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ARTICLE



# Complexes of ($\eta^5$-Cp*)Ir(III) with 1-benzyl-3-phenylthio / selenomethyl-1,3-dihydrobenzoimidazole-2-thione/selenone: catalyst for oxidation and 1,2-substituted benzimidazole synthesis

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The treatment of 1-benzyl-3-phenylthio/selenomethyl-1,3-dihydrobenzoimidazole-2-thione/selenone [**L1**–**L4**] with [($\eta^5$-Cp*)IrCl(μ-Cl)]$_2$, at 25°C, followed by $NH_4PF_6$, results in [($\eta^5$-Cp*)Ir(**L**)Cl][$PF_6$] (**1**–**4** for **L** = **L1** to **L4**) authenticated with HR-MS and multi nuclei NMR ($^1$H, $^{13}$C{$^1$H} and $^{77}$Se{$^1$H}). The structures of **1-4,** established with single crystal X-ray diffraction reveal geometry around Ir as "piano-stool" type. The Ir–thio/selenoether (Ir−S/Ir−Se) bond distances (Å) are 2.347(18)-2.355(4)/ 2.4663(12)-2.4663(13)and Ir−thione/selenone (Ir-S/Ir-Se) ones, 2.4146(19)-2.417(2)/2.5141(16)-2.5159(12). The reaction of 1,2-phenylenediamine with benzylic alcohols and furfuryl alcohol under mild and ambient condition, catalyzed efficiently with complexes **1**–**4** generates, in situ, bisimine. The cyclization and rearrangement via 1,3-hydride shift triggered by its electrophilic activation with Ir(III) species finally result in 1,2-disubstituted benzimidazole. The yield of the heterocycles in this one pot synthesis is excellent to good. The aldehydes generated in situ by aerial oxidation of alcohols in the presence of **1**–**4** as catalysts, are precursor to the bisimine as the protocols of this heterocycle synthesis carried out in the absence of 1,2-phenylenediamine give them in excellent to good yield. The oxidation of alcohols by hydrogen transfer to acetone was catalyzed efficiently with complexes **1**–**4** and resulted in aldehyde/ketone in excellent to good yield. Each catalytic process is marginally more efficient with **1** than its counterparts.

## Introduction

Metal complexes of organosulfur/selenium ligands as a single source precursor for metal sulfide/selenide phases[1a-c] and catalyst for various chemical transformations[1d-f] are of current interest. The efficiency as a catalyst appears to be contributed by strong donor properties of S/Se atom. Half sandwich complexes of iridium(III) with ligands having combination of hard donor(s), viz. N and O with one or more of S, Se and Te, have been explored more than those of (E, E') type ligands (E / E' = S or Se).[2] No half sandwich complex of Ir(III) with a bidentate ligand having a combination of thio/selenoether and thione/selenone donor site is in our knowledge. Four such half sandwich complexes of Ir(III) with (E, E') ligands (E / E' = thione or selenone / thioether or selenoether) are reported herein for the first time. They efficiently catalyze the reaction between 1,2-phenylenediamine and benzylic and furfuryl alcohols, resulting in 1,2-disubstituted benzimidazole., oxidation of alcohols aerobic and *via* hydrogen transfer to acetone under mild reaction conditions.

The continuous interest in 1,2-disubstituted benzimidazoles is due to their broad spectrum biological and pharmacological properties,[3-5] which may result in clinical medicines. The methods known for synthesis of benzimidazole skeleton involve, reaction of a carboxylic acid and its derivatives with 1,2-phenylendiamine under harsh dehydrating condition,[6] a combinatorial approach forming them on solid-phase,[7] *o*-nitroaniline as intermediate and direct *N*-alkylation of benzimidazole.[8] The protocols that involve *o*-nitroaniline as an intermediate have resulted in these heterocycles on solid support.[9] The reactions of 1,2-phenylenediamine with aldehydes catalyzed with acidic catalysts give benzimidazoles.[10] However, many of these methods are poor in selectivity due to several side reactions, resulting in low yield (contributed by multistep work-up procedure also), inspite of using exotic reagents, harsh organic solvents, and long reaction time. The aldehyde used in the synthesis of 1,2-disubstituted benzimidazole may be replaced with an alcohol, if a suitable catalyst is available to promote both its selective oxidation and subsequent condensation. Transition-metal-catalyzed *N*-alkylation of an amine with alcohol, affords a short route for C−N bond formation and involves in situ aldehyde formation.[11-13] Recently some reports have appeared on one pot synthesis of pyrrole[14a-b] and pyridine[14c-d] from alcohol (via in situ generated aldehyde). These reports strongly motivated us to explore alcohol in the preparation of 1,2-disubstituted benzimidazole

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Electronic Supplementary Information (ESI) available: *Spectral data and single crystal data for complexes **1**–**4**. CCDC 1474646 (**1**), 1474647 (**2**), 1499034 (**3**) and 1474648(**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt01406b*

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under ambient conditions and design a catalyst so that it's in situ oxidation (preferably aerobic) produces required aldehyde. This has resulted in [($\eta^5$-Cp*) Ir(**L**)Cl][$PF_6$] (**1**–**4** for **L** = **L1** to **L4**) catalyzed synthesis of 1,2-disubstituted benzimidazole from alcohol reported herein. The reactivity of $O_2$ in its triplet ground state is kinetically poor and transition metal-based catalysts are reported to activate it as an oxidant[15] with and without co-oxidant.[15a-g,17] The examples of catalysts for aerobic oxidation of alcohols without any co-oxidant are $Pd(OAc)_2$/*li*Pr-$HBF_4$,[15f] [Imim-TEMPO][$FeCl_4$][15g], Ru/HAP (hydroxylapatite)[15h], [$\eta^5$-Cp*Ir(Cl)(bpy)]OTf and [$\eta^5$-Cp*Ir(Cl)(bpym)]OTf.[16a] The Cu-Mn oxide/C-TEMPO[17a], Ru/quinine/Co−salen complex[17b] and Cu-NHC-TEMPO[17c] are examples of efficient catalysts for aerobic oxidation with co-oxidant. The catalysts based on Ir, are good[16] for aerobic oxidation of alcohols, but little explored and therefore present investigations on complexes **1-4** for this purpose are worthwhile.

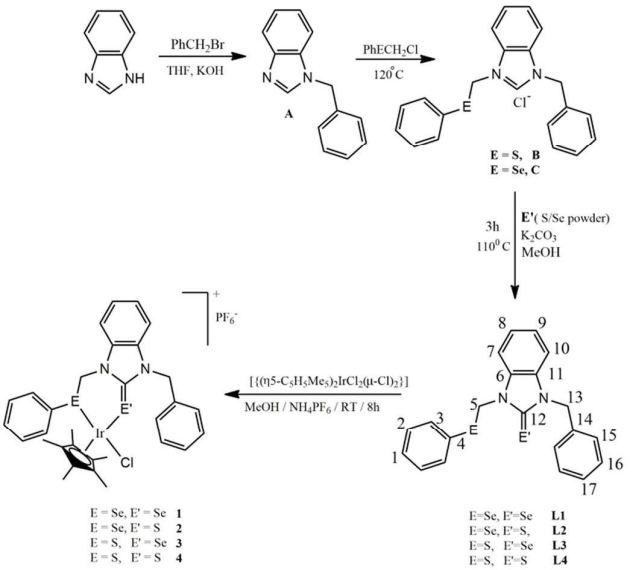
The aldehyde production by aerial oxidation with water as sole by-product is environmentally benign in comparison to oxidation with *N*-methylmorpholine *N*-oxide (NMO), *tert*-butyl hydroperoxide, NaOCl, $NaIO_4$ and $H_2O_2$[18] which are toxic and often release toxic by-product(s). The complexes **1-4** are also suitable catalysts for oxidation of alcohols by transfer of their hydrogen to acetone[19] which acts as a solvent cum oxidizing agent. Its protocol is also environment friendly[20] and economical compared to conventional oxidants.[21] Several transition metal complexes of different ligands can catalyze such transfer of hydrogen.[22-23] The efficient ones for such oxidation include Ru(II) complexes[24] including Rh(I)−Ru(II) type species and some complexes of *N*-heterocyclic carbene (NHC) with $\eta^5$-Cp*Ir(III) and $\eta^5$-Cp*Rh(III).[25]

## Results and discussion

The preparation of complexes [($\eta^5$-Cp*)Ir(**L**)Cl][$PF_6$] (**1**–**4** for **L** = **L1** to **L4**) carried out at room temperature is shown in Scheme 1. The **L1**−**L4,** were synthesized by reported procedure**.**[26] The **1-4** were formed by chloro bridge cleavage of [($\eta^5$-Cp*)IrCl(μ-Cl)]$_2$, followed by reaction with **L1**-**L4**, which was facilitated by chloride extraction with $NH_4PF_6$. The **1**−**4,** moderately soluble in $CHCl_3$, $CH_2Cl_2$, and $CH_3OH$, have good solubility in DMSO and $CH_3CN$. They can be stored under ambient conditions at 25°C for several months.

### NMR and mass spectra

The $^1$H, $^{13}$C{$^1$H} and $^{77}$Se{$^1$H} NMR and mass spectra of **1**−**4** (See ESI) are consistent with their molecular structures (Scheme 1) supported by single-crystal X-ray diffraction. The signals in $^{77}$Se{$^1$H} NMR spectra of **1** and **2** due to selenoether group are at a higher frequency by 7.5 and 11.5 ppm, respectively, with respect to those of free **L1** and **L2**. In $^{77}$Se{$^1$H} NMR of **1** and **3** the signals of selenone are at a lower frequency by 58.9 and 46.5 ppm, respectively, with respect to those of free **L1** and **L3**. This probably occurs due to weakening of >C=Se double bond character. The signals of C5 and C13 (both methylene) in $^{13}$C{$^1$H} NMR spectra of **1**-**4** appear at a higher frequency (~0.5 to 6.5 ppm respectively) relative to those of free **L1**−**L4.** It is probably due to




**Scheme 1.** Synthesis of **1**–**4**

coordination of ligands with Ir(III).[27e] The singlet due to $\eta^5$-pentamethylcyclopentadienyl ring in both $^1$H and $^{13}$C{$^1$H} NMR of all four complexes is shifted to a lower frequency (maximum shift 0.3 and 2.3 ppm respectively) relative to those of [$\eta^5$-(Cp*)$IrCl_2$]$_2$. This probably results due to substitution of Cl with relatively less electronegative S or Se, which have strong donor ability also.

In mass spectra of complexes **1**, **2, 3** and **4**, the peaks are observed at m/z, 821.0281 773.0862, 773.0839 and 725.1392 respectively which correspond to their cations ($M^+$) and authenticate them.

### Crystal structures

The slow evaporation of concentrated solutions of **1-4** made in a methanol–acetonitrile mixture (1:4 v/v) resulted in their single crystals, suitable for X-ray diffraction. In ESI (Tables S1 and S2) single crystal data and refinement parameters for **1-4** are given and molecular structures of their cations are shown in Figs. **1-4** with selected bond distances and angles. The H and $PF_6^-$ anion are omitted in these structures for clarity. All ligands form six membered chelate ring in all these complexes due to their coordination with iridium through two S, (S, Se) or two Se. Thus in the cation of all four half-sandwich complexes, donor atoms make pseudo-octahedral "piano stool" type geometry around Ir. The $\eta^5$-Cp* ring occupies symmetrically three octahedral sites. With S/Se of the ligand and chlorine six coordination number is completed. The Ir−S bond lengths (Å) of **3** [2.355(4)] and **4** [2.3469(18)] fall in the range [2.318(1)−2.3872(10)] in which such bond distances of [$\eta^5$-Cp*Ir(CO)(μ-STol)Pt(STol)($PPh_3$)],[27a] [$\eta^5$-Cp*Ir($\eta^2$-ppy-S-*p*-tol)($H_2O$)][OTf]$_2$,[27b] [$\eta^5$-Cp*Ir(4,6-di-*t*-butyl-(2-methylthio-phenylimino)-*o*-benzoquinone][$PF_6$].$CH_2Cl_2$,[27c] and [$\eta^5$-Cp*Ir

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Cl{2-(phenylthiomethyl)pyridine}]$PF_6$[27d] have been reported. The Ir–Se bond lengths in **1** and **2** [2.4663(12) and 2.4663(13) Å] are similar to the values reported for [$\eta^5$-Cp*IrCl{2-(phenylselenomethyl)pyridine}]$PF_6$ [2.4531(10) Å],[27d] [$\eta^5$-Cp*IrCl(μ-$SeCOC_6H_5$)-($\kappa^2$-$SeCOC_6H_4$–)Ir($\eta^5$-Cp*)] [2.445(2)–2.495(1)Å],[27e] and [$\eta^5$-Cp*Ir($\mu_3$-Se)$_2${PtTol(PPh$_3$)}$_2$] [2.416(1)–2.422(1) Å][27a] but longer than the values reported for [$\eta^5$-Cp*Ir-{$Se_2C_2(CO_2Me)_2$}] [2.3494(7) and 2.3520(7) Å].[27f] The $PF_6^-$ is responsible for C–H···F secondary interactions in all complexes **1-4** resulting in chains. In Fig. 5 it is shown for **1**. For **2-4** see ESI (Table S3 for C–H···F distances and Figs. S1, S2 and S3 for the resulting framework).

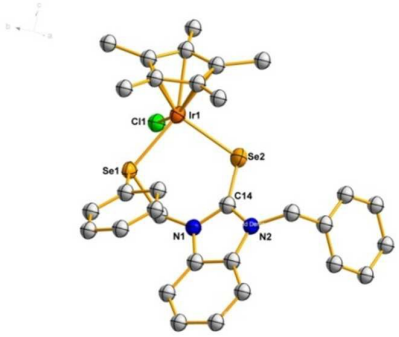


**Fig. 1** Molecular structure of **1**. Bond lengths (Å): Ir1–Se1, 2.4663(12), Ir1–Se2, 2.5159(12), Ir1–Cl1, 2.439(3), Se2–C14, 1.840(11). Bond angles (º): Se1–Ir1–Se2, 95.99(4), Cl1–Ir1–Se2, 90.79(8). Cl1— Ir1— Se1, 78.31(8).

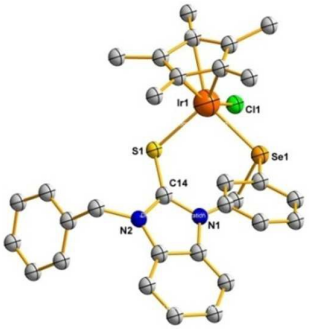


**Fig. 2** Molecular structure of **2**, Bond lengths (Å): Molecular structure of **2**, Bond lengths (Å): Ir1–S1, 2.417(2), Ir1–Se1, 2.4663(13), Cl1–Ir1, 2.436(3), C14–S1, 1.692(10). Bond angle (º): S1–Ir1–Se1, 95.41(7), Cl1–Ir1–Se1, 78.08(7), S1–Ir1–Cl1, 90.69(10)..

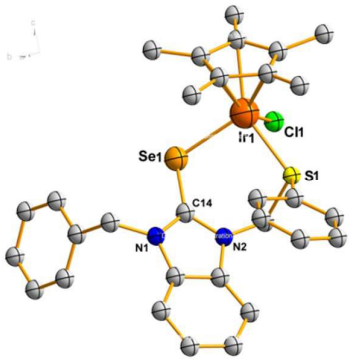


**Fig. 3** Molecular structure of **3**. Bond lengths (Å): Ir1–Se1, 2.5141(16), Ir1–S1, 2.355(4), Ir1–Cl1, 2.427(4), Se1–C14, 1.844(15). Bond angles (º): Se1–Ir1–S1, 94.99(9), Se1–Ir1–Cl1, 90.85(12), S1–Ir1–Cl1, 79.62(14).

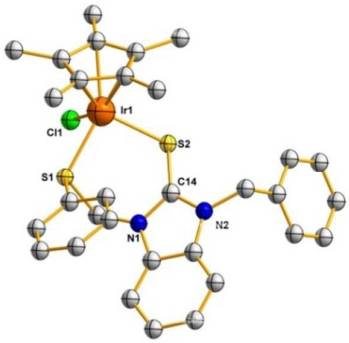


**Fig. 4**. Molecular structure of **4**. Bond lengths (Å): Ir1–S1, 2.3469(18), Ir1–S2, 2.4146(19), Ir1–Cl1, 2.4244(19), S2–C14, 1.685(7). Bond angles (º): S1–Ir1–S2, 94.61(6), S1–Ir1–Cl1, 79.33(7), S2–Ir1–Cl1, 90.55(8)

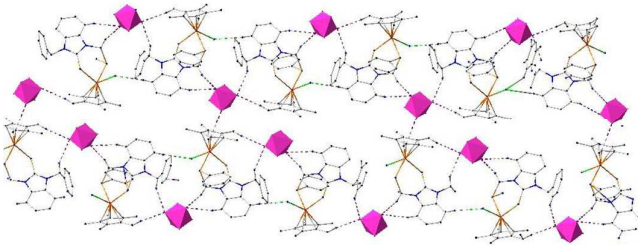

**Fig. 5.** Non-covalent C–H···F interactions in **1.**

**Catalytic applications of complexes 1-4**

**Synthesis of 1, 2-disubstituted benzimidazole**

The complexes **1-4** have been applied to catalyze one pot synthesis of 1,2-disubstituted benzimidazole from 1,2-phenylenediamine and alcohol. Optimum conditions were first established using the reaction between 1,2-phenylenediamine and benzyl alcohol (Scheme 2).

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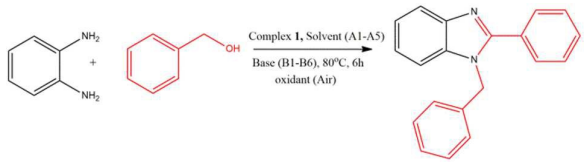



**Scheme 2**: Synthesis of 1,2-disubstituted benzimidazole

**Table 1**. Optimization of solvent, base and substrate: base ratio[a]

| Entry | A | | B | | C | |
|---|---|---|---|---|---|---|
| | Solvent | Yield [%][b] | Base | Yield [%][b] | Substrate/Base | Yield [%][b] |
| 1. | DMSO | 13 | NaOH | 14 | 1:0.5 | 10 |
| 2. | THF | nd | KOH | 27 | 1: 1 | 60 |
| 3. | Toluene | 92 | NaO$^t$Bu | 79 | 1:2 | 92 |
| 4. | DMF | 8 | $Et_3N$ | nd | 1:3 | 92 |
| 5. | $CH_3CN$ | nd | $K_2CO_3$ | 75 | | |
| 6. | | | KO$^t$Bu | 92 | | |

[a]Reaction conditions: 1,2-phenylenediamine (1.0 mmol), benzyl alcohol (2 mmol), catalyst **1** (0.1 mol%) in all cases, **[A]** KO$^t$Bu (2 mmol), solvent (2 mL), 80 ºC, 6 h. **[B]** Base (2 mmol), solvent: toluene (2 mL), 80 ºC, 6 h, **[C]** KO$^t$Bu, toluene (2 mL), 80ºC, 6 h; [b]isolated yield; nd = not detected.

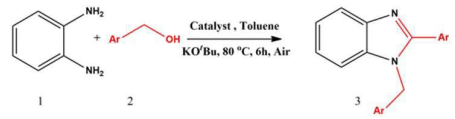
Various organic solvents were screened to carry out the reaction. In toluene the conversion was ~92% (Table 1, Entry A-3) making it most suitable. In DMSO and DMF the conversion to the desired product was low ~8-13 % (Table 1, Entries A-1 and A-4). In THF and $CH_3CN$ no conversion was detected (Table 1, Entries A-2 and A-5). Of the various bases the presence of NaO$^t$Bu and KO$^t$Bu gave good conversion (79 and 92% respectively) to the desired product (Table 1, Entries B-3 and B-6). With the use of NaOH and KOH conversion was only ~14 and 27% respectively (Table 1, Entries B-1 and B-2). In the presence of $K_2CO_3$ conversion was moderate but with $Et_3N$ it was negligible (Table 1, Entries B-4 and B-5). Probably the best results with KO$^t$Bu are due to its higher miscibility with toluene than other bases. The influence of substrate: base ratio was investigated to know the optimum amount of base needed for maximum conversion. The results given in Table 1 (Entries C-1–C-4) suggest that optimum value of the ratio is 1:2.

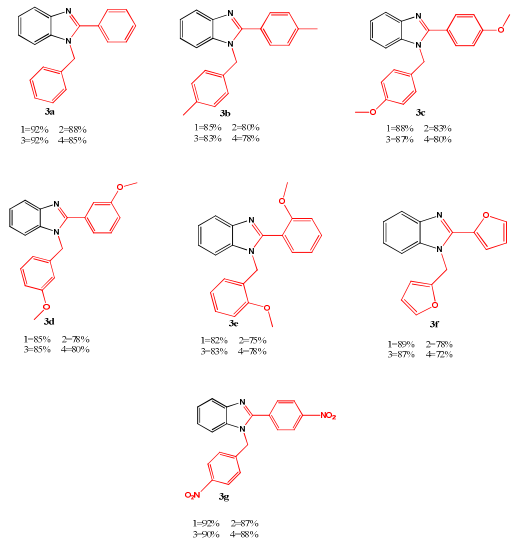
**Table 2:** Control experiments[a]

| Entry | Substrate | Base[#] | Temperature | Catalyst* | Yield%[c] |
|---|---|---|---|---|---|
| 1 | Benzyl alcohol | - | 80˚C | **1** | nd |
| 2 | Benzyl alcohol | KO$^t$Bu | RT | **1** | 8 |
| 3 | Benzyl alcohol | KO$^t$Bu | 80˚C | - | nd |
| 4 | Benzyl alcohol | KO$^t$Bu | 80˚C | $[Cp^*IrCl_2]_2$ | nd |
| 5[b] | Bisimine | KO$^t$Bu | 80˚C | **1** | 95 |

[a]Reaction condition: Benzyl alcohol (2 mmol), 1,2-phenylenediamine (1 mmol), Toluene (2 ml), *0.1 mol %,[#]KO$^t$Bu (2 mmol), time 6 h. [b]Bisimine (1mmol), Toluene (2 ml), *0.1 mol %,[#]KO*t*Bu (2 mmol), time 6 h, [c]isolated yield; nd = not detected.

**Table 3:** Synthesis of 1,2-disubstituted benzimidazoles from 1,2-phenylenediamine and benzylic and furfuryl alcohol




[a] Reaction conditions: 1,2-phenylenediamine (1.0 mmol), benzylic alcohol (2 mmol), KO$^t$Bu (2 mmol), toluene (2 mL), catalyst (**1-4**) (0.1 mol%), temperature, 80$^o$C, time, 6 h, isolated yield in % are below each structure.

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The control experiments were carried in absence of each of the three, base, catalyst and heating. The results given in Table 2 show that yield was insignificant after 6 h, when the reaction was carried out under optimum conditions in the absence of a catalyst (Table 2, Entry 3). In the absence of base no conversion was observed (Table 2, Entry 1). At room temperature only 8% conversion to the desired product was achieved (Table 2, Entry 2). On using $[Cp^*IrCl_2]_2$ as a catalyst, no conversion was observed. This reaffirms the role of ligand in the catalytic activation by complexes **1-4** in the present condensation reaction. The direct reaction of bisimine with complex **1,** gives 1,2-disubstituted benzimidazole in good yield (Table 2).

The scope of this catalytic reaction was studied, using a series of benzylic alcohols and furfuryl alcohol. The optimum reaction conditions were used in each case. 1,2-Disubstituted benzimidazoles with various functional groups resulted in excellent to good yield as summarized in Table 3. No by product was noticed with the formation of any 1,2-disubstituted benzimidazole. The nature and position of the substituent group(s) on the ring of benzylic alcohol affect yield of the condensation product. The electron withdrawing substituent groups like $-NO_2$ gave better results than those of electron donating groups such as, $OCH_3$ and $CH_3$ (Table 3, Entries 3b-c, 3g). The substitution at a *para* position gave better yield of the desired product compared to *ortho* or *meta* (Table 3, Entries 3c-3e). The yield of furfural derivative (Table 3, Entries 3f) was found good. The conversion (Table 3) was found high in the case of benzyl alcohol (up to 92 %, Table 3, Entry 3a), with all the catalysts **1**−**4**. Complex **1** (Ir bonded with two Se atoms) is marginally more efficient as catalyst among all the four, as its low loading (0.1%) is sufficient for good conversion.

For the reaction leading to 1,2-disubstituted benzimidazole from 1,2-phenylenediamine and benzylic and furfural alcohols employing complexes **1-4** as pre-catalysts most probably $[Cp^*Ir^{III}(\mathbf{L})]^{2+}$ (**A**) is the real catalytic species. It is formed by dissociation of cation of **1-4**, $[Cp^*Ir^{III}(\mathbf{L})Cl]^+$ (**B**) into $[Cp^*Ir^{III}(\mathbf{L})]^{2+}$ (**A**) and $Cl^-$ and remains in equilibrium shown below.

$$\underset{\textbf{(B)}}{[Cp^*Ir^{III}(\mathbf{L})Cl]^+} \rightleftharpoons \underset{\textbf{(A)}}{[Cp^*Ir^{III}(\mathbf{L})]^{2+}} + Cl^-$$

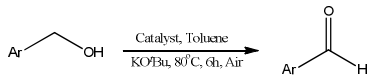
In the presence of a base, **B** forms alkoxide $[Cp^*Ir^{III}(OCH_2Ar)(\mathbf{L})]^+$ which gives aldehyde along with $[Cp^*Ir(H)(\mathbf{L})]^+$. The formation of aldehyde is supported by $^1H$ NMR of reaction mixture taken midway of the catalytic process (See Figures S31- S33 in ESI). The iridium hydride (Ir-H) formation is supported by the presence of a signal at -11.41 ppm in $^1H$ NMR spectrum (See Figs. S30 in ESI) of the reaction mixture of $[Cp^*Ir^{III}(\mathbf{L})Cl]^+$ and benzyl alcohol, consistent with literature report.[16a] Iridium hydride species liberates $H_2$ as evidenced by a signal in $^1H$ NMR spectra of reaction mixtures at ~4.5 ppm and is converted back to $[Cp^*Ir^{III}(\mathbf{L})]^{2+}$(**A**). The $[Cp^*Ir^{III}Cl_2]_2$ does not catalyze the synthesis of 1,2-disubstitutedbenzimidazole. Thus there is a role of **L** in the catalysis. Most probably electrophilic activation of aldehyde (oxygen of >C=O) by iridium(III) of species **A** makes it to react with *o*-phenylenediamine resulting bisimine (in good yield) as evidenced by $^1H$ NMR spectra recorded after 30 and 90 min of progress of the reaction (See ESI for the spectra Figures S31-S33). Of course formation of some bisimine by direct reaction is also possible. Thereafter electrophilic activation of nitrogen of bisimine with Ir(III) of **A** results in cyclization leading to 1,2-disubstitutedbenzimidazole as proposed earlier for its synthesis promoted by electrophilic activation with hydrogen of fluorous alcohols.[28]

**Aerobic oxidation of alcohols**

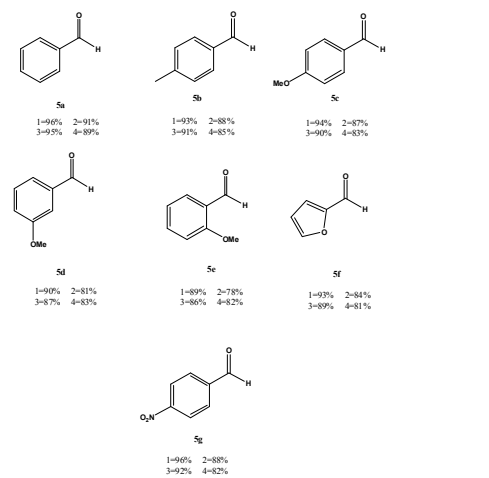
The complexes **1-4** catalyze aerobic oxidation of benzylic alcohols to aldehyde if the protocol of 1,2-disubstituted benzimidazole synthesis (Table 3) is executed in the absence of the diamine. Therefore catalytic aerobic oxidation of benzylic alcohol with **1-4** was studied in detail and found efficient. Optimum conditions and effect of substituent on the ring of aromatic alcohol are as in the case of benzimidazole synthesis. The results are given in Table 4. The oxidation is promoted by **B** mentioned above

For aerobic oxidation of alcohols complexes **1-4** show good catalytic conversion with 0.1 mol% loading without any co-oxidant/additive. This loading is lower compared to earlier reported values (given in parentheses) for transition metal based catalysts viz Cu-Mn oxide/C-TEMPO (0.5 mol%),[17a] Ru/quinine/Co−salen complex (0.5mol%),[17b] Cu-NHC-TEMPO (10 mol%),[17c] $Pd(OAc)_2$/I*i*Pr-$HBF_4$ (0.5 mol%),[15f] [Imim-TEMPO][$FeCl_4$] (2.5 mol%)[15g] and Ru/HAP (hydroxyapatite) (17mol%).[15h] Among the Ir species used for this purpose [Cp*Ir(Cl)(bpy)]OTf and [Cp*Ir(Cl)(bpym)]OTf[16a] are worth comparing with **1-4.** However they are explored for few substrates and TON values are low. The $[Cp^*IrCl_2]_2$ at 2.5-5 mol%, loading gives poor conversion even after a reaction for 15 h.[16b]

**Table 4:** Aerobic oxidation of benzylic alcohols




4 5



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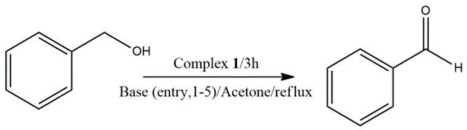
[a] Reaction conditions: benzylic alcohol (1 mmol), KO$^t$Bu (1 mmol), toluene (2 mL), catalyst (**1-4**) (0.1 mol%), temperature, 80$^o$C, time, 6 h, isolated yield in % are given below each structure.

**Oxidation alcohols via hydrogen transfer to acetone:**




**Scheme 3**: **Oxidation of alcohols H transfer to acetone**

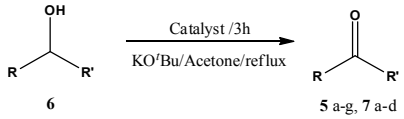
The oxidation of alcohols *via* hydrogen transfer to acetone (Scheme 3) catalyzed with 0.01 mol % of **1**−**4** was studied. To optimize the reaction conditions benzyl alcohol and complex **1** were taken. Potassium *tert*-butoxide was found the best base among all species explored. In the presence of alternatives, viz. $K_2CO_3$, KOH, $Cs_2CO_3$ or $CH_3ONa$, yield was relatively low under identical reaction conditions (Table 5).

**Table 5**. Optimization of base for oxidation of alcohols via hydrogen transfer to acetone [a]

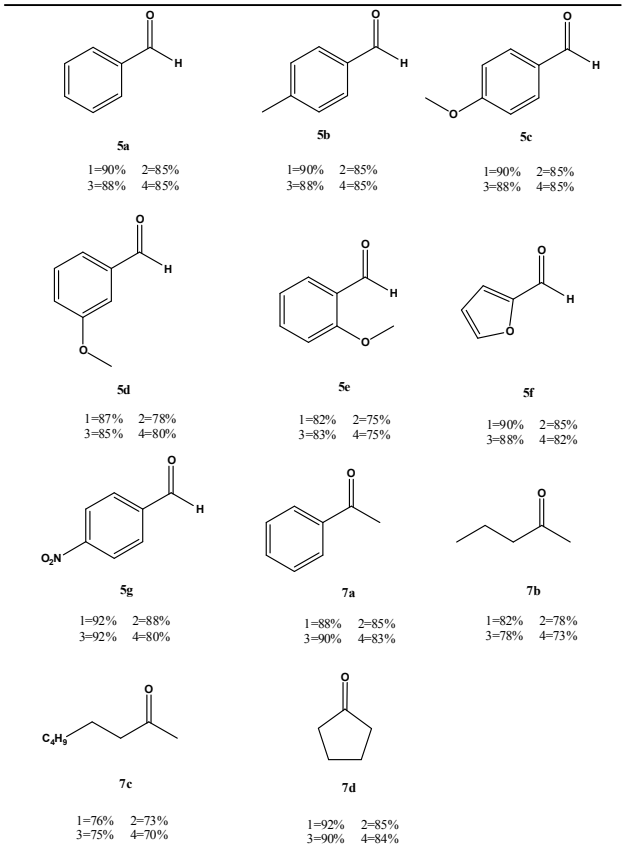
| Entry | Base | Yield% |
|---|---|---|
| 1 | KOH | 25 |
| 2 | $K_2CO_3$ | 40 |
| 3 | KO$^t$Bu | 90 |
| 4 | $Cs_2CO_3$ | 8 |
| 5 | $CH_3ONa$ | 12 |
| [a]Reaction conditions: catalyst **1** (0.01 mol %), benzyl alcohol (1 mmol), 15 mL of acetone, base (1 mmol), 80 °C, time 3 h. | | |

The substrates explored for oxidation of alcohols *via* hydrogen transfer to acetone are summarized in Table 6. The signals in $^{77}Se\{^1H\}$ NMR spectra recorded when the reaction progressed in the presence of **1-3** as a catalyst, were noticed at a 21 - 28 ppm higher frequency, relative to those of free **1-3**. New signal at ≈ δ −11.36 ppm, observed in the $^1H$ NMR spectra recorded during progress of reaction, may be ascribed to the formation of metal hydride species.[25] These two observations indicate that in this oxidation formation of metal alkoxide is involved, as reported earlier.[25] Complex **1** gives somewhat high conversion in comparison to complex **2-4** (Table 6).

**Table 6** Oxidation of alcohols via hydrogen transfer to acetone




**6** **5** a-g, **7** a-d




[a] Reaction conditions: alcohol (1 mmol), KO$^t$Bu (1 mmol), catalyst (**1-4**) (0.01 mol %), acetone (15 mL), 80$^o$ C, time 3h, isolated yield in % are given below each structure.

The effect of nature and position of the substituent on the benzene ring of benzylic alcohol on the yield in hydrogen transfer to acetone is similar to that of synthesis of 1,2-disubstituted benzimidazole. The presence of $–NO_2$ gave somewhat better yield than $–OCH_3$ or $–CH_3$ (Table 6, entries 5b, 5c, 5g). The alcohols having substituent at a *para* position gave better yield of the oxidized product compared to *ortho*/*meta* substituted derivatives (Table 6, entries 5c-e). All the four complexes are efficient as a catalyst for primary and secondary aliphatic alcohols, as revealed by good yield in both the cases (Table 6, entries 7a-7d). The yield of the product was also good with heteroaromatic derivative (Table 6, entry 5f). In comparison to aerobic oxidation, hydrogen transfer to acetone oxidizes alcohols quickly i.e. maximum conversion occurs in nearly half of the time required in the case of aerobic.

**Conclusion**

The four complexes of ($\eta^5$-$CpMe_5$)Ir(III) with 1-benzyl-3-phenylthio/selenomethyl-1,3-dihydrobenzoimidazole-2-thione /selenone [**L** = **L1**–**L4**] have been synthesized and characterized with NMR, HR-MS and single-crystal X-ray diffraction studies. These are the first examples of Ir(III) complexes (**1-4**) with unsymmetrical sulfur-selenium ligands having a unique combination of thio/selenoether and thione/selenone donor sites. They are also

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first examples of complexes of (E, E') (E and E' = S and Se) ligands with Ir(III), efficient to catalyze one pot synthesis of a series of 1,2-disubstituted benzimidazoles from benzylic alcohol in excellent to good yield under mild and aerobic conditions. The aerobic oxidation of benzylic alcohols catalyzed with **1-4** independently gave good to excellent yield. Transfer of hydrogen from alcohols to acetone catalyzed with **1-4** results in carbonyl compounds in good yield under mild reaction conditions. In comparison to aerobic oxidation, hydrogen transfer is fast, i.e. maximum conversion occurs in nearly half of the time required in case of aerobic.

## Experimental

### Physical measurements

The $^{1}H$, $^{13}C\{^{1}H\}$, and $^{77}Se\{^{1}H\}$ NMR spectra were recorded at 300.13, 75.47, and 57.24 MHz respectively on a Bruker Spectrospin DPX-300 NMR. The C, H, and N analyses were carried out with a Perkin–Elmer Series II C, H and N analyzer. Single crystal data were collected on Bruker AXS SMART Apex CCD diffractometer diffractometer using Mo Kα (0.71073 Å) radiation at 298(2) K. The software SADABS[29] was used for absorption correction and SHELXTL for space group, structure determination, and refinements.[29] Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached in all cases. The least-squares refinement cycles on $F^2$ were performed until the model converged. High resolution mass spectral measurements were performed on Bruker microtof-Q II with electron spray ionization (10 eV, 180 °C source temperature, sodium formate as reference compound) taking sample in $CH_3CN$. Nitrogen atmosphere, was created with commercial nitrogen purified by passing it successively through traps containing (as solutions/solid) alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated $H_2SO_4$ and KOH, using Schlenk techniques. The glassware dried in an oven, were used for various reactions under ambient conditions. The preparation of **L1**–**L4** was carried out in nitrogen atmosphere by reported procedure.[26a]

### Chemicals and reagents

The reported methods were used for the synthesis of $[\{(\eta^5\text{-}C_5H_5Me_5)IrCl(\mu\text{-}Cl)\}_2]$[30] and ligands **L1-L4**[26a]. All the solvents were dried and distilled before use by standard procedures.[31] The common reagents and chemicals available commercially within the country were used.

### Synthesis of complex $[Ir\{(\eta^5\text{-}Cp^*\}Cl(L)]PF_6$ ( L = L1-L4)

The solution of **L1** (0.091 g, 0.2 mmol)/ **L2** (0.082 g, 0.2 mmol)/ **L3** (0.082 g, 0.2 mmol)/ **L4** (0.072 g, 0.2 mmol) made in $CH_3OH$ (5 mL) was mixed with a solution of $[(\eta^5\text{-}C_5(CH_3)_5IrCl(\mu\text{-}Cl)]_2$ (0.080 g, 0.1 mmol) in $CH_3OH$ (5 mL) and stirred for 8 h at 25 °C giving a yellow solution. It was filtered, volume of the filtrate reduced (~7 mL) with a rotary evaporator and mixed with solid $NH_4PF_6$ (0.032 g, 0.2 mmol). The resulting yellow coloured microcrystalline solid was filtered, washed with 5 mL of ice-cold $CH_3OH$ and dried in vacuo. Single crystals of **1-4** were grown by slow evaporation of their solutions made in a mixture of $CH_3OH$ and $CH_3CN$ (1:4).

**1**: Yield: 0.164g, (0.17mmol), 85% Anal. Calc. for $C_{31}H_{33}ClF_6IrN_2PSe_2$: C, 40.25; H, 3.09; N, 3.43. Found: C, 40.68; H, 3.32; N, 3.75. Mp: 200.0 °C. $^{1}H$ NMR (DMSO, 25°C vs $Me_4Si$): $\delta$ (ppm) 1.54 {(s, 15H, Me(Cp)}, 5.27 (s, 2H, $CH_2$-Ph), 6.03 (s, 2H, $CH_2$-Se), 7.86-7.84 (m,1H), 7.58-7.33 (m, 8H), 7.28-7.20 (m, 3H), 7.11-6.97 (m, 2H). $^{13}C\{^{1}H\}$NMR (DMSO, 25°C vs $Me_4Si$): 169.4, 135.9, 132.8, 131.2, 130.5, 129.1, 128.5, 128.3, 127.6, 127.3, 123.2, 122.8, 110.6, 109.9, 92.9 (C of Cp*), 48.7, 47.1, 8.1 {C of Me(Cp*)}. $^{77}Se\{^{1}H\}$ NMR (DMSO, 25°C, $Me_2Se$) δ (ppm): 396.75, 55.57. HR-MS ($CH_3CN$) $[C_{31}H_{33}ClIrN_2Se_2]^+$ (*m/z*)= 821.0281; calculated value for $[C_{31}H_{33}ClIrN_2Se2]^+$ = 821.0276 ($\delta$: -0.8 ppm).

**2**: Yield: 0.161g, (0.176mmol), 88%. Anal. Calc. for $C_{31}H_{33}ClF_6IrN_2PSeS$: C, 40.59; H, 3.63; N, 3.05. Found: C, 41.35; H, 3.47; N, 3.32. Mp: 190 °C. $^{1}H$ NMR (DMSO, 25°C vs $Me_4Si$): $\delta$ (ppm) 1.43 {(s, 15H, Me(Cp)}, 5.50 (S, 2H, $CH_2$-Ph), 5.86 (S, 2H, $CH_2$-Se), 7.51-7.43 (m, 3H), 7.40-7.28 (m, 8H), 7.23-7.17 (m, 3H). $^{13}C\{^{1}H\}$NMR (DMSO, 25°C vs $Me_4Si$): 167.1, 135.3, 133.8, 133.3, 132.1, 129.8, 129.4, 129.1, 128.9, 128.3, 127.9, 126.0, 125.5, 112.2, 111.3, 92.5 (C of Cp*) , 49.5, 47.8. 8.7 {C of Me(Cp*)}. $^{77}Se\{^{1}H\}$ NMR (DMSO, 25 °C, $Me_2Se$) δ (ppm): 394.8. HR-MS ($CH_3CN$) $[C_{31}H_{33}ClIrN_2SSe]^+$ (*m/z*)= 773.0862; calculated value for $[C_{31}H_{33}ClIrN_2SSe]^+$ = 733.0833 ($\delta$: -1.9 ppm).

**3**: Yield: 0.148g, (0.162mmol), 81%.Anal. Calc. for $C_{31}H_{33}ClF_6IrN_2PSeS$: C, 40.59; H, 3.63; N, 3.05. Found: C, 40.50; H, 3.70; N, 3.24. Mp: 185.0 °C.$^{1}H$ NMR (DMSO, 25°C vs $Me_4Si$): $\delta$ (ppm) 1.46 {(s, 15H, Me(Cp)}, 5.66 (S, 2H, $CH_2$-Ph), 6.00 (S, 2H, $CH_2$-S), 7.44-7.34 (m, 3H), 7.30-7.28 (m, 6H), 7.23-7.21 (m, 2H), 7.19 (m, 3H). $^{13}C\{^{1}H\}$NMR (DMSO, 25°C vs $Me_4Si$): 167.1, 135.6, 133.0, 129.2, 129.1, 129.0, 128.5, 128.3, 128.2, 127.7, 127.3, 123.6, 123.2, 111.2, 110.5, 92.9 (C of Cp*) 53.8, 49.9, 8.3 {C of Me(Cp*)}. $^{77}Se\{^{1}H\}$ NMR (DMSO, 25 °C, $Me_2Se$) δ (ppm): 60.34. HR-MS ($CH_3CN$) $[C_{31}H_{33}ClIrN_2SSe]^+$ (*m/z*)= 773.0839; calculated value for $[C_{31}H_{33}ClIrN_2SSe]^+$ = 733.0833 ($\delta$: -0.8 ppm).

**4**: Yield: 0.156g, (0.18 mmol), 90% Anal. Calc. for $C_{31}H_{33}ClF_6IrN_2PS_2$: C, 47.78; H, 3.82; N, 3.22. Found: C, 46.14; H, 3.87.; N, 3.46. Mp: 205.0 °C. $^{1}H$ NMR (DMSO, 25°C vs $Me_4Si$): $\delta$ (ppm) 1.50 {(s, 15H, Me(Cp)} 5.58 (S, 2H, $CH_2$-Ph), 5.95 (S, 2H, $CH_2$-S), 7.55-7.48 (m, 8H), 7.34-7.20 (m, 6H). $^{13}C\{^{1}H\}$ NMR (DMSO, 25°C vs $Me_4Si$): 169.5, 135.9, 132.7, 132.2, 131.2, 129.1, 129.0, 128.5, 128.3, 128.1, 127.6, 127.3, 123.2, 122.8, 110.7, 109.9, 92.9 (C of Cp*) 48.7, 47.0, 8.1 {C of Me(Cp*)}. HR-MS ($CH_3CN$) $[C_{31}H_{33}\ ClIrN_2S_2]^+$ (*m/z*)= 725.1392; calculated value for $[C_{31}H_{33}\ ClIrN_2S_2]^+$ = 725.1388 ($\delta$: -0.6ppm).

### General procedure for the synthesis of 1,2-disubstituted benzimidazole:

An oven-dried flask was charged with a benzylic alcohol /furfuryl alcohol(2 mmol), 1,2-phenylenediamine (1 mmol), KO$^t$Bu (2 mmol), catalyst **1-4** (0.1 mol%) and toluene (2 mL). The mixture was stirred at 80°C for 6 h. Thereafter its solvent was evaporated off with a

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rotary evaporator and the residue extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with water (3 × 50 mL) and dried over anhydrous $Na_2SO_4$. The solvent of the extract was removed with a rotary evaporator and the resulting residue was purified by flash column chromatography on silica gel using ethyl acetate:hexane mixture (2:98) as eluent. The isolated products (yield between 72 and 92% ) were authenticated with $^1$H NMR (ESI, Page no. 22).

**General procedure for the aerobic oxidation of substituted alcohols:**

An oven-dried flask was charged with alcohol (1 mmol), KO$^t$Bu (1 mmol), catalyst **1-4** (0.1 mol%) and toluene (2 mL) .The reaction mixture was stirred at 80°C for 6 h. After a work up similar to that of synthesis of 1,2-disubstituted benzimidazole. Product were isolated (yield between 78 and 96%) and authenticated with $^1$H NMR (ESI, Page no. 23).

**General procedure for catalytic hydrogen transfer from alcohols to acetone**

In 15 mL of acetone, catalyst **1-4** (0.01 mol %) was dissolved and mixed with alcohol substrate (1 mmol) and KO$^t$Bu (1 mmol). The mixture was refluxed for 3 h. After a work up similar to that of synthesis of 1,2-disubstituted benzimidazole, The isolated products (yield between 70 and 92% ) were authenticated with $^1$H NMR (ESI, Page no. 23).

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# Complexes of ($\eta^5$-Cp*)Ir(III) with 1-benzyl-3-phenylthio / selenomethyl-1,3-dihydrobenzoimidazole-2-thione/selenone: catalyst for oxidation and 1,2-substituted benzimidazole synthesis

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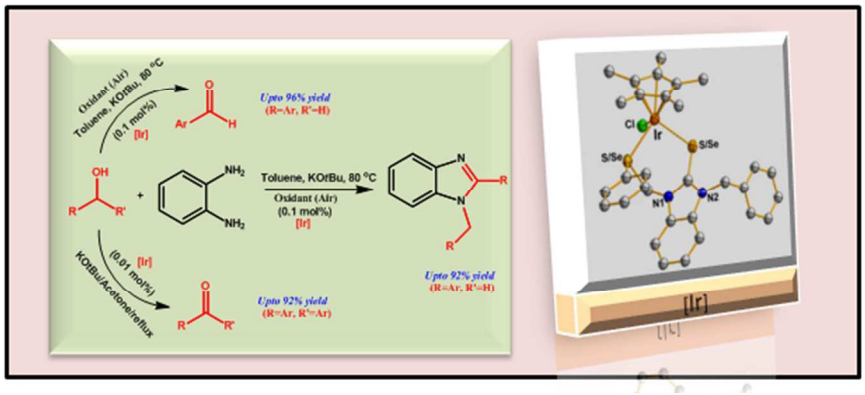


($\eta^5$-Cp*)Ir(III)-1-benzyl-3-phenylthio/selenomethyl-1,3-dihydrobenzoimidazole-2-thione/selenone complexes catalyze at 0.01-0.1 mol%, reactions of 1,2-phenylenediamine with benzylic/furfuryl alcohol and oxidation of alcohols (conditions: mild and ambient).