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Introduction

Platinum nanoparticles have attracted considerable attention due to their versatile catalytic performance in exhaust gas conof automobiles, fuel verters cells, and organic transformations.¹⁻⁴ To improve the catalytic efficiency of platinum nanoparticles, the size of the platinum particles must be reduced to nano-scale because minimization of the particle size to close to or less than 1 nm induces a drastic change in the activity and selectivity in catalysis,^{5,6} but precise size control for extremely small particles is difficult. In fact, a finely designed macromolecular template led to the formation of platinum particles in a subnanometer scale,⁷⁻⁹ but removal of the template induced substantial platinum sintering.^{10,15}

Cluster complexes in which the number of metal atoms is precisely controlled at the molecular level as characterized by X-ray analysis as well as spectroscopic measurements have been utilized as precursors for size-controlled metal nanoparticles.^{11–15} The merit of cluster precursors is that

Tetraplatinum cluster complexes bearing hydrophilic anchors as precursors for γ-Al₂O₃-supported platinum nanoparticles†

Shinji Tanaka,^a Naoto Nagata,^b Naoki Tagawa,^a Hirohito Hirata,^b Shin-ichi Matsumoto,^b Hayato Tsurugi^a and Kazushi Mashima^{*a}

Tetraplatinum cluster complexes bearing hydrophilic anchors, $[Pt_4(\mu-OCOCH_3)_4(\mu-OCOC_6H_4OH-4)_4]$ (2a), $[Pt_4(\mu-OCOCH_3)_4(\mu-OCOC_6H_4B(OH)_2-4)_4]$ (2b), and $[Pt_4(\mu-OCOCH_3)_4(\mu-OCOC_6H_4NH_2-4)_4]$ (2c), were successfully prepared by a selective substitution reaction of four *in-plane* acetates of $[Pt_4(\mu-OCOCH_3)_8]$ (1) with the corresponding *p*-substituted benzoic acids. Solid-state structure determination of 2a revealed the 3D network structure through intermolecular hydrogen bonding between the hydroxy group of the *p*-hydroxybenzoate ligand and the oxygen atom of the carboxylate ligand of 2a. UV-vis analysis of 2a–c in CH₃CN or CH₃CN–H₂O in the presence of γ -Al₂O₃ clearly indicated the adsorption efficiency of these platinum clusters on γ -Al₂O₃ from CH₃CN solution, whereas less than 40% of 1 and 2c were chemically adsorbed onto γ -Al₂O₃. Highly dispersed and very small platinum nanoparticles (less than 1 nm) on γ -Al₂O₃ were obtained by thermal treatment of Pt₄-deposited γ -Al₂O₃ at 500 °C.

peripheral modification by ligand substituents allows for metal clusters to be adsorbed onto solid surfaces.^{12*a*,16} We considered the tetraplatinum cluster complex $[Pt_4(\mu\text{-OCOCH}_3)_8]$ (1)^{17,18} to be a well-defined precursor for introducing platinum nanoparticles on surfaces,¹⁹ because four *in-plane* acetate ligands of 1 can be selectively substituted by other carboxylic acids, amidinates, and so on.²⁰ We previously demonstrated that such a labile property of the four acetate ligands of 1 was applicable for not only selective modification by redox active units²¹ but also rational construction of supramolecular assemblies of Pt₄ units.²² Herein, we synthesized tetraplatinum cluster complexes bearing hydrophilic functional groups at four *in-plane* sides of the square Pt₄ entity as precursors for introducing monodispersed Pt₄ onto a γ -Al₂O₃ surface, and characterized the calcined platinum nanoparticles by STEM and CO absorption studies.



Results and discussion

Synthesis and characterization of Pt₄ clusters bearing hydrophilic groups

We previously reported a substitution reaction of *in-plane* acetate ligands of $\mathbf{1}$ by other carboxylate ligands:^{22b} reaction of

^aDepartment of Chemistry, Graduate School of Engineering Science, Osaka University, and CREST, JST, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. E-mail: mashima@chem.osaka-u.ac.jp

^bToyota Motor Corporation, 1 Toyota-cho, Toyota, Aichi 471-8572, Japan

[†]Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format for complex **2a**, tables of crystal data and refinement parameters for **2a**. CCDC 924685. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50670c

1 with an excess of *p*-hydroxybenzoic acid in a mixture of CH_2Cl_2 and MeOH followed by treatment under reduced pressure to remove the liberated acetic acid afforded $[Pt_4(\mu\text{-O-COCH}_3)_4(\mu\text{-OCOC}_6H_4OH-4)_4]$ (**2a**) in quantitative yield (eqn (1)). The ¹H NMR spectrum of **2a** in DMSO-d₆ showed one singlet resonance assignable to the methyl group of *out-plane* acetate ligands, and AB type doublet signals at δ 6.88 and 8.13 (³*J*_{HH} = 8.8 Hz) assignable to *ortho-* and *meta-*aromatic protons. The overall molecular structure was further determined by single crystal X-ray analysis (*vide infra*). In a similar manner, $[Pt_4(\mu\text{-OCOCH}_3)_4(\mu\text{-OCOC}_6H_4B(OH)_2-4)_4]$ (**2b**) and $[Pt_4(\mu\text{-O-COCH}_3)_4(\mu\text{-OCOC}_6H_4NH_2-4)_4]$ (**2c**) were prepared by treating **1** with an excess of *p*-boronobenzoic acid and *p*-aminobenzoic acid, respectively.



Fig. 1 shows the molecular structure of complex 2a, where four *p*-hydroxybenzoate ligands coordinate to *in-plane* sides of a Pt₄ square in a bridging manner with Pt–O bond distances of 2.110–2.176 Å. The Pt–Pt bond distances of 2a, 2.484–2.494 Å, are comparable to those of 1 and reported tetracarboxylate complexes^{20–22} and thus two adjacent Pt^{II} ions are bound to each other with single bonds. Four aromatic rings of the *p*-hydroxybenzoate ligands are parallel to the Pt₄ square plane: angles between the best plane of the Pt₄ core and the four aromatic rings lie in the range of 1.52–15.16°, being much



Fig. 1 Molecular structure of complex **2a** with thermal ellipsoids at 50% probability. All H atoms and solvent molecules (H_2O and Et_2O) were omitted for the sake of clarity. Selected bond distances [Å]: Pt(1)–Pt(2) 2.4943(8), Pt(2)–Pt(3) 2.4947(8), Pt(3)–Pt(4) 2.4906(8), Pt(1)–Pt(4) 2.4984(8), Pt(1)–O(2) 2.154(12), Pt(1)–O(3) 2.110(15), Pt(2)–O(4) 2.176(17), Pt(2)–O(5) 2.173(11), Pt(3)–O(6) 2.165(12), Pt(3)–O(7) 2.120(15), Pt(4)–O(8) 2.171(15), Pt(4)–O(1) 2.167(13).



Fig. 2 Schematic drawing of the intermolecular hydrogen bonding network in complex **2a** (a), and that of stack structure (b). *Out-plane* acetate ligands were omitted.

smaller than those of the 2,6-diphenylbenzoate derivative.^{22b} A notable feature of **2a** is the one-dimensional hydrogen bonding network, in which solvated water bridges the hydroxy group of *p*-hydroxyphenyl ligands and the oxygen atom of an *in-plane* carboxylate ligand attached to another Pt₄ unit to make a one-dimensional flat network where a dihedral angle between two consecutive Pt₄ squares is 0° with distances of O (phenoxy)–O(water) (2.732 Å) and O(water)–O(carboxylate) (2.992 Å) (Fig. 2a). The other intermolecular hydrogen bonding network is between the hydroxy group of *p*-hydroxyphenyl ligands and the oxygen atom of the *in-plane* carboxylate ligand, making a zig-zag one-dimensional network where the dihedral angles between two Pt₄ squares are 75.96° with the distance of O(phenoxy)–O(carboxylate) (2.889 Å) (Fig. 2a and b).

Adsorption of Pt₄ clusters 1 and 2a-c on γ-Al₂O₃

We performed an adsorption test of these Pt₄ complexes **1** and **2a–c** onto the γ -Al₂O₃ surface by monitoring the absorption spectra of **1** and **2a–c** in CH₃CN or CH₃CN–H₂O and those for which γ -Al₂O₃ was added in 0.5 wt% Pt– γ -Al₂O₃. Notably, absorption peaks at 262 and 277 nm for **2a** and 253 nm for **2b** with large ε values (>4 × 10⁴) decreased upon the addition of γ -Al₂O₃, indicating that Pt₄ complexes in solution were efficiently adsorbed onto the γ -Al₂O₃ surface with a grafting efficiency of 99% for **2a** and 80% for **2b** (Fig. 3b and 3c). In sharp contrast, the addition of γ -Al₂O₃ to complexes **1** and **2c** in CH₃CN resulted in a partial decrease of their absorbance (Fig. 3a and 3c) and grafting efficiency, estimated to be 39% for **1** and 36% for **2c** (Table 1). Accordingly, the hydroxy groups attached to the Pt₄ core acted as anchors suitable for interacting with the



Fig. 3 UV-vis spectra of complexes 1 (a), 2a (b), 2b (c), and 2c (d) in CH₃CN (13 μ M) for 1, 2a, 2c and CH₃CN–H₂O (15/1) (12 μ M) for 2b, and those of the supernatant in a mixture with γ -Al₂O₃ (0.5 wt% on Pt) in CH₃CN.

Table 1 λ_{max} values, absorbance at λ_{max} grafting efficiency based on UV-vismeasurement of complexes 1 and 2a-c

		1	2a	2b	2c
λ_{\max} (nm) Absorbance at λ_{\max}	Without γ -Al ₂ O ₃ With γ -Al ₂ O ₂	246 0.60 0.37	$262 \\ 1.28 \\ 0.02$	253 1.35 0.27	301 1.61 1.04
Grafting efficiency (%)		39	99	80	36

 $\gamma\text{-}Al_2O_3$ surface through hydrogen bonding interactions, and promoted the spontaneous adsorption of Pt_4 clusters onto $\gamma\text{-}Al_2O_3$ surfaces.

Characterization of Pt/γ -Al₂O₃

Based on the grafting efficiency of these Pt₄ complexes on γ -Al₂O₃, we prepared several Pt/ γ -Al₂O₃ samples (0.5 wt% on Pt) up to the maximum adsorption under operations by filtration from CH₃CN, drying under vacuum at 120 °C, and calcination at 500 °C for 2 h under air. ICP analysis of the resulting solid samples derived from complexes **2a–c** indicated that the platinum content of each sample was 0.49 wt% for **2a**, 0.45 wt% for **2b**, and less than 0.10 wt% for **2c** (Table 2). Platinum particles on γ -Al₂O₃ derived from complexes **2a** and **2b**

Table 2 Pt content and size of Pt particles in Pt/γ-Al₂O₃ prepared from 2a-c

	2a	2b	2 c
Pt content $(wt\%)^a$	0.49	$\begin{array}{c} 0.45\\ 0.80\end{array}$	<0.10
Size of Pt particles $(nm)^b$	0.71		—

 a Determined by ICP analysis. b Determined by CO absorption measurement.





Fig. 4 STEM images of Pt nanoparticles on $\gamma\text{-}Al_2O_3$ prepared from 2a (a) and 2b (b).

were further analyzed by STEM (Fig. 4a and b) and were in a highly dispersed form. The sizes of the particles were calculated to be 0.71 nm for complex **2a** and 0.80 nm for complex **2b** based on CO absorption studies (Table 2), suggesting that platinum particles of a size less than 1 nm were efficiently generated by highly dispersed grafting of Pt₄ cluster complexes on γ -Al₂O₃ *via* multiple hydrogen bonds between hydrophilic functional groups and the surface.

Conclusions

We successfully prepared Pt₄ cluster complexes bearing OH group **2a**, $B(OH)_2$ group **2b**, and NH₂ group **2c** by selective substitution reactions of **1** with benzoic acid derivatives. The solid-state structure of **2a** was determined by a single crystal X-ray analysis, revealing a unique hydrogen bond network *via* OH and carboxylate groups. Complexes **2a** and **2b** in CH₃CN were efficiently adsorbed onto γ -Al₂O₃. The sizes of platinum particles derived from thermal treatment of grafted materials were well controlled at less than 1 nm. This methodology for

generating subnanometer platinum particles is thus simple and controllable.

Experimental section

General procedures

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using standard Schlenk techniques or in an argon-filled glovebox. $[Pt_4(\mu - OCOCH_3)_8]$ (1) was prepared according to literature procedures.²⁰ p-Hydroxybenzoic acid, p-aminobenzoic acid, and p-boronobenzoic acid were purchased and used as received. γ -Al₂O₃ powder (57 m² g^{-1}) was purchased from Nanotek. Dehydrated hexane, Et₂O, and CH₂Cl₂ were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.²³ Dehydrated MeOH and DMSO-d₆ were degassed and stored under an argon over activated 3 Å (MeOH) and 4 Å (DMSO-d₆) molecular sieves. ¹H NMR (400 MHz) and ¹³C¹H} NMR (100 MHz) were measured on Bruker AVANCEIII-400 spectrometers, and all spectra were recorded at 30 °C unless mentioned otherwise and referenced to an internal solvent. Elemental analyses were recorded on a Perkin-Elmer 2400II microanalyzer in the Department of Chemistry, Faculty of Engineering Science, Osaka University. Mass spectrometric data were obtained using ESI techniques on a BRUKER micrOTOF spectrometer. Melting points were measured in sealed tubes and were not corrected.

Preparation of $[Pt_4(\mu - OCOCH_3)_4(\mu - OCOC_6H_4OH - 4)_4]$ (2a)

To a solution of $[Pt_4(\mu\text{-OCOCH}_3)_8]$ (86.8 mg, 0.0693 mmol) in CH₂Cl₂ (6 mL) was added a solution of *p*-hydroxybenzoic acid (76.2 mg, 0.552 mmol, 8 equiv.) in MeOH (5 mL). The reaction mixture was stirred for 20 h at ambient temperature under reduced pressure. During this operation, a mixture of CH₂Cl₂ (6 mL) and MeOH (6 mL) was repeatedly added before all volatiles were completely removed. Removal of all volatiles gave the solid, which was washed with Et₂O (8 mL, three times) to leave complex 2a as orange powders (110 mg, quant.), mp 210-212 °C (decomp.). ¹H NMR (400 MHz, DMSO-d₆, 30 °C, δ /ppm): 1.99 (s, 12H, ^{ax}CH₃CO₂), 6.88 (d, ³J_{HH} = 8.6 Hz, 8H, Ar H), 8.13 (d, ${}^{3}J_{HH}$ = 8.6 Hz, 8H, Ar H). MS (ESI positive, CH₃CN, m/z): 1587 ($[M + Na]^+$), 1427 ($[M - O_2CC_6H_4OH]^+$). Anal. Calcd for C36H32O20Pt4: C 27.63, H 2.06. Found: 27.83, H 1.99, N 0.08.

Preparation of $[Pt_4(\mu \text{-OCOCH}_3)_4(\mu \text{-OCOC}_6H_4B(OH)_2-4)_4]$ (2b)

This compound was prepared in a similar manner as for compound **2a** using *p*-boronobenzoic acid instead of *p*-hydroxybenzoic acid. Orange powders (87% yield), mp 212–215 °C (decomp.). ¹H NMR (400 MHz, DMSO-d₆/D₂O, 30 °C, δ /ppm): 2.02 (s, 12H, ^{ax}CH₃CO₂), 7.97 (d, ³J_{HH} = 7.6 Hz, 8H, Ar H), 8.25 (d, ³J_{HH} = 7.6 Hz, 8H, Ar H). MS (ESI positive, CH₃CN/H₂O, *m*/z): 1669 ([*M* + Na]⁺), 1511 ([*M* – O₂CC₆H₄B(OH)₂]⁺). Anal. Calcd for C₃₆H₃₆B₄O₂₄Pt₄: C 25.79, H 2.16. Found: C 25.83, H 2.30, N 0.07.

Preparation of $[Pt_4(\mu - OCOCH_3)_4(\mu - OCOC_6H_4NH_2 - 4)_4](2c)$

This compound was prepared in a similar manner as for compound **2a** using *p*-aminobenzoic acid instead of *p*-hydroxybenzoic acid. Orange powders (98% yield), mp 204–206 °C (decomp.). ¹H NMR (400 MHz, DMSO-d₆, 30 °C, δ /ppm): 1.96 (s, 12H, ^{ax}CH₃CO₂), 5.91 (s, 8H, -NH₂), 6.61 (d, ³*J*_{HH} = 8.8 Hz, 8H, Ar H), 7.95 (d, ³*J*_{HH} = 8.8 Hz, 8H, Ar H). MS (ESI positive, CH₃CN, *m*/*z*): 1583 ([*M* + Na]⁺), 1562 ([*M* + H]⁺), 1424 ([*M* - O₂CC₆H₄NH₂]⁺). Anal. Calcd for C₃₆H₃₆N₄O₁₆Pt₄: C 27.70, H 2.32, N 3.59. Found: 28.01, H 1.95, N 3.37.

UV-vis spectroscopy

UV-vis spectra were recorded on an Agilent 8453 spectrometer. Complexes (9.7 µmol) were dissolved in CH₃CN (30 mL) for **1**, **2a**, and **2c** and CH₃CN/H₂O (30 mL + 2 mL) for **2b**, and each solution was diluted by 4% (1.3×10^{-5} M) before to measure UV-vis spectra. For grafted samples, 1.5 g of γ -Al₂O₃ was added to the CH₃CN solution, and the suspension was stirred for 30 min. After filtration, the filtered solution diluted by 4% was used for UV-vis spectroscopy.

Crystallographic determination of 2a

Crystals of 2a (red, block) were obtained via diffusion of diethyl ether into the acetonitrile solution of 2a. A crystal was mounted on the CryoLoop (Hampton ReseArCh Corp.) with a layer of mineral oil and placed in a nitrogen stream. Complex 2a was measured with a Rigaku RAXIS-RAPID Imaging Plate equipped with a sealed tube X-ray generator (40 kV, 50 mA) with graphite monochromated Mo-Kα (0.71075 Å) radiation in a nitrogen stream at 113(1) K. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement with the setting angles, which are listed in Table S1.[†] The structure was solved by direct methods on SIR97,²⁴ after being refined on F^2 by full-matrix least-squares methods using SHELXL-97.25 Measured nonequivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. The hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w (F_o^2 - F_c^2)]$ (w = $1/[\sigma^2(F_o^2) + (aP)^2 + bP])$, where $P = (Max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_0^2)$ from counting statistics. The functions R_1 and wR_2 were $(\Sigma ||F_{\rm o}| - |F_{\rm c}||)/\Sigma |F_{\rm o}|$ and $[\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma (w F_{\rm o}^4)]^{1/2}$, respectively. In crystals of 2a, a disordered diethyl ether molecule with its occupancy of 0.75 is involved. We refined those atoms in an isotropic form because their separation into a disordered form and anisotropic refinement were unsuccessful. ADP ratio values of atoms O7 and O10 were relatively high, presumably due to the location of those atoms near the disordered diethyl ether molecule. The ORTEP-3 program was used to draw molecules.²⁶ CCDC 924685 (2a) contains the supplementary crystallographic data for this paper.

Preparation and characterization of Pt/γ-Al₂O₃

 γ -Al₂O₃ powder (1.5 g) was added to a solution of 2a (15 mg, 9.6 µmol) in CH₃CN (30 mL). The mixture was kept under stirring at room temperature for 2 h. After filtration, the residue was washed with CH₃CN, dried at 120 °C overnight, and calcined at 500 °C in air for 2 h. Other catalysts were prepared in a similar manner to that of the 2a/Al₂O₃. The Pt concentration was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Shimadzu ICPV-8100 after decomposing the catalyst with aqua regia. A scanning transmission electron microscopy (STEM) image was measured on a Hitachi HD2000 STEM operated at 200 kV in the z-contrast mode. CO chemisorption for the estimation of Pt particle size was measured using an Okura Riken R6015 apparatus equipped with a thermal conductivity detector (TCD). A sample of 150 mg was introduced into a glass tube and pretreated sequentially in O₂ for 15 min, H₂ for 15 min, He for 15 min at 400 °C and then cooled to 50 °C under a He flow. Adsorbed CO was counted using a pulse injection method at 50 °C.

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