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SELECTIVE REDUCTION OF DIENES TO MONOENES VIA HYDROGEN TRANSFER REACTION IN THE PRESENCE OF CARBONYL CLUSTERS

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Summary

1,5-Cyclooctadiene and 1,5-hexadiene are selectively reduced by hydrogen transfer from i-PrOH using $Rh_6(CO)_{16}$ as procatalyst. The first step of the reaction appears to be the formation of conjugated diene isomers, which are subsequently reduced to monoenes. Carbonyl clusters of Os, Ru and Ir can also be used, but their activities are lower and they predominantly catalyze isomerization.

Introduction

Selective hydrogenation of dienes to monoenes homogeneously catalyzed by transition metal compounds has been extensively studied and reviewed [1]. Selectivity is often due to thermodynamic or kinetic factors which in some way reduce the rate of formation of saturated hydrocarbons. Complete selectivity, however, requires a catalyst able to hydrogenate dienes but unreactive towards monoenes. Catalytic systems include, for example $[Co(CN)_5]^{3-}$ [2], $[PdCl(PPh_3)(\eta^3\text{-allyl})]$ [3]. Ruthenium(0) polyolefin complexes can also bring about selective hydrogenation of 1,3- and 1,5-cyclooctadiene to cyclooctene [4]. A similar behaviour is shown by $Ni(acac)_2$ in the presence of $Al_2Et_3Cl_2$ and PPh_3 [5]. Dienes very rapidly isomerized to the thermodynamically more stable conjugated systems when platinum(II)-$SnCl_3^-$ was used as catalyst, and it was initially proposed that conjugated systems gave rise to the selective monoene product [6]. More careful studies of a range of dienes and monoenes, showed that this is not necessarily so, since it was found that non-isomerizable dienes are selectively hydrogenated to the corresponding monoenes [1]. Selective reduction to monoenes via hydrogen transfer, together with some isomerisation, is catalyzed by cationic rhodium(I) complexes of the type $[Rh(diene)L_2]^+$ [7]. Metal clusters have been widely used as homogeneous catalyst (or catalyst precursor) in many organic reactions [8], and have also been much studied as models for chemisorption process in heterogeneous catalysis.

We have used few carbonyl metal clusters namely $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$,

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$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in various experimental conditions as catalyst precursors for selective transfer hydrogenation of diolefins (1,5-cyclooctadiene and 1,5-hexadiene) to monoolefins.

Results and discussion

Results obtained for the reduction of 1,5-cyclooctadiene (COD) to cyclooctene (COE) via hydrogen transfer from i-PrOH as donor molecule catalyzed by $Rh_6(CO)_{16}$ are shown in Table 1. Cyclooctene is selectively formed (run 1, Table 1), and after 23 h no trace of saturated species can be detected. The first step of the reaction is a comparatively fast isomerization, mainly to the 1,3-isomer, along with some 1,4-cyclooctadiene which is formed at the beginning of the reaction (see Fig. 1). Carbon monoxide is always present to prevent metal formation, and the CO pressure also

TABLE 1

REDUCTION OF 1,5-CYCLOOCTADIENE CATALYZED BY $Rh_6(CO)_{16}$ [a]

Run	Reaction time (h)	Product composition (%) [b]				
		COE	1,3-COD	1,4-COD	1,5-COD	
1	1	2	75	5	18	Cycles/hour = 66
	3	17	83			(5 h)
	5	35	66			
	23	99				
2	1	3	49	18	30	Cycles/hour = 93 (5 h)
	3	27	72		1	P(CO) 17 atm
	5	47	53			
	23	99				
3	1	3	82	2	14	Cycles/hour = 20 (5 h)
	5	49	50			[Rh] = 5×10^{-4} M Sub/Rh = 200
4	1	2	69	6	23	Cycles/hour = 120 (5 h)
	2	4	90		6	[Rh] = 0.5×10^{-4} M
	5	30	70			Sub/Rh = 2000
5	1	2.5	73	4	21	$PPh_3/Rh_6 = 1$
	5	34	66			
6	1	2.5	73	4	20	$PPh_3/Rh_6 = 2$
	5	35	65			
7	1	2	54	20	25	$PPh_3/Rh_6 = 10$
	5	9	90			
8	1	2.5	75	4	18	diphos/Rh_6 = 1
	2	7	89		3	
	5	30	70			
9	1	1	30	26	43	diphos/Rh_6 = 5
	5	4	87	5	4	
10	1	3	97			substrate/1,3-COD
	3	20	80			sub/Rh = 990
	23	97	3			
11	1	4	95			substrate/1,3-COD
	3	28	71			sub/Rh = 990
	23	99				P(CO) 17 atm

[a] Reaction conditions: solvent i-PrOH, temperature 145°C, P(CO) 45 atm, [Rh] = 10^{-4} M, substrate/Rh = 1000. Cycles/hour are calculated measuring the amount of cyclooctene formed. [b] COE = cyclooctene, COD = cyclooctadiene.

influences the catalytic activity of the system. The number of catalytic cycles per hour, as given by the amount of cyclooctene formed (cf. Table 1), increases with decreasing CO pressure, but at the same time the total catalytic activity, based on the disappearance of 1,5-cyclooctadiene decreases with decreasing CO pressure. During the first hour, the numbers of catalytic cycles based on the disappearance of the 1,5-cyclooctadiene, were 820 (p(CO) 45 atm; run 1) and 700 (p(CO) 17 atm; run 2). These results could be attributed to the presence of some equilibria among the species present in the solution which are formed by cluster fragmentation and have different catalytic activities. To confirm this hypothesis we carried out the reduction with various concentration of the carbonyl cluster (runs 1–4, Table 1). Upon increasing the cluster concentration by a factor of ten, the number of catalytic cycles per hour based on the disappearance of 1,5-cyclooctadiene during the first hour of reaction, fell from a value of 1540 to 172, and the numbers based on the appearance of cyclooctene fell from 120 to 20. These results indicate that the cluster breaks down during the catalytic process and species with lower nuclearity are obtained [9]. As above reported, isomerization occurs initially, to give some 1,4- and a large amount of 1,3-COD (see Fig. 1). Then the reaction proceeds slowly with selective hydrogenation to monoene. The same reduction rate was observed using 1,3-COD as substrate (runs 10, 11, Table 1). All the results are consistent with the hypothesis that selectivity of this catalytic system is based on its inability to hydrogenate monoolefins. To check this point we used 1,5-hexadiene and hexene as substrate under the experimental conditions used to reduce 1,5-cyclooctadiene. These results are shown in Table 2. The overall rate is lower (see Fig. 2), and this is probably related to the different coordinating abilities of the two ligands or to the large number of isomers formed during the first stage of the reaction. The separate components of the mixture were distinguished by GLC: *trans,trans*-2,4-hexadiene was the predominant isomer, reaching 44% of the total after 5 h of reaction, other isomers are also formed, especially *trans*-1,4-hexadiene (maximum 20% after 2 h of

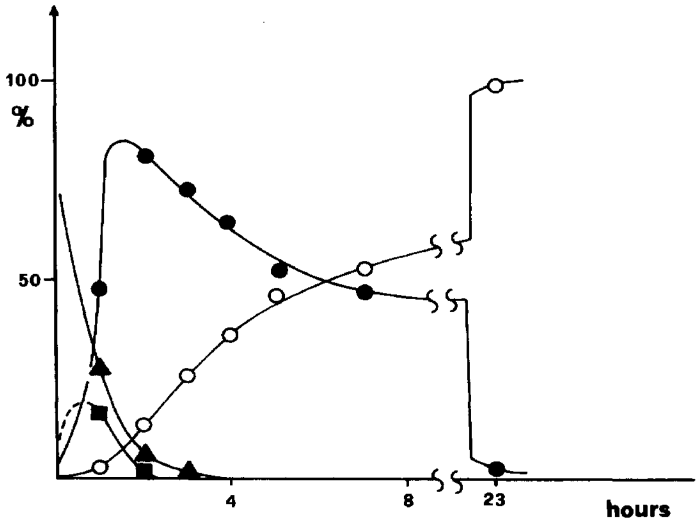

Fig. 1. Reduction of 1,5-cyclooctadiene in i-PrOH at 145°C. P(CO) 45 atm. (○) Cyclooctene, (●) 1,3-cyclooctadiene, (■) 1,4-cyclooctadiene, (▲) 1,5-cyclooctadiene.

TABLE 2

REDUCTION OF 1,5-HEXADIENE CATALYZED BY $Rh_6(CO)_{16}$ [a]

Run	Reaction time (h)	Product composition (%)			Notes
		1,5-Hexadiene	Hexenes	Hexadienes	
1	1	70	1	30	P(CO) 17 atm
	5	1	10	89	
	22	1	53	46	
	55		95	4	
2	1	16	1	82	P(CO) 45 atm
	5		9	90	
	22		49	50	
	55		97	3	
3	1	73	3	14	P(CO) 17 atm
	7	1	12	82	$PPh_3/Rh_6 = 10$
	22		27	72	
	54		47	52	
4	1	89	1	10	P(CO) 17 atm
	7	16	8	75	$PPh_3/Rh_6 = 60$
	22	1	11	88	
	46		12	87	
5	2	70	1	30	P(CO) 17 atm
	7	26	1	72	$PPh_3/Rh_6 = 300$
	22	6	2	92	
	96		5	95	
6	1	74	2	24	P(CO) 17 atm
	7	1	12	87	diphos/Rh_6 1
	22		33	67	
	94		99		

[a] Reaction conditions, solvent i-PrOH, Temperature 145°C, $[Rh] = 10^{-4}$ M, Substrate/Rh = 1000.

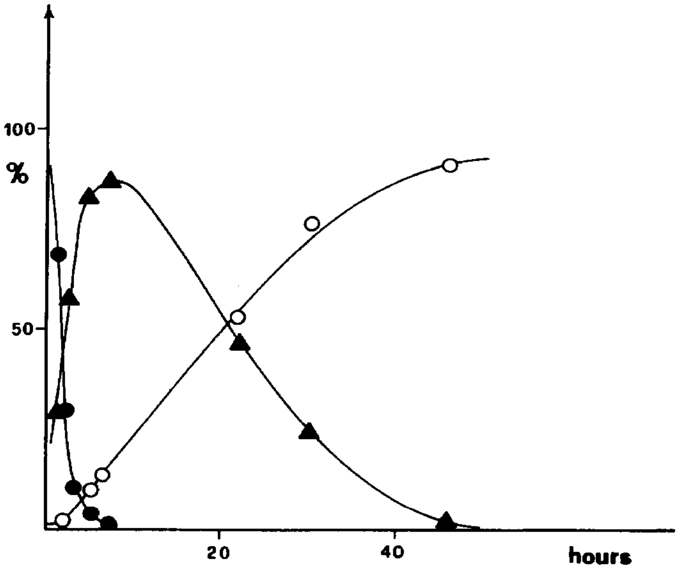

Fig. 2. Reduction of 1,5-hexadiene in i-PrOH at 145°C. p(CO) 17 atm. (○) Hexenes, (▲) hexadienes, (●) 1,5-hexadiene. Composition of the final mixture: *trans*-3-hexene (19%), *cis*-2-hexene (21%), *trans*-2- and *cis*-3-hexene (56%). Composition of the hexadienes mixture (maximum value (%)): *trans*-1,4- (20% in 2 h), *cis*-1,4- (7% in 2 h), *cis*- and *trans*-1,3- (8% in 4 h), *trans,trans*-2,4- (44% in 5 h), *cis,trans*-2,4- (29% in 5 h), *cis,cis*-2,4- (4.5% in 7 h).

reaction) and *cis,trans*-2,4-hexadiene (29% after 5 h). Smaller amounts of other isomers were detected, and the complete composition of the mixture is reported in the caption to Fig. 2. The hexadienes are then reduced to a mixture of hexenes, and the final product contain *trans*-3-hexene (19%), *cis*-2-hexene (21%); the remaining 56% is a mixture of *trans*-2- and *cis*-3-hexene, which we could not separate. 1-Hexene under the same conditions gave no hydrogenation product, but isomerized to the same mixture finally present after the reduction of hexadienes. For reductions of 1,5-COD and 1,5-hexadiene we examined the effect of changes in carbon monoxide pressure and of addition of phosphines. Changes in CO pressure have no significant effect (at least in the range we explored) on the reduction of 1,5-hexadiene. When 1,5-COD is used as substrate, increase in the CO pressure favours the isomerization with respect to the hydrogenation (Table 1, run 1,2). Addition of phosphines slows down the overall reaction, and at the same time favours the isomerization (Table 1 and 2).

$Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were also used as catalyst precursor for the reduction of 1,5-cyclooctadiene. In every case the activity in the reduction is rather poor and the isomerization is always favoured. $Os_3(CO)_{12}$ becomes deactivated during the reaction (Table 3, run 6), but if the cluster is kept for several hours at 145°C under CO atmosphere before the addition of the substrate, the catalyst completely isomerizes 1,5-cyclooctadiene into the 1,3- and 1,4-isomers. We think that a new species is obtained in this way which does not lose its catalytic activity in the presence of the substrate. It is known that $Os_3(CO)_{12}$ reacts in i-PrOH to give

TABLE 3

REDUCTION OF 1,5-CYCLOOCTADIENE CATALYZED BY $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ AND $Os_3(CO)_{12}$ [a]

Run	Catalyst	Reaction time (h)	Product composition (%)				Notes
			COE	1,3-COD	1,4-COD	1,5-COD	
1	$Ru_3(CO)_{12}$	3		3	6	91	
		57		33	30	36	
		144	1	75	5	18	
2	$Ru_3(CO)_{12}$	21		2	9	89	$PPh_3/Ru_3(CO)_{12} = 10$
3	$Ir_4(CO)_{12}$	3		6	20	74	$[Ir] = 10^{-4}$ *M*
		5	1	11	26	62	
		21	1	30	29	38	
4	$Ir_4(CO)_{12}$	3		4	18	78	$[Ir] = 10^{-4}$ *M*
		7		15	30	55	sub/Ir = 200
		21		47	28	24	react.temp. 165°C
5	$Ir_4(CO)_{12}$	3	1	27	31	40	$[Ir] = 0.5 \times 10^{-4}$ *M*
		7	3	50	23	24	sub/Ir = 2000
		21	5	86	2	7	react.temp. 165°C
6	$Os_3(CO)_{12}$	3	1	6	16	77	*P*(CO) 17 atm
		7	1	10	25	64	
		22	1	11	26	63	
7	$Os_3(CO)_{12}$ [b]	3	2	9	16	73	*P*(CO) 17 atm
		7	2	25	28	44	
		24	8	72	6	13	
		54	20	78		2	

[a] Reaction conditions: solvent i-PrOH, *T* 145°C, *P*(CO) 45 atm, $[metal] = 10^{-4}$ *M*. Substrate/metal = 1000. [b] $Os_3(CO)_{12}$ was kept at 145°C under CO atmosphere for 15 h before the addition of the substrate.

$[HOs_3(CO)_{10}OR]$ [10], a species which could be formed during the activation time. A further indication of the formation of species having lower nuclearity is given in Table 3 for runs 3, 4 and 5, in which a lower catalyst concentration gives a more active system. We think that in this system also there is evidence that catalysis is due to cluster fragmentation, which gives species having different activities and selectivities, and that the selectivity is related to the inability of these systems to reduce monoolefins.

Experimental section

Chemicals

Isopropanol was distilled over CaO and stored under an inert atmosphere. Substrates were purified by low pressure distillation over sodium and stored under an inert atmosphere. $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were purchased from Strem Chemicals.

Procedure

Two autoclaves (100 and 190 ml) equipped with a magnetic stirrer and heating mantle were used. The appropriate amount of the catalyst was placed into the autoclave, while the solution of the substrate in i-PrOH was prepared separately. Carbon monoxide was bubbled into the deareated solution for 30 min and the solution was then added to the catalyst in the autoclave.

Analyses were performed on a Perkin–Elmer Sigma 3B gas-chromatograph equipped with a thermal conductivity detector and using helium as carrier. Analyses of cyclooctadienes were carried out with a 2 m column packed with 15% Carbowax 20M on Chromosorb WAW, 80–100 mesh. Analyses of the hexenes and the hexadienes employed a 9 m column packed with 20% of TCEP (1,2,3-tris(2-cyanoethoxy)-propane) on Chromosorb P, 80–100 mesh. All the products were identified by comparison with authentic samples.

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