duced species with lower redox potentials than the free protein (Table 1). The midpoint potential of the cyanide adduct could not be determined by this method because of competitive oxidation of cyanide. The lower potentials of the two anion adducts relative to Met121Gly azurin could be rationalized by inferring electrostatic stabilization of the higher copper oxidation state by the negatively charged ligands.

The spectroscopic properties of the Met121Gly azurin–anion adducts indicate the presence of a novel form of protein-bound copper having spectroscopic properties distinct from those of either blue or type 2 copper proteins. According to a computer-generated model of the Met121Gly active site,[14] coordination of external ligands to the copper(II) ion in the space previously occupied by the Met121 side chain should result in a distorted tetrahedral environment for the metal center. Binding of anionic species to the copper(II) ion should also result in lengthening of the other metal–ligand bonds. Absorption and resonance Raman spectra of the Met121Gly azurin–anion complexes reflect substantial axial displacement of the copper atom from the plane of the His_2Cys ligand set along with elongation of the S_{cys}–Cu bond.[10, 12] The values for the parallel hyperfine splittings in the EPR spectra of the 1:1 complexes are consistent with diminished covalency in the S_{cys}–Cu bond relative to the uncomplexed form, resulting from S–Cu bond lengthening.[15] In natural blue copper proteins with distorted tetrahedral metal centers and short axial interactions with neutral ligating atoms, absorption spectra display intense bands at about 450 nm, and EPR spectra suggest a rhombic g tensor.[2] Absorption spectra with λ_{max} at about 420 nm and EPR spectra with axial symmetry for the Met121Gly azurin–anion adducts signify a unique electronic structure of the copper centers in these proteins as a result of the anionic character of the axial ligands. Further support for the proposed model of the Met121Gly azurin–anion adduct copper centers comes from properties of structurally characterized, pseudo-tetrahedral copper complexes, which display spectroscopic characteristics remarkably similar to those of the adducts reported here.[16]

A variety of unusual copper proteins can be easily created through addition of anions to the azurin mutant Met121Gly. The ability to create ligand-accessible metal centers in coordinatively saturated metalloproteins by directed mutagenesis holds promise for the preparation of metalloproteins with selective ion-sensing capabilities. Further studies aimed at detailed characterization of the electronic and geometric structure, as well as the electron-transfer properties of the active sites of these unusual proteins are in progress.

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A Redox-Switchable Hemilabile Ligand: Electrochemical Control of the Coordination Environment of a Rh^I Complex**

Elizabeth T. Singewald, Chad A. Mirkin,* and Charlotte L. Stern

We report the synthesis and characterization of a redox-switchable hemilabile ligand (RHL), $FcOCH_2CH_2PPh_2$ (**1**, $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, and its complexation to Rh^I to form the square-planar, *cis*-phosphane, *cis*-ether Rh^I complex **2** (Scheme 1). This new ligand type can yield electrochemical con-

[*] Prof. C. A. Mirkin, E. T. Singewald, C. L. Stern
Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113 (USA)
Telefax: Int. code + (708)491-7713

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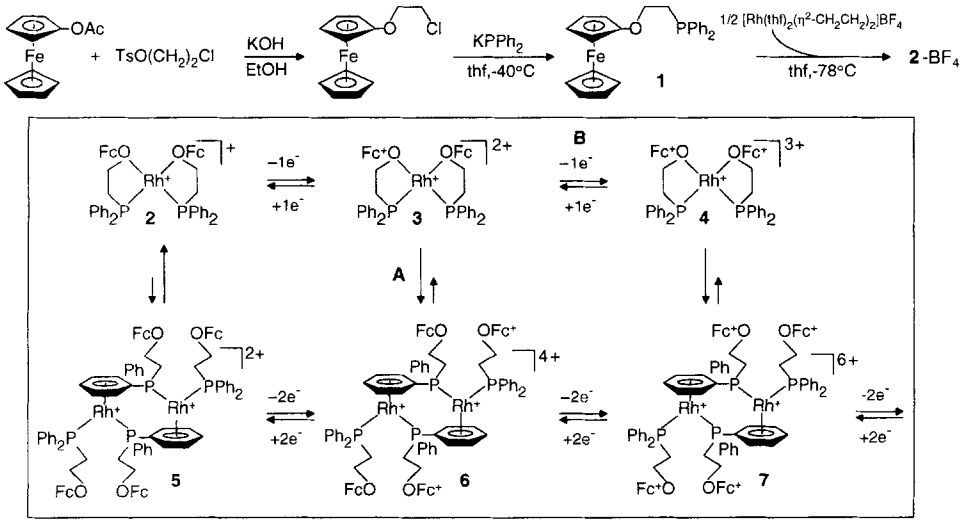


Scheme 1. Synthesis of ligand **1** and complex **2** (top) and proposed electrochemical transformations for **2** (in frame). Formal charges are denoted at appropriate atoms; overall charge is denoted outside the bracket.

trol over the electronic and steric environments of the Rh^I center. Bidentate ligand **1**, which was designed for complexation to late transition metals, has two important characteristics. First, for the example reported herein (**2**), ligand **1** is hemilabile because the phosphane moiety binds strongly to Rh^I to form a substitutionally inert bond, while the ether functionality forms a weak bond to Rh^I, which is substitutionally labile; hemilabile ligands have been studied extensively.[1] Second, the ferrocenyl group in **1** is covalently attached to the ether moiety; therefore, the binding affinity of the O atom for Rh is dependent on the oxidation state of the ferrocenyl group. With this RHL design, coordination sites at the transition-metal center to which **1** is chelated can be labilized selectively by applying a potential that can oxidize the ferrocenyl group, thereby yielding electrochemical control over transition-metal coordination environment. Electrochemical control over the coordination environment of the transition-metal complex controls the reactivity of the complex and in principle, its catalytic properties. To this end, we are designing a series of new electrocatalysts based on the RHL concept. This work complements the work of others involving 1) the design of redox-switchable ligands for sensor probes and ion transport membranes[2] and 2) the use of *substitutionally inert* redox-active ligands to tune the reactivity of transition metals.[3] The approach reported herein is fundamentally different from the latter work, because it focuses on controlling ligand binding characteristics rather than the electronic character of the transition-metal center to which the redox-active ligands are bound.[4]

The synthesis of **2**-BF_4 begins with the reaction between ferrocenylacetate[5] (5.8 mmol), KOH (5.8 mmol), and $TsOCH_2CH_2Cl$ (Ts = *p*-$(CH_3C_6H_4)SO_2$, 23 mmol) in ethanol (30 mL) at reflux for 20 h to form $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4OCH_2CH_2Cl)]$ in 65% yield (Scheme 1). The reaction of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4OCH_2CH_2Cl)]$ (6.9 mmol) with one equivalent of $KPPh_2$ in 60 mL of THF at −40 °C gives ligand **1** in 92% yield. Compound **2** is then formed from the reaction between ligand **1** (0.52 mmol) and $[(\eta^2\text{-}C_2H_4)_2Rh(thf)_2]BF_4$[6] (0.26 mmol) in THF (100 mL) at −78 °C. Compound **2**-BF_4 was isolated in 55% yield as an orange-red crystalline salt by recrystallization from CH_2Cl_2/pentane.

Spectroscopic data for **2**-BF_4 in dilute CD_2Cl_2 solutions (10 mM) are fully consistent with its proposed structure (see Experimental). For example, the ^{31}P NMR resonance signal and Rh–P coupling constant are highly diagnostic of a square-planar *cis*-phosphane, *cis*-ether Rh^I complex[1, 7a] and compare well with the ^{31}P NMR data for crystallographically characterized, isoelectronic $[Rh(\eta^4\text{-}(\{\eta^5\text{-}C_5H_4\}OCH_2CH_2PPh_2)_2Fe)]BF_4$, ($^{31}P\{^1H\}$ NMR: $\delta = 61.2$, d, $J_{Rh,P} = 210.6$ Hz).[7b]

Slow diffusion of pentane into a CH_2Cl_2 solution of **2** (0.9 mM) yielded X-ray quality single crystals. Surprisingly, a single crystal X-ray diffraction study shows that **2** forms a μ_2-η^6-arene dimer (**5**) in the solid state (Fig. 1).[12] Bis(phosphane), η^6-arene pianostool dimers similar to **5** have been reported by others, although all of these examples involve chelating bis(phosphane) ligands.[8] Significantly, upon dissolving 2 mg of crystalline **5** in CD_2Cl_2 (0.5 mL), it cleanly reverts to the monomeric species **2** as shown by its ^{31}P NMR spectrum. Apparently **2** and **5** are in equilibrium (Fig. 1), and at high concentrations (for example, single crystals) the dimer **5** is favored over the monomer **2**.

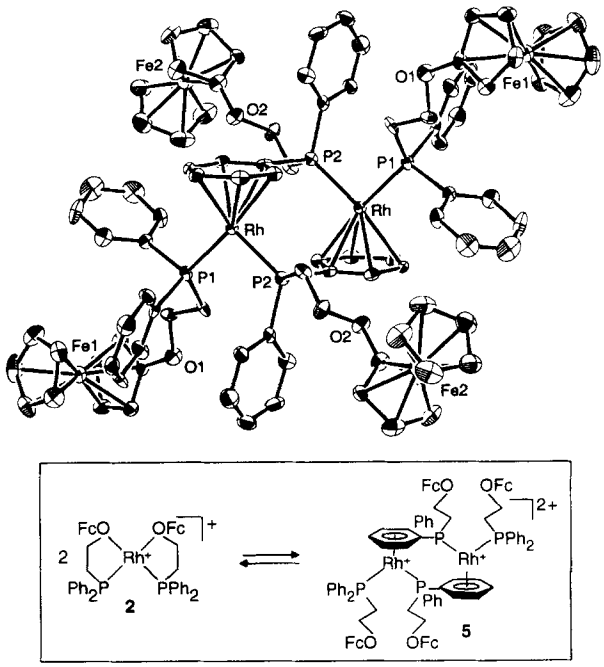


Fig. 1. Structure of **5** (ORTEP drawing; thermal ellipsoids are drawn at 50% probability; BF_4 anions and CH_2Cl_2 molecules are omitted for clarity). Selected distances [Å] and angles [°]: Rh–Rh 4.238(2), Rh–P1 2.260(3), Rh–P2 2.239(3), Rh–C(centroid) 1.423; P1-Rh-P2 95.08(9).

Cyclic voltammetry of complex **2** at concentrations at which only **2** is detected in solution by spectroscopy (1 mM) is dependent on the scan rate (Fig. 2). At a sweep rate of 20 mVs^{-1} the cyclic voltammogram of **2** exhibits two reversible waves at 260 mV and 980 mV vs. Ag wire (Fig. 2A). Initially, one might be inclined to assign the wave at 260 mV, a two-electron transfer

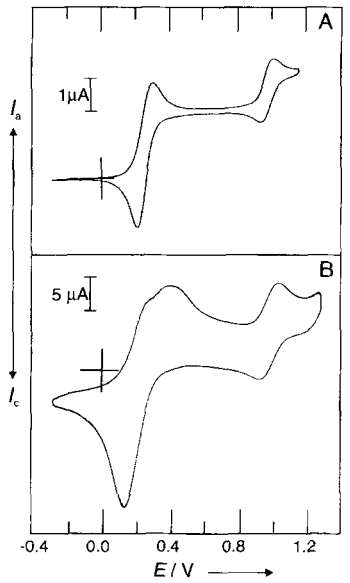
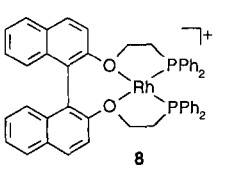


Fig. 2. Cyclic voltammogram for **2**-BF_4 (1 mM) with 0.1 M nBu_4NPF_6 in CH_2Cl_2 as supporting electrolyte, a Au disk as working electrode (0.03 cm^2), and a Ag reference electrode: A) sweep rate 20 mVs^{-1}, B) 1 Vs^{-1}.

process (see below), to the oxidation of the two Fc groups of **2** and the wave at 980 mV to a one-electron, Rh-centered oxidation/reduction of $\mathbf{2}^{2+}$ (that is, **4** in Scheme 1). However, a reversible Rh^I/Rh^{II} redox couple for **4** would be highly unusual since there are only a few examples of mononuclear Rh^{II} complexes. Although some of these compounds have square-planar geometry around Rh, there are no examples of square-planar *cis*-phosphane, *cis*-ether Rh^{II} complexes.[9] In fact, a model Rh^I tetrafluoroborate compound (**8**), which is isoelectronic with **2**, exhibits an *irreversible* Rh-centered oxidation ($E_p = 890$ mV vs. Ag wire).[10] Therefore, we conclude that the species being oxidized at 980 mV in Figure 2A is *not* a square-planar *cis*-phosphane, *cis*-ether Rh^I complex.



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For compound **2**, as the scan rate is increased to 1 Vs^{-1}, the oxidative wave assigned to the two Fc-centered oxidations at 20 mVs^{-1} broadens and then splits into two distinct waves (Fig. 2B). On the reverse scan only one cathodic wave is observed for the Fc/Fc^+ couples. At 1 Vs^{-1} the wave assigned to Rh oxidation also appears reversible (Fig. 2B).

The electrochemical response for compound **2** is highly consistent with an electrochemically induced, haptotropic rearrangement and dimerization that ultimately results in the formation of complex **7** (Scheme 1). According to our proposed scheme, at a sweep rate of 20 mVs^{-1}, **2** undergoes a Fc-centered oxidation to form **3**. This weakens the Fc^+O–Rh bond, and on the time scale of the experiment, the Fc^+O group of **3** along with its FcO group are displaced by an arene ligand in a dimerization reaction to form **6** (path A in Scheme 1). Once displaced, the unoxidized FcO groups in **6** are immediately oxidized, which results in the formation of compound **7**. If on the time scale of the electrochemical experiment the dimerization is fast, a single wave associated with oxidation of two Fc groups per Rh center for **2** would be expected (Fig. 2A). The spontaneous oxidation of the uncomplexed FcO groups in **6** is reasonable; they should be more electron-rich than the Rh^+-complexed FcO group in **3** and therefore more easily oxidized. The wave at 980 mV is attributed to a Rh^I/Rh^{II} redox couple for **7** (Fig. 2A). Note that the Rh centers of complex **7** are not square-planar ones but have adopted piano-stool geometries. We have shown that a series of isoelectronic mononuclear *cis*-phosphane, η^6-arene piano-stool complexes exhibit reversible Rh^I/Rh^{II} redox couples.[11] A comparison of the current passed for the oxidation of **7** (Scheme 1 and Fig. 2) and the current associated with the **7** to **5** conversion (1:2) indicates that oxidation of **7** is a two-electron transfer process. The nature of the product formed from the oxidation of **7** is currently under investigation.

At 1 Vs^{-1} (Fig. 2B), the electrochemical reaction sequence for **2** follows a different pathway (path B in Scheme 1), but ultimately yields the same dimer (**7**) that formed in path A. The first step is a Fc-centered oxidation of **2** to form **3**, but before dimerization occurs, a second Fc-centered oxidation forms **4**. Since the Fc^+O group in **3** remains bound to Rh on the time scale of the electrochemical experiment, the FcO group in **3** is oxidized at a more positive potential than the FcO group(s) in **2** (or **6** in path A, Scheme 1). In short, at fast scan rates the second FcO group in **2** is more difficult to oxidize than the first because they are in electronic communication with each other through their interaction with the Rh center. Compound **4** then dimerizes by arene displacement of its labile Fc^+O groups to form **7**. As at a sweep rate of 20 mVs^{-1}, the oxidation of **7** at 1 Vs^{-1} is a reversible process. On the return sweep at both 20 mVs^{-1} and 1 Vs^{-1}, all Fc^+O groups of **7** are reduced at one potential to form **5**, because all are dissociated from the Rh centers and therefore are not in electronic communication with each other. Once **5** is formed, it deoligomerizes to reform **2**, which makes the entire electrochemical sequence a chemically reversible process. This deoligomerization step is analogous to the dissolution of crystals of **5** in CD_2Cl_2 to form **2** (see above).

These experiments clearly show that RHLs may be used to control transition-metal coordination environment (both steric and electronic), and in the case of **2**–**7**, they may be used to control the position of the monomer/dimer equilibrium.

Experimental Procedure

All NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer at 20 °C. For all ^{31}P NMR spectra 85% H_3PO_4 was the external reference.

(2-chloroethyl)ferrocenyl ether: ^1H NMR (C_6D_6): $\delta = 3.20$ (t, $J(H,H) = 5.6$ Hz, 2H, CH_2Cl), 3.50 (t, $J(H,H) = 5.6$ Hz, 2H, CH_2O), 3.62 (t, $J(H,H) = 1.9$ Hz, 2H, Fc protons), 3.89 (t, $J(H,H) = 1.9$ Hz, 2H, Fc protons), 4.08 (s, 5H, Fc protons); MS(EI) (60 eV, 190 °C): m/z 264 [M^+]. Elemental analysis: calcd for $C_{12}H_{13}ClFeO$: C 54.49, H 4.95; found: C 54.67, H 4.98.

1: ^1H NMR (C_6D_6): $\delta = 2.43$ (t, $J(H,H) = 7.5$ Hz, 2H, CH_2P), 3.63 (t, $J(H,H) = 1.9$ Hz, 2H, Fc protons), 3.86 (dt, $J(H,H) = J(H,P) = 7.6$ Hz, 2H, CH_2O), 3.92 (t, $J(H,H) = 1.9$ Hz, 2H, Fc protons), 4.02 (s, 5H, Fc protons), 7.00–7.45 (m, 10H, Ph); ^{31}P NMR (C_6D_6): $\delta = -21.3$ (s); FAB-MS: m/z 414 [M^+]. Elemental analysis: calcd for $C_{24}H_{23}FeOP$: C 69.58, H 5.59; found: C 69.78, H 5.67.

2: ^1H NMR (CD_2Cl_2): $\delta = 2.78$ (m, 4H, CH_2P), 3.82 (m, 4H, Fc protons), 3.98 (s, 10H, Fc protons), 4.20 (m, 8H, CH_2O and Fc protons), 7.27–7.42 (m, 20H, Ph); ^{31}P NMR (CD_2Cl_2): $\delta = 61.0$ (d, $J(Rh,P) = 211.3$ Hz); FAB-HRMS: m/z calcd 931.0727 [M^+], found 931.0703 [M^+].

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[12] Crystal data for **5**-$(BF_4)_2$: $C_{96}H_{92}Fe_4B_2F_8O_4P_4Rh_2 \cdot 4CH_2Cl_2$, $M_r = 2206.34$, $0.29 \times 0.14 \times 0.05$ mm, triclinic, space group $P\bar{1}$, $a = 10.934(2)$, $b = 14.322(3)$, $c = 16.956(4)$ Å, $\alpha = 73.29(2)$, $\beta = 83.43(2)$, $\gamma = 81.66(2)$ Å, $V = 2509(2)$ Å^3, $\rho_{calcd} = 1.460$ g cm^{-3}, $Z = 1$, $\theta_{max} = 22.60°$, $\mu(Mo_{K\alpha}) = 11.11$ cm^{-1}, $\lambda = 0.71069$ Å, $F(000) = 1120$. Data were collected on an Enraf-Nonius CAD-4 diffractometer at -120 ± 1 °C using the ω–θ scan technique ($2\theta \leq 45.9°$). The data were corrected for Lorentz and polarization effects. In addition, an analytical absorption correction was applied with transmission factors ranging from 0.84–0.95. The structure was solved by direct methods (SHELXS-86). Of the 6959 reflections, 4065 with $I > 3.00\sigma(I)$ were used in the refinement. Refinement of 589 variable parameters (TEXAN 5.0) converged with the residuals of $R = 0.051$ and $R_w = 0.052$. Four dichloromethane solvent molecules were found in the unit cell; two remained disordered after refinement. The highest peaks left in the final difference map were located in the vicinity of the disordered solvent molecules. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

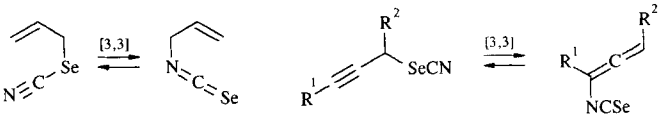
Synthesis and Reactions of Vinyl Isoselenocyanates**

Klaus Banert* and Christoph Toth

Dedicated to Professor Harald Günther on the occasion of his 60th birthday

The existence of isoselenocyanates ("seleno mustard oils") was doubted for a long time,[1] but the synthesis of several aryl and alkyl derivatives has been achieved in recent years.[2] To the best of our knowledge, however, vinyl isoselenocyanates have not yet been prepared. We now report on isomerization reactions that are derived from the known equilibration[3] of allyl selenocyanate **1** and allyl isoselenocyanate **2**, but direct the isoselenocyanato function to a *vinylic* position for the first time. These [3,3]sigmatropic rearrangements provide access to the highly reactive allenyl isoselenocyanates **4** and the isoselenocyanate-substituted 1,3-butadienes **11** and **15**.

An equilibrium of prop-2-ynyl selenocyanates **3** and allenes **4** is established on gas-phase thermolysis[4] of **3**[5] (Scheme 1). Due to their pronounced tendency to polymerize, the isoselenocyanates **4** can only be handled in solution. They can nevertheless be purified by flash chromatography (SiO_2, hexane/Et_2O 10:1; for characterization of **4**, see Table 1). The equilibrium **3a** $\rightleftharpoons$ **4a**[6] is verified by renewed gas-phase thermolysis of **4a**.



1 **2** **3** **4**

Scheme 1. **3a**, **4a**: $R^1 = R^2 = H$; **3b**, **4b**: $R^1 = H$, $R^2 = Me$; **3c**, **4c**: $R^1 = Me$, $R^2 = H$; yields based on converted **3**: **4a** 80%, **4b** 82%, **4c** 76%; ratios at equilibrium: **3a**/**4a** = 37:63; **3b**/**4b** = 17:83; **3c**/**4c** = 79:21.

Table 1. Selected physical data of compounds **4a–c**, **5**, and **9** [a].

4a: ^{1}H NMR: $\delta = 5.44$ (d, $^4J = 6.4$, 2 H; H-3), 6.16 (t, $^4J = 6.4$, 1 H; H-1); ^{13}C NMR: $\delta = 86.30$ (t; C-3), 89.51 (br. d; C-1), 128.40 (v. br. s; NCSe), 210.88 (s; C-2); GC-MS: *m/z* (%): 145 (82) [M^+], 118 (38) [$M^+ - HCN$], 39 (100) [$C_3H_3^+$]; IR (CCl_4): $\tilde{\nu} = 2080$ (NCSe).

4b: ^{1}H NMR: $\delta = 1.79$ (dd, $^3J = 7.4$, $^5J = 2.7$, 3 H; H-4), 5.80 (dq, $^3J = 7.4$, $^4J = 5.9$, 1 H; H-3), 6.03 (dq, $^4J = 5.9$, $^5J = 2.7$, 1 H; H-1); ^{13}C NMR: $\delta = 13.62$ (q; C-4), 87.94 (br. d; C-1), 97.63 (d; C-3), 126.90 (br. s; NCSe), 206.26 (s; C-2).

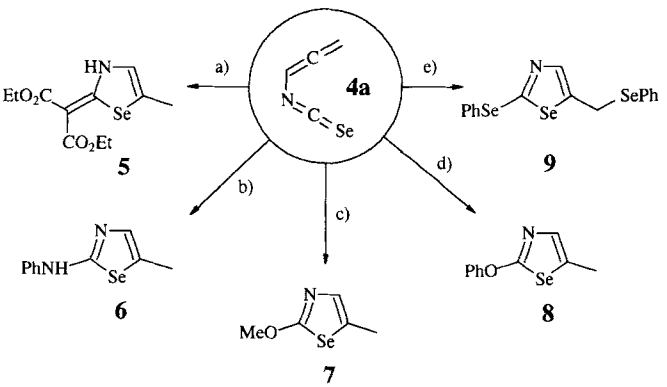
4c: ^{1}H NMR: $\delta = 1.96$ (t, $^5J = 3.2$, 3 H; CH_3), 5.24 (q, $^5J = 3.2$, 2 H; CH_2); ^{13}C NMR: $\delta = 18.97$ (q; CH_3), 83.73 (t; CH_2), 98.75 (br. s; *c*-NCSe), 128.18 (br. s; NCSe), 208.03 (s; C-2).

5: yellow crystals: m.p. 128 °C; ^{1}H NMR: $\delta = 1.35$ (t, $^3J = 7.1$, 6 H; CH_2CH_3), 2.37 (d, $^4J = 1.5$, 3 H; 5-CH_3), 4.27 (q, $^3J = 7.1$, 4 H; CH_2), 6.92 (q, $^4J = 1.5$, 1 H; H-4), 12.70 (s, 1 H; NH); ^{13}C NMR: $\delta = 13.68$ (q, 2 C; CH_2CH_3), 14.36 (q; 5-CH_3), 60.10 (t, 2 C; CH_2CH_3), 87.62 (s; $C(CO_2Et)_2$), 122.48 (d; C-4), 128.40 (s; C-5), 168.00 (s), 175.00 (s); IR (CCl_4): $\tilde{\nu} = 1650$ (C=O), 1620 (C=O), 1250 (C–O); correct elemental analysis based on $C_{11}H_{15}NO_4Se$.

9: light-red, viscous liquid: ^{1}H NMR: $\delta = 4.21$ (d, $^4J = 0.9$, 2 H; CH_2), 7.20–7.80 (m, 11 H; 2 × Ph and H-4); ^{13}C NMR: $\delta = 25.35$ (t; CH_2), 127.85 (d; Ph), 128.56 (s; C-5), 129.34 (d; Ph), 129.50 (d; Ph), 129.80 (d; Ph), 133.80 (d; Ph), 135.98 (d; Ph), 142.37 (d; C-4), 143.59 (s; *i*-Ph), 146.15 (s; *i*-Ph), 164.85 (s; C-2); correct elemental analysis of the picrate based on $C_{22}H_{16}N_4O_7Se_2$.

[a] ^{1}H NMR ($CDCl_3$, 300 or 200 MHz, *J* in Hz), ^{13}C NMR ($CDCl_3$, 75 or 50 MHz, *J* in Hz), MS (EI, 70 eV, correct isotopic distribution), IR ($\tilde{\nu}$ in cm^{-1}), elemental analyses (C,H,N).

In contrast to allenyl isocyanates[7] but similar to allenyl isothiocyanates,[8] compounds **4** afford heterocyclic products on treatment with carbon-, nitrogen-, oxygen-, or seleno-containing nucleophiles (Scheme 2). The syntheses of selenazoles[9] **5**–**9** (Table 1) show that **4a** reacts distinctly more slowly with nucleophiles than the unusually reactive allenyl isothiocyanate.[8]



Scheme 2. Reactions of **4a** with nucleophiles to give the selenazoles **5**–**9**; a) NaH, THF, $CH_2(CO_2Et)_2$, then **4a**, 20 °C, 2 h, then NH_4Cl, H_2O (65%); b) $PhNH_2$, Et_2O, hexane, 60 °C, 17 h (60%); c) MeOH, 60 °C, 24 h (50%); d) PhOH, NEt_3, Et_2O, hexane, 60 °C, 48 h (88%); e) NaH, THF, Ph_2Se_2 (excess), 75 °C, 1.5 h, then **4a** 40 °C, 5 h and 20 °C, 16 h, then NH_4Cl, H_2O (50%).

[*] Prof. Dr. K. Banert, Dipl.-Chem. C. Toth
Lehrstuhl für Organische Chemie der Technischen Universität Chemnitz-Zwickau
Strasse der Nationen 62, D-09111 Chemnitz (Germany)
Telefax: Int. code + (371) 531-1839
e-mail: email@chemie.tu-chemnitz.de

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