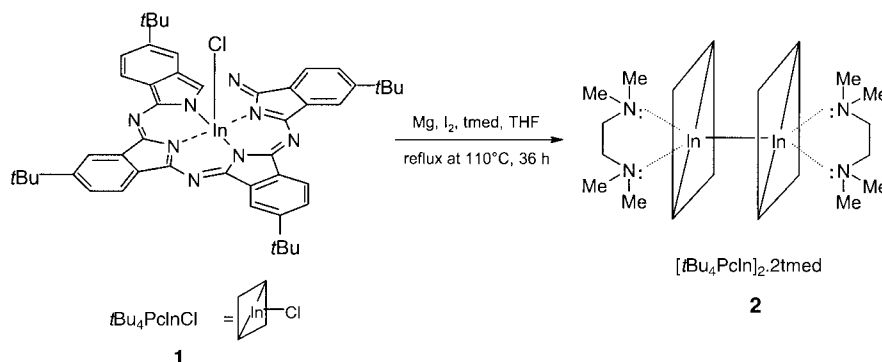


An Axially Bridged Indium Phthalocyanine Dimer with an In–In Bond**

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New nonlinear optical (NLO) materials are essential to the development of optoelectronic technologies, such as optical communications, high-speed electrooptical information processing, short optical-pulse generation, and all-optical switching.^[1] For practical NLO devices, such as optical limiting devices, only a few appropriate nonlinear materials are currently available. This has been a primary barrier to the development of these optical devices, which can control the amplitude, phase, polarization, or direction of optical beams.^[2–4]

Among the large number of NLO absorbers that have been identified, metallophthalocyanines and related compounds have emerged as the most promising materials owing to their large nonlinearities (originating from optical pumping of low-lying electronic states), ultrafast response times, and easy processability.^[2,4] $[\text{tBu}_4\text{PcInCl}]$ (Pc = phthalocyanine) has been used to prepare optical limiters,^[4] which can reduce optical damage to elements that are sensitive to sudden high-intensity light, such as sensors or human eyes. The effect of axial substitution on the optical properties of indium(III) phthalocyanines was studied systematically in our research group, and by Shirk and co-workers.^[3] The optical-limiting properties of the axially substituted indium phthalocyanine monomers were surprisingly robust to structural changes in the axial position.^[3] Dimers, in comparison with monomeric phthalocyanines (Pcs), may show increased third-order nonlinearities as a result of intramolecular π – π interactions of the Pc units. Additionally, the optical-limiting properties of these compounds are influenced by the dimeric structure. In this regard, we report here for the first time an axially linked indium phthalocyanine dimer with a direct In–In bond.



Scheme 1. Synthesis of **2**.

Organometallic compounds containing metal–metal single bonds between the metallic elements of Group 3A (Al, Ga, In, and Tl) are quite unusual,^[5a] but also of great interest in materials science.^[5] So far, only metallophthalocyanine dimers with transition-metal–transition-metal bonds, for example, $\text{Ru}=\text{Ru}$,^[6,7] $\text{Os}=\text{Os}$,^[8] $\text{Mo}=\text{Mo}$,^[9] $\text{Rh}=\text{Rh}$,^[10] $\text{Ir}=\text{Ir}$,^[11] and $\text{Re}=\text{Re}$ ^[12] are known. Kobayashi et al claimed to have prepared $(\text{PcSiX})_2$ with a direct Si–Si bonding interaction^[13a] but this has since been proved to be incorrect.^[13b] Very recently, however, the same research group have again reported to have obtained Pc dimers linked by an Si–Si bond.^[13c]

We attempted to prepare a dimeric indium phthalocyanine complex with an In–In bond, by the reaction of soluble $[\text{tBu}_4\text{PcInCl}]$ (**1**)^[3a] with activated magnesium turnings in freshly dried THF in the presence of a catalytic amount of iodine, but all efforts were unsuccessful. Further investigations showed that the pure dimer $[\text{tBu}_4\text{PcIn}(\text{InPc}(\text{tBu}_4))]_2$, that is, without an associated N donor ligand, is unstable in solution under the classical Wurtz coupling conditions. These findings are in agreement with the observations of Tuck and co-workers,^[14] who successfully prepared stable N,N,N',N' -tetramethylethylenediamine (tmed) adducts of In_2X_4 ($\text{X} = \text{Br}, \text{I}$), which possess In–In bonds. The role of the neutral tmed ligand in stabilizing In_2X_4 or In_2XY_3 molecules is mainly to promote maximum coordinative saturation at the indium center.^[14] Accordingly, we successfully prepared $[\text{tBu}_4\text{PcIn}(\text{tmed})]_2$ (**2**) by a Wurtz coupling reaction of **1** in the presence of tmed (Scheme 1). To remove any inorganic impurities, the crude product was dissolved in anhydrous toluene, stirred, filtered (this procedure was repeated several

times), and dried at 80°C in vacuo to afford a blackish-green powder in 93% yield.

The formation of an indium–indium bond in **2** was confirmed by Raman spectroscopy and by transmission extended X-ray absorption fine structure (EXAFS) spectroscopy. The strong peak at 110 cm^{-1} in the Raman spectrum of **2** (Figure 1) is ascribed to an In–In bond vibration,^[14b] but suggests that the In–In interaction is rather weak. The band at 148 cm^{-1} is assigned to the isotopic peak of the $\nu(\text{In}(\text{In}))$ mode.

Despite several attempts, compound **2** could not be obtained as a single crystal for an X-ray structural determination. EXAFS is considered to be a powerful technique for determining the local atomic environment of a specific atom,

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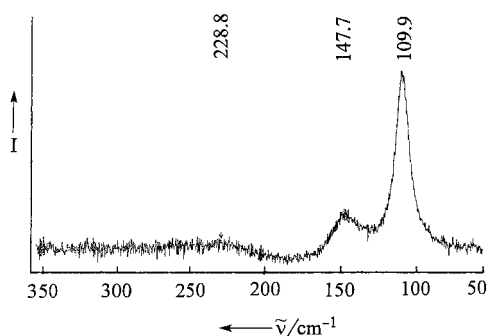


Figure 1. Resonance Raman spectrum ($\lambda_{\text{exc}} = 647.10 \text{ nm}$) of $[\text{tBu}_4\text{PcIn}(\text{tmed})]_2$ (**2**).

regardless of the state of the sample. EXAFS analysis provides information on the bond distance, the coordination number, the Debye–Waller factor, and the nature of the scattering atoms that surround the excited atom.^[15] Thus, EXAFS measurements were performed on **2** at the In–K edge at 27940 eV and 20 °C with an Si(311) double-crystal monochromator under ambient conditions (5.46 GeV, beam current 115 mA) and an inert atmosphere (beamline X1.1 at the Hamburger Synchrotron-Strahlungslabor (HASYLAB) at DESY, Hamburg). Data were collected in transmission mode with ion chambers. Energy calibration was monitored using 20- μm thick indium metal foil, also at the In–K edge at 27940 eV.

The experimental data and the fitted functions of **2** are shown in k space as well as by Fourier transformations in real space in Figure 2. The structural parameters and the EXAFS-determined molecular structure of **2** are given in Table 1 and Figure 3, respectively. In agreement with the well-known

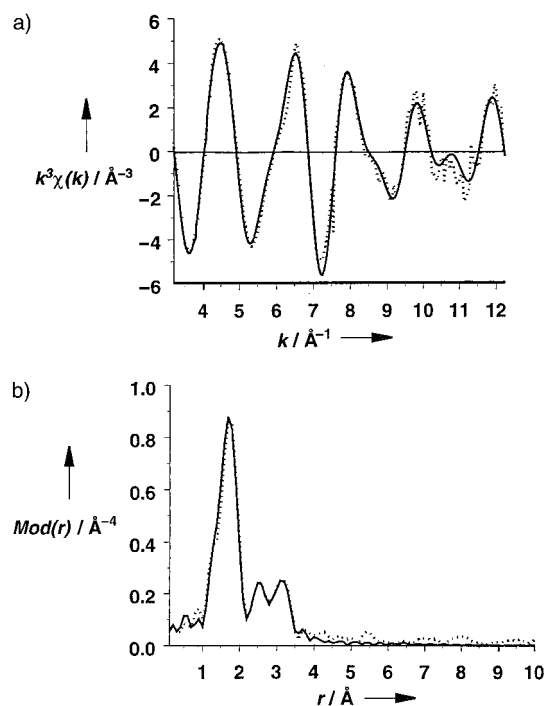


Figure 2. Experimental (dotted line) and calculated (solid line) $k^3\chi(k)$ functions (a) (k range = 3.18–12.29 $\text{\AA}^{-1}$, fit-index = 16.30, $E_0 = 18.78 \text{ eV}$) and their Fourier transforms (b) for $[\text{tBu}_4\text{PcIn}(\text{tmed})]_2$ (In–K edge, see Table 1 for fit parameters).

Table 1. EXAFS-determined structural data of $[\text{tBu}_4\text{PcIn}(\text{tmed})]_2$ (**2**). The letters in parentheses refer to **2** and indicate the molecule where the back-scattering atom is located.

	$N^{[a]}$	$r \text{ [\AA]}^{[b]}$	$\sigma \text{ [\AA]}^{[c]}$
In–(N ₁)	4	2.12 ± 0.02	0.067 ± 0.010
In–(N ₂)	2	2.59 ± 0.03	0.050 ± 0.005
In–(C ₂)	8	2.90 ± 0.03	0.102 ± 0.025
In–(N ₃)	4	3.05 ± 0.03	0.074 ± 0.011
In–(In')	1	3.24 ± 0.03	0.092 ± 0.002
In–(N ₁ ')	4	3.40 ± 0.03	0.122 ± 0.018
$\eta \text{ [}^\circ\text{]}^{[d]}$			14.5 ± 2.0
$\text{In}_{\text{out}} \text{ [\AA]}^{[e]}$			0.78 ± 0.3

[a] N = coordination number. [b] r = Absorber–backscatterer distance. [c] σ = Debye–Waller factor with calculated standard deviations. [d] η = tilting angle. [e] In_{out} = the out-of-plane displacement of the In atom.

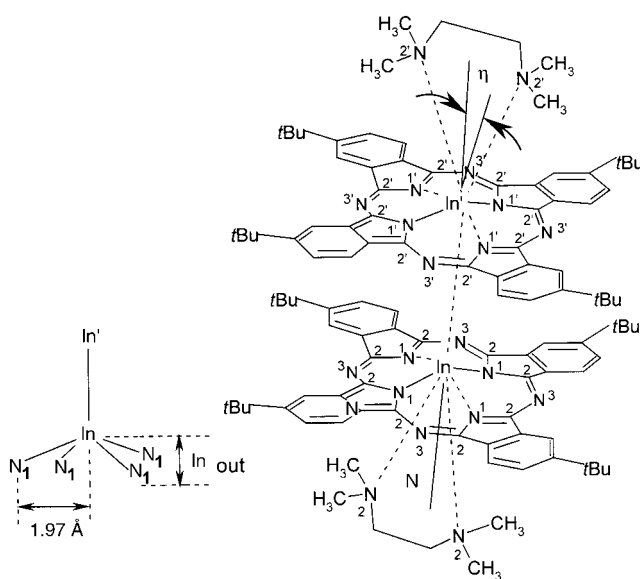


Figure 3. EXAFS-determined molecular structure of $[\text{tBu}_4\text{PcIn}(\text{tmed})]_2$.

structure of phthalocyanine complexes, we found four equivalent indium–nitrogen atomic separations of 2.12 and 3.05 $\text{\AA}$, and two equivalent indium–nitrogen atomic separations of 2.59 $\text{\AA}$. An additional shell, consisting of eight equivalent indium–carbon atomic separations at 2.90 $\text{\AA}$ gives good agreement between the experimental and the calculated parameters for **2**. The fit is significantly improved using an indium–indium separation of 3.24 $\text{\AA}$ (for comparison, reported In–In bond lengths are, for example, 2.775,^[16] 2.828,^[17] 3.631,^[18] and 3.952 $\text{\AA}$ ^[19]), and an additional indium–nitrogen interaction at 3.40 $\text{\AA}$. This is the shortest separation observed between an indium atom and a nitrogen atom situated in the neighboring phthalocyanine moiety within the dimer. The structural data acquired by the fitting procedure of **2** are listed in Table 1. Since an intermolecular In–In' separation was found, it can be deduced that two phthalocyanine molecules are arranged as a dimer. The relative orientation of the neighboring molecules can be calculated from the determined separations and the length of the intramolecular In–N₁ interaction. The molecular planes are tilted, with respect to the axis connecting the center of the molecules, by an angle of 14.5°. To check this result we calculated the shortest

intermolecular In–(N') distance, which is 3.87 Å for a parallel arrangement of the molecular planes perpendicularly oriented to the axis connecting the molecular centers. This separation, however, was not found in the spectra. If we assume a rigid phthalocyanine molecule, which is not deformed by the metal atom, the shortest indium–nitrogen distance amounts to 1.97 ± 0.02 Å;^[20–22] our results indicate an In–N₁ separation of 2.12 Å. We therefore conclude that the indium center is located 0.78 Å out of the plane described by the four nitrogen atoms directly bonded to it (In_{out}).

The IR spectrum of **2** is similar to that of **1**, and gives little structural information. As expected, the weak absorption band of the In–Cl stretching mode at 336 cm^{-1} is absent in the IR spectrum of the dimer; a new pair of split, low-intensity peaks are observed, centered at 368 and 399 cm^{-1} . Some characteristic absorption peaks, for example, at 1613, 1087, 1023, and 568 cm^{-1} appear to increase in intensity. A new intense peak at 802 cm^{-1} was also observed, and may be associated with the coordination of the tmed ligands to the indium centers.

Field-desorption mass spectrometry (FDMS) of $[\text{tBu}_4\text{PcIn}(\text{tmed})_2]$ (**2**) (m/z calcd for $\text{C}_{108}\text{H}_{128}\text{N}_{20}\text{In}_2$: 1935) only shows a single peak at m/z 978, whereas the m/z value of a singly charged monomer, that is, $[\text{tBu}_4\text{PcIn}]^+$, is 851. In general, peaks containing ^{23}Na are always detected because of its ubiquitous nature. Hence, the peak at m/z 978 can be logically assigned to $[M^{2+} + ^{23}\text{Na}]$. We also employed FDMS to investigate the in situ hydrolyzed product of **2** in analytically pure THF containing a trace of water, and found that the original signal at m/z 978 disappears, followed by the appearance of a new strong peak at m/z 1703, which can be unambiguously attributed to $[\text{tBu}_4\text{PcIn}]_2$. This pure Pc dimer, without tmed ligands, is extremely unstable in solution and, thus, can not be obtained from the hydrolyzed product of **2**.

A series of highly soluble axially substituted or bridged phthalocyanine compounds have been prepared under mild conditions utilizing the chemical reactivity of M–Cl (M = Ga^{3+} , In^{3+}) and M=O (M = for example, Ti^{4+}) bonds.^[3,23] The axial ligands did not affect the linear optical properties; in fact the Q and B bands in the UV/Vis spectra are shifted only by a few nanometers on exchanging the axial ligands.^[3] Similarly, the formation of the axial In–In bond in the phthalocyanine dimer **2** displayed similar linear optical properties as the starting material **1**. The observed red-shifts of the Q and B bands in the UV/Vis spectrum of **2** in anhydrous THF are only of the order of 4–5 nm relative to **1**.^[3a] This observation can be explained by the fact that the average mutual polarization effect is close to zero as a result of near free rotation of the two Pc macrocycles around the In–In single bond. Consequently, the spectrum of **2** is similar to that of Pc monomer **1**. In addition, we measured the UV/Vis spectra of compounds **1** and **2** in anhydrous THF and analytically pure THF containing a trace amount of water. No matter what type of THF was used, the UV/Vis spectrum of **1** was the same. However, the UV/Vis spectrum of **2** in analytically pure THF is apparently shifted to short wavelengths relative to **1**. This blue-shift is related to protonation of the coordinated tmed.

The UV/Vis absorption bands of a thin film of **2** are marginally broader, but the position of the Q band is only slightly shifted (1–2 nm) towards longer wavelengths, compared to a dilute solution in anhydrous THF. This result is suggestive of only weak aggregation of **2**. Dimer **2** is susceptible to photochemical degradation in common organic solvents, for example, THF, CH_2Cl_2 , and CHCl_3 . After exposure of the solution of **2** in THF to daylight for 48 h, the B and Q bands of **2** decrease significantly in intensity, the Q band is blue-shifted by approximately 7–8 nm, and a new, weak absorption peak near 740 nm is observed. However, in the absence of light, the solution of **2** in THF does not show a significant or apparent decrease in absorbance for up to 72 hours.

The ^1H NMR spectrum of **2** is more complicated than that of **1** because of ring-current effects^[24] caused by the two macrocycles and the existence of possible rotational isomers. The spectrum shows two broad groups of multiplet signals for the aromatic protons and one intense singlet for the *t*Bu protons, a slight downfield shift is observed for the aromatic protons in the plane of the macrocycle relative to those of **1**.^[3a] A slight deshielding effect is also observed in the ^{13}C NMR spectrum of **2** for the carbon atoms close to the indium atom. The presence of coordinated ligands is apparent from the NMR spectra of **2**. In comparison with the ^{13}C NMR spectrum of free tmed, which displays resonances at 57.34 (CH_2N) and 45.53 ppm (NCH_3), the equivalent signals for coordinated tmed in **2** are shifted upfield to $\delta = 54.75$ and 44.72 ppm, respectively. ^1H NMR signals for free tmed appear at $\delta = 2.23$ (CH_2) and 2.09 ppm (CH_3), whereas the corresponding proton signals for the coordinated tmed ligands in **2** are located at $\delta = 2.91$ and 2.50 ppm. The observed downfield shift would not normally be expected; here it may be explained by the fact that the coordinating molecules do not fit into the cone of the ring-current.^[24] In addition, the possible protonation of the coordinated tmed during measurement also leads to a downfield shift of its proton signals. To provide evidence for this, we have measured the ^1H NMR spectrum of protonated tmed, and found that after treatment of free tmed with HCl, the measured ^1H NMR signals are shifted downfield, and appear at $\delta = 2.39$ and 2.23 ppm, respectively.

Excitation of **1** and **2** in toluene with a nanosecond laser at 355 nm results in almost identical transient absorption spectra being observed. The transient absorption bands appearing at about 520 nm can be attributed to the transition from the lowest triplet excited state to the upper triplet excited states (T–T absorption).^[25] The triplet-state-maximum of each sample occurs in the region of 400–610 nm, which is located just inside the high-transmission region between the intense Q and B bands in the UV/Vis absorption spectra (of all samples). This region is of great interest for optical limiting based on reverse saturable absorption^[3b,4] since it ensures that the excited-state absorption always exceeds the ground-state absorption cross-section.^[26]

The Z scans for all samples in toluene at 532 nm indicate that **2** shows a much stronger positive NLO response at relatively low powers than starting material **1**. This NLO response can be attributed to reverse saturable absorption.^[3b] The optical-limiting properties of **1** and **2**, as well as the tmed

adduct of **1** [*t*Bu₄PcInCl(tmed)], have been studied in toluene with laser pulses at 410 nm. These preliminary results show that **2** exhibits good optical-limiting response at this laser wavelength, whereas no response was found for compound **1** and its tmed adduct. Further studies on the NLO properties (including optical-limiting properties) displayed by **2** are currently in progress.

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- [1] a) J. Zyss, *Nonlinear Optics: Materials, Physics, and Devices*, Academic Press, Boston, **1993**; b) H. S. Nalwa, S. Miyata, *Nonlinear optics of organic molecules and polymers*, CRC, Boca Raton, **1997**.
- [2] a) H. S. Nalwa, M. Hanack, G. Pawlowski, M. K. Engel, *Chem. Phys.* **1999**, *245*, 17–26; b) E. S. Manas, F. C. Spano, L. X. Chen, *J. Chem. Phys.* **1997**, *107*, 707–719; c) H. Tajalli, J. P. Jiang, J. T. Murray, N. R. Armstrong, A. Schmidt, M. Chandross, S. Mazumdar, N. Peyghambarian, *Appl. Phys. Lett.* **1995**, *67*, 1639–1641.
- [3] a) M. Hanack, H. Heckmann, *Eur. J. Inorg. Chem.* **1998**, 367–373; b) J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann, M. Hanack, *J. Phys. Chem. A* **2000**, *104*, 1438–1449; c) T. Schneider, H. Heckmann, M. Barthel, M. Hanack, *Eur. J. Org. Chem.* **2001**, 3055–3065; d) D. Dini, M. Barthel, M. Hanack, *Eur. J. Org. Chem.* **2001**, 20, 3759–3769; e) M. Barthel, M. Hanack, *J. Porphyrins Phthalocyanines* **2000**, *4*, 635–638; f) Y. Chen, L. R. Subramanian, M. Barthel, M. Hanack, *Eur. J. Inorg. Chem.* **2002**, 1032–1034; h) Y. Chen, L. R. Subramanian, M. Fujitsuka, O. Ito, S. O'Flaherty, W. J. Blau, T. Schneider, D. Dini, M. Hanack, *Chem. Eur. J.* **2002**, in press.
- [4] a) H. S. Nalwa, J. S. Shirk in *Phthalocyanines: Properties and Applications, Vol. 4* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1996**, pp. 79–181; b) J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, *Science* **1996**, *273*, 1533–1536; c) G. de la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *J. Mater. Chem.* **1998**, *8*, 1671–1683.
- [5] a) W. Uhl, *Coord. Chem. Rev.* **1997**, *163*, 1–32; b) M. J. Taylor, P. J. Brothers in *Chemistry of Aluminium, Gallium, Indium, and Thallium* (Ed.: A. J. Downs), Blackie-Chapman-Hall, London, **1993**.
- [6] H. Bertagnolli, A. Weber, W. Hörner, T. S. Ertel, U. Reinöhl, M. Hanack, M. Hees, R. Polley, *Inorg. Chem.* **1997**, *36*, 6397–6400.
- [7] A. Weber, T. S. Ertel, U. Reinöhl, H. Bertagnolli, M. Leuze, M. Hees, M. Hanack, *Eur. J. Inorg. Chem.* **2000**, 2289–2294.
- [8] R. Caminiti, M. P. Donzello, C. Ercolani, C. Sadun, *Inorg. Chem.* **1998**, *37*, 4210–4213.
- [9] M. Gorsch, H. Homborg, *Z. Anorg. Allg. Chem.* **1998**, *624*, 634–641.
- [10] a) H. Hückstädt, C. Bruhn, H. Homborg, *J. Porphyrins Phthalocyanines* **1997**, *1*, 367–378; b) M. J. Chen, J. W. Rathke, *Organometallics* **1994**, *13*, 4875–4880.
- [11] H. Hückstädt, H. Homborg, *Z. Anorg. Allg. Chem.* **1997**, *623*, 369–378.
- [12] M. Göldner, H. Hückstädt, K. S. Murray, B. Moubaraki, H. Homborg, *Z. Anorg. Allg. Chem.* **1998**, *624*, 288–294.
- [13] a) N. Kobayashi, F. Furuya, G. C. Yug, *J. Porphyrins Phthalocyanines* **1999**, *3*, 433–438; b) J. Li, L. R. Subramanian, M. Hanack, *J. Porphyrins Phthalocyanines* **2000**, *4*, 739–741; c) N. Kobayashi, F. Furuya, G. C. Yug, H. Wakita, M. Yokomizo, N. Ishikawa, *Chem. Eur. J.* **2002**, *8*, 1474–1484.
- [14] a) M. J. Taylor, D. G. Tuck, L. Victoriano, *Can. J. Chem.* **1982**, *60*, 690–694; b) C. Peppe, D. G. Tuck, *Can. J. Chem.* **1984**, *62*, 2793–2797.
- [15] a) E. A. Stern, *Phys. Rev. B* **1974**, *10*, 3027–3036; b) F. W. Lytle, D. E. Sayers, E. A. Stern, *Phys. Rev. B* **1975**, *11*, 4825–4835.
- [16] P. J. Brothers, K. Hübner, B. C. Noll, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1996**, *108*, 2528–2530; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2355–2357.
- [17] W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139–154.
- [18] H. Schumann, C. Janiak, F. Görlitz, J. Loebel, A. Dietrich, *J. Organomet. Chem.* **1989**, *363*, 243–251.
- [19] O. T. Beachley, Jr., M. R. Churchill, J. C. Fettinger, J. C. Pazik, L. Victoriano, *J. Am. Chem. Soc.* **1986**, *108*, 4666–4668.
- [20] L. H. Vogt, Jr., A. Zalkin, D. H. Templeton, *Inorg. Chem.* **1967**, *6*, 1725–1730.
- [21] J. S. Miller, C. Vazquez, J. C. Calabrese, R. S. McLean, A. J. Epstein, *Adv. Mater.* **1994**, *6*, 217–221.
- [22] D. Wöhrle, G. Mayer, *Kontakte (Darmstadt)* **1985**, 38–48.
- [23] M. J. Plater, A. Jeremiah, G. Bourhill, *J. Chem. Soc. Perkin Trans. 1* **2002**, 91–96.
- [24] a) T. R. Janson, A. R. Kone, J. F. Sullivan, K. Knox, M. E. Kenney, *J. Am. Chem. Soc.* **1969**, *91*, 5210–5214; b) U. Keppeler, W. Kobel, H. U. Siehl, M. Hanack, *Chem. Ber.* **1985**, *118*, 2095–2104.
- [25] M. Fujitsuka, O. Ito, H. Konami, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1–7.
- [26] a) L. W. Tutt, T. F. Boggess, *Prog. Quantum Electron.* **1993**, *17*, 299–315; b) C. Liu, X. Wang, Q. Gong, K. Tang, X. Jin, H. Yan, P. Cui, *Adv. Mater.* **2001**, *13*, 1687–1690.

Samarium Diiodide-Mediated Reductive Coupling of Epoxides and Carbonyl Compounds: A Stereocontrolled Synthesis of C-Glycosides from 1,2-Anhydro Sugars**

Jose Luis Chiara* and Esther Sesnilo

Dedicated to Professor Antonio Gómez-Sánchez on the occasion of his 75th birthday

The significant advances in the understanding of the biological function of carbohydrates and glycoconjugates achieved during the last two decades have stimulated the development of glycomimetics as fundamental tools for biological research and as potential agents for therapeutic intervention.^[1] C-Glycosides are of special relevance in this context because of their resistance to hydrolysis and their occurrence in a number of natural products with interesting biological activities. Methods for their preparation using anomeric anions, cations, radicals, and carbenes have been extensively studied.^[2] 1,2-Anhydro sugars, readily available and well-known donors for the stereoselective preparation of O-glycosides,^[3] have also found application in the stereoselective synthesis of C-glycosides.^[2] Because of their electrophilic nature, in all examples described to date, 1,2-anhydro sugars have reacted with metalated C-nucleophilic partners, which are often unstable and not readily available with a wide range of functionality. The regioselective and stereodefined umpolung of 1,2-anhydro sugars into nucleophilic C-glycosyl donors by reductive metalation could greatly extend the scope of these useful donors, by allowing the introduction of an expanded set of substituents at the anomeric position in a stereoselective way.^[4,5]

To test the feasibility of this approach, we performed exploratory experiments with epoxide **2a**, readily available from the protected D-glucal **1a** by oxidation with DMDO

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