Current Topics in Electrochemistry
Vol. 16, 2011

Original Communication

Direct electrochemical reduction of azolium salts into *N*-heterocyclic carbenes and their subsequent trapping

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ABSTRACT

Azolium salts such as imidazolium, triazolium and benzothiazolium halides can be directly cathodically reduced in DMF solution yielding the corresponding *N*-heterocylic carbenes (NHCs). A voltamperometric study shows that the reduction potential is linked to the nature of the azolium salt. Preparative electrolyses using an undivided cell allow the preparation of NHCs which can be trapped either by selenium to yield a selenourea derivative with good yields or by a nickel salt to yield a *bis*-NHC Ni(II) complex.

KEYWORDS: azolium salts, *N*-heterocyclic carbenes, voltamperometric study, preparative electrolysis

1. INTRODUCTION

Azolium salts have reached great interest in the organic chemistry field for two main purposes: as precursors of *N*-heterocyclic carbenes (NHCs) and as highly polar solvents, also referred to as ionic liquids. Azolium salts are indeed common precursors to NHCs used as ligands [1] for transition metals or as organocatalysts [2]. A simple deprotonation of the acidic C-H bond between the two heteroatoms leads to the formation of NHCs. Depending on the heterocyclic structures, the *p*Kas of the azolium salts vary from 22 to 12. Therefore the strength of the base used ranges from very strong (*n*BuLi, LDA…) for the deprotonation of dihydroimidazolium salts, to weak (Et_3N, AcONa) for thiazolium or triazolium salts [3]. The former class of heterocyclic structure is commonly used as ligand precursors which are among the strongest σ-donor ligands, whilst the latter is employed as organocatalysts. In some specific cases, the nature of the strong base may drive the deprotonation to either normal or abnormal NHCs [4].

Azolium salts, and more especially imidazolium salts, are also interestingly used as solvents called ionic liquids (ILs) because of their low melting point (typically below 100°C), low volatility, and high polarity [5]. These three main features allow their recycling as well as the rate increase of many reactions. They are also used as solvents in electrochemistry as they are conductive and therefore no supporting electrolyte is required [6]. They may however be reduced, and this may restrict their use for cathodic processes occurring at quite negative potentials [7]. Clyburne and Coll. have shown by voltamperometric analysis that imidazolium salts are reduced to NHCs [8]. However electrochemistry has not been used preparatively so far to access to NHCs. This is the purpose of this study.

2. EXPERIMENTAL

2.1. General methods

All reactions were carried out under inert atmosphere (N_2) and using commercially available

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reagents without further purification. All compounds were characterized by their ^{1}H and ^{13}C NMR spectra and compared to literature data for already described compounds. Full analyses have been carried out and are reported below for new compounds.

IR spectra were recorded on a FT-IR Bruker Tensor 27 and values of the most characteristic bands are given in cm^{-1}. NMR spectra (^{1}H, ^{13}C, COSY, NOESY, HSQC, HMBC) were recorded on a Bruker spectrometer AV2-400. Data are given in the following order: chemical shift (ppm); coupling figure; integration; coupling constant (Hz); attribution. The atom of the given signal is written in italic. Ipso, ortho (*o*-), meta (*m*-) and para (*p*-) position are given relatively to the bond with the heterocycle. Nitrogens are numbered following the IUPAC rules. Voltamperometric analysis was carried out with a Voltalab PST 006 education equipped with the software VoltaLab.

Azolium salts **1** and **4** were prepared following literature protocols [9].

2.2 Procedures and products characterization

2.2.1. 1-Benzyl-4,5-diphenyl-1*H*-imidazole: 6

4,5-Dibenzylimidazole (2.20 g, 10 mmol, 1 eq.) was dissolved in DMF (10 mL) at 0°C, then NaH was added (1.1 eq.) before addition of benzylbromide (1.5 mL, 15 mmol, 1.5 eq.). The reaction mixture was then warmed up to RT for 3h before addition of brine (50 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL), then the combined organic layers were washed with water (2 × 50 mL) and brine (50 mL) before being dried over $MgSO_4$ and concentrated under vacuum. The resulting oil was purified by column chromatography with CH_2Cl_2 (DCM) as eluent. **6** was obtained as a yellow powder (2.52 g: 81%). **F:** 128-129°C; **R*f*:** 0.20 (CH_2Cl_2); **IR:** 3050, 1601, 1494; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.51 (s, 1H, *H*-imidazole), 7.41 (d, 2H, *J* = 7.3 Hz, *o*-*H*-Ar), 7.23 (m, 3H, *H*-Ar), 6.97-7.14 (m, 8H, *H*-Ar), 6.82 (m, 2H, *H*-Ar), 4.80 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): 138.1 (C^{IV}), 137.0 (*C*H), 135.4 (C^{IV}), 134.4 (C^{IV}), 130.7 (*C*H), 130.3 (C^{IV}), 128.7 (*C*-H), 128.7 (*C*-H), 128.6 (C^{IV}), 128.5 (*C*-H), 128.0 (*C*-H), 127.7 (*C*-H), 126.7 (*C*-H), 126.3 (*C*-H), 126.2 (*C*-H), 48.5 (CH_2);

Elemental analysis for $C_{22}H_{18}N_2$**:** *Calc.* %C: 85.13, %H: 5.85, %N: 18.32*; fd.* %C: 85.02, %H: 5.91, %N: 18.11.

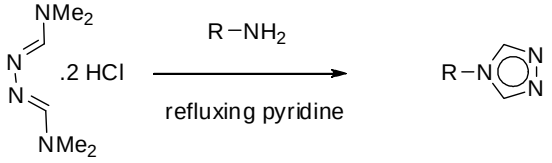
2.2.2. Typical procedure for the synthesis of triazoles

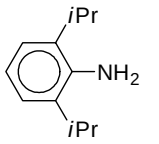
Bis 1,2-*bis*-(*N*,*N*-dimethylaminomethylidene)-hydrazine [10] (12.90 g, 60 mmol, 1.5 eq.) and the amine (40 mmol, 1 eq.) were mixed in pyridine (40 mL) and warmed up to reflux for the reaction time indicated in Table 1. The solution was then concentrated under reduced pressure and the resulting oil was diluted with ethyl acetate (100 mL) and 5% KOH aqueous solution (100 mL). The aqueous phase was extracted with ether (3 × 100 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to yield an oil which was then dissolved in a minimum of boiling DCM prior to addition of pentane to precipitate the triazole. After filtration and washing with pentane, triazoles were obtained as solids after being dried under vacuum.

2.2.2.1. 4-Benzyl-4*H*-[1,2,4]triazole: 8

Starting from benzylamine (6.40 mL, 58.3 mmol, 1 eq.) and after one hour in refluxing pyridine, typical procedure led to **8** as a white powder (6.97 g, 44 mmol, 75%). **F:** 112-113°C; **R*f*:** 0.13 (AcOEt); **IR:** 3084, 3029, 1534, 1496; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.11 (s, 2H, *H*-triazole), 7.32 (m, 3H, *m*-*H*-Ar and *p*-*H*-Ar), 7.12 (d, *J* = 7.2 Hz, 2H, *o*-*H*-Ar), 5.12 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): 142.8 (*C*-triazole), 134.1 (C^{IV}-Ar),

Table 1. Triazoles synthesis.



Entry	R-NH_2	Time	Product	Yield[a]
1	Bn-NH_2	1h	**8**	75%
2	Ph-NH_2	4 h	**9**	82%
3		15 days	**10**	51%

[a]: isolated yields after crystallization.

129.3 (*C*-Ar), 129.2 (*C*-Ar), 127.6 (*o*-*C*-Ar), 49.1 (*C*H_2); **MS (EI):** 159 (36%), 132 (27%), 91 (100%), 65 (22%), 51 (8%).

2.2.2.2. 4-Phenyl-4*H*-[1,2,4]triazole: 9

Starting from aniline (9.20 mL, 100 mmol, 1 eq.) and after 4 h in refluxing pyridine, typical procedure led to **9** as a white powder (11.90 g, 82 mmol, 82%). **F:** 120-121°C; **R*f*:** 0.34 (AcOEt); **IR:** 3119, 1658, 1590; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.32 (s, 2H, *H*-triazole), 7.52 (t, 2H, *J* = 7.4 Hz, *m*-*H*-Ar), 7.44 (t, 1H, *J* = 7.4 Hz, *m*-*H*-Ar), 7.35 (d, 2H, *J* = 7.4 Hz, *o*-*H*-Ar); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.4 (*C*-triazole), 133.7 (*C*^{IV}-Ar), 130.3 (*m*-*C*-Ar), 129.0 (*p*-*C*-Ar), 122.2 (*o*-*C*-Ar); **MS (EI):** 145 (100 %), 118 (23%), 91 (28%); 77 (6%).

2.2.2.3. 4-(2,6-Di*iso*propyl-phenyl)-4*H*-[1,2,4] triazole : 10

Starting from *o*,*o*'-di*iso*propylaniline (5.66 mL, 30 mmol, 1 eq.) and after 15 days in refluxing pyridine, typical procedure led to **10** as a off-white fiber (7.41 g, 15.3 mmol, 51%). **F:** 246-248°C; **R*f*:** 0.68 (AcOEt); **IR:** 3150, 2961, 1645, 1590; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.12 (s, 2H, *H*-triazole), 7.48 (t, 1H, *J* = 7.7 Hz, *m*-*H*-Ar), 7.29 (d, 2H, *J* = 7.7 Hz, *m*-*H*-Ar), 2.33 (heptet, 2H, *J* = 6.8 Hz, -C*H*Me_2), 1.06 (d, 12H, *J* = 6.7 Hz, -CH(C*H*)$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.2 (*o*-*C*^{IV}-Ar), 143.9 (*C*-triazole), 130.8 (*p*-*C*-Ar), 128.9 (*ipso*-*C*^{IV}-Ar), 124.2 (*m*-*C*-Ar), 28.2 (*C*H-Me_2), 24.2 (CH-(*C*H_3)$_2$); **MS (EI):** 228 (3%), 214 (4%), 201 (28%), 186 (100%), 172 (37%), 158 (13%), 145 (9%), 128 (9%), 115 (10%); **Elemental analysis** for $C_{14}H_{19}N_3$**:** *Calc.* %C: 73.33, %H: 8.35, %N: 18.32*; fd.* %C: 73.02, %H: 8.16, %N: 18.26.

2.2.3. Typical procedure for benzylation or alkylation of azole using benzyl halide or *iso*propyl iodide

The azole (10 mmol, 1 eq.) was heated to reflux for 2-17 h (see result and discussion) in toluene (20 mL) in the presence of the alkylating agent (1-2 eq.; see result and discussion). Then, the surnatant was taken off at room temperature and the pasty solid was dissolved in boiling DCM prior addition of Et_2O. The azolium salt was isolated by filtration.

2.2.3.1. 1,3-Dibenzylimidazolium chloride: 5

Starting from benzylimidazole, following the typical procedure with benzylchloride, **5** was obtained as a off-white solid (87%). **F:** >250°C; **IR:** 2984, 1602, 1557, 1449, 1185; **^{1}H NMR** (400 MHz, $CDCl_3$): 10.83 (s, 1H, N-C*H*-N), 7.47 (d, 4H, *J* = 6.9 Hz, *o*-*H*-Ar), 7.37 (m, 6H, *H*-Ar), 7.25 (s, 2H, N-C*H*-C); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.1 (N-*C*H-N), 132.7 (*C*^{IV}-Ar), 129.6 (*m*-*C*-Ar), 129.1 (*p*-*C*-Ar), 121.8 (N-*C*H-C-), 53.4 (CH_2).

2.2.3.2. 1,3-Dibenzylimidazolium bromide: 5'

Starting from benzylimidazole, following the typical procedure with benzylbromide, **5'** was obtained as a white solid (93%). **F:** 228-230°C; **IR:** 2986, 1609, 1555, 1450; **^{1}H NMR** (400 MHz, $CDCl_3$): 10.89 (s, 1H, N-C*H*-N), 7.45 (d, 4H, *J* = 6.9 Hz, *o*-*H*-Ar), 7.37 (m, 6H, *H*-Ar); 7.21 (s, 2H, N-C*H*-C); **^{13}C NMR** (100 MHz, $CDCl_3$): 136.2 (N-*C*H-N), 131.9 (*C*^{IV}-Ar), 129.5 (*m*-*C*-Ar), 129.0 (*p*-*C*-Ar), 121.4 (N-*C*H-C-), 53.2 (CH_2).

2.2.3.3. 1,3-Dibenzyl-4,5-diphenylimidazolium chloride: 7

Starting from **6**, following the typical procedure with benzylchloride, **7** was obtained as a off-white solid (99%). **F:** 248-250°C; **IR:** 3030, 2960, 1556, 1488; **^{1}H NMR** (400 MHz, $CDCl_3$): 11.21 (s, 1H, N-C*H*-N), 7.42 (t, *J* = 7.2 Hz, 2H, *H*-Ar), 7.33 (m, 4H, *H*-Ar), 7.25 (m, 6H, *H*-Ar), 7.10 (m, 8H, *H*-Ar), 5.51 (s, 4H, C*H*$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.5 (N-*C*H-N), 133.2 (*C*^{IV}-Ar), 132.2 (*C*^{IV}-imidazolium), 130.7 (*C*-Ar), 130.5 (*C*-Ar), 129.1 (*C*-Ar), 129.0 (*C*-Ar), 128.5 (*C*-Ar), 124.7 (*C*^{IV}-Ar), 51.4 (*C*H_2); **Elemental analysis** for $C_{29}H_{25}N_2Cl$**:** *Calc. %*C: 79.71, %H: 5.77, %N: 6.41*; fd.* %C: 79.91, %H: 5.71, %N: 6.89.

2.2.3.4. 1,4-Dibenzyl-4*H*-1,2,4-triazol-1-ium chloride: 11

Starting from **8**, following the typical procedure with benzyl chloride, **11** was obtained as a off-white solid (93%). **F:** 166-167°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 11.78 (s, 1H, $N^{(1)}$-C*H*-$N^{(4)}$), 8.67 (s, 1H, $N^{(2)}$-C*H*-$N^{(4)}$), 7.59-7.55 (m, 2H, *H*-Ar), 7.54-7.50 (m, 2H, *H*-Ar), 7.38-7.35 (m, 3H, *H*-Ar), 7.35-7.31 (m, 3H, *H*-Ar), 5.76 (s, 2H, C*H*$_2$), 5.65 (s, 2H, C*H*$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$): 143.4 ($N^{(1)}$-*C*H-$N^{(4)}$), 142.8 ($N^{(2)}$-*C*H-$N^{(4)}$), 131.7 (*C*-Ar), 131.7 (*C*-Ar), 130.0 (*C*-Ar), 129.7 (*C*-Ar),

129.7 (*C*-Ar), 129.5 (*C*-Ar), 129.5 (*C*-Ar), 129.3 (*C*-Ar), 56.4 (CH_2), 52.2 (CH_2).

2.2.3.5. 4-Phenyl-1-*iso*propyl-1,2,4-triazol-1-ium iodide: 12

Starting from **9**, following the typical procedure with *iso*propyliodide, **12** was obtained as a pale yellow solid (91%). **F:** 202-204°C; **IR:** 3039, 2995, 1561, 1488; **^{1}H NMR** (400 MHz, $CDCl_3$): 12.02 (s, 1H, $N^{(1)}$-C*H*-$N^{(4)}$), 8.84 (s, 1H, $N^{(2)}$-C*H*-$N^{(4)}$), 7.96 (d, 2H, *J* = 7.7 Hz, *o*-*H*-Ar), 7.63 (m, 3H, *H*-Ar), 5.53 (heptet, 1H, *J* = 6.5 Hz, -C*H*Me_2), 1.76 (d, 6H, *J* = 6.5 Hz, -CH(CH_3)$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.9 ($N^{(1)}$-*C*H-$N^{(4)}$), 140.6 ($N^{(2)}$-*C*H-$N^{(4)}$), 131.3(C^{IV}-Ar), 130.8 (*p*-*C*-Ar),125.2 (*C*-Ar), 122.6 (*C*-Ar), 57.4 (-*C*HMe_2), 21.1 (-CH(CH_3)$_2$); **Elemental analysis** for $C_{11}H_{14}N_3I$**:** *Calc.* %C: 41.92, %H: 4.48, %N: 13.33*; fd.* %C: 42.02, %H: 4.41, %N: 13.08.

2.2.3.6. 4-(2,6-Di*iso*propylphenyl)-1-*iso*propyl -1,2,4-triazol-1-ium iodide: 13

Starting from **10**, following the typical procedure with *iso*propyliodide, **13** was obtained as a pale blue solid (91%). **F:** 234-236°C; **IR:** 3061, 2960, 1589, 1408; **^{1}H NMR** (400 MHz, $CDCl_3$): 12.05 (s, 1H, $N^{(1)}$-C*H*-$N^{(4)}$), 8.26 (s, 1H, $N^{(2)}$-C*H*-$N^{(4)}$), 7.60 (t, 1H, *J* = 7.9 Hz, *p*-*H*-Ar), 7.37 (d, 2H, *J* = 7.9 Hz, *m*-*H*-Ar), 5.89 (heptet, 2H, *J* = 6.8 Hz, Ar-C*H*$(Me)_2$), 2,25 (heptet, 1H, *J* = 6.7 Hz, N-C*H*$(Me)_2$), 1.76 (d, 6H, *J* = 6.7 Hz, N-CH(CH_3)$_2$), 1.31 (d, 6H, *J* = 6.8 Hz, Ar-CH(CH_3)$_2$), 1.17 (d, 6H, *J* = 6.8 Hz, Ar-CH(CH_3)$_2$); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.2 ($N^{(1)}$-*C*H-$N^{(4)}$), 143.7 ($N^{(2)}$-*C*H-$N^{(4)}$), 143.0 ($N^{(4)}$-*C*^{IV}-Ar), 132.9 (*p*-*C*-Ar), 126.5 (*i*Pr-C^{IV}-Ar), 126.1 (*m*-*C*-Ar), 57.3 ($N^{(1)}$-*C*HMe_2), 29.0 (Ar-*C*HMe_2), 24.3 (Ar-CH(CH_3)$_2$), 24.2 (Ar-CH(CH_3)$_2$), 22.1 (N-CH(CH_3)$_2$); **Elemental analysis** for $C_{17}H_{26}N_3I$**:** *Calc.* %C: 51.13, %H: 6.56, %N: 10.58*; fd.* %C: 51.07, %H: 6.62, %N: 10.32.

2.2.3.7. 3-Benzylbenzo[d]thiazol-3-ium bromide: 14

Starting from benzo[d]thiazole, following the typical procedure in refluxing *p*-xylene instead of toluene, with benzylbromide (5 eq.), **14** was obtained as a pale purple solid (69%). **F:** 187-188°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 10.92 (s, 1H, S-C*H*-N), 8.59 (d, 1H, *J* = 8.0 Hz, *H*-Ar benzothiazole), 8.34 (d, 1H, *J* = 8.0 Hz, *H*-Ar benzothiazole), 7.87 (dd, 1H, *J* = 7.5 Hz, *J* = 8.0 Hz, *H*-Ar benzothiazole), 7.81 (t, 1H, *J* = 8.0 Hz, *H*-Ar benzothiazole), 7.50 (d, 2H, *J* = 7.0 Hz, *H*-Ph), 7.41(t, 2H, *J* = 7.0 Hz, *H*-Ph), 7.37 (t, 1H, *J* = 7.0 Hz, *H*-Ph), 6.22 (s, 2H, CH_2);**^{13}C NMR** (100 MHz, $CDCl_3$): 165.3 (S-*C*H-N), 140.0 (C^{IV}-Ar benzothiazole), 132.9 (C^{IV}-Ar), 131.8 (C^{IV}-Ar benzothiazole), 129.6 (*C*-Ar benzothiazole), 129.1 (*C*-Ar), 129.0 (*C*-Ar), 128.4 (*C*-Ar benzothiazole), 128.3 (*C*-Ar), 125.5 (*C*-Ar benzothiazole), 117.4 (*C*-Ar benzothiazole), 55.1 (CH_2); **Elemental analysis** for $C_{14}H_{12}NSBr$**:** *Calc.* %C: 54.91, %H: 3.95, %N: 4.57; *fd.* %C: 55.07, %H: 4.07, %N: 4.64.

2.2.4. Typical procedure for the synthesis of selenourea

Within a 25 mL undivided electrochemical cell, equipped with a magnesium anode and a glassy carbone cathode, was placed under argon at 0°C, a DMF solution (20 mL) containing the supporting electrolyte (1.1 M of *n*Bu_4NBF_4) and the azolium salt (0.1 M, 1 eq.). Then the current intensity was fixed at 50 mA and was switched off after 1.2 Faraday (1.2 eq.) was passed. Then, selenium powder (2 eq.) was added and the mixture was stirred at RT for 1 h before being transferred into a separating funnel. The organic layer was diluted with ether (100 mL), and washed with water (2 x 50 mL) and brine (50 mL) before being dried over $MgSO_4$ and concentrated under reduced pressure. The resulting paste was purified by column chromatography using DCM as eluent to afford the selenourea.

2.2.4.1. 1,3-*Bis*(2,6-di*iso*propylphenyl)-1*H*-imidazole-2(3*H*)-selenone: 15

Starting from **4**, typical procedure led to **15** as a yellow powder (51*%*). **F:** 112-113°C; **R*f*:** 0.60 (CH_2Cl_2); **IR:** 3084, 3029, 1534, 1496; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.40 (t, 2H, *J* =7.9 Hz, *p*-*H*-Ar), 7.23 (d, 4H, *J* =7.9 Hz ; *o*-*H*-Ar), 7.19 (s, 2H, C*H*-N), 2.61 (heptet, 4H, *J* = 6.8 Hz, -C*H*(CH_3)), 1.26 (d, 12H, *J* = 6.8 Hz ; -CH(C*H*$_3$)), 1.12 (d, 12H, *J* = 6.8 Hz ; -CH(C*H*$_3$)); **^{13}C NMR** (100 MHz, $CDCl_3$): 162.1 (*C*=Se), 146.1 (*o*-C^{IV}-Ar), 134.4 (*ipso*-C^{IV}-Ar), 130.2 (*p*-*C*-Ar), 124.2 (*m*-*C*-Ar), 121.0 (*C*H-N), 29.0 (-*C*H(CH_3)), 24.3 (-CH(*C*H$_3$)), 23.3(-CH(*C*H$_3$)); **Elemental analysis** for $C_{27}H_{36}N_2Se$**:** *Calc.* %C: 69.36, %H: 7.76, %N: 5.99*; fd.* %C: 69.19, %H: 7.64, %N: 5.86.

2.2.4.2. 1,4-Dibenzyl-1*H*-1,2,4-triazole-5(4*H*)-selenone: 16

Starting from **11**, typical procedure led to **16** as a pale yellow powder (73%). **F:** 51-53°C; **R*f* :** 0.55 (CH_2Cl_2); **IR:** 3109, 2926, 1598, 1417; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.01 (s, 1H, $N^{(5)}$-C*H*=$N^{(3)}$), 7.28-7.13 (m, 10H, *H*-Ar), 5.23 (s, 2H,CH_2), 4.93 (s, 2H,CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.8 (*C*=Se), 140.6 (N-*C*H=N), 136.8 (C^{IV}-Ar), 135.1 (C^{IV}-Ar), 128.2 (*C*-Ar), 127.9 (*C*-Ar), 127.1 (*C*-Ar), 126.9 (*C*-Ar), 125.8 (*C*-Ar), 125.2 (*C*-Ar), 55.2 (*C*H_2), 52.9 (*C*H_2); **Elemental analysis** for $C_{16}H_{15}N_3Se$**:** *Calc.* %C: 58.54, %H: 4.61, %N: 12.80; *fd.* %C: 58.59, %H: 4.69, %N: 13.01.

2.2.4.3. 3-Benzylbenzo[d]thiazole-2(3*H*)-selenone: 17

Starting from **14**, typical procedure led to **17** as pale-yellow thin needles (75%). **F:** 122-123°C; **R*f* :** 0.65 (CH_2Cl_2); **IR:** 3080, 3021, 1539, 1456; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.85 (d, 1H, *J* = 8.2 Hz, *H*-benzothiazole), 7.57 (d, 1H, *J* = 8.1 Hz, *H*-benzothiazole), 7.49 (t, 1H, *J* = 8.1 Hz, *H*-benzothiazole), 7.38-7.23 (m, 6H, *H*-benzyl and *H*-benzothiazole), 4.89 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$): 170.5 (*C*=Se), 139.1 (N-C^{IV}-benzothiazole), 137.1 (C^{IV}-benzyl), 128.1 (*C*-benzyl), 127.3 (*C*-benzyl), 126.8 (*C*-benzyl), 126.3 (*C*-benzothiazole), 122.9 (S-C^{IV}-benzothiazole), 122.1 (*C*-benzothiazole) 116.8 (*C*-benzothiazole), 116.3 (*C*-benzothiazole), 52.9 (*C*H_2); **Elemental analysis** for $C_{14}H_{11}NSSe$**:** *Calc.* %C: 55.26, %H: 3.64, %N: 4.60; *fd.* %C: 55.29, %H: 3.51, %N: 4.55.

2.2.5. Synthesis of the *bis*-NHC $NiBr_2$ complex: 18

Within an undivided electrochemical cell, fitted with a magnesium rod as the anode and a glassy carbon as the cathode, the azolium salt (0.1 M, 1 eq.) was dissolved in DMF containing the supporting electrolyte (1.1 M of nBu_4NBF_4). Then the current intensity was fixed at 50 mA and was switched off after 1.2 Faraday (1.2 eq.) was passed. Then, $NiBr_2$ (0.5 eq.) was added and the mixture was stirred at RT for 1 h before being concentrated under reduced pressure. The resulting paste was extracted with THF (3 x 20 mL) and the THF fractions were concentrated under vacuum. Finally, the crude compound was dissolved in the minimum of DCM before addition of pentane. After filtration the solid was dried under vacuum to afford **18** as a pale yellow solid (47%). **F:** >250°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.41 (t, 4H, *J* = 6.9 Hz, *p*-*H*-Ar), 7.13 (d, 8H, *J* = 6.9 Hz, *m*-*H*-Ar), 6.58 (s, 4H, C*H*-N), 2.91 (heptet, 8H, *J* = 6.8 Hz ; (-C*H*(CH_3)), 0.98 (d, 24 H, *J* = 6.8 Hz ; -CH(CH_3)), 0.82 (d, 24 H, *J* = 6.8 Hz ; -CH(CH_3)); **^{13}C NMR** (100 MHz, $CDCl_3$): 170.4 (N-C^{IV}-N), 146.7 (*ipso*-C^{IV}-Ar), 136.7 (*ortho*-C^{IV}-Ar), 129.3 (*p*-*C*-Ar), 124.5 (*m*-C^{IV}-Ar), 123.9 (*C*H-N), 28.3 (-*C*H(CH_3)), 26.1 (-CH(*C*H_3)), 22.9 (-CH(*C*H_3)).

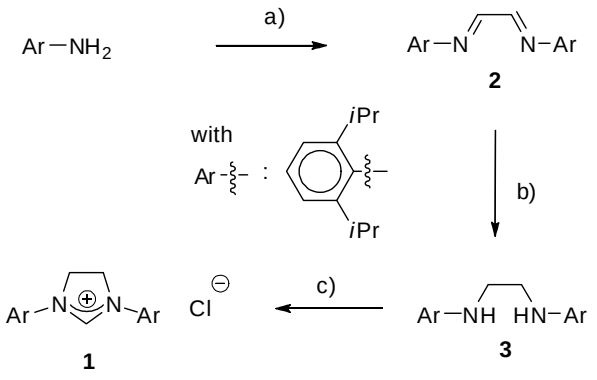
3. RESULTS AND DISCUSSION

Imidazolium salts are the conjugated acid of NHCs, as water is the conjugated acid of hydroxide anion. If water can be reduced electrochemically, a similar process could be applied to imidazolium salts and the acidity of the C-H bond be correlated to the reduction potential. To ascertain this point of view, we investigated four classes of azolium salts: dihydroimidazolium, imidazolium, triazolium, and benzothiazolium salts. We also included a few variations on the *N*-substitution or heterocycle substitution, as well as on the counter-anion.

3.1. Synthesis of azolium salts

3.1.1. Synthesis of dihydroimidazolium salt 1

Dihydroimidazolium chloride salts **1** have been prepared according to a literature procedure described in Scheme 1 [9]. This procedure led to an optimized overall yield of 74% in 3 steps.



Scheme 1. Reagents and conditions: a) aqueous glyoxal, HCO_2H (cat), EtOH, RT, 3 days, 94%; b) $LiAlH_4$, refluxing THF then KOH aq., 93%; c) $HC(OEt)_3$, NH_4Cl, HCO_2H (cat) reflux, 2 days, 85%.

3.1.2. Synthesis of *N,N'*-diarylimidazolium salt 4

N,N'-diarylimidazolium chloride salt **4** has been prepared in 72% yield from **2** according to a literature method [9] (see Scheme 2).

3.1.3. Synthesis of *N,N*-dibenzylimidazolium salts 5, 5' and 7

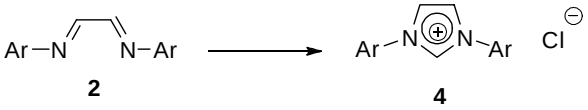
N,N'-dibenzylimidazolium chloride salt **5** and the bromide salt **5'** were prepared from benzylimidazole [11] by alkylation with benzylchloride or benzylbromide respectively (see Scheme 3).

The corresponding diphenyl analogue **7** was prepared following the same procedure (see Scheme 4).

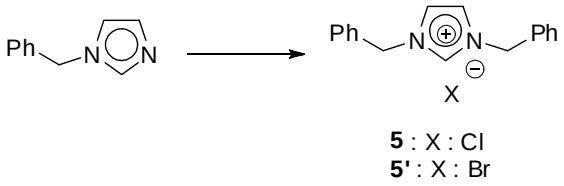
3.1.4. Synthesis of triazolium salts 11, 12 and 13

First, three triazoles have been prepared according to Lassaletta procedure [1] from benzylamine, aniline, and 2,6-di*iso*propylaniline respectively. As reported in Table 1, the reaction time is very dependent on the nucleophile (electronic and/or steric factors).

Then their alkylation was performed with benzylchloride or *iso*propyl iodide. No lack of regioselectivity was observed as far as both nucleophile nitrogens $N^{(1)}$ and $N^{(2)}$ are equivalents and that $N^{(4)}$ lone pair is part of the aromaticity therefore non nucleophile. Yields are given in Table 2.



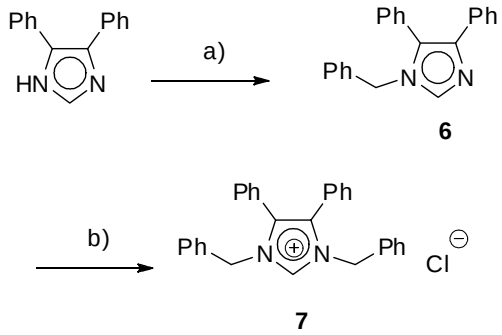
Scheme 2. Reagents and conditions: -$(CH_2O)_n$- toluene then HCl/dioxane RT, 3 days, 72%.



Scheme 3. Reagents and conditions: Ph-CH_2X (2 eq.) refluxing toluene, 2h, X: Cl yield: 87%; X: Br yield: 93%.

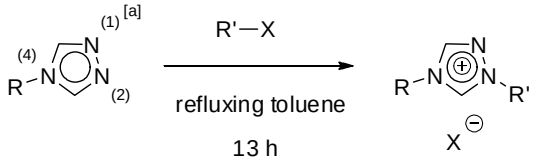
3.1.5. Synthesis of benzothiazolium salt 14

The alkylation of benzothiazole required harsh reaction conditions (see Scheme 5). After 4 days in refluxing *p*-xylene with a large excess of benzylbromide, the salt **14** has been isolated with 69% yield.



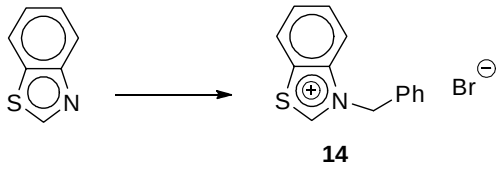
Scheme 4. Reagents and conditions: a) NaH, DMF then $PhCH_2Cl$ 1.5 eq., 81%; b) Ph-CH_2Cl (1 eq.) refluxing toluene 5h, 99%.

Table 2. Triazolium salts synthesis.

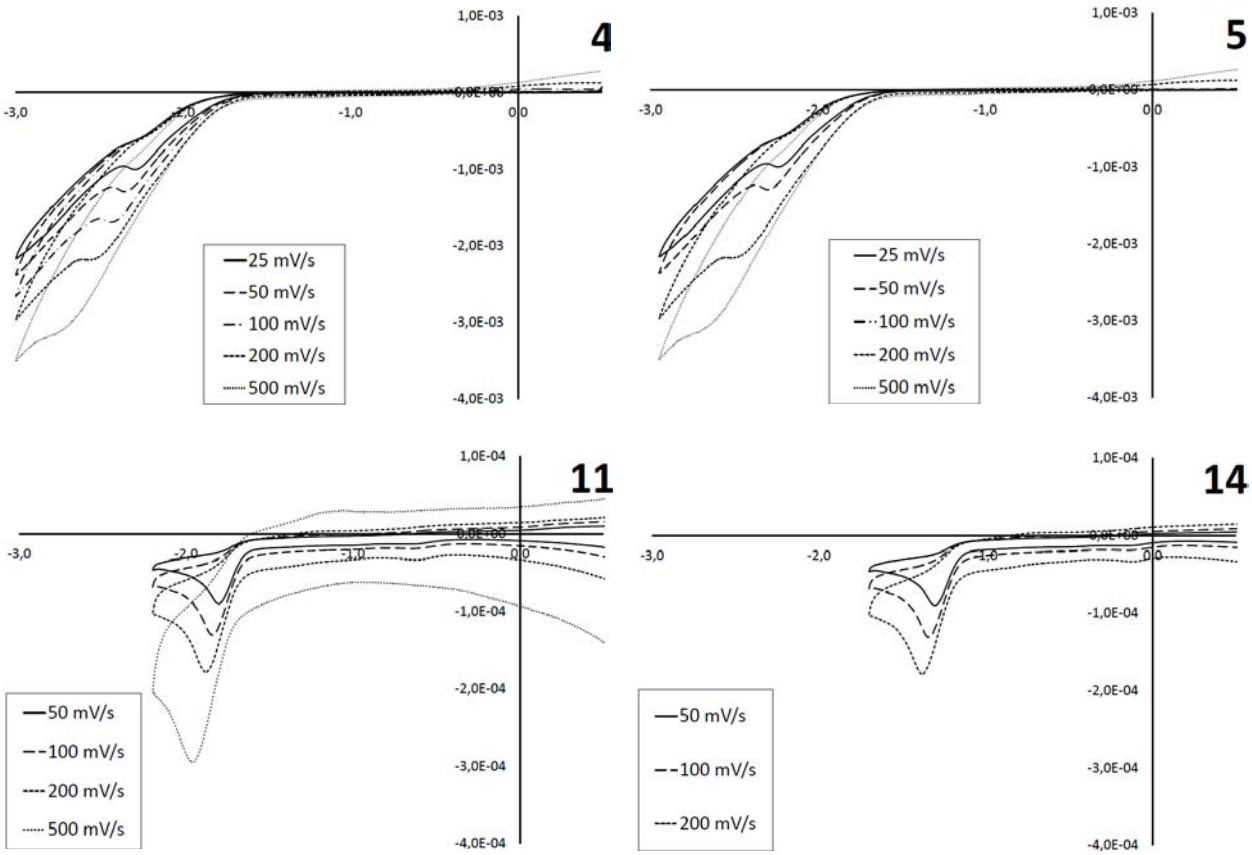


Entry	triazole	R'-X	Product	Yield[b]
1	**8**	Bn-Cl	**11**	93%
2	**9**	*i*Pr-I	**12**	91%
3	**10**	*i*Pr-I	**13**	91%

[a]: numbers follow the IUPAC rules and are also used in the experimental part (NMR); [b]: isolated yields after crystallization.



Scheme 5. Reagents and conditions: Ph-CH_2Br (5 eq.), refluxing *p*-xylene, 4 days, 69%.



Scheme 6. Voltamperograms for **4**, **5**, **11** and **14**. 0.3 mM of the salt into 0.1 M nBu$_4$NBF$_4$ solution in DMF; working electrode: glassy carbon (S = 2.5 mm²); counter electrode: gold wire; reference electrode: Ag/AgCl. Current intensities (A) are given *versus* voltages (V) at various scan rates (v = 25, 50, 100, 200, 500 mV.s^{-1}).

3.2. Voltamperometric study

All the salts prepared have been subjected to voltamperometric study using the following standard procedure: 0.3 mM of the salt was added into degassed 0.1 M nBu$_4$NBF$_4$ DMF solution; the working electrode was made of glassy carbon (S = 2.5 mm²), the counter electrode was a gold wire and the reference electrode was Ag/AgCl. The voltamperograms were recorded at various scan rates. Typical voltamperograms are given in Scheme 6.

Apart from the dihydroimidazolium salt **1**, all salts display an irreversible reduction peak in their cyclic voltamperogram (CV). The process is only under diffusion as $I_p = f(v)^{1/2}$ is linear. Coulometric analysis, using ferrocene as external standard, shows that the reduction peaks correspond to a single electron transfer. The potential peaks from CVs recorded at 200 mV.s^{-1} and referred to Ag/AgCl are collected in Table 3.

The reduction potentials are typical of the azolium series. The dihydroimidazolium salt **1** does not display a reduction peak before the solvent reduction wall. The reduction peak potentials of the imidazolium series (compounds **4**, **5**, **5'**, and **7**) are between -2.45 V and -2.20 V, -1.90 V and -1.85 V for the triazolium series (compounds **11**, **12**, and **13**) and -1.40 V for the benzothiazolium salt (**14**). We can notice that the counter-anion has no effect on the reduction potential (**5** versus **5'**). Also, the substitution on the nitrogen has little effect. Thus, replacing an aryl substituent by an alkyl increases the potential by only 50 mV (**5** versus **4**). On the other hand, the substitution on the imidazolium ring by two phenyls decreased the potential (**7** versus **5**).

Table 3. Reduction peak potential of various azolium salts.

Salts	**1**	**4**	**5**	**5'**	**7**	**11**	**12**	**13**	**14**
E_{red} (V *vs* Ag/AgCl	<-2,85	-2,45	-2,40	-2,40	-2,20	-1,90	-1,85	-1,85	-1,40

These results are consistent with the relative electron density on the azolium ring. A low electron density requires a less energetic potential for the reduction as compared to an electron-rich azolium ring. The imidazolium ring is richer in electron than the triazolium, which is itself richer than the benzothiazolium. This nicely follows the sequence of the potential peaks. In a polar solvent, the cation and the anion are not tightly associated and therefore the counter anion does not affect the reduction of the cation. Replacing an aromatic group by an alkyl group on the nitrogen does not influence much the reduction potential, because the aromatic ring is not conjugated with the nitrogen lone electron pair for steric reason.

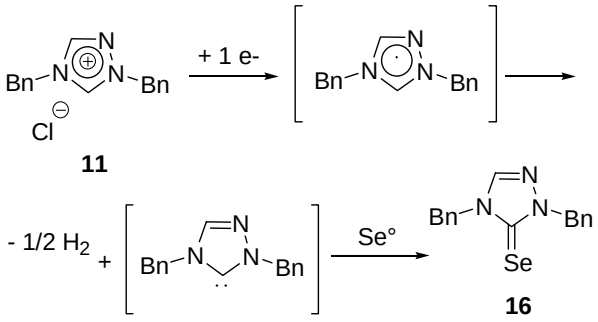
Clyburne and Coll [8] reported that the electrochemical reduction of an imidazolium salt leads first to the formation of a radical intermediate that can lose very quickly a hydrogen atom to yield the *N*-heterocyclic carbene. A proof of the formation of the NHC was supported by the appearance of its oxidation peak on the CV, and confirmed by the voltamperogram recorded from an authentic sample independently prepared. However the authors did not explained exactly how the hydrogen atom is lost.

3.3. Preparative electrolysis

Our main aim is to investigate an electrochemical process to produce NHCs in solution that can be subsequently trapped.

Preliminary attempts of preparative electrolysis have then been carried out with the triazolium salt **11**. As the corresponding NHC is not easy to isolate, it was directly oxidized with selenium to yield the corresponding selenourea **16** (see Scheme 7) [12]. That was the way we used to follow the optimization of the preparative electrolysis using GC/MS analysis with an internal standard (*n*-hexadecane).

Experimental conditions have been selected on the basis of the know-how available in this laboratory. Notably, a method called the sacrificial anode process enables to conduct electrosyntheses in an undivided electrochemical cell [13], with the consequence that, along with the cathodic reduction, the anodic process generates equimolar amounts of a metallic cation and which has to be compatible with the cathodic process. Alternatively, several electrolyses have been carried out in a divided electrochemical cell.



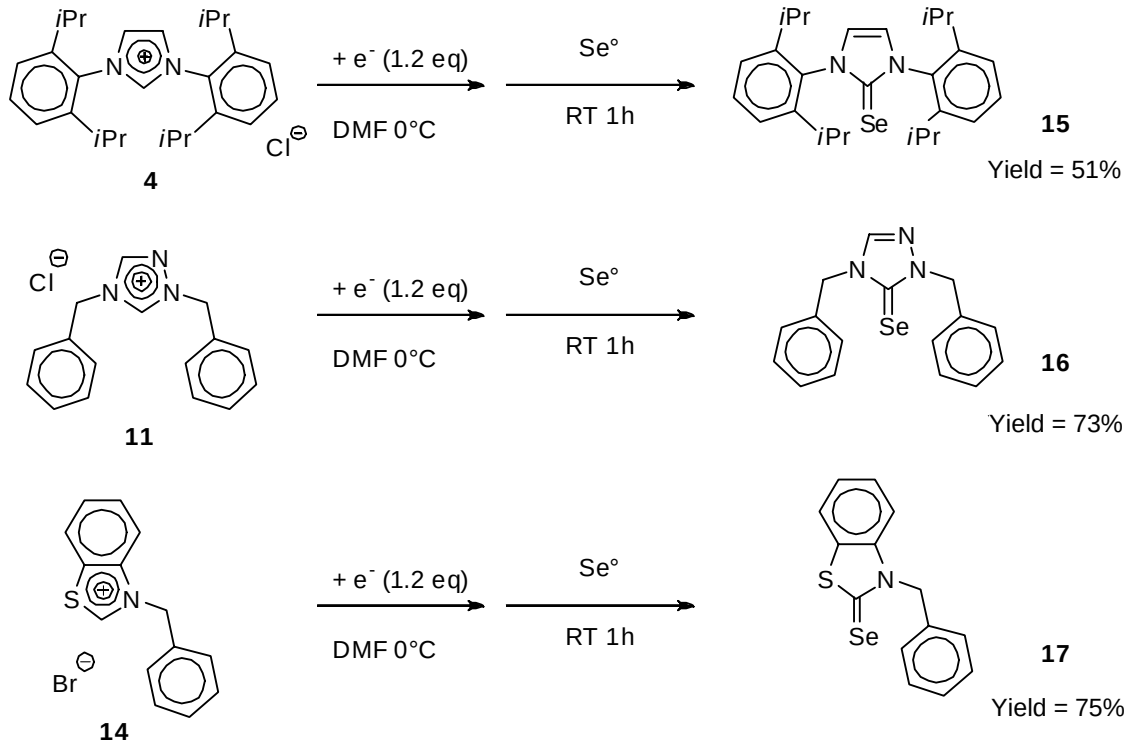
Scheme 7. Electroreduction of triazolium salt **11** to NHC and further trapping.

All results are given after 1.1 Faraday.

Several parameters have been looked at such as solvent, temperature, nature of the anode, and current density.

A first set of experiments with various solvents (DMF, MeCN or DMAc) (0.1 M of **11**; I = 50 mA, cathode: glassy carbon, anode: Zn, nBu$_4$NBF$_4$ 1.1 M, 20°C) led to choose DMF as most convenient solvent. In acetonitrile no selenourea was formed, possibly because acetonitrile can protonate the corresponding NHC back to the salt **11**. DMF led to slightly higher yield (53%) than DMAc (49%).

Next we looked at the effect of the anode (Zn, Mg or Duralumin) (0.1 M of **11**, I = 50 mA. Solvent: DMF; cathode: glassy carbon, nBu$_4$NBF$_4$ 1.1 M; 20°C). The derived cations may have more or less



Scheme 8. Range extension of the electrochemical reduction to imidazolium- and benzothiazolium chloride salts.

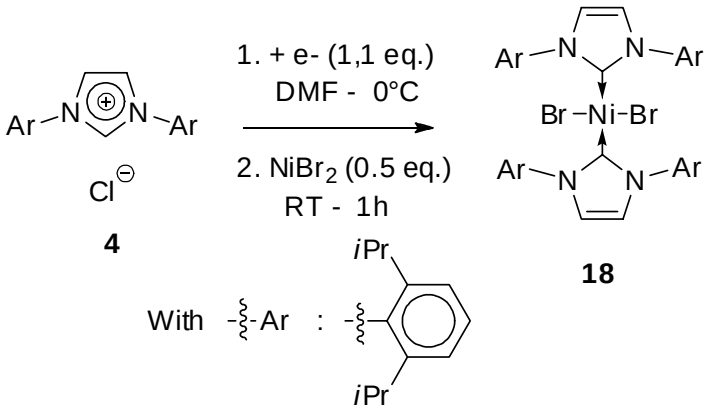
a stabilizing effect for the cathodically formed NHC by complexation. The best results were obtained with magnesium (59%) and zinc anode (53%) whilst Duralumin led to low yields (12%). Further experiments were conducted with magnesium anode.

We also looked at the effect of the temperature from -20°C to 20°C (0.1 M of **11**; 50 mA. Solvent: DMF, Cathode: glassy carbon, Anode: Mg; nBu$_4$NBF$_4$ 1,1 M). The best results were obtained at 0°C (73%), while at RT and at -20°C lower yields were obtained, 53 and 41% respectively.

Finally we looked at the influence of the current intensity from 10 mA to 200 mA (0.1 M of **11**; solvent: DMF; cathode: glassy carbon; anode: Mg; nBu$_4$NBF$_4$ 1.1 M, 0°C). The best results were obtained at 50 mA. A higher current intensity led to slightly lower yields (200 mA: 58% yield) but a lower one led to the increase of the reaction time that favors the decomposition of the NHC (10 mA: 45% yield).

Other studies have been carried out within a divided cell, but no gain was obtained. Similar yields were obtained but the process was less easy to run. Finally the optimized procedure is the electrolysis of 0.1 M of azolium salt solution in DMF at 0°C in an undivided cell with a magnesium anode and I = 50 mA. In these reaction conditions, 73% of the selenourea **16** was obtained, indicating that at least 73% of the salt led to the corresponding NHC. This method has then been applied to imidazolium chloride **4** and benzothiazolium bromide **14** to show the range of application of this process.

The corresponding selenourea **15**-**17** were obtained in good yields (see Scheme 8). The lower yield for **15** may be explained by the low reduction potential of the salt, close to the DMF reduction potential: a lack of selectivity may therefore occur.



Scheme 9. Synthesis of a *bis*-NHC Ni(II) complex.

In all reactions we noticed the formation of a colorless gas at the electrode that may be molecular hydrogen. Its formation may be due to adsorption of atomic hydrogen on the surface of the glassy carbon and release of molecular hydrogen.

To assess the value of our method in the field of organometallic complexes preparation, we have compared it to classical purely chemical process. As a preliminary investigation, the electrochemically produced NHC was subsequently trapped with a nickel (II) source to prepare a *bis*-NHC nickel complex. Various sources of nickel have been used, salt ($NiBr_2$) and complexes ($NiCl_2$bpy, $NiCl_2$dppe). The best yield in **18** (47%) (see Scheme 9) was obtained from the nickel salt, and this is already good as long as the reported chemical procedure gives 49% [14].

CONCLUSION

Imidazolium, triazolium, and benzothialium salts can be reduced electrochemically into the corresponding *N*-heterocyclic carbene. An analytical voltamperometric study shows that the reduction potential is closely linked to the electron density of the azolium salt. Furthermore preparative electrolysis using the undivided cell process led to the corresponding NHC which was characterized in the form of a selenourea derivative using 1D-2D ^{1}H, ^{13}C NMR techniques and GC/MS analysis. This procedure was applied to the one-pot synthesis of a Ni NHC complex.

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