Inorganica Chimica Acta, 31 (1978) 177–179

Isomerisation of Pentenes Catalysed by $H_2Os_3(CO)_{10}$*

R. P. FERRARI, G. A. VAGLIO** and M. VALLE
Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy
Received March 21, 1978

$H_2Os_3(CO)_{10}$ converts 1-pentene to its isomers in toluene at 70.4 °C at an initial rate which is not appreciably dependent on the carbon monoxide partial pressure and on the presence of weak acids and polar substances. Reactions of $H_2Os_3(CO)_{10}$ with trans-$C_2H_2D_2$ *and [1,2-D_2]1-pentene suggest the operation of σ-alkyl intermediates. The large increase of the isomerising ability of $H_2Os_3(CO)_{10}$ with respect to $Os_3(CO)_{12}$, compared with the relatively similar catalytic behaviour of $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$, is ascribed to the different nature of the coordination step of the alkene.*

Introduction

The coordination of alkenes to metal carbonyl complexes, which exhibit catalytic activity in isomerisation processes, usually occurs after the cleavage of metal–CO bonds [1–5]. As part of a research on the catalytic properties of metal-cluster compounds [3–5], we have investigated the isomerisation of pentenes catalysed by $H_2Os_3(CO)_{10}$, which shows a high reactivity towards unsaturated organic molecules [6–9].

In this paper we report some results about the behaviour of $H_2Os_3(CO)_{10}$ in this process and compare it with that of hydridocarbonylruthenium-clusters [3–5]. While this work was in progress some results about the isomerising ability of $H_2Os_3(CO)_{10}$ have been published [7].

Experimental

The proton n.m.r., mass and gas chromatographic analyses were carried on as described previously [4]. Dihydridodecacarbonyltriosmium, *trans*-[D_2]ethylene and [1,2-D_2]1-pentene were prepared by published methods [10–12]. Toluene was distilled from sodium and stored on molecular sieves. 1-pentene, 2-*cis*-pentene and 2-*trans*-pentene were Fluka pure grade reagents.

The isomerisation of 1-pentene, [1,2-D_2]1-pentene and *trans*-D_2-ethylene was performed by using the same apparatus and experimental techniques as reported previously [4, 5].

TABLE I. Initial Isomerisation Rates of 1-Pentene (46 m*M*) with $H_2Os_3(CO)_{10}$ at 70.4 °C in Toluene Solution.

	$H_2Os_3(CO)_{10}$ m*M*	CO m*M*	L^a m*M*	Initial Rate mmol l^{-1} h^{-1}
1	0.37			1.9
2	0.50			2.6
3	1.82			9.6
4	3.7			22.0
5	1.82	5.0×10^{-2}		8.5
6	1.82		41	7.5
7	1.82		52	7.9

^{a}L is ethyl acetate for reaction 6 and acetic acid for reaction 7.

Results and Discussion

In Table I the initial rates of isomerisation of 1-pentene with $H_2Os_3(CO)_{10}$ are reported. The initial rate, proportional to the catalyst concentration, is not appreciably affected by the carbon monoxide partial pressure and by the presence of acetic acid or polar substances, such as ethyl acetate. Under the reaction conditions reported in Table I $H_2Os_3(CO)_{11}$ is not formed in detectable extent and the dependence of the initial rate on the carbon monoxide partial pressure is completely different from that of hydridocarbonylruthenium-clusters under similar reaction conditions [4, 5]. This is in accordance with the hypothesis of a double osmium–osmium bond [6, 13], which makes possible the coordination of the alkene molecule without any

---

*This work was in part presented at the 9th Meeting of the Italian Association of Inorganic Chemistry, Marina del Cantone, September 20, 1976.

**To whom correspondence should be addressed.

TABLE II. Distribution of Deuterium in the Reaction of $H_2Os_3(CO)_{10}$ with *trans*-$C_2H_2D_2$ at 70.4 °C in Toluene Solution.[a]

Time, min	% Distribution				
	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4
0	0.4	2.3	97.3	0.0	0.0
40	2.7	27.2	55.3	13.3	1.5
75	10.3	24.6	44.7	17.4	2.9

[a] $[H_2Os_3(CO)_{10}]$ = 1.82 m*M*, [*trans*-$C_2H_2D_2$] = 22.1 m*M*.

cleavage of Os—CO bonds. The isomerising ability of $H_2Os_3(CO)_{10}$ is one order of magnitude lower than that of some hydridocarbonylrutheniumclusters 4, 5] and it is likely that the different coordination process of the alkene is an important factor responsible for this different reactivity, provided the other reaction steps are similar. In order to clarify the reaction mechanism, we have investigated the nature of the active intermediate by the reactions of $H_2Os_3(CO)_{10}$ with *trans*-$C_2H_2D_2$ and [1,2-D_2]1-pentene. As can be seen in Table II, redistribution of hydrogen isotopes of *trans*-$C_2H_2D_2$ takes place to a large extent when *trans*-$C_2H_2D_2$ is treated with $H_2Os_3(CO)_{10}$ in toluene at 70.4 °C, and it shows that σ-alkyl intermediates are involved in the isomerisation of pentenes catalysed by $H_2Os_3(CO)_{10}$. In addition, these results indicate that the supposed intermediate $HOs_3(C_2H_5)(CO)_{10}$ [7] is in equilibrium with $H_2Os_3(CO)_{10}$ and that the formation of C_2H_6 and $HOs_3(C_2H_3)(CO)_{10}$ [6, 14] is slower than the exchange of ethylene.

The operation of σ-alkyl intermediates has been confirmed by the results of the conversion to its isomers of [1,2-D_2]1-pentene with $H_2Os_3(CO)_{10}$. As shown in Table III the isomerisation is accompanied by intermolecular rearrangements of hydrogen and deuterium atoms. When the reaction is stopped, also the catalyst appears to be partially deuterated. Accumulation of deuterium on C-1 of 1-pentene and loss of deuterium on C-2 are likely to be due to σ-alkyl intermediates originated by both Markownikov and *anti*-Markownikov additions. The distribution and location of deuterium in 2-*cis*- and 2-*trans*-pentene are in agreement with this hypothesis. Similar results have been reported for the alkene isomerisation catalysed by monohydridomonometal complexes [15].

Transfer of deuterium to C-3 of 1-pentene occurs in good extent. A strictly similar behaviour has been previously observed for the isomerisation of 1-pentene with $H_4Ru_4(CO)_{12}$ and with other polyhydridocarbonyl clusters and ascribed to the exchange, in the σ-alkyl intermediates, of a hydrogen on C-3 of the deuterated 1-pentene with a deuterium linked to the metal cluster [4].

The isomerisation of 1-pentene catalysed by $H_2Os_3(CO)_{10}$ proceeds via σ-alkyl intermediates, as found for the isomerisation of pentenes with $H_4Ru_4(CO)_{12}$ and related clusters and with monometal complexes, but the coordination step of the alkene does not involve the cleavage of metal—ligand bonds. The isomerising ability of $H_2Os_3(CO)_{10}$ is much higher than that of $Os_3(CO)_{12}$, similarly to the higher reactivity of $H_2Os_3(CO)_{10}$ with unsaturated organic molecules, whilst the initial rate of isomerisation of 1-pentene with $Ru_3(CO)_{12}$ is lower than that with $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ by one order of magnitude. This change in the isomerisation ability, which can be observed passing from the dodecarbonyltrimetals to their hydride derivatives, can be attributed to the different nature of the coordination step, which is strictly linked to the different structures of the hydrido species.

TABLE III. Distribution and Location of Deuterium in the Pentene Fractions.[a]

Conversion %		% Distribution					A.D.N. at Each Carbon Atom[b]				
		C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$	C-1	C-2	C-3	C-4	C-5
0	1-pentene	0.0	0.7	99.0	0.3	0.0	0.98	1.02	0.0	0.0	0.0
12.3	1-pentene	0.0	8.8	88.5	2.6	0.0	1.05	0.79	0.10	0.0	0.0
26.0	1-pentene	1.6	15.2	78.1	4.7	0.4	1.10	0.70	0.13	0.0	0.0
34.5	1-pentene	1.0	17.6	76.1	5.5	0.0	1.08	0.64	0.17	0.0	0.0
60.0	1-pentene	3.7	26.8	61.7	7.1	0.6	1.13	0.41	0.20	0.0	0.0
							C-1	C-2 + C-3		C-4	C-5
34.5	2-*trans*-	2.9	15.2	58.5	21.0	2.3	1.16	0.84		0.04	0.0
60.0	2-*trans*-	5.2	17.6	46.9	27.3	2.8	1.28	0.66		0.0	0.0
60.0	2-*cis*-	4.3	18.4	54.2	21.1	1.9	1.34	0.64		0.0	0.0

[a] Experimental conditions are as follows: $[H_2Os_3(CO)_{10}]$ = 5.5 m*M*; [(1,2-D_2)1-pentene] = 2.20 *M*; solvent, toluene; temperature, 70.4 °C. [b] Average deuterium number at each carbon atom; values uncertain to ±0.05.

References

1 G. F. Pregaglia, A. Andreatta, G. F. Ferrari, G. Montorsi and R. Ugo, *J. Organometal. Chem., 33,* 73 (1971).
2 D. Bingham, B. Hudson, D. E. Webster and P. B. Wells, *J. Chem. Soc. Dalton,* 1521 (1974).
3 M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio and M. Valle, *Inorg. Chem., 15,* 294 (1976).
4 M. Valle, D. Osella and G. A. Vaglio, *Inorg. Chim. Acta, 20,* 213 (1976).
5 G. A. Vaglio, D. Osella and M. Valle, *Transition Met. Chem., 2,* 94 (1977).
6 A. J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc. Dalton,* 1614 (1975).
7 A. J. Deeming, S. Hasso, *J. Organometal. Chem., 114,* 313 (1976).
8 E. G. Bryan, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton,* 1328 (1977).
9 W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis and K. T. Schorpp, *J. Organometal. Chem., 88,* C17 (1975).
10 H. D. Kaesz, S. A. R. Knox, J. W. Koopke and R. B. Saillant, *Chem. Comm.,* 477 (1971).
11 W. I. Patterson and V. du Vigneaud, *J. Biol. Chem., 123,* 327 (1938).
12 J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc., 46,* 60 (1968).
13 B. F. G. Johnson, J. Lewis and P. A. Kilty, *J. Chem. Soc. A,* 2859 (1968).
14 J. B. Keister and J. R. Shapley, *J. Organometal. Chem., 85,* C29 (1975).
15 D. Bingham, D. E. Webster and P. B. Wells, *J. Chem. Soc. Dalton,* 1514 (1974).