[4] a) L. Nyulászi, *Inorg. Chem.* **1996**, *35*, 4690; b) M. N. Glokhotsev, A. Dransfeld, P. von R. Schleyer, *J. Phys. Chem.* **1996**, *100*, 13447.

[5] F. G. N. Cloke, P. B. Hitchcock, P. Hunnable, J. F. Nixon, L. Nyulászi, E. Niecke, V. Thelen, *Angew. Chem.* **1998**, *110*, 1139; *Angew. Chem. Int. Ed.* **1998**, *37*, 1083.

[6] F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, B. Wibbeling, *Angew. Chem.* **2000**, *112*, 2393; *Angew. Chem. Int. Ed.* **2000**, *39*, 2307.

[7] 2*H*-1,2-Azaphospholes: a) R. Streubel, H. Wilkens, A. Ostrowski, C. Neumann, F. Ruthe, P. G. Jones, *Angew. Chem.* **1997**, *109*, 1549; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1492; b) H. Wilkens, A. Ostrowski, J. Jeske, F. Ruthe, P. G. Jones, R. Streubel, *Organometallics* **1999**, *18*, 5627.

[8] 2*H*-1,3,2-Diazaphospholes: a) H. Wilkens, F. Ruthe, P. G. Jones, R. Streubel, *Chem. Eur. J.* **1998**, *4*, 1542; b) R. Streubel, U. Schiemann, N. Hoffmann, Y. Schiemann, P. G. Jones, D. Gudat, *Organometallics* **2000**, *19*, 475.

[9] 2*H*-1,4,2-Diazaphospholes: R. Streubel, H. Wilkens, P. G. Jones, *Chem. Eur. J.* **2000**, *6*, 3997.

[10] 2*H*-1,2,3-Azadiphospholes: G. N. Cloke, P. B. Hitchcock, U. Schiemann, R. Streubel, J. F. Nixon, D. J. Wilson, *Chem. Commun.* **2000**, 1659.

[11] R. Appel, M. Poppe, *Angew. Chem.* **1989**, *101*, 70; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 53.

[12] R. Streubel, L. Ernst, J. Jeske, P. G. Jones, *J. Chem. Soc. Chem. Commun.* **1995**, 2113.

[13] F. Mercier, L. Ricard, F. Mathey, M. Regitz, *J. Chem. Soc. Chem. Commun.* **1991**, 1305.

[14] M. Julino, M. Slany, U. Bergsträßer, F. Mercier, F. Mathey, M. Regitz, *Chem. Ber.* **1995**, *128*, 991.

[15] R. Matos, M. F. Meidine, J. F. Nixon, B. F. Trigo Passos, E. Niecke, D. Barion, *J. Organomet. Chem.* **1990**, *390*, C89.

[16] **1**: MS (EI, 70 eV, ^{182}W): m/z (%): 613 (18) $[M]^+$; **3**: MS (EI, 70 eV, 10000 resolution (10%-Tal-Def.)) m/z (%): 788.1188 ± 2 ppm (16) $[M]^+$ $C_{23}H_{43}N_2O_5P_3Si_3{}^{184}W$; negative-ion MS (CI, NH$_3$, ^{182}W): m/z (%): 785 (6) $[M-H]^-$, 713 (9) $[M-H-(H_3C)_2SiCH_2]^-$, 627 (78) $[M-H-(H_3C)_2SiCH_2\text{-}(H_3C)_2SiCHCH_3]^-$, 555 (69) $[\{(i\text{Pr}(H)N)_2C_2P_3\}^{182}W(CO)_5]^-$.

[17] Crystal structure analysis of complex **1** ($C_{16}H_{27}NO_5P_2Si_2W$): triclinic, space group $P\bar{1}$, $a = 10.577(4)$, $b = 11.441(4)$, $c = 11.970(4)$ Å, $\alpha = 70.47(2)$, $\beta = 79.07(2)$, $\gamma = 62.66(2)°$, $V = 1211.6$ Å^3, $Z = 2$, $\mu = 5.0$ mm^{-1}, $T = -130$ °C. A crystal (yellow plate, ca. 0.5 × 0.4 × 0.2 mm) was mounted in perfluoropolyether at −130 °C on a Stoe STADI-4 diffractometer. Intensities were registered up to $2\theta_{max}$ 50° using Mo$_{K\alpha}$ radiation; 4277 reflections of a total of 5117 were independent ($R_{int} = 0.015$). After a semiempirical absorption correction (ψ scans, transmittance 0.61–0.96), the structure was solved by the heavy-atom method and refined with full-matrix least-squares methods on F^2 (program SHELXL-93, G. M. Sheldrick, Universität Göttingen). The hydrogen atom at the nitrogen center was refined free, all others with a riding model or as rigid methyl groups. The final $wR2$ based on F^2 for all data was 0.045, and the conventional $R(F)$ value was $R1 = 0.019$; 257 parameters, $S = 1.07$, max. residual electron density 0.85 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160390. 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). Note: The crystal structure of **4** will be published elsewhere in the near future.

[18] R. Streubel, N. H. T. Huy, L. Ricard, F. Mathey, *Phosphorus Sulfur Relat. Elem.* **1993**, *77*, 229.

[19] R. Streubel, U. Schiemann, unpublished results.

[20] Several attempts were made to determine the crystal structure of **3**; the measurement (at −130 °C) gave a value of 322° for the sum of bond angles at the $\sigma^3\lambda^3$-phosphorus atoms in two independent molecules which matches approximately the value found for a 3,4-bisphosphonio-1,2-diphosphole: G. Jochem, H. Nöth, A. Schmidpeter, *Chem. Ber.* **1996**, *129*, 1083.

[21] The key to the assignment of the conformation was the appearance of cross peaks that connect the protons in the *N*-*i*Pr and *N*-SiMe$_3$ groups, respectively, with *only one* of the anisochronous CSiMe$_3$ groups. This suggested a static, quasi-orthogonal orientation of the (Me$_3$Si)$_2$CH and *i*Pr(Me$_3$Si)N groups with respect to the plane of the five-membered ring. The onset of rotation with increasing temperature led to the appearance of the missing cross peaks. Analysis of the cross peaks originating from the N(H)*i*Pr signals revealed that the amino group has either a static and coplanar orientation relative to the ring, or undergoes fast rotation.

[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[23] Gaussian98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998** Note: The barrier which was determined here for **8** with the B3LYP/6-31+G(d)-method lies approximately 2.5 kcal mol^{-1} higher than the earlier results;[3, 4] it is known, however, that the MP2/6-31G(d)-method underestimates the P-inversion barrier by 8–12 kJ mol^{-1}.

Unexpected Splitting of ansa-Ytterboacene and ansa-Calcoacene: Formation of $[(\eta^2\text{-}C_{12}H_8)ZrCl_2(thf)_3]$ and $(Me_3Si)_2C_{12}H_8$**

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Herbert Schumann*

Recently we reported on the synthesis of the C_2-symmetric *trans-rac*-ansa-lanthanoacenes[1] $[(\eta^5\text{-}C_{12}H_8)_2M(thf)_2]$ (M = Yb, **1**; Sm, **2**) by reductive coupling of acenaphthylene (acene) with activated metallic ytterbium or samarium.[2] The acenyl radical anions formed in the course of these redox reactions dimerize to biacenyl dianions which stereoselectively coordinate the simultaneously formed M^{2+} cations. In contrast, the

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[**] Organometallic Compounds of the Lanthanides, Part 148. This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt Foundation (I.L.F.), and the Russian Foundation for Basic Research (Grant No. 01-03-32631). We thank Dr. Yuri A. Kurskii and Dr. Vladimir I. Nevodchikov for assistance with recording NMR and ESR spectra. Part 147: I. L. Fedushkin, T. V. Petrovskaya, F. Girgsdies, V. I. Nevodchikov, R. Weimann, H. Schumann, M. N. Bochkarev, *Izv. Akad. Nauk Ser. Khim.* **2000**, 1897–1904; *Russ. Chem. Bull. Int. Ed.* **2000**, *49*, 1869-1876.

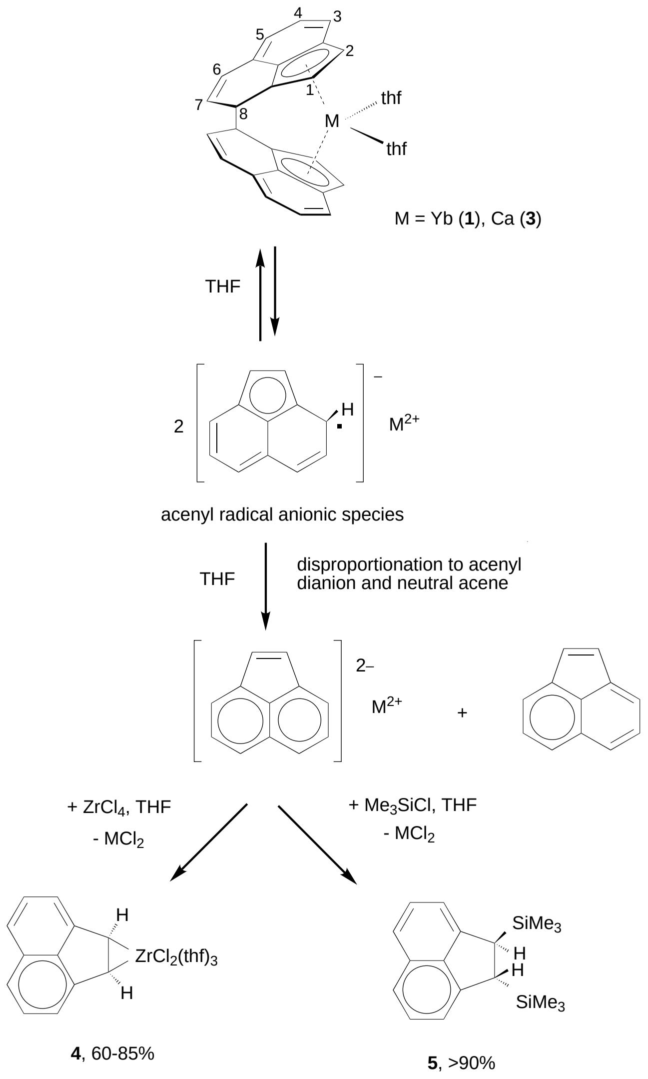
reduction of acene with alkali metals stops with the formation of adducts of the acenyl radical anions and the respective metal cations.[3] Also naphthalene and alkali metals form radical anion/metal cation adducts, but the latter react with lanthanide halides to give lanthanide complexes that contain naphthalene dianions.[4] Considering the similarities in the reactivity of acene and naphthalene towards metals one can suggest that the ansa-lanthanoacenes **1** and **2** may disclose a combination of the chemical features of both cyclopentadienyl and naphthalene complexes, thus reacting either with retention of the ansa-ligand framework or acting as reducing agents. Here we report on the unexpected reactivity of the ytterboacene complex **1** and of the analogeous calcium complex which was prepared for the first time.

The calcoacene complex $[(\eta^5\text{-}C_{12}H_8)_2Ca(thf)_2]$ (**3**) is formed with yields of about 80% by reduction of acene with metallic calcium activated by iodine in THF. It crystallizes from THF or benzene as yellow thin plates which, unfortunately, were not suitable for an X-ray diffraction analysis. However, since the ^{1}H NMR spectrum of **3**, like that of the diamagnetic complex **1**, shows only one set of eight resonance signals for the ring protons, and since its IR spectrum is identical with those of **1** and **2**, the obvious supposition is that the molecular structure of **3** is similar to that of its structurally characterized lanthanide analogues **1** and **2**.

In the course of our investigations on catalytically active ansa-zirconocenes,[5] we studied the reactions of the ansa complexes **1** and **3** with $ZrCl_4$. The reaction of equimolar amounts of the ytterbium complex **1** and $ZrCl_4$ in THF immediately proceeds, already at ambient temperature, and dark-green crystals can be isolated from the solution. The crystal structure analysis of the product reveals that it is not the corresponding ansa-zirconoacene. In contrast to our expectation the ansa-biacenyl ligand was split, leading to the formation of $[(C_{12}H_8)ZrCl_2(thf)_3]$ (**4**) in 86% yield. The reaction of the calcoacene **3** with $ZrCl_4$ also produces compound **4**, but in lower yield.

Shapiro et al.[6] have demonstrated the successful transfer of the ansa-bisindenyl ligand framework of $[\{Ph_2C_2H_2(\eta^5\text{-}4,7\text{-}Me_2C_9H_4)_2\}Ca(thf)_2]$ from the calcium center to the iron center, whereas the reaction with $[ZrCl_4(SMe_2)_2]$ or $[ZrCl_4(thf)_2]$ produced a complex mixture of products which could not be separated and identified.

Compound **4** is extremely sensitive to air and moisture. In contrast to the ^{1}H NMR spectra of **1** and **3** which show one set of eight resonance signals for the protons of the ansa ligand, the ^{1}H NMR spectrum of **4** shows only four ring proton signals, thus indicating that the framework of the ansa-biacenyl ligand undergoes a decoupling process in the course of the transmetalation reaction. The weak ESR signal, which is obtained for solutions of **1** in THF and which is assigned to the acene radical anion $C_{12}H_8^-$ ($A_H = 0.06, 0.3, 0.54, 0.64$ mT; $g = 2.0027$), demonstrates that already in solution an equilibrium exists between complex **1**, decoupled acenyl radical anions, and divalent ytterbium cations. In the presence of $ZrCl_4$, the acenyl radical anions evidently disproportionate into neutral acenaphthylene and aromatic acenyl dianions; the latter form compound **4** under elimination of ytterbium dichloride (Scheme 1).



Scheme 1. Mechanism of the formation of **4** and **5**.

A similar decoupling of the ansa-biacenyl ligand takes place when **1** or **3** react with Me_3SiCl in THF; the product 1,2-bis(trimethylsilyl)-substituted acenaphthene $(Me_3Si)_2C_{12}H_8$ (**5**) is formed in more than 90% yield.

The molecular structures of **4** (Figure 1) and **5** (Figure 2) were determined by single-crystal X-ray diffraction[7] on crystals obtained from THF or hexane, respectively.

In **4** the coordination geometry around the zirconium atom is that of a slightly distorted pentagonal bipyramid in which the two Cl atoms adopt the apical positions (Cl1-Zr-Cl2 165.4°) and the three THF molecules and the acenyl ligand form the equatorial plane. The bond lengths Zr–C1 (2.270 Å), Zr–C5 (2.288 Å), and C1–C5 (1.495 Å) indicate that the Zr-C1-C5 fragment can be described as a metallacycle with a $\sigma\text{-}\eta^2$-bonding mode rather than with a $\pi\text{-}\eta^2$ coordination of the zirconium atom. Similar $\sigma\text{-}\eta^2$-bonding modes were described by Alt et al. for $[(\eta^5\text{-}C_5H_4CMe_2H)(\eta^5{:}\eta^2\text{-}C_5H_4CMe_2C_9H_7)Zr(PMe_3)]$[12a] and $[(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}C_2H_4)(PMe_3)]$,[12b] whereas for [CpRh(acene)$_2$] the $\pi\text{-}\eta^2$-bonding mode is well documented.[13]

The molecular structure of compound **5** shows the two trimethylsilyl groups σ-bonded to C7 and C11. They are *trans*-positioned, perhaps because of steric factors. The C–C bond lengths in **5** are in the range of the corresponding bond lengths in acenaphthene.

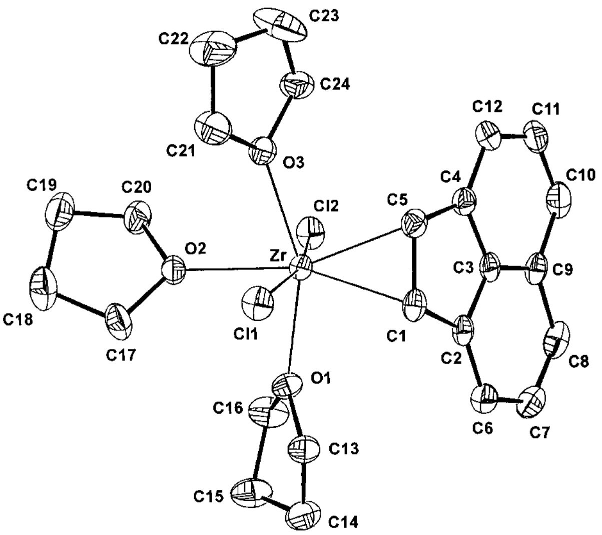


Figure 1. Molecular structure (ORTEP drawing) of **4** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are omitted for clarity. Relevant bond length [Å] and angles [°]: Zr-Cl1 2.4748(10), Zr-Cl2 2.4498(9), Zr-O1 2.269(2), Zr-O2 2.375(2), Zr-O3 2.292(2), Zr-C1 2.270(3), Zr-C5 2.288(4), C1-C2 1.480(5), C2-C3 1.420(5), C3-C4 1.423(5), C4-C5 1.476(5), C1-C5 1.495(5), C2-C6 1.379(5), C6-C7 1.416(5), C7-C8 1.381(5), C8-C9 1.428(5), C9-C10 1.416(5), C10-C11 1.365(6), C11-C12 1.416(6), C3-C9 1.399(5), C4-C12 1.376(5); Cl2-Zr-Cl1 165.36(3), O1-Zr-C1 84.04(11), C5-Zr-O3 83.68(11), O1-Zr-O2 78.69(8), O2-Zr-O3 77.06(9), O1-Zr-O3 155.59(9).

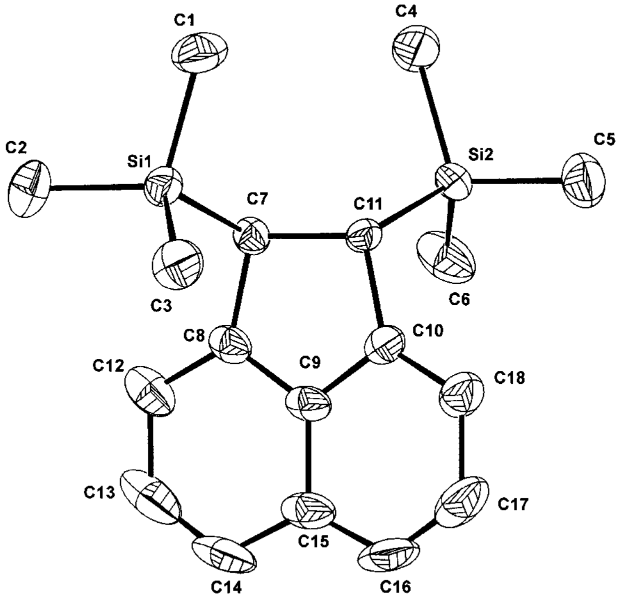


Figure 2. Molecular structure (ORTEP drawing) of **5** (thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Relevant bond length [Å] and angles [°]: Si1-C7 1.894(4), Si2-C11 1.886(5), C7-C8 1.501(7), C8-C9 1.402(7), C9-C10 1.404(7), C10-C11 1.501(6), C7-C11 1.578(6), C8-C12 1.373(7), C12-C13 1.395(10), C13-C14 1.340(10), C14-C15 1.424(9), C10-C11 1.501(6), C7-C11 1.578(6), C8-C12 1.373(7), C12-C13 1.395(10), C13-C14 1.340(10), C14-C15 1.424(9), C15-C16 1.389(10), C16-C17 1.340(10), C17-C18 1.421(9), C10-C18 1.372(7), C9-C15 1.416(7); C11-C7-Si1 110.3(3), C7-C11-Si2 112.0(3).

Experimental Section

All manipulations were performed under a nitrogen atmosphere or in vacuum. Elemental analyses were obtained by using a Perkin-Elmer Series II CHNS/O 2400 Analyzer. The extreme sensitivity of **4** towards air and moisture prevented satisfying results for its elemental analysis. NMR spectra were recorded on a Bruker DPX 200 instrument, ESR spectra on a Bruker 200D-SRC spectrometer. The commercially available acenaphthylene (Aldrich; purity 75%) was further purified 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 are calculated on pure acenaphthylene.

3: A mixture of calcium filings (2.7 g, 67.3 mmol) and iodine (1.5 g, 5.91 mmol) was stirred in THF (50 mL) at room temperature until the color of iodine disappeared. The main part of the CaI_2 formed was extracted with refluxing THF (ca. 100 mL) leaving only a small amount (1 to 2 mmol) as reaction accelerator. Acenaphthylene (1.14 g, 5.9 mmol) in THF (25 mL) was added to the calcium metal, and the mixture was stirred for 4 h at 50 °C. Extraction of the yellow crystalline precipitate with refluxing THF followed by cooling and concentration of the extract gave **3** (1.42 g; 78%); m.p. > 140 °C (decomp); ^1H NMR (200 MHz, $[D_8]THF$, 20 °C, TMS): $\delta = 6.86$ (d, $^3J(H,H) = 8.2$ Hz, 2H; CH, H^3), 6.60 (dd, $^3J(H,H) = 9.6$, 2.0 Hz, 2H; CH, H^6), 6.39 (dd, $^3J(H,H) = 8.2$, 6.4 Hz, 2H; CH, H^4), 6.31 (d, $^3J(H,H) = 3.0$ Hz, 2H; CH, H^1), 6.21 (d, $^3J(H,H) = 6.4$ Hz, 2H; CH, H^5), 5.98 (dd, $^3J(H,H) = 9.6$, 3.4 Hz, 2H; CH, H^7), 5.58 (d, $^3J(H,H) = 3.0$ Hz, 2H; CH, H^2), 4.54 (s, 2H; CH, H^8), 3.7 (m, 8H; CH_2), 1.6 (m, 8H; CH_2); IR (Nujol): $\tilde{\nu} = 1180$ w, 1030 s, 880 s, 720 w, 795 s, 745 s, 715 s cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{32}O_2Ca$ (488.68): C 78.65, H 6.60; found: C 77.81, H 6.38.

4: A mixture of **1** (1.65 g, 2.65 mmol) and $ZrCl_4$ (0.63 g, 2.7 mmol) was stirred in THF (35 mL) at 20 °C for a few minutes. Filtration and concentration of the solution in vacuum to 5 mL gave **4** (1.21 g; 86%) as dark green crystals; m. p. > 110 °C (decomp); ^1H NMR (200 MHz, $[D_8]THF$, 20 °C, TMS): $\delta = 6.95$ (dd, $^3J(H,H) = 8.2$, 7.2 Hz, 2H; CH), 6.57 (d, $^3J(H,H) = 8.2$ Hz, 2H; CH), 6.34 (d, $^3J(H,H) = 7.2$ Hz, 2H; CH), 4.15 (s, 2H; CH), 3.72 (m, 12H; CH_2), 1.61 (m, 12H; CH_2); ^{13}C NMR (50.32 MHz, $[D_8]THF$, 20 °C, TMS): $\delta = 147.32$, 133.30, 127.41, 127.05, 115.34, 110.65, 87.45.

5: A mixture of **3** (2.7 g, 5.52 mmol) and Me_3SiCl (1.3 g, 11.96 mmol) in THF (15 mL) was stirred for 30 min at 20 °C and 10 min at 40 °C. The solvent was removed in vacuum and the product extracted with hexane (2 × 15 mL). Crystallization from hexane yielded **5** (1.52 g, 93%) as large colorless crystals; m. p. 121 °C; ^1H NMR (200 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 7.43$ (d, $^3J(H,H) = 7.8$ Hz, 2H; CH), 7.35 (dd, $^3J(H,H) = 7.8$, 6.6 Hz, 2H; CH), 7.06 (d, $^3J(H,H) = 6.6$ Hz, 2H; CH), 2.93 (s, 2H; CH), −0.09 (s, 18H; CH_3); elemental analysis calcd (%) for $C_{18}H_{26}Si_2$ (298.58): C 72.41, H 8.78; found: C 72.25, H 8.92.

Received: February 19, 2001 [Z16635]

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[1] The term ansa-metalloacenes denotes that these metallocenes are based on acenaphthylene.

[2] I. L. Fedushkin, S. Dechert, H. Schumann, *Angew. Chem.* **2001**, *113*, 584–586; *Angew. Chem. Int. Ed.* **2001**, *40*, 561–563.

[3] a) F. Gerson, B. Weidmann, *Helv. Chim. Acta* **1966**, *49*, 1873–1878; b) W. E. Rhine, J. H. Davis, G. Stucky, *J. Organomet. Chem.* **1977**, *134*, 139–149; c) H. Bock, C. Arad, C. Näther, *J. Organomet. Chem.* **1996**, *520*, 1–13.

[4] a) I. L. Fedushkin, M. N. Bochkarev, H. Schumann, L. Esser, G. Kociok-Köhn, *J. Organomet. Chem.* **1995**, *489*, 145–151; b) M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, H. Schumann, J. Demtschuk, *Chem. Commun.* **1997**, 1783–1784; c) M. N. Bochkarev, *Russ. Chem. Rev.* **2000**, *69*, 783–794.

[5] a) R. L. Halterman, D. R. Fahey, E. F. Bailly, D. W. Dockter, O. Stenzel, J. L. Shipman, M. A. Khan, S. Dechert, H. Schumann, *Organometallics* **2000**, *19*, 5464–5470; b) R. L. Halterman, H. Schumann, F. Dübner, *J. Organomet. Chem.* **2000**, *604*, 12–19.

[6] P. J. Shapiro, K. M. Kane, A. Vij, D. Stelck, G. J. Matare, R. L. Hubbard, B. Caron, *Organometallics* **1999**, *18*, 3468–3473.

[7] X-ray structure data: Siemens-SMART-CCD diffractometer, ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 173$ K

(**4**), 293 K (**5**), SADABS[8] for absorption correction, structure solution with direct methods (SHELXS-97[9]), refinement against F^2 (SHELXL-97[10]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2) on calculated positions. The PLATON[11] program was used for the geometric analysis of the structures. Data collection for **4**: crystal dimensions 0.42 × 0.30 × 0.24 mm, orthorhombic, space group *Pbca*, $a = 25.2916(7)$, $b = 16.8904(5)$, $c = 10.9754(3)$ Å, $V = 4688.5(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.503 \times 10^3$ kg m^{-3}, $\mu = 0.720$ mm^{-1}, $F(000) = 2192$, $3.2° \leq 2\theta \leq 52.0°$, $-31 \leq h \leq 29$, $-20 \leq k \leq 12$, $-13 \leq l \leq 13$, 29774 data collected, 4597 unique data ($R_{int} = 0.0996$), 3439 data with $I > 2\sigma(I)$, 271 refined parameters, GOF(F^2) = 1.110, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1 = 0.0483$, $wR_2 = 0.0949$, max./min. residual electron density 0.842/ – 0.829 e Å^{-3}. Data collection for **5**: crystal dimensions 0.76 × 0.58 × 0.42 mm, monoclinic, space group $P2_1/c$, $a = 9.1647(1)$, $b = 22.9299(6)$, $c = 9.3960(2)$ Å, $\beta = 111.067(1)°$, $V = 1842.55(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.076 \times 10^3$ kg m^{-3}, $\mu = 0.183$ mm^{-1}, $F(000) = 648$, $3.6° \leq 2 \leq 50.0°$, $-10 \leq h \leq 7$, $-27 \leq k \leq 26$, $-11 \leq l \leq 11$, 11114 data collected, 3206 unique data ($R_{int} = 0.1493$), 1833 data with $I > 2\sigma(I)$, 187 refined parameters, GOF(F^2) = 1.045, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1 = 0.0903$, $wR_2 = 0.2057$, max./min. residual electron density 0.519/ – 0.445 e Å^{-3}. 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-158204 (**4**) and CCDC-158205 (**5**). 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).

[8] G. M. Sheldrick, Empirical Absorption Correction Program, Universität Göttingen, **1996**.

[9] G. M. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen, **1990**.

[10] G. M. Sheldrick, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

[11] A. L. Spek, PLATON A Multipurpose Crystallographic Tool, University of Utrecht, **2000**.

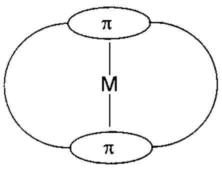
[12] a) E. H. Licht, H. G. Alt, W. Milius, S. Abu-Orabi, *J. Organomet. Chem.* **1998**, *560*, 69–75; b) H. G. Alt, C. E. Denner, U. Thewalt, M. D. Rausch, *J. Organomet. Chem.* **1988**, *356*, C83–C85.

[13] J. Müller, C. Hirsch, K. Qiao, K. Ha, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1441–1448.

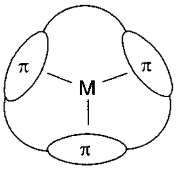
A New Strategy for Synthesizing Endohedral Metallocenophanes**

Gerald Scholz, Rolf Gleiter,* and Frank Rominger

Dedicated to Professor Edgar Heilbronner on the occasion of his 80th birthday

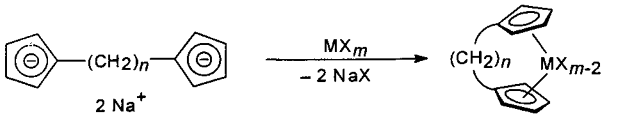


A

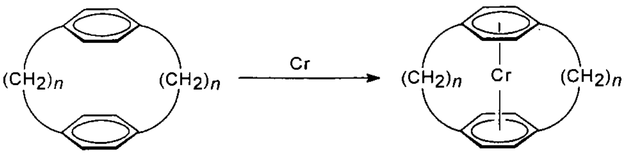


B

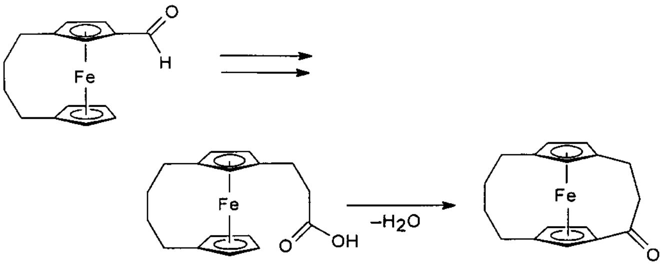
Cyclophanes are versatile ligands and are capable of including metals, as shown in **A** and **B**. Such endohedral metallocenophanes are known mostly for five- or six-membered-ring π systems, with transition metals or main group elements. Two methods have been described for the preparation of endohedral metallocenophanes:[1] the reaction of a cyclophane with metals or metal salts, or the stepwise assembly of the bridge from a metallocene. Examples for the first strategy are the preparation of bridged titanocenes, zirconocenes ($m = 4$), and ferrocenes ($m = 2$) [Eq. (1)][2, 3] as well as of chromocene derivatives ($n = 2, 3$) [Eq. (2)],[4] and complexes of Group III and IV metals with cyclophanes.[1, 5] In the second strategy [Eq. (3)], the tethers are built stepwise on the metallocene.[1, 6]



(1)



(2)



(3)

Our new protocol makes use of an intramolecular metal-catalyzed oligomerization of alkynes that are tethered to a π ligand (Scheme 1). This method is especially suited for constructing cyclobutadienes, cyclopentadienones, and benzene rings as π units, which are formed in a template reaction. We report herein the first synthesis of endohedral cobaltacyclophanes with cyclopentadienyl and cyclobutadiene rings as π units (Scheme 2 and 3). The key compounds in our protocol are the disubstituted dicarbonyl(η^5-cyclopentadienyl)cobalt derivatives **5a–c** in which two triple bonds are tethered to the Cp ring through an alkanediyl bridge. To synthesize the corresponding ligands **4a–c**, we treated 3-ethoxycyclopent-2-en-1-one (**2**)[7] with the Grignard reagents[8] derived from the ω-haloalkynes **1a–c**[9] and magnesium to yield the cyclopentenones **3a–c**. A second Grignard reaction gave the

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