Novel Urea Derivatives as Two-Step Redox Systems

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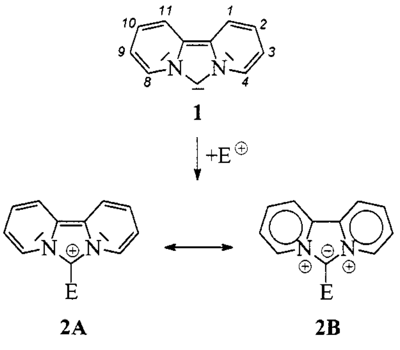
The structurally novel urea derivatives **4**–**6** have been synthesized by treating the nucleophilic dipyridoimidazol-2-ylidene **1** with elemental chalcogens Y (Y = S, Se, Te). The oxygen analogue **8** has been obtained indirectly by alkylation of the seleno urea **5**, followed by alkaline hydrolysis. All of these urea derivatives share two novel structural features: (i) their nitrogen centers represent the termini of the RED form of a two-step viologen-type redox system, and (ii) they can also be viewed as formally resulting from a cheletropic addition of CY to 2,2′-bipyridine. It has been demonstrated electrochemically that for Y = O, S, Se these ureas can be reversibly oxidized to the corresponding radical cations (SEM forms) at remarkably constant and negative potentials. This also applies to the heaviest congener of the series with Y = Te, except that in this case the oxidation process exhibits only quasi-reversibility. Electrochemical generation of the corresponding OX forms is observed quasi-reversibly at increasingly positive potentials with increasing mass of the chalcogen Y. However, the bis-oxidation of the telluro species **6** cannot be observed. These experimental results are discussed on the basis of semiempirical calculations for the RED, SEM, and OX forms under consideration. Semiempirical calculations also suggest that fragmentation of the novel urea derivatives into CY and 2,2′-bipyridine should be mildly endothermic for Y = O, but increasingly strongly endothermic with increasing mass of Y. This result is qualitatively in line with expectation considering the increasing reluctance of the heavier chalcogens to take part in multiple bonding to carbon. This phenomenon is also reflected in the mass spectrometric fragmentation patterns of the urea derivatives **4**–**6** and **8**.

Introduction

Recently, we reported on the generation of a novel type of nucleophilic carbene **1**, which alternatively can be considered as a 1:1 complex of singlet carbon and 2,2′-bipyridine.[1] In solution at −30 °C this species is stable for several hours and can be trapped by a multitude of electrophiles, both organic and inorganic, to give stable derivatives **2** (Scheme 1).



Scheme 1

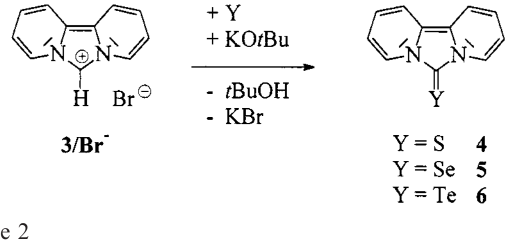
As can be inferred from inspection of the resonance structures **2A** and **2B**, the cationic substituent, which is introduced into a substrate through covalent bonding to **1**, is auto-adaptable to the electronic requirements of E. Thus, if the latter in **2** is a donor then resonance form **2A** is the major contributor, was **2B** more adequately describes the bonding situation when E is an acceptor. This unprecedented electronic flexibility intrinsic to **2** stems from the ability of the integrated two-step 2,2′-bipyridine redox system to act as an auto-umpolung device.[1]

In the present paper we report on the synthesis, structure, electrochemistry, and some reactions of adducts of **1** with S, Se, and Te as electrophiles, which represent novel redox-active urea derivatives. The synthesis of the corresponding oxygen analogue via an indirect route is also reported.

Results and Discussion

Synthesis and Characterization of Chalcogeno Ureas 4−6, 8[2]

Cyclic seleno and telluro ureas have previously been synthesized by treating Arduengo carbenes with Se and Te, respectively.[3] Similarly, dipyrido[1,2-*c*:2′,1′-*e*]imidazolylidene **1** can be transformed into the homologous chalcogeno ureas by treatment with elemental Te, Se, or even S. These orange-red to red compounds can be prepared most conveniently in yields > 80% in a one-pot reaction, where the carbene **1** is generated in situ from the imidazolium salt **3/Br**$^-$ with KO*t*Bu in the presence of the chalcogens. Compounds **4−6** are readily soluble in THF and are thus easily



Scheme 2

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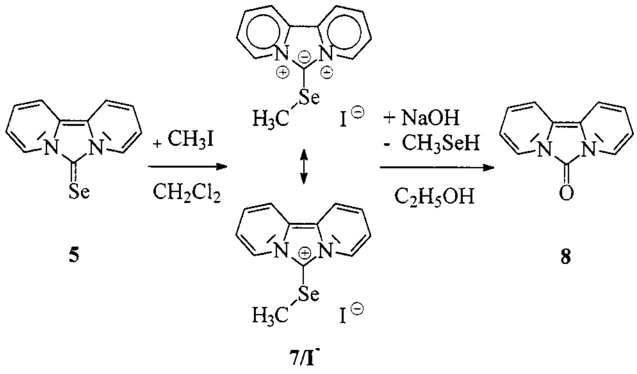
separated from salt-like components of the reaction mixture (Scheme 2).

Attempts to synthesize the parent compound of this series, i.e. the 6*H*-dipyrido[1,2-*c*:2′,1′-*e*]imidazolone **8**, by treating the carbene **1** with O_2 met with failure. However, **8** can be obtained indirectly by methylation of selenone **5** with CH_3I, followed by treatment of the resulting salt **7/I**$^-$ with NaOH in ethanol (Scheme 3).



Scheme 3

Two discrete sets of signals attributable to the 2,2′-bipyridine unit are observed in the ^1H NMR spectra of all of these urea derivatives. The set at lower field (**a** in Figure 1) can be plausibly attributed to the protons at C-1/C-11 and C-4/C-8, while that at higher field (**b** in Figure 1) can be attributed to the protons at C-2/C-10 and C-3/C-9. This is exemplified in Figure 1 in the case of the thio urea **4**.

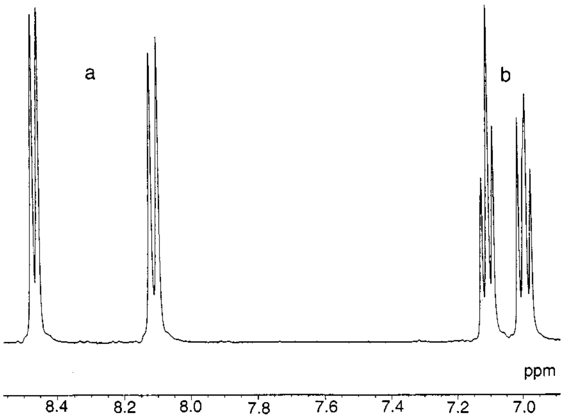


Figure 1. ^1H NMR spectrum of thio urea **4** (in [D$_6$]DMSO)

The ^{13}C NMR spectra of chalcogeno ureas **4–6**, **8** feature a set of five closely spaced signals due to the carbons of the bipyridine moiety, and one isolated signal due to the carbon atom adjacent to the chalcogen. The chemical shift of the latter varies with the nature of the chalcogen in a manner that does not lend itself to simple interpretation (see below). The complete set of data is collected in Table 1; Figure 2 shows the ^{13}C NMR spectrum of urea **8**.

Table 1. ^{13}C NMR shifts of the chalcogeno ureas **4–6** and **8**

	C=Y	C atoms of the 2,2′-bipyridine group
8 (Y = O)[a]	141.1	111.46, 112.29, 116.51, 117.24, 120.31
4 (Y = S)[b]	141.8	116.59, 118.26, 118.48, 118.92, 122.17
5 (Y = Se)[b]	133.4	117.53, 118.35, 119.69, 120.76, 123.45
6 (Y = Te)[b]	104.2	118.51, 118.64, 120.75, 123.47, 126.19

[a] in $CDCl_3$. – [b] in [D$_6$]DMSO.

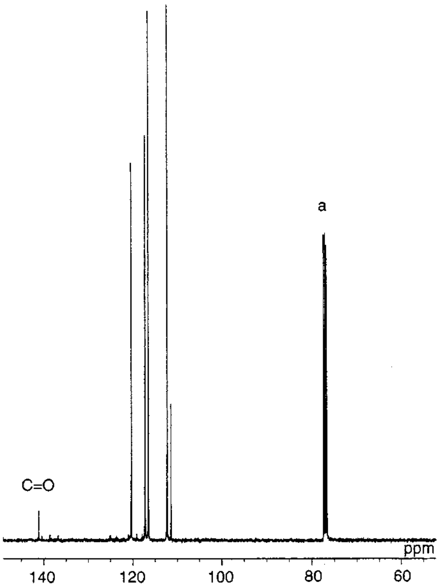
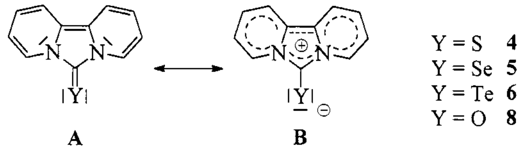


Figure 2. ^{13}C NMR spectrum of urea **8** (in $CDCl_3$ = **a**)

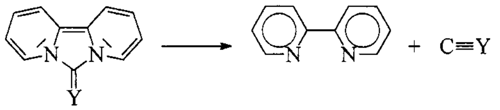
The heavy-atom effect of chalcogens Y in C=Y double bonds leads to increasingly low-field shifts of the signals of the corresponding C atoms with increasing atomic weight of Y, was the reverse is true for C–Y single bonds.[4] The data in Table 1 conform to the latter pattern, from which it can be concluded that the chalcogenones presented can best be characterized as having essentially single carbon–chalcogen bonds. This is particularly true for the heavier chalcogens Se and Te. Thus, resonance structure **B** (Scheme 4) will increasingly dominate the electron distribution in this set of chalcogenones on going from Y = O to Y = Te. This is in line with the increasingly low-field shifts observed for the ^{13}C NMR signals of the carbons of the bipyridine moiety within the same series of compounds (cf. Table 1).



Scheme 4

The radical cations of chalcogenones **4–6**, **8** figure prominently in the mass spectra of these compounds. Their further decomposition depends dramatically on the specific chalcogen present. Thus, while the radical cations of selenone **5** and tellurone **6** undergo loss of the chalcogen to yield the radical cation of carbene **1**, the corresponding radical cation of thione **4** would appear to be stable under the same mass spectrometric conditions. In contrast, the radical cation of 6*H*-dipyrido[1,2-*c*:2′,1′-*e*]imidazolone **8** decomposes into CO and the radical cation of 2,2′-bipyridine, a reaction that can be formally viewed as a C-transfer from carbene **1** to an oxygen atom.

Thermodynamic aspects of the thermal fragmentation of chalcogeno ureas **4−6** and **8** into 2,2′-bipyridine and the corresponding carbon monochalcogenides CY according to Scheme 5 have been assessed on the basis of semiempirical calculations (PM3).



Y	ΔH_R [kcal·mol^{-1}]
O	+10.19
S	+67.74
Se	+119.33
Te	+145.45

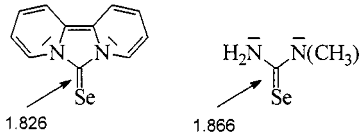
Scheme 5

For Y = O, this reaction is only moderately endothermic and would appear to be feasible either thermally or photochemically. Considering the more interesting fragmentations of **4−6**, for obvious reasons the endothermicity increases rapidly with increasing atomic weight of Y, such that these compounds do not appear to be useful precursors for the corresponding high-energy CY species (cf. Scheme 5). In any case, the reaction enthalpies given in Scheme 5 − although they are qualitatively reasonable − will have to be recalculated at higher levels of theory.

Two pieces of evidence indicate that the C−Y bonds in the novel chalcogenones presented in this paper are stronger than the corresponding bonds in known open-chain analogues:

(a) Imidazolone **8** exhibits a ν(CO) frequency of 1681 cm^{-1}, was the corresponding absorption in open-chain ureas is found at around 1660 cm^{-1}.

(b) The C−Se bond in selone **5**[1] is distinctly shorter than that in the open-chain seleno urea **9**[5] (Scheme 6).



5 (ref.1) **9** (ref.4)

Scheme 6

Theoretical calculations in conjunction with an NBO analysis[6] suggest that these effects are not due to an increase in π bond order relative to the open-chain urea analogues, but rather to an unusually high s content in the C(sp^x) orbital pointing towards the chalcogen Y. Bent's rules,[7] in agreement with the PM3 calculations, predict that the s content in this hybrid orbital should increase as the electronegativity of Y decreases. The results of calculations (PM3/NBO), as shown in Figure 3, point to an almost linear relationship between these two parameters.

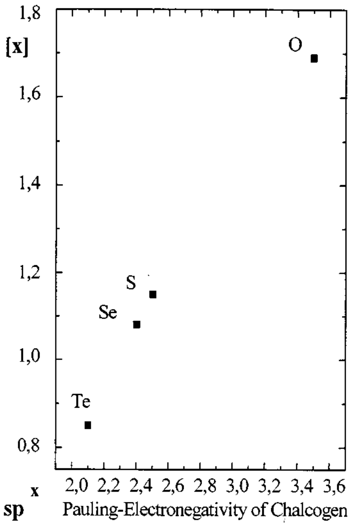


Figure 3. Hybridization C(sp^x) in the CY bond as a function of the electronegativity of the chalcogen

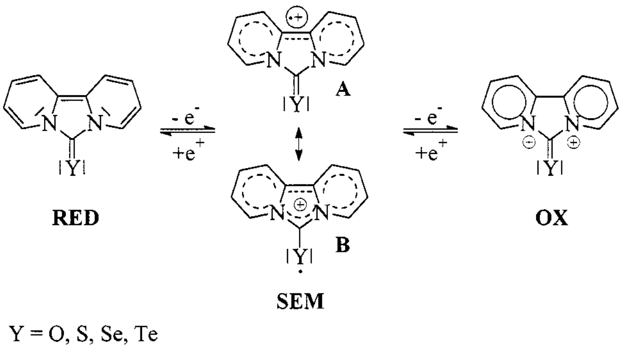
In this context, we refer to a recent communication[1] in which we presented NMR evidence showing that the carbon of the imidazolium C−H bond in **3** is virtually sp hybridized. This anomaly may be attributed to considerable angle strain in the five-membered ring, coupled with the pronounced electronegativity of the N centers. The same σ effect − albeit modulated by the nature of Y as indicated in Figure 3 − seems to be operative in the C−Y bonds of the chalcogenones considered in this paper.

Electrochemical Investigations

Chalcogenones **4−6** and **8** can be regarded as the RED[9] forms of a two-step redox system (cf. Scheme 7).

All members of the series of new chalcogenones presented show a first oxidation wave at around 0.3 V. The associated redox process is reversible for the three lighter chalcogens (see, for example, Figure 4) and quasi-reversible in the case of tellurium.

The measured $E_{1/2}$ values for the RED/SEM transition are seen to be remarkably insensitive to the nature of the chalcogen attached to the organic moiety. This is a consequence of resonance between the main contributors A and B in the SEM form (Scheme 7). The contribution of form A decreases as Y gets heavier as the bond energies of the corresponding CY double bonds rapidly increase. However, this is counterbalanced by a concomitant increase in the contribution of resonance structure B. In the latter, the high-energy structural element of a chalcogen radical center



According to cyclic voltammetric measurements, most of these redox processes can be realized electrochemically (Table 2).

Table 2. Oxidation potentials of the chalcogeno ureas **8** and **4−6** [V]

Compound	$E^{\mathrm{I}}_{1/2}$ ($E^{\mathrm{ox}}_{1/2}$ − $E^{\mathrm{red}}_{1/2}$)[a]	$E^{\mathrm{II}}_{1/2}$ [a]
8 (C=O)	+0.25 (rev, 0.059)	+0.74 (qrev)
4 (C=S)	+0.38 (rev, 0.056)	+1.27 (qrev)
5 (C=Se)	+0.25 (rev, 0.064)	+1.41 (qrev)
6 (C=Te)	+0.27 (qrev, 0.111)	−

[a] Supporting electrolyte: 0.1 N NEt_4BF_4/CH_3CN; reference electrode: Ag/AgCl; working and auxiliary electrode: platinum; standard: Ferrocene;[8] scan rate: 100 mVs^{-1}; rev = reversible; qrev = quasireversible

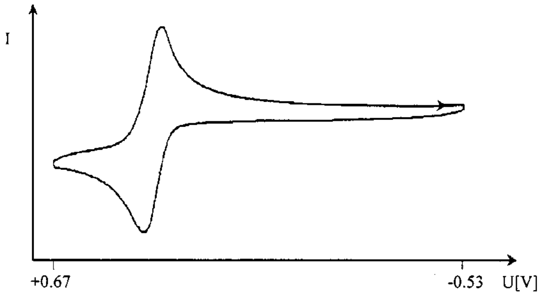


Figure 4. Cyclic voltammogram of thio urea **4**: first oxidation wave

is energetically compensated by the 14π aromatic dipyridoimidazolo substructure. As a consequence, the spin density on Y increases as Y gets heavier. This trend is corroborated by the results of calculations. An example is shown in Figure 5 and Figure 6, w the spin densities of SEM-**8** and SEM-**4** are compared.

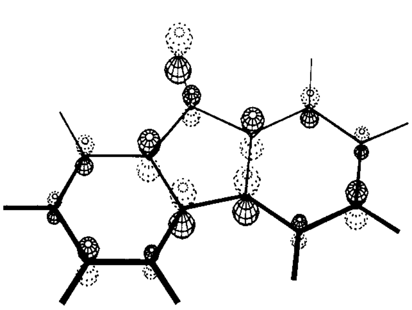


Figure 5. SOMO of the monooxidation product of **8** (Y = O, PM3)

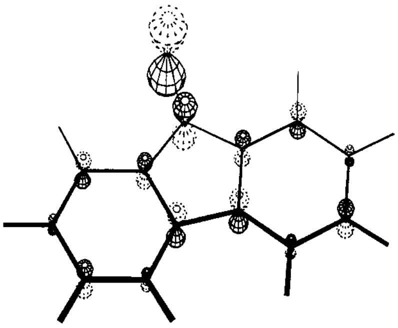


Figure 6. SOMO of the monooxidation product of **4** (Y = S, PM3)

Increasing concentration of spin density at the chalcogen center will increasingly favour dimerization of the corresponding SEM form to give a dichalcogenide. The observed loss of reversibility in the electrochemical oxidation of tellone **6** (Table 2) may be an indication of such a chemical process.

The second oxidation wave in the CV spectra corresponds in each case to the formation of the OX form. For this step, the $E_{1/2}$ values increase dramatically with increasing atomic weight of Y as a true CY double bond has to be formed − a distinct energetic disadvantage for the heavier chalcogens (see above).

Ongoing work in this area is focused on the chemical oxidation of chalcogenones **4−8**.

Experimental Section

General: All operations were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled under N_2. − IR (KBr): Bruker IFS 25; abbreviations: w (weak), m (medium), s (strong), vs (very strong). − NMR: Jeol EX 400 and Jeol GX 400 (each 400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively). For ^{1}H NMR: $CDCl_3$ as solvent, TMS as internal standard; $[D_6]DMSO$ as solvent $\delta_H = 2.49$; for ^{13}C NMR: $CDCl_3$ as solvent $\delta_C = 77.0$; $[D_6]DMSO$ as solvent $\delta_C = 39.5$. − EI-MS: Varian MAT 311A (70 eV). − Elemental analysis: Heraeus CHN-Rapid and Carlo Erba Elemental Analyser, Model 1106. Some of the compounds were found to absorb water during processing. − CV: PAR Model 170 Electrochemistry System.

***6H*-Dipyrido[1,2-*c*:2′,1′-*e*]imidazole-6-thione (4):** To a suspension of dipyrido[1,2-*c*:2′,1′-*e*]imidazolium bromide **3/Br⁻** (0.41 g, 1.65 mmol) in THF (50 mL) was added sulfur (0.05 g, 1.65 mmol) followed, at −78 °C, by KO*t*Bu (0.19 g, 1.65 mmol). After 2 h, the mixture was filtered through Celite and the solid was washed with THF (20 mL). The combined filtrate and washings were concentrated to a volume of a few mL and petroleum ether (30 mL) was added. The resulting red suspension was filtered, and the collected solid was washed with petroleum ether (10 mL) and dried in vacuo for 2 h to give 0.28 g of **4** (85%); red solid; m.p. ≈ 200 °C. − IR (KBr): $\tilde{\nu}$ = 3078 (w), 1637 (s), 1615 (s), 1524 (s), 1413 (s), 1381 (vs), 1349 (w), 1336 (s), 1327 (s), 1302 (s), 1250 (s), 1212 (s), 1154 (s), 1131 (s), 1116 (s), 1001 (vs), 989 (s), 897 (w), 810 (w), 727 (vs), 689 (s), 671 cm^{-1} (w). − ^{1}H NMR ($[D_6]DMSO$): δ = 7.04 (m, 2 H), 7.14 (m, 2 H), 8.14 (m, 2 H), 8.47 (m, 2 H). − MS: *m*/*z* =

200 [M$^+$]. − $C_{11}H_8N_2S \cdot 0.25\ H_2O$ (with 0.25 H_2O: 204.7) (200.3): calcd. C 64.52, H 4.18, N 13.68; found C 64.72, H 3.89, N 13.90.

6*H*-Dipyrido[1,2-*c*:2′,1′-*e*]imidazole-6-selone (5): To a suspension of dipyrido[1,2-*c*:2′,1′-*e*]imidazolium bromide **3/Br$^-$** (0.23 g, 0.93 mmol) in THF (50 mL) was added selenium (0.08 g, 1.03 mmol) followed, at −15 °C, by KO*t*Bu (0.13 g, 1.13 mmol). After 2 h, the mixture was filtered through Celite and the solid was washed with THF (10 mL). The combined filtrate and washings were concentrated to a volume of a few mL and pentane (30 mL) was added. The resulting red suspension was filtered, and the collected solid was washed with pentane (10 mL) and dried in vacuo for 2 h to give 0.20 g of **5** (87%); orange-red solid; m.p. ≈ 225 °C. − IR (KBr): $\tilde{\nu}$ = 3074 (w), 1644 (s), 1617 (w), 1558 (w), 1541 (w), 1524 (s), 1508 (w), 1415 (s), 1368 (vs), 1341 (w), 1325 (s), 1306 (w), 1252 (s), 1213 (s), 1154 (w), 1114 (w), 993 (s), 964 (w), 891 (w), 727 (vs), 689 cm^{-1} (w). − ^{1}H NMR ([D$_6$]DMSO): δ = 7.20 (m, 4 H), 8.28 (m, 2 H), 8.65 (m, 2 H). − MS: *m*/*z* = 248 [M$^+$], 168 [$C_{11}H_8N_2^+$ = carbene]. − $C_{11}H_8N_2Se$ (247.2): calcd. C 53.46, H 3.26, N 11.33; found C 52.97, H 3.38, N 11.47.

6*H*-Dipyrido[1,2-*c*:2′,1′-*e*]imidazole-6-tellone (6): To a suspension of dipyrido[1,2-*c*:2′,1′-*e*]imidazolium bromide **3/Br$^-$** (0.22 g, 0.87 mmol) in THF (30 mL) was added tellurium (0.123 g, 0.96 mmol) followed, at −15 °C, by KO*t*Bu (0.12 g, 1.00 mmol). After 2 h, the mixture was filtered through Celite and the solid was washed with THF (10 mL). The combined filtrate and washings were concentrated to a volume of a few mL and petroleum ether (30 mL) was added. The red suspension was filtered, and the collected solid was washed with petroleum ether (10 mL) and dried in vacuo for 2 h to give 0.21 g of **6** (87%); orange-red solid, m.p. ≈ 160 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 1645 (w), 1615 (w), 1525 (w), 1415 (s), 1350 (s), 1336 (w), 1311 (s), 1250 (s), 1214 (s), 1152 (w), 1123 (w), 1113 (w), 993 (w), 944 (w), 883 (w), 816 (w), 726 (vs), 689 cm^{-1} (w). − ^{1}H NMR ([D$_6$]DMSO): δ = 7.24 (m, 2 H), 7.35 (m, 2 H), 8.33 (m, 2 H), 8.78 (m, 2 H). − MS: *m*/*z* = 298 [M$^+$], 168 [$C_{11}H_8N_2^+$ = carbene]. − $C_{11}H_8N_2Te$ (295.8): calcd. C 44.67, H 2.73, N 9.47; found C 44.18, H 2.68, N 9.27.

6-(Methylseleno)dipyrido[1,2-*c*:2′,1′-*e*]imidazolium Iodide (7/I$^-$): To a solution of 6*H*-dipyrido[1,2-*c*:2′,1′-*e*]imidazoleselone **5** (0.14 g, 0.55 mmol) in CH_2Cl_2 (20 mL) at 0 °C, a solution of iodomethane (0.06 mL, 1.00 mmol) in CH_2Cl_2 (5 mL) was added over a period of 15 min. After 16 h, the yellow suspension was treated with Et_2O (30 mL), the mixture was filtered, and the collected solid was washed with Et_2O (10 mL) and dried in vacuo for 2 h to give 0.21 g of **7/I$^-$** (99%); yellow solid. − IR (KBr): $\tilde{\nu}$ = 3007 (s), 2987 (m), 2914 (w), 1653 (w), 1618 (m), 1531 (w), 1427 (s), 1350 (m), 1312 (m), 1258 (vs), 1223 (m), 1159 (m), 1122 (m), 1003 (w), 904 (m), 769 (m), 741 (vs), 697 cm^{-1} (s). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.41 (s, 3 H, CH_3), 7.69 (m, 4 H), 8.78 (m, 2 H), 8.99 (m, 2 H). − ^{13}C NMR ([D$_6$]DMSO): δ = 9.21 (CH_3), 112.36 (C−Se), 119.18, 121.33, 123.82, 123.85, 124.45. − MS: *m*/*z* = 247 [$C_{11}H_8N_2Se^+$ = selone], 168 [$C_{11}H_8N_2^+$ = carbene], 142 [CH_3I^+], 127 [I$^+$]. − $C_{12}H_{11}N_2ISe$ (389.1): calcd. C 37.04, H 2.85, N 7.20; found C 36.62, H 3.10, N 7.28.

6*H*-Dipyrido[1,2-*c*:2′,1′-*e*]imidazol-6-one (8): To a yellow suspension of 6-(methylseleno)dipyrido[1,2-*c*:2′,1′-*e*]imidazolium iodide **7/I$^-$** (0.28 g, 0.72 mmol) in ethanol (20 mL) was added NaOH (1.5 g). After 18 h, the solvent was removed in vacuo, the orange solid was redissolved in CH_2Cl_2 (25 mL), and this solution was extracted with H_2O (3 × 30 mL). The organic layer was concentrated to dryness in vacuo and the red residue was suspended in petroleum ether (7 mL). The suspension was filtered at −30 °C, and the collected solid was washed with petroleum ether (3 mL) and dried in vacuo for 2 h to give 0.11 g of **8** (81%); red solid; m.p. ≈ 125 °C. − IR (KBr): $\tilde{\nu}$ = 3095 (m), 3079 (m), 3052 (m), 1768 (w), 1681 [vs, ν(C=O)], 1636 (s), 1613 (s), 1529 (m), 1470 (s), 1440 (m), 1415 (w), 1349 (s), 1299 (w), 1244 (m), 1186 (m), 1151 (m), 1139 (w), 1117 (m), 1089 (w), 978 (m), 757 (m), 731 (s), 710 (s), 644 cm^{-1} (w). − ^{1}H NMR ([D$_6$]DMSO): δ = 6.44 (m, 4 H), 7.32 (m, 2 H), 7.76 (m, 2 H). − MS: *m*/*z* = 184 [M$^+$], 156 [2,2′-bipyridine$^+$]. − $C_{11}H_8N_2O \cdot 0.125\ H_2O$ (184.2, 186.4 with crystal water): calcd. C 70.86, H 4.46, N 15.02; found C 70.99, H 4.10, N 14.79.

Acknowledgments

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[1] R. Weiss, S. Reichel, M. Handke, F. Hampel, *Angew. Chem.* **1998**, *110*, 352−354; *Angew. Chem. Int. Ed.* **1998**, *37*, 344−347.

[2] B. L. Benac, E. M. Burgess, A. J. Arduengo III, *Org. Synth.* **1986**, *64*, 92−95.

[3] [3a] N. Kuhn, G. Henkel, T. Kratz, *Z. Naturforsch., Teil B* **1993**, *48*, 973−977. − [3b] N. Kuhn, G. Henkel, T. Kratz, *Chem. Ber.* **1993**, *126*, 2047−2049. − [3c] A. J. Arduengo III, F. Davison, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742−12749.

[4] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C NMR-Spektroskopie*, Thieme, Stuttgart, **1984**, p. 170f.

[5] H. M. K. K. Pathirana, T. J. Weiss, J. H. Reibenspies, R. A. Zingaro, E. A. Meyers, *Z. Kristallogr.* **1994**, *209*, 697.

[6] S. Reichel, Dissertation, Universität Erlangen-Nürnberg, **1998**.

[7] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275−311.

[8] T. Inagaki, H. S. Lee, T. A. Skotheim, Y. Okamoto, *J. Chem. Soc., Chem. Commun.* **1989**, 1181.

[9] The abbreviations RED, SEM, and OX indicate the reduced, mono-, and bis-oxidized forms of a two-step redox system, as introduced by K. Deuchert, S. Hünig, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875−886.

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