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Effect of Phosphorus-Donor Ligands on the Isomerisation of Pentenes Catalysed by Substituted Derivatives of $H_4Ru_4(CO)_{12}$

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The catalytic activity of $H_4Ru_4(CO)_{11}L$ (where L is PPh_3, $P(OEt)_3$, $P(OPh)_3$), $H_4Ru_4(CO)_{10}[P(OEt)_3]_2$ and $H_4Ru_4(CO)_8[P(OEt)_3]_4$ in the isomerisation of pentenes in toluene at 70.4 °C is described. The initial conversion rate is proportional to the catalyst concentration, decreases with increasing CO pressure, while the addition of the free ligand causes a decrease of the conversion rate, in the initial steps, ascribed to its preferential coordination on the active sites. For $H_4Ru_4(CO)_{11}L$, the isomerisation rate decreases with L in the sequence $P(OEt)_3 > P(OPh)_3 > PPh_3 > CO$. The conversion rate, moreover, decreases with n in the series $H_4Ru_4(CO)_{12-n}[P(OEt)_3]_n$ (n = 1, 2, 4). The results are interpreted by suggesting that the Ru–CO bonds are mainly involved in the active site formation and that the phosphorus-donor ligands cause a weak increase of the activity of the carbonyl groups. However, the free sites formed by Ru–CO bond cleavage of $Ru(CO)_2L$ units are considered to give a little contribution to the isomerisation for the steric hindrance of L.

Introduction

The metal cluster compounds are attracting an increasing attention as homogeneous catalysts since they can exhibit coordination modes on the active sites, such as the bridging bonding mode of biatomic species, different from those of monometal catalysts and therefore can promote new catalytic processes [1]. Such a behaviour is due to the metal–metal bonds which make the metal clusters reliable models of metal surfaces in heterogeneous catalysis [2].

As part of a work on the catalytic properties of tri- and tetrarutheniumcarbonyl clusters [3–5], in this paper we describe the effect of the substitution of carbonyl groups of $H_4Ru_4(CO)_{12}$ with different phosphines and phosphites in the catalytic isomerisation of pentenes and compare the catalytic behaviour of these cluster compounds with that of monometal complexes containing phosphorus-donor ligands.

Experimental

I.r. spectra were recorded on a double-beam Beckman IR 4230 spectrophotometer with KBr optics and with deuterochloride as calibrant. Proton n.m.r. spectra were recorded on a Jeol 60HL spectrometer. Gas chromatographic analyses were performed at 50 °C by a C. Erba Fractovap Model B using a 4m column of 20% silicon oil 720 on Chromosorb P 60–80 mesh, and at 25 °C by a C. Erba Fractovap Model M, uscng a 3m column of 11% $AgNO_3$ and 21% phenylacetonitrile on Chromosorb P 60–80 mesh. Helium was used as carrier gas at 50 cc/min. Solvents were dried over molecular sieves. All reactions were carried out in an atmosphere of nitrogen, separations were performed by preparative TLC, absorbent Kieselgel $PF_{254+368}$ Merck. Tetrahydridododecacarbonyltetraruthenium was prepared according to the literature [6]. 1-pentene, 2-*cis*-pentene, 2-*trans*-pentene, phosphine and phosphites were Fluka pure grade.

Reaction of $H_4Ru_4(CO)_{12}$ with Triphenylphosphine

A cyclohexane solution of $H_4Ru_4(CO)_{12}$ (0.200 g, 0.268 mmol) and triphenylphosphine (0.060 g, 0.228 mmol) was heated at 55 °C for 4 h. After cooling, the solution was filtered and dried under reduced pressure. The residue was dissolved by chloroform and separated by preparative TLC, eluent n-hexane and dichloromethane (1:1) to give unreacted $H_4Ru_4(CO)_{12}$, (I) (0.018 g) as yellow crystals and small amounts of unidentified products. *Anal.* Calcd. for $C_{29}H_{19}O_{11}PRu_4$: C, 35.58; H, 1.96; O, 17.98; P, 3.16; Ru, 41.31. Found for (I): C, 35.72; H, 2.14; O, 18.02; P, 3.11; Ru, 40.3%.

Reaction of $H_4Ru_4(CO)_{12}$ with Triethylphosphite

$H_4Ru_4(CO)_{12}$ (0.200 g, 0.268 mmol) and triethylphosphite (0.100 g, 0.575 mmol), dissolved in n-hep-

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TABLE I. I.r. and Proton N.m.r. Spectra.

Compound	$\nu(CO)^a$ cm^{-1}	Chemical Shift^{b,c} τ
(I)	2094m, 2088w, 2067vs, 2057vs, 3031shm, 2026vs, 2013m, 2007s, 1965w	2.55m(15), 27.1d(4)
(II)	2096m, 2089w, 2067vs, 2058vs, 2032m, 2026vs, 2015m, 2007s, 1990w, 1972w	5.91m(6), 8.62t(9), 27.6d(4)
(III)	2085w, 2078m, 2056vs, 2035w, 2020vs, 2016s, 1997s, 1952w	5.95m(6), 8.70t(9), 27.6t(2)
(IV)	2021vs, 1982m, 1965s	5.90m(6), 8.72t(9), 27.5q^d (1)
(V)	2098m, 2092shw, 2071vs, 2060vs, 2050w, 2035vs, 2011sbr, 1990w, 1978w	2.55s, br(15), 27.3d(4)

^{a}Cyclohexane solution. ^{b}CCl_4 solution. ^{c}Relative intensities in parentheses. ^{d}q = quintet.

tane, were refluxed for 1 h. After cooling, the solution was filtered and dried under reduced pressure. The residue, extracted with chloroform, was separated as above to yield unreacted $H_4Ru_4(CO)_{12}$, (II) (0.015 g) as orange crystals, (III) (0.013 g) as orange crystals, (IV) (0.006 g) as yellow crystals and little amounts of other compounds not completely identified. *Anal.* Calcd. for $C_{17}H_{19}O_{14}PRu_4$: C, 23.12; H, 2.17; O, 25.38; P, 3.51; Ru, 45.81. Found for (II): C, 23.61; H, 2.29; O, 25.07; P, 3.70; Ru, 45.41%. Calcd. for $C_{22}H_{34}O_{16}P_2Ru_4$: C, 25.88; H, 3.36; O, 25.08; P, 6.07; Ru, 39.61. Found for (III): C, 25.15; H, 3.52; O, 25.21; P, 5.93; Ru, 39.73%. Calcd. for $C_{32}H_{64}O_{20}P_4Ru_4$: C, 29.63; H, 4.97; O, 24.67; P, 9.55; Ru, 31.18. Found for (IV): C, 30.02; H, 3.36; O, 25.08; P, 6.07; Ru, 39.61%.

Reaction of $H_4Ru_4(CO)_{12}$ with Triphenylphosphite

A cyclohexane solution of $H_4Ru_4(CO)_{12}$ (0.200 g, 0.268 mmol) and triphenylphosphite (0.100 ml, 0.380 mmol) was heated at 60 °C for 5 h. After filtration, the solution was dried and separated as above. In addition to unreacted $H_4Ru_4(CO)_{12}$, (V) (0.017 g) was obtained as yellow crystals with little amounts of other compounds. *Anal.* Calcd. for $C_{29}H_{19}O_{14}PRu_4$: C, 33.92; H, 1.87; O, 21.81; P, 3.01; Ru, 39.38. Found for (V): C, 33.71; H, 1.98; O, 22.01; P, 3.09; Ru, 39.67%.

Kinetic Measurements

The kinetic measurements were performed as described previously [4, 5]. When 6.0 mg of (V) were dissolved with 3.0 ml of toluene at 70.4 °C and triethylphosphite and 1-pentene added to give a molar ratio catalyst: $P(OEt)_3$: 1-pentene of 2:1:200, the isomerisation was very slow for about 2 hours. Then the conversion of 1-pentene occurred to the extent of 12.7%, after 30 more minutes, and 20.4%, after 65 minutes, of 2-*cis*- and 2-*trans*-pentene with a *cis/trans* ratio of 1.20 and 1.09 respectively. Aliquots of solution were analyzed by TLC, eluent as above, and the i.r. spectra of the eluted fractions were run.

Results and Discussion

The following compounds have been examined: $H_4Ru_4(CO)_{11}PPh_3$ (I), $H_4Ru_4(CO)_{11}P(OEt)_3$ (II), $H_4Ru_4(CO)_{10}[P(OEt(_3]_2$ (III), $H_4Ru_4(CO)_8[P(OEt)_3]_4$ (IV), and $H_4Ru_4(CO)_{11}P(OPh)_3$ (V). Their i.r. and proton n.m.r. spectra are reported in Table I. As previously assumed for trimethylphosphite derivatives [7], only one of the possible isomers of (III) and (IV) is formed and the ligands are bonded each to a different metal atom.

The isomerisation initial rates of pentenes with (I) to (V), in toluene at 70.4 °C, are collected in Table II. For all these runs the i.r. spectrum of the solution shows that the catalyst is unchanged at the end of the reaction. The conversion rate of 1-pentene to 2-*cis*- and 2-*trans*-pentene is always proportional to the catalyst concentration and decreases with increasing carbon monoxide partial pressure. Addition of the free ligand to the solution of the monosubstituted complexes causes an initial large decrease in the conversion rate of 1-pentene, followed by isomerisation at about the same initial rate as in the absence of the free ligand, provided its initial concentration is low with respect to the catalyst. When the concentrations of the catalyst and of the added ligand are of the same order of magnitude the isomerisation process is inhibited for a longer period and subsequently takes place at a rate which is significantly lower than that measured in absence of ligand.

Addition of oxygen does not affect the isomerisation rate and this rules out the operation, in these systems, of radical species, which have been recently suggested to be active in reactions of metal carbonyl compounds [8, 9].

TABLE II. Isomerisation of Pentenes Catalysed by Complexes (I)–(V) at 70.4 °C in Toluene.

Complex	Complex Concentration m*M*	Alkene	Alkene Concentration m*M*	CO *µM*	Initial Rate mmol l^{-1} h^{-1}
(I)	0.34	1-pentene	46		25.0
(I)	0.086	1-pentene	46		5.5
(I)	0.34	1-pentene	46	9.6	0.83
(I)	0.44	1-pentene	46	22	0.74
(I)	0.34	1-pentene	230		67.8
(II)	0.37	1-pentene	46		62.0
(II)	0.121	1-pentene	46		19.7
(II)	0.028	1-pentene	46		5.7
(II)	0.37	1-pentene	46	11.3	0.40
(II)	0.37	1-pentene	230		147
(II)	0.37	2-*cis*-pentene	46		0.26
(II)	0.37	2-*trans*-pentene	46		0.09
(III)	0.38	1-pentene	46		3.9
(III)	0.38	1-pentene	46	11.4	0.10
(III)[a]	0.38	1-pentene	46		2.1
(IV)	0.34	1-pentene	46		0.40
(IV)[b]	0.34	1-pentene	46		1.0
(V)	0.35	1-pentene	46		29.2
(V)	0.13	1-pentene	46		9.6
(V)	0.35	1-pentene	46		0.26
(V)	0.35	2-*cis*-pentene	46		0.22

[a] In presence of acetic acid 97m*M*. [b] Reaction temperature of 80.0 °C.

The conversion rate of 1-pentene, in the presence of $H_4Ru_4(CO)_{11}L$, (I), (II), and (V), depends on L and decreases in the order $P(OEt)_3 > P(OPh)_3 > PPh_3$, while it is 22.1 mmol l^{-1} h^{-1} with $H_4Ru_4(CO)_{12}$ under similar experimental conditions [4]. The substitution of one CO group of $H_4Ru_4(CO)_{12}$ with any of these ligands causes an increase in the isomerising ability, but the catalytic activity of these compounds is mainly affected by the number of the replaced carbonyl groups, as shown in the series of triethylphosphite derivatives.

The isomerisation initial rate of 2-*cis*-pentene is slower than that of 1-pentene by two orders of magnitude and even slower is the conversion rate of 2-*trans*-pentene.

The effect of carbon monoxide and of free phosphine or phosphite may suggest that the active sites are formed by the cleavage of both Ru–CO and Ru–P bonds and the variation of the conversion rate with (I), (II) and (V) may be ascribed both to the different dissociation energy of L and to the effect of different L's on the Ru–CO bond strength. On the other hand, two additional points must be considered. First, the higher substituted clusters show a decrease in the isomerisation rate with increasing number of substituted CO groups. Secondly, the conversion of 1-pentene catalysed by (V) with added $P(OEt)_3$, under the conditions described in the experimental section, takes place without any exchange of the coordinated $P(OPh)_3$ with the free $P(OEt)_3$. As shown by TLC and i.r. spectra, after more than 20% conversion of 1-pentene, only unchanged (V) with bi- and trisubstituted complexes are present in the solution. Indeed, a large dissociation of Ru–P bonds of (V) should presumably yield (II) to a detectable extent. On the basis of these results the dissociation of the phosphorus ligands cannot be excluded, but it is more likely not to give a major contribution to the formation of the active sites. The large decrease of the initial rate caused by addition of the free ligand can, in fact, be ascribed to its preferential coordination, with respect to the alkenes, on the vacant sites of the catalyst. As observed by TLC, in these experiments the concentration of free ligand is reduced to very low values, while higher substituted complexes are formed.

The catalytic activity of the three $H_4Ru_4(CO)_{11}L$ complexes, (II) in particular, is higher than that of $H_4Ru_4(CO)_{12}$. This could be correlated, as is usually done, to the increased electron density on the metal due to the good electron donor properties of L. However, a comparison of the isomerising ability of (I), (II) and (V) shows that such a behaviour cannot be simply explained by the electronic properties of the ligands, as reported for other systems [10].

In the isomerisation of 1-pentene, *cis*/*trans* ratios of 0.3–0.4, unchanged during the course of the process, are indicative of π-allyl intermediates, while higher initial values, decreasing to about 0.35 at the equilibrium, are typical of σ-alkyl intermediates [11]. In presence of (I), (II), (III) and (IV) the initial *cis/trans* ratio is in the range 0.7–0.8, whilst (V) gives an initial ratio of 1.4–1.5. Therefore these data suggest that an addition–elimination process is involved, as usually found for hydrido complexes. The higher figure for (V) should indicate a higher congestion on the active site [11]. This explanation is, however, rather uncertain, since the initial *cis/trans* ratio is 0.8 with (IV), where the active sites are heavily hindered.

The very large decrease of the conversion rate of 1-pentene for n increasing from one to four in $H_4Ru_4(CO)_{12-n}[P(OEt)_3]_n$ can be interpreted to mean that the phosphite affects in different ways the ruthenium atoms having different environments. The experimental evidence suggests an activation of the carbonyl groups of the $Ru(CO)_3$ units, by the electronic effects of the ligand transmitted through the metal–metal bonds and a decrease of activity of the $Ru(CO)_2L$ units. This could be ascribed to a decreased lability of carbonyl groups of $Ru(CO)_2L$, but it is much more likely that the bulkiness of L is the major factor reducing the coordination on the active sites of $Ru(CO)_2L$. Further studies on analogous series are, however, required to clarify the mechanisms involved in these processes and the possible influence of the steric position of L. A parallel behaviour has been observed by variable temperature ^{13}C n.m.r. spectra of $FeCo_2(CO)_9S_2$ and their tributylphosphite substituted derivatives. It appears that the substitution slows down the localised exchange at the metal where the substitution occurs, whilst the mobility of CO groups bonded to non-substituted metals is increased [12].

Several monometal complexes, used as catalysts in different processes, contain carbonyl groups and phosphorus-donor ligands and usually give active sites by dissociation of phosphines and phosphites [13]. On the opposite, the phosphorus-donor ligands of these complexes do not seem to give a large dissociation and we suggest that their main effect is to enhance the coordination of alkenes, mainly on non-L-substituted metal atoms, by labilising the Ru–CO bonds. Labilisation of CO by phosphorus ligands has been recently reported in *cis*-$MBr(CO)_4L$ (M = Mn, Re) complexes [14].

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