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Pt-Pd Nanoalloy for the Unprecedented Activation of Carbon-Fluorine Bond at Low Temperature

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Abstract

Carbon-Fluorine bonds are considered the most inert organic functionality and their selective transformation under mild conditions remains challenging. Herein, we report a highly active Pt-Pd nanoalloy as a robust catalyst for the transformation of C-F bonds into C-H bonds at low temperature, a reaction that has hitherto often required harsh conditions. The alloying of Pt with Pd is crucial to promote the overall C-F bond. DFT calculations elucidated that the key step is the selective oxidative addition of the O-H bond of 2-propanol to a Pd center prior to C-F bond activation at a Pt site, which crucially reduces the activation energy of the C-F bond cleavage. Therefore, both Pt and Pd work independently but synergistically to promote the overall reaction.

Keywords: Pt/Pd nanoalloy, C-F bond activation, protodefluorination

1. Introduction

Homogeneous mixtures of two metals, also known as alloys, are commonly used as catalysts for a number of applications¹. Alloying two metals may give rise to unique catalytic activities and novel properties.² Alloying of Pd with other metals often improves its catalytic activity, stability, and product selectivity owing to "synergistic effects" with the foreign metallic atoms present in the single particles.^{2b,3} Previously, we have shown an example of the unique catalytic activity of Au-Pd nanoalloy for the Ullmann coupling of chloroarenes at low temperature.⁴ As part of our ongoing efforts to extend the utility of nanoalloys in terms of unique reactivity, we herein report that a poly(*N*-vinylpyrrolidone) (PVP)-stabilized Pt-Pd nanoalloy serves as an effective and robust catalyst for the activation of the C-F bonds in aryl fluorides at low temperature (Scheme 1b).

The high electronegativity of fluorine induces a significant ionic bond character, which results in the strongest and shortest sigma bond to carbon. Therefore, C-F bonds are among the most inert functionalities and their transformation at low temperature remains challenging.⁵ Despite these

difficulties, the fact that a significant number of pharmaceuticals^{5a, 6} and functional materials contain fluorinated moieties has fueled intense interest in the activation of C-F bonds.

(a) Previous work: (Hydride addition)



L_n = Phosphine type, pyridinyl type, *N*-heterocyclic carbene, imidazolylpyridine (b) This work: (Proton addition)



Scheme 1. Different approaches to cleavage C-F bond

The simplest modification of the C-F bond is its transformation into a C-H bond, hereafter referred to as hydrodefluorination (HDF; Scheme 1a).⁷ This process often involves the use of harsh reductants at high temperature or electrochemical conditions, which leads to a wide mechanistic diversity. Aryl fluorides are defluorinated by homogeneous or heterogeneous transition-metal-catalyzed hydride transfer in the presence of hydride sources.⁸ Fluorophilic reagents, including boron/aluminum hydrides and silanes, are also used for the defluorination of aryl fluorides, where the fluoride is replaced with hydride.⁹ Electron-rich metal centers are preferred for the activation of C-F bonds and many transition-metal complexes

have been developed in combination with electron donating, bulky, and nucleophilic ligands.¹⁰ Recent developments in hydrodehalogenation reactions involve the use of 2-propanol,¹¹ HCOOK,¹² or $(C_2H_5)_2$ CHONa¹³ as greener reductants or hydride sources in combination with nucleophilic ligand-bearing metals.¹⁴ Some examples have been recently reported where HDF proceeds at ambient temperature.¹⁵

In view of the key role that ligands play in the homogeneous catalysis promoted by metal catalysts,¹⁰ we developed a conceptually different approach to activate C-F bonds using a heterobimetallic system to mimic the steric and/or electronic environment provided by ligands in a single particle.^{2b}

2. Experimental

2.1 General. All chemicals and solvents were used as received without further purification unless otherwise noticed. Hexachloroplatinate (H2PtCl4•4H2O Tanaka Kikinzoku), palladium chloride (PdCl₂, FUJIFILM Wako Pure Chemical) and poly(N-vinylpyrrolidone) (PVP-K-30) (Kishida chemicals) were used as precursors for the preparation of monometallic and bimetallic nanoclusters (NCs). Ethyl acetate, ether and hexane were obtained from FUJIFILM Wako Pure Chemical. Cesium carbonate was obtained from Aldrich. Other bases such as NaOH, KOH, and anhydrous t-BuOK were obtained from the FUJIFILM Wako Pure Chemical. Aryl fluorides were obtained from TCI. Ultrapure water (Milli-Q, 18.2 MΩ) was used in all experiments. All glassware was cleaned by freshly prepared aqua-regia (3:1 mixture of conc. HCl and conc. HNO₃) and rinsed by Milli-Q (18.2 M Ω) water before preparation of catalysts.

2.2 Preparation of PtxPdy nanoalloy. 160 mg (1.25 mmol, monomer unit of polymer) of PVP (K-30) was placed in a hard glass test tube (q=42 mm) and dissolved in ethanol water mixed solvent (32 mL ethanol+6 mL water). To the solution was added required amount of aqueous PdCl2 and H2PtCl6 (from 12.5 mM stock solution) solution (1:58 metal to monomer unit of polymer) and final ratio of ethanol/water was made 4:1. The resulting solution was stirred (in organic synthesizer, EYELA, PPS-2510) for 15 min at 25 °C under argon. The solution was then refluxed at 92 °C for 3 hours under vigorous stirring (1000 rpm) under argon atmosphere. The color of the mixture turned from pale yellow to brown, indicating the formation of bimetallic clusters. The thus-obtained PtxPdy:PVP clusters were subsequently dialyzed using membrane filter with a cut-off molecular weight of 10 kDa (Vivaspin 15R, United Kingdom) at 4000 rpm to remove the inorganic impurities and organic solvent, which is a crucial treatment to enhance the stability of the clusters against coalescence. The dialyzed hydrosol of Pt_xPd_y was dried using a lyophilizer and then vacuum at 45 °C for 3 h.

For the preparation of other catalysts, please see the Supporting Information.

2.3 Transmission electron microscopy analysis (TEM). A drop of aqueous $Pt_{1.0}$ or $Pd_{1.0}$ or Pt_xPd_y nanoalloy (1 mM) was placed on the carbon coated copper grid followed by vacuum drying. The sample was then analyzed using a transmission electron microscope (TEM). By counting more than 300 particles, histograms were plotted and the average diameters (in nanometers, nm) of the series of clusters were calculated. The observed TEM images and corresponding histogram plots of monometallic and bimetallic catalysts are shown in Figure 1. For the STEM-EDS measurements and other characterization,

please see the Supporting Information.



Figure 1. TEM images and corresponding histogram plots of a) Pt_{1.0} NCs, b) Pt_{0.8}Pd_{0.2} c) Pt_{0.5}Pd_{0.5} d) Pt_{0.2}Pd_{0.8} and e) Pd_{1.0} NCs.

2.4 Typical procedure for de-fluorination of aryl fluorides. De-fluorination reaction was carried out using an organic synthesizer (EYELA, PPS-2510). Aryl fluoride (0.25 mmol), bases (200 mol%, 0.50 mmol) and catalyst (2 atom%) were placed in a test tube (φ =20 mm) under argon conditions. To the mixture, anhydrous 2-propanol was added and the solution was stirred vigorously (1300 rpm) at required temperature for desired times under argon (from balloon). Reaction was quenched by HCl (1 M) and the product was extracted with

ethyl acetate or ether (4x10 mL). The extracted organic layer was diluted up to 50 mL and the content of products was quantified using gas chromatography. Hexadecane was used as the internal standard. For the confirmation of products, the crude was dissolved in acetone- d_6 or CDCl₃ and analyzed by NMR. The product was isolated by preparative thin layer chromatography (WAKO gel B-5F; ethyl acetate and hexane as eluent).

For the details of the kinetic studies, please see the Supporting Information.

2.5 General information for theoretical studies. The reaction mechanism of this catalytic cycle proposed in Scheme 2 was examined using density functional theory (DFT) calculations with M06-L functional.¹⁶ The model clusters of Pt₇Pd₆ and Pt₁₁Pd₂ in nearly icosahedral structures which are usually stable and less reactive were adopted for calculating the reaction pathways and simulating the Pt0.5Pd0.5 and Pt0.8Pd0.2 cases, respectively. The results obtained for the Pt7Pd6 NC were mostly presented and those for the Pt11Pd2 NC were essentially the same as Pt₇Pd₆ NC and not reported here, except for some cases specified. The relativistic effective core potential (RECP) with LANL2DZ basis sets¹⁷ were adopted for Pt and Pd, while the 6-31G(d,p) basis sets¹⁸ were used for other atoms. The stable geometrical structures and the spin states of bare bimetallic NCs were examined using the Birmingham genetic algorithm (GA)¹⁹ using Gupta potential followed by the DFT calculations. All the DFT calculations were conducted using Gaussian09 suit of programs.²⁰

The structure and spin state of bare Pt_7Pd_6 NC were examined using the GA and DFT calculations. Nearly symmetric icosahedral structures were obtained and the alloy structure was more stable than the phase separated structure. The structure with nonet spin state was found to be most stable in bare Pt_7Pd_6 NC. The present computational protocol with M06-L was found to be suitable for metal NC with high spin state previously.²¹

For more details about the calculations, please see the Supporting Information.

3. Results and Discussion

A series of PVP-stabilized monometallic nanoparticles and bimetallic nanoalloys was prepared *via* a wet chemical approach (Supporting Information). Typically, the transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images of Pt-Pd nanoalloys (Figure 1) show a approximately uniform distribution and crystallinity. The energy dispersive X-ray spectroscopy (EDS) pattern of Pt_{0.5}Pd_{0.5}:PVP (Figure S2) shows the stoichiometric presence of Pt and Pd (50% on average) in the particles, which is consistent with the observed experimental inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Table S1). The EDS/STEM images show that both Pt (red dots) and Pd (green dots) species (Figure S1) are mixed in a single particle that forms a nanoalloy.

Our investigation started by monitoring the defluorination of 4-fluoroanisole (**1a**) in 2-propanol as the hydrogen source at 27 °C, and results are shown in Table 1. The defluorinated product, anisole (**2a**), was not obtained using pure metal (Au, Pt, Pd) particles and bimetallic (Au_{0.5}-Pd_{0.5}, Au_{0.5}-Pt_{0.5}, Pt_{0.2}Pd_{0.8}) nanoalloys (entries 1-6). To our delight, the Pt_{0.5}Pd_{0.5}:PVP(mean size 2.7 ± 0.3 nm) showed remarkable catalytic activity and the conversion into **2a** was accomplished after 28 h (entry 7). With other bimetallic combinations, such as nanoalloy containing 20% of Pd (Pt_{0.8}Pd_{0.2}:PVP, mean size 2.1 ± 0.2 nm), the yield of **2** reached 95% after 40 h (entry 8). In contrast, a physical mixture of Pt:PVP and Pd:PVP did not exhibit any catalytic activity, which indicates that a bimetallic surface is indispensable for the reaction (entry 9).

Table1.ComparisonoftheCatalyticDefluorination of 1a.

MeO	F Catalyst (2 aton KOH (200 mol%) KOH (200 mol%) 1a 2-PrOH 27 °C, time, Ar	n%) ➤ MeO- 6)	- Данияна 2a
Entry ^a	Catalyst	Time (h)	Yield (%) ^b
1	Au _{1.0} :PVP	24	0
2	Pd _{1.0} :PVP	24	0
3	Pt _{1.0} :PVP	24	0
4	Au0.5Pd0.5:PVP	24	0
5	Au0.5Pt0.5:PVP	24	0
6	Pt _{0.2} Pd _{0.8} :PVP	24	0
7	Pt0.5Pd0.5:PVP	28	97
8	Pt _{0.8} Pd _{0.2} :PVP	40	95
9c	Pt _{1.0} :PVP +Pd _{1.0} :PVP	24	0

^aReactions conditions: 0.25 mmol of **1**, 2 mL of 2-propanol. ^bYield was determined by using gas chromatography, hexadecane was used as external standard. ^cPd_{1.0}:PVP (1 atom%)+Pt_{1.0}:PVP (1 atom%) was used.

The method was extended to a wide variety of aryl fluorides in order to verify the generality and scope of the current protocol. As shown in Table 2, aryl fluorides bearing different functional groups were successfully converted into the hydroarenes in excellent yield. In particular, inactive Ar-F compounds containing a deactivating group showed better reactivity than those bearing activating substituents. For example. the observed reaction rates for 1-fluoro-4-methoxybenzene (1a), fluorobenzene (1b), and 4-fluorobenzoic acid (1c) (Figure S6) follow the order 1a > 1b> 1c, which strongly indicates that C-F bond activation step is not the rate determining step and that the reaction mechanism does not involve an aromatic nucleophilic substitution reaction. To gain further insight into the mechanism, the reaction of 1a was carried out in deuterium-labeled 2-propanol at 45 °C using t-BuOK as the base. The nearly-identical initial rates for the consumption of 1a at all reaction times (Figure S7) suggest that the reaction is zero order with respect to 1a, ruling out the oxidative addition of Ar-F as the rate determining step. The hydrogen source for the product from 1a was investigated using various 2-propanol solvents deuterated (Table 3). Characterization of the product resulting from the reaction with D1 (entry 1) confirmed the substitution of fluoride by deuterium (60% deuterium incorporation), indicating that the alcoholic proton of 2-propanol is the major hydrogen source. In addition, 92% of the incorporation in the product was observed from the reaction with (CD₃)₂CDOH (D7), further confirming that the source of hydrogen is the alcoholic proton (entry 2).

\nearrow Pt _{0.5} Pd _{0.5} :PVP (2 atom%)					
R	KOH (200 mol%) 1 2-PrOH, time temp, Ar	,	R 2	Π	
Entry ^a	Reactant (1)	T (°C)	Time (h)	Yield (%) ^b	
1 ^c	MeO	27	28	97 (2a)	
2	F (1b)	50	10	92 (2b)	
3 ^d	$HO_2C \longrightarrow F$ (1c) HO_2C	50	7	99 (2c)	
4 ^d	F (1d)	50	12	97 (2d)	
5 ^d	F (1e)	50	10	98 (2e)	
6	MeO F (1f) OMe	50	4	97 (2f)	
7	F (1g)	50	4.5	94 (2g)	
8 ^c	Me — F (1h)	27	18	98 (2h)	
9 ^e	H ₂ N- F (1i)	50	10	98 (2i)	
10 ^e	F (1j)	50	10	93 (2j)	
11 ^e	SiMe ₃	27	36	95 (2k)	
12	CF ₃ —F (11)	50	3.25	96 (2I)	
13	F (1m)	60	5	99 (2m)	
14 ^c	F	60	18	92 (2n)	

Table 2. Substrate Scope

^aReactions conditions: 0.25 mmol of **1**, 2 mL of 2-propanol, and 200 mol% of KOH under argon. ^bYield determined by GC using hexadecane or anisole as the internal standard. ^c300 mol% of KOH was used. ^dIsolated yield. ^ePt_{0.8}Pd_{0.2}:PVP was used as catalyst.





Therefore, we refer to this reaction as "protodefluorination" instead of hydrodefluorination (HDF) (Scheme 1b). The

observed kinetic isotope effect $(k_{\rm H}/k_{\rm D}=2.41)$ indicates that the hydrogen at the 1-position of 2-propanol participates in the rate-determining step of the overall process, although this hydrogen is not mainly introduced in the product (Figure S7). In contrast, we observed an inverse KIE ($k_{\rm H}/k_{\rm D}$ =0.93), where the hydrogen stems from the alcoholic proton (-OD). Subsequently, the initial rate of consumption of 1a was found to depend linearly on the concentration of the catalyst (first order with respect to the catalyst) (Figure S8), providing additional evidence that the oxidative addition step occurs on the surface of the alloy.²² In addition, the concentration of both metals after the reaction was confirmed by ICP-AES to be under the detection limit (<40 ppb). To elucidate the reaction mechanism, we performed DFT calculations. Scheme 2 shows the proposed mechanism for the catalytic cycle and Figure 2 provides the calculated free energy profile using a Pt-Pd model cluster. Both Pt and Pd sites are present on the cluster surface, which is supported by the EDS and XRD data and genetic algorithm calculations. The oxidative addition of 2-propanol under concomitant O-H dissociation occurs selectively at the Pd sites prior to the C-F activation with an energy barrier of 18.3 kcal/mol. This step is an endothermic equilibrium process prior to the high energy barrier process, which would explain the inverse KIE (Figure S7). Owing to the effect of electron-donative adsorption at nearby Pd site, C-F activation occurs selectively at the Pt sites²³ with an energy barrier of 18.1 kcal/mol, which is sufficiently low for the bond activation even at room temperature: this step is thus not the rate-determining step. The C-F activation prior to the O-H oxidative addition, on the other hand, requires 26.3 kcal/mol, while the energy barrier for C-F activation without adsorption of KOH on the Pt-Pd cluster is 23.5 kcal/mol. Potassium ion coordinates to C-F and supports to abstract F atom. These results indicate that the O-H dissociation of 2-propanol and the adsorption of KOH as well as the activation of the cluster surface under similar reaction conditions, are crucial for the activation of the C-F bond.

The LUMO of the C-F activation transition state is delocalized over the Pt-C bond in anti-phase, indicating that the reduction of the energy barrier should be attributed to a stabilization of the LUMO. In contrast, the HOMO is delocalized over the Pt-Pd cluster and related to its nucleophilicity. The energy level of HOMO is almost constant even after co-adsorption, suggesting that the oxidative addition of 2-propanol does not affect the subsequent oxidative addition (Figure S15). Since the migration of H easily occurs from Pd to Pt, the reductive elimination of benzene follows through a low-energy barrier, which is exothermic by 17.2 kcal/mol. The obtained results clearly demonstrate that the hydrogen atom introduced into the product is derived mainly from the alcoholic proton of 2-propanol, although experimentally H/D scrambling was observed due to multiple sites on the same particle surface.

Finally, the β -H transfers from the adsorbed 2-propoxy group is followed by elimination of H₂O to complete the catalytic cycle. Notably, 2-propanol acts as the reductant via a β -H transfer to the cluster surface, where it is oxidized into acetone, as confirmed experimentally (Figure S10) as well as the formation of KF (Figure S11). These results are also consistent with another kinetic observation (Figure S9). In short, the aforementioned theoretical results and derived mechanism show excellent agreement with the experimental findings. The oxidative addition of 2-propanol on Pd occurs before Pt activates the C-F bond. The most important thing to note is that Pd and Pt play cooperative roles and the bimetallic effects stand in sharp contrast to the conventional behavior observed for Au-Pd alloys.²⁴



Scheme 2. Possible Mechanism. Only the reactive site is shown in the Pt₇Pd₆ model.



Figure 2. Calculated free energy profile (ΔG) for the activation of C-F bonds together with the schematic structures of the intermediates. The optimized structures are shown only for the reactive site of the Pt₇Pd₆ model.

4. Conclusion

In conclusion, we have demonstrated that Pt-Pd nanoalloy exhibits superior catalytic activity for the activation of C-F bonds at room temperature. The present reaction (C-F activation by Pt-Pd) seems similar to our previously reported C-Cl activation by Au-Pd, but the two reaction mechanisms are totally different.⁴ In the latter case, the catalytic center is Pd and the major role of Au is to anchor the Pd centers onto the bimetallic surface to avoid leaching (deactivation) processes, in addition to accelerate the migration process of the Cl atoms.^{4a,} ¹⁸ In contrast, in the current reaction, the C-F activation occurs at the Pt sites, but this is only possible once the neighboring Pd atoms are activated upon oxidative addition of 2-propanol, which also provides the coupling partner "H" for the exothermic reductive elimination. Therefore, Pt and Pd play independent and cooperative roles to accomplish the effective activation of C-F bonds.

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