

Cite this: *New J. Chem.*, 2017, 41, 10299

Optical and XPS evidence for the electrochemical generation of an N-heterocyclic carbene and its CS₂ adduct from the ionic liquid [bmim][PF₆][†]

P. Aydogan Gokturk,[†] S. E. Donmez, B. Ulgut,[†] Y. E. Türkmen[†] * and S. Suzer[†] *

Room temperature ionic liquids continue to be at the forefront of chemistry, covering a broad spectrum of research areas from electrochemistry and energy to catalysis and green chemistry. Therefore, it is of great value to fully understand the chemical and electrochemical reactivity and stability of ionic liquids utilized in these applications. In this context, we have investigated the electrochemical generation of an N-heterocyclic carbene and its CS₂ adduct from the ionic liquid [bmim][PF₆], and X-ray photoelectron spectroscopy (XPS) proved to be a highly effective spectroscopic tool to study such systems. Initially, the dithiocarboxylate adduct was chemically synthesized as a reference compound starting from both [bmim][PF₆] and [bmim][OAc], and characterized by HRMS, and ¹H- and ¹³C-NMR, FTIR, visible and X-ray photoelectron spectroscopy. While a simple mixture of [bmim][PF₆] and CS₂ revealed no evidence of adduct formation, the application of an electrochemical stimulus led to the formation of the dithiocarboxylate adduct as evidenced optically and through the newly formed S2p peak in the XP spectrum. Further evidence for the electrochemical reduction of [bmim][PF₆] to the corresponding N-heterocyclic carbene came from the XPS analysis *via* the appearance of a new N1s peak in the XP spectrum.

Received 5th June 2017,
Accepted 10th August 2017

DOI: 10.1039/c7nj01996c

rsc.li/njc

Introduction

Within the last two decades, there has been an overwhelming growing interest in the application of room-temperature ionic liquids (ILs) across various disciplines of chemistry.^{1–7} ILs have found widespread use as reaction solvents in the area of green chemistry due to their unique properties such as extremely low vapor pressure, structural tunability, and thermal stability.⁸ Being composed of purely anions and cations and having a reasonable ionic conductivity (10^{−2} S cm^{−1}) together with an enlarged electrochemical window, ILs have also found a unique place in the field of electrochemistry, notably in energy storage, such as batteries, supercapacitors, *etc.*^{9–17} Among the numerous favorable physicochemical properties of ILs, the ability to capture CO₂ as alternative solvents of conventional amines is also noteworthy of mention.^{18–22} The reasons are attributed to ILs' non-volatile, non-corrosive and non-flammable nature, together with their high thermal stability and recyclability, enabling them to

reduce the energy consumption in CO₂ capture processes.²³ This was demonstrated by Wappel *et al.*, where the energy demand for a carbon capture process using ILs was found to be lower than the process using the amine solvent.²⁰ ILs are also classified as low-melting organic salts, and among the 'onium' cations, imidazolium rings with positive nitrogen(s) turned out to be the most convenient and resourceful starting material for producing numerous useful combinations.¹²

An important class of compounds structurally related to imidazolium-based ILs consists of N-heterocyclic carbenes (NHCs), as schematically shown in Fig. 1.^{24,25} The groundbreaking work of Arduengo and co-workers in the early 1990s on the preparation and isolation of stable NHCs opened up new avenues in carbene chemistry.^{26,27} Due to their strong σ-donor properties, NHCs serve as excellent ligands for transition metal-catalyzed reactions including cross-coupling and olefin metathesis

Department of Chemistry, Bilkent University, Ankara 06800, Turkey.
E-mail: yeturkmen@bilkent.edu.tr, suzer@fen.bilkent.edu.tr;
Tel: +90-312-290 24 51, +90-312-290 14 76

[†] Electronic supplementary information (ESI) available: Additional data and spectra. See DOI: 10.1039/c7nj01996c

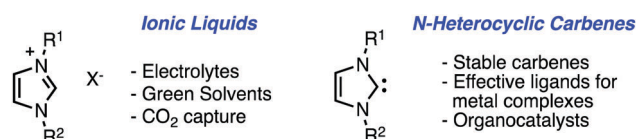


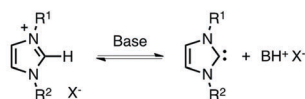
Fig. 1 Imidazolium-based ionic liquids and N-heterocyclic carbenes.

reactions as well as a number of asymmetric transformations.^{28–30} The NHCs were also discovered to stabilize metal nanoparticles and self-assembled monolayers, and found use as ligands in heterogeneous nanocatalysis.^{31–34} Recently, the coordination chemistry space of NHCs has been further expanded to include non-metals where p-block elements were shown to be stabilized by the coordination of NHCs.^{35–38} Finally, NHCs proved to be highly effective organocatalysts and have been utilized in a wide range of organic reactions.^{39–41}

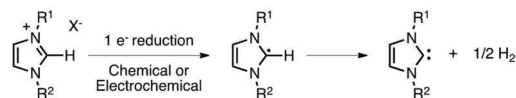
Traditionally, deprotonation of imidazolium salts using a strong base such as NaH, KOtBu, *etc.* has been the preferred method for the preparation of the corresponding NHCs (Scheme 1a). Alternatively, it was shown that such NHC compounds could be prepared *via* one-electron chemical or electrochemical reduction of imidazolium salts (Scheme 1b). In a pioneering work reported in 2004, Clyburne and co-workers investigated the electrochemical reduction of a bis(mesityl)-substituted imidazolium cations by cyclic voltammetry (CV), and demonstrated the large-scale preparation of two NHC products by chemical reduction of the corresponding imidazolium salts using potassium metal.⁴² The organocatalytic activities of the electrochemically generated NHCs have been elegantly showcased in a variety of organic transformations.^{43–49}

NHCs are known to react with a broad range of electrophiles such as carbon dioxide, carbon disulfide, isocyanates, and isothiocyanates to form stable zwitterionic betaine adducts.⁵⁰ Imidazolium-2-dithiocarboxylates, CS₂ adducts of imidazole-based NHCs, have been used as ligands in coordination complexes of transition metals such as ruthenium, osmium, palladium, and gold.^{51–55} In addition, the coordination of such zwitterionic imidazolium-2-dithiocarboxylates to gold nanoparticles and gold surfaces has been investigated.^{53,56} Due to the reactive nature of the carbenes, their formation is usually inferred by mostly indirect experimental evidence, based on their reaction products.

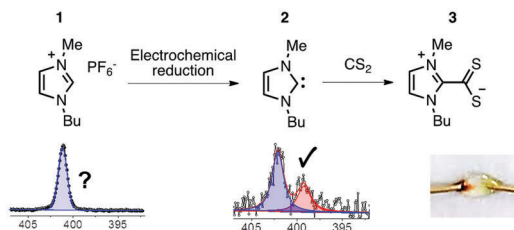
a. Generation of NHCs via deprotonation:



b. Generation of NHCs via reduction:



c. This work:



Scheme 1 Chemical and electrochemical generation of NHCs, and the present work.

Hence, the adduct formation *via* its unique coloration is generally used as one experimental proof for the presence of carbenes.⁵⁷ However, great care has to be exercised for its correct interpretation, since the process also interferes with the delicate acid–base equilibrium of the imidazolium salt(s). The basicity of the corresponding anion plays a critical role, which will be discussed in more detail in the next section.

As a part of our ongoing research program on electrochemical studies using ionic liquids,⁵⁸ we report herein our recent studies on the electrochemical generation of NHC **2** from the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bvim][PF₆], **1**). Along with direct XPS evidence for the electrochemical formation of carbene **2**, we present NMR, FTIR, Visible, and XP spectroscopic evidence for the dithiocarboxylate adduct **3** that is obtained by the trapping of the *ex situ*-generated carbene **2** (Scheme 1c).

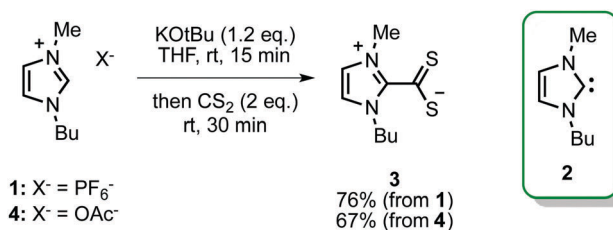
Results and discussion

Chemical preparation of the dithiocarboxylate adduct

For this purpose, the adduct **3** was prepared as shown in Scheme 2, by the deprotonation of 1-butyl-3-methylimidazolium hexafluorophosphate ([bvim][PF₆], **1**) using potassium *tert*-butoxide in THF followed by treatment with CS₂. This process gave dithiocarboxylate product **3** in 76% yield after purification by column chromatography. A similar procedure applied to the imidazolium acetate salt ([bvim][OAc], **4**) afforded the same product **3**, albeit in a slightly lower yield (67%). Based on literature precedence, both reactions are expected to proceed *via* the intermediacy of carbene **2**, which is generated upon the deprotonation of the imidazolium salts.²⁵

The structure of the imidazolium dithiocarboxylate product **3** was confirmed by HRMS, and ¹H- and ¹³C-NMR, FTIR, visible and X-ray photoelectron spectroscopy.⁵⁹ High-resolution mass spectrometric analysis showed the expected [M + H]⁺ signal (*m/z* 215.0676). The incorporation of the CS₂ unit into the imidazolium structure has been confirmed by the dithiocarboxylate carbon signal at 224.7 ppm in the ¹³C-NMR spectrum of **3** (Fig. 2).

This is further supported by the FTIR spectrum that exhibits the expected band for the –CS₂[–] moiety at around 1050 cm^{–1} (Fig. 3b). It should also be noted that compound **3** exhibits the characteristic red color (see Scheme 1c and also Fig. 6) of similar imidazolium dithiocarboxylate derivatives.^{50,56,60–62} In accordance with this observation, the visible spectrum of **3** recorded in CH₂Cl₂ shows the presence of two intense absorption bands at 530 nm and 430 nm, as shown in Fig. 3a.



Scheme 2 Synthesis of imidazolium dithiocarboxylate **3** starting from [bvim][PF₆] (**1**) and [bvim][OAc] (**4**).

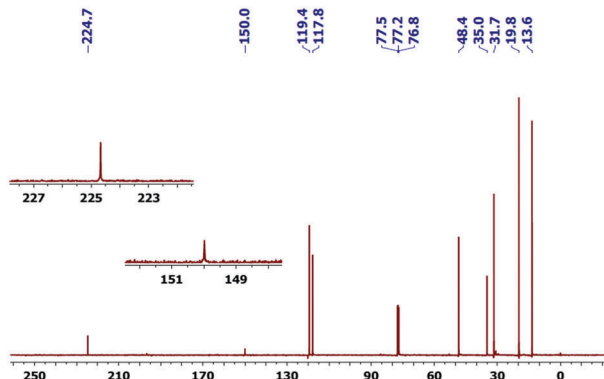


Fig. 2 ^{13}C -NMR spectrum of imidazolium dithiocarboxylate **3** recorded in CDCl_3 .

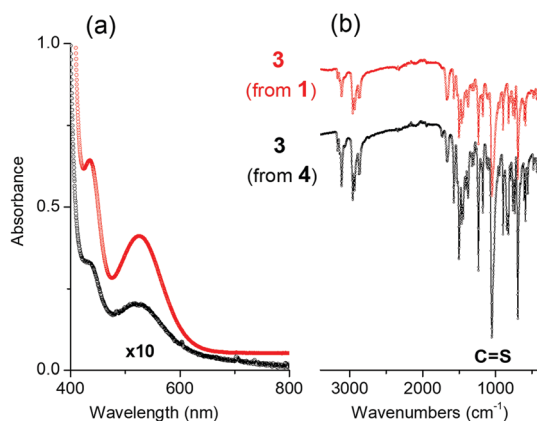


Fig. 3 (a) Vis and (b) IR spectra of the imidazolium dithiocarboxylate **3** starting from $[\text{bmim}][\text{PF}_6]$ (**1**) and $[\text{bmim}][\text{OAc}]$ (**4**).

Additional support is obtained from the XP spectrum of the compound **3** as depicted in Fig. 4, by the presence of the strong and broad (multiple) S2p peaks, and the absence of the P2p and F1s peaks. Consistent with the literature data, only one N1s peak at 402.0 eV is observed representing the two equivalent nitrogen atoms of the imidazolium ring, but carrying one unit of positive charge.^{63–66} The multiple structure of the S2p region is deconvoluted to three spin-orbit doublets; two of the major ones (designated as A and B in the figure) have binding energies assignable to the CS_2 adduct, but the third one (C) with much smaller intensity and at a higher energy position can

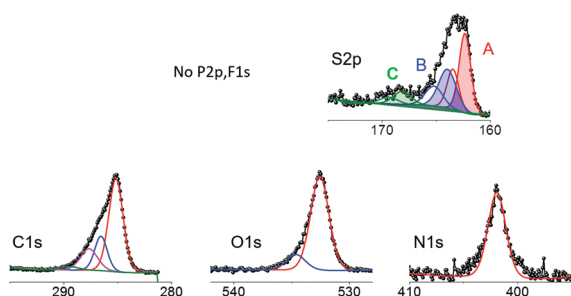


Fig. 4 XP spectrum of imidazolium dithiocarboxylate **3**.

best be assigned to oxidized sulfur atoms. One explanation for the appearance of two sulfur components can be given as partial conversion of CS_2 to OCS, either during generation of the adduct in air-ambient and/or transformation to the XPS chamber afterwards. This issue has been recently investigated in detail and discussed by Cabaço *et al.*⁶¹

Electrochemical preparation of the dithiocarboxylate adduct

The nature of the anions of imidazolium-based ionic liquids was shown to have a strong effect on the reactivity patterns of such compounds. For instance, in a study reported by Nyulászi and co-workers in 2011, 1-ethyl-3-methylimidazolium acetate was shown to be an effective organocatalytic ionic liquid for benzoin condensation and hydroacylation reaction.^{67–69} This catalytic activity was attributed to the *in situ* formation of the corresponding N-heterocyclic carbene with the help of the basic acetate anion, which was supported by the lack of catalytic activity when non-basic anions were used. The non-innocent nature of the acetate anion in ionic liquids was also demonstrated by Cabaço and co-workers, where the reactions of $[\text{bmim}][\text{OAc}]$ with CS_2 and OCS were investigated.^{60–62} Through detailed spectroscopic analysis, the authors showed that the OAc^- anion, in addition to its role as a base, reacted with CS_2 to form OCS and CO_2 *in situ* that led eventually to the formation of $[\text{bmim}]\text{CO}_2$ and $[\text{bmim}]\text{OCS}$ adducts. With these considerations in mind, we next sought to investigate the electrochemical generation of carbene **2** through its conversion to the CS_2 adduct.

For this purpose, we selected to use $[\text{bmim}][\text{PF}_6]$ ionic liquid as the carbene precursor due to the non-basic nature of the PF_6^- anion and to avoid any potential complications that would be caused by the OAc^- anion. Indeed, when neat $[\text{bmim}][\text{PF}_6]$ was mixed with CS_2 , no red color formation was observed. Moreover, the analysis of the mixture by X-ray photoelectron spectroscopy confirmed the absence of sulfur (Fig. 5), while revealing close to a stoichiometric compound.^{63–66} Note that the CS_2 , originally introduced to the mixture in air, is expected to evaporate away once introduced to the vacuum environment of the XPS-chamber. These two observations clearly show that $[\text{bmim}][\text{PF}_6]$ does not react with CS_2 in the absence of a base or a reducing agent.

Having previous experience regarding the successful preparation of a carbene intermediate from a similar IL using electrochemical means only,⁵⁸ our next move focused on first

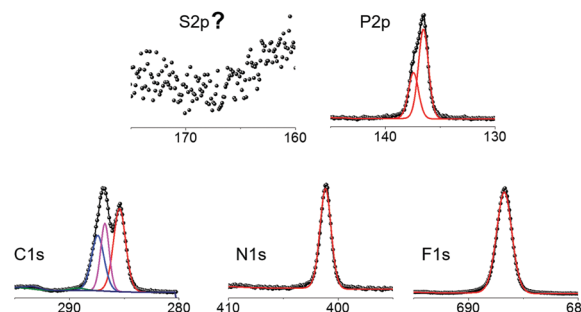


Fig. 5 XP spectra of the mixture of $[\text{bmim}][\text{PF}_6]$ and CS_2 .

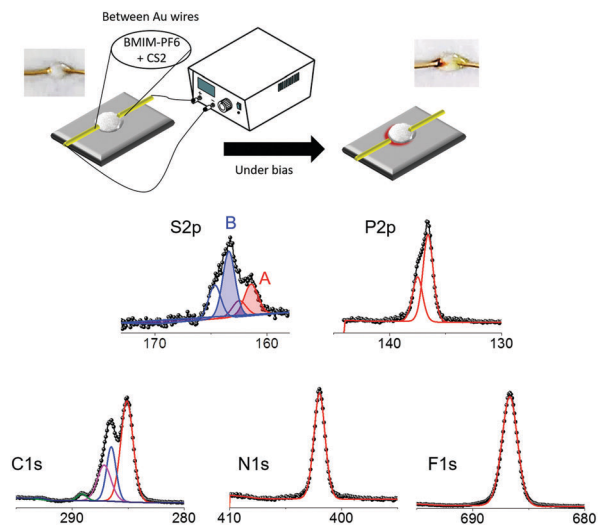


Fig. 6 Schematics of *ex situ* electrochemical preparation of the adduct **3**, and the XP spectrum of the mixture of [bmim][PF₆] and CS₂ after the electrochemical process.

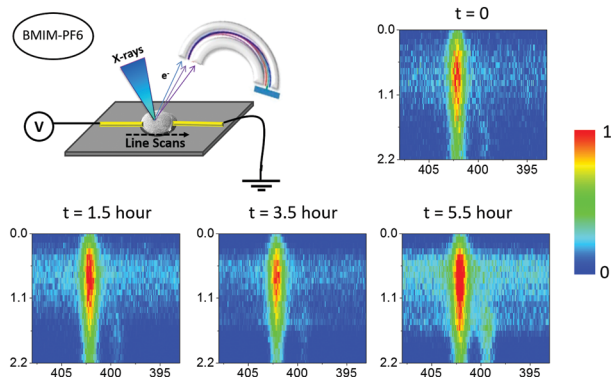


Fig. 7 XP spectra of [bmim][PF₆] during the electrochemical process. The spectra are recorded in the line scan mode, at different time-intervals and across the two gold electrodes spanning a distance of 2.2 mm. The normalized color bar represents the peak intensity.

producing the carbene in the same mixture as above *ex situ*, thus hoping that the presence of CS₂ in the mixture would signal the carbene formation through appearance of the intense coloration. As expected and displayed in Fig. 6, the electrochemical reaction started in the negatively polarized electrode (*i.e.* reduction) and the coloration became intense after ~30 min, and continued for a while in air-ambient. After the incorporated CS₂ is in the form of a stable adduct, its XPS analysis could be successfully carried out. The XP spectrum of the adduct depicts again the two S2p spin-orbit doublet peaks (A and B), as shown in Fig. 6. The other observed XP peaks, P2p, C1s, N1s and F1s, have binding energy positions and intensities that are consistent with the published data.^{63–66}

Electrochemical preparation of the carbene under vacuum

Similar to our previous work,⁵⁸ we have finally attempted and succeeded in generating the carbene intermediate inside the

XPS analysis chamber by electrochemical means, through application of a 3V d.c. bias, which caused ~0.2 μ A of current. The process is slow but the direct spectroscopic evidence is very strong through the appearance of a new N1s peak representing the carbene at 399.3 eV after 3–4 hours, as depicted in Fig. 7. Note that at the beginning only the positively charged N1s peak of the imidazolium ring at 402.0 eV is dominant, but after a few hours the carbene peak of ~20% intensity prevails.

Conclusions

In summary, we present direct optical and X-ray photoelectron spectroscopic evidence for the electrochemical generation of an N-heterocyclic carbene and its CS₂ adduct from the ionic liquid [bmim][PF₆]. The zwitterionic imidazolium dithiocarboxylate **3** was chemically synthesized and isolated starting from both [bmim][PF₆] (**1**) and [bmim][OAc] (**4**). This adduct was fully characterized by HRMS, and ¹H- and ¹³C-NMR, FTIR, Visible and X-ray photoelectron spectroscopy. In a control experiment, a mixture of [bmim][PF₆] (**1**) and CS₂ revealed no red coloration in addition to the absence of a sulfur signal in the XP spectrum, which together confirm that these two compounds do not react to give the adduct **3** in the absence of a chemical or electrochemical stimulus. On the other hand, electrochemical reduction of [bmim][PF₆] (**1**) in the presence of CS₂ resulted in the formation of the dithiocarboxylate adduct **3**, supported optically by the formation of red color and through XP spectroscopy exhibiting the expected S2p peak. To the best of our knowledge, this is the first example of the formation of a CS₂ adduct *via* an electrochemically generated N-heterocyclic carbene. Finally, we provide evidence for the electrochemical-generation of the carbene intermediate **2** inside the XPS analysis chamber *via* the emergence of a new N1s peak in the XP spectrum. These results underscore the utility and potential of X-ray photoelectron spectroscopy for investigating the electrochemical reactivity of ionic liquids.

Experimental section

The ionic liquids [bmim][PF₆] and [bmim][OAc] were purchased from Sigma-Aldrich and used as received. The NMR spectra were recorded using a Bruker Avance 400 spectrometer. The FTIR, Visible, and XP spectroscopic data were recorded using Bruker Alpha-Platinum-ATR, Cary 300, and Thermo Scientific K-Alpha spectrometers respectively. The XP spectrometer was modified to implement the electrochemical process under vacuum.

Synthesis

A 100 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar was charged with 1-butyl-3-methylimidazolium hexafluorophosphate **1** (300 mg, 1.06 mmol). The flask was evacuated and refilled with nitrogen three times. The ionic liquid was dissolved in 20 mL of anhydrous THF, and KOtBu (142 mg, 1.27 mmol) was added as a solid. The resulting clear, light yellow solution was stirred for 15 min at room temperature under nitrogen.

Afterwards, CS₂ (128 μL, 2.11 mmol) was added *via* syringe, and the color turned dark red immediately. The reaction mixture was stirred for 30 min, and directly concentrated under reduced pressure using a rotary evaporator. Purification by flash column chromatography (silica gel, CH₂Cl₂:EtOAc 1:1) gave pure imidazolium dithiocarboxylate **3** (173 mg, 76%) as a red-colored solid: mp 99–102 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.88 (1H, d, *J* = 2.1 Hz), 6.87 (1H, d, *J* = 2.1 Hz), 4.12 (2H, t, *J* = 7.6 Hz), 3.78 (3H, s), 1.90–1.83 (2H, m), 1.38 (2H, sext, *J* = 7.5 Hz), 0.93 (3H, t, *J* = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 224.7, 150.0, 119.4, 117.8, 48.4, 35.0, 31.7, 19.8, 13.6; FTIR (ATR, solid): 1572, 1502, 1235, 1175, 1050 cm⁻¹; HRMS (APCI): *m/z* = 215.0676 [M + H]⁺ (*m/z* calcd for C₉H₁₅N₂S₂ = 215.0671).

Conflicts of interest

There are no conflicts to declare.

References

- 1 K. Dong, X. Liu, H. Dong, X. Zhang and S. Zhang, *Chem. Rev.*, 2017, **117**, 6636–6695.
- 2 C. Dai, J. Zhang, C. Huang and Z. Lei, *Chem. Rev.*, 2017, **117**, 6929–6983.
- 3 Y. Qiao, W. Ma, N. Theyssen, C. Chen and Z. Hou, *Chem. Rev.*, 2017, **117**, 6881–6928.
- 4 K. S. Egorova, E. G. Gordeev and V. P. Ananikov, *Chem. Rev.*, 2017, **117**, 7132–7189.
- 5 M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda and K. Dokko, *Chem. Rev.*, 2017, **117**, 7190–7239.
- 6 S. Zhang, J. Zhang, Y. Zhang and Y. Deng, *Chem. Rev.*, 2017, **117**, 6755–6833.
- 7 Z. Zhang, J. Song and B. Han, *Chem. Rev.*, 2017, **117**, 6834–6880.
- 8 F. M. Kerton, *Alternative Solvents for Green Chemistry*, The Royal Society of Chemistry, Cambridge, 2009, ch. 6, pp. 118–142.
- 9 M. Galiński, A. Lewandowski and I. Stepniak, *Electrochim. Acta*, 2006, **51**, 5567–5580.
- 10 D. R. MacFarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil and E. I. Izgorodina, *Acc. Chem. Res.*, 2007, **40**, 1165–1173.
- 11 E. I. Rogers, B. Šljukić, C. Hardacre and R. G. Compton, *J. Chem. Eng. Data*, 2009, **54**, 2049–2053.
- 12 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
- 13 H. Liu, Y. Liu and J. Li, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1685–1697.
- 14 X. Lu, G. Burrell, F. Separovic and C. Zhao, *J. Phys. Chem. B*, 2012, **116**, 9160–9170.
- 15 D. R. M. Angel and A. J. Torriero, *Electrochemistry in Ionic Liquids: Applications*, Springer International Publishing, Switzerland, 2015.
- 16 D. R. MacFarlane, M. Forsyth, P. C. Howlett, M. Kar, S. Passerini, J. M. Pringle, H. Ohno, M. Watanabe, F. Yan, W. Zheng, S. Zhang and J. Zhang, *Nat. Rev. Mater.*, 2016, **1**, 15005.
- 17 M. Forsyth, G. M. A. Girard, A. Basile, M. Hilder, D. R. MacFarlane, F. Chen and P. C. Howlett, *Electrochim. Acta*, 2016, **220**, 609–617.
- 18 J. L. Anderson, J. K. Dixon and J. F. Brennecke, *Acc. Chem. Res.*, 2007, **40**, 1208–1216.
- 19 F. Karadas, M. Atilhan and S. Aparicio, *Energy Fuels*, 2010, **24**, 5817–5828.
- 20 D. Wappel, G. Gronald, R. Kalb and J. Draxler, *Int. J. Greenhouse Gas Control*, 2010, **4**, 486–494.
- 21 M. Ramdin, T. W. de Loos and T. J. H. Vlugt, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149–8177.
- 22 M. Isik, S. Zulfikar, F. Edhaim, F. Ruiperez, A. Rothenberger and D. Mecerreyes, *ACS Sustainable Chem. Eng.*, 2016, **4**, 7200–7208.
- 23 F. K. Chong, V. Andiappan, D. K. S. Ng, D. C. Y. Foo, F. T. Eljack, M. Atilhan and N. G. Chemmangattuvalappil, *ACS Sustainable Chem. Eng.*, 2017, **5**, 5241–5252.
- 24 O. Hollóczki and L. Nyulászi, in *Electronic Effects in Organic Chemistry*, ed. B. Kirchner, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014, pp. 1–24, DOI: 10.1007/128_2012_416.
- 25 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496.
- 26 A. J. Arduengo, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530–5534.
- 27 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361–363.
- 28 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371–2374.
- 29 G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151–5169.
- 30 F. Wang, S. Li, M. Qu, M.-X. Zhao, L.-J. Liu and M. Shi, *Beilstein J. Org. Chem.*, 2012, **8**, 726–731.
- 31 J. Vignolle and T. D. Tilley, *Chem. Commun.*, 2009, 7230–7232, DOI: 10.1039/B913884F.
- 32 K. V. S. Ranganath, J. Kloesges, A. H. Schäfer and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 7786–7789.
- 33 P. Lara, O. Rivada-Wheelaghan, S. Conejero, R. Poteau, K. Philippot and B. Chaudret, *Angew. Chem., Int. Ed.*, 2011, **50**, 12080–12084.
- 34 C. M. Crudden, J. H. Horton, I. I. Ebraldidze, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H.-B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb and G. Wu, *Nat. Chem.*, 2014, **6**, 409–414.
- 35 C. A. Dyker, V. Lavallo, B. Donnadiou and G. Bertrand, *Angew. Chem., Int. Ed.*, 2008, **47**, 3206–3209.
- 36 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 14970–14971.
- 37 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. von R. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069–1071.
- 38 R. Kinjo, B. Donnadiou, M. A. Celik, G. Frenking and G. Bertrand, *Science*, 2011, **333**, 610–613.
- 39 D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655.
- 40 D. M. Flanagan, F. Romanov-Michailidis, N. A. White and T. Rovis, *Chem. Rev.*, 2015, **115**, 9307–9387.
- 41 C. Zhang, J. F. Hooper and D. W. Lupton, *ACS Catal.*, 2017, **7**, 2583–2596.

- 42 B. Gorodetsky, T. Ramnial, N. R. Branda and J. A. C. Clyburne, *Chem. Commun.*, 2004, 1972–1973, DOI: 10.1039/B407386J.
- 43 M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu and A. Inesi, *Adv. Synth. Catal.*, 2008, **350**, 1355–1359.
- 44 M. Orsini, I. Chiarotto, M. N. Elinson, G. Sotgiu and A. Inesi, *Electrochem. Commun.*, 2009, **11**, 1013–1017.
- 45 I. Chiarotto, M. M. M. Feeney, M. Feroci and A. Inesi, *Electrochim. Acta*, 2009, **54**, 1638–1644.
- 46 M. Feroci, I. Chiarotto, M. Orsini and A. Inesi, *Chem. Commun.*, 2010, **46**, 4121–4123.
- 47 M. Feroci, I. Chiarotto, M. Orsini, R. Pelagalli and A. Inesi, *Chem. Commun.*, 2012, **48**, 5361–5363.
- 48 I. Chiarotto, M. Feroci, G. Sotgiu and A. Inesi, *Eur. J. Org. Chem.*, 2013, 326–331.
- 49 M. Feroci, I. Chiarotto, F. D'Anna, G. Forte, R. Noto and A. Inesi, *Electrochim. Acta*, 2015, **153**, 122–129.
- 50 L. Delaude, *Eur. J. Inorg. Chem.*, 2009, 1681–1699.
- 51 L. Delaude, X. Sauvage, A. Demonceau and J. Wouters, *Organometallics*, 2009, **28**, 4056–4064.
- 52 S. Naeem, A. L. Thompson, L. Delaude and J. D. E. T. Wilton-Ely, *Chem. – Eur. J.*, 2010, **16**, 10971–10974.
- 53 S. Naeem, L. Delaude, A. J. P. White and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2010, **49**, 1784–1793.
- 54 S. Naeem, A. L. Thompson, A. J. P. White, L. Delaude and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2011, **40**, 3737–3747.
- 55 M. J. D. Champion, R. Solanki, L. Delaude, A. J. P. White and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2012, **41**, 12386–12394.
- 56 U. Siemeling, H. Memczak, C. Bruhn, F. Vogel, F. Trager, J. E. Baio and T. Weidner, *Dalton Trans.*, 2012, **41**, 2986–2994.
- 57 L. Di Marco, M. Hans, L. Delaude and J.-C. M. Monbaliu, *Chem. – Eur. J.*, 2016, **22**, 4508–4514.
- 58 P. Aydogan Gokturk, U. Salzner, L. Nyulászi, B. Ulgut, C. Kocabas and S. Suzer, *Electrochim. Acta*, 2017, **234**, 37–42.
- 59 Please see the ESI† for further details.
- 60 M. Isabel Cabaco, M. Besnard, F. V. Chavez, N. Pinaud, P. J. Sebastiao, J. A. P. Coutinho, J. Mascetti and Y. Danten, *Chem. Commun.*, 2013, **49**, 11083–11085.
- 61 M. I. Cabaço, M. Besnard, F. V. Chávez, N. Pinaud, P. J. Sebastião, J. A. P. Coutinho and Y. Danten, *J. Chem. Phys.*, 2014, **140**, 244307.
- 62 Y. Danten, M. I. Cabaço, J. A. P. Coutinho, N. Pinaud and M. Besnard, *J. Phys. Chem. B*, 2016, **120**, 5243–5254.
- 63 E. F. Smith, F. J. M. Rutten, I. J. Villar-Garcia, D. Briggs and P. Licence, *Langmuir*, 2006, **22**, 9386–9392.
- 64 K. R. J. Lovelock, I. J. Villar-Garcia, F. Maier, H.-P. Steinrück and P. Licence, *Chem. Rev.*, 2010, **110**, 5158–5190.
- 65 I. J. Villar-Garcia, K. R. J. Lovelock, S. Men and P. Licence, *Chem. Sci.*, 2014, **5**, 2573–2579.
- 66 S. Men, D. S. Mitchell, K. R. J. Lovelock and P. Licence, *ChemPhysChem*, 2015, **16**, 2211–2218.
- 67 O. Holloczki, D. Gerhard, K. Massone, L. Szarvas, B. Nemeth, T. Veszpremi and L. Nyulaszi, *New J. Chem.*, 2010, **34**, 3004–3009.
- 68 Z. Kelemen, O. Holloczki, J. Nagy and L. Nyulaszi, *Org. Biomol. Chem.*, 2011, **9**, 5362–5364.
- 69 Z. Kelemen, B. Péter-Szabó, E. Székely, O. Hollóczki, D. S. Firaha, B. Kirchner, J. Nagy and L. Nyulászi, *Chem. – Eur. J.*, 2014, **20**, 13002–13008.