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Catalytic Tail-to-Tail Selective Dimerization of Methyl Methacrylate Promoted by a Ruthenium(0) Complex

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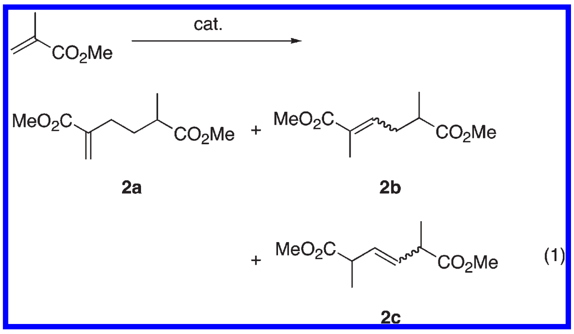
*Summary: Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**) (10 mol %) catalyzes the tail-to-tail dimerization of methyl methacrylate (MMA) in MeCN in 74% yield at 70 °C for 4 h. Without use of solvent complex **1** (1 mol %) rapidly catalyzes the tail-to-tail dimerization and trimerization of MMA in 59% and 23% yields, respectively, at 70 °C for 5 min.*

The tail-to-tail dimers of substituted olefins are potential precursors to monomers for condensation polymerization, and a variety of transition metal complexes have been documented to catalyze such tail-to-tail dimerization.[1] Although such examples involve dimerization of methyl acrylate,[2] acrolein,[3] and acrylonitrile,[4] the catalytic tail-to-tail dimerization of methyl methacrylate (MMA) is generally very difficult even though the product is potentially important.[5] To the best of our knowledge, only a few examples have been reported of the dimerization of MMA by transition-metal-based catalysts, and the catalytic activities are generally poor. For examples, these pioneering works report the dimerization of MMA promoted by $[\mathrm{Pd(NCMe)_4}]^{2+}[\mathrm{PF_6}]^-{}_2$ in the presence of $\mathrm{LiBF_4}$ to give of *E*/*Z*-**2b** (59%) and **2c** (4%) at 25 °C for 3 days,[6] by $[\mathrm{Pd}(\eta^3\text{-allyl})(1,5\text{-COD})]^+\mathrm{BF_4}^-/\mathrm{PR_3}$ (COD = cyclooctadiene ($\mathrm{C_8H_{12}}$)) to give *E*/*Z*-**2b** with 12% conversion of MMA at 80 °C,[7] by *in situ* formed Ni(II) to give *E*/*Z*-**2b** (26%) at rt for 20 h,[8] and by $\mathrm{PdCl_2}(p\text{-nonyl-}\mathrm{C_6H_4CN})_2/\mathrm{LiBF_4}$ to give a 6:94 mixture of **2a** and *Z*/*E*-**2b** with 50% conversion of MMA at 20−50 °C (eq 1).[9] Quite recently, catalytic tail-to-tail dimerization of MMA by *N*-heterocyclic carbene as an organic catalyst has been reported.[10]



We have documented the first solid evidence for an oxidative coupling mechanism in the selective tail-to-tail coupling reaction of methyl acrylate promoted by Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**).[11] As an extension of this study, we have found that complex **1** also catalyzes the tail-to-tail dimerization of MMA, and interestingly, this process occurs much faster than the corresponding reaction with methyl acrylate. We disclose details of this work here and discuss possible mechanisms.

The naphthalene complex of ruthenium(0), **1** (10 mol %), catalyzed the tail-to-tail dimerization of MMA in the presence of MeCN (10 equiv to **1**) at 70 °C for 4 h in 74% yield (**2a**/*Z*-**2b**/*E*-**2b** = 3/5/92) with concomitant formation of trimers in 13% yield (**3x**/*Z*-**3a**/*E*-**3a** = 54/38/8) (eq 2, entry 1 in Table 1).[12] The tail-to-tail dimers **2a**, *Z*-**2b**, and *E*-**2b** and the trimer **3a** were characterized by GC-MS, ^{1}H NMR, ^{1}H−^{1}H COSY, ^{13}C NMR, DEPT135, and ^{1}H−^{13}C HETCOR NMR spectra, and *E*-**2b** and **3a** were separated by silica gel column chromatography and preparative GLC. A small amount of

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[1] Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992; pp 82−85.

[2] (a) DiRenzo, G. M.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 6225. (b) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. (c) Broookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437. (d) Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038. (e) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080. (f) Strehblow, C.; Schupp, T.; Sustmann, R. *J. Organomet. Chem.* **1998**, *561*, 181. (g) Guibert, I.; Neibecker, D.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1989**, 1850. (h) Picquet, M.; Stutzmann, S.; Tkachenko, I.; Tommasi, I.; Zimmermann, J.; Wasserscheid, P. *Green Chem.* **2003**, *5*, 153. (i) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565.

[3] Ohgomori, Y.; Ichikawa, S.; Sumitani, N. *Organometallics* **1994**, *13*, 3758.

[4] (a) Fukuoka, A.; Nagano, T.; Furuta, S.; Yoshizawa, M.; Hirano, M.; Komiya, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1409. (b) Kashiwagi, K.; Sugise, R.; Shimakawa, T.; Matuura, T.; Shirai, M.; Kakiuchi, F.; Murai, S. *Organometallics* **1997**, *16*, 2233. (c) Tembe, G. L.; Ganeshpure, P. A.; Satish, S. *React. Kinet. Catal. Lett.* **1998**, *63*, 151.

[5] Thermal dimerizations of MMA (ref 5a) and calcium methacrylate followed by treatment of diazomethane were reported (ref 5b). (a) Albisetti, C. J.; England, D. C.; Hogsed, M. J.; Joyce, J. *J. Am. Chem. Soc.* **1956**, *78*, 472. (b) Naruchi, K.; Yamamoto, O.; Miura, M.; Nagakubo, K. *Nippon Kagakukaishi* (*J. Chem. Soc. Jpn, Chem. Ind. Chem.*) **1976**, *11*, 1794.

[6] Nugent, W. A. U.S. Patent, 4 451 665, 1984.

[7] Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* **1984**, *3*, 1130.

[8] Wilke, G.; Sperling, K. Ger. Patent 3336691, 1985.

[9] (a) Oehme, G. *J. Prakt. Chem.* **1984**, *5*, 779. (b) Oehme, G.; Grassert, I.; Mennenga, H.; Baudisch, H. *J. Mol. Catal.* **1986**, *37*, 53.

[10] Matsuoka, S.; Washio, A.; Ohta, Z.; Katada, A.; Ichioka, K.; Takagi, K.; Suzuki, M. Abstracts of Papers, the 90th Annual Meeting of the Chemical Society of Japan, Osaka, **2010**; 3F703.

[11] Hirano, M.; Sakate, Y.; Komine, N.; Komiya, S.; Bennett, M. A. *Organometallcs* **2009**, *28*, 4902.

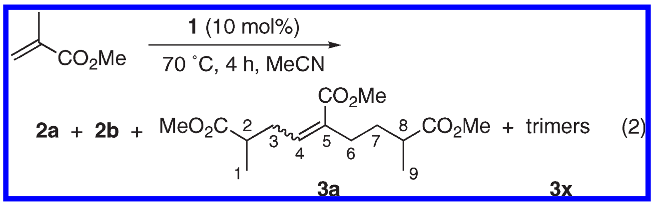
[12] The structure of trimer **3x** is not clear at present, but **3x** is estimated to be two regioisomers of trimer **3a** on the basis of the GC-MS analysis. The yield of **3x** was calculated on the basis of the GLC analysis with assumption of the same relative intensity as **3a**.

Table 1. Catalytic Tail-to-Tail Dimerization of MMA Promoted by 1[a]

	conditions				dimers		trimers	
entry	cat., %	temp, °C	time, h	solvent	yield, %	**2a**/*Z*-**2b**/*E*-**2b**, %	yield, %	**3x**/*Z*-**3a**/*E*-**3a**, %
1	10	70	4	MeCN	74	3/5/92	13	54/38/8
2	1	140	4	MeCN	33	3/9/88	1	0/64/36
3	1	0	97	neat	40	15/35/50	60	2/58/40
4	1	30	24	neat	47	2/13/85	54	7/33/60
5	1	50	2	neat	55	3/22/75	40	9/39/56
6	1	70	2	neat	66	2/11/87	24	13/25/62
7	1	90	2	neat	67	3/7/90	20	20/10/70
8	1	70	8	C_6H_6	61	2/7/91	15	13/13/74
9[b]	1	70	2	neat	65	2/23/75	20	10/45/55
10[c]	1	70	2	neat	trace		trace	
11[d]	1	70	2	neat	trace		trace	
12[e]	1	70	6	neat	62	2/10/88	23	12/23/65

[a] Yields are estimated on the basis of MMA. [b] 1,5-COD (5 mol %) added. [c] PPh_3 (5 mol %) added. [d] $P(OMe)_3$ (5 mol %) added. [e] NEt_3 (100 mol %) added. Typical conditions: **1** (0.100 mmol), MMA (10.0 mmol).

isobutyric acid (2%) was observed and compound **2c** was not observed in this catalysis.



Without use of MeCN, complex **1** (1 mol %) at 70 °C catalyzed the reaction to give a mixture of the tail-to-tail dimer in 59% yield (tail-to-tail selectivity: 100%, **2a**/*Z*-**2b**/*E*-**2b** = 14/30/56) *in 5 min*, with concomitant formation of the trimers in 23% yield (**3x**/*Z*-**3a**/*E*-**3a** = 4/63/33). After 1 h, the product ratios changed to **2a**/*Z*-**2b**/*E*-**2b** = 2/15/83 (61% yield) and **3x**/*Z*-**3a**/*E*-**3a** = 11/37/62 (27% yield), and after 24 h to **2a**/*Z*-**2b**/*E*-**2b** = 2/5/93 (56% yield) and **3x**/*Z*-**3a**/*E*-**3a** = 3/7/90 (27% yield). The transient formations of **2a**, *Z*-**2b**, and *Z*-**3a** suggest that **2a** is converted into **2b** and/or **3a** and that *Z*-**2b** and *Z*-**3a** are similarly converted into *E*-**2b** and *E*-**3a**, respectively.

This catalysis proceeded even at 0 °C, but the trimers became the dominant product (entry 3 in Table 1). The dimer/trimer ratio increased at higher temperature (entries 3−7), but the conversion decreased due to catalyst deactivation (entry 2). The change of the dimer/trimer ratio depending on the reaction temperature may be due to rapid isomerization of the initial product **2a** to **2b** at high temperature, while **2a** is converted into the trimers by the coupling with MMA (*vide infra*). Addition of 1,5-COD did not cause significant change in this catalysis (entry 9), but trivalent phosphorus compounds, such as PPh_3 or $P(OMe)_3$, were found to inhibit the reaction, probably by preventing coordination of MMA to the ruthenium center or by displacement of the 1,5-COD ligand (entries 10, 11).

In order to clarify the mechanism of the tail-to-tail dimerization of MMA promoted by **1**, we performed a stoichiometric reaction of **1** with MMA. Treatment of **1** with 3 equiv of MMA in C_6D_6 resulted in the tail-to-tail dimer in 74% yield (**2a**/*Z*-**2b**/*E*-**2b** = 2/5/93) along with Ru(η^6-C_6D_6)(η^4-1,5-COD) (**4**)[13] (23%) and [Ru(η^4-1,5-COD)]$_2$(η^6:η^4-naphthalene) (**5**)[14] (3%) in 57% conversion of **1** without any indication of intermediates. Although the catalyst precursor **1** does not give a single product during this process, the formation of **4** and **5** suggests formation of a zerovalent ruthenium species such as "Ru(η^4-1,5-COD)".[15] When **1** was treated with 2 equiv of MMA in the presence of 2 equiv of PMe_3 at 50 °C for 1 day in benzene, the zerovalent complex Ru(κ^4-*cisoid*-MMA)(η^2-*cisoid*-MMA)$(PMe_3)_2$ (**6**) was isolated as pale yellow plates in 32% yield. It was characterized by IR and NMR spectroscopy and, most unambiguously, by X-ray structure analysis (Figure 1).

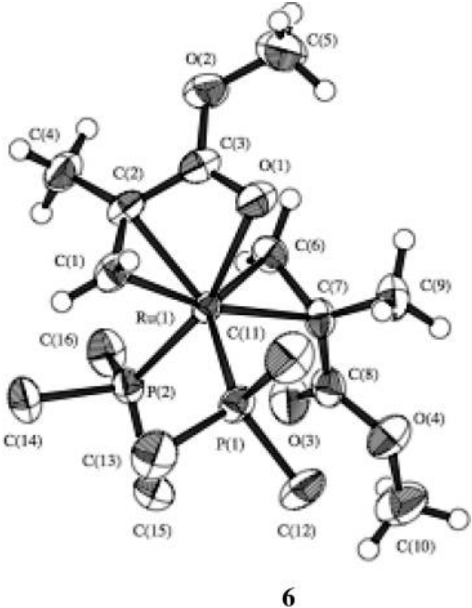


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Figure 1. Molecular structure of Ru(κ^4-*cisoid*-MMA)(η^2-*cisoid*-MMA)$(PMe_3)_2$ (**6**). Hydrogen atoms in the PMe_3 ligands were omitted for clarity. Ellipsoids represent 50% probability. Although two crystallographically independent molecules are observed in a unit cell, one of them is depicted because they are isostructural to each other.

In complex **6**, two MMA fragments are coordinated to the ruthenium center, but the bonding modes are different—κ^4-*cisoid* and η^2-*cisoid*—and the original 1,5-COD fragment has been displaced by two PMe_3 ligands. The bond distances to the side-bonded C═O group of the κ^4-MMA ligand

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(13) Vitulli, G.; Pertici, P.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2255.

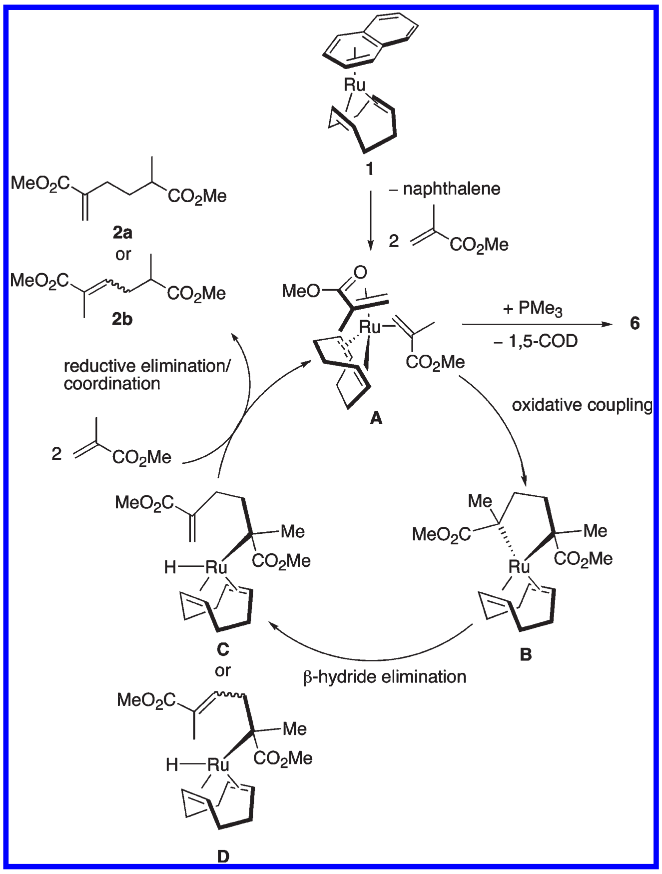
(14) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X.-Q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237.

(15) Bennett, M. A.; Lu, Z.; Wang, X. Q.; Bown, M.; Hockless, D. C. R. *J. Am. Chem. Soc.* **1998**, *120*, 10409.

[Ru(1)−C(3) = 2.448(4) Å and Ru(1)−O(1) = 2.333(2) Å] are significantly longer than those to the C=C group of this ligand [Ru(1)−C(1) = 2.125(3) Å and Ru(1)−C(2) = 2.169(3) Å]. This feature suggests that the κ^4-MMA unit in **6** is close to the η^2-C=C extreme. On the other hand, in the η^2-MMA unit in **6**, the distances Ru(1)−C(6) [2.141(3) Å] and Ru(1)−C(7) [2.221(3) Å] clearly show the η^2-coordination through the C=C bond, while the Ru(1)−C(8) [3.186(3) Å] and Ru(1)−O(3) [3.699(3) Å] distances clearly rule out C=O coordination. In the NMR spectrum of **6** in benzene-d_6, these two MMA fragments were observed separately at room temperature, showing that they do not exchange rapidly on the NMR time scale. Complex **6** does not bring about dimerization (or trimerization) of MMA, when it is heated either alone or in the presence of excess MMA at 70 °C. We believe that complex **6** is obtained as an isolable species by displacement of the 1,5-COD ligand of an active species with PMe_3. It is worth noting that complexes of general formula [Ru(L)(η^2-1,5-COD)(κ^4-MMA)] (L = PMe_3, PEt_3, $P(OMe)_3$) have also been isolated as yellow, crystalline solids from the reaction of **1** with MMA in the presence of the P-donor ligands.[16]

The isolation of complex **6** in the case of MMA and of the ruthenacyclopentane in the case of methyl acrylate[11] are consistent with the catalytic cycle shown in Scheme 1 for dimerization of MMA on Ru(0). In the first step, MMA initiates displacement of the naphthalene ligand in **1** to give Ru(η^2-MMA)$_2$(η^4-1,5-COD) (**A**). Interestingly, the two MMA molecules in complex **6** are coordinated through different prochiral faces (*si* and *re*), whereas the observed *trans*-configuration of the ruthenacyclopentane indicates that the two methyl acrylate molecules coordinate through the same prochiral faces.[11] Although the face selectivity of MMA in the active species is unknown, the oxidative coupling reaction should proceed with retention of configuration to give a ruthenacyclopentane **B**. In this cycle, we believe the 1,5-COD ligand remains attached because (i) addition of 1,5-COD does not affect the catalysis (entry 9 in Table 1), (ii) formation of the "Ru(1,5-COD)" fragment is observed in the stoichiometric reaction, (iii) *in situ* generated naked Ru(0) species by reduction of $RuCl_3\cdot 3H_2O$ with Zn[2e] does not give dimers and trimers of MMA under these conditions at all, and (iv) an analogue of **B** has been isolated in the case of methyl acrylate. Then, successive β-hydride elimination and the reductive elimination release the tail-to-tail dimer **2a** or **2b**. It is noteworthy that the dimerization of MMA occurs under much milder conditions (even at 0 °C) than dimerization of methyl acrylate (at 140 °C) in this system. We believe this is because the α-methyl groups induce facile β-hydride elimination, thus producing the dimer rapidly. Distortion of the ruthenacyclopentane caused by the methyl and methoxycarbonyl groups at the 2- and 5-positions may also promote β-hydride elimination from the methylene protons in the ruthenacyclopentane.[17]

Scheme 1



The dominant trimer in the mixture of trimers also observed in this catalysis was characterized as a *E*/*Z*-mixture of 2,5,8-trimethoxycarbonylnon-4-ene (**3a**) (eq 2). We believe that the formation of **3a** also supports the previously suggested[11] oxidative coupling mechanism for this catalysis, for the following reasons: (i) the yield of **3a** increased with decrease of the exomethylene compound **2a** as described above; (ii) **3a** has the trimer structure that formally formed two C−C bonds at the methylene and the methyl carbons of a MMA molecule, and (iii) **3a** has a C=C bond at the 4-position. These features can best be explained only by co-dimerization between **2a** and MMA, as illustrated in path 1 in Scheme 2, where the tail-to-tail type oxidative coupling reaction between **2a** and MMA gives ruthenacyclopentane **E**, from which subsequent β-hydride elimination and reductive elimination between the hydride and alkyl groups release the trimer **3a**. The predominant formation of **E** over **F** may be caused by the coordination of the methoxycarbonyl groups at the 2- and 5-positions, or the difficulty in achieving the C−C bond formation in the oxidative coupling reaction prevents the formation of ruthenacyclopentane **F**.

An alternative insertion mechanism, in which a MMA molecule inserts into the M−C bond in the ruthenacyclopentane **B**, giving the putative ruthenacycloheptane **G** or **H**, can also be considered. Subsequent β-hydride elimination and reductive elimination between the hydride and alkyl would then give the trimers (path 2). However, it is not possible to account for the formation of compound **3a** from either **G** or **H**. Although we cannot rule out the formation of trimers from intermediates **G** and **H**, the dominant process for the formation of the trimer seems to be the oxidative coupling reaction between **2a** and MMA, which is also consistent with the time course for the formation of **3a** with decrease of **2a**.[18]

Another potential mechanism may be the hydride-insertion mechanism and the C−H bond activation mechanism.

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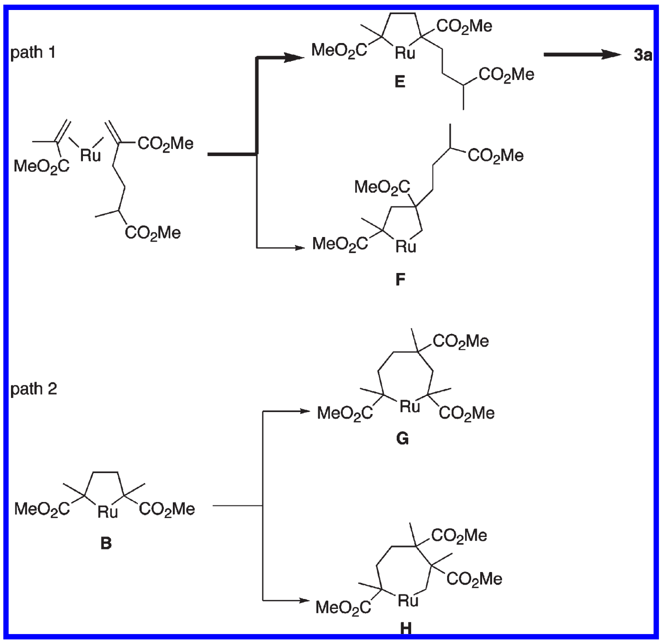
[16] Lu, Z. Ph.D. Thesis, Australian National University, Canberra, 1998.

[17] One of the reviewers mentioned a possibility for the formation of dimers by degradation of the trimer at high temperature because the selectivity of the dimer was increased with increase of the temperature. Because **3a** is thermally stable under these conditions, we can rule out this possibility (see SI Figure S8).

Scheme 2. Possible Pathways for the Formation of 3a[a]



[a] The 1,5-COD ligand is omitted.

Brookhart and his co-workers reported a detailed mechanistic study for dimerization of methyl acrylate promoted by the combination of $[RhCp^*(C_2H_4)_2]$ with a proton.[2d] Although they have proposed the hydride-insertion mechanism with solid evidence, in the present case unexpected protonation of the catalyst precursor, leading to the hydride-insertion mechanism, is less likely because the catalysis in the presence of a large excess of NEt_3 does not give a significant change (Table 1, entry 12). Moreover, Mitsudo and his co-workers proposed the hydride-insertion mechanism for the stoichiometric dimerization of dimethyl fumarate in $Ru(\eta^6$-1,3,5-COT)(η^2-dimethyl fumarate)$_2$ (COT = cyclooctatriene (C_8H_{10})) via intramolecular C−H bond oxidative addition.[19] We believe this is also less likely because it is not possible to account for the formation of **3a** by this mechanism.

In summary, the present work provides a rare example of the catalytic tail-to-tail dimerization of MMA promoted by a Ru(0) precursor that is considered to be carried out by the oxidative coupling mechanism, although the other potential mechanisms cannot be completely excluded. While the dimerization of methyl acrylate promoted by **1** requires high temperature (ca. 140 °C), this process proceeds even at 0 °C. The key step is expected to be the facile β-hydrogen elimination from the α-methyl group and/or the methylene groups in the ruthenacyclopentane ring formed by the oxidative coupling reaction. Further detailed mechanistic studies are now in progress.

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Supporting Information Available: Text, tables, and figures giving full experimental details involving the characterizations of **2a**, **2b**, **3a**, and **6**, crystallographic analyses of **6**, a CIF file giving X-ray crystal data, and time−yield curves for this catalysis at 0 and 70 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Characteristic time−yield curves, initial formation of **2a** followed by increase of **3a** and **2b** with decrease of **2a**, was observed at 0 °C (see SI Figure S7).

(19) Shiotsuki, M.; Suzuki, T.; Kondo, T.; Wada, K.; Mitsudo, T. *Organometallics* **2000**, *19*, 5733.