The Importance of Imidazolium Substituents in the Use of Imidazolium-Based Room-Temperature Ionic Liquids as Solvents for Palladium-Catalyzed Telomerization of Butadiene with Methanol

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Room-temperature ionic liquids are used as cosolvents in the palladium-catalyzed telomerization of butadiene with methanol. The basic catalyst is palladium(II) acetate with either triphenylphosphine or sodium diphenylphosphinobenzene-3-sulfonate (TPPMS), which was reacted with butadiene and methanol at 85 °C. It was found that the addition of several equivalents of 1,3-dialkylimidazolium salts per palladium leads to complete deactivation of the catalyst. It was suspected that the deactivation of the catalyst was due to the formation of highly stable palladium imidazolylidene complexes, but no direct evidence of this species was obtained. On the basis of this hypothesis, the use of pyridinium and 1,2,3-trialkylimidazolium salts was studied in an attempt to limit the formation of such species. It was found, particularly for the 1,2,3-trialkylimidazolium salts, that highly active and selective systems for the telomerization of butadiene with methanol were obtained. Furthermore, a biphasic catalytic system composed of palladium(II) acetate, TPPMS, heptane, and 1-butyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imidate, [BMMI][TF_2N], was used. In this case, after the telomerization reaction, the methoxyoctadiene products were recovered by simple decantation and the ionic liquid phase reintroduced to the reactor. In this way the catalyst was recycled four times (to total turnover number of 10 000) with little loss of activity.

Introduction

The catalytic dimerization of dienes under the concomitant addition of a nucleophilic reagent was reported simultaneously in 1967 by Smutny at Shell[1] and Takahashi[2−4] at Osaka University. The reaction is defined under the general term of telomerization as the dimerization of two conjugate diolefins (taxogen) together with the addition of a third molecule (telogen) over one double-bond equivalent (Scheme 1). Individual reports can be found in which various telogens have been used, for example, alcohols,[2,5−10] nitroalkanes,[11,12] hydrosilanes,[13] carboxylic acids,[14,15] amines,[16−19] and water,[20−23] leading to valuable functionalized octadienes with 100% atom economy. The subject of the telomerization of butadiene with those telogen agents has been reviewed.[24−27] A variety of metals have been shown to be active for telomerization including cobalt, rhodium, nickel, and platinum, but by far it is palladium-based systems that are superior in terms of both activity and selectivity.

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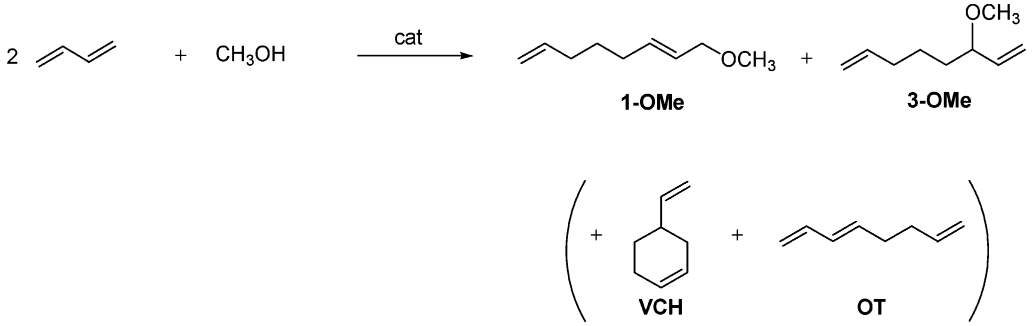
Scheme 1. Products Obtained by Telomerization of Butadiene with Methanol



The separation of the homogeneous catalyst from the products is a significant factor in the economics of the application of a catalytic reaction. It is now generally accepted that the use of two-phase catalytic systems is a logical approach that could overcome the separation problems by allowing the phase separation of the products from the catalyst phase.[16,17,28] Recently, nonaqueous ionic liquids have been attracting attention for the application of many homogeneous reactions to biphasic systems.[29−32] Those based on the imidazolium cation are largely the most widely investigated. In the palladium-catalyzed telomerization reaction, the catalytic cycle is thought to pass through a low coordination palladium(0) intermediate,[33] and so the general problem of catalyst separation is exacerbated by the formation of palladium black. In our laboratory, we have been studying reactions using imidazolium-based ionic liquid in palladium-mediated carbon−carbon bond formation reactions (e.g., dimerization of ethylene), and we observed that palladium can be stabilized somewhat by these solvents and that hydrocarbon products can be easily separated from the catalytically active solution.[34] It was thus interesting to try to adapt existing aqueous biphasic catalytic telomerization technology to ionic liquid media and thus perhaps solve some of the catalyst stability and leaching problems reported.

Telomerization of butadiene with methanol has been extensively investigated.[3,23,25] The reaction leads to the formation of *trans*- and *cis*-1-methoxy-2,7-octadiene and 3-methoxy-1,7-octadiene, with the butadiene dimers 1,3,7-octatriene and 4-vinylcyclohexene often detected as side products. In the period since we filed our patent for this reaction, Beller and co-workers have reported some extremely active catalytic systems for the telomerization of butadiene with methanol using palladium catalysts.[9,35] The systematic optimization of the conventional $Pd(OAc)_2/PPh_3$/base catalyst system leads eventually to very high catalyst productivity with turnover numbers in excess of 225 000. A much higher level of activity was obtained for bulky monocarbene palladium complexes, allowing astonishingly high levels of activity and productivity, even at 50 °C.[35]

The best basic catalytic system available at the time of this study was also derived from the work of Beller's group,[23] which we modified by the incorporation of room-temperature ionic liquids. It was found that the alkyl substituent pattern of the imidazolium cation was key to obtain active systems. A biphasic system was then developed. The results in this paper have previously been disclosed in a patent;[36] this reports serves to expand upon and explain in detail one part of the study behind the invention.

Results and Discussion

In a typical catalysis test, a stirred stainless steel autoclave was charged with a solution of the catalyst ($Pd(OAc)_2$ and phosphine) in methanol and any cosolvents (ionic liquids, eventually heptane). The desired mass of butadiene was transferred from a weighed lecture bottle. The reactor was then heated to the desired reaction temperature. After 3 h of reaction (or if the pressure in the reactor dropped suddenly), the autoclave was cooled to 40 °C and degassed to a volumetric glass cylinder cooled to −78 °C. The volume of the liquid condensed in the cylinder (determined to be almost pure butadiene) was noted. The autoclave was then warmed to room temperature. The remaining liquid phases in the autoclave were recovered, weighed, and further analyzed (GC, GC−MS, and NMR). Thus butadiene conversion was determined in two ways, from the volume of unreacted butadiene condensed in the graduated cylinder (abbreviated as conv A in the tables herein) and by the mass increase of the liquid solution in the autoclave (conv B). We will see that conversion A is very often higher than conversion B due to possible loss of butadiene during trapping. In the discussion, conversion values mentioned are an average of the two measured conversions.

In Table 1, some reactions using a classical homogeneous system were performed. The main goal of these experiments was to validate the procedure used for telomerization of butadiene with methanol and so have

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Table 1. Reference Experiments[a]

					selectivity determined by GC (mol %)					
run	ligand	time (h)	conv A	conv B	1-OMe + 3-OMe	VCH	OT	oligo	ratio 1/3	TON
1	TPP	0.75	98	96	90.3	4.6	4.3	0.8	5	2525
2	TPPMS	0.75	98	94	85.3		8.9	5.8	13	2581
3	TPPDS	3	33	28	49.2	2.6	13.1	35.1	12	797

[a] Reaction conditions: $Pd(OAc)_2$ = 30 mg (0.134 mmol); phosphine = 3 equiv/Pd; MeOH = 15 mL (370 mmol); C_4H_6 = 20 g (370 mmol); T = 85 °C. Abbreviations used are TPP = triphenylphosphine; TPPME = (*m*-sulfophenyl)diphenylphosphine sodium salt; TPPDS = bis(*p*-sulfophenyl)phenylphosphine dipotassium salt; 1-OMe = sum of all isomers of 1-methoxy-2,7-octadiene; 3-OMe = 3-methoxy-1,7-; VCH = vinylcyclohexene; OT = sum of 1,3,7-octatriene and 1,3,6-octatriene; ratio 1:3 = ratio of linear to branched telomerization product. Conversion A is defined as the difference between the mass of butadiene introduced and recovered divided by the mass of butadiene introduced. Conversion B is defined as the difference in the mass of the solution in the reactor between the introduction of catalysts, solvents, and methanol and the withdrawal of contents after degassing divided by the mass of butadiene introduced. The selectivity of a given product was the molar amount of the product divided by the total molar amount of all products. Turnover number is defined as the molar amount of butadiene converted (average of conversion A and B) divided by the molar amount of palladium used.

at our disposal references of catalytic activity and selectivity of the studied reaction performed in the lab apparatus.

First, one can see that we chose to use both neutral (triphenylphosphine, TPP) and charged phosphine (mono-, bis-, and tris-sulfonated triphenylphosphines, TPPMS, TPPDS, and TPPTS respectively). Triphenylphosphine is the common ligand used for the telomerization reaction.[23] Its sulfonated derivatives were also tested because their ionic character is potentially much more adapted to the ionic liquid than a neutral ligand.[19,37] The amount of phosphine (3 equiv/Pd) was determined in accordance with previous studies[23,38] and a short validation study within our lab.

Performances of the systems using TPP and TPPMS are very similar. Conversions reach 96% after 0.75 h of reaction. This represents a turnover number ([mol butadiene consumed]/[2 mol Pd introduced], TON) of around 2550 for a single batch run. Selectivities toward telomers were respectively 90.3% for TPP and 85.3% for TPPMS. At the end of each run, a single-phase, yellow medium without any trace of palladium black was recovered. For systems using TPPDS, conversion dramatically decreases: 31% in 3 h in this case. The low solubility of TPPDS in the reaction medium might explain the reaction rate decrease; that is, yellow particles were present in the reaction mixture. This phenomenon is exacerbated when the trisodium salt of tris(*m*-sulfophenyl)phosphine (TPPTS) is used because of its insolubility in methanol even at high temperature. Extensive formation of palladium black was observed by heating the mixture before the run. The latter system was thus not tested.

Also of some interest is the change in the regioselectivity of the reaction. In run 1, the 1-methoxy to 3-methoxy product ratio (ratio 1:3) was only 5, whereas in run 2, this ratio was much higher, 13. The recent report by Vollmüller and co-workers[23] explained in their study that higher concentrations of phosphines or butadiene lead to lower linear to branched product ratios. In their explanation of the effect, based on Jolly's mechanism,[33] the regioselectivity is determined in the step of nucleophilic attack on an allyl fragment of a C_8 allyl-olefin ligand and depends on the extent to which this intermediate is chelating through the olefin function. Chelation is thought to favor the linear product, and thus this hypothesis can be extrapolated to explain that a less coordinating ligand (TPPMS vs TPP) would be less able to open the C_8 allyl-olefin chelation, and thus would lead to more linear product.

The use of ionic liquid for two-phase catalysis represents a new approach for catalyst separation and recycling. Air- and moisture-stable room-temperature ionic liquids based on 1,3-dialkylimidazolium cation associated with organic or inorganic anions have attracted growing interest in the past few years.[31] Many catalytic reactions were performed in those media. Recent applications include Diels–Alder reactions,[39] olefin dimerization and oligomerization,[40] hydrogenation,[37] Heck reaction,[41] hydroformylation,[37] and epoxidation.[42,43] Our study was naturally first conducted using salts derived from this structure. The lab had at its disposal a number of such salts: 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imidate, $[EMI][TF_2N]$, 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imidate, $[BMI][TF_2N]$, 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMI][BF_4]$, 1-ethyl-3-methylimidazolium hexafluorophosphate $[EMI][PF_6]$, and 1-butyl-3-methylimidazolium hexafluorophosphate $[BMI][PF_6]$, and these were tested for the telomerization of butadiene with methanol. Results are summarized in Table 2.

Conversions were extremely low. There was, however, no obvious formation of palladium black: systems at the end of the reaction appear as homogeneous, quite colorless liquids. (Note that we did not otherwise test the solution for the presence of palladium clusters or nanoparticles.) The "palladium-phosphine" catalyst supposed to be formed in situ certainly suffered from some modifications and thus deactivation. The possible contamination by halide impurities was considered, as the synthesis of some of these ionic liquids is based on the use of chloride intermediates and it has been reported that chloride ions poison the telomerization reaction.[25] The halide contents of our solvents were always under the detection limit (250 ppm) in microanalysis measurements, which would be too little for total deactivation of the catalyst.

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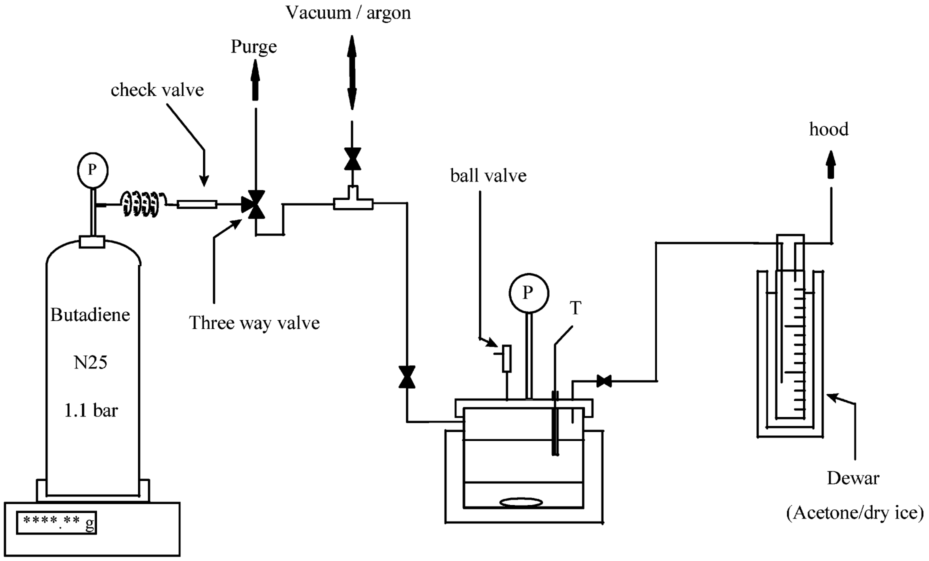


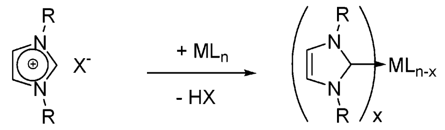
Figure 1. Apparatus used for telomerization of butadiene.

Table 2. Use of 1,3-Dialkylimidazolium Salts[a]

				selectivity determined by GC (mol %)					
run	ionic liquid	conv A	conv B	1-OMe + 3-OMe	VCH	OT	oligo	ratio **1**/**3**	TON
4	[BMI][TF$_2$N][b]	10	7	62.0	18.4	3.5	16.1	8	241
5	[EMI][TF$_2$N][b]	7	3	66.1	21.6	1.7	10.6	6	146
6	[EMI][TF$_2$N][c]	16	6	27.5	44.7	0.6	27.1	7	271
7	[BMI][BF$_4$][c]	15	−1	49.6	33.9	1.2	15.4	6	165
8	[EMI][PF$_6$][d]	13	2	38.0	49.8	8.2	4.0	7	184

[a] Reaction conditions: $Pd(OAc)_2$ = 30 mg (0.134 mmol); PPh_3 = 105 mg (0.400 mmol); MeOH = 15 mL (370 mmol); C_4H_6 = 20 g (370 mmol); T = 85 °C; t = 22 h. [b] 1 mL of ionic liquid. [c] 4 mL of ionic liquid. [d] Solid, 0.725 g. For explanation of abbreviations, see Table 1.

Scheme 2. Carbene Formation



In light of recent developments in the chemistry of imidazolium salts[41,44−47] it was considered that perhaps the inactivity of these systems was due to the reaction of the imidazolium cation with the palladium catalyst to form 1,3-dialkylimidazol-2-ylidene palladium complexes (Scheme 2). This proposition has been reinforced by the observation of Welton of the direct formation of such complexes from room-temperature ionic liquids.[45] Given the remarkable stability of the metal−imidazolylidene bond with respect to dissociation,[44] this type of reactivity, if present, would quickly lead to inactive polycarbene palladium complexes. Attempts were made to detect such species in used catalyst solutions or to generate them under similar conditions, but they have proven elusive.

Nevertheless, we wished to establish that catalyst deactivation was due to a stoichiometric reaction between the salt and palladium; thus a poisoning study was undertaken. In this series of experiments, the organic/aqueous control experiment (run 1 in Table 1) was compared to experiments run under the same conditions except that stoitciometric (with respect to palladium) amounts of the ionic liquid [BMI][TF$_2$N] were added to the solution (Figure 2). Note that the reaction was run in this case for 22 h rather than the 45 min required for completion in run 1. Catalyst activity was significantly degraded by the addition of even 1 equiv of [BMI][TF$_2$N], the reaction rate being dramatically slower (from 97% in 0.75 h to 92% in 22 h). Given Beller and co-workers' findings on the activity of the palladium carbene complex mentioned above,[35] one might expect *increased* activity for this test. One should note that in the previous study the ligand is the symmetric, bulky 1,3-dimesitylimidazol-2-ylidene carbene, and direct comparison with a putative 1-methyl-3-butylimidazol-2-ylidene complex is risky. Significantly, the Beller group showed that alkyl-substituted

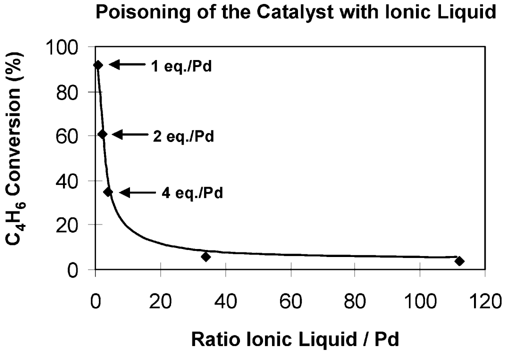


Figure 2. Poisoning of the catalyst by 1,3-dialkylimidazolium ionic liquids.

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Table 3. Study of Different Ionic Liquids[a]

run	ionic liquid	conv A	conv B	time (h)	selectivity determined by GC (mol %)				ratio **1**/**3**	TON
					1-OMe + 3-OMe	VCH	OT	oligo		
9	[EMI][TF$_2$N]	7	0	22	27.5	44.7	0.6	27.1	7	271
10	[BuPy][PF$_6$][b]	100	81	5	56.8	1.0	28.1	14.1	18	2403
11	[BMMI][BF$_4$]	100	92	1	81.8	0.2	15.1	2.9	8	2619
12	[BMMI][TF$_2$N]	100	89	1	84.0	0.2	13.7	2.1	9	2537

[a] Reaction conditions: Pd(OAc)$_2$ = 30 mg (0.134 mmol); PPh$_3$ = 105 mg (0.400 mmol); ionic liquid (4 mL); MeOH = 15 mL (370 mmol); C$_4$H$_6$ = 20 g (370 mmol); T = 85 °C. [a] Solid, 1.63 g. For explanation of abbreviations, see Table 1.

Table 4. Study of Common Phosphines[a]

run	P	time (h)	conv A	conv B	selectivity determined by GC (mol %)				ratio **1**/**3**	TON
					1-OMe + 3-OMe	VCH	OT	oligo		
13	TPP	1	100	89	84.0	0.2	13.7	2.1	9	2537
14	TPPMS	1	100	93	77.9	0.3	17.1	4.7	14	2769

[a] Reaction conditions: Pd(OAc)$_2$ = 30 mg (0.134 mmol); phosphine = 3 equiv/Pd; [BMMI][TF$_2$N] (4 mL); MeOH = 15 mL (370 mmol); C$_4$H$_6$ = 20 g (370 mmol); T = 85 °C. For explanation of abbreviations, see Table 1.

imidazol-2-ylidene monocarbene complexes were much less active and furthermore that that excess carbene ligand leads to deactivation.[48] What is clear in our case is that the deactivation of the system continues with the addition of further equivalents of salt, very quickly leading to completely inactive systems (Figure 2). We believe that this indicates a stoichiometric reactivity between 1,3-dialkylimidazolium salt and palladium, leading eventually to an inactive, soluble palladium form, perhaps a polycarbene species.

Given the problem of stoichiometric deactivation of the catalyst by the ionic liquid solvent, it was imperative to study different types of ionic liquids. A key hypothesis guiding this exploration was that the proton in the 2-position of the imidazolium cation (that is, the proton on the carbon between the nitrogen atoms) could be responsible for the deactivation. It is well known that this proton is labile, and if deprotonated, imidazolium salts produce a stable carbene which can form very stable, that is, inactive, palladium complexes. Two approaches were taken to avoid such reactivity. A radically different cation was used, in the form of the 1-butylpyridinium hexafluorophosphate ([BuPy][PF$_6$]) ionic liquid. Alternatively, modified imidazolium salts were studied in which acidic hydrogen in the 2-position was replaced by a methyl group, leading to the 1-butyl-2,3-dimethylimidazolium ionic liquids ([BMMI][BF$_4$] and [BMMI][TF$_2$N]). Results of these tests are summarized in Table 3.

For the pyridinium salt, the reaction was complete after 5 h, but selectivity toward telomers is not very high (56.8%). Thus, the activity of the system was reestablished, but formation of palladium black was observed together with increased selectivity for linear dimerization and oligomerization. This result can be explained by the transfer of an alkyl group from pyridinium to triphenylphosphine,[49,50] thus producing phosphonium salts, which cannot stabilize palladium(0), thus the appearance of palladium black. One should also note that the regioselectivity of the telomerization reaction has changed, the 1-OMe/3-OMe ratio of the telomerization products being 18 for the pyridinium salt.

The best results were found for the 1,2,3-trialkylimidazolium ionic liquids; conversions and reaction rates are perfectly comparable with the reference system without ionic liquid (Table 1). Quantitative conversions were achieved after 1 h for the two solvents [BMMI]-[TF$_2$N] and [BMMI][BF$_4$]. Selectivity toward telomers is around 83%, and there is a slight effect on the regioselectivity of the telomerization reaction. It seems that the nature of the anion of the salts, between the hydrophobic bis(triflyl)imidate and the hydrophilic tetrafluoroborate, does not induce any notable difference in terms of activity and selectivity. Furthermore, at the end of these reactions, absolutely no palladium black was observed. A two-phase liquid−liquid system remains in the case of 1,2,3-trialkylimidazolium salts. The lower phase corresponds to the ionic liquid, whereas the upper one is a mixture of products and unreacted methanol. The two phases are yellow in color to about the same degree, which indicates roughly that the catalyst is evenly distributed between the organic and the ionic liquid phases. This was confirmed by the titration of palladium in each phase. Around 56% of the initial palladium is present in the organic phase for run 12 (Table 3), for example.

This partition of palladium is undesirable if one wishes to easily separate catalyst from products. Sulfonated phosphines, TPPMS in particular, were studied as a possible solution[37] to the catalyst partitioning problem (Table 4). Surprisingly (and unfortunately), the use of TPPMS leads to a single-phase system at 96% conversion. Apparently, the TPPMS serves as a surfactant. Selectivity toward telomers is lower with TPPMS than with TPP, 77.9 versus 84.0. However with TPPMS the ratio 1-OMe/3-OMe is largely better, 14.

At the end of the TPPMS reaction, it was determined that the addition of 16% wt (10 mL) of heptane to the solution leads to a clean separation of an ionic liquid phase from the product/MeOH/heptane phase. To ensure a two-phase system throughout the reaction and simplify the entire process, this minimum amount of heptane necessary for phase separation at 100% conversion was added prior to reaction. Another step taken to ensure phase separation was the use of a strict 2:1 ratio of butadiene/methanol (in previous studies, an excess of methanol was used). Furthermore, several combinations of ligand/solvent were tried to probe the effect of

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Table 5. Phosphine Effect on the Partitioning of the Catalyst[a]

				selectivity determined by GC (mol %)						
run	P	conv A	conv B	1-OMe + 3-OMe	VCH	OT	oligo	ratio **1**/**3**	% Pd leaching	TON
15	TPP	82	71	53.3		40.6	6.1	14.6	14.2	2127
16	TPPMS	74	66	70.3	0.6	14.1	15.0	13.1	1.9	1816
17	TPPDS	56	51	58.6	1.2	17.5	22.8	15.0	1.8	1373

[a] Reaction conditions: $Pd(OAc)_2$ = 30 mg (0.134 mmol); phosphine = 3 equiv/Pd; [BMMI][TF_2N] (4 mL); MeOH = 7.5 mL (185 mmol); heptane = 10 mL; C_4H_6 = 20 g (370 mmol); t = 3 h; T = 85 °C. For explanation of abbreviations, see Table 1.

Table 6. Recycling of Ionic Liquid Phase[a]

			selectivity determined by GC (mol %)					
run	conv A	conv B	1-OMe + 3-OMe	VCH	OT	oligo	ratio **1**/**3**	TON
16	74	66	70.3	0.6	14.1	15.0	13.1	1816
18	82	73	72.2	0.5	13.2	14.2	12.4	3817
19	89	81	72.4	0.4	15.9	11.3	15.4	6066
20	80	68	75.6	0.5	16.2	7.7	16.3	7973
21	70	63	78.8	0.9	17.3	3.1	18.6	9682

[a] Reaction conditions: $Pd(OAc)_2$ = 30 mg (0.134 mmol); TPPMS = 146 mg (0.401 mmol); [BMMI][TF_2N] (4 mL); MeOH = 7.5 mL (185 mmol); heptane = 10 mL; C_4H_6 = 20 g (370 mmol); T = 85 °C; t = 3 h. For explanation of abbreviations, see Table 1.

varying solubilities on performance. Experiments performed with this objective are summarized in Table 5.

In general, the systems were less active. This could be due, in part, to phase transfer limitations which would accompany the isolation of palladium in an ionic liquid phase. A certain limit on activity is also the depletion of methanol at high conversion. Table 5 summarizes the test of three common phosphines. Surprisingly, very different results were obtained with TPP and TPPMS. In these two cases, conversions are comparable, but for TPP, selectivity toward telomers falls to only 53.3%. This result can be linked to the partial solubility of the Pd/TPP catalyst in heptane, in which a lower concentration of methanol is observed, forming a large amount of dimers. As expected, the use of heptane as cosolvent yields at the end of the reaction a perfect two-phase system with a yellow lower phase and a totally colorless higher phase. In the cases report in Table 5, titration of the palladium in each phase was realized. With TPP, 14.2% of the initial palladium is present in the organic phase, whereas with TPPMS and TPPDS palladium leaching is respectively 1.9% and 1.8%. TPPMS performs better than TPPDS perhaps because its ligand is more soluble in the ionic liquid phase.

The question must logically concern the recycling of this catalytic system (Table 6). At the end of run 16 (Pd($OAc)_2$/TPPMS/heptane/methanol/butadiene) product phase was decanted and the palladium contained in the ionic liquid phase was reintroduced to the reactor with fresh reactants and cosolvent (runs 18−21).

Slight changes in activity were observed with each cycle. At first, activities are actually higher (runs 16, 18, and 19) perhaps as the initiation reactions (conversion of $Pd(OAc)_2$ to the active species) reach completion. Recall that no amine is added to facilitate the formation of the Pd(0) active species, which is described as an important factor in some reports.[23] Then, activity slowly degrades in runs 20 and 21, in part perhaps due to the mechanical difficulty of quantitatively recuperating the ionic liquid phase (drops of the liquid can remain in the Schlenck tube used for decantation and/or the syringe), palladium leaching (microanalysis of the organic phase at the end of each run indicates 1−4% leaching of palladium to the organic phase), or some palladium deactivation. In no case was there obvious evidence for the formation of palladium black.

Finally, preliminary reactions have probed the effect of palladium concentration and of reaction temperature on system performance, but no full study of the optimization of reaction parameters (which would also include lower temperatures, methanol/butadiene ratio, and palladium/ligand ratio) has yet been undertaken (Table 7).

The only clear conclusion of the dilution study was that the reaction seems to be roughly first-order in palladium. We also observed that the presence of ionic liquid does not permit stabilization of palladium catalyst at temperatures higher than 85 °C (a lot of palladium black in the reaction mixture is formed at 110 °C). A very recent publication of Beller, in which optimization of C_4H_6/MeOH is described with $Pd(OAc)_2/PPh_3$ catalyst, gives us food for thought that performances of our system with ionic liquids could be greatly improved, notably in terms of selectivity (by decreasing temperatures to 50 °C for example).[23] Optimization of reaction conditions will be further investigated in the laboratory.

Conclusion

In this work, the telomerization of butadiene with methanol was investigated. The existence of a reactivity between the palladium catalyst and 1,3-dialkylimidazolium ionic liquids has been demonstrated. The putative formation of a “carbene-Pd” complex was evoked to explain inactivity of systems using this kind of ionic liquids. Taking into account this reactivity, we have developed other kinds of ionic liquids in which the “carbene-Pd” formation became unlikely. By using [BMMI][TF_2N] and [BMMI][BF_4], active systems were obtained, although activities were generally inferior to

Table 7. Influence of Reaction Parameters[a]

						selectivity determined by GC (mol %)					
run	$Pd(OAc)_2$ (mmol)	temp (°C)	time (h)	conv A	conv B	1-OMe + 3-OMe	VCH	OT	oligo	ratio **1**/**3**	TON
14	0.134	85	1	100	93	77.9	0.3	17.1	4.7	13.7	2769
22	0.028	85	5.75	85	80	77.7	0.8	20.9	0.6	16.0	11092
23	0.025	110	5.75	89	75	50.4	3.0	41.8	4.8	11.7	11953

[a] Reaction conditions: TPPMS = 3 equiv/Pd; [BMMI][TF_2N] (4 mL); MeOH = 15 mL (370 mmol); C_4H_6 = 20 g (370 mmol). For explanation of abbreviations, see Table 1.

systems not containing ionic liquid cosolvents. To transpose this homogeneous system to a biphasic one, addition of cosolvent like heptane was necessary. A reasonably performing biphasic system in which the catalyst was immobilized in the ionic liquid phase was obtained, whereas the products were recovered in the organic phase. The catalytic phase was recycled by simple decantation, with each cycle yielding very little modification of performances. (Note that for the time being the system has not at all been optimized: different cosolvent combinations, different phosphine ligands, and other reaction parameters that may affect mass transfer and catalyst stability could well lead to much better performing systems with less leaching.) On the fringe of this study, we have also demonstrated the interest of using monosulfonated phosphine TPPMS instead of neutral TPP to stabilize the Pd(0) complex in the reaction mixture. This phosphine increases considerably the selectivity toward the linear telomer and permits through its ionic character a better retention of the palladium in the ionic liquid phase.

Experimental Section

Syntheses. All the syntheses were carried out under dry argon using standard Schlenck techniques. Dichloromethane was distilled from the appropriate drying agent: P_2O_5. It was then stored over 3 Å molecular sieves under argon. Water used in all experiments was deionized and degassed by freeze-pumping and bubbling of argon. All other reagents (1,2-dimethylimidazole, pyridine, HPF_6, etc.) were purchased from Aldrich and used as is unless otherwise indicated. Classical neutral alumina for further chromatography was used for purification of salts when necessary (if, for example, the product has significant color).

Proton and carbon NMR were recorded on a Bruker AC 300 MHz using CD_2Cl_2 (from SDS) as solvent and $SiMe_4$ (from Aldrich) as internal standard. Elemental analyses and free halide content of the salts were performed by the Central Analysis Service of the CNRS at Solaize. Melting points of solid salts were measured on a digital apparatus from Electrothermal.

The ionic liquids [EMI][TF_2N],[51] [BMI][PF_6],[52] [BMI][TF_2N],[51] and [BMI][BF_4][52] were synthesized as described in the literature. [EMI][PF_6] was obtained from Aldrich and was used as received. The syntheses of other salts are derived from general protocols described by Bonhôte.[51] Ionic liquids were systematically dried by heating under vacuum at 60 °C for 4 h. Water content was controlled by Karl-Fischer titration. The ionic liquids were systematically controlled for halide impurities by elemental analysis and in some cases by electrochemical means.

1-Butyl-2,3-dimethylimidazolium Chloride [BMMI][Cl]. Freshly distilled 1-chlorobutane (88 g, 0.96 mol) was added in one portion to a 500 mL thick walled glass reactor equipped with a magnetic stirrer containing 1,2-dimethylimidazole (65 g, 0.68 mol). The reactor was sealed, and the solution was stirred for 16 h at 100 °C (note: the reaction pressure was in excess of 2 atm). The reactor was degassed, and the hot solution was transferred (under argon) in a round-bottom flask containing acetonitrile (95 mL). The solution was added dropwise under vigorous stirring to toluene (500 mL). A precipitate formed and was filtered, washed with toluene (3 × 100 mL), and dried overnight under vacuum. [BMMI][Cl] was obtained (89.73 g, 70% yield) as a white hygroscopic solid. ^{1}H NMR (CD_2Cl_2): δ 0.97 [t, $J = 7.15$ Hz, $\mathrm{NCH_2CH_2CH_2C}H_3$]; 1.39 [sext, $J = 7.5$ Hz, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$]; 1.80 [quint, $J = 7.4$ Hz, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$]; 2.75 [s,$\mathrm{CC}H_3$]; 4.00 [s, $\mathrm{NC}H_3$]; 4.19 [t, $J = 7.1$ Hz, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$]; 7.52 [s, $\mathrm{C}H$]; 7.84 [s, $\mathrm{C}H$]. ^{13}C NMR (CD_2Cl_2): δ 10.70 [$\mathrm{NCH_2CH_2CH_2}C\mathrm{H_3}$]; 13.74 [$\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$]; 19.96 [$\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$]; 32.26 [$C\mathrm{CH_3}$]; 36.09 [$\mathrm{N}C\mathrm{H_3}$]; 48.94 [$\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$]; 121.72 [$C\mathrm{H}$]; 123.64 [$C\mathrm{H}$]; 144.03 [$C\mathrm{CH_3}$]. Anal. Calcd: C 57.14 (57.29), H 9.08 (9.08), N 14.85 (14.85). Mp = 104−105 °C.

1-Butyl-2,3-dimethylimidazolium Bis((trifluoromethyl)sulfonyl)imidate [BMMI][TF_2N]. A solution of lithium bis((trifluoromethyl)sulfonyl)imidate (41.9 g, 0.149 mol) in 100 mL of H_2O was added dropwise to a solution of [BMMI][Cl] (24.32 g, 0.129 mol) in 150 mL of H_2O. The solution was stirred at 70 °C for 2 h and then cooled to room temperature. Methylene dichloride (50 mL) was added, and all was transferred to a separatory funnel. The lower phase (ionic liquid + CH_2Cl_2) was collected. Ionic liquid was purified through a short alumina column, and the CH_2Cl_2 removed on a Rotavapor. The resultant hydrophobic liquid was washed three times with 150 mL of H_2O and dried for 3 h at 50 °C under vacuum to afford [BMMI][TF_2N] (44.1 g, 78.9% yield) as a colorless liquid. ^{1}H NMR (CD_2Cl_2): δ 0.97 [t, $J = 7.15$ Hz, $\mathrm{NCH_2CH_2CH_2C}H_3$]; 1.37 [sext, $J = 7.5$ Hz, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$]; 1.78 [quint, $J = 7.4$ Hz, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$]; 2.59 [s, $\mathrm{CC}H_3$]; 3.79 [s, $\mathrm{NC}H_3$]; 4.04 [t, $J = 7.1$ Hz, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$]; 7.19 [s, $\mathrm{C}H$]; 7.21 [s, $\mathrm{C}H$]. ^{13}C NMR (CD_2Cl_2): δ 9.78 [$\mathrm{NCH_2CH_2CH_2}C\mathrm{H_3}$]; 13.53 [$\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$]; 19.86 [$\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$]; 31.90 [$C\mathrm{CH_3}$]; 35.60 [$\mathrm{N}C\mathrm{H_3}$]; 49.00 [$\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$]; 121.37 [$C\mathrm{H}$]; 122.91 [$C\mathrm{H}$]; 144.21 [$C\mathrm{CH_3}$]; 120.50 [q, $J_{\mathrm{C-F}} = 321.4$ Hz, $(C\mathrm{F_3SO_2})_2\mathrm{N}$]. Anal. Calcd: C 30.68 (30.49), H 3.96 (3.95), N = 9.66 (9.70), Cl < 250 ppm (0).

1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate [BMMI][BF_4]. The procedure previously described for the synthesis of [BMMI][TF_2N] was used (except the washes with water). From 22.23 g (0.118 mol) of [BMMI][Cl] and 15.52 g (0.141 mol) of sodium tetrafluoroborate was obtained 25.33 g (90% yield) of [BMMI][BF_4] as a colorless, very viscous and hydrophilic liquid. ^{1}H NMR (CD_2Cl_2): δ 0.96 [t, $J = 7.15$ Hz, $\mathrm{NCH_2CH_2CH_2C}H_3$]; 1.38 [sext, $J = 7.5$ Hz, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$]; 1.78 [quint, $J = 7.4$ Hz, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$]; 2.60 [s, $\mathrm{CC}H_3$]; 3.80 [s, $\mathrm{NC}H_3$]; 4.06 [t, $J = 7.1$ Hz, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$]; 7.25 [dd, $\mathrm{C}H$]; 7.30 [dd, $\mathrm{C}H$]. ^{13}C NMR (CD_2Cl_2): δ 9.58 [$\mathrm{NCH_2CH_2CH_2}\boldsymbol{C}\mathrm{H_3}$]; 13.61 [$\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$]; 19.79 [$\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$]; 31.94 [$C\mathrm{CH_3}$]; 35.36 [$\mathrm{N}C\mathrm{H_3}$]; 48.70 [$\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$]; 121.30 [$C\mathrm{H}$]; 122.88 [$C\mathrm{H}$]; 144.31 [$C\mathrm{CH_3}$]. Anal. Calcd: C 45.09 (45.03), H 7.25 (7.14), N 11.52 (11.67), Cl 0.11 (0).

1-Butylpyridinium Chloride [BuPy][Cl]. The procedure previously described for the synthesis of [BMMI][Cl] was used. From 48.9 g (0.618 mol) of pyridine and 57.4 g (0.62 mol) of 1-chlorobutane, [BuPy][Cl] (85.4 g, 80.5% yield) was obtained as a white solid. ^{1}H NMR (CD_2Cl_2): δ 0.97 [t, $J = 7.4$ Hz, $\mathrm{NCH_2CH_2CH_2C}H_3$]; 1.42 [sext, $J = 7.5$ Hz, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$]; 2.04 [quint, $J = 7.6$ Hz, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$]; 5.06 [t, $J = 7.4$ Hz, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$]; 8.14 [t, $J = 7.2$ Hz, 2 $\mathrm{C}H_{\mathrm{ar}}$]; 8.51 [t, $J = 7.7$ Hz, $1\mathrm{C}H_{\mathrm{ar}}$]; 9.76 [d, $J = 5.5$ Hz, $2\mathrm{NC}H_{\mathrm{ar}}$]. ^{13}C NMR ($CD_2Cl_2$): δ 13.62 [$\mathrm{NCH_2CH_2CH_2}C\mathrm{H_3}$]; 19.46 [$\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$]; 34.13 [$\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$]; 61.21 [$\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$]; 128.53 [$2C\mathrm{H_{ar}}$]; 145.48 [$1C\mathrm{H_{ar}}$]; 145.87 [$2\mathrm{N}C\mathrm{H_{ar}}$]. Anal. Calcd: C 59.47 (62.97), H 8.62 (8.22), N 7.91 (8.16). Mp = 137−138 °C.

1-Butylpyridinium Hexafluorophosphate [BuPy][PF_6]. A solution of hexafluorophosphoric acid (60 wt % in water) (10 cm^3) was added dropwise to a solution of [BuPy][Cl] (5.77 g, 33.6 mmol) in 100 mL of distilled water. The solution was stirred at room temperature for 1 h. The white precipitate formed was filtered off, washed several times with 50 mL of H_2O, and dried overnight at room temperature under vacuum to afford [BuPy][PF_6] (4.45 g, 47.1% yield) as a white solid. ^{1}H NMR (CD_2Cl_2): δ 0.99 [t, $J = 7.4$ Hz, $\mathrm{NCH_2CH_2CH_2C}H_3$]; 1.41 [sex, $J = 7.5$ Hz, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$]; 2.01 [quint, $J = 7.6$ Hz,

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$NCH_2C\mathit{H}_2CH_2CH_3$]; 4.58 [t, $J = 7.4$ Hz, $NC\mathit{H}_2CH_2CH_2CH_3$]; 8.08 [t, $J = 6.9$ Hz, 2 $C\mathit{H}_{ar}$]; 8.51 [t, $J = 7.7$ Hz, 1$C\mathit{H}_{ar}$]; 8.68 [d, $J = 5.5$ Hz, 2$NC\mathit{H}_{ar}$]. ^{13}C NMR (CD_2Cl_2): δ 13.38 [$NCH_2CH_2CH_2\mathit{C}H_3$]; 19.58 [$NCH_2CH_2\boldsymbol{C}H_2CH_3$]; 33.56 [$NCH_2\mathit{C}H_2CH_2CH_3$]; 62.81 [$N\mathit{C}H_2CH_2CH_2CH_3$]; 129.06 [2 $\mathit{C}H_{ar}$]; 144.34 [1 $\mathit{C}H_{ar}$]; 146.05 [2 $N\mathit{C}H_{ar}$]; Anal. (Calcd): C 38.70 (38.44), H 5.09 (5.02), N 5.06 (4.98). Mp = 78−79 °C.

Catalysis. Palladium(II) acetate (98%) was purchased from Strem Chemicals, stored under argon, and used without further purification. Triphenylphosphine (TPP) was obtained from Aldrich, dipotassium bis(*p*-sulfonatophenyl)phenylphosphine dihydrate (TPPDS) from Strem Chemical, and sodium diphenylphosphinobenzene-3-sulfonate (TPPMS) from TCI. Trisodium tris((*m*-sulfonatophenyl)phosphine) (TPPTS) was synthesized by the Hoechst method and obtained as a mixture with a 4% phosphine oxide impurity.[53] All phosphines were stored under argon and used as is. Methanol was dried by refluxing over Mg/I_2 and stored over 3 Å molecular sieves. Heptane was distilled over Na/K and stored over 3 Å molecular sieves under argon. Butadiene (N25) was obtained from Air-Liquide and used without further purification

All catalytic reactions were performed in a 100 mL magnetically stirred stainless steel autoclave equipped with an inner glass sleeve and an internal thermocouple under argon atmosphere (Figure 1). In a typical reaction, $Pd(OAc)_2$, phosphine, ionic liquid, methanol, and eventually heptane were introduced in a Schlenck and then transferred into the purged autoclave via a ball valve. The autoclave was cooled to below −10 °C, and the desired mass of butadiene was transferred from a lecture bottle resting on a scale. The reactor was then heated to the desired reaction temperature. After the selected reaction time, the autoclave was cooled to 40 °C and butadiene was condensed in a volumetric glass cylinder cooled to −78 °C. The volume of the liquid condensed in the cylinder (determined to be nearly pure butadiene) was noted. The autoclave was then warmed to room temperature. The remaining liquid phases in the autoclave were recovered, weighed, and further analyzed (GC, GC−MS, and NMR).

Thus we have two measures of butadiene conversion: from the volume of unreacted butadiene condensed in the graduated cylinder (conv A) and the mass increase of the liquid solution in the autoclave (conv B). We will see that conversion A is very often higher than conversion B due to possible loss of butadiene during trapping.

When at the end of a run only a single liquid phase was present, a sample was analyzed without further treatment. When multiple phases were present, only the upper phase was analyzed for product. Where distinct phases were present, the palladium content of each was determined by elemental analysis.

The identification of the telomerization products was carried out by both Hewlett-Packard GC−MS and NMR analyses. Finally they were quantitatively analyzed by gas chromatography on a HP6890 chromatograph equipped with FID detector and a HP1 column ($L = 30$ m, $\phi_{int} = 0.32$ mm, film thickness = 0.25 μm). Injector temperature was 170 °C, and detector temperature was 180 °C. The temperature program was from 60 °C (3 min) to 100 °C (0 min) at a heating rate of 10 °C/min to 220 °C (30 min) at a heating rate of 5 °C/min.

In a typical sample, 500 mg of reaction mixture and 150 mg of tetradecane (internal standard) were introduced in 2 mL of tetrahydrofuran. The relative response factors of those different products were determined from pure samples when possible. When products were not commercial, they were isolated from the reaction mixture by distillation. From those relative response factors and the mass of the organic phase at the end of the reaction, the mass of each product was determined.

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