Selective Tail-to-Tail Dimerization of Ethyl Acrylate Catalyzed by Dirhodium Complexes

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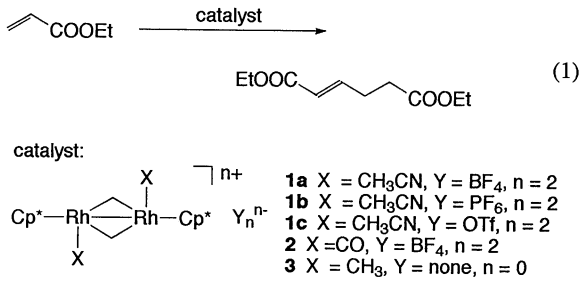
A catalytic selective tail-to-tail dimerization of ethyl acrylate was achieved by using dinuclear rhodium complexes, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2](BF_4)_2$ ($Cp^* = C_5Me_5$) (**1a**) and $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CO)_2](BF_4)_2$ (**2**). The corresponding dimethyl complex, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (**3**), showed catalytic ability only in the presence of $HBF_4{\cdot}OEt_2$.

The catalytic C-C bond forming reaction promoted by metal complexes in homogenous systems has been investigated for its remarkable utility to organic synthesis. However, the customary studies were concentrated on mononuclear metal complex catalysts. Use of higher nuclearity metallic complexes like metal cluster compounds for catalytic organic reaction is very attractive, because it is expected that they have potential ability for unique reactivity and selectivity of organic reactions caused by multi-active sites.[1] We recently found the C-C bond forming reaction between the bridging methylene group on the dirhodium complex, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$ ($Cp^* = C_5Me_5$) (**1**),[2,3] and phenylacetylene to form the novel organic ligand on the dirhodium complex.[4] In this reaction replacement of the relatively labile acetonitrile ligands by phenylacetylene should trigger the C-C bond formation. Employing electron deficient olefins for the reaction with complex **1** caused selective oligomerization of the olefins to take place.[5] Here we report a selective tail-to-tail dimerization of ethyl acrylate[6,7] catalyzed by dinuclear rhodium complexes (eq 1).



The results of the catalytic dimerization are summarized in Table 1. We first observed the dimerization of ethyl acrylate in the presence of complex **1a**. At ambient temperature only 14 equivalents of ethyl acrylate relative to the catalyst were transformed to the dimer (entry 1). The catalysis is not efficient under the mild conditions. The improvement of the catalysis, however, was achieved at higher reaction temperature. Furthermore, the striking effect of H_2 was observed and the best turnover number, 3290, based on ethyl acrylate was obtained under 1 atm of H_2 at 80 °C (entry 3: 3550 equivalents of ethyl acrylate relative to the catalyst was used).[8] The reaction was perfectly controlled to form the tail-to-tail dimerization product with the E isomer excess and reduction of the olefinic part was not observed.[9]

The counter anions of the cationic dirhodium complex affect remarkably the catalysis. A bis(acetonitrile) complex possessing OTf^- ($Tf = CF_3SO_2$) counter part, **1b**, showed poor catalytic activity compared with corresponding BF_4 complex **1a** (entry 4). Probably, the counter anion, OTf^-, which is nucleophilic competes with ethyl acrylate for the coordination to the metal centers, hence the dimerization reaction is depressed. For PF_6 complex **1c**, inefficiency was also observed (entry 5). It is worthwhile to note that PF_6^- generates sometimes F^-, as reported for the zirconium catalytic system by Jordan,[10] which can interrupt the coordination of olefins. The feature of the interruption by PF_6^- may be nearly the same as the case of OTf^-. A dirhodium complex with another neutral CO ligand, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CO)_2](BF_4)_2$ (**2**)[2] was used for the reaction (entry 6). It showed the catalytic activity, but the ability was less than that of complex **1a**. In this compound coordination of the CO ligands to the rhodium centers is quite weak but stronger than that of acetonitrile ligands.

Complexes with relatively rigid ligands, i. e., alkyl, halide, or thiolate, instead of the acetonitrile ligand can not promote the catalytic dimerization. However, treatment of a dimethyl complex, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3)_2]$ (**3**),[11] with 2 molar amounts of $HBF_4{\cdot}OEt_2$ is effective for the dimerization (entries 7-9). The reaction was performed as follows: To a solution of ethyl acrylate (13.15 g, 1.31 mol) and complex **3** (20 mg, 0.037 mmol) in CH_2ClCH_2Cl (20 mL) a 0.2 M CH_2ClCH_2Cl solution of $HBF_4{\cdot}OEt_2$ (0.37 mL, 0.074 mmol) was added at -20 °C. After the reaction system was filled with H_2, the mixture was stirred for 12 h at 80 °C. Then the solvent was removed *in vacuo* at ambient temperature, and ether (200 mL) was introduced into the reaction mixture. A precipitate produced was filtered off and the filtrate was concentrated to give the crude dimer product. Yield and selectivity were determined after purification by silica-gel column chromatography (9.68 g, 73.6% conversion).

When complex **3** was treated with 2 equivalents of $HBF_4{\cdot}OEt_2$ in acetonitrile, the formation of complex **1a** proceeded quantitatively. Treatment of complex **3** with the suitable amounts of the protonic acid in uncoordinating solvents leads to the Rh-Me bond cleavage to form free coordination sites which are open to the unsaturated organic compounds. The acid, of course, does not destroy the μ-methylene framework.[2,12] The results for the catalytic reactions with complex **3** and $HBF_4{\cdot}OEt_2$ practically corresponds to those for the reactions with complex **1a** (entries 1-3 versus 7-9). This fact suggests that the reaction conditions closely resemble each other and in the case of complex **1a** the replacement of the acetonitrile ligands by ethyl acrylate is essential at an initial step of the catalytic reaction. As mentioned above, it is reasonable that the system of complex **3** with trifric acid showed no catalytic ability (entry 10).

This is the first observation for the catalytic dimerization of acrylate ester by using dinuclear metal complex, to our knowledge. The catalytic efficiency of our system is superior to

Table 1. Dimerization of ethyl acrylate catalyzed by dirhodium complexes **1** - **3**

entry	catalyst	equiv of acrylate/catalyst	conditions[a]	% conv[b] (E/Z)[c]	turnover number[d]
1	**1a**	32	25 °C, 60 h, N_2	43.8 (82/18)	14
2	**1a**	1180	80 °C, 12 h, N_2	61.0 (91/9)	720
3	**1a**	3550	80 °C, 15 h, H_2	92.6 (91/9)	3290
4	**1b**	780	80 °C, 12 h, N_2	16.8 (82/18)	131
5	**1c**	780	80 °C, 12 h, N_2	8.8 (83/17)	69
6	**2**	780	80 °C, 15 h, N_2	39.0 (82/18)	304
7	**3**[e]	32	25 °C, 12 h, N_2	65.8 (87/13)	21
8	**3**[e]	1070	80 °C, 60 h, N_2	66.3 (85/15)	705
9	**3**[e]	3550	80 °C, 12 h, H_2	73.6 (88/12)	2610
10	**3**[f]	1070	80 °C, 12 h, N_2	<1	

[a] All reactions except for entries 1 and 7 were carried out in CH_2ClCH_2Cl. For entries 1 and 7, carried out in CH_2Cl_2. [b] Calculated from isolated yields. [c] Determined by ^1H NMR. [d] Based on mol of ethyl acrylate converted. [e] In the presence of 2 equivalents of $HBF_4{\cdot}OEt_2$. [f] In the presence of 2 equivalents of CF_3SO_3H.

the previous reports, except for the prominent report of the acrylate dimerization by cationic hydride complexes of rhodium (III) prepared from rhodium (I) complexes with a special protonation method.[7i] In contrast with the dirhodium complexes, a mononuclear Cp*-rhodium (III) complex, $[RhCp^*(CH_3CN)_3]^{2+}$, showed a poor reactivity. The turnover number was <40. The fact again emphasizes that our dirhodium catalysts have remarkable ability to the acrylate dimerization. Although the details and the role of H_2 in the catalysis of the dinuclear rhodium complexes are not obvious at the present, our system is available for practical synthesis of adipate analogues.

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References and Notes

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