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Palladium catalyzed cycloisomerization of 2,2-diallylmalonates in imidazolium ionic liquids

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Abstract

A series of palladium salts and complexes, including $PdCl_2$, $PdCl_2/AgPF_6$, $PdCl_2(PhCN)_2$, $PdBr_2$ and $Pd_2(dba)_3$ were used in imidazolium ionic liquids as catalysts for the cycloisomerization of diethyl 2,2-diallylmalonate. The order of reactivity follows the expected Pd atom hardness and, therefore, "naked" Pd^{2+} generated from $PdCl_2 + AgPF_6$ gives the highest turnover frequencies. The system comprising Pd species dissolved in ionic liquid can be reused with minor decrease in conversion, but with an apparent variation in the product distribution. The latter comes from a diminished catalytic activity and from formation of Brönsted acid sites. Finally, by using 1,10-undecadiene derivative we have observed that this Lewis acid induced cycloisomerization is specific for the formation of five-member rings.

Keywords: Ionic liquids; Recoverable and reusable catalyst; Palladium catalyst; Cycloisomerization

1. Introduction

Ionic liquids have been widely used as a medium in which homogeneous catalysts can be separated from the reaction products and the system reused in consecutive runs [1–6]. The necessary pre-requisite in order to develop a reusable homogeneous catalytic system is that the reaction products should be isolable while the catalyst should remain in the ionic liquid during the recovery of the reaction products.

This pre-requisite is fulfilled in many catalytic processes based on ionic liquids in where metal halides are used as Lewis acids and the reaction products are soluble in hexane or diethyl ether. In the present work, we report the use of palladium halides and complexes dissolved in *N*-butyl-*N*′-methylimidazolium (bmim) ionic liquid as a homogeneous and reusable catalytic system for the cycloisomerization of 1,6-heptadiene derivatives.

Palladium cycloisomerization of heptadienes is an important reaction from the synthetic point of view [7–11]. In addition, it is closely related to the ruthenium catalyzed ring closure metathesis, the difference being in that the ruthenium catalysis leads to a cyclopentene product in where the C=C double bond is located in a precise position and the two terminal carbon atoms of the heptadiene are cleaved in the process. In contrast, all the carbon atoms of the starting material are present in the product using palladium complexes as catalysts, while the reaction mixture contains a distribution of cyclopentene isomers differing in the position of the C=C double bond.

Working with $bmimPF_6$ ionic liquid we have found that this cycloisomerization is efficiently promoted by palladium Lewis acid sites, typical Brönsted acids being inefficient as cycloisomerization catalyst. Also, the catalytic activity of the palladium atoms depends on the

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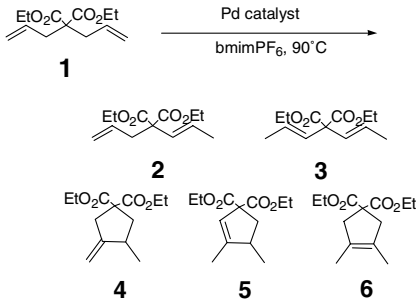
softness–hardness of the complex, hard Lewis acid Pd^{2+} ions being more active than soft Lewis palladium complexes.

2. Results and discussion

For the cycloisomerization reactions we have selected a series of palladium salts and complexes in which we have varied the metal oxidation state and the nature ligands. The actual palladium catalysts are listed in Table 1. One previous point to be considered is that not all the palladium salts were completely soluble in $bmimPF_6$ at room temperature. Elemental analysis of palladium in $bmimPF_6$ saturated with the palladium salt at 90 °C shows that $Pd_2(dba)_3$, $PdBr_2$ and $PdCl_2$ exhibit similar solubility and it was considerably smaller than that of the $PdCl_2(PhCN)_2$ complex (see Section 3 for values).

The catalytic diallylmalonate cycloiosomerization was carried out in palladium-saturated $bmimPF_6$ and the catalytic activity interpreted considering exclusively the amount of catalyst dissolved. In order to compare the catalyst efficiency, the turnover frequency (TOF) rather than the yield at the final reaction time was the figure of merit. The TOF was defined as the initial reaction rate divided by the amount of palladium atoms present in the solution dissolved in the ionic liquid. This definition assumes that solid undissolved palladium salt would not contribute to the catalysis that would be exclusively due to dissolved palladium species. The products observed are indicated in Eq. (1) and the final yields are summarized in Table 1. Although colloidal palladium particles arising from the undissolved palladium salt could contribute to the final yield at long reaction times, the use of TOF values based on the initial reaction rate as parameter to compare the catalyst efficiency practically exclude the influence of nanoparticles that could be formed after prolonged reaction times.



(1)

In agreement with earlier literature reports [10], in where the cycloisomerization was carried out in toluene, treatment of diallylmalonate **1** in $bmimPF_6$ using $PdCl_2(PhCN)_2$ as catalyst leads to a complex mixture in where two types of products were formed. One type corresponds to acyclic malonate isomers in where one or two of the C–C double bond have undergone a migration from the terminal to the internal position of the allylic moieties of **1**, as well as acyclic compounds arising from ester hydrolysis. Together with these products, the second type of compounds corresponds to the terminal alkene **4** and to the isomeric cyclopentenes **5** and **6**, in where the endocyclic C–C double bond is tri- or tetra-substituted. Table 1 shows the results of the catalytic reactions and the resulting product distribution. For the sake of comparison we have also reacted 2,2-diallylmalonate with a conventional Brönsted acid and with $AgPF_6$. In the case of triflic acid, the predominant compounds correspond to acyclic malonate isomers, with only low amount of cyclopentenes. This behavior is in agreement with early precedents that have reported that Brönsted acids mostly catalyzed C–C double bonds isomerizations and ester hydrolysis without promoting cycloisomerization [12]. In the case considered here the relative high conversion achieved with triflic acid in ionic liquid has allowed us to detect the formation of lesser quantities of cyclopentenes. On the other hand, $AgPF_6$ is also very inefficient to catalyze the formation of cyclopentenes. However, in accordance with the Lewis nature of $AgPF_6$, its activity towards cycloisomerization is higher than that of triflic acid. In contrast

Table 1
Results for the cycloisomerization of diethyl 2,2-diallylmalonate (60.5 μl, 0.25 mmol) in *N*-butyl-*N*′-methylimidazolium hexafluorophosphate (500 mg) at 90 °C for 24 h using different acid catalysts (0.025 mmol, 10 mol%)

Catalyst	Pd dissolved (mmol × 10^3)	Conversion (%)	**2** + **3** (%)	**4** (%)	**5** (%)	**6** (%)	TOF[a]
No catalyst	–	<1	–	–	–	–	–
Triflic acid	–	48	31	3	3	11	4[b]
$AgPF_6$	–	79	48	–	4	27	–
$PdCl_2 + AgPF_6$	1.0	100	–	–	6	94	365.0
$PdCl_2$	3.8	100	–	–	21	79	29.4
$PdBr_2$	2.8	100	2	–	9	89	28.6
$PdCl_2(PhCN)_2$	19.8	100	–	–	7	93	15.6
Pd_2dba_3	2.1	94	34	–	7	53	1.8

[a] (mol isomer **6**) × (mol soluble Pd × h)$^{-1}$.
[b] (mol isomer **6**) × (mol triflic acid × h)$^{-1}$.

to triflic acid and $AgPF_6$, all the palladium catalysts, except $Pd_2(dba)_3$, exhibit high activity for the C–C bond formation leading to cyclopentenes. One way to rank the catalyst activity for the most active palladium halides that give essentially 100% conversion and almost complete selectivity towards cyclopentenes is to follow the course of the reaction and determine the TOF values in each case. Fig. 1 shows the time-conversion plot for four palladium catalysts that exhibit high conversion and selectivity. Each data point of these plots corresponds to an independent run that has been stopped at the appropriate time and fully analyzed.

In this way the TOF values show that the most active catalyst is $PdCl_2$ followed by $PdBr_2$ and $PdCl_2(PhCN)_2$. These values can be rationalized considering that the harder the palladium atom, the more active the catalyst is. It has been demonstrated [12] using a series of palladium catalyst adsorbed in zeolites in where the softness–hardness of the framework has been varied systematically that hard palladium Lewis acid sites are more active than soft Lewis acid sites. In our case $PdCl_2$ will be the hardest catalyst of the series followed by $PdBr_2$ and this order matches with the catalytic activity. The presence of benzonitrile as ligand or the change in the oxidation state from +2 to 0 should increase the softness of the palladium metal by giving it some extra electron density from the ligands. According to this rationalization, addition of $AgPF_6$ to $PdCl_2$ should increase further the hardness of the palladium by precipitating AgCl and giving Pd^{2+} as "naked" cation. Pd^{2+} should be even more active than the previous halides. In agreement with the order of hardness, Table 1 shows that the presence of $AgPF_6$ has a remarkable beneficial influence in the catalytic activity of $PdCl_2$.

Recovery of palladium complexes dissolved in $bmimPF_6$ and isolation from the reaction products was simply achieved by liquid–liquid extraction using hexane as solvent. The resulting bmim ionic liquid was submitted to a series of reuses. $PdCl_2(PhCN)_2$ was selected for this study given the complete solubility of this palladium complex in $bmimPF_6$. A productivity higher than 50 mol of converted diallyl malonate per mol of palladium was obtained with this simple catalytic system based on imidazolium ionic liquids. As indicated in Eq. (1), the presence of by-products arising from C=C isomerization were also observed in minor amounts upon reuse. The results are summarized in Table 2.

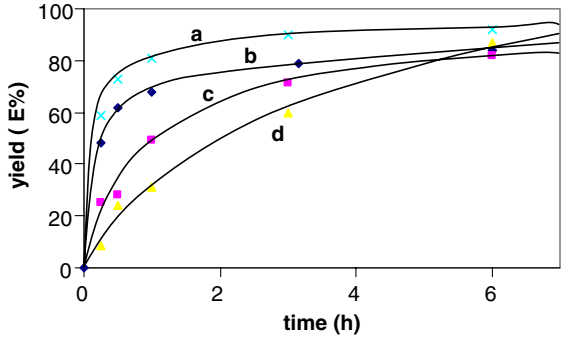


Fig. 1. Time-conversion plot for the cycloisomerization of diethyl 2,2-diallylmalonate (60.5 μl, 0.25 mmol) in *N*-butyl-*N*′-methylimidazolium hexafluorophosphate (500 mg) at 90 °C using as palladium catalysts (0.025 mmol, 10 mol%): (a) $PdCl_2 + AgPF_6$, (b) $PdCl_2(PhCN)_2$, (c) $PdCl_2$ and (d) $PdBr_2$. Each data point was obtained by an independent run stopped at the required time. Some of the catalysts were only partly solved.

Two features of the reusability data deserve some comment. The first one is the variation in the product distribution. The predominant product in the first three reuses is the corresponding tetra-substituted cyclopentene **6**, whose proportion is decreasing upon reuse while the tri-substituted cyclopentene **5** experiences a concomitant increase. Giving that the tetra-substituted cyclopentene exhibits, according to the time-conversion plots, a character of primary and secondary stable product, the changes upon reusing appear to point to a decrease in the catalytic activity for the secondary process interconverting cyclopentene **5** into cyclopentene **6**. However, the primary process in where cyclopentenes are formed directly from the starting material diallyl malonate seems to work equally well upon reuse considering that there is nor a drop in the reaction conversion neither in the combined **5** + **6** selectivity in those runs 1–4 in where the **5**-to-**6** proportion varies.

The second feature from Table 2, over imposed to the product distribution variation, is a drop in the conversion of the starting material. This drop seems not to be related with the decomposition of the palladium complex, since the addition of benzonitrile does not result in any conversion increase. PhCN, whose origin is $PdCl_2(PhCN)_2$, is observed as free ligand in the reaction mixture and addition of extra amounts of PhCN should shift the equilibrium towards $PdCl_2(PhCN)_2$. Most probably the decrease in the conversion of malonate **1** is due to a loss of the catalyst activity arising in part from the depletion in the concentration of palladium catalyst on the ionic liquid. The loss of Pd upon reuse was confirmed by chemical analysis after the fifth reuse, that shows a diminution of about 13% of the initial palladium amount present in the fresh bmim solution. On the other hand, the appearance of detectable amounts of acyclic isomers of diallyl malonate seems to point the generation of adventitious Brönsted acid sites upon reusing of ionic liquid. Acyclic isomers of the diallylmalonate **1** in where one or two of the C–C double bond has migrated from the terminal to the internal position are not observed in the presence of active palladium Lewis acids, in where cyclization is the only process observed. In contrast, Brönsted acids tend to form significant amounts of acyclic isomers **2** and **3**. These Brönsted acids can be generated from the Lewis acid sites by hydrolysis in the presence of water or alternatively from

Table 2
Reuses for the cycloisomerization of diethyl 2,2-diallylmalonate (121 μl, 0.5 mmol) in bmimPF_6 (1 g) at 90 °C using $PdCl_2(PhCN)_2$ (19.2 mg, 0.05 mmol, 10 mol%) as catalyst

	Time (h)	Conversion[a] (%)	**2** (%)	**3** (%)	**4** (%)	**5** (%)	**6** (%)
1 use	23	100	–	–	–	11	88
2 use	23.5	100	–	–	–	30	70
3 use	23.5	100	–	–	–	43	57
4 use	23	97	2	–	–	58	37
4 use (+ 1 equiv. PhCN)	23	93	3	–	–	58	32
5 use	23	77	4	<1	<1	56	17

Palladium analysis from the extracts: 12.6 % leached from the original.
[a] Mass balance: ca. 80–100%. Non-ionic liquid detected in the extract (by ^{1}H NMR).

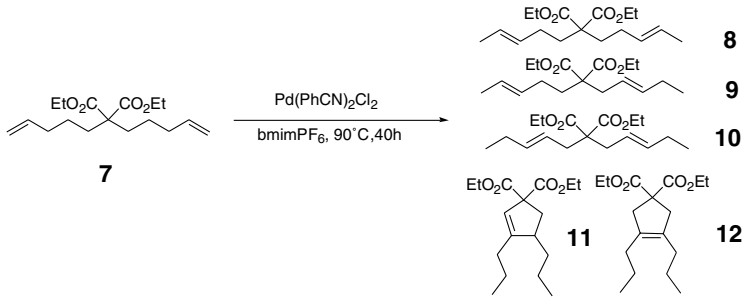
PF_6 by hydrolysis and formation of hydrofluoric acid and phosphate [13].

One of the differences between ruthenium-catalyzed ring closure metathesis and palladium-catalyzed cycloisomerization is that the former had shown applicability to form macrocycles. Here we wanted to determine the applicability of the palladium catalyst dissolved in ionic liquid to promote the cyclization of starting dienic compounds others than 1,6-heptadienes with the hope that larger carbocycles could also be formed. For this reason, we studied the reaction of diethyl 2,2-di-(4-pentenyl) malonate. Scheme 1 shows the structure of the characterized reaction products. From this product distribution it becomes clear that, in contrast to Ru-catalyzed reactions, large ring cycloalkanes are absent from the reaction products. The products observed are indicated in Scheme 1. The mol percentage was (8 + 9 + 10):(11 + 12) 50:50. This product distribution can be rationalized assuming that palladium is able to promote specifically cyclization to five-membered rings, but not to larger size cycloalkanes. The formation of five-membered rings requires the location of the C=C double bonds in relative 1,6-positions. When no cyclization is possible, C=C double bond isomerization along the pentyl chain starts to occur until the appropriate position to form cyclopentenes is achieved.

In conclusion, palladium salts and complexes can be dissolved in imidazolium ionic liquids in a sufficiently large extent to promote the cycloisomerization of 1,6-heptadienes. The system can be reused maintaining high conversions but with significant variation in the product distribution, that arises from a decrease of catalytic activity, depletion of the palladium concentration and influence of generated Brönsted acids. More than 50 mol of diallylmalonate can be converted per mol of Pd. This reaction seems to be specific for the formation of five-member rings even when the starting diene could lead to large macrocycles.

3. Experimental

The ionic liquid 1-butyl-3-methyl imidazolium hexafluorophosphate (bmimPF_6) was supplied by Solvent Innovation Co. (purity grade 99%). The reagents were obtained from commercial sources and were used without further purification. Gas chromatographic analyses were performed on a HP 5890 instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on an Agilent 5973 N spectrometer equipped with the same column and in the same conditions as GC. ^{1}H-, ^{1}H-COSY, DEPT and ^{13}C NMR were recorded in a 300 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. IR spectra were recorded on a Jasko 460plus spectrophotometer using CaF_2



Scheme 1.

windows. Elemental analysis was determined by combustion chemical analysis using a Fisons CHNS analyzer. Palladium chemical analysis was determined by dissolving the residue of the different extracts or the ionic liquid filtrate in a mixture of HCl:HNO_3 conc. (ca. 2:2 ml), diluting the solution in water (60 mL) and measuring by quantitative atomic absorption spectroscopy (Varian SpectrAA 10 plus). Quantification was achieved by comparing the response with a calibration plot.

3.1. Procedure for the cycloisomerization of diethyl 2,2-diallylmalonate in N-butyl-N′-methyl imidazolium ionic liquid

Catalyst (0.025 mmol, 10 mol%), bmimPF_6 (500 mg) and diethyl 2,2-diallylmalonate (60.5 μl, 0.25 mmol) were placed in a screw cap vial and magnetically stirred in a pre-heated oil bath at 90 °C for 24 h. Then, the mixture was extracted with hexane (4 ml × 3), the extract was concentrated under reduced pressure and analyzed by GC, GC-MS and ^{1}H NMR. When $AgPF_6$ was used as catalyst, the reactants were placed and the reaction performed under protection from the light. The different runs in kinetic experiments were performed independently and placed in the same pre-heated bath oil under identical magnetic stirring conditions. To assess the amount of palladium dissolved in bmimPF_6, palladium complex or salt (0.5 mmol) and ionic liquid (1 g) were placed in a screw cap vial and magnetically stirred in a pre-heated oil bath at 90 °C for 30 min, filtering the mixture in hot through a microfilter Swinney 13 mm (Millipore), weighing the filtrate and measuring the palladium by quantitative atomic absorbance spectrophotometry. Solubility (%): $PdCl_2(PhCN)_2$: 79.1; $PdCl_2$: 15.5; $PdBr_2$: 11.2; $Pd_2(dba)_3$: 8.5 and $PdCl_2/AgPF_6$: 4.1. To calculate the TOFs the initial reaction rate obtained from the slope of the time-conversion plot at zero time was divided by the mols of Pd catalyst dissolved in the ionic liquid.

3.2. Reuses for the cycloisomerization of diethyl 2,2-diallylmalonate in N-butyl-N′-methylimidazolium ionic liquid using $PdCl_2(PhCN)_2$ as catalyst

$Pd(PhCNCl)_2$ (19.2 mg, 0.05 mmol, 10 mol%), bmimPF_6 (1 g) and diethyl 2,2-diallylmalonate (121 μl, 0.5 mmol) were placed in a round-bottomed flask and stirred magnetically in a pre-heated oil bath at 90 °C for 24 h. Then, the mixture was cooled and extracted with hexane (5 ml × 5), the extracts being concentrated under reduced pressure and the crude weighed and analyzed by GC and ^{1}H NMR. The residual hexane in the ionic liquid phase was removed under reduced pressure and then a new feed of diethyl 2,2-diallylmalonate (121 μl, 0.5 mmol) was added for the next run. After the fifth reuse, the consecutive extracts were joined in a flask, hexane was removed and the palladium content of the residue was analyzed by quantitative atomic absorbance spectrophotometry.

3.3. Synthesis of diethyl 2,2-di-(4-pentenyl) malonate

Diethyl malonate (1.52 ml, 1.60 g, 10 mmol) and sodium ethoxide (6.8 g, 100 mmol) were placed in a previously dried double-necked round-bottomed flask. Then, anhydrous toluene (20 ml) was added under nitrogen atmosphere and the mixture was magnetically stirred in a pre-heated oil bath at 110 °C under nitrogen atmosphere for 15 min. Then, 5-bromo-pent-1-ene (5.92 ml, 7.45 g, 50 mmol) was added and the reaction was left to react at 110 °C under inert atmosphere. The course of the reaction was followed by GC until no further conversion was observed. At this time the mixture was filtered and the filtrate was concentrated under reduced pressure. The crude was dissolved in dichloromethane and extracted with 5% HCl (50 ml × 3) and brine (50 ml × 2), dried on magnesium sulphate and filtered through a 20 nm pore diameter Teflon membrane. After removing the solvent under reduced pressure, 2,2-di-(4-pentenyl)-malonic acid diethyl ester was obtained as a yellow oil (1.18 g, 40%, purity >95% by ^{1}H NMR). IR (neat, cm^{-1}): 3075, 2979, 2956, 2931, 2864, 1731 (vs), 1641, 1462, 1450, 1298, 1252, 1261, 1186, 1093, 1038, 993, 910. ^{1}H NMR δ_H (ppm, 300 MHz, $CDCl_3$): 5.80 (2H, m), 5.05 (2H, d), 4.95 (2H, d), 4.10 (4H, q), 2.00 (4H, m), 1.85 (4H, m), 1.20 (6H, t). ^{13}C NMR δ_C (ppm, 300 MHz, $CDCl_3$): 172.2, 138.8, 138.5, 115.3, 115.0, 61.4, 57.8, 34.2, 34.0, 32.3, 32.2, 23.7, 14.5. MS (*m*/*z*): $M^{+\cdot}$ 296 (<1%), other peaks: 251, 223, 182, 173 (more intense). *Anal.* calc. for $C_{17}H_{28}O_4$ (296.20): C, 68.89; H, 9.52. Found: C, 67.68; H, 9.68%.

3.4. Procedure for the cycloisomerization of diethyl 2,2-di-(4-pentenyl) malonate in N-butyl-N′-methylimidazolium ionic liquid using $PdCl_2(PhCN)_2$ as catalyst

Diethyl 2,2-di-(4-pentenyl) malonate (74.1 mg, 0.25 mmol), $PdCl_2(PhCN)_2$ (9.6 mg, 0.025 mmol, 10 mol%) and bmimPF_6 (500 mg) were placed in a round-bottomed flask and magnetically stirred in a pre-heated oil bath at 90 °C for 40 h, taking a control sample at 24 h. The mixture was cooled and extracted with hexane (5 ml × 5), the extracts being concentrated under reduced pressure and the crude weighed and analyzed by GC, GC-MS and ^{1}H-, ^{13}C-, DEPT and ^{1}H-COSY NMR (see spectra in Supporting Information). This mixture was too complicated to be purified and the product distribution was determined from the mixture as follows. The GC and GC-MS analyses reveal that the reactant has disappeared and five chromatographic peaks with similar pattern than that observed

for the mixture of acyclic and cyclic isomers for 2,2-diallyl diethylmalonate was found. The MS spectra show that all the peaks are isomers (*m*/*z* 296) with very similar fragmentation scheme. The $M^{+\cdot}$ has low intensity in the first three peaks, but it was more intense in the latter two peaks, suggesting that more stable cyclic cations are present. Common fragmentation pattern in MS (*m*/*z*): 296, 251, 228, 222, 182, 173, 160, 149. The ^{1}H NMR shows that not vinylic C=C double bond remains in the product mixture, this being confirmed for the absence of any CH_2 in the Csp^2 region in ^{13}C and DEPT. The presence of the three-substituted isomer cyclic is clearly confirmed by the appearance of a new signal at 154 ppm in ^{13}C NMR, that disappears in DEPT, suggesting that corresponds to the completely substituted C–C double bond position of the cyclic compounds, together with the presence of the different peaks in ^{1}H and ^{13}C NMR spectra. The presence of the tetra-substituted cyclic isomer is confirmed by the appearance of a neat singlet around 3.0 ppm in ^{1}H NMR and a signal at 46 ppm in ^{13}C NMR, that disappears in DEPT, corresponding to the tetra-substituted saturated carbon in the carbocycle. The integration of the characteristic peaks in ^{1}H NMR for each isomer is in good agreement with the distribution calculated by GC. The interactions observed by ^{1}HCOSY NMR are in accordance with the proposed products distribution.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.02.044.

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