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Dimerization of methyl acrylate by homogeneous transition metal catalysis. Part II *. Activation of dihydridoruthenium(II)phosphane complexes by CF_3SO_3H

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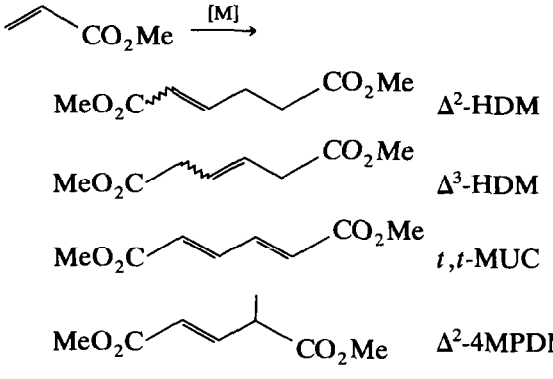
Abstract

The tail-to-tail dimerization of methyl acrylate (MA) in the presence of $H_2Ru(PPh_3)_4$ (1) or $H_2(CO)Ru(PPh_3)_3$ (2) and CF_3SO_3H to give a mixture of linear dimers is described. In neat methyl acrylate at 85°C the reaction shows turnover numbers of 300 in 20 h and 640 in 7 d. Mechanistic studies show that the initial step of the reaction is the reduction of $H_2Ru(PPh_3)_4$ (1) by MA to form $Ru(MA)_2(PPh_3)_2$ (5). After activation with CF_3SO_3H the catalytically active species contains only one phosphane ligand. The basic mechanistic features of the dimerization reaction have been revealed by ^2H NMR spectroscopy involving the use of CF_3SO_3D. The deuterium-labelling studies indicate the intermediate formation of a ruthenium(II) hydride complex. Subsequent olefin insertions in this complex, followed by β-hydride elimination, lead to the linear dimeric products.

Key words: Ruthenium; Methyl acrylate; Catalysis; Transition metals; Nuclear magnetic resonance; Phosphane complexes

1. Introduction

The tail-to-tail dimerization of methyl acrylate or acrylonitrile provides an attractive route to bifunctional C_6 compounds that are precursors for adipic acid or hexamethylenediamine, intermediates in Nylon-6,6 production. The transition-metal catalyzed dimerization of methyl acrylate [eqn. (1)] yields a mixture of 2- and 3-hexene-1,6-dioic acid dimethyl ester, 2,4-hexadiene-1,6-dioic acid dimethyl ester and 4-methylpentene-1,5-dioic acid dimethyl ester. This reaction [eqn. (1)] has been reported for various catalytic systems based on Ni [2,3], Pd [4–13], Rh [14–17] and Ru [18–21]. Most of these systems require the use of Lewis acids as co-catalysts or of other additives to initiate the dimerization. Up to now, ruthenium catalysts have been generated rather unspecifically from $RuCl_3$ or $Ru_3(CO)_{12}$ and various additives *in situ*.



(1)

Recently, we reported the dimerization of methyl acrylate in the presence of $RuH(CO)Cl[P(^iPr)_3]_2$ and $AgCF_3SO_3$ [1]. The silver salt activates the ruthenium–hydride complex by removal of the chloro ligand. This provides a free ligand site for π coordination of methyl acrylate prior to its insertion into the metal–hydrogen bond.

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TABLE 1. Dimerization of MA with various ruthenium complexes activated by CF_3SO_3H

Ru complex		Reactant ratio	TON [a]	Time (h)	Dimer distribution (%)				
		Ru/MA/H^+			t-Δ^2-HDM	c-Δ^2-HDM	t-Δ^3-HDM	c-Δ^3-HDM	t-Δ^2-4MPDM
$H_2Ru(PPh_3)_4$	(1)	1.0:910:3.2	310	20	89.6	5.3	3.9	1.0	< 0.2
			640 [b]	168	90.4	5.0	3.5	0.9	< 0.2
$H_2RuCO(PPh_3)_3$	(2)	1.0:940:3.9	62	24	89.7	7.4	1.2	0.3	1.4
$H_2Ru(PPh_2Me)_4$	(3)	1.0:620:4.2	0	20	–	–	–	–	–
$Ru(MA)_2(PPh_3)_2$	(5)	1.0:800:1.3	290	24	91.1	5.7	3.0	< 0.2	traces

[a] Turnover number (TON) = n(dimer)/n([Ru]). [b] Addition of further 1080 equiv. MA after 24 h.

Dihydridotetrakis(triphenylphosphane)ruthenium (II) (**1**), or its ruthenium–dihydride derivatives, are known to be active catalysts or catalyst precursors for a wide range of reactions such as hydrogenation [22], hydroformylation [23], hydrogen transfer [24], CC-coupling [25] and polymerization [26]. In view of the versatility of $H_2Ru(PPh_3)_4$ and prompted by the fact that metal–hydrido species have been postulated as catalytically active intermediates in the dimerization of methyl acrylate, we have begun a systematic study of the dimerization of methyl acrylate catalyzed by $H_2Ru(PPh_3)_4$ and some of its derivatives. Here, we describe a detailed analysis of the behaviour of $H_2Ru(PPh_3)_4$ as a catalyst precursor.

2. Results and discussion

The complex $H_2Ru(PPh_3)_4$ (**1**) reacts with neat methyl acrylate (MA) to yield a deep red solution which turns bright yellow on addition of more than 3 equiv. of CF_3SO_3H. At 85°C this solution leads to a mixture of linear tail-to-tail dimers (> 99%), whose main component is *trans*-2-hexene-1,6-dioic acid dimethyl ester (t-Δ^2-HDM) (Table 1). Dimethyl muconate (t,t-MUC), the branched dimer 2-methylenepentane-1,5-dioic acid dimethyl ester, and trimers of methyl acrylate are only formed in traces. After 20 h, the turnover number (TON) is ca. 300. Prolonging the reaction for 7 d increases the TON to 640. We have not been able to confirm that $H_2Ru(PPh_3)_4$ initiates the polymerization of methyl acrylate as reported by Komiya *et al.* [26].

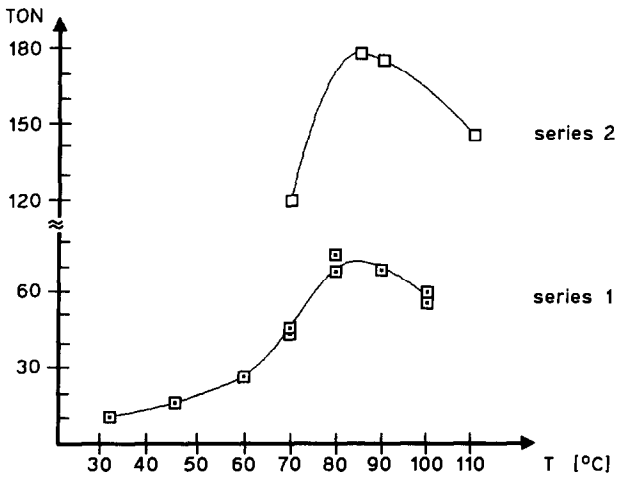


Fig. 1. Turnover numbers (TON) for the catalytic dimerization of MA with $H_2Ru(PPh_3)_4/CF_3SO_3H$ as a function of temperature (⊡ Ru/MA/H^+ = 1.0:1070:3.4, 6 h; □ Ru/MA/H^+ = 1.0:860:3.7, 20h).

Under the same conditions, *i.e.* reaction in neat methyl acrylate and activation with 3–4 equiv. of CF_3SO_3H (Table 1), methyl acrylate is also dimerized by $H_2RuCO(PPh_3)_3$ (**2**), with a turnover number of 60 in 24 h. In contrast, $H_2Ru(PPh_2Me)_4$ (**3**) showed no catalytical activity.

Since the $H_2Ru(PPh_3)_4/CF_3SO_3H$ system displayed the highest activity in the dimerization of methyl acrylate, it has been studied in more detail.

2.1. The effect of temperature

The effect of temperature on the rate of dimerization was studied in the range 32–110°C. The experiments were carried out in such a manner that for each series a stock solution containing $H_2Ru(PPh_3)_4$, methyl acrylate and CF_3SO_3H was prepared. Aliquots were taken from each stock solution in order to avoid any

TABLE 2. Effect of CF_3SO_3H concentration on the dimerization of MA in the presence of $H_2Ru(PPh_3)_4$ (**1**) at 85°C

Entry No.	Reactant ratio Ru/MA/H^+	Reaction time (h)	TON	TON (h^{-1})
1	1.00:990	1 [a]	1 [b]	
2	1.00:906:1.77	24	27	1.1
3	1.00:880:3.03	18	178	9.9
4	1.00:963:3.63	20	176	8.8
5	1.00:908:4.11	24	198	8.2
6	1.00:936:4.27	22	173	7.7
7	1.00:864:5.50	17	67	3.9
8	1.00:936:6.81	22	81	3.7
9	1.00:917:12.3	17	54	3.1

[a] No further conversion, reaction terminated after 1 h. [b] Formation of t-Δ^2-HDM and MUC (1:1).

changes in component concentration. The reaction times were 6 h and 20 h for the first and second series, respectively. The formation of dimers was observed over the whole range of temperatures, with an optimum temperature of *ca.* 85°C (Fig. 1).

2.2. The influence of CF_3SO_3H

The effect of the activator concentration was determined at several ratios of [Ru]/[CF_3SO_3H] (Table 2). When the acid was omitted, only the dimers Δ^2-HDM and *t,t*-MUC were produced in stoichiometric amounts in a 1:1 ratio. Thus, the catalytically active ruthenium complex is only formed in the presence of CF_3SO_3H. The highest TON was achieved by adding slightly more than 3 equiv. of CF_3SO_3H. An increase in the amount of CF_3SO_3H to the ratio $H^+/Ru > 4:1$ resulted in decreased turnover numbers.

2.3. Reaction profile

A typical concentration–time profile for the products is shown in Fig. 2. The initial turnover frequency was 20 h^{-1}. The five isomeric dimers were produced in a constant ratio, the rate of dimer formation decreasing continuously during the progress of the reaction. This can be attributed to a continuous decrease in the amount of the catalytically active ruthenium complex. Further addition of methyl acrylate in order to lower the dimer concentration or viscosity of the solution had no effect on the overall TON.

2.4. The effect of additives

In order to elucidate the scope of this catalytic system and to find the reason for the deactivation, we carried out a series of reactions to explore the effect of various additives added to the solution after the activation step. The results obtained are listed in Table 3.

2.4.1. The role of PPh_3

As was shown earlier $H_2Ru(PPh_3)_4$ (**1**) reacts in neat methyl acrylate to give $Ru(MA)_2(PPh_3)_2$ (**5**) with the liberation of PPh_3 [27]. In the presence of CF_3SO_3H, the phosphane is converted into the phosphonium salt **4** [eqn. (2)], which may be isolated from the reaction mixture (see Experimental details).

$$MA + PPh_3 + CF_3SO_3H \longrightarrow \underset{\textbf{(4)}}{\left\{Ph_3P\!\!\sim\!\!\sim\!\!CO_2CH_3\right\}^+} \{CF_3SO_3\}^- \quad (2)$$

There is evidence (see below) that in the dimerization of methyl acrylate activation by $H_2Ru(PPh_3)_4$ (**1**) requires the removal of 3 equiv. of PPh_3 (via reaction 2) and protonation of the resulting ruthenium complex; thus 3–4 equiv. of CF_3SO_3H are necessary. Therefore, if external PPh_3 is added it consumes CF_3SO_3H and lowers the catalytic activity. Addition of the phosphonium salt **4** has no effect on the catalytic activity.

TABLE 3. Effect of additives on the dimerization of MA in the presence of $H_2Ru(PPh_3)_4$ (**1**) and CF_3SO_3H at 85°C

Entry No.	Reactant ratio Ru/MA/H^+	Additive	No. of equiv.	Reaction time (h)	TON
1	1.0:960:3.6	PPh_3	1.2	8	4
2	1.0:960:3.6	H_2O	16.2	20	22
3	1.0:910:3.4	CH_2CHCO_2H	6.5	72	46
4	1.0:800:3.4	CH_3CO_2Na	2.6	24	6
5	1.0:810:3.8	CH_3CO_2H	5.1	24	24
6	1.0:910:3.2 [a]	**4**	2.5	27	350
7	1.0:910:3.2 [a]	MeOH	6.0	20	310
8	1.0:910:3.2 [a]	–	–	26	360

[a] CF_3SO_3H dried over P_2O_5 prior to use.

Because of the hygroscopic nature of CF_3SO_3H, the presence of traces of water cannot be excluded. For this reason, we also examined the influence of water. An inhibitory effect was observed as well as the formation of acrylic acid. As acrylic acid shows the same inhibitory effect as water, it can be assumed that the actual influence of water is due to acrylic acid formed by the hydrolysis of methyl acrylate. Acrylic acid can coordinate to ruthenium as a η^2 ligand through the carboxylate group [22], possibly blocking the coordination sites necessary for the dimerization process. The similar effects of sodium acetate and acetic acid support this assumption. To exclude the effect of moisture, CF_3SO_3H was dried over P_2O_5 prior to each run, and this resulted in an increase in the reaction rate and in the maximum TON. However, the deactivation could not be completely prevented.

Systems for methyl acrylate dimerization based on $RuCl_3 \cdot 3H_2O$ require methanol [17,18]. In our system the presence of methanol was unnecessary, and its addition to the reaction mixture had no effect.

2.5. Mechanistic studies

$H_2Ru(PPh_3)_4$ (**1**) reacted in neat methyl acrylate (MA) to yield a deep red solution of $Ru(MA)_2(PPh_3)_2$ (**5**) [27]. ^1H NMR and ^{31}P NMR spectroscopy revealed that 1 equiv. of methyl acrylate was hydrogenated, with release of 2 equiv. of triphenylphosphane [eqn. (3)].

$$\underset{\textbf{(1)}}{H_2Ru(PPh_3)_4} + 3MA \xrightarrow[5\ min]{20°C} \underset{\textbf{(5)}}{Ru(MA)_2(PPh_3)_2} + 2PPh_3 + CH_3CH_2CO_2CH_3 \quad (3)$$

The complex $Ru(MA)_2(PPh_3)_2$ (**5**) was isolated in 82%

yield as a yellow, fairly air-stable powder. The properties of this new olefin–ruthenium(0) complex **5** and the structure of a mono-aqua adduct of **5** have been reported recently [27]. The formation of $Ru(MA)_2(PPh_3)_2$ (**5**) indicates that ruthenium was reduced by methyl acrylate to oxidation state zero and that no ruthenium hydride was present prior to activation with CF_3SO_3H. However, since $Ru(MA)_2(PPh_3)_2$ (**5**) exhibited catalytic activity only after the addition of slightly more than 1 equiv. of CF_3SO_3H (Table 1), complex **5** as well as $H_2Ru(PPh_3)_4$ must be a precatalyst for the dimerization. In the absence of CF_3SO_3H, only stoichiometric amounts of the dimers Δ^2-HDM and MUC (molar ratio 1 : 1) were obtained.

After the addition of 3.5 equiv. of CF_3SO_3H the ^1H NMR and ^{31}P NMR spectra of the catalytic mixture from $H_2Ru(PPh_3)_4$ in neat methyl acrylate showed that 3 equiv. of the phosphonium salt **4** [^1H NMR δ: 3.97 ppm (dt, $-PCH_2-$); 2.96 (dt, $-CH_2CO_2-$) ppm; ^{31}P NMR δ: 26.6 ppm] had been formed, and that the fourth equivalent of PPh_3 was still coordinated to ruthenium. This analysis involved the assumption that the sum of all the ^{31}P signals corresponded to the 4 equiv. of PPh_3 originally bound to Ru in $H_2Ru(PPh_3)_4$. In addition to the singlet due to the phosphonium salt **4**, five additional singlets were found in the range δ 22–72 ppm, indicating the presence of several ruthenium phosphane complexes. It is, therefore, reasonable to postulate that the catalytically active ruthenium species contain one triphenylphosphane ligand. We present a rationalization of the activation of $H_2Ru(PPh_3)_4$ by CF_3SO_3H in eqn. (4).

$$\underset{(1)}{H_2Ru(PPh_3)_4} \xrightarrow[-CH_3CH_2CO_2CH_3]{MA} \underset{(5)}{Ru(MA)_2(PPh_3)_2} + 2PPh_3$$

$$\underset{(5)}{Ru(PPh_3)_2(MA)_2} + 2PPh_3 + 3CF_3SO_3H \xrightarrow{H^+,\,MA} \underset{(6)}{\{RuPPh_3(MA)_n\}} + 3[Ph_3P^+CH_2CH_2CO_2CH_3][CF_3SO_3^-] \quad (4)$$

The ^1H NMR spectra provided no evidence for any acidic hydrogens. Thus, it may be assumed that the protons arising from excess CF_3SO_3H were consumed by the ruthenium phosphane complexes to give cationic ruthenium hydride complexes. Presumably, complexes **6** are the species that are protonated, giving **7** [eqn. (5)].

$$\underset{(6)}{\{RuPPh_3(MA)_n\}} + CF_3SO_3H \xrightarrow{MA} \underset{(7)}{\{HRuPPh_3(MA)_n^+\}} + \{CF_3SO_3^-\} \quad (5)$$

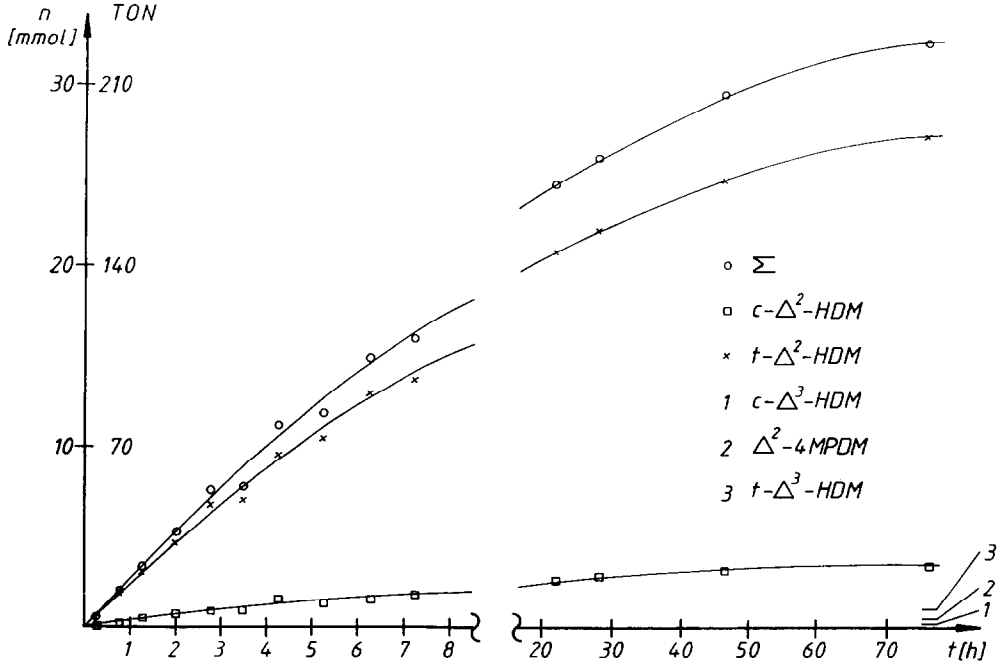


Fig. 2. Reaction profile for methyl acrylate dimerization in the presence of $H_2Ru(PPh_3)_4$ and CF_3SO_3H.

The existence of complexes such as **7** could not be verified directly by ^{1}H NMR spectroscopy because no hydride signals were observed in the expected region (< 0 ppm). However, the absence of a high-field signal does not necessarily exclude the intermediate formation of a ruthenium hydride species, because the short-lived cationic hydride complexes might possibly react rapidly by insertion of a π-coordinated methyl acrylate to give a ruthenium alkyl complex **8** [eqn. (6)].

$$\underset{(7)}{\{HRuPPh_3(MA)_n^+\}} \rightleftharpoons \underset{(8)}{\{Ph_3P(MA)_{n-1}Ru(CH_2CH_2CO_2CH_3)^+\}} \quad (6)$$

The intramolecular insertion of a coordinated olefin into a transition metal hydride bond is usually a very facile process compared with that into a metal–carbon bond [28]. Because of this, the second insertion reaction to give the 6C unit must be rate-determining. Hence, the stationary concentration of ruthenium alkyl complexes **8** should be higher than that of the ruthenium hydride complexes **7**. A weak multiplet in the ^{1}H NMR spectrum at δ 1.8 ppm, presumably due to ($RuCH_2CH_2$–), might be an indication of the presence of such a complex. If ruthenium hydride complexes **7** are formed by the oxidative addition of CF_3SO_3H to the ruthenium phosphane complexes **6** [eqn. (5)], the acid will be the activator as well as a co-catalyst for the dimerization.

^{31}P NMR spectra taken during the progress of the dimerization reaction indicated that the concentration of phosphonium salt **4** increased continuously. The ^{31}P NMR spectra of several deactivated catalysis mixtures showed that all the phosphane ligands had been converted into the phosphonium salt. Formal reductive elimination of **4** from **8** seems to be responsible for deactivation of the catalyst. The formal description of the deactivation as a reductive elimination process is not necessarily related to the actual mechanism of the reaction. Since an increase in the concentration of CF_3SO_3H ($H^+/Ru > 4:1$) resulted in lower turnover numbers, the deactivation reaction (a reaction in competition with the dimerization) must be bimolecular. Realizing that the catalytically inactive complex derives from the loss of PPh_3 and H^+, we tried to re-activate the catalysis by the addition of PPh_3 (in order to generate a ruthenium phosphane complex), followed by addition of CF_3SO_3H; however re-activation could not be achieved in this way.

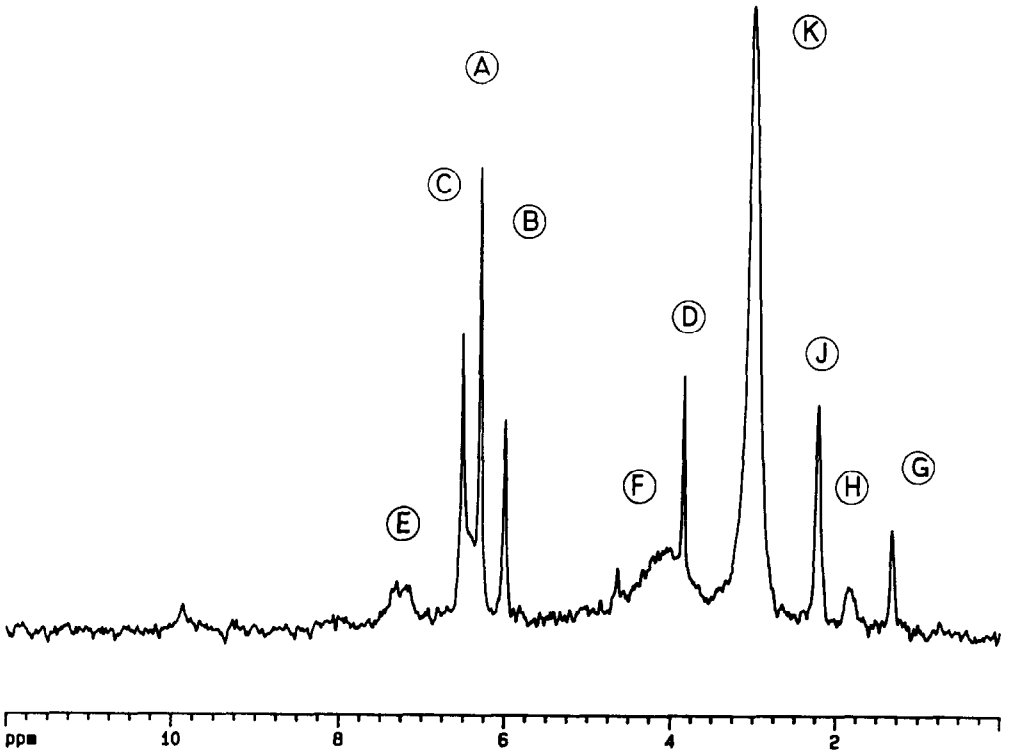


Fig. 3. ^{2}H NMR spectrum of the catalysis mixture $[H_2Ru(PPh_3)_4]/[CF_3SO_3D] = 1.0:3.5$ after 1 h.

2.6. Deuterium labelling studies

In order to determine the role of the acid in the catalytic cycle, we carried out a deuterium labelling study using CF_3SO_3D. The deuterium distribution during catalysis (Fig. 3) and the incorporation of deuterium into the resulting dimers (Fig. 4) was followed by ^2H NMR spectroscopy.

If it is assumed that isotopic exchange at the methoxy group of methyl acrylate does not occur, this group may be taken as the internal standard. In the presence of CF_3SO_3D alone, a very slight isotopic exchange was observed. The deuterium ratio $^2H(\beta cis)/^2H(\alpha)/^2H(\beta trans)/^2H(CH_3) = 1:1:1:3$ (natural abundance) changed to 1.9:1.3:1.5:3.0 after 1 h. The signal from the acidic deuteron of CF_3SO_3D appeared at δ 14.0 ppm.

The ^2H NMR spectrum (Fig. 3) of the catalytic mixture ($Ru/D^+ = 1:3.5$) may be interpreted in terms

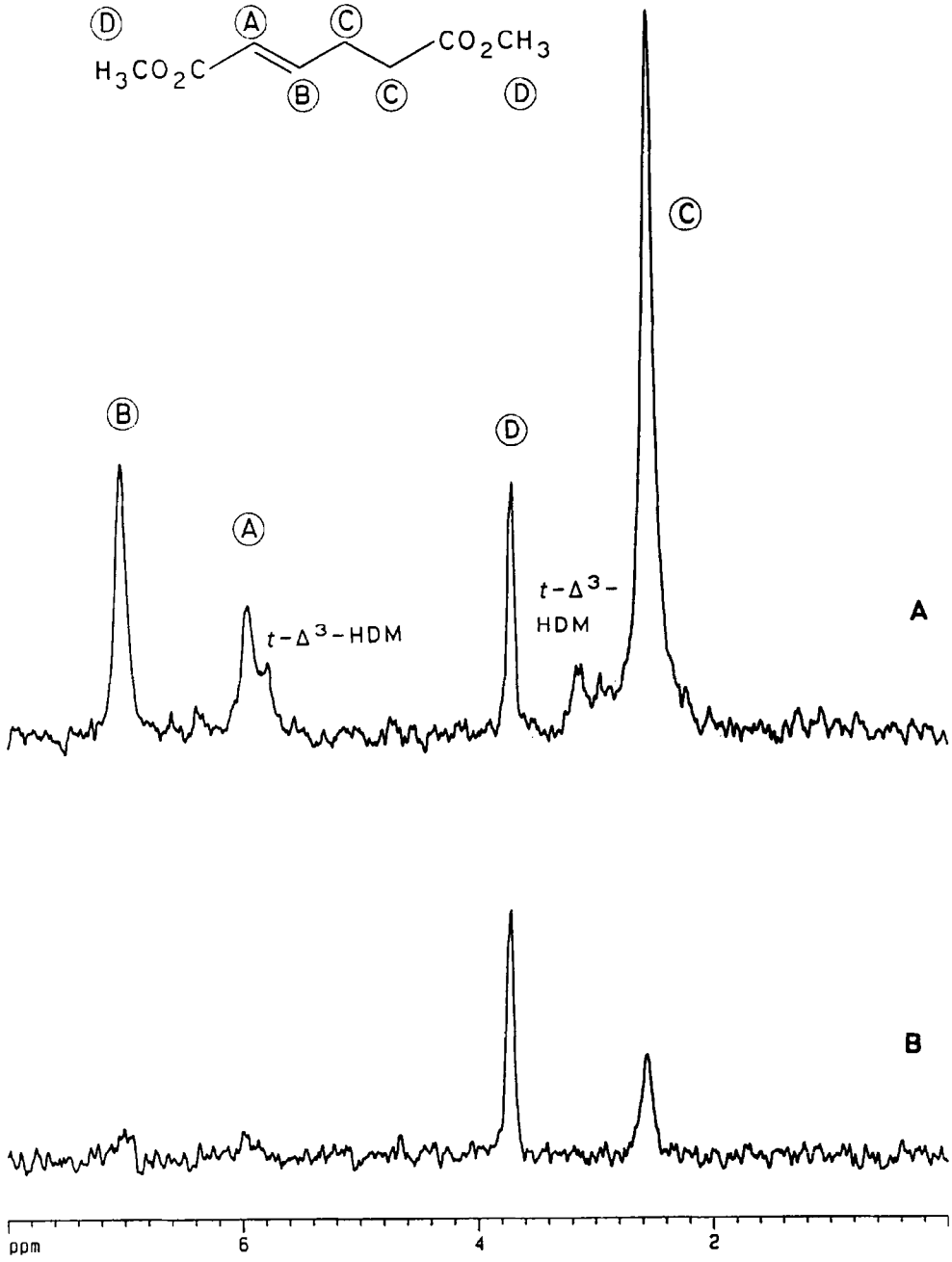
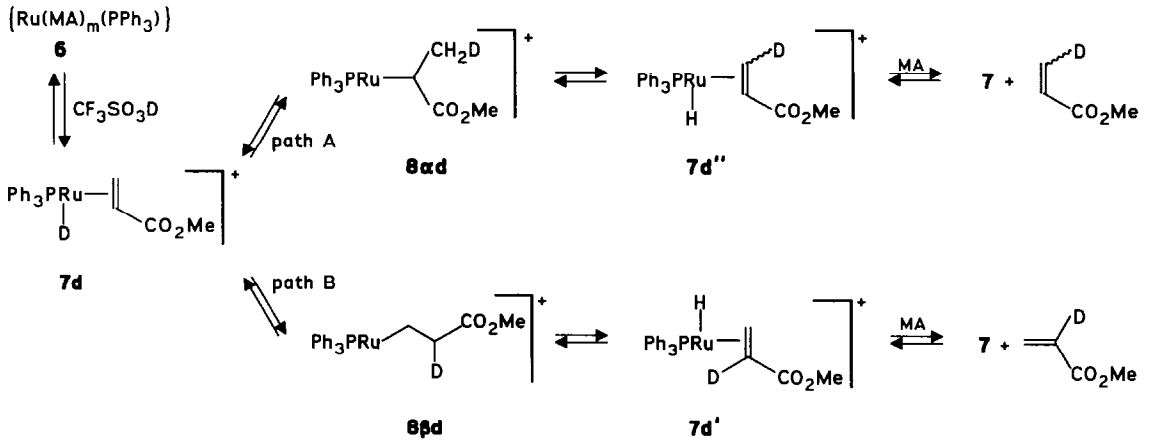


Fig. 4. ^2H NMR spectra of the dimers of MA. (**A**) Catalysis with CF_3SO_3D. (**B**) Catalysis with CF_3SO_3H.

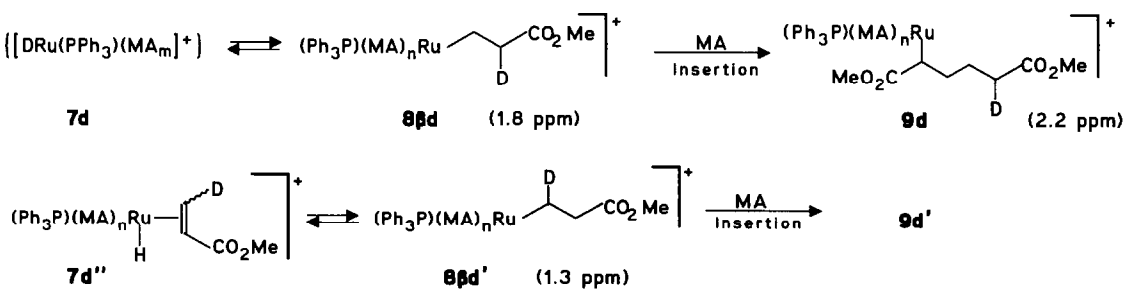


Scheme 1.

of Schemes 1 and 2. By comparison with the integral signal of the methoxy group (D) of methyl acrylate, the ^2H NMR spectrum indicated a significant increase in the deuterium content at the α-(A) as well as at the β-carbon atom (B, C) of methyl acrylate. The ^2H NMR spectrum displays a ratio $^2H(\beta cis)/^2H(\alpha)/^2H(\beta trans)/^2H(CH_3)$ of 5:8:3:3 after 1 h. As the acid immediately reacts to form the phosphonium salt **4d** and no signal from the surplus acidic deuteron at δ 14 ppm can be observed, the isotope exchange reaction must be catalyzed by ruthenium. This can be regarded as an indication of the intermediate formation of a ruthenium hydride complex **7d**. Methyl acrylate can insert into the ruthenium–deuteride bond of **7d** in two ways [28] (Scheme 1). *Anti*-Markownikov addition (path B) leads to β-methoxycarbonylethylruthenium (**8βd**), a primary alkyl ruthenium complex. The secondary alkyl ruthenium complex **8αd** is formed by Markownikov addition (path A). The reverse reaction, β-hydride elimination, leads to the incorporation of deuterium into methyl acrylate if hydrogen (^1H) is removed from **8αd** or **8βd**. The observed deuterium distribution after 1 h suggests that the isotope exchange process occurs via both pathways (Scheme 1).

A broad signal (F in Fig. 3) at δ 3.5–4.5 ppm may be assigned to a π-coordinated methyl acrylate involved in the isotopic exchange process. The signals at δ 1.3 ppm (G) and δ 1.8 ppm (H) are attributed to the methylene groups of the insertion complexes **8βd** or **8βd'** or to the methyl group of an insertion complex **8αd**. This assignment is based on a comparison with literature data. For example, the ^1H NMR spectrum of the analogous primary ruthenium–alkyl complex $(Ph_3P)_2$-(Cl)(CO)Ru($CH_2CH_2CO_2CH_3$) exhibited a triplet at δ 1.95 ppm for the methylene group β to ruthenium ($RuCH_2CH_2$–) and a broad triplet at δ 1.25 ppm for the methylene group in the α position ($RuCH_2$–) [29]. In the secondary alkyl iron complex $Cp(Ph_3P)(CO)Fe$-$CH(CH_3)CN$, the methyl group was observed at δ 1.3 ppm [30] (Scheme 2).

Signal J at δ 2.2 ppm (Fig. 3) may be assigned to a methylene group of a second ruthenium alkyl complex **9d** (or **9d'**) formed by the insertion of methyl acrylate into the ruthenium carbon bond of **8βd** (or **8βd'**) (Scheme 2). Relative to the dimers (Δ^2-HDM) whose methylene groups appear at δ 2.6 ppm, these groups are shifted to high field by *ca.* 0.4 ppm as a result of coordination to ruthenium.



Scheme 2.

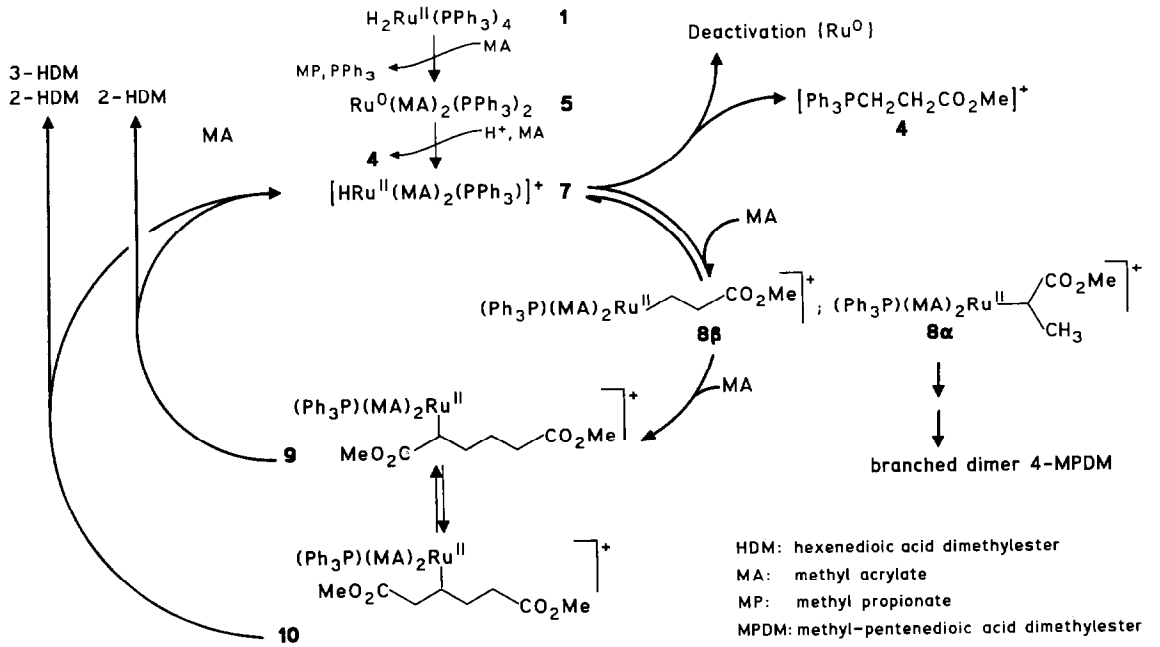
The deuterium atom of the phosphonium salt **4d** (δ 3.0 ppm) exhibited the most intense signal (K). Signals corresponding to the triphenylphosphane ligands (deuterium in natural abundance) appear in the range δ 7.0–7.5 ppm (E).

The ^{2}H NMR spectra of the dimeric esters (89% t-Δ^2-HDM) obtained with CF_3SO_3D (spectrum A) and CF_3SO_3H (spectrum B) are shown in Fig. 4. Spectrum A shows the incorporation of deuterium at positions A–C. The largest fraction of the deuterium is found at the methylene carbon atoms (increased by a factor of 11). Owing to the identical chemical shifts of the two methylene groups, no data can be given for the isotope distribution at these positions. Deuterium incorporation was also found at the methine carbon atoms (A, B). Relative to the methoxy group (D), the deuterium content was increased by a factor of six and eight for α (A) and β position (B), respectively. Thus, the isotopic exchange reaction must be much faster than the insertion of the second methyl acrylate molecule.

2.7. *Mechanistic conclusions*

The results of the deuterium labelling study are summarized in Scheme 3. The complex $H_2Ru(PPh_3)_4$ (**1**) reacts with methyl acrylate to give the ruthenium(0) complex $Ru(MA)_2(PPh_3)_2$ (**5**). Oxidative addition of CF_3SO_3H to **5** with formation of the phosphonium salt **4**, produces a cationic ruthenium(II) hydride complex **7** bearing one phosphane ligand. Insertion of a π-coordinated methyl acrylate, in a *cis* orientation with respect to the hydride, into the Ru–H bond produces the α- or β-(methoxycarbonyl)ethylruthenium(II) intermediate **8**α or **8**β, respectively. According to the information obtained from the isotopic exchange reaction, this insertion is reversible. Irreversible insertion of a second π-coordinated methyl acrylate into the Ru–C bond of **8**β produces the 1,4-di(methoxycarbonyl)butylruthenium(II) intermediate **9**. The latter complex can isomerize to **10** by β-H elimination and re-insertion into the newly formed Ru–H bond. Finally, β-H elimination from **9** or **10** yields Δ^2-HDM or Δ^3-HDM and the ruthenium(II) hydride complex **7**. Although the secondary ruthenium alkyl complex **8**α is formed, only traces of the branched dimer 4-MPDM are produced. Hence, insertion of methyl acrylate into the Ru–C bond of **8**α or **9** to form branched dimers or trimers is inhibited, probably by steric effects. Deactivation of the ruthenium alkyl species **8** occurs by formal reductive elimination of the phosphonium salt **4**. During catalysis the active ruthenium species **7**–**10** have a formal +2 oxidation state. Therefore, cationic ruthenium(II)–hydride or –alkyl complexes should be active catalysts for the dimerization of methyl acrylate provided free coordination sites are available for the coordination of methyl acrylate prior to its insertion (Scheme 3).

In contrast to $H_2Ru(PPh_3)_4$ (**1**), $H_2Ru(Ph_2Me)_4$ (**3**) shows no catalytic activity in the dimerization reaction because it does not react with methyl acrylate. As a



Scheme 3. Ruthenium-catalyzed dimerization of methyl acrylate with **1** and/or **5**.

consequence, ruthenium is not reduced to the zero oxidation state, a necessary step for the formation of the catalytically active species. In contrast to $H_2Ru(PPh_2Me)_4$ (3), $H_2Ru(PPh_3)_4$ (1) dissociates in solution by release of one phosphane ligand, producing a coordinatively unsaturated species [31]. This process is necessary for initiating the reaction since methyl acrylate can now π-coordinate prior to its insertion into the Ru–H bond [29]. Owing to the stability of 3 towards ligand dissociation, CF_3SO_3H should react with this complex to give a cationic ruthenium(II) complex, probably $\{Ru(PPh_2Me)_2(MA)_n^{2+}\}\{CF_3SO_3^-\}_2$ [22]. Formal oxidative addition of CF_3SO_3H would produce a ruthenium(IV) species and not a ruthenium hydride complex of +2 oxidation state which seems to be necessary for the dimerization.

3. Experimental details

All manipulations were carried out under dry argon using standard Schlenk tube techniques. Complexes $H_2Ru(PPh_3)_4$ (1) [32], $H_2(CO)Ru(PPh_3)_3$ (2) [33] and $H_2Ru(PPh_2Me)_4$ (3) [34] were prepared as previously described. Methyl acrylate was dried over calcium hydride, distilled and stored under argon. CF_3SO_3H was dried over P_2O_5 and distilled (fraction: b.p. 42°C/133 Pa) prior to use. MeOH was dried over Mg. ^1H, ^2H, $^{31}P\{^1H\}$ and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer. Assignment of the various resonances was achieved by ^1H, ^1H COSY, ^1H, ^{13}C COSY and ^{13}C (BB, DEPT 135, DEPT 90) spectra.

3.1. Typical preparation of a catalyst mixture

To the red solution of 348.0 mg (0.302 mmol) of $H_2Ru(PPh_3)_4$ and 41.6 mg (0.327 mmol) of hydroquinone monoethyl ether in 21.9 ml (243 mmol) of methyl acrylate was added 142.6 mg (0.951 mmol) of CF_3SO_3H (Table 3, Run 8). The yellow solution was stored for 26 h at 85°C. Product formation was monitored by GLC (capillary column SE 52 [25 m × 0.32 mml]). Diethyl ether (*ca.* 20 ml) was added to the deactivated solution to precipitate the crystalline phosphonium salt 4. After removal of diethyl ether and residual methyl acrylate, distillation at 64–72°C 66 Pa gave 18.1 g (105 mmol) of dimers (TON 350; by GC TON 360). Catalyst mixtures with other ruthenium complexes (Table 1) were prepared similarly. Additives were always added after the CF_3SO_3H.

The dimers were identified by ^1H NMR and ^{13}C NMR spectra, including (^1H, ^1H) and (^1H, ^{13}C) COSY spectra, and by comparison with published MS data [35].

Dimer *t*-Δ^2-HDM: $C(1)H_3C(2)O_2C(3)HC(4)HC(5)H_2C(6)H_2C(7)O_2C(8)H_3$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.96 (dt, ^1H, H^4, $^3J(H^3, H^4) = 15.68$ Hz, $^3J(H^4, H^5) = 6.69$ Hz); 5.87 (dt, 1H, H^3, $^4J(H^3, H^5) = 1.65$ Hz); 3.731 (s, 3H, H^1); 3.694 (t, 3H, H^8, $^5J(H^6, H^8) = 0.24$ Hz); 2.46–2.59 (m, 4H, H^5, H^6) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 172.67 (C^7); 166.74 (C^2); 146.96 (C^4); 121.89 (C^3); 51.77 (C^1); 51.49 (C^8); 32.23 (C^6); 27.24 (C^5) ppm.

Dimer *c*-Δ^2-HDM: $C(1)H_3C(2)O_2C(3)HC(4)HC(5)H_2C(6)H_2C(7)O_2C(8)H_3$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.26 (dtt, 1H, H^4, $^3J(H^4, H^3) = 11.45$ Hz, $^3J(H^4, H^5) = 7.45$ Hz, $^4J(H^4, H^6) = 0.27$ Hz); 5.85 (dt, 1H, H^3, $^3J(H^3, H^4) = 11.46$ Hz, $^4J(H^3, H^5) = 1.69$ Hz); 3.718 (s, 3H, H^1); 3.686 (t, 3H, H^8, $^5J(H^6, H^8) = 0.25$ Hz); 2.96 (tdd, 2H, H^5, $^3J(H^5, H^4) = {}^3J(H^5, H^6) = 7.36$ Hz, $^4J(H^5, H^3) = 1.69$ Hz); 2.49 (br t, 2H, H^6) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 173.10 (C^7); 166.48 (C^2); 148.00 (C^4); 120.52 (C^3); 51.66 (C^1); 51.13 (C^8); 33.15 (C^6); 24.32 (C^5) ppm.

Dimer *t*-Δ^3-HDM: $C(1)H_3C(2)O_2C(3)H_2C(4)HC(5)HC(6)H_2C(7)O_2C(8)H_3$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 5.70 (m (ddd), 2H, H^4, H^5, $^3J(H^4, H^5) = 5.52$ Hz, $^3J(H^3, H^4) = 3.87$ Hz, $^4J(H^3, H^5) = 1.65$ Hz); 3.72 (s, 6H, H^1,H^8); 3.10 (m, 4H, H^3,H^6) ($A_2A'_2XX'$ system) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 171.93 (C^2, C^7); 125.99 (C^4, C^5); 51.83 (C^1, C^8); 37.66 (C^3, C^6) ppm.

Dimer *c*-Δ^3-HDM: $C(1)H_3C(2)O_2C(3)H_2C(4)HC(5)HC(6)H_2C(7)O_2C(8)H_3$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 5.79 (m, 2H, H^4, H^5); 3.68 (s, 6H, H^1, H^8); 3.13 (m (dd), 4H, H^3, H^6) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 171.6 (C^2, C^7); 124.55 (C^4, C^5); 51.93 (C^1, C^8); 32.86 (C^3, C^6) ppm.

Phosphonium salt 4: $\{Ph_3PC(5)H_2C(6)H_2C(7)O_2C(8)H3\}\{C(9)F_3SO_3\}$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.81–7.66 (m, 15H, PPh_3); 3.71 (dt, 2H, H^5, $^2J(P, H^5) = 12.71$ Hz, $^3J(H^5, H^6) = 7.18$ Hz); 3.47 (3H, s, CH_3); 2.79 (dt, 2H, H^6, $^3J(P, H^6) = 16.09$ Hz, $^3J(H^5, H^6) = 7.18$ Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 170.46 (C^7, d, $^3J(P,C^7) = 11.30$ Hz); 135.35 (C^4, d, $^4J(P, C^4) = 3.07$ Hz); 133.42 (C^2, d, $^2J(P, C^2) = 10.20$ Hz); 130.58 (C^3, d, $^3J(P, C^3) = 12.65$ Hz); 120.74 (C^9, q, $^1J(F, C^9) = 320.7$ Hz); 117.33 (C^1, d, $^1J(P, C^1) = 86.53$ Hz); 52.40 (C^8, s); 26.70 (C^6, d, $^2J(P, C^6) = 3.14$ Hz); 17.75 (C^5, d, $^1J(P,C^5) = 55.39$ Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) δ: 25.16 (s) ppm. Analysis: $C_{23}H_{22}F_3O_5PS$ requires: C, 55.42; H, 4.45%. Found: C, 55.46; H, 4.34%.

Phosphonium salt 4d: $\{Ph_3PC(5)H_2C(6)HDC(7)O_2C(8)H_3\}\{C(9)F_3SO_3\}$: ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.76 (dd, $^2J(P,H^5) = 12.7$ Hz, $^3J(H^5, H^6) = 7.1$ Hz); 2.84 (dt, 1.16 H, H^6, $^3J(P, H^6) = 16.3$ Hz, $^3J(H^5, H^6) = 7.1$ Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.55 (C^6 (CHD), td, $^1J(D, C^6) = 18.7$ Hz, $^2J(P, C^6) = 3.2$ Hz) ppm.

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