7 \le h \le 7$	$-11 \le h \le 11$	$-22 \le h \le 22$	$-13 \le h \le 13$	$-23 \le h \le 23$
	$-21 \le k \le 21$	$-17 \le k \le 17$	$-12 \le k \le 12$	$-15 \le k \le 15$	$-13 \le k \le 13$
	$-13 \le l \le 13$	$-13 \le l \le 13$	$-16 \le l \le 16$	$-17 \le l \le 17$	$-12 \le l \le 12$
reflections collected	10543	12779	10465	15837	18460
independent reflections	2306	2668	2429	3780	4498
	(R(int) = 0.0299)	(R(int) = 0.0581)	(R(int) = 0.0588)	(R(int) = 0.0321)	(R(int) = 0.0395)
observed reflections	1941 ($I > 2\sigma(I)$	1979 ($I > 2\sigma(I)$	1973 ($I > 2\sigma(I)$	3212 ($I > 2\sigma(I)$	3274 ($I > 2\sigma(I)$
max, min transmission	0.99 and 0.94	0.99 and 0.94	0.84 and 0.61	0.95 and 0.91	1.00 and 0.97
data/restraints/params	2306/94/213	2668/436/402	2429/0/128	3780/0/213	4498/0/237
goodness-of-fit on F^2	1.05	1.05	1.05	1.05	1.03
final R indices ($I > 2\sigma(I)$)	$R_1 = 0.067$, w$R_2 = 0.178$	$R_1 = 0.046$, w$R_2 = 0.106$	$R_1 = 0.029$, w$R_2 = 0.062$	$R_1 = 0.042$, w$R_2 = 0.109$	$R_1 = 0.048$, w$R_2 = 0.118$
largest diff peak, hole (e Å^{-3})	0.36 and –0.31	0.18 and –0.18	0.57 and –0.79	0.57 and –0.26	0.26 and –0.18

[a] In all cases: refinement method was full-matrix least-squares on F^2. [b] The low theta$_{max}$ value is due to the low resolution of the experiment and the poor data/parameter value is a direct consequence thereof. Local symmetry restraints and rigid bond restraints were applied to the BF_4^- moiety.

Table 4 Crystal data and structure refinement details for **12**, **13**, **14**, **15**, **17** and **18**[a]

	12[b]	**13**[c]	**14**[d]	**15**[e]	**17**	**18**[f]
empirical formula	$C_{20}H_{19}AgBF_4N_7$	$C_{20}H_{22}Ag_3I_3N_6OS$	$C_{30}H_{24}Ag_2Cl_2N_6$	$C_{20}H_{20}B_2F_8N_6Pd$	$C_{21}H_{30}Cl_2N_3O_3PdS_3$	$C_{22}H_{23}BCuF_4N$
formula weight	552.10	1098.81	755.19	624.44	645.96	535.82
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	*Pmma*	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2/c$
Z	4	2	4	2	2	4
unit cell dimensions						
a (Å), α (°)	12.7785(3), 90.0	6.7715(4), 90.0	27.896(7), 90.0	6.0175(5), 99.511(1)	9.8168(10), 67.107(2)	23.200(2), 90.0
b (Å), β (°)	25.2891(6), 105.638(1)	15.2581(5), 90.0	9.701(2), 113.895(4)	10.1458(8), 98.775(1)	12.4495(12), 80.082(2)	8.9069(8), 107.756(2)
c (Å), γ (°)	6.9458(2), 90.0	14.6406(7), 90.0	11.654(3), 90.0	19.3685(14), 99.397(1)	12.8901(13), 69.636(2)	24.425(2), 90.0
volume (Å^3)	2161.50(10)	1512.67(13)	2883.4(12)	1130.83(15)	1359.3(2)	4806.7(8)
density (calculated) (g cm^{-3})	1.70	2.41	1.74	1.83	1.58	1.48
absorption coefficient (mm^{-1})	0.99	5.08	1.58	0.91	1.14	0.96
crystal colour	pale yellow	colourless	colourless	colourless	yellow	red
crystal shape	needle	polyhedron	polyhedron	polyhedron	polyhedron	polyhedron
theta range for data collection (°)	1.6 to 27.5	1.9 to 20.9	1.6 to 28.3	2.1 to 28.3	1.9 to 28.3	1.8 to 25.1
index ranges	$-16 \leq h \leq 16$ $-32 \leq k \leq 32$ $-8 \leq l \leq 9$	$-5 \leq h \leq 6$ $-15 \leq k \leq 15$ $-11 \leq l \leq 14$	$-37 \leq h \leq 37$ $-12 \leq k \leq 10$ $-10 \leq l \leq 15$	$-8 \leq h \leq 8$, $-13 \leq k \leq 13$ $-25 \leq l \leq 25$	$-13 \leq h \leq 13$ $-16 \leq k \leq 16$ $-17 \leq l \leq 17$	$-27 \leq h \leq 27$ $-10 \leq k \leq 10$ $-28 \leq l \leq 29$
reflections collected	22162	3768	9643	11901	14408	38103
independent reflections	4938 (R(int) = 0.1793)	928 (R(int) = 0.1007)	3553 (R(int) = 0.0762)	5562 (R(int) = 0.0191)	6706 (R(int) = 0.0288)	8522 (R(int) = 0.0747)
observed reflections	3200 ($I > 2\sigma(I)$)	596 ($I > 2\sigma(I)$)	2521 ($I > 2\sigma(I)$)	5341 ($I > 2\sigma(I)$)	5909 ($I > 2\sigma(I)$)	6414 ($I > 2\sigma(I)$)
max, min transmission	0.97 and 0.61	0.95 and 0.35	0.97 and 0.64	0.88 and 0.76	0.90 and 0.87	0.94 and 0.83
data/restraints/params	4938/0/301	928/0/65	3553/0/182	5562/219/353	6706/0/309	8522/423/695
goodness-of-fit on F^2	1.10	1.06	1.37	1.07	1.11	1.20
final R indices ($I > 2\sigma(I)$)	$R_1 = 0.068$, w$R_2 = 0.142$	$R_1 = 0.088$, w$R_2 = 0.230$	$R_1 = 0.139$, w$R_2 = 0.268$	$R_1 = 0.025$, w$R_2 = 0.064$	$R_1 = 0.040$, w$R_2 = 0.085$	$R_1 = 0.090$, w$R_2 = 0.164$
largest diff peak, hole (e Å^{-3})	1.08 and −1.84	1.72 and −1.24	1.62 and −1.12	0.52 and −0.54	0.57 and −0.46	0.69 and-0.81

[a] in all cases: refinement method was full-matrix least-squares on F^2. [b] The diffracting intensities for this crystal were very weak, especially at higher theta. Improving the R_{int} by cutting the dataset at a lower resolution was not performed in order to get a higher data/parameter ratio and therefore more reliable results. [c] The quality of the this structure determination result is definitely poor, however it is a clean proof of the constitution. [d] All available crystal were twinned. Split reflections were integrated as composed intensities and splitted mathematically. A twin fraction of 6% is found which is the main reason for the low precision, the anomalous weighting scheme and the high R values. [e] All restraints used are local symmetry restraints for the model of two orientations of the BF_4^- anion. [f] All restraints used are local symmetry restraints for the disordered BF_4^- anions and "similar bond and angles restraints" for the separated ethyl groups.

$^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): $\delta = 40.3$ (CH_3), 114.5 (C-5), 119.5 (C-5′), 121.6 (C-3), 125.4 (C-4′), 146.3 (C-4), 151.1 (C-6), 154.7 (C-2), 162.5 (C-2′), spectrum contains impurities; MS (ESI$^+$): *m*/*z* (%) = 509.2 $[M - BF_4]^+$ (100); 687.0 $[M - BF_4 + PdCl_2]^+$ (25); 1103.1 $[2M - BF_4]^+$ (18).

Synthesis of [SP-4-3]-tetrachloro[μ-(2,2′-bipyridin-6,6-diyl)-bis(3-benzyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-1κ*C*:2κ*C*′)]-bis-[(sulfinyl-κ*S*)bis(methan)] dipalladium(II) $[Pd_2Cl_4(\mu\text{-}Bn_2NHC_2^{bipy})(DMSO)_2]$ (17) as NMR experiment. A Young® NMR tube was charged with $[Ag_2Cl_2(\mu\text{-}Bn_2NHC_2^{bipy})]$ **14** (15.0 mg, 19.9 μmol), $[PdCl_2(CH_3CN)_2]$ (10.3 mg, 39.7 μmol) and 0.5 mL of CD_3CN under glovebox atmosphere. A lot of grey solid precipitated. As the reaction progress could not be monitored by ^1H NMR spectroscopy in CD_3CN, the solvent was evaporated *in vacuo*. The residue was subsequently suspended in 0.5 mL of DMSO-d_6. After four weeks at room temperature big yellow crystals had grown out of the suspension. ^1H NMR (300 MHz, DMSO-d_6, 100 °C): $\delta = 5.89$ (m, CH_2), 7.30–7.47 (m, *m*/*p*-Ph), 7.54–7.62 (m, *o*-Ph), 8.07–8.17 (m), 8.26–8.41 (m), poor solubility causes bad resolution. Crystals suitable for X-ray analysis were obtained from the DMSO-d_6 suspension at rt.

Synthesis of [T-4]-[bis-(μ-1,1′-(2,2′-bipyridin-6,6-diyl-1κ*N*:2κ*N*′)bis(3-ethyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene-1κ*C*:2κ*C*′) di-copper(I)]-ditetrafluoroborate $[Cu_2(\mu\text{-}Et_2NHC_2^{bipy})_2](BF_4)_2$ (18). A solution of $[Ag_2(Et_2NHC_2^{bipy})](BF_4)_2$ **11** (100 mg, 136 μmol) in 5 mL of acetonitrile were cooled to −35 °C. Copper(I)-chloride (27.0 mg, 273 μmol) was added. Immediately a large amount of grey solid precipitated. The mixture was kept under nitrogen atmosphere at rt for 16 h without stirring. The solution was decanted and filtered over Celite®. The Celite® pad was extracted with an additional 5 mL of acetonitrile. The solvent was evaporated and the product was obtained as a copper-red solid which was dried *in vacuo* for 12 h. The orange-coloured residue was dissolved in 5 mL of acetonitrile and the addition of 2 mL of thf and pentane causing a copper-red precipitate to form. After 24 h without stirring, the solid was filtered, washed with pentane and dried *in vacuo* over night to yield the product in 55 mg (82%) as a copper-red solid. M.p. 275 °C; ^1H NMR (300 MHz, CD_3CN): $\delta = 1.15$ (t, $^3J_{HH} = 7.3$ Hz, 12H, CH_3), 3.62 (q, $^3J_{HH} = 7.3$ Hz, 8H, CH_2), 7.10 (d, $^3J_{HH} = 1.9$ Hz, 4H, H-4′), 7.40 (d, $^3J_{HH} = 8.1$ Hz, 4H, H-5), 7.54 (d, $^3J_{HH} = 8.1$ Hz, 4H, H-3), 7.56 (d, $^3J_{HH} = 1.9$ Hz, 4H, H-5′), 7.83 (t, $^3J_{HH} = 8.1$ Hz, 4H, H-4); $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): $\delta = 16.0$ (CH_3), 47.5 (CH_2), 112.6 (C-5), 116.8 (C-5′), 122.1 (C-3), 123.2 (C-4′), 141.0 (C-4), 150.5 (C-6), 155.1 (C-2), 185.0 (C-2′); IR (KBr): $\nu = 3164$ (w), 3134 (w), 3114 (w), 2983 (m), 1601 (m), 1572 (m), 1486 (m), 1469 (m), 1443 (m), 1415 (m), 1346 (m), 1262 (s), 1228 (m), 1084 (vs br), 806 (s) cm^{-1}; HR-MS (ESI$^+$) calcd for $C_{40}H_{40}N_{12}Cu_2BF_4$: *m*/*z* 901.21146 (%); found: *m*/*z* 901.21149 $[2M - BF_4]^+$ (52); calcd for $\frac{1}{2}(C_{40}H_{40}N_{12}Cu_2)$: *m*/*z* 407.10400 (%); found: *m*/*z* 407.10413, $[M]^{2+}$ (100); elemental analysis calcd for $C_{20}H_{20}N_6CuBF_4\cdot CuBF_4\cdot CH_3CN$: C 38.51, H 3.38, N 14.29; found: C 38.48, H 3.60, N 14.34; Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution at rt.

X-Ray crystal data and refinement details for 3–6, 8, 12–15, 17–18 (Tables 3 and 4)

X-Ray structures were obtained with a Bruker Smart diffractometer (**4–6**, **12**, **13**,) or a Bruker APEX diffractometer (**3**, **8**, **14**, **15**, **17**, **18**) at 200 K, both equipped with a Mo Kα radiation source ($\lambda = 0.71073$ Å) and a graphite monochromator. All intensities were corrected for Lorentz and polarisation effects, and an absorption correction was applied in each case using SADABS[24] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non hydrogen atoms were refined anisotropically according to a full-matrix least squares technique against F^2 with exception of the light atoms of **13**, which could only be described isotropically. The hydrogen atom locations were calculated according to stereochemical aspects. We have observed and modelled some disorder in the anions or incorporated solvent molecules. Structure solution and refinement were carried out with the SHELXTL (6.10) software package.[25]

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