The study of alkene isomerization catalyzed by the system: rhodium dimeric complex—tertiary phosphine—tin dichloride

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Rhodium(I) dimeric complexes, $[(Ph_3P)_4Rh_2Cl_2]$ and $[(C_2H_4)_4Rh_2Cl_2]$, form active catalysts for alkenes isomerization on interaction with tertiary phosphine and tin dichloride in CH_2Cl_2. Besides 2-methylbut-2-ene, which is the normal product of 1,2-double bond migration, 3-methylbut-1-ene gives the product of unusual 1,3-double bond migration, 2-methylbut-1-ene, which is formed at early stages of the reaction under kinetic control in over-equilibrium quantities. The proposed mechanism for 1,3-double bond migration includes the methyl C—H bond activation, followed by intramolecular transfer hydrogenation.

Key words: alkene, isomerization; rhodium, binuclear complexes; catalysis.

The migration of double bond is a widespread reaction, accompanying homogeneous hydrogenation, hydroformylation, and other catalytic reactions of alkenes. In some cases, this reaction can be of industrial importance, *e.g.*, in production of *tert*-butylmethyl ether or motor fuels.[1,2]

Using this reaction, convenient routes were proposed to silyl dienol ethers, [3] amides and esters of dienoic acids and dienones,[4,5] α,β-unsaturated aldehydes and ketones from propargyl alcohols.[6,7] The enantioselective isomerization of allylamines to enamines was carried out with use of chiral rhodium catalyst.[8,9] The isomerizations of allyl alcohols catalyzed by ruthenium carbonyls afford a simple route to aldehydes.[10]

Polynuclear transition metal complexes, both bridged and cluster, are in many cases more active in low-pressure hydroformylation of formaldehyde [11] and alkenes[12—14] compared with monomer analogs. The high activity was explained in terms of cooperative effects and template mechanisms,[15] though the exact nature of these effects was not suggested. Also evidence for mononuclear active species was obtained.[16]

Bridged dirhodium chlorostannato complexes are active in dehydrogenation of isopropyl alcohol,[17,18] alkanes and cycloalkanes.[19] The mononuclear Wilkinson catalyst is also active in analogous reaction.[20]

As we have shown earlier, the trichlorostannato analog of the Wilkinson catalyst, $[(Ph_3P)_3RhSnCl_3]$ is active in alkene isomerization *via* the π-allyl-hydride mechanism.[21] Moreover, the system $[(Ph_3P)_4Rh_2Cl_2]$ + $SnCl_2$ is much more active in this reaction. Isomerization of 3-methylbut-1-ene by this system gives 2-methylbut-1-ene in a quantity slightly more than equilibrium concentration, which is 11% at 300 K.[22] This product was identified by its ^{13}C NMR spectrum,[23] and is clearly detected in the ^1H spectrum due to its olefin CH_2 protons *.

This paper is devoted to the study of catalytic activity of binuclear bridged rhodium complexes as a function of ligand environment and basicity of phosphine.

Experimental

The ^1H and ^{13}C NMR spectra (79.54 and 20.0 MHz, respectively) were recorded on a Varian FT-80A spectrometer (TMS and CD_2Cl_2 were used as internal standards). The kinetic measurements were performed by integration of the corresponding signals in ^1H NMR spectrum. Several points up to 10% of conversion were used for the calculation of initial rates of the reaction. The whole set of kinetic data points was then processed by standard least-squares method, assuming the first-order kinetics.

The rhodium dimers,[24,25] $[(Ph_3P)_4Rh_2Cl_2]$ (**1**) and $[(C_2H_4)_4Rh_2Cl_2]$ (**2**) and 3-methylbut-1-ene, [26a] were obtained as described earlier. Tin dichloride[26b] and CD_2Cl_2[27] were purified according to standard procedures. The preparation of samples and the isomerization of 3-methylbut-1-ene were carried out in the absence of oxygen and moisture using a standard vacuum technique. All liquids were dried and degassed before use; solids were dried for several hours and stored under vacuum.

The solutions of catalysts for isomerizations were prepared according to procedures ***A*** and ***B***.

A. The complex **2** was dissolved in CD_2Cl_2, a weighted amount of phosphine was added and stirred for 5 min, then

* NMR spectral parameters for alkene region (CD_2Cl_2), δ: 3-methylbut-1-ene, δ ^1H: 4.99—4.85 (m, 2 H; $=CH_2$), 5.87—5.78 (m, 1 H, =CH); δ ^{13}C: 111.25 (t, $=CH_2$), 146.49 (d, =CH). 2-Methylbut-1-ene, δ ^1H: 4.70—4.66 (m, 2 H, $=CH_2$); δ ^{13}C: 108.45 (t, $=CH_2$), 148.24 (s, =C). 2-Methylbut-2-ene, δ ^1H: 5.23 —5.16 (m, 1 H, =CH); δ ^{13}C: 123.19 (d, =CH), 132.4 (s, =C).

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the resulting solution was stirred for 30 min with two-fold mole amount of anhydrous $SnCl_2$, until a clear deep-red solution was formed.

B. The complex **1** was suspended in CD_2Cl_2 together with $SnCl_2$ and stirred for 10 min until a deep-red clear solution was formed.

The solutions thus obtained were then transferred to NMR tubes and the 3-methylbut-1-ene was condensed thereupon. The ^1H spectra were taken directly for reaction solutions, whereas the ^{13}C spectra were taken after removal of the non-volatiles and addition of 10 mg of $Cr(acac)_3$ as relaxation agent.

Results and Discussion

The formation of catalytic active system. The system based on complex **1** and $SnCl_2$ (procedure ***B***) contains exactly two moles of PPh_3 per mole of rhodium. Since the dimers of the type $(R_3P)_4Rh_2Cl_2$ in general are hardly available, this direct method of generation can be easily applied only for the Ph_3P complex. Furthermore, this procedure does not make it possible to study the catalysts containing less than 2 moles of phosphine per mole of rhodium. These problems can be avoided by use of procedure ***A***. We choose the ethylene Rh^I dimer as starting material, since the ethylene molecule is readily displaced with phosphine ligands. According to,[28] the interaction of Rh^I ethylene or norbornadiene dimers with diphosphines retains the dimeric chloride-bridged structure. In our experiments with P : Rh_2 ratio 2—4 we also observed the formation of the phosphine-containing species, identified as dimeric complexes based on the ^{31}P NMR spectra. On addition of 6 or more moles of R_3P per mole of ethylene Rh dimer, the formation of triphosphine mononuclear complexes $(R_3P)_3RhCl$ also was detected. The resulting deep-colored solutions produced on addition of $SnCl_2$ showed unfortunately, the substantial line broadening in ^{31}P NMR spectra in CD_2Cl_2, thus precluding more detailed information on the solution structure of the active species.

Isomerization of 3-methylbut-1-ene. The isomerization proceeds at temperatures 0—45° C and results in a mixture of the normal isomerization product 2-methylbut-2-ene, together with substantial amounts of 2-methylbut-1-ene, the relative quantities of the two products being dependent on the particular phosphine ligand and on the phosphine/Rh ratio. At low degrees of transformation the ratio (2-methylbut-1-ene)/(2-methylbut-2-ene) is higher than at equillibrium state (11% according to[22] Table 1, 2). This finding indicates that the formation of 2-methylbut-1-ene is a result of kinetically controlled one-step 1,3-migration of the double bond, rather than two consecutive 1,2-migrations.

To clarify the mechanism of the 1,3-double bond migration, the partial kinetic orders with respect to the catalyst and the substrate for the **1**—$SnCl_2$ system were determined using the method of initial rates (see Table 1). The values obtained are in the range 1—1.3, which can be the result of absence of substantial pre-equilibrium dissociation of the rhodium dimers to form the active species. The values of k_1(1,3-migration)/k_1(1,2-migration) ratios in Table 1 are calculated assuming the first-order kinetics for both reactions.

Table 1. The initial reaction rates of the 3-methylbut-1-ene isomerization catalyzed by $[(Ph_3P)_4Rh_2Cl_2]$—$SnCl_2$ at various reaction conditions

$[Rh_2]\cdot10^3$	[Alkene]	$W_{tot}\cdot10^4$ [a]	$W_{1,2}\cdot10^4$ [b]	$W_{1,3}\cdot10^4$ [c]
mol L^{-1}		mol L^{-1} min^{-1}		
12.9	0.0947	0.312	0.301	0.142
12.0	0.689	2.79	1.43	1.88
11.9	0.926	5.32	3.45	2.064
11.5	1.37	7.34	3.47	4.35
3.8	0.653	0.67	0.455	0.839
5.3	0.667	1.49	0.713	1.16
7.7	0.666	3.95	2.54	2.49
17.4	0.668	5.03	3.59	5.73
20.61	0.667	7.0	4.48	6.15

[a] The initial rate of 3-methylbut-1-ene consumption.
[b] The initial rate of 1,2-double bond migration.
[c] The initial rate of 1,3-double bond migration.

Table 2. The composition of reaction products at approx. 30% conversion of 3-methylbut-1-ene in various reaction conditions ([Alkene] = 1 mol L^{-1}; $[Rh_2] = 10.8\cdot10^{-3}$ mol L^{-1}; CD_2Cl_2)

R_3P	R_3P/Rh_2	T /°C	t /min	2-Methyl-but-2-ene (%)	2-Methyl-but-1-ene (%)	Selectivity[a]
Ph_3P[b]	4	0	159	24.0	19.8	—
Ph_3P[b]	4	0	1204[c]	13.6	16.4	1.0
Ph_3P[b]	4	0	575[d]	9.1	20.9	—
Ph_3P[b]	4	0	368[e]	13.0	17.0	0.85
Et_3P	2.8	35	280	12.0	21.0	4.8
Ph_2PMe	2.9	35	93	16.0	14.4	0.85
Ph_2PMe	4	35	70	10.0	23.6	1.75
Ph_2PMe	5	35	254	23.4	9.0	0.14
Ph_2PMe	3.45	45	203	6.9	25.3	2.8
Ph_2PMe	3.9	45	69	8.5	22.0	—
Ph_2PMe	4.2	45	373	26.5	9.9	—
Ph_2PMe	5	45	377	23.8	12.6	0.42

[a] Ratio k_1(1,3-migration)/k_1(1,2-migration).
[b] The catalyst derived from $[(Ph_3P)_4Rh_2Cl_2]$+2 $SnCl_2$.
[c] $[Rh_2] = 1.98\cdot10^{-3}$ mol L^{-1}.
[d] $[Rh_2] = 6.58\cdot10^{-3}$ mol L^{-1}; [Alkene] = 0.109 mol L^{-1}.
[e] $[Rh_2] = 5.58\cdot10^{-3}$ mol L^{-1}; [Alkene] = 1.46 mol L^{-1}.

We suggest that these data can be rationalized as the insertion of chlorostannato rhodium complexes into $C(sp^3)$—H methyl bond, *i.e.*, methyl C—H bond activation as a first step. An analogous mechanism is apparently operative in dehydrogenation of alkanes and cycloalkanes,[19,20] and for the *o*-tolylphosphine and tolyl platinum complexes.[29] The further transformations of active intermediates could occur *via* several reaction

steps, resulting in the intramolecular 1,3-shift of hydrogen molecule. This reaction could be kinetically more favored than the known allyl-hydride transformation,[21] due to steric hindrances around the methyne hydrogen of the particular substrate.

The suggestion that dimeric rhodium species could be catalytically active in this reaction is supported by the fact that the increase of R_3P : Rh_2 ratio up to 4 and greater causes a sharp decrease in the rate of 1,2- and particularly, 1,3-migration (see Table 2). The apparent reason could be the formation of $[(R_3P)_3RhSnCl_3]$ complexes, which are the catalysts of π-allyl-hydride type alkenes isomerization[21], being less active than the corresponding dimers. This fact however, even together with the determined partial reaction orders, cannot be regarded as a straightforward test for the dimeric nature of active species. The optimum P : Rh_2 ratio both for total reaction rate and for 1,3-migration selectivity is close to 4. The change of phosphine from Ph_3P to Ph_2PMe causes a decrease in the isomerization rate, but the ratio 1,3-/1,2-products increases, being about 1 for Ph_3P and reaching values of 3 and 4 for Ph_2PMe and Et_3P.

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