

# Nonredox Metal-Ion-Accelerated Olefin Isomerization by Palladium(II) Catalysts: Density Functional Theory (DFT) Calculations Supporting the Experimental Data

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**Supporting Information** 

**ABSTRACT:** Redox metal-ion-catalyzed olefin isomerization represents one of the important chemical processes. This work illustrates that nonredox metal ions can sharply accelerate Pd(II)-catalyzed olefin isomerization, while Pd(II) alone is very sluggish. Nuclear magnetic resonance (NMR) and ultraviolet-visible light (UV-vis) characterizations disclosed that the acceleration effect originates from the formation of heterobimetallic Pd(II) species with added nonredox metal ions, which improves the C-H activation capability of the Pd(II) moiety. Density functional theory (DFT) calculations further confirmed the sharp decrease of the energy barrier in C-H activation by the heterobimetallic Pd(II)/Al(III) species.



KEYWORDS: olefins, isomerization, density functional theory, energy barrier, nonredox metal ions

ate-transition-metal ions play significant roles in versatile ∠C−H activation and functionalization, and in certain cases, the counteranion of the redox metal ions may significantly affect the reactivity.<sup>1</sup> To achieve the efficient oxidative C-H bond activation by palladium(II) catalyst, copper(II) salts were popularly employed as stoichiometric oxidant or co-catalyst when dioxygen was employed as the terminal oxidant.<sup>2,3</sup> Unprecedentedly, we recently observed that, in Wacker-type oxidations, nonredox metal ions like Sc(III) can accelerate Pd(II)-catalyzed olefin oxidation even better than Cu(II), implicating that the Lewis acid properties of Cu(II) may play significant role as well as its redox properties, and a heterobimetallic Pd(II)/Sc(III) dimer having diacetate bridge was proposed as the key active species for oxidation. In fact, bimetallic catalysis has been applied in versatile organic synthesis as well as Ziegler catalysis.<sup>5</sup> We also observed that adding nonredox metal ions can substantially accelerate redox metal ions such as manganese- and iron-mediated catalytic oxidations, and adding Al(III) to the Pd<sup>II</sup>(bpym) complex can promote its benzene hydroxylation to phenol (bpym = 2,2'bipyrimidine), whereas Pd<sup>II</sup>(bpym) alone is very sluggish in activating the C-H bond of benzene.<sup>6,7</sup> The recovered C-H activation ability of the Pd<sup>II</sup>(bpym) was attributed to binding of nonredox Al<sup>3+</sup> through two remote N atoms in the bpym ligand to generate Pd<sup>II</sup>-bpym-Al<sup>3+</sup> complex, which positively shifts the redox potential of Pd(II) species. Inspired by these Lewis-acidpromoted C-H bond activations, herein, we report a nonredox

metal-ion-promoted olefin isomerization by simple  $Pd(OAc)_2$  catalyst. It was found that adding nonredox metal ions can sharply accelerate Pd(II)-catalyzed olefin isomerization, and the catalytic efficiency is highly Lewis acidity strength-dependent, whereas  $Pd(OAc)_2$  alone is very sluggish. Detailed density functional theory (DFT) calculations provided more-detailed information about the roles of the nonredox metal ions in improving the catalytic efficiency of Pd(II) in olefin isomerization. The strategy of catalyst design demonstrated here may offer those sluggish Pd(II)-based catalysts new opportunity in olefin isomerization, which has a great market in the perfumery, fragrance, and food industries.

To explore nonredox metal-ion-promoted olefin isomerization with Pd(II) catalyst, we first focused on allylbenzene as a substrate, using simple  $Pd(OAc)_2$  as a catalyst, and the results are summarized in Table 1. In acetonitrile at 30 °C, in the absence of Lewis acid,  $Pd(OAc)_2$  alone as a catalyst is inactive for olefin isomerization. It can be rationalized by the fact that there is no extra protonic source such as alcohol in the reaction mixture to facilitate the formation of the Pd(II) hydride moiety to initialize the [1,2]-hydrogen shift mechanism, while the Pd(II)/Pd(IV) catalytic cycle for the [1,3]-hydrogen shift

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# Table 1. Nonredox Metal-Ion-Promoted Allylbenzene Isomerization by $Pd(OAc)_2$ Catalyst<sup>a</sup>

	у́ —	-> Cis	+ trans	~
			Yield (%)	
entry	Lewis acid	conversion (%)	trans	cis
1	Na(OTf)	0.09	0.02	
2	$Mg(OTf)_2$	46.5	40.2	1.9
3	$Ca(OTf)_2$	44.2	37.3	2.5
4	$Zn(OTf)_2$	55.4	45.9	3.5
5	$Cu(OTf)_2$	85.6	82.5	1.2
6	$Al(OTf)_3$	98.9	97,2	0.7
7	$Sc(OTf)_3$	87.1	85.0	1.9
8	$Y(OTf)_3$	81.5	77.8	1.2
9 <sup>b</sup>	$Al(OTf)_3$	12.5	9.2	

<sup>*a*</sup>Conditions: acetonitrile volume, 3 mL;  $Pd(OAc)_2$  concentration, 1 mM; Lewis acid concentration, 2 mM; allylbenzene 100 mM, 30 °C under air, 2 h. <sup>*b*</sup>Using isopropanol (3 mL) as the solvent.

mechanism is energetically unfavorable, as are those in the literature.<sup>8</sup> Adding monovalent NaOTf to the Pd(OAc)<sub>2</sub> catalyst does not generate any improvement for isomerization. However, adding divalent metal ions such as Mg(II), Ca(II), and Zn(II) substantially promote the catalytic activity of the Pd(II) catalyst, providing 40.2%, 37.3%, and 45.9% of transmethylstyrene product (E isomer) with 1.9%, 2.5%, and 3.5% cis-methylstyrene product (Z isomer), respectively. In particular, adding Cu(OTf)<sub>2</sub> can offer 82.5% E isomer with 1.2% Z isomer within 2 h. Compared with other divalent metal ions such as Zn(II), Cu(II) is redox active and widely employed as stoichiometric oxidant or co-catalyst in versatile Pd(II)catalyzed oxidative C-H activations.<sup>2,3</sup> Here, in Pd(II)catalyzed olefin isomerization, the redox properties of Cu(II) are apparently not essential, since there is no extra oxidant required for olefin isomerization. More importantly, nonredox trivalent metal ions such as Al(III) can accelerate Pd(II)catalyzed olefin isomerization more efficiently than Cu(II), providing 97.2% E isomer with 0.7% Z isomer within 2 h; adding Sc(III) to Pd(OAc)<sub>2</sub> also gave 85% E isomer with 1.9% Z isomer. In control experiments, using  $Al(OTf)_3$  alone as a catalyst is inactive for olefin isomerization. Clearly, adding nonredox metal ions would greatly promote Pd(II)-catalyzed olefin isomerization, and the improvement is highly Lewis-acidstrength-dependent on added metal ions. Compared with acetonitrile solvent, using isopropanol as a solvent sharply retards the reaction, providing only 9.2% E isomer within 2 h, with no detectable Z isomer with Pd(II)/Al(III) catalyst. In addition, the preliminary DFT calculations also support that isopropanol is a poor solvent for this catalysis (see Figures S15 and S16 in the Supporting Information). In the literature, isopropanol and other protonic solvents were generally employed as co-catalysts or additives for in situ generation of the active metal-hydride moiety to initiate olefin isomerization.<sup>8</sup> Apparently, the invalidity of isopropanol as a solvent indicates an alternative mechanism other than [1,2]-hydrogen shift operates here.

Reaction kinetics further confirmed the promotional effect of nonredox metal ions in Pd(II)-catalyzed olefin isomerization. As shown in Figure S1 in the Supporting Information, adding NaOTf does not show any promotional effect, while other metal ions substantially accelerate isomerization. Notably, as well-disclosed in Table 1, Figure 1 further confirms that the isomerization rate increases in the order of added monovalent,



Figure 1. UV-vis spectra of (a) kinetic formation of heterobimetallic Pd(II)/Al(III) dimer and (b)  $Pd(OAc)_2$ ,  $Al(OTf)_3$ , or final Pd- $(OAc)_2/Al(OTf)_3$  in acetonitrile.

divalent, and trivalent metal ions, which is consistent with their increased Lewis acidity. The influence of the Al(III)/Pd(II) ratio on the Pd(II)-catalyzed allylbenzene isomerization was also investigated (see Figure S2 in the Supporting Information). It was found that increasing the ratio of Al(III)/Pd(II) from 0 to 1 sharply accelerates the isomerization reaction, while increasing the ratio to 2 just slightly improves the catalytic efficiency; further increasing the ratio to 3 or 4 demonstrates a slightly negative effect, which is different from Pd(II)/Sc(III)catalyzed Wacker-type oxidation.<sup>4</sup> In Pd(II)/Sc(III)-catalyzed olefin oxidation, the ratio of 4 is much more efficient than that of 1. In that reaction, the roles of Sc(III) cation were explained in two aspects: one is to ligate with Pd(II) through two acetate bridges to accelerate Pd(II)-catalyzed olefin oxidation, and the other is to generate a Sc(III)…H-Pd(II) intermediate, thus facilitating the insertion of dioxygen to generate the HOO-Pd(II) intermediate. Thereof, the presence of excess Sc(III) is critical for efficient Pd(II)-catalyzed Wacker-type oxidation. In this work, dioxygen insertion of the H-Pd(II) bond is not an elementary step in olefin isomerization, thus extra amounts of Al(III) are not essential for the Pd(II) catalyst here.

Next, the substrate scope of olefin isomerization was investigated, and the results are summarized in Table 2. One may see that, as well as allylbenzene, its derivatives can also be isomerized feasibly at ambient temperature. For example, isomerization of 2,4-dimethoxyl allylbenzene offered 99.5%

# Table 2. Substrate Scope of Olefin Isomerization by $Pd(OAc)_2/Al(OTf)_3^{a}$

			Yield	(%)	
entry	substrate	time (h)	conversion (%)	trans	cis
1	allybenzene	2	98.9	97.2	0.7
2	4-methoxyl allylbenzene	2	99.9	98.7	0.9
3	2,4-dimethoxyl allylbenzene	4	99.5	97.8 (87)	1.7
4	eugenol	4	99.7	94.2 (83)	5.1
5	1-hexene	0.3	99.5	95.3 (ison	ners)
6	1-dodecene	0.3	99.8	94.1 (ison	ners)
7	1-octene	0.3	99.9	95.2 (ison	ners)
8	4-methylpentene	0.3	99.9	95.2 (ison	ners)
9 <sup>b</sup>	1,5-COD	24	99.2	95.6 <sup>c</sup>	2.3 <sup>d</sup>

<sup>*a*</sup>Conditions: acetonitrile, 3 mL;  $Pd(OAc)_{2^{j}}$  1 mM;  $Al(OTf)_{3^{j}}$  2 mM; olefin, 100 mM; 30 °C, data in brackets represent isolated yield. <sup>*b*</sup>2 mM Pd(OAc)\_{2^{j}} 4 mM Al(OTf)<sub>3</sub>, 100 mM olefin, 90 °C. °Yield of 1,3-COD. <sup>*d*</sup>Yield of 1,4-COD.

conversion with 97.8% yield of the E isomer and 1.7% yield of Z isomer at 30 °C within 4 h. In particular, it is worth mentioning that the ratio of E:Z isomer generated here is remarkably high. Also, in the isomerization of eugenol, the yield of trans-isoeugenol is 94.2% with a 5.1% yield of cis-isoeugenol when  $Al(OTf)_3$  was employed as additives. More importantly, in a 10 g scale isomerization of eugenol with only 0.1 mmol %  $Pd(OAc)_2$  and 0.2 mmol %  $Al(OTf)_3$  loading, a yield of 96% can be achieved with an E/Z isomer ratio of 95:5 in 12 h at 50 °C. It was reported that the ongoing commercial process with H<sub>2</sub>SO<sub>4</sub> and KOH generally only gives a 82:18 ratio of E/Z isoeugenol, with a total yield of 56%, and the reaction temperature is as high as 200 °C.9 Because cis-isoeugenol has an unpleasant taste and, in some cases, a toxic character in food industries, the content of cis-isoeugenol should be <1%. Apparently, the Pd(II)/Al(III) catalyst demonstrated here is much more attractive than the ongoing commercial process, not only because of the high ratio of E/Z isomer formation, but also its simplicity and more environmentally benign process. As well as arylalkenes, linear olefins, such as 1-hexene, 1-octene, 1dodecene, and even 4-methylpentene can be feasibly isomerized to the corresponding internal olefin mixtures in 20 min at 30 °C. Isomerization of cyclic olefin is generally very sluggish, because of its steric hindrance. Here, isomerization of 1,5-cyclooctadiene (1,5-COD) required 24 h at 90 °C to achieve 99.2% conversion, providing a 95.6% yield of 1,3cyclootadiene (1,3-COD) with a 2.3% yield of 1,4-cyclooctadiene (1,4-COD), and the Pd(II)/Al(III) loading must be doubled. Because of serious steric hindrance, 4-ethenylcyclohexene cannot be isomerized by the Pd(II)/Al(III) catalyst here.

In UV-vis characterizations of the catalyst (Figure 1), adding  $AI(OTf)_3$  to the acetonitrile solution of  $Pd(OAc)_2$  triggered the immediate formation of an intermediate, having the absorbance band maximum at 278 nm. This intermediate decays gradually to form a stable species having a characteristic absorbance band at ~310 nm, and the original yellow color of the Pd(II) species changes to a pale yellow of the new species. In particular, adding olefin to this new species in acetonitrile can immediately trigger the formation of the above intermediate again (see Figure S3 in the Supporting Information). In <sup>1</sup>H NMR spectra (Figure 2), Pd(OAc)<sub>2</sub> alone in acetonitrile- $d_3$  reveals a chemical

	B Pd(C	OAc) <sub>2</sub> + Al(OTf) <sub>3</sub>	$\begin{array}{c} Pd(OAc)_2 + Al(0) \\ 173.10 \\ 181.78 \\ 167.48 \\ 167.48 \\ 167.48 \\ 181.78 \\ 167.48 \\ 181.78 \\ 167.48 \\ 181.78 \\ 100$	OTf) <sub>3</sub> 24.49 21.05
1.97		Pd(OAc) <sub>2</sub>	173.73 Pd(OAc)2	21.15
1.98	u	СН <sub>3</sub> СООН	176.23 СН3СООН	21.14
	1.81	CH <sub>3</sub> COONH <sub>4</sub>	180.43 CH3COONa	23.02
	1.82	CH <sub>3</sub> COONa	Al(OTf)3	Jun marine
2.1 2.0	1.9 1.8	1.7 1.6	180 170 130 1	20 20

**Figure 2.** NMR spectra of  $Pd(OAc)_2/Al(OTf)_3$  with related compounds in acetonitrile- $d_3$ .

shift of 1.97 ppm, which can be assigned to the methyl group of acetate in  $Pd_3(OAc)_6$  trimer in which all of the acetates serve as a bridge like those in the literature.<sup>10</sup> Adding Al(OTf)<sub>3</sub> to the acetonitrile solution of  $Pd(OAc)_2$  slightly shifts the chemical shift of methyl group of acetate from 1.97 ppm to 1.98 ppm with another chemical shift at 2.06 ppm, indicating the formation of the new species. In <sup>13</sup>C NMR spectra, adding Al(OTf)<sub>3</sub> causes the chemical shifts at 173.73 and 21.15 ppm for  $Pd(OAc)_2$  in acetonitrile- $d_3$  to become complicated. It

demonstrates three chemical shifts for the carbonyl group (181.78, 173.10, and 167.48 ppm) and two for the methyl group (24.49 and 21.05 ppm), indicating the occurrence of three categories of acetate in this Pd(II)/Al(III) solution. The downshifts of carbonyl at 181.78 ppm with methyl at 24.49 ppm suggest that a more electron-deficient group than Pd(II) has become linked to acetate, while the chemical shifts at 173.10 and 21.05 ppm indicate that free  $Pd_3(OAc)_6$  trimer still exists. However, the shift at 167.48 ppm for carbonyl group further implies that the third category of acetate exists in solution, which has indistinguishable methyl chemical shifts in both <sup>1</sup>H and <sup>13</sup>C NMR graphs from those of Pd<sub>3</sub>(OAc)<sub>6</sub> trimer, which was further evidenced by 1H-13C HSQC NMR (see Figure S4 in the Supporting Information). In the complementary experiments, the <sup>27</sup>Al NMR studies were conducted as shown in Figure S9 in the Supporting Information. In acetonitrile, Al(OTf)<sub>3</sub> alone displayed several peaks between 10 ppm and -20 ppm, indicating the presence of several Al<sup>3+</sup> species having an octahedral coordination environment;<sup>11</sup> however, in  $Pd(OAc)_2/Al(OTf)_3$  solution (ratio 1:1), the peaks change sharply to a broadened resonance between 10 ppm and -10 ppm, clearly indicating that an interaction between Pd(II) and Al(III) cations exists. According to these changes with DFT calculations (vide infra), the acetate ligands in this Pd(II)/Al(III) system can be assigned in three forms: (a) heterobimetallic Pd(II)/Al(III) dimer, having two acetate bridges; (b) heterobimetallic Pd(II)/Al(III) dimer, having one acetate bridge with another acetate ligated to Pd(II) cation (Figure 3); and (c) original  $Pd_3(OAc)_6$ .



Figure 3. Proposed heterobimetallic Pd(II)/Al(III) dimer having (a) two acetate bridges and (b) one acetate bridge, based on NMR studies.

In order to understand the effect of Lewis acid on the Pd(II)catalyzed allylbenzene isomerization, we performed DFT calculations<sup>12'</sup> for the catalytic systems with and without Al(OTf)<sub>3</sub>. The calculated Gibbs free energy diagram is shown in Figure 4 (for optimized structures, see Figures S11-S19). The most striking difference between catalytic systems with and without  $Al(OTf)_3$  comes from the energetics for the generation of the active catalytic species. For  $Pd(OAc)_2$  alone, the trimeric form  $Pd_3(OAc)_6$  is the most stable form in solution,<sup>10,13</sup> and the formation of the monomeric species  $Pd(OAc)_2$  is endergonic by 14.8 kcal/mol. The addition of Al(OTf)<sub>3</sub> facilitates the decomposition of  $Pd_3(OAc)_6$  to generate a dimeric Pd(II)/Al(III) species, and this process becomes exergonic by as much as 22.8 kcal/mol. The calculations agree quite well with our NMR studies, which suggest a heterobimetallic Pd(II)/Al(III) dimeric species.

For Pd(OAc)<sub>2</sub>-catalyzed isomerization, the reaction starts with the coordination of the substrate allyl double bond to Pd(II), This is followed by proton transfer (**TS1**) from C1 to acetate to form a  $\eta^3$ -allyl Pd(II) intermediate, and no stable Pd(IV)-hydride intermediate can be located. This type of base-assisted C–H activation mechanism has also been observed in several Pd-, Ir-, and Ru-catalyzed reactions.<sup>14,15</sup> Importantly,



Figure 4. Calculated Gibbs free-energy diagram for (top)  $Pd(OAc)_2$ catalyzed allylbenzene isomerization and (bottom)  $Pd(OAc)_2/Al$ -(OTf)<sub>3</sub>-catalyzed allylbenzene isomerization.

the oxidation addition mechanism to generate Pd(IV)-hydride was found to be unfavorable.<sup>15</sup> Subsequently, isomerization and proton transfer (**TS2**) proceed to form the final product. The first step (**TS1**) was calculated to be the rate-limiting step, with a total barrier of 29.5 kcal/mol for the *trans* pathway. The corresponding barrier for the *cis* pathway is 3.7 kcal/mol higher. It is pertinent to mention that constrained geometry optimization could obtain a Pd(IV)-hydride-like structure, but its energy is much higher than that of **TS1**<sub>t</sub> (see Figure S13 in the Supporting Information), which further supports the proton transfer mechanism.

The overall mechanism of the Pd(II)/Al(III)<sub>3</sub>-catalyzed allylbenzene isomerization is quite similar to that without  $Al(OTf)_{3}$ , but with very different energetics.  $TS2'_{t}$  is now the rate-determining step for the trans pathway, with a barrier of 24.9 kcal/mol. For the *cis* pathway,  $TS1'_c$  is rate-limiting with a barrier of 25.3 kcal/mol. The barrier is 4.6 kcal/mol lower than that without Al(OTf)<sub>3</sub>, suggesting a critical role of Lewis acid in the Pd(II)-catalyzed isomerization reaction. In addition, it is very important to point out that TS1' is the selectivitydetermining step, which favors the *trans* pathway, with a barrier difference of 5.5 kcal/mol. Our experimental data (98.8% trans vs 0.8% cis) gives a barrier difference of 2.85 kcal/mol. The calculations thus somewhat overestimate the difference. If Int2<sup>+</sup> and  $Int2'_c$  can be easily interconverted, then TS2' is the selectivity-determining step, which would give the wrong selectivity. However, interconversion between  $Int2'_t$  and  $Int2'_c$ should be very difficult as the rotation of a double bond is very energy-demanding. Notably, formation of the C1 intermediate requires the dissociation of one acetate bridge between Pd(II) and Al(III). This is very consistent with the experimental fact that adding olefin to the acetonitrile solution of Pd(II)/Al(III)catalyst will generate an intermediate having absorbance identical to that adding  $Al(OTf)_3$  to  $Pd(OAc)_2$  solution, which has been proposed as the heterobimetallic Pd(II)/Al(III)dimer having two acetate bridge by NMR studies (see Figure 3).

In summary, this work demonstrated the first example that bridging nonredox metal ions to the simple Pd(II) catalyst can sharply promote its activity in olefin isomerization, and DFT calculations convincingly support the experimental data. The catalyst strategy introduced here may offer new opportunities for versatile olefin isomerization processes, which has a great market in the perfumery, fragrance, and food industries.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b01061.

Detailed experimental procedures, UV-vis, NMR graphs, and calculation procedures (PDF)

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## Notes

The authors declare no competing financial interest.

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(12) Computational details are given in the Supporting Information.
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