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Abstract

During our exploration, we have found that fluorous metal complexes can be readily and directly intercalated into α-zirconium phosphate (ZrP) layered compound. The interlayer distance of neat ZrP is 7.6 Å. After the uptake of polyfluorinated Pd complexes, the original 7.6 Å interlayer distance was increased to ca. 10.6 Å, suggesting the successful intercalation of polyfluorinated Pd complexes within the ZrP galleries. The reason why polyfluorinated Pd complexes can be readily intercalated into ZrP is probably owing to the formation of hydrogen bonds between the hydroxyl groups of ZrP and the fluorous segments of the metal complexes. The intercalation of polyfluorinated Pd complexes into ZrP converted the metal complexes to be heterogeneous catalysts, which were evaluated for Sonogashira and Heck reactions. Such intercalation compounds exhibited high performance in terms of both yield and recyclability, which suggested that intercalation into layered compounds (such as ZrP) can be a promising route to form heterogeneous catalysts for polyfluorinated metal complexes for various reactions.

Keywords: polyfluorinated Pd complexes; α-zirconium phosphate; intercalation; heterogeneous

1. Introduction

Homogeneous catalysis offers several advantages in comparison to heterogeneous catalysis, including higher efficiency, better tuning of chemoselectivity, regioselectivity and stereoselectivity for most organic reactions.[1-3] However, majority of catalytic processes in industry are still heterogeneous, because the separation of the catalyst from the product is much easier than under homogeneous conditions.[4,5] Therefore, parallel to the development of highly efficient homogeneous catalysts (for which the catalyst quantity needed is at ppm level, and thus separation becomes not necessary), huge efforts have been made to create heterogeneous systems that require catalysts to be immobilized onto a solid support.[1,3]

Besides the most typical porous supports, layered materials,[6-9] which comprise multiple layers of thin sheets, with graphite and clay as the most representative examples, have emerged to be another group of ideal supports for catalysts. The most typical strategy to immobilize catalysts in layered compounds is to intercalate catalysts into the galleries of layered compounds, leading to the formation of a heterogeneous system. In this study, we explored to use α-zirconium phosphate (ZrP) as the catalyst support. ZrP is a versatile layered compound owing to its synthetic nature (in contrast to natural clays) and rich surface chemistry.[10] Both the lateral dimension[11] and interlayer structure of ZrP can be tailored.[12] As such, ZrP has found many functional applications,[13a-j] including as support for catalysts.[14] We anticipate ZrP is a particularly ideal support for fluorinated catalyst system because ZrP contains a high concentration of hydroxyl groups on each of its layers, which can form hydrogen bonds with fluorous segments, resulting in a facile intercalation process.

In this study, the catalysts of interest are polyfluorinated Pd complexes. Fluorine-containing materials have been known as a group of special materials, which have attracted significant interest in the past few years.[15-17] Lu's group has been working on various fluorous metal complexes for almost a decade. For practical industrial applications, the catalysts are desirable to be separated from the reaction media at the end of the reaction. That is the reason why the fluorous technology plays an important and crucial role in recovering and reusing the precious metal catalysts during the biphasic or thermomorphic catalysis.[16] However, in order to reach the goal of fluorous catalysis, the very high fluorous contents are usually required. Reported here, we have found a way to moderately secure the short fluorous catalysts into the ZrP gallery, which enables to form heterogeneous catalysts and to be used for other applications. Formation of polyfluorinated metal complexes based heterogeneous catalysts have been explored recently[16] and have also gained great attention in the areas of crystal engineering,[15c] medicinal chemistry,[17a] and functional materials.[17b] The unusual interactions of polyfluorinated metal complexes involve C–F…H, F…F, C–F…π_F, C–F…π, C–F…C=O and anion–π_F interactions, as well as other halogen bonds.[18] Thus, the application of special interactions of these polyfluorinated metal complexes can be used to enable a number of reactions, to improve materials properties, to tune its physical properties by so called "fluorous chemistry"[18] and even open up new fields of research. The intercalation of fluorous metal complexes into ZrP seems to benefit from these unusual weak fluorine-related interactions. To the best of our knowledge, this report serves the first example to directly intercalate planar fluorous metal complexes into layered ZrP for catalysis applications.

2. Experimental Section

2.1. Synthesis

Synthetic procedure for **2a-c**, [4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy]PdX_2: Equal molar [$PdCl_2(CH_3CN)_2$] or K_2PdBr_4 (0.144 mmol) and ligand 4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy [0.144 mmol; R_f= HCF_2 (**1a**), HC_2F_4 (**1b**), C_2F_5 (**1c**)], were charged into a round bottomed flask, and CH_2Cl_2 (8 mL) was added as the solvent. The color of the solution changed from pale yellow to bright yellow after mixing for several minutes. The solution was further stirred at 25 °C for 24 h before the solvents and volatiles were removed under vacuum. The resulting bright yellow solid was collected as spectroscopically pure product [4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy]PdX_2 [R_f= HCF_2 (**1a**), HC_2F_4 (**1b**), C_2F_5 (**1c**); X=Br, Cl]. Complex of **2b** which is also labeled as 44-4F-$PdCl_2$, was soluble in polar solvent (e.g., DMF), but insoluble in methanol. Accordingly, recrystallization proceeded with a dissolution of Pd complex **2b** in DMF to form a yellow solution, to which a methanol overlayer (5 cm^3) was placed. Solvent diffusion, over a period of 10 days at 25 °C, afforded pale yellow crystals of 44-4F-$PdCl_2$.

2.1.1. Analytical data of **2a** (also labeled as 44-2F-$PdBr_2$; from [$PdCl_2(CH_3CN)_2$] and ligand **1a**): Yield 83%, yellow solid; 1H NMR (300 MHz, d-Me_2SO): δ= 9.30 (2H, d, $3J_{H–H}$ = 5.9 Hz, H-6), 8.47 (2H, s, H-3), 7.73 (2H, d, $3J_{H–H}$ = 5.9 Hz, H-5), 6.28 (2H, tt, $^2J_{HF}$= 54.7, $^3J_{HF}$= 3.3, 2 x HCF_2), 4.86

(4H, s, bpy–CH$_2$), 3.89 (4H, q, 3J$_{H–F}$ = 15.2 Hz, HCF$_2$CH$_2$). 19F NMR (470.5 MHz, d-Me$_2$SO): δ= -125.7 ~ -125.9 (4F, d, ^{2}J$_{HF}$ 54.7, 2 x HCF$_2$). 13C NMR (126 MHz, d-Me2SO): δ= 71 (bpy-CH$_2$), 69 (bpy-CH$_2$OCH$_2$), 114.7 (116.6 ~ 112.7, 2C, t, $^1J_{CF}$ = 239.2 Hz, -CH$_2$CF$_2$H), 156, 153, 151, 125, 122 (bpy); FT-IR [ν_{max}(KBr)/cm^{-1}]: 1621m, 1560s, 1428m (νbpy), 1250vs, 1121vs (νCF$_2$). HR-MS (FAB): [M]+ $C_{16}H_{16}{}^{79}Br_2F_4N_2O_2Pd$ calcd m/z 607.8549, found 607.8553; $C_{16}H_{16}{}^{79}Br^{81}BrF_4N_2O_2Pd$ calcd m/z 609.8529, found 609.8528; $C_{16}H_{16}{}^{81}Br_2F_4N_2O_2Pd$ calcd m/z 611.8509, found 611.8507.

; m.p. = 234 °C.

2.1.2. Analytical data of **2b** (also labeled as 44-4F-PdCl$_2$; its structure was very briefly mentioned for the comparison purpose in ref. 15c): Yield 82.3%; 1H NMR (500 MHz; d-Me$_2$SO; Me4Si) δ= 8.98 (2H, dd, ^{3}J$_{HH}$ 6, 2 x H$_6$), 8.42 (2H, s, 2 xH$_3$), 7.72 (2H, dd, ^{3}J$_{HH}$ 6, 2 x H$_5$), 6.65 (2H, tt, ^{2}J$_{HF}$ 52, ^{3}J$_{HF}$ 5.5, 2 x HCF$_2$), 4.91 (4H, s, 2 x bpy–CH$_2$), 4.16 (4H, t, ^{3}J$_{HF}$ 14, 2xCF$_2$CH$_2$); 19F NMR (470.5 MHz; d-Me$_2$SO; CFCl$_3$) δ= -125.3 (4F, t, ^{3}J$_{HF}$ 5.5, 2 x CH$_2$CF$_2$), -140.1 (4F, d, ^{2}J$_{HF}$ 52, 2 x HCF$_2$); 13C NMR (126 MHz; d-Me$_2$SO; CHCl$_3$) δ= 71 (bpy-CH$_2$), 67 (bpy–CH$_2$OCH$_2$), 107-112 (CF$_2$)$_2$, 121, 125, 149, 152 and 156 (bpy); FT-IR [ν_{max} (KBr)/cm^{-1}]: 1625m, 1561, 1424m (bpy), 1235vs, 1205vs, 1190vs and 1144vs (CF$_2$). HR-MS (FAB): [M]$^+$ $C_{18}N_2H_{16}F_8O_2Pd^{35}Cl_2$ calcd m/z 619.9496, found m/z 619.9482; $C_{18}N_2H_{16}F_8O_2Pd^{37}Cl^{35}Cl$ calcd m/z 621.9466, found m/z 621.9452; $C_{18}N_2H_{16}F_8O_2Pd^{37}Cl_2$ calcd m/z 623.9437, found m/z 623.9440. m.p. = 180 °C.

Single crystal X-Ray structure analysis of **2b** (CCDC988755): C18N2H16F8O2PdCl2 Mr 621.63, P -1, Wavelength 0.71073 Å (Mo Kα), a=9.3497(3), b=9.9160(4), c=12.4927(4) Å, alpha=93.291(2), beta=111.275(1), gamma=91.890(2)°, V 1075.70(7) Å^3, Z = 2, T = 150 K, ρ_{calcd} = 1.919 g.cm^{-3}, 2θ_{max} = 50.04°, No of reflns. = 3757 [I_o > 2□I)], R = 0.0323, Rw = 0.0976, GoF = 1.119.

2.1.3. Analytical data of **2c** (also labeled as 44-5F-PdCl$_2$ (from [PdCl$_2$(CH$_3$CN)$_2$] and ligand **1c**): This complex has been synthesized using the method described in our previous publication.[19] Yield 96%, yellow solid.

2.2. Synthesis of α-zirconium phosphate (ZrP)

Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 98%, Aldrich) and phosphoric acid (85%, Aldrich) were used as received. ZrP micro-crystals with a lateral dimension of 60-80 nm were synthesized according to the procedures described in an earlier report.[20] Briefly, a sample of 10.0 g of $ZrOCl_2 \cdot 8H_2O$ was refluxed with 100.0 mL of 3.0 M H_3PO_4 at 100 °C for 24 h to synthesize ZrP micro-crystals.

2.3. Intercalation of polyfluorinated Pd complexes into ZrP

The synthesized ZrP was first well dispersed in dimethyl sulfate oxide (DMSO) with the assistance of ultra-sonication for 1 hour. A solution of polyfluorinated Pd complexes in DMSO was added into the dispersion of ZrP at 1:1 molar ratio, followed by ultrasonication for another 2 hours to obtain the Pd complex intercalated ZrP. After the uptake, the solid phase was separated by centrifugation, washed with DMSO to eliminate the excessive complex on ZrP surface, and then dried at 60 °C overnight.

2.4. Characterization

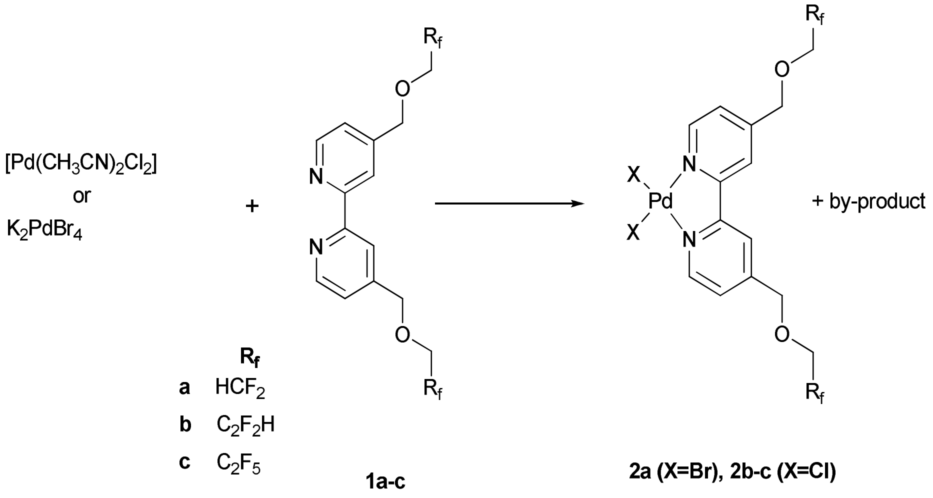
These Pd complexes intercalated ZrP were mainly characterized by X-ray diffraction (XRD). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Bragg-Brentano θ-2θ geometry using a graphite monochromator with Cu Kα radiation. The thermal properties of the samples were characterized by a thermogravimetric analyzer (TGA, TA Instruments model Q50) under an air atmosphere (40 mL/min) at a heating rate of 10 °C/min. IR spectra were obtained on a Perkin-Elmer RX I FT-IR spectrophotometer; and ATR data reported here were taken with a ZnSe crystal plate. Additionally, high-resolution transmission electron microscopy (TEM) samples were prepared by dropping a dilute DMSO solution of neat ZrP or ZrP/44-4F-PdCl$_2$ onto copper grids coated with a thin Formvar-carbon film with subsequent evaporation of the solvent in air at room temperature. TEM imaging was carried out on a Philips Tecnai G2 F20 microscope (Philips, Holland).

3. Results and Discussion

3.1. Intercalation of polyfluorinated Pd complexes into layered ZrP

3.1.1. The polyfluorinated Pd complexes

Scheme 1. Synthesis of 2a-c



As shown in Scheme 1, the reaction of [Pd(CH_3CN)$_2$$Cl_2$] or K_2PdBr_4 with polyfluorinated bipyridines, 4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy **1a-c** [R_f= *n*-HCF_2 (**1a**), *n*-C_2F_4H (**1b**), *n*-C_2F_5 (**1c**)] resulted in the synthesis of pale yellow solids of Pd complexes, [PdX_2(4,4′-bis-($R_fCH_2OCH_2$)-2,2′-bpy)] **2a-c,** respectively (**2a** X= Br, **2b-c** X= Cl). The fluorine contents of these polyfluorinated Pd complexes are 16.4%, 32.2% and 36.2%, respectively. Due to their low fluorine content, these Pd complexes are all quite soluble in most organic solvents. Using the diffusion crystallization, the structure of **2b** has been obtained by solving its single crystal using X-ray crystallography.

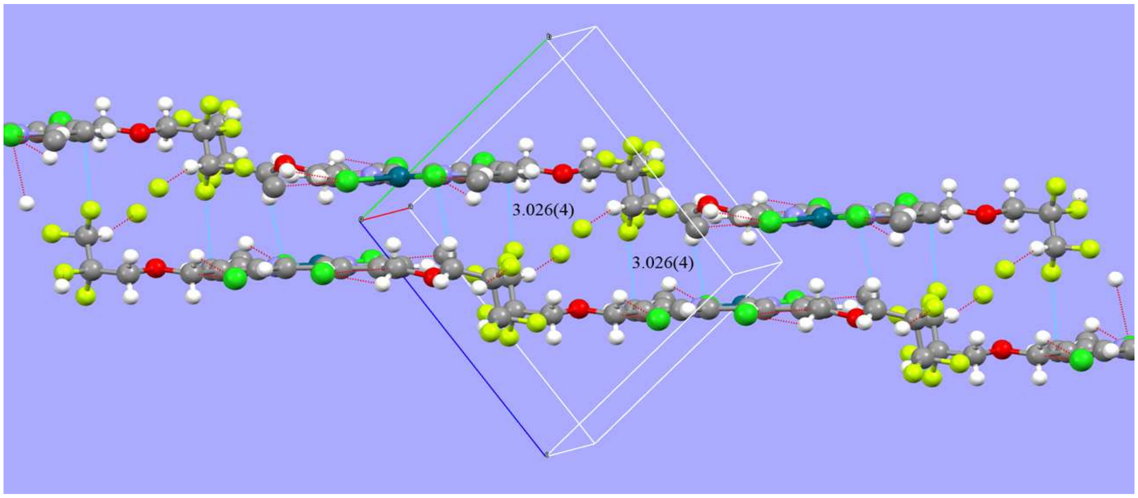


Figure 1. The two-dimensional structural arrangement of crystal 44-4F-PdCl_2, **2b**. (Note: C: grey; H: white; O: yellow: F: yellow; Cl: green; Pd: pink.)

As shown in Figure 1, this structure shows some interesting features. First of all, the fluorous chains containing four fluorine atoms form the fluorous domain around the –C_2F_4H segment. Second, this type of fluorous square planar Pd complex has the tendency to form a dimer pair.[15d] The weak forces, which mainly include bipyridyl π-π stacking and H…Cl hydrogen bonding, make the dimeric structure possible. As shown in Figure 1, there are mainly two sets of dimeric structures aligned from left to right. Each set of dimeric structure is half a step lower than its left neighboring set of dimer. Third, two –C_2F_4H groups from two different Pd complexes of each dimeric pair, inside the unit cell, not only form the fluorous domain but also form the unusual synthon. This rectangular-shaped synthon as shown at the centre of Figure 1 is mainly formed by two sets of weak C-F… aromatic carbon interactions vertically situated within the unit cell. It is this type of attractive force that brings together two immediately neighboring set of dimeric complexes. The distance of F atom (from F-C bond) and C atom (from aromatic ring) is 3.026(4) Å, which is shorter than the sum

(1.47 + 1.70 = 3.17 Å) of van der Waals radii of fluorine and carbon atoms.

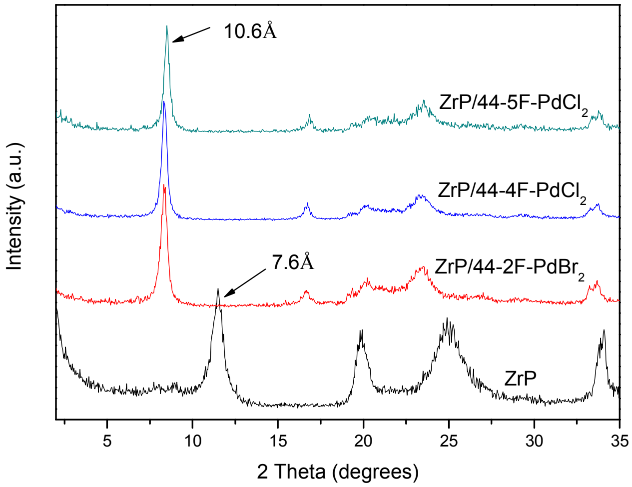
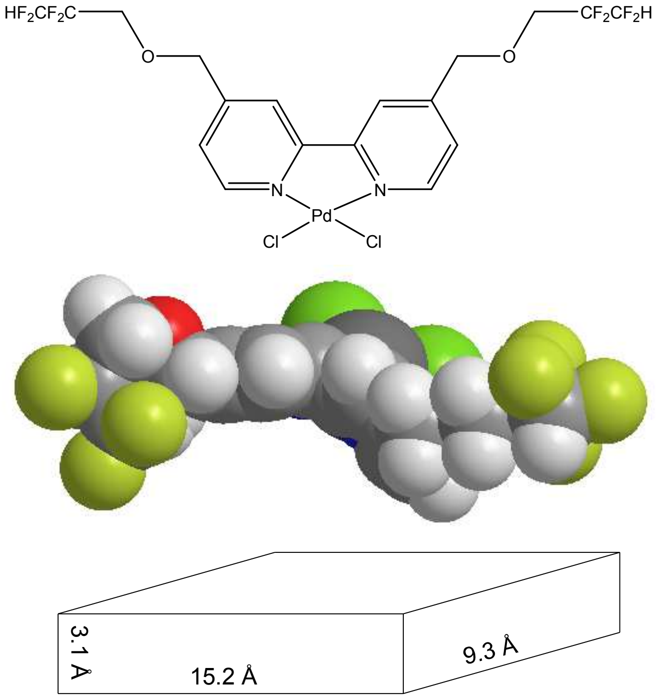


Figure 2. XRD patterns of the intercalated complexes

The XRD characterization was performed to verify the intercalation of Pd-complex within the layers of ZrP,[21] and the results are presented in Figure 2. The diffraction pattern of the ZrP sample is highly consistent with the literature, and it exhibited an interlayer distance of 7.6 Å. After the uptake of the Pd complexes, the diffraction patterns show a new peak at ca. 8.5°, corresponding to a new phase with an interlayer distance of ca. 10.6 Å. Meanwhile the original ca. 7.6 Å peak completely disappeared. The above result strongly supports that the poly-fluorinated Pd-complexes have been successfully intercalated into the galleries of ZrP. The dimension of the Pd-complexes was simulated by Chem3D Pro.2010 under minimized energy (Figure 3). The simulated thickness of these Pd complexes is ca. 3Å. The interlayer distances of Pd-complex intercalated ZrP are ca. 10.6 Å. Therefore, the results indicate that the planar Pd-complexes were intercalated into the ZrP galleries virtually perfectly parallel to the layer surface.

The XRD patterns shown in Figure 3 suggest that the planar fluorous Pd complexes can be readily intercalated into the layered ZrP, with no neat ZrP phase left. There are probably several favorable factors that facilitate the intercalation of such fluorous Pd complexes into ZrP, including the hydrogen bonding between the fluorous side chains and the hydroxyl groups on ZrP layers, and the suitable geometry to situate inside ZrP. To the best of our knowledge,[22-24] *this direct intercalation of fluorous metal complexes is the first example of its kind in the intercalation chemistry*. This kind of facile and direct intercalation might open up several practical applications, because 1) the metal complexes can be moderately secured after intercalation; 2) this type of intercalation renders the immobilized metal complexes certain mechanical strength for possible future material applications.



44-4F-PdCl$_2$ (**2b**)

Figure 3. Dimension of 44-4F-PdCl$_2$, **2b,** under minimized energy (Chem3D Pro.2004). (Note: Dimension of figures of **2a,c** are shown in Electronic Supplementary Information **A**, ESI **A**.)

Both ZrP and fluorous Pd complexes show quite different IR peaks, but the phosphate part of ZrP shows strong peaks in the range of 1300 and 900 cm^{-1} as shown in black trace of Figure 4. This region covers most of vibrational peaks of 44-4F-PdCl$_2$, so the intercalated fluorous Pd complex can then be confirmed by the ring stretching peaks around 1424 cm^{-1} where ZrP shows no peak as shown in Figure 4.

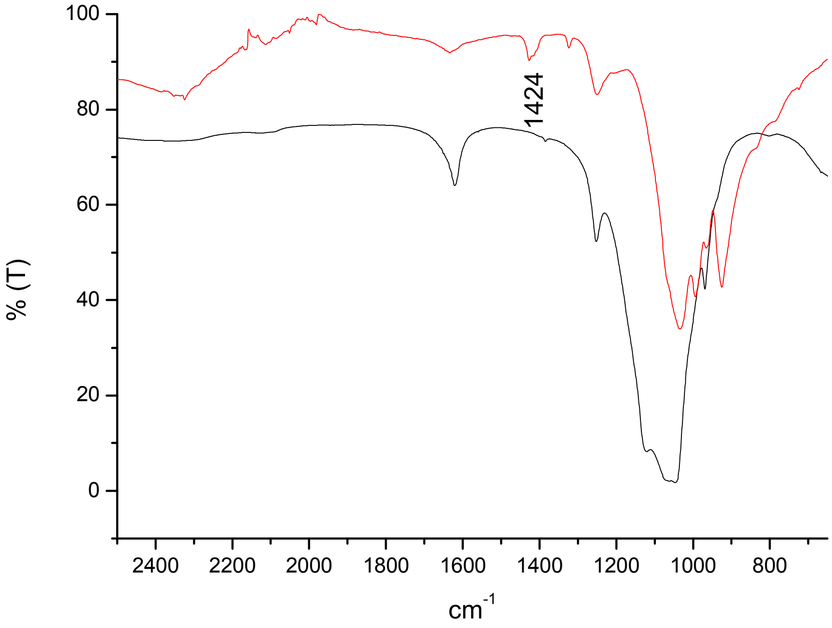


Figure 4. FT-IR overlay spectra of ZrP/44-4F-PdCl$_2$ (in red trace) and ZrP (in black trace).

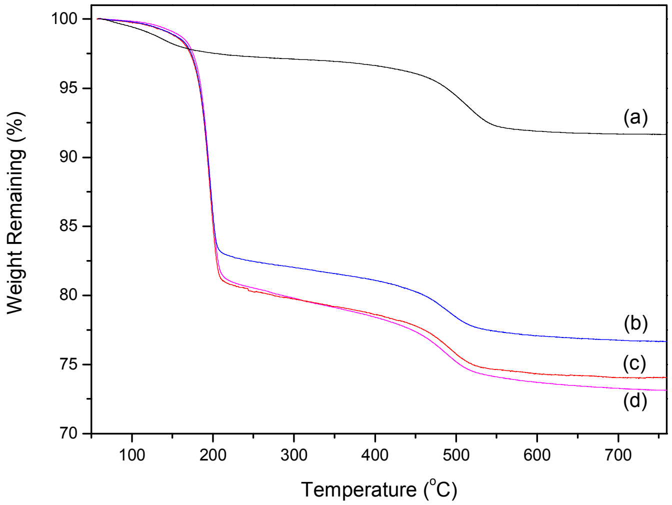


Figure 5. TGA thermograms of (a) ZrP; (b) ZrP/44-2F-PdBr$_2$; (c) ZrP/44-5F-PdCl$_2$; (d) ZrP/44-4F-PdCl$_2$.

The thermal stability of the samples was characterized by TGA. As shown in Figure 5, ZrP went through two major weight losses in 100-170 and 420-600 °C range, corresponding to the loss of hydration water and condensation water in ZrP, respectively.[14a] The Pd complexes intercalated ZrP samples, including ZrP/44-2F-PdBr$_2$, ZrP/44-4F-PdCl$_2$ and ZrP/44-5F-PdCl$_2$, showed very similar TGA patterns. The weight percentage of these three intercalated samples is estimated to be 15.0, 18.5 and 17.6 %, respectively.

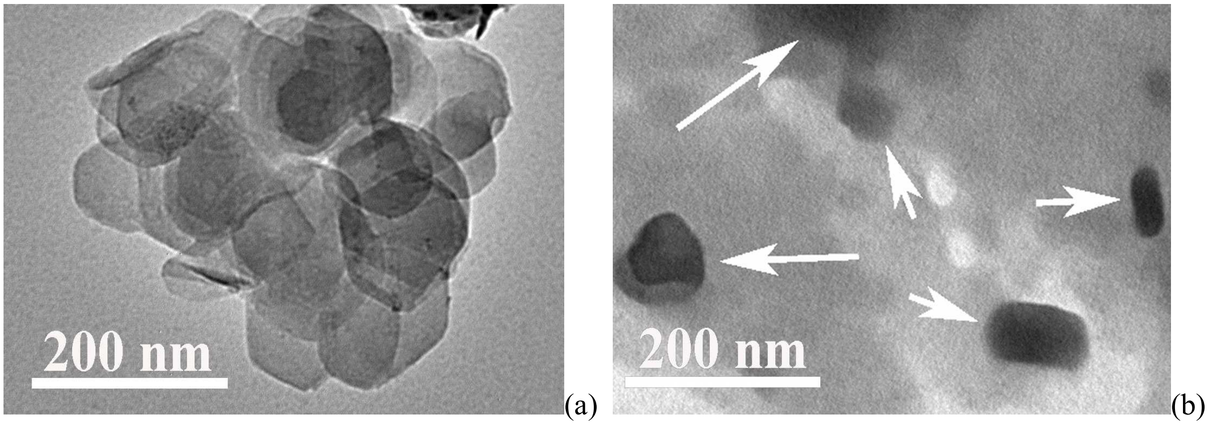


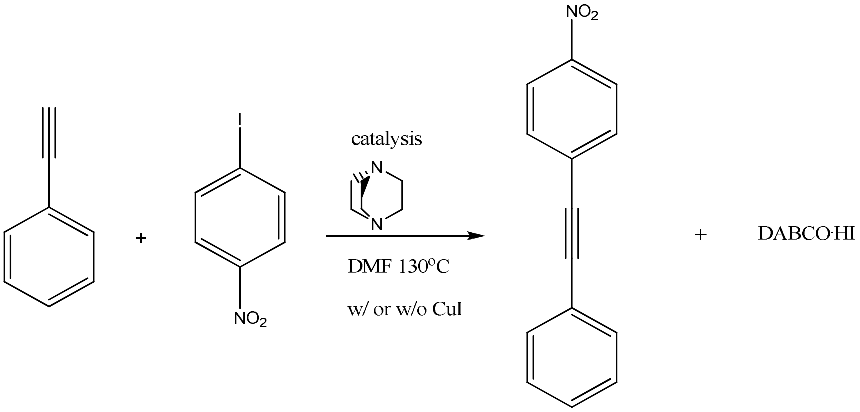
Figure 6. TEM images of (a) neat ZrP and (b) ZrP/44-4F-PdCl$_2$.

Additionally, the TEM images of neat ZrP and ZrP/44-4F-PdCl$_2$ have been obtained, and are shown in Figure 6(a) and Figure 6(b), respectively. ZrP microcrystals exist as nano-sized particles in 80-100 nm in diameter. As shown in Figure 6(b), the Pd complex intercalated ZrP remains to be well dispersed.

4. Reactivity

4.1. Sonogashira reaction

Scheme 2. Pd complexes intercalated ZrP-catalyzed Sonogashira reactions



In **Scheme 2**, the intercalated Pd-catalyzed Sonogashira reactions of phenylacetylene with aryl iodides were selected to demonstrate the feasibility of recycling usage with Pd complex immobilized

ZrP as the catalyst using 10% CuI, at ca. 130-140 °C in DMF for several hours varying in each cycle. As shown in Table 1, immobilized Pd-catalyzed Sonogashira reaction of 4-nitro-iodobenzene can be easily carried out and reused for a total of 8 times at ca. 140 °C under heterogeneous condition. Most importantly, the reactions can be completed within several hours for the first 5 runs, with turnover number of 100, as shown in the last column of Table 1. The reaction can be easily repeated for a few times with high yields using the recovered catalyst, Pd complex intercalated ZrP. We also find that it is *under the direct, non-covalently intercalation method* that immobilized Pd complex-catalyzed Sonogashira reaction of aryl iodide could be carried out, recovered and reused with the high yield for the first 5 runs as shown in Table 1. Their general procedures are described in ESI **B**.

Table 1. Recycling results of Sonogashira reaction of aryl iodide using Pd complex intercalated ZrP, ZrP/44-4F-PdCl$_2$.

Cycle[a]	Time (h)	Temperature (°C)	Yield (%)	TON
1	4	140	100	100
2	4	140	100	100
3	4	140	100	100
4	4	140	100	100
5	4	140	100	100
6	4	140	69	69
7	4	140	62	62
8	4	140	37	37

[a] Reaction conditions: DMF (4 ml); 1-iodo-4-nitrobenzene (0.45 mmol, 112.05 mg), phenylacetylene (0.54 mmol, 55.08 mg), DABCO (0.675 mmol, 75.7 mg), with 10% CuI (0.045 mmol), intercalated Pd complex on ZrP (16 mg, 1 mol %).

These results are new and exciting in several ways. First of all, we were successfully in using simple, non-covalently bound method in intercalating poly-fluorinated Pd complexes into the multilayered materials of ZrP. Secondly, this type of metal intercalation[22,23] into ZrP could usually provide a local ZrP matrix for the metal-catalyzed oxidation in a way that the catalyst can also be prevented from being deactivated by the strong oxidizers. Although this moderate non-covalent intercalation is not robust in nature, it was still strong enough to hold the catalyst inside the ZrP matrix for several cycles of Pd-catalyzed C-C forming reactions. Thus, the catalyst could be recovered for up to 5 times while the catalytic abilities still remained high. It was well known that the metal complexes have the rich catalytic chemistry in solution phase in addition to their other applications as self-stand film in areas such as material science, light-emitting materials, optoelectronic devices, vapochromic sensors, organic transistors etc.[24,25] Thirdly, it was possible that the oxidation state change between Pd(0) and Pd(2) during redox process, the weak electrostatic force was formed between Pd moiety and ZrP to help to secure the Pd complex in place. Thus, this research will certainly shed new light on the immobilized metal complex catalysis, their recycling and separation. Additionally, the easy intercalation onto ZrP will sufficiently provide the strength to this type of metal complexes which in general are known to be lack of mechanical strength and film forming abilities. In view of the successful results above, we further evaluate the similar Pd complex intercalated ZrP in catalyzing Sonogashira reaction. Other similar Pd complex used was 44-2F-$PdBr_2$. As shown in Table 2, the similar ZrP-immobilized complex could also catalyze the same reaction with decent recyclabilities although the yield fell off in the 4th run. Additionally, the few samples taken from Table 1 and Table 2 were submitted for ICP-MS analysis. The metal leaching studies showed that the metal leaching problem was small and ranged from 0.0054-0.091%.

Table 2. Recycling results of Sonogashira reaction of aryl iodide using another intercalated Pd complex ZrP, ZrP/44-2F-$PdBr_2$.

Cycle[a]	Time[b] (h)	Temperature (°C)	Yield (%)	TON
1	3	140	100	100
2	3	140	92	92
3	4	140	90	90
4	4	140	27	27

[a]Reaction conditions: DMF (4 ml); 1-iodo-4-nitrobenzene (0.45 mmol), phenylacetylene (0.54 mmol, 55.08 mg), DABCO (0.675 mmol, 75.7 mg), with 10% CuI (0.045 mmol), intercalated Pd complex on ZrP (1 mol %). [b]Time was lengthened when the yield seemed decreasing.

Lastly, due to the success of ZrP/44-4F-$PdCl_2$-catalyzed Sonogashira reactions, we also evaluated ZrP/44-4F-$PdCl_2$-catalyzed Sonogashira reactions without using CuI. It is known that the CuI-free Pd-catalyzed Sonogashira reaction was proceeded by using a slightly different mechanism from that of the normal Sonogashira reaction. The condition required for CuI-free Sonogashira reaction is certainly more harsh than that of the normal Sonogashira reaction. Even so, as shown in Table 3, the Pd complex intercalated ZrP still catalyzed the CuI-free Sonogashira reaction 4 times with high yieldings. In view of these good outcomes, other intercalations and more effectively covalently bonded immobilization of ZrP are under the further investigations.

Table 3. Recycling results of Sonogashira reaction of aryl iodide using Pd complex intercalated ZrP, ZrP/44-4F-PdCl$_2$, without using CuI.

Cycle[a]	Time[b] (h)	Temperature (°C)	Yield (%)	TON
1	3	140	100	100
2	3	140	89	89
3	3	140	86	86
4	3	140	42	42
5	4	140	51	51

[a] Reaction conditions: DMF (4 ml); 1-iodo-4-nitrobenzene (0.45 mmol), phenylacetylene (0.54 mmol, 55.08 mg), DABCO (0.675 mmol, 75.7 mg), without using CuI, intercalated Pd complex on ZrP (1 mol %). [b]Time was lengthened when the yield seemed decreasing.

Besides the heterogeneous catalysis applications, these non-covalently intercalated Pd complexes might find other useful applications in areas like lithium batteries,[10] fuel cells,[11] biomedical devices,[12] optoelectronic systems,[10] etc. Reported above are mainly evaluations of these immobilized Pd complex as a heterogeneous catalyst in the Pd-catalyzed Sonogashira reactions.

4.2. Heck reaction

Scheme 3. Pd complexes intercalated ZrP-catalyzed Heck reactions

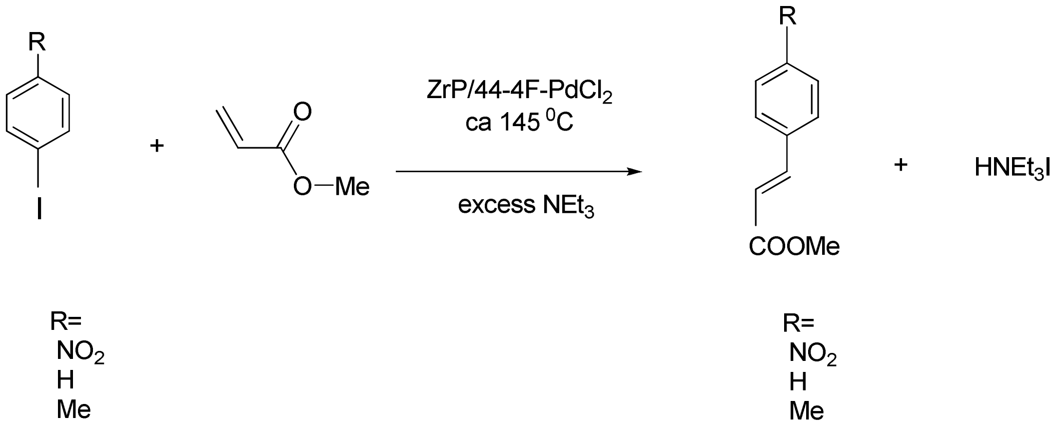


Table 4. Recycling results of ZrP/44-4F-$PdCl_2$-catalyzed Heck reaction of methyl acrylate with three iodobenzene derivatives,[a] 4-X-C_6H_4-I, (X= NO_2, H or CH_3).

entry	Cycle[b]	Reactant A[a]: (when X=)	Reactant B:	Time (h)	Temperature (°C)	Yield (%)	TON
1	1st	NO_2	Methyl acrylate	2	145	100	100
2	2nd	NO_2	Methyl acrylate	2	145	100	100
3	3rd	NO_2	Methyl acrylate	2	145	100	100
4	1st	H	Methyl acrylate	3	145	100	100
5	2nd	H	Methyl acrylate	3	145	97	97
6	1st	CH_3	Methyl acrylate	6	145	100	100
7	2nd	CH_3	Methyl acrylate	7	145	88	88

[a] (Reactant A=) derivatives of iodobenzene, 4-X-C_6H_4-I, (X= NO_2, H or CH_3).

[b] Reaction conditions: DMF (4 ml); 4-X-C_6H_4-I, (X= NO_2, H or CH_3) (0.45 mmol), methyl acrylate (0.90 mmol, 77.5 mg), NEt_3 (2.25 mmol, 227.7 mg), intercalated Pd complex on ZrP (16 mg, 1 mol %).

We also evaluated ZrP/44-4F-$PdCl_2$ in Heck reactions. The results showed that ZrP/44-4F-$PdCl_2$ can effectively catalyze the Heck reactions as shown in Table 4. The catalyst could be recycled and reused for several times. It is known that the electron-withdrawing NO_2 substituent on aryl halide could speed up Heck reaction. Thus, the entries 1-3 in Table 4 were tested first for ZrP-supported Pd complex-catalyzed Heck reaction of 4-nitro-iodobenzene (when X= NO_2). After the 1st run, the recovered catalyst was subject to the normal washing steps and then reused for the next runs. For these three runs, the reactions were all completed within 2 hours at 145 °C with 100% yield. For entries 4 & 5, it was iodobenzene (when X=H) that was used as the substrate for the ZrP-supported Pd complex-catalyzed Heck reaction. The results demonstrated that this ZrP-supported Pd complex, ZrP/44-4F-$PdCl_2$, was a good recoverable catalyst for the two runs with a yield better than 97% under the conditions outlined in Scheme 3. For entries 6 & 7, these two results also showed that

ZrP-supported Pd complex-catalyzed Heck reactions were efficient and recyclable. Although these two Heck reactions using the less reactive 4-methyl-iodobenzene (when X= CH_3) required slightly longer time to proceed, the yields were 100 and 88% for entries 6 and 7, respectively. Thus, the results in Tables 1 to 4 have clearly demonstrated that the ZrP-supported Pd complex is an excellent heterogeneous catalyst for C-C forming reactions.

5. Conclusions

Tradition intercalation of metal complexes in layered compounds is typically a two-step process.[25-27] The layered compounds are usually pre-intercalated by certain chemicals to increase the interlayer distance to facilitate the second step intercalation of metal complex. Such pre-intercalants often bring negative impact for the practical applications of the intercalation compounds. Interestingly, we found a direct method to simply and effectively intercalate the planar fluorous metal complexes into ZrP gallery. The Pd complexes immobilized into ZrP have been successfully characterized by XRD, FT-IR, TGA etc. The short fluorous chain has been believed to help to immobilize the neutral Pd complexes inside the galleries by the fluorous related H-bonding interactions. The Pd complex immobilized ZrP was evaluated for Sonogashira/Heck reaction in DMF. At the end of each cycle, the product mixtures were cooled to 0 °C and centrifuged, and the catalyst was recovered and reused. The results of immobilized Pd-catalyzed Sonogashira/Heck reactions turned out to be efficient and recyclable.

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Electronic supplementary information (ESI) available: **A** and **B** contain, respectively, Figure S1 and general Sonogashira recycling procedures. CCDC reference number of complex **2b** is CCDC 988755. For ESI and crystallographic data in CIF or other electronic format see DOI:

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Graphical Abstract

A direct method was used to effectively intercalate the short fluorous-ponytailed Pd complexes into ZrP gallery, and that the resulting Pd intercalated ZrP could be used as a recoverable catalyst for Sonogashira reactions.