molecular plane (Figure 4). This effect can be described by means of two ring currents circulating at a certain distance of the molecular plane. In this paper, instead, we have observed one highly aromatic disrotatory ring closure in which there is only one maximum diamagnetic shielding above the molecular plane. In a formal sense this transition structure corresponds to π aromaticity involving only one ring current circulating on the side where the disrotatory movement allows a close proximity between the terminal p atomic orbitals (pAO). We therefore propose the terms π^1 aromaticity and π^2 aromaticity to describe these two different kinds of aromatic transition structures.

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Stereoselective Formation of C_2-Symmetric ansa-Lanthanocenes by Reductive Coupling of Acenaphthylene with Activated Ytterbium or Samarium[**]

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Dedicated to Professor Jörn Müller
on the occasion of his 65th birthday

C_2-symmetric ansa-metallocenes have been studied intensively because of their potential use as catalysts for stereoselective olefin polymerization processes.[1] Edelmann et al. and, later on, Shapiro et al. and Eisch et al. reported on a method to synthesize interannular ethano-bridged ansa-metallocenes by the reductive coupling of 6-substituted or 6,6′-disubstituted fulvenes with metallic calcium, lanthanide metals, or the dihalides of titanium and zirconium.[2] The reaction with 6-substituted fulvenes results in the formation of mixtures of *rac* and *meso* isomers. The exclusive formation of just one isomer by fulvene-type coupling has not yet been observed.[2e] The synthesis of ansa-metallocenes from bridged cyclopentadienyl dianions also produces only mixtures of isomers of variable *rac*:*meso* ratios.[3] We now suggest that the reductive coupling of a ligand in which the coupling exocyclic carbon atom of the fulvene moiety is fixed by incorporation into a condensed aromatic ring system such as in acenaphthylene (acene) would probably allow the isolation of an isomerically pure ansa-metallocene. Acene combines one five- and two six-membered rings and its resonance structures reveal the fulvene pattern. The only reductive coupling process of acene known so far is its reaction with $[V(CO)_6]$ which produces the double half-sandwich vanadium complex $(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_{24}H_{16})[V(CO)_4]_2$.[4] Here we report the reductive coupling of acene by activated metallic ytterbium and samarium, which yields the respective C_2-symmetric *trans-rac*-ansa-lanthanocenes.

The high electron affinity of acene ($E_{1/2} = -1.65$ V)[5] allows its reduction with activated metallic ytterbium or samarium, affording the ansa-lanthanocenes $[(\eta^5\text{-}C_{12}H_8)_2Ln(thf)_2]$ as dark red (Ln = Yb, **1**) or dark brown crystals (Ln = Sm, **2**) in yields of about 90% (Scheme 1). The ytterbium and samarium are activated by addition of iodine to the respective

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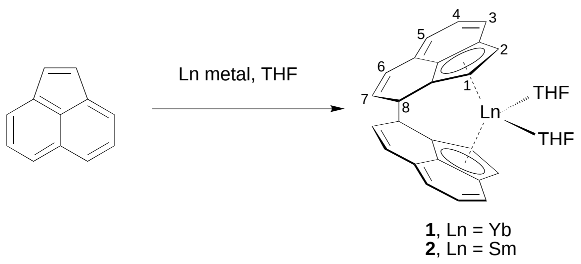

Scheme 1.

suspension of the metal in THF. The release of two electrons from each metal atom leading to the formation of Ln^{II} ions, uptake of one of these electrons per acene molecule, dimerization of the acenyl radicals to give biacenyl dianions, and coordination of the two cyclopentadienyl ring units of the dianion to the Ln^{II} ion are expected as the reaction steps on the way to the isolated ansa-metallocene complexes.

According to the two different possibilities for the orientation of the two acenyl ring units of the ligand, C_s-symmetric *meso-* and/or C_2-symmetric *rac*-ansa complexes may be expected. In contrast to the results of the reductive coupling of indenylidenes with metallic calcium[2c,e] or titanium and zirconium dihalides,[2d] the described coupling of acene with Yb or Sm, exclusively gives the respective C_2-symmetric *trans-rac*-ansa complex as confirmed by ^{1}H NMR spectroscopic measurements and X-ray diffraction analysis of **1** and **2**.

The ^{1}H NMR spectrum of **1** in [D$_8$]THF shows only one set of eight resonances for the ring protons. Compound **1** could not be chatracterized by ^{171}Yb NMR spectroscopy because it was not sufficiently soluble in THF or in toluene. As expected, the ^{1}H NMR signals of the paramagnetic samarium complex **2** in the range from $\delta = 17$ to -10 are broadened, thus preventing the observation of ^{1}H–^{1}H couplings. However, a clear assignment of the ^{1}H NMR spectrum of **2** could be achieved by ^{1}H–^{1}H COSY experiments and by comparison with the ^{1}H–^{1}H coupling scheme of the diamagnetic complex **1**.

The molecular structures of **1** (Figure 1) and **2** (Figure 2) were determined by single-crystal X-ray diffraction[6] on crystals obtained from THF. Both complexes crystallize in a centrosymmetric space group, **1** in $P\bar{1}$ and **2** in $P2_1/c$, each with four molecules (two pairs of *R*,*R* and *S*,*S* enantiomers) in the unit cell. The two crystallographically independent molecules in **1** show very similar molecular parameters. The lanthanide atoms in **1** and **2** are coordinated to the two cyclopentadienyl units of the biacenyl ligand and to two THF molecules in a distorted tetrahedral fashion with the THF molecules lying in the equatorial wedge of the ansa-lanthanocene moiety. The ansa-metallocene unit of both **1** and **2** is rather constrained as seen by the C$_g$-Ln-C$_g$ angles (C$_g$ defines the center of the five-membered ring units of the ligand) of 119.8° for **1** and 115.0° for **2**. Unexpectedly, these C$_g$-Ln-C$_g$ angles are smaller than those of the two-atom bridged ethylenebis(indenyl)(ebi) complexes [(*meso*-ebi)YbN(SiMe$_3$)$_2$][3] (122.0°) and [(*meso*-ebi)ZrCl$_2$][11] (125.4°) which are already considered as strained molecules. Generally, the C$_g$-Ln-C$_g$ angle decreases with increasing size of the metal cation, which in the case of **2** leads to a pronounced slippage of the samarium atom from

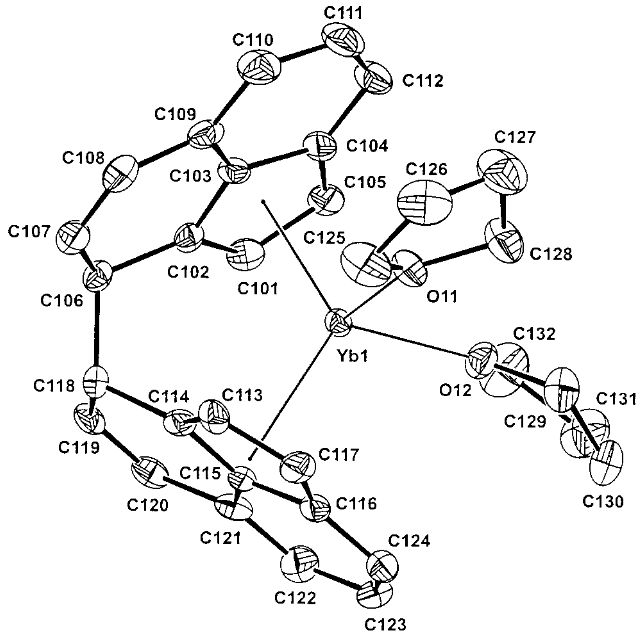

Figure 1. Molecular structure (ORTEP drawing) of one of the two crystallographically independent molecules of **1** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are omitted for clarity. Relevant bond lengths [Å] and angles [°]: Yb1-C$_g$(1) 2.4436(18), Yb1-C$_g$(2) 2.449(2), Yb1-O11 2.396(3), Yb1-O12 2.364(3), Yb1-C101 2.721(4), Yb1-C102 2.688(4), Yb(1)-C103 2.705(5), Yb1-C104 2.759(5), Yb1-C105 2.752(4), Yb1-C113 2.714(4), Yb1-C114 2.725(4), Yb1-C115 2.740(5), Yb1-C116 2.759(5), Yb1-C117 2.709(4); C$_g$(1)-Yb1-C$_g$(2) 119.18(6), O11-Yb1-O12 92.91(12), C$_g$(1)-Yb1-O11 112.89(10), C$_g$(1)-Yb1-O12 110.20(10), C$_g$(2)-Yb1-O11 106.74(9), C$_g$(2)-Yb1-O12 111.79(10); ring slippage [Å]: 0.082 (C$_g$(1)), 0.019 (C$_g$(2)).

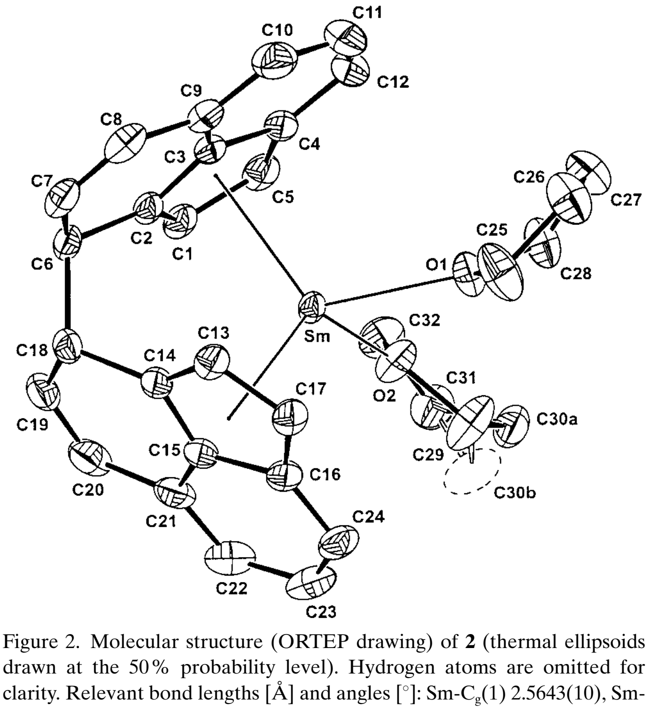

Figure 2. Molecular structure (ORTEP drawing) of **2** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are omitted for clarity. Relevant bond lengths [Å] and angles [°]: Sm-C$_g$(1) 2.5643(10), Sm-O1 2.5167(18), Sm-C1 2.834(2), Sm-C2 2.852(2), Sm-C3 2.827(2), Sm-C4 2.835(2), Sm-C5 2.827(2), Sm-C$_g$(2) 2.5686(11), Sm-O2 2.5483(18), Sm-C13 2.879(3), Sm-C14 2.825(2), Sm-C15 2.779(2), Sm-C16 2.831(2), Sm-C17 2.876(2); C$_g$(1)-Sm-C$_g$(2) 115.04(4), O1-Sm-O2 83.47(6), C$_g$(1)-Sm-O1 117.12(5), C$_g$(2)-Sm-O1 111.82(5), C$_g$(2)-Sm-O2 120.91(5), C$_g$(1)-Sm-O2 104.90(5); ring slippage [Å]: 0.022 (C$_g$(1)), 0.124 (C$_g$(2)).

the center of one of the two cyclopentadienyl rings (0.124 Å). The C_g-Ln-C_g angles of the less constrained five-atom-bridged bis(indenyl)lanthanocenes $[\{O(CH_2CH_2C_9H_6)_2\}LnCl(thf)]$[12] (131.4° Ln = Nd, 132.3° Gd, 132.6° Ho) are larger and show little dependence on the size of the central metal cation.

It is expected that **1** and **2** will be useful as reducing agents due to the presence of minor quantities of uncoupled acene radical anionic species in solution, detected by ESR spectroscopy. Reactiviy studies of both complexes are in progress.

Experimental Section

All manipulations were performed under nitrogen atmosphere or in vacuum. Elemental analyses were obtained by using a Perkin-Elmer Series II CHNS/O 2400 Analyzer, NMR spectra were recorded on a Bruker ARX 200 instrument. The commercially available acenaphthylene (Aldrich; purity 75 %) was purified further to 85 % (10 to 15 % acenaphthene as impurity) by sublimation (80/10^{-1} Torr). The given quantities of acenaphthylene and the yields of the products refer to pure acenaphthylene.

1: A mixture of ytterbium metal (7.8 g, 45 mmol) and iodine (1.85 g, 14.6 mmol) in THF (30 mL) was stirred for 1 h at 50 °C, and the resulting suspension of YbI_2 was decanted off. The residual activated metal was washed with warm THF (2 × 30 mL), and then a solution of acenaphthylene (1.23 g, 6.37 mmol) in THF (50 mL) was added. The mixture was stirred for 1 h at reflux. The warm, dark red-brown solution was filtered and then concentrated to 15 mL which yielded **1** as dark red almost black crystals. Yield: 2.34 g (93 %); m.p. > 180 °C (decomp); ^1H NMR (200 MHz, $[D_8]$THF, 20 °C, TMS): $\delta = 6.87$ (d, $^3J(H,H) = 8.26$ Hz, 2H; CH, H^3), 6.65 (dd, $^3J(H,H) = 9.7$, 2.0 Hz, 2H; CH, H^6), 6.45 (dd, $^3J(H,H) = 8.24$, 8.26 Hz, 2H; CH, H^4), 6.29 (s, 2H; CH, H^1), 6.26 (d, $^3J(H,H) = 4.54$ Hz, 2H; CH, H^5), 6.02 (dd, $^3J(H,H) = 9.7$, 3.56 Hz, 2H; CH, H^7), 5.59 (d, $^3J(H,H) = 3.14$ Hz, 2H; CH, H^2), 4.45 (s, 2H; CH, H^8), 3.71 (m, 8H; CH_2), 1.59 (m, 8H; CH_2); elemental analysis (%): calcd for $C_{32}H_{32}O_2Yb$ (621.62): C 61.83, H 5.19; found: C 60.79, H 4.25.

2: The dark brown crystalline compound **2** was prepared as described for **1** using samarium (4.2 g, 28 mmol), iodine (1.3 g, 10.24 mmol), and acenaphthylene (0.76 g, 5 mmol) in THF (50 mL). Yield: 1.34 g (90 %); m.p. > 180 °C (decomp); ^1H NMR (200 MHz, $[D_8]$THF, 20 °C, TMS): $\delta = 17.67$ (s, 2H; CH, H^3), 15.52 (s, 2H; CH, H^1), 12.84 (s, 2H; CH, H^6), 12.01 (s, 2H; CH, H^4), 6.89 (s, 2H; CH, H^2), 5.12 (s, 2H; CH, H^5), 3.6 (s, 8H; CH_2), 1.73 (s, 8H; CH_2), 0.72 (s, 2H; CH, H^7), −9,88 (s, 2H; CH, H^8); elemental analysis (%): calcd for $C_{32}H_{32}O_2Sm$ (598.93): C 64.17, H 5.38; found: C 63.37, H 5.42.

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[6] X-ray structure analyses: Siemens-SMART-CCD diffractometer, ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71093$ Å), graphite monochromator, $T = 173$ K, absorption correction with SADABS,[7] structure solution with direct methods (SHELXS-97[8]), refinement against F^2 (SHELXL-97[9]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2) at calculated positions. The PLATON[10] program was used for the geometric analysis of the structures. Data collection for **1**: crystal dimensions 0.48 × 0.30 × 0.04 mm, triclinic, space group $P\bar{1}$, $a = 8.1967(1)$, $b = 15.6420(3)$, $c = 19.9504(2)$ Å, $\alpha = 81.668(1)$, $\beta = 83.920(1)$, $\gamma = 89.921(1)°$, $V = 2516.41(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.641 \times 10^3$ kg m^{-3}, $\mu = 3.744$ mm^{-1}, $F(000) = 1240$, $2.08° \leq 2\theta \leq 55.0°$, $-10 \leq h \leq 10$, $-20 \leq k \leq 20$, $-25 \leq l \leq 24$, 19188 data collected, 11429 unique data ($R_{int} = 0.0438$), 8209 data with $I > 2\sigma(I)$, 631 refined parameters, GOF(F^2) = 0.925, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$): $R_1 = 0.0348$, $wR_2 = 0.0658$; max./min. residual electron density 1.203/−1.597 e Å^{-3}. Data collection for **2**: crystal dimensions 0.50 × 0.42 × 0.22 mm, monoclinic, space group $P2_1/c$, $a = 17.8614(3)$, $b = 8.6231(1)$, $c = 16.4556(2)$ Å, $\beta = 96.452(1)°$, $V = 2518.45(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.580 \times 10^3$ kg m^{-3}, $\mu = 2.359$ mm^{-1}, $F(000) = 1208$, $2.30° \leq 2\theta \leq 55.0°$, $-23 \leq h \leq 23$, $-11 \leq k \leq 8$, $-20 \leq l \leq 21$, 18413 data collected, 5780 unique data ($R_{int} = 0.0374$), 4938 data with $I > 2\sigma(I)$, 326 refined parameters, GOF(F^2) = 1.024, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$): $R_1 = 0.0240$, $wR_2 = 0.0537$; max./min. residual electron density 0.692/−0.641 e Å^{-3}. The C30 carbon atom of one of the THF molecules in **2** is disordered about two positions, with occupancy factors of 0.627(18) and 0.373(18). 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-149098 (**1**) and CCDC-149099 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Fabrication and Properties of Gold Single-Crystal Ultramicroelectrodes**

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Ultramicroelectrodes (UMEs) are important in electrochemistry and electroanalysis because of the special mass transfer conditions observed with respect to those at electrodes of normal dimensions.[1] This property has been used to facilitate the measurement of very fast electron transfer kinetics, a well-known example being the electrooxidation of ferrocene.[2] On the other hand UMEs made from metals in the usual way are necessarily polycrystalline in nature. As a

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