Tetraplatinum precursors for supramolecular assemblies: syntheses, crystal structures, and stereoselective self-assemblies of [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-N_4-DArBp)] (DArBp = 1,3-bis(arylbenzamidinate)propane)†

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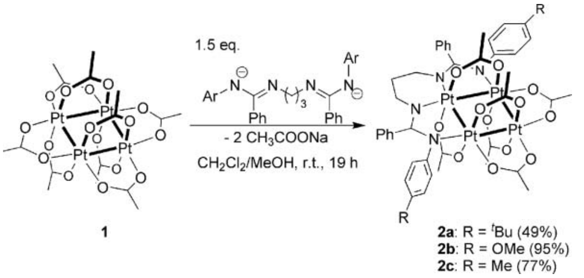
Treatment of the *cisoid*-capped complex [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-N_4-DAr′Bp)] (2a), which was obtained from the reaction of [Pt_4(μ-$OCOCH_3$)$_8$] (1) with Na_2D^{t}BuPhBp (D^{t}BuPhBp = 1,3-bis(*para-tert*-butylphenylbenzamidinate)propane), with an equimolar amount of 1,1′-ferrocenedicarboxylic acid undergoes a stereoselective self-assembly to afford an indented-quadrangle tetramer [Pt_4(μ-$OCOCH_3$)$_4$(κ^4-N_4-D^{t}BuPhBp){Fe(C_5H_4COO)$_2$}]$_4$ (4) as a single diastereomer.

Supramolecular assemblies of metal centers as entities are a major focus of attention because the molecular architecture is tunable through not only varying the types of metal fragments and organic linkers in the assembly, but their composition ratio as well.[1–11] Mononuclear units are still used as major building blocks, while multinuclear units, especially metal-metal bonded clusters with three or more metal centers, are rarely used.[12–15] We have constructed a new series of supramolecular arrays composed of a tetraplatinum cluster, [Pt_4(μ-$OCOCH_3$)$_8$] (**1**),[16] which is a suitable building block because four platinum atoms lie at the four corners of a square and four *in*-plane acetate ligands are selectively replaced by free carboxylic acids in solution.[17] We recently reported that the selective mono-substitution of the *in*-plane acetates of **1** with α,ω-alkenyl carboxylic acids and the subsequent metathesis coupling reaction lead to well-defined Pt_8 clusters, [{Pt_4(μ-$OCOCH_3$)$_7$}$_2${μ-OCO(CH_2)$_n$CH=CH(CH_2)$_n$(μ-OCO)}] (n = 2 and 3),[18] whereas treatment of **1** with half the amount of dicarboxylic acid, which was considered to be the simplest and shortest route for the synthesis of a Pt_4–Pt_4 cluster linked with the dicarboxylate spacer, results in the precipitation of insoluble black organoplatinum compounds.[18] This result led us to introduce appropriate *nonlabile* ligands into the tetraplatinum system to design and synthesize further systematic architectures. *N*,*N*′-Diarylformamidinates are used as inert bridges in dinuclear paddlewheel system,[7,13] and therefore, its derivatives are expected to be nonlabile ligands even in our system because the nitrogen atom, in general, coordinates more tightly to late transition metals than the oxygen atom. In addition, their steric hindrance, which arises from bulky aromatic rings on the nitrogen atoms, enables regioselective modification of the Pt_4 framework. Herein, we report the synthesis of tetraplatinum complexes with a *cisoid* arrangement of nonlabile tetradendate ligand, DArBp, which is consist of two amidinates linked with a trimethylene chain. We also disclose that the self-assembly of the *cisoid*-capped tetraplatinum precursor with dicarboxylic acids gave the tetramer [Pt_4(μ-$OCOCH_3$)$_4$(κ^4-N_4-D^{t}BuPhBp)(μ-OCO-R-OCO-μ)]$_4$ (D^{t}BuPhBp = 1,3-bis(*para-tert*-butylphenylbenzamidinate)propane).

A novel building unit [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-N_4-D^{t}BuPhBp)] (**2a**) with a *cisoid* arrangement was prepared by reacting **1** with an excess amount of Na_2D^{t}BuPhBp in CH_2Cl_2–MeOH (eqn (1)). Notably, the steric hindrance attributable to the aromatic rings on the N atoms prevents the incorporation of the second D^{t}BuPhBp ligand into the Pt_4 frame. Similar complexes [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-N_4-DAniBp)] (**2b**) (DAniBp = 1,3-bis(*para*-methoxyphenylbenzamidinate)propane) and [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-N_4-DTolBp)] (**2c**) (DTolBp = 1,3-bis(*para*-tolylbenzamidinate)propane) with the *cisoid* geometry were prepared.



(1)

The ^{1}H NMR spectrum of **2a** displayed three singlet signals attributable to the acetate ligands at δ 1.79 (*out*-plane), 2.05 (*out*-plane), and 2.18 (*in*-plane) with the same intensity of 6H. Characteristics resonances due to the D^{t}BuPhBp moiety were observed at δ 1.18 (s, 18H) assigned to the *t*-butyl groups. The X-ray structural determination of **2a** confirmed that two amidinate ligands bridge two platinum atoms on the adjacent sides of the Pt_4 square, and two *in*-plane acetates remain intact (Fig. 1).‡ The square planar geometry of the Pt_4 moiety is consistent with the four Pt–Pt bond distances of *ca.* 2.513 Å and a sum of the internal angles of 355.73°. The averaged Pt–Pt bond distance was comparable to that of the parent complex **1** (2.495 Å).[16] The averaged Pt–O_{eq} value of 2.23 Å in **2a**, where O_{eq} was the coordinating atom of the *in*-plane acetate, is longer than that of **1** (about 2.17 Å), probably due to a *trans* influence through the Pt–Pt sequence. This finding indicated that the *in*-plane acetates of

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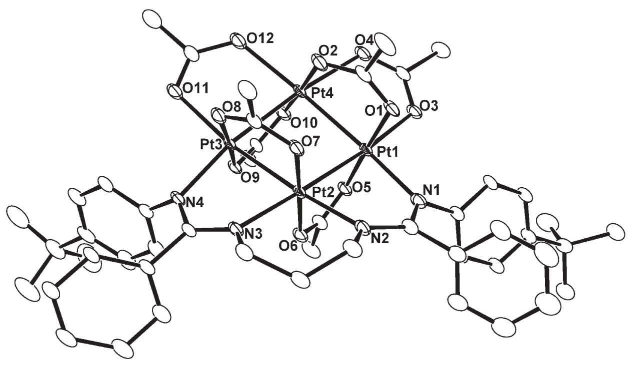
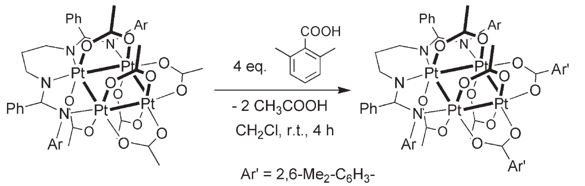


Fig. 1 Molecular structure of **2a** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules are omitted for clarity.

2a are more labile and more easily replaced by other carboxylates than those of **1**. It should be mentioned that complex **2** consists of an enantiomeric pair (called the Λ form and Δ form, Scheme 1).§

Reaction of **2** with a slight excess of 2,6-dimethylbenzoic acid in dichloromethane at ambient temperature selectively replaced the *in*-plane acetates to give [$Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-}N_4\text{-}DArBp)(\mu\text{-}OCOAr')_2$] (**3**: Ar′ = $2,6\text{-}C_6H_3(CH_3)_2$) (eqn (2)). It is critical not only that the DArBp ligand in **2** is not replaced even when an excess amount of 2,6-dimethylbenzoic acid has been added but also that the protection ligand doesn't disturb the replacement of the *in*-plane acetates. The molecular structure of the *cisoid*-oriented bisbenzoate derivative **3a** was determined by X-ray analysis.¶ This analysis clearly indicated that the introduced amidinates have a role in controlling the *in*-plane reaction site in which the substitution reactions occurred.



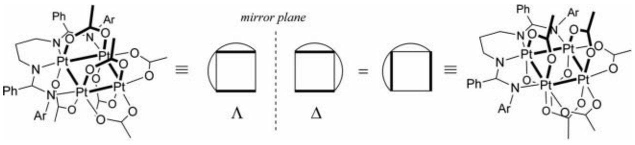
(2)

Ar′ = $2,6\text{-}Me_2\text{-}C_6H_3\text{-}$

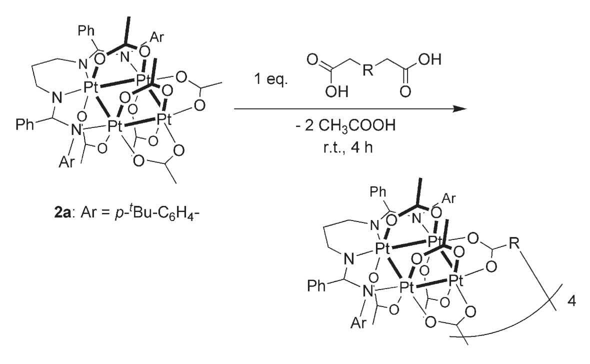
2a: Ar = $p\text{-}{}^tBu\text{-}C_6H_4\text{-}$
2b: Ar = $p\text{-}MeO\text{-}C_6H_4\text{-}$
2c: Ar = $p\text{-}Me\text{-}C_6H_4\text{-}$

3a (70%)
3b (86%)
3c (48%)

Self-assembly of the Pt_4 precursor was accomplished by treating **2a** with an equimolar amount of 1,1′-ferrocenedicarboxylic acid in a CH_2Cl_2–MeOH solution, giving the tetramer [$Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-}N_4\text{-}D^tBuPhBp)\{Fe(C_5H_4COO)_2\}$]$_4$ (**4**) in 46% isolated yield (eqn (3)).[19] It was unexpected that tetramer **4** is obtained as a single diastereomer,[20] in which all of the tetraplatinum entities in **4** are the same enantiomer, though four diastereomeric (and their enantiomeric isomers) candidates result from their combination with the enantiomers (Λ and Δ) of **2a**, indicating that molecular recognition proceeds during this reaction.



Scheme 1 Enantiomeric pairs of the *cisoid*-capped complex **2**. Two arcs represent a DArBp ligand, and heavy-lines and solid-lines are *out*-plane acetates upward and downward from the Pt_4 plane, respectively.



2a: Ar = $p\text{-}{}^tBu\text{-}C_6H_4\text{-}$

(3)

4: R = $1,1'\text{-}(C_5H_4)_2Fe$ (46%)
5: R = 4,4′-biphenyl (87%)

The most appropriate representation of the molecular form of **4** is an indented quadrangle composed of four Pt_4 entities and four 1,1′-ferrocenedicarboxylic acids (Fig. 2),‖ the former of which compose the four corners of the quadrangle and the latter of which act as linkers to connect the two Pt_4 units in two different manners alternately (Scheme 2). If the angles formed by two intramolecular carboxylate groups in the ferrocene linkers were 180°, the self-assembled structure would be an uneven quadrangle, as outlined in

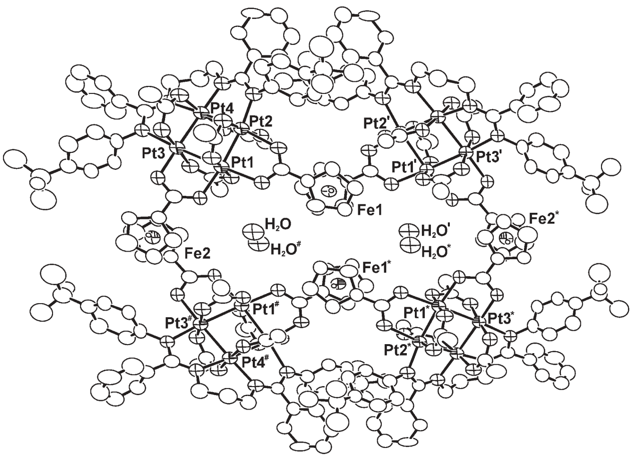
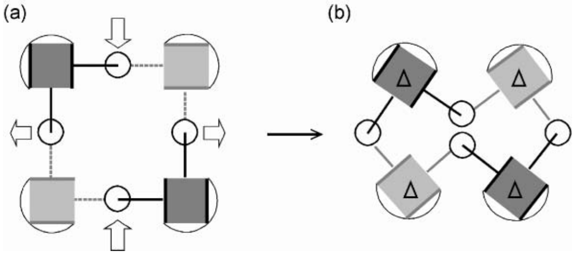


Fig. 2 Molecular structure of **4** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity. One of the two independent tetramers in a unit cell of **4** is depicted. Symmetry transformations used to generate equivalent atoms Pt*: x, $-y + 1/4$, $-z + 1/4$; Pt$^{\#}$: $-x + 1/4$, y, $-z + 1/4$; Pt′: $-x + 1/4$, $-y + 1/4$, z.



Scheme 2 Views showing frame formats: (a) plausible structure of **4** with straight angles formed by two intramolecular carboxylate groups in 1,1′-ferrocenedicarboxylic acid, and (b) the actual structure of **4** with bent angles.

Scheme 2a, however, the observed angles of Fc1 and Fc2 in complex **7** are 125.6° and 115.9°, respectively (Scheme 2b).[21] Based on the observation of two nonequivalent *tert*-butyl signals at δ 1.09 and 1.34 in the NMR spectrum of **4** measured in $CDCl_3$ at 35 °C, the indented framework of **4** is maintained in solution.

On the other hand, when the *cisoid*-capped complex **2a** was treated with 4,4′-biphenyldicarboxylic acid in a molar ratio of 1 : 1, an orange precipitate was isolated, whose ^1H NMR spectrum showed no signals due to *in*-plane acetates. Although the poor solubility of the product prevented us from determining its molecular weight, its ^1H NMR spectrum along with combustion analysis strongly suggested that self-assembly of **2a** with 4,4′-biphenyldicarboxylic dicarboxylic acid gives the highly-symmetric quadrangular Pt_4 tetramer, like the structure described in Scheme 2a, with the composition of $[Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-}N_4\text{-}D^tBuPhBp)\{(4,4'\text{-}C_{12}H_8)(\mu\text{-}OCO)_2\}]_4$ (**5**).[22] The difference between the self-assembled structures **4** and **5** might be attributed to the flexibility of the dicarboxylic acid linkers.

In conclusion, successful construction of Pt_4-based assemblies was achieved through the following two advances: (a) selective replacement of the *in*-plane acetates of **1** by 1,3-bis(benzamidino)-propane derivatives afforded *cisoid*-capped complexes $[Pt_4(\mu\text{-}OCOCH_3)_6(\kappa^4\text{-}N_4\text{-}DArBp)]$ (**2**) and (b) treatment of *cisoid*-capped building block **2a** with an equimolar amount of dicarboxylic acid induced the well-controlled assembly to give the Pt_4 tetramers **4** and **5**. Further modifications of **1** as well as the assemblies of *cisoid* and *transoid* Pt_4 units are in progress.

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Notes and references

‡ Crystal data for **2a**: $C_{49}H_{60}N_4O_{12}Pt_4\cdot3(CHCl_3)$, M_r = 2035.47, red platelet (0.50 × 0.50 × 0.10 mm), triclinic, space group $P\bar{1}$ (#2), a = 14.6652(18), b = 14.8635(18), c = 18.169(3) Å, α = 94.640(7), β = 105.681(6), γ = 117.743(5)°, V = 3273.9(7) $Å^3$, Z = 2, ρ_{calcd} = 2.065 g cm^{-3}, T = 120(1) K, $\lambda(Mo_{K\alpha})$ = 0.71075 Å, $\mu(Mo_{K\alpha})$ = 8.944 mm^{-1}, F(000) = 1928, 84182 reflections collected, 19892 were unique reflections (R_{int} = 0.1015), 730 parameters, R_1 = 0.0463 for 18413 reflections ($I_o > 2\sigma(I_o)$), wR_2 = 0.0972 for all data, GOF = 1.055, min./max. residual electron density −4.205/2.366 e $Å^{-3}$. CCDC 634657. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703730a

§ **2b** CCDC 634656. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703730a

¶ CCDC 634659. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703730a

|| Crystal data for **4**: $C_{228}H_{248}Fe_4N_{16}O_{48}Pt_{16}\cdot4(H_2O)$, M_r = 7397.33; red platelet (0.15 × 0.10 × 0.05 mm); orthorhombic, space group *Fddd* (#70), a = 15.8027(14), b = 62.629(6), c = 76.415(7) Å, V = 75628(12) $Å^3$, Z = 8, ρ_{calcd} = 1.299 g cm^{-3}, T = 120(1) K, $\lambda(Mo_{K\alpha})$ = 0.71075 Å, $\mu(Mo_{K\alpha})$ = 6.088 mm^{-1}, F(000) = 28032, 259037 reflections collected, 21678 were unique reflections (R_{int} = 0.2740), 678 parameters, R_1 = 0.0808 for 7212 reflections ($I_o > 2\sigma(I_o)$), wR_2 = 0.3098 for all data, GOF = 0.950, min./max. residual electron density −0.598/0.918 e $Å^{-3}$.CCDC 634660. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703730a

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19 The ^1H NMR observation of the crude product of this reaction showed the formation of an unidentified minor by-product. The major product, tetramer **4**, was finally isolated by recrystallization from THF–hexane solution. The minor product might be another oligomer (such as dimer) or the other diastereomeric tetramer to be hereinafter described.

20 The complex **4** should be represented as ΔΔΔΔ (and its enantiomer ΛΛΛΛ; Scheme 2). Other possible diastereomers of the tetramer are described in the ESI†.

21 These angle values were calculated from the torsion angle of C(carboxyl)-CEN-CEN′-C′(carboxyl), where CEN and CEN′ represent the centroids of the two cyclopentadienyl rings in the 1,1′-ferrocenedicarboxylic acid.

22 One of the two acetate signals was observed as multiplet (while the other one was singlet), indicating that the complex **5** is obtained as a mixture of diastereoisomers (See ESI†).