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Platinum clusters with precise numbers of atoms for preparative-scale catalysis

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Madhuri Jash
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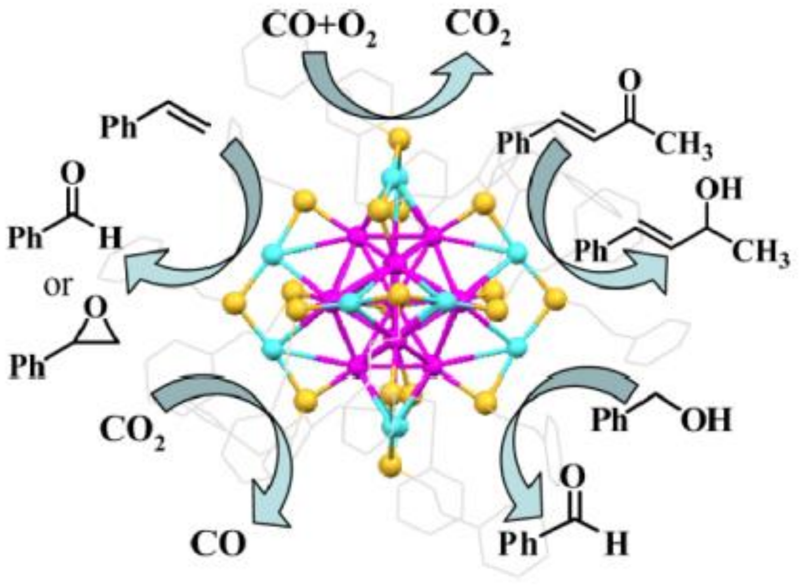
ACCOUNTS of chemical research

Atomically Precise Gold Nanoclusters as New Model Catalysts

GAO LI AND RONGCHAO JIN*

Vol. 46, No. 8 ■ 2013 ■ 1749–1758 ■ ACCOUNTS OF CHEMICAL RESEARCH



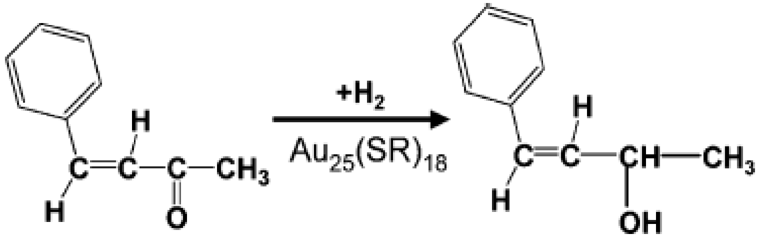
Gold Nanocatalysts

DOI: 10.1002/anie.200906249

Atomically Precise $Au_{25}(SR)_{18}$ Nanoparticles as Catalysts for the Selective Hydrogenation of α,β-Unsaturated Ketones and Aldehydes**

*Yan Zhu, Huifeng Qian, Bethany A. Drake, and Rongchao Jin**

Angew. Chem., Int. Ed. **2010**, *49*, 1295–1298



Nanoscale

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Cite this: *Nanoscale*, 2013, **5**, 12558

Green synthesis of silver nanoclusters supported on carbon nanodots: enhanced photoluminescence and high catalytic activity for oxygen reduction reaction†

Minmin Liu[ab] and Wei Chen[*a]

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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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One-Pot Synthesis, Photoluminescence, and Electrocatalytic Properties of Subnanometer-Sized Copper Clusters

Wentao Wei,[†,§] Yizhong Lu,[†,‡,§] Wei Chen,[*,†] and Shaowei Chen[*,#]

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ARTICLE

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Structure sensitivity in the nonscalable regime explored via catalysed ethylene hydrogenation on supported platinum nanoclusters

Andrew S. Crampton[1], Marian D. Rötzer[1], Claron J. Ridge[1,2], Florian F. Schweinberger[1], Ueli Heiz[1], Bokwon Yoon[3] & Uzi Landman[3]

Relevant to the group:

- The synthesis pathway for making naked cluster from ligand protected clusters in a preparative scale can be applicable for our thiolate protected clusters of Au and Ag or Pd etc.

- Again only for Pt, there is report of $Pt_{11}(BBS)_8$ from our group.

Nanoscale

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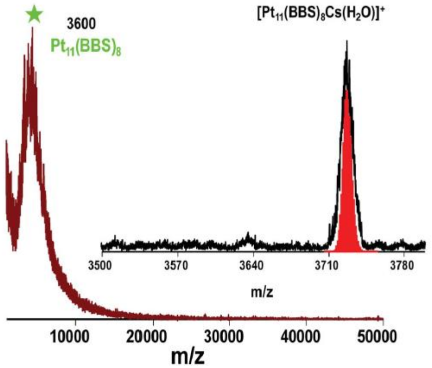
Blue emitting undecaplatinum clusters†

Indranath Chakraborty, Radha Gobinda Bhuin, Shridevi Bhat and T. Pradeep*

Cite this: *Nanoscale*, 2014, 6, 8561



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INTRODUCTION:

- The ultimate approach is the extreme miniaturization of the particle because subnanometer particles consequently have a specific structure that has no periodicity against crystalline nanoparticles.

- Clusters on a subnanometer scale indeed showed distinct properties especially for catalytic applications due to the geometric nature or electronically induced superatomic character.

- To study the specific activities, a gas-phase synthesis with the mass selection of each cluster has been the only way providing the atomicity control with satisfactory precision and scalability. However, this approach is applicable for analytical scale catalysis due to the limited throughput of the mass selection.

In this paper…

- Platinum is the most important metal element for nanoparticle catalysis. As the precursors of such ultrasmall platinum subnanoparticles, platinum thiolates are currently being investigated because of the reductive metal-sulfur bond cleavage.

- They showed the scalable synthesis, characterization, and fundamental properties of platinum tiara-like complexes with octanethiol ligands, synthesis of monodispersed subnanometer platinum clusters and their catalytic activity for preparative-scale reactions.

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Experimental Method:

Synthesis of platinum thiolate complexes:

$PtCl_4$ in (1/1) monochlorobenzene /acetonitrile

$\xrightarrow[\text{90 °C, 1 h}]{\text{N,N-diisopropylamine, n-octanethiol}}$

The crude product was again dissolved in monochlorobenzene containing n-octanethiol

$\downarrow$ 200 °C, 1 h

Solution was centrifuged and the soluble part includes tiara-like complexes with various ring numbers $[Pt(\mu\text{-}SC_8H_{17})_2]_n$ as a mixture

Synthesis of Pt_n clusters:

A preparative recycling HPLC was used for the purification using chloroform as the eluent. After the recycling processes, each tiara-like complex was collected in order

→

After purification in HPLC the hexane solution of particular $[Pt(SC_8H_{17})_2]_n$ was added to the Ketjenblack, KB and stirred for 15 min

→

After filtration, the cluster supported on KB was treated with hydrogen gas at 250 °C in a tube furnace for 18 h

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RESULTS AND DISCUSSION:

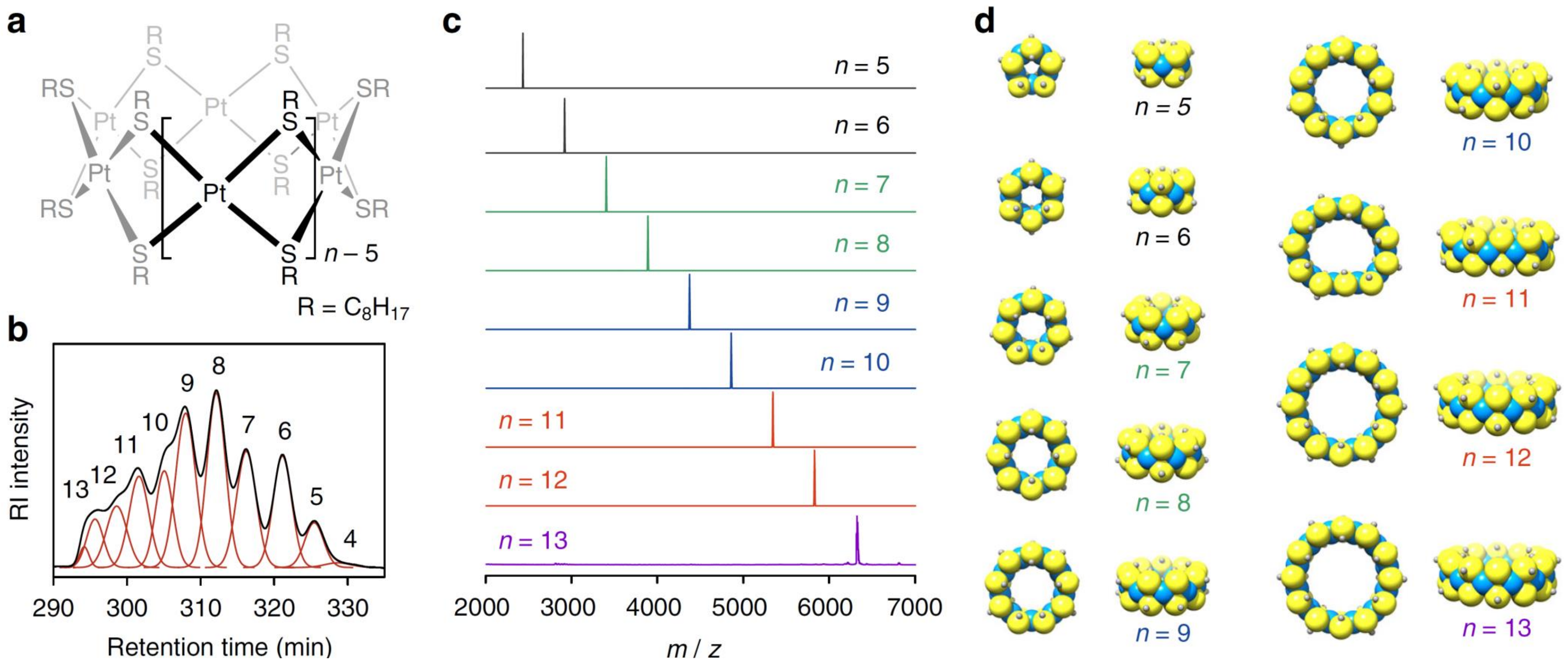

Fig. 1 Tiara-like platinum octanethiolate complexes $[Pt(\mu\text{-}SC_8H_{17})_2]_n$. **a** Chemical structure of the complexes. **b** Chromatogram of the preparative HPLC separation with size-exclusion columns (*SEC*) monitored by a refractive index detector. This chromatogram was recorded at five cycles of the recycling processes. **c** MALDI-TOF-mass spectra of the isolated $[Pt(\mu\text{-}SC_8H_{17})_2]_n$ ($n = 5$–13) measured with DCTB matrix. **d** Optimized geometric structures at the B3LYP/LanL2DZ level. Platinum, sulphur, and α-carbon atoms are shown as *blue*, *yellow*, and *gray spheres*, respectively. The hydrogen atoms are omitted for clarity

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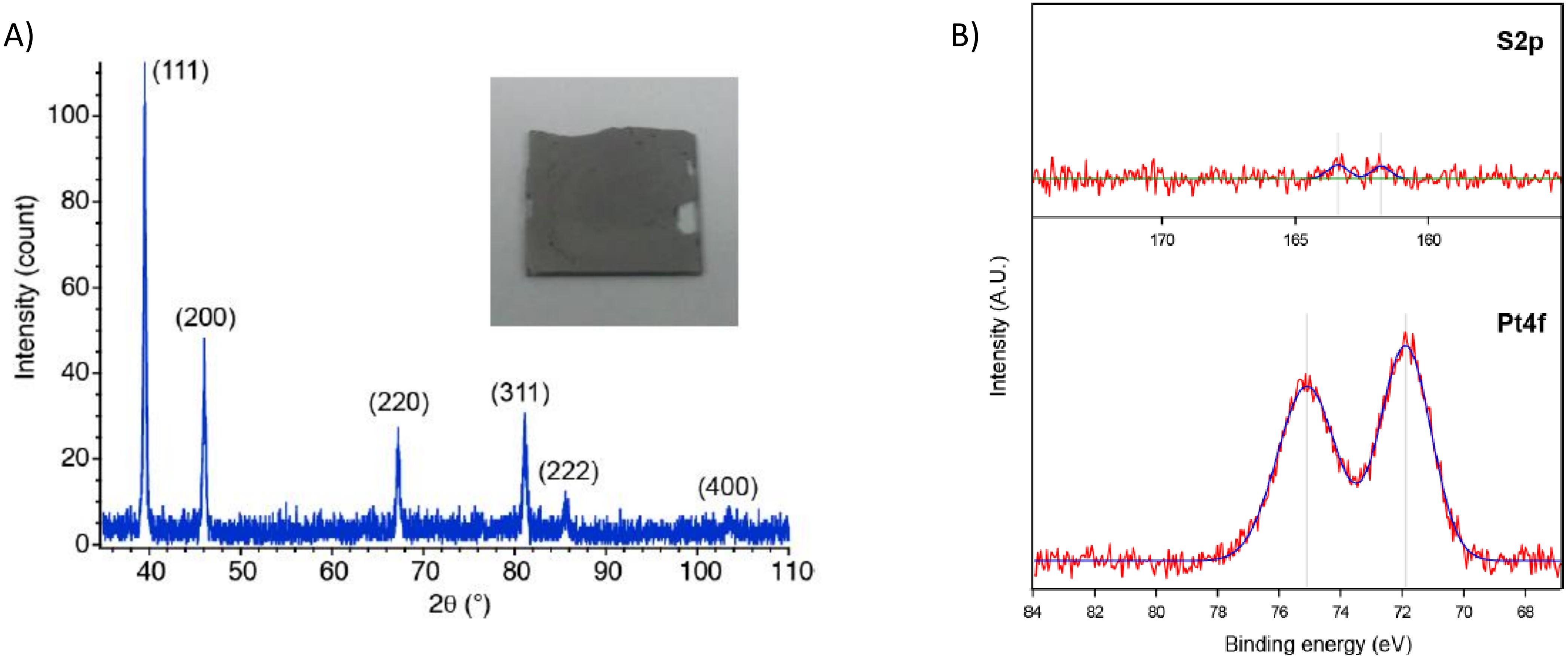

Fig. 2 A) Powder X-ray diffraction (XRD) of a thick [Pt(C8H17S)2]n (mixture of different *n* products) film after a treatment under a hydrogen atmosphere at 250°C. Inset picture is a photograph of the as-prepared product. **B)** X-ray photoelectron spectra (S 2*p* and Pt *4f*) of Pt8 after the calcination under a hydrogen (3%) / nitrogen (97%) atmosphere at 250°C for 16 hours. Only a trace amount of sulfur was remained after the calcination.

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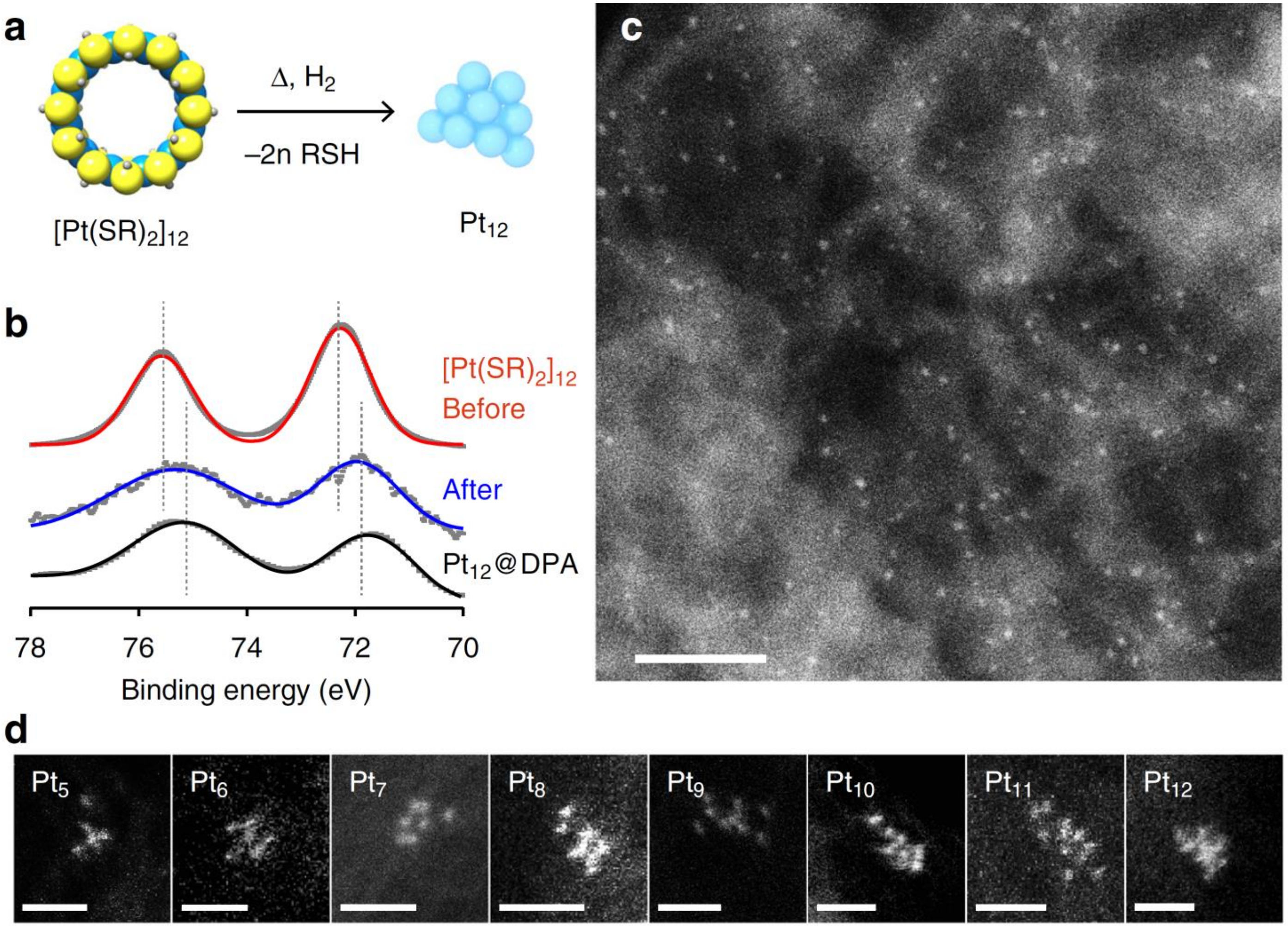

Fig 3 Preparation of monodispersed Pt_{12} clusters from $[Pt(\mu\text{-}SC_8H_{17})_2]_{12}$ complexes. **a** Direct conversion scheme from a complex to a cluster by reduction in a hydrogen atmosphere. **b** XPS of the $[Pt(\mu\text{-}SC_8H_{17})_2]_{12}$ complexes in Pt $4f_{7/2}$ and Pt $4f_{5/2}$ regions before and after calcination at 250 °C under a hydrogen stream. Pt_{12}@DPA is the previously synthesized sample prepared with a phenylazomethine dendrimer in ref. [19]. **c** A dark-field STEM image of the calcined sample supported on carbon (Ketjenblack). Inset shows a high-magnification aberration-corrected STEM image. *Scale bar*, 20 nm. **d** Atomic scale high-magnification STEM images of the monodispersed clusters (Pt_5–Pt_{12}). *Scale bar*, 1 nm

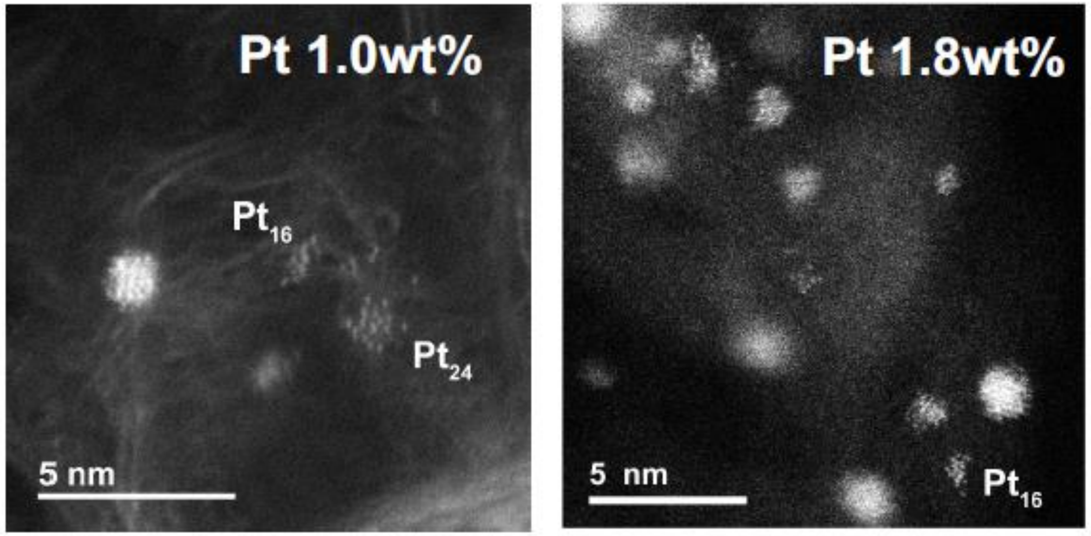

Fig. 4 Atomic scale HAADF-STEM images of Pt8 at higher weight percentages (Pt: 1.0 and 1.8 wt%) of platium loading on Ketjenblack. Most of the resulting clusters are aggregated producing larger clusters and nanoparticles.

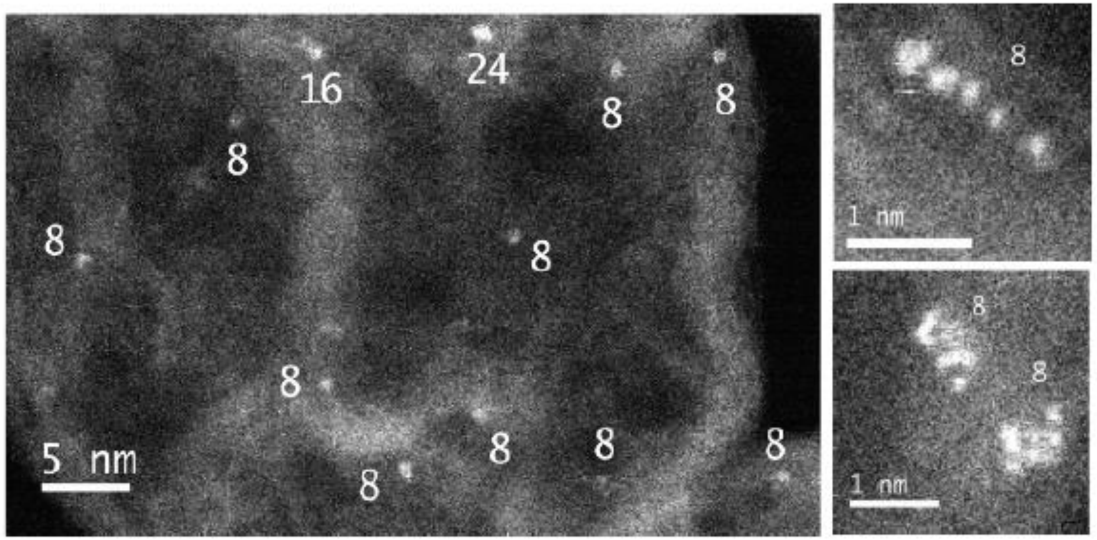

Fig. 5 A sub-atomic scale HAADF-STEM image of Pt8 on Ketjenblack (Pt: 0.4 wt%) and the magnifications of the respective clusters.

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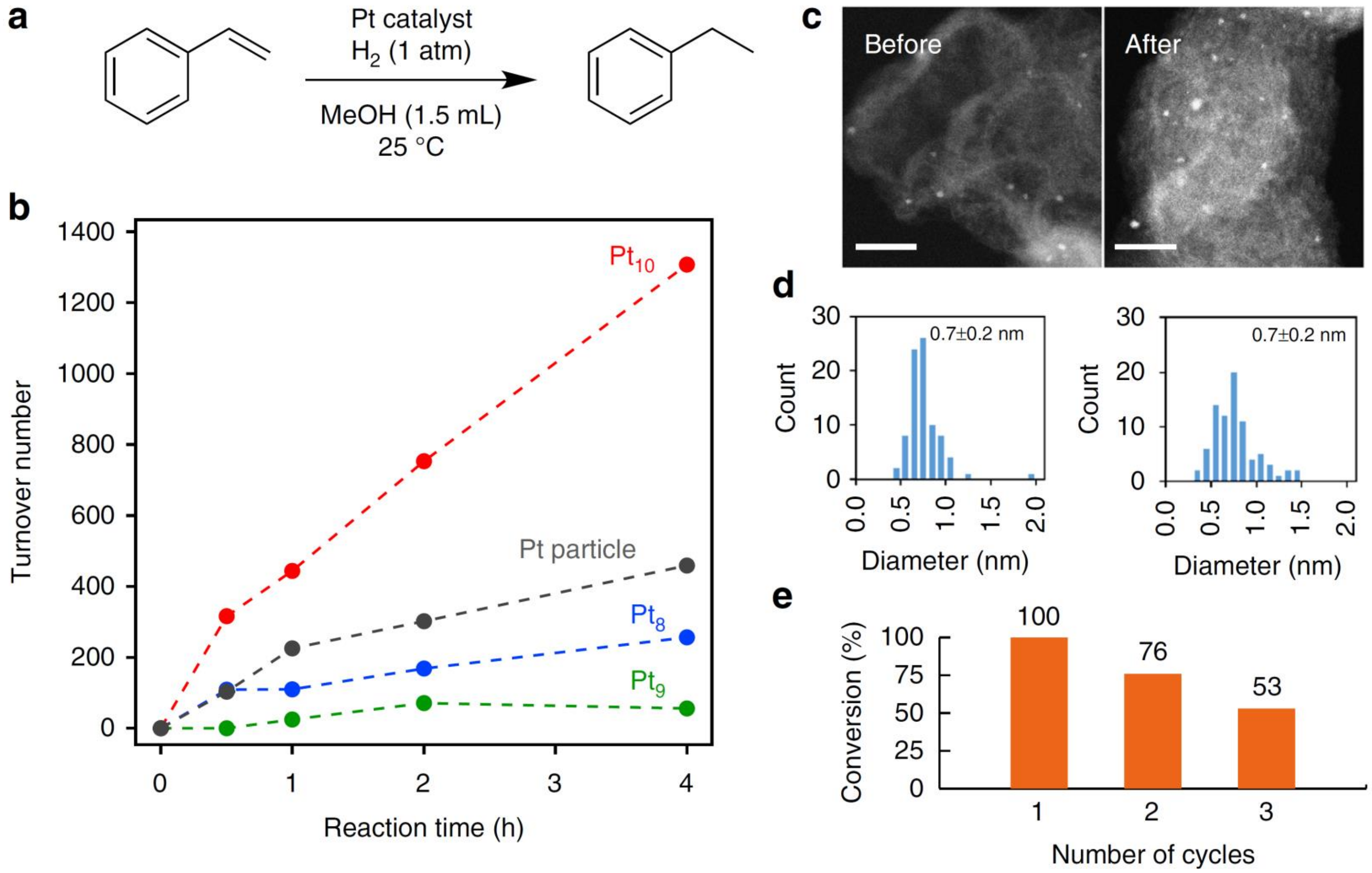

Fig 6 Hydrogenation reaction of styrene catalyzed by platinum clusters. **a** A scheme of the conversion. **b** Turnover numbers of the styrene conversion catalyzed by platinum clusters (Pt_8, Pt_9, and Pt_{10}) on Ketjenblack (Pt: 0.02 mol%). Pt particle represents the platinum nanoparticles (1.1 ± 0.2 nm) prepared from $[Pt(\mu\text{-}SC_8H_{17})_2]_9$ at higher concentration (1.8 wt% Pt) on Ketjenblack. **c** HAADF-STEM images of the Pt_{10} catalyst before and after (2 h) the hydrogenation reaction. *Scale bar*, 10 nm. **d** The particle size histograms from the images on panel **c** and other views. **e** Styrene conversions at the end of the cycles during repeated uses of Pt_{10}/KB. The reaction conditions are the same as those in panel **b**, but the amount of catalyst (Pt: 0.1 mol%) is different

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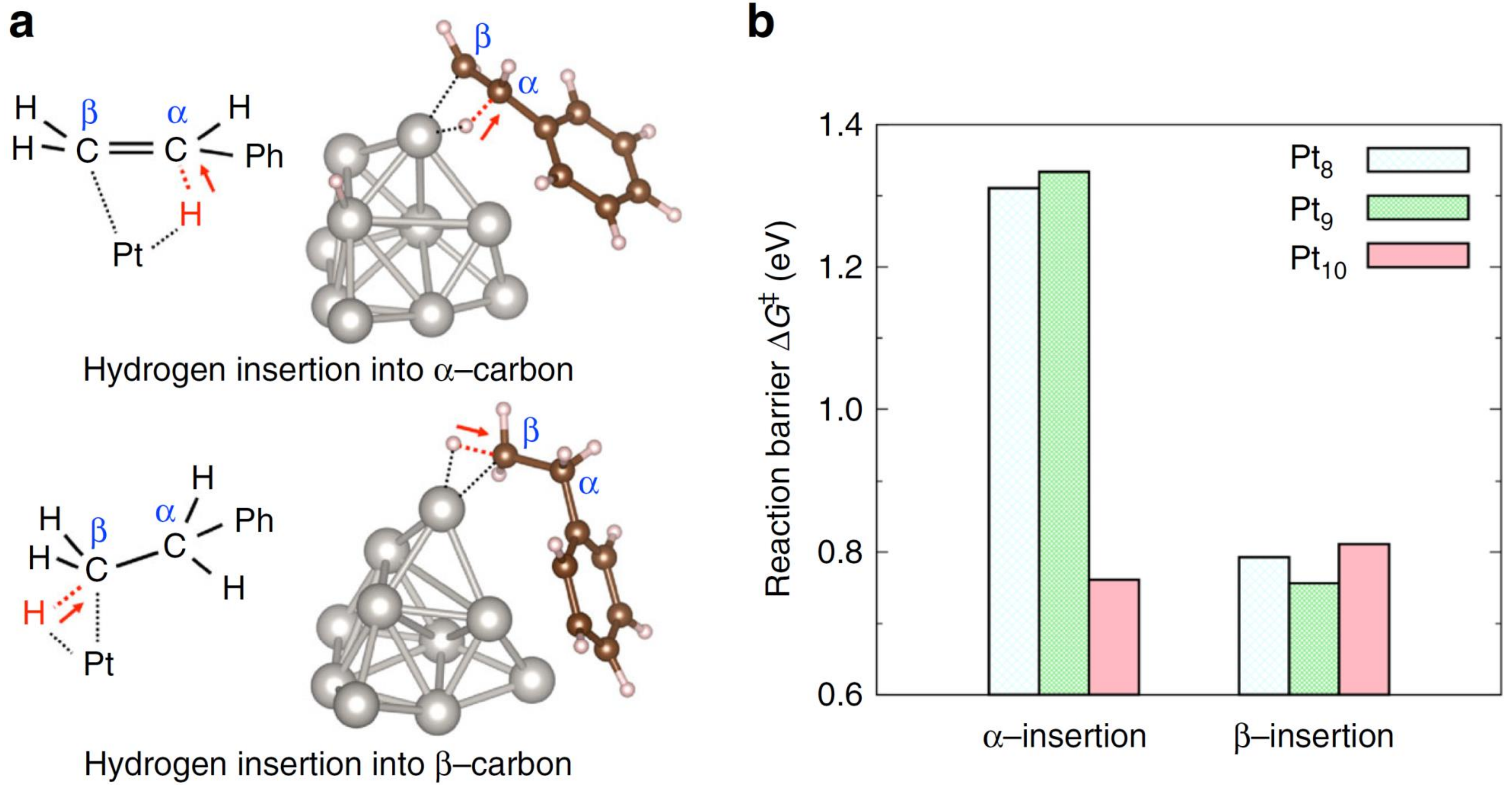

Fig 7 Styrene hydrogenation and its reaction barriers under the existence of platinum catalysts. **a** Hydrogen insertion processes into α-carbon and β-carbon, and the corresponding transition states with Pt_{10} catalyst. **b** Calculated reaction barriers under the existence of Pt_8, Pt_9, or Pt_{10} catalyst. Density functional theory calculations were performed at the B3LYP/LanL2DZ and 6-31 G (d, p) level of theory

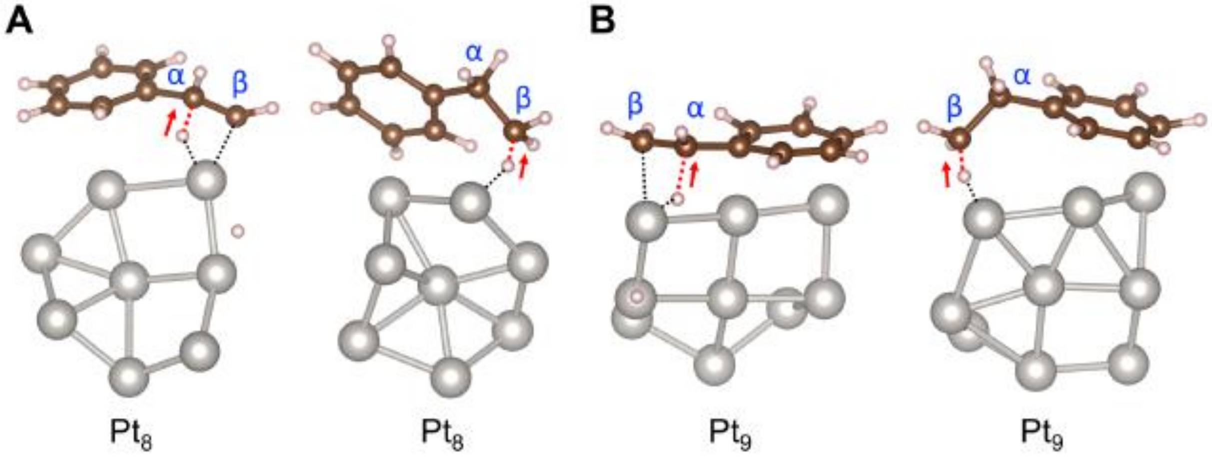

Fig. 8 Transition states of hydrogen insertions into α–carbon and β–carbon of styrene with (A) Pt8 or (B) Pt9. Density-functional-theory calculations were performed at the B3LYP/LanL2DZ and 6–31G (d, p) level of theory.

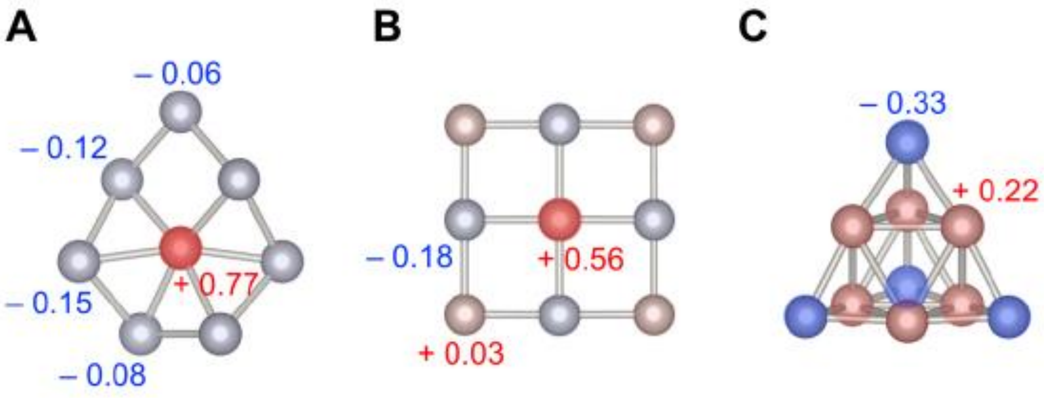

Fig. 9 Mulliken charge distributions of (A) Pt8, (B) Pt9, and (C) Pt10. Density-functional-theory calculations were performed at the B3LYP/LanL2DZ level of theory.

CONCLUSIONS:

- They successfully isolated various tiara-like platinum thiolate complexes, whose atomicity ranged between 5 and 13.

- A study on the thermal chemical conversion revealed that the tiara-like platinum thiolate complexes were suitable precursors for the synthesis of monodispersed zero-valent platinum clusters with a specific atomicity (n = 5–12), which had been inaccessible by previous chemical methods.

- Especially, the Pt_{10} cluster prepared from the tiara-like complex exhibited an exceptionally high catalytic activity for the hydrogenation reaction of styrene relative to the other clusters (Pt_8, Pt_9, or larger one).

- This is the first example demonstrating a preparative-scale reaction using atom-precise clusters with a single-digit atomicity.


THANK
YOU...