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Preliminary communication

THE HYDROGENATION OF *cis*- AND *trans*-1,3-PENTADIENE IN THE PRESENCE OF $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$. A NEW METHOD TO CARRY OUT HOMOGENEOUS OR HETEROGENEOUS CATALYSIS AND THE ANALYSIS OF THE PRODUCTS IN A GAS-CHROMATOGRAPHIC APPARATUS

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Summary

The title complex, a very stable cluster, is active in the hydrogenation of alkynes, alkenes and pentadienes in homogeneous conditions. When supported onto Chromosorb P, the complex hydrogenates the pentadienes with high efficiency. There is evidence for operation of both homogeneous or heterogeneous processes, the relative contributions depending on the temperature and the ageing of the system.

With a flow of hydrogen, coupling of the hydrogenating vessel with an analytical column forms a versatile catalytic-analytical system which may be operated from room temperature to about 150°C.

The title cluster (complex I) [1,2], a very stable species, is active and selective in the hydrogenation of alkynes and alkenes under homogeneous conditions [1]. When supported on alumina it is also an efficient catalyst for the methanation of CO and CO_2 [3]. We report below some preliminary observations on the behaviour of I in the presence of H_2 and of *cis*- or *trans*-1,3-pentadiene in hydrocarbon solutions, and the development of a new catalytic and analytical system formed by I supported on gas-chromatographic materials.

The homogeneous hydrogenation of *cis*- and *trans*-1,3-pentadiene* in the

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*Both purchased from Fluka and used without purification. Tests for impurities were performed on the GLC chromatograph. Complex I was prepared and purified as described in ref. 1.

presence of I was performed in sealed glass vials containing octane solutions of I and the ligands under 0.9 atm of hydrogen. These vials were kept in a thermostatted oven at 120° C. The solutions were analyzed by means of a Carlo Erba 4200 instrument equipped with a 0.6 mm × 2 m n-octane/Porasil C column and a F.I.D. detector, and operated with N_2 as carrier gas (25 ml/min) with the following temperature program: 10 min at 75° C, then 20° C per minute till 155° C, and another 10 min at 155° C. The nature of the eluted products was established by comparison with authentic samples. The results of these experiments are listed in Table 1.

TABLE 1

HYDROGENATION OF *cis*- AND *trans*-1,3-PENTADIENE IN THE PRESENCE OF COMPLEX I

Reaction	t (°C)	time (h)	Composition of the reaction mixtures (%)				
			pentane	1-pentene	*trans*-2-pentene	*cis*-2-pentene	substrate
cis-1,3-pentadiene							
Complex I [a]	120	1	0.26	1.27	2.26	1.65	94.55
	120	2	0.35	1.86	3.02	2.16	92.60
	120	4	0.59	11.15	27.03	21.07	40.16
	120	6	0.72	14.93	27.90	21.51	35.94
System A	see text	see text	72.68	27.32	—	—	—
System B	75	see text	—	—	—	—	100.0
System C	45	see text	26.30	7.79	27.76	30.77	7.38
(90 min) [b]	60	see text	38.54	2.91	29.75	28.79	—
	93	see text	22.14	11.04	35.39	31.42	—
	116	see text	12.47	16.72	32.64	38.69	—
(6 h) [b]	23	see text	21.80	6.01	20.33	28.67	23.08
(20 h) [b]	22	see text	100.0	—	—	—	—
System D	88	see text	tr [c]	tr	tr	—	99.0
	102	see text	tr	tr	1.70	1.0	97.3
	120	see text	tr	tr	8.30	5.28	86.42
trans-1,3-Pentadiene							
Complex I [a]	120	1	0.02	0.28	3.99	0.33	95.38
	120	2	0.06	0.40	4.22	0.45	94.87
	120	4	0.26	1.78	9.57	1.99	86.40
	120	6	0.41	13.35	28.31	9.17	48.74
System A	see text	see text	43.34	56.66	—	—	—
System B	see text	see text	—	—	—	—	100.0
System C	79	see text	43.79	1.25	52.20	2.75	—
(90 min) [b]	139	see text	15.32	15.04	65.04	4.60	—
(210 min) [b]	26	see text	42.77	tr	53.20	4.03	—
(20 h) [b]	22	see text	100.0	—	—	—	—

[a] Sealed vials. [b] Pre-treatment time. [c] tr = trace amounts.

The results can be summarized as follows: (i) pentenes and small amounts of pentane are obtained, so that selective hydrogenation of one double bond occurs; (ii) the efficiency of I towards the dienes is higher than that towards alkenes and alkynes [1]; (iii) the reaction of I with the *cis*-diene is faster than that with the *trans*-homologue; (iv) both of the reactions stop after a few hours, probably because of cluster modifications.

The hydrogenation of *cis*- and *trans*-1,3-pentadiene was also attempted in the presence of I supported on gas-chromatographic materials. The system (System A) was formed by a 0.6 mm × 1 m glass coil containing about 7.0 g of silanized Chromosorb P (J. Manville; 60/80 mesh, superficial area 4 m^2 /g) to which 20 mg of I had been attached by dissolving the complex in light petroleum, adding the Chromosorb, and then taking to dryness at room temperature in a Rotavapor. The system was attached directly to a Porasil analytical column, as described above. Hydrogen was used as reactant and carrier gas and, after injections of octane solutions of the dienes, at 75°C, the previously described temperature program was used. Blank experiments showed that the Chromosorb and the Porasil are inactive in the hydrogenation of the substrates.

With System A, rapid and complete hydrogenation of the dienes occurs (Table 1); the efficiency is comparable to that observed for I supported on alumina [3]. However, the low selectivity suggests that a heterogeneous process, involving metal particles derived from partial decomposition of I, operates. Both the sections making up A were in the oven of the chromatograph, and above 140°C slow sublimation of I from the Chromosorb to the beginning of the Porasil column was observed; although washing with $CHCl_3$ resulted in the recovery of unaltered I, doubt about partial decomposition still remained (vide infra).

In order to evaluate the effects of possible decomposition of I, we tested the following systems based on two independent sections:

(a) System B, consisting of an hydrogenating section identical to that of A, but independently thermostatted in an oil bath at 75°C.

(b) System C consisting of the same hydrogenating section, which was pretreated at 155°C with hydrogen flow for various times. The analyses were performed at temperatures of 22 to 140°C (oil bath).

(c) System D formed by a hydrogenating section obtained by dissolving 40 mg of I in chloroform, suspending 15 g of Chromosorb into the solution, adding 2% (0.3 g) of silicone oil 702, and then taking to dryness. An oil bath was used as a thermostat.

The analytical sections coupled with Systems B—D were identical to those previously described.

The results obtained (Table 1), may be summarized as follows: (i) with system B no hydrogenation is observed, probably because no pre-treatment was carried out; at 75°C no homogeneous processes appear to take place (vide infra); (ii) with system D, where the silicone oil may act as a solvent for I, the products are comparable to those observed under homogeneous conditions; (iii) with system C the results depend on the temperature and on the pre-treatment times; for the same pre-treatment time, the proportion of pentane increases to a maximum and then decreases when the temperature is raised. After very long pre-treatment times only pentane is observed, even at room temperature.

A tentative explanation for the results with system C is that various competitive processes may operate. Short pre-treatment times may result in partial decomposition of I. At low temperatures heterogeneous catalysis by the decomposition products may occur, leading to high proportions of pentane; the rise in the temperature may then result in homogeneous catalysis on the unmodified I still present, leading to *cis*- and *trans*-2-pentenes. The latter process occurs at 80—120°C. Finally, higher temperatures or very long pretreatments may result in complete decomposition of I, and in heterogeneous, non selective total hydrogenation to pentane.

Evidence for decomposition of I during the "ageing" of the columns was obtained. Careful extraction with octane of the Chromosorb P on which I had been supported, followed by IR analysis, showed that the material pretreated for 20 h contains less than 25% of unaltered I after taking account of the amount of I used in the catalytic reactions.

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