Journal of Organometallic Chemistry, 385 (1990) 173–184
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20424

Rhodium catalyzed dimerization of vinyl ketones. NMR study of the dynamic behaviour of intermediate η^2- and η^4-methyl vinyl ketone complexes of rhodium(I)

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(Received September 20th, 1989)

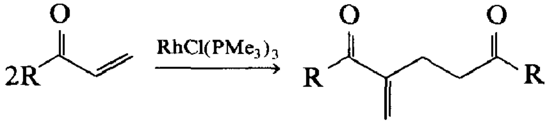
Abstract

The equilibrium between five-coordinated Rh^I π-complexes I–VI is established at −35 °C in organic solvents (acetone, MeCN, MeOH) containing $RhCl(PMe_3)_3$ and methyl vinyl ketone (MVK). The structures and dynamic behaviour of complexes I–VI in solution have been studied by ^1H, ^{31}P and ^{35}Cl NMR spectroscopy. The nature of the solvent influences the equilibrium strongly. In acetone only complexes with η^2-bonded MVK I–III are present. On the other hand, the only structure to be detected in MeOH by NMR spectroscopy was the η^4-MVK complex VI. Both η^2- and η^4-complexes exist in MeCN and in an acetone/H_2O mixture (70/30). The complex $[(\eta^4\text{-MVK})Rh\text{-}(PMe_3)_3]BPh_4$ VIb has been obtained from $(\eta^2\text{-MVK})RhCl(PMe_3)_3$ and $Na[BPh_4]$ in MeOH. The equilibrium between VI and a solvent complex $[(\eta^2\text{-MVK})Rh(Sol)(PMe_3)_3]BPh_4$ is established in MeCN. The role of rhodium intermediates with η^2- and η^4-bonded MVK in the mechanism of vinyl ketone catalytic dimerization is discussed.

Introduction

Dimerization of olefins and dienes is an intensively developing field of metallocomplex catalysis. But the dimerization of olefins containing functional groups has hardly been investigated in detail [1,2].

It has been shown previously that under mild conditions (60–80 °C) $RhCl(PMe_3)_3$ catalyzes the dimerization of vinyl ketones in a "head-to-tail" manner [3]. This reaction is a convenient method of synthesizing α-methylene-substituted 1,5-diketones [4]:



The present paper elaborates on the study of the vinyl ketone catalytic dimerization mechanism, or, to be exact, on the study of the first stage of this reaction, i.e. vinyl ketone coordination with $RhCl(PMe_3)_3$ and the dynamic behaviour of the solution π-complexes that are formed.

Results and discussion

Dynamic behaviour of π-complexes $(\eta^2\text{-}MVK)RhCl(PMe_3)_3$ and $[(\eta^4\text{-}MVK)Rh(PMe_3)_3]BPh_4$ in organic solvents

$RhCl(PMe_3)_3$ with methyl vinyl ketone (MVK) in organic solvents at −35 °C forms five-coordinate π-complexes of η^2-bonded MVK I–III, cationic complexes of η^2-bonded MVK IV, V, and a cationic complex of η^4-bonded MVK VI * (Scheme 1).

In solutions containing $RhCl(PMe_3)_3(MVK)$, neither free MVK (^1H NMR) nor species of the $[Rh(PMe_3)_3(Sol)_2]^+$ (^{31}P NMR) type [8] were observed, i.e. under these conditions (Table 1) the formation of complexes I–VI from $RhCl(PMe_3)_3$ and MVK proceeds practically as an irreversible reaction.

When a solid complex, VIa, isolated from methanol was then dissolved in acetone, the resulting solution contained a mixture of complexes I–III in a proportion equal to that of the reaction products from $RhCl(PMe_3)_3$ and MVK in the same solvent. This indicates that a rapid equilibrium is established between complexes I–III. The composition of this equilibrium mixture was found to depend on the solvent used.

The ratio of (I + II)/III in the equilibrium mixture is equal to (8–10)/1 and does not actually depend on the solvent (Table 1). On the contrary, the (I + II + III)/(IV + V + VI) and (IV + V)/VI ratios change greatly in different solvents, owing to their varying abilities to coordinate with the metal. So, in acetone with a low water content (about 0.5%) the $RhCl(PMe_3)_3(MVK)$ complex exists only in non-dissociated forms (I–III), whereas in aqueous acetone (acetone/water 70/30) the cationic complex VI is formed, whose content is 20–25% in the equilibrium mixture (Table 1). It should be noted that π-complexes with a non-ionized Rh–Cl bond I, II are present in different solvents chiefly in the trigonal-bipyramidal form; only 5–15% of complexes with the square-pyramidal geometry III have been found in solution. However, a square-pyramidal geometry (V–VI) is preferable for cationic-type complexes (Table 1). The cationic complexes IV–VI have also been obtained independently by interaction of $RhCl(PMe_3)_3(MVK)$ with $Na[BPh_4]$.

The equilibrium between the cationic complexes IV, V and VI in MeOH and in acetone is almost completely (according to ^{31}P NMR) shifted to the η^4-complex VI (Table 1). On the contrary, in MeCN, owing to its high ability to coordinate with metals, the η^2-complexes IV and V prevail. In other solvents (except MeCN), the formation of solvent complexes of types IV and VI was not observed.

Spectral characteristics of MVK and butadiene rhodium complexes

The structures of the MVK rhodium π-complexes were determined by IR and ^1H,

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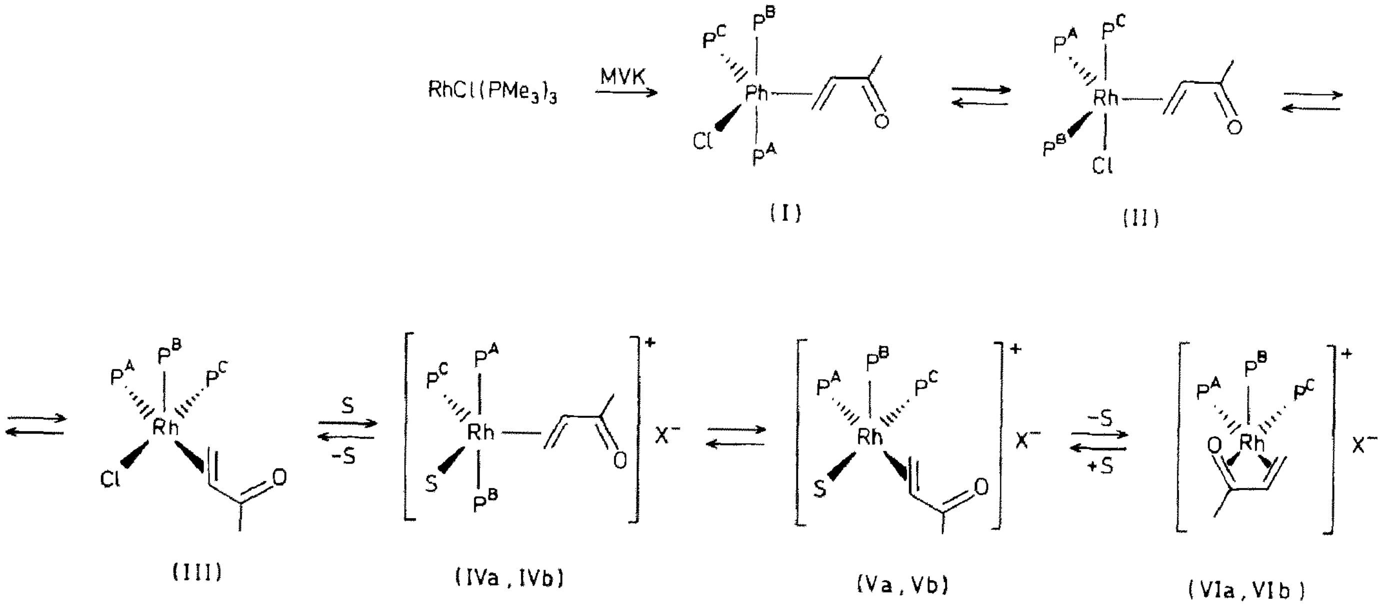
* It is well known that a fast equilibrium between square-pyramidal and trigonal-bipyramidal configurations is often observed for five-coordinated complexes in solution owing to the small energy barrier between them [5]. Therefore, only little information on the real configuration of five-coordinated complexes in solutions can be obtained from NMR data, even at low temperatures [6,7].



Scheme 1. a: $X = Cl$, b: $X = BPh_4$; $P = PMe_3$; $S = MeCN$.

Table 1

Influence of the solvents on the composition of equilibrium mixtures of π-complexes (according to $^{31}P\{^1H\}$ NMR data at −35 ° C)

π-Complex	Solvent	I	II	III	IV	V	VI
$RhCl(PMe_3)_3(MVK)$	acetone	75–85	5–10	10–15	–	–	–
$RhCl(PMe_3)_3(MVK)$	acetone/H_2O (70/30)	60–70	5–10	5	–	–	20–25
$RhCl(PMe_3)_3(MVK)$	MeOH	–	–	–	–	–	100
$RhCl(PMe_3)_3(MVK)$	MeCN	50–55	5	5	5	35–40	5–10
$[Rh(PMe_3)_3(MVK)]BPh_4$	acetone	–	–	–	–	–	100
$[Rh(PMe_3)_3(MVK)]BPh_4$	MeCN	–	–	–	20–25	65–75	5–10

^{31}P and ^{35}Cl NMR spectroscopy. In the IR spectrum of I, ν(C=O) 1610 cm^{-1}, i.e. it is considerably lower than that of free MVK (ν(C=O) 1680 cm^{-1}). The observed increase in the vibration frequency (Δν 70 cm^{-1}) is typical for the π-complexes of α, β-unsaturated carbonyl compounds with transition metals, in which the carbonyl group does not participate directly in the coordinated [9,10]. In the ^1H NMR spectrum of complex I, the signal assigned to protons of the η^2-coordinated ethylene bond are at 3.16, 2.10 and 2.02 ppm. The absence of a signal of a chlorine-free anion in the ^{35}Cl NMR spectra of complexes I–III in acetone indicates the σ-character of the chlorine–rhodium bond.

Figure 1 shows the experimental and calculated $^{31}P\{^1H\}$ NMR spectra of complexes I and II (the spectral parameters are listed in Table 2). All three phosphine ligands in I are non-equivalent (spin system ABMX). The presence of two groups of close signals in the 0–3 ppm area and the high value of the coupling constant ($^2J(P^A–P^B)$ 435 Hz) indicate a trigonal-bipyramidal geometry of complex I with phosphine ligands in the *trans*-positions [11,12]. For comparison, we synthesized a square-planar *cis*-$RhCl(PEt_3)(PMe_3)_2$ complex in which the coupling constant between *trans*-positioned PMe_3 and PEt_3 $^2J(P–P)$ 360 Hz.

In complex II, the phosphine ligands are also non-equivalent; the coupling constants between the ^{31}P nuclei have rather low values ($^2J(P–P)$ 26–34 Hz). This indicates that in the trigonal-bipyramidal structure all the phosphine ligands are situated in a *cis*-position to each other. The MVK ligand in II lies in the equatorial plane, since, according to ^{31}P NMR, the chlorine atom is in a *trans*-position to one of the phosphine ligands. The ^{31}P chemical shift for this phosphine was recorded downfield due to the *trans*-influence of the chlorine.

In addition, in the already described trigonal-bipyramidal Rh^I π-complexes [13] the ethylene bond is disposed in the equatorial plane, thus also confirming the suggested geometries of I and II [14]. The non-equivalence of the phosphine ligands in I and II indicates the absence of free rotation of the π-coordinate MVK ligand. At the same time, the recorded NMR spectra do not allow us to conclude which of the two possible rotamers, distinguished by the position of the aceto-group at the ethylene π-bond, to assign to the observed signals in the ^{31}P NMR spectra of complexes I and II [15].

The chemical shift values and $^1J(Rh–P)$ in the ^{31}P NMR spectra of trigonal-bipyramidal complexes I and II are very different from the corresponding values in the spectra of complexes III, V and VI, which, according to the spectral data analysis (Table 2), have a square-pyramidal geometry. For complexes III, V and VI,

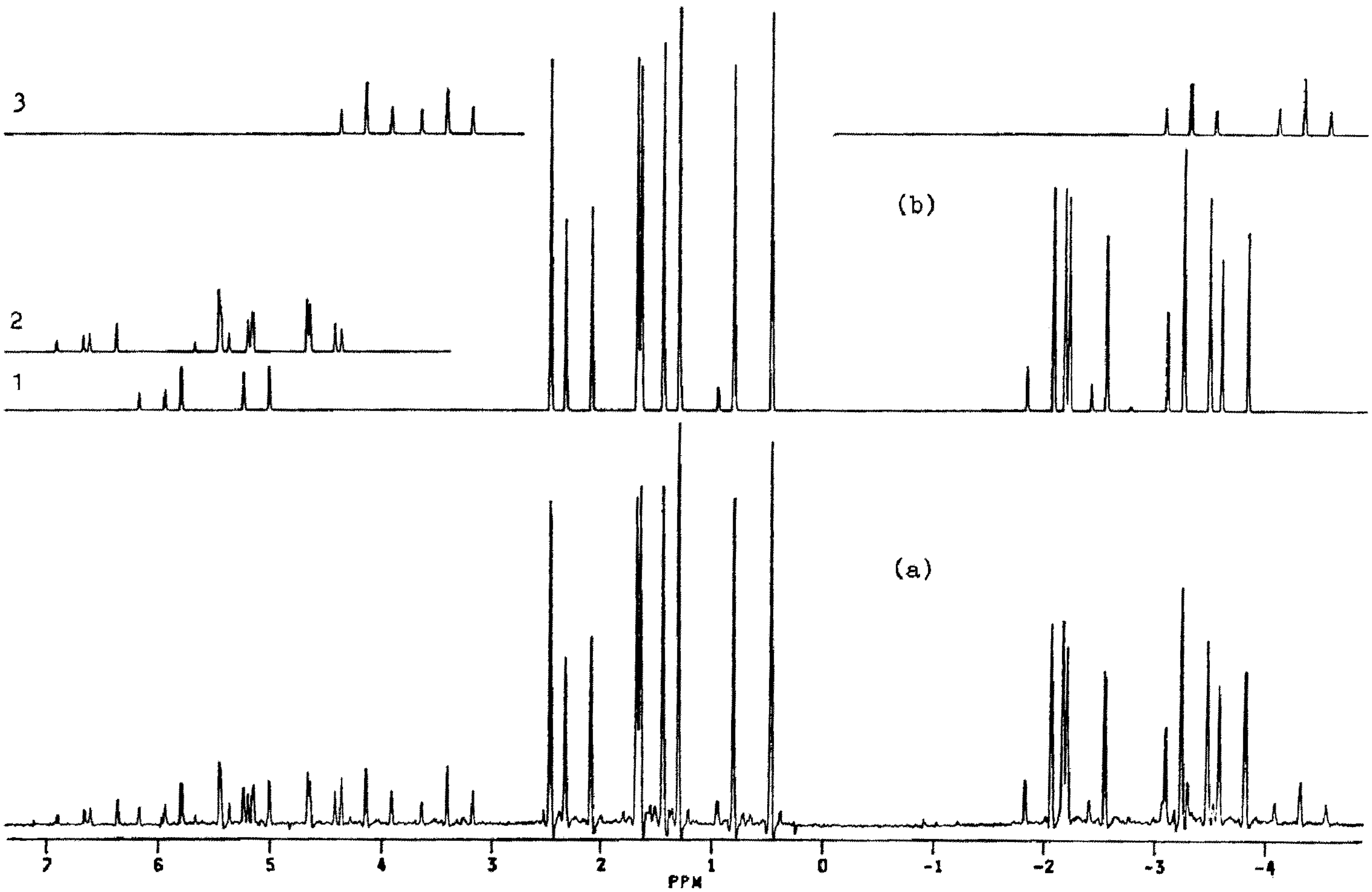


Fig. 1. Observed (a) and calculated (b) $^{31}P\{^1H\}$ spectrum of $RhCl(PMe_3)_3$ (η^2-MVK): 1 ≡ I, 2 ≡ II, 3 ≡ $[Rh(PMe_3)_4O_2]Cl$.

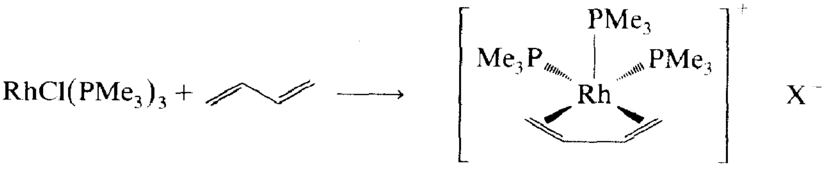
none of the coupling constant values ^2J(P–P) are higher than 59 Hz. This indicates that all the phosphine ligands are in a *cis*-position to each other in these complexes (Table 2). Consequently, one of the phosphines in III, V and VI is in an axial position, the other two in a *cis*-equatorial one.

ν(C=O) 1630 cm^{-1} ($\Delta\nu$(C=O) 50 cm^{-1}) has been observed in the IR spectrum of cationic complex Vb (in CD_3CN) (cf. the value for complex I given above).

In the IR spectra of complex VIb in the solid state and VIa in CD_3OD, absorption bands at 1500–1700 cm^{-1} are not observed, indicating η^4-coordination of MVK in VI [16,17]. The considerable downfield shift of the signal of one of the phosphorus atoms (P^C) in the ^{31}P NMR spectrum is due to the *trans*-influence of an electron-acceptor ligand. This effect is similar to the *trans*-influence of chlorine and MeCN on the P^C shift in the square-pyramidal complexes III and V. This is also in accordance with the suggested geometry of complex VI.

The NMR spectrum of complex VI (in CD_3OD) obtained using two-dimensional COSY spectroscopy shows the presence of three non-equivalent protons (1.62, 1.77 and 5.38 ppm) in the coordinated MVK molecule. A spin–spin interaction of the proton with δ 5.38 ppm with methyl group protons (^4J 2.5 Hz) was also observed, additionally confirming the η^4-coordination of MVK in VI. The $^{31}P\{^1H\}$ NMR spectra of complexes VIa and VIb coincide, indicating their ionic structure. The ^{35}Cl NMR spectrum of VIa represents a narrow singlet, which is typical for a free-chlorine anion (Table 2).

We synthesized the cationic complex VII containing η^4-coordinated butadiene * in order to assign more accurately the ^{31}P signals of the phosphine ligands in VI.



VII a,b (X = Cl(a), BPh_4(b))

The chemical shifts of ^{31}P of phosphine ligands in the $^{31}P\{^1H\}$ NMR spectrum of this symmetric complex (Fig. 2) are close to those of $^{31}P^A$ and $^{31}P^B$ nuclei in complex VI. The coupling constants ^1J(Rh–P) for phosphine ligands in the *trans*-position to the double bond in all the square-pyramidal complexes (III, V–VII) have similar values equal to 116 ± 3 Hz (Table 2).

Complex VI is the first example of a rhodium π-complex with a η^4-monoheterodiene ligand.

The role of intermediate π-complexes in the catalytic dimerization of MVK

The equilibrium shown in Scheme 1 obviously plays an important role in the catalytic dimerization of MVK. As follows from Fig. 3, the selectivity of the formation of 3-methylen-2,5-heptandione increases drastically with increasing water content in acetone, i.e. under conditions favourable for the dissociation of $RhCl(PMe_3)_3(MVK)$. This is likely to result from the stronger bonding of ligands to

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* A similar $[Co(PMe_3)_3(butadiene)]BPh_4$ complex has been obtained earlier [18].

Table 2

^{31}P{^{1}H} and ^{35}Cl NMR spectral data of complexes I–VII [a]

Complex	Solvent	δ (^{31}P (ppm))			J (Hz) [b]						δ^{35}Cl (ppm)
		P^A	P^B	P^C	Rh–P^A	Rh–P^B	Rh–P^C	P^A–P^B	P^A–P^C	P^B–P^C	
I	acetone	2.82	0.14	−2.87	+94.3	+102.3	+154.4	+435.7	−26.8	−45.8	– [c]
I	MeCN	2.39	−0.34	−2.37	+94.1	+102.3	+155.7	+431.9	−27.0	−45.3	– [c]
II	acetone	4.92	4.91	5.97	+94.9	+94.9	+150.1	−26.0	−31.3	−33.9	– [c]
III	acetone	−24.20	−10.52	20.32	116.9	134.9	134.4	59.1	38.2	31.1	– [c]
III	MeCN	−24.56	−10.09	20.84	116.4	135.3	135.5	58.0	38.4	31.2	– [c]
IV	MeCN	−2.49	−2.55	−3.26	+82.6	+114.1	+111.8	+300.0	−25.9	−39.7	–
V	MeCN	−27.16	−12.45	15.70	113.3	129.1	119.9	45.7	40.6	27.3	–
VI	MeCN	−14.59	−6.76	19.65	119.2	147.8	134.5	14.3	29.3	31.9	–
VIa	MeOH	−16.20	−8.07	19.14	119.1	147.7	133.7	12.6	29.0	32.4	−23.1
VIb	acetone	−14.50	−6.56	19.68	119.1	148.5	134.5	14.3	29.4	31.5	–
VIa	acetone + H_2O	−15.33	−7.32	19.29	119.1	148.0	133.9	13.1	29.2	31.8	31.8
VII	MeOH	−11.32 (P^A and P^C), J(Rh–P) = 116.6, ^2J(P–P) = 12.2, −10.84 (P^B), J(Rh–P) = 159.5									−29.2

[a] Temperature −35 °C; deuterium solvents were used. [b] The signs of the spin–spin coupling constants were obtained by calculation. [c] The Cl^- signal in the ^{35}Cl NMR spectrum is not observed.

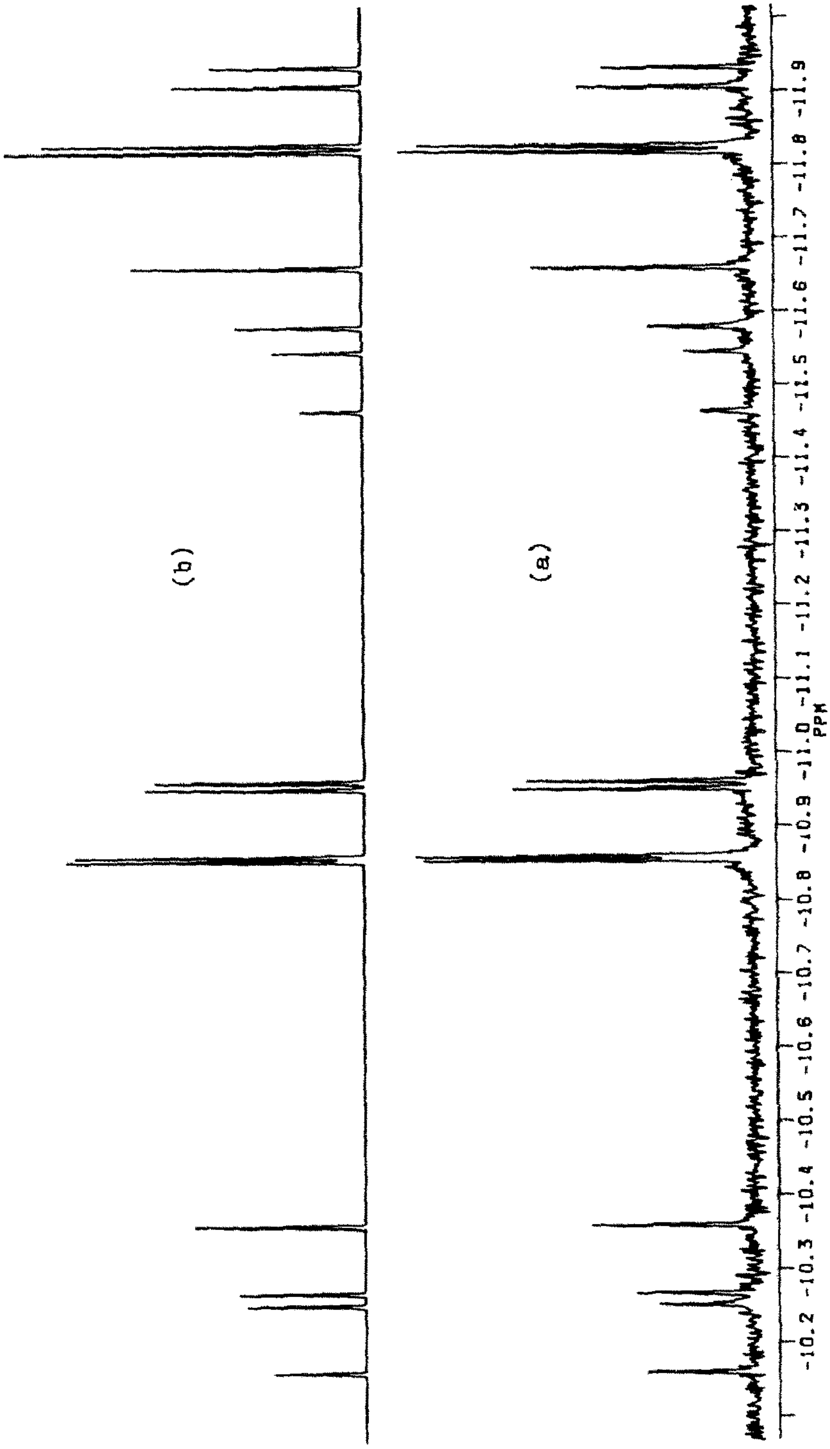


Fig. 2. Observed (a) and calculated (b) $^{31}P\{^1H\}$ spectrum of $Rh(PMe_3)_3(\eta^4\text{-butadiene})Cl$ (VIIa).

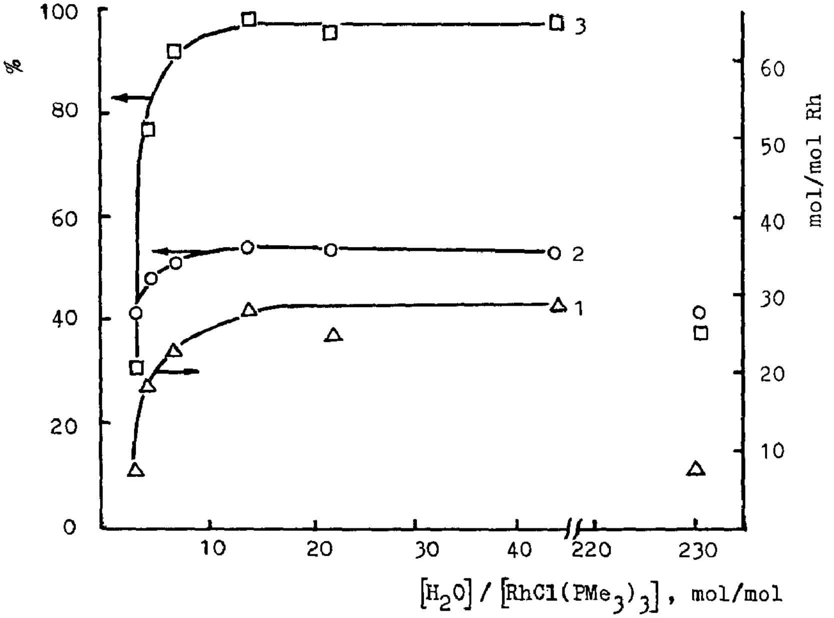
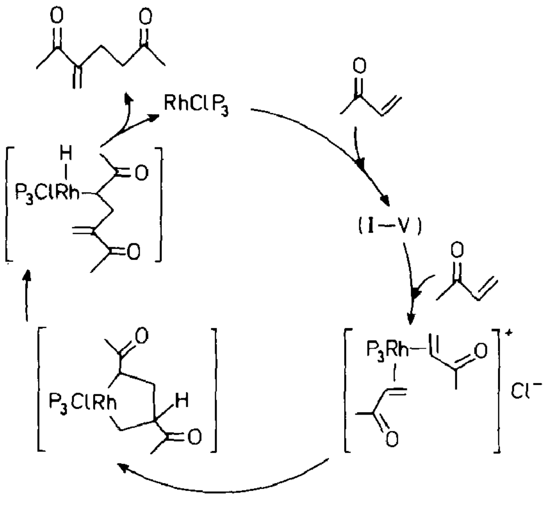


Fig. 3. Influence of the molar ratio $H_2O/RhCl(PMe_3)_3$ on the conversion of MVK (2) and the yield of 3-methylen-2,6-heptandione (1, 3). MVK (0.42 g, 6 mmol), $RhCl(PMe_3)_3$ (0.022 g, 0.06 mmol), acetone (3 ml), 60 ° C, 5 h.

rhodium in cationic complex V than in complexes I–III, thus impeding the displacement of PMe_3 which, as reported in [3], causes a side-reaction of MVK polymerization.

The ability of $RhCl(PMe_3)_3(MVK)$ to catalyse the formation of 3-methylen-2,5-heptandione from MVK indicates that complexes I–III are real intermediates in the catalytic dimerization.



P = PMe_3

Scheme 2. The probable mechanism of vinyl ketone catalytic dimerization.

In contrast to $RhCl(PMe_3)_3(MVK)$, the η^4-complex VIb does not catalyze this reaction in acetone. In this solvent, for $X = BPh_4$ the equilibrium in Scheme 1 shifts completely to η^4-complex VIb (see Table 1).

At the same time, during MVK dimerization in MeCN (in this solvent the equilibrium between IV, V and VI shifts to η^2-complexes (Table 2)) $[Rh(PMe_3)_3(MVK)]BPh_4$ is capable of catalysing this reaction.

Hence we can assume that only η^2-MVK complexes of rhodium – probably square-pyramidal III and V – participate in MVK dimerization.

The probable mechanism of vinyl ketone catalytic dimerization is presented in Scheme 2.

We failed to find a π-complex with two η^2-coordinated MVK molecules in the MVK + $RhCl(PMe_3)_3$ system at −35°C, even with a 15-fold excess of MVK. This complex, as well as products of the oxidative addition of two molecules of MVK to Rh(I) [9,19], is probably formed at higher temperatures when catalytic dimerization of vinyl ketones takes place. The mechanism of the following stages of this reaction is still under study.

Experimental

^1H (300.14), ^{31}P (121.50) and ^{35}Cl (29.41 MHz) NMR spectra were recorded with a Bruker AM 300 spectrometer using D_2O, $(CD_3)_2CO$, CD_3OD and CD_3CN as solvents (internal standard TMS, external standard 85% H_3PO_4 and 1M solution of NaCl, respectively). $^{31}P\{^1H\}$ NMR spectra for complexes I, II and IV were calculated by means of the PANIC program. IR spectra were recorded on a Specord M 80 instrument in CsI pills and CD_3OD or CD_3CN solution between CsI plates. All procedures were carried out under argon. Organic solvents were preliminarily dried. All solvents were degassed directly before use. $RhCl(PMe_3)_3$ was obtained according to [20].

$RhCl(PMe_3)_3(\eta^2$-MVK). MVK (0.2 g) was added to a solution of $RhCl(PMe_3)_3$ (0.05 g, 0.14 mmol) in acetone (3 ml) at −40 to −35°C. The mixture was kept for 30 min at the same temperature. The solvent and excess MVK were then removed slowly in vacuum under the same conditions. The orange solid residue was dried in vacuo for 4 h, m.p. 103–105°C (dec.). $^{31}P\{^1H\}$ and ^{35}Cl NMR spectral data are given in Table 2. ^1H NMR (δ (ppm), acetone-d_6, −35°C): 1.30 (m, 9H, PMe_3); 1.50 (m, 9H, PMe_3); 1.60 (m, 9H, PMe_3); 2.00 (d, J(HP) 2.8 Hz, 3H, Me); 2.02 (m, 1H); 2.10 (m, 1H); 3.16 (m, 1H). IR (ν (cm^{-1})): 3018w, 2970w, 2905m, 1610s, 1456m, 1420m, 1392m, 1338w, 1280s, 1200m, 1076w, 950vs, 855m, 785w, 730s, 618m, 606m, 520w, 360m. Found: C, 35.44; H, 7.36; Cl, 8.14. $C_{13}H_{33}ClOP_3Rh$ calcd: C, 35.76; H, 7.62; Cl, 8.12%.

$[Rh(PMe_3)_3(\eta^4$-MVK)]Cl (VIa) Complex VIa was afforded only in solution by dissolving $RhCl(PMe_3)_3(\eta^2$-MVK) in MeOH. It is formed quantitatively. $^{31}P\{^1H\}$ and ^{35}Cl NMR spectral data are given in Table 2. ^1H NMR (δ (ppm), CD_3OD, −35°C): 1.47 (dt, ^2J(PH) 11.2, ^3J(RhH) = ^4J(PH) 1.0 Hz, 9H, P^CMe_3); 1.48 (dd, ^2J(PH) 8.8, ^3J(RhH) 0.6 Hz, 9H, P^AMe_3); 1.60 (m, 1H); 1.67 (dd, ^2J(PH) 9.7, ^3J(RhH) 0.9 Hz, 9H, P^BMe_3); 1.70 (m, 1H); 2.34 (dd, J(PH) 6.4, ^4J(HH) 2.6 Hz, 3H, Me); 5.34 (m, 1H). In the ^1H NMR spectrum, the assignment of signals of protons of methyl groups to the corresponding phosphine ligands was carried out

using selective suppression of the ^{31}P–^{1}H spin–spin interaction. The vibrations assigned to the carbonyl group were absent in the IR spectrum in methanol-d_4.

[Rh(PMe$_3$)$_3$(η^4-MVK)]BPh$_4$ (VIb). Na[BPh$_4$] (0.039 g, 0.11 mmol) in water (2 ml) was added, under stirring, to a solution of RhCl(PMe$_3$)$_3$(η^2-MVK) (0.05 g, 0.11 mmol) in MeOH (3 ml). The resulting yellow residue was filtered off, washed with MeOH (2 × 1 ml) and dried in vacuo. 0.078 g (96%) of complex VIb was obtained in yellow powder form, m.p. 139–145 °C (dec.). ^{31}P{^{1}H} NMR spectral data are given in Table 2. ^{1}H NMR (δ (ppm), acetone-d_6, −35 °C): 1.55 (dd, ^2J(PH) 8.8, ^3J(RhH) 0.6 Hz, 9H, PMe$_3$); 1.56 (dt, ^2J(PH) 11.3, ^3J(RhH) = ^4J(PH) 1.0 Hz, 9H, PMe$_3$); 1.62 (m, 1H); 1.74 (dd, ^2J(PH) 9.7, ^3J(RhH) 0.9 Hz, 9H, PMe$_3$); 1.77 (m, 1H); 2.35 (dd, J(PH) 6.0, ^4J(HH) 2.5 Hz, 3H, Me); 5.38 (m, 1H); 6.85 (tt, ^3J 7.3, ^4J 1.6 Hz, 4H); 7.01 (t, J 7.3 Hz, 8H); 7.28 (m, 8H). IR (ν (cm^{-1})): 3050m, 2996w, 2980m, 2906w, 1580w, 1480m, 1420m, 1365w, 1305w, 1290m, 1030w, 940s, 845m, 735s, 705s, 670w, 610m, 578w. Found: C, 61.23; H, 7.40; B, 1.51. $C_{37}H_{53}BOP_3Rh$ calcd.: C, 61.68; H, 7.42; B, 1.50%.

cis-RhCl(PMe$_3$)$_2$(PEt$_3$). PEt$_3$ (0.12 g, 1.26 mmol) was added dropwise, under stirring, to a [RhCl(PMe$_3$)$_2$]$_2$ (0.29 g, 0.63 mmol) [21] solution in C_6D_6 (10 ml). The solution was stirred at room temperature for 2 h. ^{31}P NMR analysis showed that in addition to *cis*-RhCl(PMe$_3$)$_2$(PEt$_3$) 10–15% *trans*-RhCl(PMe$_3$)$_2$(PEt$_3$) was present in the solution. ^{31}P{^{1}H} NMR of the *cis*-complex (δ (ppm), 25 °C): −12.47 (ddd, J(RhP) 132.4, J(PP) 361.6, 47.2 Hz, PMe$_3$ *trans* to PEt$_3$); −1.70 (ddd, J(RhP) 179.7, J(PP) 43.6, 47.2 Hz, PMe$_3$ *trans* to Cl); 22.05 (ddd, J(RhP) 133.9, J(PP) 43.6, 361.7 Hz, PEt$_3$). ^{31}P{^{1}H} NMR of the *trans*-complex (δ (ppm), 25 °C): −12.48 (dd, J(RhP) 132.1, J(PP) 44.4 Hz, 2PMe$_3$); 41.99 (dt, J(RhP) 182.6, J(PP) 44.3 Hz, PEt$_3$).

[Rh(PMe$_3$)$_3$(η^4-CH$_2$=CHCH=CH$_2$)]Cl (VIIa). Butadiene (0.5 ml) was added to a solution of RhCl(PMe$_3$)$_3$ (0.03 g, 0.082 mmol) in acetone (3 ml) at −20 °C. The afforded mixture was maintained at the same temperature for 20 min. Then the solvent and excess butadiene were removed slowly in vacuo at −30 to −20 °C. The light-orange solid residue was dried in vacuo for 2 hours, m.p. 170–171 °C (dec.). ^{31}P{^{1}H} and ^{35}Cl NMR spectra data are presented in Table 2. ^{1}H NMR (δ (ppm), CD$_3$OD, −35 °C): 0.71 (m, 2H); 1.63 (m, 18H, 2PMe$_3$); 1.70 (m, 9H, PMe$_3$); 2.02 (m, 2H); 5.61 (m, 2H). IR (ν (cm^{-1})): 3065w, 3018w, 2964w, 2900m, 1482w, 1426m, 1315w, 1304w, 1288m, 1040w, 948vs, 860m, 852w, 794w, 728s, 672s, 656w, 458w, 398w, 354w, Found: C, 37.07; H, 7.70; Cl, 8.84. $C_{13}H_{33}ClP_3Rh$ calcd.: C, 37.12; H, 7.91; Cl, 8.48%.

[Rh(PMe$_3$)$_3$(η^4-CH$_2$=CHCH=CH$_2$)]BPh$_4$ (VIIb). Na[BPh$_4$] (0.038 g, 0.11 mmol) in MeOH (2 ml) was added to a solution of VIIa (0.047g, 0.11 mmol) in MeOH (1 ml). The precipitated cream-coloured residue was filtered off, washed with aqueous methanol (2 × 1ml) and 1 ml of ether, and dried in vacuo, mp 250–251 °C (dec.). ^{31}P{^{1}H} NMR spectral data are given in Table 2. ^{1}H NMR (δ (ppm), acetone-d_6, −35 °C): 0.69 (m, 2H); 1.52 (m, 18H, 2PMe$_3$); 1.70 (m, 9H, PMe$_3$); 2.04 (m, 2H); 5.53 (m, 2H); 6.62 (m, 4H); 6.96 (m, 8H); 7.34 (m, 8H). Found: C, 62.59; H, 7.64; B, 1.47; P, 12.74; Rh, 14.12. $C_{37}H_{53}BP_3Rh$ calcd.: C, 63.12; H, 7.52; B, 1.53; P, 13.19; Rh, 14.61%.

MVK dimerization. MVK (0.42 g, 6 mmol) and acetone (3 ml) containing a certain amount of water were placed in a glass tube with RhCl(PMe$_3$)$_3$ (0.022 g, 0.06 mmol). The sealed tube was maintained at 60 °C for 5 h. MVK conversion and the yield of 3-methylen-2,6-heptandione were determined using GC. The results are given in Fig. 3. The spectral characteristics of the dimer are listed in ref. 3.

MVK dimerization catalysed with $RhCl(PMe_3)_3(MVK)$. MVK (0.28 g, 4 mmol) was added to $RhCl(PMe_3)_3(MVK)$ (0.018 g, 0.04 mmol) in 3 ml of acetone. The afforded solution was heated in a glass tube at 60 °C for 5 h, yield 0.1 g of dimer (96% to converted MVK, 18 mol/mol Rh), MVK conversion 37%.

MVK dimerization catalysed with complex VIb. MVK (0.1 g, 0.014 mmol) was added to VIb (0.005 g, 0.007 mmol) in MeCN (2.5 ml). The afforded solution was heated in a glass tube at 80 °C for 5 h. GC gave the following data: MVK conversion 18%; yield of dimer 8% to converted MVK; 2 mol/mol Rh [3].

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