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Dinuclear Tetrapyrazolyl Palladium Complexes Exhibiting Facile Tandem Transfer Hydrogenation/Suzuki Coupling Reaction of Fluoroarylketone

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Supporting Information Place holder

ABSTRACT: Herein, we report an example of dinuclear pyrazolyl-based Pd complexes exhibiting facile tandem catalysis for fluoroarylketone: Tetrapyrazolyl di-palladium complexes with varying Pd-Pd distances efficiently catalyze the tandem reaction involving transfer hydrogenation of fluoroarylketone to the corresponding alcohol and Suzuki-Miyaura cross coupling reaction of the resulting fluoroarylalcohol under moderate reaction conditions, to biaryl alcohol. The complex with the shortest Pd-Pd distance exhibits the highest tandem activity among its di-metallic analogues, and exceeds in terms of activity and selectivity the analogous mononuclear compound. The kinetics of the reaction indicates clearly that reductive transformation of haloarylketone into haloaryalcohol is the rate determining step in the tandem reaction. Interestingly while fluoroarylketone undergoes the multistep tandem catalysis, the chloro- and bromo-arylketones undergo only a single step C-C coupling reaction resulting in biarylketone as the final product. Unlike the pyrazole based Pd compounds, the precursor $PdCl_2$ and the phosphine based relevant complexes $(PPh_3)_2PdCl_2$ and $(PPh_3)_4Pd$ are found to be unable to exhibit the tandem catalysis.

KEYWORDS: tetrapyrazolyl, dipalladium complex, fluoroarylketone, tandem catalysis, transfer hydrogenation, Suzuki coupling.

INTRODUCTION

With the strongest σ-bond among the carbon-hetero atoms,[1] the C-F bond activation of organofluoro compounds followed by their transformation into new functionalized molecules has been a great challenge in synthetic organic chemistry.[2] In this context, a significant effort has been put forward for the development of new and efficient synthetic strategies. Among the various approaches, catalytic transformations of organofluoro compounds is one of the most challenging subject. The well-known catalytic transformations, such as hydrodefluorination,[3] Suzuki-Miyaura,[4] and Stille[5] C-C cross-coupling, amination reaction,[5] C–F bond activations of multi fluorinated compounds,[6] nucleophilic substitution of electron deficient fluoroarenes[7] and metallofluoroarene complexes,[8] cross-coupling reaction of perfluoro organic compounds,[9] etc. are already well documented in literature.

Nevertheless, one-pot multi-step tandem transformations of organofluoro compounds comprising C-F activation is rare.[10] Such type of catalysis, owing to their advantage in improving atom economy, saving chemicals, reduction of waste, energy and time has emerged as a fascinating tool in the synthesis of complex organic frameworks.[11] Thus, development of single, well-defined multifunctional catalytic system capable of conducting tandem reactions is highly demanding, however, challenging due to the requirement of compatibility between mechanistically diverse reaction steps.

Besides, combining multiple catalytic metals in close proximity in order to improve local concentration of the active sites,[12] and to promote cooperativity and/or synergism between the two reaction centers is also highly challenging.[13] Therefore, design of new ligand framework and the resulting synthesis of the corresponding polynuclear metal complexes with varying metal-metal distances is a difficult target.

In parallel, there has been a gradual demand for alternate ligands to replace the existing expensive, toxic and/or unstable phosphine or carbene based systems.[14] In this aspect, N,N donating polypyrazolyl-based homoscorpionate ligands have been developed and extensively employed for the preparation of precatalysts or catalysts in studying numerous homogeneous catalytic processeses.[15] In contrast, the use of multidentate bis-heteroscorpionate based multimetallic system is relatively rare.[16] Moreover, to the best of our knowledge, the catalytic tandem transformation of organofluoro compounds utilizing such heteroscorpionate ligand-based coordination compound is not known.

Tandem catalysis using heterometallic systems are much common as the metal centers are compatible to conduct mechanistically diverse reactions.[17] Palladium based catalysts are well known for their efficiency in a wide range of reactions, such as C-C coupling,[18] reduction of various organic functionalities,[19] dehydrogenation of alcohols, etc. Combining Pd with other metal centers a varieties of heterometallic tandem catalysts have been developed.[16-17] Therefore, although a considerable number of reports comprising heterometallic systems are available,[17a-k] tandem catalysis using homodimetallic system is rare.[20] In particular, homodinuclear Pd complexes catalyzing tandem reactions are not known.

In the current contribution we present such examples of new inexpensive, air-stable bis-heteroscorpionate-di-palladium complexes (Figure 1) and their efficient use towards tandem transfer

hydrogenation/Suzuki coupling reaction of fluoroarylketone. The influence of two metal centers with varying Pd-Pd distances on the tandem reactivity has also been scrutinized. The advantage of N-donor pyrazolyl-based complexes over their non-ligated precursor $PdCl_2$, as well as the phosphine based analogous complexes $[(PPh_3)_2PdCl_2]$ and $[(PPh_3)_4Pd]$ is investigated here. Additionally, kinetics experiments has been carried out to shed light over the sequence of such multi-step reactions involving both carbonyl (C=O) reduction and C-F bond activation.

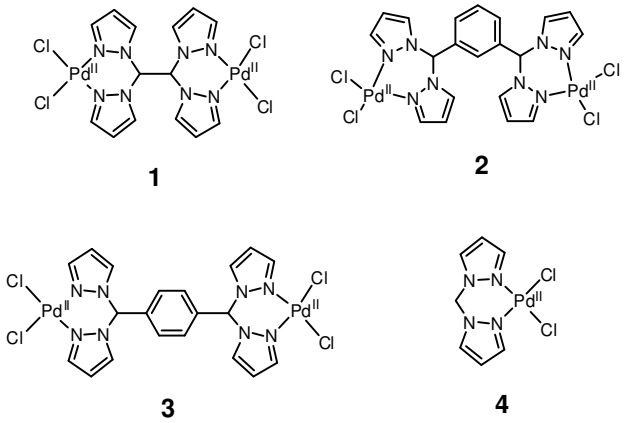


Figure 1. Dimetallic (**1**-**3**) and monometallic (**4**) Pd complexes with polypyrazolyl framework.

RESULTS AND DISCUSSION

Synthesis and characterization of pyrazolyl Pd complexes 1-4. The dinuclear tetrapyrazolyl Pd complexes **1**-**3** have been prepared by reacting $Li_2[PdCl_4]$ with suitable ligands in appropriate ratio (2:1, respectively) in methanol followed by repeated washing of the precipitate using cold methanol (Scheme S1, see in the Supporting Information (SI)). These resulting neutral complexes show satisfactory microanalytical data, and display the proton (^{1}H) and carbon (^{13}C) resonances corresponding to the half of the molecule (Figures S1 and S2, SI). The mononuclear **4** has been prepared and characterized by following the reported procedure.[21] The formations of complexes **1**, **2** and **3** have been further authenticated by their single crystal X-ray structure (Figure 2). Important crystallographic and bond parameters are depicted in Tables S1 and S2 (SI). These complexes are crystallized out in monoclinic (**1**, **2**) and triclinic (**3**) geometry with p21/n, C2/c and p-1 space group, respectively. The Pd centers in all the compounds display distorted square planner geometry with pyrazole units, which forms six membered metallacycle with boat conformation. The Pd-N and Pd-Cl bond distances are in good agreement with the structurally similar complexes.[16,22] The observed N-Pd-N and Cl-Pd-Cl bite angles and dihedral angles are also in the range observed with structurally similar compounds.[16,22] The intermetallic Pd-Pd distances for **1**, **2** and **3** are 6.479 Å, 6.870 Å and 8.871 Å, respectively.

Evaluation of transfer hydrogenation activities of pyrazolyl Pd complexes. The present set of complexes **1**-**4** were evaluated for their activity in tandem transfer hydrogenation and Suzuki-Miyaura C-C cross coupling reaction for fluoroarylketone. Initially, the reduction of 4-fluoroacetophenone (**A**), comprising C-F and C=O functionalities, was monitored in the presence of **1** (Table 1, entries 1-6). The reaction conditions were screened for a range of bases and solvents (as the source of hydrogen) at 80 °C.

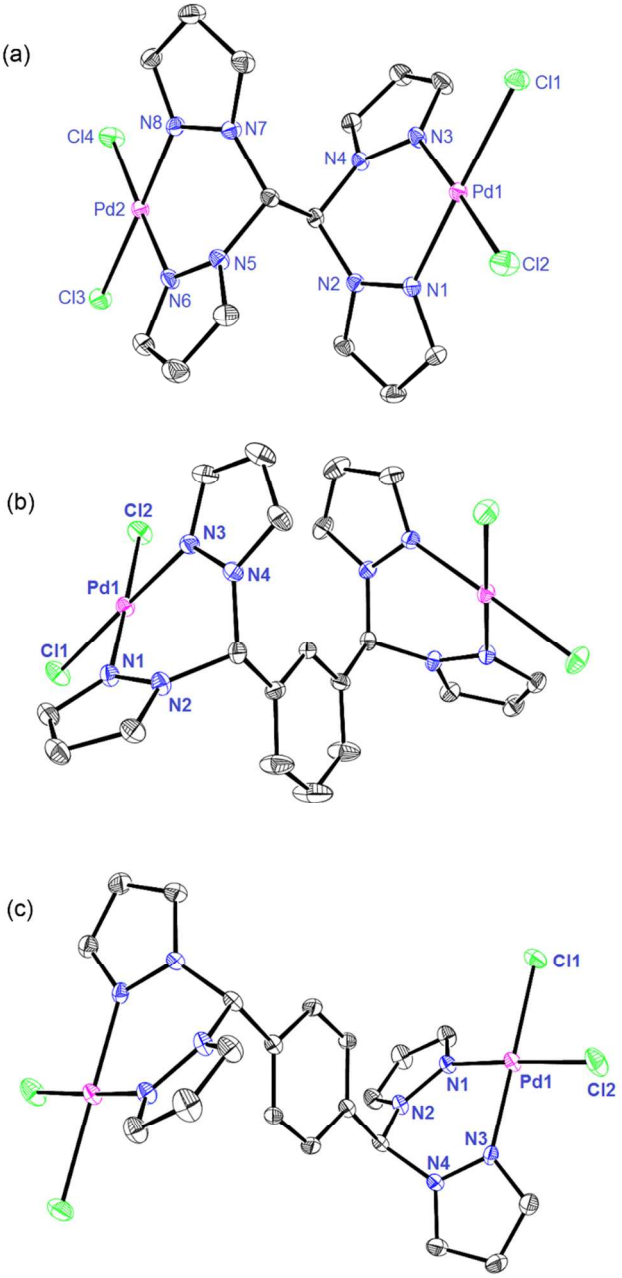
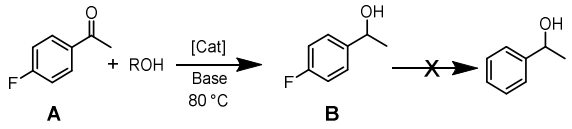


Figure 2. ORTEP diagram of complexes (a) **1**, (b) **2** and (c) **3**. Ellipsoids are drawn at 20% probability level. Hydrogen atoms are eliminated for clarity.

Employing alcohols as the source of hydrogen via transition metals catalyzing the dehydrogenation process are well known in the literature.[23] It appears from the screening results in Table 1 that complex **1** exhibits the best catalytic efficiency for the transfer hydrogenation of **A** for the combination of KO*t*Bu and *i*PrOH (entry 1). It is also observed that under such conditions reduction occurs only to the carbonyl group to produce 1-(4-fluorophenyl)ethanol (**B**) barring the hydrodehalogenation process of either the reagent or the product.

Reaction conditions could thus be identified to achieve the transfer hydrogenation before the tandem reaction (Pd/4-fluoroacetophenone/KO*t*Bu = 1/1000/2500 (molar ratio), catalyst (0.1 mol% Pd), 4-fluoroacetophenone (0.5 mmol), KO*t*Bu (1.25 mmol), *i*PrOH (1 mL), 80 °C).

Table 1. Catalytic transfer hydrogenation of 4-fluoroacetophenone[a]



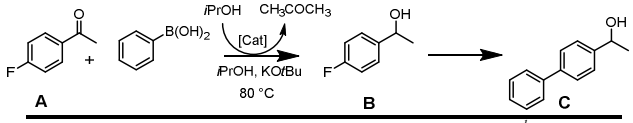
Entry	Catalyst	ROH	Base	Yield (%)[b] B
1	**1**	*i*PrOH	KO*t*Bu	98
2	**1**	*i*PrOH	KOH	21
3	**1**	*i*PrOH	Na_2CO_3	16
4	**1**	*n*PrOH	KO*t*Bu	12
5	**1**	MeOH	KO*t*Bu	0
6	**1**	$PhCH_2OH$	KO*t*Bu	0
7	**2**	*i*PrOH	KO*t*Bu	95
8	**3**	*i*PrOH	KO*t*Bu	92
9	**4**	*i*PrOH	KO*t*Bu	67
10	**$PdCl_2$**	*i*PrOH	KO*t*Bu	13
11	**$(PPh_3)_2PdCl_2$**	*i*PrOH	KO*t*Bu	0
12	**$(PPh_3)_4Pd$**	*i*PrOH	KO*t*Bu	0
13	-	*i*PrOH	KO*t*Bu	0

[a] Reaction conditions: Pd/4-fluoroacetophenone/Base = 1/1000/2500 (molar ratio), catalyst (0.1 mol% Pd), 4-fluoroacetophenone (0.5 mmol), base (1.25 mmol), ROH (1 mL), 80 °C, reaction time = 8 h. [b] Isolated yields after preparatory thin layered chromatography.

The other dinuclear Pd complexes (**2**, **3**) as well as the analogous mononuclear **4** also showed good catalytic efficiencies (entries 7-9) under the identical conditions. Catalytic activities were also monitored for the precursor $PdCl_2$ (entry 10), and the phosphine based palladium complexes $(PPh_3)_2PdCl_2$ and $(PPh_3)_4Pd$ (entries 11 and 12). Notably, the reaction did not proceed at all in the presence of phosphine based complexes, or under blank condition (entry 13). A much lower yield (13%) of **B** was obtained using $PdCl_2$ as compared to its pyrazolyl analogues **1**-**4** (98-67%).

Evaluation of tandem activities of pyrazolyl Pd complexes. Next, we extended our study to examine whether **1**-**4** can initiate tandem transfer hydrogenation/Suzuki-Miyaura cross coupling reaction. Substrate 4-fluoroacetophenone (**A**, having C=O and C-F functionalities) was reacted with phenylboronic acid in presence of the complexes under the conditions given in Table 2. A high yield (92%) of the tandem product, 1-(4-biphenylyl)ethanol (**C**), was obtained using the dinuclear Pd complex **1** (entry 1) after a reaction period of 20 h. The analogous **2** (80%), **3** (73 %) with higher internuclear Pd-Pd distances (6.870 and 8.871 Å, respectively), or mononuclear **4** (58 %) showed lower activities (entries 2-4) than **1** (Pd-Pd distance 6.479 Å, see Table S2 in the SI). This is very likely due to the proximity among the dinuclear centers in the set of complexes **1**-**3** and the assistance of proximal metallic centers for a stepwise mechanism (*vide infra*).
Expectedly, the precursor $PdCl_2$ resulted in a very low yield (12%, entry 5) of transfer hydrogenation product (**B**), however devoid of further C-C coupling to produce **C**. Reaction did not proceed at all with the phosphine based complexes (entries 6 and 7). Therefore, neither $PdCl_2$ nor $(PPh_3)_2PdCl_2$ and $(PPh_3)_4Pd$ were able to conduct the desired tandem catalysis. It should be mentioned that none of the complexes listed in Table 2 was active to catalyze direct C-C coupling between 4-fluoroacetophenone (**A**) and phenylboronic acid to produce 4-acetylbiphenyl.

Table 2. Tandem transfer hydrogenation/Suzuki coupling of 4-fluoroacetophenone[a]



Entry	Catalyst	Yield (%)[b] B	C
1	**1**	6	92
2	**2**	15	80
3	**3**	22	73
4	**4**	22	58
5	**$PdCl_2$**	12	0
6	**$(PPh_3)_2PdCl_2$**	0	0
7	**$(PPh_3)_4Pd$**	0	0

[a] Reaction conditions: Pd/4-fluoroacetophenone/$PhB(OH)_2$/ KO*t*Bu = 1/1000/1200/2500 (molar ratio), catalyst (0.1 mol% Pd), 4-fluoroacetophenone (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), KO*t*Bu (1.25 mmol), *i*PrOH (1 mL), 80 °C, reaction time = 20 h. [b] Isolated yields after preparatory thin layered chromatography.

In order to get more insight into the pyrazolyl Pd complex mediated tandem catalysis, time monitored reaction profile was studied for the reaction between 4-fluoroacetophenone (**A**) and phenylboronic acid in the presence of KO*t*Bu and *i*PrOH at 80 °C (Figure 3). It is evident from the figure that in this multistep catalytic process hydrogenation of the carbonyl group of the substrate (line through the red points) precedes the reactions to produce 1-(4-fluorophenyl)ethanol (**B**, line through the blue points). Next, the C–C coupling occurs between **B** and phenylboronic acid to yield the tandem product 1-(4-biphenylyl)ethanol (**C**, line through the green points). In fact, the coupling reaction follows an induction period of 2h, which suggests that the hydrogenation of the carbonyl group of 4-fluoroacetophenone is more facile than C-F activation. Indeed, the coupling product 4-acetylbiphenyl could not be detected, which would arise if direct C-C coupling between 4-fluoroacetophenone and phenylboronic acid would proceed. These results clearly suggest a consecutive nature of the two reactions mechanistically independent, where the hydrogenation of carbonyl group leads the tandem process in step I with subsequent coupling occurring between the corresponding fluoroarylalcohol and phenylboronic acid in step II (Scheme S2, SI).

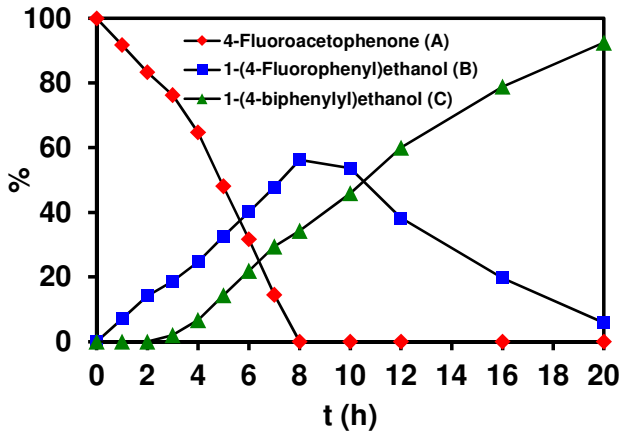
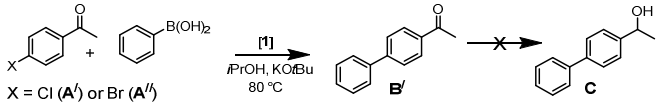


Figure 3. Reaction kinetics for tandem transfer hydrogenation/Suzuki coupling of 4-fluorocetophenones. Reaction conditions: 4-fluoroacetophenone (**A**, 0.5 mmol), $PhB(OH)_2$ (0.6 mmol), KO*t*Bu (1.25 mmol), *i*PrOH (1 mL), **1** (0.1 mol% Pd) at 80 °C.

To explore whether this tandem catalysis is effective on other haloderivatives, we followed the reactions of 4-chloro- and 4-bromoacetophenone ($\mathbf{A}^{I}$ and $\mathbf{A}^{II}$, respectively) with phenylboronic acid in the presence of **1** under identical conditions (Scheme 1). Interestingly, for both the substrates 4-acetylbiphenyl ($\mathbf{B}^{I}$) was obtained as the sole product in high yield (99 %, Table 3, entries 2 and 3). Reduction of keto group did not proceed at all to produce the desired tandem product **C** even after prolonging the reaction time. It therefore appears that reductive transformation of haloarylketone into haloaryalcohol is the first key step to proceed the reaction to **C**. To prove this, a control reaction between (4-halophenyl)ethanol (i.e. (4-chloro-) and (4-bromophenyl)ethanol) and phenylboronic acid was examined in the presence of **1** (Table S3, SI). Indeed, the reactions led to the formation of tandem product **C** in high yield (≥ 92 %) for both reagents within 12 h. Additionally, an attempt towards transfer hydrogenation of 4-acetylbiphenyl ($\mathbf{B}^{I}$) on **1** resulted in no hydrogenation of the keto group (Table S3, SI) even after a longer period of time (20 h).

Overall, these experimental results suggest that no tandem reaction could be achieved for 4-haloacetophenones with weaker electron withdrawing Cl and Br substituents than F, using the present Pd based catalytic systems. The weaker C-halide (halide = Cl and Br) bond in the substrates favors C-C cross coupling with phenylboronic acid involving oxidative addition, σ-bond metathesis with KO*t*Bu, trans-metalation and reductive elimination (Scheme S2, SI) to produce 4-acetylbiphenyl (Scheme 1). In contrast, with F once the alcohol is formed the oxidative addition of the C-F on Pd is kinetically favored because the transfer hydrogenation is slower than the C-C coupling.



Scheme 1. Reaction sequence of 4-chloro- and 4-bromoacetophenone under identical reaction conditions for fluoro-analogue.

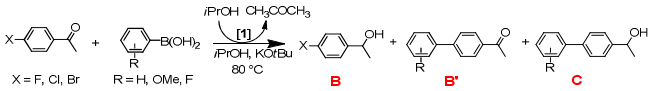
To further support these hypotheses, we investigated the electronic effect of the halo groups (-F, -Cl and -Br) on to the reduction of carbonyl functionality in the substrates 4-haloacetophenones. The transfer hydrogenation reaction was conducted in the absence of phenylboronic acid (Table 3, entries 4-6). It is observed that the fluoro-substituted substrate is the most active (98% yield) to produce the corresponding alcohol, followed by the chloro-substituted substrate (65% yield). The bromo-substituted compound remained unreactive. Indeed, a similar order of reactivity was reported with higher transfer hydrogenation activity for 4-fluoroacetophenone compared to its bromo-analogues.[24] These results suggest that fluoro substituent in 4-haloacetophenone induces highest activity in reductive hydrogenation of its carbonyl group into alcohol.

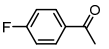
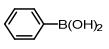
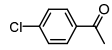
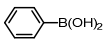
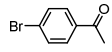
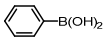
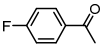
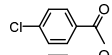
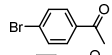
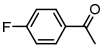
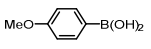
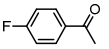
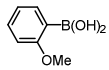
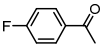
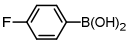
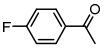
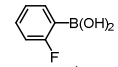
We, therefore, suggest that the productive tandem reaction for 4-fluoroacetophenone, unlike its chloro- and bromo-analogues, is due to the result of a facile reductive transformation of keto group into alcohol, which undergo a subsequent C-C coupling reaction with phenylboronic acid (see the reaction sequence under caption of Table 2). On the other hand, with weaker C-halide bond, both chloro- and bromo-substrates favor C-C coupling over reduction of ketone, which result in 4-acetylbiphenyl as the end product (Scheme 1).

Furthermore, the tandem reaction has been extended for the combination of 4-fluoroacetophenone and varieties of arylboronic acids (Table 3, entries 7–10). Under the moderate reaction conditions **1** is active towards all the reactants with good yields of the tandem products.

Finally, to check the homogeneous nature of the catalytic hydrogenation or tandem reactions mercury drop test was conducted (SI) for **1** (as representative complex).[25] However, no significant change in the yield of the final product (**C**) was observed (Table S4) from that of the normal reaction. This suggests the homogeneous nature of the present catalytic systems.

Table 3. Scope of tandem transfer hydrogenation/Suzuki coupling for 4-haloarylketones[a]



Entry	ArX	$Ar^{I}B(OH)_2$	% Conversion of ArX	Product (B/B^{I}/C) % Yield[b]
1			100	6/0/92
2			100	0/99/0
3			100	0/99/0
4[c]		-	100	98/0/0
5[c]		-	68	65/0/0
6[c]		-	<1	0/0/0
7			100	50/0/47
8			100	52/0/43
9			100	35/0/61
10			100	41/0/52

[a] Reaction conditions: Pd/ArX/$Ar^{I}B(OH)_2$/KO*t*Bu = 1/1000/1200/1500 (molar ratio), **1** (0.1 mol% Pd), ArX (0.5 mmol), $Ar^{I}B(OH)_2$ (0.6 mmol), KO*t*Bu (1.25 mmol), *i*PrOH (1 mL), 80 °C, reaction time = 20 h. [b] Isolated yields after preparatory thin layered chromatography. [c] Reaction time = 8 h.

CONCLUSIONS

In summary, the results of this work emphasize that we have developed tetrapyrazolyl based air-stable dinuclear Pd complexes **1**-**3** with gradual increase in intermetallic distances. The structures of **1**, **2** and **3** have been authenticated by single crystal X-ray diffraction. Superior catalytic activity (tandem transfer hydrogenation/Suzuki coupling of 4-fluoroacetophenone as model substrate) of **1** as compared to other dinuclear Pd complexes (**2** and **3**) is anticipated due to the shortest inter Pd-Pd distance. Activities of all the dinuclear complexes (**1**-**3**) are higher than those of the mononuclear compound **4**, suggesting that a well-defined multinuclear catalytic system is more efficient compared to its analogous mononuclear complex. While the pyrazolyl based complexes exhibit tandem catalysis, the precursor complex $PdCl_2$ (without any ligand) and the palladium phosphine complexes $(PPh_3)_2PdCl_2$ and $(PPh_3)_4Pd$ were found to be inactive. These results suggest the significance of pyrazole-based ligand frameworks for achieving sustainable active catalytic system. Time monitored reaction profile and controlled reactions inicate that reductive transformation of haloarylketone into haloaryalcohol is the rate determining step to proceed desired tandem reaction. The productive tandem reaction of fluoroarylketone over chloro- and bromo-analogues may open new avenues for the development of desired one-pot multi-step reactions utilizing varieties of organofluoro compounds as starting reagents.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data of all new complexes and catalysis products, crystallographic details of complexes **1**, **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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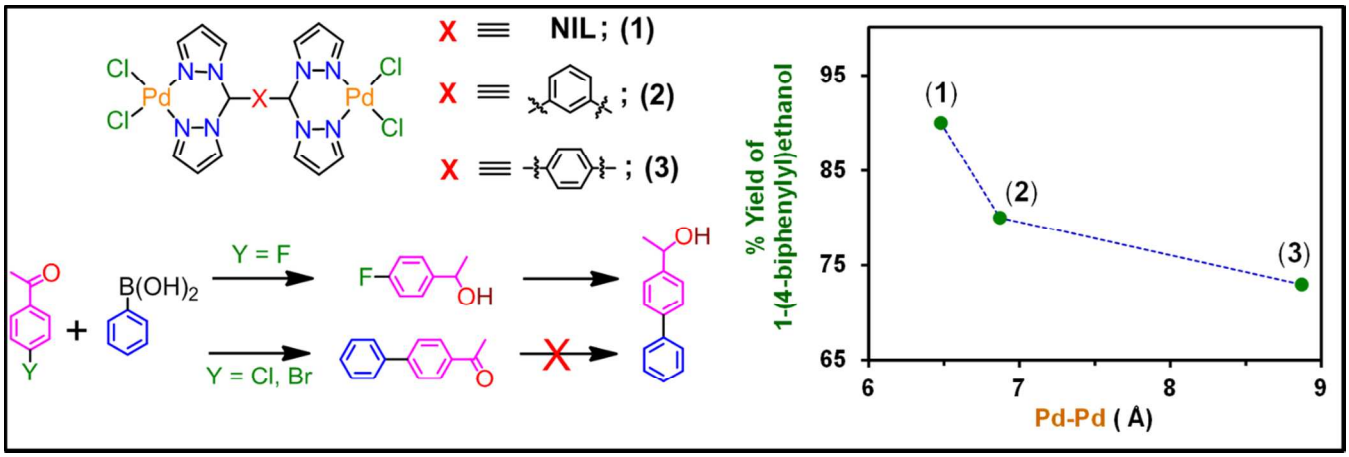

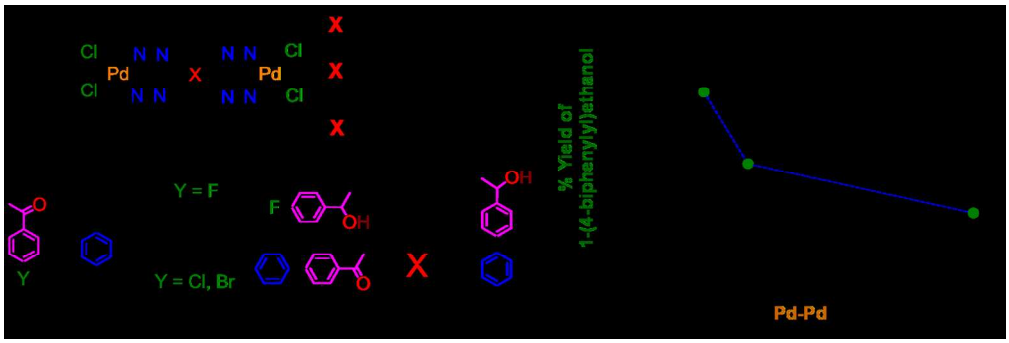

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