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Confinement of a Au–N-heterocyclic carbene in a Pd₆L₁₂ metal–organic cage⁺

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A Au(I)–N-heterocyclic-carbene (NHC)-edged Pd₆L₁₂ molecular metal–organic cage is assembled from a Au(I)–NHC-based bipyridyl bent ligand and Pd²⁺. The octahedral cage structure is unambiguously established by NMR, electrospray ionization-mass spectrometry and single crystal X-ray crystallography. The electrochemical behaviour was analyzed by cyclic voltammetry. The octahedral cage has a central cavity for guest binding, and is capable of encapsulating PF_6^- and BF_4^- anions within the cavity.

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Introduction

The self-assembly of metal-organic cages (MOCs)¹⁻³ has been investigated for diverse potential applications, such as catalysis,⁴ sensing,^{5,6} molecular storage and sequestration,⁷ drug delivery,8 and so on. For MOCs the shape, cavity size, and ligand can influence their guest binding and transformation capability.9-11 N-heterocyclic-carbenes (NHCs) are a class of electrondonating ligands,12 and have been applied in catalyzing various organic transformations.13,14 Discrete assemblies based on NHC ligands including molecular metallocycles and cages have received increasing attention¹⁵⁻¹⁸ because they may induce reactivity change, selectivity and product distribution variation.19,20 However, few molecular cages with well-defined cavities are reported in the literature.²¹⁻²³ Remarkably, Nitschke et al. reported M_4L_6 (M = Zn(II), Cd(II)) cages with Au(I)-NHCbased ligand.23 In our effort to build NHC-based cages with large cavity, we wish to report herein that a Pd₆L₁₂ metalorganic cage containing twelve Au(I)-NHC centres is assembled from a rigid, bent N-heterocyclic-carbene-based bispyridyl ligand and palladium(II) ions.

Results and discussion

For the self-assembly of Pd_6L_{12} cage, bis(pyridyl)-functionalised Au(i)-NHC ligand L was designed and synthesized (Fig. 1a). First diiodo-functionalised imidazolium chloride (b) was synthesized from bis-Schiff's compound a^{24} and paraformaldehyde *via* a ring-closing step in the presence of

chlorotrimethylsilane. Then Au(1)-NHC compound c^{25} was synthesized by the reaction of imidazolium salt b with HAuCl₄·4H₂O and 3-chloropyridine in the presence of base (Na₂CO₃). Subsequently, L was synthesized by Suzuki-Miyaura cross-coupling reaction between c and 3-pyridylboronic acid (Fig. S1-S10[†]). ¹H NMR shows that the imidazolium C-H resonance appeared at δ 10.34 for **b** and disappeared for **L**. ¹³C NMR spectra show the resonance of the imidazolium C-H carbon at 139.60 ppm for **b** and the resonance of the metallated carbenecarbon atoms at 185.55 ppm. The coordination cage Pd₆L₁₂ was successfully assembled by heating a 2:1 mixture of L and Pd(NO₃)₂·2H₂O in DMSO at 70 °C for 6 h. ¹H NMR indicates that the quantitative formation of Pd_6L_{12} (12 NO_3^- anions are omitted for clarity, the same hereinafter) (Fig. 2 and S11[†]). The cage is highly symmetric. Compared with the free ligand L the original sharp signals of pyridine moieties turn into broad peaks and shift downfield, for example the signals at 9.05, 8.64 and 8.26 ppm for the H_i, H_h and H_c pyridyl protons are downfield-shifted to 9.74, 9.09 and 8.62 ppm, respectively, which is ascribed to the coordination of palladium(II) ions to the ligand.

Gratifyingly, single crystals of Pd_6L_{12} (NO_3^- salt) suitable for X-ray diffraction analysis were obtained over one month by slow diffusion of ethyl acetate vapour into a solution of Pd_6L_{12} in DMSO (Table S1†). The crystals crystallize in the trigonal space group $R\bar{3}$. The cubic symmetric unit is composed of six Pd(n)metal centres linked by twelve L ligands, forming the octahedron edges (Fig. 1b). Nevertheless, nitrate ions and solvent molecules could not be reasonably located in this highly disordered structure. The bend angle between pyridine rings and central Au–NHC ring is 174.1°. Two pyridyl donors on the same ligands adopt *syn*-conformation. The bond angles $C_{carbene}$ –Au–I_{trans} range from 176 to 179° are in fact close to linearity (C18–Au1–I1 176.1(11)°) and the Au1–C18 bond length of 1.96(3) Å, which is close to those of the reported (NHC)gold(1) complexes.²⁶ Each Pd(π) has a square planar geometry with Pd–

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Fig. 1 (a) Synthetic route of L, single crystal X-ray structures of Pd_6L_{12} , (b) sticks, (c) ball-and-stick model, (d) space-filling model. Anions, solvent molecules and hydrogen atoms are omitted for clarity. Color coding: C: gray; N: red; I: purple; Au: orange; Pd: blue.



Fig. 2 $\,^{1}\text{H}$ NMR spectra of (a) L and (b) $\text{Pd}_{6}\text{L}_{12}$ in DMSO- d_{6} (400 MHz, 298 K).

N bond distances of 1.98(2)–2.03(2) Å and the angle between the two 3-pyridyl coordinating motifs in L is 88–93°, within the normal range for those reported analogous pyridine-based ligand assembled Pd_6L_{12} complexes.^{27,28} The cavity size is approximately $20.2 \times 20.4 \times 28.7$ Å³, which is defined by the six $Pd(\pi)$ ions. The opposing $Pd(\pi)$ – $Pd(\pi)$ distance is 28.7 Å and adjacent Pd–Pd distances are 20.2–20.4 Å. One of the two diisopropyl groups on each ligand points to the cavity, and the C–C distance of diisopropyl groups on opposite ligands is 16.3 Å.

Further evidence for Pd₆L₁₂ was provided by ¹H-¹H homonuclear correlation spectroscopy (COSY) and ¹H-¹H nuclear overhauser effect spectroscopy (NOESY), which both reveal important cross peaks between the two observed sets of NMR signals (e.g. H_c-H_b and H_c-H_b) (Fig. S12 and S13[†]). In addition, diffusion-ordered NMR spectroscopy (DOSY) shows the selective formation of a single species (Fig. S14[†]). The same diffusion coefficient at $D = 5.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ corresponds to the dynamic radius of 19.0 Å according to the Stokes-Einstein equation.28 Further structural evidence was given by electrospray ionization-mass spectrometry (ESI-MS) (Fig. 3). After anion exchange of NO_3^- for PF_6^- ions in DMSO solution, a series of prominent peaks with continuous charge states of $[\mathbf{M} - (\mathbf{PF_6}^{-})_n]^{n+}$ (n = 4 - 8) were detected for $\mathbf{Pd_6L_{12}}$. The isotopic distribution patterns of each peak agreed well with the simulated patterns.

The chemical composition of L and Pd_6L_{12} were characterized by Fourier transform infrared spectroscopy (FT-IR) (Fig. S15†). The absorption of Pd_6L_{12} at 1632 cm⁻¹ corresponding to the C=N in-ring stretching in the pyridine rings shifts to lower energy compare with L at 1638 cm⁻¹, which is attributed to the coordination of L to Pd^{2+} *via* the nitrogen atom. Both L and Pd_6L_{12} exhibit characteristic C-N_{carbene} bands typically at 1467 and 1443 cm⁻¹.²⁹ The strong absorption band at approximately 1384 cm⁻¹ is attributed to the NO₃⁻ ions for Pd_6L_{12} .

To investigate the electrochemical behaviour, cyclic voltammetry analyses were carried out in the potential range from -2.0 Paper



Fig. 3 (a) ESI-TOF-MS spectrum of Pd_6L_{12} (M) (PF_6^- as counterion) and (b) measured (top) and calculated (bottom) isotope patterns for various charge states observed for $[Pd_6L_{12}]^{12+} \cdot 12PF_6^-$.

to +2.0 V at a scan rate of 50 mV s⁻¹ in a solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in dry DMSO $(0.10 \text{ mol } L^{-1})$ as a supporting electrolyte on glassy carbon electrode (3 mm in diameter) (Fig. 4). L gave a reduction wave at a potential of -1.068 V, indicating the reduction of Au(I) to metallic Au(0) corresponding to previously reported Au(1)-NHC analogues.^{30,31} The analogous process was significantly shifted to a more anodic potential at -0.890 V for Pd₆L₁₂. In addition to the reduction processes, a single irreversible oxidation peak was also observed at 0.812 V for Pd₆L₁₂, positively shifted by 0.287 V from L (+0.525 V), which is consistent with the oxidation processes of I⁻ to I₂ on clean glassy carbon surface.^{32,33} It is worth noting that a new irreversible cathodic potential appeared at -0.732 V, attributed to the reduction process of NO₃⁻ to NO₂⁻ within the cage,³⁴ perhaps owing to the change of ionic status in the cavity after coordination.35 The reduction



Fig. 4 Cyclic voltammograms of (a) L and (b) Pd_6L_{12} in DMSO solution at a scan rate of 50 mV s⁻¹, results are reported *versus* Ag wire.

current for Pd_6L_{12} were acquired at scan rates of 50–200 mV s⁻¹, showing that two reduction waves are located below the scan rates of 100 mV s⁻¹ (Fig. S16†). With the increase in the sweep rate, the two waves merge into one broad peak, suggesting that the redox process takes place under simple diffusion-control for the cage.³⁶

The resulting cage structure of Pd₆L₁₂ was further investigated to explore its encapsulation of anions. The original nitrate anions are difficult to detect by NMR, so anion exchange of nitrate with other anions were performed. Various anions (20 equiv., excess) were added to a DMSO solution of Pd_6L_{12} $(0.75 \text{ mmol } L^{-1})$ and the mixture was allowed to react for 4 h at room temperature, then diethyl ether was added to precipitate out pale yellow solid prior to the acquisition of NMR spectroscopy. After the introduction of NaPF₆ ³¹P NMR spectroscopy shows that phosphorus resonances from PF_6^- in DMSO appear expected sharp septet, with the main peak at δ –144.19 ppm with coupling constant of $J_{\rm PF} = 711.2 \text{ Hz}$,³⁷ while bound $PF_6^$ anions display the multiplets centred on δ –142.70 ppm, shifted by $\Delta \delta = 1.49$ ppm with $J_{\rm PF} = 719.3$ Hz to lower field (Fig. 5a and S17[†]). Moreover, ¹⁹F NMR shows that one new set of peaks at -65.19 ppm ($J_{\rm FP} = 725.7$ Hz) are downshifted with free PF₆⁻ $(-70.15 \text{ ppm}, J_{\text{FP}} = 710.6 \text{ Hz})$ (Fig. 5b and S18[†]). Additionally for ¹H NMR H_i proton resonance inside the central cavity is upfield shifted by 0.70 ppm (Fig. S19[†]), while other proton resonances are essentially unaffected. These results demonstrate that two types of PF₆⁻ anions are present in the solution, some are



Fig. 5 (a) 31 P NMR (162 MHz, 298 K), and (b) 19 F NMR (376 MHz, 298 K) spectra of PF₆⁻@Pd₆L₁₂ in DMSO-*d*₆.

encapsulated within the cavity, and others are free in the solution.

BF₄⁻ anions can also be encapsulated inside the cavity. With the addition of KBF₄ to Pd₆L₁₂, ¹⁹F NMR shows two signals, one strong signal at –148.27 ppm corresponding well with the peak of free BF₄⁻ in DMSO-*d*₆ (–148.3 ppm), and the other new signal at –144.1 ppm (Fig. S20 and S21†). ¹¹B NMR show that a new signal at 2.79 ppm is also assigned to bound BF₄⁻ in the cavity (Fig. S22 and S23†).^{38,39} Simultaneously ¹H NMR reveals that the proton resonance of H_i inside the central cavity is shifted upfield ($\Delta \delta = 0.30$ ppm) compared to Pd₆L₁₂ (Fig. S19†). These results suggest that some BF₄⁻ anions are bound within the cavity of Pd₆L₁₂. However, addition of OTf⁻ to Pd₆L₁₂ causes neither new signals nor notable shifts, and ¹⁹F NMR gives only one sharp signal corresponding to free OTf⁻, suggesting that the nitrate ions in the cage was unaffected by OTf⁻ (Fig. S19 and S24†).

Conclusions

In summary, we have successfully synthesized Au(1)–NHC bispyridine ligand (L) and Au(1)–NHC-edged Pd₆L₁₂ coordination cage has been assembled from L and Pd²⁺. The cage Pd₆L₁₂ has been fully characterized by NMR, diffusion-ordered NMR spectroscopy, FT-IR, mass spectrometry and cyclic voltammogram. The single crystal X-ray diffraction confirms unequivocally the octahedral structure of Pd₆L₁₂. The octahedral cage has central cavity for guest binding, and has been shown to be capable of encapsulating PF₆⁻ and BF₄⁻ anions within the cavity. It paves a way to build NHC-based metal-organic container molecules with large cavity for subsequent guest binding and transformation.

Experimental

Synthesis of L

A mixture of c (689.1 mg, 0.715 mmol), 3-pyridylboronic acid (357.5 mg, 2.86 mmol), anhydrous potassium carbonate (988.1 mg, 7.15 mmol), tetrakistriphenylphosphine palladium(0) (0.00715 mmol, 8.3 mg) in 18 mL degassed DMF-H₂O (v/v = 5:1) was stirred at 100 °C for 24 h under argon atmosphere, the progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed and the residue was dispersed in water and extracted with CH₂Cl₂. The CH₂Cl₂ solution was washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography on silica gel (ethyl acetate : hexane 1:1) to give the product as white powder which was further purified by washing with hexane (464 mg, 75%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.05 (s, 2H), 8.64 (s, 2H), 8.27-8.22 (m, 2H), 8.08 (s, 2H), 7.76 (s, 4H), 7.57-7.53 (m, 2H), 2.59 (dt, J =14.0, 6.9 Hz, 4H), 1.36 (d, J = 6.8 Hz, 12H), 1.30 (d, J = 6.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃): δ 185.55, 149.02, 148.43, 146.49, 140.41, 136.25, 134.79, 133.79, 123.65, 123.29, 123.14, 29.04, 24.48, 24.06. Q-TOF-MS(ESI⁺) (m/z): calcd. for $[M + H]^+$ $[C_{37}H_{43}N_4AuI + H]^+$ 867.2198, found 867.2206 and calcd for [M-AuI + H]⁺ $[C_{41}H_{44}N_2O_2 + H]^+$ 543.3488, found 543.3471.

Synthesis of Pd₆L₁₂

L (174.0 mg, 0.2 mmol) and Pd(NO₃)₂·2H₂O (27.0 mg, 0.1 mmol) were dissolved in DMSO (10.0 mL) were mixed. Each time 1 mL of the mixture was taken and stirred at 70 °C for 6 h. The quantitative formation of Pd₆L₁₂ was confirmed by ¹H NMR and ¹H DOSY NMR. The addition of diethyl ether to the yellow homogeneous solution precipitated the product, and it was collected by filtration, washed with diethyl ether, and dried in vacuo to give a pale yellow solid (13.8 mg, 70%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.74 (s, 2H), 9.08 (s, 2H), 8.60 (s, 2H), 7.88 (d, J = 39.1 Hz, 8H), 2.55 (s, 4H), 1.35 (s, 24H). ¹H DOSY NMR (400 MHz, DMSO- d_6): $D = 7.16 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Pd₆L₁₂ (PF₆⁻ salt) was prepared by adding excess NaPF₆ to the DMSO solution of Pd₆L₁₂. Electrospray ionization mass spectra were recorded for $Pd_{6}L_{12}$ (PF_{6}^{-} salt). m/z calcd for $C_{444}H_{504}N_{48}Au_{12}I_{12}P_{8}F_{48}Pd_{6}$ [M- $4(PF_6)$ ⁴⁺ 3049.4240, found 3049.4123; m/z calcd for C₄₄₄H₅₀₄- $N_{48}Au_{12}I_{12}P_7F_{42}Pd_6 [M-5(PF_6)]^{5+}$ 2410.5462, found 2410.5425; m/z calcd for $C_{444}H_{504}N_{48}Au_{12}I_{12}P_6F_{36}Pd_6$ $[M-6(PF_6)]^{6+}$ 1984.6278, found 1984.6254; *m/z* calcd for C₄₄₄H₅₀₄N₄₈Au₁₂I₁₂- $P_5F_{30}Pd_6[M-7(PF_6)]^{7+}$ 1680.4003, found 1680.3982; m/z calcd for $C_{444}H_{504}N_{48}Au_{12}I_{12}P_4F_{24}Pd_6$ [M-8(PF₆)]⁸⁺ 1452.2296, found 1452.2276; m/z calcd for $C_{74}H_{84}N_8Au_2I [2L-I]^+$ 1605.5190, found 1605.5175.

X-ray crystallography for Pd_6L_{12}

Quality single crystals were obtained by the slow diffusion of ethyl acetate vapour into a DMSO solution of Pd₆L₁₂ (NO₃⁻ salt) to give colourless crystals of Pd₆L₁₂ over one month. A crystal was picked $(0.2 \times 0.2 \times 0.2 \text{ mm}^3)$ and coated in paratone oil, attached to a glass silk which was inserted in a stainless steel stick, then quickly transferred to the Agilent Technologies SuperNova X-ray diffractometer with the Enhance X-ray Source of Cu Ka radiation ($\lambda = 1.54184$ Å) using the ω - ϕ scan technique. Data collection were measured at 150.00 (10) K. The unit cell parameters were solved by direct methods and the unit cell parameters refined against all data by anisotropic full-matrix least-squares methods on F² with the SHELXL program.⁴⁰ Hydrogen atoms were calculated in ideal positions (riding model). All nitrate ions and solvent molecules could not be reasonably located because of highly disordered structures, and were removed by PLATON/SQUEEZE routine.41

Crystallographic data for Pd_6L_{12} : $C_{74}H_{84}Au_2I_2N_8Pd$ FW = 1839.62, trigonal, $R\bar{3}$, a = 29.8768 (16) Å, b = 29.8768 (16) Å, c = 74.341 (3) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 120^{\circ}$, V = 57 468 (7) Å³, Z = 18, T = 150.00 (10) K, $\lambda = 1.54184$ Å, $\rho_{calcd} = 0.957$ mg m⁻³, $\mu = 9.349$ mm⁻¹, 13 205 reflections were collected (7693 were unique) for $6.856 < 2\theta < 79.938$, R(int) = 0.0372, $R_1 = 0.0888$, w $R_2 = 0.2668$ [$I \ge 2\sigma(I)$], $R_1 = 0.1033$, w $R_2 = 0.2821$ (all data) for 725 parameters and 825 restraints, GOF = 1.059. Selected bond lengths and bond angles are presented in Table S1.† The crystal structure was submitted to the Cambridge Structural Database under the CCDC number 2013514.

Conflicts of interest

There are no conflicts to declare.

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