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Racemo-selective formation of *ansa*-zirconocene in the reaction of dimethylbis(5-phenyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)silane dilithium salt with $ZrCl_4$: X-ray and DFT argumentation for stereocontrol

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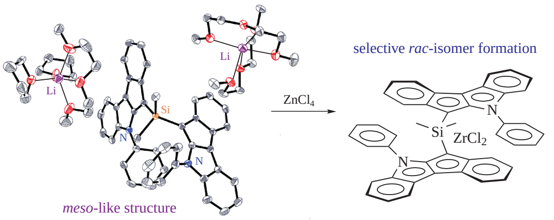
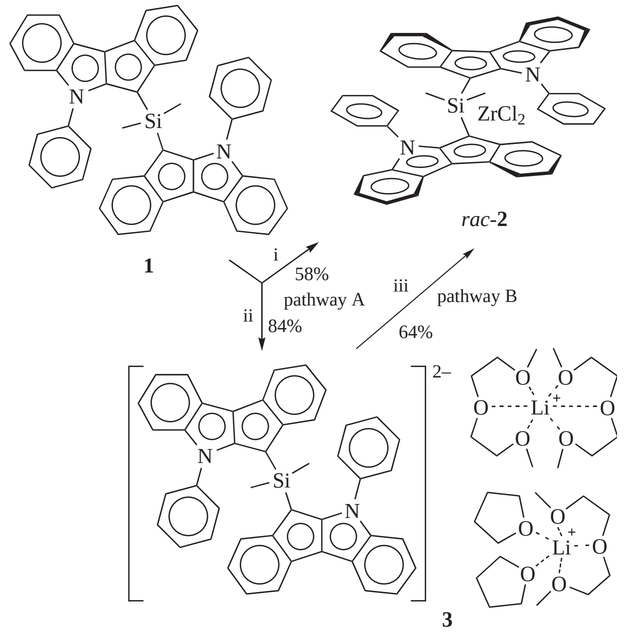
The reaction of bis[(5a,6,6a,10a,10b-η)-5-phenyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl]dimethylsilane dilithium salt with $ZrCl_4$ results in the formation of zirconium *ansa*-complex with > 95% *rac*-selectivity, presumably due to specific crystal structure of the dilithium salt, which was established by X-ray diffraction.



The synthesis of pure diastereomeric forms of *ansa*-zirconocenes is important for their application as pre-catalysts in the polymerization of α-olefins.[1–3] To achieve the required diastereomeric purity, four general approaches have been developed. The first one involves the use of bridged ligand as a precursor, which has a structure making possible the formation of C_2-symmetric *ansa*-complexes only, examples are biphenylene-bridged and structurally similar C_2-symmetrical zirconocenes.[4–9] The second approach utilizes pro-chiral or chiral zirconium complexes that provide stereochemical induction at the stage of Li–Zr transmetallation, by this way dichlorozirconium diamide,[10–13] dichlorozirconium biphenolate[14] and trichlorozirconium *tert*-butylamide[15,16] have been successfully applied to the synthesis of *rac*-isomers of bis(cyclopentadienyl) and bis(indenyl) *ansa*-complexes. The third approach is the initial separation of *rac*- and *meso*-like stereoisomers of disilicon- or ditin-substituted bridged ligands, followed by their stereoselective Si–Zr or Sn–Zr transmetallation.[17–19] Finally, the fourth approach consists in the stereoselective reaction of dilithium salts with $ZrCl_4$,[20–22] with the selectivity being driven by a higher stability of *rac*-zirconocene compared with the *meso*-isomer.



Scheme 1 *Reagents and conditions:* i, BuLi, Et_2O, hexane, –60 °C to room temperature, 30 min, then $ZrCl_4$, –60 °C to room temperature, 12 h; ii, BuLi, Et_2O, hexane, –60 °C to room temperature, 30 min, then evaporation, then THF, diglyme, hexane, 1 week; iii, Et_2O, $ZrCl_4$, –60 °C to 0 °C, 24 h.

The latter approach formally corresponds to our recent results[1] on the synthesis of six $SiMe_2$-bridged zirconium *ansa*-complexes, bearing η^5-coordinated 5,6-dihydroindeno[2,1-*b*]indole and 5,10-dihydroindeno[1,2-*b*]indole ligands, by the reaction of dilithium derivatives of the corresponding ligands with $ZrCl_4$. In that case, the dilithium derivative of $SiMe_2$-bridged ligand **1** reacted with $ZrCl_4$ in diethyl ether with an unexpected formation of single *rac*-isomer of zirconium *ansa*-complex **2** (Scheme 1, conditions i), while for five other investigated zirconocenes, the *rac*- and *meso*-products were detected in equal ratio.

Indeed, it seems that the stereoselective formation of *rac*-**2** can be explained by less stability of the *meso*-counterpart due to the strain originated from repulsion of two phenyl groups. Therefore, we examined the apparent instability of *meso*-**2** by quantum chemical modeling. For DFT calculations, we chosen an M06-2X functional of Minnesota 06 family,[23] as one of the most accurate tools for the modeling of zirconocenes,[24] and a DGTZVP basis set.[25] A Gaussian-09 program package[26] was used for the optimization of the structures of complexes *rac*-**2** and *meso*-**2**. The calculated geometry for isomer *rac*-**2** was in good agreement with its molecular structure determined by X-ray diffraction.[1] The molecular structures for isomeric *rac*-**2** and *meso*-**2** are presented in Figure 1. The comparative analysis of their geometric parameters did not reveal any repulsion between structural groups.

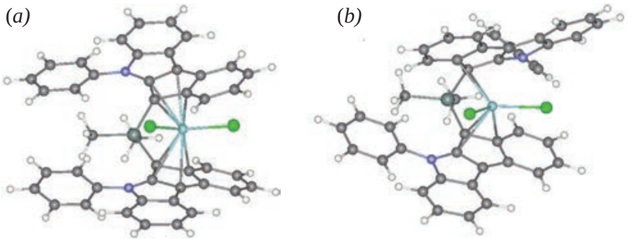


Figure 1 The molecular geometries of compounds (*a*) *meso*-**2** and (*b*) *rac*-**2** optimized by DFT calculations at an M06-2X/DGTZVP level of theory.

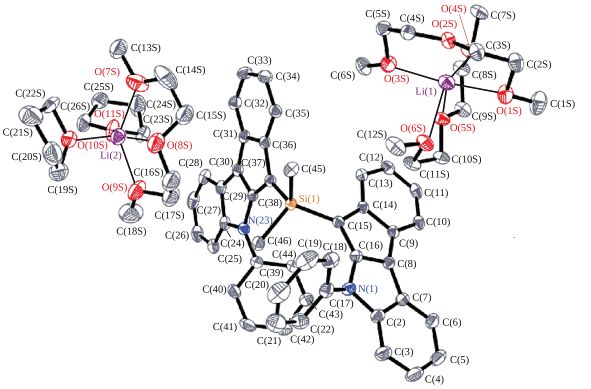


Figure 2 Molecular structure of cations and dianion of compound **3**.

The absence of repulsions was confirmed by the comparison of free energies and enthalpies of the diastereomers: the differences in *G* and *H* values were only 1.9 and 1.7 kcal mol^{-1}, respectively. Such a little gap hardly explains the high selectivity for the formation of pure *rac*-form in the reaction of the dilithium salt with $ZrCl_4$. We proposed that the reason for the *rac*-selectivity originates from crystallographic considerations, namely the packing of the dilithium salt that is insoluble in diethyl ether as the reaction solvent, contrary to partially soluble $ZrCl_4$.

We failed to prepare the high quality crystals of the intermediate dilithium salt from pure diethyl ether or from diethyl ether–THF mixture, and used diglyme as a chelating solvent to facilitate the crystals precipitation (see Scheme 1, conditions ii). As a result, we obtained perfectly shaped single crystals of dilithium compound **3** and investigated its molecular structure as well as its packing in the crystal cell by X-ray diffraction (Figure 2).[†]

In the crystal of compound **3**, the dianion moiety occupies the cell in *meso*-like conformation with *anti*-placement of lithium cations that are solvated in different coordination modes. The first, fully chelated, lithium cation is coordinated by two diglyme moieties, and the second, partially chelated one, is coordinated by one diglyme and two THF moieties. We assume that the initial stage of Li–Zr transmetallation process involves the interaction of the partially chelated lithium cation *via* Zr···Cl···Li intermediate with retaining the configuration, and the following stage is the Zr–η^{5}Cp bond formation. In the whole, the reaction of *meso*-like **3** with $ZrCl_4$ results in the *rac*-form of zirconocene **2** (Figure 3).

This assumption was verified by the reaction of compound **3** with $ZrCl_4$ in diethyl ether affording nearly pure compound *rac*-**2** (see Scheme 1, conditions iii, see the Online Supplementary Materials for details). The isolated yield of complex *rac*-**2** was higher than the reported one,[1] namely 64% *vs*. 58%. Therefore, we have demonstrated that the effect of crystal packing can control the stereoselectivity in the synthesis of *ansa*-zirconocenes.

The application of this direct Li–Zr transmetallation approach in the synthesis of required stereoisomers of *ansa*-zirconocenes is generally limited by the following two factors. The first one is the uncertainty of the preferable type of dilithium salt packing, *rac*-like or *meso*-like, which depends on the effects of molecular geometry of the ligand, metal–solvent coordination as well as the arrangement of metal atom and solvent moiety in the crystal cell. The second factor refers to the low solubility of the dilithium salts resulting in the formation of amorphous precipitates with unpredictable type of the basic metal–ligand coordination. The introduction of solvating moiety, ensuring mostly ionic type of

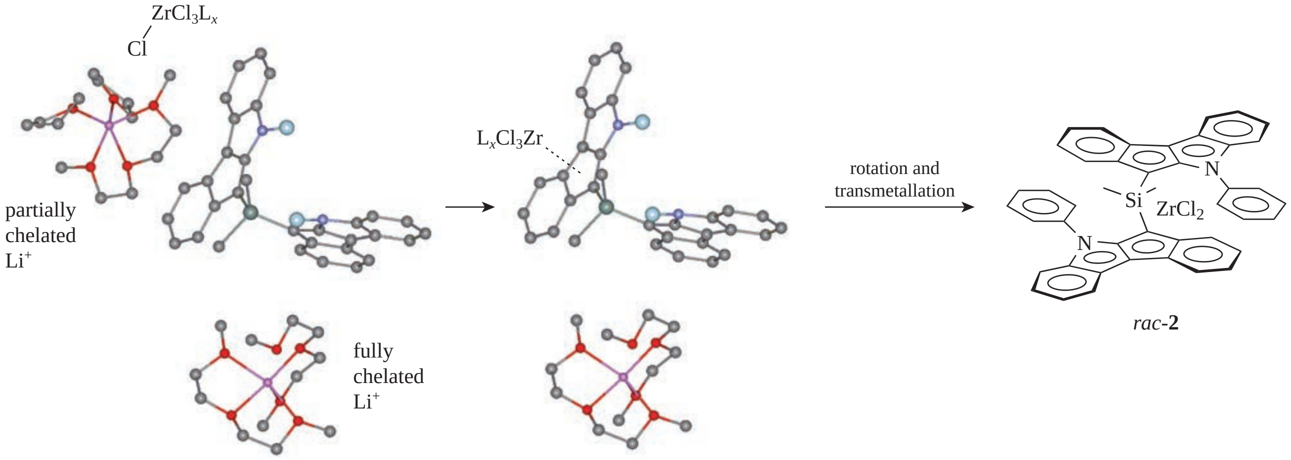


Figure 3 Proposed mechanism for **3** → **2** transmetallation. Phenyl groups in **3** are omitted for clarity.

[†] *Crystal data for* **3**. $C_{75}H_{101}Li_2N_2O_{11.5}Si$ (*M* = 1256.54), monoclinic, space group *C*2/*c*, at 120(2) K: *a* = 47.412(3), *b* = 11.6851(7) and *c* = 28.2569(16) Å, *β* = 110.2852(12)°, *V* = 14683.8(15) Å^3, *Z* = 8, d_{calc} = = 1.137 g cm^{-3}, μ(MoKα) = 0.090 mm^{-1}, *F*(000) = 5416. Total of 78499 reflections were measured and 16866 independent reflections (R_{int} = 0.0367) were used in a further refinement. The refinement converged to wR_2 = = 0.1448 and GOF = 1.020 for all independent reflections [R_1 = 0.0561 was calculated against *F* for 13196 observed reflections with $I > 2\sigma(I)$]. The measurements were performed on a SMART APEX II area-detector diffractometer (graphite monochromator, *ω*-scan technique) using MoKα radiation (λ = 0.71073 Å).

The structure was solved by direct method using SHELXS[27]and refined by full-matrix least squares on F^2 using SHELXL.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in geometrically calculated positions (C–H distance is 0.950 Å for aromatic, 0.980 Å for methyl and 0.990 Å for methylene hydrogen atoms) and refined using a riding model with relative isotropic displacement parameters [U_{iso}(H) = 1.5 U_{eq}(C) for methyl hydrogen atoms and 1.2U_{eq}(C) otherwise].

CCDC 1882527 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

metal coordination, can result in the uniformity of the crystal structure.

In conclusion, the design and synthesis of new biscyclopentadienyls should be accompanied by the structural study of their dilithium salt solvates, or at least by the investigation of the solvates interaction with $ZrCl_4$ to establish possible stereoselectivity of transmetallation, which can finally facilitate the synthesis of pure diastereomeric forms of *ansa*-zirconocenes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.008.

References

1 I. E. Nifant'ev, A. A. Vinogradov, A. A. Vinogradov, A. V. Churakov, V. V. Bagrov, I. A. Kashulin, V. A. Roznyatovsky, Y. K. Grishin and P. V. Ivchenko, *Appl. Catal., A*, 2019, **571**, 12.
2 G. W. Coates, *Chem. Rev.*, 2000, **100**, 1223.
3 S. Prashar, A. Antiñolo and A. Otero, *Coord. Chem. Rev.*, 2006, **250**, 133.
4 M. J. Burk, S. L. Colletti and R. L. Halterman, *Organometallics*, 1991, **10**, 2998.
5 W. W. Ellis, T. K. Hollis, W. Odenkirk, J. Whelan, R. Ostrander, A. L. Rheingold and B. Bosnich, *Organometallics*, 1993, **12**, 4391.
6 M. E. Huttenloch, J. Diebold, U. Rief, H. H. Brintzinger, A. M. Gilbert and T. J. Katz, *Organometallics*, 1992, **11**, 3600.
7 M. E. Huttenloch, B. Dorer, U. Rief, M.-H. Prosenc, K. Schmidt and H. H. Brintzinger, *J. Organomet. Chem.*, 1997, **541**, 219.
8 R. L. Halterman and T. M. Ramsey, *J. Organomet. Chem.*, 1997, **530**, 225.
9 M. Könemann, G. Erker, R. Fröhlich and S. Kotila, *Organometallics*, 1997, **16**, 2900.
10 M. D. LoCoco, X. Zhang and R. F. Jordan, *J. Am. Chem. Soc.*, 2004, **126**, 15231.
11 X. Zhang, Q. Zhu, I. A. Guzei and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 8093.
12 M. D. LoCoco and R. F. Jordan, *Organometallics*, 2003, **22**, 5498.
13 M. D. LoCoco and R. F. Jordan, *J. Am. Chem. Soc.*, 2004, **126**, 13918.
14 H.-R. H. Damrau, E. Royo, S. Obert, F. Schaper, A. Weeber and H.-H. Brintzinger, *Organometallics*, 2001, **20**, 5258.
15 I. E. Nifant'ev, P. V. Ivchenko, V. V. Bagrov, A. V. Churakov and R. Chevalier, *Organometallics*, 2012, **31**, 4340.
16 I. E. Nifant'ev, P. V. Ivchenko, V. V. Bagrov, A. V. Churakov and P. Mercandelli, *Organometallics*, 2012, **31**, 4962.
17 I. E. Nifant'ev and P. V. Ivchenko, *Organometallics*, 1997, **16**, 713.
18 M. Hüttenhofer, A. Weeber and H.-H. Brintzinger, *J. Organomet. Chem.*, 2002, **663**, 58.
19 M. Hüttenhofer, F. Schaper and H.-H. Brintzinger, *J. Organomet. Chem*., 2002, **660**, 85.
20 L. Resconi, I. Camurati, C. Fiori, D. Balboni, P. Mercandelli and A. Sironi, *Helv. Chim. Acta*, 2006, **89**, 1497.
21 P. V. Ivchenko, I. E. Nifant'ev, O. V. Smetannikov, A. A. Ivanyuk and A. V. Churakov, *Mendeleev Commun.*, 2015, **25**, 435.
22 S. T. Chacon, E. B. Coughlin, L. M. Henling and J. E. Bercaw, *J. Organomet. Chem.*, 1995, **497**, 171.
23 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
24 Y. Sun and H. Chen, *J. Chem. Theory Comput.*, 2013, **9**, 4735.
25 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09, Revision A.01*, Gaussian, Inc., Wallingford CT, 2016.
27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008, **64**, 112.
28 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.

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