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Homogeneous and two-phase dimerization of olefins catalyzed by tungsten complexes. The role of imido ligands and Lewis acids

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Abstract

Organoimido $Cl_4W^{VI} = NAr$ (Ar = aryl) (**1**) complexes catalyze the dimerization of propene and ethene in presence of alkylaluminum derivatives. Similar results are obtained with the in situ formed tungsten system based on the mixture WCl_6/aniline/alkylaluminum. For most cases, 2,3-dimethylbutenes are the main dimers formed from propene. However, in some instances, propene metathesis reactions can be promoted. The $Cl_2W^{IV} = NPh(PMe_3)_3$ **3** complex is an efficient catalyst for ethene dimerization when promoted by $AlCl_3$. The reaction can be carried out using acidic chloroaluminates as the solvent with **3** without an additional cocatalyst. Cationic species are proposed as the active intermediate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tungsten; Ionic liquids; Chloroaluminates; Organoimido; Metathesis; Dimerization

1. Introduction

Tungsten and molybdenum complexes have been known for a long time as homogeneous catalysts for the metathesis of cyclic and acyclic olefins [1,2]. Very early it appeared that oxo or alkoxo and/or imido anionic ligands could improve catalyst efficiency. Thanks to Schrock's brilliant work, it has been demonstrated that the active species is a W(VI) alkylidene complex [3]. The alkoxo and/or imido ligands play an important role in the stabilization of the four member metallacyclic intermediate and prevent

intermolecular reactions [4]. Rappé and Goddard [5] have suggested in a theoretical mechanistic study that the spectator oxo makes the metallocycle formation favourable.

However in the middle of the seventies, Lawson and Menapace et al. from Goodyear [6–10] pointed out that the catalyst system based on WCl_6 and aniline, which is efficient for olefin metathesis reactions, could be changed into an olefin dimerization catalyst system. As an example, a mixture of tungsten hexachloride, aniline (aniline/W molar ratio = 2) and ethylaluminum dichloride (Al/W = 10) catalyzes the dimerization of propene into a mixture of 2,3-dimethylbutene and 2-methylpentene, using chlorobenzene as the solvent. More recently,

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this reaction has been reexamined, in the hope that an industrial process based on a tungsten catalyst might be developed [11].

We undertook to revisit the 'Goodyear reaction' and to transfer the catalytic system into an ionic liquid, with the aim of increasing the catalyst turn-over number by using the two-phase catalysis concept. This technique has been used in a similar way for the dimerization of propene catalyzed by cationic nickel complexes [12].

2. Experiment

All the manipulations were conducted under argon atmosphere using the Schlenk tube technique. Most of the reagents are commercially available. Chlorobenzene was dried over P_2O_5 and other liquids over molecular sieves.

2.1. Preparation of catalytic systems

$WOCl_4$ was prepared according to Gibson et al.'s procedure [13]. Imidotetrachloro tungsten complexes were synthesized by reacting the corresponding isocyanate with oxotetrachloro

tungsten, which provided the $Cl_4W=NAr$ (**1**) (Ar = aryl group) complexes. These complexes are further reduced to $Cl_3W=NAr(PMe_3)_2$ complexes **2** upon addition of PMe_3. The corresponding $Cl_2W=NAr(PMe_3)_3$ complexes **3** were obtained by the reduction of **1** using sodium–mercury amalgam in the presence of PMe_3, as described by Nielson [14].

2.2. Preparation of the ionic liquid

1-Butyl-3-methylimidazolium tetrachloroaluminate was obtained by reacting 1-butyl-3-methylimidazolium chloride (BMIC) with aluminum chloride as previously described [15].

2.3. Catalytic experiments

The catalytic reactions were conducted in a 100 ml double walled stainless steel autoclave equipped with a magnetic stirring bar. In a typical experiment, the reactor purged of both air and moisture, was maintained under an atmosphere of olefin. Then a solution containing the catalytic system was introduced, the reactor was heated to the desired temperature and a constant pressure of gaseous olefin was applied.

Table 1
Reaction of propene with $WCl_6/ArNH_2/EADC$ (1:2:11) catalytic system

Entry	1	2	3	4	5	6
Catalyst (nature of Ar)	C_6H_5	$4\text{-}FC_6H_4$	$2,6\text{-}Cl_2C_6H_3$	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}{}^iPr_2C_6H_3$	$3,5\text{-}(CF_3)_2C_6H_3$
Reaction time (mn)	175	180	150	135	145	210
TON (mol mol^{-1})	4250	5660	3650	700	530	1100
Products (wt.%)						
ethene						1
n-butenes	traces	traces	traces	traces		41
pentenes	traces	traces	traces			14
i-hexenes	96	96	95	77	74	22
heavier olefins	4	4	5	23	26	22
Distribution of dimers[a]						
DMB	62	59	87	81	78	51
4MP	5	5	5	13	15	43
2MP	33	36	8	6	17	6

Reaction conditions: Solvent: chlorobenzene. Pressure: 0.8 MPa. $T = 60°C$.
[a]Analysis of the liquid phase: DMB: 2,3-dimethyl but-1-ene and 2,3-dimethyl but-2-ene; 4MP: 4-methylpent-1-ene and 4-methylpent-2-ene; 2MP: 2-methylpent-1-ene.

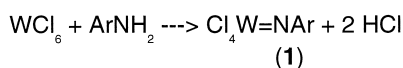$$WCl_6 + ArNH_2 \longrightarrow Cl_4W=NAr + 2 HCl$$
$$(1)$$

Fig. 1. Formation of the imido W(VI) complexes.

At the end of the reaction, the catalyst was deactivated by injecting gaseous ammonia.

Hydrocarbons were analyzed by means of gas chromatography on a HP5890 apparatus equipped with a PONA column (length 50 m, internal diameter 0.2 mm, FID detector).

3. Results and discussion

3.1. WCl_6 and aniline ('Goodyear type' catalyst)

In the first series of experiments, propene was reacted under 0.8 MPa and 50°C with a 'Goodyear-type' catalyst resulting from the interaction of WCl_6, aniline or derivatives and $AlEtCl_2$ (EADC), using chlorobenzene as the solvent. The results obtained with an excess of EADC (Al/W = 11) are summarized in Table 1. Dimerization is the prevalent reaction for almost all the anilines used. 2,3-Dimethyl-butenes (tail-to-tail dimers) are the main products but 2-methylpent-1-ene (head-to-tail) is important for the 2,6-unsubstituted aryl group of the aniline derivatives (entries 1 and 2). 4-Methylpentenes (head-to-tail) are also formed but in minor quantities. No n-hexenes were observed. The best selectivity in 2,3-dimethylbutenes is obtained with o-substitution of the aromatic group of the aniline by two chlorine atoms (entry 3). On the other hand, substitution in o-position with an alkyl group (entries 4 and 5) considerably reduces the dimerization reaction rate. Unexpectedly, using bis 3,5-trifluoro-methyl aniline (entry 6), metathesis is the main reaction pathway. In this case, but-2-ene is the primary product and n-pentenes probably arise from the subsequent reaction of but-1-ene with propene.

When EADC is used with Al/W molar ratio of 1, under the same operating conditions as previously described, the catalyst activity decreases considerably.

3.2. $Cl_4W=NAr$ as catalyst precursors

The reaction of a suspension of WCl_6 in chlorobenzene with one equivalent of aniline

Table 2

Reaction of propene with ArN = WCl_4/EADC (Al/W = 11) catalytic system

Entry	7	8	9	10
Catalyst (nature of Ar)	C_6H_5[a]	4-FC_6H_4	$2,6\text{-Me}_2C_6H_3$	$2,6\text{-}^iPr_2C_6H_3$[b]
Reaction time (mn)	148	80	152	210
TON (mol mol^{-1})	3400	4150	1190	360
Products (wt.%)				
ethene				1
n-butenes	traces	traces		1
pentenes	traces	traces		1
i-hexenes	86	97	91	79
heavier olefins	13	3	9	18
Dimer distribution				
DMB	74	65	85	80
4MP	4	5	11	12
2MP	22	30	6	8

Operating conditions see Table 1.
[a] Solvent: toluene.
[b] Complex recrystallized from tetrahydrofuran.

Table 3
Reaction of ethene with $(2,6\text{-}Me_2C_6H_3)N = WCl_4/AlEt_nCl_{2-n}$ catalytic system

Entry	11	12	13
Nature of the alkylaluminum	$AlEtCl_2$	$AlEtCl_2$	$AlEt_2Cl$
Al/W (molar ratio)	11	40[a]	40[a]
Reaction time (mn)	240	450	274
TON (mol mol^{-1})	0	14000	22300
Products (wt.%)			
n-butenes		63 (97% but-1-ene)	83 (99% but-1-ene)
i-hexenes		17 (7% hex-1-ene)	16 (3% hex-1-ene)
heavier olefins		20	1

Reaction conditions: Solvent: chlorobenzene. $T = 40°C$, $P = 6$ MPa.
[a] 0.2 MPa ethene was applied over night before starting the reaction.

under reflux (140°C), in the presence of a stream of argon, yields a brownish orange solution. HCl simultaneously evolves. Depending on the reaction conditions and on aniline substituents, 1.6 to 2.2 moles of HCl per mole of W were formed. From these results, it may be suspected that the active species precursor is the monoimido W(VI) complex formed as depicted in Fig. 1. However, we were not able to isolate any definite compound from this solution.

For this reason, we synthesized complexes **1** by a well known method, i.e., the reaction of isocyanates with $WOCl_4$ [13,14]. Reacting **1** with EADC in quite similar conditions to those previously used, affords clear orange to red solutions. Table 2 shows the results obtained with different arylimido groups using EADC in excess (Al/W = 11). The results compare rather well with the results in Table 1.

In a similar way, in the presence of EADC, complexes **1** catalyze the dimerization of ethene (Table 3). Surprisingly, activity was only observed for Al/W = 40. $AlEt_2Cl$ proved to be a better cocatalyst (entry 13). Higher TON are obtained. Selectivities both in *n*-butenes and but-1-ene are high. Using similar operating conditions, $W(=O)Cl_4$ complex, associated with $AlEt_2Cl$ (Al/W = 40) is not reactive.

3.3. Catalysis with low oxidation state tungsten complexes

In order to specify the valence of the active species we have synthesized the corresponding

Table 4
Reaction of ethene catalyzed by $Cl_2W = NPh(PMe_3)_3$

Entry	14	15
Solvent	Chlorobenzene	$BMIC/AlCl_3$ (1:1.08)
Volume of solvent (ml)	15	4
Cocatalyst	$AlCl_3$ (Al/W = 4.5)	
TON (mol mol^{-1})	1740	1280
Products (wt.%)		
butenes	80 (but-1-ene 60%)	81 (but-1-ene 65%)
i-hexenes	18 (hex-1-ene 85%)	18 (hex-1-ene 92%)
heavier olefins	2	1

Operating conditions: W:0.25 mmole, $T = 60°C$; $P = 4$ MPa; reaction time: 230 mn.

$Cl_3W = NPh(PMe_3)_2$ **2** and $Cl_2W = NPh$-$(PMe_3)_3$ **3** imido complexes. These complexes are not active per se, but reacting a solution of **3**, in chlorobenzene, with an excess of aluminum chloride $(Al/W = 4.5)$ yields an orange–brown solution which dimerizes ethene (Table 4). Under these conditions, a part of the phosphine ligand coordinates to aluminum chloride as shown by the ^{31}P NMR spectra (sextuplet between -52.1 and -35.8 ppm resulting from $^{27}Al-^{31}P$ coupling; $J = 290$ Hz). On the other hand, complex **2** did not yield to an active species but it can be activated by EADC in the same conditions and with similar results as **1**.

Acidic ionic liquids composed of the mixture of butyl-1 methyl-3 imidazolium chloride and aluminium chloride $(AlCl_3/BMIC > 1)$, are liquid at room temperature. They contain the $Al_2Cl_7^-$ anion which is in equilibrium with $AlCl_3$ and the $AlCl_4^-$ anion. Complex **3** dissolves in acidic organochloroaluminate ionic liquids. It forms a homogeneous brown solution which also catalyzes the dimerization of ethene without the addition of $AlEtCl_2$. The supernatant hydrocarbon layer (oligomers) is quite colorless. We can then assume that the catalysis occurs in the ionic phase. The products can be easily separated by simple decantation and the ionic liquid containing the catalyst may be reused. Complex **1** also dissolves in acidic $BMIC/AlCl_3$ based ionic liquids. It can be reduced directly in the ionic liquid by the addition of EADC and catalyzes the dimerization of

propene. However, in this case and contrary to experiment starting from complex **3**, the organic phase is colored which suggests that some tungsten species has been extracted. This may be ascribed to the fact that the reduction of W(VI) to W(IV) is not selective in the ionic liquid.

In the case of **3**, the following reaction scheme can be suggested (Fig. 2).

Starting from complex **1** and EADC, the same type of W(IV) active intermediates may be formed on account of a double alkylation of W(VI) followed by β–H transfer yielding a W(IV) complex [16,17]. In the 'Goodyear system', the role of the excess aniline is probably to neutralize a part of the HCl that is formed. As could be expected, sterically demanding arylimido groups (o-disubstituted phenyl) favor tail-to-tail coupling of two moles of propene yielding 2,3-DMB.

Metallocyclopentane formation has also been invoked in the case of zirconium complexes and may explain the obtained selectivity in the alkene–alkene coupling reaction [18].

In some instances (e.g., bis 3,5-trifluoromethyl aniline), the α–H elimination could be promoted in the intermediate 'ArN=W(X$_2$)Et$_2$' and could generate the metallacarbene responsible for the metathesis reaction.

The metathesis of olefins results from the conversion of a π-olefin-metallocarbene species into a metallacyclobutane intermediate. The change of tungsten based catalyst reaction pathway from metathesis to dimerization could be
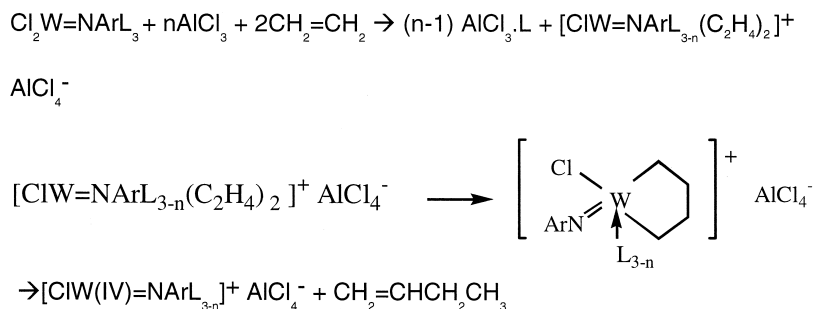
$$Cl_2W=NArL_3 + nAlCl_3 + 2CH_2=CH_2 \rightarrow (n-1)\ AlCl_3.L + [ClW=NArL_{3-n}(C_2H_4)_2]^+$$

$$AlCl_4^-$$

$$[ClW=NArL_{3-n}(C_2H_4)_2]^+\ AlCl_4^- \longrightarrow \left[\begin{array}{c} Cl \\ ArN \end{array} \underset{L_{3-n}}{\overset{}{W}} \right]^+ AlCl_4^-$$

$$\rightarrow [ClW(IV)=NArL_{3-n}]^+\ AlCl_4^- + CH_2=CHCH_2CH_3$$

Fig. 2. Proposed reaction pathway for ethene dimerization catalyzed by complex **3** (L = PMe$_3$).

ascribed to the relative instability of the metallocarbene in the presence of a strong Lewis acid. The instability of the carbene would result in the π-coordination of a second molecule of olefin, and the consecutive oxidative coupling forming a metallacyclopentane. Clearly, the substitution of aniline with two trifluoromethyl groups stabilizes the carbene intermediate in spite of the presence of a Lewis acid and then favors the metathesis pathway. The role of the imido ligand in the dimerization reaction could be the same as in a metathesis catalyst i.e., it stabilizes a W(VI) species with two metal–carbon bonds either C–W–C or C=W bonds.

4. Conclusion

We have specified the nature of the active species in the dimerization of olefins by the mixture of $Cl_4W=NAr$/EADC. The same active intermediates may be involved in the reaction with the mixture of WCl_6/aniline/EADC previously described by Menapace et al. The cationic nature of this complex is confirmed by its solubility in an ionic liquid and its insolubility in aliphatic hydrocarbons. Unfortunately, the instability of the active species precludes both a more accurate characterization and an industrial development. As the nature of the ligand seems to be of prime importance in stabilizing the active intermediates, other types of ligands need to be examined.

References

[1] G. Natta, G. Dall'Asta, G. Mazzanti, Angew. Chem. Int. Ed. 3 (1964) 723.
[2] N. Calderon, E.A. Ofstead, J.P. Ward, W.A. Judy, K.W. Scott, J. Am. Chem. Soc. 90 (1968) 4133.
[3] R.R. Schrock, J. Organomet. Chem. 300 (1986) 249.
[4] R.R. Schrock, Acc. Chem. Res. 23 (1990) 158.
[5] A.K. Rappé, W.A. Goddard, J. Am. Chem. Soc. 104 (1982) 448.
[6] U.S. Patent 3,784,629, 30 and 31 (1972) to Goodyear Tire and Rubber Inv. H.R. Menapace, G.S. Benner, N.A. Maly.
[7] U.S. Patent 3,897,512 (1973) to Goodyear Tire and Rubber Inv. M. Brown, H.R. Menapace, N.A. Maly.
[8] U.S. Patent 3,813,453 (1974) to Goodyear Tire and Rubber Inv. G.W. Lawson.
[9] U.S. Patent 3,903,193 (1975) to Goodyear Tire and Rubber Inv. N.A. Maly, H.R. Menapace, G.S. Benner.
[10] H.R. Menapace, N.A. Maly, J.L. Wang, L.G. Wideman, J. Org. Chem. 40 (1975) 2983.
[11] US Patent 5,059,739 (1989) to Exxon Chemical Inv. D.E. Hendriksen.
[12] Y. Chauvin, S. Einloft, H. Olivier, Ind. Eng. Chem. Res. 34 (1995) 1149.
[13] V.C. Gibson, T.E. Kee, A. Shaw, Polyhedron 7 (1988) 579.
[14] A.J. Nielson, Inorg. Synth. 24 (1986) 194.
[15] B. Gilbert, Y. Chauvin, I. Guibard, Vib. Spectrosc. 1 (1991) 299.
[16] S.S. Wang, K.A. Abboud, J.M. Boncella, J. Am. Chem. Soc. 119 (1997) 11990.
[17] S.S. Wang, D.D. Vanderlende, K.A. Abboud, J.M. Boncella, Organometallics 17 (1998) 2628.
[18] E. Negishi, T. Takahashi, Acc. Chem. Res. 27 (1994) 124.