Journal of Organometallic Chemistry, 164 (1979) 1—10

HYDROGENATION CATALYSTS FROM ALUMINUM HYDRIDE DERIVATIVES AND TRANSITION METAL COMPOUNDS

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(Received June 12th, 1978)

Summary

New homogeneous catalysts based on aluminum hydride derivatives and transition metal compounds for the hydrogenation of unsaturated hydrocarbon substrates are described. A feature of these catalysts is their high activity under very mild experimental conditions. Some aspects of the activity of aluminum hydrides cocatalysts are discussed, with particular reference to their molecular structure and to the hydridic hydrogen/transition metal atomic ratio.

Introduction

The catalytic hydrogenation of mono-olefins by alkylaluminum—transition metal systems was described some years ago by Sloan et al. [1]. Later a number of active systems involving alkylaluminums [2], as well as alkyllithium [3], Grignard reagent [4], lithium aluminum hydride [5] and its alkoxy derivatives [6], sodium bis(2-methoxyethoxy)aluminum hydride [7] and sodium boron hydride [8] are reported. However, the simpler derivatives of aluminum hydride have not been considered as hydrogenation cocatalysts. It is known that the complexation of AlH_3 with organic Lewis bases or the partial substitution of its hydridic hydrogens by various ligands, (e.g., halogen, NR_2 and NR groups) leads to compounds with significantly different properties [9]. The behaviour of simpler aluminum hydrides as components of catalytic systems for the stereospecific polymerization of mono- or di-olefins varies in activity with the nature of the aluminum hydride derivative [10]. The fact that these compounds are usually soluble in hydrocarbons and that some of them, i.e. $HAl(NR_2)_2$, $(HAlNR)_n$ (n = 4—10) can now be synthesized directly from aluminum, amines and hydrogen [11,12] have heightened interest in this class of reducing agents. We therefore extended the research to the use of such hydrides to the homoge-

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TABLE 1

HYDROGENATION[a] OF MONO- AND DI-OLEFINS WITH CATALYTIC SYSTEMS BASED ON ALUMINUM HYDRIDE DERIVATIVES AND COBALT(III) COMPOUNDS

Olefin	Hydrogenation product	Hydrogenation yield with different catalytic systems[b]										
		TMMA	DMMA	t-BuPIA	i-PrPIA	n-PrPIA	TMMA	DMMA	DCA	t-BuPIA	i-PrPIA	n-PrPIA
		Coacac$_2$	Coacac$_2$	Coacac$_2$	Coacac$_2$	Coacac$_2$	Cohex$_2$	Cohex$_2$	Cohex$_2$	Cohex$_2$	Cohex$_2$	Cohex$_2$
1-Octene	n-Octane		100	100	100	100						
Cyclohexene	Cyclohexane			90 [c]	100	85				100	100 [d]	100
2-Methyl-2-butene	Isopentane			42	99	83				57	100	100
4-Vinylcyclohexene	4-Ethylcyclohexene		85 [e]				3	17	6	93 [e, f]	41 [e]	
	4-Ethylcyclohexane		15				97	83	93	7	58	
Isoprene	2-Methyl-2-butene	4	34							22	5	10
	Isopentane	94	66				100			78	95	90
2,3-Dimethyl-2-butene	2,3-Dimethylbutane										34 [g]	

[a] Reaction conditions generally used: toluene 20 ml, cobalt compound 0.1 mmol, mono-olefin 20 mmol or diolefin 10 mmol, H*/Co atomic ratio 6; 1 h, 30°C, 2 atm of H_2. The reaction components were mixed in the following order: solvent, olefin, cobalt compound, alane and H_2. [b] TMMA = $AlH_3 \cdot N(CH_3)_3$; DMMA = $AlH_2N(CH_3)_2$; t-BuPIA = $(HAlN\text{-}t\text{-}C_4H_9)_4$; i-PrPIA = $(HAlN\text{-}i\text{-}C_3H_7)_6$; n-PrPIA = $(HAlN\text{-}n\text{-}C_3H_7)_8$; DCA = $AlHCl_2 \cdot O(C_2H_5)_2$; Coacac$_2$ = cobaltbis(acetylacetonate); Cohex$_2$ = cobaltbis(2-ethylhexanoate). [c] 4 atm of H_2. [d] 0.5 h. [e] Diolefin 20 mmol. [f] 1.5 atm of H_2. [g] 2 h, 50°C.

neous catalytic hydrogenation of unsaturated hydrocarbons. This paper describes some results obtained with binary catalysts based on aluminum hydride derivatives and transition metal compounds, involving some comparisons also with analogous systems based on alkylaluminum compounds.

Results and discussion

$AlH_3 \cdot N(CH_3)_3$, $AlHCl_2 \cdot O(C_2H_5)_2$, $AlH_2N(CH_3)_2$, $HAl[N(CH_3)_2]_2$ and $(HAlNR)_n$ ($R = t\text{-}C_4H_9$, $n = 4$; $R = i\text{-}C_3H_7$, $n = 6$; $R = n\text{-}C_3H_7$, $n = 8$) were suitable for investigation. These show significant differences in physico-chemical properties, arising from varying nature of the ligands and thus the varying degrees of acidity of the aluminum atoms [9,10]. After combination with derivatives of cobalt, nickel, iron, titanium and vanadium, the activity of the resulting catalysts was tested in the hydrogenation of olefins with different steric hindrances. In every case the catalysts were soluble and so hydrogenation occurred in solution.

Table 1 lists some results obtained with catalytic systems based on aluminum hydride derivatives and organic salts of cobalt(II). As expected from the results with trialkylaluminums [1], the hydrogenation reactivity is in the following order: terminal > disubstituted > trisubstituted > tetrasubstituted olefins. The systems based on $Cohex_2$ were more active than those based on $Coacac_2$. At constant atomic ratio H */Co (H * = hydridic hydrogen) the nature of the aluminum hydride derivatives influences the activity. In particular, for the hydrogenation of 4-vinylcyclohexene the order of activity is $AlH_3 \cdot N(CH_3)_3 \simeq AlHCl_2 \cdot O(C_2H_5)_2 > AlH_2N(CH_3)_2 > (HAlN\text{-}i\text{-}C_3H_7)_6 \geqslant (HAlN\text{-}n\text{-}C_3H_7)_8 > (HAlN\text{-}t\text{-}C_4H_9)_4$. A rather different order was found for the hydrogenation of isoprene, with $AlH_2N(CH_3)_2$ less active than $(HAlN\text{-}i\text{-}C_3H_7)_6$ and $(HAlN\text{-}n\text{-}C_3H_7)_8$.

Thus the right choice of the aluminum compound can favour selective partial or complete hydrogenation of a diolefin; for example 4-vinylcyclohexene is reduced primarily to 4-ethylcyclohexane using $AlH_3 \cdot N(CH_3)_3/Cohex_2$ and to 4-ethylcyclohexene by using $(HAlN\text{-}t\text{-}C_4H_9)_4$.

Under our conditions, these reactivity differences are apparent for hydrogenation of diolefins, but do not show up with α-olefins, because of the high activity of the catalytic systems investigated. It is noteworthy that diolefins can be quantitatively hydrogenated, without secondary oligomerization reactions, under milder conditions than are needed for trialkylaluminums, which were reported [2] to reduce butadiene and isoprene at 90–110° C and at 40 kg/cm^2 of hydrogen pressure.

The catalytic activity depends on the aluminum/transition metal ratio, as is usual in other binary systems [2,7]. However, the variation of the hydrogenation activity with this ratio appears to be influenced by the nature of the aluminum hydride derivative. Our studies were limited to the activities of various nitrogen derivatives, i.e. $AlH_3 \cdot N(CH_3)_3$, $HAl[N(CH_3)_2]_2$ and $(HAlN\text{-}i\text{-}C_3H_7)_6$, with $Cohex_2$ (as a function of the atomic ratio H */Co) in the hydrogenation of 1-hexene, cyclohexene (Fig. 1) and isoprene (Fig. 2, 3 and 4). $AlH_3 \cdot N(CH_3)_3$ is more active than $(HAlN\text{-}i\text{-}C_3H_7)_6$, which is more active than $HAl[N(CH_3)_2]_2$. However, the activities of $AlH_3 \cdot N(CH_3)_3$ and $HAl[N(CH_3)_2]_2$ peak at H */Co =

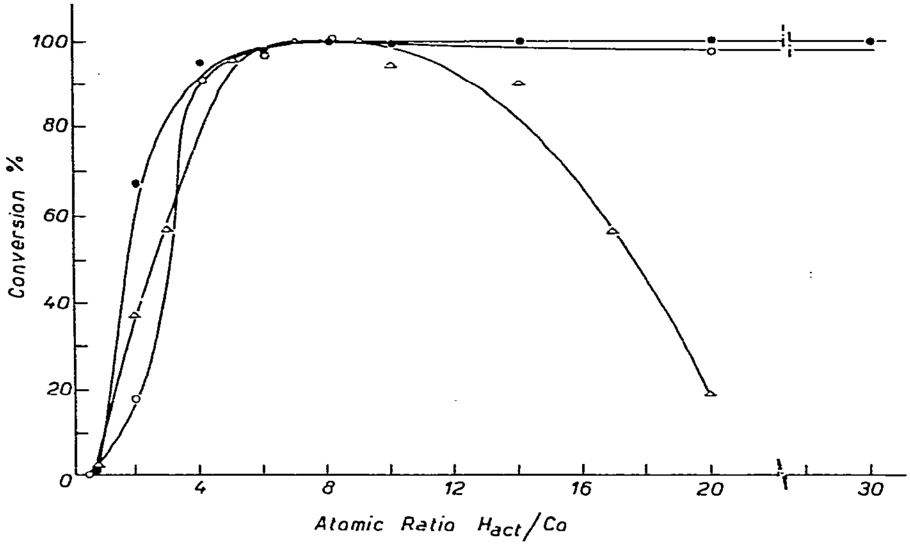


Fig. 1. Hydrogenation of 1-hexene to n-hexane and of cyclohexene to cyclohexane as a function of the H_{active}/cobalt atomic ratio with aluminum hydride derivatives/cobalt(II) 2-ethylhexanoate systems. Conditions: toluene 20 ml; $Cohex_2$ 0.1 mmol; H_2 pressure 2 atm; 30°C and △: 1-hexene 20 mmol; $AlH_3 \cdot N(CH_3)_3$; time, 15 min; ● 1-hexene 20 mmol; $(HAlN\text{-}i\text{-}C_3H_7)_6$, time 15 min; ○: cyclohexene 20 mmol, $(HAlN\text{-}i\text{-}C_3H_7)_6$, time 30 min. The reaction components were mixed in the following order: solvent, cobalt compound, alane and olefin, then the reaction mixture was pressured with hydrogen.

6–7 and 3, respectively, whereas the activity of $(HAlN\text{-}i\text{-}C_3H_7)_6$ is greatest at H */Co = 6; this activity then remains constant or decreases very slowly. The literature contains a brief report [6] of similar behaviour for lithium butoxyaluminum hydrides, which when used in conjunction with cobalt salts show a

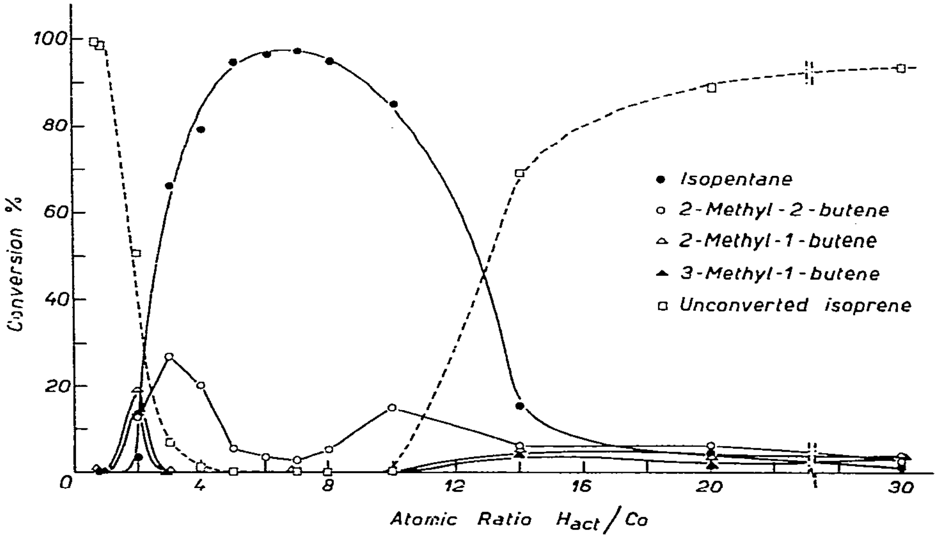


Fig. 2. Hydrogenation of isoprene as a function of the H_{active}/cobalt atomic ratio with $AlH_3 \cdot N(CH_3)_3$/$Cohex_2$ catalytic systems. Conditions: toluene 20 ml; $Cohex_2$ 0.1 mmol; isoprene 10 mmol; H_2 pressure 2 atm, time 30 min. The reaction components were mixed as indicated in Fig. 1.

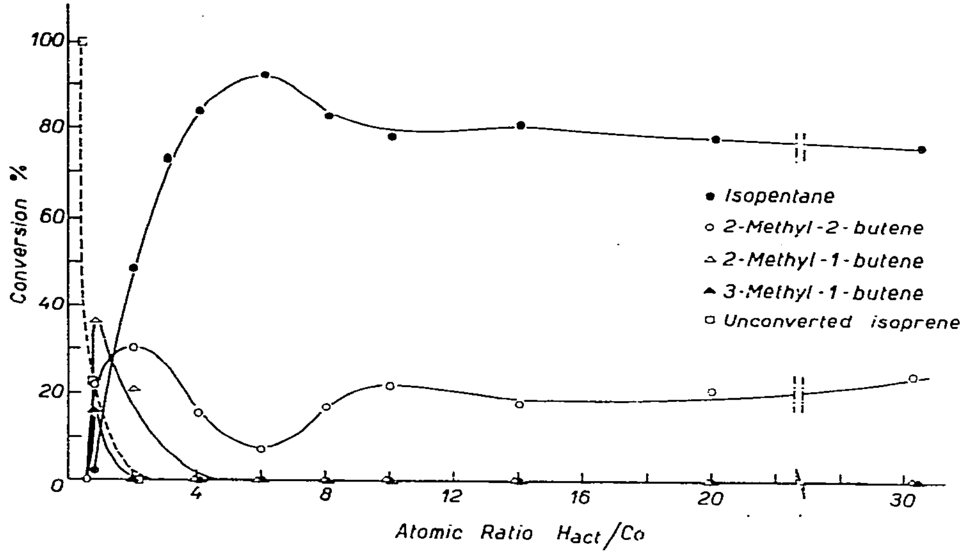


Fig. 3. Hydrogenation of isoprene as a function of the H_{active}/cobalt atomic ratio with $(HAlN\text{-}i\text{-}C_3H_7)_6$/ Cohex$_2$ catalytic systems. Conditions as indicated in Fig. 2.

constant reaction rate for Al/Co ⩾ 4. In our opinion structural differences are responsible for the varying behaviour of the nitrogen derivatives of aluminum hydride rather than the chemical nature of the ligands on the aluminum atom. In both $HAl[N(CH_3)_2]_2$ and $(HAlN\text{-}i\text{-}C_3H_7)_6$ the aluminum atoms are tetracoordinated by three nitrogen atoms and one hydridic hydrogen, but the molecular structures of these compounds are different: $HAl[N(CH_3)_2]_2$ is associated as a mixture of dimer I and trimer II [9,13] whereas $(HAlN\text{-}i\text{-}C_3H_7)_6$ [14] has a hexa-

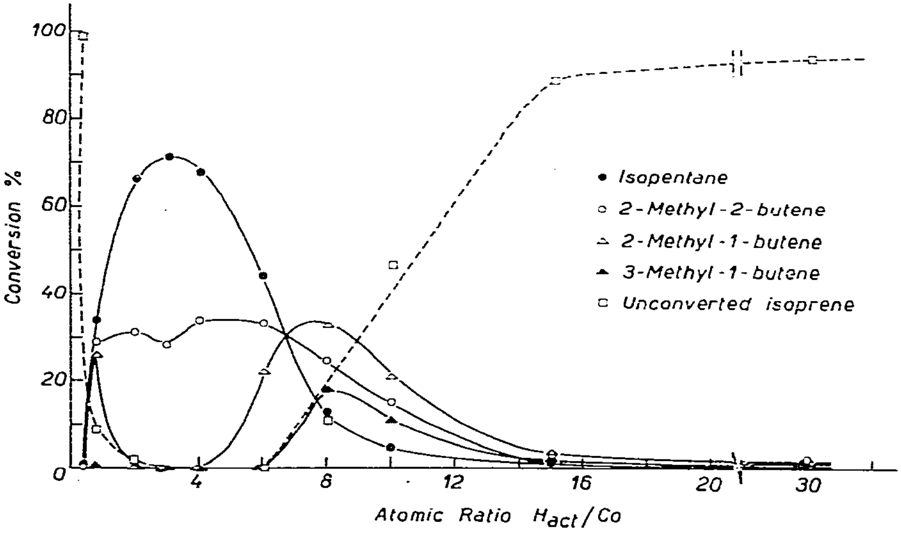
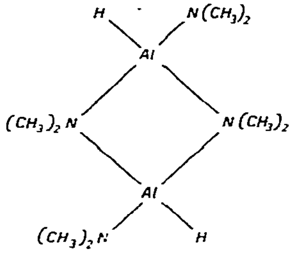
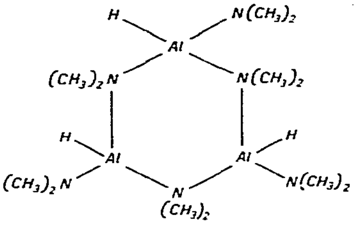


Fig. 4. Hydrogenation of isoprene as a function of the H_{active}/cobalt atomic ratio with $HAl[N(CH_3)_2]_2$/ Cohex$_2$ catalytic systems. Conditions as indicated in Fig. 2.

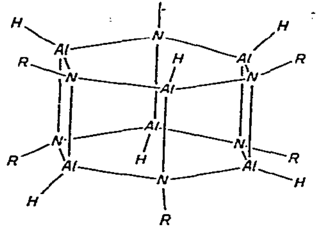
gonal cage structure (III). On the other hand, $HAl[N(CH_3)_2]_2$ behaves like $AlH_3 \cdot N(CH_3)_3$ in spite of the different ligands.



(I)



(II)



(III)

The results for the hydrogenation of 4-vinylcyclohexene or isoprene with $(HAlN\text{-}i\text{-}C_3H_7)_6$/Cohex$_2$ (Table 2) indicate that the activity decreases upon use of ethereal in place of aromatic solvents and also upon addition of primary amines or alcohols. The latter also allows partial hydrogenation. Furthermore pre-formed catalysts are generally more active than those prepared in the presence of olefin. The $(HAlN\text{-}i\text{-}C_3H_7)_6$/Cohex$_2$ system retains a high activity after use, allowing successive hydrogenations (Table 3).

Table 4 lists results with Niacac$_2$. Its activity is generally similar to that of aluminum hydrides/Coacac$_2$ systems and lower than that of analogous systems based on Cohex$_2$. As with the cobalt systems, the order of activity is AlH_3·N-

TABLE 2

YIELDS IN THE HYDROGENATION OF DIOLEFINS WITH $(HAlN\text{-}i\text{-}C_3H_7)_6$/Cohex$_2$ SYSTEM IN VARIOUS SOLVENTS OR IN THE PRESENCE OF ADDITIVES[a]

Diolefin	Catalyst[b]	Additive (mmol)	Hydrogenation product	Yield in different solvents		
				Toluene	Diethyl ether	Tetrahydrofuran
4-Vinylcyclohexene	S	—	4-Ethylcyclohexene	42.5[c]		74
			4-Ethylcyclohexane	57.5		26
4-Vinylcyclohexene	S	$i\text{-}C_3H_7NH_2$ (0.6)	4-Ethylcyclohexene	77		
			4-Ethylcyclohexane	23		
4-Vinylcyclohexene	S	C_2H_5OH (0.6)	4-Ethylcyclohexene	99		
			4-Ethylcyclohexane	1		
4-Vinylcyclohexene	P	—	4-Ethylcyclohexene	13.5	45	
			4-Ethylcyclohexane	86.5	55	
Isoprene	S	—	3-Methyl-1-butene	—	12	—
			2-Methyl-1-butene	—	40	32
			2-Methyl-2-butene	5	30	38
			Isopentane	95	18	30
Isoprene	P	—	2-Methyl-2-butene		25.5	
			Isopentane	100	74.5	

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[a] See Table 1 for the conditions generally used. [b] S = catalyst "in situ"; the reaction components were mixed in the following order: solvent, olefin, cobalt compound, $(HAlN\text{-}i\text{-}C_3H_7)_6$, and additive if any. P = preformed catalyst; order of mixing: solvent, Cohex$_2$, $(HAlN\text{-}i\text{-}C_3H_7)_6$ and olefin. [c] Diolefin 20 mmol.

TABLE 3

HYDROGENATION OF OLEFINS FED IN SUCCESSIVE STEPS WITH $(HAlN\text{-}i\text{-}C_3H_7)_6/Cohex_2$ [a]

Olefin addition	Olefin (mmol)	Reaction time (min)	Hydrogenation product (yield (%))
1st	1-Octene (20)	10	n-Octane (100)
2nd	1-Octene (20)	15	n-Octane (100)
3rd	1-Octene (20)	20	n-Octane (100)
4th	1-Octene (20)	30	n-Octane (100)
5th	Cyclohexene (20)	60	Cyclohexane (100)

[a] Initially toluene (20 ml), $Cohex_2$ (0.1 mmol), $(HAlN\text{-}i\text{-}C_3H_7)_6$ (0.6 mmol) were mixed and 1-octene was then added. The mixture was pressured with H_2 (2 atm) and stirred at 30°C to complete hydrogenation. Then olefin solutions in toluene (12 ml) were added successively and hydrogenated under the same conditions.

TABLE 4

HYDROGENATION OF OLEFINS WITH CATALYTIC SYSTEMS BASED ON ALUMINUM HYDRIDE DERIVATIVES AND NICKELBIS(ACETYLACETONATE) [a]

Olefin	Hydrogenation product	Hydrogenation yield with different alanes		
		$AlH_3 \cdot N(CH_3)_3$	$AlH_2N(CH_3)_2$	$(HAlN\text{-}i\text{-}C_3H_7)_6$
4-Vinylcyclohexene	4-Ethylcyclohexene	19	27	74.5
	4-Ethylcyclohexane	81	73	25.5
Isoprene	2-Methyl-2-butene	34.5	17	56
	Isopentane	65.5	35	44

[a] See Table 1 for reaction conditions.

$(CH_3)_3 > AlH_2N(CH_3)_2 > (HAlN\text{-}i\text{-}C_3H_7)_6$ in the hydrogenation of 4-vinylcyclohexene and $AlH_3 \cdot N(CH_3)_3 > (HAlN\text{-}i\text{-}C_3H_7)_6 > AlH_2N(CH_3)_2$ in the hydrogenation of isoprene.

Table 5 summarizes the more significant results with compounds of other transition metals. Fairly good results were obtained with Cp_2TiCl_2 or $Ti(O\text{-}i\text{-}C_3H_7)_4$; however, activities were lower than with Co and Ni systems, and the catalyst had to be aged with an excess of hydride at high temperatures. Systems based on vanadium and iron compounds were not very active. This distinguishes aluminum hydrides from trialkylaluminums; $Al(i\text{-}C_4H_9)_3/Feacac_3$ has been reported to have a high hydrogenating activity [2], approaching that of trialkylaluminum—cobalt compounds systems. Thus, with the exception of iron, the catalytic activity of various transition metals when combined with aluminum hydrides is the same as with trialkylaluminums, viz. $Co \simeq Ni > Ti > V$.

Experimental

Reagents and solvents

(a) Aluminum hydride derivatives. $AlH_3 \cdot N(CH_3)_3$ was prepared from $LiAlH_4$ and $(CH_3)_3N \cdot HCl$ [15], and treated with $t\text{-}C_4H_9NH_2$ or $(CH_3)_2NH$, to give $(HAlN\text{-}t\text{-}C_4H_9)_4$ [16] or dimethylaminoalanes [9,13]. $HAlCl_2 \cdot O(C_2H_5)_2$ was

TABLE 5

HYDROGENATION OF OLEFINS WITH CATALYTIC SYSTEMS BASED ON ALUMINUM HYDRIDES AND COMPOUNDS OF DIFFERENT TRANSITION METALS[a]

Transition metal compound (mmol)	Alane	H*/M[b] atomic ratio	Catalyst aging	Olefin (mmol)	Reaction conditions			Hydrogenation products (yield (%))
					PH_2 (atm)	Tempe-ature (°C)	Time (h)	
Cp_2TiCl_2 (0.1)	$AlH_3 \cdot N(CH_3)_3$	12	1 h at 80°C	Isoprene (10)	3	70	1	Isopentane (93) 2-Methyl-2-butene (7)
Cp_2TiCl_2 (0.1)	$AlH_2N(CH_3)_2$	12	1 h at 80°C	1-Octene (20)	3	70	1	n-Octane (100)
Cp_2TiCl_2 (0.1)	$AlH_2N(CH_3)_2$	12	1 h at 80°C	Cyclohexene (20)	3	70	1	Cyclohexane (100)
Cp_2TiCl_2 (0.1)	$AlH_2N(CH_3)_2$	6	1 h at 80°C	Isoprene (10)	3	70	1	Isopentane (91) 2-Methyl-2-butene (9)
Cp_2TiCl_2 (0.1)	$(HAlN\text{-}i\text{-}C_3H_7)_6$	12	1 h at 80°C	Cyclohexene (20)	3	70	1	Cyclohexane (100)
Cp_2TiCl_2 (0.1)	$(HAlN\text{-}i\text{-}C_3H_7)_6$	12	1 h at 80°C	Isoprene (10)	3	70	1	Isopentane (41) 2-Methyl-2-butene (59)
Cp_2TiCl_2 (0.1)	$(HAlN\text{-}n\text{-}C_3H_7)_8$	6	1 h at 70°C	Cyclohexene (20)	3	70	1	Cyclohexane (94)
$Ti(O\text{-}i\text{-}C_3H_7)_4$ (0.33)	$AlH_2N(CH_3)_2$	9	—	1-Octene (20)	4	25	20	n-Octane (83)
$VO(O\text{-}n\text{-}C_4H_9)_3$ (0.2)	$AlH_3 \cdot N(CH_3)_3$	12	10 min at 25°C	1-Octene (20)	4	70	2	n-Octane (93)
$VO(O\text{-}n\text{-}C_4H_9)_3$ (0.4)	$AlH_2N(CH_3)_2$	9	10 min at 25°C	1-Octene (20)	5	40	2	n-Octane (69.5)
$VO(O\text{-}n\text{-}C_4H_9)_3$ (0.4)	$(HAlN\text{-}i\text{-}C_3H_7)_6$	9	10 min at 25°C	1-Octene (20)	5	40	2	n-Octane (23.5)
$V[N(C_2H_5)_2]_4$ (0.1)	$AlH_3 \cdot N(CH_3)_3$	6	10 min at 25°C	1-Octene (20)	3	30	21	n-Octane (40)
$Fe[OC(CH_3)=CHCOCH_3]_2$ (0.5)	$AlH_3 \cdot N(CH_3)_3$	9	—	1-Octene (20)	4	30	1	n-Octane (93)
$Fe[OC(CH_3)=CHCOCH_3]_2$ (0.1)	$(HAlN\text{-}i\text{-}C_3H_7)_6$	12	—	1-Octene (20)	3	30	20	n-Octane (13)
$Fe[OC(CH_3)=CHCOCH_3]_3$ (0.5)	$AlH_3 \cdot N(CH_3)_3$	9	—	1-Octene (20)	4	30	1	n-Octane (94)
$Fe[OC(CH_3)=CHCOCH_3]_3$ (0.5)	$AlH_2N(CH_3)_2$	9	—	1-Octene (20)	4	30	1	n-Octane (64)

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[a] The components were mixed in the following order: toluene (20 ml), transition metal compound, aluminum hydride and, after aging, olefin. [b] H* = hydridic hydrogen; M = transition metal.

made by reaction of $LiAlH_4$ with $AlCl_3$ [17] (HAlN-i-$C_3H_7)_6$ and HAln-n-$C_3H_7)_8$ were obtained by direct synthesis from aluminum and the corresponding amine under a pressure of hydrogen [12].

(b) Transition metal compounds. $V[N(C_2H_5)_2]_4$ was prepared by a published method [18]. The other compounds were commercial products: Co(acetylacetonate)$_2$ Merck-Schuchardt, dried under vacuum; Co(2-ethyl hexanoate)$_2$ K&K, Ni(acetylacetonate)$_2$ Merck-Schuchardt, Cp_2TiCl_2 Fluka, after crystallization from THF, Ti(O-i-$C_3H_7)_4$ Schuchardt after distillation, VO(O-n-$C_4H_9)_3$ Fluka, after distillation.

(c) Olefins. Pure commercial products were dried over molecular sieves and distilled.

(d) Solvents were purified and dried by standard methods. All reactions were carried under nitrogen.

Analytical measurements

Aluminum and transition metal compounds were analyzed by known methods.

The products from the hydrogenation were analysed by gas chromatography (Fractovap, C.Erba apparatus); β,β'-oxydipropionitrile (30%) supported on Chromosorb P (5 m) was used for products from 1-hexane, 2-methyl-2-butene, and isoprene (2 m) for products from 1-octene, cyclohexene and 4-vinylcyclohexene and of Carbowax 20 M + terephthalic acid (10%) on Chromosorb P, (3 m) for products from 1-octene and cyclohexene.

Hydrogenation tests

Hydrogenations were carried out in a 0.25 l autoclave provided with an inlet valve for hydrogen and manometer and thermostatted by immersion in an oil bath. The reaction mixture was stirred magnetically.

A typical run was as follows. At room temperature, Coacac$_2$ (0.1 mmol) in toluene (1.5 ml) and then $AlH_3 \cdot N(CH_3)_3$ (0.2 mmol) in toluene (1 ml) were added to a stirred solution of 4-vinylcyclohexene (10 mmol) in toluene (17.5 ml) in a 50 ml two-necked flask. The mixture was introduced into the autoclave thermostatted at 30° C under vacuum, pressured with H_2 at 2 atm and stirred for 1 h under these conditions. Hydrogen was then removed and the solution analyzed by gas-chromatography. The conversion of 4-vinylcyclohexene was quantitative, giving 4-ethylcyclohexane (96% yield) and 4-ethylcyclohexene (4%).

Acknowledgements

We thank SNAMPROGETTI for allowing publication of these results.

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