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Ruthenium-mediated selective head-to-tail dimerization of acrylic and α,β-unsaturated carbonyl compounds: generation of an acrylate-hydride complex $C_5Me_5Ru(PCy_3)(CH_2=CHCO_2Et)H$

Chae S. Yi *, Nianhong Liu

Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881, USA

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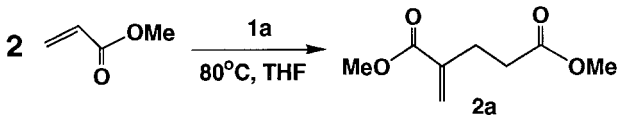
Abstract

The ruthenium-hydride complex $C_5Me_5Ru(PCy_3)H_3$ (**1a**) was found to be a selective catalyst precursor for the head-to-tail dimerization of acrylic and α,β-unsaturated carbonyl compounds to produce bifunctional 1,5-dicarbonyl compounds. A new ruthenium species $C_5Me_5Ru(PCy_3)(CH_2=CHCO_2Et)H$ (**6a**) was independently generated from the substitution reaction of **1a** with ethyl acrylate. The exclusive formation of the head-to-tail dimers suggested that, the tertiary phosphine, generated from the substitution reaction of **6a** with an olefin, was the active species for the dimerization reaction. © 1998 Elsevier Science S.A.

Keywords: Head-to-tail dimerization of acrylic compounds; Ruthenium-hydride complexes

1. Introduction

The transition metal-catalyzed dimerization of acrylic compounds has been extensively studied as an alternate way of forming commercially important hexendioates and adiponitriles [1–9]. [1] Currently, Brookhart's cationic rhodium catalyst is the most active system for the selective tail-to-tail dimerization of acrylates, and the mechanism of this dimerization reaction has been well-established [10]. In contrast to the tail-to-tail dimerization, however, the synthetic utility for the head-to-tail dimerization of acrylic compounds has been limited due to low selectivity and yields on the dimeric products [5–9]. While tertiary phosphines are known to catalyze the head-to-tail dimerization of acrylates, the reactions typically require elevated temperatures and often yield mixtures of dimeric and oligomeric products [4–9]. Selective head-to-tail dimerization of acrylic compounds would in principle produce bifunctional 1,5-dicarbonyl compounds, a useful class of substrates in aldol-type condensation and other annulation reactions [14,15]. Herein, we report the ruthenium-mediated selective head-to-tail dimerization of acrylic and α,β-unsaturated carbonyl compounds to produce 1,5-dicarbonyl compounds and the formation of ruthenium acrylate-hydride intermediate species.



2. Results and discussion

We recently reported that the ruthenium-hydride complexes $C_5Me_5(L)RuH_3$ (L=PCy_3 (**1a**), PPh_3 (**1b**), PMe_3 (**1c**)) [16–18] were effective catalysts for the dimerization of terminal alkynes [19]. The same ruthe-

* Corresponding author.

[1] For leading examples on the metal-catalyzed tail-to-tail dimerization reactions, see Refs. [10–13].

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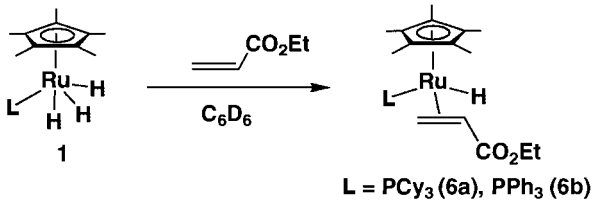
Table 1
The ruthenium complex **1a**-catalyzed dimerization of acrylic and α,β-unsaturated carbonyl compounds[a]

Entry	Olefin substrate	Product	Yield (%)
1	$CH_2=CHCO_2Me$	**2a**	91
2	$CH_2=CHCO_2Et$	**2b**	86
3	$CH_2=CHCOMe$	**3**	88
4	$CH_2=CHCHO$[b]	**4**[c]	57[d]
5	$CH_2=CHCN$	**5**[c]	73

[a]Reaction conditions: THF (5 ml); 4–8 mmol of an alkene; 3–5 mol% of the catalyst **1a**; 80°C; 24 h. The isolated product yield after a simple silica gel column chromatography.
[b]The commercial olefin substrate contained ~3% of water and 0.1% of hydroquinone.
[c]Approximately 10–20% of white polymeric products was formed.
[d]The yield was determined by the ^{1}H NMR.

nium-hydride complex **1a** was found to be a selective catalyst precursor for the dimerization of acrylic compounds. In a typical catalytic reaction, a THF (5 ml) solution of **1a** (10 mg, 0.019 mmol) and an excess of methyl acrylate (0.7 ml, 7.8 mmol) was stirred at 80°C for 24 h. The branched dimer **2a** (91%) was isolated after a simple column chromatography on a silica gel (3: 1 hexanes/Et_2O). The structure of **2a** was established from the observation of two vinyl proton resonances at δ 6.04 and 5.31 ($J_{gem}\sim 1$ Hz) by the ^{1}H NMR and the detection of M^+ ($m/z=172$) by the GC-MS. [2] An analogous dimerization reaction of ethyl acrylate by **1a** also yielded **2b** in 86% yield. No other dimeric or oligomeric products has been detected during an NMR tube reaction of **1a** and methyl acrylate in C_6D_6 as monitored by ^{1}H NMR in the temperature range of 25–75°C. The catalysts **1b** and **1c** were inactive toward the catalytic dimerization of methyl acrylate under similar reaction conditions, giving mostly recovered starting materials after 3 days.

Some functional group tolerance have been observed toward the dimerization of other olefins. The dimerization reactions of methyl vinyl ketone, acrolein, and acrylonitrile by **1a** exclusively produced the branched dimers **3**, **4** and **5**, respectively, with good to high yields (Table 1, [2]). None of the head-to-head dimers or higher oligomers was detected by the ^{1}H NMR, but 10–20% of the polymeric products was formed during the dimerization of acrolein and acrylonitrile (entries 4 and 5). The dimerization reactions of the substituted acrylates such as methyl methacrylate and *trans*-ethyl crotonate, methyl butenoate, and *N,N*-dimethylacrylamide by **1a** failed to give dimeric products under similar reaction conditions. The metal-catalyzed tail-to-tail dimerization of acrolein has recently been reported [13].



The hydrogen ligand in ruthenium-polyhydride complexes are well known to interconvert between the η^2-H_2 and the classical metal-hydride coordination modes [19–23], and we thought that the hydride ligand of **1a** could be substituted by an acrylate ligand. The treatment of **1a** (50 mg, 0.096 mmol) and 5 equivalents of ethyl acrylate in C_6D_6 at 80°C for 4 h cleanly produced the new metal-hydride species along with the hydrogenated ethyl propionate (~10%). The new ruthenium-hydride signal at δ −10.31 (d, $J_{P-H}=36.8$ Hz) and the diastereotopic OCH_2 proton resonances at δ 4.34 and 4.07 (dq, $J=11.4$, 7.4 Hz) by ^{1}H NMR were consistent with the acrylate-hydride complex **6a** (81% yield by NMR), but the olefinic proton peaks were completely masked by the cyclohexyl group. To establish the coordinated olefin resonances, PPh_3-substituted **6b** was prepared from an analogous reaction of **1b** with ethyl acrylate. In this case, the ^{1}H NMR of **6b** clearly exhibited the coordinated olefinic resonances at δ 1.76 (d, $J=10.0$ Hz), 1.68 (br t, $J=7.1$ Hz) and 1.26 (dd, $J=10.0$, 7.1 Hz) along with the Ru-H resonance at δ −10.15 (d, $J_{PH}=36.0$ Hz). Both **6a** and **6b** were stable in solid state at room temperature under N_2 atmosphere, but the complexes slowly decomposed in C_6D_6 solution ($t_{1/2}\sim 2$ days).

The independently formed **6a** was subsequently shown to be active toward the catalytic dimerization of acrylic compounds. The treatment of **6a** (50 mg, 0.081 mmol) with an excess of ethyl acrylate (0.3 ml, 4.2 mmol) in 5 ml of C_6H_6 solution at 80°C produced the dimer **2b** in a similar rate as before (>95% conversion after 24 h). Initially, a new ruthenium species was formed along with free PCy_3 at the expense of the resonances due to **6a**. The spectroscopic data of the new ruthenium species suggested of the olefin complex **7**, [3] but its structure could not be unambiguously assigned due to the masked resonances by PCy_3 group and the

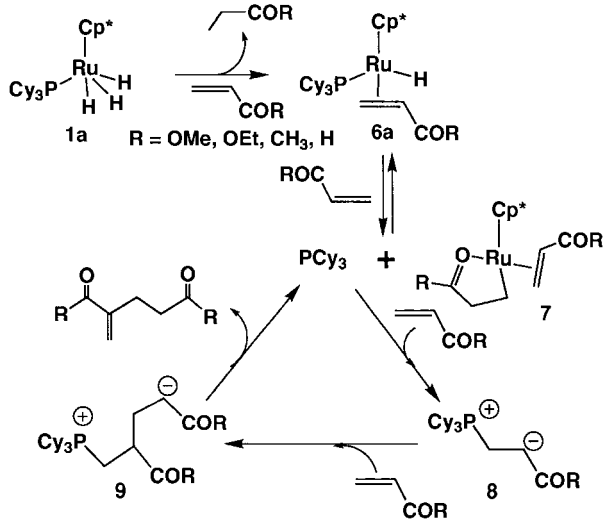
[2] The spectroscopic data for some of these compounds have been previously reported in Refs. [5–9].

[3] Selected spectroscopic data for **7**: ^{1}H NMR (C_6D_6, 300 MHz) δ 3.96 (q, $J=7.2$ Hz, $CO_2CH_2CH_3$), 1.49 (s, C_5Me_5) olefinic protons were masked by cyclohexyl group. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 173.9 (CO_2Et), 86.3 (C_5Me_5), 60.1 ($CO_2CH_2CH_3$), 9.7 ($CO_2CH_2CH_3$), 9.2 (C_5Me_5), olefinic carbons were overlapped with cyclohexyl group.

dimer **2b**. Several attempts to isolate this species thus far have been unsuccessful. Similar dimerization reaction of ethyl acrylate by **6b** failed to yield any dimeric products under a similar reaction condition, although the dimerization of methyl vinyl ketone by **1b** yielded approximately 10% of the dimeric product **3** after 3 days.

A series of control experiments was conducted using PCy_3 as a catalyst to compare the activity with that of **1a**. In general, the catalytic activity of PCy_3 toward the dimerization reaction of acrylic compounds was considerably lower than **1a**. For example, the dimerization of methyl acrylate catalyzed by PCy_3 (6 mg, 0.02 mmol) under otherwise same reaction condition resulted in 49% of the product **2a** after 24 h. Much less dimeric products ($\sim$10%) were isolated in the PCy_3-catalyzed reactions of methyl vinyl ketone, acrolein and acrylonitrile, as in these cases, gave mostly insoluble polymeric products.

Both the formation of the head-to-tail dimers **2**–**5** and the generation of the acrylate-hydride **6** suggest the mechanism as illustrated in Scheme 1. It is well-established that the tertiary phosphines selectively catalyzed the head-to-tail dimerization of acrylic compounds [3,5–9]. In this case, the exclusive formation of the head-to-tail dimers **2**–**5** suggests that the dimerization reaction was probably catalyzed by the free phosphine PCy_3 generated during the reaction. The substitution of another olefin substrate from the acrylate complex **6a** would generate free PCy_3 and the ruthenium complex **7**. Sterically demanding and soft PCy_3 ligand should favor the 1,4-addition to the olefin substrate to form the zwitterionic intermediate **8**. The similar mechanism involving zwitterionic phophonium intermediate has been commonly proposed in phosphine-catalyzed dimerization reactions [3]. Addition of another acrylate molecule and the 1,3-hydrogen migration and the elimination of PCy_3 from **9** would yield the head-to-tail dimers.



Scheme 1. A plausible mechanism of the ruthenium-mediated head-to-tail dimerization of acrylic compounds.

The reasons for higher activity and selectivity of **1a** compared to the phosphine-catalyzed reactions toward the dimerization of acrylic compounds are not clear. One possible explanation is that the ruthenium complex might be involved in controlling the phosphine concentration during the reaction. Initially, the equilibrium between the acrylate-hydride **6a** and **7** would be shifted toward the generation of free PCy_3 when the monomer concentration is high. Toward end of the reaction, the acrylate concentration would become low as most of the monomer was converted to the dimer, and the equilibrium would be shifted back toward **6a**, thereby minimizing the secondary and other side reactions catalyzed by free PCy_3. The PCy_3-substituted **1a** was much better catalyst than **1b** because sterically demanding and nucleophilic PCy_3 ligand would be readily dissociated from **6a** under relatively mild reaction conditions.

In summary, the bifunctional 1,5-dicarbonyl compounds **2**–**5** have been selectively obtained from the ruthenium-mediated head-to-tail dimerization of acrylic and α,β-unsaturated carbonyl compounds. Catalytically active acrylate-hydride complex **6a** was successfully generated from the substitution reaction of **1a** with an acrylate compound. The exclusive formation of the head-to-tail dimers suggested that the free PCy_3 was the active species during the dimerization reaction. Further studies on improving the catalytic activity and on understanding a detailed reaction mechanism are currently in progress.

3. Experimental

3.1. General

All materials were manipulated in an inert-atmosphere glove box or by standard high vacuum and Schlenk line techniques unless otherwise mentioned. Tetrahydrofuran and benzene were distilled from purple solutions of sodium and benzophenone immediately prior to use. C_6D_6 was dried from activated molecular sieves (4 Å). The ruthenium complexes $C_5Me_5Ru(L)H_3$ (L=PCy_3 (**1a**), PPh_3 (**1b**), PMe_3 (**1c**)) were prepared according to literature procedures [16–18]. The olefin compounds were received from the commercial sources and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass Spectra were recorded on a Hewlett-Packard HP 5970 GC/MS spectrometer or on a FAB-MS spectrometer (Center of Mass Spectrometry, Washington University). Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

3.2. General experimental procedure for the catalytic dimerization reaction of acrylic compounds

In a 25 ml Teflon-joint Schlenk tube equipped with a magnetic stirring bar, the ruthenium complex **1a** (10 mg, 0.019 mmol) and C_6Me_6 (internal standard, 10 mg) were dissolved in 5 ml of dried THF. Excess alkene monomer (7–8 mmol) was added via a syringe to the solution. The reaction mixture was stirred for 24 h in an oil bath at 80°C under a closed system. After the solution was cooled to room temperature, a small sample was drawn out from the solution for GC-MS analysis. Volatiles were removed under a vacuum. The dimeric organic product was isolated by the column chromatography on a silica gel (hexanes: Et_2O = 3: 1).

$CH_2=C(CO_2Me)CH_2CH_2CO_2Me$ (**2a**). ^1H NMR (C_6D_6, 300 MHz): δ 6.04 (s, C*H*H=), 5.31 (s, CH*H*=), 3.38 (s, $=CCO_2CH_3$), 3.34 (s, $CH_2CO_2CH_3$), 2.31 (t, J = 7.4 Hz, $=CCH_2$), 2.26 (t, J = 7.4 Hz, $CH_2CO_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 172.4 ($=CCO_2Me$), 166.7 (CH_2CO_2Me), 139.5 ($CH_2=C$), 125.4 ($CH_2=C$), 51.4 ($=CCO_2CH_3$), 51.0 ($CH_2CO_2CH_3$), 32.9 ($CH_2CO_2CH_3$), 27.6 ($=CCH_2$). GC-MS m/z = 172 (M^+).

$CH_2=C(CO_2Et)CH_2CH_2CO_2Et$ (**2b**). ^1H NMR (C_6D_6, 300 MHz): δ 6.09 (s, C*H*H=), 5.31 (s, CH*H*=), 3.93 (q, J = 7.4 Hz, $=CCO_2CH_2CH_3$), 3.90 (q, J = 7.4 Hz, $CH_2CO_2CH_2CH_3$), 2.58 (t, J = 7.4 Hz, $=CCH_2$), 2.34 (t, J = 7.4 Hz, $CH_2CO_2CH_2CH_3$), 0.94 and 0.93 (t, J = 7.4 Hz, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 172.0 ($=CCO_2Et$), 166.2 (CH_2CO_2Et), 139.8 ($CH_2=C$), 125.1 ($CH_2=C$), 60.5 ($=CCO_2CH_2CH_3$), 60.1 ($CH_2CO_2CH_2CH_3$), 33.2 (CH_2CO_2Et), 27.5 ($=CCH_2$), 14.2 and 14.1 ($CO_2CH_2CH_3$). GC-MS m/z = 200 (M^+).

$CH_2=C(COCH_3)CH_2CH_2COCH_3$ (**3**). ^1H NMR (C_6D_6, 300 MHz): δ 5.45 (s, C*H*H=), 5.35 (s, CH*H*=), 2.47 (t, J = 7.4 Hz, CH_2COCH_3), 2.15 (t, J = 7.4 Hz, $=CCH_2$), 1.89 (s, $=CCOCH_3$), 1.62 (s, CH_2COCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 206.0 ($=CCOMe$), 198.4 (CH_2COMe), 148.0 ($CH_2=C$), 125.3 ($CH_2=C$), 42.1 (CH_2COCH_3), 29.2 ($=CCH_2$), 25.4 ($=CCOCH_3$), 25.3 (CH_2COCH_3). GC-MS m/z = 140 (M^+).

$CH_2=C(CHO)CH_2CH_2CHO$ (**4**). ^1H NMR (C_6D_6, 300 MHz): δ 9.12 (s, $=CCHO$), 9.08 (CH_2CHO), 5.49 (s, C*H*H=), 5.16 (s, CH*H*=), 2.20 (t, J = 7.4 Hz, CH_2CHO), 1.88 (t, J = 7.4 Hz, $=CCH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 199.4 ($=CCHO$), 193.1 (CH_2CHO), 133.5 ($CH_2=C$), 127.6 ($CH_2=C$), 41.5 (CH_2CHO), 20.8 ($=CCH_2$). GC-MS m/z = 112 (M^+).

$CH_2=C(CN)CH_2CH_2CN$ (**5**). ^1H NMR (C_6D_6, 300 MHz): δ 5.27 (s, C*H*H=), 5.00 (s, CH*H*=), 1.67 (t, J = 5.2 Hz, $=CCH_2$), 1.63 (t, J = 5.2 Hz, CH_2CN). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 132.3 ($CH_2=C$), 119.4 ($CH_2=C$), 117.7 ($=CCN$), 117.3 (CH_2CN), 29.8 ($=CCH_2$), 15.4 (CH_2CN). GC-MS m/z = 106 (M^+).

3.3. General procedure for $C_5Me_5Ru(L)(CH_2=CHCO_2Et)H$ (L = PCy_3 (6a), PPh_3 (6b))

In a 25 ml Teflon-joint Schlenk tube equipped with a magnetic stirring bar, the ruthenium-hydride complex **1** (1.63 mmol) and 10 equiv. of an acrylate compound (16.3 mmol) were mixed in 10 ml of C_6H_6. The reaction mixture was stirred at 80°C for 12 h under a closed vessel. The solvent was removed under a high vacuum. The resulting brown residue was triturated with ~5 ml of Et_2O, and the precipitate was washed several times with a small amount of Et_2O. Recrystallization from Et_2O (~5 ml) at −78°C gave **6** as an analytically pure pale-yellow solid (52–60% yield).

For **6a**: ^1H NMR (C_6D_6, 300 MHz): δ 4.34 (dq, J = 11.4, 7.4 Hz, OC*H*HCH$_3$), 4.07 (dq, J = 11.4, 7.4 Hz, OCH*H*CH$_3$), 2.20–1.00 (m, Cy), 1.86 (s, C_5Me_5), 0.98 (t, J = 7.4 Hz, OCH_2CH_3), −10.31 (d, J_{P-H} = 36.8 Hz, Ru–H), olefinic protons were masked by Cy group. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 178.5 (CO_2Et), 94.0 (C_5Me_5), 59.9 ($CO_2CH_2CH_3$), 38.9 (d, J = 22.0 Hz, Cy), 30.6 ($CH_2=CH$), 30.3, 28.2, and 27.1 (Cy), 26.4 ($CH_2=CH$), 15.1 ($CO_2CH_2CH_3$), 11.0 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.6 MHz). δ 63.8. FAB-MS m/z = 618 (M^+). Anal. Calcd. for $C_{33}H_{57}O_2PRu$: C, 64.15; H, 9.30. Found C, 65.06; H, 9.05.

For **6b**: ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.70–7.30 (m, Ph), 4.07 (dq, J = 11.1, 7.4 Hz, OC*H*HCH$_3$), 3.95 (dq, J = 11.1, 7.4 Hz, OCH*H*CH$_3$),1.76 (d, J = 10.0 Hz, CH*H*=CH), 1.68 (br t, $J = J_{P-H}$ = 7.1 Hz, C*H*H=CH), 1.52 (s, C_5Me_5), 1.26 (dd, J = 10.0, 7.1 Hz, $CH_2=CH$), 1.21 (t, J = 7.4 Hz, OCH_2CH_3), −10.15 (d, J_{H-P} = 36.0 Hz, Ru-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 177.4 (CO_2Et), 136.0, 135.4, 134.4 and 129.1 (Ph), 94.9 (C_5Me_5), 58.8 ($CO_2CH_2CH_3$), 33.6 ($CH_2=CH$), 28.5 ($CH_2=CH$), 15.0 ($CO_2CH_2CH_3$), 10.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.6 MHz): δ 74.8. FAB-MS m/z = 600 (M^+). Anal. Calcd. for $C_{33}H_{39}O_2PRu$: C, 66.09; H, 6.55. Found C, 65.90; H, 6.71.

Acknowledgements

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