(4 mmol) in dry CH_2Cl_2 (4 mL) and the reaction was stirred at room temperature for 5 – 10 min. The appropriate alcohol (4 mmol) was added and stirring continued until the reaction was completed (as judged by RPLC and ^{31}P NMR). The reaction mixture was then evaporated to dryness under reduced pressure (maximum 40 °C), dissolved in acetonitrile, and applied to a semi-preparative RP-HPLC column. Appropriate fractions (2′- and 3′-isomers can be collected separately) were evaporated immediately (reduced pressure, maximum 40 °C), dried several times by co-evaporation with dry acetonitrile or CH_2Cl_2, and kept in a desiccator. The pure samples of the triesters **13** – **18** were prepared by dry extraction from the inorganic buffer salts in acetonitrile or CH_2Cl_2. ^1H and ^{31}P NMR spectra and chromatographic properties of all isolated compounds were identical with the corresponding phosphotriesters obtained by an alternative procedure (see references [4 – 6]).

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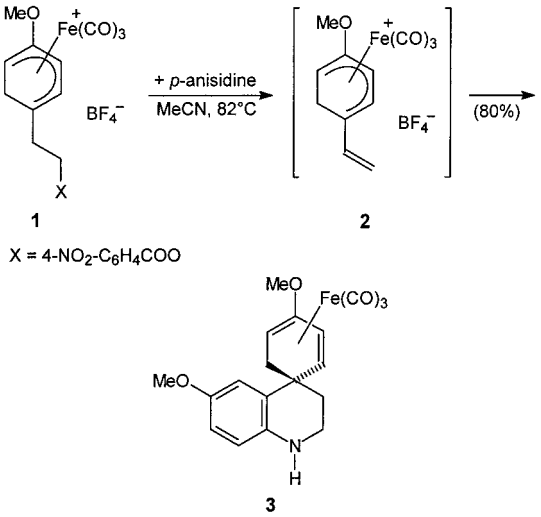
[1] B. N. Tawrick, A. T. Dauher, J. K. Bashkin, *Chem. Rev.* **1998**, *98*, 939 – 960.
[2] a) W. P. Jencks, *Chem. Rev.* **1985**, *85*, 511 – 527; b) E. Bunsel, H. Wilson, *Adv. Phys. Org. Chem.* **1977**, *14*, 133 – 202.
[3] C.-W. Su, J. M. Watson, *J. Am. Chem. Soc.* **1974**, *96*, 1854 – 1857, and references therein.
[4] M. Kosonen, M. Oivanen, H. Lönnberg, *J. Org. Chem.* **1994**, *59*, 3704 – 3708.
[5] M. Kosonen, H. Lönnberg, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1203 – 1209.
[6] A. Kraszewski, J. Stawinski, *Tetrahedron Lett.* **1980**, *21*, 2935 – 2936.
[7] R. Magolda, P. Johnson, *Tetrahedron Lett.* **1985**, *26*, 1167 – 1170.
[8] M. J. Robins, S. R. Naik, A. S. K. Lee, *J. Org. Chem.* **1974**, *39*, 1891 – 1899.
[9] D. M. Brown, D. I. Magrath, A. H. Nielson, A. R. Todd, *Nature* **1956**, *177*, 1124 – 1128.
[10] D. M. Brown, *Basic Princ. Nucleic Acid Chem.* **1974**, *2*, 1 – 90.
[11] D. Herschlag, F. Ekstein, T. R. Cech, *Biochemistry* **1993**, *32*, 8312 – 8321.
[12] a) S. B. Tzokov, I. T. Devedjiev, E. K. Bratovanova, D. D. Petkov, *Angew. Chem.* **1994**, *106*, 2401 – 2402; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2302 – 2303; b) S. B. Tzokov, I. T. Devedjiev, D. D. Petkov, *J. Org. Chem.* **1996**, *61*, 12 – 13; c) S. B. Tzokov, R. T. Momtcheva, N. G. Vassilev, J. Kaneti, D. D. Petkov, *J. Am. Chem. Soc.* **1999**, *121*, 5103 – 5107.
[13] T. C. Bruice, T. H. Fife, *J. Am. Chem. Soc.* **1962**, *84*, 1973 – 1979.
[14] a) E. Ciuffarin, A. Loi, *J. Org. Chem.* **1983**, *48*, 1047 – 1051; b) R. L. Snell, C. D. Chanler, J. T. Leach, R. Lossin, *J. Org. Chem.* **1983**, *48*, 5106 – 5107.
[15] J. G. Verkade, L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, FL, USA, **1987**, pp. 365 – 389.

Iron-Mediated Diastereoselective Spiroannelations with Vinylogous Urethanes – A Novel Access to Spiroannelated Carbo- and Heterocycles**

Hans-Joachim Knölker,* Elke Baum, Helmut Goesmann, Hella Gössel, Konrad Hartmann, Mike Kosub, Ulrike Locher, and Thomas Sommer

Tricarbonyl(η^4-1,3-diene)iron complexes are widely used in organic synthesis;[1] applications include stereoselective spirocyclization.[2] A few years ago, we reported the diastereoselective iron-mediated spiroannelation of arylamines to spirotetrahydroquinolines.[3, 4] The reaction of the iron complex salt **1** with *p*-anisidine provided the tricarbonyliron complex **3** containing a spiro[quinoline-4,1′-cyclohexane] framework (Scheme 1).[3] Through a deuterium labelling



Scheme 1. Iron-mediated spiroannelation of *p*-anisidine.

study, the one-pot spiroannelation was recently shown to proceed via the intermediate tricarbonyliron-complexed 1-vinyl-4-methoxycyclohexadienyl cation **2**.[5] Moreover, it was demonstrated that arylamines which are more nucleophilic in the *ortho*-amino position show a regioselectivity reversal in their reaction with **1** and afford the spiro[quinoline-2,1′-cyclohexane] framework.[4] The iron-mediated spiroannelation of arylamines was applied to the synthesis of a tetracyclic

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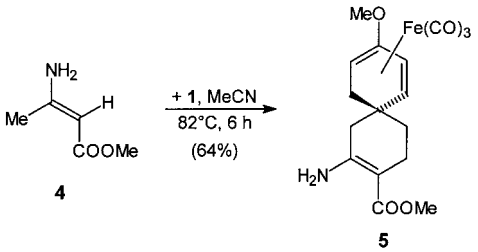
substructure of the discorhabdin alkaloids.[6] Here, we describe a remarkable extension of the scope of the iron-mediated spiroannelation by using vinylogous urethanes as substrates for the reaction with the complex salt **1**.

The reaction of methyl β-aminocrotonate **4** with **1** in acetonitrile under reflux afforded diastereoselectively the spiro[5.5]undecane derivative **5** (Scheme 2). The chemical



Scheme 2. Iron-mediated spiroannelation of methyl β-aminocrotonate **4**.

shift for the signal of the spiro carbon atom at $\delta = 36.27$ in the ^{13}C NMR spectrum indicated immediately that a carbocyclic, rather than a heterocyclic, ring system had been formed (Table 1). The structure (with respect to the orientation of the methyl β-aminocrotonate unit) and configuration (with respect to the spiroannelation) of the product **5** were determined by comparison of the ^{13}C NMR data with those of the compounds described below.

Table 1. Selected spectroscopic data of the spirocyclic tricarbonyliron complexes **5**, **7**, **8**, **10a**, and **10b**.

5: ^{13}C NMR and DEPT (75 MHz, $CDCl_3$): $\delta = 20.33$ (CH_2), 34.92 (CH_2), 36.27 (C), 38.42 (CH_2), 47.94 (CH_2), 50.48 (CH_3), 53.47 (CH), 54.45 (CH_3), 60.77 (CH), 64.19 (CH), 91.41 (C), 140.66 (C), 155.52 (C), 170.44 (C=O), 211.16 (3 CO)

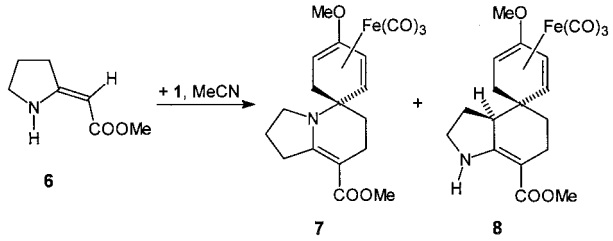
7: ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): $\delta = 19.36$ (CH_2), 20.87 (CH_2), 33.34 (CH_2), 35.38 (CH_2), 38.87 (CH_2), 47.99 (CH_2), 50.21 (CH_3), 51.80 (CH), 53.10 (CH), 54.63 (CH_3), 57.94 (C), 64.72 (CH), 88.62 (C), 140.63 (C), 158.81 (C), 168.94 (C=O), 210.67 (3 CO); elemental analysis for $C_{19}H_{21}FeNO_6$ (%): calcd: C 54.96, H 5.10, N 3.37; found: C 54.92, H 5.06, N 3.51

8: ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): $\delta = 19.96$ (CH_2), 27.09 (CH_2), 32.09 (CH_2), 36.49 (CH_2), 38.57 (C), 44.44 (CH_2), 50.27 (CH_3), 51.71 (CH), 53.90 (CH), 54.43 (CH_3), 60.76 (CH), 64.42 (CH), 85.23 (C), 140.58 (C), 161.36 (C), 170.08 (C=O), 211.26 (3 CO)

10a: ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): $\delta = 20.41$ (CH_2), 22.94 (CH_2), 23.02 (CH_2), 32.04 (CH_2), 36.98 (CH_2), 40.01 (C), 41.36 (CH_2), 45.86 (CH), 50.32 (CH_3), 54.11 (CH), 54.43 (CH_3), 60.95 (CH), 66.45 (CH), 87.98 (C), 139.96 (C), 159.80 (C), 170.90 (C=O), 211.44 (3 CO); elemental analysis for $C_{20}H_{23}FeNO_6$ (%): calcd: C 55.96, H 5.40, N 3.26; found: C 56.21, H 5.41, N 3.49

10b: ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): $\delta = 20.67$ (CH_2), 23.42 (2 CH_2), 36.76 (CH_2), 39.29 (C), 41.11 (CH_2), 41.32 (CH_2), 46.18 (CH), 50.31 (CH_3), 53.17 (CH), 53.72 (CH), 54.40 (CH_3), 66.15 (CH), 86.78 (C), 140.06 (C), 160.19 (C), 170.98 (C=O), 211.42 (3 CO); elemental analysis for $C_{20}H_{23}FeNO_6$ (%): calcd: C 55.96, H 5.40, N 3.26; found: C 56.10, H 5.38, N 3.49

Spiroannelation of the 2-(methoxycarbonylmethylene)pyrrolidine **6**[7] with the complex salt **1** in acetonitrile provided the spiro[indolizidine-5,1′-cyclohexane] **7** and the spiro[indole-4,1′-cyclohexane] **8** (Scheme 3). In this case, the ratio of the two products was dependent on the reaction time and the temperature. At lower temperatures and shorter reaction



Scheme 3. Synthesis of the spiroindolizidine **7** and the spiroindole **8**.

times the spiroindolizidine **7** was generally preferred. Reaction for 10 h at room temperature and subsequently 13 h under reflux afforded **7** and **8** in 80% yield and a ratio of 6:1. After 4 d in acetonitrile under reflux the spiroindole **8** was formed predominantly (78% yield, ratio of **7** to **8** = 1:5). A temperature-induced reversal of the regioselectivity of the spiroannelation was already found for the reaction of arylamines with **1**.[4, 6]

The regioselectivity for the spiroannelation of **6** leading to the spiroindolizidine **7** becomes clear by the chemical shift for the signal of the spiro carbon atom at $\delta = 57.94$ (Table 1), characteristic for a 1-azaspiro[5.5]undecane framework.[4] The configuration of **7** was deduced from the steric requirements of the tricarbonyliron fragment. The ^{13}C NMR spectrum of the spiroindole **8**, with a signal for the spiro carbon atom at $\delta = 38.57$ (Table 1), indicated that **8** contains a spiro[5.5]undecane core related to **5**. Although **8** has an additional stereogenic center, it was obtained surprisingly as a single diastereoisomer. The configuration of the spiroindole **8** was unequivocally confirmed by an X-ray crystal structure analysis (Figure 1).[8] This analysis shows that compound **8** was

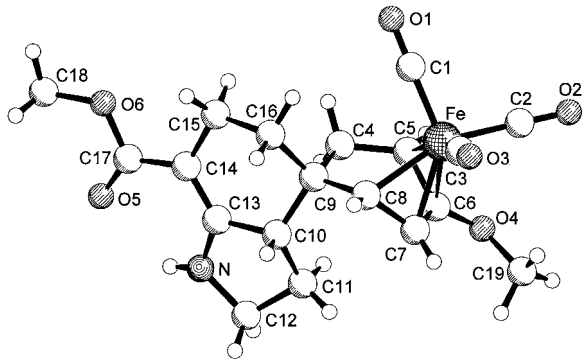


Figure 1. Molecular structure of **8** in the crystal. Selected bond lengths [Å]: Fe–C5 2.122(2), Fe–C6 2.103(2), Fe–C7 2.042(2), Fe–C8 2.065(2), C5–C6 1.417(3), C6–C7 1.406(3), C7–C8 1.431(3).

formed by an approach of **6** to **1** from the face *anti* to the tricarbonyliron fragment. Moreover, it determines the configuration of the newly generated additional stereogenic center C10 adjacent to the spiro carbon C9 (crystallographic numbering). The angular proton at C10 is oriented *syn* relative to the terminal carbon of the coordinated 4′-methoxycyclohexa-2′,4′-diene moiety (C8).

The spiroannelation of the homologous 2-(methoxycarbonylmethylene)piperidine **9**[9] with the complex salt **1** in acetonitrile for 2 d under reflux afforded the two diastereoisomeric spiroquinoline complexes **10a** and **10b** in a 1:1 ratio and 88% yield (Scheme 4).

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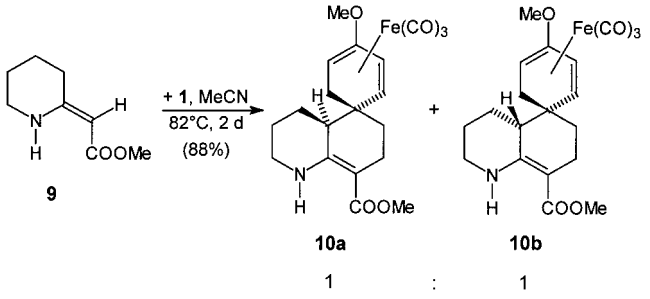
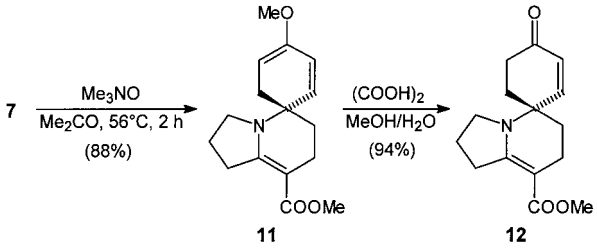


Scheme 4. Synthesis of the spiroquinolines **10**.

The structural assignment of the spiroquinolines **10** is based on the characteristic ^{13}C NMR spectra with signals for the spiro carbon atoms at $\delta = 40.01$ for **10a** and $\delta = 39.29$ for **10b** (Table 1), which suggest again a spiro[5.5]undecane subunit. The X-ray crystal structure determinations of **10a** and **10b** unambiguously confirmed that both compounds have a spiro[quinoline-5,1′-cyclohexane] framework with the vinylogous urethane oriented *anti* relative to the tricarbonyliron fragment. Both complexes differ only in the configuration of the additional stereogenic center C10 (Figure 2).[8] Thus, compound **10a** has a stereochemical arrangement related to **8**, in which the angular proton at C10 is *syn* relative to the terminal carbon atom (C8) of the coordinated 4′-methoxycyclohexa-2′,4′-diene moiety, while in **10b** this stereochemical relationship is *anti*.

In order to demonstrate the utility of the spirocyclic tricarbonyliron complexes for further synthetic transformations, the spiroindolizidine **7** was smoothly converted to the corresponding free ligand **11** by reaction with anhydrous trimethylamine *N*-oxide in acetone under reflux (Scheme 5).[10] Hydrolysis of the enol ether using oxalic acid in aqueous methanol[2b] provided the spirocyclohexenone **12**, which represents a promising substrate for additional functionalization by nucleophilic additions.



Scheme 5. Transformation of complex **7** to the spirocyclohexenone **12**.

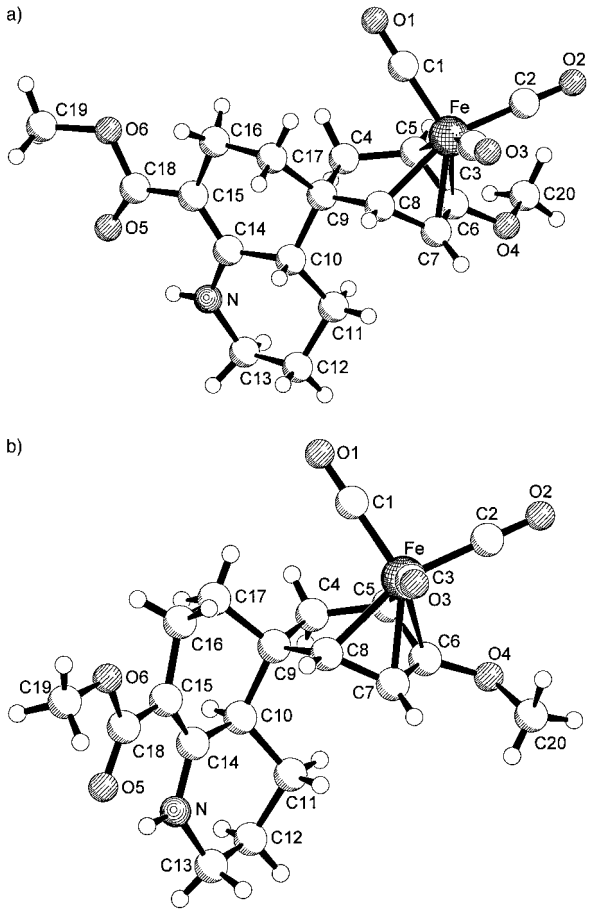


Figure 2. a) Molecular structure of **10a** in the crystal. Selected bond lengths [Å]: Fe–C5 2.110(3), Fe–C6 2.111(3), Fe–C7 2.042(3), Fe–C8 2.088(3), C5–C6 1.417(4), C6–C7 1.402(4), C7–C8 1.427(4). b) Molecular structure of **10b** in the crystal. Selected bond lengths [Å]: Fe–C5 2.115(2), Fe–C6 2.102(2), Fe–C7 2.048(2), Fe–C8 2.082(2), C5–C6 1.419(3), C6–C7 1.402(2), C7–C8 1.434(2).

In conclusion, the method described above offers an easy access to a broad range of carbo- and heterospirocyclic frameworks for the synthesis of biologically active compounds. Taking advantage of the asymmetric catalytic complexation of the appropriate diene precursor for **1**, enantioselective syntheses of the products are feasible.[11]

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[1] A. J. Pearson, *Acc. Chem. Res.* **1980**, *13*, 463; H.-J. Knölker, *Synlett* **1992**, 371; A. J. Pearson, *Iron Compounds in Organic Synthesis*, Academic Press, London, **1994**, chap. 4 and 5; R. Grée, J. P. Lellouche in *Advances in Metal-Organic Chemistry*, *Vol. 4* (Ed.: L. S. Liebeskind), JAI, Greenwich, CT, **1995**, p. 129; H.-J. Knölker, *Chem. Soc. Rev.* **1999**, *28*, 151.

[2] a) A. J. Pearson, *J. Chem. Soc. Perkin Trans. 1* **1979**, 1255; A. J. Pearson, *J. Chem. Soc. Perkin Trans. 1* **1980**, 400; A. J. Pearson, M. Chandler, *J. Chem. Soc. Perkin Trans. 1* **1980**, 2238; b) A. J. Pearson, D. C. Rees, *Tetrahedron Lett.* **1980**, *21*, 3937; A. J. Pearson, P. Ham, D. C. Rees, *Tetrahedron Lett.* **1980**, *21*, 4637; A. J. Pearson, P. Ham, D. C. Rees, *J. Chem. Soc. Perkin Trans. 1* **1982**, 489.

[3] H.-J. Knölker, R. Boese, K. Hartmann, *Angew. Chem.* **1989**, *101*, 1745; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1678.

[4] H.-J. Knölker, R. Boese, K. Hartmann, *Tetrahedron Lett.* **1991**, *32*, 1953.

[5] C. Guillou, F. Bintein, J.-P. Biron, C. Thal, *Tetrahedron Lett.* **1999**, *40*, 4331.

[6] H.-J. Knölker, K. Hartmann, *Synlett* **1991**, 428.

[7] A. Eschenmoser, *Quart. Rev.* **1970**, *24*, 366; L. F. Tietze, T. Eicher, *Reaktionen und Synthesen*, Thieme, Stuttgart, **1991**, p. 180.

[8] X-ray crystal structure analyses: **8**: $C_{19}H_{21}FeNO_6$, $M_r = 415.22\ g\,mol^{-1}$, monoclinic, space group $P2_1/n$, $\lambda = 0.71073$ Å, $a = 10.401(2)$, $b = 11.480(4)$, $c = 16.260(3)$ Å, $\beta = 108.26(2)^\circ$, $V = 1843.7(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.496\ g\,cm^{-3}$, $\mu = 0.831\ mm^{-1}$, $T = 293(2)$ K, θ range: 5.22–28.09°; 4118 independent reflections; full-matrix least-squares refinement; R indices [$I > 2\sigma(I)$]: $R_1 = 0.0443$, $wR_2 = 0.1001$; max. residual electron density: 0.419 e Å^{-3}. **10a**: $C_{20}H_{23}FeNO_6$, $M_r = 429.24\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$, $\lambda = 0.71073$ Å, $a = 8.232(4)$, $b = 10.759(5)$, $c = 12.318(5)$ Å, $\alpha = 74.98(3)$, $\beta = 84.86(4)$, $\gamma = 73.25(4)^\circ$, $V = 1008.9(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.413\ g\,cm^{-3}$, $\mu = 0.783\ mm^{-1}$, $T =$

293(2) K, θ range: 1.71–25.99°; 3966 independent reflections; full-matrix least-squares refinement; R indices [$I > 2\sigma(I)$]: $R_1 = 0.0408$, $wR_2 = 0.1036$; max. residual electron density: 0.431 e Å^{-3}. **10b**: $C_{20}H_{23}FeNO_6$, $M_r = 429.24$ g mol^{-1}, monoclinic, space group $C2/c$, $\lambda = 0.71073$ Å, $a = 19.630(10)$, $b = 15.928(11)$, $c = 15.375(5)$ Å, $\beta = 124.12(2)°$, $V = 3979.8(37)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.433$ g cm^{-3}, $\mu = 0.773$ mm^{-1}, $T = 293(2)$ K, θ range: 1.79–27.50°; 4473 independent reflections; full-matrix least-squares refinement; R indices [$I > 2\sigma(I)$]: $R_1 = 0.0384$, $wR_2 = 0.1075$; max. residual electron density: 0.372 e Å^{-3}. Programs: G. M. Sheldrick, SHELXS-86, Göttingen, Germany, **1986**; G. M. Sheldrick, SHELXL-93, Göttingen, Germany, **1993**; E. Keller, SCHAKAL-97, Freiburg im Breisgau, Germany, **1997**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-134504 (**8**), -134505 (**10a**), and -134506 (**10b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] P. H. Lambert, M. Vaultier, R. Carrié, *J. Chem. Soc. Chem. Commun.* **1982**, 1224; N. Knouzi, M. Vaultier, R. Carrié, *Bull. Chim. Soc. Fr.* **1985**, 815; N. Khoukhi, M. Vaultier, R. Carrié, *Tetrahedron* **1987**, *43*, 1811.

[10] Y. Shvo, E. Hazum, *J. Chem. Soc. Chem. Commun.* **1974**, 336; H.-J. Knölker, *J. Prakt. Chem.* **1996**, *338*, 190.

[11] H.-J. Knölker, H. Hermann, *Angew. Chem.* **1996**, *108*, 363; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 341; H.-J. Knölker, P. Gonser, T. Koegler, *Tetrahedron Lett.* **1996**, *37*, 2405; H.-J. Knölker, H. Goesmann, H. Hermann, D. Herzberg, G. Rohde, *Synlett* **1999**, 421; H.-J. Knölker, H. Hermann, D. Herzberg, *Chem. Commun.* **1999**, 831.

Intracellular Degradation of Diorganomercury Compounds by Biological Thiols—Insights from Model Reactions**

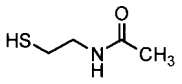
Henry Strasdeit,* Angelika von Döllen, Wolfgang Saak, and Michaela Wilhelm

Dimethylmercury, $HgMe_2$, the simplest diorganomercury compound, is classified as a "super poison"—only a few drops on the skin is fatal for an adult.[1,2] It is noteworthy that several months pass after exposure before the first characteristic symptoms of severe damage to the central nervous system (CNS) appear. In contrast, the onset of the toxic action of diphenylmercury, $HgPh_2$, is rapid and is associated with a different symptomology; it resembles inorganic Hg^{II} salts.[3] At a molecular level these results may only be explained piecemeal, although the extent and rate of degradation of HgR_2 compounds to RHg^+ and finally to Hg^{2+} would appear to play a central role.[4]

We have occupied ourselves with the question as to the possible nature of the degradation reactions in humans from the viewpoint of complexation chemistry. The polar character of Hg–C bonds ($Hg^{\delta+}$–$C^{\delta-}$), which has been confirmed inter alia by quantum-mechanical calculations on $HgMe_2$ and $HgPh_2$,[5] and the protic conditions of most biological compartments suggest that reactions with Brønsted acids are likely. Because of their acidity, their frequent intracellular occurrence, and in particular because of the high thermodynamic stability of the Hg–S bond ("thiophilia" of Hg^{II}), biological thiols have been assumed to be the most important reaction partners [Eq. (1)].

$$HgR_2 \xrightarrow[-RH]{+R'SH} RHg(SR') \xrightarrow[-RH]{+R'SH} Hg(SR')_2 \quad (1)$$

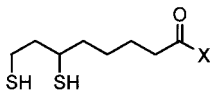
Indeed, we have been able to isolate sequentially the two dearylation stages as $PhHgL^1$ and HgL_2^1 from reactions of $HgPh_2$ with the thiol *N*-acetylcysteamine HL^1 ($HgPh_2$:HL^1 = 1:2, room temperature, tetrahydrofuran (THF), see the Experimental Section), a model for the biological monothiols glutathione and coenzyme A. Moreover, it was also possible to detect the symmetrization of $PhHgL^1$ by NMR spectroscopy in [D_7]*N*,*N*-dimethylformamide [Eq. (2)].



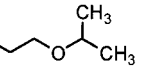
HL^1

$$2\,PhHgL^1 \rightleftharpoons HgPh_2 + HgL_2^1 \quad (2)$$

Accordingly, HgL_2^1 need not necessarily be formed by the direct attack of HL^1 on $PhHgL^1$. Alternatively HL^1 could react solely with $HgPh_2$, first with that initially available and later with that provided by symmetrization. These results show that $HgPh_2$ can be completely dearylated by a suitable thiol under mild conditions.[6]



H_3L^2: X = OH

H_2L^3: X = 

An analogous reaction of $HgPh_2$ with the coenzyme dihydrolipoic acid H_3L^2 also led to the two dearylation stages. However, in this case they appeared unexpectedly as components of the same complex. This complex, $[Hg(PhHg)_2(HL^2)_2]$ (**1**) was isolated in good yield as the poorly soluble THF adduct. [Eq (3), see the Experimental Section].

$$3\,HgPh_2 + 2\,H_3L^2 \xrightarrow{THF} \mathbf{1}\cdot THF\downarrow + 4\,C_6H_6 \quad (3)$$

The formation of **1**·THF is essentially independent of the stoichiometric ratio of the reagents. $HgPh_2$ also formed a complex of analogous composition with the amide H_2L^3, which we synthesized as a sterically equivalent model for the dihydrolipoyl-lysyl side chain (swinging arm) in enzymes. This excludes the possibility that the carboxyl functionality of dihydrolipoic acid is critical for the formation of **1**. The crystal structure analysis[7] showed that **1** is a trinuclear, centrosymmetric complex (Figure 1). Each of the two peripheral mercury atoms Hg1 and Hg1′ is bound to a phenyl group and to a thiolate sulfur atom; the S-Hg-C arrangement

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