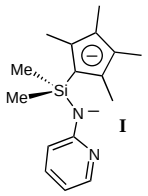
Maynard, E. R. Hickey, R. D. Rogers, *J. Org. Chem.* **1991**, *56*, 2449 – 2455.
[3] a) R. Durr, O. De Lucchi, S. Cossu, V. Lucchini, *Chem. Commun.* **1996**, 2447 – 2448; b) C. Zonta, S. Cossu, P. Peluso, O. De Lucchi, *Tetrahedron Lett.* **1999**, *40*, 8185 – 8188; c) A. Paulon, S. Cossu, O. De Lucchi, C. Zonta, *Chem. Commun.* **2000**, 1837 – 1838; d) C. Zonta, S. Cossu, O. De Lucchi, *Eur. J. Org. Chem.* **2000**, 1965 – 1971; e) S. Cossu, O. De Lucchi, A. Paulon, P. Peluso, C. Zonta, *Tetrahedron Lett.* **2001**, *42*, 3515 – 3518.
[4] a) P. G. Gassman, I. Gennick, *J. Am. Chem. Soc.* **1980**, *102*, 6863 – 6964; b) S. B. Singh, H. Hart, *J. Org. Chem.* **1990**, *55*, 3412 – 3415; c) K. Komatsu, S. Aonuma, Y. Jinbu, R. Tsuji, C. Hirosawa, K. Takeuchi, *J. Org. Chem.* **1991**, *56*, 195 – 203; d) N. L. Franck, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1995**, *117*, 2102 – 2103; e) F. Cardullo, D. Giuffrida, F. H. Kohnke, F. M. Raymo, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1996**, *108*, 347 – 349; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 339 – 341; f) R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6012 – 6018.
[5] F.-G. Klärner, U. Burkert, M. Kamieth, R. Boese, J. Benet-Bucholz, *Chem. Eur. J.* **1999**, *5*, 1700 – 1707.
[6] a) J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston, R. S. Burkhalter, *J. Am. Chem. Soc.* **1994**, *116*, 10346 – 10347; b) J.-F. Nierengarten, L. Oswald, J.-C. Eckert, J.-F. Nicoud, N. Armaroli, *Tetrahedron Lett.* **1999**, *40*, 5681 – 5684.
[7] a) R. Faust, K. P. C. Vollhardt, *J. Chem. Soc. Chem. Commun.* **1993**, 1471 – 1473; b) J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, 368, 229 – 231; c) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1997**, *109*, 288 – 290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 259 – 260; d) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1998**, *110*, 1044 – 1046; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 997 – 998; e) P. E. Georghiou, S. Mizyed, S. Chowdhury, *Tetrahedron Lett.* **1999**, *40*, 611 – 614.
[8] a) D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud, J.-F. Nierengarten, *Chem. Eur. J.* **2000**, *6*, 3501 – 3507; b) G. Cooke, N. Kaushal, N. Boden, R. J. Bushby, Z. Lu, O. Lozman, *Tetrahedron Lett.* **2000**, *41*, 7955 – 7959; c) S. J. Holder, J. A. A. Elemans, J. J. J. M. Donners, M. J. Boerakker, R. de Gelder, J. Barberá, A. E. Rowan, R. J. M. Nolte, *J. Org. Chem.* **2001**, *66*, 391 – 399.
[9] E. Piers, P. L. Gladstone, J. G. K. Yee, E. J. McEachern, *Tetrahedron* **1998**, *54*, 10609 – 10626.
[10] a) V. Farina, S. Kapadia, B.Krishnan, C. Wang, L. S. Liebeskind, *J. Org. Chem.* **1994**, *59*, 5905 – 5911; b) J. R. Falck, R. K. Bhatt, J. Ye, *J. Am. Chem. Soc.* **1995**, *117*, 5973 – 5982; c) X. Han, B. M. Stolz, E. J. Corey, *J. Am. Chem. Soc.* **1999**, *121*, 7600 – 7605.
[11] a) E. Piers, T. Wong, *J. Org. Chem.* **1993**, *58*, 3609 – 3610; b) G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748 – 2749.
[12] Enantiopure **1a** was obtained by resolution of the racemate by means of HPLC chiral separation on Chiralcel OT(+), with methanol as eluant.
[13] a) M. A. Bennett, H. P. Schwemlein, *Angew. Chem.* **1989**, *101*, 1349 – 1373; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1296 – 1320; b) K. Komatsu, H. Kamo, R. Tsuji, H. Masuda, K. Takeuchi, *J. Chem. Soc. Chem. Commun.* **1991**, 71 – 72; c) K. Albrecht, D. C. R. Hockless, B. König, H. Neumann, M. A. Bennett, A. de Meijere, *Chem. Commun.* **1996**, 543 – 544.
[14] a) Hydroboration: K. Burgess, W. A. van der Donk in *Advanced Asymmetric Synthesis* (Ed.: G. R. Stephenson), Chapman & Hall, London, **1996**, chapt. 9, p. 181 – 211; b) Hydrosilylation: E. Campi, P. Perlmutter in *Advanced Asymmetric Synthesis* (Ed.: G. R. Stephenson), Chapman & Hall, London, **1996**, chapt. 10, p. 212 – 221; c) S. Cossu, P. Pasetto, O. De Lucchi, *Angew. Chem.* **1997**, *109*, 1598 – 1601; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1504 – 1506; d) S. Cossu, O. De Lucchi, P. Peluso, R. Volpicelli, *Tetrahedron Lett.* **1999**, *40*, 8705 – 8709; e) S. Cossu, O. De Lucchi, P. Peluso, R. Volpicelli, *Tetrahedron Lett.* **2000**, *41*, 7263 – 7266.
[15] General review on enantioselective desymmetrization: M. C. Willis, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1765 – 1784.

Yttrate Metathesis: Ligand Design for the Controlled Synthesis of f-Block Heterobimetallic Compounds**

Michael S. Hill* and Peter B. Hitchcock

Heterobinuclear derivatives in which one of the constituent metals is a member of Group 3 or the lanthanide series display unusual cooperative properties for a variety of diverse applications.[1] Approaches to bimetallic rare earth complexes that comprise metals other than those of Group 1 are however uncommon and usually inflexible with regard to the identity and coordination requirements of the second metal.[2] We describe here a simple and readily modified ligand design that permits the synthesis of molecules containing a trivalent rare earth element with a defined and proximal disposition to a second metal center. Our adopted strategy exploits the tendency of these large cations to form uninegative "ate" complexes, through the attachment of two amido-cyclopentadienyl dianions, **I**. Further bimetallic systems may then be synthesized by metathesis of the initial alkali metal derivative with a metal halide.



I

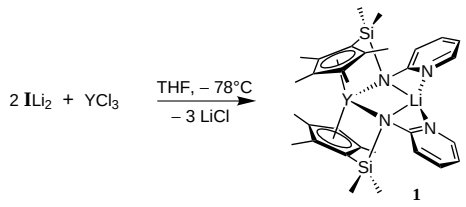
For this approach to succeed, the ligand design must suppress fragmentation of the lanthanide ate anion. Kempe et al. have shown that metathesis of a variety of early and late transition metal halides with aminopyridinato-based lanthanide ate complexes results in complete ligand transfer (albeit via unstable bimetallic intermediates).[3] This reactivity may be perturbed, however, permitting the synthesis of Nd/Rh and Nd/Pd bimetallic compounds, through the use of chelating bis-aminopyridinato ligands.[2d]

Dianion **I** is based upon the ligand framework applied by Bercaw et al. to the synthesis of "constrained geometry" olefin polymerization catalysts.[4] Our ligand constitution is determined by the demonstrated ability of Bercaw's and similar ligands to saturate the coordination sphere of Group 3 metals.[5] The amido functionality of **I** results from the deprotonation of a 2-aminopyridine substituent, selected for the capacity of 2-aminopyridinato ligands to bind a wide variety of metal centers.[6] For the initial investigation of the ligating properties of **I**, we chose to study the chemistry of trivalent yttrium derivatives, mindful of the diagnostic solution-state NMR data derived from observation of the ^{89}Y nucleus and its attendant internuclear couplings.

Reaction of YCl_3 and two equivalents of the dilithium derivative of **I** in THF afforded the colorless complex **1** [Eq. (1)]. Complex **1** is very soluble in THF and aromatic solvents but poorly soluble in aliphatic hydrocarbons. The

[*] Dr. M. S. Hill, Dr. P. B. Hitchcock
School of Chemistry, Physics and Environmental Science
University of Sussex
Brighton BN1 9QJ (UK)
Fax: (+44) 1273-677196
E-mail: m.s.hill@sussex.ac.uk

[**] We thank the Royal Society for the provision of a University Research Fellowship (M.S.H.) and Dr. A. G. Avent for assistance with NMR spectra.



(1)

observation of four ring methyl resonance signals in the ^{1}H and ^{13}C NMR spectra and five cyclopentadienyl ring signals, identified by their coupling to the yttrium nucleus ($^{1}J_{Y,C}$ = 0.5 – 2.0 Hz), in the ^{13}C NMR spectrum were consistent with a C_2-symmetric structure in which yttrium is bound by η^5-cyclopentadienyl and η^1-amido interactions.[7] The ^{6}Li and ^{7}Li NMR spectra consist of a single resonance signal at $\delta = 3.1$. Cooling of a [D_8]toluene solution of **1** to 248 K did not result in any perceptible changes to the NMR spectra, indicating a static solution geometry. The robust nature of **1** in solution was further reflected by a $^{2}J_{Y,Si}$ coupling of 2.1 Hz in the ^{29}Si NMR spectrum and in the vapor phase by a 100 % intensity molecular ion at 636 in the mass spectrum.

A bent metallocene structure for **1** was confirmed by a single-crystal X-ray diffraction analysis (Figure 1).[8a] The yttrium atom is coordinated in a pseudotetrahedral fashion by two pairs of cyclopentadienyl and amido donors. The Y–C(Cp) bond lengths (2.576(3) – 2.758(3) Å) and the Cp_{cent}-Y-Cp_{cent} angle (137.0(1)°) are comparable to those in Li[Y(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe)_2$] (**II**).[5d] The Y–N bond lengths (2.332(3), 2.349(3) Å) are only about 0.02 Å longer than those of **II**, despite the potential for enhanced delocalization of charge from the amido donors onto the 2-pyridyl substituents. The pendant aminopyridinato groups both chelate the lithium countercation. In contrast to other lithiated aminopyridines,[6a] the lithium center is preferentially bound by the pyridyl nitrogen atoms of the N_4-donor set (Li–N1 2.308(7), Li–N3 2.256(7), Li–N2 1.995(6), Li–N4 1.990(6) Å). This results in a displacement of the lithium atom away from the yttrate anion and a Y–Li separation of 3.136 Å. Evidently the steric demands of the yttrate fragment and the "bite" provided by the pendant aminopyridinato substituents are such that further coordination of THF solvent is prevented.

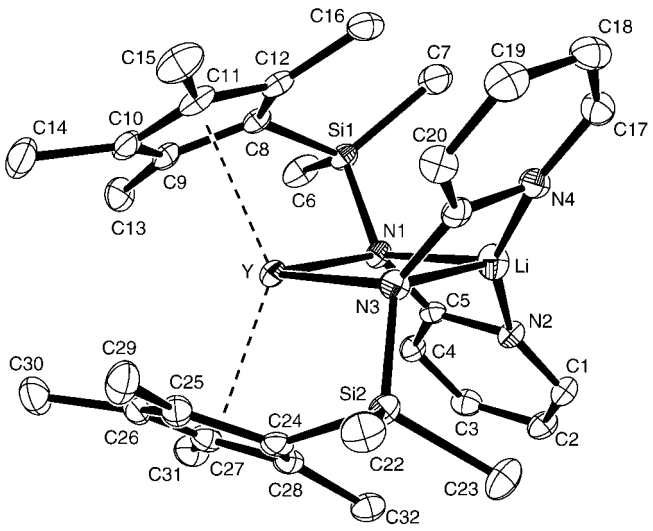
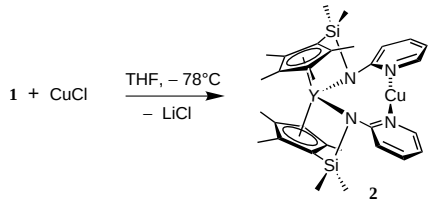


Figure 1. Structure of **1** (ORTEP plot; 30 % probability ellipsoids). H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Y-N1 2.349(3), Y-N3 2.332(3), Y-C8 2.576(3), Y-C9 2.617(3), Y-C10 2.734(3), Y-C11 2.752(3), Y-C12 2.673(3), Y-C24 2.588(3), Y-C25 2.599(4), Y-C26 2.722(4), Y-C27 2.758(3), Y-C28 2.704(3), Y-M1 2.380(4), Y-M2 2.385(4), Li-N1 2.308(7), Li-N2 1.995(6), Li-N3 2.256(7), Li-N4 1.990(6), Y···Li 3.136(6); N1-Y-N3 92.99(10), N1-Y-M1 95.2(1), N1-Y-M2 114.4(1), N3-Y-M1 114.3(1), N3-Y-M2 95.3(1), M1-Y-M2 137.0(1), N1-Li-N3 96.1(3), N1-Li-N2 65.0(2), N2-Li-N4 155.9(4), N4-Li-N3 66.0(2), N1-Li-N4 135.6(3), N2-Li-N3 132.0(3). M1 and M2 are the centroids of the C8 to C12 and C24 to C28 rings respectively.

Reaction of **1** with one equivalent of CuCl in THF provided, after crystallization from toluene, the colorless heterobinuclear compound **2** [Eq. (2)]. The formation of this



(2)

unusual Y/Cu species was indicated by a strong peak for the molecular ion at m/z 692 in the mass spectrum. Furthermore, retention of the C_2 symmetry of the molecule was deduced from the similarity of the solution-state NMR spectra to those of **1**. The ^{89}Y chemical shift of **2** is little altered from that of **1** ($\Delta\delta = 10.1$ ppm) indicating that substitution of copper for lithium causes little disruption to the yttrium coordination environment.[9]

An X-ray structural analysis confirmed the incorporation of copper into the pendant aminopyridinato coordination environment of the yttrate anion (Figure 2).[8b] The structural parameters relating to the yttrium coordination sphere are

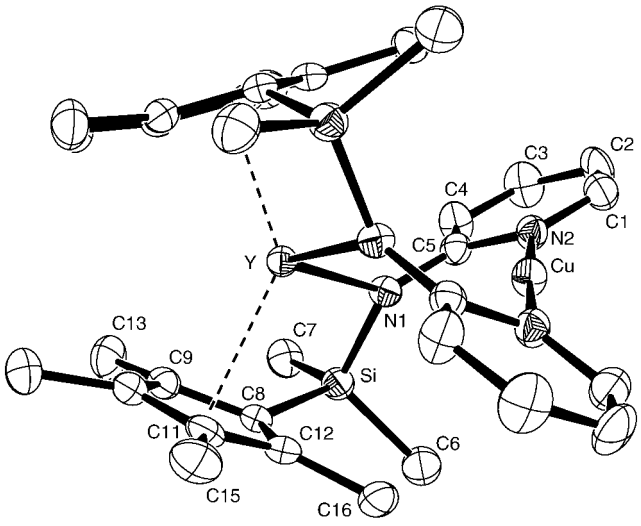


Figure 2. Structure of **2** (ORTEP plot; 50 % probability ellipsoids). H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Y-N1 2.358(3), Y-C8 2.585(4), Y-C9 2.678(4), Y-C10 2.759(4), Y-C11 2.732(4), Y-C12 2.630(4), Y-M1 2.388(4), Cu-N2 1.879(3), Y···Cu 3.458(6); N1-Y-N1′ 107.8(2), N1-Y-M1 94.4(2), N1′-Y-M1 111.9(2), M1-Y-M1′ 135.2(2), N2-Cu-N2′ 177.6(2). M1 is the centroid of the C8 to C12 ring.

  0044-8249/01/11321-4214 $ 17.50+.50/0 *Angew. Chem.* **2001**, *113*, Nr. 21

very similar to those of **1** apart from a widening of the N1-Y-N1′ angle to 107.8(2)° (from 92.99(10)° for the equivalent N1-Y-N3 measurement in **1**). This adjustment to the yttrate configuration is due to the almost linear (N-Cu-N 177.6(2)°) 2-coordination of the copper atom provided exclusively by the pyridyl N donors of the aminopyridinato substituents. This also results in a lengthening of the intermetallic Y–Cu distance to 3.458 Å.

In conclusion, the isolation of **2** indicates that the kinetic stabilization afforded by the sterically demanding architecture of **I** is suitable for the intact metathetical transfer of an yttrium-centered anion. This simple synthetic method holds promise for the assembly of a range of unusual and unprecedented combinations of metal centers. To further understand the pendant coordination environment of **1**, we are exploring the generality of its metathesis reactions with a range of main group and d-block metal halides. Preliminary mass spectral studies indicate that reactions of **1** with $AlCl_3$, $FeBr_2$ and $PdCl_2$ also result in the replacement of lithium and the formation of mixed-metal species. This is most clearly apparent for the reaction with $AlCl_3$, which displays a strong peak for the molecular ion at *m*/*z* 726. However in this case each signal in the ^{1}H NMR spectrum splits into two demonstrating that the C_2 symmetry of **1** and **2** is lost, due, most likely, to coordination by a single aminopyridine. This latter observation indicates that "tuning" of the pendant donor environment to the coordination requirements of particular metal centers will be a major consideration in the realization of certain combinations of metals. With this in mind, the simplicity of **I** allows straightforward modification of ligand bite and donor identity by, for example, the inclusion of methylene spacers between the amido nitrogen atoms and the pyridyl substituents.

Experimental Section

All reactions and manipulations were performed under rigorous exclusion of water and oxygen, either on a double manifold vacuum line or a N_2-filled drybox operating at <1 ppm O_2. All reagents and solvents were purified by standard procedures.

1: YCl_3 (0.34 g, 1,.76 mmol) and $Li_2(C_5Me_4SiMe_2NC_5H_4N\text{-}2)$ (1.0 g, 3.52 mmol) were combined in a flask, and precooled THF (30 mL) was added at −78 °C with stirring. The resulting mixture was allowed to warm to room temperature and stirred for 14 h to give a pale yellow solution. The solvent was removed and the resultant pale yellow glass extracted with toluene (30 mL). This was filtered from LiCl, and the clear pale yellow solution concentrated to 5 mL. Storage at −30 °C for one week resulted in the formation of mono-toluene solvated **1** as air-sensitive colorless crystals suitable for an X-ray diffraction study. The included toluene was removed by storage of a ground sample under vacuum: yield; 0.95 g, 85 %. M.p. 138 °C (decomp); elemental analysis: $C_{32}H_{44}LiN_4Si_2Y$: calcd: C 60.29, H 6.90, N 8.79; found: C 60.39, H 7.00, N 8.68; ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 0.47, 0.60$ (s, 6H; SiMe), 1.55, 1.85, 2.13, 2.26 (s, 6H; C_5Me_5), 6.29 (t, 2H; 4-H, C_5H_4N), 6.61 (d, 2H; 3-H, C_5H_4N), 7.06 (m, 2H; 5-H, C_5H_4N), 7.85 (d, 2H; 6-H, C_5H_4N); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 4.1$, 5.8 (SiMe), 10.4, 11.5, 13.1, 13.2 (ring CH_3), 104.4 (ring C attached to $SiMe_2$), 114.2 (4-C; C_5H_4N), 119.1 (3-C, C_5H_4N), 121.4 ($^1J_{Y,C} = 2.0$ Hz, ring C), 122.2 ($^1J_{Y,C} = 0.5$ Hz, ring C), 122.4 ($^1J_{Y,C} = 0.8$ Hz, ring C), 126.8 ($^1J_{Y,C} = 1.9$ Hz, ring C), 138.0 (5-C, C_5H_4N), 146.7 (6-C, C_5H_4N), 171.6 (2-C, C_5H_4N); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 25 °C): $\delta = -16.46$ ($^2J_{Y,si} = 2.2$ Hz); $^{6/7}$Li NMR (194.5 MHz, C_6D_6, 25 °C): $\delta = 3.1$; ^{89}Y{^{1}H} NMR (24.5 MHz, C_6D_6, 25 °C): $\delta = -82.4$; MS (70 eV): *m*/*z* (%): 636 (100) [M^+], 509 (60), 458 (15), 359 (55) [RY], 277 (6), 151 (35).

2: Precooled THF (20 mL) was added at −78 °C to a solid mixture of **1** (0.35 g, 0.55 mmol) and CuCl (0.06 g, 0.57 mmol) to give a pale yellow solution that turned deep red-brown on warming to room temperature. After stirring for a further 2 h the solvent was removed to give a red-brown glass. This was extracted with toluene (15 mL) and filtered. Concentration to about 5 mL followed by storage at −30 °C for one week provided **2** as colorless block crystals suitable for an X-ray diffraction study: yield 0.22 g, 58 %. M.p. softens 175 °C, melts 225 °C (decomp); elemental analysis: $C_{32}H_{44}CuN_4Si_2Y$: calcd: C 55.38, H 6.35, N 8.08; found: C 55.48, H 6.32, N 7.96; ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 0.56, 0.73$ (s, 6H; SiMe), 1.84, 1.85, 2.17, 2.32 (s, 6H; C_5Me_5), 6.10 (t, 2H; 4-H, C_5H_4N), 6.68 (d, 2H; 3-H, C_5H_4N), 6.91 (m, 2H; 5-H, C_5H_4N), 7.20 (d, 2H; 6-H, C_5H_4N); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 3.7$, 6.0 (SiMe), 11.1, 11.8, 14.1, 14.7 (ring CH_3), 104.8 (ring C attached to $SiMe_2$), 113.1 (4-C, C_5H_4N), 119.4 ($^3J_{Y,C} = 1.1$ Hz, 3-C, C_5H_4N), 121.2 ($^1J_{Y,C} = 0.7$ Hz, ring C), 122.9 ($^1J_{Y,C} = 1.8$ Hz, ring C), 123.7 ($^1J_{Y,C} = 0.5$ Hz, ring C), 125.3 ($^1J_{Y,C} = 1.9$ Hz, ring C), 137.6 (5-C, C_5H_4N), 147.4 (6-C, C_5H_4N), 171.8 (2-C, C_5H_4N); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 25 °C): $\delta = -17.91$ ($^2J_{Y,si} = 2.1$ Hz); ^{89}Y{^{1}H} NMR (24.5 MHz, C_6D_6, 25 °C): $\delta = -72.3$; MS (70 eV): *m*/*z* (%): 692 (60) [M^+], 509 (35), 359 (15) [RY], 285 (98), 207 (20), 151 (100), 120 (20).

Received: August 13, 2001 [Z17717]

[1] Examples of asymmetric catalysis: a) H. C. Aspinall, J. F. Bickley, J. L. M. Dwyer, N. Greeves, R. V. Kelly, A. Steiner, *Organometallics* **2000**, *19*, 5416; b) H. C. Aspinall, J. L. M. Dwyer, N. Greeves, A. Steiner, *Organometallics* **1999**, *18*, 1366; c) H. Gröger, Y. Saida, H. Sasai, K. Yamaguchi, J. Martens, M. Shibasaki, *J. Am. Chem. Soc.* **1998**, *120*, 3089; d) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1236; e) H. Sasai, T. Arai, Y. Satow, K. N. Houk, M. Shibasaki, *J. Am. Chem. Soc.* **1995**, *117*, 6194; energy conversion by f–d complexes: f) C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **2000**, 3999; g) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347.

[2] For example: a) S. Rigault, C. Piguet, G. Bernardinelli, G. Hopfgartner, *Angew. Chem.* **1998**, *110*, 178; *Angew. Chem. Int. Ed.* **1998**, *37*, 169; b) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681; c) C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **1997**, 421; d) A. Spannenberg, M. Oberthür, H. Noss, A. Tillack, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 2190; *Angew. Chem. Int. Ed.* **1998**, *37*, 2079.

[3] a) A. Spannenberg, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 824; *Angew. Chem. Int. Ed.* **1998**, *37*, 832; R. Kempe, H. Noss, H. Fuhrmann, *Chem. Eur. J.* **2001**, *7*, 1630.

[4] a) P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867; b) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1994**, *116*, 4623.

[5] a) K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228; b) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem.* **1999**, *111*, 163; *Angew. Chem. Int. Ed.* **1999**, *38*, 227; c) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1998**, *17*, 485; d) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845.

[6] See, for example, ref. [2d] and a) L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1988**, 1011; b) L. M. Engelhardt, G. E. Jacobsen, W. C. Patalinghug, B. W. Skelton, C. L. Raston, A. H. White, *J. Chem. Soc. Dalton Trans.* **1991**, 2859; c) C. L. Raston, B. W. Skelton, V.-A. Tolhurst, A. H. White, *Polyhedron* **1998**, *17*, 935; d) A. Spannenberg, H. Fuhrmann, P. Arndt, W. Baumann, R. Kempe, *Angew. Chem.* **1998**, *110*, 3565; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3363; e) H. K. Lee, Y.-L. Wong, Z.-Y. Zhou, Z.-Y. Zhang, D. K. P. Ng, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **2000**, 539; f) M. Oberthür, G. Hillebrand, P. Arndt, R. Kempe, *Chem. Ber.* **1997**, *130*, 789.

[7] H. Schumann, E. C. E, Rosenthal, J. Demtschuk, G. A. Molander, *Organometallics* **1998**, *17*, 5324.

[8] Data for the X-ray structural analyses of **1** and **2** were collected on a KappaCCD diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å), solved by direct

methods (SHELXS-97) and refined against all F^2 using SHELXL-97) with non hydrogen atoms anisotropic and hydrogen atoms in riding mode. a) Crystallographic data for **1** at 173(2) K: ($C_{39}H_{52}LiN_4Si_2Y$, $M_r = 728.88$) crystal dimensions $0.4 \times 0.4 \times 0.3$ mm^3: triclinic, space group $P\bar{1}$ (no. 2), $a = 11.2801(6)$, $b = 12.5170(8)$, $c = 14.0742(9)$ Å, $\alpha = 106.916(3)$, $\beta = 92.003(4)$, $\gamma = 93.380(3)^\circ$, $V = 1895.1(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.28$ Mg m^{-3}, $\mu = 1.63$ mm^{-1}. Of 12364 reflections measured ($3.75 < \theta < 24.10^\circ$), 5977 were independent ($R_{int} = 0.051$). $wR2 = 0.093$ (all data), $R1 = 0.045$ (for 4962 reflections with $I > 2\sigma(I)$), 436 parameters, GOF = 1.049. b) Crystallographic data for **2** at 173(2) K: ($C_{32}H_{44}CuN_4Si_2Y$, $M_r = 693.34$) crystal dimensions $0.1 \times 0.1 \times 0.1$ mm^3: orthorhombic, space group *Pbcn* (no. 60), $a = 11.9268(5)$, $b = 17.0281(6)$, $c = 16.0764(7)$ Å, $V = 3265(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.41$ Mg m^{-3}, $\mu = 2.52$ mm^{-1}. Of 15424 reflections measured ($3.84 < \theta < 25.01^\circ$), 2872 were independent ($R_{int} = 0.079$). The molecule lies on a twofold rotation axis. $wR2 = 0.098$ (all data), $R1 = 0.041$ (for 1907 reflections with $I > 2\sigma(I)$), 188 parameters, GOF = 1.025. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168596 and CCDC-168597 for **1** and **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] a) W. J. Evans, J. H. Meadows, A. G. Kostka, G. L. Closs, *Organometallics* **1985**, *4*, 324; b) C. J. Schaverien, J. H. G. Frijns, H. J. Heeres, J. R. van den Hende, J. H. Teuben, A. L. Spek, *J. Chem. Soc. Chem. Commun*. **1991**, 642.

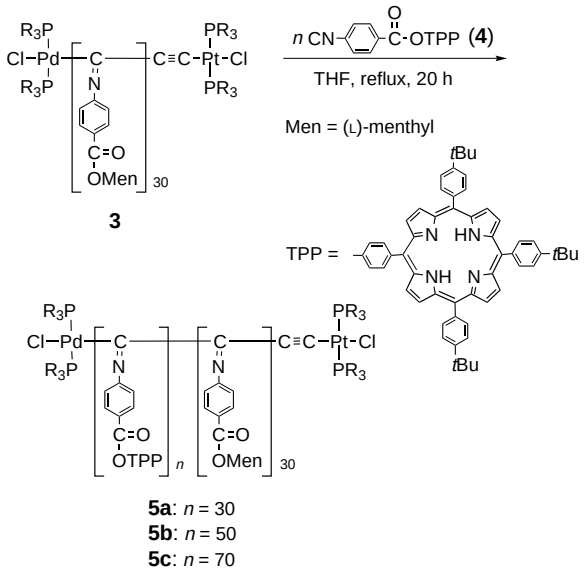
Helical Chiral Polyisocyanides Possessing Porphyrin Pendants: Determination of Helicity by Exciton-Coupled Circular Dichroism**

Fumie Takei, Hiroko Hayashi, Kiyotaka Onitsuka, Nagao Kobayashi, and Shigetoshi Takahashi*

There has been considerable interest in helical chiral polymers because of their unique functions that are applicable to a wide range of scientific disciplines, such as molecular recognition and asymmetric syntheses.[1] Although the helical structure is often found in biopolymers, only a limited number of artificial polymers that maintain a stable helical conformation in solution have so far been reported. Polyisocyanide with bulky substituents is a representative example of such helical polymers.[2] In recent years, interesting studies on the selective syntheses of single-handed helical polyisocyanides using chiral monomers, chiral initiators, and chiral additives have been reported.[3–6] Many problems associated with helical polymers, however, still remain to be solved. One such problem is the determination of the helical sense. Although theoretical circular dichroism (CD) calculations provide useful information on the helical sense, experimental determination of the helical sense is quite rare.[7, 8] We previously developed a living polymerization of aryl isocyanides by the use of a Pd/Pt μ-ethynediyl complex (**1**) as an initiator.[9] This living polymerization system is applicable to aryl isocyanides bearing various kinds of substituents, and poly(aryl isocyanide)s with porphyrin pendants in their side chains have been prepared.[10] Herein we present a novel method of determining the helical sense of poly(aryl isocyanide)s that is based on exciton-coupled CD of the porphyrin Soret band.

It is well-known that the CD sign arising from exciton coupling is a useful probe for the assignment of the absolute configuration of chiral organic molecules.[11] Porphyrin derivatives are one of the best candidates since they exhibit a sharp and intense absorption band (the Soret band) at around 420 nm.[12] Thus, we started our study from the preparation of helical chiral poly(aryl isocyanide)s having porphyrin pendants. Since we had already shown that helical chiral poly(aryl isocyanide)s are selectively synthesized by block copolymerization between chiral and achiral isocyanides[13], aryl isocyanide (**4**), which has a tetraphenylporphyrin derivative linked through an ester group,[10] was polymerized using a helical chiral initiator (**3**; $M_n = 7000$, $M_w/M_n = 1.12$, $\Delta\varepsilon_{364} = 9.60$ dm^3 cm^{-1} mol^{-1}) prepared from complex **1** and 30 equivalents of the chiral isocyanide (**2a**) with a (L)-menthyl group.

Treatment of **4** with **3** in refluxing THF for 20 h resulted in the quantitative formation of block copolymers (**5a**–**5c**) with a narrow polydispersity index (Scheme 1). The CD spectra of



5a: $n = 30$
5b: $n = 50$
5c: $n = 70$

Scheme 1.

the resulting polymers **5a**–**5c** exhibited a Cotton effect at 364 nm, which is characteristic of helical chiral polyisocyanides and assignable to the n–π^* transition of the imino chromophore.[2] The $\Delta\varepsilon_{364}$ values of **5a**–**5c** are smaller than that of the helical chiral initiator **3**, but almost constant and

[*] Prof. Dr. S. Takahashi, Dr. F. Takei, H. Hayashi, Dr. K. Onitsuka
The Institute of Scientific and Industrial Research
Osaka University, Mihogaoka, Ibaraki
Osaka 567-0047 (Japan)
Fax: (+81) 6-6879-8459
E-mail: takahashi@sanken.osaka-u.ac.jp
Prof. Dr. N. Kobayashi
Department of Chemistry, Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-8578 (Japan)

[**] This work was supported by a Grant-in-Aid for COE Research and Scientific Research from the Ministry of Education, Science, Sports, and Culture. F.T. gratefully acknowledges partial support of this work by the Hayashi Memorial Foundation for Female Natural Scientists.