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Molecular Mechanism on the Activation of Au₂₅(SCH₂CH₂Ph)₁₈ Nanoclusters by Imidazolium-based Ionic Liquids for Catalysis

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ABSTRACT:

Unavailable surface structures of nanocatalysts often pose a challenge to molecular-level understanding of the catalytic mechanism. Recent progress in the structural characterization of gold nanoclusters with atomic precision has enabled them to serve as excellent model systems to scrutinize structure-reactivity correlation. Herein a case study is reported, in which the full structure of the Au₂₅(SCH₂CH₂Ph)₁₈ nanocluster catalyst allows detailed mechanistic insight into the Suzuki cross-coupling reaction pathways at the atomic/molecular level, in particular, the promotional effect by imidazolium-based ionic liquids (ILs) for the coupling reaction between phenylboronic acid and *p*-iodoanisole. The catalytic mechanisms are studied using UV-vis spectroscopy, MALDI mass spectrometry, density functional theory (DFT) calculations, and classical molecular dynamics (MD) simulations. Partial removal of thiolate ligands (-SR) and “Au-SR” units from the protected Au₂₅ cluster through interactions with imidazolium cations is deemed the promotion mechanism in the cross-coupling reaction. Both the experiment and DFT calculation indicate that the acidic proton at the position-2 of the imidazolium ions plays an important role in the detachment of SR ligands and Au atoms from the nanocluster surface, which in turn enables the cross-coupling reaction at a much milder temperature than in the absence of the IL promoter. Results suggest that oxidation of the active gold species not only prevents further fragmentation of the nanoparticles by the ILs but also increases the interaction of reactants with the catalysts, thereby improving the conversion rate.

Keywords: Gold nanocluster, Au₂₅, Suzuki Cross-Coupling, Ionic Liquid, DFT calculation, MD simulation

1. Introduction

Mechanistic understanding of the catalytic reactions usually requires precise knowledge of the surface atomic-structure of nanocatalysts. Although a variety of metal nanoparticle-based catalysts have been explored for a wide range of reactions, molecular-level understanding of the catalytic mechanisms has been acquired with limited success. Among the chemical transformation reactions, metal-catalyzed carbon-carbon coupling reactions, such as the Suzuki cross-coupling reactions—which lead to the formation of a carbon-carbon bond between an organic halide and a boronic acid—are strategically important in organic chemical transformation processes [1-3]. Traditionally, the carbon-carbon coupling is catalyzed by palladium (Pd) complexes via homogeneous catalysis, which unfortunately has several disadvantages, including the poor reusability of catalysts and the difficulty of removing catalysts from the products [4]. In recent years, a new trend based on heterogeneous catalysis has emerged, which aims to address the issues of homogeneous catalysis. Metal nanoparticles (e.g., Pd, Au, etc.) have been actively developed for the coupling and other reactions as heterogeneous nanocatalysts, which show high atom efficiency, simplified isolation of products, and facile recovery and excellent recyclability of catalysts [1-8].

Understanding the mechanisms of the carbon-carbon coupling reactions is of major importance. Extensive attention has been paid recently to the coupling reactions catalyzed by palladium nanoparticles and complexes [9]. It is generally accepted that these reactions proceed in three stages: oxidative addition, transmetalation, and reductive elimination. The oxidative addition process is usually regarded as the rate-limiting one [9-11]. In contrast, the mechanistic study of the coupling reactions

catalyzed by gold nanoparticle catalysts is still in an early stage, although there are speculations that the mechanism would be similar to the Pd nanoparticle case [5-7]. For example, Corma and coworkers investigated oxidative homo- and cross-coupling reactions by employing naked and/or partially oxidized gold nanoclusters [12,13]. They found that gold nanoparticles show intrinsic activity toward the coupling reactions. Nevertheless, the truncated octahedral Au₃₈ nanocluster model used in their computational analysis is rather different from the real catalysts in terms of size and structure.

Well-defined gold nanoclusters with fully determined structures, e.g., [Au₂₅(SCH₂CH₂Ph)₁₈]⁻ (denoted as the Au₂₅(SR)₁₈ hereafter) have recently emerged as a new promising class of catalysts for the carbon-carbon coupling and other reactions [14-19]. Catalytic effectiveness of such nanoclusters has been demonstrated in reactions such as Ullmann homo-coupling of iodobenzene [15], Sonogashira cross-coupling between iodobenzene and phenylacetylene [16], and selective oxidation reactions [17]. Additionally, the small size and crystallographically characterized structure of the Au₂₅(SR)₁₈ nanocluster enable efficient and accurate electronic structure calculations [20]. This allows for a quantitative comparison of theoretical predictions with minimal approximations with experiments to study reaction mechanisms [21], such as the adsorption of reactant molecules (e.g., iodobenzene and/or phenylacetylene) onto the nanocluster surface. Thus, atomically-precise nanoclusters provide an excellent molecular system to investigate catalytic mechanisms and to understand relationships between the structure and properties of catalysts in catalytic processes, e.g., the coupling reactions.

In this work we explore the potential catalytic effect of ionic liquids (ILs) in the nanocluster-catalyzed reactions. The ILs have received a considerable attention as an alternative to traditional organic solvents due to the unique properties of ILs, such as non-volatility, non-flammability, high chemical and thermal stability, low toxicity, high ion conductivity and wide electrochemical window [22-27]. It is known that the hydrogen atom at the position-2 of imidazolium ions, hereafter referred to as H₂, is acidic. It thus tends to interact strongly with negatively charged sites compared to other ring or alkyl chain hydrogen atoms and to form a hydrogen bond. This property is believed to play an important

role in, for example, CO₂ capture with the ionic liquid, 1-alkyl-3-methylimidazolium acetate [28-30]. It also opens up the possibility of activating the thiolate-protected gold nanoclusters by tailoring these interactions toward sulfur, which has potential applications in heterogeneous catalysis. Herein we pursue this possibility further and consider the Suzuki cross-coupling reaction between *p*-iodoanisole and phenylboronic acid catalyzed by TiO₂-supported Au₂₅(SR)₁₈ nanoclusters. It is discovered that the addition of imidazolium-based ILs can markedly enhance the product conversion at mild temperatures (e.g., at 90 °C). The catalytic mechanisms, in particular, the roles played by ILs, are studied via a combined approach of experiment and theory. The mechanism of imidazolium cation-induced removal of thiolate ligands (-SR) and “-SR-Au-” units of the Au₂₅ is found to be energetically more favorable than an alternative mechanism of imidazolium cation-induced protonation/dissociation of thiolate group. The as-generated low-coordinated gold atoms adsorb and activate the reactant *p*-iodoanisole for the subsequent Suzuki cross coupling.

2. Experimental

2.1. Synthesis of the Au₂₅(SR)₁₈ nanocluster and preparation of the supported catalyst.

The synthesis of Au₂₅(SR)₁₈ nanoclusters followed a literature method [31]. Of note, the counterion of the cluster is tetraoctylammonium (TOA⁺). The UV-vis absorption spectra were recorded on a Hewlett-Packard (HP) 8543 diode array spectrophotometer. MALDI-TOF mass spectrometry analysis was performed with a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer using DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix.

The Au₂₅(SR)₁₈/TiO₂ catalyst was made by impregnation of TiO₂ powders (Hombikat, Aldrich) in a dichloromethane solution of Au₂₅(SR)₁₈ nanoclusters, followed by drying and annealing at 150 °C for 1 hour in a vacuum oven. The gold cluster loading on the oxide support was determined by thermogravimetric analysis (TGA) [32], which indicated 0.94 wt.% clusters in the Au₂₅(SR)₁₈/TiO₂

catalyst by converting the ligand loss amount to the cluster amount according to the cluster formula. The $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ sample was further characterized by high-resolution scanning transmission electron microscopy (HR-STEM). As shown in Fig. S1 in the Supporting Information, the average particle size of TiO_2 oxide is ca. 15 nm. The interplanar spacing is found to be ~ 0.35 nm which corresponds to the prominent $\{101\}$ lattice of anatase TiO_2 . The size of the gold clusters is estimated to be ~ 1.3 nm, which is consistent with the size of unsupported $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters reported in literature [16].

2.2. Stability test of the unsupported $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters in the presence of the $\text{BMIM}\cdot\text{BF}_4$.

In this test, typically, 0.5 mg $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ nanoclusters was dissolved in CH_2Cl_2 and then 5 equiv $\text{BMIM}\cdot\text{BF}_4$ was added. The mixture was stirred at 400 rpm for 4h at room temperature. Further, the mixture sample was characterized by UV-vis and MALDI-MS. Of note, the laser intensity in the MALDI-MS of the three samples is same.

2.3. Typical Procedure for Suzuki Cross-Coupling Reaction.

In a typical coupling reaction, *p*-iodoanisole (0.1 mmol), phenylboronic acid (0.12 mmol), K_2CO_3 (0.36 mmol), $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ (100 mg, 1 wt.% loading $\text{Au}_{25}(\text{SR})_{18}$) and 1 mL ethanol (EtOH) and ionic liquids were added to a 5 mL vial. The mixture was stirred under N_2 atmosphere at 90 °C for 18h as indicated in Table 1. The $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ was separated by centrifugation. Then ethanol was removed by rotary evaporation, and extracted by 2 mL ether for three times. The products were obtained after removal of the ether, and then characterized by ^1H NMR (300 MHz). The conversion of *p*-iodoanisole was determined by NMR spectroscopic analysis.

2.4. DFT Calculations.

DFT calculations were performed to investigate oxidative addition of $\text{Au}_{25}(\text{SCH}_3)_{18}$ to a halide. All ground state geometry optimizations were carried out with the B3PW91 hybrid density functional and 6-31G(d,p) (H, C, N, O, S) and LANL2DZ (Au and I) basis sets [33-37]. To assess the accuracy of the

optimized geometries for gold nanoclusters, a time-dependent DFT (TD-DFT) calculation was performed for $\text{Au}_{25}(\text{SCH}_3)_{18}$ and its optical properties were compared with experimental results (see Fig. S2 in the Supporting Information) [20]. We have also used MIDI! basis set for I to examine the effect of basis sets on the iodine-incorporated structures [38]. The integral equation formalism polarizable continuum model (IEFPCM) was applied to study how solvation may influence the stabilization of a complex formed by a removed thiolate ligand and DMI, EtOH, or DMF [39]. All calculations were carried out with the Gaussian 09 package [36]. The crystal structure of $\text{Au}_{25}(\text{SR})_{18}$ was employed as a starting point for DFT calculations for nanoclusters [20].

2.5. MD Simulations.

Solvation structure of BMIM·BF₄ in ethanol was studied via MD. Four different IL concentrations, 0.083, 0.057, 0.029, 0.014 M, were considered. The number of ethanol molecules in the simulation system was 500 in all cases. At each IL concentration, energy optimization, annealing from 800 K to 363 K and equilibration for 2 ns were first conducted, followed by a 10 ns production run in the *NPT* ensemble at 1 *atm* and 363 K. All simulations were performed using the NAMD package [40]. The Langevin dynamics and Nose-Hoover Langevin piston methods were used to keep the temperature and pressure constant, respectively [41]. The particle mesh Ewald (PME) algorithm was used to calculate the long-range electrostatic interactions [42]. The van der Waals forces were truncated using a cutoff of 12 Å. The all-atom potential model based on OPLS-AA parameters was employed to compute intermolecular forces [43,44].

3. Results and Discussion

3.1. Imidazolium-promoted Suzuki Cross-Coupling.

The $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ nanocluster was synthesized following a literature procedure [21]. The atomic structure [20] of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ exhibits an icosahedral 13-gold-atom kernel and six staple-like

motifs of “-(SR2)-Au-(SR1)-Au-(SR2)-”, where 1 and 2 refer to the chemically nonequivalent positions (Scheme 1A). The $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst was made by impregnation of TiO_2 powders in a dichloromethane solution of $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters, followed by drying and annealing at 150 °C for 1 hour in a vacuum oven. The supported $\text{Au}_{25}(\text{SR})_{18}$ nanocluster remains intact (i.e. no decomposition) after the thermal treatment, as analyzed previously [19]. Four different imidazolium-based ionic liquids, i.e., BMIM•X (BMIM = 1-butyl-3-methylimidazolium) with X = Cl, Br, and BF_4 , and BDiMIM• BF_4 (BDiMIM = 1-butyl-2,3-dimethylimidazolium) in Scheme 1B are considered in this work.

Scheme 1. (A) Crystal structure of $\text{Au}_{25}(\text{SR})_{18}$ (= $\text{Au}_{25}(\text{SR1})_6(\text{SR2})_{12}$) nanoclusters in the ball-stick mode. Color codes: Au, cyan; S, yellow and orange. Carbon and hydrogen atoms are omitted for clarity. There are two non-equivalent types of thiolate ligands on the staple motif “-(SR2)-Au-(SR1)-Au-(SR2)-”. The ligand position on the staple motif is the only difference between the two types. (B) Imidazolium-based ionic liquids used in this work (top panel: 1-butyl-3-methylimidazolium, and bottom panel: 1-butyl-2,3-dimethylimidazolium).

To gain insight into the stability of the $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters in the presence of imidazolium-based ionic liquids, the unsupported nanoclusters were studied in three different solutions: *i*) a dichloromethane solution of $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters, *ii*) the same solution but in the presence of only BMIM• BF_4 , and *iii*) the same solution but in the presence of both BMIM• BF_4 and K_2CO_3 stirring for 4 h under the same conditions. As seen from Fig. 1A, the peak positions of the optical absorption spectrum

are similar for the three solutions. However, there are some differences in the peak intensities before/after the treatment with the IL and the base. This may indicate that the $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters undergo electronic/structural changes after the treatment with $\text{BMIM}\cdot\text{BF}_4$. In this context, it is worth noting that the change of the nanocluster charge from -1 (i.e., $[\text{Au}_{25}(\text{SR})_{18}]^-$) to 0 (i.e., neutral $\text{Au}_{25}(\text{SR})_{18}$) results in changes in the peak intensities at 400, 450 and 670 nm but not in the peak positions [14]. For further insight, we performed MALDI-MS analysis of the solutions. For solution *i*, two main peaks are observed (Fig. 1B, black line), one signal at $m/z = 7394.4$ (assigned to the molecular ion peak of $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters, theoretical molecular weight: $m/z = 7393.8$) and one at 6056.5 (assigned to $\text{Au}_{21}(\text{SR})_{14}$ fragment, theoretical m/z : 6057.3, after losing one $\text{Au}_4(\text{SR})_4$ unit from $\text{Au}_{25}(\text{SR})_{18}$ caused by the somewhat destructive MALDI method) [14,31]. In the case of solutions *ii* and *iii*, several peaks are observed (Fig. 1B, red and blue lines). The positions of these peaks are the same in the two solutions. The zoom-in spectrum of the nanoclusters treated in solution *ii* is shown in Fig. 1C (the spectrum in solution *iii* is very similar and thus is not shown). The peaks are assigned as follows: peak I at $m/z = 7394.4$ to $\text{Au}_{25}(\text{SR})_{18}$ (theoretical m/z : 7393.8), peak II at $m/z = 7061.2$ to $\text{Au}_{24}(\text{SR})_{17}$ (theoretical m/z : 7060.0), peak III at $m/z = 6725.1$ to $\text{Au}_{23}(\text{SR})_{16}$ (theoretical m/z : 6725.7), peak IV at $m/z = 6391.7$ to $\text{Au}_{22}(\text{SR})_{15}$ (theoretical m/z : 6391.5), and peak V to $\text{Au}_{21}(\text{SR})_{14}$ (theoretical m/z : 6057.3). This strongly indicates the generation of $\text{Au}_{25-n}(\text{SR})_{18-n}$ ($n = 1-4$). We note that the intensity of peak V (i.e., the $\text{Au}_{21}(\text{SR})_{14}$ species) was enhanced considerably in solutions *ii* and *iii*, compared to that of solution *i* (Fig. 1B, red/blue lines vs. black line). This suggests that the ILs may assist the formation of $\text{Au}_{21}(\text{SR})_{14}$ species during the MALDI-MS measurement. Of note, the laser intensity in the MALDI-MS analysis of the three solutions was the same.

Fig. 1. (A) UV-vis absorption spectra and (B) Positive mode MALDI mass spectra of the initial $[\text{Au}_{25}(\text{SR})_{18}]^-$ (in dichloromethane) and samples after the treatment with $\text{BMIM}\cdot\text{BF}_4$ or with $\text{BMIM}\cdot\text{BF}_4$ and K_2CO_3 . (C) Zoom-in of the MALDI mass spectrum of the sample after the treatment of $[\text{Au}_{25}(\text{SR})_{18}]^-$ with $\text{BMIM}\cdot\text{BF}_4$. The peak, in B, marked with an asterisk (*) is a fragment (i.e., the $\text{Au}_{21}(\text{SR})_{14}$ species) caused by MALDI method, rather than an impurity. Of note, the laser intensity in the MALDI-MS of the three samples is the same.

The catalytic process of the Suzuki cross-coupling reaction was carried out under the following conditions: 0.1 mmol iodoanisole, 0.12 mmol phenylboronic acid, 0.36 mmol K_2CO_3 , and 100 mg $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ (~1 wt.% loading of the ligand-protected nanoclusters) in different solvents at 90 °C for 18 hours (see details in the Experimental section). For regular organic solvents (Table 1, entries 1-4), reaction was performed in an EtOH:H₂O mixture, which is helpful to dissolve K_2CO_3 . We noted K_2CO_3 does not dissolve in common organic solvents (e.g., $\text{PhCH}_3 + \text{EtOH}$) in the absence of water. The reaction product was analyzed by ^1H NMR (Fig. S3 in the Supporting Information). The experimental results of the Suzuki cross-coupling reaction between phenylboronic acid and *p*-iodoanisole are compiled in Table 1. The most salient feature is that BMIM-based ILs exerted a major influence on the conversion of *p*-iodoanisole to the product. Specifically, in common organic solvents such as ethanol, toluene, *o*-xylene, and dimethylformamide (DMF), the $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst exhibits very low catalytic activity (<5% conversion of the *p*-iodoanisole) at 90 °C (Table 1, entries 1-4). When $\text{BMIM}\cdot\text{X}$ is added to the solvents (e.g. ethanol), the catalytic activity shows a drastic increase to 89–99% (Table 1, entries 5-8). Thus, $\text{BMIM}\cdot\text{X}$ acts as an excellent catalytic promoter for the Suzuki coupling reaction.

Another noteworthy aspect is that anions of BMIM•X only have a minor effect. This strongly indicates that it is the BMIM cation that effects the catalytic promotion of the Suzuki coupling reaction. Also notable is that the presence of water can increase the promotional effect of ionic liquids on the reaction conversion (Table 1, entry 7 vs 8). A possible reason includes better solvation of the base (K₂CO₃) in the presence of H₂O, thereby producing a higher concentration of hydroxide (OH⁻) ions in the reaction medium.

Table 1. Catalytic performance of thiolate-capped Au₂₅ cluster supported on titania as catalysts for Suzuki cross-coupling reaction of iodoanisole and phenylboronic acid.^a

Entry	Solvent	Conversion [%] ^b
1	EtOH:H ₂ O	<0.5
2	<i>o</i> -xylene + EtOH:H ₂ O	<0.5
3	PhCH ₃ + EtOH:H ₂ O	<0.5
4	DMF + EtOH:H ₂ O	4
5	BMIM•Br + EtOH	89
6	BMIM•Cl + EtOH	90
7	BMIM•BF ₄ + EtOH	94
8	BMIM•BF ₄ + EtOH:H ₂ O	>99
9	BDiMIM•BF ₄ + EtOH	<0.5

^aReaction conditions: 0.1 mmol iodoanisole, 0.12 mmol phenylboronic acid, 0.36 mmol K₂CO₃, 100 mg Au₂₅(SR)₁₈/TiO₂ (~1 wt.% cluster loading), solvents (1 mL EtOH or EtOH:H₂O (10:1, v/v), and 0.2 mL IL or other organic solvents), 90 °C, 18h. ^bThe conversion of iodoanisole was determined by ¹H NMR.

The molecular structure of BMIM led us to believe that its acidic hydrogen at the position-2 (Scheme 1B, top panel), hereafter referred to as H₂, plays an important role. To test this hypothesis, we studied the reaction with the ionic liquid BDiMIM•BF₄, which has no acidic hydrogen, added to the solvent ethanol. As shown in Table 1 (entry 9), no product conversion was observed in this case. This strongly suggests that H₂ of the BMIM is mainly responsible for the catalytic promotion of the Suzuki

cross-coupling reaction in the mixture of polar solvents and BMIM•X. We next consider the mechanism of this promotion.

3.2. Mechanism of Imidazolium-promoted Suzuki cross-coupling.

Extensive studies on bare gold clusters with no ligands attached have revealed that low-coordinated naked gold atoms on the surface are the main active sites for catalytic reactions. As noted above, while the mechanism of Suzuki cross-coupling reactions catalyzed by gold nanoclusters is not fully understood yet [5-7], oxidative addition (in which the catalyst is oxidized by dissociation of a carbon-halogen bond on the catalyst) is believed to be the first key process that is often rate-limiting [7,9-11,13]. We therefore restrict our attention to oxidative addition of the Suzuki coupling reaction and analyze the roles played by imidazolium-based ILs via the DFT method. For efficient calculations, $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$, iodoanisole, and BMIM are modeled as $\text{Au}_{25}(\text{SCH}_3)_{18}$, iodobenzene, and 1,3-dimethylimidazolium ($\text{DMI}-\text{H}_2^+$), respectively.

We first investigated possible active sites on $\text{Au}_{25}(\text{SCH}_3)_{18}$ for oxidative addition. DFT results indicate that the protected Au_{25} cluster is inert toward the activation of the C-I bond. This strongly suggests that structural/electronic changes are necessary to activate the gold cluster towards the oxidative addition.

In **Mechanism 1**, we consider removal of fragments of Au_{25} cluster such as thiolate ligands and “-Au-SR” units via imidazolium cations. We first examine how a $\text{DMI}-\text{H}_2^+$ cation interacts with and removes the fragments of the nanocluster, thereby producing low-coordinated gold atoms for iodobenzene adsorption. We should also note that Corma and coworkers reported the detection of H_2 formation during homo-coupling reaction on nanoclusters, indicating the possibility of gold oxidation [45]. In view of the protic nature of the solvents employed in the present work, it would be prudent to consider similar gold oxidation by H^+ for our system, especially at high temperatures, because the proton activity (chemical potential) increases with temperature. Thus in **Mechanism 2**, two different pathways

for protonation of gold nanoclusters that can also produce active sites for iodobenzene adsorption are considered.

As illustrated in Scheme 1A, there are two types of thiolate ligands on the staple motifs of $\text{Au}_{25}(\text{SR})_{18} = \text{Au}_{25}(\text{SR1})_6(\text{SR2})_{12}$, i.e., $-\text{SR}$ ligands bridging two exterior Au atoms (SR1) and those bridging an exterior Au atom and Au_{13} icosahedral core (SR2). The average Au-S bond lengths in the $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ nanocluster are 2.372 and 2.308 Å for $\text{Au}(\text{core})-\text{S}(\text{R2})$ and $\text{Au}(\text{staple})-\text{S}(\text{R1})$, respectively (Table 2). The DFT results for optimized $\text{Au}_{25}(\text{SR1})_5(\text{SR2})_{12}$ and $\text{Au}_{25}(\text{SR1})_6(\text{SR2})_{11}$ ($\text{R} = \text{CH}_3$) in the gas phase indicate that the removal of $-\text{SR2}$ is energetically favored by 18.6 kcal/mol over that of $-\text{SR1}$, as expected from the Au-S bond length differences (Table 2).

Table 2. Experimental results for $\text{Au}(\text{core})-\text{S}(\text{R2})$ and $\text{Au}(\text{staple})-\text{S}(\text{R1})$ bond lengths in the $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ nanoclusters.²⁰

Bond	Average length (Å)	Range (Å)
$\text{Au}(\text{core})-\text{S}(\text{R2})$	2.372	2.362 to 2.382
$\text{Au}(\text{staple})-\text{S}(\text{R1})$	2.308	2.300 to 2.313

With these results in mind, we consider *Mechanism 1* in Fig. 2. The first step (**Reac** $\rightarrow$ **Int1**) is adsorption of $\text{DMI}-\text{H}_2^+$ onto $-\text{SR2}$ through the interaction between H2 of the former and S of the latter with interatomic distance of 2.47 Å. This in turn induces a considerable elongation (0.04 Å) of the $\text{Au}(\text{core})-\text{SR2}$ bond. According to DFT calculations, the adsorption energy ΔE_{ad} (defined as $E(\text{NC}/\text{ad}) - E(\text{NC}) - E(\text{ad})$) is -59.0 kcal/mol, where $E(\text{NC}/\text{ad})$, $E(\text{NC})$, and $E(\text{ad})$ are the energies of the adsorbed system, isolated gold nanocluster and isolated adsorbate, respectively (Table 3). The energy released from this exothermic step can assist the removal of the interacting $-\text{SR2}/\text{DMIM}$ pair and thus the formation of $\text{Au}_{25}(\text{SR1})_6(\text{SR2})_{11} = \text{Au}_{25}(\text{SR})_{17}$ in the ensuing step (**Int1** $\rightarrow$ **Int2**), which is 45.5 kcal/mol endothermic. In Fig. S4 in the Supporting Information, another pathway of thiolate removal assisted by $\text{DMI}-\text{H}_2^+$ is considered. Upon $\text{DMI}-\text{H}_2^+$ adsorption, the thiolate group is first protonated (**Int1** $\rightarrow$

Int1*), and then detached from the nanoparticle (**Int1*** → **Int2**). DFT predicts that this stepwise ligand removal is about 7 kcal/mol more endothermic than the single-step removal **Int1** → **Int2** in Fig. 2. The higher endothermicity, in the stepwise process, is mainly due to the complete proton transfer from DMI—H₂⁺ to the thiolate group. The thiolate group removal yields a gold atom site, *G1* (Fig. 2), with only one ligand attached to it. Two hydroxide ([OH][−]) ions produced in the reaction media by K₂CO₃ (or IL anions) can coordinate to *G1* with Au—O distance of 2.02 Å and energy release of 178.3 kcal/mol (**Int2** → **Int3**). The coordinating [OH][−] ions (or IL anions) eventually displace the Au atom from the nanocluster in an exothermic step with Δ*E* = -2.9 kcal/mol, where Δ*E* is the energy difference between the product and reactant states. This results in the formation of [Au(OH)₂][−] and [Au₂₄(SCH₃)₁₇][−] with a possible active metal site, *G2*, on the icosahedral Au₁₃ core (**Int3** → **Int4**).

Upon adsorption of DMI—H₂⁺ onto −SR₂ (**Int1**), a hydroxide (or other anion) can attack the gold atom bonded to the −SR₂ on the same staple motif. This step, which yields DMI—H₂⁺, [HOAuSCH₃][−], and [Au₂₄(SCH₃)₁₇][−] (**Int1** → **Int4**, Fig. 2), is found to be endothermic by 6.0 kcal/mol. Comparison with **Int1** → **Int2** suggests that the **Int1** → **Int4** step is more favorable from energetics point of view, in good agreement with the MALDI-MS results of the unsupported gold nanoclusters, i.e., [Au₂₄(SR)₁₇][−] is detected but not Au₂₅(SR)₁₇. Furthermore, DFT shows that site *G1*, if produced, is not stable and thus is likely to react with the solvent media and ultimately detach from the nanocluster to form [Au₂₄(SR)₁₇][−]. Nonetheless, since the catalyst's support (TiO₂) can stabilize the nanoclusters which are not stable thermodynamically in the solution phase, we do not rule out the possibility that *G1* functions as a catalytically active site (see Table 4 below). Of note, the exposed gold atom in the core (**Int2**) that was bonded to the (removed) thiolate group becomes partially shielded by another staple motif situated nearby (cf. Scheme 1A). As such, it becomes less exposed and thus less active than the low-coordinated Au atom on the staple motif.

For completeness, we also considered the possibility of “-Au-SR” removal via N-heterocyclic carbene that can be formed from the imidazolium cation (Fig. S5 in the Supporting Information) [46,47].

DFT results obtained with the all-electron 6-31G(d,p) basis set for sulfur indicate that 1,3-dimethylimidazol (DMI) does not show appreciable interactions with –SR groups or with Au atoms. However, when the corresponding valence basis set 6-31G(d,p) together with the appropriate Stuttgart-Dresden effective core potentials (ECPs) is employed for S [48,49], DMI can interact strongly with Au on the staple motif. This can lead to cleavage of the Au-SR1 bond with $\Delta E = -22.1$ kcal/mol (**Reac** $\rightarrow$ **Int5**, Fig. 2). The DMI–Au–SCH₃ moiety eventually detaches from the nanoparticle with $\Delta E = +26.4$ kcal/mol (**Int5** $\rightarrow$ **Int4**). The detached complex may undergo a hydrolysis to form DMI–H₂⁺ and [HOAuSCH₃][–] with $\Delta E = +103.0$ kcal/mol. In view of their strong basis-set dependence, however, care should be taken in the interpretation of the results for the carbene pathway presented here.

While [Au₂₄(SR)₁₇][–] with *G2* (**Int4**) can catalyze cross-coupling reactions, it can also interact with DMI–H₂⁺ and form [Au_{25–n}(SR)_{18–n}][–] through a sequential removal of “–Au-SR” units. Among different thiolate groups of **Int4**, the –SR1 group of the staple motif with a “–Au-SR2” unit removed probably provides the best site for DMI–H₂⁺ to interact with in the formation of [Au₂₃(SR)₁₆][–]. Because it is linked to only one Au, it is well exposed to the solvent media. Furthermore, the partial atomic charge for sulfur of the –SR1 group determined with the electro-static potential (ESP) method is -0.51, while that of the –SR2 groups is on average -0.34 (Fig. S6 in the Supporting Information). Thus the Coulomb interaction of the former with positively charged DMI–H₂⁺ will be stronger than that of the latter. The resulting [Au₂₃(SR)₁₆][–] nanocluster can lose two more “–Au-SR” units from a nearby stable motif in the same way and become [Au₂₁(SR)₁₄][–] (**Int4** $\rightarrow$ **Int8**) with an active site, *G4* (Fig. S7 in the Supporting Information).

shown in Fig. 2 using PCM (polarizable continuum model) calculations. It should be mentioned that the small complexes were fully re-optimized using DFT/PCM calculations. Due to the high computational cost for the models containing the gold nanoclusters, only single point DFT/PCM calculation was conducted on the gas-phase optimized structures. Because of this approximation and due to the fact that the continuum approach tends to overestimate the solvation effect [51], our results offer qualitative insights rather than accurately quantifying the actual exothermicity/endothemicity in the solution phase. As Table 3 indicates, solvation in a highly polar solvent can stabilize charged species like DMI—H_2^+ and $[\text{Au}_{25-n}(\text{SR})_{18-n}]^-$ significantly. For example, the **Reac** $\rightarrow$ **Int1** $\rightarrow$ **Int2** step becomes 35.2 kcal/mol endothermic in a polar solvent even though it is 13.5 kcal/mol exothermic in the gas phase! A considerably lesser solvation effect is expected for steps where the charge species are not produced or consumed (e.g. **Reac** $\rightarrow$ **Int5**, **Int4** $\rightarrow$ **Int6**, and **Int6** $\rightarrow$ **Int7**). Consistent with the gas phase calculations and experimental results, DFT/PCM also indicates that the **Int1** $\rightarrow$ **Int2** step is less favorable than **Int1** $\rightarrow$ **Int4**.

Table 3. DFT results for ΔE (kcal/mol) for elementary steps of *Mechanism 1* (Fig. 2) in the gas and solution phases (PCM calculations, solvent = ethanol)

Steps	Gas phase	Solution phase
Reac $\rightarrow$ Int1	-59.0	+0.9
Int1 $\rightarrow$ Int2	+45.5	+34.3
Int2 $\rightarrow$ Int3	-178.3	-111.6
Int3 $\rightarrow$ Int4	-2.9	+12.1
Int1 $\rightarrow$ Int4	+6.0	-28.2
Reac $\rightarrow$ Int5	-22.1	-23.1
Int5 $\rightarrow$ Int4	+26.4	+15.5
Int4 $\rightarrow$ Int6	+0.9	+5.9
Int6 $\rightarrow$ Int7	+20.2	+13.4
Hydrolysis of DMI—Au—SCH ₃	+103.0	+20.4

We also examined the ligand removal by regular solvents, in particular, ethanol and DMF. The adsorption energies are $\Delta E_{\text{ad}} = -4.9$ and -1.9 kcal/mol for EtOH and DMF, respectively. Comparison with the DMI—H₂⁺ case ($\Delta E_{\text{ad}} = -59.0$ kcal/mol) shows that the adsorption of DMI—H₂⁺ is strongly favored over that of EtOH or DMF. As for the interaction of the removed thiolate group ([–SCH₃][–]) with the solvents, we found that its bond energy is 19.3 kcal/mol with an EtOH molecule and 13.8 kcal/mol with a DMF molecule (Fig. S8 in Supporting Information). This is much weaker than the interaction of the removed thiolate group with DMI—H₂⁺, which has a bond energy of 101.9 kcal/mol. The results for the adsorption and bond energies thus indicate that imidazolium cations are much more effective in removing thiolate ligands than polar solvent molecules. Even with the inclusion of the solvation effect (Supporting Information), this conclusion appears to be valid.

To gain insight into ion pairing of BMIM and X (X= Cl, Br, BF₄) and its influence on BMIM reactivity towards thiolate ligands, we analyzed the distribution of anions X around H2 of BMIM using molecular dynamics (MD) simulations. The results for X= BF₄ (Fig. S9 in the Supporting Information) show that ion pairing via H2 is reduced substantially in EtOH, compared to pure IL. This suggests that solvation in polar solvents tends to break IL ion pairs and make H2 of BMIM available to interact with thiolate ligands of the nanoclusters; viz., solvation enhances BMIM's adsorption capability.

The low-coordinated Au atoms (*G1*, *G2*, *G3*, and *G4*) on the nanoclusters that are produced with the help of ionic liquids may act as active sites to adsorb iodobenzene. For insight into their catalytic activity, we examined adsorption energy, ΔE_{ad} , of iodobenzene on these sites. DFT with the LANL2DZ basis set for iodine (and gold) yields ΔE_{ad} of -3.5 , -3.5 , -7.5 , and -9.1 kcal/mol for *G1*, *G2*, *G3*, and *G4*, respectively (Table 4). With the MIDI! basis set employed for iodine, ΔE_{ad} becomes -10.8 , -12.3 , -18.5 , and -19.1 kcal/mol, respectively. This increase in the magnitude of ΔE_{ad} is attributed to the polarization functions included in the MIDI! basis set, which allow iodine to be hypervalent (with carbon and gold). We note that with the exception of [Au₂₅(SR)₁₇]⁰ which is neutral, nanoclusters carry a net charge of -1 (see Fig. 2). However, in a protic solvent such as ethanol and water, it would be prudent to consider the

oxidation of Au particles. Although the redox potential (E_0) for such a reaction is not high enough for spontaneous oxidation of bulk gold, previous studies indicate that the oxidation potential of metal nanoclusters is usually size-dependent and tends to decrease as they become smaller [52-55]. This decrease is attributed to change in Gibbs free energy, which is associated with a high surface-to-volume ratio and chemical potential of the particles. Such a change in the oxidation potential is shown for small metal clusters that can reduce organics [56]. Our analysis shows that the oxidation of the Au nanoclusters usually leads to a superior interaction between iodobenzene and the active sites (see Table 4). Among all active sites studied here, $G3$ and $G4$ on the neutral Au nanoclusters, $[\text{Au}_{24}(\text{SR})_{17}]^0$ and $[\text{Au}_{21}(\text{SR})_{14}]^0$, show the strongest interaction with iodobenzene.

Table 4. Adsorption energy (ΔE_{ad} , kcal/mol) of iodobenzene on different active sites shown in Fig. 2 at different oxidation states. Units for Au—I: Å. The stronger interaction between iodine and the active gold sites can be tracked by the shorter Au—I bond length.

Active site	Cluster	ΔE_{ad}	Au—I
$G1$	$[\text{Au}_{25}(\text{SR})_{17}]^0$	-3.5 (-10.8)	3.116 (2.859)
	$[\text{Au}_{25}(\text{SR})_{17}]^+$	-5.7	2.992
$G2$	$[\text{Au}_{24}(\text{SR})_{17}]^-$	-3.5 (-12.3)	3.025 (2.802)
	$[\text{Au}_{24}(\text{SR})_{17}]^0$	-4.8	2.974
	$[\text{Au}_{24}(\text{SR})_{17}]^+$	-6.6	2.946
$G3$	$[\text{Au}_{24}(\text{SR})_{17}]^-$	-7.5 (-18.9)	2.920 (2.686)
	$[\text{Au}_{24}(\text{SR})_{17}]^0$	-13.3	2.759
$G4$	$[\text{Au}_{21}(\text{SR})_{14}]^-$	-9.1 (-19.1)	2.912 (2.754)
	$[\text{Au}_{21}(\text{SR})_{14}]^0$	-11.8	2.854
	$[\text{Au}_{21}(\text{SR})_{14}]^+$	-5.2	3.375

We also studied how oxidation of the gold cluster may influence the interaction between the IL cations and nanoclusters. DFT predicts that the interaction of DMI—H_2^+ with -SR2 group of

$[\text{Au}_{25}(\text{SR})_{18}]^0$ and $[\text{Au}_{25}(\text{SR})_{18}]^+$ in the gas phase is -20.3 and +23.2 kcal/mol, respectively. These interactions are considerably weaker than that between $\text{DMI}-\text{H}_2^+$ and -SR2 group of $[\text{Au}_{25}(\text{SR})_{18}]^-$ (-59.0 kcal/mol, **Reac** $\rightarrow$ **Int1**, Table 3). We can qualitatively understand the results as follows: All other things being equal, the interaction of two opposite charges ($\text{DMI}-\text{H}_2^+$ and $[\text{Au}_{25}(\text{SR})_{18}]^-$) is stronger than that of two like charges ($\text{DMI}-\text{H}_2^+$ and $[\text{Au}_{25}(\text{SR})_{18}]^+$) or of a neutral ($[\text{Au}_{25}(\text{SR})_{18}]^0$) and a charge ($\text{DMI}-\text{H}_2^+$). Our analysis indicates that oxidation of the Au nanoclusters may prevent further fragmentation of the nanoparticles induced by ILs.

Finally, we consider the activation of Au nanoclusters via protonation (Fig. S10 in the Supporting Information). There are three different possible sites on the Au nanocluster that can adsorb protons generated in the media: sulfur atoms of two different thiolate groups (-SR1 and -SR2) and the surface gold atoms. According to the DFT calculations, protonation of -SR2 is more favorable by 12.4 and 17.0 kcal/mol than the protonation of -SR1 and surface gold atoms, respectively. Removal of protonated -SR1 and -SR2 was found to be endothermic by 7.7 and 1.5 kcal/mol, respectively. As such, protonated thiolate groups (-SR2) may eventually be dissociated from the nanocluster, yielding low coordinated gold atoms for the catalytic reaction (Fig. S10A), similar to **Int2** in Fig. 2. Since the increase in temperature lowers proton adsorption selectivity, one should also consider protonation of gold atoms, especially at elevated temperatures (**Reac*** in Fig. S10B). The adsorbed H^+ on the gold is capable of interacting with iodine of iodobenzene with energy release 3.2 kcal/mol (**Reac*** $\rightarrow$ **Int11**). With MIDI! basis set for I, the result becomes $\Delta E = -5.9$ kcal/mol.

Since any protic solvent molecules can be the source of proton, our theoretical analysis here predicts that a weak acid, such as acetic acid, is a better promoter than regular solvents. Specifically, the DFT result for interaction energy between CH_3COOH and a removed thiolate group ($[-\text{SCH}_3]^-$) is -25.0 kcal/mol. Although this interaction is considerably weaker than that of the removed thiolate group with $\text{DMI}-\text{H}_2^+$ (-101.9 kcal/mol), it is stronger than the interaction of DMF, EtOH, or water with $[-\text{SCH}_3]^-$ (Fig. S8). Therefore, CH_3COOH would promote the cross coupling reaction better than the regular

solvents, even though not as well as ILs. To test this, we proceeded: The $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst was stirred for 12h at room temperature in a solution of ethanol/acetic acid ($\text{Au}_{25}(\text{SR})_{18}:\text{CH}_3\text{COOH} = 1:100$, mol/mol). Next, the $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst was separated by centrifugation and washed with ethanol for three times. The treated catalyst was then examined for the coupling reaction in a mixture solution of DMF/EtOH/water (same as entry 4 of Table 1). The reaction conversion was found to reach 9%, more than twice the result in entry 4 of Table 1, in good agreement with theoretical predictions. This indicates that our computational analysis via DFT/PCM, though qualitative, properly captures energetics of Suzuki cross coupling reactions in solution.

4. Conclusion

In summary, we have investigated the Suzuki cross-coupling reaction of phenylboronic acid and *p*-iodoanisole catalyzed by TiO_2 -supported $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ nanoclusters. A pronounced promotion of the reaction was attained with the addition of imidazolium-based ionic liquids to the solvent media. Both the experimental and computational results suggest that the acidic hydrogen atom H2 of imidazolium cations plays a central role in promoting the cross-coupling reaction. Based on DFT simulations, two different mechanisms for oxidative addition of protected gold nanoclusters were proposed. The pathway based on the removal of thiolate ligands of the protected Au_{25} (**Mechanism 1**) is believed to be the main catalytic mechanism under the reaction condition we studied. Specifically, imidazolium cations adsorb onto ligands $-\text{SR}_2$ and remove fragments of the gold cluster, producing active gold sites to catalyze cross-coupling reactions. Compared to common solvents (ethanol and DMF), the imidazolium cations of the ionic liquids engender strong interactions with the surface thiolate ligands on the cluster, which is the key for the promotional role of the imidazolium cations. Our work reported here shows that the $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ catalyst can successfully enable molecular-level understanding of the promotional effect of ionic liquids in the nanocluster-catalyzed Suzuki cross-coupling reaction. It would thus be worthwhile in the future to extend the present approach based on

nanocluster catalysts and the structure-based DFT with account of solvation effects to other catalytic reactions to understand their molecular mechanisms. The mechanistic understanding of the IL-induced activation/promotion is significant, as it suggests the possibility of applying ILs in the harsh and difficult reactions (such as Sonogashira coupling reaction) to achieve high catalytic activity under mild conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi: xxx. STEM image of $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst, optimized structure and theoretical absorption spectrum of $[\text{Au}_{25}(\text{SCH}_3)_{18}]^-$, TEM image of $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst after the treatment with BMIM• BF_4 and K_2CO_3 , ^1H NMR spectrum, proposed reaction based on thiolate removal in the form of H-SCH_3 , formation of 1,3-dimethylimidazol by treatment of ionic liquid DMI— H_2^+ with a base (OH^-), structure of $[\text{Au}_{24}(\text{SR})_{17}]^-$, molecular structure of $[\text{Au}_{21}(\text{SR})_{14}]^-$ with a possible active site (G4) on the Au_{13} -core, interaction energy of a $-\text{SCH}_3$ group with DMI— H_2^+ , ethanol, DMF, TriMIM, and H_2O in gas phase, solvation effects on the energy species compared to gas phase, average coordination number of H_2 (BMIM) with respect to BF_4^- , and proposed reaction *Mechanism 2* based on protonation of gold nanoclusters.

Notes

The authors declare no competing financial interest.

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