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Palladium complexes of heterobidentate ligands: Active catalysts for direct acylation of aryl halides with aldehydes via C(sp^2)-H activation

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ABSTRACT

Heterobidentate P-S donor ligands [P-S = {2-(methylthio) phenyl}diphenylphosphine (**a**) and {2-((methylthio) methyl) phenyl}diphenylphosphine (**b**)], and their palladium complexes of the type [Pdη^2-(P-S)Cl_2] (**1a**, **1b**) have been synthesised and characterised. Single crystal X-ray diffraction shows that in both the complexes, Pd occupies the centre of a slightly distorted square planar geometry. **1a** forms a planner ring structure, whereas, the hexagonal ring of **1b** bends from planarity to adjust any ring strain. Interesting differences between the complexes were observed in terms of the intermolecular forces. The catalytic activities of the synthesised complexes towards the direct acylation of aryl halides with aldehydes via C(sp^2)-H activation were good to excellent. **1b** shows better catalytic activity over **1a** which may be attributed to the higher stability of the pentagonal ring of **1a**. Aryl halides containing electron withdrawing group enhance the reaction, while electron donating substituent tend to retard the desired product formation. The difference in the bond lengths of Pd-P and Pd-S of the chelate complexes may impart hemilabile behaviour in the catalytic cycle by dissociating the weaker bond (Pd-S) to generate vacant coordination site at the metal centre and reassociate after the completion of the reaction.

1. Introduction

The C—H bond activation has emerged as a useful tool in organic synthesis for providing desired transformations [1–8]. Insertion of metal into the carbon-hydrogen bonds via oxidative addition has long been investigated, which often is the key step for majority of transformations leading to many pioneering discoveries in the field of catalysis [9,10]. Several transition metal catalysts based on rhodium [11], nickel [12], ruthenium [13] etc. have been deployed for the C—H activation reactions. The aldehyde C—H activation by direct acylation of aryl halides with aliphatic aldehydes is an interesting prospect to get alkyl-aryl ketones; which are potential intermediates in different pharmaceutical, fragrance, dye and agrochemical industries [14–22]. Friedel-Crafts acylation has been a traditional way of acylating arenes, which has the strict limitation of reacting with activated benzene derivatives only [23].

Synthesis of alkyl-aryl ketones by direct acylation of aryl halides with aliphatic aldehydes have been reported by using palladium complexes of phosphine ligands as well as palladium nanopaticles [16–21]. Selection of ligands plays an important role in determining the efficiency of the catalysts for generating the Pd(0) species for the reaction cycle to start. Different monodentate and bidentate phosphine ligands such as Q-phos, xantphos, DPEphos, dppp, BINAP etc., were studied for the catalysis of acylation of aryl bromides with aldehydes [16–18]. Bidentate ligands having wider bite angle tend to destabilize the divalent square planner complexes and favour zerovalent complexes [24]. Most of the C—H activation reactions have been carried out by using phosphine ligands which are known to reduce Pd(II) to Pd(0) to initiate the oxidative addition step of the catalytic cycle. However, as per our knowledge, no heterobidentate hemilabile P-S ligands have been reported in the past for the catalysis of direct acylation of aromatic halides with aliphatic aldehydes.

We chose two palladium metal complexes of heterobidentate P-S ligand systems {2-(methylthio) phenyl}diphenylphosphine (**a**) and {2-(methylthio) methyl)phenyl}diphenyl-phosphine (**b**) for catalyzing C—H functionalization of aliphatic aldehyde by aryl halides to form alkyl-aryl ketone. Although palladium complexes of these ligands have been synthesized in the past [25,26], their catalytic activities towards C—H activation reactions have not been studied. Heterobidentate ligands like **a** and **b** tend to show hemilability at the metal centre by dissociating the weaker bond during the catalytic cycles to step up the oxidative addition [27–29]. In our continued efforts [30–39] to develop new catalysts for

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different coupling reactions, herein, we report synthesis and characterization of two palladium complexes of heterobidentate P-S ligand systems, and their catalytic activity towards acylation of aryl halides with aldehydes.

2. Experimental

2.1. General information

All the solvents were distilled under N_2 prior to use. $PdCl_2$ was purchased from M/S Arrora Matthey Ltd., Kolkata, India. Elemental analyses were performed on a PerkinElmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded as thin film using NaCl cell in a Shimadzu IR Affinity-1 FTIR spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solution on a Bruker DPX-300 spectrometer, and chemical shifts were reported relative to $SiMe_4$ and 85% H_3PO_4 as internal and external standard respectively. Mass spectra of complexes were recorded on an ESQUIRE 3000 mass spectrometer. Melting points were measured in melting point apparatus Buchi M-560.

2.2. Synthesis of the ligands

Ligands **a** and **b** were synthesized by adapting the literature [26,40].

2.3. Analytical data for the ligands *a* and *b*

a: ^1H NMR ($CDCl_3$, ppm): δ 2.53 (s, 3H, CH_3), δ 7.26, 7.78 (m, 14H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 15.1 (CH_3), δ 125.1-140.8 (Ph), $^{31}P\{^1H\}$NMR ($CDCl_3$, ppm): δ -14.67 [s, P^{III}] Elemental analyses: Found (Cald. for $C_{19}H_{17}PS$), C 73.92 (74.0); H 4.98 (5.56). Mass: 307.7 [m/z^+].

b: ^1H NMR ($CDCl_3$, ppm): δ 2.14 (s, 3H, CH_3), δ 3.56 (s, 2H, CH_2), δ 7.24, 7.98 (m, 14H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 14.9 (CH_3), δ 40.9 (CH_2), δ 127.41-143.8 (Ph), $^{31}P\{^1H\}$NMR ($CDCl_3$, ppm): δ -16.52 [s, P^{III}] Elemental analyses: Found (Cald. for $C_{20}H_{19}PS$), C 73.90 (74.6); H 5.09 (5.89). Mass: 320.5 [m/z^+].

2.4. Synthesis of the complexes

$PdCl_2$ (0.05 mmol, 8.86 mg) was dissolved in acetonitrile (15 cm^3). The ligands [0.05 mmol, 15.41 mg (**a**) and 16.1 mg (**b**)] were dissolved in dichloromethane (10 cm^3) to prepare corresponding solutions. Both the solutions were mixed together and stirred for 30 min at room temperature. The solvent was removed under reduced pressure and washed with diethyl ether. The resulting yellowish orange compounds were recrystalized from dichloromethane and hexane to obtain the complexes **1a** and **1b**.

2.5. Analytical data for the complexes *1a* and *1b*

1a: ^1H NMR ($CDCl_3$, ppm): δ 7.36–7.83 (m, Ph), δ 2.59 (s, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 127.7–142.2 (Ar), δ 15.47 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 40.83 (s) Elemental analyses: Found (Cald. for $PdC_{19}H_{17}C_{l2}PS$), C 46.31 (47.01); H 5.09 (5.96). *m/z*: 484.63 [M^+].

1b: ^1H NMR ($CDCl_3$, ppm): δ 7.31-7.91 (m, Ph), δ 2.19 (s, CH_3), δ 3.86 (s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 128.4–142.8 (Ar). $^{31}P\{^1H\}$NMR ($CDCl_3$, ppm): δ 89.997 (s). Elemental analyses: Found (Cald. for $PdC_{20}H_{19}C_{l2}PS$), C 47.42 (48.09); H 3.71 (3.8). *m/z*: 498.46 [M^+].

2.6. X-ray structural analysis

Single crystals of **1a** and **1b** suitable for X-ray crystallographic analysis were obtained by layering a dichloromethane solution of the respective compounds with hexane. Intensity data of **1a** and **1b** were collected on a Bruker Smart-CCD with Mo-Kα radiation (λ = 0.71073 Å) at 150 and 293 K respectively. The structures were solved with SHELXS-97 and refined by full-matrix least squares on F^2 using the SHELXL-97 computer program. Hydrogen atoms were idealised by using the riding models.

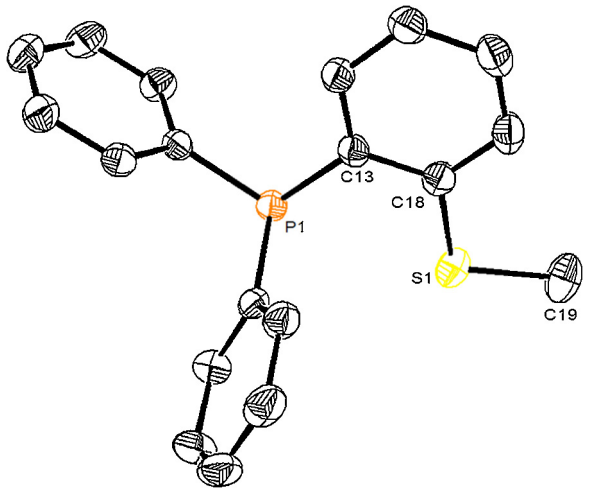


Fig. 1. Ortep diagram of a (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms and uncoordinatated molecules are omitted for clarity.

2.7. Catalytic activity of *1a* and *1b* in acylation reaction

Aryl halides (2 mmol) and aldehydes (2.4 mmol) in 1, 4 - dioxane (20 cm^3) were mixed together. The base cesium carbonate (6 mmol) and the respective catalyst (0.004 mmol) in dichloromethane (5 cm^3) were then added to the solution and stirred at 100 °C. The reactions were monitored by TLC and the products were isolated by silica gel column chromatography using ethyl acetate and hexane as eluents. The products were characterized by ^1H NMR, ^{13}C NMR and melting point determination followed by their comparison with the standard literature data.

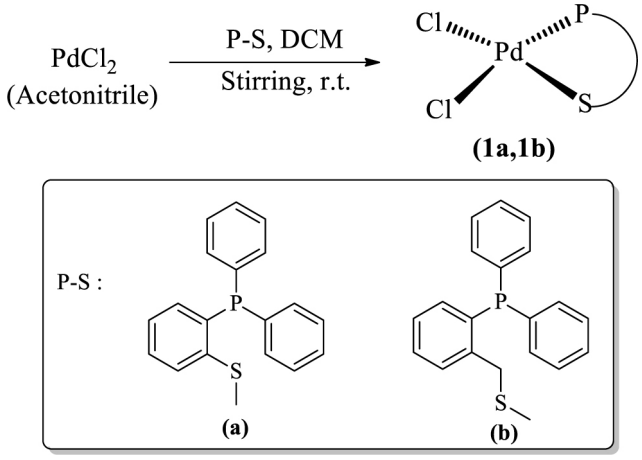
3. Results and discussion

3.1. Synthesis and characterization

The ligands **a** and **b** were synthesised according to the literature methods. Elemental analyses and mass spectrometric results demonstrate the observed molecular composition of **a** and **b**. The ^1H NMR spectra of both **a** and **b** show characteristic phenylic multiplets in the region 7.24–7.98 ppm. The characteristic methylic singlet in the range 2.14–2.51 ppm, and methylene singlet at 3.56 ppm confirm the formation of **b**. $^{31}P\{^1H\}$ NMR spectra of **a** and **b** show characteristic resonances at δ −14.67 and −16.52 respectively, corresponding to the trivalent phosphines. In ^{13}C NMR spectra, the chemical shifts due to the phenylic and methyl carbons of both the ligands are found in the range 125.1–143.8 ppm and 14.9-15.1 ppm respectively. The appearance of singlet at 40.9 ppm for the methylene carbon in the ^{13}C NMR spectra further confirms the formation of the ligand **b**. The ligand **a** is also structurally characterized by single crystal X-ray diffraction, which crystallizes in monoclinic crystal system (Fig. 1, Table 1). However, the structure of ligand **b** could not be determined due to its liquid state. Palladium complexes **1a** and **1b** were prepared by stirring acetonitrile solution of palladium dichloride with dichloromethane solution of ligands **a** and **b** in 1:1 mol ratio at room temperature (Scheme 1).

Table 1
Crystallographic data and structure refinement details for **a**, **1a** and **1b**.

	a	1a	1b
Emphirical formula	$C_{19}H_{17}PS$	$PdCl_2C_{19}H_{17}PS$	$PdCl_2C_{20}H_{19}PS$
Formula weight	308.37	485.67	499.68
Temperature (K)	150 K	150 K	293 K
λ (Å)	0.71073	0.71073	0.71073
Crystal syst.	Monoclinic	Monoclinic	Monoclinic
Space group	*P* 21/*C*	*P* 21/*C*	*P* 21/*C*
Z	4	4	4
a (Å)	11.3199 (13)	10.5589 (8)	11.1276 (16)
b (Å)	15.8299 (19)	17.2956 (12)	10.0382 (15)
c (Å)	9.5357 (11)	20.9978 (15)	17.648(3)
α (°)	90	90	90
β (°)	108.069(2)	99.799 (2)	95.995(3)
γ (°)	90	90	90
μ (Mo Kα) mm^{-1}	0.288	1.458	1.408
Reflections collected	3525	7395	3843
R1 (observed data)	0.0384 (3256)	0.0473 (6733)	0.0841 (3101)
wR2 (all data)	0.1138 (3525)	0.0950 (7395)	0.1603 (3843)



Scheme 1. Synthesis of the Palladium complexes.

Elemental analyses and mass spectrometric results of the complexes support the observed molecular composition of **1a** and **1b**. The ^{31}P NMR spectra of **1a** and **1b** show two sharp singlets at δ 40.83 and 89.99 ppm respectively for the corresponding metal bonded P atoms. Both the complexes were structurally characterized by single crystal X-ray diffraction using full-matrix least squares on F^2 using the SHELXL-97 computer program (Fig. 2, Table 1) [41,42]. In both the complexes, Pd atom occupies the centre of a slightly distorted square planar geometry formed by a P atom, a S atom and two Cl atoms. The spatial P-S distance of **1a** (3.112 Å) is almost equal to that of the free ligand **a** (3.115 Å), which demonstrates the ideal space **a** provides for the formation of **1a**. The ligands **a** and **b** form chelate through P-S donors with palladium centre and show bite angles P(1)-Pd(1)-S(1) 88.42 (**1a**) and P(1)-Pd(1)-S(1) 94.05 (**1b**); for the pentagonal and hexagonal rings respectively. **1a** forms a planner ring structure, whereas, the hexagonal ring of **1b** bends from planarity to adjust any ring strain. The Pd-S {2.270 (**1a**) and 2.274 Å (**1b**)} bonds are longer than the respective Pd—P bond lengths {2.217 (**1a**) and 2.239 Å (**1b**)} in both the complexes, implying the possibility of Pd-S bond cleavage during the catalytic cycle. Interesting differences between the complexes were observed in terms of the intermolecular forces. Intermolecular weak bonds between one Cl-atom and two H-atoms were observed in both the complexes. In addition, **1a** has other intermolecular interactions involving different atoms of the complex (see Suppoting information).

*3.2. Catalytic activity of **1a** and **1b** towards acylation of aryl halides with aldehydes*

Catalytic activity of the synthesised complexes were investigated towards the acylation of aryl halides with aldehydes at elevated temperature. Optimization of the catalytic reaction conditions was carried out by acylation of iodobenzene with pentanal using **1a** as catalyst precursor in presence of a base. The desired ketone was obtained in small amounts when secondary amines and $KOBu^t$ were used as base, while with Cs_2CO_3, maximum yield up to 76 % was observed. Use of piperidine as base in 1,4-dioxane as solvent yields about 20 % of the desired ketone. Similarly, effect of solvent on the reaction was significant, 1,4-dioxane yielding the best results. Use of dimethyl formamide (DMF) and Cs_2CO_3 as solvent and base respectively yielded 25 % product. The effects of the combinations of different solvents with different bases were also tested and the results are summarized in Table 2. It therefore appears that the reaction proceeds efficiently in the presence of Cs_2CO_3 as base and 1,4-dioxane as solvent.

Having established the optimized conditions, acylation of different halides with aldehydes were tested. Good to excellent results were obtained (Table 3). Both **1a** and **1b** show better catalytic activity over $PdCl_2$, indicating the dictation of the coordinating ligands in the catalytic performance of the complexes. The better activity of **1b** over **1a** may be attributed to the higher stability of the pentagonal ring of **1a**. The hexagonal ring of **1b** twists from planarity to offer more space as well as a greater bite angle (Fig. 1); thereby enhancing more probability of the oxidative addition at the metal centre. As oxidative addition is often the first step of the catalytic cycle [1,18], greater flexibility of **1b** offers geometrical favour during the reaction cycle than **1a**. The wider bite angle of **1b** tends to

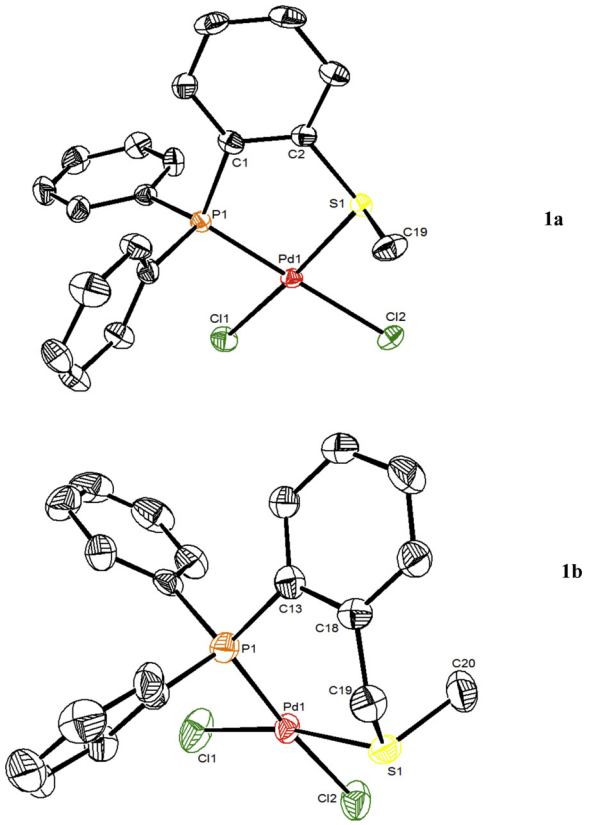
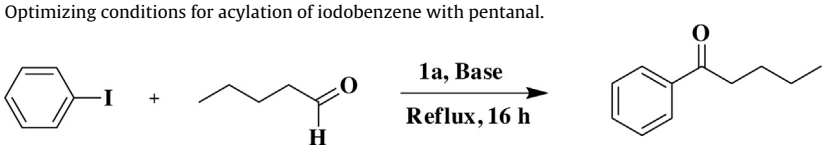


Fig. 2. Ortep diagram of 1a and 1b (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms and uncoordinatated molecules are omitted for clarity.

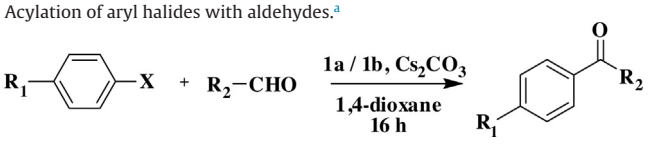
Table 2
Optimizing conditions for acylation of iodobenzene with pentanal.



Entry	Base	Solvent	Yield (%)
1	Pyrrolidine	DMF	<15
2	Piperidine	DMF	<15
3	$KOBu^t$	DMF	<3
4	Cs_2CO_3	DMF	25
5	Piperidine	Toluene	<5
6	$KOBu^t$	Toluene	0
7	Piperidine	1,4-dioxane	<20
8	Cs_2CO_3	1,4-dioxane	76
9	Cs_2CO_3	Toluene	10
10	$KOBu^t$	1,4-dioxane	<5

Reactions were carried out with 1 mmol of halide and 1.2 mmol of aldehyde, 3 mmol of base and 1 mol% **1a** at refluxed temperature for 16 h.

Table 3
Acylation of aryl halides with aldehydes.[a]



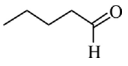
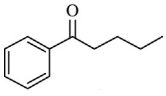
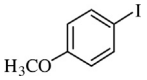
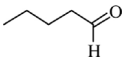
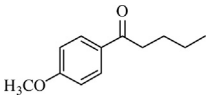
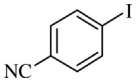
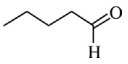
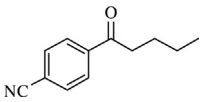
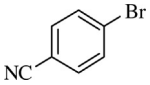
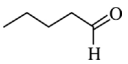
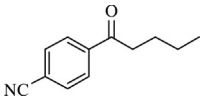
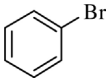
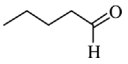
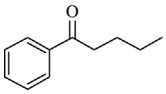
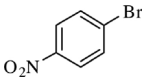
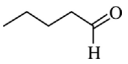
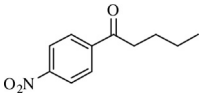
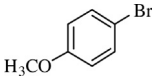
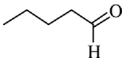
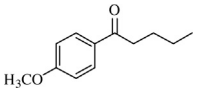
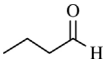
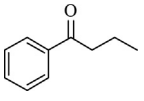
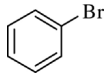
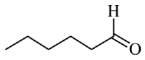
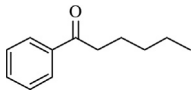
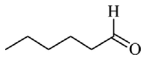
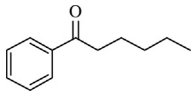
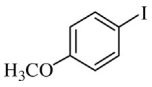
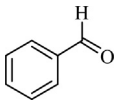
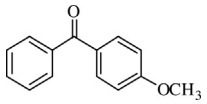
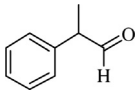
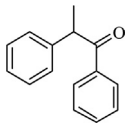
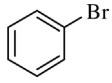
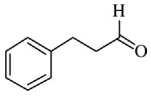
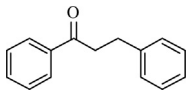
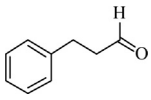
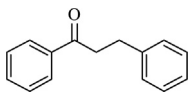
Entry	Halides	Aldehyde	Desired product	Yield (%)[b]
1				76 **1a** 79 **1b** 56 $PdCl_2$
2				72 **1a** 76 **1b** 53 $PdCl_2$
3				80 **1a** 88 **1b**
4				78 **1a** 80 **1b**
5				63 **1a** 74 **1b**
6				75 **1a** 81 **1b**
7				62 **1a** 69 **1b**
8				52 **1a** 59 **1b**

Table 3 (*Continued*)

Entry	Halides	Aldehyde	Desired product	Yield (%)[b]
9				77 **1a**
				82 **1b**
10				80 **1a**
				88 **1b**
11				0 **1a**
				0 **1b**
12				0 **1a**
				0 **1b**
13				65 **1a**
				78 **1b**
14				69 **1a**
				80 **1b**

[a] Reactions were carried out with 1 mmol of halide and 1.2 mmol of aldehyde, 3 mmol Cs_2CO_3 and 1 mol% catalyst in 1,4-dioxane at refluxed temperature for 16 h.
[b] Isolated yields were calculated in respect of halides.

favour the Pd(0), which accelerates the reductive elimination step [24]. This fastens the catalytic cycle of **1b** over **1a**.

Since, iodide is a better leaving group than bromide, the acylation reactions (Table 3) shows the higher yields in case of iodo-containing substrates. It appears that aryl halides containing electron withdrawing group enhance the reaction, while electron donating substituent tend to retard the desired product formation. This is in accordance with the deactivating nature of the electron withdrawing groups, which remove electron density from the para position and make it less nucleophillic. ^{1}H NMR spectrum of the reaction mixture containing **1a** shows a peak at −44.99 ppm, which may be due to formation of the hydride complex during the reaction. As the Pd—S bonds are weaker than the corresponding Pd—P bonds, it is possible of the complexes to show hemilabile behaviour in the catalytic cycle by dissociating the weaker bond to generate vacant coordination site at the metal centre and reassociate after the completion of the reaction. This is worth mentioning that, under the given reaction conditions, the desired ketone was not obtained when benzaldehyde and 2-phenylpropanal are used as substrates (entry 11, 12); while using 3-phenylpropanal, substantial amount of the desired product was obtained (entry 13, 14). Though we could not make a precise study of the reaction mechanism, the lack of activity of benzaldehyde and 2-phenylpropanal may be due to the steric hindrance at the α-carbon of benzaldehyde and 2-phenylpropanal, which inhibit the coordination of palladium of the complex with the carbonyl carbon, resulting the failure to yield the desired ketone. Moreover, benzaldehyde does not have any α-hydrogen to form enolate anion which may be the nucleophile to bind to the metal centre during the reaction cycle.

4. Conclusions

In conclusion, we have developed two new palladium complexes of heterobidentate P-S ligand systems which show good to excellent catalytic activity towards C—H activation of aliphatic aldehydes by the acylation of aryl halides to form alkyl - aryl ketones. The hexagonal chelate complex (**1b**) shows better catalytic activity over the pentagonal one (**1a**) owing to the deviation of the hexagonal ring from planarity. Cs_2CO_3 yields better results than secondary amines and KOBu^t, when used as base. The chelating heterobidentate ligands may show hemilabile behavior during the catalytic cycle by dissociating the weaker Pd—S bond to generate vacant coordination site at the metal centre and reassociate after the completion of the reaction. Mechanistic investigations of the reaction will be the focus of our future work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.07.007

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