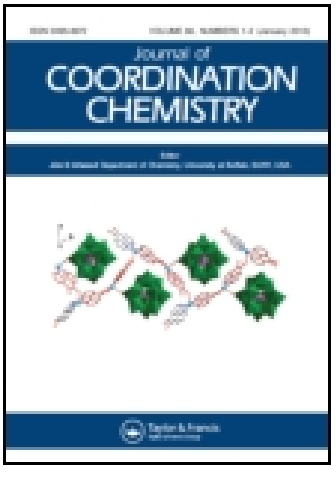

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Tail-to-tail dimerization of methyl acrylate in the presence of triphenylarsine ruthenium complexes

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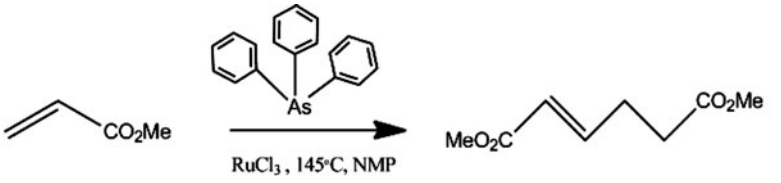

Dimerization of methyl acrylate by ruthenium-based homogenous catalysts. The effect of the addition of supporting ligands on selectivity was studied. Conversion and selectivity were significantly affected by using triphenyl arsine. Possible reaction mechanism to achieve the tail to tail product was discussed.

Catalytic dimerization of methyl acrylate by homogenous ruthenium catalysts was investigated. The effect of the addition of acidic additives, supporting ligands, polymerization inhibitor, and reaction conditions on the selectivity of dimerization was studied, and possible reaction mechanism was discussed. Conversion and selectivity were significantly affected by using triphenylarsine as supporting ligand. Under mild conditions, conversion up to 98% with good selectivity to tail-to-tail product was achieved.

Keywords: Ruthenium complex; Methyl acrylate dimerization; Triphenylarsine; Homogenous catalyst

1. Introduction

The selective tail-to-tail dimerization of acrylic compounds such as methyl acrylate, ethyl acrylate, and acrylonitrile is a profitable way to synthesize an industrially important intermediate, adipic acid [1], which is an intermediate for nylon-66 production, fine chemicals [2], biologically active materials [3], and pharmaceutical materials [4]. Acrylic compounds are easily made from cheap raw materials such as propylene and light alcohols; therefore, it is worthwhile to use these cheap compounds in organic synthesis. Numerous homogeneous and heterogeneous catalysts have been used in these dimerizations, most of which are based on noble metals (Rh [5], Ru [6], Pd [7]), and Ni [8]. For example, Fukuoka *et al.* in 1998 used [Ru(cod)(cot)] and [Ru(cod)(benzene)] as effective catalyst precursors for the tail-to-tail dimerization of acrylonitrile under 25 atmospheres of hydrogen pressure [9]. Methyl acrylate

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also can be smoothly dimerized at 0 °C using a nickel catalyst containing BF_4^- [10]. In 1970, Barlow *et al*. described that palladium complexes can catalyze the linear dimerization of methyl acrylate. They used dichlorobis(benzonitrile) palladium(II) at 113 °C for 23 h and obtained 93% dimerization yield with a very high selectivity, but observed rapid reductive decomposition of the palladium catalyst [11]. Pracejus *et al.* [12] stabilized a similar catalytic system to prolong its lifetime by the addition of Lewis acids and $AgBF_4$ for the complete removal of chloride from the palladium catalyst; however, it was impractical for large scale applications. So far, the most effective catalytic system for dimerization of methyl acrylate is (η^5-1,2,3-trimethylindenyl)-bis(ethene) rhodium in the presence of a proton source, that was developed by Brookhart. This catalytic system operates between room temperature and 60 °C with high selectivity toward tail-to-tail linear dimers; however, after a while, this catalyst is deactivated; therefore, this system requires H_2 pressure to improve the catalyst's lifetime [13]. Among precious metals, ruthenium has been studied extensively in organometallic and coordination chemistry due to its stability and catalytic activities [14]. In 1990, phosphines were used as additives in $Ru_3(CO)_{12}$-catalyzed dimerization reactions in order to raise the yield [15]. Phosphine complexes display good solubility in organic solvents and are compatible with metal ions in multiple oxidation states. They generally do not participate in reactions, except to dissociate from the metal center, and are widely used as ligands in transition metal catalysts [16].

In this article, we have used ruthenium complexes as catalysts for the tail-to-tail dimerization of methyl acrylate; to increase the amount of tail-to-tail dimers, different types of additives such as acids, donor ligands, and reducing agents were examined under a wide range of reaction conditions.

2. Experimental

2.1. *General remarks*

Triruthenium dodecacarbonyl [17], dichlorotris(triphenylphosphine)ruthenium(II) [18], chloro(pentamethylcyclopentadienyl)bis(triphenylphosphine)ruthenium(II) [19], dichloro (*p*-cymene) ruthenium(II) dimer [20], triphenylantimony, and triphenylbismuth [21] were prepared according to literature procedures and characterized by IR spectra. Methyl acrylate, ruthenium(III) chloride hydrate, triphenylphosphine, dodecane, and acids were purchased from Merck and Strem chemical companies. Methyl acrylate and all solvents were dried and distilled under argon. For monitoring reaction products, a gas chromatograph (Agilent Technologies 7890A Instrument) equipped with a HP-1 capillary column, a FID detector, and a mass spectrometer model 5975C with a triple-axis detector was used. Yields of methyl acrylate dimers were obtained with the use of dodecane as an internal standard. Melting points are uncorrected and were obtained with an Electrothermal 9200 melting point apparatus.

2.2. *Synthesis methods*

2.2.1. Synthesis of triphenylarsine. Triphenylarsine was prepared according to previously published methods for synthesis of triphenylantimony [21]. In a round-bottomed, three-necked flask fitted with a separatory funnel, 4 g (0.165 M) of magnesium was suspended into 20 mL of dry diethyl ether; then 10 mL of a mixture of 26 g (0.165 M) dry bromobenzene and 80 mL of dry diethylether was added. The remaining bromobenzene solution was added

during 2 h to the mixture. When the addition was finished, a solution of 9 g (0.05 M) of freshly distilled arsenic trichloride in 30 mL of dry diethylether was added slowly through the separatory funnel and then the mixture was heated on the steam bath for one hour. After cooling the mixture, the reaction mixture was poured slowly, with stirring, into a mixture of ice and water. The hydrolyzed mixture was filtered through a funnel and the residue on the filter extracted with 30 mL of diethyl ether. The aqueous layer was separated and extracted with diethylether. The ether layer was dried and evaporated slowly to 5 mL. After cooling, crystals of triphenylarsine separated. Yield: 65%, m.p. 58–61 °C.

2.2.2. Synthesis of bis(benzaldehyde)dichloro(triphenylarsine)ruthenium, ({[$RuCl_2(AsPh_3)(C_6H_5CHO)_2$]}. ({[$RuCl_2(AsPh_3)(C_6H_5CHO)_2$]} was prepared according to previously published methods with slight modifications [22]. To a solution of ruthenium trichloride hydrate ($RuCl_3.3H_2O$) (0.1 g, 3.8×10^{-4} M) in n-butanol (10 mL, 0.1 M), benzaldehyde (2 mL, 0.02 M) was added. A solution of triphenylarsine (0.6 g, 0.002 M) in n-butanol (5 mL, 0.05 M) was added to the hot solution of ruthenium trichloride. The resulting solution was then refluxed for 2 h. The reaction mixture was cooled overnight and after that, a brownish-yellow crystalline compound was obtained. The compound was separated by centrifugation and washed first with methanol and then with diethylether, and dried under vacuum. Yield: 70%, brownish-yellow crystal, m.p. 188–192 °C, Elemental Anal. Calcd for $C_{35}H_{25}AsCl_2O_2Ru$: C, 55.83; H, 3.66. Found: C, 55.66; H, 3.48. ^1H NMR ($CDCl_3$, δ): 7.31–7.5 (15H, phenyl groups of $AsPh_3$) 7.6–7.9 (8H, phenyl groups of benzaldehyde) 9.87 (2H of aldehyde).

2.2.3. Synthesis of chloro, cyclopentadienyl triphenylphosphine, triphenylarsine ruthenium(II) {[(η^5-C_5H_5)RuCl($AsPh_3$)(PPh_3)]}. A solution of [(η^5-C_5H_5)RuCl(PPh_3)$_2$] [19] (0.5 g, 7×10^{-4} M) and $AsPh_3$ (0.4 g, 1.3×10^{-4} M) in 60 mL benzene was heated to reflux for 24 h. The resulting solution was concentrated to near dryness, the residue extracted by CH_2Cl_2 and the complex precipitated by addition of petroleum ether. It was centrifuged and purified by recrystallization from CH_2Cl_2–petroleum ether. Yield: 75%, orange-yellow crystal, m.p. 140 °C decom. Elemental Anal. Calcd for $C_{41}H_{35}AsClPRu$: C, 63.94; H, 4.58. Found: C, 63.8; H, 4.4. ^1H NMR ($CDCl_3$, δ): 4.1 (5H of Cp) 7.3–7.8 (30H, m, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): 40.1 (s, PPh_3).

Table 1. Dimerization of methyl acrylate catalyzed by $RuCl_3$ and $Ru_3(CO)_{12}$ in the presence of acidic additives.

Run	Acidic additive	Time (h)	Conversion (%)		Selectivity (%)[a]	
			$RuCl_3$	$Ru_3(CO)_{12}$	$RuCl_3$	$Ru_3(CO)_{12}$
1	p-Toluenesulfonic acid	24	95	42	44.2	53.5
2	p-Toluenesulfonic acid	48	68	24	42.7	66.6
3	Methanesulfonic acid	24	70	52	11.4	24.1
4	Methanesulfonic acid	48	47	41	33	33.8
5	Trifluoromethanesulfonic acid	24	44	32	20.2	47.7
6	Trifluoromethanesulfonic acid	48	31	20	22.6	33.3
7	Trifluoroacetic anhydride	24	33	27	52.3	63.3
8	Trifluoroacetic anhydride	48	27	12	439	38.4

Notes: Reaction condition: catalyst (0.06 mM), methyl acrylate (22.2 mM), N-methylpyrrolidone (0.02 mM), hydroquinone (0.1 g).
[a]Selectivity to tail-to-tail product.

2.3. *Catalytic reaction*

All experiments were carried out three times in order to be sure about reproducibility. In a typical experiment, a solution of 0.06 mM metal catalyst, 0.1 g hydroquinone, as polymerization inhibitor, 2 mL N-methyl-2-pyrrolidone, 0.016 mL methanol (if needed), and 2 mL methyl acrylate were heated in a stainless steel reactor. For reactions given in Table 1, 0.076 mM of acidic additives, and for reactions given in Table 3, 0.12 mM of supporting ligands, were added to the reaction mixture. Decane was added as an internal standard, and the products were analyzed by GC–mass spectroscopy.

3. Results and discussion

Catalytic dimerization of methyl acrylate leads to a mixture of linear tail-to-tail dimers of dimethyl hexenedioate (DHD) and branched head-to-tail dimers of dimethyl 2-methylenepentanedioate (MPD), as shown in scheme 1. It is clear that each catalyst system suffers from one or more drawbacks, such as high reaction temperature, short catalyst lifetime, and formation of branched dimers and oligomers. Selectivity to the desired product, linear tail-to-tail dimer, is our main concern in developing an efficient catalytic system.

Various mechanisms for the catalytic dimerization of an olefinic compound with an electron-withdrawing group such as methyl acrylate [5–8] and acrylonitrile [23] were proposed. One possible mechanism is the abstraction of a coordinated ligand to create a vacant site for the coordination of methylacrylate followed by coupling of two methyl acrylates and the formation of a ruthenacyclopentane. Transfer of hydride to carbon bearing the CO_2Me group completes the cycle. Reductive elimination of the ruthenium complex gives the dimer and catalytically active species. In scheme 2, a proposed mechanism for the linear dimerization of methyl acrylate, which is the main product in our reactions, is shown.

We examined different kinds of acidic additives with different pK_a, such as para-toluenesulfonic acid, methanesulfonic acid, trifluoroacetic anhydride, and trifluoromethanesulfonic acid, as cocatalysts with $RuCl_3$ and $Ru_3(CO)_{12}$. According to Table 1, by using CF_3SO_3H, which is the strongest acid (pK_a ~ −12) in this series, conversion reached the lowest amount, in conflict with previously published work [24] where CF_3SO_3H was used in order to activate the dihydridoruthenium(II) complex. Based on their observations, $H_2Ru(PPh_3)_3$ reacts with neat methyl acrylate and the catalytically active ruthenium complex is only formed in the presence of CF_3SO_3H. We conclude that our conversion has a reverse order with the acidity in dimerization reactions. Tembe *et al.* [25] observed that acid addition completely inhibits $Ru(CO)_3(PPh_3)_2$-catalyzed acrylate dimerization, while addition of acid in similar reactions catalyzed by $Ru_3(CO)_{12}$ showed only a small decrease in conversion. An inhibitory effect was also observed by the formation of acrylic acid through hydrolysis of acrylate esters. Acrylic acid can coordinate to ruthenium as a ligand through the carboxylate group, possibly blocking the coordination sites necessary for dimerization. Because of the hygroscopic nature of CF_3SO_3H, the presence of traces of water cannot be excluded. To exclude the effect of moisture, CF_3SO_3H was dried over P_2O_5 prior to each run; however, the deactivation could not be completely prevented.

We observed that by using acidic cocatalyst, $RuCl_3$ has better conversion than $Ru_3(CO)_{12}$. Generally speaking, acidic catalysts show good conversion, at least in some cases, but suffer from low selectivity, as shown in figure 1. Furthermore, prolonging the

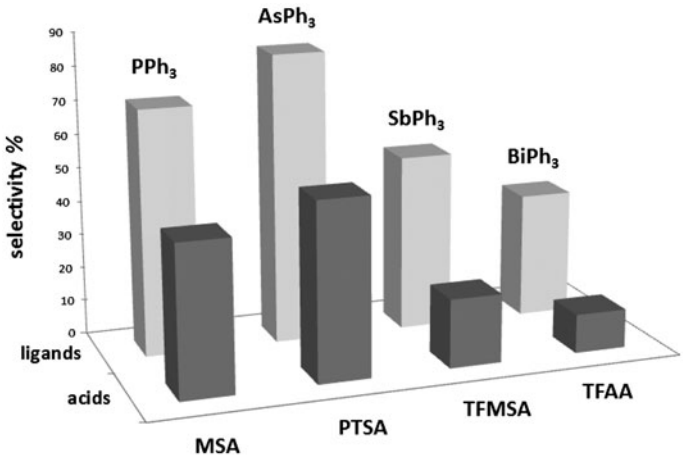
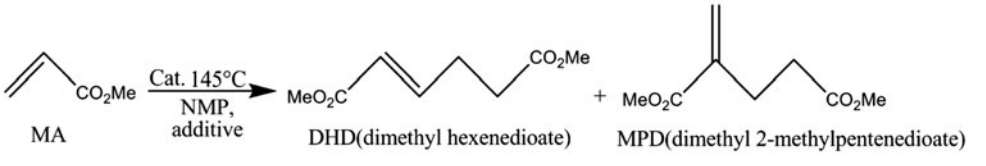


Figure 1. Comparison of selectivity of ligands with different acids (MSA = methanesulfonic acid, PTSA = para-toluenesulfonic acid, TFMSA = trifluoromethanesulfonic acid, TFAA = trifluoroacetic anhydride).

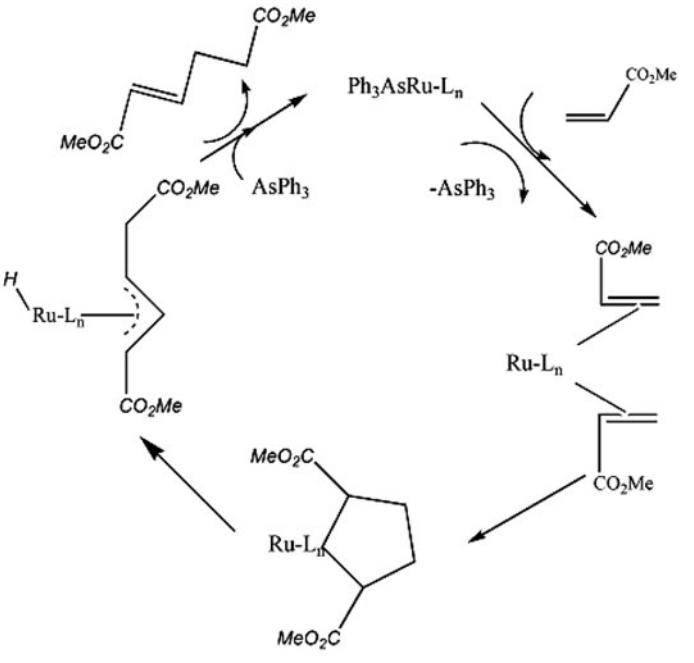


Scheme 1. Dimerization of methyl acrylate.

reaction time for these reactions leads to decrease in conversion probably because of the formation of heavy byproducts.

In order to increase the conversion and selectivity to desired tail-to-tail dimer, we investigated effect of addition of triphenyl pnictogen ligands (PPh_3, $AsPh_3$, $SbPh_3$, $BiPh_3$) with different electronic and steric demands in the course of the catalytic reaction. As shown in the mechanism, free ligands will coordinate and will dissociate to open a coordination site for approaching methyl acrylate. Therefore, the electronic and steric characters of coordinating ligands have strong impact on catalytic activity. This means by modifying electronic character of catalyst species through coordination of ligands with good steric demands, we can tune catalytic activities.

After testing different ruthenium complexes in conjunction with free ligands, we found that $RuCl_3$–triphenylarsine combination displays very high activity and selectivity for the dimerization of methyl acrylate, because of differences in metal-to-pnictogen bond dissociation energy and donor ability of these ligands [26]. Triphenylarsine and triphenylbismuth exhibit lower basicities than triphenylphosphine and triphenylantimony; therefore, arsenic compounds have poorer coordination abilities than the phosphorus and stibine analogs [27]. Triphenylarsine, which has the desired donor ability and bond energy, is found to be the most reactive. Also the cone angles show a decrease as atom becomes heavier, and in general, this will affect how strong it will be as a coordinated ligand; when using PPh_3 as a ligand the coordination site has been blocked more than $AsPh_3$, and this may cause dimers not to reach the space around ruthenium catalyst easily.



Scheme 2. Proposed catalytic cycles for the dimerization of methyl acrylate.

Special activity enhancement of some ruthenium complexes by using triphenylarsine is shown in Table 2. Catalytic activity of ruthenium complexes with different electron counts and coordination numbers was investigated. In the case of 18-electron ruthenium complexes such as $Ru_3(CO)_{12}$, $RuCl(PPh_3)_2Cp$, $RuCl(Cp)(AsPh_3)(PPh_3)$, and $RuH_2CO(PPh_3)_3$, at least one ligand should be dissociated to make a vacant site for coordination of methyl arylate, so we expect lower conversion for these complexes. In the complexes containing triphenylarsine initial triphenylarsine dissociation begins the reaction.

Table 2. Dimerization of methyl acrylate with various ruthenium complexes in the presence of triphenylarsine.

	Complex	Conversion (%)	
		Without $AsPh_3$	With $AsPh_3$
1	$RuCl_3$	18	89
2	$Ru_3(CO)_{12}$	55	82
3	$RuCl_2(PPh_3)_3$	52	79
4	$RuCl(PPh_3)_2Cp$	11	27
5	$[Ru(cymene)Cl_2]_2$	15	33
6	$RuH_2CO(PPh_3)_3$	5	22
7	$RuCl(Cp)(AsPh_3)(PPh_3)$	15	50
8	$RuCl_2(AsPh_3)(C_6H_5CHO)_2$	7	21

Notes: Reaction condition: ruthenium complex (0.06 mM), methyl acrylate (22.2 mM), N-methyl-pyrrolidone (0.02 mM), hydroquinone (0.1 g), $AsPh_3$ (0.12 mM), reaction temperature 145 °C, time 24 h.

For finding optimum reaction condition, further experiments were done by using different amounts of free ligands. The results are shown in Table 3. Dimerization yield and selectivity increases in the order $BiPh_3 < SbPh_3 < AsPh_3 > PPh_3$, suggesting importance of both metal-to-pnictogen bond dissociation energy and donor ability. Effect of $AsPh_3$ on $RuCl_3$ is more than Ru_3CO_{12}, related to close structure of ruthenium carbonyl complex.

We determined that the optimum ratio of ruthenium to $AsPh_3$ is 0.12 mM. When the amount of ligand was increased to 0.15 mM, the conversion and selectivity to tail-to-tail dimers decreased significantly. For increasing conversion, we tested the experiments with 0.12 mM $AsPh_3$ in longer reaction times and found that by prolonging the reaction time, the reaction is completed. As is clear from Table 3, pnictogens were very helpful supporting ligands as they can coordinate to metal center and dissociate to create a vacant site. In other experiments, we used diphosphine ligands such as xantphos, diphenyphosphinopropane, and diphenylphosphinoferrocene, instead of monophosphines; these diphosphines showed no activity for dimerization, probably strongly chelating metal center and blocking free coordination site. Using donor ligands such as $AsPh_3$ and acidic components together in one reaction vessel forms insoluble salt, which may be isolated from the reaction mixture.

Ruthenium trichloride must reduce to a lower oxidation state to have reactivity in this reaction; for this reason, we add a small amount of methanol for reduction of ruthenium. A large amount of methanol is unnecessary because it can inhibit the reaction by competing with free ligands and lower the selectivity; omitting methanol from the reaction mixture, no tail-to-tail products were detected. Solvent has a striking effect on conversion and selectivity. In polar solvents, such as THF and NMP, dimerization proceeds much faster than in nonpolar solvents such as benzene or pentane. In the former two solvents, the reactions were complete after 24 h. Also, with changing from nonpolar to polar solvent (NMP), the ratio of linear (DHD) to branched dimer (MPD) increases from 10 to 84%. We examined different temperatures in the range of 90–170 °C for these catalytic experiments. Under 90 °C, no dimer formation occurred, and above 170 °C, the rate of production of undesired byproducts and catalyst deactivation increased. We found 145 °C as the optimum reaction

Table 3. Dimerization of methyl acrylate catalyzed by $RuCl_3$ in the presence of free ligands.

Run	Ligand	Metal/ligand mole ratio	Time (h)	Conversion (%)	Tail-to-tail dimers/other products
1	–	–	24	11	1.2
2	PPh_3	1	24	43	3.4
3	PPh_3	2	24	62	5.1
4	PPh_3	2	48	71	3.5
5	PPh_3	2.5	24	55	4.2
6	$AsPh_3$	1	24	65	5.7
7	$AsPh_3$	2	24	89	8.8
8	$AsPh_3$	2	48	98	7.2
9	$AsPh_3$	2.5	24	61	5.6
10	$SbPh_3$	1	24	34	3.2
11	$SbPh_3$	2	24	52	4.5
12	$SbPh_3$	2	48	58	3.3
13	$SbPh_3$	2.5	24	40	4.2
14	$BiPh_3$	1	24	21	3.2
15	$BiPh_3$	2	24	37	4.5
16	$BiPh_3$	2	48	43	3.3
17	$BiPh_3$	2.5	24	32	4.2

Notes: Reaction condition: $RuCl_3$ (0.06 mM), methyl acrylate (22.2 mM), N-methylpyrrolidone (0.02 mM), hydroquinone (0.1 g), methanol (0.039 mM), reaction temperature 145 °C.

temperature. All experiments were performed in two different reaction times, 24 and 48 h, and conversion increased and selectivity to DHD decreased in longer reaction times.

4. Conclusion

Here, we used a new catalytic system based on ruthenium complexes to improve the yield of tail-to-tail methyl acrylate dimerization. High conversion and good selectivity for dimethyl hexenedioate was obtained in the presence of $AsPh_3$ as supporting ligand. This new catalytic system showed better selectivity than previously reported methods using acidic additives. Up to 90% selectivity to tail-to-tail product was obtained. Further examinations on dimerization of acrylonitrile by this methodology are in progress.

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