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Novel C_2-symmetric chiral ligands: enantioselective transformation of cyclic 1,2-diols into 1,2-bis(phenylsulfenyl) and 1,2-bis(phenylselenyl) derivatives

Elżbieta Wojaczyńska and Jacek Skarżewski*

Department of Organic Chemistry, Faculty Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland

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Abstract—Chiral C_2-symmetric S,S- and Se,Se-donating ligands as well as the C_1 mixed S,Se-donating ligands were prepared from optically active 1,2-cyclohexanediol and 1,2-cyclopentanediol via the respective S_N2 reactions. The bis(chalcogen) ligands obtained effectively catalyze the asymmetric allylic alkylation with enantioselectivities of up to 50% ee.
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1. Introduction

Chiral chelating ligands with both nitrogen- and phosphorus-donating atoms are regarded as the most effective catalysts in various transition-metal catalyzed asymmetric reactions.[1] Generally, chiral C_2-symmetric derivatives with a rigid, cyclic structure constitute the best ligands, such as *trans*-1,2-diaminocyclohexane derivatives.[2] Recently, sulfur- and selenium-donating ligands have also been developed with much success.[3] In particular, hetero-donating C_1-symmetric chalcogen/nitrogen and chalcogen/phosphorous ligands have performed well in the Pd-catalyzed asymmetric allylic alkylation (AAA) due to the *trans*-effect additionally stereodifferentiating the intermediate Pd-complex.[4] On the other hand, a few C_2-symmetric homo-donating sulfur ligands have already been tested, in some cases even outperforming others in catalytic activity.[5] This has stimulated interest in the synthesis of new compounds of this type.[6] Within our program to explore the preparation and use of chiral organochalcogen compounds in asymmetric catalysis, we have synthesized optically active 1,2-bis(phenylsulfenyl)cyclopentane and its heterocyclic analogues.[7] However, when we attempted to obtain the corresponding chiral *vic*-cyclohexane derivative, simple synthetic methods failed.[7a] Herein, we report the successful preparation of the sulfur–sulfur, selenium–selenium, and sulfur–selenium donor five- and six-membered cyclic ligands and their use in the AAA reaction.

2. Results and discussion

Commercially available *trans*-diols: 1,2-cyclopentanediol **1** and 1,2-cyclohexanediol **2** were chosen as substrates for the title transformations. It should be noted that attempted substitution of the corresponding bis-sulfonyl esters gave a complex mixture. Thus, we introduced phenylsulfenyl group into these molecules using the Hata reaction.[7,8] As we reported previously, the nucleophilic substitution of enantiomerically pure (1*R*,2*R*)-**1** with $(PhS)_2/Bu_3P$ in benzene gave exclusively (1*S*,2*S*)-bis(phenylsulfenyl)cyclopentane **3**; both de and ee exceeded 95%.[7] However, the corresponding reaction of (*S*,*S*)-1,2-cyclohexanediol resulted in a mixture containing 1,2-bis(phenylsulfenyl)-cyclohexane **4** (42% yield) along with the elimination side-products and butyl phenyl sulfide. The disubstituted product obtained was mainly *trans*-**4** (83% de), containing also the *cis-meso*-isomer (by GC/MS), and was considerably racemized (22% ee by chiral HPLC).[7a] The reasons for this outcome have already been discussed there.[7a] The reaction of (1*R*,2*R*)-**2** with 6 equiv of $(PhS)_2/Bu_3P$ in toluene yielded bis(phenylsulfenyl)cyclohexane **4**, still formed as a diastereomeric mixture (Scheme 1).

However, when we treated (1*R*,2*R*)-**2** with 3 equiv of $(PhS)_2/Bu_3P$, the nucleophilic substitution of one hydroxy

* Corresponding author. Tel.: +48 71 320 2464; fax: +48 71 328 4064; e-mail: jacek.skarzewski@pwr.wroc.pl

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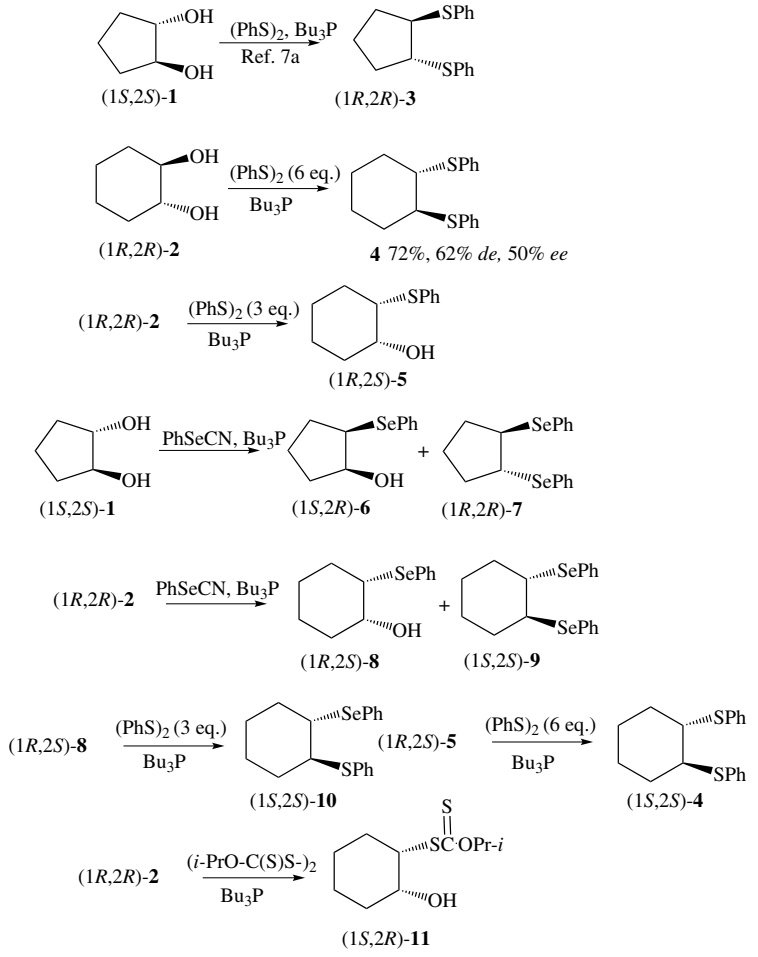


Scheme 1.

group proceeded in a highly stereoselective manner and furnished *cis*-(1*R*,2*S*)-2-phenylsulfenylcyclohexanol **5** in 34% yield and >95% ee. Recently, this enantiomeric product has also been obtained via bromomandelation of cyclohexene.[9]

We were also interested in the preparation of the corresponding 1,2-bis(phenylselenyl) derivatives. Thus, (1*S*,2*S*)-*trans*-1,2-cyclopentanediol **1** reacted smoothly with $PhSeCN/Bu_3P$ according to Grieco protocol[10] and stereoselectively gave both, mono- **6** (37%) and bis-substituted **7** (43%) products (>98% de, >95% ee).

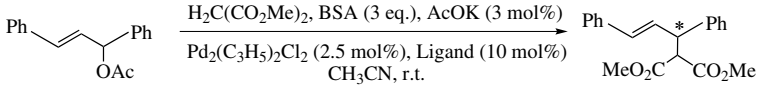
Surprisingly, under similar reaction conditions, also both mono-**8** (25%) and bis-phenylselenyl cyclohexane derivatives **9** (23%) were obtained from (1*R*,2*R*)-**2** and $PhSeCN/Bu_3P$ with a de and ee exceeding 97%.

Additionally, when (1*R*,2*S*)-2-phenylselenylcyclohexanol **8** was treated with 3 equiv of $(PhS)_2/Bu_3P$, it was converted to the mixed sulfide–selenide derivative (1*S*,2*S*)-1-phenylsulfanyl-2-phenylselenylcyclohexane **10** with complete inversion of configuration at the 1-C atom (42% yield).

These outcomes prompted us to examine a similar reaction with the mono-phenylsulfenyl derivative **5**. When this pure *cis*-(1*R*,2*S*)-**5** was submitted to a Hata reaction with 6 equiv of $(PhS)_2/Bu_3P$, the desired (1*S*,2*S*)-bis(phenylsulfenyl)cyclohexane **4** (80% yield, >95% ee) was formed. Apparently, the Hata reaction of **2** should be conducted in a two-step manner, while the isolation of monosubstituted product is required to achieve complete stereoselectivity.

Moreover, facing failures in our earlier substitution experiments,[7a] we have separately developed a protocol for the resolution of racemic 1,2-bis(phenylsulfenyl)cyclohexane **4**, comprising of an enantioselective sulfoxidation, separation of diastereomeric bissulfoxides, and subsequent deoxygenation of pure diastereomers.[11] The product proved to be identical to that obtained via the two-step substitution procedure.

We then tested the influence of sulfur nucleophiles on the reactivity and stereoselectivity of substitution of hydroxy groups in (1*R*,2*R*)-1,2-cyclohexanediol **2**. When we used 6 equiv of isopropylxanthicdisulfide in a Hata reaction, we observed the formation of (1*S*,2*R*) *O*-isopropyl-*S*-(2-hydroxycyclohexyl) dithiocarbonate **11**, that is, the monosubstitution product, as a single enantiomer. Identical results were obtained when 3 equiv of the reagents was used. Another independent attempts with sulfur nucleo-



Scheme 2.

philes, namely diethyl dithiophosphate $(EtO)_2P(S)SH$ and potassium thiocyanate, under Mitsunobu reaction conditions were unsuccessful and led to the complete recovery of unreacted substrate.

Thus, as yet, the stereoselective introduction of two sulfhydryl groups into *trans–vic*-cyclohexane positions could not be accomplished. Nevertheless, the enantiomeric monochalcogen-functionalized cyclic alcohols obtained **5**, **6**, **8**, and **11** offer various possibilities for further transformations into interesting chiral building blocks and ligands.

Next, we tested enantiomerically pure sulfides and selenides **3**, **4**, **7**, **9**, and **10** as ligands in the Pd-catalyzed allylic substitution reaction (AAA reaction, Scheme 2).[4] The results obtained for the reaction of dimethyl malonate with *rac*-1,3-diphenyl-2-propenyl acetate, using 3 mol % of *N*,*O*-bis(trimethylsilyl)acetamide-potassium acetate as a base, 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, and 10 mol % chiral ligand in acetonitrile solution, are collected in Table 1. The reaction yield documents palladium complexation to the ligands, because in the absence of ligands no reaction occurs. The moderate enantioselectivities observed are in agreement with the fact that metal complexation to sulfur makes these donors stereogenic, and even in the case of C_2-symmetric S,S-donating ligands multiply the number of diastereomeric complexes that can be formed. Moreover, these stereogenic centers can rapidly epimerize. It is noteworthy that the softer selenium donors performed better than their sulfur analogues. In both the cases, the same type of complexed species prevail since the same sense of stereoinduction (configuration of product vs configuration of ligand) was observed.

Table 1. Pd-catalyzed alkylation of dimethyl malonate with 1,3-diphenyl-2-propenyl acetate in the presence of S,S-, S,Se-, and Se,Se-donating ligands[a]

Entry	Ligand	Yield (%)	ee (%)	Configuration of product
1[b]	(1*R*,2*R*)-**3**	68	42	(−)-(*S*)
2	(1*R*,2*R*)-**7**	88	42	(−)-(*S*)
3	(1*S*,2*S*)-**4**	92	30	(+)-(*R*)
4	(1*S*,2*S*)-**10**	90	34	(+)-(*R*)
5	(1*S*,2*S*)-**9**	90	50	(+)-(*R*)

[a] For the catalytic procedure and product analysis, see Ref. 7b.
[b] The results for entry 1 were taken from Ref. 7b.

Additionally, the results obtained seem to support our earlier conclusions concerning the catalytic performance of 3,4-bis(phenylsulfenyl)pyrrolidines. Those ligands gave in the same reaction with up to 90% ee, thus acting rather as N,S- other than S,S-donors.[7b]

3. Conclusions

In conclusion, the successful enantioselective displacement of one hydroxy group in enantiomeric *trans*-1,2-cyclopentanediol and *trans*-1,2-cyclohexanediol leading to the corresponding *cis*-2-phenylchalcogen cyclic alcohols opens up a route for the synthesis of a series of chiral homo- and hetero-donor ligands. Accordingly, chiral C_2-symmetric S,S- and Se,Se-donating ligands and the C_1 mixed S, Se-donating one were easily prepared. The asymmetric allylic alkylation was effectively catalyzed by these compounds; however, the obtained enantioselectivities were rather moderate. Further applications of the obtained compounds in asymmetric reactions are currently under investigation.

4. Experimental

4.1. General

Melting points were determined using a Boetius hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Bruker CPX (^1H, 300 MHz) or a Bruker Avance (^1H, 500 MHz) spectrometer using TMS as an internal standard. ^{77}Se NMR spectra were recorded at 115 MHz on a Bruker Avance spectrometer using dimethyl selenide as an external standard. Optical rotations were measured using an Optical Activity Ltd, Model AA-5 automatic polarimeter. High resolution mass spectra were recorded using a microTOF-Q instrument utilizing electrospray ionization mode. Separations of products by chromatography were performed on Silica Gel 60 (230–400 mesh) purchased from Merck. Thin layer chromatography analyses were performed using Silica Gel 60 precoated plates (Merck). HPLC measurements were performed on a Knauer HPLC Pump 64 using a Knauer Variable Wavelength Monitor and CHIRACEL OD-H column.

4.2. Preparation of sulfides

Tributylphosphine (3.2 mmol, 0.65 g, 0.80 mL) was added via syringe to a solution of diol **2** (0.8 mmol) and diphenyldisulfide (2.4 mmol, 0.52 g) in dry toluene. The mixture was transferred to an ampoule, filled with argon and sealed. This reaction mixture was kept at the at 80 °C in an oil for three days. Diethyl ether (20 mL) was added to the cooled solution, the organic layer was washed with 10% aqueous NaOH, water, and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the monosubstituted product **5** was purified by column

chromatography. This compound was converted to bissulfide **4** using a similar procedure, using 0.48 mmol (0.1 g) of **5**, 3.84 mmol of tributylphosphine, and 2.88 mmol of diphenyldisulfide.

4.2.1. (1*S*,2*S*)-1,2-Bis(phenylsulfenyl)cyclohexane 4. Yield 80%. $[\alpha]_D = +120.0$ (*c* 2.20, CH_2Cl_2) >95% ee. Spectral characteristics in agreement with those described for the less enantioenriched product **4**.[7a]

4.2.2. (1*R*,2*S*)-2-Phenylsulfenylcyclohexanol 5. Yield 34%. Mp = 48–49 °C; $[\alpha]_D = -23.0$ (*c* 1.04, CH_2Cl_2), >95% ee, lit. $[\alpha]_D = -25.2$ (*c* 1.15, $CHCl_3$).[9] IR (KBr): 3404, 2916, 2852, 1579, 1436, 1066, 734, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.33–1.37 (m, 2H, cyclohexane ring), 1.62–1.80 (m, 6H, cyclohexane ring), 2.43 (m, 1H, OH), 3.30–3.32 (m, 1H, CHS), 3.74 (dd, $J_1 = 5.8$ Hz, $J_2 = 3.2$ Hz, 1H, CHOH), 7.23–7.26 (m, 3H, ArH), 7.40–7.43 (m, 2H, ArH).

4.3. Preparation of selenides

PhSeCN (1.5 mL, 12 mmol) was added via syringe to the solution of diol **1** or **2** (5 mmol) in dry toluene (80 mL) under an argon atmosphere. The mixture was cooled to 0 °C in an ice bath, and tributylphosphine (0.74 mL, 3 mmol) was injected to the stirred solution. The mixture was kept at room temperature for 20 h. After evaporation of the solvent, chloroform (30 mL) was added to the reaction mixture, and washed with 10% aqueous NaOH, water, and brine. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the product purified by column chromatography. Elution with *n*-hexane yields two separate fractions containing products of bis- and monosubstitution.

A mixed sulfide–selenide derivative **10** was prepared from (1*R*,2*S*)-2-phenylselenylcyclohexanol **8** using the Hata reaction as described above (Section 4.2), using 0.58 mmol of **8**, 2.35 mmol of tributylphosphine, and 1.76 mmol of diphenyldisulfide.

4.3.1. (1*S*,2*R*)-2-Phenylselenylcyclopentanol 6. Yield 37%, de = 100%. $[\alpha]_D = +49.3$ (*c* 1.52, CH_2Cl_2) >95% ee. IR(film): 3439, 2962, 2869, 1579, 1478, 1437, 1301, 1022, 1007, 738, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.61–1.65 (m, 1H, cyclopentane ring), 1.75–1.81 (m, 2H, cyclopentane ring), 1.88–1.92 (m, 2H, cyclopentane ring), 2.08–2.13 (m, 1H, cyclopentane ring), 2.48 (s, 1H, OH), 3.49–3.54 (m, 1H, cyclopentane ring), 4.07 (br s, 1H, cyclopentane ring), 7.12–7.28 (m, 3H, ArH), 7.55–7.65 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 22.4, 29.8, 32.5, 52.5 (CHSe), 72.9 (CHOH), 127.9, 129.6, 134.1, 134.2; ^{77}Se NMR ($CDCl_3$): δ 254.3. Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found: C, 54.55; H, 5.74. R_f 0.25 (hexane/ethyl acetate = 9:1).

4.3.2. (1*R*,2*R*)-1,2-Bis(phenylselenyl)cyclopentane 7. Yield 43%, de = 100%. $[\alpha]_D = -18.0$ (*c* 1.00, CH_2Cl_2) >95% ee. IR(film): 3375, 3069, 3055, 2958, 2931, 2870, 1578, 1476, 1437, 1150, 1022, 736, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.76–1.87 (m, 4H, cyclopentane ring), 2.39–2.47 (m, 2H, cyclopentane ring), 3.75–3.77 (m, 2H, CHSe), 7.16–7.36 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$): δ 23.8 (C-4), 31.5 (C-3, C-5), 49.4 (C-1,C-2), 127.7, 129.5, 129.6, 134.5; ^{77}Se NMR ($CDCl_3$): δ 401.4. Anal. Calcd for $C_{17}H_{18}Se_2$: C, 53.70; H, 4.77. Found: C, 53.64; H, 4.85. R_f 0.68 (hexane/ethyl acetate = 9:1).

4.3.3. (1*R*,2*S*)-2-Phenylselenylcyclohexanol 8. Yield 25%, de = 100%. $[\alpha]_D = -8.3$ (*c* 1.08, CH_2Cl_2) >95% ee. IR-(film): 3445, 2933, 2855, 1578, 1477, 1437, 991, 739, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.29–1.33 (m, 2H, cyclohexane ring), 1.53–1.86 (m, 6H, cyclohexane ring), 2.36–2.37 (d, 1H, $J = 4.7$ Hz, OH), 3.41–3.44 (m, 1H, cyclohexane ring), 3.62–3.64 (m, 1H, cyclohexane ring), 7.15–7.20 (m, 3H, ArH), 7.47–7.50 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 21.0, 24.5, 29.1, 32.5, 53.7 (CHSe), 68.3 (CHOH), 127.5, 127.7, 129.2, 134.5; ^{77}Se NMR ($CDCl_3$): δ 355.5. Anal. Calcd for $C_{12}H_{16}OSe$: C, 56.47; H, 6.32. Found: C, 56.55; H, 6.24.

4.3.4. (1*S*,2*S*)-1,2-Bis(phenylselenyl)cyclohexane 9. Yield 23%, de = 100%. $[\alpha]_D = +90.8$ (*c* 0.98, CH_2Cl_2) >95% ee. Spectral characteristics in agreement with the literature data for *rac*-**9**.[12] IR(film): 3068, 2931, 2852, 1578, 1476, 1436, 1173, 1022, 999, 737, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.39–1.54 (m, 4H, cyclohexane ring), 1.72–1.77 (m, 2H, cyclohexane ring), 2.21–2.23 (m, 2H, cyclohexane ring), 3.47–3.49 (m, 2H, CHSe), 7.09–7.18 (m, 6H, ArH), 7.31–7.34 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$): δ 24.2, 30.5, 47.7 (C-1,C-2), 127.5, 129.1, 129.6, 134.7; ^{77}Se NMR ($CDCl_3$): δ 393. Anal. Calcd for $C_{18}H_{20}Se_2$: C, 54.83; H, 5.11. Found: C, 55.14; H, 5.10.

4.3.5. (1*S*,2*S*)-1-Phenylsulfanyl-2-phenylselenylcyclohexane 10. Yield 42%; >98% de; $[\alpha]_D = +100.0$ (*c* 0.91, CH_2Cl_2) >95% ee. Spectral characteristics in agreement with the literature data for *rac*-**10**.[13] IR(film): 3070, 3056, 2932, 2853, 1579, 1476, 1437, 1023, 738, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.20–1.67 (m, 6H, cyclohexane ring), 2.17–2.26 (m, 2H, cyclohexane ring), 3.30–3.40 (m, 2H, cyclohexane ring), 7.14–7.25 (m, 8H, ArH), 7.39–7.42 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 22.4, 23.3, 29.2, 29.3, 45.6, 49.5, 125.9, 126.6, 127.9, 128.0, 128.3, 131.1, 133.8, 134.0; ^{77}Se NMR ($CDCl_3$): δ 391.0. Anal. Calcd for $C_{18}H_{20}Ss$: C, 62.24; H, 5.80, S, 9.23. Found: C, 62.02; H, 5.74, S 9.70. R_f 0.23 (*n*-hexane).

4.4. Preparation of xanthic derivative

A similar procedure as for sulfide preparation (Section 4.2) was used with 1.0 mmol of *trans*-1,2-cyclohexanol **2**, 8.0 mmol of tributylphosphine, and 6.0 mmol of isopropylxanthicdisulfide. Only the product of monosubstitution was observed.

4.4.1. (1*S*,2*R*)-*O*-Isopropyl-*S*-(2-hydroxycyclohexyl) dithiocarbonate 11. Yield 54%, de = 100%. $[\alpha]_D = -27.9$ (*c* 1.02, CH_2Cl_2) >95% ee. IR(film): 3416, 2981, 2940, 2864, 1453, 1354, 1275, 1248, 1176, 1110, 1057, 963, 908, 834, 619 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.23–1.39 (m, 10H), 1.69–1.72 (m, 2H), 2.01–2.06 (m, 1H), 2.20–2.24 (m, 2H), 3.69–3.77 (m, 1H), 4.99–5.04 (m, 1H), 5.42 (septet,

1H, $J = 6.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 21.7, 24.1, 24.2, 29.5, 33.2, 72.9, 77.9, 86.9, 194.9 (C=S). HRMS (ESI) calcd for $C_{10}H_{19}O_2S_2$ ($[M+H]^+$) 235.0818, found 235.0771. R_f 0.22 (hexane/ethyl acetate = 9:1).

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