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Tetrahedral Cage Complex with Planar Vertices: Selective Synthesis of Pt₄L₆ Cage Complexes Involving Hydrogen Bonds Driven by Halide Binding†

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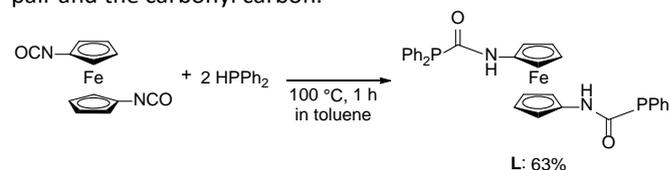
The reaction of Fe(η -C₅H₄NHC(O)PPh₂)₂ (L) with PtX₂(PPh₃)₂ selectively formed cage-shaped complexes formulated as [(PtX)₄(L)₆]X₄·CHCl₃ (X = Cl, Br), in which the four square-planar Pt fragments were situated at each vertex and the six Ls were located in each side of a tetrahedral framework and hydrogen bonds existed between the NH groups in Ls and X⁻ ions inside the cage.

In the last few decades, the chemistry of metal-organic cage complexes has developed rapidly because of their fascinating structures and potential applications,¹ and controllable synthesis of metal-organic cage complexes is still a great challenge. Many systems involve using *rigid* frameworks to control the geometry and symmetry of the final architecture (e.g., 4,4'-bipyridine,² 1,3,5-tris((4-(diphenylphosphino)ethynyl)phenyl)benzene³). Recently, some discrete assemblies were synthesized by introducing organic ligands with *flexible* arms such as methylene, but these were restricted to ligands with three or more coordination atoms.⁴ A template-directed strategy is also a powerful method for selective construction of molecular assemblies.^{4g-i, 4k-n, 5} However, the template molecule should be removed in order to use the internal cavity, since it occupies the internal space in many cases.

Herein, we report an unprecedented selective synthesis of M₄L₆ cage complexes using a flexible ligand with two coordination parts and without addition of a particular template molecule. The reaction of new 1,1'-ferrocene derivative Fe(η -C₅H₄NHC(O)PPh₂)₂ (L) with PtX₂(PPh₃)₂ gave [(PtX)₄(L)₆]X₄, adopting a tetrahedral framework. In the cavity, hydrogen bonds formed between the NH groups of phosphinecarboxamidyl moieties and halide ions derived from PtX₂(PPh₃)₂ immediately below each vertex of the cage.

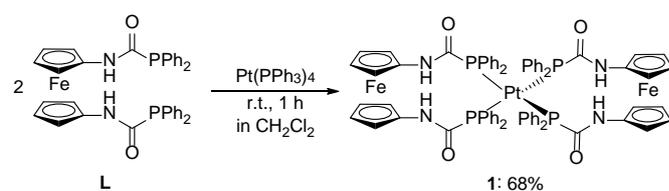
First, 1,1'-bis(phosphinecarboxamidyl)ferrocene, L, was

prepared via the reaction of Fe(η -C₅H₄NCO)₂ with diphenylphosphine for 1 h at 100 °C in toluene (Scheme 1). Ligand L was characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy, and elemental analysis. In the ³¹P{¹H} NMR spectrum, L showed a singlet at δ = -2.06 ppm in the range expected for a phosphinecarboxamide.⁶ The molecular structure was confirmed by single-crystal X-ray structure analysis (see ESI, Fig. S22). No intramolecular hydrogen bond was observed. The P–C bond length was 1.886(2) Å, which was slightly longer than the sum of the single-bond covalent radii for the elements (1.80–1.86 Å).⁷ The C–O and C–N bond distances were consistent with those of other carboxamides in the literature.⁸ These results indicate significant delocalization of π -electron density between the carbonyl and amide groups and no significant π -interaction between the phosphine lone pair and the carbonyl carbon.



Scheme 1 Synthesis of ligand L.

Next, we attempted a reaction of L with zero-valent platinum complex Pt(PPh₃)₄ because Goicoechea's group has reported the first transition metal complexes of phosphinecarboxamide (H₂NC(O)PH₂) in which a phosphorus atom coordinates to the transition metal.⁹ The reaction shown in Scheme 2 afforded poorly soluble complex **1** identified by EA and X-ray structure analyses (see ESI, Fig. S23). Complex **1** has a four-coordinate tetrahedral geometry around the platinum center and L behaves as a bidentate ligand.

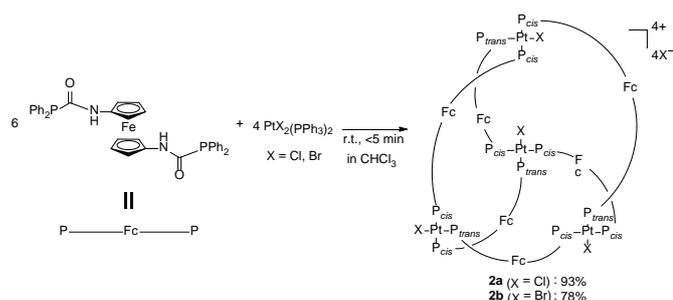


Scheme 2 Reaction of L with Pt(PPh₃)₄.

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In contrast, the reaction of **L** with divalent platinum complex $\text{PtX}_2(\text{PPh}_3)_2$ in chloroform led to unexpected results (Scheme 3). The suspension was vigorously stirred at room temperature to provide a red solution within a few minutes. Red crystals were obtained upon diffusion of *n*-hexane vapor into the chloroform solution. The crystal structures revealed that the M_4L_6 cage complexes were formed and one solvent molecule and four X^- ions from Pt centers were encapsulated ($[\text{CHCl}_3\text{c-2a}]$: Fig. 1, $[\text{CHCl}_3\text{c-2b}]$: Fig. 2). The four square-planar Pt(II) centers were bridged by six **L**s. The structure displays S_4 symmetry. This is the first report of an M_4L_6 platinum-organic cage complex.¹⁰



Scheme 3 Reaction of **L** with $\text{PtX}_2(\text{PPh}_3)_2$.

The N–Cl and N–Br distances were 3.120(10)–3.339(9) and 3.238(10)–3.402(9) Å, respectively. These results indicate the existence of a hydrogen bond, which is shown as $(\text{N}-\text{H})_3 \cdots \text{X}^-$. Molina's group has reported a ferrocene-based urea in which the NH group acted as a strong hydrogen-bonding site for F^- or H_2PO_4^- .^{11, 12} Hydrogen bonding is a well-precedented strategy for multicomponent self-assembly.^{4k, 4l, 5f} In the crystal structure of $[\text{CHCl}_3\text{c-2a}]$, three chloroform chlorine atoms are facing Cl^- ions in the cage, and the $\text{Cl} \cdots \text{Cl}$ interaction (halogen bonding)¹³ is formed (Pt–Cl \cdots Cl–C distance is 3.110(6)–3.308(6); these distances are shorter than that reported previously^{13a, 13b}). In contrast, the chloroform is arranged to be separated from Br^- ions in the structure of $[\text{CHCl}_3\text{c-2b}]$.

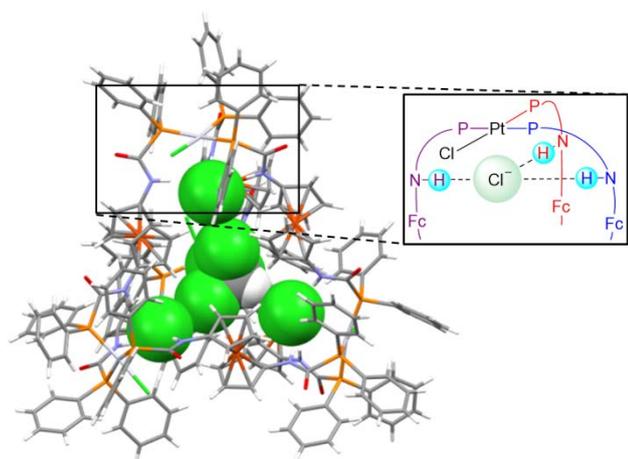


Fig. 1 Crystal structure of $[\text{CHCl}_3\text{c-2a}]$. All solvent molecules except one in the cavity are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt– P_{trans} = 2.256(3)–2.270(2), Pt– P_{cis} = 2.323(2)–2.344(3), Pt–Cl = 2.350(3)–2.364(3), P–C(O) = 1.866(12)–1.935(11), N–C(O) = 1.316(17)–1.360(12), N–Cl = 3.120(10)–3.339(9); $\text{P}_{\text{cis}}-\text{Pt}-\text{P}_{\text{trans}}$ = 93.74(9)–98.02(10), $\text{P}_{\text{cis}}-\text{Pt}-\text{Cl}$ = 80.09(9)–88.63(10).

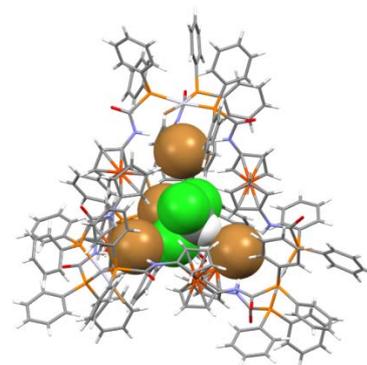


Fig. 2 Crystal structure of $[\text{CHCl}_3\text{c-2b}]$. All solvent molecules except one in the cavity are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt– P_{trans} = 2.267(3)–2.286(2), Pt– P_{cis} = 2.327(3)–2.366(3), Pt–Br = 2.4804(12)–2.5030(10), P–C(O) = 1.862(17)–1.921(9), N–C(O) = 1.310(13)–1.351(13), N–Br = 3.238(10)–3.402(9); $\text{P}_{\text{cis}}-\text{Pt}-\text{P}_{\text{trans}}$ = 93.50(8)–96.47(9), $\text{P}_{\text{cis}}-\text{Pt}-\text{Br}$ = 80.49(6)–89.25(7).

Leaving crystals of $[\text{CHCl}_3\text{c-2a}]$ and $[\text{CHCl}_3\text{c-2b}]$ under reduced pressure gave orange powders of **2a** and **2b**, respectively, containing no guest molecule (CHCl_3). Complicated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2a** and **2b** were observed in solution at room temperature (Fig. 3a and ESI). Each signal was accompanied by broad ^{195}Pt satellite signals. The gNMR simulations of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were in excellent agreement with the observed spectra (Fig. 3b and ESI). The corresponding gNMR simulated spectra have been fitted to ABX spin systems where A, B = $^{31}\text{P}_{\text{cis1, cis2}}$ and X = $^{31}\text{P}_{\text{trans}}$. These results indicate that there are three chemically inequivalent phosphorus atoms in our cage molecules. In the ^1H NMR spectra of **2a** and **2b** in Fig. 3c and ESI, the twelve peaks for Cp rings are sharp, indicating the cage structure rather than a non-discrete aggregate. The obvious down-field shift assigned to NH protons in the ^1H NMR spectrum suggests the presence of strong hydrogen bonding between the NH groups and Cl^- .¹⁴ Cl^- would be immobilized in the cage. The NMR spectra revealed that the X-ray structure was maintained in solution. The fact that M_4L_6 -type compounds **2a** and **2b** exist in solution was also supported by high-resolution electrospray mass spectrometry (ESI-MS) (see ESI, Figs. S10 and S17). The distinct peaks observed correspond to $[\mathbf{2a}]^{2+}$ and $[\mathbf{2b}]^{2+}$, and matched the simulated isotopic patterns well.

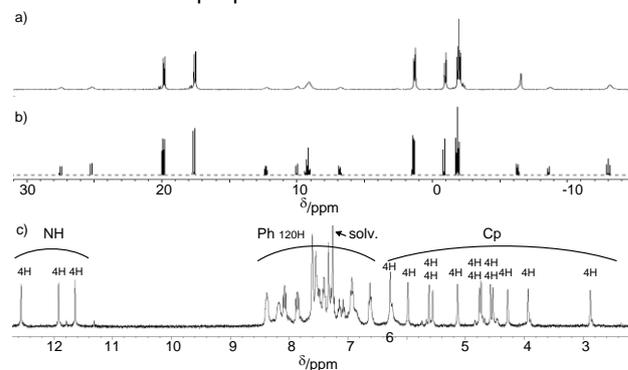


Fig. 3 (a) $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , rt, 161.7 MHz) and (b) gNMR simulated spectra of **2a**. (c) ^1H NMR spectrum (CDCl_3 , 40 °C, 400 MHz) of **2a**.

In metal-organic cage complexes^{1–5} and metal-organic frameworks¹⁵ reported thus far, the vertex or intersection component in molecular assemblies is a metal atom that roughly regulates the angle (Fig. 4, left). The construction of an M_4L_6 tetrahedral cage containing a square-planar metal center as the vertex component is far from easy because each vertex angle of a tetrahedron is 109.5° . Therefore, square-planar complexes have not been used at the vertex positions when constructing tetrahedral cage complexes. Complexes $[\text{CHCl}_3\text{-}2\mathbf{a}]$ and $[\text{CHCl}_3\text{-}2\mathbf{b}]$ reported in this paper are quite unique because they are tetrahedral cage complexes and four square-planar Pt complexes are located at the vertex positions (Fig. 4, right). Moreover, each Pt plane is perpendicular to the axis passing through the center of the cage and the vertex, showing that the L–Pt–L angle (ca. 90°) is not involved in the vertex angle of the cage structure. Another unique characteristic of our system is that a halide ion derived from the starting Pt complex is situated immediately below the Pt plane (in other words, just inside the cage structure) and forms hydrogen bonds with three NH groups in the three ligands of the Pt complex. These $(\text{NH})_3\cdots\text{X}^-$ hydrogen bonds keep the Pt complex at the vertex position, namely halide ions bind the ligands (halide binding), and eventually construct the tetrahedral cage complex. One halide out of two in the starting square planar $\text{PtCl}_2(\text{PPh}_3)_2$ moves, during the reaction, to the position below a Pt coordination plane (inside the cage), but still keeps a space available for a guest molecule (CHCl_3 in our case).

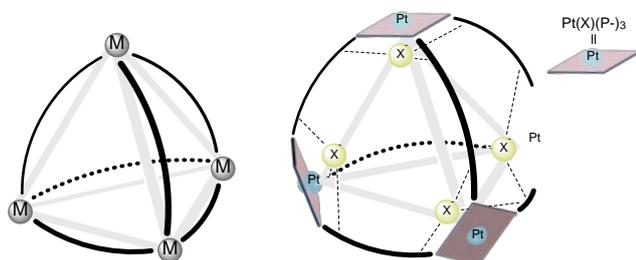
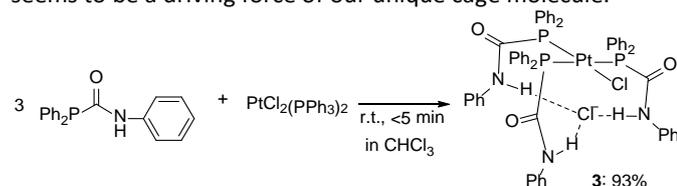


Fig. 4 Difference in the vertex for M_4L_6 tetrahedral cage complexes.

On the basis of the crystal structure of $[\text{CHCl}_3\text{-}2\mathbf{a}]$, the Pt fragment shown in the inset in Fig. 1 is considered as a basic unit; $2\mathbf{a}$ consists of four of the basic units. The phosphinecarboxamide $\text{PhNHC}(\text{O})\text{PPh}_2$ is a simplified version of \mathbf{L} , where the ferrocenyl group is replaced by a phenyl group. The reaction of $\text{PhNHC}(\text{O})\text{PPh}_2$ in place of \mathbf{L} with $\text{PtCl}_2(\text{PPh}_3)_2$ was expected to afford a Pt complex similar to that shown in the inset in Fig. 1. The reaction took place immediately and gave $\mathbf{3}$ in excellent yield (Scheme 4). The X-ray structure (Fig. 5) revealed that $\mathbf{3}$ corresponded to the Pt complex at the vertex position of $[\text{CHCl}_3\text{-}2\mathbf{a}]$. Therefore, the formation of $\mathbf{3}$ seems to be a driving force of our unique cage molecule.



Scheme 4 Reaction of $\text{PhNHC}(\text{O})\text{PPh}_2$ with $\text{PtCl}_2(\text{PPh}_3)_2$.

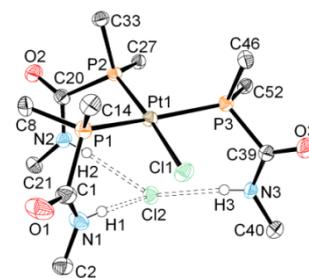


Fig. 5 ORTEP drawing of $\mathbf{3}$ (thermal ellipsoids at 50% probability). All hydrogen atoms, solvent molecules, and Ph rings (except *ipso*-C) are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Pt(1)–P(1) = 2.3116(7), Pt(1)–P(2) = 2.2568(8), Pt(1)–P(3) = 2.3448(7), Pt(1)–Cl(1) = 2.3591(7), P(1)–C(1) = 1.883(3), P(2)–C(20) = 1.904(3), P(3)–C(39) = 1.893(3), N(1)–C(1) = 1.352(4), N(2)–C(20) = 1.362(4), N(3)–C(39) = 1.352(4), N(1)–Cl(2) = 3.395(3), N(2)–Cl(2) = 3.224(3), N(3)–Cl(3) = 3.227(3); P(1)–Pt(1)–P(2) = $94.15(3)$, P(2)–Pt(1)–P(3) = $101.27(3)$, P(1)–Pt(1)–Cl(1) = $81.13(3)$, P(3)–Pt(1)–Cl(1) = $83.50(3)$.

We examined two reactions in order to explore the importance of hydrogen bonds between NH groups and halide ions in our synthetic system. First, the reaction of diiodo-platinum complex $\text{PtI}_2(\text{PPh}_3)_2$ with \mathbf{L} was examined, and it was found that the corresponding cage complex was not obtained. The reaction of $\text{PhNHC}(\text{O})\text{PPh}_2$ with $\text{PtI}_2(\text{PPh}_3)_2$ also did not give corresponding complex to $\mathbf{3}$. The lower electronegativity of I compared to Cl or Br might be responsible for the lack of a hydrogen bond. These results indicate that the hydrogen bond between the phosphinecarboxamide ($\text{RNHC}(\text{O})\text{PR}'_2$) and a halide ion lead to the formation of the cage structure. Next, the reaction of $\text{PtCl}_2(\text{PPh}_3)_2$ with phosphinethiocarboxamide ligand $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{NHC}(\text{S})\text{PPh}_2)_2$ (\mathbf{L}'), which was synthesized according to a previously reported method,⁶ was examined. The NMR spectrum of the reaction mixture showed that a complicated mixture was obtained although an NH group in thioamide is expected to bind an anion such as Cl^- stronger than that in amide.¹⁶ This result indicates that appropriate acidity of an NH group is important to keep the cage-shaped molecule.

In summary, we have succeeded in the selective synthesis of unprecedented tetrahedral organic cage complexes involving square-planar Pt complexes. The hydrogen bond between a phosphinecarboxamide and a halide ion plays a significant role in the formation of the cage structure.

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