Head-to-tail dimerization of acrylates catalyzed by iridium complexes

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Head-to-tail dimerizations of acrylates and vinyl ketone were successfully performed by the use of iridium complexes in good yields. An iridium hydride complex generated *in situ* from [IrCl(cod)]$_2$ and alcohols in the presence of Na$_2$CO$_3$ and (MeO)$_3$P was found to be an active species promoting the head-to-tail dimerization of acrylates. Thus, butyl acrylate afforded the corresponding head-to-tail dimer in 86% yield.

The dimerization of functional alkenes like acrylates and acrylonitrile is an attractive route to obtain bifunctional compounds like dicarboxylates and diamine, respectively. For example, the dimerization of acrylates affords generally a mixture of tail-to-tail dimers, **1a** and **1b**, and head-to-tail dimers, **1c–1e**, whose ratio depends on the catalyst and ligand used. It has been reported that the tail-to-tail dimerization of acrylates can be achieved by various transition metal compounds like Co,[1] Ni,[2] Ru,[3] Rh[4] and Pd.[5] However, a limited number of reports have appeared on the selective head-to-tail dimerization leading to the latter dimers (**1c–1e**).[6] Tertiaryl phosphines are known to enhance the formation of the head-to-tail products, but the selectivity of the reaction is generally low.[7] There have been a number of reports on the dimerization of acrylates and acrylonitrile catalyzed by Ru and Pd compounds, but, to our best knowledge, no report has appeared on the Ir-catalyzed dimerization of acrylates (Scheme 1).

Scheme 1
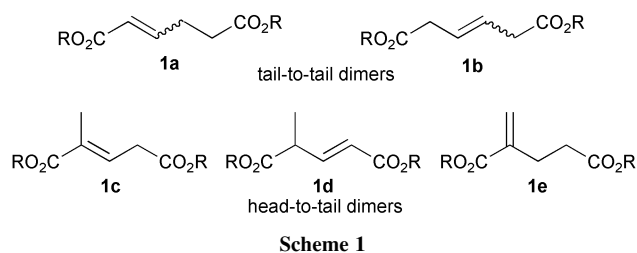
In this paper, we wish to report the first selective Ir-catalyzed head-to-tail dimerization of acrylates and methyl vinyl ketone [eqn. (1)].

(1)
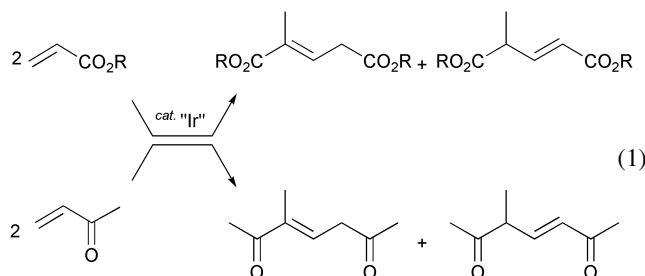
In order to confirm optimum reaction conditions for the dimerization, butyl acrylate (**2**) was chosen as a model substrate and allowed to react using [IrCl(cod)]$_2$ as the catalyst under various reaction conditions (Table 1).

In the first place, the reaction of **2** (1 mmol) was carried out in the presence of [IrCl(cod)]$_2$ (1 mol%) and base (2 mol%) in several solvents at 100 °C for 15 h. Among the solvents used,

1-butanol was found to be a good solvent, and dimer **1c** was obtained as a main product along with butyl propionate (**3**) formed by the hydrogen transfer from 1-butanol to **2** (Meerwein–Ponndorf–Verley type reaction) (Run 1). Although the reaction in 1,4-dioxane afforded **1c** in low yields, no reaction took place in THF, benzene, ethyl acetate, acetonitrile and acetic acid (Runs 2 to 4). The present dimerization called for the coexistence of a base like sodium carbonate. Thus, when sodium carbonate was removed from the catalytic system, no dimerization was completely induced (Run 5). The effect of several carbonates on the dimerization was examined, and Na$_2$CO$_3$ was found to be the best additive (Runs 6 and 7). It is believed that the presence of an alcohol like 1-butanol and a base like sodium carbonate is essential for the *in situ* generation of an iridium hydride complex, which promotes the dimerization of **2**, from [IrCl(cod)]$_2$.

As shown in Run 1 of Table 1, the reaction in 1-butanol was accompanied by an undesired transfer hydrogenation from 1-butanol to **2**. In a previous paper, we showed that the transfer hydrogenation of α,β-unsaturated carbonyl compounds with 2-propanol is efficiently catalyzed by [IrCl(cod)]$_2$ in the presence of a small amount of Cs$_2$CO$_3$, and that an iridium hydride complex is a real active species generated *in situ* from the [IrCl(cod)]$_2$ under above conditions.[8] In the present dimerization, an iridium hydride complex derived from [IrCl(cod)]$_2$ and 1-butanol in the presence of Na$_2$CO$_3$ is thought to be an active species promoting the dimerization of **2** as well as the transfer hydrogenation from 1-butanol to **2**.

Table 2 shows the effect of ligands on the dimerization of **2** by [IrCl(cod)]$_2$. In order to avoid the Meerwein–Ponndorf–Verley type reaction between 1-butanol and **2**, 1-butanol was removed from the catalytic solution. After treatment of [IrCl(cod)]$_2$ with 1-butanol in the presence of small amounts of Na$_2$CO$_3$ and (MeO)$_3$P at 100 °C for 1 h, 1-butanol was removed under reduced pressure to give a brown solid involving an iridium hydride, and toluene and **2** were added to the iridium hydride complex thus obtained.† The mixture was stirred at 100 °C for 5 h to give dimer **1c** involving a small amount of **1d** in high yield (86%), and the formation of butyl propionate **3** could

Table 1 Dimerization of butyl acrylate (**2**) catalyzed by [IrCl(cod)]$_2$ under several solvents[a]

Run	Solvent	Base	Conv./%	Yield/%[b]	
				1c	**3**
1	1-Butanol	Na$_2$CO$_3$	99	53 (9)	35
2	1,4-Dioxane	Na$_2$CO$_3$	24	6 (<1)	2
3[c]	THF	Na$_2$CO$_3$	4	nd	nd
4	AcOH	Na$_2$CO$_3$	1	nd	nd
5	1-Butanol	—	5	nd	nd
6	1-Butanol	Li$_2$CO$_3$	79	4 (trace)	48
7	1-Butanol	K$_2$CO$_3$	98	33 (5)	40
8	1-Butanol	Cs$_2$CO$_3$	71	11 (2)	50

[a] Butyl acrylate **2** (1 mmol) was reacted in the presence of [IrCl(cod)]$_2$ (0.01 mmol) and base (0.02 mmol) in solvent (1 mL) at 100 °C for 15 h. [b] Parenthesis shows the yield of dimers other than **1c**. [c] 65 °C

Table 2 Effect of ligands for the dimerization of butyl acrylate (**2**) by *in situ* generated iridium hydride complex[a]

Run	Ligand	Conv./%	Yield/%[b]	
			1c	**3**
1	—	32	10 (< 1)	4
2	(MeO)₃P	98	86 (10)	1
3	(BuO)₃P	71	60 (7)	4
4	(PhO)₃P	9	2 (trace)	3
5	Bu₃P	77	4 (< 1)	4
6	Cy₃P	71	nd	2
7	Ph₃P	11	nd	4
8[c]	dppe	14	2 (trace)	2

[a] After treatment of [IrCl(cod)]₂ (0.01 mmol) with 1-butanol (1 mL) in the presence of Na₂CO₃ (0.02 mmol) and ligand (0.04 mmol) at 100 °C for 1 h, 1-butanol was removed under reduced pressure, and then toluene (1 mL) and **2** (1 mmol) were added. The reaction mixture was stirred at 100 °C for 5 h. [b] Parenthesis shows the yield of dimers other than **1c**. [c] Dppe (0.02 mmol) was used.

be controlled lower than 1% (Run 2).‡ The reaction in the absence of a ligand under these conditions resulted in the considerable decrease of the conversion of **2** to **1** (Run 1). Although the head-to-tail dimerization was accelerated by PCy₃,[7] the reaction catalyzed by (MeO)₃P alone did not take place at all under these reaction conditions.

It was found that phosphites serve as good ligands of the iridium hydride complex generated *in situ* from [IrCl(cod)]₂ and 1-butanol in the presence of Na₂CO₃ (Runs 2 and 3). When phosphine ligands like tributylphosphine and tricyclohex-ylphophine were employed, the polymerization of **2** was induced rather than the dimerization (Runs 5 and 6). Triphenyl-phosphine and bidentate ligand, dppe, were inert for the promotion of the dimerization (Runs 7 and 8).

The effect of alcohols on the generation of an active iridium hydride complex was examined (Table 3). The reactions by the [IrCl(cod)]₂ upon treatment with methanol and ethanol gave almost the same results, but no reaction took place when water was employed in place of alcohols. 2-Butanol was also effective for the generation of an iridium hydride, while *tert*-butyl alcohol did not promote the dimerization of **2** probably because of the difficulty for the generation of the iridium hydride complex which catalyzes the dimerization. This shows that the alcohols possessing α-hydrogen requires to generate the iridium hydride complex from the [IrCl(cod)]₂.

Methyl, ethyl and isobutyl acrylates dimerized in the same fashion as **2** under the conditions shown in Table 2, Run 2 to

Table 3 Effect of alcohols on the activation of [IrCl(cod)]₂ for dimerization of **2**[a]

Run	Alcohol	Conv./%	Yield/%		
			1c	**1d**	**3**
1	MeOH	94	72	10	4
2	EtOH	91	68	9	7
3	1-BuOH	98	86	10	1
4	2-BuOH	71	61	10	2
5	*t*-BuOH	22	8	2	nd
6	Water	no reaction			

[a] After [IrCl(cod)]₂ (0.01 mmol) was treated in the presence of Na₂CO₃ (0.02 mmol) and (MeO)₃P (0.04 mmol) in alcohol (1 mL) at refluxing temperature for 1 h, the alcohol was removed under reduced pressure, and then toluene (1 mL) and **2** (1 mmol) was added to the reactant. The reaction was run at 100 °C for 5 h.

form the corresponding head-to-tail products in 86%, 88% and 82% yields, respectively. Methyl vinyl ketone (**4**) similarly dimerized under these conditions to give 1,5-diketone (**5**) in 79% yield [eqn. (2)].§ However, acrylonitrile was difficult to dimerize due to the strong coordination of cyano group to the iridium complex.

$$(2)$$
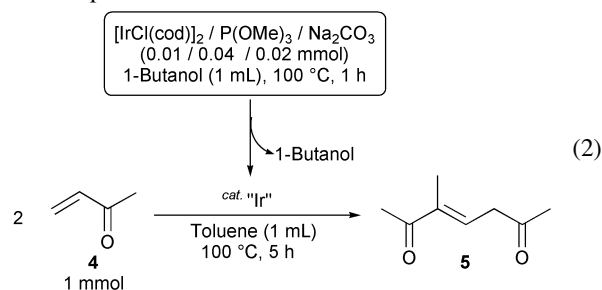
Owing to the complexity of the present catalytic system, we cannot propose a detail reaction path, but the present reaction is thought to proceed through a similar pathway to that proposed for the dimerization of acrylates by Ru,[3] Rh,[4] and Pd.[5]

In conclusion, we have found that an iridium hydride complex generated *in situ* from [IrCl(cod)]₂ complex and 1-butanol in the presence of small amounts of Na₂CO₃ and (MeO)₃P catalyzes the head-to-tail dimerization of acrylates and methyl vinyl ketone in high selectivity.

Notes and references

† A procedure for the dimerization reaction of **2**: The solution of a dry 1-butanol (1 mL) containing [IrCl(cod)]₂ (0.01 mmol), (MeO)₃P (0.04 mmol), and Na₂CO₃ (0.02 mmol) under Ar were stirred at 100 °C for 1 h. After 1-butanol was removed under reduced pressure, a solution of a dry toluene (1 mL) and **2** (1 mmol) was added, then the reaction mixture was allowed to react at 100 °C for 5 h.

‡ *Spectral data for* **1c**: ¹H NMR δ 6.86–6.80 (m, 1H), 4.09–4.04 (m, 4H), 3.13 (d, *J* = 7.1 Hz, 2H), 1.79 (s, 3H), 1.63–1.50 (m, 4H), 1.40–1.24 (m, 4H), 0.86 (t, *J* = 7.3 Hz, 3H); ¹³C NMR δ170.2, 167.2, 132.5, 130.5, 64.85, 64.52, 34.2, 30.6, 30.5, 19.24, 19.11, 13.74, 13.69, 12.7; MS (70 eV) *m/z* = 182 (M⁺), 126, 106, 57, 41.

§ *Spectral data for* **5**: ¹H NMR δ 6.86–6.80 (m, 1H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 2.07 (s, 3H), 1.89 (s, 3H); ¹³C NMR δ206.0, 196.5, 139.6, 130.2, 36.3, 25.5, 23.1, 11.8; MS (70 eV) *m/z* = 112 (M⁺), 81, 59, 53, 43.

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