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Synthesis and reactivity of subvalent compounds. Part 13: Reaction of triethyl orthoformate with amines and selenium—a convenient one-step three-component synthesis for selenoureas☆

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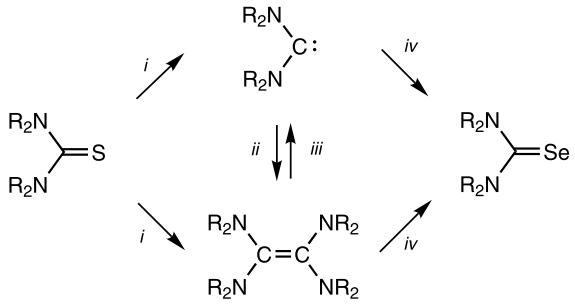
Abstract—Selenoureas are obtained by a novel three-component condensation reaction from metallic selenium, triethyl orthoformate and a primary or secondary amine. The reaction is carried out as solvent-free one pot-procedure at 180–190°C under inert gas with a reaction time of 8 h. The reaction was tested for piperidine, isopropylamine, *N*,*N*′-dimethylpropylenediamine (Me-NH-CH_2-CH_2-CH_2-NH-Me) and *N*,*N*′-disubstituted ethylenediamines (R-NH-CH_2-CH_2-NH-R, R = Me, Et, ^{i}Pr, ^{t}Bu, Ph).

1. Introduction

The reduction of thioureas with potassium (Scheme 1)[1–3] is a convenient method for the synthesis of diamino carbenes[1–4] and enetetramines.[2,5] A disadvantage of this approach are the low yields encountered in the synthesis of thioureas bearing bulky substituents.[6] Previous research on stable diamino carbenes[2,6,7] and related species[8] in our laboratory has therefore prompted us to investigate new methods for the synthesis of thioureas[6] and, more recently, selenoureas.[9–12] The reductive deselenation of selenoureas should proceed under milder reaction conditions than the analogous reduction of thioureas,[1–3] but will be attractive only if the respective selenoureas are readily accessible. We now report the reaction of metallic selenium with amines and triethylorthoformate as new solvent-free one-pot synthesis of symmetric selenoureas.



Scheme 1. Interconversion of thioureas, diaminocarbenes, enetetramines and selenoureas. *Reagents and conditions*: (i) THF, Δ, K, -K_2S.[1] (ii) rt.[2,3] (iii) 180°C.[2,3,7e] (iv) metallic selenium, rt.[4,5,20–22]

Previously published methods for the synthesis of selenoureas are largely analogous to those of thioureas. However, the required selenium reagents like hydrogen selenide,[13] carbon diselenide[14] bis(trimethylsilyl)-selenide[15] or isoselenocyanates R-N=C=Se[16] are significantly more toxic and also thermally less stable than their sulfur analogs. A number of selenium reagents[15,17–19] like Woollin's Reagent[17] or P_4Se_{10}[18] allow the conversion of carbonyl groups into the analogous selenocarbonyl functionalities but ureas are often inert or give selenoureas only in poor yields.

Due to its low volatility and ready accessibility, metallic selenium is the least problematic starting material for the synthesis of other selenium compounds. Selenoureas can indeed be obtained under ambient reaction conditions by reacting selenium with diamino carbenes[20] or enetetramines.[21,22] (Scheme 1). Although the yields are

Keywords: selenoureas; selenium; enetetramines; solvent-free; amine; carbene.

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generally good, the enetetramines or diamino carbenes are not readily available and typically require multi-step syntheses.

2. Results and discussion

The starting point of our synthetic investigation was the reaction of *N*,*N*′-diphenyl-ethylenediamine, triethyl orthoformate and sulfur reported by Wanzlick et al.[23] This remarkably simple method gives 1,3-diphenyl-imidazolidine-2-thione in excellent yield and purity but has apparently never been applied to other amines. Our own attempts using a variety of primary and secondary amines were indeed unpromising and led to thioureas only in poor yields (<10%). Much to our surprise, we discovered that the same approach works very well with metallic selenium. Selenoureas were obtained from cyclic and non-cyclic amines in fair (**3**, **6**, **7**) to excellent (**1**, **2**, **4**, **5**) yields (Scheme 2).

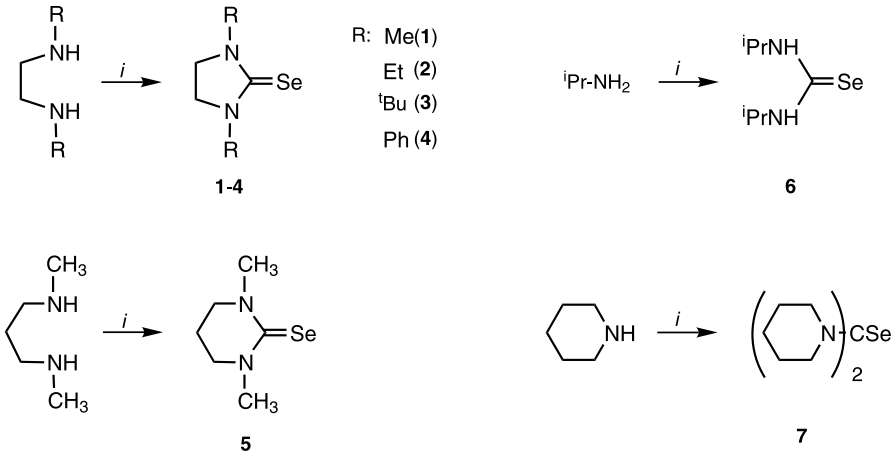
To avoid evaporation losses and to contain the toxic selenium materials, the reactions are carried out in stainless steel Swagelock® cylinders. The use of inert gas conditions was found to be necessary to avoid oxidation of the metallic selenium or hydrolysis of the selenoureas during the reaction.

The reactions do not require a solvent, the yields did in fact decrease when toluene or octane was employed. GC–MS analysis of crude reaction mixtures showed that the minimum temperature required for the reaction was in fact 150°C, but 180–190°C for a duration of 8 h is required for synthetically useful conversion rates. Despite the high reaction temperatures, the selenoureas are obtained in excellent purity. The crude products were homogeneous by ^{1}H, ^{13}C NMR and GC and showed melting points that were very close (ΔT<2°C) to literature data. Trace impurities of volatile selenium contaminants seem to give rise to a slow discoloration of the crude selenoureas upon exposure to air or light. Subjecting the crude reaction mixtures to a 3 h pumping cycle at 0.1 Torr was found to be sufficient to eliminate these contaminants. The selenoureas can be mechanically removed from the reaction vessel but extraction with a suitable solvent was found to be more efficient. Yellowish to greenish discolorations of the solutions were observed on a few occasions, presumably due to inefficient removal of the volatile impurities, but are readily eliminated by decolorizing the solutions with activated charcoal. Selenoureas obtained from these solutions remain colorless even after prolonged storage. The absence of solvents minimizes the required reaction volume and facilitates scale-up of the reaction.

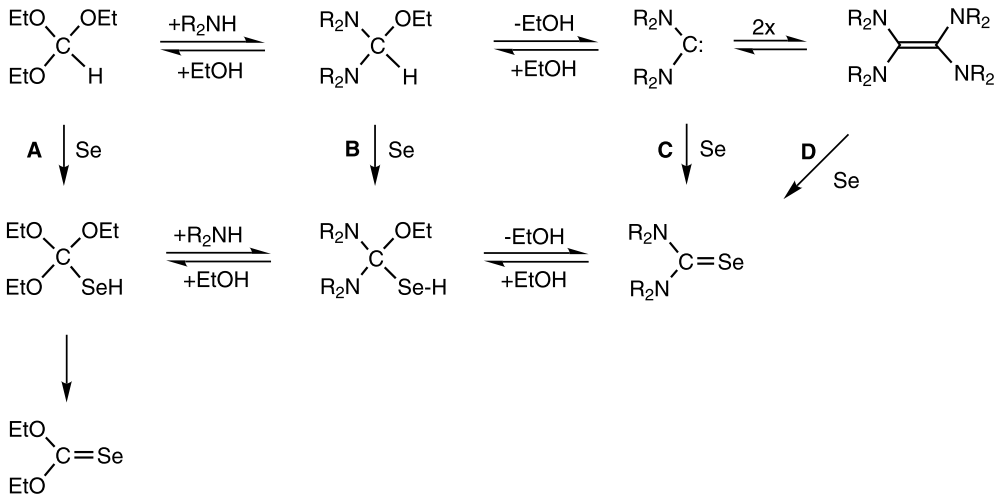
A number of different reaction pathways seem to be compatible with the formation of selenoureas (Scheme 3). Diaminocarbenes[4,20] and enetetramines[5,21] are known to react with elemental selenium and enetetramines can in fact be obtained from triethylorthoformate and diamines under reaction conditions similar to those employed for the selenourea procedure.[24] The formation of selenoureas may thus involve the in situ formation of diamino carbenes or enetetramines (pathways **C** or **D**). However, alternative pathways involving the CH activation of triethylorthoformate (**A**) or its amino substituted derivatives (**B**) by selenium have to be considered as well.

The fact that selenoureas are also obtained from primary amines is difficult to reconcile with the intermediacy of enetetramines or carbenes. The enetetramines obtained from primary amines would contain an unstable RNH-C=C fragment and would rapidly tautomerize to the respective imines RN=C-CH). The analogous tautomerization of the carbenes (R-NH-C:-NH-R → R-NH-CH=NH-R) on the other hand may possess a rather high activation barrier (ca. 40 kcal mol^{-1}).[29] The carbenes R-NH-C:-NH-R are therefore plausibile intermediates in the formation of the respective selenoureas R-NH-CSe-NH-R.

Indirect evidence for the feasibility of pathway **A** was obtained from a control experiment in which selenium was reacted with pure triethyl orthoformate. A trace amount of a newly formed compound was observed in



Scheme 2. Synthesis of selenoureas from primary and secondary amines. *Reagents and conditions*: (i) 2 equiv. of triethyl orthoformate/1 equiv. of metallic selenium/190°C/8 h. Yields: 89% (**1**), 95% (**2**), 39% (**3**), 95% (**4**), 91% (**5**), 34% (**6**), 30% (**7**).



Scheme 3. Possible pathways for the formation of selenoureas from orthoesters.

the GC of the crude reaction mixture (0.1% based on total ion count) and identified as $(EtO)_2C{=}Se$ by its mass spectrum (characteristic isotope pattern for one selenium atom). This concentration is too small to account for a complete conversion, but step **A** may be catalyzed by the amine (reversible formation of the carbanion) and should thus not be prematurely ruled out. Precedence for **B** is the formation of the respective selenoureas from the orthoamides $HC(NMePh)_3$[25] $HC(NMe_2)_3$[26] or $^tBuOCH(NMe_2)_2$[26] and metallic selenium reported by Kantlehner and Schönberg although these reactions may also proceed through the carbene pathway **C**.

3. Experimental

Caution! Selenium compounds are highly toxic. All operations (including the cleaning of equipment) should be carried out in an efficient fume hood.

Melting points were recorded in sealed capillaries and are uncorrected. EI-MS spectra were obtained with a Shimadzu 5050 GC–MS instrument at an ionizing voltage of 70 eV. NMR spectra were recorded on Varian Gemini 200 (^{1}H), Bruker 500 MHz (^{13}C) or Varian 400 MHz spectrometers (^{13}C) at normal spectrometer temperature. The spectra are referenced versus TMS (^{1}H and ^{13}C, internal). Selenium powder -100 mesh (99.5%) and all other starting materials were obtained from Aldrich Inc. and used as received. The synthesis of the selenoureas was conducted under an atmosphere of nitrogen or argon (purity 99.994 or better). Yields are not optimized. Contaminated equipment and the rubber gloves used in the preparations were cleaned with household bleach. The cleaning solutions were left to evaporate in the fume hood and the remaining solids disposed of as selenium waste.

General procedure for the synthesis of selenoureas from amines and triethyl orthoformate. A mixture of the amine (50.0 mmol for monoamines, 25.0 mmol for diamines) triethylorthoformate (50 mmol, 100% excess) and selenium (25.0 mmol) is sealed in a Swagelock® stainless steel cylinder and heated to 180–190°C for 8 h. The cold reaction mixture is dried under oil vacuum for 3 h, dissolved in the minimum amount of ether–ethanol (3:1), decolorized with charcoal and filtered. Slow evaporation gives the selenoureas as colorless, crystalline solids. **1,3-Dimethyl-imidazolidine-2-selenone** (**1**): Yield 89%, colorless crystals, mp 146–147°C from EtOH. ^{1}H NMR: 3.24 (s, 6H, NC$\underline{H}_3$), 3.60 (s, 4H, NC$\underline{H}_2$). ^{13}C NMR: 36.9 (CH_3), 49.4 (CH_2), 181.9 (s, $\underline{C}$=Se). EI-MS: 178 (M^+, 100), 120 (6), 97 (14), 83 (7), 69 (69), 56 (32), 42 (70). **1,3-Diethyl-imidazolidine-2-selenone** (**2**): Yield 95%, colorless crystals, mp 85.5–86°C from Et_2O. ^{1}H NMR: 1.18 (t, ^3J(H,H) = 7 Hz, C$\underline{H}_3$), 3.60 (s, 4H, C$\underline{H}_2$C$\underline{H}_2$), 3.75, (q, ^3J(H,H) = 7 Hz, NC$\underline{H}_2$CH$_3$). ^{13}C NMR: 12.6 (q, ^1J(C,H) = 127 Hz, $\underline{C}H_3$), 44.4 (t, ^1J(C,H) = 138 Hz, N$\underline{C}H_2$), 46.7 (t, ^1J(C,H) = 145 Hz, N$\underline{C}H_2$), 179.6 (s, $\underline{C}$=Se). EI-MS: 206 (M^+, 100), 177 (11), 125 (81), 108 (5), 97 (40), 83 (28), 69 (52), 56 (40), 42 (71). **1,3-Di-*tert*-butyl-imidazolidine-2-selenone** (**3**): Yield 39%, colorless crystals, mp 174–175°C (EtOH). ^{1}H NMR: 1.69 (s, 18H, C$\underline{H}_3$), 3.48 (s, 4H, C$\underline{H}_2$). ^{13}C NMR: 29.3 (q, ^1J(C,H) = 127 Hz, $\underline{C}H_3$), 46.1 (t, ^1J(C,H) = 145 Hz, N$\underline{C}H_2$), 58.4 (s, $\underline{C}(CH_3)_3$), 178.9 (s, $\underline{C}$=Se). EI-MS: 262 (M^+, 36), 205 (19), 150 (100), 126 (7), 111 (26), 84 (9), 70 (18), 57 (40), 41 (62). **1,3-Diphenyl-imidazolidine-2-selenone** (**4**): Yield 95%, off-white crystals, mp 185–186°C (CH_2Cl_2), 186°C,[27a] 183–185°C[21]). ^{1}H NMR ($CDCl_3$): 4.03 (s, $\underline{C}H_2$, 4H), 7.52–7.22 (M, phenyl-$\underline{H}$). ^{13}C NMR ($CDCl_3$): 51.3 (t, ^1J(C,H) = 147 Hz, $\underline{C}H_2$), 126.6 (d, 161 Hz, $\underline{C}H_{meta}$), 127.4 (d, ^1J(C,H) = 161 Hz, $\underline{C}H_{para}$), 129.5 (d, ^1J(C,H) = 161 Hz, $\underline{C}H_{ortho}$), 141.5 (s, C_{ipso}), 180.6 (s, $\underline{C}$=Se). EI-MS: 301 (34), 194 (7), 238 (100), 118 (26), 105 (36), 91 (83), 77 (85), 51 (28). **1,3-Dimethyl-2,4,5,6-tetrahydropyrimidine-2-selenone** (**5**): Yield 91%, colorless crystals, mp 100–101°C from Et_2O–EtOH (1:1). ^{1}H NMR: 2.07 (quin, ^3J(H,H) = 6 Hz, $CH_2C\underline{H}_2$), 3.39 (t, ^3J(H,H) = 6 Hz, NC$\underline{H}_2$), 3.54 (s, NC$\underline{H}_3$). ^{13}C NMR: 21.2 (t, ^1J(C,H) = 132 Hz, $CH_2\underline{C}H_2CH_2$), 47.2 (q, ^1J(C,H) = 139 Hz, N$\underline{C}H_3$), 48.7 (t, ^1J(C,H) = 141 Hz,

NCH_2), 177.4 (s, C=Se). EI-MS: 192 (M^+, 78), 121 (7), 111 (22), 97 (22), 83 (14), 70 (20), 55 (21), 42 (100). ***N,N′*-Diisopropyl selenourea** (**6**): Yield 34%, off-white crystals, mp 173–174°C from Et_2O–EtOH (3:1). Lit: 173°C,[14c] 167.5–168°C.[16a] ^1H NMR: 1.23 (d, $^3J(H,H) = 7$ Hz, 6H, CH_3), 4.26 (septet, $^3J(H,H) = 7$ Hz, CH), 6.1 (br. NH). ^{13}C NMR: 23.1 (q, $^1J(C,H) = 127$ Hz, CH_3), 46.5 (d, $^1J(C,H) = 140$ Hz, CH), 179.5 (s, C=Se). EI-MS: 160 (34), 85 (6), 69 (10), 58 (100), 43 (54). **1,1′-Selenocarbonyl-bis-piperidine** (**7**): Yield 30%, off-white crystals, mp 80–81°C from Et_2O–EtOH (3:1) g. Lit.: 79–80°C,[14d] 78–79°C[28]). ^1H NMR: 1.56 (m, 12H, $CH_2CH_2CH_2$+$CH_2CH_2CH_2$), 3.58 (m, 4H, NCH_2). ^{13}C NMR: 25.0 (t, $^1J(C,H) = 127$ Hz, $CH_2CH_2CH_2$), 26.3 (t, $^1J(C,H) = 128$ Hz, 8H, NCH_2CH_2), 54.9 (t, $^1J(C,H) = 139$ Hz, CH_2N), 194.5 (s, C=Se). EI-MS: 260 (M^+, 32), 179 (28), 111 (11), 96 (20), 84 (100), 69 (25), 55 (25), 41 (71).

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References

1. Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561–562.
2. Denk, M. K.; Thadani, A.; Hatano, K.; Lough, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2607–2609; *Angew. Chem.* **1997**, *109*, 2719–2721.
3. Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, *5*, 1931–1935.
4. For recent reviews, see: (a) Regitz, M. *Angew. Chem.* **1996**, *108*, 791–794; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725–728; (b) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162–2187; (b) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913–921; (c) Warkentin, J. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Jai Press: London, 1998; Vol. 2, p. 245; (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
5. For reviews on tetraaminoethenes ('enetetramines'), see: (a) Wiberg, N. *Angew. Chem.* **1968**, *80*, 809; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 766–779; (b) Hoffmann, R. W. *Angew. Chem.* **1968**, *80*, 823; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 754–765. (c) Hocker, J.; Merten, R. *Angew. Chem.* **1972**, *84*, 1022; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 964–973; (d) Haug, E.; Kantlehner, W. In Houben-Weyl, *Methoden der Organischen Chemie*, E15, *3*, 2898–2931, Thieme Verlag: Stuttgart, 1993; (e) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185–214.
6. Denk, M. K.; Gupta, S.; Brownie, J.; Tajammul, S.; Lough, A. J. *Chem. Eur. J.* **2001**, *20*, 4477–4486.
7. (a) Denk, M. K.; Rodezno, J. *J. Organomet. Chem.* **2001**, *617–618*, 737–740; (b) Denk, M. K.; Rodezno, J. *J. Organomet. Chem.* **2000**, *608*, 122–125; (c) Denk, M. K.; Rodezno, J.; Gupta, S.; Lough, A. J. *J. Organomet. Chem.* **2001**, *617–618*, 242–253; (d) Lehmann, J. F.; Urquhart, S. G.; Ennis, L. E.; Hitchcock, A. P.; Hatano, K.; Gupta, S.; Denk, M. K. *Organometallics* **1999**, *18*, 1862–1872; (e) Denk, M. K.; Hatano, K.; Ma, M. J. *Tetrahedron Lett.* **1999**, *40*, 2057–2060; (f) Denk, M. K.; Thadani, A.; Hatano, K.; Lough, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2607–2609; *Angew. Chem.* **1997**, *109*, 2719–2721.
8. (a) Hitchcock, A. P.; Ennis, L. E.; Lehmann, J. F.; Denk, M. K. *J. El. Spec.* **2001**, *114*, 1037–1041; (b) Leites, L. A.; Bukalov, S. S.; Denk, M. K.; West, R.; Haaf, M. *J. Mol. Struct. Theochem.* **2000**, *550*, 329–335; (c) Denk, M. K.; Gupta, S.; Ramachandran, R. *Eur. J. Inorg. Chem.* **1999**, 41–49; (d) Denk, M. K.; Hatano, K.; Lough, A. J. *Eur. J. Inorg. Chem.* **1998**, 1067–1070; (e) Urquhart, S.; Hitchcock, A. P.; Denk, M. K. *Organometallics* **1998**, *17*, 2352–2360; (f) Denk, M. K.; Gupta, S.; Ramachandran, R. *Tetrahedron Lett.* **1996**, *37*, 9025–9028; (g) Metzler, N.; Denk, M. K. *Chem. Commun.* **1996**, 2657–2658; (h) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Haaland, A.; Belyakov, A. V.; Verne, H. P.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692; (i) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813–10814; (j) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410; (k) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33–34.
9. Attempts to oxidize diaminomethanes $R_2N\text{-}CH_2\text{-}NR_2$ with selenium gave selenoureas but only in poor yields (<10%, contrast to oxidation with S_8[6]).
10. For recent reviews on selenium compounds, see: (a) Murai, T.; Kato, S. *Top. Curr. Chem.* **2000**, *208*, 177–199; (b) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons, 1987; Vol. 2; (c) Nishibayashi, Y.; Uemura, S. *Top. Curr. Chem.* **2000**, *208*, 235–255; (d) Wirth, T. *Tetrahedron* **1999**, *55*, 1–28. (Tetrahedron Report Nr. 47).
11. For the synthesis of selenium-heterocycles from selenoureas, see: (a) Weber, M.; Hartmann, H. *Z. Chem.* **1987**, *27*, 95–96; (b) Comrie, A. M. *J. Chem. Soc.* **1963**, 5713–5717; (c) Günther, W. H. H.; Searle, R.; Sieber, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 417–424; (d) Arca, M.; Demartin, F.; Devillanova, F. A.; Isaia, F.; Lelj, F.; Lippolis, V.; Verani, G. *Can. J. Chem.* **2000**, *78*, 1147–1157.
12. For the use of selenoureas as building blocks for organic conductors, see: (a) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A; Trogu, E. F. *Gazz. Chim. Ital.* **1994**, *124*, 445–454; (b) Bigoli, F.; Dematin, F.; Deplano, P.; Devillanova, F. A.; Isaia, A. F.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chem.* **1996**, *35*, 3194–3201; (c) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Girlando, A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chem.* **1996**, *35*, 5403–5406; (d) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Girlando, A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Synth. Met.* **1997**, *86*, 1853–1854; (e) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Eur. J. Inorg. Chem.* **1998**, 137–141; (f) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Girlando, A.; Lippolis, V.; Mercuri, M. L.;

Pellinghelli, M. A.; Trogu, E. F. *J. Mater. Chem.* **1998**, *8*, 1145–1150; (g) Boyle, P. D.; Cross, W. I.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Teat, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2845–2852.

13. (a) Hope, H. *Acta Chem. Scand.* **1964**, *18*, 1800–1800; (b) Guziec, F. S. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons, 1987; Vol. 2, p. 255.
14. (a) Grimm, H. G.; Metzger, H. *Chem. Ber.* **1936**, *69*, 1356–1364; (b) Warner, J. S. *J. Org. Chem.* **1963**, *28*, 1642–1644; (c) Rosenbaum, A. *J. Prakt. Chem.* **1968**, *37*, 200–205; (d) Henriksen, L. *Synthesis* **1982**, *9*, 773–776; (e) Pan, W. H.; Fackler, J. P., Jr. *Inorg. Synth.* **1985**, *21*, 6–11.
15. Takikawa, Y.; Watanabe, H.; Sasaki, R; Shimada, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 876–878.
16. (a) Jensen, K. A.; Nielsen, P. H. *Acta Chem. Scand.* **1966**, *20*, 597–629; (b) Zhou, Y. H.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **2000**, *83*, 1576–1598; (c) Review: Petrov, M. L.; Zmitrovich, N. I. *Russ. J. Gen. Chem.* **1999**, *69*, 245–256.
17. (a) Wood, P. T.; Woollins, J. D. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 51–56; (b) Fitzmaurice, J. C.; Williams, D. J.; Wood, P. T.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1988**, *11*, 741–743.
18. Jensen, K. A.; Felbert, G.; Kägi, B. *Acta Chem. Scand.* **1966**, *20*, 281–282.
19. (a) Shimada, K.; Jin, N.; Kawaguchi, M.; Dobashi, K.; Nagano, Y.; Fujimura, M.; Kudoh, E.; Kai, T.; Saito, N.; Masuda, J.; Iwaya, M.; Fujiisawa, H.; Aoyagi, S.; Takikawa, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 197–206; (b) Yoshifuji, M.; Higeta, N.; An, D.-L.; Toyota, K. *Chem. Lett.* **1998**, 17–18; (c) Michael, J. P.; Reid, D. H.; Rose, B. G.; Speirs, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1494–1496; (d) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095–2097.
20. (a) Kuhn, N.; Henkel, G.; Kratz, T. *Z. Naturforsch. B* **1993**, *48*, 973–977; (b) Williams, D. J.; Fawcett-Brown, M. R.; Raye, R. R.; Vanderveer, D.; Pang, Y. T.; Jones, R. L.; Bergbauer, K. L. *Heteroatom Chem.* **1993**, *4*, 409–414.
21. Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1983**, *116*, 2068–2073.
22. An early example for the chemical cleavage of electron rich olefins by sulfur was described by A. Schönberg in 1925: Schönberg, A.; Rosenbach, A.; Krüll, H.; Ostwaldt, U. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 1793–1801; Schönberg, A.; Asker, W. *J. Chem. Soc. (London)* **1942**, 272–274. For an excellent account of Schönberg's research see the obituary by Singer: Singer, E. *Chem. Ber.* **1987**, *120*, I–XIX. For early research on stabilized carbenes see the obituary for H. Scheibler: Wanzlick, H.-W. *Chem. Ber.* **1969**, *102*, XVII–XXXIX.
23. Wanzlick, H.-W.; Lachmann, B.; Schikora, E. *Chem. Ber.* **1965**, *98*, 3170–3177.
24. Wanzlick, H.-W.; Esser, F.; Kleiner, H.-J. *Chem. Ber.* **1963**, *96*, 1208–1212. For the formation of enetetramines from DMF acetals and 1,2-diaminoethanes see: Çetinkaya, B.; Çetinkaya, E.; Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Kücükbay, H.; Lappert, M. F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2047–2054.
25. Schönberg, A.; Singer, E.; Stephan, W. *Chem. Ber.* **1987**, *120*, 1581–1588.
26. Kantlehner, W.; Hauber, M.; Vettel, M. *J. Prakt. Chem. Chem. Z.* **1996**, *338*, 403–413.
27. (a) Maas, G.; Singer, B. *Chem. Ber.* **1983**, *116*, 3659–3674; (b) Cetinkaya, B.; Cetinkaya, E.; Kucukbay, H.; Durmaz, R. *Arzneim. Forsch.* **1996**, *46*, 1154–1158.
28. Shimada, K.; Yamaguchi, M.; Sasaki, T.; Ohnishi, K.; Takikawa, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2235–2242.
29. An activation barrier of 41.5 kcal mol^{-1} was calculated for the isomerization of imidazole-2-ylidene to imidazole: Maier, G.; Endres, J. *Eur. J. Org. Chem.* **1998**, 1517–1520.