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Selective Catalytic Hydrodimerization of 1,3-Butadiene by Palladium Compounds Dissolved in Ionic Liquids

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Palladium(II) compounds dissolved in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI{\cdot}BF_4$) ionic liquid are shown to be able to catalyze the hydrodimerization of 1,3-butadiene. In most of the cases, only the 1,3-butadiene dimer 1,3,6-octatriene and the telomer octa-2,7-dien-1-ol have been obtained. The products' selectivity and catalytic activity depend on the reaction conditions. 1,3-Butadiene conversion up to 28%, a turnover frequency (TOF) of 118 h^{-1}, and a selectivity of 94% on telomer were achieved with $(BMI)_2PdCl_4$ dissolved in $BMI{\cdot}BF_4$. The 1,3-butadiene conversion and TOF were significantly increased to 49% and 204 h^{-1}, respectively, by a 5-atm pressure of carbon dioxide. The reactions were performed under homogeneous conditions at 70 °C. However, at temperatures below 5 °C, a two-phase system is formed and the products are easily removed from the reaction mixture by simple decanting. The recovered ionic catalyst solution can be reused several times without any significant changes in the catalytic performance. The structure of the new catalyst precursor $(BMI)_2PdCl_4$ has been determined by X-ray diffraction analysis.

Introduction

It is well-known that the homogeneous catalytic hydrodimerization of 1,3-butadiene with soluble palladium complexes in the presence of carbon dioxide affords in most of the cases octa-2,7-dien-1-ol.[1] It has also been demonstrated that palladium-water-soluble phosphine compounds are also able to hydrodimerize 1,3-butadiene in typical two-phase (liquid−liquid) catalytic reactions.[2] In this respect, various patents[3] have recently appeared and a pilot plant based on two-phase catalytic systems is operated by the Kuraray Co.[4] In both catalytic systems (homogeneous and two-phase), the use of carbon dioxide is essential for the production of octa-2,7-dien-1-ol from 1,3-butadiene.[1−4] Despite the relatively vast number of studies over the past 20 years on the use of water as solvent for two-phase catalysis, limitations such as lower reaction rates due to poor solvent properties of water for organic substrates or the necessity to use special water-soluble ligands associated with the transition metal catalyst precursors remain the basic problem of these liquid−liquid catalytic systems.[5] We[6] and others[7] have recently demonstrated that ionic liquids based on the 1-*n*-butyl-3-methylimidazolium cation are an important alternative to water as solvents for the two-phase catalytic oligomerization, hydroform-

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Chart 1

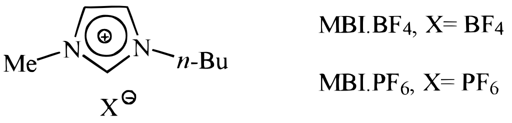


Table 1. Physical−Chemical Properties of Ionic Liquids BMI·BF$_4$ and BMI·PF$_6$ at 30 °C

ionic liquid	η^a (P)	d^b (g mL^{-1})	κ^c (S cm^{-1})	T^d (°C)	solubility^e water	hydrocarbons	alcohols^f
BMI·BF$_4$	2.33	1.17	0.0023	−81	yes	no	yes
BMI·PF$_6$	3.12	1.37	0.0019	−61	no	no	yes

^{a} Viscosity. ^{b} Density. ^{c} Specific conductivity. ^{d} Glass transition. ^{e} 50% weight solutions. ^{f} For methanol and ethanol.

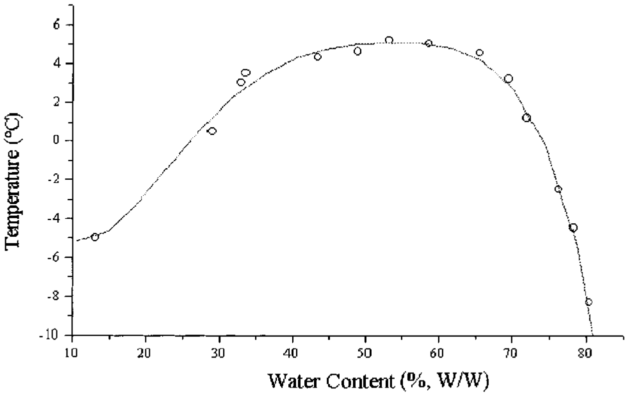


Figure 1. Partial miscibility of MBI·BF$_4$ in water (w/w).

ylation, and hydrogenation of olefins by transition metal complexes. In this work, we show that palladium(II) compounds immobilized in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate are able to hydrodimerize selectively 1,3-butadiene in the absence of carbon dioxide.

Results and Discussion

Ionic Liquids. The ionic liquids 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF$_4$) and hexafluorophosphate (BMI·PF$_6$) (Chart 1) have been chosen for this study due to their distinct physical-chemical properties (Table 1).

The BMI·BF$_4$ is particularly interesting because of its partial miscibility with water. Indeed, the miscibility of this ionic liquid depends on the composition ratio (molten salt/water) and on the temperature (Figure 1). For example, a homogeneous mixture of 1/1 (w/w, molten salt/water) is formed at temperatures above 5 °C and a two-phase mixture at temperatures below 5 °C. This allows one to perform the catalytic reaction under homogeneous conditions in a relative large range of temperatures and also to separate the products from the catalytic solution at temperatures below 5 °C.

Moreover, classic palladium compounds such as [(η^3-C$_4$H$_7$)Pd-μ-Cl]$_2$ (**1**) [(η^3-C$_4$H$_7$Pd(1,5-cyclooctadiene)][BF$_4$] (**2**), and palladium acetate (**3**), which are known to catalyze 1,3-butadiene telomerization reactions, are completely soluble and stable, at room temperature, in this ionic liquid.

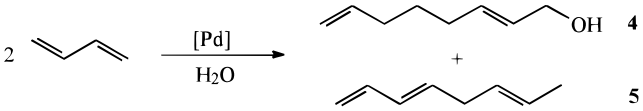
Catalytic Experiments. The catalytic systems were prepared by mixing the palladium compound and the ionic liquid at room temperature. The results obtained with these catalytic systems in the hydrodimerization of 1,3-butadiene under different reaction conditions are summarized in Table 2. In most of the cases, only the telomer octa-2,7-dien-1-ol (**4**) and the 1,3-butadiene dimer 1,3,6-octatriene (**5**) have been obtained (Scheme 1).

Table 2. Selectivity, Conversion, and Turnover Frequency (TOF) of the Hydrodimerization of 1,3-Butadiene by Palladium(II) Compounds Dissolved in Ionic Liquids under Various Reaction Conditions^a

entry	catalyst precursor	T (°C)	P_{CO_2} (atm)	t (h)	selectivity (%)		conversn (%)	TOF (h^{-1})
					4	**5**		
1	**1**	70		24	89	11	28	15
2	**2**	70		24	88	12	23	12
3	**3**	70		24	90	10	27	14
4	**1**	70	5	3	85	15	36	152
5	**2**	70	5	3	88	12	38	161
6	**3**	70	5	3	90	10	19	82
7	**6**	40	5	3	88	12	29	118
8	**6**	70	5	3	84	16	49	204
9	**6**	100	5	3	88	12	19	81
10	**6**	70	10	3	89	11	40	169
11	**6**	70		3	94	6	28	118
12	**6**^{b}	70		3	60^f	10	17	73
13	**6**^{b,c}	70		3	92	8	22	93
14	**6**^{b,d}	70		3	95	5	29	122
15	**6**	70		24	92	8	31	16
16	**7**	70		3	90	10	26	110
17	**6**^{e}	70		24	46^f	12	22	11

^{a} Reaction conditions: 1,3-butadiene (125 mmol); water (125 mmol); catalyst precursor (0.1 mmol). Molten salt: BMI·BF$_4$ (15 mmol), [Pd] = 0.035 mol/L. ^{b} Molten salt: BMI·PF$_6$. ^{c} [Pd] = 0.015 mol/L. ^{d} [Pd] = 0.050 mol/L. ^{e} Reaction in absence of molten salt. ^{f} Formation of oligomers containing three to eight butadiene units.

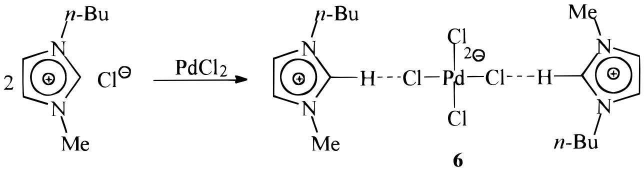
Scheme 1



It is noteworthy that both the alcohol and the 1,3-butadiene dimer formed are soluble in this medium at room temperature, but they are insoluble at temperatures below 5 °C. The products can be easily separated by simply decanting the reaction mixture at temperatures below 5 °C. In the performed reactions using the catalyst precursors **1**−**3**, metallic palladium was detected at the end of the reaction, thus limiting the reutilization of this catalytic system. This can be attributed to the instability of these palladium catalyst precursors toward water. Nevertheless, it is important to note that the hydrodimerization is effective even in the absence of carbon dioxide (entries 1−3), but with lower turnover frequency (TOF) as compared to the reactions performed under carbon dioxide pressure (entries 4−6).

The formation of metallic palladium could be suppressed almost completely by the use of the new catalyst precursor (BMI)$_2$PdCl$_4$ (**6**) (see later for its synthesis and characterization). Atomic absorption analysis of metal contents in the ionic and organic phases, after the reaction, indicated that more then 97% of the palladium is retained in the ionic phase. The recovered ionic catalyst phase could be reused several times (at least four) without any significant losses in catalytic efficiency. The increase of the reaction temperature from 40 to 70 °C (entries 7 and 8, respectively) causes an

Scheme 2



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enhancement of the 1,3-butadiene conversion without any significant change in selectivity. However, at 100 °C, there is a dramatic decrease in the 1,3-butadiene conversion. This is probably related to the instability of the catalytic palladium-active species at higher temperatures (100 °C). Indeed, metallic palladium was observed at the end of the reactions performed at temperatures above 100 °C (entry 9).

The use of carbon dioxide on the catalytic system—a classical procedure in 1,3-butadiene hydrodimerization[1-4]—increases the 1,3-butadiene conversion (entries 8, 10, and 11), however, accompanied by a relative decrease in octa-2,7-dien-1-ol selectivity from 94 to 84%. The role of carbon dioxide in the hydrodimerization of 1,3-butadiene is not well understood: it is generally accepted that CO$_2$ facilitates the nucleophilic attack of water on the η^3-allylpalladium intermediates through HCO$_3^-$ species.[2] The 1,3-butadiene hydrodimerization catalyzed by palladium compounds dissolved in ionic liquids occurs in the absence of carbon dioxide. In this case, it is reasonable to assume that the ionic liquid facilitates the ionization of water. This may also explain the lower 1,3-butadiene conversion, catalytic activity, and selectivity observed in the 1,3-butadiene hydrodimerization reaction with **6** dissolved in BMI·PF$_6$, which is insoluble in water and much less ionic then its tetrafluoroborate analogue (see entry 12 of Table 2 and also Table 1).

There is no significant change in the catalytic selectivity with increasing palladium concentration in the ionic liquid (entries 11, 13, and 14). However, the TOF increases with increase of the catalyst precursor concentrations to 0.035 mol/L. In concentrations higher than 0.050 mol/L, metallic palladium was observed at the end of the reaction. This behavior is probably related to the saturation of the ionic phase by the palladium species. This result suggests that the ionic liquid also supports the stabilization of the catalytic palladium active species.

Preparation, Characterization and Crystal Structure of 6. Compound **6** has been prepared in almost quantitative yield by the reaction of palladium chloride with 2 molar excesses of 1-*n*-butyl-3-methylimidazolium chloride in acetonitrile at reflux temperature (Scheme 2). The palladium adduct **6** has been fully characterized by means of C, H, N combustion analysis and IR, UV–visible, ^{1}H and ^{13}C NMR spectroscopies. The IR spectrum of **6** shows the bands between 3100 and 3200 cm^{-1} (see Experimental Section) characteristic of hydrogen bonding (C–H···Cl interactions), already observed in analogous compounds[8] of Ni(II) and Co(II) containing the 1-ethyl-3-methylimidazolium cation. The crystal structure of the adduct **6** has been determined by X-ray diffraction analysis. Crystallographic data and details of the structure determination of **6** are presented in Table 3. Selected bond lengths and angles of **6** are given in Table 4. The ORTEP drawing of **6** is shown in Figure 2.

Table 3. X-ray Experimental Data

formula	C$_{16}$H$_{30}$N$_4$Cl$_4$Pd
mol w	526.66 g/mol
cryst syst	monoclinic
space group	P 1 21/n 1
a (Å)	8.833(2)
b (Å)	10.689(3)
c (Å)	11.766(3)
β (deg)	91.26(2)
V (Å^3)	1110.6(9)
Z	2
color	orange
crystal dimens (mm)	0.30 × 0.30 × 0.25
d$_{calc}$ (g cm^{-3})	1.57
F_{000}	536
μ (mm^{-1})	1.318
trans min/max	0.9062/1.0000
temp (K)	294
wavelength (Å)	0.710 73
radiation	Mo Kα graphite monochromated
diffractometer	Nonius CAD4-MACH3
scan mode	$\theta/2\theta$
hkl limits	−12, 12/0, 15/0, 16
θ limits(deg)	2.5/30.40
no. of data meas	3679
no. of data with $I > 3\sigma(I)$	2598
weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0016\, F_o^4)$
no. variables	115
R	0.022
R_w	0.033
GOF	1.189
largest peak in final diff (e Å^{-3})	0.625

Table 4. Bond Lengths and Angles of 6

bond lengths (Å)		bond angles (deg)	
Pd–Cl1	2.2974(4)	Cl1–Pd–Cl2	90.05(2)
Pd–Cl2	2.3096(5)	Cl1–Pd–Cl2	89.95(2)
C1–N1	1.325(2)	N1–C1–N2	108.4(2)
C1–N2	1.328(2)	C1–N1–C2	108.8(1)
N1–C2	1.367(2)	C1–N1–C4	125.8(2)
N1–C4	1.465(2)	C2–N1–C4	125.4(2)
C2–C3	1.340(3)	N1–C2–C3	107.3(2)
C3–N2	1.376(2)	C2–C3–N2	107.2(1)
N2–C5	1.472(2)	C1–N2–C3	108.3(1)
C5–C6	1.510(3)	C1–N2–C5	125.7(1)
C6–C7	1.512(3)	C3–N2–C5	126.0(1)
C7–C8	1.508(3)	N2–C5–C6	112.1(1)
		C5–C6–C7	112.9(2)
		C6–C7–C8	114.8(2)

Compound **6** is constituted by a tetrachloropalladate anion in which the coordination sphere of Pd including the four chlorine atoms can be considered as essentially planar. The two imidazolium cations adopted an eclipsed conformation (with respect to the 1-butyl group). It is interesting to note the relatively short distance between the Cl2 atoms and the C1 carbon of the imidazolium ring and that the Cl2-Pd bond length is ~0.1 Å shorter than Cl1-Pd. This can be attributed to the relative strong hydrogen bonds existing between the ionic pair through the chlorine atom and the hydrogen at C1 of the imidazolium cation. These hydrogen bonds were also corroborated by the presence of characteristic peaks in the IR spectrum.

Chemical Behavior of 6 Dissolved in BMI·BF$_4$. When water was added to an orange solution of **6** in BMI·BF$_4$, the color slowly turned to light yellow with evolution of a volatile product (Scheme 3). Compound

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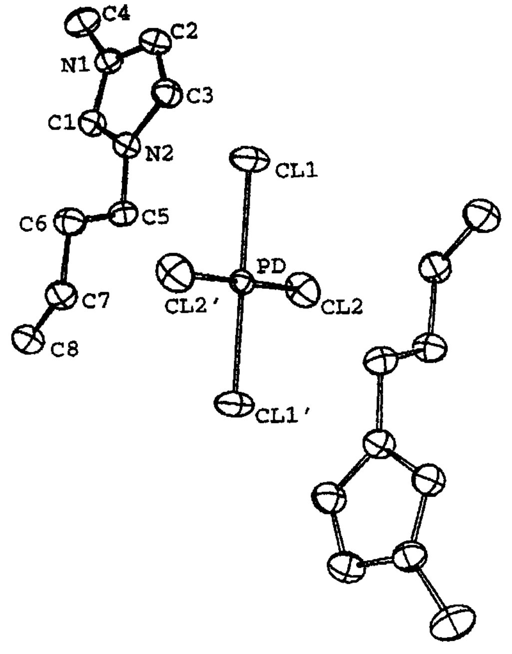


Figure 2. ORTEP plot with atom labling scheme of the structure of **6**. H atoms are omitted for clarity.

Scheme 3

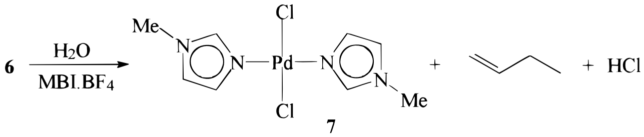
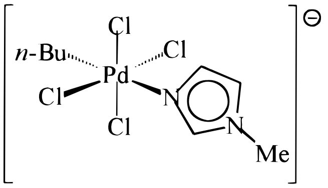


Chart 2



7, whose crystal structure has already been reported,[9] was isolated from the ionic solution and characterized by C, H, N combustion analysis and IR, UV–visible and ^{1}H and ^{13}C NMR spectroscopy (see Experimental Section). The formation of **7** is concomitant with the evolution of but-1-ene (identified by CG/MS spectrometry) and followed by the increase of the medium acidity (pH changes from 7 to 3). It is important to note that the transformation of **6** into **7** only occurs in the presence of both BMI·BF$_4$ and water.

These results can be explained in terms of two successive processes of oxidative addition reaction of the imidazolium nitrogen–butyl bond to afford Pd(IV)–n-butyl species (Chart 2), which undergo β-elimination affording but-1-ene, followed by reductive elimination of HCl. The ionic liquid should act as an ionizing agent and is probably responsible for the stabilization of the palladium species involved in this process.

Compound **7** was also isolated from the ionic catalyst solution after the catalytic reaction. This compound has a catalytic performance very similar (1,3-butadiene conversion, activity, and selectivity) to **6** (entries 15 and 16, Table 2) under the same reaction conditions. These results clearly indicate that the true catalyst precursor on the hydrodimerization of 1,3-butadiene is in fact **7**.

Conclusions. The palladium compounds immobilized in BMI·BF$_4$ ionic liquid catalyze the selective transformation of 1,3-butadiene into octa-2,7-dien-1-ol. This reaction was performed in homogeneous media at 70 °C, and the reaction products could be easily separated from the reaction mixture by simply cooling the system to temperatures below 5 °C followed by decantation. The recovered ionic catalyst solution could be reused several times without any significant loss of the catalytic performance. The complex BMI$_2$PdCl$_4$ undergoes dealkylation in the presence of the ionic liquid and water to produce the catalyst precursor *trans*-[PdCl$_2$(MI)$_2$]. Moreover, the hydrodimerization of 1,3-butadiene could be performed even in the absence of carbon dioxide. The selective hydrodimerization of 1,3-butadiene described in this work, associated with the simplicity of the system, catalyst recovery, and separation of the products from the reaction mixture is an outstanding example of technical applicability of molten salts as immobilizing agents for transition metal catalysts.[10]

Experimental Section

General Considerations. All manipulations were performed under dry, oxygen-free argon using standard techniques. All solvents were dried and distilled under argon prior to use. Infrared (Nujol mulls or KBr pellets) spectra were recorded in the region 4000–400 cm^{-1} using a Mattson 3020 FT-IR spectrophotometer. The ^{1}H and ^{13}C–{^{1}H} NMR spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Varian VXR-200 instrument. Proton and carbon shifts (δ/ppm, *J*/Hz), are positive downfield relative to external SiMe$_4$. Elemental analyses were carried out by the Central Analítica IQ/UFRGS (Porto Alegre, Brazil). Mass spectra were obtained with GC/MS HP5988A (EI, 70 eV). The palladium contents in both ionic and organic phases were determined by atomic absorption analysis using a Perkin-Elmer 2380, HGA 400, atomic absorption spectrometer with graphite tube atomizer and autosampler. The reaction products were analyzed by gas chromatography on a Varian 3400 chromatograph equipped with an OV1 column, 30 m × 0.25 mm × 0.2 μm, and FID detector; N$_2$ was the carrier (1 mL/min); the temperature program ranged from 50 (5 min) to 180 °C (5 min) at a heating rate of 10 °C/min.

The (η^3-allyl)palladium(II) derivatives[11] **1** and **2** and the ionic liquids[6b] were prepared according to procedures described in the literature. All other reagents were obtained from commercial sources and were used as received without further purification.

Syntheses. Bis(1-butyl-3-methylimidazolium) tetrachloropalladate (6). A mixture of 1-butyl-3-methylimidazolium chloride (1000 mg, 5.7 mmol) and palladium chloride (507 mg, 2.8 mmol) in acetonitrile (75 mL) was heated at reflux temperature for 24 h. The formed orange solution was concentrated to ~3 mL under reduced pressure. Addition of toluene (25 mL) affords an yellow-orange solid that was recovered by filtration, washed with toluene (2 × 10 mL), and dried in vacuo (1.4 g, 93% based on Pd). Crystals suitable for X-ray diffraction study were obtained by slow diffusion of

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toluene into an acetonitrile solution of the compound, at room temperature. Anal. Calcd for $C_{16}H_{30}Cl_4N_4Pd$: C, 36.49; H, 5.74; N,10.64. Found: C, 36.31; H, 5.65; N, 10.57. IR (KBr): 3133, 3097, 3064 (ν_{C-H} aromatic); 2992, 2952, 2933, and 2871 (ν_{C-H} aliphatic); 1728 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 8.95 (s, 1H, imidazolium ring); 7.39 (s, 1H, imidazolium ring); 7.36 (s, 1H, imidazolium ring); 4.19 (t, 2H, $^3J_{HH} = 5.9$ Hz, CH_2N); 3.88 (s, 3H, NCH_3); 1.86 and 1.34 (2m, 4H, $2CH_2$); 0.93 (t, 3H, $^3J_{HH} = 7.2$ Hz, CH_3). ^{13}C−{^{1}H} NMR ($CDCl_3$): δ 137.5, 124.4, and 123.1 (C-imidazolium ring); 50.2 (CH_2N); 36.9 (NCH_3); 32.7 and 20.0 ($2CH_2$) and 13.7 (CH_3).

Isolation of Bis(methylimidazole) Dichloropalladate (7). To an orange solution of **6** (53 mg, 0.1 mmol) in BMI·BF_4 (3 mL, 15 mmol) water (2.3 mL, 125 mmol) was added at room temperature, immediately producing a light yellow solution. After 24 h standing at room temperature, yellow-orange crystals were formed which were recovered by filtration washed with hexanes (10 mL) and dried in vacuo (15 mg, 44%). Anal. Cald for $C_8H_{12}Cl_2N_4Pd$: C, 28.13; H, 3.55; N, 16.41. Found: C, 29.05; H, 3.66; N, 17.12. IR (KBr): 3140, 3110, 3053 (ν_{C-H} aromatic); 2952, 2917 (ν_{C-H} aliphatic); 1698 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 7.98 (s, 1H, imidazolium ring); 7.41 (d, 1H, $^3J_{HH} = 1.3$ Hz, imidazolium ring); 6.78 (d, 1H, imidazolium ring); 4.19 (s, 3H, NCH_3); 1.86 and 1.34 (2m, 4H, $2CH_2$); 0.93 (t, 3H, $^3J_{HH} = 7.2$ Hz, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 139.2, 130.2, 119.4 (C-imidazolium ring); 34.4 (NCH_3).

Catalytic Experiments. In a typical experiment, **6** (53 mg, 0.1 mmol) was dissolved in the ionic liquid (3 mL) with water (2.3 mL, 125 mmol), affording a light yellow solution. To this solution, 1,3-butadiene (10 mL, 125 mmol) was introduced, under an argon atmosphere, in a 100-mL stainless steel autoclave equipped with a magnetic stirring bar. The autoclave was pressurized with 10 bar of carbon dioxide and heated at 70 °C for 3 h. The autoclave was then cooled and degassed. The crude reaction mixture contained a single phase that upon cooling to ~5 °C produced two phases. The upper phase was analyzed by gas chromatography. The 1,3-butadiene conversion and butene selectivity were determined by gas chromatography using 2,4-pentanedione as internal standard. The remaining light yellow catalytic ionic solution could be reused several times.

Crystallographic Data Collection and Structure Determination of 6. Single crystals of **6** ($C_{16}H_{30}N_4Cl_4Pd$, MW = 526.7), were obtained as described above. Data were collected at room temperature using Mo Kα graphite-monochromated radiation, $\lambda = 0.7107$ Å, on a Nonius CAD4-MACH3 diffractometer. The orange compound crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 8.833(2)$, $b = 10.689(3)$, and $c = 11.766(3)$ Å, $\beta = 91.26(2)$, $V = 1110.6$ Å,^{3} $d_{calcd} = 1.575$ g cm^{-3}, $Z = 2$, and $\mu = 13\,177$ cm^{-1}. A total number of 3679 reflections were collected in the range $2° < \theta < 30°$. Three standard reflections measured every hour during the data collection period showed no significant trend. The data were corrected for Lorentz, polarization, and absorption factors (ψ scan of four reflections). A total of 2598 reflections with $I > 3\,\sigma(I)$ were used. The structure was solved using the heavy atom method. Hydrogen atoms were introduced as fixed contributors (C−H = 0.95 Å, B(H) = 1.3 Beqv(C) Å^2). For all computations the Nonius MolEN package was used.[12] Crystal data and details on intensity collection parameters are indicated in Table 3. Full-matrix least squares led to the final values of $R(F) = 0.022$, and $R_w(F) = 0.33$.

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Supporting Information Available: Tables of positional parameters for non-hydrogen and for hydrogen atoms, thermal parameters for anisotropic atoms, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

OM970982P

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