A stereoselective isomerization of allyl silyl ethers to (*E*)- or (*Z*)-silyl enol ethers using cationic iridium complexes

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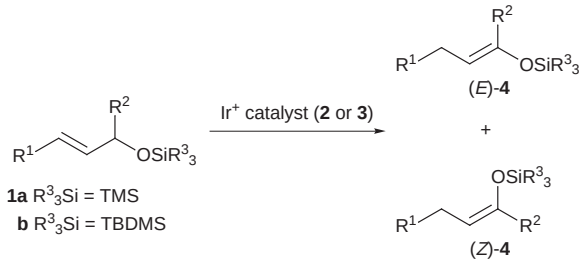
A cationic iridium complex, prepared *via* the hydrogenation of $[Ir(cod)_2]PF_6$–$2PPr_3$ is found to be an excellent catalyst for the stereoselective isomerization of primary allyl silyl ethers to (*E*)-enol ethers and secondary allyl ethers to (*Z*)-enol ethers.

The transition metal-catalyzed positional isomerization of double bonds is an excellent method which has been used in a variety of organic transformations,[1] such as the synthesis of ketones or aldehydes from allylic alcohols, the conversion of allylic ethers to enol ethers, and the transfer of double bonds to the carbon adjacent to carbonyl groups. Among them, the catalytic isomerization of allyl ethers to enol ethers has been studied quite extensively because the procedure is convenient and straightforward and uses readily available substrates, although their stereoselective transformation has not received much attention. The enol ethers thus obtained are either (*Z*)- or (*E*)-isomers, or a mixture of two in most cases. For example, a ruthenium complex gives an equilibrium mixture with the (*Z*)-enol ether predominating (*Z* > 55–68%),[2] while a cationic iridium(III) complex, in contrast, stereoselectively produces (*E*)-enol ethers (*E* > 97%).[3]



Scheme 1

We have recently demonstrated the efficiency of a cationic iridium catalyst for the stereoselective preparation of (*E*)-γ-alkoxyallylboronates from (3-alkoxy-1-alkenyl)boronates.[4] However, the difficulty in reproducing high stereoselectivities on various substrates prompted us to re-investigate the reactioin detail. One of the early, and still one of the most frequently used, routes to (*E*)- or (*Z*)-silyl enol ethers is the trapping of ketone or aldehyde enolates generated under conditions of either kinetic or equilibrium control conditions.[5] However, the catalytic isomerization may offer a reliable and economical route from readily available allylic alcohols (Scheme 1).

The cationic iridium(III) complex **2** generated *in situ* by hydrogenation of $[Ir(cod)(PMePh_2)_2]PF_6$ in THF, produced a very active catalyst, reported by Felkin, which isomerizes primary allyl ethers to (*E*)-enol ethers, but it was unfortunately

Table 1 Effect of catalysts on the isomerization of **1b** (R^1 = H, R^2 = Ph)[a]

Entry	Catalyst	Yield (%)	*E* : *Z*
1	$[Ir(cod)(PPh_2Me)_2]PF_6/H_2$	trace	
2	$[Ir(cod)(PPh_2Me)_2]PF_6$/catecholborane	12	36 : 64
3	$[Ir(cod)(PPh_3)_2]PF_6$/catecholborane	10	42 : 58
4	$[Ir(cod)_2]PF_6$–$2PMe_3/H_2$	0	
5	$[Ir(cod)_2]PF_6$–$2PEt_3/H_2$	76	8 : 92
6	$[Ir(cod)_2]PF_6$–$2PPr_3/H_2$	92	12 : 88
7	$[Ir(cod)_2]PF_6$–$2PBu_3/H_2$	96	10 : 90
8	$[Ir(cod)_2]PF_6$–$2PCy_3/H_2$	0	
9	$[Ir(cod)_2]PF_6$–dppe/H_2	0	

[a] To a solution of catalyst (3 mol%) in CH_2Cl_2 (3 ml)–acetone (0.5 mmol) was added **1b** (R^1 = H, R^2 = Ph) (0.5 mmol), and the resulting solution was then stirred for 30 min at room temperature. The catalysts were prepared *in situ* by bubbling hydrogen into a solution of $[Ir(cod)(PR_3)_2]PF_6$ or into a mixture of $[Ir(cod)_2]PF_6$ (0.015 mmol) and R_3P (0.03 mmol) (entries 1 and 4–9). To a solution of $[Ir(cod)(PR_3)_2]PF_6$ (3 mol%) and **1b** (0.5 mmol) was added catecholborane (3 mol%) at room temperature (entries 2 and 3).

Table 2 Synthesis of silyl enol ethers[a]

		Acetone		CH_2Cl_2–acetone	
Entry	Allyl silyl ether **1**	Yield (%)	*E* : *Z*	Yield (%)	*E* : *Z*
1	CH_2=CHCH$_2$OTBDMS	74	99 : 1	90	24 : 76
2	MeCH=CHCH$_2$OTBDMS	92	99 : 1[b]		
3	PrCH=CHCH$_2$OTBDMS	97	99 : 1[b]		
4	PrCH=CHCH$_2$OTBDMS	85	99 : 1[c]		
5	PhCH=CHCH$_2$OTBDMS	77	96 : 4		
6	CH_2=CHCHMeOTMS	—		71[d]	26 : 74
7	CH_2=CHCHMeOTBDMS	—		89[d]	28 : 72
8	CH_2=CHCHPr^{i}OTMS	—		89	*Z* > 99
9	CH_2=CHCHCyOTMS	—		96	*Z* > 99
10	CH_2=CHCHPhOTMS	—		96	18 : 82

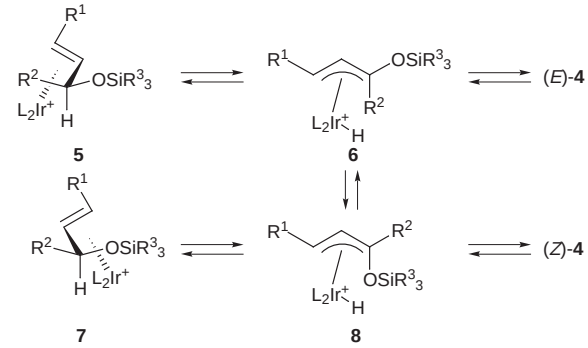
[a] Hydrogen was bubbled into a mixture of $[Ir(cod)_2]PF_6$ (0.015 mmol) and PPr_3 (0.03 mmol) in acetone (3 ml) or CH_2Cl_2 (3 ml)–acetone (0.5 mmol) to give a pale yellow solution of the catalyst **3**. The excess hydrogen was then removed by bubbling argon into the solution. An allyl silyl ether (0.5 mmol) was added and the resulting mixture was then stirred for 30 min at room temperature. [b] The reaction was carried out for 10 min in the presence of 1 mol% of the catalyst because the conditions using 3 mol% catalyst for 30 min resulted in lower selectivity (*E* = 87–93%). [c] Catecholborane (0.015 mmol) was added to a mixture of $[Ir(cod)(PPh_2Me)_2]PF_6$ (0.015 mmol) and allyl silyl ether (0.5 mmol) in acetone. [d] The reaction accompanied by 5–6% of CH_2=CEtOSiR$^3{}_3$.

not effective for secondary allyl ethers such as **1b** (R^1 = H, R^2 = Ph) (entry 1 in Table 1). Similarly to the treatment with hydrogen, various metal hydrides were found to activate the Ir-cod complexes, presumably by removing the cod ligand *via* hydrometalation. The addition of catecholborane or DIBAL-H (1 equiv.) generated the more active catalyst solution than treatment with hydrogen, but the arylphosphine derivatives did not give good results due to their large steric hindrance (entries 2 and 3). Finally, Ir–trialkylphosphine complexes **3** obtained by hydrogenation of a mixture of $[Ir(cod)_2]PF_6$[6] and R_3P (R = Et, Pr, Bu) (2 equiv.) gave an excellent catalyst for the isomerization of secondary allyl ethers with (*Z*)-**4** predominating (*Z* = 88–92%) (entries 5–7). Trimethylphosphine, tricyclohexylphosphine (PCy_3) and bidentate phosphine ligands such as dppe are not effective (entries 4, 8 and 9).

The isomerization of the representative allyl silyl ethers with **3** (R = Pr) is summarized in Table 2. In an acetone solution, the isomerization of primary allyl ethers was completed within 30 min, provided (*E*)-**4** in high yields and with high selectivity, results which were comparable to those obtained for reactions catalyzed by **2** (entries 1–5). The reaction was further accelerated in a mixed solvent of acetone and CH_2Cl_2 giving (*Z*)-**4** predominantly (*E* : *Z* = 24 : 76) (entry 1), although all attempts for the stereoselective preparation of (*Z*)-**4** were unsuccessful. The *Z*-selectivity further improved for secondary allyl trimethylsilyl ethers (entries 6–10), especially when R^2 was a secondary alkyl unit (entries 8 and 9). Both catalysts reported by Felkin (**2**) and **3** worked well for primary allyl ethers (entry 4), but **3** demonstrated a higher catalytic efficiency for secondary allyl ethers.

The iridium-catalyzed isomerization of allyl ethers proceeds through the oxidative addition of an allylic C–H bond to the iridium(I) metal center giving a *syn*-π-allyliridium complex **6** which selectively led to (*E*)-**4** (Scheme 2).[1–3]

The ^1H NMR study reveled that the isomerization involves two process: the first and selective formation of (*E*)-**4** (kinetically controlled process) is followed by equilibration to a mixture of (*E*)- and (*Z*)-**4** through the *anti*-π-allyl intermediate (thermodynamically controlled process) which is slow in a solvent coordinating to the iridium metal center such as acetone.[7] Thus, the stereochemistry of **4** is highly dependent on the solvents and the substrates. When primary allyl ethers were



Scheme 2

reacted in acetone, the kinetic products [(*E*)-**4**] were obtained through the *syn*-π-allyl intermediate [**5** → **6** → (*E*)-**4**]. On the other hand, high *Z*-selectivity was achieved for secondary allyl ethers under conditions leading to equilibration, where the steric difference between the R^2 and R_3Si groups controls the stereochemistry of the products [**5** → **6** → **8** or **7** → **8** → (*Z*)-**4**].

Notes and References

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