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"Head-to-head" dimerization and dehydrodimerization of vinyl ketones catalyzed by modified rhodium(I) complexes

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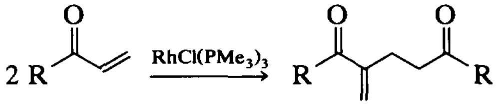
Abstract

The dimerization of vinyl ketones RC(O)CH=CH$_2$, I (R = Me, ^{t}Bu, Ph, p-MeC$_6$H$_4$, cyclopropyl, 2-(5-methylfuryl)) at 80 °C in the presence of the catalytic system [RhCl(C$_2$H$_4$)$_2$]$_2$–MCl$_2$ leads preferably to either α,β-unsaturated 1,6-diketones RC(O)CH=CHCH$_2$CH$_2$C(O)R, II when M = Ge or to diene 1,6-diketones RC(O)CH=CHCH=CHC(O)R, III when M = Sn. The yields of II and III are 20–85% to converted I, the conversion of vinyl ketones being 10–50%. The intermediate rhodium and rhodium–tin complexes including η^2-coordinated methyl vinyl ketone have been isolated and characterized by ^{1}H, ^{119}Sn NMR and IR spectroscopy.

Introduction

It has been shown previously that RhCl(PMe$_3$)$_3$ catalyzes the dimerization of vinyl ketones in a "head-to-tail" manner [1].



However, no data have been reported about "head-to-head" dimerization and dehydrodimerization of vinyl ketones promoted by transition metal complexes. At the same time the dimerization of acrylic monomers catalyzed by Pd [2–7] and Rh [8–10] has been described.

Results and discussion

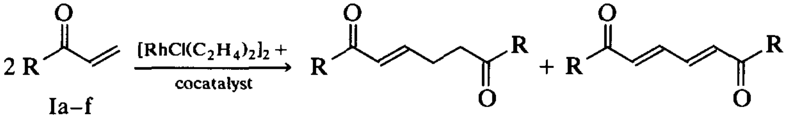
We report here about a "head-to-head" dimerization of vinyl ketones I using rhodium catalysts obtained *in situ* from [RhCl(C$_2$H$_4$)$_2$]$_2$ and acid modifier (preliminary communication see [11,12]).

Table 1

Dimerization and dehydrodimerization of methyl vinyl ketone Ia catalyzed by $[RhCl(C_2H_4)_2]_2$–MX_n [a]

Co-catalyst MX_n	Solvent	Conversion of MVK (%)	% Yield to converted Ia (mol/g at Rh)		IIa/IIIa
			IIa	IIIa	
–	Acetone	20	38 (8)	12 (2.6)	3.16
HBF_4	Acetone	17	50 (8.6)	14 (2.4)	3.59
HBF_4 [b]	Acetone	9	38 (3.5)	26 (2.4)	1.46
$AlCl_3$	Acetone	11	55 (6)	16 (1.8)	3.43
$FeBr_2$	Acetone	16	55 (9)	17 (3)	3.22
$AgNO_3$	Acetone	19	16 (3)	14 (2.8)	1.14
$SnCl_4$ [c]	Acetone	29	7 (2)	10 (3)	0.70
$GeCl_2$	CH_2Cl_2	12	54 (6.5)	2 (0.3)	27.00
$GeCl_2$	Toluene	17	31 (5.2)	2 (0.35)	15.50
$GeCl_2$	EtOAc	24	23 (5.6)	2.5 (0.6)	9.33
$HGeCl_3$	Toluene	15	22 (3.3)	0.2 (0.19)	110.00
$GeCl_2$	THF	10	33 (3.4)	17 (1.7)	1.94
$BF_3 \cdot Et_2O$	Toluene	25	2 (0.5)	26 (6.5)	0.08
$SnCl_2$	Acetone	14	10 (1.4)	36 (5.2)	0.28
$SnCl_2$ [b]	Acetone	21	5 (1.1)	21 (4.3)	0.24
$SnCl_2$	THF	13	16 (2)	21 (2.6)	0.76
$SnCl_2$	EtOAc	24	37 (9)	15 (3.7)	2.46

[a] 0.015 mmol of $[RhCl(C_2H_4)_2]_2$, 0.03 mmol of MX_n, 6 mmol of Ia, 3 ml of solvent, at 80 °C for 5 h. [b] $(acac)Rh(C_2H_4)_2$ was used. [c] 0.075 mmol of MX_n.



Ia–f

IIa–c,f

IIIa–f

R = Me (a), ${}^tBu$ (b), cyclopropyl (c), Ph (d), p-MeC_6H_4 (e), 2-(5-methylfuryl) (f)

Catalytic dimerization of the methyl vinyl ketone Ia

Vinyl ketone Ia in the presence of catalytic amounts of $[RhCl(C_2H_4)_2]_2$ transforms into unsaturated 1,6-diketone IIa and IIIa, the diketone IIa being the main product (IIa/IIIa = 3.16 in acetone) (Table 1). The ratio IIa/IIIa has been found to be very sensitive to various additives (cocatalyst) as well as to the solvent used.

By changing the reaction conditions, each of these compounds (IIa or IIIa) can be obtained from vinyl ketone Ia as the major product. Thus, when $GeCl_2$ or $HGeCl_3$ are used as cocatalysts and CH_2Cl_2 as a solvent, 1,6-diketone IIa is a main product. Alternatively, diene diketone IIIa was formed as a principal product when rhodium catalyst modified by $SnCl_2$ (acetone) or $BF_3 \cdot Et_2O$ (toluene) was used (IIa/IIIa = 0.2 and 0.08). Maximum yields of IIa and IIIa have been achieved with Rh^I–Ge^{II} and Rh^I–Sn^{II} catalytic systems (54 and 36%, to the Ia consumed respectively). It has been shown in a special experiment that IIIa does not form via IIa dehydrogenation reaction.

Such cocatalysts as HBF_4, $AlCl_3$, $FeBr_2$ have only a slight influence on the IIa/IIIa ratio, the total yield of IIa and IIIa being higher in the presence of these cocatalysts than without. When $AgNO_3$ and $SnCl_4$ were used as components in a

Table 2

Synthesis of the unsaturated 1,6-diketones II and III by catalytic dimerization of vinyl ketones [a]

Vinyl ketone I	Conversion of I (%)	% Yield of dimers to converted vinyl ketone (mol/g-at Rg) [b]	
		II	III
Catalytic system $[RhCl(C_2H_4)_2]_2-2\ SnCl_2$ *(in acetone)*			
Ia	24	5 (1,3)	23 (5,3)
Ib	15	75 (12)	20 (5,3)
Ic	26	29 (7,5)	66 (17)
Id	49	–	80 (40)
Ie	13	–	60 (7,8)
If	46	–	20 (9)
Catalytic system $[RhCl(C_2H_4)_2]_2-2\ GeCl_2$ *(in* CH_2Cl_2*)*			
Ia	12	54 (6,5)	2 (0,3)
Ib	12	84 (10,4)	3,5 (0,4)
Ic	30	70 (21)	–
If	17	43 (7,4)	–

[a] 6 mmol of I, 0.015 mmol of $[RhCl(C_2H_4)_2]_2$, 0.03 mmol of $SnCl_2\cdot 2H_2O$ (or $GeCl_2\cdot$dioxane), 3 ml of solvent, at 80 °C for 10 h. [b] For IIa–c and IIIa–c according to GC data, the isolated yields for IIf and IIId–f.

catalytic system, the total yield of IIa and IIIa was found to decrease sharply and the reaction was supressed almost completely using $CuCl_2$ and $TiCl_4$ as cocatalysts.

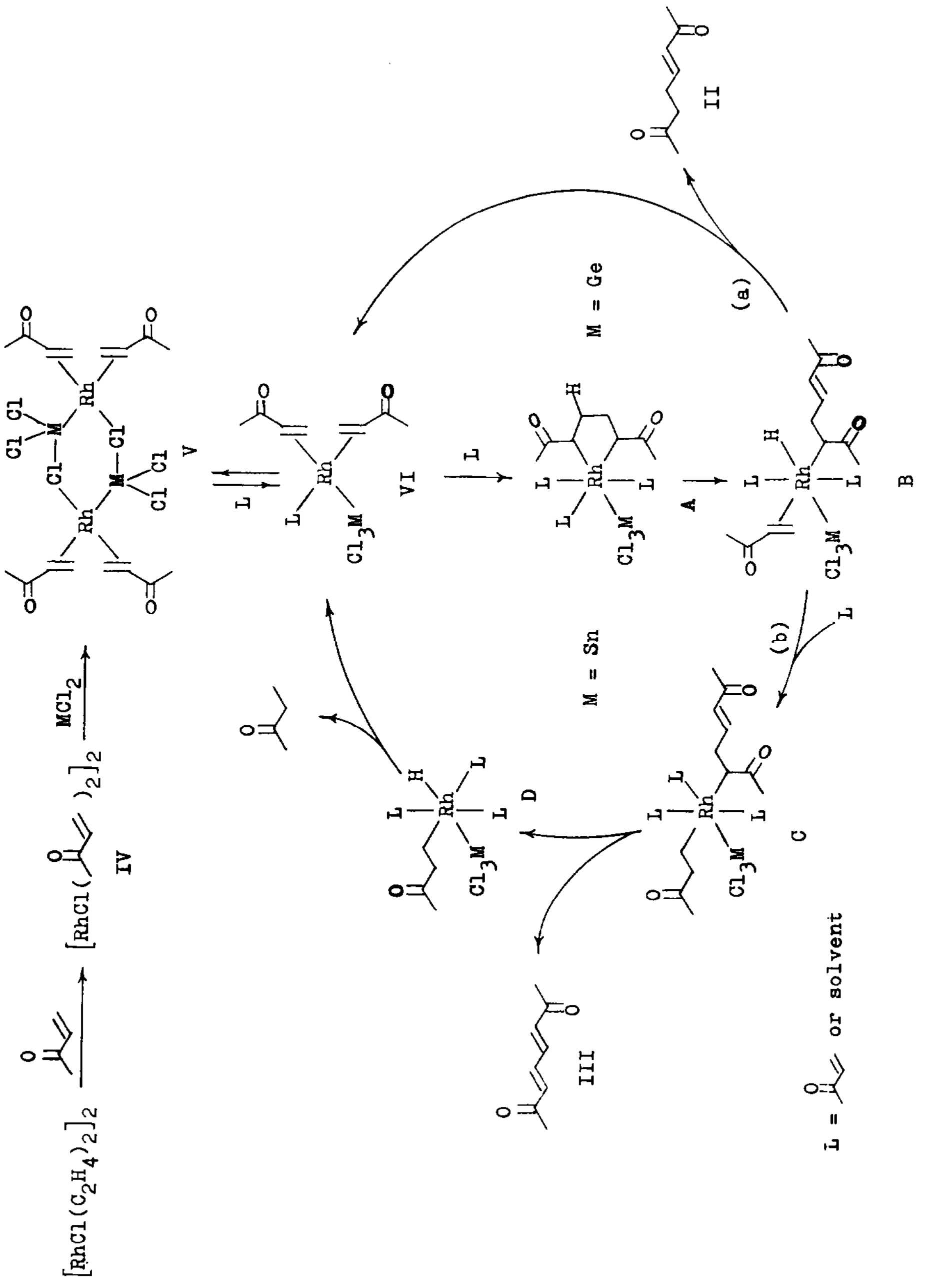
The results (Table 1) illustrate the important role of the solvent in the Ia catalytic dimerization. The replacement of acetone by ethyl acetate in the Rh^I–Sn^{II} catalytic system causes a dramatic change in distribution of products (IIa/IIIa is 0.27 in acetone and 2.4 in ethyl acetate). With MeCN the reaction did not proceed practically, while with MeOH, 4-methoxy-2-butanone was predominantly formed as a result of nucleophilic addition to the vinyl ketone double bond.

Compared with head-to-tail vinyl ketone dimerization catalyzed by Rh^I phosphine complexes [1], the head-to-head dimerization and dehydrodimerization of Ia promoted by a $[RhCl(C_2H_4)_2]_2$–cocatalyst system is more sensitive to temperature. Thus, diketones IIa and IIIa are formed from Ia at temperatures ranging from 60 to 80 °C. At 50 °C the reaction did not proceed practically and at 100 °C the rhodium complex decomposition took place.

Synthesis of α,β-unsaturated and diene 1,6-diketones

Under optimum conditions for synthesis of IIa and IIIa (see above) various α,β-unsaturated and diene 1,6-diketones II and III have been prepared.

As follows from the data shown in Table 2, head-to-head dimeric 1,6-diketones II are predominantly obtained from all the vinyl ketones used, in the presence of a Rh^I–Ge^{II} catalytic system. Alternatively linear diene 1,6-diketones III were found to be the main products of Rh^I–Sn^{II} catalyzed reactions, except for vinyl ketone Ib for which dimerization remains a dominant reaction route even under conditions favourable for the dehydrodimerization reaction. It may be due to the effect of a steric tert-butyl group on the configuration of intermediate organorhodium complexes.


[RhCl(C2H4)2]2
[RhCl( )2]2
IV
MCl2
V
VI
L
A
B
C
D
II
III
(a)
(b)
M = Ge
M = Sn
L = or solvent

Scheme 1.

Aromatic vinyl ketones react most smoothly when a catalytic Rh^I–Sn^{II} system is used to yield dehydrodimers III selectively.

It should be noted that Rh^I–Sn^{II} promoted dehydrodimerization of vinyl ketones is a new catalytic reaction with reference to α,β-unsaturated carbonyl compounds. (There is poor information in literature about catalytic dehydrodimerization of compounds with terminal C=C bonds [13,14].)

This reaction is obviously the most convenient route to conjugated 1,6-diketones from accessible vinyl ketones [15,16].

A mechanism of catalytic dimerization and dehydrodimerization of vinyl ketones

The simplest mechanism of vinyl ketone transformation promoted by a Rh–M (M = Sn, Ge) catalyst, which should explain the competition between dimerization (a) and dehydrodimerization (b) pathways, is outline in Scheme 1.

The assumed mechanism includes ligand exchange between bis-ethylene rhodium π-complex and substrate to give bis-(vinyl ketone)rhodium complex IV. This intermediate compound has been isolated from the reaction mixture containing rhodium complex without co-catalyst.

The ^1H NMR spectrum of IV shows (−90 °C) unsplit broad multiple signals centered at 5.4–5.8, 4.6–5.2, 2.4–2.8 ppm showing the presence of π-bonded vinyl groups. The signal pattern indicates that compound IV is stereochemically unrigid because of π-bonded ligand rotation.

ν(C=O) 1690 cm^{-1} and ν(C=C) 1654 cm^{-1} have been observed in the IR spectrum of complex IV (cf. ν(C=O) 1680 and ν(C=C) 1630 cm^{-1} for free methyl vinyl ketone). $SnCl_2$ modification of rhodium catalyst gives rise to complex V (M = Sn), which has been isolated in crystalline form (cf. [17,18]). This compound probably has dimeric structure. That is consistent with poor solubility of V in non-polar solvents (acetone, benzene, toluene, THF) and good solubility in polar solvents (MeCN, DMF) in which solvated monomeric complexes of type VI have been fixed spectroscopically.

The ^1H NMR spectrum of complex VI in CD_3CN (−35 °C) has been recorded using two-dimensional COSY spectroscopy. It shows four groups of non-equivalent protons corresponding to four isomers VIa–d distinguished by mutual position and configuration of ligands within this complex. The coupling constant $^1J(^{103}Rh-^{119}Sn)$ in the ^{119}Sn NMR spectrum of complex VI equals 663 Hz which is similar to that for compounds of this type [18].

According to the postulated mechanism, the catalytic reaction starts from oxidative addition of two π-bonded substrate ligands within complex VI to form metallacycle **A** which is converted to transient alkyl hydride rhodium **B** via hydrogen β-elimination. Complex **B** is a key intermediate because its further transformation determines the nature of the reaction products. When M = Ge, liberation of α,β-unsaturated diketone II takes place preferentially (pathway a), complex VI being regenerated. On the other hand, if M = Sn the course of the reaction is controlled by pathway b which suggests the insurtion of π-bonded substrate into the Rh–H bond in complex **B** to afford dialkyl rhodium intermediate C followed by successive liberation of diketone III and methyl ethyl ketone to give back complex VI. Methyl ethyl ketone has been indentified in the reaction mixture by chromatomass-spectroscopy. No detectable amount of molecular hydrogen in the gas phase has been found.

Experimental section

^1H (300.14), ^{13}C (75.47), ^{119}Sn (111.87 MHz) NMR spectra were recorded with a Bruker AM 300 spectrometer using $CDCl_3$, $C_6D_5CD_3$ and CD_3CN as solvents (internal standard TMS and external standard $SnMe_4$). IR spectra were recorded on a Specord M 80 instrument in KBr pills or in films between KBr plates if not indicated in addition. The GC analysis was carried out in LHM-8MD(5) using a 300 × 0.3 cm column with 10% PEGS on Chromosorb P and a 200 × 0.3 cm column with 5% SE-30 on Inerton Super. Mass spectra were recorded with a Finnigan MAT INCOS 50.

2,2-Dimethyl-4-penten-3-one Ib, 1-cyclopropyl-2-propen-1-one Ic, 1-(4-methylphenyl)-2-propen-1-one Ie, 1-(5-methyl-2-furyl)-2-propen-1-one If [20,21], $(acac)Rh(C_2H_4)_2$ [22], $[RhCl(C_2H_4)_2]_2$ [23] and $GeCl_2 \cdot$dioxane [24] were prepared as described previously.

All operations were carried out under argon. Solvents and initial reagents were dried and degassed before use.

Dimerization and dehydrodimerization of vinyl ketones

Vinyl ketone was added to a mixture (0.0039 g, 0.01 mmol) of $[RhCl(C_2H_4)_2]_2$ and (0.02 mmol) of co-catalyst in 3 ml of the relevant solvent and the resulting solution was heated for 10 h in a sealed glass tube at 80 ° C. Conversion of vinyl ketone was detected by GC. Chromatomass spectrum data showed that the reaction mixture contains a methyl ethyl ketone (from Ia, co-catalyst $SnCl_2$). MS of methyl ethyl ketone: m/z 72 (M^+), 57, 43 (base), 29, 15. The diketones IIa,b and IIIb were isolated by chromatography on a silica gel column using a hexane/ether (5:2) solvent mixture as an eluent. All other dimers and dehydrodimers were isolated by crystallysation at −20 to −25 ° C. The results are listed in Tables 1 and 2. ^1H and ^{13}C NMR data are listed in Tables 3 and 4.

*3*E*-Octen-2,7-dione IIa.* b.p. 103–105 ° C/6 mmHg. IR (ν(cm^{-1})): 1630 (C=C), 1676 and 1718 (C=O).

*3*E*,5*E*-Octadien-2,7-dione IIIa.* m.p. 121–123 ° C. IR (ν(cm^{-1})): 1632 (C=C), 1660 (C=O).

*2,2,9,9-Tetramethyl-4*E*-decen-3,8-dione IIb.* m.p. 44–46 ° C. IR (ν(cm^{-1})): 1630 (C=C), 1690 and 1705 (C=O). Found: C, 75.10; H, 9.57. $C_{14}H_{22}O_2$ calc.: C, 75.69; H, 9.90%.

*2,2,9,9-Tetramethyl-4*E*,6*E*-decadien-2,8-dione IIIb.* m.p. 88–90 ° C. IR (ν(cm^{-1})): 1590 (C=C), 1675 (C=O). Found: C, 76.57; H, 9.36. $C_{14}H_{20}O_2$ calc.: C, 76.32; H, 9.15%.

*1,6-Dicyclopropyl-2*E*-hexen-1,6-dione IIc.* m.p. 16–18 ° C. IR (ν(cm^{-1})): 1630 (C=C), 1665 and 1698 (C=O). Found: C, 74.65; H, 8.47. $C_{12}H_{16}O_2$ calc.: C, 74.97; H, 8.39%.

*1,6-Dicyclopropyl-2*E*,4*E*-hexadien-1,6-dione IIIc.* m.p. 121–122 ° C. IR (ν(cm^{-1})): 1580 (C=C), 1665 (C=O). Found: C, 75.07; H, 7.65. $C_{12}H_{14}O_2$ calc.: C, 75.81; H, 7.36%.

*1,6-Diphenyl-2*E*,4*E*-hexadien-1,6-dione IIId.* m.p. 180–181 ° C. IR (ν(cm^{-1})): 1580 (C=C), 1650 (C=O).

*1,6-Di(4-methylphenyl)-2*E*,4*E*-hexadien-1,6-dione IIIe.* m.p. 214–216 ° C. IR (ν(cm^{-1})): 1580 (C=C), 1655 (C=O). Found: C, 82.13; H, 6.11. $C_{20}H_{18}O_2$ calc.: C, 82.77; H, 6.20%.

Table 3

^{1}H NMR data for diketones II and III, in $CDCl_3$ (δ in ppm, J in Hz)

Compound	(O)C–CH=	=CH	=C–CH_2	CH_2–C(O)	R
IIa	6.02 dt $^3J = 16.5$ $^4J = 1.5$	6.75 dt $^3J = 16.5$ $^3J = 6.5$	2.44 m	2.60 m	2.13 s, 2.18 s (6H, 2 Me)
IIIa	6.42 m	7.12 m			2.26 s (6H, 2 Me)
IIb	6.52 dt $^3J = 15$ $^4J = 1.5$	6.88 dt $^3J = 15$ $^3J = 7$	2.47 m	2.65 m	1.14 s, 1.17 s (18H, 6 Me)
IIIb	6.90 m	7.39 m			1.80 s (18H, 6 Me)
IIc	6.22 dt $^3J = 16$ $^4J = 1.5$	6.87 dt $^3J = 16$ $^3J = 7$	2.51 m	2.76 t	0.87 m, 1.03 m (8H), 1.92 tt (1H, $^3J_{cis} = 4.5$; $^3J_{trans} = 8$), 2.10 m (1H)
IIIc[a]	6.62 m $^3J = 15.44$ $^4J = -0.84$ $^5J = 0.73$	7.25 m $^3J = 15.44$ $^3J = 11.30$ $^4J = -0.84$			2.26 tt (2H, $^3J_{trans} = 8$; $^3J_{cis} = 4.5$), 1.15 m (4H), 1.00 m (4H)
IIId	7.34 m	7.52 m			7.56 m (6H), 8.00 m (4H in C_6H_5)
IIIe	7.27 m	7.42 m			7.17 d (4H, $J = 8$), 7.77 d (4H, $J = 8$)
IIf	6.81 dt $^3J = 15$ $^4J = 1.5$	7.07 dt $^3J = 15$ $^3J = 6.5$	2.72 m	3.00 m	2.40 m (6H, 2 Me), 6.16 m (2H), 7.15 m (2H)
IIIf	7.15 m	7.55 m			2.36 s (6H, 2 Me), 6.14 dq (2H, $^3J = 3.5$, $^4J = 1.0$), 7.10 d (2H, $^3J = 3.5$)

[a] Coupling constants were calculated using the PANIC program for IIIc (spin system AA′BB′ for the diene part of the diketones IIIa–f).

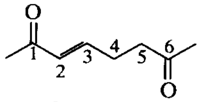
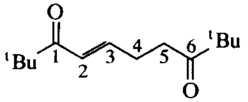
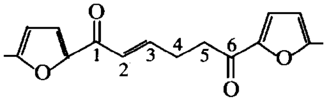
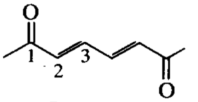
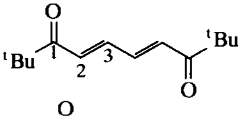
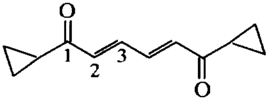
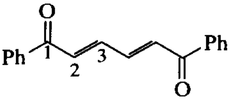
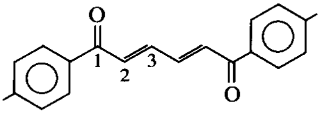
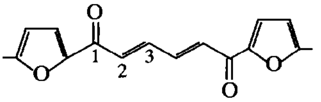
*1,6-Di-2(5-methylfuryl)-2*E*-hexen-1,6-dione IIf.* m.p. 117–119 °C. IR (ν(cm^{-1})): 1580 (C=C), 1613 and 1661 (C=O). Found: C, 70.39; H, 5.65. $C_{16}H_{16}O_4$ calc.: C, 70.61; H, 5.87%.

*1,6-Di-2(5-methylfuryl)-2*E*,4*E*-hexadien-1,6-dione IIIf.* m.p. 202–204 °C. IR (ν(cm^{-1})): 1580 (C=C), 1630 (C=O). Found: C, 70.72; H, 5.43. $C_{16}H_{14}O_4$ calc.: C, 71.13; H, 5.18%.

$\{RhCl[\eta^2\text{-}(CH_2{=}CHCOCH_3)]_2\}_2$ IV. To a solution of $[RhCl(C_2H_4)_2]_2$ (0.1 g, 0.26 mmol) in benzene (10 ml), methyl vinyl ketone Ia (0.63 g, 9.3 mmol) was added at room temperature. The mixture was stirred at the same temperature for 30 min. The benzene and excess of Ia were then removed slowly *in vacuo*. The solid residue was dried *in vacuo* for 3 h; yield of IV was 100% (0.145 g), m.p. 68–75 °C(dec.). ^{1}H NMR (δ (ppm), toluene-d_8, −90 °C): 5.4–5.8 (m, 1H); 4.6–5.2 (m, 1H); 2.4–2.8 (m, 1H); 2.29 (s, 3H, CH_3). IR (ν(cm^{-1})): 3000w, 2920w, 2848w, 1690vs, 1564s, 1466s, 1390s, 1366s, 1272w, 1224m, 1194s, 1072w, 976w, 772w, 684m, 592w, 416w, 380w; (in Nujol between polyethylene plates): 326w, 288w, 282w. Found: C, 34.90; H, 4.52; Cl, 13.28; Rh, 36.10. $C_{16}H_{24}Cl_2O_4Rh_2$ calc.: C, 34.50; H, 4.34; Cl, 12.73; Rh, 36.90%.

Table 4

$^{13}C\{^1H\}$ NMR data for diketones IIa,b,f and IIIa–f in $CDCl_3$ (δ in ppm)

Diketone	1	2	3	4	5	6	R
	198.2	146.1	131.6	29.6	41.4	208.6	26.6, 26.0
	190.6	145.8	124.9	26.7	35.0	204.1	26.4(2), 26.2, 26.1
	180.9	125.8	146.0	27.0	36.2	189.9	14.1, 151.4, 109.1, 119.8, 157.9, 158.1, 119.2, 109,0, 151.9, 14.0
	197.5	139.6	136.7				27.8
	204.2	139.6	131.8				29.5, 26.0
	199.6	138.5	136.1				20.0, 11.8
	189.8	141.1	133.3				137.5, 128.7, 128.6, 132.6
	180.8	141.0	132.6				137.2, 128.8(2), 129.6, 21.8
	176.1	139.3	131.7				158.7, 120,3, 109.3, 151.9, 13.8

$\{Rh[\eta^2\text{-}(CH_2{=}CHCOCH_3)]_2SnCl_3\}_2$ V. $[RhCl(C_2H_4)_2]_2$ (0.0783 g, 0.2 mmol) and $SnCl_2 \cdot 2H_2O$ (0.0832 g, 0.4 mmol) were dissolved in acetone (4 ml). Vinyl ketone Ia (0.28 g, 4 mmol) was added to the resulting solution and the mixture was stirred at room temperature for 3 h. The resulting orange crystals were filtered off, washed with acetone (2 × 1 ml) and dried *in vacuo*; 0.12 g (60%) of complex V were obtained, m.p. 210–216 °C(dec.). Complex V in MeCN exists as a mixture of four stereoisomers (VIa–d). ^1H NMR (CD_3CN, −35 °C) VIa (δ (ppm)): 4.85 (dd, $^3J_{cis}$ 8.1, $^3J_{trans}$ 11.6 Hz, 1H); 4.47 (d, $1H_{trans}$); 3.60 (d, $1H_{cis}$); VIb (δ (ppm)): 4.65 (dd, $^3J_{cis}$ 8.1, $^3J_{trans}$ 11.7 Hz, 1H); 3.26 (d, $1H_{cis}$); 3.06 (d, $1H_{trans}$); 4.28 (dd, $^3J_{cis}$ 8.1, $^3J_{trans}$ 11.6 Hz, 1H); 4.13 (d, $1H_{trans}$); 3.38 (d, $1H_{cis}$); VIc (δ (ppm)): 4.88 (dd, $^3J_{cis}$ 7.6, $^3J_{trans}$ 11.5 Hz, 1H); 3.96 (d, $1H_{trans}$); 3.65 (d, $1H_{cis}$); VId (δ (ppm)): 4.90 (dd, $^3J_{cis}$ 8.1, $^{J}{}_{trans}$ 11.7 Hz, 1H); 4.31 (d, $1H_{cis}$); 3.70 (d, $1H_{trans}$); 4.87 (dd, $^3J_{cis}$ 7.2, $^3J_{trans}$ 12.5 Hz, 1H); 3.82 (d, $1H_{trans}$); 3.72 (d, $1H_{cis}$).

The reciprocal attribution of the protons of the double bond in the coordinated MVK molecules in complexes VIa–d has been made by using two-dimensional COSY spectroscopy. The chemical shifts of the methyl groups of coordinated Ia in the complexes VIa–d are 2.10 s and 2.31 s ppm. $^{119}Sn\{^1H\}$ NMR for VIa–d (δ (ppm) CD_3CN, $-35\,^\circ C$): 44.3 (d, $^1J(^{119}Sn^{103}Rh$ 663 Hz). IR of V ($\nu(cm^{-1})$): 3048w, 3000w, 2910w, 1714s, 1568s, 1454s, 1376vs, 1220m, 1194vs, 1090w, 1072w, 1038m, 968s, 902m, 810w, 804w, 656m, 634s, 604w, 548w, 530w, 508w, 474w, 436s, 424w, 366s; (in Nujol between polyethylene plates): 276w, 248w, 226w, 214w. Found: C, 20.75; H, 2.20; Cl, 23.30; Rh, 20.19; Sn, 25.13. $C_{16}H_{24}Cl_6O_4Rh_2Sn_2$ calc.: C, 20.53; H, 2.58; Cl, 22.72; Rh, 21.99; Sn, 25.34%.

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