N,N'-Di(alkyloxy)imidazolium Salts: New Patent-free Ionic Liquids and NHC Precatalysts

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

1-Hydroxyimidazole-3-oxides (2-H, 2-Me) were alkylated with $(RO)_2SO_2$ (R = Me, Et) to give the new 1,3-di(alkyloxy)imidazolium cations which were isolated as hexafluorophosphates. Ion metathesis yielded new hydrophobic ionic liquids (bis(trifluoromethanesulfonyl)imides, tris(pentafluoroethyl)trifluorophosphates). Bromination afforded 2-bromo derivatives which were converted to Ni and Pd *N*-heterocyclic carbene complexes by oxidative insertion. Fifteen crystal structures were determined by X-ray diffraction. The *N*-alkyloxy groups are twisted out of the imidazole ring plane and adopt either *syn* or *anti* conformations in the solid state.

Key words: Carbene, Imidazolium Salt, Ionic Liquid, NHC, Nickel, Palladium

Introduction

Imidazoles and, in particular, imidazolium salts are extremely important and versatile compounds. In recent years, they have found manifold uses in the fields of ionic liquids (ILs), as electrolytes, and as carbene ligand precursors for transition metal complexes. As a consequence, tremendous commercial interest in this group of compounds has developed which is reflected by the immense number of patents granted. Needless to say that these patents exhibit varying degrees of inventive ingenuity and originality.

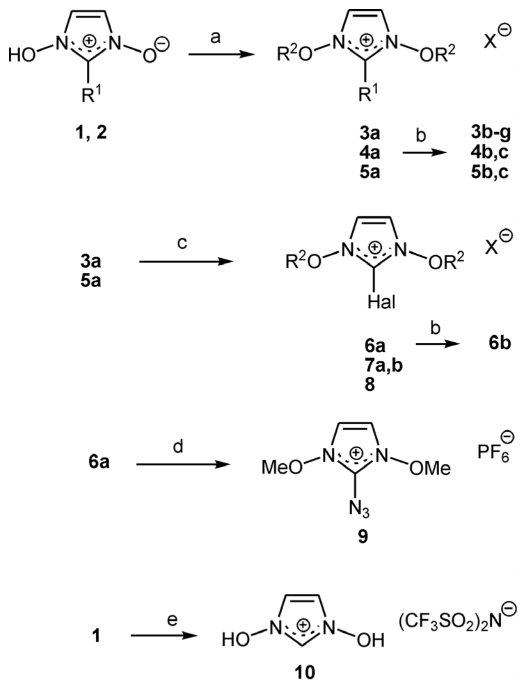
Liquid imidazolium salts have been long known [1 – 5] and praised for industrial applications due to their low volatility, although their observed antiseptic properties [1] and toxicity [6] make their postulated environmental benignity appear questionable. Nevertheless, their potential is huge, and exciting developments can be expected such as task-specific [7, 8] and organometallic ILs [9]. In particular, new hydrophobic ionic liquids, containing bis(trifluoromethanesulfonyl)imide ('triflimide') [10] or tris(pentafluoroethyl) trifluorophosphate ('FAP') anions [11, 12], are promising reaction and extraction media.

On the other hand, imidazolium salts are easily converted to *N*-heterocyclic carbenes ('NHC') [13 – 18] which are valuable ligands for homogeneous catalysts for cross-coupling reactions [19]. Typically, the conversion to carbene complexes is effected either by metallation, especially lithiation, and subsequent transmetallation [20 – 22], or by oxidative insertion [23 – 26]. Therefore, imidazolium-based ILs could serve both as solvents and catalysts [27 – 32]. A catalytically active organometallic IL has been described previously [33].

In this work we present a new class of imidazolium salts and patent-free ionic liquids as well as 2-halogen derivatives thereof and derived NHC complexes.

Results and Discussion

1-Hydroxyimidazole-3-oxides **1** and **2** were readily prepared [34, 35] and alkylated to give the not yet described 1,3-di(alkyloxy)imidazolium salts which could be conveniently purified by precipitation as hexafluorophosphates from aqueous solution, as exemplified by compounds **3a**, **4a**, and **5a** (Scheme 1). These salts were then transformed into new ILs by ion metathesis. Thus, the hydrophobic triflimides **3b**, **4b**, **5b**, and **6b** were obtained in high purity by reaction of the corresponding hexafluorophosphates with lithium triflimide. Treatment of **3a** and **4a** with potassium FAP afforded the hydrophobic salts **3c** and **4c** containing the FAP anion. Compound **4c** was actually crystalline but with a melting point below 100 °C still qualified as an IL. These anions impart highly desirable properties on the ILs, such as low residual water content, hydrolytic and electrochemical stability, and low viscosity. The IL **3b** was subjected to more detailed investigation; it exhibited a relatively large electrochemical window (from −1.5 to +0.5 V *versus* Ag/AgCl by cyclic voltammetry). Dynamic viscosity (η) and specific conductivity (σ) data at different temperatures are summarized in Table 1. For comparison, 1,3-diethylimidazolium triflimide features an η of 35 cP and a σ of 8.5 mS cm^{-1} at 20 °C [10]. Thermal stability was assessed by differential scanning calorimetry, and the IL **3b** was found to be stable up to 160 °C.



a. $(R^2O)_2SO_2$, NH_4PF_6; b. ion metathesis; c. Br_2 or ICl; d. NaN_3; e. $(CF_3SO_2)_2NH$.

	R^1	R^2	X
1	H		
2	Me		
3a	H	Me	PF_6
3b	H	Me	Tf_2N
3c	H	Me	$P(C_2F_5)_3F_3$
3d	H	Me	$PhBF_3$
3e	H	Me	*t*-BuC_2BF_3
3f	H	Me	Br
3g	H	Me	ClO_4
4a	Me	Me	PF_6
4b	Me	Me	Tf_2N
4c	Me	Me	$P(C_2F_5)_3F_3$
5a	H	Et	PF_6
5b	H	Et	Tf_2N
5c	H	Et	BF_4
6a	Br	Me	PF_6
6b	Br	Me	Tf_2N
7a	Br	Et	PF_6
7b	Br	Et	Br
8	I	Me	$(PF_6)_{2/3}Cl_{1/3}$

Scheme 1.

Table 1. Conductivity σ and viscosity η of 1,3-dimethoxyimidazolium bis(trifluoromethanesulfonyl)imide (**3b**).

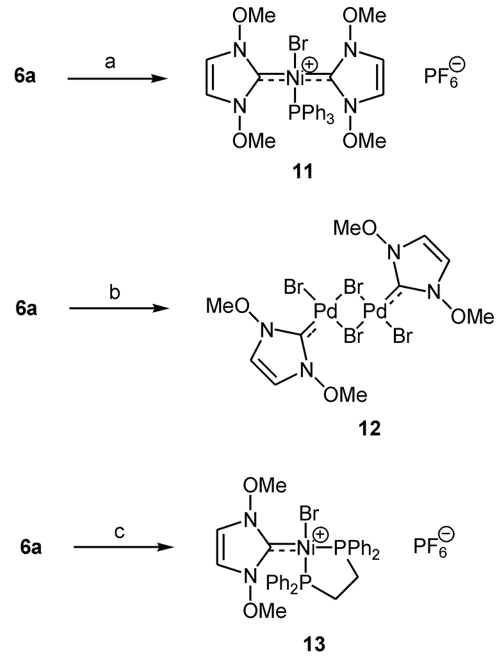
T [°C]	σ [mS cm^{-1}]	η [mPa s]	T [°C]	σ [mS cm^{-1}]	η [mPa s]
30	4.3	94.3	70	16.3	22.1
40	6.9	60.9	80	20.0	16.9
50	9.7	42.0	90	24.0	13.8
60	12.9	29.9			

Furthermore, the triflimides are valuable intermediates for further ion exchange when other pathways are not viable. Thus, sulfuric acid liberated from **3b** the corresponding amine and gave the water-soluble hydrogen sulfate which, in turn, could be converted to the phenyltrifluoroboronate **3d** and *tert*-butylethynyltrifluoroboronate **3e** which also qualify as ILs. Analogous treatment of **3b** with hydrobromic acid yielded the bromide **3f** which was transformed into the perchlorate **3g** by the silver salt method.

The bromination of imidazolium cations reportedly occurs in the 4,5-positions [36], but since bromination of 1-hydroxyimidazole-3-oxide gave the 2-bromo derivative [37], we anticipated that in our case halogenation would also yield the 2-halogenoimidazolium salts as functionalized building blocks for further derivatization. Thus, addition of bromine to an aqueous solution of 1,3-dialkoxyimidazolium salts **3a** or **5a** resulted at first in precipitation of an adduct of yet unknown composition which upon further addition of bromine and sodium carbonate proceeded to give the desired 2-bromoimidazolium salts **6a** and **7a**. The reaction did not work well when acetate was used as a buffer. The analogous reaction with iodine was not successful, but iodination took place when iodine chloride was used instead to afford the crystalline 2-iodo compound **8**. The novel azide **9** was obtained by reaction of the bromo compound **6a** with sodium azide. Arylazides can act as ligands on their own in azido-metal complexes or as sources of the nitrene fragment [38], as precursors for iminophosphines [39] and iminoimidazolines and derived complexes [40 – 42].

Unexpectedly, even the polar parent compound, 1-hydroxyimidazole-3-oxide (**1**), liquefied on contact with bis(trifluoromethanesulfonyl)amine to give the Brønsted-acidic IL 1,3-dihydroxyimidazolium triflimide (**10**), a novel protic hydrophobic IL. To mention a discovery which is not exactly within the scope of this paper but which we like to report anyway, we found that the highly polar 1,3-diaminoimidazolium chloride [43] also yielded a hydrophobic IL on contact with lithium bis(trifluoromethanesulfonyl)imide. Another fortunate observation in the course of this work which we like to disclose here was that by simple combination of commercially available solids, *i. e.* 1-ethyl-3-methylimidazolium chloride and potassium benzenetrifluoroboronate, a new IL was produced. It is also noteworthy that a few liquid 1-alkyloxy-3-alkylimidazolium salts, *e. g.* 1-methoxy-3-methylimidazolium iodide, 1-ethoxy-3-methylimidazolium tosylate, or 1-benzyloxy-3-butylimidazolium bromide, have been observed earlier [44]. Finally, imidazolium-based ILs with alkyloxyalkyl substituents have been reported [45] but, to the best of our knowledge, the present di(alkyloxy)imidazolium ions have not yet been described, or claimed in the patent literature. In preliminary experiments, we also looked at the possible use of bulky silyloxy- and trityloxy-substituted imidazolium salts for the synthesis of free carbenes. These results will be communicated in due course.

Of course, the 2-bromoimidazolium salts lend themselves to the construction of metal-NHC complexes by oxidative addition to metal(0) precursors (Scheme 2). Thus, $Ni(cod)_2$ reacted with one equivalent of **6a** in the presence of two equivalents of triphenylphosphine [24] to afford the mixed nickel(II) bis(carbene)/phosphine complex **11**. As a result of multiple ligand exchange, the reaction is obviously more complex than a sole stoichiometric insertion of the cod/phosphine system which would lead to a monocarbene species. Evidently, the second carbene must originate from another Ni(0)/Ni(II) oxidation cycle and replace a phosphine molecule. Similar substitution of phosphine by NHC has been observed in related Ni complexes [46]. Presumably, the electron-rich carbene further facilitates the ligand exchange.



a. $Ni(cod)_2$, PPh_3; b. $Pd(dmdba)_2$; c. $Ni(cod)_2$, dppe.

Scheme 2.

Reaction of $Pd(tmdba)_2$ with the carbene-forming oxidant **6a** afforded the binuclear palladium complex **12**. Again, this dimer is not the primary product of the insertion since four equivalents of **6a** are required to contribute the necessary bromide ions. The fate of the other imidazolium units is unclear at this point. An analogous complex with 1,3-dialkylimidazolin-2-ylidene ligands has been described previously [30].

In contrast, $Ni(cod)_2$ in the presence of 1,2-bis(diphenylphosphino)ethane gave the expected product. In this case, it is likely that one cod ligand was replaced by the bidentate phosphine followed by oxidative addition of **6a**, and the Ni-NHC complex **13** was obtained. However, the compound $Ni(dppe)Br_2$ was isolated as a byproduct and characterized by X-ray crystal structure determination. Therefore, bromide/phosphine ligand scrambling must have been involved as well. The structure of a CH_2Cl_2 solvate of this byproduct has been reported earlier [47].

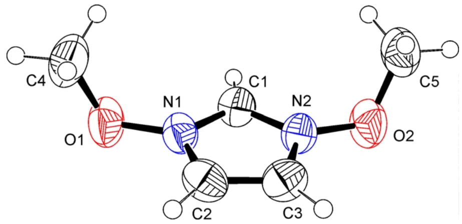


Fig. 1. The molecular structure of the cation in **3a** (*syn* conformation) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

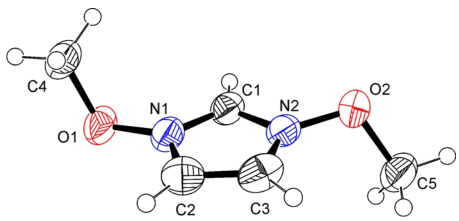


Fig. 2. The molecular structure of the cation in **3a** (*anti* conformation) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

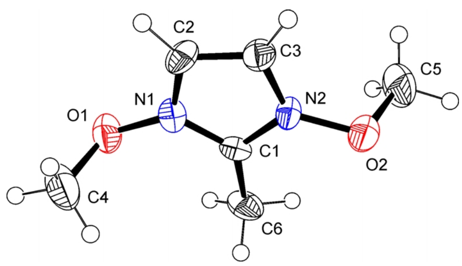


Fig. 3. The molecular structure of the cation in **4a** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

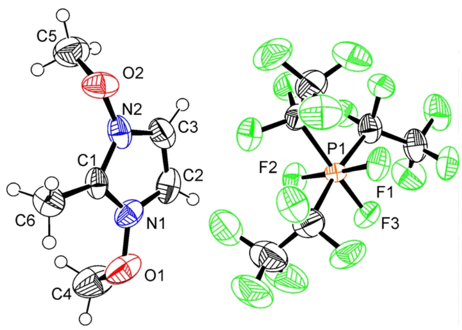


Fig. 4. The molecular structure of the ionic components in **4c** showing part of the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

The catalytic activity of these NHC complexes has yet to be tested.

Due to the high crystallinity of the complexes and their precursors, a number of crystal structures could

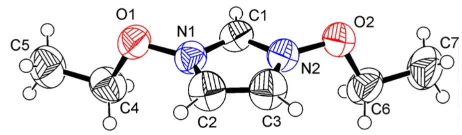


Fig. 5. The molecular structure of the cation in **5a** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

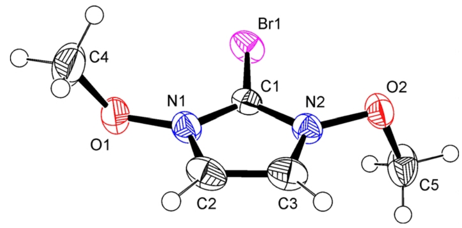


Fig. 6. The molecular structure of the cation in **6a** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

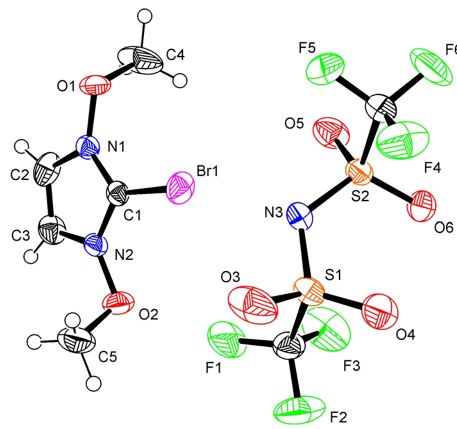


Fig. 7. The molecular structure of the ionic components in **6b** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

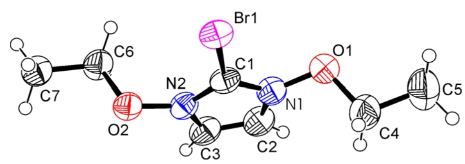


Fig. 8. The molecular structure of the cation in **7b** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

be determined by X-ray diffraction. Key bond lengths in 1,3-di(alkyloxy)imidazolium cations are: N–O typically 1.36 to 1.38 Å, C1–N 1.32 to 1.33 Å, C2–N 1.36 to 1.37 Å, C2–C3 1.33 to 1.36 Å, C–Br 1.82 Å. Typical values of N–C–N angles are around 105°. Some of these parameters are slightly different in the carbene complexes: C1–N 1.32 to 1.35 Å, C2–N 1.37 to 1.38 Å,

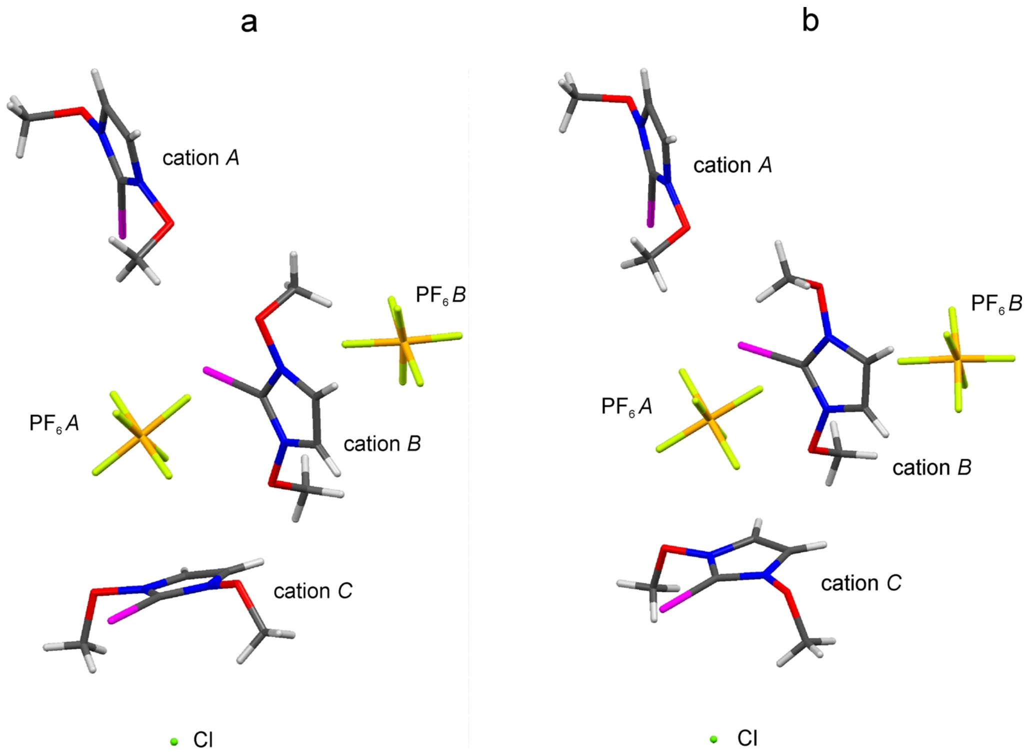


Fig. 9. Packing diagram of the asymmetric unit of **8** at (a) r. t. and (b) at −40 °C.

N–C–N 101° (with Ni) and 103° (with Pd). The tetrafluoroborate and FAP ions in **5c** and **4c** are disordered, and the hexafluorophosphate ions are disordered in most of the structures. Interestingly, we observed two distinct conformations of the alkyloxy groups with respect to the imidazolium ring plane. They are twisted out of the plane in either *syn* or *anti* conformations. We were fortunate to obtain single crystal data of two polymorphs of 1,3-dimethoxyimidazolium hexafluorophosphate **3a**, one adopting the *syn* conformation with MeO-plane angles of 79.9° and 82.6° (Fig. 1) and the other *anti* with respective angles of 88.8° and 63.2° (Fig. 2). X-ray powder diffraction data of three batches of **3a** confirmed the dominance of the *syn* conformer in the bulk material, though in varying proportions. By temperature-dependent XRPD it was demonstrated that the conformation does not change between 173 and 233 K (the temperatures at which the single crystals were measured). The analogous 2-methyl compound **4a**, however, occurred only in *anti* conformation (MeO-plane angles of 82.0° and 85.2°) (Fig. 3), since no phase transition between 133 and 273 K could be observed by DSC and XRPD. The cation in the FAP salt **4c** displayed again the *syn* geometry (MeO-plane angles of 81.8° and 72.8°) (Fig. 4). The 1,3-diethoxyimidazolium hexafluorophosphate **5a** also exhibited the *syn* conformation (CH_2O-plane angles of 84.0° and 78.7°) (Fig. 5). The 2-bromo derivative **6a** crystallized as the *anti* conformer (MeO-plane angles of 89.5° and 68.3°) (Fig. 6). The related triflimide **6b** showed two ion pairs in the asymmetric unit, with both cations in *anti* orientation (MeO-plane angles of 81.4°, 81.8°, and 79.3°, 87.3°). The S–N bond lengths are between 1.542 and 1.608 Å. The S–N–S angles are 124.5° and 124.9° (Fig. 7). In crystals of 2-bromo-1,3-diethoxyimidazolium bromide **7b** the substituents are also *anti* oriented (CH_2O-plane angles of 80.3° and 70.9°) (Fig. 8). Surprisingly, a temperature dependence of the conformation was observed in crystals of the 2-iodo compound **8**. The asymmetric unit contains three cations, all of which adopt *syn* conformations at 25 °C (MeO-plane angles in cation *A*: 88.9°, 87.3°; cation *B*: 85.2°, 83.9°; cation *C*: 88.2°, 85.3°) (Fig. 9a), whereas one of the cations (cation *B*) switches to an *anti* conformation at −40 °C (MeO-plane angles in cation *A*: 87.6°, 86.8°; cation *B*: 85.1,

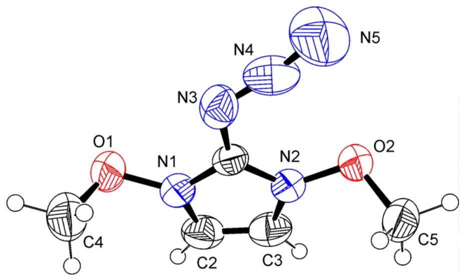


Fig. 10. The molecular structure of the cation in **9** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

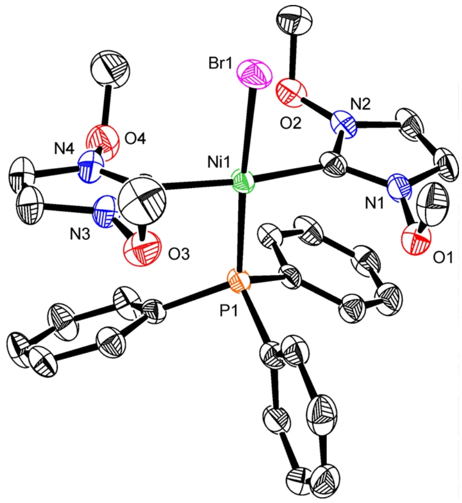


Fig. 11. The molecular structure of the cationic nickel-carbene complex **11** showing part of the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and the anion are omitted for clarity.

84.2°; cation *C*: 88.3°, 85.4°) (Fig. 9b). In the crystal structure of the azide **9**, the C–N–N and N–N–N angles have values of 115.8° and 170.3°, the methoxy groups are *syn* oriented (MeO-plane angles of 88.7° and 66.5°) (Fig. 10).

In the molecular structure of the Ni-NHC complex **11**, the carbene ligands occupy *trans* positions. The square planar configuration around the central Ni atom is noticeably distorted. Thus, the C–Ni–C angle is 170.6° and P–Ni–Br is 173.3°, whereas both C–Ni–Br angles are 89.5°, and C–Ni–P angles are 90.0° and 92.1°, respectively. The mean distances of the ligands from the least-squares plane are 0.14 Å (carbene C atoms on one side, P and Br on the other side of the plane). As in related complexes of this type [48], the torsion angles between the ligand plane and the carbene planes are 81.8° and 82.4°, resulting

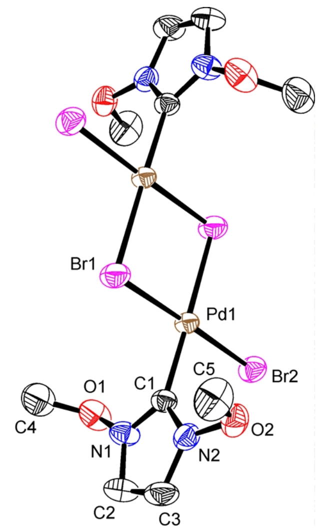


Fig. 12. The molecular structure of the dinuclear palladium-carbene complex **12** showing part of the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and the solvent molecule are omitted for clarity.

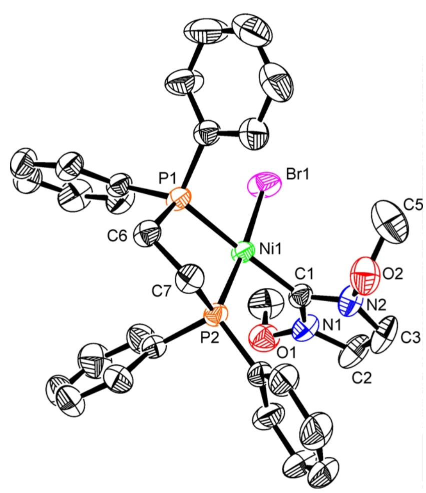


Fig. 13. The molecular structure of the cationic nickel-carbene complex **13** showing part of the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms and the anion are omitted for clarity.

in a dihedral angle between the two carbenes of 15.8°. The Ni–C bond lengths are 1.899 and 1.893 Å, Ni–P is 2.181 Å, and Ni–Br is 2.341 Å. The methoxy groups of the imidazolylidene rings adopt *syn* conformations and are rotated out of the ring planes by 72.4°, 89.9° and 75.6°, 83.6°, respectively (Fig. 11).

In contrast, the μ-Br-bridged dimeric Pd-NHC complex **12** possesses a center of inversion and, therefore, the four-membered Pd–Br–Pd–Br ring is perfectly planar. The Pd–Br–Pd and Br–Pd–Br angles within the ring are 91.4° and 88.6°, respectively. The Pd atoms coordinate in square planar geometry with mean deviations of the ligands from the plane of only 0.03 Å. The Pd–C distance is 1.956 Å, Pd–Br is 2.405 Å, and the Pd–μ-Br bond lengths are 2.450 and 2.516 Å. The ring plane and the ligand plane are slightly tilted by 0.92°. The imidazolylidene rings are almost perpendicular to the molecular reference plane with a torsion angle of 89.8°. Again, the methoxy groups adopt *syn* conformations with out-of-plane angles of 80.1° and 85.0° (Fig. 12).

The Ni-NHC complex **13** again presents an approximately square planar environment around the Ni atom. Distances to the coordinating ligands are Ni–C 1.893, Ni–Br 2.327, Ni–P 2.146 and 2.202 Å. Mean deviation from the ligand plane is 0.07 Å, angles C–Ni–P1 and Br–Ni–P2 are 173.3° and 175.6°, respectively. Other angles are C–Ni–Br 92.4°, C–Ni–P2 91.8°, P1–Ni–Br 90.8°, and the P–Ni–P bite angle of the chelating dppe ligand is 85.3°. The five-membered chelate ring is nearest to a C7-envelope with the C6 and C7 atoms lying out of the coordination plane by 0.31 and 0.89 Å. The torsion angle between the imidazolylidene ring and the ligand plane is 82.8°, and the methoxy groups adopt a *syn* orientation (MeO-plane angles 86.1° and 88.7°) (Fig. 13).

In summary, new imidazole-based ILs and NHC complexes were prepared by facile and inexpensive processes. The 1,3-di(alkyloxy)imidazolium salts open a plethora of possibilities in the fields of IL research and catalysis. Although the synthetic potential has not yet been fully exploited and the experimental procedures have not yet been fully optimized, it is clear that a new chapter in imidazole chemistry has been written.

Experimental Section

The starting 1-hydroxyimidazole-3-oxides **1** and **2** were prepared according to [34]. The crystal structures were determined using Nonius KappaCCD and STOE IPDS 2 diffractometers. The experimental conditions and crystallographic data are listed in Table 2. NMR spectra were recorded with Bruker AC 300 and Varian Unity 500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to internal TMS, whereas ^{31}P and ^{19}F spectra were calibrated with external 85 % H_3PO_4 and CCl_3F, respectively. IR spectra were obtained with a Nicolet 5700 FT instrument.

*General procedure for the preparation of compounds **3a**, **4a**, and **5a***

A mixture of dimethyl sulfate (15.2 mL, 0.16 mol) and freshly prepared 1-hydroxyimidazole-3-oxide (8.0 g, 0.08 mol) was stirred at ambient temperature for 1 h. Then $NaHCO_3$ (6.7 g, 0.08 mol) was added and stirring was continued for 12 h. Addition of H_2O (20 mL) and more stirring yielded a clear solution to which NH_4PF_6 (13.0 g, 0.08 mol) was added. The precipitate was ultrasonicated for 1 h, filtered, and recrystallized from MeOH to give **3a** as a colorless powder (16.0 g; 73 %). The compounds **4a** (from 1-hydroxy-2-methylimidazole-3-oxide), and **5a** (using diethyl sulfate) were prepared on a smaller scale with similar yields. Crystals of the imidazolium hexafluorophosphates suitable for X-ray diffraction studies were obtained by slow evaporation of MeOH solutions.

*1,3-Dimethoxyimidazolium hexafluorophosphate (**3a**):* m. p. 83–84 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.26 (s, 6H), 8.29 (d, J = 2.1 Hz, 2H), 10.29 (t, J = 2.1 Hz, 1H). – IR (neat): ν = 3163, 1556, 1455, 1015, 944, 827, 718, 706, 582, 555 cm^{-1}.

*1,3-Dimethoxy-2-methylimidazolium hexafluorophosphate (**4a**):* m. p. 128–129 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.59 (s, 3H), 4.16 (s, 6H), 8.19 (s, 2H). – IR (neat): ν = 3155, 1595, 1460, 1444, 1117, 964, 944, 820, 733, 709, 650, 555 cm^{-1}.

*1,3-Diethoxyimidazolium hexafluorophosphate (**5a**):* m. p. 99–102 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.32 (t, J = 7.0 Hz, 6H), 4.49 (q, J = 7.0 Hz, 4H), 8.26 (s, 2H), 10.26 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 13.0 (2C), 78.4 (2C), 117.9 (2C), 130.4. – IR (neat): ν = 3155, 1478, 1446, 1395, 1119, 1006, 810, 743, 726, 598, 554 cm^{-1}.

*General procedure for the preparation of compounds **3b**, **4b**, **5b**, and **6b***

A mixture of **3a** (11.0 g, 0.04 mol) and lithium bis (trifluoromethanesulfonyl)imide (11.5 g, 0.04 mol) in H_2O (70 mL) was ultrasonicated for 1 h and then extracted with CH_2Cl_2. The extract was dried with anhydrous Na_2SO_4 and filtered. After removal of the solvent the residue was dried by means of a vacuum pump to yield **3b** as a colorless oil (12.8 g; 78 %). The compounds **4b**, **5b**, and **6b** were prepared accordingly on a smaller scale with similar yields.

*1,3-Dimethoxyimidazolium bis(trifluoromethanesulfonyl) imide (**3b**):* n_D^{20} = 1.4240. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.25 (s, 6H), 8.28 (s, 2H), 10.29 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.5 (2C), 117.1 (2C), 119.6 (q, J_{C-F} = 320 Hz, 2C), 129.5. – IR (neat): ν = 3138, 1666, 1556, 1457, 1346, 1328, 1177, 1132, 1052, 1013, 943, 845, 789, 612, 569, 510 cm^{-1}.

Table 2. Crystal data and structure refinement details.

Compound	**3a** (*syn*)	**3a** (*anti*)	**4a**	**4c**	**5a**	**5c**
CCDC no.	629553	629554	629555	629556	629557	629558
Chemical formula	$C_5H_9F_6N_2O_2P$	$C_5H_9F_6N_2O_2P$	$C_6H_{11}F_6N_2O_2P$	$C_{12}H_{11}F_{18}N_2O_2P$	$C_7H_{13}F_6N_2O_2P$	$C_7H_{13}BF_4N_2O_2$
M_r	274.11	274.11	288.14	588.20	302.16	244.00
Crystal syst., space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1$	monoclinic, $P2_1/n$	orthorhombic, *Pbca*	orthorhombic, *Pbca*
a [Å]	6.5168(3)	7.082(2)	6.4340(14)	9.4101(4)	10.1450(3)	9.2625(12)
b [Å]	11.6929(3)	16.565(3)	11.830(2)	13.8039(8)	14.9480(5)	14.668(2)
c [Å]	14.3448(5)	9.0009(2)	8.1290(13)	16.2881(9)	17.2941(5)	16.834(4)
β [deg]	95.202(2)	99.75(2)	111.684(14)	102.951(3)	90	90
V [Å^3]	1088.58(7)	1040.7(4)	574.94(19)	2061.94(19)	2622.61(14)	2287.1(7)
Z	4	4	2	4	8	8
D_x [g cm^{-3}]	1.673	1.750	1.669	1.895	1.531	1.417
μ [mm^{-1}]	0.33	0.34	0.31	0.31	0.28	0.14
$F(000)$ [e]	552	552	292	1160	1232	1008
Crystal form, color	plate, colorless	plate, colorless	plate, colorless	plate, colorless	prism, colorless	plate, colorless
Crystal size [mm^3]	$0.3 \times 0.2 \times 0.08$	$0.28 \times 0.24 \times 0.04$	$0.44 \times 0.22 \times 0.10$	$0.3 \times 0.15 \times 0.07$	$0.30 \times 0.15 \times 0.08$	$0.34 \times 0.32 \times 0.10$
Diffractometer	Nonius KappaCCD	STOE IPDS 2	STOE IPDS 2	Nonius KappaCCD	Nonius KappaCCD	STOE IPDS 2
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Data collection method	ϕ- and ω-scans	rotation method	rotation method	ϕ- and ω-scans	ϕ- and ω-scans	rotation method
Temperature [K]	233(2)	173(2)	173 (2)	233(2)	233(2)	173(2)
θ_{max} [deg]	25.0	24.7	24.7	23.0	24.0	24.8
h, k, l Ranges	$\pm 7, \pm 13, -16 \rightarrow 17$	$\pm 8, \pm 19, \pm 10$	$\pm 7, \pm 13, -8 \rightarrow 9$	$-9 \rightarrow 10, -14 \rightarrow 15, \pm 17$	$\pm 11, \pm 17, -18 \rightarrow 19$	$\pm 10, \pm 17, \pm 19$
Absorption correction	none	multi-scan	none	none	none	none
Measured reflections	6243	6134	3225	9645	12813	10943
Independent reflections	1889 ($R_{int} = 0.023$)	1758 ($R_{int} = 0.068$)	1778 ($R_{int} = 0.025$)	2869 ($R_{int} = 0.044$)	2050 ($R_{int} = 0.038$)	1942 ($R_{int} = 0.102$)
Observed reflections [$I \geq 2\sigma(I)$]	1615	1093	1527	2304	1565	1145
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
Data, restraints, parameters	1889, 0, 203	1758, 0, 147	1778, 1, 237	2869, 0, 416	2050, 0, 218	1942, 8, 184
R [$F^2 \geq 2\sigma(F^2)$]	$R_1 = 0.0392$, $wR_2 = 0.1034$	$R_1 = 0.0737$, $wR_2 = 0.1444$	$R_1 = 0.0352$, $wR_2 = 0.0589$	$R_1 = 0.0915$, $wR_2 = 0.2394$	$R_1 = 0.0449$, $wR_2 = 0.1084$	$R_1 = 0.0624$, $wR_2 = 0.1066$
R (all data)	$R_1 = 0.0466$, $wR_2 = 0.1083$	$R_1 = 0.1308$, $wR_2 = 0.1671$	$R_1 = 0.0457$, $wR_2 = 0.0620$	$R_1 = 0.1045$, $wR_2 = 0.2538$	$R_1 = 0.0634$, $wR_2 = 0.1172$	$R_1 = 0.1213$, $wR_2 = 0.1218$
Goodness of fit	1.07	1.09	1.08	1.12	1.06	1.07
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.26, −0.25	0.63, −0.24	0.12, −0.13	1.21, −0.37	0.23, −0.20	0.23, −0.16

Table 2 (continued).

Compound	**6a**	**6b**	**7b**	**8** (298 K)	**8** (233 K)	**9**
CCDC no.	629559	629560	629561	629562	629563	629564
Chemical formula	$C_5H_8BrF_6N_2O_2P$	$C_7H_8BrF_6N_3O_6S_2$	$C_7H_{12}Br_2N_2O_2$	$3(C_5H_8IN_2O_2)\cdot 2(F_6P)\cdot Cl$	$3(C_5H_8IN_2O_2)\cdot 2(F_6P)\cdot Cl$	$C_5H_8F_6N_5O_2P$
M_r	353.01	488.20	316.01	1090.49	1090.49	315.13
Crystal syst., space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	orthorhombic, *Pcab*	orthorhombic, *Pcab*	monoclinic, $P2_1/n$
a [Å]	6.7533(9)	9.3740(10)	7.1414(2)	12.0978(16)	11.1107(6)	8.0924(4)
b [Å]	16.2559(19)	13.0160(10)	18.9159(5)	16.037(2)	16.7476(8)	13.3202(5)
c [Å]	10.6281(14)	14.9920(10)	8.7042(2)	36.792(4)	37.553(2)	11.6471(6)
α [deg]	90	107.230(10)	90	90	90	90
β [deg]	97.813(11)	99.859(8)	92.393(2)	90	90	102.10782)
γ [deg]	90	93.312(8)	90	90	90	90
V [Å^3]	1155.9(3)	1709.8(3)	1174.79(5)	7138.2(16)	6987.7(6)	1227.54(10)
Z	4	4	4	8	8	4
D_x [g cm^{-3}]	2.028	1.896	1.787	2.029	2.073	1.705
μ [mm^{-1}]	3.77	2.74	6.875	2.89	2.95	0.308
$F(000)$ [e]	688	960	616	4144	4144	632
Crystal form, color	plate, colorless	plate, colorless	prism, colorless	plate, colorless	plate, colorless	prism, colorless
Crystal size [mm^3]	$0.40 \times 0.24 \times 0.12$	$0.40 \times 0.32 \times 0.06$	$0.35 \times 0.3 \times 0.15$	$0.30 \times 0.27 \times 0.03$	$0.30 \times 0.27 \times 0.03$	$0.30 \times 0.20 \times 0.10$
Diffractometer	STOE IPDS 2	STOE IPDS 2	Nonius KappaCCD	STOE IPDS 2	STOE IPDS 2	Nonius KappaCCD
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Data collection method	rotation method	rotation method	ϕ- and ω-scans	rotation method	rotation method	ϕ- and ω-scans
Temperature [K]	293(2)	173(2)	233(2)	298(2)	233(2)	233(2)
θ_{max} [deg]	24.6	24.7	26.0	24.7	23.8	25.00
h, k, l Ranges	$\pm 7, \pm 19, \pm 12$	$\pm 10, \pm 14, -17 \rightarrow 16$	$\pm 8, -22 \rightarrow 23, -9 \rightarrow 10$	$-13 \rightarrow 14, \pm 18, -43 \rightarrow 42$	$\pm 12, -17 \rightarrow 18, \pm 42$	$-8 \rightarrow 9, \pm 15, \pm 13$
Absorption correction	multi-scan	integration	none	multi-scan	multi-scan	none
Measured reflections	6932	10016	6901	15911	29209	6380
Independent reflections	1943 (R_{int}=0.024)	5344 (R_{int}=0.034)	2309 (R_{int}=0.0353)	4992 (R_{int} = 0.066)	5062 (R_{int}= 0.062)	2139 (R_{int} = 0.0249)
Observed reflections [$I \geq 2\sigma(I)$]	1677	3936	2062	3130	3850	1811
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
Data, restraints, parameters	1943, 0, 156	5344, 0, 455	2309, 0, 119	4992, 0, 467	5062, 0, 467	2139, 0, 212
R [$F^2 \geq 2\sigma(F^2)$]	$R_1 = 0.0265$, $wR_2 = 0.0591$	$R_1 = 0.0547$, $wR_2 = 0.1065$	$R_1 = 0.0256$, $wR_2 = 0.0638$	$R_1 = 0.0577$, $wR_2 = 0.1188$	$R_1 = 0.0350$, $wR_2 = 0.0718$	$R_1 = 0.0446$, $wR_2 = 0.1150$
R (all data)	$R_1 = 0.0345$, $wR_2 = 0.0616$	$R_1 = 0.0824$, $wR_2 = 0.1171$	$R_1 = 0.0299$, $wR_2 = 0.0659$	$R_1 = 0.1017$, $wR_2 = 0.1326$	$R_1 = 0.0557$, $wR_2 = 0.0780$	$R_1 = 0.0536$, $wR_2 = 0.1204$
Goodness of fit	1.03	1.07	1.04	1.04	1.04	1.02
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.29, −0.22	0.93, −0.53	0.480, −0.408	0.56, −0.32	0.43, −0.30	0.44, −0.19

Table 2 (continued).

Compound	**11**	**12**	**13**
CCDC no.	629565	629566	629567
Chemical formula	$C_{28}H_{31}BrF_6N_4NiO_4P_2$	$C_{10}H_{16}Br_4N_4O_4Pd_2 \cdot C_4H_{10}O$	$C_{31}H_{32}BrF_6N_2NiO_2P_3$
M_r	802.13	862.83	810.12
Crystal syst., space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$	monoclinic, $C2/c$
a [Å]	12.2927(6)	19.9922(3)	34.2172(2)
b [Å]	18.5705(8)	8.5719(3)	9.1512(3)
c [Å]	14.8605(8)	15.6670(6)	23.0333(4)
β [deg]	93.707(4)	104.477(2)	105.637(2)
V [Å^3]	3385.3(3)	2599.62(14)	6945.4(3)
Z	4	4	8
D_x [g cm^{-3}]	1.574	2.205	1.549
μ [mm^{-1}]	1.92	7.561	1.911
$F(000)$ [e]	1624	1640	3280
Crystal form, color	plate, yellow-brown	prism, red	prism, yellow
Crystal size [mm^3]	$0.36 \times 0.26 \times 0.10$	$0.40 \times 0.10 \times 0.07$	$0.4 \times 0.35 \times 0.08$
Diffractometer	STOE IPDS 2	Nonius KappaCCD	Nonius KappaCCD
Radiation type	Mo-K_α	MoK_α	MoK_α
Data collection method	rotation method	ϕ- and ω-scans	ϕ- and ω-scans
Temperature [K]	173(2)	233(2)	233(2)
θ_{max} [deg]	24.7	25.00	26.0
h, k, l Ranges	$\pm14, \pm21, \pm17$	$\pm23, \pm10, -18 \rightarrow 17$	$-42 \rightarrow 39, \pm11, \pm28$
Absorption correction	multi-scan	none	none
Measured reflections	20258	7111	21029
Independent reflections	5675 (R_{int} = 0.035)	2288 (R_{int} = 0.0414)	6807 (R_{int} = 0.0351)
Observed reflections [$I \ge 2\sigma(I)$]	4730	1912	5654
Refinement on	F^2	F^2	F^2
Data, restraints, parameters	5675, 0, 419	2288, 0, 134	6807, 0, 454
R [$F^2 \ge 2\sigma(F^2)$]	R_1 = 0.0406, wR_2 = 0.0839	R_1 = 0.0321, wR_2 = 0.0766	R_1 = 0.0343, wR_2 = 0.0806
R (all data)	R_1 = 0.0542, wR_2 = 0.0884	R_1 = 0.0416, wR_2 = 0.0796	R_1 = 0.0459, wR_2 = 0.0853
Goodness of fit	1.06	1.05	1.03
$\Delta\rho_{max}, \Delta\rho_{min}$ [e Å^{-3}]	1.02, −0.30	0.87, −0.67	0.48, −0.37

*1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethanesulfonyl)imide (**4b**):* n_D^{20} = 1.4250. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.62 (s, 3H), 4.19 (s, 6H), 8.22 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 7.6, 68.7 (2C), 115.6 (2C), 119.6 (q, J_{C-F} = 320 Hz, 2C), 138.9. – IR (neat): ν = 3153, 1594, 1460, 1434, 1389, 1347, 1180, 1133, 1052, 979, 957, 831, 741, 711, 603, 569, 505 cm^{-1}.

*1,3-Diethoxyimidazolium bis(trifluoromethanesulfonyl)imide (**5b**):* n_D^{20} = 1.4250. – ^{1}H NMR (300 MHz, [D$_6$] DMSO): δ = 1.32 (t, J = 7.0 Hz, 6H), 4.49 (q, J = 7.0 Hz, 4H), 8.25 (d, J = 1.9 Hz, 2H), 10.26 (t, J = 1.9 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 13.0 (2C), 78.4 (2C), 117.9 (2C), 119.6 (q, J_{C-F} = 320 Hz, 2C), 130.4. – IR (neat): ν = 3142, 1554, 1479, 1393, 1347, 1328, 1179, 1133, 1052, 1006, 844, 789, 740, 611, 599, 569, 558, 509 cm^{-1}.

*2-Bromo-1,3-dimethoxyimidazolium bis(trifluoromethanesulfonyl)imide (**6b**):* The triflimide crystallized from the biphasic mixture before extraction. Yield: 99 %. – n_D^{20} = 1.4469 (subcooled melt). – M. p. 28 – 30 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.23 (s, 6H), 8.48 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.0 (2C), 116.9, 118.3 (2C), 119.5 (q, J_{C-F} = 322 Hz, 2C). – IR (neat): ν = 3135, 1556, 1457, 1446, 1345, 1327, 1177, 1132, 1048, 937, 789, 739, 611, 600, 569, 510 cm^{-1}.

*General procedure for the preparation of compounds **3c** and **4c***

A mixture of **3a** (0.55 g, 0.002 mol) and potassium tris (pentafluoroethyl)trifluorophosphate (0.97 g, 0.002 mol) in H_2O (5 mL) was ultrasonicated for 1 h and then extracted with CH_2Cl_2. The extract was dried with anhydrous Na_2SO_4 and filtered. After removal of the solvent the residue was dried by means of a vacuum pump to yield **3c** as a colorless oil (0.96 g; 84 %). The compound **4c** (from **4a**) was prepared accordingly on a smaller scale with similar yield.

*1,3-Dimethoxyimidazolium tris(pentafluoroethyl)trifluorophosphate (**3c**):* n_D^{20} = 1.3730. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.25 (s, 6H), 8.28 (d, J = 2.1 Hz, 2H), 10.32 (t, J = 2.1 Hz, 1H). – IR (neat): ν = 3165, 1556, 1459, 1296, 1181, 1126, 1098, 1014, 961, 944, 803, 760, 712, 616, 580 cm^{-1}.

*1,3-Dimethoxy-2-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (**4c**):* The FAP salt crystallized from Et_2O. M. p. 75 – 76 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.63 (s, 3H), 4.20 (s, 6H), 8.23 (s, 2H). – ^{19}F NMR (470 MHz, [D$_6$]DMSO): δ = −42.5 (md, J_{F-P} = 894 Hz, 1F), −77.7 (m, 3F), −79.3 (m, 6F), −85.7 (md, J_{F-P} = 894 Hz, 2F), −113.8 (md, J_{F-P} = 85 Hz, 2F), −114.3 (md, J_{F-P} = 99 Hz, 4F). – IR (neat): ν = 3168, 1462, 1294, 1210, 1180, 1135, 1121, 1098, 954, 802, 762, 722, 617, 581, 531, 495 cm^{-1}.

Preparation of potassium (tert-butyl-ethynyl)trifluoroboronate: (3,3-Dimethyl-1-butynyl)di-(*iso*-propoxy)borane (2.10 g, 10.0 mmol) was added dropwise to a solution of KHF_2 (4.60 g, 58.9 mmol) in H_2O (12 mL). A white precipitate formed immediately. The suspension was stirred for 15 min. The crude product was isolated by filtration, washed with cold methanol, and recrystallized from CH_3CN (10 mL) to yield 1.57 g (84 %). – IR (neat): ν = 2969, 2869, 1456, 1223, 1066, 953, 890 cm^{-1}.

Solution of 1,3-dimethoxyimidazolium hydrogensulfate: 1,3-Dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide **3b** (5.89 g, 14.4 mmol) and concentrated H_2SO_4 (5.5 mL) were combined in a 50 mL flask. The evolving bis(trifluoromethylsulfonyl)amine was removed by vacuum distillation at 70 °C. After several h the remaining solution was cooled in an ice bath and H_2O was added to a volume of 20 mL. The resulting 0.72 M solution was used for further anion exchange.

*1,3-Dimethoxyimidazolium phenyltrifluoroboronate (**3d**):* A portion of the above solution of 1,3-dimethoxyimidazolium hydrogensulfate (5.0 mL, 3.6 mmol) was diluted with H_2O, and $NaHCO_3$ (370 mg, 4.4 mmol) was added. After gas evolution had ceased, potassium phenyltrifluoroboronate [49 – 51] (760 mg, 4.1 mmol) was introduced. Complete dissolution was achieved by ultrasonication. The resulting aqueous solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The product was finally dried by means of a vacuum pump to yield **3d** as a colorless liquid (260 mg, 26 %). n^D_{17} = 1.4809. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.23 (s, 6H), 7.08 (m, 3H), 7.33 (m, 2H), 8.25 (s, 2H), 10.25 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.5 (2C), 117.0 (2C), 125.0, 126.3 (2C), 129.5, 131.3 (2C). – IR (neat): ν = 3127, 2953, 1554, 1453, 1351, 1191, 1137, 1058, 1015, 938, 754, 706, 615, 597, 570, 512 cm^{-1}.

*1,3-Dimethoxyimidazolium (tert-butyl-ethynyl)trifluoroboronate (**3e**):* A portion of the above solution of 1,3-dimethoxyimidazolium hydrogensulfate (3.0 mL, 2.2 mmol) was diluted with H_2O, and $NaHCO_3$ (260 mg, 3.1 mmol) was added. After gas evolution had ceased, potassium (*tert*-butyl-ethynyl)trifluoroboronate (410 mg, 2.2 mmol) was introduced. Complete dissolution was achieved by ultrasonication. The resulting aqueous solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The product was finally dried by means of a vacuum pump to give **3e** as colorless crystals (140 mg, 23 %). M. p. 62 – 64 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.07 (s, 9H), 4.25 (s, 6H), 8.27 (d, J = 2.0 Hz), 10.24 (t, J = 2.0 Hz). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 26.9, 31.6 (3C), 69.6 (2C), 117.1 (2C), 129.5. – IR (neat): ν = 3129, 2966, 1554, 1456, 1352, 1254, 1195, 1142, 1043, 986, 939, 890, 816, 732, 703, 616, 581, 506 cm^{-1}.

*1,3-Dimethoxyimidazolium bromide (**3f**):* A mixture of the triflimide **3b** (2.34 g, 5.7 mmol), aqueous HBr (47 %, 0.98 g, 5.7 mmol) and Et_2O (5 mL) was stirred for 15 h at r. t. Then, H_2O was added, and the solution was repeatedly extracted with Et_2O (8 × 10 mL). The aqueous phase was taken to dryness to give the crude product **3f** as a hygroscopic oil which was dried in vacuum. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.25 (s, 6H), 8.33 (d, J = 2.0 Hz, 2H), 10.38 (t, J = 2.0 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.6 (2C), 117.1 (2C), 129.6. – IR (neat): ν = 3066, 2947, 1552, 1452, 1229, 1144, 1010, 939, 702, 580 cm^{-1}.

*1,3-Dimethoxyimidazolium perchlorate (**3g**):* $AgClO_4$ (0.59 g, 2.9 mmol) was added to a solution of the crude bromide **3f** (0.60 g, 2.9 mmol) in H_2O (15 mL), the mixture was ultrasonicated and filtered. The filtrate was taken to dryness, and the residue was recrystallized from MeOH to give **3g** as a colorless powder. M. p. 238 – 242 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.24 (s, 6H), 8.29 (d, J = 2.0 Hz, 2H), 10.31 (t, J = 2.0 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.6 (2C), 117.1 (2C), 129.6. – IR (neat): ν = 3163, 3143, 3122, 3042, 1555, 1469, 1073, 1010, 936, 773, 721, 705, 619, 528, 516 cm^{-1}.

*1,3-Diethoxyimidazolium tetrafluoroborate (**5c**):* Potassium imidazole-1,3-dioxide (2.61 g, 18.9 mmol; prepared from **1** and KOMe in MeOH) was suspended in dry CH_2Cl_2 (15 mL). A solution of triethyloxonium tetrafluoroborate (7.18 g, 37.8 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise. The mixture gradually turned yellow, and the suspended reagent dissolved. Simultaneously, a voluminous precipitate was formed. The solid was removed by filtration, and the solvent was evaporated to give **5c** as a brown oil which crystallized on standing (3.76 g, 82 %). M. p. 40 – 46 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.32 (t, J = 7.0 Hz, 6H), 4.49 (q, J = 7.0 Hz, 4H), 8.24 (d, J = 1.8 Hz, 2H), 10.24 (t, J = 1.8 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 12.9 (2C), 78.3 (2C), 117.8 (2C), 130.3. – IR (neat): ν = 3146, 2992, 1555, 1477, 1393, 1049, 1005, 967, 856, 791, 727, 596, 520 cm^{-1}.

*General procedure for the preparation of compounds **6a** and **7a***

1,3-Dimethoxy-1*H*-imidazolium hexafluorophosphate **3a** (3.19 g, 11.7 mmol) was suspended in a mixture of H_2O

(10 mL) and MeOH (5 mL). Bromine (0.60 mL, 11.7 mmol) was added at once, and the mixture was stirred for 24 h. To the resulting yellow solution with a dark red precipitate Na_2CO_3 (1.23 g, 11.7 mmol) was added. Gas evolution was observed. Subsequently, another equivalent of bromine was added (0.60 mL) and stirring was continued for 24 h. During the first five minutes, more gas evolved and the red solid dissolved. Simultaneously, a voluminous yellow precipitate formed. The solid was filtered off, washed with H_2O (10 mL) and dissolved in hot MeOH (30 mL). The product was precipitated by addition of Et_2O (250 mL) and collected by filtration after cooling the suspension to −18 °C to yield **6a** as a white powder (3.1 g, 75 %). Compound **7a** was prepared accordingly from **5a** on a smaller scale with similar yield. A small amount of the related bromide **7b** was isolated after concentrating the aqueous filtrate and washing the resulting precipitate repeatedly with H_2O.

*2-Bromo-1,3-dimethoxyimidazolium hexafluorophosphate (**6a**):* m. p. 148 – 149 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.23 (s, 6H), 8.50 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 69.0 (2C), 117.0, 118.3 (2C). – IR (neat): ν = 3170, 3149, 1557, 1458, 1441, 1049, 941, 837, 733, 650, 556 cm^{-1}.

*2-Bromo-1,3-diethoxyimidazolium hexafluorophosphate (**7a**):* m. p. 84 – 86 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.36 (t, J = 7.0 Hz, 6H), 4.49 (q, J = 7.0 Hz, 4H), 8.47 (s, 2H). – IR (neat): ν = 3135, 3113, 1546, 1466, 1386, 1345, 1108, 1044, 999, 852, 729, 615 cm^{-1}.

*2-Bromo-1,3-diethoxyimidazolium bromide (**7b**):* m. p. 145 – 148 °C. – IR (neat): ν = 3016, 2994, 2963, 2888, 1552, 1472, 1387, 1115, 1039, 1006, 864, 777, 757, 637 cm^{-1}.

*2-Iodo-1,3-dimethoxyimidazolium hexafluorophosphate (**8**):* A solution of ICl in CH_2Cl_2 (0.73 mL 1.0 M) was added to a mixture of **3a** (0.2 g, 0.7 mmol) in H_2O (3 mL) and CH_2Cl_2 (3 mL) which was stirred for 3 d at r. t. The organic layer was separated and the solvent removed. The residue was treated with Et_2O to remove I_2, then dissolved in MeOH, and the product precipitated with Et_2O. M. p. 148 – 150 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.19 (s, 6H), 8.44 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 68.9 (2C), 117.0, 119.2 (2C). – IR (neat): ν = 3166, 3146, 1455, 1042, 945, 823, 732, 648, 557 cm^{-1}.

*2-Azido-1,3-dimethoxyimidazolium hexafluorophosphate (**9**):* To a suspension of 2-bromo-1,3-dimethoxyimidazolium hexafluorophosphate **6a** (1.0 g, 2.8 mmol) in acetone (20 mL) was added NaN_3 (0.18 g, 2.8 mmol). After stirring the reaction mixture for 72 h at r. t., a yellow solution with a white precipitate was obtained. After addition of anhydrous Na_2SO_4 the solution was filtered and the solvent evaporated. The brown solid residue was recrystallized from MeOH (2 mL) and washed with Et_2O to yield **9** as colorless crystals (0.20 g, 22 %). M. p. 92 °C (dec). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.22 (6H, s), 8.18 (2H, s). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 68.9 (2C), 113.9 (2C), 132.0. – IR (neat): ν = 3180, 3160, 2161, 1602, 1262, 1071, 825, 555 cm^{-1}.

*1,3-Dihydroxyimidazolium bis(trifluoromethanesulfonyl) imide (**10**):* 1-Hydroxyimidazole-3-oxide (1.50 g, 14.9 mmol) was added to bis(trifluoromethanesulfonyl)amine (4.20 g, 14.9 mmol) in a Schlenk vessel. After stirring for 2 h, the resulting liquid was filtered to give **10** as a colorless clear liquid (5.6 g, 98 %). n_D^{20} = 1.4185. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.83 (2H, s), 9.73 (1H, s). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 118.4 (2C), 119.8 (2C, q, J = 322 Hz), 128.3. – IR (neat): ν = 3522, 3156, 1471, 1341, 1184, 1125, 1050, 1013, 792, 743, 727, 594, 569 cm^{-1}.

*Bis(1,3-dimethoxyimidazolin-2-ylidene)(triphenylphosphine)bromonickel(II) hexafluorophosphate (**11**):* A solution of bis(cyclooctadiene)nickel(0) (113 mg, 0.41 mmol) and triphenylphosphine (215 mg, 0.82 mmol) in dry THF was stirred for 20 min at r. t. 2-Bromo-1,3-dimethoxyimidazolium hexafluorophosphate (**6a**; 145 mg, 0.41 mmol) was added and stirring was continued for 3 h. The yellow precipitate was collected by filtration, washed with Et_2O and dried in vacuum. It was redissolved in CH_2Cl_2, and single crystals were grown by vapor diffusion with pentane. M. p. 202 – 205 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.25 (s, 12H), 7.06 (s, 4H), 7.3 – 7.6 (m, 15H). – ^{31}P NMR (121 MHz, [D$_6$]DMSO): δ = 22.0. – IR (neat): ν = 3168, 2961, 1436, 1261, 1094, 1063, 836, 693, 557 cm^{-1}.

*trans-[Bis(1,3-dimethoxyimidazolin-2-ylidene)]dibromo-μ,μ'-dibromo-dipalladium(II) diethylether solvate (**12**):* 2-Bromo-1,3-dimethoxyimidazolium hexafluorophosphate **6a** (22 mg, 0.06 mmol) was added to a solution of bis-(3, 5, 3′, 5′-tetramethoxydibenzylideneacetone) palladium(0) (50 mg, 0.06 mmol) in CH_2Cl_2 (2 mL) under argon. The mixture was stirred at r. t. overnight. The black precipitate was removed by centrifugation, and the supernatant was taken to dryness. The residue was extracted twice with Et_2O (2 × 1 mL) to remove the tmdba ligand. The remainder was dissolved in CH_2Cl_2 (1 mL), and red crystals were grown by vapor diffusion of Et_2O. Yield: 10 mg (19 %). M. p. 106 – 110 °C (dec). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.01 (t, J = 7.0 Hz, 6H), 3.28 (q, J = 7.0 Hz, 4H), 4.22 (s, 12H), 7.32 (s, 4H). – IR (neat): ν = 3151, 3119, 3078, 2968, 2937, 2859, 1594, 1557, 1446, 1432, 1149, 1113, 1030, 949, 835, 719, 671, 613, 557 cm^{-1}.

*[1,2-Bis(diphenylphosphino)ethane](1,3-dimethoxyimidazolin-2-ylidene)bromonickel(II) hexafluorophosphate (**13**):* A solution of bis(cyclooctadiene)nickel(0) (98 mg, 0.36 mmol) and 1,2-bis(diphenylphosphino)ethane (142 mg, 0.36 mmol) in dry THF was stirred for 20 min at r. t. 2-Bromo-1,3-dimethoxyimidazolium hexafluorophosphate **6a** (126 mg, 0.36 mmol) was added and stirring was continued overnight. The yellow precipitate was removed by filtration and found to be Ni(dppe)Br_2. Slow evaporation of

the filtrate yielded single crystals of complex **13**. M. p. 228 – 230 °C. – ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 2.1 – 2.3 (m, 2H), 2.5 – 2.8 (m, 2H), 4.05 (s, 6H), 7.13 (s, 2H), 7.3 – 7.9 (m, 20H). – ^{31}P NMR (121 MHz, [D$_8$]THF): δ = 53.7 (d, J_{P-P} = 58 Hz), 67.2 (d, J_{P-P} = 58 Hz). – IR (neat): ν = 3150, 2962, 1437, 1260, 1099, 1019, 834, 754, 693, 556, 526, 492 cm^{-1}.

1-Ethyl-3-methylimidazolium phenyltrifluoroboronate: 1-Ethyl-3-methylimidazolium chloride (7.42 g, 50.6 mmol) and potassium phenyltrifluoroboronate [49 – 51] (9.31 g, 50.6 mmol) were dissolved in distilled water and the resulting mixture was stirred at r. t. for 2 h. Subsequently, this solution was extracted six times with small portions of CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The product was finally dried in vacuum. Yield: 7.28 g (56 %). – n_D^{20} = 1.4953. – ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.30 (t, J = 7.0 Hz, 3H), 3.59 (s, 3H), 3.90 (q, J = 7.0 Hz, 2H), 7.08 – 7.18 (m, 5H), 7.46 (d, J = 6.5 Hz, 2H), 8.33 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 14.9, 35.6, 44.5, 121.8, 123.5, 126.0, 127.1 (2C), 131.5 (2C), 136.0, 148.7 (broad). – IR (neat): ν = 3154, 3117, 3006, 1571, 1432, 1193, 1168, 945, 752, 707, 647, 621, 597 cm^{-1}.

Supplementary material

CCDC 629553 – 629567 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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