

Liquid–liquid two-phase cyclodimerization of 1,3-dienes by iron-nitrosyl dissolved in ionic liquids

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Received 24 May 2000; received in revised form 24 November 2000; accepted 24 November 2000

Abstract

The 1,3-butadiene cyclodimerization reaction by iron complexes, prepared in situ by reduction of $[\text{Fe}(\text{NO})_2\text{Cl}]_2$ with metallic zinc, diethylaluminum chloride or *n*-butyllithium, dissolved in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄, **1**) or hexafluorophosphate (BMI-PF₆, **2**) ionic liquids is a typical two-phase catalytic reaction. The reaction performed in BMI-PF₆, at 50°C, furnished 4-vinyl-1-cyclohexene with 100% selectivity and TOF up to 1404 per hour. The 1,3-butadiene conversion is dependent on the nature of ionic liquid, reaction temperature and added phosphine. The products are removed from the reaction mixture by simple decanting. The recovered ionic catalyst solution can be reused several times without any significant changes in catalytic performance. Under similar reaction conditions, isoprene leads quantitatively to the mixture of cyclic dimers: 2-methyl-4-(1-methylethenyl)cyclohexene (**3a**), 1-methyl-4-(1-methylethenyl)cyclohexene (**3b**), 2,4-dimethyl-4-vinylcyclohexene (**4a**) and 1,4-dimethyl-4-vinylcyclohexene (**4b**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Two-phase catalysis; 1,3-Dienes cyclodimerization; Ionic liquids; Iron-nitrosyl; Imidazolium salts

1. Introduction

For economic and ecological reasons, synthetic chemists face an increasing obligation to optimize their synthetic methods in order to produce the desired product in 100% yield and selectivity through a safe and environmentally acceptable process. Addition and cycloaddition reactions, especially those catalyzed by transition metal complexes, are potentially the best candidates for atom economy in organic synthesis [1,2]. Organometallic catalysis offers one of the best

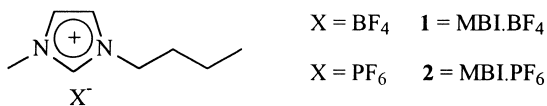
ways to promote these C–C and C-heteroatom bond forming reactions [3], however, the separation of the products from the reaction mixture and the recovery of the catalysts are the major disadvantages of these homogeneous processes. This is why, despite the benefits, many homogeneous processes are not used on the industrial scale. Among the various approaches addressed to solve these problems, the liquid–liquid two-phase catalysis has emerged as one of the most important alternatives [4].

The advent of water-soluble organometallic complexes, especially those based on sulphonated phosphorus ligands, has made possible for various two-phase catalytic reactions to be conducted on an industrial scale [4]. However, the use of water as a catalyst-immobilizing phase has its limitations: (i) it represents a highly polar and coordinating

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Scheme 1.

protic solvent; (ii) it is reactive towards many organometallic complexes and substrates. Moreover, the synthesis of especially designed water soluble ligands/organometallic complexes is essential for its use. More recently, perfluorocarbons have been used as the non-aqueous phase for liquid–liquid two-phase hydroformylation [5] and oxidation reactions. Electrocatalytic reactions using propylene carbonate as solvent has been described as a valuable tool in this field [6]. Although, ionic liquids, especially those based on the 1-*n*-butyl-3-methylimidazolium cation (Scheme 1) has been shown to be immobilizing agents of choice for the oligomerization, hydrogenation, hydroformylation and hydrodimerization of carbon–carbon double bonds [7–12].

In these systems the products are easily separated from the reaction mixture and the recovered ionic catalyst solution can be reused several times without any significant changes in the catalytic performance. However, these systems have limitations such as the necessity of organic co-solvents and limited conversions and/or selectivities. We describe herein the cyclodimerization of 1,3-butadiene and isoprene by iron-nitrosyl complex immobilized in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate ionic liquids (BMI·BF₄, **1**, and BMI·PF₆, **2**), a typical liquid–liquid two-phase catalytic reaction. The product is continuously separated from the reaction mixture by simple decanting and the remaining catalyst solution can be reused several times, enabling the reaction to be considered as an ideal process within the atom economy concept.

2. Experimental section

2.1. General considerations

All manipulations were performed under dry, oxygen-free argon using standard Schlenk tube techniques. All solvents were dried and distilled under

argon immediately prior to use. Infrared (nujol mulls or KBr pellets) spectra were recorded in the region 4000–400 cm⁻¹ region with a Bomem FTIR spectrophotometer. The ¹H and ¹³C {¹H} NMR spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Varian VXR-200 instrument. Proton and carbon resonances (δ (ppm), *J* (Hz)), are shifted positively downfield relative to external SiMe₄. The reaction products were analyzed by gas chromatography on a Varian 3400 CX chromatograph equipped with a DB-1 column (30 m long, i.d.: 0.20 mm, 0.5 μ m film thickness), equipped with a FID detector; N₂ was the carrier (1 ml min⁻¹); the temperature program was: 35°C (5 min) to 250°C (10 min) at a heating rate of 10°C min⁻¹.

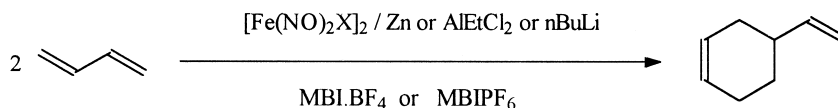
The ionic liquids [8] and the iron catalyst precursor [13] were prepared according to procedures described in literature. All other reagents were obtained from commercial sources and were used as received without further purification.

2.2. Catalytic experiments

In a typical experiment 163 mg (2.5 mmol) of Zn, (Qualitec, 99%) and 78 mg of the complex [Fe(NO)₂Cl]₂ (0.26 mmol) were introduced into the 100 ml stainless steel autoclave equipped with a magnetic stirring bar. Thereafter, the autoclave was cooled to 10°C and the ionic liquid (2 ml) was added followed by 25 ml 1,3-butadiene (314 mmol). The reaction mixture was heated to the desired temperature. The crude reaction mixture contains two-phases. The upper phase was analyzed by gas chromatography. The 1,3-butadiene conversion and 4-vinyl-1-cyclohexene selectivity were determined by gas chromatography using cyclohexane as the external standard.

3. Results and discussion

The cyclodimerization of conjugated dienes catalyzed by soluble transition metal catalyst precursors, especially those based on iron complexes, is a well-known reaction. For example 4-vinyl-1-cyclohexene can be easily produced by cyclodimerization of 1,3-butadiene [14–17]. Considering that iron-nitrosyl complexes are soluble and stable in ionic liquids and that a two-phase system is constituted upon forming



a mixture of alkenes and dienes with the catalyst solution in the ionic liquid, we studied the potential of this system as a technological improvement in this field. Therefore we have investigated the transposition of these homogeneous reactions to a liquid–liquid two-phase system by immobilizing the iron catalyst precursor in the ionic liquids **1** and **2**. These two ionic liquids were chosen for this study due to their distinct physical-chemical properties [18], in particular the difference in the ionic character of such ionic liquids.

3.1. 1,3-Butadiene cyclodimerization

The catalytic 1,3-butadiene cyclodimerization was performed by dissolving the catalyst precursor $[\text{Fe}(\text{NO})_2\text{Cl}]_2$ and a reducing agent in the ionic

liquid and this affords 4-vinyl-1-cyclohexene as the sole product (Scheme 2).

Table 1 shows the data on the catalytic performance of $[\text{Fe}(\text{NO})_2\text{Cl}]_2$ in the cyclodimerization of 1,3-butadiene.

It becomes evident that metallic Zn is a better reducing agent than *n*-butyllithium, and this is evidenced either from the 1,3-butadiene conversion or the 4-vinyl-1-cyclohexene selectivity (compare entries 2 and 5). In the case of diethylaluminum chloride (entry 4) the conversion and turnover frequencies are similar to those obtained using Zn as reducing agent, but there is some formation of 1,3-butadiene linear oligomers.

The nature of the ionic liquid affects the reactivity of the system. At 10°C the system shows higher turnover frequencies (TOF) in $\text{MBI}\cdot\text{BF}_4$ than in $\text{MBI}\cdot\text{PF}_6$, as

Table 1

Cyclodimerization of 1,3-butadiene by $[\text{Fe}_2(\text{NO})_4\text{Cl}_2]$ dissolved in $\text{MBI}\cdot\text{PF}_6$ (**1**) and $\text{MBI}\cdot\text{BF}_4$ (**2**) ionic liquids under various reaction conditions^a

Entry	Solvent	Fe (mmol)	Phosphine (mmol)	P/Fe	Reducing agent (mmol)	C ₄ H ₆ (mmol)	Temperature (°C)	Time (h)	Conversions (%)	Selectivities (%)	TOF (per hour)
1	2	0.32	0	0	Zn (3.3)	220	10	3.0	23	100	53
2	2	0.33	0	0	Zn (3.3)	296	30	1.2	65	100	486
3	2	0.26	0	0	Zn (2.5)	466	50	1.2	94	100	1404
4	2	0.13	0	0	AlEt_2Cl (2.0) ^b	229	30	2.0	72	96	634
5	2	0.17	0	0	<i>n</i> -BuLi (0.6) ^c	444	30	4.7	11	88	61
6	1	0.36	0	0	Zn (3.5)	263	10	3.0	99	100	241
7	1	0.36	0	0	Zn (3.5)	364	50	2.0	85	100	430
8	PhMe	0.35	0	0	Zn (2.0)	295	50	3.0	90	100	253
9	2	0.48	PPh_3 (0.38)	0.8	Zn (3.8)	353	50	3.0	87	100	213
10	2	0.70	Pcy_3 (0.54)	0.8	Zn (5.5)	310	50	3.0	44	100	65
11	2	0.43	Pcy_3 (0.41)	1.0	Zn (4.0)	268	50	24	63	100	16
12	2	0.28	S-BINAP ^d (0.24)	0.8	Zn (4.3)	315	50	3.0	5	100	19
13	2	0.43	S-BINAP (0.42)	1.0	Zn (4.1)	296	50	24	60	100	17
14	2	1.3	PPh_2Cl (1.3)	1.0	Zn (23)	315	50	0.25	93	100	908
15	2	0.19	PPh_2Cl (0.23)	1.0	Zn (1.8)	357	50	3.0	72	100	451

^a Reaction conditions: volume of ionic liquid, 2.0 ml; volume of PhMe, 20 ml.

^b Co-catalyst added as a 0.5 M solution in toluene.

^c Co-catalyst added as a 1.4 M solution in *n*-hexane.

^d S-(–)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

Table 2
Cyclodimerization of isoprene by $[\text{Fe}_2(\text{NO})_4\text{Cl}_2]$ dissolved in BMI-PF₆ (**1**) and BMI-BF₄ (**2**) ionic liquids under various reaction conditions^a

Entry	Solvent	Fe (mmol)	Phosphine (mmol)	Fe/P	Reducing agent (mmol)	C ₅ H ₈ (mmol)	Temperature (°C)	Time (h)	Conversions (%)	Selectivities (%)				TOF (per hour)
										3a	3b	4a	4b	
16	1	0.36	0	0	Zn (3.8)	145	30	5.0	91	4.0	4.0	40	52	73
17	1	0.31	0	0	AlEt ₂ Cl (2.0) ^b	131	30	2.5	7	30	11	13	46	12
18	PhMe	0.16	0	0	Zn (4.2)	67	30	6.0	72	4.0	4.0	40	52	50
19	2	0.30	0	0	Zn (3.5)	150	30	0.7	99	4.0	4.0	40	52	707
20	2	0.31	0	0	AlEt ₂ Cl (2.0) ^b	131	30	4.7	19	30	10	13	47	17
21	PhMe	0.16	0	0	Zn (1.8)	177	50	6.0	83	9.4	4.6	22	64	153
22	2	0.29	–	–	Zn (3.0)	349	30	3.5	96	5.5	3.5	26	65	330
23	2	0.68	0	0	Zn (6.5)	152	50	3.0	99	5.8	3.2	39	52	74
24	2	0.40	PPh ₃ (0.39)	1.0	Zn (3.4)	110	50	3.0	45	6.0	5.0	21	68	38
25	2	0.40	S-BINAP ^c (0.38)	1.0	Zn (4.2)	160	50	3.0	7	6.0	5.0	21	68	9
26	2	0.20	NMDPP ^d (0.20)	1.0	Zn (4.0)	250	30	6.0	66	4.9	3.1	22	70	138
27	2	0.47	PPh ₂ Cl (0.48)	1.0	Zn (3.0)	150	50	3.0	70	6.0	4.0	25	65	74
28	2	0.37	P(<i>o</i> -MePh) ₃ (0.36)	1.0	Zn (5.1)	258	50	3.0	96	5.5	3.5	25	66	223
29	2	0.26	P(<i>p</i> -MePh) ₃ (0.26)	1.0	Zn (5.4)	268	50	3.0	61	5.4	3.6	23	68	210

^a Reaction conditions: volume of ionic liquid, 2.0 ml; volume of PhMe, 20 ml.

^b Co-catalyst added as a 0.5 M solution in toluene.

^c S-(–)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

^d S-(+)-neomenthylidiphenyl phosphine.

can be seen comparing entries 1 and 6. At 50°C the trend is reversed, the higher TOF being obtained in MBI-PF₆ when compared with MBI-BF₄ (compare entries 3 and 7).

It is noteworthy that the 1,3-butadiene conversion and, the turnover frequency obtained in the two-phase system are higher than those obtained under homogeneous conditions (compare entries 3 and 8). The catalytic system described in entry 7 has been recovered and used in 3 successive batches of cyclodimerization of 1,3-butadiene, without any loss in the catalytic activity or selectivity.

Entries 9 to 15 of Table 1 describe the catalytic performance obtained from the cyclodimerization of 1,3-butadiene by [Fe(NO)₂Cl]₂ in presence of phosphine ligands. It can be noticed that varying the phosphine does not lead to changes in selectivity, which is still 100% for 4-vinyl-1-cyclohexene in all cases. In opposition, the turnover frequencies change to 213 per hour with PPh₃ (entry 9), a value which is of the same order of magnitude as that obtained under homogeneous conditions (253 per hour, entry 8), but lower than the biphasic phosphine-free system (1404 per hour, entry 3). This decrease in the TOF is observed also with PCy₃ (entry 10) and S-BINAP (entry 12) and, in a lower extent, with PPh₂Cl (entry 15).

The effect of phosphines, leading to lower activities than the original system can be attributed to the formation of iron-phosphine species that are less active in the cyclodimerization reaction. The same trend has been observed in one-phase butadiene cyclodimerization reaction [15].

3.2. Isoprene cyclodimerization

The results obtained in the cyclodimerization of isoprene are summarized in Table 2. In these reactions a

mixture of 2-methyl-4-(1-methylethenyl)cyclohexene and 1-methyl-4-(1-methylethenyl)cyclohexene (**3a** and **3b**, respectively) and 2,4-dimethyl-4-vinylcyclohexene and 1,4-dimethyl-4-vinylcyclohexene (**4a** and **4b**, respectively) were obtained (Scheme 3).

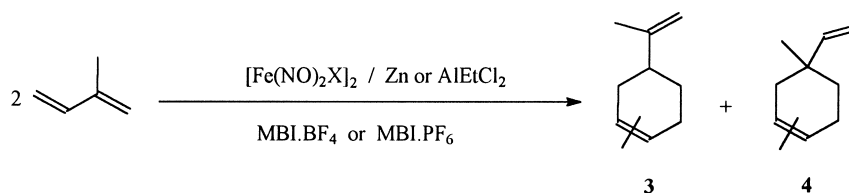
Table 2 shows the catalytic performance of [Fe(NO)₂Cl]₂ dissolved in different ionic liquids and with the addition of phosphines.

Metallic zinc has been shown to be a better reducing agent than diethylaluminum chloride, as already observed in the case of 1,3-butadiene. Both isoprene conversion and the selectivity in 1,4-dimethyl-4-vinylcyclohexene (**4b**) and 2,4-dimethyl-4-vinylcyclohexene (**4a**) significantly decreases when AlEt₂Cl is used (from 92%, entry 16, to 59 or 60%, entries 17 and 20).

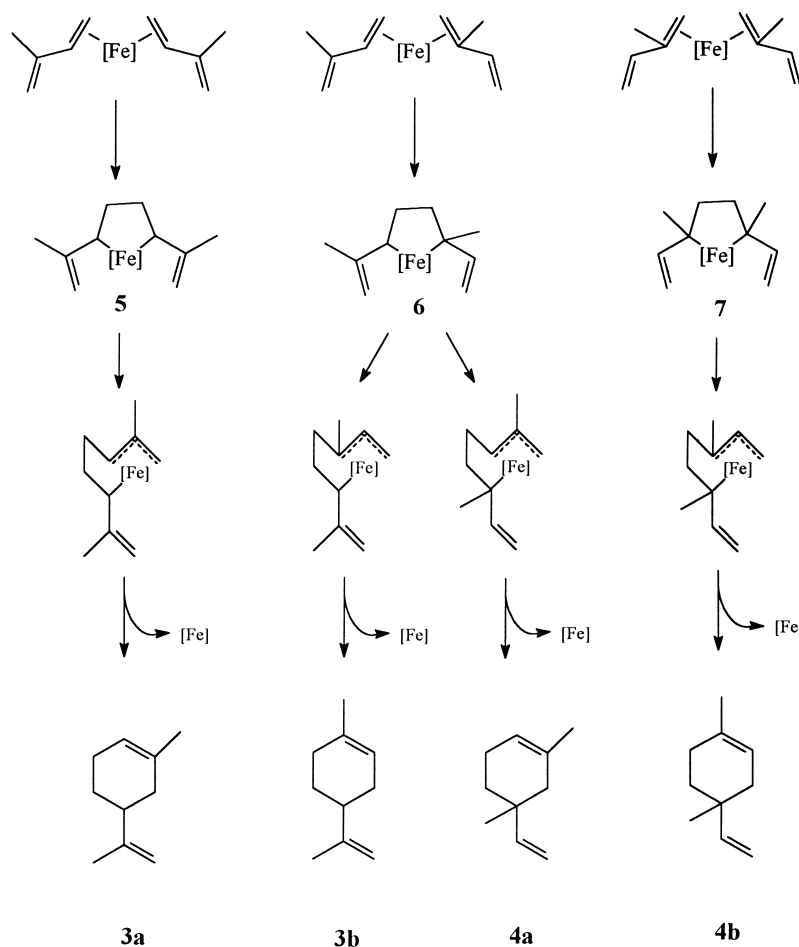
The selectivity found with metallic zinc is similar to those achieved under homogeneous conditions, i.e. 90% of **4** and 10% of **3** as shown in entries 16 and 19 and these values agree with those previously described by Petit and co-workers [15]. This shows that **4** is formed from the more stable metallacycle intermediate (**7**) when using iron-nitrosyl complex associated with Zn. When Zn is replaced by AlEt₂Cl, 40% of **3** is formed as shown in entry 17 or 20.

From Scheme 4 it can be seen that **3a** derived from the tail-to-tail coupling of isoprene. Whereas **4b** is produced by a head-to-head coupling and the other two products, **3b** and **4a** are formed by a head-to-tail carbon-carbon bond formation. It is noteworthy that **3b** and **4a** are formed from the same intermediate species **6**, which can lead to two possible η³-allylic moieties [19] (Scheme 4).

It is also clear from Table 2 that the TOF decreases with the addition of phosphine ligands (see entries 24–29). This effect is best observed on Fig. 1, where the variation of conversion with reaction time is shown



Scheme 3.



Scheme 4.

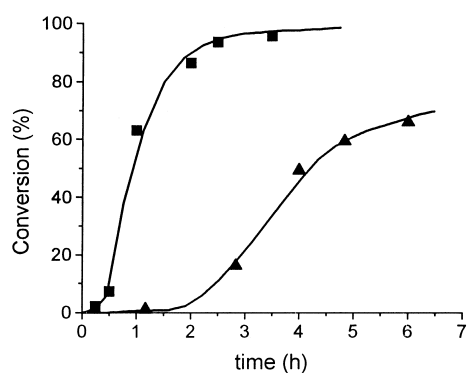


Fig. 1. Dependence of the conversion with the reaction time in the cyclodimerization of isoprene; (■) without phosphine (entry 22, Table 2); (▲) with addition of NMDPP phosphine (entry 26, Table 2).

for the reaction with NMDPP phosphine (entry 26²) and without phosphine (entry 22).

However the ratio **4b/4a** is significantly enhanced with the addition of phosphines from 1.3 (entry 23) up to 3.2 (entry 24). Note that this behavior is independent of the steric and/or electronic properties of the added phosphine. At present we have no explanation for this effect. However it is clear that the addition of external ligands favor the intermediate metallacycle **7** over **6** (Scheme 4).

² It is worthnoting that the specific rotation of the mixture of products **3a**, **3b**, **4a** and **4b** obtained with NMDPP (entry 26) was +0.35° (*c* = 4.46; C₂H₅OH) and with S-BINAP (entry 25) was +0.13° (*c* = 4.20; C₂H₅OH).

4. Conclusions

4-Vinyl-1-cyclohexene, the cyclodimer of 1,3-butadiene, has been obtained in 100% yield and selectivity using iron nitrosyl complexes and different reducing agents immobilized in 1-*n*-butyl-3-methylimidazolium ionic liquids. The two-phase reaction conditions enable higher conversions of 1,3-butadiene than those observed under homogeneous conditions, attaining values of 1404 per hour under very mild reaction conditions. The product is continuously separated from the reaction mixture by simple decanting, in a typical two-phase catalytic reaction. The recovered ionic catalyst solution may be reused several times without any changes in the catalytic activity and selectivity.

The cyclodimerization of isoprene can also be performed under two-phase conditions, yielding 1,4-dimethyl-4-vinylcyclohexene (**4b**) in 70% selectivity upon improvement by the addition of phosphines.

Acknowledgements

The authors are grateful to FINEP-PADCT and FAPERGS for financial support and to PETROFLEX for a gift of isoprene. RAL is grateful to UNESP and CNPq for a fellowship.

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