

New insight into role of *ortho*-metallation in rhodium triphenylphosphite complexes. Hydrogen mobility in hydrogenation and isomerization of unsaturated substrates

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Received 3 August 1999; received in revised form 24 September 1999

Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday.

Abstract

The hydrogen transfer from two rhodium(I) hydrido complexes $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ to methyl acrylate and/or allylbenzene leads to the formation of *ortho*-metallated complexes $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$ (**I**) and $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}(\text{CO})\{\text{P}(\text{OPh})_3\}_2$ (**II**), respectively. During these reactions unsaturated substrates, methyl acrylate or allylbenzene undergo stoichiometric hydrogenation. A similar reaction was also observed for $\text{HRh}\{\text{P}(\text{OR})_3\}_4$ complexes ($\text{R} = 3\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$). The complex $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ catalyses the isomerization of hex-1-ene to hex-2-ene in the absence of H_2 ; however at 1 atm of H_2 the formation of hexane is observed. Hydrido complexes of the type $\text{HRh}\{\text{P}(\text{OR})_3\}_4$ in D_2 atmosphere undergo H/D exchange at the *ortho* position of coordinated triarylphosphite. Deuteration of the *ortho* protons in complexes with $\text{R} = \text{Ph}$, $3,5\text{-(CH}_3)_2\text{C}_6\text{H}_3$ and $4\text{-CH}_3\text{C}_6\text{H}_4$ is total, whereas only one *ortho* hydrogen is replaced in the case of $\text{R} = 3\text{-CH}_3\text{C}_6\text{H}_4$. The formation of an *ortho*-metallated chelating ring causes a downfield shift in the ^1H -NMR signal of one proton from the phenyl ring to δ ca. 8 ppm. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium complexes; *ortho*-Metallation; Triarylphosphite; Hydrogenation; Isomerization

1. Introduction

The formation of *ortho*-metallated bonding by a triarylphosphite ligand coordinated to the metal is one of the most typical reactions of transition metals with that ligand. Formation of the five-membered metallacycle favours stabilization of the *ortho*-metallated complex. A number of well-characterized (with spectroscopic and/or diffractometric methods) *ortho*-metallated complexes are known for iridium [1–4]. In the case of rhodium, until now only three monomeric *ortho*-metallated complexes are described in the literature:

- $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$ (**I**) of trigonal bipyramidal structure [5] obtained by heating of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ in *n*-alkanes [6–8];

- $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_2$ (**Ia**) obtained in the reaction of $\text{RhCl}\{\text{P}(\text{OPh})_3\}_3$ with PhMgCl [9] and rhodium(III) complex of formula $[(\text{C}_5\text{Me}_5)\text{-Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3]\text{PF}_6$ [10].

Recently van Leeuwen and co-workers repeated the synthesis of **I** and **Ia** and on the basis on $^{31}\text{P}\{^1\text{H}\}$ -NMR spectral analysis postulated that both complexes are identical [5].

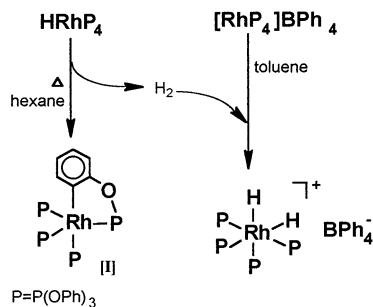
Several *ortho*-metallated complexes with tri-phenylphosphine, mainly dimeric rhodium(II) complexes, are also known [11].

The *ortho*-metallated structure is strongly supported by H/D exchange at the *ortho* positions of phenyl ring of triphenylphosphite coordinated to rhodium [6,9,12].

In this paper we present a new synthetic route to *ortho*-metallated complexes based on hydrogen transfer from hydrido complexes of rhodium(I), $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$, to the olefins. The studies of the above-mentioned hydrogen-transfer reac-

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Scheme 1.

tion is important for understanding the reactivity of $\text{HRh}\{\text{P(OPh)}_3\}_4$ and $\text{HRh(CO)}\{\text{P(OPh)}_3\}_3$ complexes, known as active catalysts of hydrogenation and hydroformylation [5,13–16].

2. Results and discussion

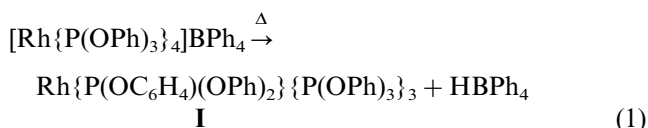
2.1. Preparation of *ortho*-metallated complexes

Complex **I** may be easily obtained by heating of a $\text{HRh}\{\text{P(OPh)}_3\}_4$ suspension in boiling heptane [6] as well as in benzene or toluene. We have found that dihydrogen evolved in this reaction passed through the benzene solution of $[\text{Rh}\{\text{P(OPh)}_3\}_4]\text{BPh}_4$ formed $[(\text{H})_2\text{Rh}\{\text{P(OPh)}_3\}_4]\text{BPh}_4$ (Scheme 1). The ^1H -NMR spectrum of

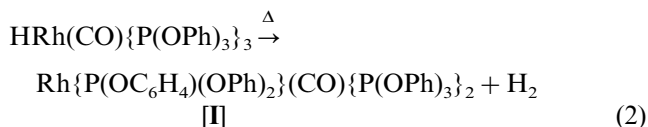
the dihydrido complex showed a resonance at $\delta -9.5$ ppm, split into two multiplets as a result of P–H coupling characteristic for the *cis* arrangement of two hydrido ligands in the $[(\text{H})_2\text{Rh}\{\text{P(OPh)}_3\}_4]\text{BPh}_4$ complex.

Two new complexes, **Ib** and **Ic**, the analogs of **I**, have been obtained applying a similar procedure (boiling heptane) to $\text{HRh}\{\text{P(O-3-CH}_3\text{C}_6\text{H}_4)_3\}_4$ and $\text{HRh}\{\text{P(O-4-CH}_3\text{C}_6\text{H}_4)_3\}_4$, respectively. All three compounds (**I**, **Ib** and **Ic**), although with slightly different phosphito ligands, have almost identical $^{31}\text{P}\{^1\text{H}\}$ -NMR spectral parameters according to a computer simulation (Table 1). The typical downfield resonances at δ ca. 150 ppm of the phosphorus atom involved in the metallacycle [17] are detected in all spectra.

In further studies we found that complex **I** is also formed in boiling benzene or toluene solution of $[\text{Rh}\{\text{P(OPh)}_3\}_4]\text{BPh}_4$ complex. However, dihydrogen is not produced and the formation of the *ortho*-metallated complex can be explained by *ortho*-proton abstraction and HBPh_4 formation:



The new *ortho*-metallated compound of formula $\text{Rh}\{\text{P(OC}_6\text{H}_4)(\text{OPh})_2\}(\text{CO})\{\text{P(OPh)}_3\}_2$ (**II**) was obtained when hydrido–carbonyl complex, $\text{HRh(CO)}\{\text{P(OPh)}_3\}_3$, was heated in benzene solution or as a suspension in heptane.



Similar complexes **Ib** and **Ic** with $\text{P(O-3-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{P(O-4-CH}_3\text{C}_6\text{H}_4)_3$ ligands, respectively, have been synthesized applying an identical procedure. In the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of complexes **II**, **Ib** and **Ic**, the multiplet found at δ 160 ppm was assigned to the phosphorus of the *ortho*-metallated five-membered ring (Table 2). Two other triphenylphosphites are equivalent and display a doublet of doublets at δ 128 ppm (Fig. 1). The analysis of $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra allows one to propose for those complexes a trigonal bipyramidal structure with CO and the *ortho* carbon atom of the phenyl ring occupying apical positions. It is interesting to note that all coupling constants are positive, whereas $J(\text{P}_\text{A}-\text{P}_\text{C})$ in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **I** (and **Ib**, **Ic**) is negative.

Reaction of **II** with P(OPh)_3 produces **I**, whereas the reverse reaction occurs when a solution of **I** is saturated with CO. Both transformations are observed in $^{31}\text{P}\{^1\text{H}\}$ -NMR experiments within a few minutes (Scheme 2).

Table 1
 $^{31}\text{P}\{^1\text{H}\}$ -NMR data (C_6D_6 , δ/ppm ($J(\text{Rh}-\text{P})/\text{Hz}$) of complexes **I**, **Ib**, **Ic** and **Ie**

	I ^a	Ib ^b	Ic ^c	Ie ^d
δ_A	151.6 (236)	154.5 (242)	151.1 (241)	146.5 (249)
$J(\text{P}_\text{A}-\text{P}_\text{B})$	78	72	83	56
δ_B	123.6 (159)	127.2 (158)	129.1 (166)	41.5 (98)
$J(\text{P}_\text{B}-\text{P}_\text{C})$	71	71	73	50
δ_C	115.3 (236)	117.6 (242)	118.4 (241)	115.9 (250)
$J(\text{P}_\text{A}-\text{P}_\text{C})$	−314	−314	−308	−336

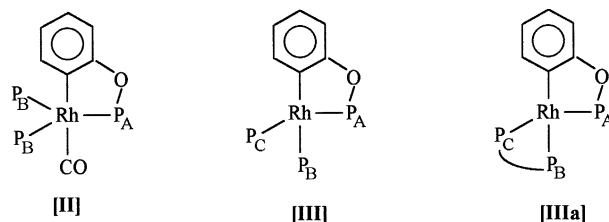
^a **I**, $\text{P}_{\text{B,C}} = \text{P(OPh)}_3$, $\text{P}_\text{A} = \text{P(OC}_6\text{H}_4)(\text{OPh})_2$ [5].

^b **Ib**, $\text{P}_{\text{B,C}} = \text{P(O-3-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}_\text{A} = \text{P(O-3-CH}_3\text{C}_6\text{H}_3)(\text{O-3-CH}_3\text{C}_6\text{H}_4)_2$.

^c **Ic**, $\text{P}_{\text{B,C}} = \text{P(O-4-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}_\text{A} = \text{P(O-4-CH}_3\text{C}_6\text{H}_3)(\text{O-4-CH}_3\text{C}_6\text{H}_4)_2$.

^d **Ie**, $\text{P}_\text{A} = \text{P(OC}_6\text{H}_4)(\text{OPh})_2$, $\text{P}_\text{C} = \text{P(OPh)}_3$, $\text{P}_\text{B} = \text{PPh}_3$.

Table 2

 $^{31}\text{P}\{^1\text{H}\}$ -NMR data (C_6D_6 , δ/ppm ($J(\text{Rh}-\text{P})/\text{Hz}$) of complexes **II**, **IIb**, **IIc**, **III** and **IIIa**

	II ^a	IIb ^b	IIc ^c	III ^d	IIIa ^e
δ_{A}	161.3 (231)	161.3 (231)	161.6 (233)	153.1 (221)	152.2 (228)
$J(\text{P}_{\text{A}}-\text{P}_{\text{B}})$	295	295	292	84	36
δ_{B}	127.8 (234)	127.8 (234)	128.9 (233)	116.9 (227)	38.1 (130)
$J(\text{P}_{\text{B}}-\text{P}_{\text{C}})$				28	17
δ_{C}				21.7 (73)	-7.1 (74)
$J(\text{P}_{\text{A}}-\text{P}_{\text{C}})$				28	36

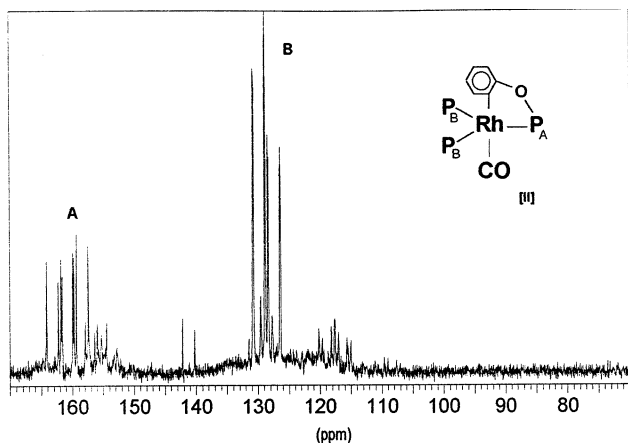
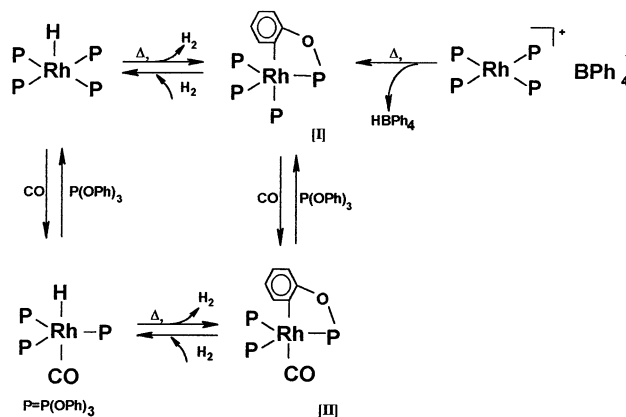
^a **II**, $\text{P}_{\text{B}} = \text{P}(\text{OPh})_3$, $\text{P}_{\text{A}} = \text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2$.^b **IIb**, $\text{P}_{\text{B}} = \text{P}(\text{O}-3\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}_{\text{A}} = \text{P}(\text{O}-3\text{-CH}_3\text{C}_6\text{H}_3)(\text{O}-3\text{-CH}_3\text{C}_6\text{H}_4)_2$.^c **IIc**, $\text{P}_{\text{B}} = \text{P}(\text{O}-4\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}_{\text{A}} = \text{P}(\text{O}-4\text{-CH}_3\text{C}_6\text{H}_3)(\text{O}-4\text{-CH}_3\text{C}_6\text{H}_4)_2$.^d **III**, $\text{P}_{\text{A}} = \text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2$, $\text{P}_{\text{B}} = \text{P}(\text{OPh})_3$, $\text{P}_{\text{C}} = \text{PPh}_3$.^e **IIIa**, $\text{P}_{\text{A}} = \text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2$, $\text{P}_{\text{B,C}} = \text{dppb}$.

The complexes **I** and **II**, respectively, are slowly formed in benzene solutions of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ or $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ left under nitrogen at room temperature. According to $^{31}\text{P}\{^1\text{H}\}$ -NMR up to 10% of the *ortho*-metallated complexes were obtained in 2 h. Both *ortho*-metallated complexes, **I** and **II**, react quickly with H_2 forming the corresponding hydrido complexes (Scheme 2). This explains why heating $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ or $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ in closed vessels always gives a lower yield of **I** or **II** if compared with reactions carried out in open vessels with simultaneous removal of dihydrogen from the solution. For example, the benzene solution of $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ heated for ca. 20 min in a closed vessel produced ca. 50% of **II** (according to ^{31}P -NMR), whereas 10 min of heating is enough for 100% conversion of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ into **I** when

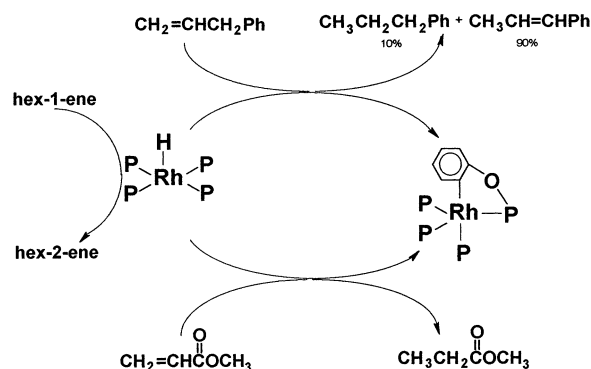
evolved dihydrogen is removed from the reaction medium.

2.2. Reactions of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ or $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ with unsaturated substrates: methyl acrylate, allylbenzene, styrene and hex-1-ene

We have found that in the absence of free H_2 both rhodium hydrido complexes, $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$, react with equimolar amounts of unsaturated substrates as stoichiometric hydrogenating reagents (each mole of the rhodium complex donates one mole of dihydrogen). Stoichiometric hydrogenation is observed when methyl acrylate, styrene or allylbenzene are used as substrates and methyl propionate, ethylbenzene and propylbenzene are formed, respec-

Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of complex **II** in C_6D_6 .

Scheme 2.



Scheme 3.

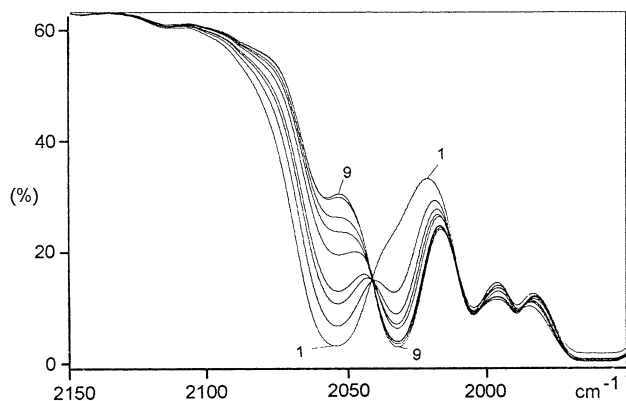
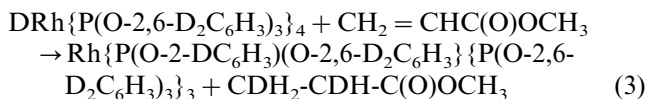


Fig. 2. IR spectra in the region 1950–2150 cm^{-1} measured during the reaction of $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3 + \text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$. Reaction time: 1, 3 min; 9, 85 min.

tively. Allylbenzene additionally undergoes catalytic isomerization to methylstyrene, whereas hex-1-ene is only isomerized to hex-2-ene (Scheme 3).

Hydrogenation (deuteration) of methyl acrylate was demonstrated in the reaction with $\text{DRh}\{\text{P}(\text{O}-2,6\text{-D}_2\text{C}_6\text{H}_3)_3\}_4$ (Reaction (3)) and reaction product $\text{CH}_2\text{D}-\text{CHD}-\text{C}(\text{O})\text{OCH}_3$ was identified by MS.



During stoichiometric hydrogenation of unsaturated substrates the hydrido complexes $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ are transformed into **I** and **II**, respectively. In the reaction of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ with allylbenzene leading to propylbenzene (hydrogenation product) and methylstyrene (isomerization product), the existence of both rhodium complexes — the starting hydrido complex (in higher concentration) and complex **I** — were detected in the reaction mixture. During isomerization of hex-1-ene only $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ was found in solution.

The rate of the hydrogen-transfer reaction increases with increasing unsaturated substrate concentration.

When a ca. ten-fold excess of $\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$ was added to the solution of $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ after 2 h only complex **II** was found. In this reaction traces of aldehyde were also detected as a result of CO transfer from $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ to methyl acrylate.

The above reaction was monitored by IR spectroscopy and the ν_{CO} region of the spectrum is shown in Fig. 2. The intensity of the ν_{CO} band at 2056 cm^{-1} , characteristic for the starting complex ($\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$), decreased over time and a new band at 2032 cm^{-1} (**II**) appeared. The presence of an isosbestic point (at 2042 cm^{-1}) may suggest a quantitative transformation of the starting complex $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ into **II**.

The addition of free triphenylphosphite caused a decrease in the rates of hydrogen transfer as well as in the transformation of $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ into **I**. In addition, in the reaction mixture the other rhodium complex [18] with a characteristic $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum showing signals at ca. 80 ppm was found (Fig. 3(b)).

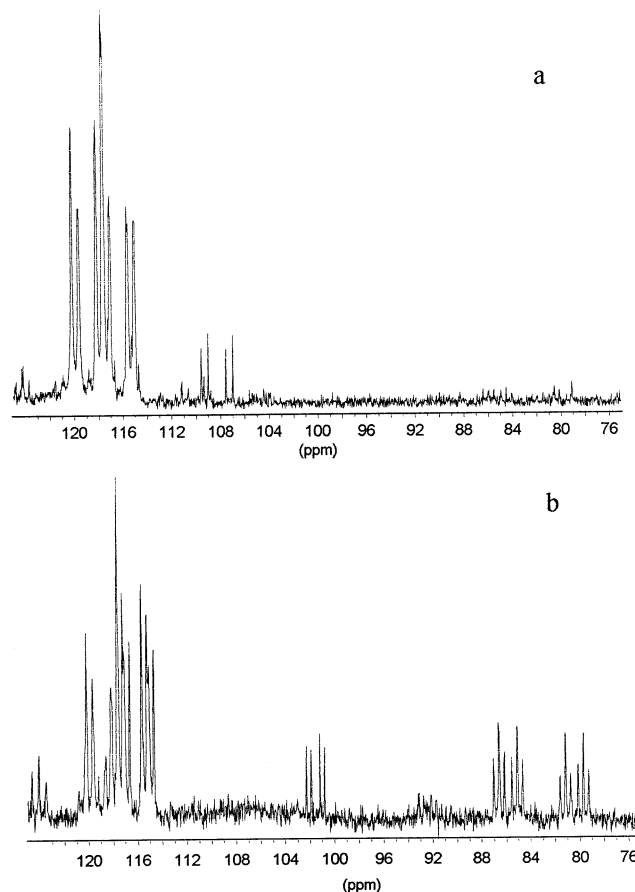


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra in C_6D_6 in the region 75–125 ppm for the systems (a) $\text{HRh}\{\text{P}(\text{OPh})_3\}_4 + \text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$ and (b) $\text{HRh}\{\text{P}(\text{OPh})_3\}_4 + 3 \text{P}(\text{OPh})_3 + \text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$.

Table 3

Products of hydrogenation/isomerization of hex-1-ene with rhodium(I) catalysts at 40°C, 1 atm H₂ after 2 h

Rh(I) catalyst	Reaction yield (%)	
	Hexane	Hex-2-ene
[Rh{P(OPh) ₃ } ₄]ClO ₄	15	6
[Rh{P(OPh) ₃ } ₄]ClO ₄ + N(ⁱ Pr) ₃	18	71
[Rh{P(OPh) ₃ } ₄]ClO ₄ + NEt ₃	24	72
HRh(P(OPh) ₃) ₄	18	81
HRh(CO){P(OPh) ₃ } ₃	8	92 ^a

^a 20% of hex-3-ene.

It must be noted that all the stoichiometric hydrogenation reactions described above proceed with the HRh{P(OR)₃}₄ and HRh(CO){P(OR)₃}₃ types of complex only. The hydrogenation of methyl acrylate did not occur with in situ prepared [(H)₂Rh{P(OPh)₃}₄](BPh₄) as well as with [Rh{P(OPh)₃}₄](BPh₄), although the latter forms *ortho*-metallated complex **I** when heated (Reaction (1)).

The rhodium triphenylphosphito complexes exhibit different reactivity in reactions with hex-1-ene under 1 atm of H₂ (Table 3). The conversion of hex-1-ene to hex-2-ene with HRh{P(OPh)₃}₄ as well as with HRh(CO){P(OPh)₃}₃ is complete. In the case of HRh(CO){P(OPh)₃}₃ some amounts (20%) of hex-3-ene were also found. In comparable conditions [Rh{P(OPh)₃}₄]ClO₄ is much less active; however in the presence of amines its activity increases and may compete with that of HRh{P(OPh)₃}₄. The addition of amine facilitates heterolytic splitting of H₂ and the formation of HRh{P(OPh)₃}₄ [9].

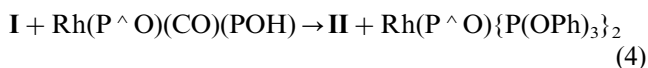
2.3. Ligand exchange in complexes **I** and **II**

Triphenylphosphito ligands coordinated to rhodium(I) in complexes **I** and **II** can be partially substituted by PPh₃ or diphenylphosphinobutane (dppb); however the *ortho*-metallated fragment remains unchanged.

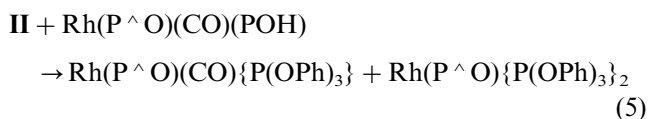
A new complex with an identical trigonal bipyramidal structure of formula Rh{P(OC₆H₄)(OPh)₂}{P(OPh)₃}₂ (PPh₃) (**Ie**) is formed in reaction of **I** with PPh₃. The ³¹P{¹H}-NMR spectrum parameters of **Ie** are very similar to those of **I** and according to them (Table 1) triphenylphosphine is coordinated in a *trans* position to the carbon atom of the *ortho*-metallated ring. Application of a large excess of PPh₃ in the reaction with **I** ([PPh₃]: **I** = 5) leads to the formation of some amounts of a tetracoordinated complex Rh{P(OC₆H₄)(OPh)₂}{P(OPh)₃}(PPh₃) (**III**), which is the only product of the reaction of **II** with PPh₃ ([PPh₃]: **II** = 2). It is worth noting that complex **III** is not square planar although such symmetry was expected, since C–M–P [2] in the metallacycle is ca. 80°. Low values of *J*(P–P) in the ³¹P{¹H}-

NMR spectrum of complex **III** exclude a mutual *trans* position for the two phosphorus atoms in the molecule. The *J*(P(PPh₃)–P(P(OPh)₃)) coupling constants were found to be close to 400 Hz in octahedral complexes of Os [19], Ru [20] and square planar complexes of Rh [21] with phosphine coordinated *trans* to phosphite. According to this criterion, the complex of formula Rh{P(OC₆H₄)(OPh)₂}(dppb) (**IIIa**) is not a square planar structure (Table 2).

The interesting process of ligand exchange between **I** and Rh(P[^]O)(CO)(POH) (POH = PPh₂C₆H₄OH) produces complex **II** and Rh(P[^]O){P(OPh)₃}₂ (Reaction (4)):



It was surprising that the *ortho*-metallated fragment remained unchanged during ca. 3 h in the presence of a weak proton donor like coordinated (2-hydroxyphenyl)-diphenylphosphine. However in a similar reaction of **II** with Rh(P[^]O)(CO)(POH) the *ortho*-metallated ring was protonated and the mixture of Rh(P[^]O)(CO){P(OPh)₃} and Rh(P[^]O){P(OPh)₃}₂ was identified by ³¹P{¹H}-NMR (Reaction (5)):



Complex **I** reacts easily with stronger proton donors like HClO₄ or HCl producing well-known Rh(I) complexes: [Rh{P(OPh)₃}₄]ClO₄ and Rh{P(OPh)₃}₃Cl, respectively. In the reaction of **I** with formic acid a mixture of Rh{P(OPh)₃}₄(HCO₂) and Rh{P(OPh)₃}₃(HCO₂) was obtained.

2.4. H/D exchange in Rh-phosphito complexes

Reaction of **I** with D₂ (1 atm) at room temperature leads to the formation of DRh{P(O-2,6-D₂C₆H₃)₃} (100%) in 5 h, which is in agreement with literature data [6,9]. Similarly the complex HRh(CO){P(OPh)₃}₃ reacts with D₂ giving an analogous H/D exchange product. Unexpectedly H/D exchange in HRh{P(O-3-CH₃-C₆H₄)₃}₄ is not complete since the proton neighbouring the methyl group is not exchanged. This was concluded from ¹H-NMR spectrum measured during H/D exchange, in which the singlet assigned to the *ortho* proton at 7.18 ppm (H⁴) remained, whereas the doublet of (H¹) at 7.28 ppm disappeared (Fig. 4). It is interesting to note that in the HRh{P(O-3,5-(CH₃)₂C₆H₃)₃}₄ complex the total deuteration of the *ortho* protons is realized in 2 h.

In reaction of [Rh{P(OPh)₃}₄]ClO₄ with D₂ (1 atm at room temperature) only [(D)₂Rh{P(OPh)₃}₄]ClO₄ was obtained but H/D exchange in phenyl rings was not observed.

2.5. ^1H -NMR spectra of *ortho*-metallated complexes **I** and **II**

Both *ortho*-metallated complexes, **I** and **II**, have rather complicated ^1H -NMR spectra in the phenyl proton region, which is caused by the unequivalency of coordinated triphenylphosphites. The most obvious characteristic seems to be the appearance of downfield-shifted resonances (at 8.1 ppm for **I** and 8.6 ppm **II** if compared with the spectra of parent hydrido complexes $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$, respectively) (Fig. 5).

A similar signal was also observed in the ^1H -NMR spectrum of the cobalt(I) analog, $\text{Co}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\text{-}\{\text{P}(\text{OPh})_3\}_3$ [22].

Applying COSY and homodecoupling, we have found that the doublets at 7.61, 7.42 and 7.24 ppm are a result of the *ortho* protons of phosphite ligands A, B and C of complex **I**, respectively (Fig. 5). This interpretation was confirmed by analysis of the ^1H -NMR spectrum of the *ortho*-metallated complex obtained by heating of $\text{DRh}\{\text{P}(\text{O-2,6-}\text{D}_2\text{C}_6\text{H}_3)\}_4$ in heptane (Reaction (6)). In

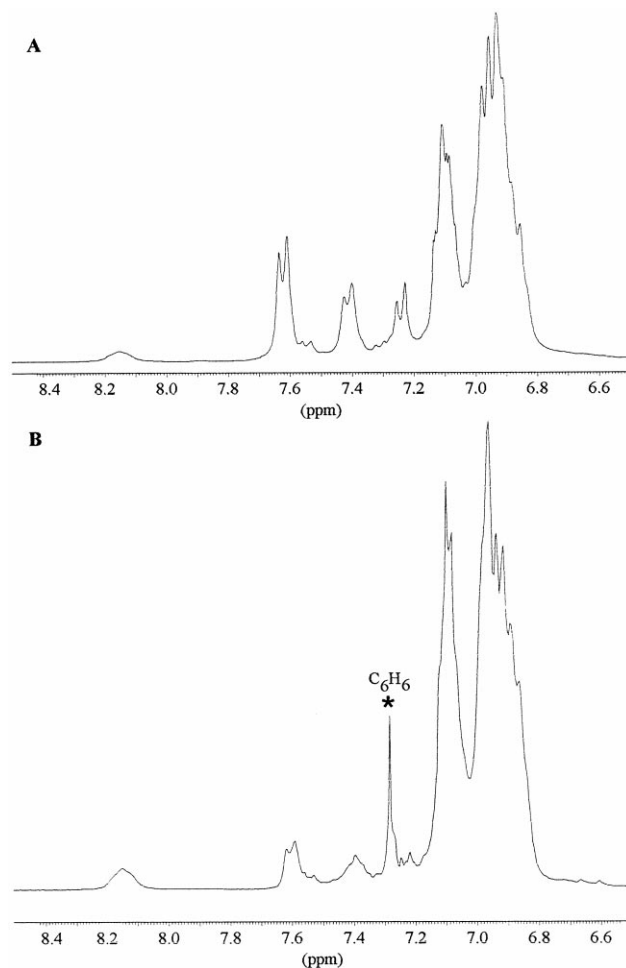
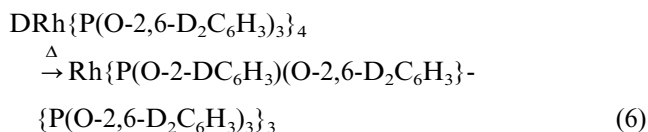


Fig. 5. ^1H -NMR spectra of $\text{Rh}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}_3$ (**I**), (A) and $\text{Rh}\{\text{P}(\text{O-2-DC}_6\text{H}_3)(\text{O-2,6-}\text{D}_2\text{C}_6\text{H}_3)_2\}\{\text{P}(\text{O-2,6-}\text{D}_2\text{C}_6\text{H}_3)_3\}_3$ (**B**) in C_6D_6 in the phenyl proton region (* traces of C_6H_6 in C_6D_6).

that spectrum the multiplet at 8.1 ppm was found, but doublets in the region 7.6–7.2 ppm were not observed (Fig. 5).



The downfield resonances were observed in all *ortho*-metallated complexes investigated by us, which may suggest their assignment to *meta* protons; however the final interpretation needs additional study. In fact we were not able to prepare the *ortho*-metallated complex by heating of $\text{HRh}\{\text{P}(\text{O-3,5-}(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\}_4$ as well as by its reaction with methyl acrylate.

3. Experimental

All reactions were carried out in inert atmosphere using the standard Schlenk technique.

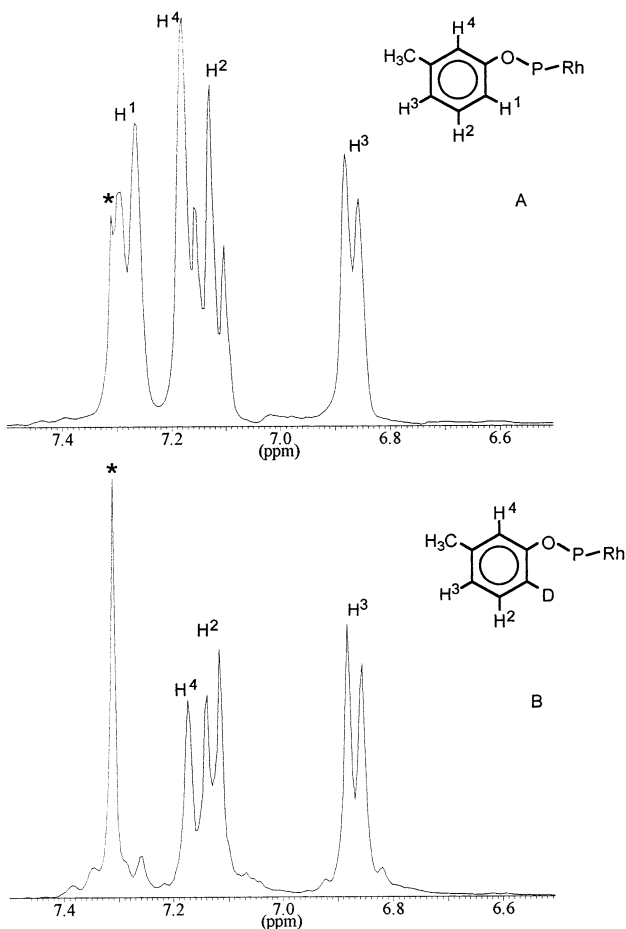


Fig. 4. ^1H -NMR spectra of $\text{HRh}\{\text{P}(\text{O-3-CH}_3\text{C}_6\text{H}_4)_3\}_4$ (A) and $\text{DRh}\{\text{P}(\text{O-2-D, 3-CH}_3\text{C}_6\text{H}_3)_3\}_4$ (B) in C_6D_6 in the phenyl proton region (* traces of C_6H_6 in C_6D_6).

Rhodium complexes were prepared according to literature methods: $\text{HRh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4$ [23], $\text{HRh}(\text{CO})\{\text{P}(\text{O}^i\text{Ph})_3\}_3$ [24], $\text{Rh}(\text{acac})(\text{CO})_2$ [25], $[\text{Rh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4]\text{BPh}_4$ [26], $[\text{Rh}\{\text{P}(\text{O}-3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\}_4]\text{BPh}_4$ [26] $\text{Rh}(\text{P}^i\text{O})(\text{CO})(\text{POH})$ [21].

$\text{HRh}\{\text{P}(\text{O}-3-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$ and $\text{HRh}\{\text{P}(\text{O}-4-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$ complexes have been prepared by the method described for $\text{HRh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4$ [23], in the reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with $\text{P}(\text{OR})_3$ under 1 atm of H_2 . Complexes have been characterized with ^1H -NMR.

3.1. $\text{HRh}\{\text{P}(\text{O}-3-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$

^1H -NMR data (C_6D_6), δ/ppm : -10.2 (q of d; $^1J(\text{Rh}-\text{H})$ 7 Hz, $^1J(\text{P}-\text{H})$ 45 Hz; $\text{Rh}-\text{H}$); 2.12 (s, CH_3); 6.83 (d, $^1J(\text{H}-\text{H})$ 6.8 Hz; $p-\text{H}$); 7.09 (t, $^1J(\text{H}-\text{H})$ 7.9 Hz; $m-\text{H}$); 7.14 (s, $o-\text{H}$); 7.24 (d, $^1J(\text{H}-\text{H})$ 7.9 Hz; $o-\text{H}$).

3.2. $\text{HRh}\{\text{P}(\text{O}-4-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$

^1H -NMR data (C_6D_6), δ/ppm : -10.6 (q of d; $^1J(\text{Rh}-\text{H})$ 6 Hz, $^1J(\text{P}-\text{H})$ 41 Hz; $\text{Rh}-\text{H}$); 2.13 (s, CH_3); 6.91 (d, $^1J(\text{H}-\text{H})$ 8.1 Hz; $m-\text{H}$); 7.24 (d, $^1J(\text{H}-\text{H})$ 8.0 Hz; $o-\text{H}$).

3.3. $\text{HRh}\{\text{P}(\text{O}-3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\}_4$

To a suspension of 0.11 g of $[\text{Rh}\{\text{P}(\text{O}-3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\}_4]\text{BPh}_4$ in 3 cm^3 of ethanol 0.5 cm^3 of ethanol containing 0.003 g NaBH_4 was added. During stirring the colour changed from yellow to white. The white precipitate was filtrated and washed with ethanol. ^1H -NMR data (C_6D_6), δ/ppm : -10.05 (q of d; $^1J(\text{Rh}-\text{H})$ 6 Hz, $^1J(\text{P}-\text{H})$ 45 Hz; $\text{Rh}-\text{H}$); 2.1 (s, CH_3); 6.67 (s, $p-\text{H}$); 7.1 (s, $o-\text{H}$).

3.4. Hydrogen-transfer reactions

The reactions were carried out at room temperature (r.t.) in Schlenk or in NMR tubes. The typical reaction solution contained $4.1 - 4.6 \times 10^{-5}$ mol of $\text{HRh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4$ or $\text{HRh}(\text{CO})\{\text{P}(\text{O}^i\text{Ph})_3\}_3$ and 1×10^{-4} mol of unsaturated substrate like styrene or hex-1-ene or 2.6×10^{-4} mol of methyl acrylate in 0.5 cm^3 of C_6H_6 or C_6D_6 . The reaction was monitored with ^1H -NMR (or/and ^{31}P -NMR) and final organic products were analysed with GC-MS after separation from the rhodium complexes by vacuum transfer.

3.5. H/D exchange

The reactions were carried out at r.t. in Schlenk tubes under 1 atm of D_2 . Typically, a solution of 0.02 g of rhodium complex in 1 cm^3 of C_6H_6 or C_6D_6 was prepared under dinitrogen, the tube was evacuated and D_2 was introduced. The mixture was stirred during the

reaction. Small samples after solvent evaporation were analysed by IR spectroscopy using KBr disks. The average reaction time was 3 h, the longest time for H/D exchange was 12 h. After that time the solvent was evaporated and the isolated complex analysed by IR spectroscopy and/or ^1H -NMR. In some experiments the reaction course was monitored with ^1H -NMR directly in C_6D_6 solution without isolation of the complex.

3.6. Monitoring of H/D exchange with IR

It was found that H/D exchange can be easily observed in the IR spectra in the region $1400 - 1600 \text{ cm}^{-1}$. The following changes in the IR spectra are detected during deuteration:

$\text{HRh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4$: the intensity of the band at 1490 cm^{-1} decreases and a new band at 1440 cm^{-1} appears.

$\text{HRh}(\text{CO})\{\text{P}(\text{O}^i\text{Ph})_3\}_3$: the intensity of the band at 1490 cm^{-1} decreases and a new band at 1443 cm^{-1} appears; ν_{CO} 2030.5; 2039 cm^{-1} .

$\text{HRh}\{\text{P}(\text{O}-3-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$: the intensity of the band at 1480 cm^{-1} decreases and the new band at 1400 cm^{-1} appears.

$\text{HRh}\{\text{P}(\text{O}-4-\text{CH}_3\text{C}_6\text{H}_4)_3\}_4$: the intensity of the band at 1510 cm^{-1} decreases and a new band at 1460 cm^{-1} appears.

$\text{HRh}\{\text{P}(\text{O}-3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\}_4$: the intensity of the band at 1450 cm^{-1} decreases and a new band at 1400 cm^{-1} appears;

3.7. Identification of rhodium complexes formed in reactions

3.7.1. $\text{Rh}\{\text{P}(\text{O}^i\text{Ph})_3\}_3(\text{HCO}_2)$

$^{31}\text{P}\{^1\text{H}\}$ -NMR δ_1 : 118.1 ppm, dt, $J(\text{Rh}-\text{P}) = 277 \text{ Hz}$; δ_2 106.7 ppm, dd, $J(\text{Rh}-\text{P}) = 230 \text{ Hz}$, $J(\text{P}-\text{P}) = 64 \text{ Hz}$.

3.7.2. $[\text{Rh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4](\text{HCO}_2)$

$^{31}\text{P}\{^1\text{H}\}$ -NMR δ : 108.6 ppm, d, $J(\text{Rh}-\text{P}) = 214 \text{ Hz}$.

3.7.3. $[(\text{H})_2\text{Rh}\{\text{P}(\text{O}^i\text{Ph})_3\}_4](\text{BPh}_4)$

$^{31}\text{P}\{^1\text{H}\}$ -NMR δ_1 : 118.7 ppm, dt, $J(\text{Rh}-\text{P}) = 169 \text{ Hz}$; $J(\text{P}-\text{P}) = 48 \text{ Hz}$, δ_2 110.5 ppm, dt, $J(\text{Rh}-\text{P}) = 145.0 \text{ Hz}$. ^1H -NMR: δ : -9.5 ppm , d of m, $J(\text{P}-\text{H}_{\text{trans}}) = 230 \text{ Hz}$.

3.7.4. $\text{RhCl}[\text{P}(\text{O}^i\text{Ph})_3]_3$

$^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_1 117 ppm, dt, $J(\text{Rh}-\text{P}) = 279 \text{ Hz}$, $J(\text{P}-\text{P}) = 54 \text{ Hz}$; δ_2 109 ppm, dd, $J(\text{Rh}-\text{P}) = 223.1 \text{ Hz}$.

3.7.5. $\text{Rh}(\text{P}^i\text{O})(\text{CO})\{\text{P}(\text{O}^i\text{Ph})_3\}$

$^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_1 121.6 ppm, dd, $J(\text{Rh}-\text{P}) = 236 \text{ Hz}$, $J(\text{P}-\text{P}) = 476 \text{ Hz}$; δ_2 41.6 ppm, dd, $J(\text{Rh}-\text{P}) = 130 \text{ Hz}$.

3.7.6. Deuterium transfer from $DRh\{P(O-2,6-D_2-C_6H_3)_3\}_4$ to $CH_2=CHC(O)OCH_3$

MS data of $CDH_2-CDH-C(O)OCH_3$: 90 [3, M^+], 89(17), 88(17), 59(35), 58(46), 57(46) $CH_3-CH_2-C(O)O-CH_3$: 86 [2, M^+], 85(10), 58(15), 56(10), 55(47).

4. Instruments

The following instruments were used: IR spectra: FT-IR Nicolet Impact 400; GC-MS, Hewlett-Packard 5890 II; NMR, Bruker 300 MHz (121.5 MHz for $^{31}P\{^1H\}$ -NMR). TMS was used as an internal standard in 1H and 85% H_3PO_4 as an external standard in $^{31}P\{^1H\}$ -NMR measurements.

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