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Non-redox metal ions can promote Wacker-type oxidations even better than copper(II): a new opportunity in catalyst design

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In Wacker oxidation and inspired Pd(II)/Cu(II)-catalyzed C-H activations, copper(II) is believed to serve re-oxidizing of Pd(0) in the catalytic cycle. Herein we report that non-redox metal ions like Sc(III) can promote Wacker-type oxidations even better than Cu(II), both Sc(III) and Cu(II) can greatly promote Pd(II)-catalyzed olefin isomerization in which the redox properties of Cu(II) are not essential, indicating that the Lewis acid properties of Cu(II) can play significant role in Pd(II)-catalyzed C-H activations in addition to its redox properties. Characterizations of catalysts with UV-Vis and NMR indicated that adding $Sc(OTf)_3$ to the acetonitrile solution of $Pd(OAc)_2$ generates a new Pd(II)/Sc(III) bimetallic complex having diacetate bridge which serves as the key active species for Wacker-type oxidation and olefin isomerization. Linkage of trivalent Sc(III) to the Pd(II) species makes it more electron-deficient, thus facilitates the coordination of olefin to the Pd(II) cation. Due to the improved electron transfer from olefin to the Pd(II) cation, it benefits the nucleophilic attack of water on the olefinic double bond, leading to efficient olefin oxidation. The presence of excess Sc(III) prevents the palladium(0) black formation, which has been rationalized by the formation of the Sc(III)•••H-Pd(II) intermediate. This intermediate inhibits the reductive elimination of the H-Pd(II) bond, and facilitates the oxygen insertion to form the HOO-Pd(II) intermediate, thus avoids the formation of the inactive palladium(0) black. The Lewis acid promoted Wacker-type oxidation and olefin isomerization demonstrated here may open up a new opportunity in catalyst design for versatile C-H activations.

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Introduction

Wacker oxidation is a classic process in homogeneous catalysis which transforms ethylene to acetaldehyde by aerobic oxidation.[1] In this reaction, $PdCl_2$ is the catalyst responsible for olefin oxidation, and $CuCl_2$ is believed to promote re-oxidation of the reduced Pd(0) back to the active Pd(II) species, after which the reduced Cu(I) is feasibly oxidized by O_2 to complete the catalytic cycle. Up to now, Wacker-type oxidations have been widely applied in olefin functionalization,[2-6] and inspired Pd(II)-catalyzed C-H activations with Cu(II) as the stoichiometric oxidant or cocatalyst have been extensively explored in organic synthesis.[7] Although above mechanism has been widely accepted, there still exist arguments including the assumption that the active Pd(II) species is dimeric rather than monomeric, or the suspicion that Cu(II) cation is linked to the Pd(II) species, and several Pd(II)/Cu(II) bimetallic clusters including $[(PdCl_2)_2CuCl_2(DMF)_4]_n$ and $Pd_6Cu_4Cl_{12}O_4(HMPA)_4$, $[(HMPA)_2CuCl_2(PdCl_2)_2]_n$, (HMPA: hexamethylphosphoramide) were isolated by Hosokawa with X-ray identifications.[8,9] In investigating the kinetics of Wacker oxidation, Sigman also observed that the concentration of Cu(II) can significantly affect the reaction order on olefin, thus suggested that Cu(II) plays a complex role in Wacker chemistry.[10] However, due to the mask of its redox properties, the alternative roles of Cu(II) in Wacker-type oxidations have not been clearly evidenced.

Recently, non-redox metal ions functioning as Lewis acid and promoting high oxidation state metal ion mediated oxidations has attracted much attention. Adding these non-redox metal ions to the synthetic transition metal complexes at high oxidation state can substantially accelerate their oxidations in electron transfer, oxygenation, and/or hydrogen abstraction.[11-14] The promotional effect was attributed to the linkage of a Lewis acid to the active intermediate, which positively shifts its redox potential, thus improves the oxidizing ability of the active metal ion. Inspired by these studies and our earlier works in elucidating the reactivity relationships of different metal intermediates in oxidation,[15] we explored Lewis acid promoted catalytic oxygenation with manganese complexes, dioxygen activation by iron complexes and selective benzene hydroxylation by Pd^{II}(bpym) (bpym: 2,2'-pyrimidine) catalyst.[16] In particular, non-redox metal ion, Al^{3+}, can promote Pd^{II}(bpym) catalyzed selective hydroxylation of benzene to phenol, whereas Pd^{II}(bpym) alone is inactive. The promotional effect was attributed to the ligation of Al^{3+} to the two remote nitrogen atoms of the Pd^{II}(bpym) complex, which positively shifts the redox potential of the Pd(II) cation in the Pd^{II}(bpym) complex, thus improves its capability in C-H activation.

Herein, we demonstrate that certain non-redox metal ions like Sc(III) can promote Pd(II)-catalyzed Wacker-type oxidations even better than Cu(II), and both non-redox metal ions and Cu(II) can promote Pd(II)-catalyzed olefin isomerization in which the redox properties of Cu(II) is not essential, suggesting that Cu(II) may play multiple roles in Wacker-type oxidations in addition to oxidize Pd(0) as described in textbooks. Taken together with previous findings in literatures,[11-14,16] this work has not only evidenced that the Lewis properties of the Cu(II) cation can play significant role in Wacker-type oxidations, but also implicated that these non-redox metal ions can play significant roles in versatile transition metal ion mediated homogeneous catalysis, for example, C-H activation, thus provides new opportunities for catalyst design which was not fully recognized before.

Experimental

General information All chemical reagents are commercially available and used without further purification. Palladium(II) acetate ($Pd(OAc)_2$) was purchased from Strem Chemicals Inc. Copper(II) trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$) and 1,4-cyclohexadiene came from Alfa Aesar; sodium trifluoromethanesulfonate ($NaCF_3SO_3$), magnesium(II) trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$), 1-hexene, 2-hexanone, 1-octene, 4-hexene, 2-octanone, 3-octanone, cyclohexene and cyclopentene were purchased from Aladdin. Scandium trifluoromethanesulfonate ($Sc(CF_3SO_3)_3$) was purchased from Shanghai Shaoyuan Co. Ltd. 3-Hexanone, 4-octanone and trans-3-hexene were purchased from TCI Shanghai, Other trifluoromethanesulfonates including $Ca(CF_3SO_3)_2$, $Zn(CF_3SO_3)_2$, $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, and $Yb(CF_3SO_3)_3$ came from Shanghai Dibai Chemical Co. 1-Dodecene, 1,5-cyclooctadiene, and 4-octanone were purchased from J&K Scientific Ltd. Toluene, dimethylsulfoxide, acetonitrile and acetic acid were purchased from local Sinopharm Chemical Reagent. UV-Vis spectra were studied on Analytikjena specord 205 UV-Vis spectrometer, GC-MS analysis was performed on an Agilent 7890A/5975C spectrometer, and NMR analysis was performed on Bruker AV400.

General procedure for catalytic olefin oxidation by $Pd(OAc)_2$ with $Sc(OTf)_3$ In a typical experiment, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Sc(OTf)_3$ (19.7 mg, 0.04 mmol) were dissolved in 5 mL of acetonitrile in a glass tube, after stirred for 10 min, 1-hexene (0. 25 mL, 2 mmol) and 0.2 mL of water were added. The glass tube was put into a 50 mL stainless autoclave which was then charged with 20 atm of oxygen. Next, the reaction solution was magnetically stirred at 80 °C in oil bath for 2 h. After the reaction, the autoclave was cooled to room temperature and carefully depressurized to normal pressure. The product analysis was performed by GC using the internal standard method. Control experiments including using $Pd(OAc)_2$, or $Sc(OTf)_3$ alone, or $Pd(OAc)_2$ plus $Cu(OTf)_2$ as catalyst were carried out in parallel.

General procedure for catalytic kinetics of styrene oxidation by $Pd(OAc)_2$ with $Sc(OTf)_3$ $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Sc(OTf)_3$ (19.7 mg, 0.04 mmol) were dissolved in 5 mL of acetonitrile in a glass tube, after stirred for 10 min, styrene (42.0 mg, 0.4 mmol) and 0.2 mL of water were added. The glass tube was connected with O_2 balloon. Then, the reaction solution was magnetically stirred at 55 °C in oil bath for 10 h. The product analysis was performed by GC using the internal standard method at set intervals. Control experiments using $Pd(OAc)_2$ plus $Cu(OTf)_2$ or $Pd(OAc)_2$ alone as catalyst were carried out in parallel.

General procedure for catalytic isomerization of terminal olefin by $Pd(OAc)_2$ with $Sc(OTf)_3$ In 0.5 mL of acetonitrile-d_3 containing 4 mM $Pd(OAc)_2$ and 8 mM $Sc(OTf)_3$, 0.02 mmol of 1-hexene were added by syringe. Then, the reaction mixture was monitored by ^1H NMR at 25 °C, and the yield of internal olefins was determined using TMS as an internal standard. Control experiments using $Pd(OAc)_2$ or $Sc(OTf)_3$ alone, or using $Pd(OAc)_2/Cu(OTf)_2$ as catalyst were carried out in parallel.

General procedure for catalytic isomerization of 1,5-cyclooctadiene by $Pd(OAc)_2$ with $Sc(OTf)_3$ In a typical experiment, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Sc(OTf)_3$ (19.7 mg, 0.04 mmol) were dissolved in 5 mL of acetonitrile in a glass tube, after stirred for 10 min, 1,5-cyclooctadiene (0.12 mL, 1 mmol) was added. The reaction solution was magnetically stirred at 90 °C in oil bath for 24 h. The yield was determined by GC analysis using direct integral method. Control experiments using $Pd(OAc)_2$ plus $Cu(OTf)_2$, and $Pd(OAc)_2$, $Sc(OTf)_3$ or $Cu(OTf)_2$ alone as catalyst were carried out in parallel.

General procedure for catalytic kinetics of 1,5-cyclooctadiene isomerization by $Pd(OAc)_2$ with $Sc(OTf)_3$ $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Sc(OTf)_3$ (19.7 mg, 0.04 mmol) were dissolved in 5 mL of acetonitrile in a glass tube, after stirred for 10 min, 1,5-cyclooctadiene (108.0 mg, 1 mmol) was added. The reaction solution was magnetically stirred at 90 °C in oil bath. The yield was determined by GC analysis using direct integral method at the set intervals. Control experiments using $Pd(OAc)_2$ plus $Cu(OTf)_2$, or using $Pd(OAc)_2$, $Sc(OTf)_3$ or $Cu(OTf)_2$ alone as catalyst were carried out in parallel.

Results and discussion

Non-redox metal ion promoted olefin oxidations by $Pd(OAc)_2$ Olefin oxidations were performed in acetonitrile containing water (v/v, 5/0.2), oxygen was employed as oxidant, and various non-redox metal ions were tested to investigate their influence on Pd(II)-catalyzed Wacker-type oxidation. Using 1-hexene as substrate, we first found that non-redox tervalent metal ions can greatly promote Pd(II)-catalyzed olefin oxidation, and adding bivalent metal ions also slightly improves the efficiency, while the catalytic efficiency of $Pd(OAc)_2$ alone is very poor (Table 1). In particular, adding 2 equiv. of $Sc(OTf)_3$ to $Pd(OAc)_2$ achieves >99% conversion with 53.1% yield of 2-hexanone and 29.3% of 3-hexanone in 2 h at 80 ^{o}C by GC analysis of the reaction mixture. The loss of 1-hexene mass balance is due to its vaporizing into gas phase under the reaction conditions, and formation of 3-hexanone can be attributed to the isomerization of 1-hexene prior to Wacker-type oxidation (*vide infra*). In control experiment, Sc(III) alone is inactive for olefin conversion, which is consistent with its non-redox properties. However, increasing the ratio of Sc(III)/Pd(II) can substantially accelerate olefin oxidation and prohibit palladium black formation (See Table S3). For examples, in oxidation of 1-hexene at 60 ^{o}C, adding 0.5 equiv. of $Sc(OTf)_3$ to $Pd(OAc)_2$ provided only 8.1% of 2-hexanone and 2.0% of 3-hexanone with 25.7% conversion in 2 h, and some palladium(0) black was observed after the reaction, while adding 3 equiv. of $Sc(OTf)_3$ offers 53.3% and 28.8% of 2- and 3-hexanone, respectively, with 98.2% conversion under identical conditions, and no palladium black formation was observed.

Table 1. Wacker-type oxidation of 1-hexene by $Pd(OAc)_2$ in the presence of non-redox metal ions[a]

Entries	Lewis acid	Conv. (%)	Yield of 3-hexanone (%)	Yield of 2-hexanone (%)
1	-	13.7	trace	1.3
2[b]	Na^{+}	14.8	trace	1.8
3	Mg^{2+}	23.4	trace	4.2
4	Ca^{2+}	21.1	trace	4.0
5	Zn^{2+}	21.3	trace	3.8
6	Y^{3+}	30.5	1.1	7.9
7	Yb^{3+}	32.4	1.6	8.4
8	Al^{3+}	55.1	9.1	24.8
9	Sc^{3+}	>99	29.3	53.1
10	Cu^{2+}	62.0	11.3	28.3
11[c]	Sc^{3+}+Cu^{2+}	86.0	22.9	47.6

[a] Conditions: 1-hexene (2 mmol), $Pd(OAc)_2$ (0.02 mmol), trifluoromethane sulfonate (0.04 mmol), acetonitrile (5 mL), H_2O (0.2 mL), O_2 (20 atm), 80 ^{o}C, 2 h; [b] NaOTf (0.12 mmol); [c] 0.04 mmol of $Sc(OTf)_3$ and $Cu(OTf)_2$ added.

Because adding 6 equiv. of NaOTf, which contain the same amount of OTf^{-} as those in 2 equiv. of $Sc(OTf)_3$, does not generate an obviously promotional effect (Table 1, entry 2), it clearly suggests that the promotional effect originates from non-redox metal ions like Sc(III) rather than OTf^{-} anion. In comparison, adding 2 equiv. of $Cu(OTf)_2$ yields 28.3% of 2-hexanone and 11.3% of 3-hexanone with only 62.0% conversion in 2 h, which is similar to the results by adding Al(III) (Table 1, entries 8 vs 10). Notably, adding Cu(II) to the Pd(II)/Sc(III) system decreases the conversion, and the yields are lower than those by only using Pd(II)/Sc(III) catalyst (Table 1, entry 11), clearly suggesting that re-oxidation of Pd(0) by Cu(II) is not essential here. In addition, the catalytic kinetics of styrene oxidation using oxygen balloon also disclosed that adding Sc(III) displays a faster oxidation rate than Cu(II) although their initial rates look similar. As shown in Figure 1, in the absence of Lewis acid, oxidation of styrene by $Pd(OAc)_2$ alone is very sluggish, while adding Cu(II) or Sc(III) greatly accelerates the oxidation, and Sc(III) demonstrates a relatively higher promotional effect than Cu(II). *Unambiguously*, non-redox metal ions like Sc(III) can greatly promote Pd(II)-catalyzed Wacker-type oxidations even better than Cu(II), and this challenges the long believed textbook role of Cu(II) in Wacker-type cycles.

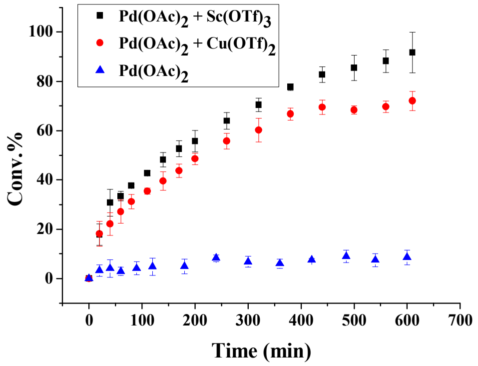


Figure 1 Catalytic kinetics for styrene oxidation to acetophenone by Pd(II)/(Sc(III) or Pd(II)/Cu(II) catalyst. Reaction conditions: CH_3CN (5.0 mL), styrene (0.4 mmol), $Pd(OAc)_2$ (0.02 mmol), $Sc(OTf)_3$ or $Cu(OTf)_2$ (0.04 mmol), H_2O (0.2 mL), O_2 balloon, 55 ^{o}C.

Table 2. Wacker-type oxidation of different olefins by $Pd(OAc)_2$ in the presence of $Sc(OTf)_3$[a]

Entries	Substrate	Time (h)	Conv. (%)[b]	Products	Yield (%)[b]
1	1 -hexene	2	99.8 (62.0)	2-hexanone 3-hexanone	53.1(28.3) 29.3 (11.3)
2	3 -hexene	5	99.6 (65.4)	2-hexanone 3-hexanone	56.0 (27.1) 33.9 (13.4)
3	1 -octene	12	99.3 (48.2)	2-octanone 3-octanone 4-octanone	39.0 (16.1) 27.0 (10.2) 20.6 (7.2)
4	4 -octene	16	99.8 (60.5)	2-octanone 3-octanone 4-octanone	37.4 (21.4) 26.9 (15.2) 22.5 (12.6)
5	styrene	2	99.7 (60.4)	acetophenone benzaldehyde	87.3 (49.9) 7.0 (5.8)
6[c]	cyclohexene	16	99.7 (62.9)	cyclohexanone cyclohexenone	86.3 (45.8) 7.4 (5.7)
7[c]	cyclopentene	16	99.8 (99.1)	cyclopentanone	80.2 (72.2)

[a] Conditions: olefin (2 mmol), $Pd(OAc)_2$ (0.02 mmol), $Sc(OTf)_3$ (0.04 mmol), acetonitrile (5 mL), H_2O (0.2 mL), O_2 (20 atm), 80 ^{o}C. [b] The data in parentheses comes from control experiments using $Cu(OTf)_2$ instead of $Sc(OTf)_3$. [c] olefin (1 mmol).

Catalytic oxidations of other olefins also clearly support that Sc(III) produces much more efficient substrate conversion than Cu(II) in most cases (Table 2). For example, in styrene oxidation, Pd(II)/Sc(III) catalyst achieves >99% conversion with 87.3% yield of acetophenone and 7.4% yield of benzaldehyde in 2 h at 80 °C, whereas Pd(II)/Cu(II) catalyst can only convert 60.4% of styrene under the identical conditions, providing 49.9% and 5.8% yields of acetophenone and benzaldehyde, respectively. Notably, unlike the olefin oxidations reported by Kaneda and others in which oxidation of terminal olefin produced solely methyl ketone,[2b,6d] here, Pd(II)/Sc(III) catalyzed oxidations of terminal olefins provided both methyl ketone and other internal ketones as those in oxidation of internal olefins. For example, in oxidation of 1-hexene, the yields of 2-hexanone and 3-hexanone are 53.1% and 29.3%, respectively, while they are 56.0% and 33.9% for 3-hexene (Table 2, entries 1 and 2), suggesting that a rapid olefin isomerization occurs prior to oxidation, which makes 1-hexene and 3-hexene to give similar product distributions.

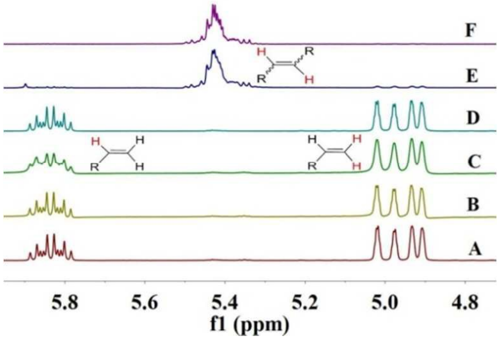


Figure 2. The ^{1}H NMR spectra of olefin isomerization in CD_3CN at 25 °C. A: 1-octene (40 mM); B: 1-octene (40 mM) with $Pd(OAc)_2$ (4 mM), 1 h; C: 1-octene (40 mM) with $Cu(OTf)_2$ (8 mM), 1 h; D: 1-octene (40 mM) with $Sc(OTf)_3$ (8 mM), 1 h; E: 1-octene (40 mM) with $Pd(OAc)_2$ (4 mM) and $Cu(OTf)_2$ (8 mM), 10 min; F: 1-octene (40 mM) with $Pd(OAc)_2$ (4 mM) and $Sc(OTf)_3$ (8 mM), 4 min.

Non-redox metal ions promoted olefin isomerization by $Pd(OAc)_2$ Figure 2 demonstrates Pd(II)-catalyzed 1-octene isomerization by ^{1}H NMR detection in the presence/absence of $Sc(OTf)_3$ or $Cu(OTf)_2$. The spectrum A shows the ^{1}H NMR chemical shifts of olefinic bond in 1-octone, in which the peaks at 4.9-5.1 ppm represent the chemical shifts of the methylene group in olefinic bond, while the peaks at 5.8-5.9 ppm represent the chemical shifts of the internal H-C(R) unit of the olefinic bond. Spectra B, C and D confirm that none of Pd(II), Cu(II) and Sc(III) alone can efficiently isomerize 1-octene to internal octene in 1 h at 25 °C. However, adding 2 equiv. of $Cu(OTf)_2$ to $Pd(OAc)_2$ isomerizes most of 1-octene to internal octenes in 10 min which have the chemical shifts of olefinic bond between 5.3 and 5.5 ppm, while adding $Sc(OTf)_3$ to $Pd(OAc)_2$ achieves complete isomerization in 4 min, much faster than Cu(II). Similar promotional effects have also been observed in isomerization of other olefins as shown in Table 3. In isomerization of 1-hexene, adding 2 equiv. of $Sc(OTf)_3$ to $Pd(OAc)_2$ provided 89.5% of internal olefins with 98.2% conversion in 6 min at 25 °C, while adding $Cu(OTf)_2$ offered only 49.3% of internal olefins with 55.8% conversion under the identical conditions. In the case of 1,5-cyclooctadiene (1,5-COD), the promotional effects of Sc(III) and Cu(II) are comparable, providing 89.0% yield of 1,3-cyclooctadiene (1,3-COD) with 4.7% of 1,4-cyclooctadiene (1,4-COD), and 88.0% of 1,3-COD with 4.1% of 1,4-COD, respectively. In control experiments, neither $Pd(OAc)_2$ nor Lewis acid alone is active for olefin isomerization (Table S4-S7), which is consistent with that, in literature, oxidation of terminal olefins with $Pd(OAc)_2$ alone generally provided methyl ketones with no isomerized ketone formation,[2b,6d] thus confirms the critical role of Sc(III) and Cu(II) in Pd(II)-catalyzed olefin isomerization. *Undoubtedly*, the role of Cu(II) in Pd(II)-catalyzed olefin isomerization is distinctly different from that proposed of re-oxidizing Pd(0) in Wacker-type processes, because its redox properties are unnecessary here. As evidence, Sc(III), a non-redox metal ion but a stronger Lewis acid than Cu(II), demonstrates a better promotional effect in most cases, and other metal ions like Al(III), Mg(II) and Zn(II) can also accelerate Pd(II)-catalyzed olefin isomerization (Table S7).

Table 3 The influence of Lewis acid on Pd(II)-catalyzed olefin isomerization.[a]

Substrate	Lewis acid	Time	Conv. (%)	Product yield (%)
1-hexene	$Sc(OTf)_3$ $Cu(OTf)_2$	6 min 6 min	98.2 55.8	Internal olefins (89.5) Internal olefins (49.3)
1-octene	$Sc(OTf)_3$ $Cu(OTf)_2$	4 min 6 min	94.5 75.7	Internal olefins (90.3) Internal olefins (63.2)
1-dodecene	$Sc(OTf)_3$ $Cu(OTf)_2$	6 min 6 min	99.6 48.4	Internal olefins 84.4) Internal olefins (41.4)
1,5-COD[b]	$Sc(OTf)_3$	24 h	95.2	1,3-COD (89.0) 1,4-COD (4.7)
	$Cu(OTf)_2$	24 h	93.0	1,3-COD (88.0) 1,4-COD (4.1)

[a] Conditions: acetonitrile-d_3 (0.5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), olefin (40 mM), reaction performed in NMR tube at 25 °C, yield determined by ^{1}H NMR. [b] CH_3CN (5 mL), $Pd(OAc)_2$ (4 mM), Lewis acid (8 mM), 1,5-cyclooctadiene (0.2 M), reaction performed in oil bath at 90 °C, yield determined by GC analysis .

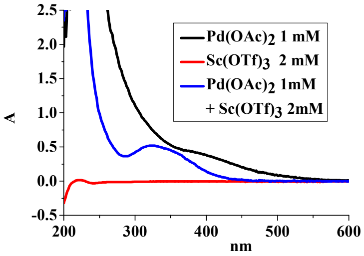


Figure 3. UV-Vis spectra of $Pd(OAc)_2$ and $Sc(OTf)_3$ with their mixture in acetonitrile containing water (v/v, 0.5/0.02 mL).

Characterizations of Pd(II)/Sc(III) catalyst with mechanistic proposal for olefin oxidation The UV-Vis spectra of Pd(II)/Sc(III) catalyst are displayed in Figure 3. In acetonitrile containing water (v/v, 0.5/0.02) which is the reaction solvent for olefin oxidation, $Pd(OAc)_2$ demonstrates a yellowish colour, having an absorbance band around 400 nm involving the ligand-to-metal charge transfer as expected to take place from acetate ligand to Pd(II) cation. Adding 2 equiv. of $Sc(OTf)_3$ to $Pd(OAc)_2$ turns its original yellowish colour to pale yellow, and yields a new absorbance band with maximum near 320 nm, indicating the formation of a new Pd(II) species. Similar $Sc(OTf)_3$ concentration dependent shifts have been observed on the UV-Vis and ^{1}H NMR spectral features (Fig. S3 and S4). In ^{1}H NMR spectra (Fig. 4), $Pd(OAc)_2$ alone in acetonitrile-d_3 reveals a chemical shift of 1.965 ppm, assigning to the methyl group of acetate in $Pd_3(OAc)_6$ trimer in which all of the acetates serve as bridges like those in the literature.[8b,17] Adding $Sc(OTf)_3$ to the $Pd(OAc)_2$ solution downshifts this methyl group to 1.989 ppm, indicating a more electron-deficient group than bivalent Pd(II) has bound to acetate, while in monomeric NaOAc or NH_4OAc, the chemical shift of acetate is upshifted, giving the chemical shifts of 1.817 and 1.814 ppm, respectively, and it is 1.958 ppm for $Sc(OAc)_3$. In ^{13}C NMR spectra (Fig. 5), $Pd(OAc)_2$ in acetonitrile-d_3 displays one chemical shift at 21.15 ppm and another at 173.73 ppm, corresponding to the methyl and carbonyl groups of acetate bridges in $Pd_3(OAc)_6$, respectively. Adding $Sc(OTf)_3$ downshifts the carbonyl group to 179.49 ppm which is still a singlet peak, while the methyl group also downshifts but demonstrates multiple peaks between 21.44 and 22.24 ppm which have been evidenced by ^{1}H-^{13}C HSQC NMR (see Fig. S2). Since the carbonyl group of acetate is a singlet peak, it apparently suggests that there is only one type of acetate in solution, thereof, the multiple methyl peaks between 21.44 and 22.23 ppm could be attributed to its different orientation in the new species.

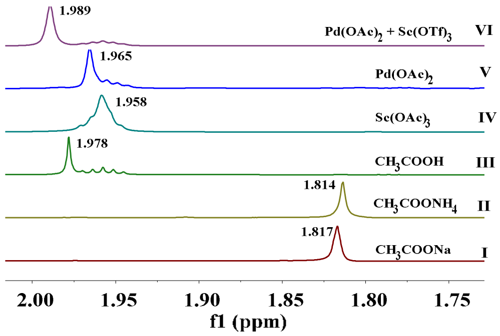


Figure 4. ^{1}H NMR spectra of $Pd(OAc)_2/Sc(OTf)_3$ with related compounds in acetonitrile containing water-d (v/v, 0.5/0.02 mL).

Taken together, the down-shifts of the ^{1}H and ^{13}C NMR peaks of $Pd_3(OAc)_6$ trimer by adding $Sc(OTf)_3$ clearly indicate that a more electron-deficient group than Pd(II) has linked to acetate. In literature, breakdown of trimeric $Pd_3(OAc)_6$ by adding metal salts, including Ba^{2+}, Sr^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Nd^{2+}, Zn^{2+} and Ce^{4+}, etc., to generate heterobimetallic palladium(II) salts with acetate bridge was widely observed,[18] and several Pd(II)/Cu(II) bimetallic clusters were also isolated and well characterized by Hosokawa.[9] Based on this information with our characterizations, the new species generated here can be assigned to the bimetallic Pd(II)/Sc(III) dimers having two acetate bridges with two free sites on Pd(II) for solvent or substrate coordination (Fig. 6). Replacing one bivalent Pd(II) by tervalent Sc(III) can account for the downshifts of the chemical shift of the carbonyl and methyl groups in acetate bridges, and the multiple methyl peaks in ^{13}C NMR can be putatively attributed to its different orientation caused by bulky OTf$^-$ groups ligated to Sc(III), but is not conclusive.

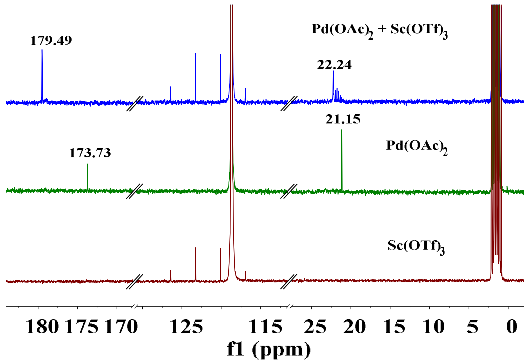


Figure 5. ^{13}C NMR spectra of $Pd(OAc)_2$, $Sc(OTf)_3$ and their mixture in acetonitrile containing water-d (v/v, 0.5/0.02 mL).

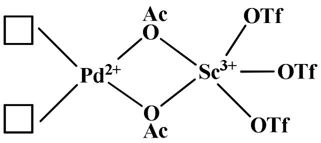
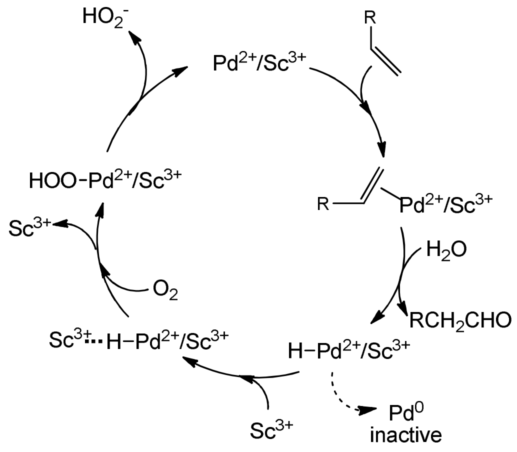


Figure 6. Proposed bimetallic Pd(II)/Sc(III) core for olefin oxidation.

In Pd(II)/Sc(III)-catalyzed olefin oxidation, since Sc(III) is redox inactive, it cannot re-oxidize Pd(0) back to the active Pd(II) species; however, Sc(III) demonstrates a more efficient promotional effect than Cu(II), and adding Cu(II) to Pd(II)/Sc(III) system does not further accelerate olefin oxidation (see Table 1, entry 11). These observations strongly suggest that Pd(0) may not essentially occur in the catalytic cycle. Taken together, an alternative Wacker-type mechanism was proposed for Pd(II)/Sc(III)-catalyzed olefin oxidation (Scheme 1). In this mechanism, the key active species for olefin activation is a bimetallic Pd(II)/Sc(III) species as shown in Figure 6. The presence of Sc(III) makes Pd(II) more electron-deficient, thus improves its olefin oxidation and C-H activation ability in two aspects: 1) improving the electron transfer from olefin to Pd(II) cation, thus benefiting its attack by water, and 2) accelerating C-H activation by Pd(II) in β-hydrogen elimination to form the enol intermediate. The enhanced C-H activation capability of Pd(II) by Sc(III) has been evidenced in olefin isomerization (*vide supra*), and similar improvement was also observed by adding Al(III) to Pd^{II}(bpym) in benzene hydroxylation.[16c] More importantly, the presence of excess Sc(III) has prevented palladium black formation (see Table S3), indicating that it can prohibit the reductive elimination of H-Pd(II) intermediate in Wacker-type cycle (Note: Sc(III) is redox inactive). To rationalize this phenomenon, we propose the role of excess Sc(III) as forming a Sc(III)•••H-Pd(II) intermediate which weakens the H-Pd(II) bond, thus facilitating dioxygen insertion to generate the HOO-Pd(II) intermediate. Finally, releasing of HO_2^- re-generates the active Pd(II) species, thereof, formation of Pd(0) does not necessarily occur in catalytic cycle. In literature, dioxygen insertion of the H-Pd(II) intermediate to generate the corresponding HOO-Pd(II) bond have also been reported by Stahl and Goldberg, and the insertion pathways are highly ligand dependent of the H-Pd(II) intermediates.[19] Here, formation of the Sc(III)•••H-Pd(II) intermediate may prevent the reduction elimination of the Pd(II) hydride intermediate to yield the inactive palladium(0) black, and meanwhile weaken the H-Pd(II) bond, thus facilitate the dioxygen insertion, leading to efficient Wacker-type oxidation. However, it is also worth to mention that the reduced amount of Pd black with Sc(III) is not known, since there is no obvious Pd(0) formation observed.



Scheme 1. Proposed mechanism for Sc(III) promoted Wacker-type oxidation.

Conclusions and perspective

This work revealed that certain trivalent metal ions like Sc(III) can substantially promote Pd(II)-catalyzed Wacker-type oxidation even better than Cu(II), and the promotional effect is apparently Lewis acid strength dependent. Both Sc(III) and Cu(II) can greatly promote Pd(II)-catalyzed olefin isomerization, whereas Pd(II) alone is very sluggish. Because the redox properties of Cu(II) is not essential in promoting Pd(II)-catalyzed olefin isomerization, and stronger Lewis acid like Sc(III) demonstrates more efficient promotional effect than Cu(II) in most cases, it clearly indicates that the Lewis properties of Cu(II) plays significant role in Wacker-type oxidations in addition to its redox properties. The origin of the promotional effect has been attributed to the formation of a bimetallic Pd(II)/Sc(III) dimer which serves as the key active species in C-H activation. Linkage of Sc(III) cation to Pd(II) through diacetate bridge makes Pd(II) more electron-deficient, thus improves its capability in olefin coordination and C-H activation, and it also benefits the nucleophilic attack of water on olefin.

In fact, non-redox metal ions have been extensively employed as additives to modify the reactivity and improve the stability of redox catalysts in heterogeneous catalysis,[20] and they also occur in certain active sites of redox enzymes like Ca^{2+} in the oxygen evolution center of Photosystem II.[21] However, they have not been fully recognized in homogeneous oxidations, for example, in C-H activation. Recent findings have disclosed that these non-redox metal ions can promote active metal oxo intermediates mediated stoichiometric and catalytic oxidations.[11-14,16] Here, we further revealed that the Lewis acid properties of Cu(II) cation, as well as its redox properties, can play significant role in Wacker-type oxidations, which appeals for the attention of the Lewis acid properties of the Cu(II) cation in many Pd(II)-catalyzed C-H activations where Cu(II) salts were generally employed and recognized as stoichiometric oxidant or cocatalyst for re-oxidizing of Pd(0) back to the active Pd(II) species.[7] Finally, this knowledge may open up new opportunities in catalyst design for versatile Pd(II)-catalyzed C-H activations in which non-redox metal ions as Lewis acid can play significant roles.

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Notes and references

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Electronic Supplementary Information (ESI) available: Reaction optimizations for olefin oxidations; GC-MS graphs of olefin oxidation and isomerization products; UV-Vis spectra of $Pd(OAc)_2/Al(OTf)_3$ and $Pd(OAc)_2/Cu(OTf)_2$ in acetonitrile; ^1H-^{13}C HSQC spectra of $Pd(OAc)_2/Sc(OTf)_3$ in CD_3CN; ^1H NMR kinetics of olefin isomerization. See DOI: 10.1039/c000000x/

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Graphical Abstract

Non-redox metal ions can accelerate Pd(II)-catalyzed Wacker-type oxidations better than Cu(II), revealing a new role of Cu(II) in Wacker-type mechanism.