New bimetallic rhodium–zirconium catalysts for homogeneous olefin hydroformylation

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Abstract

Catalytic activity of bimetallic system composed with $Rh(acac)(CO)_2$ and $cp_2Zr(CH_2PPh_2)_2$ or $cp_2ZrH(CH_2PPh_2)$ (cp = C_5H_5) in hex-1-ene, 1,5-hexadiene and 1,7-octadiene hydroformylation have been studied at 80°C, 10 atm of $H_2/CO = 1$. Hydroformylation of hex-1-ene produces normal and branched aldehydes of 69–85% yield and n/iso ratio 1.8–2.0. Hydroformylation of dienes gives unsaturated monoaldehydes (ca. 30% yield). Applying ^1H, ^{31}P NMR, UV–VIS and IR spectroscopy the following complexes have been identified: $Rh(acac)(CO)_2L$ (1), $Rh(acac)(CO)(L)$ (2), and $Rh_4(CO)_xL_{12-x}$ (3) (where: L = $cp_2Zr(CH_2PPh_2)_2$, $cp_2ZrH(CH_2PPh_2)$, x = 8–11).
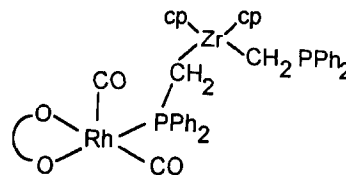
1. Introduction

Bimetallic system of d^0–d^8 metal electronic structure, composed with zirconium (IV) (d^0) complex $cp_2Zr(CH_2PPh_2)_2$ and different rhodium (I) d^8 complexes like $HRh(PPh_3)_4$ [1], $HRh(CO)(PPh_3)_3$ [2], $HRh\{P(OPh)_3\}_4$ and $HRh(CO)\{P(OPh)_3\}_3$ [3] applied for hex-1-ene hydroformylation, produced aldehydes with satisfactory yield and selectivity. Zirconium (IV) complex, $cp_2Zr(CH_2PPh_2)_2$, in all above mentioned systems is coordinated to rhodium via one or both phosphorous atoms, playing the role of modifying ligand similar to that of PPh_3 or $P(OPh)_3$.

Also, dimeric rhodium complexes obtained in the reaction of $Rh_2(\mu\text{-}SBu^t)_2(CO)_4$ with $cp_2Zr(CH_2PPh_2)_2$ [4] or $(\eta^5\text{-}Bu^t\text{-}C_5H_4)_2Zr(CH_2PPh_2)_2$ [5] are active in hydroformylation although PPh_3 or $P(OPh)_3$ ligands are not present in coordination sphere.

The main task of this paper is study of the structure and activity of catalytic systems composed with $Rh(acac)(CO)_2$ as catalyst precursor and zirconium (IV) complexes, playing the role of 'zirconium–phosphine' modifying ligand – $cp_2Zr(CH_2PPh_2)_2$ and $cp_2ZrH(CH_2PPh_2)$, respectively. Catalytic activity of $cp_2ZrH(CH_2PPh_2)$ in olefin isomerization and hydrogenation have been studied previously [6,7]. On the other hand, Zr-complexes (as well as Ti, Nb, V . . .) were never involved in hydroformylation catalysis. As strongly oxophilic metals they form catalyst poisoning Zr–O bonds.

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The above mentioned rhodium (I)–zirconium (IV) catalytic systems without any additional modifying ligands have been applied for hydroformylation of hex-1-ene, 1,5-hexadiene and 1,7-octadiene.

2. Results and discussion

2.1. Studies on reaction: $Rh(acac)(CO)_2 + cp_2Zr(CH_2PPh_2)_2$

It was published in our earlier paper that phosphines and phosphites easily substitute carbonyl ligands (one or two) in $Rh(acac)(CO)_2$ forming respective substitution reaction products [8]. Zr (IV) complex, $cp_2Zr(CH_2PPh_2)_2$, in reaction with $Rh(acac)(CO)_2$ behaves similar to triphenylphosphine, producing a monosubstituted complex of the formula $Rh(acac)(CO)(cp_2Zr(CH_2PPh_2)_2)$. However, this reaction is more complicated than that with triphenylphosphine and proceeds with the few stages monitored by ^1H, ^{31}P NMR, UV–VIS and IR measurements (Table 1).

IR and ^1H NMR studies of the reaction mixture at the concentration ratio $[cp_2Zr(CH_2PPh_2)_2]:[Rh(acac)(CO)_2] = 0.5$ have shown unreacted starting $Rh(acac)(CO)_2$ complex and also two new rhodium species $Rh(acac)(CO)_2(cp_2Zr(CH_2PPh_2)_2)$ (1), and $Rh(acac)(CO)(cp_2Zr(CH_2PPh_2)_2)$ (2). The main product, complex (1), contains two CO ligands (ν_{CO} 1990, 2055 cm^{-1}) and 'zirconium–phosphine', $cp_2Zr(CH_2PPh_2)_2$, in coordination

(1)

Fig. 1. Proposed structure of the $Rh(acac)(CO)_2(cp_2Zr(CH_2PPh_2)_2)$ complex

sphere. Coordination of zirconium (IV) complex to rhodium via phosphorous atoms is evidenced by the ^{31}P NMR spectra measurements which show the doublet at δ 33.6 ppm with J_{Rh-P} 176 Hz as well as by the shift of proton signals in ^1H NMR from 5.76 ppm (for free Zr-complex in C_6D_6) to 5.85 ppm after coordination to rhodium. The Zr-complex is monocoordinated, which was proved by the presence of the signal of a free $Zr(CH_2PPh_2)$ group at δ −2.3 ppm in ^{31}P NMR. The presence of coordinated acetylacetone was confirmed by the presence of two signals of methyl groups at δ 1.7 and 1.35 ppm and the signal at 5.1 ppm assigned for –CH proton. On the base of spectroscopic results the formula $Rh(acac)(CO)_2(cp_2Zr(CH_2PPh_2)_2)$ was proposed for complex (1). Two signals of methyl groups suggest that the complex (1) has no symmetry plane and its most probably structure is shown at (Fig. 1).

The second reaction product, complex (2), was observed in very low concentration in reaction performed at [Zr]:[Rh] ratio 0.5. At higher concentration of Zr (IV) complex up to [Zr]:[Rh]

Table 1
Spectroscopic characterization of reaction products: $Rh(acac)(CO)_2$ (S$_1$) + $cp_2Zr(CH_2PPh_2)_2$ (S$_2$) in C_6D_6

Substrate (S)/complex formed (P)	IR (ν_{CO}/cm^{-1})	^{31}P NMR (δ/ppm (J_{Rh-P}/Hz))	^1H NMR (δ/ppm)	UV–VIS (nm)
(S$_1$) Rh(acac)(CO)$_2$	2020, 2090	—	1.45; 4.9 (acac)	306, 326
(S$_2$) cp$_2$Zr(CH$_2$PPh$_2$)$_2$	—	−3.1	1.4 (CH$_2$); 5.76 (cp)	—
(P$_1$) Rh(acac)(CO)$_2$(cp$_2$Zr(CH$_2$PPh$_2$)$_2$) (1)	2055, 1990	33.6 (176); −2.3	1.7; 1.35; 5.1 (acac); 5.85 (cp)	398, 418
(P$_2$) Rh(acac)(CO)(cp$_2$Zr(CH$_2$PPh$_2$)$_2$) (2)	1980	20.4 (129)	1.55; 5.1 (acac); 5.85 (cp)	402

$cp = C_5H_5$.

(2)
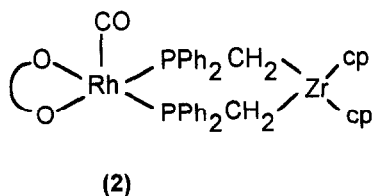
Fig. 2. Proposed structure of the Rh(acac)(CO)(cp$_2$Zr(CH$_2$PPh$_2$)$_2$) complex

$= 0.9$, the complex (2) is the main reaction product.

Complex (2) is characterized by the presence of only one carbonyl ligand frequency (ν_{CO}) in IR at 1980 cm^{-1} and the doublet in ^{31}P NMR at 20.4 ppm (J_{Rh-P} 129 Hz). The absence of the free Zr(CH$_2$$PPh_2$) group signal in ^{31}P NMR in the region δ -3 ppm is indicative for the bidentate character of Zr-complex coordination. Complex (2) has a formula Rh(acac)(CO)(cp$_2$Zr(CH$_2$PPh$_2$)$_2$) with acac and Zr-ligands located in one plane (Fig. 2).

The proposed structure is supported by the presence of only one signal of methyl groups of acac ligand in ^{1}H NMR at 1.55 ppm. Complex Rh(acac)(CO)(cp$_2$Zr(CH$_2$PPh$_2$)$_2$) was isolated in solid. Its IR spectrum shows typical chelating coordination of acetylacetonate ligand (stretching frequencies observed at 1590, 1530 and 1390 cm^{-1}).

The increase of cp$_2$Zr(CH$_2$PPh$_2$)$_2$ concentration up to [Zr]:[Rh] = 1.8 do not effect in substitution of the second CO ligand (only one ν_{CO} at 1970 cm^{-1} is observed). However the ^{31}P NMR signals at δ ca. 20 ppm ($\nu_{1/2}$ 150 Hz) and ^{1}H NMR at δ 1.55 ppm and ca. 5 ppm are distinctly broadened. It may suggest appearance of dynamic processes, like that of chemical exchange of triphenylphosphine ligand observed in the system Rh(acac)(CO)$_2$ + PPh$_3$ [9].

Because of low solubility of cp$_2$ZrH(CH$_2$PPh$_2$) in all applied solvents it was not possible to follow the reaction of Rh(acac)(CO)$_2$ with cp$_2$ZrH(CH$_2$PPh$_2$) in solution by spectroscopic methods. However, the final product of that reaction, performed in C$_6$H$_6$ at the ratio [Zr]:[Rh] = 2, was isolated and for-

mula Rh(acac)(CO)(cp$_2$ZrH(CH$_2$PPh$_2$) was assumed for it on the base of IR measurements. The bands of acac at 1600, 1530 and 1380 cm^{-1} overlap partially with broad band of ν_{Zr-H} frequency whereas ν_{CO} is observed at 1960 cm^{-1}.

2.2. Hydroformylation of hex-1-ene, 1,5-hexadiene and 1,7-octadiene

The catalytic system composed with Rh(acac)(CO)$_2$ (catalyst precursor) and

Table 2

Hydroformylation of hex-1-ene catalyzed by the system: Rh(acac)(CO)$_2$ +cp$_2$Zr(CH$_2$PPh$_2$)$_2$ [I] and Rh(acac)(CO)$_2$ + cp$_2$ZrH(CH$_2$PPh$_2$) [II].Reaction conditions: 80°C, 10 atm, H$_2$/CO = 1, [hex-1-ene]:[Rh] = 390, [Rh] = 1.4·10^{-5} mol, t = 3.5 h

[Zr] (10^{-5} mol)	[Zr]:[Rh]	Products (% mol)		
		aldehydes	hex-2-ene	hex-1-ene
0	0	14	69	17
cp$_2$Zr(CH$_2$PPh$_2$)$_2$				
2.44	—	0	0	100
1.22	0.9	52	34	14
1.69	1.2	85	13	1
cp$_2$ZrH(CH$_2$PPh$_2$)				
2.09	1.4	35	21	44
3.69	2.7	69	15	16

Table 3

Hydroformylation of 1,5-hexadiene and 1,7-octadiene catalyzed by the systems Rh(acac)(CO)$_2$ + cp$_2$Zr(CH$_2$PPh$_2$)$_2$ [I] and Rh(acac)(CO)$_2$ + cp$_2$ZrH(CH$_2$PPh$_2$) [II]. Reaction conditions: 80°C, 10 atm, H$_2$/CO = 1, [1,5-hexadiene]:[Rh] = 180, [1,7-octadiene]:[Rh] = 140, [Rh] = 1.6·10^{-5}

Substrate	[Zr] (10^{-5} mol)	[Zr]: [Rh]	Σ Aldehydes (mol%)	n / iso	Reaction time (h)
cp$_2$Zr(CH$_2$PPh$_2$)$_2$					
1,5-Hexadiene	1.8	1.1	26	2	2
	2.8	1.8	30	1.6	5
	6.4	3.9	10	1.5	4
1,7-Octadiene	6.4	3.9	3		3
cp$_2$ZrH(CH$_2$PPh$_2$)					
1,5-Hexadiene	1.6	1.0	7		4
	5.7	3.5	40	1.2	6
	8.8	5.5	25	1.7	8
1,7-Octadiene	6.5	4.0	59	1.3	6

$cp_2Zr(CH_2PPh_2)_2$ or $cp_2ZrH(CH_2PPh_2)$ as modifying ligands were used for hydroformylation of hex-1-ene (Table 2) as well as 1,5-hexadiene and 1,7-octadiene (Table 3). Generally, the yield of aldehydes increases with the increase of Zr (IV) species concentration (Tables 2 and 3). However, modifying capacity of particular 'zirconium–phosphines' are different.

The system modified with $cp_2ZrH(CH_2PPh_2)$ (system **II**) at [Zr]:[Rh] = 1.44 and 2.7, produces 35% and 69% of aldehydes, respectively. Modifying effect of $cp_2Zr(CH_2PPh_2)_2$ (system **I**) is even higher and the yield of 85% is reached at [Zr]:[Rh] = 1.2. The selectivity of hydroformylation was similar in all reactions under studies (n/iso = 1.8–2.0). It is worth to notice that the observed enhanced catalytic activity of the systems studied must be associated with the 'in situ' formation of bimetallic rhodium–zirconium complexes. The only $Rh(acac)(CO)_2$ complex has very low activity in hydroformylation (only 14% of aldehydes) and quite significant activity in hex-1-ene isomerization (69% of hex-2-ene).

Both Zr (IV) complexes, applied alone under hydroformylation reaction conditions (CO/H_2 = 10 atm), do not catalyze either hydroformylation or isomerization of hex-1-ene. The activity of the catalytic system under study is significantly lower in case of dienes hydroformylation (average yield of aldehydes do not exceeds 30% for system [I] and 59% for system [II] after 6 h). The only reaction products are unsaturated monoaldehydes, 6-heptenal and 2-Me-5-hexenal in hydroformylation of 1,5-hexadiene and 8-nonenal and 2-Me-7-octenal in hydroformylation of 1,7-octadiene, respectively. Double bond migrations in both substrates and products were not observed but hydroformylation reaction selectivity was rather low ($n/iso \leq 2$).

Catalytic activity of bimetallic Rh–Zr complexes in hex-1-ene hydroformylation is comparable to that of $Rh(acac)(CO)(PPh_3)$ + PPh_3 and $Rh(acac)\{P(OPh)_3\}_2$ + $P(OPh)_3$ systems [10], although selectivity is generally lower.

For hydroformylation of dienes, catalytic sys-

tems under study are less attractive and dialdehydes, main products of hydroformylation with $Rh(acac)(CO)(PPh_3)$ + PPh_3 systems [11], were never obtained in the systems modified with zirconium–phosphine.

2.3. The studies on catalyst in post reaction mixture

Spectroscopic studies of post-reaction mixtures led us to the statement that complexes of $Rh(acac)(CO)(L)$ type (where L = $cp_2Zr(CH_2PPh_2)_2$ or $cp_2ZrH(CH_2PPh_2)$) identified at the beginning of the catalytic process undergo transformation during hydroformylation.

^{31}P NMR studies of the $Rh(acac)(CO)_2$ + $cp_2Zr(CH_2PPh_2)_2$ or $cp_2ZrH(CH_2PPh_2)$ mixture in toluene or benzene aged during one hour under 10 atm of H_2/CO at 80°C, disclosed the doublet at δ 14.5 ppm (J_{Rh-P} = 120 Hz). From that solution, rhodium complex of approximate formula of $Rh_4(CO)_x(cp_2Zr(CH_2PPh_2)_2)_{12-x}$ (x = 8–11) was isolated in solid (IR: ν_{CO} 2040, 1990, 1970, 1810 cm^{-1}). The structure of that carbonyl cluster was proposed on the basis of IR data [12]. In comparable conditions, rhodium complex $Rh(acac)(CO)(PPh_3)$ undergoes similar transformation to $HRh(CO)(PPh_3)_3$ and $Rh_4(CO)_x(PPh_3)_{12-x}$ (ν_{CO} for $Rh_4(CO)_8(PPh_3)_4$ 2070, 2048, 1995, 1970, 1810, 1800 cm^{-1}) [13].

3. Experimental

Rhodium and zirconium complexes were prepared according to the literature methods: $Rh(acac)(CO)_2$ [14], $cp_2Zr(CH_2PPh_2)_2$ [15], $cp_2ZrH(CH_2PPh_2)$ [16]. Solvents (toluene, benzene) and olefins were distilled before use.

Hydroformylation reaction was carried out in thermostated steel autoclave (40 cm^3) with magnetic stirrer. Samples of $Rh(acac)(CO)_2$ (0.0036–0.0045 g) and zirconium complexes (0.006–0.017 g) were introduced to the auto-

clave in nitrogen atmosphere. Next, toluene (0.7 cm^3) and hex-1-ene (0.7 cm^3) or 1,5-hexadiene (0.35 cm^3) or 1,7-octadiene (0.35 cm^3) were added, respectively. Finally the autoclave was filled up with $H_2/CO = 1$ mixture at 10 atm. Reaction products were identified by ^{1}H NMR (Tesla 567 BS 100 MHz or Bruker 300 MHz, 121.5 MHz for ^{31}P NMR), and after vacuum distillation by GC-MS (Hewlett-Packard) using xylene as internal standard. The column HP-5 $\times$ 25 m $\times$ 0.2 mm $\times$ 0.33 μm (film thickness) was used for product analysis. UV–VIS spectra were recorded on 8452 A UV–VIS spectrometer (Hewlett-Packard), IR spectra on Nicolet, Impact 400.

MS and ^{1}H NMR data of reaction products:

(a) *n*-heptanal: 114 (M$^+$, 1); 96 (7); 95 (1); 86 (10); 81 (15); 71 (21); 70 (61); 68 (13); 57 (48); 55 (50); 45 (20); 44 (100); 43 (74); 42 (57); 41 (74); 39 (28). ^{1}H NMR (C$_6$D$_6$) δ 9.6 ppm (t, CHO).

(b) 2-Me-6-hexanal: 114 (M$^+$, 1); 96 (1); 91 (1); 85 (2); 81 (1); 72 (7); 71 (4); 58 (100); 57 (20); 53 (2); 43 (70); 41 (26). ^{1}H NMR (C$_6$D$_6$) δ 9.5 ppm (d, CHO).

(c) 6-heptenal: 111 (0.5); 97 (4); 94 (8); 84 (11); 83 (13); 79 (39); 70 (22); 68 (100); 67 (59); 57 (33); 56 (35); 55 (54); 53 (20); 43 (33); 42 (30); 41(100); 39 (54). ^{1}H NMR (C$_6$D$_6$) δ 9.6 ppm (CHO); 5.6 (m, CH$_2$=CH); 5.15 (m, CH_2=CH).

(d) 2-Me-7-octenal: 112 (M$^+$, 1); 94(7); 84 (4); 79 (8); 69 (8); 68 (8); 58 (100); 57 (35); 55 (48); 42 (17); 41 (63); 39 (85). ^{1}H NMR (C$_6$D$_6$) δ 9.5 ppm (CHO); 5.6 (m, CH$_2$=CH); 5.15 (m, CH_2=CH).

(e) 8-nonenal: 122 (2); 111 (6); 98 (20); 97 (13); 96 (15); 93 (17); 83 (20); 81 (41); 79 (24); 70 (22); 69 (20); 68 (30); 67 (39); 57 (28); 55 (100); 54 (52); 44 (35); 41 (85). ^{1}H NMR (C$_6$D$_6$) δ 9.6 ppm (CHO); 5.6 (m, CH$_2$=CH); 5.15 (m, CH_2=CH).

(f) 2-Me-6-octenal: 125 (3); 112 (9); 111 (9); 98 (12); 97 (15); 83 (15); 82 (24); 69 (48); 58 (100); 55 (73); 43 (55); 41 (100). ^{1}H NMR (C$_6$D$_6$) δ 9.5 ppm (CHO); 5.6 (m, CH$_2$=CH); 5.15 (m, CH_2=CH).

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