analogues. The molecular structures of *rac*-Et[Ind]$_2$HfCl$_2$ and *rac*-Et[IndH$_4$]$_2$HfCl$_2$ are displayed in Figure 1. The Hf–ring centroid distance in *rac*-Et[Ind]$_2$HfCl$_2$ is 0.02 Å longer, and its unit cell is 81.6 Å$^3$ smaller than for *rac*-Et[IndH$_4$]$_2$HfCl$_2$. The presence of the c-glide plane in the monoclinic *C*2/*c* space group means that there are two sets of molecules with opposite chirality.[15]

The ligand–metal distances for *rac*-Et[IndH$_4$]$_2$MCl$_2$ increase in the order M = Zr > Hf ≫ Ti. The Hf–ring centroid distance and Hf–Cl length are 0.02 and 0.04 Å shorter, respectively, than the corresponding distances in *rac*-Et[IndH$_4$]$_2$ZrCl$_2$. The smaller Hf ionic radius is due to the 4f$^{14}$ lanthanide contraction resulting from imperfect shielding of one electron by another in the same 4f subshell.[16] The filled 4f orbital has been speculated to result in lower Lewis acidities for hafnocenes relative to zirconocene analogues.[16a,17]

**Polymerization Results.** The yields and characterizations of the polypropylene samples are listed in Table I. The indenyl derivatives have higher activities, produce higher molecular weight polymers, and are less stereospecific than the tetrahydroindenyl complexes at equivalent polymerization conditions.[1-3,11] This ligand effect is particularly pronounced for the smaller Ti complexes.[1,2]

*rac*-Et[Ind]$_2$TiCl$_2$ is the only member of this series with a high activity at subambient conditions.[1] The higher fundamental activity for Ti is consistent with both the order of M–C $\sigma$-bond strengths (Ti < Zr < Hf)[16a] and the increased stability of Ti(IV) at low temperatures.[1] On the other hand, the zirconium oligomerization and hafnium polymerization catalysts both have high activities at 30–80 °C because of their relatively more stable M(IV) oxidation states.

**Catalyst Stereospecificities.** The polymer DSC melting points indicate that Hf produced polymers are slightly more stereoregular than those obtained with Zr (Table I). $^{13}$C NMR analyses of the polymers show that the racemic stereoisomers of Zr are 95–99% stereoselective (mole % of units with the same relative configuration = % N$_A$) at 80–20 °C.[3,19] The soluble catalysts are therefore similar to heterogeneous $\delta$-TiCl$_3$ systems in this respect.[20] However, *rac*-Et[IndH$_4$]$_2$ZrCl$_2$ and *rac*-Et[Ind]$_2$ZrCl$_2$ isomerization and/or decomposition products produce 6–15 wt % of perfectly atactic polymer at 20–80 °C, and their "as-polymerized" samples contain about 5% regioirregularities which are mostly stereoregular (meso).[3]

**Polymer Molecular Weights.** The chiral "zirconocenes" produce brittle polypropylene waxes at conditions where appreciable yields can be obtained. The soluble chiral hafnium catalysts produce plastics with high molecular weights (Table I). The differences in the degrees of polymerization obtained with these two transition metals is remarkable because hafnium and zirconium typically produce similar chemistry.[16] These are the first examples of filled 4f orbitals providing a useful advantage in a catalytic reaction.

**Supplementary Material Available:** Listings of crystal data, atomic coordinates, generated atomic coordinates for hydrogen atoms, bond distances and angles, geometry for the hafnium atoms, best planes, drawings of the unit cells, and temperature factors for the molecular structures as well as synthetic and polymerization procedures (11 pages); listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(12) The Hf complexes were prepared from 99.99% pure HfCl$_4$ on a metal–metal basis obtained from Research Organic/Inorganic Chemicals Co. with modifications (Supplementary Material) to the procedure described for preparation of the Zr analogues.[14]

(13) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233–240.

(14) Wild, F. R. W. P.; Wasiuchnek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63–67.

(15) The space group for *rac*-Et[IndH$_4$]HfCl$_2$ is the monoclinic *C*2/*c* with $a$ = 16.328 (3) Å, $b$ = 10.115 (2) Å, $c$ = 14.296 (3) Å, $\beta$ = 132.08 (2)°, and $D_c$ = 1.95 g cm$^{-3}$ for $Z$ = 4. Least-squares refinement based on 1592 observed reflections led to a final $R$ value of 0.027. We suggest that the zirconium complex (ref 14) also belongs to the space group *C*2/*c*. For *rac*-Et[Ind]$_2$HfCl$_2$ the space group is *C*2/*c* with $a$ = 15.494 (2) Å, $b$ = 10.612 (2) Å, $c$ = 11.945 (2) Å, $\beta$ = 121.71 (2)°, and $D_c$ = 2.01 g cm$^{-3}$ for $Z$ = 4. Refinement based on 1527 observed reflections led to $R$ = 0.030.

(16) (a) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; John Wiley and Sons: New York, 1986. (b) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238. (c) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *103*, 693. (d) Lappert, M. F.; Pickett, C. J.; Rilet, P. J.; Yarrow, P. I. W. *J. Chem. Soc. Dalton Trans.* **1981**, 805. (e) Atwood, J. L.; Barker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 6645.

(17) Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.

(18) Details of the polymerization procedures are included in the Supplementary Material.

(19) $N_A$ is estimated from $^{13}$C NMR data by calculating the stereoselective copolymerization parameter ($R$) from the fraction of meso placements ($m$) in the isotactic fraction ($w$)[1] of the polymer: $m = (1 + R^2)/(1 + R)^2$ and $N_A = R/(1 + R)$.[20]

(20) Kissin, Y. V. *Isospecific Polymerizations of Olefins*; Springer-Verlag: New York, Berlin, Heidelberg, Tokyo, 1985; p 259.

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## Synthesis of a Bilindionostilbenoparacyclophane as a Model for "Stretched" Bile Pigment Chromophores of Biliproteins[1]

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The most primitive oxygen-producing phototrophic microorganisms, the cyanobacteria,[2] as well as the red algae (*Rhodophyceae*) and cryptomonads utilize highly specialized light-harvesting chromoproteins—the so-called phycobiliproteins—as photosensitizers of chlorophyll *a* in the primary process of photosynthesis.[3] The chromophores of the phycobiliproteins (phycocyanins, phycoerythrins, and phycourobilins) belong to the class of bile pigments. However, two characteristic spectroscopic properties, namely intense fluorescence[4] and a higher extinction of the visible absorption band with respect to the band in the near-UV range, differentiate native (i.e., not denatured) phycobiliproteins from free bile pigment chromophores. Both theoretical calculations[5,6] and comparison with the UV–vis spectrum of isophorcabilin (an almost rigid bile pigment chromophore isolated from the butterfly *Papilio phorcas*[7]) suggest that the enhanced absorption of phycobiliproteins in the visible range depends on the occurrence of "stretched" conformations of the chromophore molecules.[8] Thus, in solution, the ratio of absorption of biliverdins and their 3,4-dihydro derivatives in the visible and UV range is higher in HMPTA than in CCl$_4$,[9] probably because of the increase of "stretched" conformations in the former solvent at the expense of the energetically more favorable helical-shaped conformation of bile pigment molecules.[10] However, the proof of a relationship between conformation of bile pigment molecules and their spectroscopic properties may be only furnished by a model which mimics the features of the phycobiliproteins without changing the structure of the chromophore. Such a prerequisite is fulfilled by

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(1) Part 14 in the series Synthesis of Bile Pigments.

(2) Olsen, J. M. *Science (Washington, D.C.)* **1970**, *168*, 438.

(3) Scheer, H. *Angew. Chem.* **1981**, *93*, 230. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 241.

(4) Oi, V. T.; Glazer, A. N.; Styer, L. *J. Cell. Biol.* **1982**, *93*, 981 and references therein.

(5) Blauer, G.; Wagniere, G. *J. Am. Chem. Soc.* **1975**, *97*, 1949.

(6) Falk, H.; Gsaller, H.; Hubauer, E.; Müller, N. *Monatsh. Chem.* **1985**, *116*, 939 and references therein.

(7) Bois-Choussy, M.; Barbier, M. *Heterocycles* **1978**, *9*, 677.

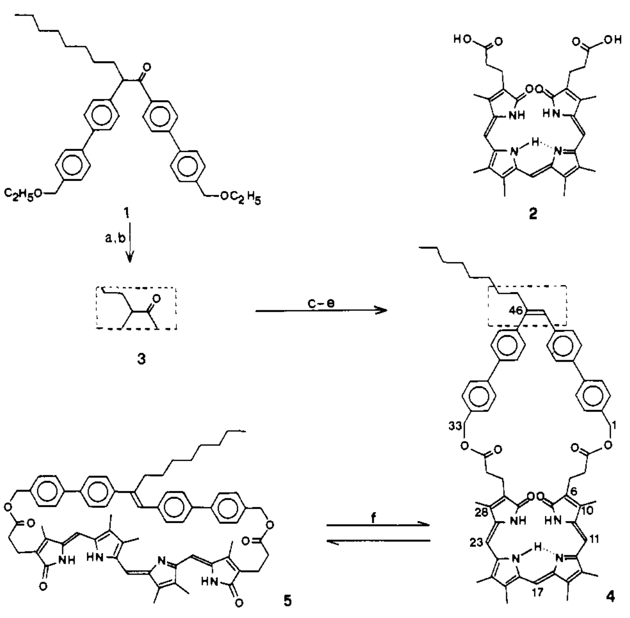
(8) Actually, the X-ray analyses of *C*-phycocyanin from *Mastigocladus laminosus*[8a] and *Agmenellum quadruplicatum*[8b] reveal the presence of "stretched" bile pigment chromophores: (a) Schirmer, T.; Bode, W.; Huber, R.; Sidler, W.; Zuber, H. *J. Mol. Biol.* **1985**, *184*, 257. (b) Schirmer, T.; Huber, R.; Schneider, M.; Bode, W.; Miller, M.; Hackert, M. L. *Ibid.* **1986**, *188*, 651.

(9) Falk, H.; Müller, N.; Wansch, S. *Monatsh. Chem.* **1986**, *116*, 1087.

(10) Falk, H.; Müller, N. *Monatsh. Chem.* **1981**, *112*, 791.

0002-7863/87/1509-6545$01.50/0

**Scheme I**[a]



[a](a) 33% HBr in AcOH (99%). (b) Reaction with **2** and DBU in DMFA ($10^{-3}$ M) (35%). (c) $NaBH_4$ in THF–MeOH. (d) DDQ in $CH_2Cl_2$–DMSO. (e) 3% TsOH on $SiO_2$ (29%) or, alternatively, *o*-$NO_2C_6H_4SeCN$, $Bu_3P$ in THF, and then $H_2O_2$ (35%). (f) $h\nu$ (high-pressure Hg lamp) in $C_6H_6$. For the sake of clarity, in **3** only the part of the molecule which is modified during the reaction is represented in the partial structure; the remainder of the molecule is shown in **4**.

[5](2,18)-1,19-{21*H*,23*H*,24*H*}bilindiono[5]paracyclo[0](4,4′)-stilbeno[0]paracyclophane (**5**),[11] whose synthesis from 1,2-bis-(4′-(ethoxymethyl)biphenyl-4-yl)decan-1-one (**1**)[12] is given in Scheme I. The octyl group of **1** serves exclusively to increase the solubility of the intermediates in the synthesis.

The biliverdin chromophores of the (*E*)-bilindionostilbeno-paracyclophane **5** and its *Z* isomer **4** are held in a "stretched" and a helical-shaped conformation, respectively, by the rigid *p,p′*-diphenylstilbene moiety. On irradiation of benzene solutions of **4** or **5** with light of $\lambda_{max}$ corresponding to the absorption range of the *p,p′*-diphenylstilbene chromophore, a mixture of the two compounds in photostationary equilibrium is obtained, from which both isomers can be separated by chromatography.[13] On the contrary, neither **4** nor **5** is photoisomerized by red light ($\lambda_{max}$ > 525 nm). Thus, the conformational changes of the bile pigment chromophore brought about by isomerization of the stilbene double bond correspond presumably to the changes which are observed on denaturation and renaturation of the phycobiliproteins.[14] As a matter of fact, the light absorption of the *blue* biliverdin derivative **4** and its *magenta* isomer **5** strikingly differs as in the natural pigments (see Figure 1). In order to emphasize the change of UV–vis absorption induced by "stretching" of the bile pigment molecules, the difference spectra which are obtained by subtraction of the absorption due to the (*Z*)- and (*E*)-*p,p′*-bis(4-(ethoxymethyl)phenyl)-α-octylstilbene chromophores (both synthesized from **1**) from the absorption curves of **4** and **5**, respectively, are represented in Figure 1c. In agreement with theoretical calculations, the absorption of the "stretched" bile pigment chromophore of **5** in the UV range is extremely weak. Interestingly, **5** absorbs in the visible range at the same frequency as phycoerythrin, whose chromophore is three C═C bonds shorter. Apparently, twisting of the chromophore equals a shortening of the conjugated system.

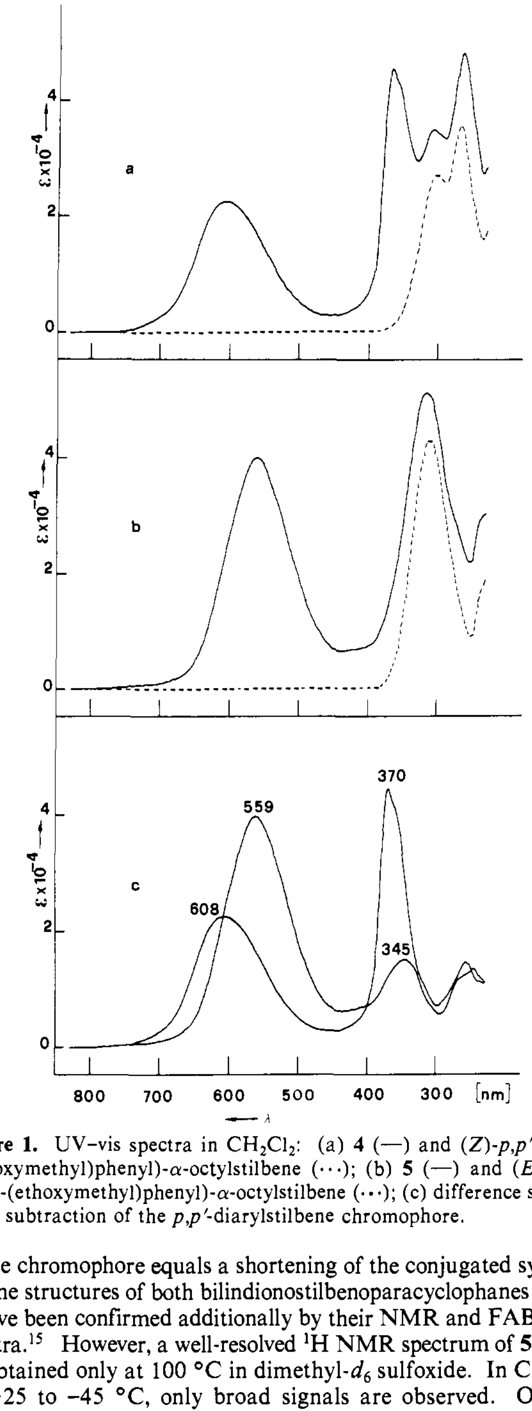


**Figure 1.** UV-vis spectra in $CH_2Cl_2$: (a) **4** (—) and (*Z*)-*p,p′*-bis(4-(ethoxymethyl)phenyl)-α-octylstilbene (···); (b) **5** (—) and (*E*)-*p,p′*-bis(4-(ethoxymethyl)phenyl)-α-octylstilbene (···); (c) difference spectra after subtraction of the *p,p′*-diarylstilbene chromophore.

The structures of both bilindionostilbenoparacyclophanes **4** and **5** have been confirmed additionally by their NMR and FAB mass spectra.[15] However, a well-resolved $^1H$ NMR spectrum of **5** could be obtained only at 100 °C in dimethyl-$d_6$ sulfoxide. In $CD_2Cl_2$ at +25 to −45 °C, only broad signals are observed. On the contrary, the $^1H$ NMR spectrum of the *Z* isomer **4** in $CDCl_3$ shows well-resolved peaks at room temperature. Accordingly, the UV–vis spectrum of **5** in $CH_2Cl_2$ at −45 °C indicates the presence of several conformers, whereas in the case of **4** no appreciable dependence of the light absorption on the temperature was detected.[16]

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(11) For nomenclature and numbering, cf.: Vögtle, G.; Neumann, P. *Tetrahedron* **1970**, *26*, 5847.

(12) Nesvadba, P. Ph.D. Thesis, University of Freiburg i.Ue. (Switzerland), Dec 1986.

(13) After 30 min of irradiation under argon, **5** (29%) and **4** (57%) were separated by preparative TLC on silica gel 60 (HPTLC plates from E. Merck, Darmstadt) using ethyl acetate as eluent.

(14) Scheer, H.; Kufer, W. *Z. Naturforsch., C. Biochem., Biophys., Biol., Virol.* **1977**, *32C*, 513.

(15) Particularly, the frequencies of vinylic protons are markedly different in both stereoisomers. $^1H$ NMR (360 MHz): **4** ($CDCl_3$ at 293 K and DMSO-$d_6$ at 373 K, respectively) δ 6.71 (6.85) (s, H17), 6.53 (6.56) (s, H47), 6.02 (6.09) and 6.00 (6.05) (2 s, each 1 H at C11 and C23); **5** (DMSO-$d_6$ at 373 K) δ 6.98 (br s, H17), 6.18 (s, H47), 5.98 and 5.87 (2 s, each 1 H at C11 and C23).

(16) UV ($CH_2Cl_2$): **4** (at 293 K) 265 nm (log ϵ = 4.66), 306 (4.51), 368 (4.62), 608 (4.32); **5** (at 293 K) 317 nm (log ϵ = 4.62), 559 (4.54); **5** (at 228 K) 319 nm (log ϵ = 4.76), 576 (4.46), 613 (4.43), 720 (4.01).