Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis of a flexible macrocyclic tetraimidazolium salt – precursor for a tetracarbene ligand with metal dependent coordination modes†

Christian Schulte to Brinke,[a] F. Ekkehardt Hahn*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The cyclic tetraimidazolium salt $(H_4$-**4**$)(PF_6)_4$ with flexible linkers between the imidazolium groups has been synthesized following a stepwise synthetic approach. *In situ* deprotonation of $(H_4$-**4**$)(PF_6)_4$ in the presence of different metal ions leads to complexes where the tetracarbene ligand shows differing coordination modes depending on the metal center. Due to its high flexibility the tetracarbene ligand folds around d^8 transition metal ions such as Ni^{II}, Pd^{II} and Pt^{II} to yield mononuclear tetracarbene complexes of type $[M(\mathbf{4})](PF_6)_2$ featuring a square-planar coordinated metal center. Reaction of **4** with metal centers that prefer a linear coordination mode such as Ag^I yields the tetranuclear silver(I) octacarbene complex $[Ag_4(\mathbf{4})_2](PF_6)_4$ featuring four silver(I) ions sandwiched in between two tetra-NHC ligands.

Introduction

The in situ deprotonation of imidazolium salts is a well known strategy for the preparation of transition metal complexes bearing N-heterocyclic carbene ligands.[1] In recent years, cyclic polyimidazaolium salts have also been studied due to their potential application as precursors for cyclic polycarbene ligands and their metal complexes.[1] In addition, cyclic polyimidazolium salts can also function as receptors for selected anions[2] and π-electron-rich neutral guests.[3]

Cyclophane-like diazolium salts, for example, have led to metal complexes with cyclic di-NHC ligands that normally act as classical bidentate ligands. Coordination of such di-NHC ligands to square-planar metal ions such as Pd^{II} gave metal complexes with the bidentate ligand bound in *cis*-fashion to the metal center.[4] In fact, there are only very few examples known for metal complexes featuring the metal ion located in the center of cyclic di-NHC ligands. Examples are Baker´s Ni^{II} complex bearing a cyclic tetradentate di-NHC/di-pyridyl ligand leading to a saddle-shaped complex[5] and the [16]ane-$P_2C^{NHC}_2$ di-NHC/diphosphine ligand coordinated to a Pt^{II} ion.[6] However, the reaction of cyclic di-NHC ligands with linearly coordinated metal ions such as Ag^I indicated that this ligand type normally cannot accommodate the metal ion in the ligand's center and the formation of bidentate dinuclear complexes is preferred.[4a,7] In summary, the coordination chemistry of cyclic di-NHC ligands depends on the number of additional donor functions present, the size of the macrocycle and its flexibility as well as the type of metal ion used.

Metal complexes bearing cyclic poly-NHC ligands with more than two carbene donor functions are less common.[1] The Pt^{II} complex bearing a macrocyclic tetra-NHC ligands has been obtained via a metal template controlled reaction starting from a tetraisocyanide complex[8] and, more recently, via metalation of the cyclic tetraimidazolium salt $(H_4$-**A**$)(OTf)_4$ (Fig. 1).[9] The tetraimidazolium salt $(H_4$-**B**$)(PF_6)_4$,[10] as well as its *o*-xylene-bridged analogon[11] turned out to be suitable precursors for mono and dinuclear Ag^I Au^I complexes. Due to the rigidity of the of macrocyclic tetracarbene ligand, the M–M distances of the resulting dinuclear Ag^I and Au^I complexes are rather short and metalophilic interactions between the two metal ions can be expected. The synthesis of mononuclear complexes with square-planar coordinated metal ions with these tetra-NHC ligands proved impossible.

A third coordination mode for macrocyclic polycarbene ligands was found in transition metal complexes bearing ligands of type **C**. Here three-dimesional cyclidrical structures composed of linearly coordinated Ag^I ions sandwiched in between two tri,[12] tetra[4a] or even hexacarbene ligands[10] have been observed. Related structures are also been oberved for acyclic tri, tetra or hexacarbene ligands.[13] Finally, deprotonation of the highly flexible cyclic tetraimidazolium salt $(H_4$-**D**$)(I)_4$ yields a tetra-NHC ligand which folds fold around metal ions with a square-planar (Pd^{II})[14] or tetrahedral (Co^{II})[15] coordination geometry.

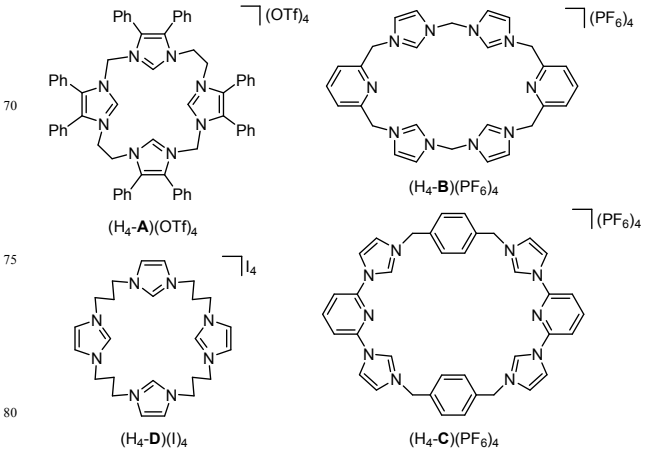
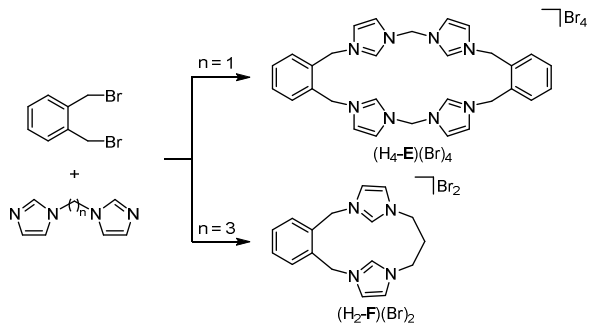


Fig. 1 Precursors for cyclic tetracarbene ligands with different coordination modes.

In this contribution we describe the preparation of the highly flexible tetraimidazolium salt $(H_4\text{-}\mathbf{4})(PF_6)_4$. Upon deprotion and metalation of $(H_4\text{-}\mathbf{4})(PF_6)_4$, complexes featuring two different coordination modes of the resulting tetra-NHC ligand, depending on the metal ion empoyed, have been isolated.

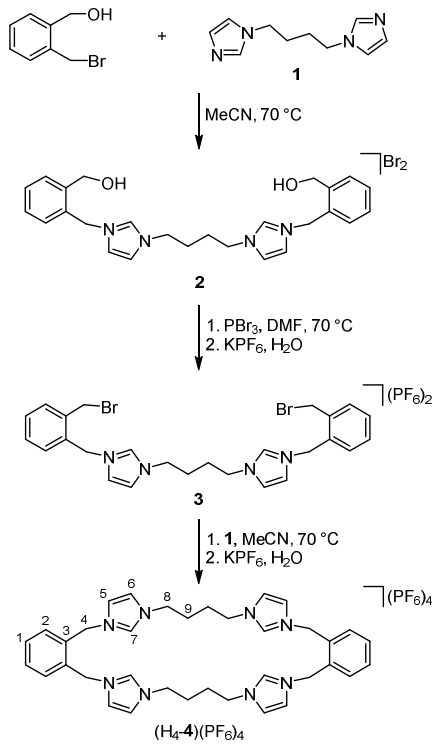
Results and Discussion

A common synthetic pathway for the preparation of macrocyclic polyimidazolium salts is the reaction of equimolar amounts of alkylene bridged diimidazoles and suitable linkers such as 2,5-di(halomethyl)pyridine[4a,5,16] or di(halomethyl)benzene.[7c,11,17] The macrocyclic tetraimidazolium salts can be obtained in a single-step reaction (Scheme 1). The ring size of the macrocycles formed depends, however, on the flexibility and size of the alkylene bridge linking the imidazoles. Reaction of equimolar amounts of 1,2-di(bromomethyl)benzene and di(1*H*-imidazol-1-yl)methane gave the rigid tetraimidazolium salt $(H_4\text{-}\mathbf{E})(Br)_4$[11] as the major product, while the reaction of the more flexible di(1*H*-imidazol-1-yl)propane yielded the diimiazolium salt $(H_2\text{-}\mathbf{F})(Br)_2$.[7c] After the synthesis of Ag^I and Au^I complexes using the rigid tetracarbene ligand **E**[11] we became interested in more flexible cyclic tetracarbenes where the methylene bridges in **E** have been substituted for longer alkyl chains and in the coordination chemisty of these ligands.



Scheme 1 Synthesis of the cyclic tetraimidazolium salt $(H_4\text{-}\mathbf{E})(Br)_4$[11] and the diimidazolium salt $(H_2\text{-}\mathbf{F})(Br)_2$[7c] via direct cyclization using rigid (n = 1) and more flexible (n = 3) alkylene bridged diimidazoles, respectively.

Given the undesirable reactivity of flexible-bridged diimidazoles regarding the preparation of tetraimidazolium macrocycles (Scheme 1) we developed a new stepwise procedure for the preparation of the cyclic tetraimidazolium salt $(H_4\text{-}\mathbf{4})(PF_6)_4$ (Scheme 2). This procedure involved the preparation of 1-(bromomethyl)-2-(hydroxymetyl)benzene by reduction of phthalic anhydride with lithium aluminum hydride to give 1,2-di(hydroxymethyl)benzene[18] followed by reaction with one equivalent of concentrated HBr[19] (Scheme 2). Subsequently, the 1-(bromomethyl)-2-(hydroxymethyl)benzene was reacted with di(1*H*-imidazol-1-yl)butane to give the diimidazolium salt **2**. Bromination of diimidazolium salt **2** with phosphorus tribromide and anion exchange with potassium hexafluorophosphate gave the imidazolium salt **3**. Cylization to give the macrocyclic tetraimidazolium salt $(H_4\text{-}\mathbf{4})(PF_6)_4$ was achieved by reaction of **3** with another equivalent of di(1*H*-imidazol-1-yl)butane in the presence of potassium hexafluorophosphate (Scheme 2).



Scheme 2 Stepwise preparation of the tetraimidazolium salt $(H_4\text{-}\mathbf{4})(PF_6)_4$ (the numbering refers to the assignment of the NMR resonances in the experimental section).

The ^1H and ^{13}C NMR spectra recorded for $(H_4\text{-}\mathbf{4})(PF_6)_4$ were consistent with the formation of the cyclic tetraimidazolium salt. Only one resonance was observed for the four NCHN protons (δ = 8.47 ppm) and NCN carbon atoms (δ = 136.8 ppm), respectively. Crystals of $(H_4\text{-}\mathbf{4})(PF_6)_4\cdot$MeCN, which were suitable for an X-ray diffraction analysis, were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the salt.

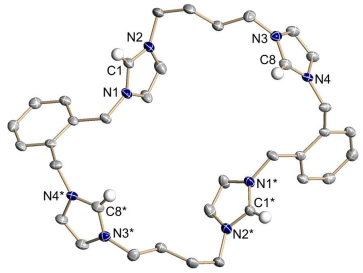
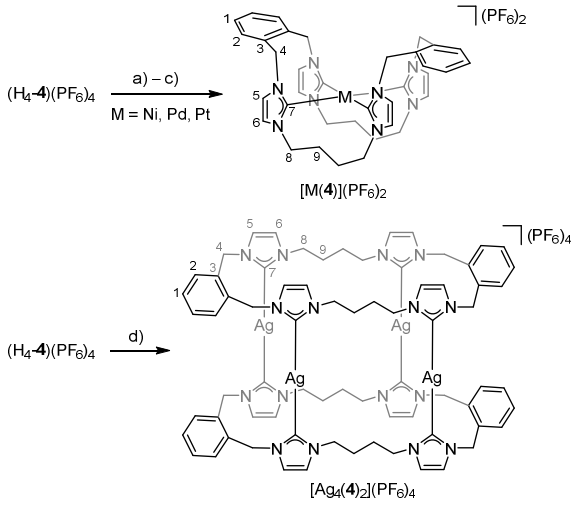


Fig. 2 Molecular structure of $(H_4\text{-}\mathbf{4})^{4+}$ in $(H_4\text{-}\mathbf{4})(PF_6)_4\cdot$MeCN. Hydrogen atoms except for the NCHN protons have been omitted for clarity. Selected bond lengths (Å) and angles (°): N1–C1 1.330(2), N2–C1 1.326(2), N3–C8 1.329(2), N4–C8 1.330(2); N1–C1–N2 108.7(2), N3–C8–N4 109.0(2).

The X-ray diffraction analysis with crystals of $(H_4\text{-}\mathbf{4})(PF_6)_4\cdot$MeCN confirmed the formation of the macrocycle (Fig. 2). Equivalent metric parameters do not differ significantly from those observed for related cyclic and non-cyclic imidazolium salts.[1c,11] The imidazolium NCHN functions in the tetracation $(H_4\text{-}\mathbf{4})^{4+}$ point alternating towards the center or away from the center of the macrocycle. This situation differs form that oberserved for the more rigid $(H_4\text{-}\mathbf{E})(Br)_4$[11] where all four

imidazolium groups point towards the center of the macrocycle. We take this observation as an indiction for the flexibility of the linkers between the imidazolium groups in $(H_4$-**4**$)(PF_6)_4$.



Scheme 3 Preparation of square-planar transition metal complexes $[M($**4**$)](PF_6)_2$ (M = Ni, Pd, Pt) and silver(I) complex $[Ag_4($**4**$)_2](PF_6)_4$ with the flexible macrocyclic tetracarbene ligand **4**. Reaction conditions: a) M = Ni, $NiBr_2 \cdot 3H_2O$, K_2CO_3, MeCN, Δ; b) M = Pd, $Pd(OAc)_2$, NaOAc, DMF, 50 °C; c) M = Pt, K_2PtCl_4, KO*t*Bu, DMF, 50 °C; d) Ag_2O, MeCN, 25 °C (the numbering refers to the assignment of the NMR resonances in the experimental section).

Deprotonation of the tetraimidazolium salt $(H_4$-**4**$)(PF_6)_4$ in presence of suitable d^8 transition metal precursors led to mononuclear complexes of type $[M($**4**$)](PF_6)_2$ (M = Ni, Pd, Pt). The complexes feature a square-planar metal center surrounded by four NHC donors. The tetracarbene macrocycle folds around the metal ion (Scheme 3).

The Ni^{II} complex $[Ni($**4**$)](PF_6)_2$ was obtained by deprotonation of $(H_4$-**4**$)(PF_6)_4$ with potassium carbonate in boiling acetonitrile in presence of $NiBr_2$. The complex formed over 3 d in 69% yield as a pale yellow solid. Formation of the tetracarbene complex was confirmed by NMR spectroscopy. The resonance for the NCHN protons of $(H_4$-**4**$)(PF_6)_4$, previously detected at $\delta = 8.47$ ppm in the ^{1}H NMR spectrum is not detectable anymore in the ^{1}H NMR spectrum of $[Ni($**4**$)](PF_6)_2$. Furthermore, the three chemically different methylene groups (4, 8 and 9 in Scheme 3) show diastereotopic behavior (6 × d or m) in the Ni^{II} complex, while only three broadened apparent singlets were detected for these protons in the tetraimidazolium salt $(H_4$-**4**$)(PF_6)_4$. The ^{13}C NMR spectrum of $[Ni($**4**$)](PF_6)_2$ shows only one resonance for all four C_{NHC} carbon atoms at $\delta = 168.8$ ppm compared to the NCHN resonance at $\delta = 136.8$ ppm for $(H_4$-**4**$)(PF_6)_4$. Formation of the Nickel(II) complex was also verified by high-resolution ESI-MS spectrometry showing strong resonances with correct isotope distribution for the cations $[\{Ni($**4**$)\}(PF_6)]^+$ and $[Ni($**4**$)]^{2+}$.

The palladium(II) complex $[Pd($**4**$)](PF_6)_2$ was prepared by treatment of the tetraimidazolium salt $(H_4$-**4**$)(PF_6)_4$ with sodium acetate and palladium(II) acetate in dimethylformamide at 50 °C for 3d. Compound $[Pd($**4**$)](PF_6)_2$ was obtained as a yellow solid in 79% yield. The ^{1}H as well as ^{13}C NMR resonances for palladium complex $[Pd($**4**$)](PF_6)_2$ were observed only slightly shifted compared to the values observed for the nickel(II) complex $[Ni($**4**$)](PF_6)_2$ (for example C_{NHC} $\delta = 168.2$ ppm). High-resolution ESI-MS spectroscopy also confirmed the formation of $[Pd($**4**$)](PF_6)_2$ with strong peaks with correct isotope distribution recorded for the cations $[\{Pd($**4**$)\}(PF_6)]^+$ and $[Pd($**4**$)]^{2+}$.

Finally, Pt^{II} complex $[Pt($**4**$)](PF_6)_2$ was prepared from $(H_4$-**4**$)(PF_6)_4$ and K_2PtCl_4 in the presence of KO*t*Bu as base in DMF at 50 °C over 3 d. The complex was isolated in 90% yield as a yellow solid. The recorded NMR data are is consistent with the formation of $[Pt($**4**$)](PF_6)_2$ with only the resonance for the carbene carbon atoms detected at $\delta = 161.9$ ppm. This resonance is significantly shifted upfield compared to the C_{NHC} resonances recorded for $[Ni($**4**$)](PF_6)_2$ ($\delta = 168.8$ ppm) and $[Pd($**4**$)](PF_6)_2$ ($\delta = 168.2$ ppm). The C_{NHC} resonance for $[Pt($**4**$)](PF_6)_2$ exhibits the typical Pt-C coupling with $^1J_{Pt,C} = 955$ Hz. In addition, $^3J_{Pt,C}$ coupling was detected involving the two chemically different NHC ring carbon atoms ($^3J_{Pt,C} = 24$, 23 Hz) and the methylene groups bound to the NHC nitrogen atoms ($^3J_{Pt,C} = 31$, 29 Hz). Both, the $^1J_{Pt,C}$ and $^3J_{Pt,C}$ coupling constants fall in the range previously observed for Pt-NHC complexes.[20] Finally compound $[Pt($**4**$)](PF_6)_2$ was detected by high-resolution ESI-MS spectrometry with strong peaks with the correct isotope distribution for $[\{Pt($**4**$)\}(PF_6)]^+$ and $[Pt($**4**$)]^{2+}$.

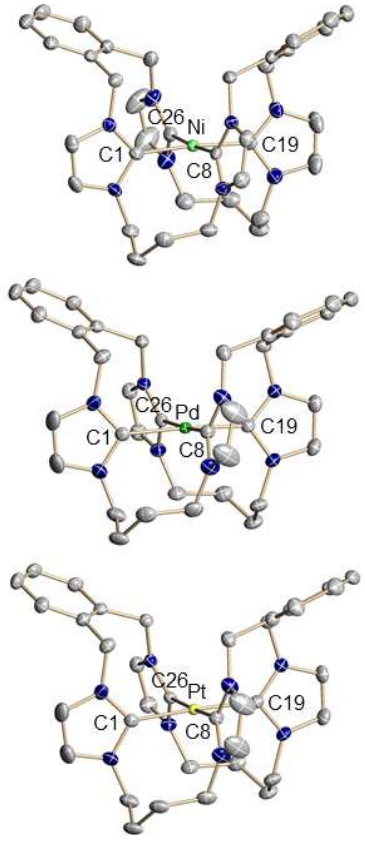


Fig. 3 Molecular structures of $[Ni($**4**$)]^{2+}$ in $[Ni($**4**$)](PF_6)_2 \cdot$MeCN (top), $[Pd($**4**$)]^{2+}$ in $[Pd($**4**$)](PF_6)_2 \cdot$MeCN (middle) and $[Pt($**4**$)]^{2+}$ in $[Pt($**4**$)](PF_6)_2 \cdot$MeCN (bottom). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for $[Ni($**4**$)]^{2+}$, $[[Pd($**4**$)]^{2+}]$ and $\{[Pt($**4**$)]^{2+}\}$: M–C1 1.939(4) [2.048(2)] {2.042(4)}, M–C8 1.931(4) [2.051(2)] {2.047(3)}, M–C19 1.933(4) [2.056(2)] {2.046(4)}, M–C26 1.931(4) [2.047(2)] {2.044(3)}, range N–$C_{carbene}$ 1.352(5)–1.364(5) [1.349(3)–1.360(3)] {1.348(5)–1.366(4)}; C1–M–C8 91.8(2) [92.6(1)] {92.6(1)}, C1–M–C19 175.1(2) [175.8(1)] {176.2(1)}, C1–M–C26 89.1(2) [86.1(1)] {86.1(1)}, C8–M–C19 86.3(2) [89.0(1)] {89.0(1)}, C8–M–C26 176.1(2) [176.4(1)] {176.6(1)}, C19–M–

C26 93.1(2) [92.5(1)] {92.5(1)}, range N–$C_{carbene}$–N 103.5(3)–104.2(3) [104.5(2)–104.8(2)] {104.4(3)–105.2(3)}.

The metal complexes of type $[M(\mathbf{4})](PF_6)_2$ have been crystallizd as MeCN adducts $[M(\mathbf{4})](PF_6)_2 \cdot MeCN$ by slow evaporation of the solvent from acetonitrile solutions of the compounds. X-ray diffraction analyses confirmed the formation of the expected mononuclear metal complexes. As expected, the tetacarbene ligand **4** is flexible enough to wrap itself around the metal center (Fig. 3). The coordination mode thus resembles the one found for the propylene-bridged tetracarbene ligand obtained after deprotonation of $(H_4\text{-}\mathbf{D})(I)_4$ (Fig. 1).[14] The molecular structures of the complexes of type $[M(\mathbf{4})](PF_6)_2$ demonstrate the highly flexible nature of the tetracarbene ligand **4**. Comparable bond distances and angles in complexes $[M(\mathbf{4})](PF_6)_2$ fall in the range previously observed for metal tetra-NHC complexes (M = Ni,[21] Pd,[4b,14] Pt[9,22]).

Contrary to the formation of mononuclear complexes from **4** and d^8 transition metals, tetracarbene precursor $(H_4\text{-}\mathbf{4})(PF_6)_4$ reacts with 2.5 equiv. of Ag_2O following a precedure described by Wang and Lin[23] to yield the tetranuclear silver(I) complex $[Ag_4(\mathbf{4})_2](PF_6)_4$ in 83% yield (Scheme 3). Complex $[Ag_4(\mathbf{4})_2](PF_6)_4$ features four linearly coordinated silver(I) ions sandwiched in between two tetracarbene ligands **4**. Formation of the silver-NHC complex was indicated by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum shown no more resonance for the NCHN protons of the tetracarbene precursor $(H_4\text{-}\mathbf{4})(PF_6)_4$. The resonance for the eight chemically equivalent C_{NHC} carbon atoms was detected at $\delta = 180.6$ ppm in the ^{13}C NMR spectrum in the typical range for C_{NHC}–Ag–C_{NHC} complexes. This resonance was observed as two doublets due to as the characteristical coupling to the two different silver isotops ^{107}Ag and ^{109}Ag ($^1J_{Ag(109),C} = 207$ Hz, $^1J_{Ag(107),C} = 178$ Hz).[7a] This coupling is an additional indication for Ag–C_{NHC} bonding. In addition, ^3J coupling between the silver ions and both of the C5 and C6 ring carbon atoms of the NHC (see Scheme 3) was observed ($^3J_{Ag,C} = 6$ Hz).

While the NMR spectra clearly indicate the presence of a silver-NHC complex featuring $Ag(NHC)_2$ units, they are not sufficient to distinguish between possible isomers. These isomers are a tetranuclear complex such as $[Ag_4(\mathbf{4})_2](PF_6)_4$ or a dinuclear complex $[Ag_2(\mathbf{4})](PF_6)_2$ where two Ag^I ions residing the center of the macrocycle are coordinated by the four NHC donors of the tetracarbene ligand in a linear fashion. Such dinuclar Ag^I and Au^I complexes have previously been obtained from the related but more rigid xylene-methylene-bridged tetracarbene ligand obtained from $(H_4\text{-}\mathbf{E})(Br)_4$ (Scheme 1).[11]

In order to establish unequivocally the composition of the reaction product from the reaction of Ag_2O with $(H_4\text{-}\mathbf{4})(PF_6)_4$, the obtained off-white solid was dissolved in acetonitrile. Slow diffusion of diethyl ether into this solution gave colorless crystals of $[Ag_4(\mathbf{4})_2](PF_6)_4 \cdot 2MeCN$.

The molecular structure determination revealed the presence of the expected tetranuclear octacarbene sandwich complex with the four Ag^I ions coordinated by two tetracarbene ligands **4** (Fig. 4). Contrary to the dinuclear Ag^I and Au^I complexes of the rigid tetracarbene ligand **E** where all four carbene donors coordinate the metal ions located in the center of the macrocycle, Ag^I complex $[Ag_4(\mathbf{4})_2](PF_6)_4$ features carbene donors rotated out of the plane of the macrocycle. These donors coordinate to four Ag^I ions located outside of the planes of the two cyclic ligands. This arrangement leads to a strain-free coordination in $[Ag_4(\mathbf{4})_2](PF_6)_4$ with the all C_{NHC}–Ag–C_{NHC} angles close to linearity while the strongly bent and thus strained C_{NHC}–Ag–C_{NHC} angles were found for the related dinuclear complex $[Ag_2(\mathbf{E})](PF_6)_2$.

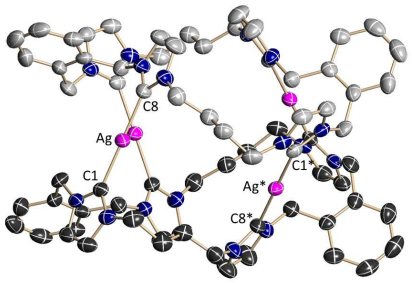


Fig. 4 Molecular structure of $[Ag_4(\mathbf{4})_2]^{4+}$ in $[Ag_4(\mathbf{4})_2](PF_6)_4 \cdot 2MeCN$. Hydrogen atoms have been omitted for clarity. The asymmetric unit contains ¼ formula unit. Selected bond lengths (Å) and angles (°): Ag–C1 2.099(4), Ag–C8 2.088(4), N1–C1 1.346(6), N2–C1 1.348(6), N3–C8 1.357(5), N4–C8 1.347(6); C1–Ag–C8 179.4(2), N1–C1–N2 104.7(4), N3–C8–N4 103.9(4).

Remarkably, high-resolution ESI-MS spectroscopy does not show peaks for the cations of the tetranuclear Ag^I complex $[Ag_4(\mathbf{4})_2](PF_6)_4$ but only peaks for dinuclear cationic complexes such as $[\{Ag_2(\mathbf{4})\}(PF_6)]^+$ or $[Ag_2(\mathbf{4})]^{2+}$. A related difference in observations between the solid state and the gas phase has been reported for some crystallographically characterized dinuclear NHC complexes where MS spectrometry only indicted the presence of mononuclear complexes in the gas phase.[7a,24] Therefore it appears reasonable to assume, that the tetracarbene ligand **4** is capable to bind four linearly coordinated metal ions in the sandwich mode found in $[Ag_4(\mathbf{4})_2](PF_6)_4$ and also two linearly coordinated metal ions inside to macrocycle with formation of a complex $[Ag_2(\mathbf{4})](PF_6)_2$. The latter binding mode appears to be less favored.

Conclusions

We present a new and stepwise synthetic pathway for the preparation of propyl/*o*-xylyl bridgd macrocyclic tetraimidazolium salts of type $(H_4\text{-}\mathbf{4})(PF_6)_4$. Macrocyclic tetraimidazolium salts featuring such flexible bridges cannot be obtained with the conventional one-step cyclization procedure. After tetra-deprotonation of the tetraimidazolium salt $(H_4\text{-}\mathbf{4})(PF_6)_4$ the resulting tetra-NHC ligand **4** showed two different, metal dependent coordination modes. In the presence of d^8 transition metal ions M^{2+} (M = Ni, Pd, Pt), the highly flexibe tetra-NHC ligand **4** wraps around the square-planar coordinated metal center with formation of mononuclear complexes of type $[M(\mathbf{4})](PF_6)_2$. Metal ions which prefer a linear coordination mode such as Ag^+ react with **4** to give the tetranuclear octacarbene sandwich complex $[Ag_4(\mathbf{4})_2](PF_6)_4$. In this case the carbene donor functions are rotated out of the ligand plane and four silver(I) ions are coordinated between two macrocycles. The coordination chemistry of tetra-NHC ligand **4** illustrates nicely, how important the flexibility of the bridging groups in macrocclic tetra-NHCs are for the resulting metal complexes.

Experimental

General

All reagents and solvents were used as received without further purification. NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm using the residual protonated solvent as an internal standard. Coupling constants are expressed in Hertz. Assignments are based on distortionless enhancement of polarization transfer (DEPT) and homo- and heteronuclear shift correlation spectroscopy. Mass spectra were obtained with MicroTof (Bruker Daltonics, ESI) and Orbitrap LTQ XL (Thermo Scientific, ESI). The syntheses of di(1*H*-imidazol-1-yl)butane,[25] 1,2-di(hydroxymethyl)benzene[18] and 1-(bromomethyl)-2-(hydroxymetyl)benzene[19] have been described. Consistent microanalytical data for the metal complexes were difficult to obtain due to the large fluorine content (PF_6^- anions).[28] A full set of NMR spectra are provided instead.

Syntheses

Preparation of diimidazolium salt 2. A sample of 1-(bromomethyl)-2-(hydroxymetyl)benzene (804 mg, 4.00 mmol)[18] and di(1*H*-imidazol-1-yl)butane (380 mg, 2.00 mmol)[25] were dissolved in acetonitrile (50 mL). The solution was stirred over for 12 h at 70 °C and subsequently cooled to ambient temperature. After removal of the solvent *in vacuo* diimidazolium salt **2** was obtained as an off-white solid in quantitative yield and used without further purification. Yield 1.18 g (2.0 mmol, 100 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (s, 2H, NCHN), 7.86 (s, 2H, C*H*=CH), 7.78 (s, 2H, CH=C*H*), 7.45–7.26 (m, 8H, Ar-H), 5.53 (s, 4H, ArCH_2N), 4.59 (s, 4H, ArCH_2OH), 4.26 (s br, 4H, NCH_2CH_2), 1.80 (s br, 4H, NCH_2CH_2), the OH protons could not be detected in DMSO-d_6). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 140.8 (NCHN), 137.0, 132.9, 129.5, 129.2, 129.1, 128.3 (Ar-C), 123.2 and 123.0 (N*C*=*C*N), 61.4 (CH_2OH), 49.9 (ArCH_2N), 48.7 (N*C*H$_2$CH$_2$), 26.5 (NCH$_2$*C*H$_2$). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 511.16947 (35, $[M–Br]^+$, 511.17086), 216.12509 (100, $[M–2Br]^{2+}$, 216.12626).

Preparation of diimidazolium salt 3. A sample of the diimidazolium salt **2** (296 mg, 0.50 mmol) was dissolved in dimethylformamide (10 mL) and phosphorus tribromide (0.094 mL, 271 mg, 1.00 mmol) was added dropwise. The reaction mixture was stirred for 12 h at 50 °C and subsequently cooled to ambient temperature. The mixture as treated with water (1 mL). After removal of the solvents *in vacuo* the crude solid obtained was dissolved in water (20 mL) and a solution of potassium hexafluorophosphate (368 mg, 2.00 mmol) in water (10 mL) was added dropwise. Filtration and washing of the obtained solid with water (3 × 5 mL) gave diimidazoliumsalt **3** as an off-white solid. Yield: 350 mg (0.41 mmol, 82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (s, 2H, NCHN), 7.81 (s br, 2H, C*H*=CH), 7.77 (s br, 2H, CH=C*H*), 7.58–7.54 (m, 2H, Ar-H), 7.46–7.42 (m, 4H, Ar-H), 7.30–7.26 (m, 2H, Ar-H), 5.58 (s, 4H, ArCH_2N), 4.85 (s, 4H, ArCH_2Br), 4.22 (s br, 4H, NCH_2CH_2), 1.78 (s br, 4H, NCH$_2$CH_2). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 136.5 (NCHN), 136.4, 132.7, 131.4, 129.7, 129.5 (Ar-C, only 5 of the 6 resonances were detected), 122.9, 122.7 (*C*H=*C*H), 49.0 (ArCH_2N), 48.1 (N*C*H$_2$CH$_2$), 31.6 (ArCH_2Br), 26.1 (NCH$_2$*C*H$_2$). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 703.04387 (70, $[M–PF_6]^+$, 703.04604), 279.03936 (100, $[M–2PF_6]^{2+}$, 279.04093).

Preparation of (H_4-4)$(PF_6)_4$. Diimidazolium salt **3** (254 mg, 0.30 mmol) and an equimolar amount of di(1*H*-imidazol-1-yl)butane (57 mg, 0.30 mmol) were dissolved in acetonitrile (50 mL) and the reaction mixture was stirred for 12 h at 70 °C. Subsequently, the reaction mixture was cooled to ambient temperature and the solvent was removed *in vacuo*. The solid residue was suspended in water (20 mL) and treated dropwise with a solution of potassium hexafluorophosphate (221 mg, 1.20 mmol) in water (10 mL). Compound (H_4-**4**)$(PF_6)_4$ precipitated and was isolated by filtration. The residue was washed with water (3 × 5 mL) to give the cyclic tetraimidazolium salt (H_4-**4**)$(PF_6)_4$ as an off-white solid. Yield: 245 mg (0.21 mmol, 70%). Crystals of (H_4-**4**)$(PF_6)_4$·MeCN suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the compound. ^{1}H NMR (400 MHz, CD_3CN): δ 8.47 (s br, 4H, H-7), 7.54 (dd, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 3.4 Hz, 4H, H-1), 7.41 (s br, 4H, H-5), 7.34 (dd, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 3.4 Hz, 4H, H-2), 7.23 (s br, 4H, H-6), 5.35 (s br, 8H, H-4), 4.18 (s br, 8H, H-8), 1.84 (s br, 8H, H-9). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ 136.8 (C-7), 132.8 (C-3), 131.6 (C-1), 131.5 (C-2), 124.1 (C-5), 123.5 (C-6), 50.9 (C-4), 50.3 (C-8), 27.0 (C-9). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 439.14719 (100, $[(H_4\text{-}4)(PF_6)_2]^{2+}$, 439.14862), 244.44316 (75, $[(H_4\text{-}4)(PF_6)]^{3+}$, 244.44436).

Preparation of [Ni(4)]$(PF_6)_2$. Tetraimidazolium salt (H_4-**4**)$(PF_6)_4$ (82 mg, 0.070 mmol), $NiBr_2·3H_2O$ (38 mg, 0.14 mmol) and potassium carbonate (193 mg, 1.40 mmol) were dissolved in acetonitrile (25 mL) and heated under reflux for 3 d. The reaction mixture was then cooled to ambient temperature. Removal of the solvent *in vacuo* yielded a yellow solid. The solid was dissolved in acetonitrile (3 mL) and this solution was added to diethyl ether (80 mL). A yellow solid precipited which was isolated by filtration and washed with water (5 × 1 mL) to give nickel complex [Ni(**4**)]$(PF_6)_2$ as a yellow solid. Yield: 45 mg (0.048 mmol, 69%). Crystals of [Ni(**4**)]$(PF_6)_2$·MeCN suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from an acetonitrile solution of the compound. ^{1}H NMR (400 MHz, CD_3CN): δ 7.86–7.82 (m, 4H, H-2), 7.58–7.53 (m, 4H, H-1), 7.32 (s, 4H, H-5), 7.07 (s, 4H, H-6), 6.94 (d, $^2J_{H,H}$ = 14.5 Hz, 4H, H-4a), 5.34 (d, $^2J_{H,H}$ = 14.5 Hz, 4H, H-4b), 5.38–5.31 (m, 4H, H-8a), 4.40–4.32 (m, 4H, H-8b), 2.28–2.20 (m, 4H, H-9a), 1.26–1.16 (m, 4H, H-9b). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ 168.8 (C-7), 136.5 (C-3), 132.7 (C-2), 131.3 (C-1), 124.9 (C-6), 124.1 (C-5), 53.3 (C-4), 48.0 (C-8), 26.8 (C-9). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 787.23682 (65, $[\{Ni(\mathbf{4})\}(PF_6)]^+$, 787.23712), 321.13599 (100, $[Ni(\mathbf{4})]^{2+}$, 321.13647).

Preparation of [Pd(4)]$(PF_6)_2$. Tetraimidazolium salt (H_4-**4**)$(PF_6)_4$ (105 mg, 0.090 mmol), palladium(II) acetate (20 mg, 0.090 mmol) and sodium acetate (148 mg, 1.80 mmol) were dissolved in dimethylformamide (10 mL). The reaction mixture was stirred for 3 d at 50 °C and subsequently cooled to ambient temperature. The solution was filtered and the solvent was revoved *in vacuo* from the filtrate. The resulting solid was dissolved in acetonitrile (2 mL) and the cloudy solution was filtered again. Palladium complex [Pd(**4**)]$(PF_6)_2$ was obtained after removal of the solvent as a yellow solid. Yield: 70 mg

(0.071 mmol, 79%). Crystals of [Pd(**4**)](PF$_6$)$_2$·MeCN suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from an acetonitrile solution of the compound. ^{1}H NMR (400 MHz, CD$_3$CN): δ 7.83 (m, 4H, H-2), 7.52 (m, 4H, H-1), 7.36 (s, 4H, H-5), 7.11 (s, 4H, H-6), 6.46 (d, $^2J_{H,}$ = 14.5 Hz, 4H, H-4a), 5.21 (d, $^2J_{H,H}$ = 14.5 Hz, 4H, H-4b), 4.88–4.80 (m, 4H, H-8a), 4.26–4.17 (m, 4H, H-8b), 2.19–2.10 (m, 4H, H-9a), 1.28–1.18 (m, 4H, H-9b). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 168.2 (C-7), 136.3 (C-3), 133.0 (C-2), 131.2 (C-1), 124.1 (C-6), 123.3 (C-5), 53.2 (C-4), 47.8 (C-8), 26.6 (C-9). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 835.20665 (100, [{Pd(**4**)}(PF$_6$)]$^+$, 835.20524), 345.12070 (95, [Pd(**4**)]$^{2+}$, 345.12121).

Preparation of [Pt(4)](PF$_6$)$_2$. Tetraimidazolium salt (H$_4$-**4**)(PF$_6$)$_4$ (82 mg, 0.070 mmol), K$_2$PtCl$_4$ (29 mg, 0.070 mmol) and potassium *tert*-butoxide (38 mg, 0.34 mmol) were dissolved in dimethylformamide (10 mL) and stirred for 3 d 50 °C. The reaction mixture was then cooled to ambient temperature. The solvent was removd *in vacuo* and the residue was dissolved in acetonitrile (3 mL). Addition of diethyl ether (80 mL) yielded a yellow solid. This solid was isolated by filtration and washed with water (5 × 1 mL) to give platinum complex [Pt(**4**)](PF$_6$)$_2$ as a yellow solid. Yield: 67 mg (0.063 mmol, 90%). Crystals of [Pt(**4**)](PF$_6$)$_2$·MeCN suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from an acetonitrile solution of the compound. ^{1}H NMR (400 MHz, CD$_3$CN): δ 7.81 (m, 4H, H-2), 7.52 (m, 4H, H-1), 7.34 (d, $^3J_{H,H}$ = 1.9 Hz, 4H, H-5), 7.08 (d, $^3J_{H,H}$ = 1.9 Hz, 4H, H-6), 6.57 (d, $^2J_{H,H}$ = 14.5 Hz, 4 H, H-4a), 5.12 (d, $^2J_{H,H}$ = 14.5 Hz, 4H, H-4b), 4.94–4.86 (m, 4H, H-8a), 4.16–4.08 (m, 4H, H-8b), 2.15–2.08 (m, 4H, H-9a), 1.27–1.16 (m, 4H, H-9b). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 161.9 (s + ^{195}Pt-satellites, $^1J_{195Pt,C}$ = 955 Hz, C-7), 136.3 (C-3), 133.0 (C-2), 131.2 (C-1), 123.6 (s + ^{195}Pt-satellites, $^3J_{195Pt,C}$ = 24 Hz, C-6), 122.8 (s + ^{195}Pt-satellites, $^3J_{195Pt,C}$ = 23 Hz, C-5), 52.8 (s + ^{195}Pt-satellites, $^3J_{195Pt,C}$ = 31 Hz, C-4), 47.5 (s + ^{195}Pt-satellites, $^3J_{195Pt,C}$ = 29 Hz, C-8), 26.5 (C-9). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 924.26361 (100, [{Pt(**4**)}(PF$_6$)]$^+$, 924.26680), 389.64930 (100, [Pt(**4**)]$^{2+}$, 389.65131).

Preparation of [Ag$_4$(4)$_2$](PF$_6$)$_4$. Tetraimidazolium salt (H$_4$-**4**)(PF$_6$)$_4$ (50 mg, 0.043 mmol) and silver oxide (25 mg, 0.11 mmol) were dissolved in acetonitrile (10 mL) and the suspension was stirred for 3 d at ambient temperature with exclusion of light. Subsequently, the solvent was removed *in vacuo* and the residue was dissolved in acetonitrile (1 mL). The resulting solution was filtered through celite (three times). Removal of the solvent gave [Ag$_4$(**4**)$_2$](PF$_6$)$_4$ as an off-white solid. Yield: 39 mg (0.0178 mmol, 83%). Crystals of [Ag$_4$(**4**)$_2$](PF$_6$)$_4$·2MeCN suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the compound. ^{1}H NMR (400 MHz, CD$_3$CN): δ 7.72–7.65 (m, 16H, H-1, H-2), 7.25 (s, 8H, H-6), 6.66 (s, 8H, H-5), 5.20 (d, $^2J_{H,H}$ = 14.0 Hz, 8H, H-4a), 5.05 (d, $^2J_{H,H}$ = 14.0 Hz, 8H, H-4b), 4.10–3.96 (m, 16H, H-8), 2.03–1.95 (m, 8H, H-9a), 1.90–1.84 (m, 8H, H-9b). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 180.6 (d + d, $^1J_{109Ag,C}$ = 207 Hz, $^1J_{107Ag,C}$ = 178 Hz, C-7), 135.0 (C-3), 134.8 (C-2), 131.6 (C-1), 124.4 (d, $^3J_{Ag,C}$ = 5.5 Hz, C-6), 121.5 (d, $^3J_{Ag,C}$ = 6 Hz, C-5), 54.3 (C-4), 51.8 (C-8), 24.3 (C-9). HRMS (ESI, positive ions): *m*/*z* (%, ion, calcd) = 945.11169 (30, [{Ag$_2$(**4**)}(PF$_6$)]$^+$, 945.11192), 400.07308 (100, [Ag$_2$(**4**)]$^{2+}$, 400.07387).

Crystal structure determinations

X-Ray diffraction data were collected with a Bruker AXS APEX (Mo-*Kα* radiation) or an AXS SMART (Cu-*Kα* radiation) diffractometer equipped with a rotation anode at 153(2) K using graphite monochromated radiation. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[26] program package. Structure solutions were found with the SHELXS-97 package[27] using the heavy-atom method and were refined with SHELXL-97[27] against all F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal data for (H$_4$-4)(PF$_6$)$_4$·MeCN. Formula $C_{38}H_{47}N_9F_{24}P_4$, M = 1209.73, colorless prism, 0.21 × 0.15 × 0.09 mm^3, a = 14.3308(8), b = 13.4896(7), c = 25.4184(14) Å, β = 100.399(4)°, V = 4833.1(5) Å^3, monoclinic, space group $C2/c$, Z = 4, ρ_{calcd} = 1.663 g cm^{-3}, Cu-*Kα* radiation (λ = 1.54178 Å), μ = 2.688 mm^{-1}, 13467 intensities measured in the range 7.1° ≤ 2θ ≤ 144.8°, 4518 independent intensities (R_{int} = 0.0440), 3965 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.602 ≤ T ≤ 0.794), refinement of 352 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0399, wR = 0.1109, R_{all} = 0.0440, wR_{all} = 0.1138. The asymmetric unit contains ½ of a formula unit (the SOF for the acetonitrile molecule in the asymmetric unit is 0.5).

Crystal data for [Ni(4)](PF$_6$)$_2$·MeCN. Formula $C_{38}H_{43}N_9F_{12}NiP_2$, M = 974.46, colorless plate, 0.31 × 0.20 × 0.05 mm^3, a = 12.0643(3), b = 12.3563(3), c = 15.4897(3) Å, α = 93.8020(10), β = 99.1400(10), γ = 113.3460(10)°, V = 2071.70(8) Å^3, triclinic, space group P–1, Z = 2, ρ_{calcd} = 1.562 g cm^{-3}, Mo-*Kα* radiation (λ = 0.71073 Å), μ = 0.642 mm^{-1}, 31462 intensities measured in the range 4.0° ≤ 2θ ≤ 55.7°, 9867 independent intensities (R_{int} = 0.0416), 7556 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.826 ≤ T ≤ 0.769), refinement of 544 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for C, N and Ni atoms and hydrogen atoms on calculated positions, R = 0.0741, wR = 0.1937, R_{all} = 0.0962, wR_{all} = 0.2112. The asymmetric unit contains one formula unit. The fluorine atoms of the PF_6^- anions are disordered. The positional parameters of the PF_6^- anions and the acetonitrile molecule in the asymmetric unit were refined with isotropic thermal parameters.

Crystal data for [Pd(4)](PF$_6$)$_2$·MeCN. Formula $C_{38}H_{43}N_9F_{12}P_2Pd$, M = 1022.15, colorless plate, 0.13 × 0.10 × 0.03 mm^3, a = 12.0953(5), b = 12.4132(5), c = 15.6467(7) Å, α = 92.8700(10), β = 99.6370(10), γ = 112.9970(10)°, V = 2114.67(15) Å^3, triclinic, space group P–1, Z = 2, ρ_{calcd} = 1.605 g cm^{-3}, Mo-*Kα* radiation (λ = 0.71073 Å), μ = 0.609 mm^{-1}, 25199 intensities measured in the range 3.6° ≤ 2θ ≤ 60.3°, 12366 independent intensities (R_{int} = 0.0198), 10812 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.925 ≤ T ≤ 0.982), refinement of 596 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R =

0.0414, wR = 0.1026, R_{all} = 0.0492, wR_{all} = 0.1080. The asymmetric unit contains one formula unit.

Crystal data for [Pt(4)](PF$_6$)$_2$·MeCN. Formula $C_{38}H_{43}N_9F_{12}P_2Pt$, M = 1110.83, yellow prism, 0.18 × 0.18 × 0.11 mm^3, a = 12.0669(2), b = 12.3711(2), c = 15.6154(3) Å, α = 92.9460(10), β = 99.6010(10), γ = 112.8670(10)°, V = 2100.40(6) Å^3, triclinic, space group P–1, Z = 2, ρ_{calcd} = 1.756 g cm^{-3}, Mo-$K\alpha$ radiation (λ = 0.71073 Å), μ = 3.512 mm^{-1}, 38228 intensities measured in the range 5.9° ≤ 2θ ≤ 62.2°, 13022 independent intensities (R_{int} = 0.0343), 11584 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.543 ≤ T ≤ 0.671), refinement of 567 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all C, N and Pt atoms and hydrogen atoms on calculated positions, R = 0.0380, wR = 0.0920, R_{all} = 0.0454, wR_{all} = 0.0951. The asymmetric unit contains one formula unit. The fluorine atoms of the PF_6^- anions are disordered. The positional parameters of the PF_6^- anions and the acetonitrile molecule in the asymmetric unit were refined with isotropic thermal parameters.

Crystal data for [Ag$_4$(4)$_2$](PF$_6$)$_4$·2MeCN. Formula $C_{76}H_{86}N_{18}Ag_4F_{24}P_4$, M = 2262.99, colorless plate, 0.15 × 0.12 × 0.08 mm^3, a = 17.1961(6), b = 19.7707(6), c = 26.2271(8) Å, V = 8916.7(5) Å^3, orthorhombic, space group $Ibam$, Z = 4, ρ_{calcd} = 1.686 g cm^{-3}, Cu-$K\alpha$ radiation (λ = 1.54178 Å), μ = 8.536 mm^{-1}, 24107 intensities measured in the range 6.7° ≤ 2θ ≤ 144.8°, 4459 independent intensities (R_{int} = 0.0521), 3729 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.361 ≤ T ≤ 0.548), refinement of 297 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0498, wR = 0.1373, R_{all} = 0.0591, wR_{all} = 0.1505. The asymmetric unit contains ¼ formula unit. The fluorine atoms of one of the PF_6^- anions are disordered.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (IRTG 2027 and SFB 858) for financial support.

Notes and references

[a] *Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany. E-Mail: fehahn@uni-muenster.de; Fax: +49-251-8333108; Tel: +49-251-8333110.*

† Electronic supplementary information (ESI) available: NMR spectra (^{1}H and ^{13}C) for all new compounds. CCDC reference numbers 1404048–1404052. For the ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

Notes and references

1 (*a*) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810–8849; (*b*) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677–3707; (*c*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.

2 (*a*) W. W. H. Wong, M. S. Vickers, A. R. Cowley, R. L. Paul and P. D. Beer, *Org. Biomol. Chem.*, 2005, **3**, 4201–4208; (*b*) J. Yoon, S. K. Kim, N. J. Singh and K. S. Kim, *Chem. Soc. Rev.,* 2006, **35**, 355–360; (*c*) Z. Xu, S. K. Kim and J. Yoon, *Chem. Soc. Rev.,* 2010, **39**, 1457–1466.

3 C. J. Serpell, J. Cookson, A. L. Thompson and P. D. Beer, *Chem. Sci.*, 2011, **2**, 494–500.

4 (*a*) C. Radloff, H.-Y. Gong, C. Schulte to Brinke, T. Pape, V. M. Lynch, J. L. Sessler and F. E. Hahn, *Chem. Eur. J.*, 2010, **16**, 13077–13081; (*b*) M. V. Baker, B. W. Skelton, A. H. White and C. C. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 111–120; (*c*) M. V. Baker, S. K. Brayshaw, B. W. Skelton, A. H. White and C. C. Williams, *J. Organomet. Chem.*, 2005, **690**, 2312–2322; (*d*) M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton, A. H. White and C. C. Williams, *J. Organomet. Chem.*, 2006, **691**, 5845–5855; (*e*) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617–618**, 546–560.

5 M. V. Baker, B. W. Skelton, A. H. White and C. C. Williams, *Organometallics*, 2002, **21**, 2674–2678.

6 A. Flores-Figueroa, T. Pape, K.-O. Feldmann and F. E. Hahn, *Chem. Commun.*, 2010, **46**, 324–326.

7 (*a*) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978–4008; (*b*) K. M. Hindi, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Chem. Rev.*, 2009, **109**, 3859–3884; (*c*) P. J. Barnard, L. E. Wedlock, M. V. Baker, S. J. Berners-Price, D. A. Joyce, B. W. Skelton and J. H. Steer, *Angew. Chem., Int. Ed.*, 2006, **45**, 5966–5970; (*d*) A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier and W. J. Youngs, *J. Am. Chem. Soc.*, 2005, **127**, 2285–2291; (*e*) J. C. Garrison, R. S. Simons, C. A. Tessier and W. J. Youngs, *J. Organomet. Chem.*, 2003, **673**, 1–4.

8 F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape and D. Le Van, *Angew. Chem., Int. Ed.*, 2005, **44**, 3759–3763.

9 H. M. Bass, S. A. Cramer, J. L. Price and D. M. Jenkins, *Organometallics*, 2010, **29**, 3235–3238.

10 (a) F. E. Hahn, C. Radloff, T. Pape and A. Hepp, *Chem. Eur. J.*, 2008, **14**, 10900–10904.

11 C, Schulte to Brinke, T. Pape and F. E. Hahn, *Dalton Trans.* 2013, **42**, 7330–7337.

12 D. Wang, B. Zhang, C. He, P. Wu and C. Duan, *Chem. Commun.*, 2010, **46**, 4728–4730.

13 (*a*) A. Rit, T. Pape, A. Hepp and F. E. Hahn, *Organometallics*, 2011, **30**, 334–347; (*b*) A. Rit, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2010, **132**, 4572–4573; (*c*) A. Rit, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 6393–6401; (*d*) C. Segarra, G. Guisado-Barrios, F. E. Hahn and E. Peris, *Organometallics*, **33**, 2014, 5077–5080.

14 R. McKie, J. A. Murphy, S. R. Park, M. D. Spicer and S.-z. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 6525–6528.

15 S. R. Park, N. J. Findlay, J. Garnier, S. Zhou, M. D. Spicer and J. A. Murphy, *Tetrahedron*, 2009, **65**, 10756–10761.

16 K. Chellappan, N. J. Singh, I.-C. Hwang, J. W. Lee and K. S. Kim, *Angew. Chem., Int. Ed.*, 2005, **44**, 2899–2903.

17 (*a*) E. Alcalde, C. Alvarez-Rúa, S. García-Granda, E. García-Rodriguez, N. Mesquida and L. Pérez-García, *Chem. Commun.*, 1999, 295–296; (*b*) S. Ramos, E. Alcalde, G. Doddi, P. Mencarelli and L. Pérez-García, *J. Org. Chem.*, 2002, **67**, 8463–8468.

18 S. J. Gharpure, S. R. B. Reddy and U. Sanyal, *Synlett*, 2007, 1889–1892.

19 W. E. Lindsell, D. D. Palmer, P. N. Preston and G. M. Rosair, *Organometallics*, 2005, **24**, 1119–1133.

20 W. P. Fehlhammer, K. Bartel, U. Plaia, A. Völkl and A. T. Liu, *Chem. Ber.*, 1985, **118**, 2235–2254.

21 (*a*) T. A. P. Paulose, S.-C. Wu, J. A. Olson, T. Chau, N. Theaker, M. Hassler, J. W. Quail and S. R. Foley, *Dalton Trans.*, 2012, **41**, 251–260; (*b*) H. V. Huynh and R. Jothibasu, *Eur. J. Inorg. Chem.*, 2009, 1926–1931.

22 (*a*) C. Lu, S. Gu, W. Chen and H. Qiu, *Dalton Trans.*, 2010, **39**, 4198–4204; (*b*) Y. Unger, A. Zeller, M. A. Taige and T. Strassner, *Dalton Trans.*, 2009, 4786–4794.

23 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972–975.

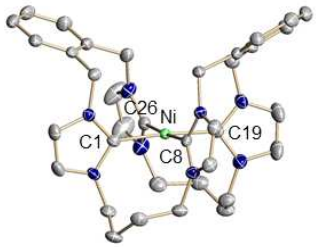
24 J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276–1278.

25 C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, **46**, 9016–9018.

26 *SMART*, Bruker AXS, 2000.

27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
28 Fadeeva, V. P.; Tikhova, V. D.; Nikulicheva, O. N. *J. Analyt. Chem.* **2008**, *63*, 1094–1106.

Graphic for table of contents



The flexibly bridged macrocyclic tetra-NHC ligand **4** reacts with d^8 transition metal ions to yield mononuclear complexes of type $[M(\mathbf{4})](PF_6)_2$ (M= Ni, Pd, Pt) while reaction with Ag^+ yields the tetranuclear sandwich-type octacarbene complex $[Ag_4(\mathbf{4})_2](PF_6)_4$.