ELSEVIER

Journal of Organometallic Chemistry 498 (1995) C10–C13

Journal of Organometallic Chemistry

Preliminary communication

Direct synthesis of acetals by rhodium catalysed hydroformylation of alkenes in the presence of orthoformate

K. Soulantica [a], S. Sirol [b], S. Koïnis [a], G. Pneumatikakis [a,*], Ph. Kalck [b,*]

[a] *Inorganic Chemistry Department, University of Athens, Panepistimiopolis, 157 71 Athens, Greece*
[b] *Laboratoire de Catalyse et de Chimie Fine, Ecole Nationale Supérieure de Chimie deToulouse, 118, route de Narbonne 31077 Toulouse cédex, France*

Received 9 January 1995

Abstract

The two catalyst precursors $[Rh_2(\mu\text{-penicillamine})_2(CO)_4][OTf]_2$ and $[Rh_2(\mu\text{-cysteine})_2(CO)_4][OTf]_2$ in the presence of 4 equivalents of $P(OPh)_3$ in triethyl orthoformate as solvent and reactant, permit the low pressure hydroformylation of various alkenes into the corresponding acetals. Apart from a few low-yield by-products resulting from isomerization of the substrates, the carbonylated products obtained directly and exclusively are acetals.

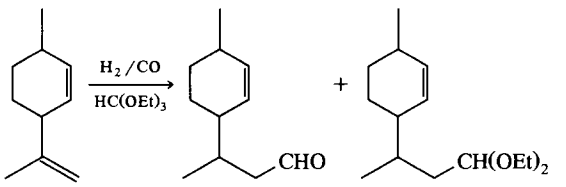
Keywords: Hydroformylation; Rhodium; Catalysis; Acetals

Acetals are protected forms of aldehydes, and several recent papers have described not only the catalytic conversion of an aldehyde into the corresponding acetal [1] but also the direct production of acetals by hydroformylation when identification of chiral compounds are required by NMR spectroscopy [2,3]. In particular, Stille and Parrinello have shown that hydroformylation of various prochiral alkenes catalysed by platinum–tin systems can be carried out in triethyl orthoformate, leading directly the diethylacetals of interest [2,3]. However, the introduction of trialkyl orthoformate as solvent or reactant causes a dramatic reduction in reaction rates. Cobalt catalysts have also been used but the yields remain very poor [4]. Recently Claver, Castillón, et al. carried out the hydroformylation of alkenes in triethyl orthoformate in the presence of pyridinium 4-toluene sulfonate and obtained high yields of the expected acetals [5,6].

In addition, Venanzi et al. have shown that aldehydes and ketones can be acetalized under mild conditions of temperature [1] using various rhodium precursors that generate species with Lewis-acid character and contain the triphosphine $H_3CC(CH_2PPh_2)_3$.

We report preliminary results where 1-octene or monoterpenes are chemoselectively converted into diethylacetals by use of cysteine- or penicillamine-bridged dicationic dirhodium complexes as catalyst precursors.

The classical hydridorhodium mononuclear complex $[HRh(CO)\{P(OPh)_3\}_3]$, in triethylorthoformate as solvent (molar alkene/rhodium ratio = 300) at 84 °C, 1.2 MPa and for 18 h gave a 31% conversion of *trans*-isolimonene into a mixture of 50% acetal and 50% aldehyde, with a small amount of isomers of the substrate (Eq. 1).



(1)

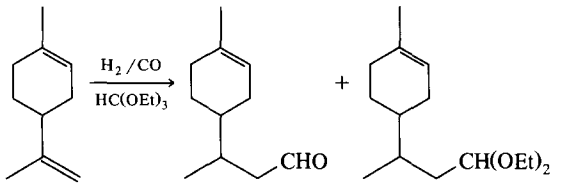
(1*R*, 4*R*)-isolimonene

The complex $[Rh_2(\mu\text{-S-}^tBu)_2(CO)_2\{P(OPh)_3\}_2]$ (molar alkene/dirhodium ratio = 600) in the presence of 10 equivalents of $P(OPh)_3$ transformed 50% of

* Corresponding author.

SSDI 0022-328X(95)05594-0

limonene into carbonylated products with selectivities of 93% in aldehyde and only 7% in acetal (Eq. 2).



(2)

(+)-*R*-limonene

A similar experiment carried out with (1*R*, 4*R*)-isolimonene (see Eq. 1) in the presence of 4 equivalents of $P(OPh)_3$ gave a 28% conversion, including 4% isomerization of the substrate, and a ratio of aldehyde/acetal of 96/4.

We have found that dinuclear precursors containing cysteine or penicillamine as bridging ligands can transform 1-octene, *trans*-isolimonene or β-pinene into acetal with complete chemoselectivity. Provided the reaction time was adjusted for each substrate, only minor amounts of isomers of the starting materials were produced (2-octene, terpinene or terpinolene..., α-pinene respectively).

The two thioamino acids $HSCR_2CH(NH_3)^+(COO)^-$ [R = H (cysteine **1**) and R = Me (penicillamine **2**)], were used as bridging ligands to prepare the two tetracarbonyl complexes $[Rh_2(\mu\text{-}\mathbf{1})_2(CO)_4][CF_3SO_3]_2$, **3**, and $[Rh_2(\mu\text{-}\mathbf{2})_2(CO)_4][CF_3SO_3]_2$, **4**, that we isolated in the solid state. Addition of $Ag(CF_3SO_3)$ to $[Rh_2Cl_2(CO)_4]$ in acetone under CO led, filtration of silver chloride and addition of **1** or **2**, to the two complexes **3** and **4**, in which the bridging ligands are $-SCR_2CH(NH_3)^+(COOH)$ (Fig. 1).

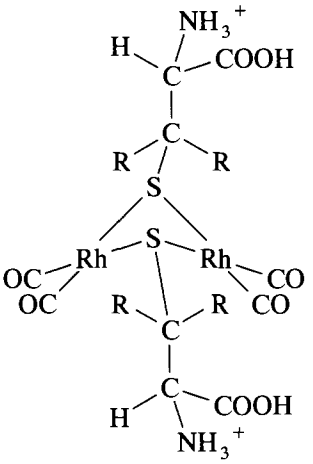


Fig. 1. Schematic diagram showing the two tetracarbonyl (μ-cysteine) or (μ-penicillamine) dirhodium complexes **3** and **4**.

Complex **3** shows three ν(CO) bands at 2096 (s), 2073 (s) and 2027 (vs) cm^{-1} (KBr pellets) consistent with a C_{2v} symmetry, and no ν(SH) band in the 2550 cm^{-1} region. The COOH group is characterized by its ν(CO) band at 1740 cm^{-1} and the NH_3^+ group by its ν(NH) band at 2955 cm^{-1}. Similarly, complex **4** has 3 ν(CO) bands at 2084 (s), 2068 (s) and 2018 (vs) cm^{-1}, a ν(CO) band at 1733 cm^{-1} for the COOH group, and a ν(NH) band at 2971 cm^{-1} consistent with a NH_3^+ group [7].

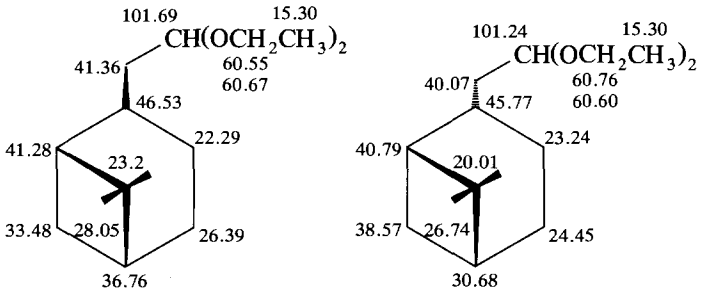
Addition of 4 equivalents of triphenylphosphite to complexes **3** and **4** in triethyl orthoformate generated active species which converted the substrates at 0.5, 1.2, or 2.1 MPa and 84 °C into the corresponding diethylacetals (Table 1). For instance **4**, 1-octene (row 1, Table 1) gave 87% conversion with only traces of 2-octene in 30 min. Two acetals were obtained with almost 100% chemoselectivity, the distribution being 1, 1-diethoxy-2-methyl-octane (18%) and 1, 1-diethoxy-nonane (82%). This catalysis corresponds to a turnover frequency of 1080 mol of product $(mol^{-1}$ of precursor$)^{-1}$ h^{-1}. (1*R*, 4*R*)-isolimonene (row 2, Table 1) reacted more slowly (53% in 3 h) and 47% of the acetal was produced. About 2% heavy-products and 4% isomers were identified.

Harsher conditions need to be used for β-pinene. Row 6, Table 1 shows that 2.1 MPa and 98 °C permit-

Table 1
Direct synthesis of acetals by hydroformylation of alkenes using $[Rh(\mu\text{-}SCR_2CH(NH_3)(COOH))]_2[OTf]_2$ [R = H (**3**), R = Me (**4**)] as catalyst precursor [a]

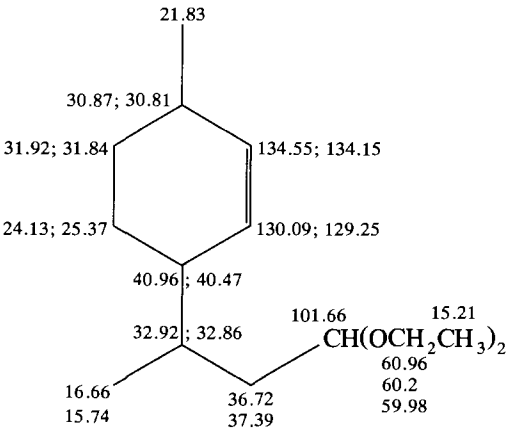
Row	Catalyst [b]	Substrate	P (MPa)	t (h)	Conversion [c] (%)	Yield [d] (%)	By-products
1	**4**	1-octene	0.5	0.5	nd	87 [e]	traces of 2-octene
2	**3**	(1*R*, 4*R*)-isolimonene	1.2	3	53	47	isomers of isolimonene
3	**3**	(1*R*, 4*R*)-isolimonene	1.2	18	97	44	isomers and heavy products
4	**4**	(1*R*, 4*R*)-isolimonene	1.2	18	95	76	isomers and heavy products
5	**4**	(−)-β-pinene	2.1	18	56	52	α-pinene
6	**4**	(−)-β-pinene	2.1	18	80 [f]	71	α-pinene

[a] Reaction conditions: 40 ml triethyl orthoformate, 60 mmol substrate, substrate/catalyst = 600, 0.4 mmol triphenyl phosphite, $CO/H_2 = 1/1$, T = 84°C.
[b] **3** or **4** prepared in triethyl orthoformate starting from 0.1 mmol of $[Rh_2Cl_2(CO)_4]$.
[c] Substrate converted measured by gas phase chromatography with an internal standart (acetophenone).
[d] Yield in acetals.
[e] Octene converted based on the total octene (1- and 2-) present, measured by gas phase chromatography with an internal standard (anisole).
[f] T = 98°C.



(1*R*,2*R*) (1*R*,2*S*)

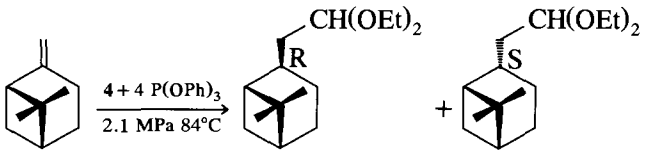
2-(2,2-diethoxyethyl)-6,6-dimethyl-bicyclo[3.1.1]heptane



(3*R*)- and (3*S*)-1,1-diethoxy-3-(4-methylcyclohex-2-enyl)butane

Fig. 2. ^{13}C NMR (62, 9 MHz, $CDCl_3$) data for acetals produced by hydroformylation of (−)-β-pinene and (1*R*, 4*R*)-isolimonene in triethylorthoformate.

ted 80% transformation of the starting material in 18 h. However, at this temperature there was 8% isomerization to α-pinene, whereas at 84 °C only 4% isomerization occured (row 5). The reaction is diastereoselective. A chiral carbon atom is formed, and the two configurations were obtained in a ratio of 87% (R) to 13% (S) i.e. a diastereoisomeric excess of 74% (Eq. 3) as observed by GC. However, in this case the two chiral bridging ligands do not improve the diastereoselectivity with regard to $[Rh_2(\mu\text{-S-}^tBu)_2(CO)_4]$ plus $P(OPh)_3$. Pittman et al. [8] have previously observed such an asymmetric induction (67% d.e.) in the absence of chiral ligands on their rhodium or cobalt precursors. However, they obtained mixtures of 3- and 10-formylpinane and the corresponding alcohols, depending on the reaction conditions.



(−)-β-pinene 87% 13% (3)

Here, the two acetals resulting from (−)-β-pinene were isolated by column chromatography on silica gel (hexane, ethyl acetate) and identified by GC/MS, and ^1H NMR, and ^{13}C NMR spectroscopy (see Fig. 2). A similar procedure was carried out for (1*R*, 4*R*)-isolimonene, and we also obtained the two acetals. In this case, no diastereoisomeric excess was observed.

The main benefit of using **3** or **4** as catalyst precursors in the hydroformylation reaction carried out in trialkyl orthoformate is to produce acetals directly in high yield with no decrease of the reaction rate.

Acknowledgements

We thank the Platon program between France and Greece for travel and subsistence, and the Comptoir-Lyon-Alemand-Louyot for a loan of rhodium trichloride.

References

[1] J. Ott, G.M. Ramos Tombo, B. Schmid, L.M. Venanzi, G. Wang and T.R. Ward, *Tetrahedron Lett., 30* (1989) 6151.

[2] G. Parrinello and J.K. Stille, *J. Am. Chem. Soc., 109* (1987) 7122.
[3] J.K. Stille, H. Su, P. Brechot, G. Parrinello and L.S. Hegedus, *Organometallics, 10* (1991) 1183.
[4] P. Pino, G. Consiglio, C. Botteghi and C. Salomon, *Adv. Chem. Ser., 132, Am. Chem. Soc. Ed.* (1974) 295.
[5] A.M. Masdeu, A. Orejón, A. Ruiz, S. Castillón and C. Claver, *J. Mol. Catal., 94* (1994) 149.
[6] E. Fernández and S. Castillón, *Tetrahedron Lett., 35* (1994) 2361.
[7] (a) A. Kay and P.C.H. Mitchell, *J. Chem. Soc. (A)* (1970) 2421; (b) K. Nakamoto, Y. Morimoto and A.E. Martell, *J. Am. Chem. Soc., 83* (1961) 4528; (c) G. Pneumatikakis and N. Hadjiliadis, *J. Inorg. Nucl. Chem., 41* (1979) 429; (d) S.T. Chow, C.A. Mc Auliffe and B.J. Sayle, *J. Inorg. Nucl. Chem., 35* (1973) 4349.
[8] E.N. dos Santos, C.U. Pittman, Jr. and H. Toghiani, *J. Mol. Cat., 83* (1993) 51.