Allyl-Functionalised Ionic Liquids: Synthesis, Characterisation, and Reactivity

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Dedicated to Professor *André E. Merbach* on the occasion of his 65th birthday

The two known Me- and allyl-substituted 1*H*-imidazol-3-ium bromides **1** and **2**, respectively, were converted to the corresponding BF_4^- and BPh_4^- salts **3**–**6** (*Scheme 1*). Compounds **3** and **4** were liquids at ambient temperature. Reaction of **1** or **2** with $[PdCl_2]$ afforded the corresponding 2:1 imidazolium/metal complexes **7** and **8**. The latter complex, melting at 58°, can be regarded as a 'true' ionic liquid. Attempts to polymerise **7** by radical promotion (AIBN) were unsuccessful, but resulted in the centrosymmetric 2:1 complex **9**. The allyl group of **1** could be arylated (giving rise to **10**) or hydrogenated (at 100 bar H_2 pressure). The solid-state structures of compounds **5**–**7** and **9** were solved by means of single-crystal X-ray analyses (*Figs. 1–4*).

Introduction. – Room-temperature ionic liquids have received considerable attention as alternative solvents for a wide range of applications, in particular as reaction media for homogeneous, heterogeneous, and enzymatic catalysis [1]. Ionic liquids that incorporate functional groups are becoming more and more important, since imparting specific chemical properties to the ionic liquid could lead to highly specific roles in synthesis and catalysis unparalleled by more-generic systems. Only a few ionic liquids with functional anions have been reported [2], whereas a large number of ionic liquids with functional cations have been published, including alkenes [3–5], alkynes [6][7], amines [8], amides [9], ethers and alcohols [10], acids [11], fluorous [12] and glycidyl [13] chains, nitriles [14], thiols [15–17], and ferrocenyl groups [18].

Functionalised ionic liquids exhibit a range of physical and chemical properties that are well-suited to specific applications. For example, ionic liquids incorporating the *O*,*O*-diethylphosphonyl functionality have been evaluated as mechanical lubricants [19], and ionic liquids with fluorous chains act as surfactants [12a]. Other applications include the use of acid-functionalised ionic liquids in the acetalisation of aldehydes [11e][20], and urea- and thiourea-functionalised ionic liquids to extract metal ions from aqueous solution [21][22]. Thiol-functionalised ionic liquids have been shown to stabilise gold and platinum nanoparticles [15][16], as have nitrile-functionalised ionic liquids with palladium nanoparticles, which also exhibit catalytic activity in various C–C coupling reactions [14][23].

It is interesting to note that the first liquid alkene- or allyl-substituted[1]) imidazolium salts were reported as early as 1971 [24]. However, at that time, the

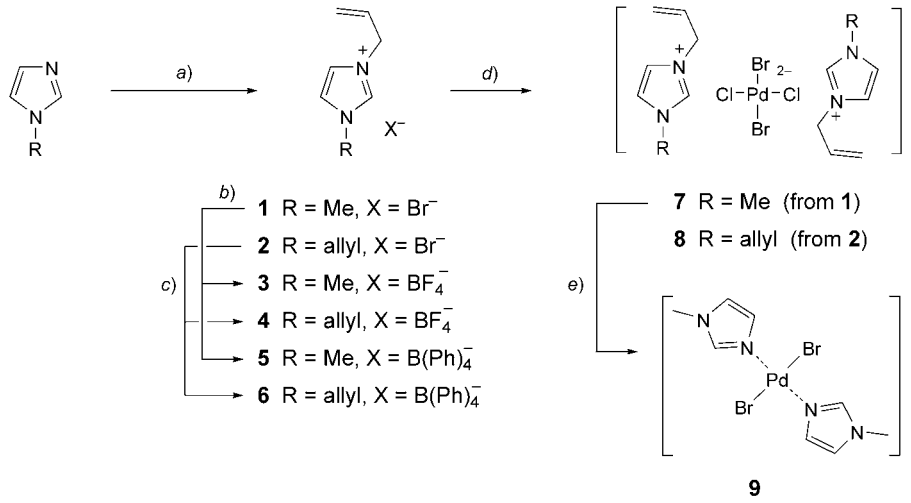
[1]) Allyl = prop-2-enyl.

liquid nature of these compounds was not appreciated and was, in part, attributed to their deliquescent nature. As yet, no extensive study of ionic liquids bearing an alkene functionality has been reported, although it has been shown that 1-allyl-3-methylimidazolium chloride can be used as solvent for cellulose acetylation [25]. In addition, a series of allyl-functionalised imidazolium halides were prepared, and their conductivities, viscosities, and thermal properties were investigated, indicating that the introduction of an *N*-allyl group effectively suppresses crystallisation [26].

We have recently reported the synthesis of an ionic liquid comprised of a functionalised fluoroborate anion and an alkene-substituted imidazolium cation [2g]. Here, we describe the synthesis and characterisation of a series of ionic liquids incorporating the allyl functionality, together with some nascent reactions that they undergo, indicating that these compounds are useful synthons to a wide range of other functionalised ionic liquids.

Results and Discussion. – *Synthesis and Characterisation.* The synthetic route used to prepare the allyl-functionalised imidazolium salts **1**–**8** is illustrated in *Scheme 1*. The 1-methyl- or 1-allyl-substituted 1*H*-imidazol-3-ium compounds **1** and **2**, respectively, have been prepared previously [26]. Ion-exchange reaction of **1** or **2** with $Na^+BF_4^-$ and $Na^+BPh_4^-$ in acetone [27] afforded the salts **3**–**6**. Compound **3** can also be prepared by a halide-free strategy (*Method B* in the *Exper. Part*) *via* methylation of 1-allylimidazole with trimethyloxonium tetrafluoroborate ($Me_3O^+BF_4^-$) [28]. Salts **1**–**4** are liquid at room temperature, with low melting points; compounds **5** and **6** are solid at ambient temperature. Presumably due to their higher symmetry, the melting points of the bis-functionalised ionic liquids **2** and **4** are higher than those of the mono-functionalised compounds **1** and **3**, which is in keeping with previous observations [29].

Scheme 1



a) Allyl bromide (1 equiv.), MeOH, r.t., 5 d. *b*) $Na^+BF_4^-$ (1 equiv.), acetone, r.t., 48 h. *c*) $Na^+BPh_4^-$, acetone, r.t., 48 h. *d*) [$PdCl_2$] (0.5 equiv.), CH_2Cl_2, r.t., 2 d. *e*) AIBN, MeCN, 80°, 10 h.

Salts **1**–**6** were characterised by means of electrospray-ionisation mass spectrometry (ESI-MS), IR, and ^{1}H- and ^{13}C-NMR spectroscopy. The positive-ion ESI mass spectra of **1**, **3** and **5**, and of **2**, **4**, and **6** exhibited parent peaks at *m*/*z* 123 and 149, respectively, corresponding to the expected organic molecular ions (M^+). In negative-ion mode, the bromide, tetrafluoroborate, and tetraphenylborate counter-ions were identified at *m*/*z* 79/81, 87, and 319, respectively. In keeping with previous observations [14], aggregates composed of the anions and cations are present in more-concentrated samples, but, upon dilution, essentially only the parent ions were observed with significant relative intensities. The IR spectra of **3**–**6** contained stretches between 3050 and 3100 cm^{-1} that correspond to =C–H vibrations, and the C=C stretch was observed at *ca*. 1645 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra of **3**–**6** were as expected, with little change in the spectra as the anion is varied.

In CH_2Cl_2 solution, [$PdCl_2$] reacted with 2 equiv. of **1** or **2** to form the mixed-halide complexes **7** or **8**, respectively (*Scheme 1*). These complexes were isolated as dark-red solids (at room temperature). They are air-stable, but slowly decompose in H_2O and alcoholic media. Both compounds are poorly soluble in chlorinated solvents such as $CHCl_3$ or CH_2Cl_2 , but are soluble in coordinating solvents such as MeCN. Complex **7** has a melting point of 134°. Complex **8**, despite its higher molecular symmetry, already melts at 58° and may, therefore, be a 'true' ionic liquid – based on the commonly accepted definition [30]. The flexibility of the four allyl side chains probably contribute to the low melting point of this compound.

The solid-state structures of compounds **5**, **6**, and **7** were established by means of single-crystal X-ray analyses. Crystals suitable for X-ray diffraction were grown at room temperature from acetone/H_2O (for **5** and **6**) or from MeCN/Et_2O (for **7**). Representations of the structures are shown in *Figs. 1–3*; key bond distances and angles are provided in *Table 1*.

There is some conformational disorder in the allyl moieties of **5** and **7**, both C(5) and C(6) being distributed over two positions[2]). Furthermore, there is disorder in the

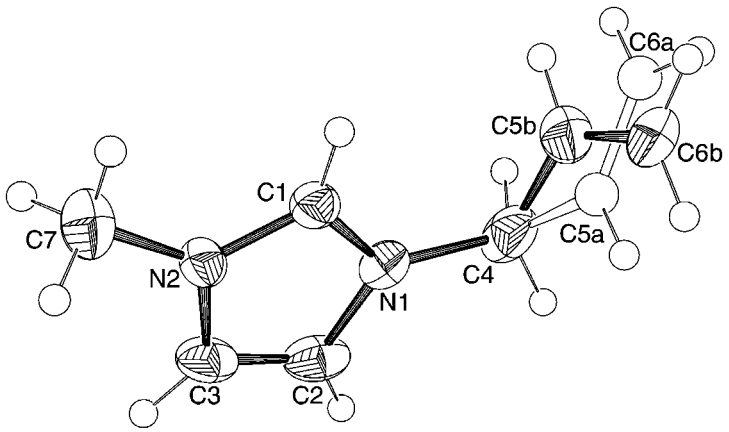


Fig. 1. *X-Ray crystal structure of compound* **5** (ORTEP plot; ellipsoids drawn at the 50% probability level)

[2]) Arbitrary atom numbering (see *Fig. 1*).

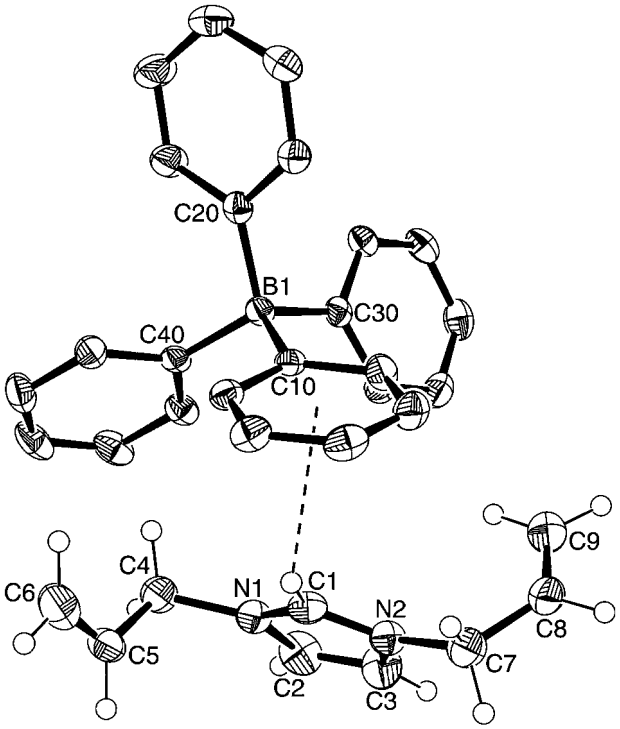


Fig. 2. *X-Ray crystal structure of compound* **6** (ORTEP plot; ellipsoids drawn at the 50% probability level)

anion of **7**, the position of the bromide being partially occupied by chloride (and *vice versa*).

Comparable structures of allyl-imidazolium cations are known, and their bonding parameters are similar to those observed in **5**, **6**, and **7** [31]. In all of these structures, bond lengths and angles of the imidazolium ring are basically identical within experimental error. The imidazolium ring is essentially planar, with no atom deviating from the least-squares plane by more than 0.0062 Å. Even atoms C(4) and C(7) deviate only slightly from that plane, except for compound **6**. In the latter, the C(4)-atom lies 0.512 Å above the imidazolium plane. In **6**, the two C=C moieties display almost identical bond distances: 1.301(2) and 1.303(2) Å, one of the double bonds being basically parallel to, the other perpendicular to the imidazolium ring. In both compounds **5** and **6**, there is a weak C–H$\cdots\pi$ contact between the acidic H(1)-atom and the negative π-cloud of one of the rings of the $[BPh_4]^-$ anion (H(1)$\cdots$C(10)–C(15) centroids of 3.019 and 2.722 Å, resp.). Furthermore, in compound **5**, there is weak π-stacking interaction between the imidazolium and one Ph ring (centroid–centroid distance = 3.77 Å).

In complex **7**, the Pd-ion resides at a centre of inversion. The complex is square-planar, with typical Pd–X (X = Cl, Br) bond lengths and angles. The halide atoms are involved in extensive H-bonding to symmetry-related cations (six close contacts <3 Å).

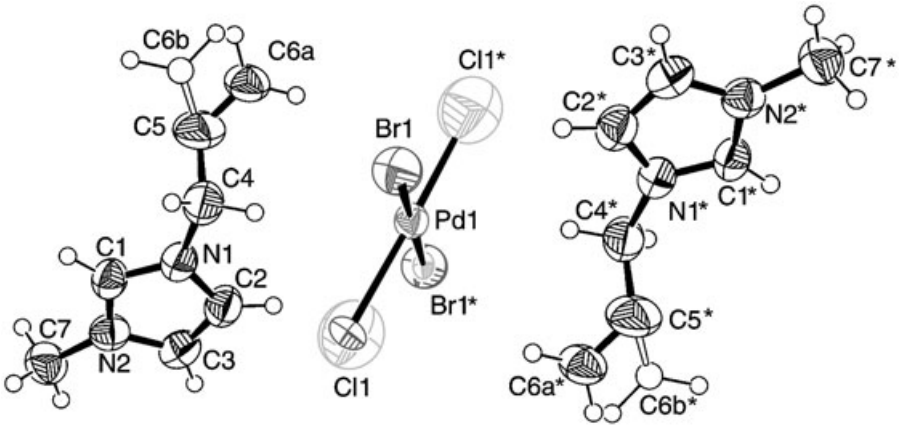


Fig. 3. *X-Ray crystal structure of compound* **7** (ORTEP plot; ellipsoids drawn at the 50% probability level). The atoms marked with asterisks (*) are symmetry-related $(-x, -y, -z+2)$.

Table 1. *Key Bond Lengths* (Å) *and Angles* (°) *for Compounds* **5**–**7** *and* **9**

	5	**6**	**7**	**9**
C(1)–N(1)	1.323(3)	1.328(2)	1.30(2)	1.325(3)
C(1)–N(2)	1.320(3)	1.328(2)	1.35(2)	1.341(4)
C(2)–N(1)	1.378(3)	1.374(2)	1.40(2)	1.379(4)
C(3)–N(2)	1.372(3)	1.376(2)	1.39(2)	1.374(4)
C(2)–C(3)	1.337(3)	1.343(2)	1.37(2)	1.351(4)
N(1)–C(4)	1.478(3)	1.482(2)	1.48(2)	–
N(2)–C(7)	1.466(3)	1.470(2)	1.46(2)	–
C(5)–C(6)	[a])	1.301(2)	[a])	–
C(8)–C(9)	–	1.303(2)	–	–
Pd–N(1)	–	–	–	2.103(2)
Pd–Br(1)	–	–	2.401(2)	2.4389(3)
Pd–Cl(1)	–	–	2.350(3)	–
N(1)–C(1)–N(2)	–	108.0(1)	109(1)	106.4(2)
C(4)–C(5)–C(6)	[a])	123.4(2)	[a])	–
C(7)–C(8)–C(9)	–	128.0(2)	–	–

[a]) Disordered.

Chemical Reactivity of Ionic Liquids. Attempts to polymerise the mono-functionalised ionic liquids **1**, **2**, and **7** by means of a known free-radical-initiator procedure [32] were unsuccessful. The reaction of **7** with '2,2′-azobis(isobutyronitrile)' (AIBN) in refluxing MeCN led, after 10 h, to the formation of **9**. The crystalline compound, investigated by single-crystal X-ray diffraction, was identified as *trans*-palladium(II)-bis(methylimidazole) dibromide (*Fig. 4*). The structure of the corresponding dichloride has been published previously [33]. Again, the Pd-atom resides at the centre of symmetry and is almost perfectly square-planar, with N(1)–Pd(1)–Br(1) angles of 89.92(7) and 90.08(7)°. The dihedral angle between the plane of the imidazole ring and the square plane around Pd is 131.9°. The Pd–N distance is slightly elongated (2.103(2) *vs.* 2.011(4) Å) due to the higher electron density at Pd, arising from the less-

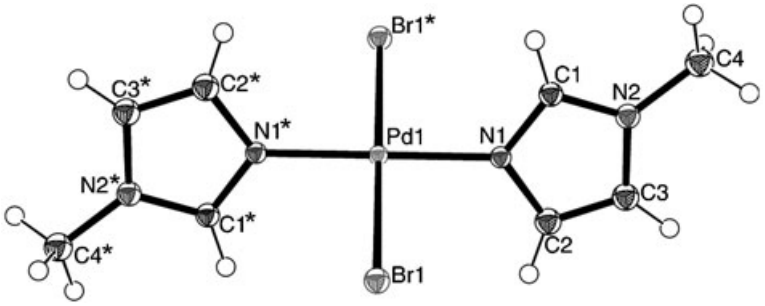


Fig. 4. *X-Ray crystal structure of the Pd complex* **9** (ORTEP plot; ellipsoids drawn at the 50% probability level). The atoms marked with asterisks (*) are symmetry-related ($-x,\ -y+1,\ -z+1$)

electronegative Br-atoms. All other bonding parameters are identical within experimental error to those of the chloro analogue [33].

In the crystal, molecules of **9** form parallel stacks, the distance between the molecules being 5.3852(5) Å (*Fig. 5*). There are no inter- or intramolecular H-bonds below 3 Å to the Br-atoms. The relatively high melting point of **9**, 249°, is, thus, a reflection of *Van der Waals* and $\pi-\pi$ stacking interactions.

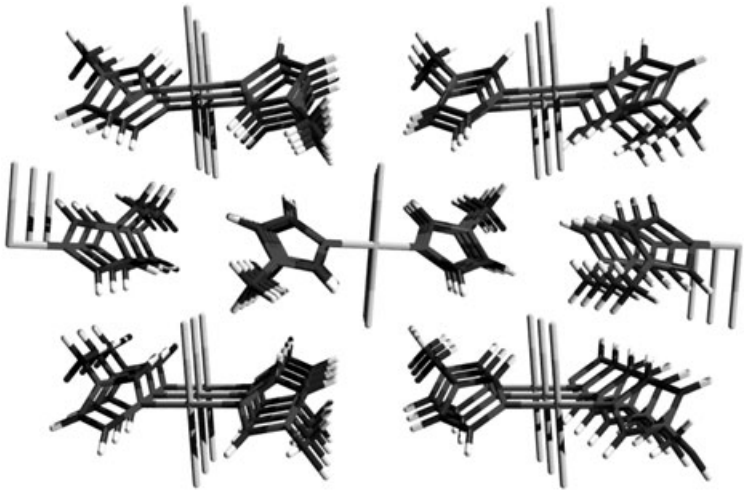


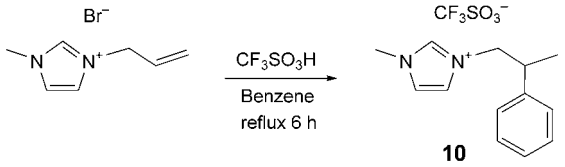
Fig. 5. *Crystal packing in the Pd complex* **9**

Additional spectroscopic and analytical data of **9** were in full agreement with the solid-state structure. The ^{1}H-NMR spectrum of **9** showed the imidazolium H-atoms at δ(H) 8.14, 7.20, and 7.16, and the Me group at δ(H) 3.72. The formation of **9** presumably results from radical reactions initiated by AIBN, which leads to the elimination of the allyl group of **7**.

Addition reactions to side chains of allyl-functionalised compounds represent an important route to a wide range of novel, potential ionic-liquid imidazolium salts. To illustrate the versatility of this approach, compound **1** was reacted with benzene in the

presence of trifluoromethanesulfonic acid (CF_3SO_3H; 'triflic acid'), following a literature protocol [34]. This reaction afforded the adduct **10** (*Scheme 2*). The positive- and negative-ion ESI mass spectra of **10** showed parent peaks at *m/z* 201 (M^+) and 149 ($CF_3SO_3^-$). The ^{1}H-NMR spectrum exhibited a *multiplet* at δ(H) 3.27 (benzylic H-atom) and a *doublet* at 1.33 ($^3J = 7.0$ Hz, Me). In addition, characteristic resonances for the Ph ring H-atoms were observed at δ(H) 7.21 – 7.34.

Scheme 2



Hydrogenation reactions in ionic liquids have been extensively investigated [35], and the solubility of elemental H_2 gas in various ionic liquids has been determined [36]. However, as far as we know, the hydrogenation of functionalised ionic liquids has not been reported. Accordingly, we investigated the hydrogenation of **1** and **3** in the presence of *Wilkinson*'s catalyst. In the neat ionic liquid, no reaction was observed after 48 h according to NMR analysis. This is possibly due to suppression of the catalyst by bromide present in **1** as the counter-ion or, in **3**, as an impurity. However, other factors cannot be fully ruled out. Inhibition or reduction of catalytic activity due to halide contamination of ionic liquids has been noted previously [37]. Upon 50% dilution (*v/v*) of **3** with CD_3OD, and at a temperature of 60° and a pressure of 100 bar H_2, hydrogenation took place rapidly[3]). The high-pressure ^{13}C-NMR spectra of the starting material and the hydrogenated product, *i.e.*, 3-butyl-1-methyl-1*H*-imidazol-3-ium tetrafluoroborate (not shown), are depicted in *Fig. 6*. The resonances of **3** at δ(C) 131.4 (*d*, =CH) and 121.6 (*t*, $=CH_2$) were no longer present in the product; instead, new aliphatic signals were observed at δ(C) 23.4 (*t*, CH_2) and 9.9 (*q*, Me).

Experimental Part

General. All chemicals were purchased from *Acros* and were used without further purification. Compounds **1** and **2** were prepared according to the literature [2g]. All reactions were performed under an inert atmosphere of dry N_2, using standard *Schlenk* techniques, in anh. solvents distilled immediately prior to use. IR Spectra were recorded on a *Perkin-Elmer FT-IR 2000* spectrophotometer; in cm^{-1}. NMR spectra were recorded at 20° on a *Bruker DRX-400* spectrometer (100/400 MHz for ^{13}C and ^{1}H, resp.); chemical shifts δ in ppm relative to $SiMe_4$ (= 0 ppm) as external standard. Electrospray-ionisation (ESI) mass spectra were recorded on a *ThermoFinnigan LCQ Deca-XP-Plus* quadrupole ion-trap instrument on samples diluted with MeOH or H_2O. Samples were infused with a syringe pump directly into the source at a rate of 5 µl/min, and the spray voltage was set to 5 kV, the capillary temp. being 50° [38]; ESI-MS signals are reported in *m/z*. Elemental analyses were carried out at the EPFL, Switzerland.

*1-Methyl-3-(prop-2-enyl)-1*H*-imidazol-3-ium Tetrafluoroborate* (**3**). *Method A*. A suspension of **1** (6.09 g, 30 mmol) and $Na^+BF_4^-$ (3.62 g, 33 mmol) in acetone (80 ml) was stirred at r.t. for 48 h. The mixture was filtered, and the solvent was removed *in vacuo:* 5.86 g (93%) of **3**. Pale-yellow, waxy solid. IR: 3155, 3117 (ν(arom. C–H)); 3088 (ν(=C–H)), 2978 (ν(aliph. C–H)); 1599 (ν(C=C)). ^{1}H-NMR ((D$_6$)acetone): 9.04 (*s*, 1 H); 7.70

[3]) The half-life for the reduction was less than 1 h under the conditions employed.

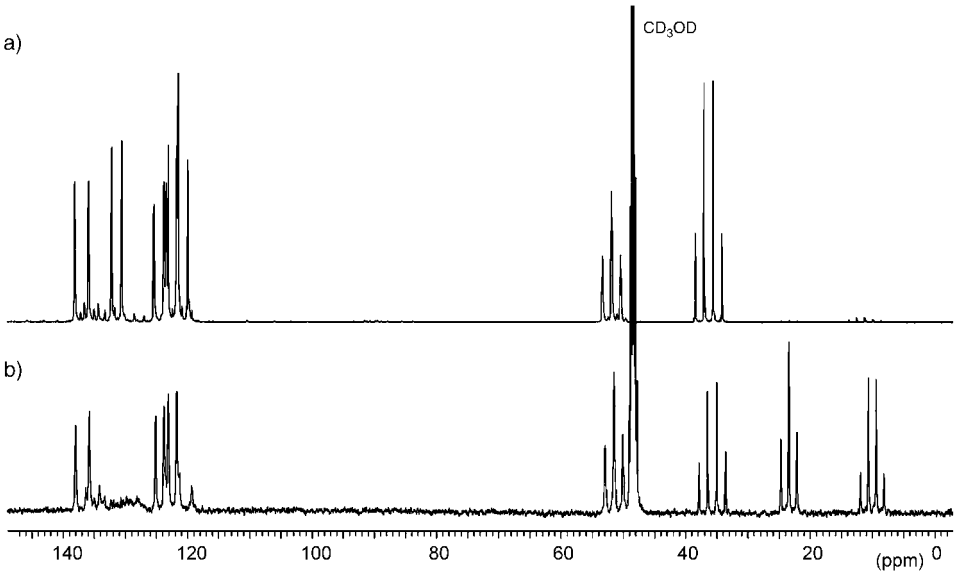


Fig. 6. *High-pressure ^{13}C-NMR spectra* (100 MHz) *of a solution of compound* **3** *recorded* a) *before and* b) *after hydrogenation at 100 bar H_2 pressure* (see *Exper. Part*)

(*s*, 1 H); 7.65 (*s*, 1 H); 6.75 (*m*, 1 H); 5.85 (*s*, 1 H); 5.25 (*m*, 2 H); 3.99 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone)): 136.2; 129.4; 124.3; 114.6; 114.4; 52.3; 35.7. ESI-MS (pos./neg.; H_2O)[4]): 123 (M^+)/87 [BF_4]$^-$. Anal. calc. for $C_7H_{11}BF_4N_2$ (209.98): C 40.03, H 5.28, N 13.34; found: C 40.02, H 5.25, N 13.26.

Method B. 1-(Prop-2-enyl)-1*H*-imidazole (5 ml) was added dropwise to a rapidly stirred suspension of trimethyloxonium tetrafluoroborate (1 equiv.) in hexane (20 ml) at $-78°$ over a period of 10 min. After the initial vigorous gas evolution had ceased, the mixture was allowed to warm to r.t. The product was washed with Et_2O (3×25 ml) and dried *in vacuo* to afford **3** quantitatively. IR: 3158, 3120, 3089, 2977, 1577. ^{1}H-NMR ((D$_6$)acetone): 8.64 (*s*, 1 H); 7.47 (*s*, 1 H); 7.43 (*s*, 1 H); 6.02 (*m*, 1 H); 5.38 (*s*, 1 H); 4.78 (*m*, 2 H); 3.93 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone)): 136.1; 130.6; 124.0; 122.6; 121.1; 51.5; 35.7. ESI-MS (pos./neg.; H_2O)[4]): 123 (M^+)/87 [BF_4]$^-$. Anal. calc. for $C_7H_{11}BF_4N_2$ (209.98): C 40.03, H 5.28, N 13.34; found: C 40.10, H 5.26, N 13.41.

*1,3-Bis(prop-2-enyl)-1*H*-imidazol-3-ium Tetrafluoroborate* (**4**). A mixture of **2** (6.87 g, 30 mmol) and $Na^+BF_4^-$ (3.62 g, 33 mmol) in acetone (80 ml) was stirred at r.t. for 48 h. The resulting solid was filtered off, and the solvent was removed *in vacuo:* 6.37 g (90%) of **4**. Pale-yellow, waxy solid. IR: 3145, 3077, 2941, 2852, 1654. ^{1}H-NMR ((D$_6$)acetone): 9.18 (*s*, 1 H); 7.71 (*s*, 2 H); 6.18 (*m*, 2 H); 5.41 (*m*, 4 H); 5.01 (*m*, 4 H). ^{13}C-NMR ((D$_6$)acetone): 136.2; 129.5; 123.4; 121.8; 52.2. ESI-MS (pos./neg.; H_2O)[4]): 149 (M^+)/87 ([BF_4]$^-$). Anal. calc. for $C_9H_{13}BF_4N_2$ (236.02): C 45.80, H 5.55, N 11.87; found: C 45.75, H 5.47, N 11.76.

*1-Methyl-3-(prop-2-enyl)-1*H*-imidazol-3-ium Tetraphenylborate* (**5**). A suspension of **1** (6.09 g, 30 mmol) and $Na^+BPh_4^-$ (11.29 g, 33 mmol) in acetone (80 ml) was stirred at r.t. for 48 h. The mixture was filtered, and H_2O (5 ml) was added to the filtrate, from which **5** crystallized over a period of 3 d: 11.8 g (89%). Colourless crystals. M.p. 145.1°. IR: 3137, 3082, 3053, 3033, 2999, 2945, 1599. ^{1}H-NMR ((D$_6$)acetone): 8.20 (*s*, 1 H); 7.48 (*s*, 2 H); 7.36 (*t*, 8 H); 6.93 (*t*, 8 H); 6.77 (*t*, 4 H); 6.02 (*m*, 1 H); 5.37 (*m*, 1 H); 4.75 (*m*, 2 H); 3.82 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone): 164.8; 164.3; 163.8; 163.3; 136.4; 136.1; 131.0; 126.0; 125.2; 122.3; 121.4; 120.5; 51.4; 35.9. ESI-MS (pos./neg.; H_2O)[4]): 123 (M^+)/319 ([BPh_4]$^-$). Anal. calc. for $C_{31}H_{31}N_2B$ (442.40): C 84.16, H 7.06, N 6.33; found: C 85.30 H 7.10, N 6.26. X-Ray crystal structure: see *Fig. 1* and *Table 1*.

*1,3-Bis(prop-2-enyl)-1*H*-imidazol-3-ium Tetraphenylborate* (**6**). A mixture of **2** (6.87 g, 30 mmol) and $Na^+BPh_4^-$ (11.29 g, 33 mmol) in acetone (80 ml) was stirred at r.t. for 48 h. The resulting solid was filtered off. H_2O (5 ml) was added to the filtrate, which led to crystallisation of **6** within 3 d: 12.4 g (88%). Colourless

[4]) M^+ Refers to the molecular ion of the cationic part (substituted imidazolium) of the salt.

crystals. M.p. 170.2°. IR: 3139, 3088, 2999, 2945, 1631. ^{1}H-NMR ((D$_6$)acetone): 8.17 (*s*, 1 H); 7.41 (*s*, 2 H); 7.38 (*t*, 8 H); 7.01 (*t*, 8 H); 6.87 (*t*, 4 H); 5.98 (*m*, 1 H); 5.37 (*m*, 1 H); 4.68 (*m*, 2 H). ^{13}C-NMR ((D$_6$)acetone): 164.9; 164.2; 163.6; 163.3; 136.3; 135.9; 131.0; 124.8; 123.2; 122.3; 120.4; 120.1; 51.4. ESI-MS (pos./neg.; $H_2O)^4$): 149 (M^+)/319 ([BPh_4]$^-$). Anal. Calc. for $C_{33}H_{33}N_2B$ (468.44): C 84.61, H 7.10, N 5.98; found: C 84.64, H 7.10, N 5.86. X-Ray crystal structure: see *Fig. 2* and *Table 1*.

Palladium Complex **7**. To a soln. of **1** (406 mg, 1.0 mmol) in CH_2Cl_2 (5.0 ml) was added [$PdCl_2$] (177 mg, 1.0 mmol). The mixture was stirred at r.t. for 2 d, during which time a dark-red suspension formed. The resulting solid was collected by filtration, washed with CH_2Cl_2 (2 × 2 ml), and dried *in vacuo:* 553 mg (95%) of **7**. Dark-red solid. M.p. 134° (dec.). IR: 3138 (arom. C–H); 3091, 3071 (=C–H); 2973 (aliph. C–H); 1632 (C=C). ^{1}H-NMR ((D$_6$)DMSO): 9.16 (*s*, 1 H); 7.65 (*m*, 2 H); 5.91 (*m*, 1 H); 5.19 (*m*, 1 H); 4.77 (*m*, 2 H); 3.78 (*s*, 3 H). ^{13}C-NMR ((D$_6$)-DMSO): 136.5; 132.1; 124.1; 121.7; 120.7; 51.4; 36.4. Anal. calc. for $C_{14}H_{22}Br_2Cl_2N_4Pd$ (583.49): C 28.82, H 3.80, N 9.60; found: C 28.80, H 3.78, N 9.69. X-Ray crystal structure: see *Fig. 3* and *Table 1*.

Palladium Complex **8**. Prepared from **2** (458 mg, 1.0 mmol) and [$PdCl_2$] (177 mg, 1.0 mmol) in analogy to **7**. Dark-red solid. Yield: 553 mg (95%). M.p. 58°. IR: 3124 (arom. C–H); 3091 (=C–H); 2981, 2960 (aliph. C–H); 1644 (C=C). ^{1}H-NMR ((D$_6$)DMSO): 9.28 (*s*, 1 H); 7.78 (*s*, 2 H); 6.02 (*m*, 2 H); 5.35 (*m*, 4 H); 5.27 (*m*, 4 H). ^{13}C-NMR ((D$_6$)DMSO): 136.7; 132.2; 123.5; 122.1; 51.4. Anal. calc. for $C_{18}H_{26}Br_2Cl_2N_4Pd$ (635.56): C 34.02, H 4.12, N 8.81; found: C 34.08, H 4.18, N 8.79.

Palladium Complex **9**. To a soln. of **7** (291.5 mg, 0.5 mmol) in MeCN (10 ml) was added '2,2′-azobis(isobutyronitrile)' (AIBN; 2 mg), and the mixture was stirred at 80° for 10 h. Upon standing at r.t. for 24 h, orange cubic crystals of **9** formed, which were collected by filtration: 20 mg (9%). M.p. 249° (dec.). IR: 3138 (arom. C–H); 2951 (aliph. C–H). ^{1}H-NMR ((D$_6$)DMSO): 8.14 (*s*, 1 H); 7.20 (*s*, 1 H); 7.16 (*s*, 1 H); 3.72 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 137.7; 131.2; 124.2; 32.4. Anal. calc. for $C_8H_{12}Br_2N_4Pd$ (430.44): C 22.32, H 2.81, N 13.01; found: C 22.08, H 2.84, N 13.09. X-Ray crystal structure: see *Figs. 4* and *5*, and *Table 1*.

*1-Methyl-3-(2-phenylpropyl)-1*H*-imidazol-3-ium Trifluoromethanesulfonate* (**10**). To a suspension of **1** (2.03 g, 10 mmol) in benzene (20 ml) was added an excess of CF_3SO_3H ('triflic acid'; 30 ml), and the mixture was heated to reflux for 6 h. After cooling to 0°, the mixture was neutralized (pH 7.1) with aq. 40% NaOH soln., and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. phases were washed with sat. aq. NH_4Cl soln., dried ($MgSO_4$), and concentrated to afford **10**: 0.8 g (22%). Pale-yellow liquid. IR: 3151 (arom. C–H), 2969 (aliph. C–H), 1574; 1256, 1163, 1029. ^{1}H-NMR (CD_3CN): 8.32 (*s*, 1 H); 7.37 (*s*, 1 H); 7.35 (*s*, 1 H); 7.30–7.34 (*m*, 2 H); 7.21–7.27 (*m*, 3 H); 4.25–4.40 (*m*, 2 H); 3.76 (*s*, 3 H); 3.27 (*m*, 1 H); 1.32 (*d*, 3 H). ^{13}C-NMR (CD_3CN): 137.8; 124.8; 123.3; 123.1; 122.1; 119.4; 118.5; 51.5; 36.5; 31.8; 13.7. ^{19}F-NMR (CD_3CN): −79.7. ESI-MS (pos./neg.; $CH_2Cl_2)^4$): 201 (M^+)/149 ([CF_3SO_3]$^-$). Anal. calc. for $C_{14}H_{17}F_3N_2O_3S$ (350.58): C 47.99, H 4.89, N 7.99; found: C 47.68, H 5.00, N 7.89.

Hydrogenation Studied by High-Pressure NMR Spectroscopy. Samples were prepared under O_2-free conditions using *Schlenk* techniques. CD_3OD was purchased from *Cambridge Isotope Laboratories*. Hyrogenation reactions were carried out *in situ* in a medium-pressure sapphire NMR tube (10 mm) [39] under 100 bar of H_2 pressure. ^{13}C-NMR Spectra were recorded on a *Bruker DRX-400* spectrometer at 100 MHz.

X-Ray Crystal-Structure Analyses. Suitable crystals were obtained at ambient temperature from acetone/H_2O 10:1 (for **5** and **6**), from MeCN/Et_2O 10:1 (for **7**), and from CH_2Cl_2 (for **9**). The single crystals were mounted on a *KUMA KM4/Sapphire CCD* diffractometer. Data reduction was performed with CrysAlis RED [40]. Structure solution and refinement were performed with the SHELX97 software package [41], and graphical representations of the structures were made with ORTEP32 [42]. Structures were solved by direct methods and successive interpretation of the difference *Fourier* maps, followed by full-matrix least-squares refinement (against F^2). All non-H-atoms were refined anisotropically. H-atoms were placed in their geometrically generated positions, and refined with a riding model. An adsorption correction (DELABS) was applied for **7** and **9**. In **5**, atoms C(5) and C(6) were split over two positions, with an occupancy factor of 0.62(2) for site A. In **7**, only C(6) was split over two positions (occupancy factor 0.51(2) for site A). The disorder for both Cl- and Br-atoms was solved for both positions, which led to the occupancy factor, followed by anisotropic refinement. The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as deposition numbers CCDC-257944 to -257947. Copies of the data can be obtained, free of charge, by application to *CCDC*, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request). Details of the structure determinations of compounds **5**–**7** and **9** are summarised in *Table 2*.

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Table 2. *Crystallographic Data and Details of Structure Determinations*

	5	**6**	**7**	**9**
Formula	$C_{31}H_{31}BN_2$	$C_{33}H_{33}BN_2$	$C_{14}H_{22}Br_2Cl_2N_4Pd$	$C_8H_{12}Br_2N_4Pd$
M_r	442.39	468.42	583.48	430.44
Crystal size [mm]	$0.10 \times 0.15 \times 0.18$	$0.11 \times 0.14 \times 0.17$	$0.05 \times 0.10 \times 0.12$	$0.09 \times 0.10 \times 0.12$
T [K]	140	140	140	140
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/c$
a [Å]	9.6409(8)	10.8209(6)	8.870(2)	5.3852(5)
b [Å]	17.647(2)	17.478(1)	12.110(4)	11.815(1)
c [Å]	15.3633(8)	13.8763(9)	9.908(4)	9.7595(8)
α [°]	90	90	90	90
β [°]	104.137(7)	90.804(5)	101.98(3)	98.139(7)
γ [°]	90	90	90	90
V [Å^3]	2534.6(3)	2624.2(3)	1041.1(6)	614.73(9)
Z	4	4	2	2
Density [Mg/m^3]	1.159	1.186	1.861	2.325
Θ Range [°]	$3.07 \leq \Theta \leq 25.03$	$3.16 \leq \Theta \leq 25.03$	$3.27 \leq \Theta \leq 25.03$	$3.45 \leq \Theta \leq 25.03$
μ [mm^{-1}]	0.067	0.068	4.989	7.983
Reflections measured	14982	15423	6349	3355
Goodness-of-fit on F^2	0.819	0.918	1.132	1.135
Unique reflections [$I > 2\sigma(I)$]	4250	4385	1844	1084
R_{int}	0.0607	0.0374	0.0422	0.0272
Final $R1$, $wR2$[$I > 2\sigma(I)$]	0.0422, 0.0641	0.0362, 0.0776	0.0419, 0.1050	0.0207, 0.0529
R (all data)	0.1285, 0.0810	0.0627, 0.0852	0.0542, 0.1133	0.0215, 0.0533
Largest diff. peak and hole	0.146, −0.170	0.157, −0.226	1.082, −0.563	0.418, −0.711

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