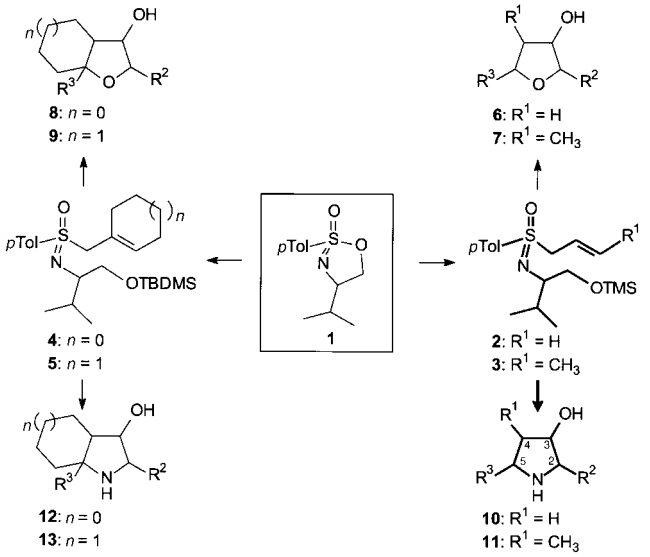
Metalated 2-Alkenylsulfoximides in Asymmetric Synthesis: Diastereoselective Preparation of Highly Substituted Pyrrolidine Derivatives**

Michael Reggelin* and Timo Heinrich

Enantiomerically pure metalated 2-alkenylsulfoximides from cyclic sulfonimidates **1**[1] were introduced in 1994 and proved to be efficient asymmetric d^3-synthons.[2, 3] The isomerically pure, highly substituted tetrahydofuranes **6** and **7**[4] (derived from the open-chain precursors **2** and **3**) as well as the oxabicyclic systems **8** and **9**[3] (derived from **4** and **5**) could be synthesized efficiently by use of reagent **1** (Scheme 1).[2, 4]

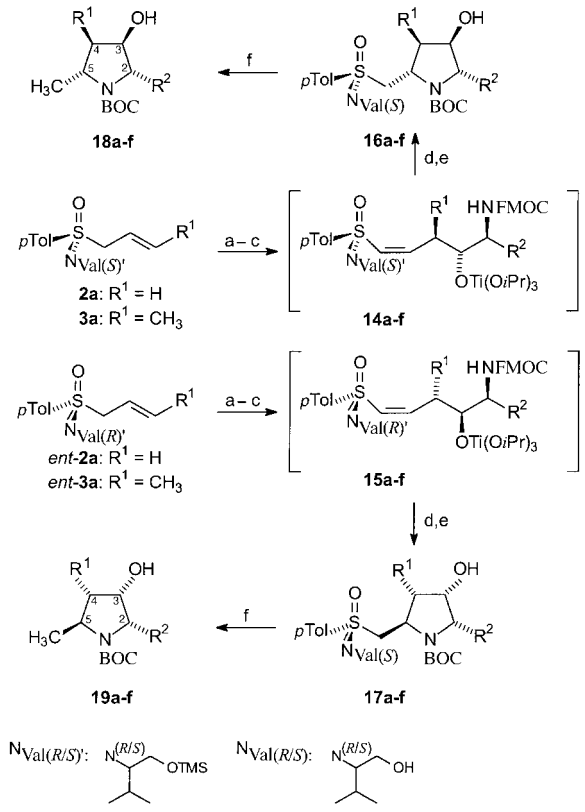


Scheme 1. Heterocyclic compounds available from the cyclic sulfonimidate **1**. R^2 = alkyl, alkaryl, alkheteroaryl; $R^3 = CH_2S(O)(p\text{Tol})N_{val}$, vinyl, methyl. TMS = trimethylsilyl, TBDMS = *tert*-butyldimethylsilyl.

Based on these results, the extension of our method to the synthesis of azamono- (**10** and **11**) and azabicycles (**12** and **13**) seems to be rather promising. Here we describe the stereoselective synthesis of enantiomerically pure, highly substituted pyrrolidine derivatives **10** and **11**. This structural element is found in various biologically active alkaloids[5] such as glycosidase inhibitors,[6] excitatoric aminoacid antagonists,[7] or ACE inhibitors (ACE = acetylcholinesterase).[8] Furthermore, pyrrolidine derivatives are important as catalysts in asymmetric synthesis, for example in the addition of dialkyltin compounds to aldehydes,[9] in the enantioselective reduction of ketones,[10] or in asymmetric Diels–Alder reactions.[11]

A number of methods are available for establishing the five-membered heterocyclic ring with two to four substituents.[12] Many of these possible entries are restricted in their constitutional and configurational versatility; these limits also hold for approaches from natural precursors.[13] The 1,3-dipolar cycloaddition of azomethine-ylides to olefins or acetylene dipolarophiles controlled by chiral auxiliaries[14] is a common way to obtain pyrrolidines. The electronic demands of the dipolarophile necessitate the formation of 2-alkoxycarbonyl-substituted derivatives. However, this method has been applied for the synthesis of combinatorial libraries, which suggests the importance of these substances for pharmaceutical purposes.[15]

Here we demonstrate that the addition of α-aminoaldehydes to titanated 2-alkenylsulfoximides offers a versatile approach to a multitude of highly substituted pyrrolidines in good yields (Scheme 2, Table 1). In contrast to the protocol



Scheme 2. Synthesis of pyrrolidines **18a–f** and **19a–f**, starting from open-chain 2-alkenylsulfoximides. a) *n*BuLi, −78 °C. b) Chlorotris(isopropoxy)-titanium, 0 °C. c) **21a–c**, −78 °C. d) Piperidine, 20 °C; $(NH_4)_2CO_3$, NH_4Cl. e) K_2CO_3, MeOH; BOC_2O, $NaHCO_3$. f) SmI_2. FMOC = (9H-fluoren-9-ylmethoxy)carbonyl.

described earlier,[2, 3] we used toluene instead of THF as solvent for the deprotonation and transmetalation of the allylsulfoximides **2a** and **3a** as well as their enantiomers (*ent*-**2a** and *ent*-**3a**). Only in this solvent are high yields and very high diastereoselectivities obtained ($ds \geq 96\%$, determined by NMR spectroscopy from the crude product). The FMOC-protected α-aminoaldehydes were generated without racemization by Dess–Martin oxidation[16] of the corresponding

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[**] This work was supported by the DFG (Re 1007/1–4) and Solvay Pharmaceuticals GmbH (Hannover, Germany). Continous support by Prof. Dr. C. Griesinger is gratefully acknowledged. We thank the Degussa AG for generous gifts of amino acids.

Table 1. Highly substituted pyrrolidines from metalated 2-alkenylsulfoximides.

Compd	R^1	R^2	Yield [%]	*ds* [%][a]	$[\alpha]_D^{20}$ [°][b]	M.p [°C]
18a	H	Bn	27	67	−37.71 (0.4)	108.5
18b	H	*i*Bu	23	65	+28.17 (0.6)	oil
18c	H	*t*BuOCH$_2$	21	68	+24.46 (0.8)	115.7
18d	CH$_3$	Bn	63	≥96	−37.29 (1.0)	127.8
18e	CH$_3$	*i*Bu	42	≥96	−19.99 (0.9)	96.9
18f	CH$_3$	*t*BuOCH$_2$	44	≥96	+14.80 (0.3)	oil
19a	H	Bn	33	59	+6.52 (1.4)	107.7
19b	H	*i*Bu	36	67	−37.29 (1.0)	oil
19c[c]	H	*t*BuOCH$_2$	31	54	+1.80 (0.3)	93.1
19d	CH$_3$	Bn	43	≥96	+26.70 (1.0)	91.0
19e	CH$_3$	*i*Bu	34	≥96	+66.20 (1.0)	97.3
19f[c]	CH$_3$	*t*BuOCH$_2$	30	≥96	−20.80 (0.3)	187.2

[a] Determined from the ^{1}H NMR spectra of the crude products. [b] *c* in dichloromethane. [c] Deprotected at nitrogen and isolated as the *p*-toluenesulfonate; optical rotation recorded in methanol.

amino alcohols, and were allowed to react without further purification.[17]

After deprotonation of the sulfoximides with *n*BuLi, transmetalation with chlorotris(isopropoxy)titanium (ClTIPT), and addition of the protected aldehydes, O-titanated 5-amino-4-hydoxyvinylsulfoximides **14a–f** and **15a–f** were formed but not isolated (Scheme 2). After one hour piperidine (10 equiv) was added at −78 °C to deprotect the nitrogen atom, which attacked the acceptor-substituted double bond of the vinylsulfoximide (Figure 1). After crystallization of the

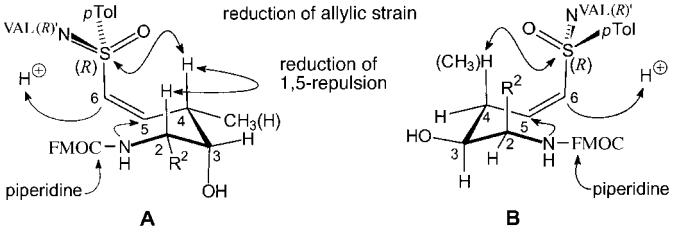

Figure 1. Stereochemical aspects of the cyclization. The topicity of the attack of the nitrogen atom on the 5-position is directed by two conformational aspects: reduction of allylic strain and 1,5-repulsion.

dibenzofulvene–piperidine adduct from methanol and column filtration, the silyl ether group in the auxiliary was cleaved by solvolysis and the pyrrolidine nitrogen atom was protected with a *tert*-butoxycarbamoyl group. The removal of the auxiliary from the resulting 5-sulfonimidoylmethyl-substituted heterocycles **16a–f** and **17a–f** was successful with samarium diiodide in methanol/THF (1/2). This way of desulfuration is described here for the first time and is superior to alternative methods described in the literature.[18] It is essential to manipulate the heteroatoms as described above. If the silyl ether is still present no reaction occurs,[19] and an open-chain homoallylamine is formed if the pyrrolidine nitrogen atom is deprotected.

After recording a ^{15}N–^{1}H HMBC spectrum[20] of **20**, the cyclization product of **14e**, we were able to verify the successful pyrrolidine synthesis (Figure 2). The pyrrolidine nitrogen atom resonates at $\delta = 56.6$ and shows two $^3J_{NH}$ correlations to the methylene group adjacent to the sulfur

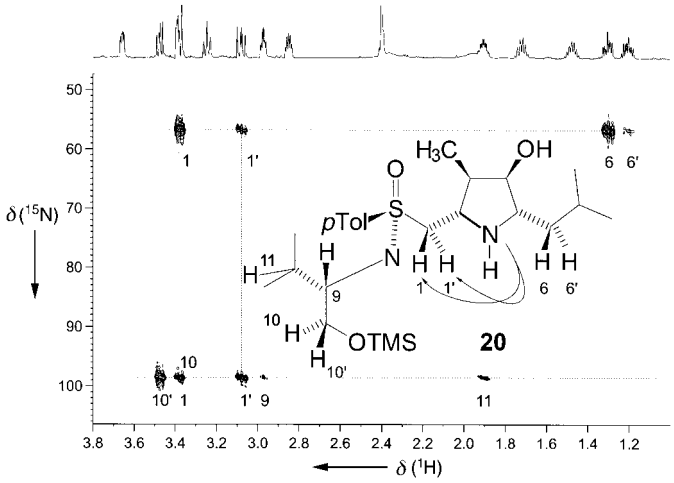

Figure 2. Part of the ^{15}N–^{1}H HMBC spectrum of **20**. Verification of the cyclization (thick bond) is provided by the correlation of the pyrrolidine nitrogen atom to the protons (1, 1′) of the sulfonimidoylmethyl group.

atom (H-1 and H-1′). This is possible only if the cyclization had taken place. The relative and absolute configuration of the pyrrolidines derived from the crotylsulfoximide **3a** (*S* configuration at sulfur) could be verified by X-ray structure analysis of the N-tosylated derivative prepared from **14d**.[21] As expected the absolute configurations of the pyrrolidine alcohol center
(C-3) and the neighboring C-4 atom resulted from a *Re*-side attack of the allyl moiety on the *Re* side of the α-aminoaldehyde (*lk* process).[2, 3] In agreement with our interpretation of the stereochemical outcome of the cyclization process, the sulfonimidoylmethyl fragment is always oriented *trans* to the hydroxyl functionality at C-3.[4] As expected, for the series of crotylsulfoximides obtained from *ent*-**3a** (*R* configuration at sulfur), the induced absolute configurations were the result of a *Si*,*Si* process. This was verified by X-ray structure analysis of the pyrrolidine **19d**.[22]

The total control of the absolute configurations at the newly formed stereogenic centers at C-3 and C-4 in the pyrrolidines **19a–f** merits comment. The addition of a 2-alkenylsulfoximide with the absolute configuration *R* at sulfur to a *S*-configurated α-aminoaldehyde represents an intermolecular "mismatched pair",[23] because the preferred topicity of the nucleophile (*Si*) does not correlate with the Cram side of the aldehyde (*Re*). In perfect agreement with our results with the lactaldehydes,[2, 3] the stereochemical bias excerted by the α-chiral aldehyde is totally overcompensated (reagent control).

The absence of the terminal methyl group in the parent systems (**2a** and *ent*-**2a**) results in a decrease in the stereocontrol at C-5, as already discussed for the THF derivatives (Figure 1).[4] The topicity of attack of the nitrogen nucleophile onto the 5-position is dominated by the attempt of the system to minimize allylic strain and 1,5-repulsion. For the vinylsulfoximides **3**, which lead to the 4-methyl-substituted pyrrolidines, there exists an optimal solution, conformation A. In contrast, derivatives **2**, which lead to the 4-unsubstituted pyrrolidines, can also react via conformation B. In this arrangement the absolute topicity of the attack on the 5-position is inverted. With respect to the 1,5-interaction, B

  1433-7851/98/3720-2884 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1998**, *37*, No. 20

is less stable than A. Within this model, the desired 3,5-*trans* product, the result of a cyclization via A, should be formed in slight excess, which is indeed the case (Table 1). Structural verification was again achieved by X-ray structure analysis of the minor compounds 5-*epi*-**19a** and 5-*epi*-**18a**, confirming the predicted 3,5-*cis* relative configuration.[24]

Our results can be summerized as follows:

1) The γ-hydroxyalkylation of the enantiomeric allyl- and crotylsulfoximides **2a**/**3a** and *ent*-**2a**/*ent*-**3a**, respectively, with α-aminoaldehydes results in the formation of isomerically pure vinylsulfoximides **14** and **15**, which can be transformed to highly substituted pyrrolidines **16** and **17** with piperidine as a deblocking agent.

2) The absolute configuration at the newly formed stereogenic centers C-3 and C-4 is controlled by the absolute configuration at sulfur (reagent control). The configuration at C-5 is the result of conformational preferences of the cyclization precursor. Therefore only 3-substituted derivatives allow total control of this stereogenic center.

3) Samarium diiodide was introducted as a superior desulfuration agent.

The expansion of this new strategy to synthesize isomerically pure, saturated nitrogen heterocycles such as substituted 1- and 2-azabi- and -tricyclic derivatives by proper combination of open-chain or cyclic 2-alkenylsulfoximides with open-chain or cyclic α-aminoaldehydes was already successful (e.g. **12**, **13**, Scheme 1) and will be published in due course. Furthermore, we found that with certain pharmacophoric substituents R^2 and after installation of such substituents at the free OH group (e.g. by benzylation), a number of biologically active substances are available.[25]

Experimental Section

18d: To a solution of **3a** (329 mg, 0.89 mmol) in toluene (2 mL) was added *n*BuLi (492 mg, 2.27 mmol g^{-1} in hexane) at $-78\,^{\circ}$C by syringe. After 15 min ClTIPT (487 mg, 2.50 mmol g^{-1}) was added, and the mixture was warmed to $0\,^{\circ}$C and stirred for 30 min. The mixture was again cooled to $-78\,^{\circ}$C, **21a** (754 mg, 1.79 mmol) dissolved in THF (3 mL) was added, and the mixture was stirred at $-78\,^{\circ}$C for 60 min. Piperidine (0.9 mL, 8.90 mmol) was added, and the temperature was raised to $0\,^{\circ}$C. After 10 h the reaction mixture was poured onto a well-mixed, saturated solution of $(NH_4)_2CO_3$ (25 mL) layered with ethyl acetate (4 mL). After 30 min two clear phases could be separated. The aqueous phase was extracted three times with ethyl acetate (10 mL), and the combined organic layers were extracted with a saturated solution of NH_4Cl. After the organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuo, the benzofulvene–piperidine adduct was crystallized from methanol. The resulting crude product was purified by column filtration (eluent: diethyl ether/hexane 1/1; ethyl acetate), and the obtained polar fraction was treated with K_2CO_3 (136 mg, 0.99 mmol) in methanol (3 mL). The pyrrolidine (desilylated **3a**) nitrogen atom was protected with di-*tert*-butoxycarbonate (BOC_2O, 350 mg, 1.60 mmol) and $NaHCO_3$ (100 mg, 1.2 mmol) in dioxane (4 mL) and water (8 mL). Then residual **3a** and unchanged BOC_2O were removed by flash chromatography.

To remove the chiral auxiliary samarium (545 mg, 3.63 mmol) was suspended in THF (12 mL), and diiodomethane (860 mg, 3.21 mmol) was added by syringe at $0\,^{\circ}$C. After 15 min the reaction was maintained at room temperature for 60 min, and the pyrrolidine was added in methanol (1.5 mL) and THF (3 mL). To quench the reaction, the mixture was poured into a saturated solution of NH_4Cl (20 mL), and 0.5 N HCl was added until two clear phases resulted. After the organic layer was extracted three times with diethyl ether (20 mL), and the pyrrolidine was purified by flash chromatography (diethyl ether/hexane 1/1) to yield 129 mg of **18d** (63 %). M.p. 127.8 °C; $[\alpha]_D^{20} = -37.29$ ($c = 1.00$ in dichloromethane); ^{1}H NMR (270 MHz, [D$_{10}$]xylol, 80 °C): $\delta = 0.849$ (d, $^3J = 6.9$ Hz, 3H; 4-CH$_3$), 1.230 (d, $^3J = 6.1$ Hz, 3H; 5-CH$_3$), 1.448 (s, 9H; C(CH$_3$)$_3$), 1.618 (dqq, $^3J = 8.8$, $^3J = 6.9$, $^3J = 6.1$ Hz, 1H; 4-H), 2.459 (dd, $^3J = 9.4$, $^2J = 13.6$ Hz, 1H; A-H), 2.988 (dd, $^3J = 4.6$, $^2J = 13.6$ Hz, 1H; B-H), 3.427 (dq, $^3J = 8.8$, $^3J = 6.1$ Hz, 1H; 5-H), 3.591 (br s, 1H; 3-H), 3.934 (ddd, $^3J = 9.4$, $^3J = 4.6$, $^3J = 5.7$ Hz, 1H; 2-H), 7.013–7.177 (m, 5H; arom.); ^{13}C NMR (67.9 MHz, [D$_{10}$]xylol, 80 °C): $\delta = 11.12$ (C-4′), 19.44 (C-5′), 28.88 (C(*C*H$_3$)), 40.97 (C-A/B), 44.62 (C-4), 59.33 (C-5), 69.46 (C-2), 75.73 (C-3), 79.00 (*C*(CH$_3$)), 126.71, 128.63, 129.23 (5C, arom.), 139.75 (*ipso*-arom.), 154.49 (C=O); IR (KBr): $\tilde{\nu} =$ 3430.1 (OH), 2973.0, 2930.6 (CH$_3$), 1672.4 (C=O) cm^{-1}; elemental analysis calcd for $C_{18}H_{27}NO_3$ (305.41): C 70.79, H 8.91, N 4.59; found: C 70.59, H 8.93, N 4.63.

Received: May 28, 1998 [Z11917IE]
German version: *Angew. Chem.* **1998**, *110*, 3005–3008

Keywords: asymmetric synthesis · heterocycles · pyrrolidines · samarium · sulfoximines

[1] a) M. Reggelin, H. Weinberger, *Tetrahedron Lett.* **1992**, *33*, 6959–6962; b) M. Reggelin, R. Welcker, *Tetrahedron Lett.* **1995**, *36*, 5885–5886.
[2] M. Reggelin, H. Weinberger, *Angew. Chem.* **1994**, *106*, 489–491; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 444–446.
[3] a) M. Reggelin, H. Weinberger, M. Gerlach, R. Welcker, *J. Am. Chem. Soc.* **1996**, *118*, 4765–4777; b) M. Reggelin, M. Gerlach, M. Vogt, unpublished results.
[4] M. Reggelin, H. Weinberger, T. Heinrich, *Liebigs Ann.* **1997**, 1881–1886.
[5] W. H. Pearson in *Studies in Natural Product Chemistry*, *Vol. 1* (Ed.: Atta-Ur-Rahman), Elsevier, Amsterdam, 1988, pp. 323–358.
[6] a) G. W. Fleet, *Top. Med. Chem.* **1988**, *65*, 149–162; b) R. T. Schwarz, R. Datema, *Trends Biochem. Sci.* **1984**, *9*, 32–34; c) V. Wehner, V. Jäger, *Angew. Chem.* **1990**, *102*, 1180–1182; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1169–1171, and references therein.
[7] R. J. Bridges, F. E. Lovering, J. M. Humphrey, M. S. Stanley, T. N. Blakely, M. F. Cristopharo, A. R. Chamberlin, *Bioorg. Med. Chem. Lett.* **1993**, *3*, 115–121, and references therein.
[8] a) E. W. Petrillo, M. A. Ondetti, *Med. Res. Rev.* **1982**, *2*, 1–41; b) H. S. Cheung, D. W. Cushman, *Biochim. Biophys. Acta.* **1973**, *293*, 451–463.
[9] K. Soai, S. Niwa, *Chem. Rev.* **1992**, *92*, 833–856.
[10] E. J. Corey, R. K. Bakshi, S. J. Shibata, *J. Am. Chem. Soc.* **1987**, *105*, 5551–5553.
[11] S. Kobayashi, M. Murakami, T. Harada, T. Mukayama, *Chem. Lett.* **1991**, 1341–1344.
[12] M. Pichon, B. Figadère, *Tetrahedron: Asymmetry* **1996**, *7*, 927–964.
[13] a) R. H. Wightman, *Tetrahedron* **1993**, *49*, 3827–3840; b) F. Nicotra, *Tetrahedron Lett.* **1993**, *34*, 4555–4558; c) C. Kibayashi, *J. Org. Chem.* **1987**, *32*, 1956–1962; d) T. Livinghouse, *J. Am. Chem. Soc.* **1993**, *115*, 11458–11489.
[14] a) P. Deprez, J. Royer, H. P. Husson, *Tetrahedron: Asymmetry* **1991**, *2*, 1189–1192; b) P. Garner, W. B. Ho, *J. Org. Chem.* **1990**, *55*, 3973–3975; c) P. Garner, F. Arya, W. B. Ho, *J. Org. Chem.* **1990**, *55*, 412–414; d) R. M. Williams, W. Zhai, D. Aldous, S. C. Aldous, *J. Org. Chem.* **1992**, 57, 6527–6532, zit. Lit.; e) W. J. Lown in *1,3-Dipolar Cycloaddition Chemistry*, *Vol. 1* (Ed.: A. Padwa), Wiley, New York, **1984**.
[15] a) G. Liu, J. A. Ellman, *J. Org. Chem.* **1995**, *60*, 7712–7713. b) M. M. Murphy, J. R. Schullek, E. M. Gordon, M. A. Gallop, *J. Am. Chem. Soc.* **1995**, *117*, 7029–7030.
[16] a) D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287; b) D. B. Dess, J. C. Martin, *J. Org. Chem.* **1983**, *48*, 4156–4158.
[17] After addition of 84 mol % of the chiral shift reagent Pr(hfc)$_3$, the enantiomeric excess of the aldehydes could be determined by integration of the ^{1}H NMR signal of the aldehyde protons: M. Reggelin, T. Heinrich, unpublished results.
[18] Raney Nickel requires a large excess (> 10 equiv) to provide satisfying results, and much of the pyrrolidine formed is absorbed. Lithium naphthalenide works fast, but ring-opened by-products are formed.

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[19] Desilyation of the TMS-protected derivative occurs by solvolysis during the desulfuration. More stable silyl ethers must be previously cleaved in an extra step.
[20] $^{13}C-^{1}H$ HMBC: A. Bax, M. F. Summers, *J. Am. Chem. Soc.* **1986**, *108*, 2093 – 2094.
[21] M. Bolte, *Acta Crystallogr. Sect. C* **1997**, *C53*, *IUC 9700029*.
[22] J. Bats, T. Heinrich, M. Reggelin, *Acta Crystallogr. Sect. C*, submitted.
[23] S. Masamune, W. Choy, J. S. Petersen, L. R. Sita, *Angew. Chem.* **1985**, *97*, 1 – 31; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1 – 30.
[24] J. Bats, T. Heinrich, M. Reggelin, *Acta Crystallogr. Sect. C*, eingereicht.
[25] M. Reggelin, T. Heinrich, B. Junker, J. Antel, U. Preuschoff, DE-B 19821418.9, **1998**.

Synthesis and Properties of Lanthanum – Pyrene Complexes—Structure of $[(Cp^*La)_3(\mu\text{-}Cl)_3(thf)(\mu\text{-}\eta^2\text{:}\eta^6\text{-}C_{16}H_{10})]$, the First Complex with a Pyrene Trianion**

Karl-Heinz Thiele,* Sergio Bambirra, Joachim Sieler, and Svea Yelonek

The reduction of polyarenes with alkali metals in ethers leads to compounds in which ether-stabilized contact-ion pairs,[1] triples,[2] or even quintuples[3] occur. The known magnesium anthracene[4] and probably also some naphthalene complexes of europium, samarium, and ytterbium[5] are similarly built. Complexes of trivalent lanthanoids with naphthalene and anthracene have also been described in the last few years.[6] In this context, the reduction of benzanthracene, pyrene, and acenaphthylene with decamethylsamarocene to form dinuclear complexes is of particular interest.[7] In these compounds, η^2, η^3, η^4, and η^5 bonds are found between the metal atom and the arene.

Most organolanthanoid compounds examined so far contain $\{(C_5H_5)_2Ln\}$ and $\{(C_5Me_5)_2Ln\}$ units. Reactions of $[CpLnX_2]$ derivatives, for which diverse conversions with condensed aromatic hydrocarbons in the presence of alkali metals can be expected, have been far less extensively investigated. We report here on the synthesis, structure, and bonding of lanthanum – pyrene complexes with partly novel and completely unexpected coordination modes.

In the reaction of $[Cp^*LaCl](\mu\text{-}Cl)_2Li(thf)_2]$ (**1**) in toluene with pyrene and potassium under the strictest exclusion of air and moisture, a red-violet solution is obtained from which the pyrene complex $[(Cp^*LaCl)_3(C_{16}H_{10})]\cdot thf$ (**2**) was isolated in the form of red-violet, extremely air-sensitive crystals ($Cp^* = C_5Me_5$). Unusual bonding modes prevail in **2**, in which La atoms are coordinated in two different ways. According to the crystal-structure analysis,[8] La1 and La2 are positioned above opposite rings of the pyrene molecule in a η^6 coordination hitherto unknown in polyarene complexes of the lanthanoids, and the La – C bond lengths lie between 2.76 and 3.07 Å (Figure 1). La3 is η^2-bound to one of the middle rings of the pyrene molecule. The La3 – C4 and La3 – C5 distances of 2.82 and 2.84 Å, respectively, are almost identical. Thus, La3 is coordinatively unsaturated and sterically less shielded, which is compensated at least in part by the addition of a THF molecule. Therefore, La1 and La2 form the centers of distorted tetrahedrons and both have a coordination number (CN) of eight, whereas La3 with CN = 7 is arranged in a distorted trigonal bypramid. Pyrene, which is planar when uncoordinated, is slightly twisted in **2**. The atoms C9 and C14 lie 0.115(9) and 0.095(9) Å, respectively, above the plane determined for the $C_{16}H_{10}$ system, with C11 and C12 both lying 0.095(10) Å below it. As with the $\{La_3(pyrene)\}$system, the pyrene unit thus adopts trianionic character.[9] Compound **2** can also be understood as a trinuclear complex with a phenanthrene bridge to which a noncoordinated double bond is attached; this view is supported by the strongly differing bond lengths C4 – C5 and C11 – C12 of 1.41 and 1.35 Å, respectively. The angles of the perpendiculars of the Cp*La and LaC_6 fragments are 128.13° and 128.56°, respectively, for La1 and La2, and thus lie between those values for $[\{Cp_3La\}_n]$[10] and $\{Cp^*_2La\}$ systems.[11]

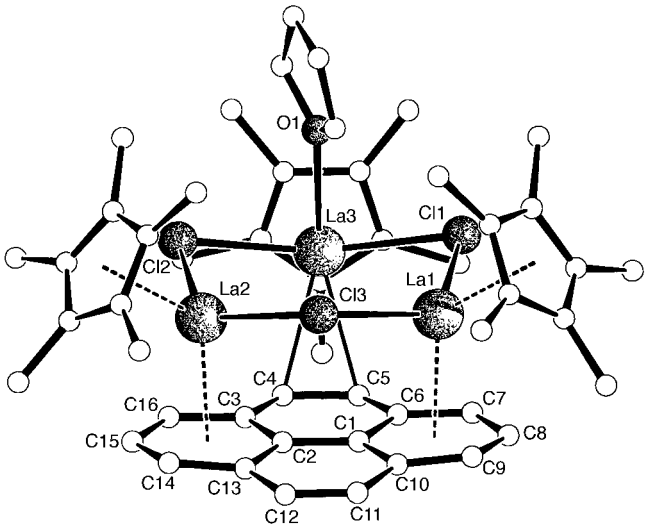

Figure 1. Structure of **2** in the crystal. Selected bond lengths [Å] and angles [°]: La1 – C1 3.047(9), La1 – C6 3.072(8), La1 – C7 2.951(8), La1 – C8 2.843(8), La1 – C9 2.766(8), La1 – C10 2.936(9), La2 – C2 3.014(8), La2 – C3 3.061(8), La2 – C16 2.951(9), La2 – C15 2.872(11), La2 – C14 2.903(10), La2 – C13 2.959(9), La3 – C4 2.823(9), La3 – C5 2.841(8), La – Cl 2.810(3) – 2.894(2), La3 – O1 2.694(7), C11 – C12 1.35(2), C4 – C5 1.417(13); La3-Cl1-La1 93.96(8), La3-Cl2-La2 94.04(6), La1-Cl3-La2 102.10(6)

These results indicate that the formation of **2**, a compound with different coordination modes for La atoms bound in the complex, can be described by Equation (1). The reaction of

$$3\,\mathbf{1} + 3\,K + C_{16}H_{10} \xrightarrow[-5\,THF]{\text{toluene}} \mathbf{2} + 3\,LiCl + 3\,KCl \qquad (1)$$

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

  1433-7851/98/3720-2886 $ 17.50+.50/0