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Alkene isomerization catalysed with platinum hydride complexes

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The mechanism of but-1-ene, pent-1-ene and 3-methylbut-1-ene isomerization catalysed with *trans*-[PtH(SnX_3)L_2] (I, L = PPh_3, $PMePh_2$, PEt_3, PPr_3; X = Cl, Br) have been studied. Stoichiometric reactions of I with the alkenes proceed even at −90°C giving *cis*-[Pt(alkyl-1) (SnX_3)L_2] (II). The equilibrium amounts of II are dependent on the nature of the phosphines, halogens and alkenes. The isomerization rates, determined at +20°C, change in parallel with the relative stabilities of II as a function of phosphine ($PMePh_2 > PPh_3 > PAlk_3$) and halogen (Br > Cl), and decrease with methyl substitution at γ- and δ-carbons of the alkenes. 2-Substituted alk-1-enes undergo no isomerization in the reactions under investigation. When L is PPh_3 or $PMePh_2$, the main platinum-containing species in the course of the isomerization are *trans*-[Pt(alkyl-1) (SnX_3)L_2], appearing as a result of *cis–trans* isomerization of II. The conversion of I, L = $PAlk_3$ into related *trans*-alkyl complexes, and oxidation of I, proceed more slowly than the isomerization of alkenes. The ratio of *cis*- to *trans*-alk-2-enes is dependent on the size of L and is a maximum for L = PPh_3.

Keywords: Isomerization, alkene, platinum hydrides, tin trihalide complexes of platinum, catalysis, phosphine, mechanism

INTRODUCTION

Platinum phosphine complexes, activated by tin dihalides, are known as active catalysts for alkene hydrogenation,[1,2] hydroformylation,[3–5] and isomerization.[6–8] The effect of tin dihalides is generally attributed to the formation of trihalogenstannato complexes of platinum,[9] which are reduced to the corresponding hydrides in the reaction conditions. Cataytic cycles of the alkene reactions include, as one of the key stages, a reversible formation of platinum σ-alkyl complexes, resulting from alkene insertion into the Pt–H bond.[10] Recently, we have studied the interaction of *trans*-[PtH(SnX_3)L_2] (I) with ethylene, propene and 2-methylpropene.[11] In the present paper we describe the catalytic activity of the hydrides I (L = PPh_3, $PMePh_2$, PEt_3, PPr_3; X = Cl, Br) in alk-1-ene isomerization (but-1-ene, pent-1-ene, 3- and 2-methylbut-1-enes, and 2,3-dimethylbut-1-ene) into the corresponding alk-2-enes, as well as the mechanism of the reaction and the composition of the products.

EXPERIMENTAL

The ^{31}P-{^{1}H}, ^{13}C-{^{1}H}, and ^{1}H NMR spectra were obtained with a Varian FT-80A instrument operating at 32.196, 20.0, and 79.542 MHz respectively. Chemical shifts, calculated in the δ-scale, were determined relative to external 85% H_3PO_4, signals of ^{13}C and residual protons of deuterodichloromethane (CD_2Cl_2); 10-mm NMR tubes with 8.5-mm sealed inserts were used with the reaction mixtures in CD_2Cl_2.

CD_2Cl_2, SnX_2 and *trans*-[PtHXL$_2$] were prepared as described.[11]

But-1-ene, pent-1-ene and 3-methylbut-1-ene were obtained by pyrolysis of trimethyl(alkyl-1) ammonium hydroxides. 2-Methylbut-1-ene and 2,3-dimethylbut-1-ene were obtained by dehydration of tertiary amyl alcohol and dimethylisopropylcarbinol with phosphorus oxychloride ($POCl_3$) and pyridine respectively.[12] Rectification gave the fractions enriched with alk-1-enes (33°C, 60% of 2-methylbut-1-ene + 40% of 2-methylbut-2-ene; 55°C, 90% of 2,3-dimethylbut-1-ene + 10% of 2,3-dimethylbut-2-ene). The purity and isomer composition of the alkenes were checked by means of ^{1}H and ^{13}C NMR spectroscopy. Before use the alkenes were additionally dried by recondensing them twice *in vacuo* over phosphorus pentoxide (P_2O_5).

Table 1 ^{31}P NMR spectra of *cis*-[PtR(SnX_3)L_2] (**II**) in CD_2Cl_2 at −90°C[a,b]

L	X	R	δ(P)	δ(P′)	^1J(Pt–P)	^1J(Pt–P′)	II (%)
PPh_3	Cl	C_4H_9	29.4	16.5	3970	1866	95
		C_5H_{11}	29.4	16.6	3980	1865	88
		i-C_5H_{11}	29.2	16.5	3970	1870	86
	Br	C_4H_9	26.0	19.5	3986	1917	100
		C_5H_{11}	26.0	19.5	3994	1954	100
		i-C_5H_{11}	25.9	19.8	3991	1921	100
$PMePh_2$	Cl	C_4H_9	11.4	0.1	3863	1807	100
		i-C_5H_{11}	11.4	0.4	3870	1805	100
		2-MeC_4H_8	10.9	−0.5	3875	1793	27
		2,3-$Me_2C_4H_7$	10.3	−0.7	—[c]	—[c]	17
	Br	C_5H_{11}	8.1	1.5	3866	1827	100
		i-C_5H_{11}	8.2	2.0	3868	1824	100
		2-MeC_4H_8	7.8	1.1	3877	1826	70

[a] Chemical shifts in ppm relative to 85% H_3PO_4; coupling constants in Hz. [b] P′ is *trans* to R, P is *cis* to R. [c] Values are not determined due to low signal intensities.

Solutions of *trans*-[PtH(SnX_3)L_2] and the catalytic isomerization of alkenes

Reactions of *trans*-[PtHXL_2] (0.025 mmol) and SnX_2 (0.025 mmol) in 1 cm^3 of CD_2Cl_2, and the subsequent reactions of **I** with an alkene (2.5 mmol) were carried out in all-glass evacuated apparatus. The handling of reagents, as well as the composition and purity of the solutions obtained, were controlled by ^{31}P NMR spectra at −90°C, and have been shown essentially to be the same as described previously.[11] The alkenes were first allowed to react with **I** for about 2 h at −90°C. After the ^{31}P NMR spectra have been recorded the solutions were warmed to +20°C, and the isomerization reaction was followed with ^{1}H NMR spectroscopy. The time required for one ^{1}H spectrum was about 4 s. After the isomerization had taken place to the extent of 50–70%, CD_2Cl_2 and alkenes were recondensed in the tube using 14 mg of Cr(acac)$_3$. The ^{13}C NMR spectrum was recorded to determine the *cis*/*trans* ratio of alk-2-enes with assignments performed in accord with Ref. 13.

The processing of kinetic data

The concentrations of alkenes were calculated from the integrated intensities of corresponding ^{1}H NMR signals. Plots of ln [alk-1-ene] versus time were linear up to 50–60% conversion and were processed with a least-squares routine, giving $k_{1\,obs}$ as a slope. The standard deviations in $k_{1\,obs}$ were about 5% of the values.

RESULTS AND DISCUSSION

The interaction of I with alkenes

The interactions of **I** (L = PPh_3, $PMePh_2$) with monosubstituted alk-1-enes leads to *cis*-complexes **II**, quite analogous from the viewpoint of their ^{31}P NMR spectra to *cis*-ethyl and *cis*-n-propyl ones described previously[11] (Table 1). The NMR data obtained lead us to the conclusion that *cis*-[Pt(alkyl-1)(SnX_3)L_2] (**II**) were formed as the result of anti-Markovnikov insertion of alk-1-enes into platinum hydride (Pt–H) bonds. The amounts of **II** formed in 2 h at −90°C, when the equilibrium amount of alkyl complex appears to be almost reached, are also quoted in Table 1. The hydrides **I** (L = PEt_3, PPr_3) do not react with the alkenes at −90°C to any noticeable extent. The insertion reactions of disubstituted alk-1-enes, 2-methylbut-1-ene and 2,3-dimethylbut-1-ene, proceed to some extent only with *trans*-[PtH($SnBr_3$)($PMePh_2$)$_2$]. The sequence of reactivities of **I** towards the alkenes as a function of L and X is similar to that described previously.[11] Complexes **II**, with 2-methylbutyl and 2,3-dimethylbutyl groups, are formed in smaller amounts than the corresponding 2-methylpropyl complexes, apparently owing to increased steric requirements caused by γ-carbon substitution. The γ-substitution has, however, little effect on the reaction of 3-methylbut-1-ene with **I** (L = PPh_3).

Table 2 Observed first-order alk-1-ene isomerization rate constants $k_{1\,\mathrm{obs}}$ and isomeric composition of reaction products[a]

L	X	Alk-1-ene	$k_{1\,\mathrm{obs}} \times 10^5$, ($s^{-1}$)	$\tau_{1/2}$ (min)	*trans*-Alk-2-ene (%)	Isomerization (%)
PPh_3	Cl	C_4H_8	8.3	150	53	50
		C_5H_{10}	4.0	250	50	15
		i-C_5H_{10}	0.31	3650	nd[b]	nd
	Br	C_4H_8	80	13	62	62
		C_5H_{10}	43	16	63	50
		i-C_5H_{10}	0.77	1310	nd	nd
$PMePh_2$	Cl	C_4H_8	760	1.5	67	90
		C_5H_{10}	240	2.8	68	65
		i-C_5H_{10}	1.5	1000	nd	nd
	Br	C_5H_{10}	nd	1	77	100
		i-C_5H_{10}	4.1	200	nd	nd
PEt_3	Cl	C_4H_8	0.31	3250	74	55
		C_5H_{10}	0.34	nd	nd	nd
	Br	C_4H_8	2.1	575	81	63
		C_5H_{10}	1.6	630	nd	nd
PPr_3	Cl	C_4H_8	0.2	nd	76	30
		C_5H_{10}	0.22	nd	74	19

[a] $[PtH(SnX_3)L_2]$, 0.025 mol dm^{-3}; alkene, 2.5 mol dm^{-3}; CD_2Cl_2, +20°C. [b] nd, value not determined.

The alkene isomerization, catalysed by I

The isomerization of but-1-ene and pent-1-ene in the presence of **I** ($L = PPh_3$, $PMePh_2$) proceeds slowly above 0°C; reaction conditions are given in Table 2. Complexes **I** ($L = PAlk_3$) exhibit only minor activity; therefore all kinetic data were obtained at +20°C. The slope of a semilogarithmic plot of alk-1-ene concentration vs time gives an observed first-order rate constant values, $\mathbf{k}_{1\,\mathrm{obs}}$ (Eqn 1), which characterizes the

$$\frac{d[\text{alk-1-ene}]}{dt} = k_{1\,\mathrm{obs}} \cdot [\text{alk-1-ene}] \qquad [1]$$

reaction rate under the chosen conditions (Table 2). The $k_{1\,\mathrm{obs}}$ values decrease with increased substitution at γ- and δ-carbon atoms of alkenes: i.e.

$$\text{but-1-ene} > \text{pent-1-ene} \gg \text{3-methylbut-1-ene} \qquad [2]$$

The activity of complexes **I** decreases in the series [3] and [4], similarly to their reactivity in the alkene insertion reaction (Table 1).[11]

$$PMePh_2 > PPh_3 > PEt_3 \geqslant PPr_3 \qquad [3]$$

$$Br > Cl \qquad [4]$$

Complex **I** ($L = PEt_3$) shows no activity in 3-methylbut-1-ene isomerization during one week at +20°C. The β-branched alk-1-enes are not isomerized even by the most active *trans*-$[PtH(SnBr_3)(PMePh_2)_2]$ complex. The series [2] correlates poorly with the alkene activities in the insertion reactions, i.e. with the equilibrium amounts of *cis*-alkyl complexes at −90°C. The data obtained can be explained by the suggestion that the key intermediate of the isomerization reaction proceeding by the hydrido-alkyl mechanism[6,7] is the secondary alkyl complex, appearing in low quantity, imperceptible by ^{31}P NMR. This quantity, as well as the rate of complex formation, should vary in the series [3] and [4] similarly to those for the primary alkyl complexes **II**. However, the stability of the secondary alkyl complexes is strongly affected by C-4 and C-3 substitutions for steric reasons, just as the stability of **II** is strongly affected by the substitution at C-2. The lack of isomerization of 2-methylalk-1-enes gives evidence for the non-existence of tertiary alkyl complexes of platinum under the conditions studied.

Table 3 Platinum phosphine complexes involved in the isomerization of alkenes, in proportion (%) to the total amounts of platinum phosphine complexes (CD_2Cl_2, −90°C)

L	X	Alkene	Alk-2-ene, %	Amount of Pt–P complexes, (% of total) I	II	III
PPh_3	Cl	C_4H_8	50	23	29	48
	Br	C_4H_8	62	9	73	18
$PMePh_2$	Cl	C_4H_8	93	0	55	45
	Cl	C_5H_{10}	65	12	0	88
	Cl	i-C_5H_{10}	35	0	0	100
PEt_3	Cl	C_4H_8	53	85	0	15

The state of the catalyst in the course of alkene isomerization and the reaction mechanism

The state of the catalyst during the alkene isomerization has been followed by ^{31}P NMR spectroscopy of the reaction solution at −90°C. The spectral lines appeared were attributed to **I**, *cis*- and *trans*-$[PtR(SnX_3)L_2]$ (**II** and **III**, respectively) on the basis of previous data (Ref. 11, and references cited therein). The results, quoted in Table 3 show that the complexes **II** formed first isomerize at +20°C to more stable **III**, the last being the predominant form of platinum containing species at moderate conversions of alk-1-enes for **I** ($L = PMePh_2$). For hydrides with trialkylphosphine ligands, when **II** is poorly formed, the graduate growth of **III** and *trans*-$[PtX(SnX_3)(PAlk_3)_2]$[9] is observed, being however slower than alkene isomerization. The appearance of the latter complex is apparently due to removal of the hydride by an alkene. The *trans* complex $[PtH(SnBr_3)(PMePh_2)_2]$ shows poor stability under the reaction conditions and in 10–15 minutes the solution contained a complex mixture of various platinum complexes. This destruction of the catalyst is due to reactions of the complex with alkene, since it is stable over at least one hour at +20°C in CD_2Cl_2 in the absence of alkene. Taking into account the data quoted in Table 3, the mechanism of alk-1-ene isomerization can be described by Scheme 1.

The side reactions of complex **III** formation play a significant role when $L = PPh_3$ and $PMePh_2$, thereby deactivating the bulk of the catalyst, but are of lesser importance when $L = PEt_3$.

The $k_{1\,obs}$ values calculated (Table 4) according to Eqn [1] obviously depend on the concentrations of the catalyst and the alkene. An estimation of this dependence was performed by determination of partial reaction orders, according to Eqn [5]:

$$k_{1\,obs} = k_1 \cdot [Pt{-}H]^n \cdot [\text{alk-1-ene}]^{m-1} \qquad [5]$$

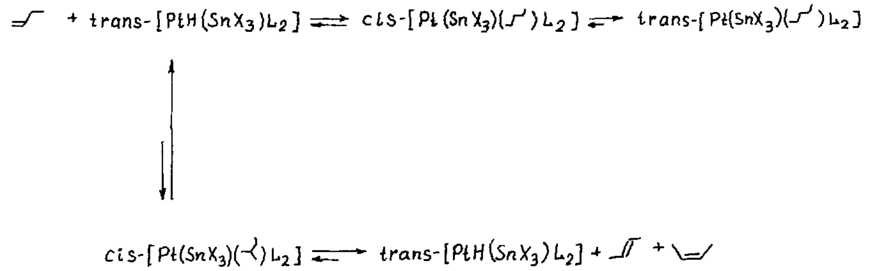
where n and m are the partial orders of the overall reaction. The treatment of the data in Table 4 gives $n = 2.6$ and $m = 0.3$. These values can be explained in terms of an increasing proportion of **III** as a consequence of an increase in the alk-1-ene/[PtH] ratio. This leads to the decrease in real catalyst concentration.

Composition of isomerization products

The isomerization of but-1-ene pent-1-ene leads to mixtures of *cis*- and *trans*-alk-2-enes, the ratio being dependent upon the catalyst. Data in Table 2 show that the percentage of *cis*-alkenes decreases in the series [6], with a minor dependence on alkene and halogen. Apparently, the

$$PPh_3 > PMePh_2 > PEt_3 \qquad [6]$$

cis/*trans* ratio of products is dependent mainly on steric interactions in the alkene elimination transition state. As was previously shown,[6] steric



Scheme 1

Table 4 Determination of partial reaction order for but-1-ene isomerization reaction {catalyst, $[PtH(SnCl_3)(PMePh_2)_2]$, CD_2Cl_2, +20°C}

c_{cat} (mol dm^{-3})	$c_{but\text{-}1\text{-}ene}$, (mol dm^{-3})	$k_{1\,obs} \times 10^5$ (s^{-1})
0.025	2.5	760
0.0037	2.5	1.92
0.0011	2.5	0.32
0.0037	0.588	5.3

interactions between alkyls attached to the forming double bond favoured *trans*-pent-2-ene elimination in amounts in excess of equilibrium ones. The formation of considerable amounts of *cis*-alkenes by platinum hydride catalysis is apparently due to steric interactions between alkyl groups and bulky ligands, which are minimized in the course of the development of the transition state for *cis*-alkene elimination. The predominance of *cis*-isomers was also observed[14] when alk-1-ene isomerization was carried out in the presence of the $Ni[P(OEt)_3]_4$–HCl system.

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