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Preparation of *meso*-1,3-diphenylallyllithium·(−)-sparteine—its crystal structure and reactions

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Abstract—The X-ray crystal structure of 1,3-diphenylallyllithium, complexed with enantiomerically pure (−)-sparteine, was determined. The crystallized complex is stereohomogeneous. Its subsequent electrophilic substitution reactions proceed with low enantioselectivity.

1. Introduction

Research into enantioselective synthesis is a prospering field of activity and has become the subject increasing attention in recent times. Within this research area, external chiral induction by cations bearing chiral ligands is a widely used methodology.[1] Different chiral ligands are used for chiral modification of organometallic reagents, and the commercially available diamine, (−)-sparteine **1**[2] has demonstrated its value particularly in enantioselective synthesis with organolithium compounds.[3]

Structural information about (−)-sparteine-modified allyllithium species is still very scarce. Two solid-state characterizations of (−)-sparteine-modified allyllithium compounds **2**[4] and **3**[5] from our laboratory and the structure of the cinnamyllithium derivative **4**[6] reported by Beak et al. (Fig. 1) provide an unambiguous link between stereostructure and the stereochemical course of electrophilic substitutions.[3b]

We thought of modifying a symmetrical allyllithium compound with a non-racemic chiral ligand in order to achieve a differentiation between originally enantiotopic positions in the anion. This concept was very successfully applied to the chiral modification of *meso*-allylpalladium complexes.[7] 1,3-Diphenylprop-2-enyl acetate is one of the most frequently used substrates for testing Pd-catalyzed asymmetric C–C bond formations;[8] the intermediate Pd–allyl complexes **5** contain a symmetrical allyl cation (Scheme 1). Structure determination for complexes **5** revealed unsymmetrical η^3-bonding of palladium as one origin of stereospecific addition of nucleophiles to yield enantioenriched products **6**. The analogous allyllithium complex **7** is an umpoled version (Scheme 1). To the best of our knowledge, up to now, no crystal structure of a chirally modified allyllithium compound with an acyclic symmetrical carbon skeleton has been reported.[9]

Encouraged by the results obtained with species (1*S*)-**3**[5] we investigated the chiral modification of complex **7** with diamine **1**.

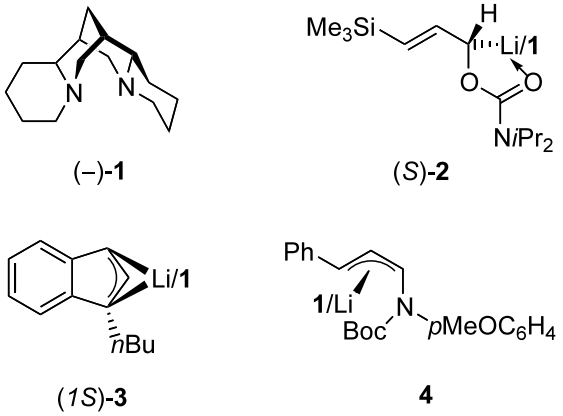

Figure 1. (−)-Sparteine allyllithium complexes.

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† X-Ray structure analysis.

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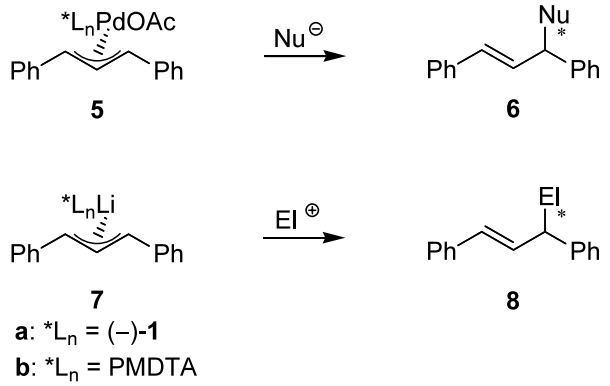


Scheme 1. Reactions of complexes of *meso*-ions of 1,3-diphenylpropene. PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

2. Results and discussion

1,3-Diphenylpropene is deprotonated smoothly with *n*-butyllithium in the presence of an amine ligand in various solvents at −78°C, the allyllithium **7a** is formed in the presence of (−)-sparteine. Crystals of **7a** suitable for X-ray structure analysis were obtained by deprotonation in concentrated solution in THF, addition of some diethyl ether at −20°C and slowly warming the reaction mixture to room temperature. Allyllithium **7a** crystallizes in space group *P*1. The unit cell contains four almost identical molecules, one of which is depicted in Fig. 2.[10]

The lithium cation in homochiral crystals of allyllithium **7a** possess (*R*) configuration,[11] it is bound to the allylic carbon atoms in a η^3-fashion as was seen for indenyllithium (1*S*)-**3**. The angles of the carbon atoms chain C76–C80 in (*R*)-**7a** of 127.5±0.5° are very similar, indicating a uniform hybridization. The allylic carbon atoms C77–C79 are in a planar vicinity (angular sums of 360.1, 360.0, and 360.0 and 359.9–360.1° for the other three molecules in the unit cell) pointing out ideal sp^2-hybridization as a consequence of charge delocalization in the allylic unit. The Li–N bond lengths of 2.008 and 2.018 Å are very similar. The different bond lengths of the lithium cation to the allylic unit are important: The C79–Li bond (2.458 Å) is substantially longer than the C78–Li bond (2.225 Å) and the C77–Li bond (2.213 Å). [For indenyllithium (1*S*)-**3** bond lengths of 2.432 Å (C1–Li) and 2.334 Å (C3–Li) were found.][5] In addition, the C77–C78 bond (1.392 Å) is marginally longer than the C78–C79 bond (1.380 Å), indicating that the negative charge of the allylic anion might be slightly displaced towards C77. The enantiomeric ratio of the substitution products is determined by the facial *and* regioselectivity of the attack by the electrophile at the diastereotopic carbon moieties C77 and C79. The mode of selection is demonstrated for the deuteration in Scheme 2 (the allyllithium is drawn orthogonally to the paper plane): Attack in (*R*)-**7a** at C77 (the right side), suprafacially to the lithium cation, leads to (*S*)-**8** (path a); an antarafacial attack can lead to the same product (*S*)-**8** if it occurs at the other end of the allyllithium (at C79; path a′). After epimerization of the complex (e.g. by rotation of the *meso*-allyl anion by 180 degrees around its horizontal axis) towards (*S*)-**7a**, electrophilic attack along these trajectories (now named b at C77 and b′ at C79, respectively) leads to the enantiomeric product (*R*)-**8**.

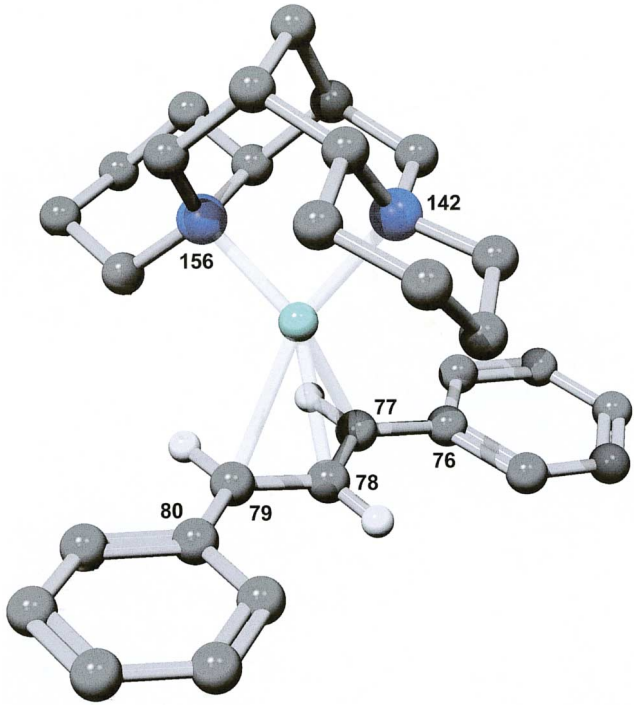
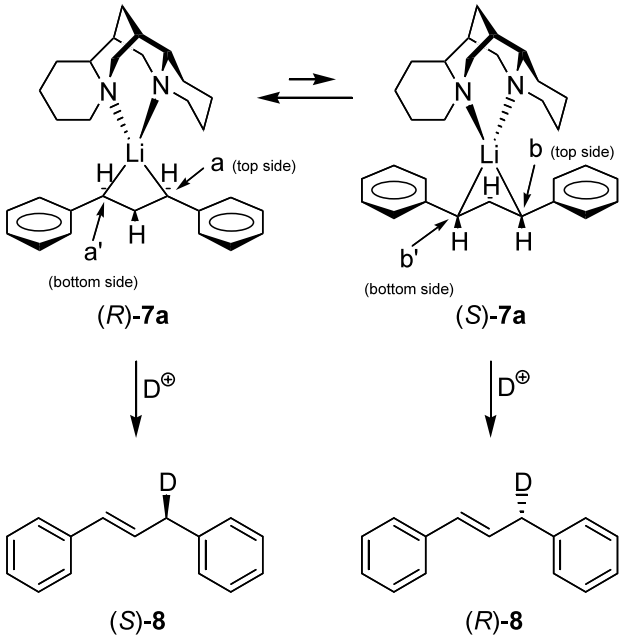


Figure 2. X-Ray crystal structure of complex (*R*)-**7a**.



Scheme 2. Stereochemical aspects of substitution at (−)-sparteine-complexed *meso*-allyllithium.

Since electrophilic substitution on the asymmetric η^3-coordinated allylic unit in crystalline indenyllithium (1*S*)-**3**[5] leads to very high ee's of the products (the same is true for some complexes **5**[8]), we expected a regioselective electrophilic attack on readily crystallizing complex (*R*)-**7a**, providing enantioenriched products **8**. Such crystallization is observed for allylic species (*S*)-**2** and (1*S*)-**3**, too. In the latter two cases a dynamic kinetic resolution process occurred in the course of the crystallization[12] leading to virtually homochiral allyllithium reagents; we expected the same behavior for (*R*)-**7a**.

Racemic allyllithium **7b** ($L_n = N,N,N',N'',N''$-pentamethyldiethylenetriamine; PMDTA) and the allyllithium complex (*R*)-**7a** were reacted with different electrophiles, yielding substitution products **8** in good yields (Table 1). Unfortunately the determined ee's of the isolated acetone adduct (−)-**8a**, and allylsilane **8h** are quite low (Table 1, entries 2, and 12-13). The specific rotation of other enantioenriched products is also negligible (only two from many examples are given: Table 1, entries 9 and 11).

The crystallization of **7a** is almost quantitative, as was checked by crystallization at rt (removal of the mother liquor with two additional washings with pentane) and drying the crystals in vacuo; 95% of the sparteine complex by weight was isolated (Table 1, entry 7).[15] Presumably the employed electrophiles do not differentiate the diastereotopic positions of complex (*R*)-**7a** in an effective manner or show a lack of facial selectivity. In addition, a base-mediated racemization is possible for the highly acidic products **8b** and **8c**. Interestingly, addition of **7a** from homogenous solution in toluene onto acetone yields adduct (+)-**8a** with opposite absolute configuration (Table 1, entry 3). It cannot be excluded, that (*S*)-**7a** is the predominant—or more reactive—species in solution formed from re-dissolved (*R*)-**7a**. Semi-empirical calculations of (*R*)-**7a** and (*S*)-**7a** show only a very small difference in their relative energies (approx. 1 kJ/mol),[16] and thus, epimerization seems likely. Replacing the solvent after crystallization with pentane, which should dissolve the solid complex (*R*)-**7a** less readily, or reacting the dried crystals with acetone in only a small amount of solvent failed to enhance the enantioselectivity (Table 1, entries 6-7). The transmetallation of lithium for titanium is often the method of choice for stereo- and regioselective addition to carbonyl compounds.[17] For (*R*)-**7a**, addition of $Ti(O\textit{i}\text{-}Pr)_4$ or $Cl(O\textit{i}\text{-}Pr)_3$ had no impact on stereoselectivity (Table 1, entries 4-5).

The inversion of the configuration of silane **8h** by changing the silylation reagent from chlorotrimethylsilane to trimethylsilyl triflate emphasizes the sensibility of the stereochemical course of the electrophilic substitution regarding changes of the reaction conditions (Table 1, entries 12-13). Changes in enantiofacial differentiation in electrophilic substitutions have also been observed for an cinnamyllithium[18] and a benzyllithium.[19]

The following reasons may account for the lack of stereoselectivity in the electrophilic attack: Rapid interconversion between the epimers (*R*)- and (*S*)-**7a** in solution, minor diastereofacial selectivity, and/or inadequate enantiotopos differentiation between the position C77 and C79. Obviously, the loose electrostatic connection between the chiral cation and the well-stabilized carbanion is insufficient to support stereoselective reactions.

Table 1. Electrophilic substitution in diethyl ether

Entry	Complex	Electrophile	El	Product	Yield (%)	$[\alpha]_D^{20}$ ($CHCl_3$)	e.r.
1	**7b**	Acetone	$COHMe_2$	*rac*-**8a**	75	–	–
2	**7a**	Acetone	$COHMe_2$	(−)-**8a**	73	−11.5	54.5:45.5 (9% ee)
3[a]	**7a**	Acetone	$COHMe_2$	(+)-**8a**	42	n.d.[b]	60.5:39.5 (21% ee)
4[c]	**7a**	Acetone	$COHMe_2$	(−)-**8a**	74	−9.9	54:46 (8% ee)
5[d]	**7a**	Acetone	$COHMe_2$	(−)-**8a**	40	−10.4	54:46 (8% ee)
6[e]	**7a**	Acetone	$COHMe_2$	(−)-**8a**	64[f]	−8.9	53.5:46.5 (7% ee)
7[g]	**7a**	Acetone	$COHMe_2$	(−)-**8a**	45[f]	−6.0	52.5:47.5 (5% ee)
8	**7b**	$ClCO\textit{t}\text{-Bu}$	$CO\textit{t}\text{-Bu}$	*rac*-**8b**	86	–	–
9	**7a**	$ClCO\textit{t}\text{-Bu}$	$CO\textit{t}\text{-Bu}$	(+)-**8b**	45	+0.3	n.d.[b]
10	**7b**	*p*-TsSPh	SPh	*rac*-**8c**	86	–	–
11	**7a**	*p*-TsSPh	SPh	(+)-**8c**	62	+0.5	n.d.[b]
12	**7a**	$ClSiMe_3$	$SiMe_3$	(*R*)-**8d**[h]	63	−1.9	52.5:47.5 (5% ee)[14]
13	**7a**	$TfOSiMe_3$	$SiMe_3$	(*S*)-**8d**	84	+7.3	61:39 (22% ee)[14]

[a] Performed in homogenous solution in toluene.
[b] n.d. = not determined.
[c] Addition of 4.3 equiv. $Ti(\textit{i}\text{-}PrO)_4$ 1 h prior to acetone.
[d] Addition of 1.8 equiv. $ClTi(\textit{i}\text{-}PrO)_3$ 1 h prior to acetone.
[e] The ether was displaced after the crystallization by pentane at rt, acetone was added at −78°C.
[f] The mother liquor of the crystallization—free from crystalline **7a**—led to 10% of (−)-**8a** with e.r. of 52.5:47.5 (5% ee).
[g] The ether was removed after the crystallization, the residue (washed with pentane) was dried in vacuo (0°C) and acetone/pentane (1: 1) was added at −78°C.
[h] Isolated as a mixture with 15% of the starting material.

3. Conclusion

In summary, we have determined the first X-ray structure of a *meso*-allyllithium compound in a complex with a non-racemic chiral diamine. Lithium/(−)-sparteine is bonded unsymmetrically in η^3-fashion in crystalline (*R*)-**7a**. However, at this time the products **8**, isolated from electrophilic substitutions on (*R*)-**7a** show only low enantiomeric purities.

4. Experimental

4.1. General

All solvents were dried and purified prior to use: Toluene and Et_2O were distilled from sodium benzophenone ketyl, THF was distilled from potassium benzophenone ketyl. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDTA) was distilled from powdered CaH_2 and stored under Ar in the dark. Acid chlorides were distilled prior to use, chlorotrimethylsilane was distilled from powdered calcium hydride, and acetone was dried by heating over phosphorus pentoxide and subsequent distillation. *n*-Butyllithium (ca. 1.6 molar in hexanes) was purchased from Acros; the content of *n*-BuLi was determined by titration.[20] All other commercially available reagents were used as received. All reactions were performed under an atmosphere of Ar in flame-dried glassware. Flash column chromatography (FCC) was performed on Merck silica gel 60, 0.040–0.063 mm, and monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F_{254}; PE = light petroleum ether, bp 36–46°C. NMR: Bruker ARX 300, AM 360 (NOE experiments), and AMX 400 (routine 2D spectra); spectra from solutions in $CDCl_3$ ($\delta_C = 77.0$ ppm) are calibrated to $SiMe_4$ ($\delta_H = 0.00$ ppm). IR: Nicolet 5 DXC. MS: Finnigan MAT 8200 (EI); Finnigan MAT 8230 (GC–MS); Varian Saturn II (GC–MS). Optical rotations: Perkin–Elmer 341 polarimeter. Melting points: Gallenkamp MFB 595 (uncorrected values). Elemental analysis: Elementar Analysensysteme Vario EL III. GC: Hewlett–Packard 5890, 25 m×0.2 mm HP 1, 107 kPa pre-column pressure N_2, 1 min at 50°C/10°C×min^{-1}/15 min at 290°C; Agilent 6890, 30 m×0.32 mm HP 5, 1.5 mL×min^{-1} H_2, start at 50°C/10°C×min^{-1}/30 min at 300°C; Hewlett–Packard 6890, 25 m×0.2 mm HP 1701, 100 kPa pre-column pressure N_2, 1 min at 50°C/10°C×min^{-1}/20 min at 270°C. HPLC: A) Knauer WellChrom Maxi-Star K-1000 pump with mixing unit A0285 and spectral photometer A0293 at 220 nm; B) Waters 600E Multisolvent Delivery System and 996 photodiode array detector.

4.2. Electrophilic substitutions

4.2.1. Synthesis of 1,3-diphenylpropene (DPP). DPP was synthesized by self-condensation of phenylacetaldehyde and purified by distillation and subsequent FCC (with pentane) providing the alkene as a colorless viscous liquid in 74% yield.[21] $R_f = 0.33$ (PE), $R_f = 0.57$ (E/PE, 1:20); t_r (HP 5) = 14.4 min. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.49$ (d, 2H, $3CH_2$); 6.31 (dt, 1H, 2CH); 6.42 (d, 1H, 1CH); 7.10–7.33 (m, 10H, ArCH). $J_{1,2} = 15.7$ Hz, $^3J_{2,3} = 6.2$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 39.29$ ($3CH_2$); 126.13, 127.04, 128.46, 128.63, 129.16, 131.09 (CH); 137.49, 140.12 (ArC). IR (film): $\tilde{\nu} = 3090$ w, 3060 m, 3030 s, 2900 w, 1600 m, 1500 s, 1430 m, 970 s, 750 s, 700 s cm^{-1}. GC–MS (EI [70 eV]): *m*/*z* (%) = 194 (65) [M$^+$]; 193 (39); 179 (32) [{M−CH_3}$^+$]; 178 (24); 116 (54); 115 (100); 103 (27) [{M−$PhCH_2$}$^+$]; 91 (55) [tropyllium: $C_7H_7^+$]; 65 (34) [$C_5H_5^+$]; 51 (23) [$C_4H_4^+$]; 39 (15) [from Ph$^+$].

4.2.2. Preparation of the (−)-sparteine complex, 7a. A solution of (−)-sparteine (420 mg, 1.8 mmol, 1.2 equiv.) in Et_2O (11 mL) in a flask sealed with a rubber septum was cooled to −78°C. *n*-BuLi (1.10 mL, 1.6 molar solution in hexane, 1.76 mmol, 1.17 equiv.) was added dropwise with stirring. After 15 min a solution of 1,3-diphenylpropene (290 mg, 1.50 mmol) in ether (3 mL) was added dropwise and stirring was continued for 30 min at −78°C. The flask was removed from the cooling bath and the reaction mixture was slowly stirred for 30 min at rt. Then the flask was placed back into the dry ice/acetone bath and after additional 30 min a solution of the electrophile (1–5 equiv.) was added and stirring was continued for 2–20 h. A solution of HOAc (2.0 mL, 1.0N in ether, 2.0 mmol, 1.3 equiv.) was added at −78°C, then the reaction mixture was warmed to rt. The diamine was extracted with aqueous HCl (20 mL, 2.0N) and the aqueous layer was extracted with ether (3×20 mL). The combined organic layers were washed with water (20 mL), dried over $MgSO_4$, filtered and the ether was removed in vacuo. The resulting residue was subjected to flash column chromatography (Merck silica gel 60, 0.040–0.063 mm; gradient Et_2O/light petroleum ether bp 36–46°C) yielding the product **8**, characterized by NMR, IR, and elemental analysis.

4.2.3. (*E*)-1-Methyl-3,5-diphenyl-4-penten-2-ol, 8a. Compound **8a** was obtained from 1.5 mmol DPP by the given procedure employing PMDTA as ligand and 5.0 mmol (0.37 mL, 3.4 equiv.) acetone as electrophile (2 h at −78°C). FCC (66 ccm) with E/PE 1:1 lead to *rac*-**8a** (282 mg, 1.12 mmol, 75%) as colorless resin-like material. The enantioenriched samples were synthesized in the same manner, some of them employing a transmetallation to titanium; conditions, yields, and enantioenrichments are given in Table 1. The ees of enantioenriched samples were determined on a Bayer ZWE-805 HPLC column (4×250 mm; 0.5 mL/min 1:40:460 H_2O/THF/cyclohexane; $t_r = 10/11$ min). $[\alpha]_D^{20} = -11.5$; $[\alpha]_{578}^{20} = -12.2$; $[\alpha]_{546}^{20} = -14.5$; $[\alpha]_{436}^{20} = -31.3$; $[\alpha]_{365}^{20} = -70.9$ (*c* 1.0, $CHCl_3$, at e.r. = 55.5: 44.5 (9% ee)). $R_f = 0.14$ (E/PE, 1:5), $R_f = 0.45$ (E/PE, 1:1); t_r (HP 5) = 17.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ (s, 3H, CH_3); 1.25 (s, 3H, CH_3'); 1.57 (s, 1H, OH); 3.42 (d, 1H, 3CH); 6.48 (d, 1H, 5CH); 6.68 (dd, 1H, 4CH); 7.14–7.43 (m, 10H, ArCH). $^3J_{3,4} = 9.5$ Hz, $^3J_{4,5} = 15.7$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.87$ (1CH_3); 28.14 (2-CH_3'); 60.86 (3CH); 72.69 (2C); 126.23, 126.67, 127.28, 128.29, 128.46, 129.13, 129.43, 132.74 (CH); 137.29, 141.26 (ArC). IR (film): $\tilde{\nu} = 3570$ s, 3450 br s, (OH); 3090 w, 3060 m, 3030 s, 2970 s, 2930 m, 2890 w,

1600 s, 1500 s, 1450 s, 1370 s, 1160 s, 970 s, 750 s, 700 s cm^{-1}. MS (EI [70 eV]): m/z (%) = 194 (100) [McLafferty: {M–acetone}$^+$]; 179 (18); 115 (33); 91 (18) [tropyllium: $C_7H_7^+$]; 59 (56) [i-PrOH$^+$]. $C_{18}H_{20}O$ (M = 252.36 g/mol): calcd C, 85.67; H, 7.99. Found: C, 85.53; H, 7.97.

4.2.4. (*E*)-2,2-Dimethyl-4,6-diphenyl-5-hexen-3-one, 8b. Compound **8b** was synthesized by the given procedure employing PMDTA or (–)-sparteine, respectively. The reaction mixture was neutralized 1 h after the addition of 2,2-dimethylpropanoyl chloride; FCC (63 ccm) of the crude products with E/PE 1:20 lead to ketone **8b** (360 mg, 1.29 mmol; 86% for the racemate; 194 mg, 0.70 mmol, 45% for (+)-**8b**) as colorless crystals.

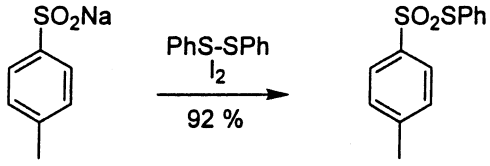
$[\alpha]_D^{20} = +0.3$; $[\alpha]_{578}^{20} = +0.2$; $[\alpha]_{546}^{20} = +0.4$; $[\alpha]_{436}^{20} = +1.0$; $[\alpha]_{365}^{20} = +2.9$ (c 0.97, $CHCl_3$; e.r. not determined). Mp = 106°C (PE/Et_2O). $R_f = 0.36$ (E/PE, 1:20); t_r (HP 5) = 18.3 min. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.17$ (s, 9H, t-Bu(CH_3)$_3$); 5.01 (d, 1H, 4CH); 6.41 (d, 1H, 6CH); 6.54 (dd, 1H, 5CH); 7.14–7.40 (m, 10H, ArCH). $^3J_{4,5} = 8.3$ Hz, $^3J_{5,6} = 15.7$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 26.42 (t-Bu(CH_3)); 45.53 (t-BuC); 56.01 (4CH); 126.37, 127.04, 127.48, 128.19, 128.46, 128.73, 130.01, 131.15 (CH); 136.88, 139.11 (ArC); 213.38 (C=O). IR (KBr): $\tilde{\nu} = 3090$ w, 3070 m, 3030 s, 2970 s, 2930 m, 2870 w, 1700 s, ν (C=O), 1600 s, 1490 s, 1450 s, 1370 m, 970 s, 750 s, 690 s cm^{-1}. MS (EI [70 eV]): m/z (%) = 278 (2) [M$^+$]; 193 (100) [{M–t-Bu(CO)}$^+$]; 178 (10); 115 (39); 91 (16) [tropyllium: $C_7H_7^+$]; 85 (9) [t-Bu(CO)$^+$]; 57 (60) [t-Bu$^+$]. $C_{20}H_{22}O$ (M = 278.39 g/mol): calcd C, 86.29; H, 7.97. Found: C, 86.14; H, 7.97.

***S*-Phenyl *p*-toluenethiosulfonate**[22] was synthesized from p-toluenesulfinic acid sodium salt and 0.5 equiv. diphenyl disulfide in CH_2Cl_2 in the presence of iodine (0.5 equiv.) at rt according to Scheme 3. Purification by FCC with E/PE gave the pure thio ester as colorless crystals in 92% yield.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.41$ (s, 3H, p-CH_3); 7.20 (d, 2H, ArCH); 7.28–7.40, 7.41–7.51 (each m, 4H+3H, ArCH). $^3J_{Ar,Ar} = 8.3$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.59$ (p-CH_3); 127.58 (o-ArCH); 128.10 (1PhC); 129.34 (o-/m-PhCH); 131.25 (p-PhCH); 136.54 (m-ArCH); 140.40 (1ArCH); 144.67 (p-ArCH); 126.84 (o-ArCH); 129.71 (m-ArCH); 140.63 (1ArC); 144.73 (p-ArC). $C_{13}H_{12}O_2S_2$ (M = 264.36 g/mol).

4.2.5. (*E*)-1,3-Diphenyl-1-prop-2-enyl phenyl sulfide, 8c. Compound **8c** was formed by reaction of the allyllithium (1 mmol) with 2.0 equiv. S-phenyl p-toluenethiosulfonate in ether, allowing the reaction mixture to warm slowly (approx. 6 h) to rt after 1 h at –78°C. Purification by FCC (53 ccm) with E/PE (gradient 1:50→1:10) lead to phenyl thioether **8c** (259 mg, 0.86 mmol, 86% *rac*-**8c** and 185 mg, 0.62 mmol, 62% in the presence of (–)-sparteine, respectively) as colorless crystals. $[\alpha]_D^{20} = +0.4$; $[\alpha]_{578}^{20} = +0.5$; $[\alpha]_{546}^{20} = +0.6$; $[\alpha]_{436}^{20} = +0.6$; $[\alpha]_{365}^{20} = +2.0$ (c 1.02, $CHCl_3$). $R_f = 0.56$ (E/PE, 1:50). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.92$ (d, 1H, 1CH); 6.29 (d, 1H, 3CH); 6.46 (dd, 1H, 2CH); 7.13–7.43 (m, 15H, ArCH). $^3J_{1,2} = 8.2$ Hz, $^3J_{2,3} = 15.6$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 56.62$ (1CH); 126.42, 127.42, 127.55, 127.95, 128.44, 128.62, 128.69, 129.16, 131.52, 133.08 (2CH/3CH/ArCH); 134.87, 136.70, 140,24 (ArC). MS (EI[70 eV]): m/z (%) = 302 (0.2) [M$^+$]; 193 (100) [{M–SPh}$^+$]; 115 (67); 91 (24) [tropyllium: $C_7H_7^+$]. $C_{21}H_{18}S$ (M = 302.43 g/mol): calcd C, 83.39; H, 6.00. Found: C, 83.17; H, 5.78.

4.2.6. (*E*)-1,3-Diphenyl-3-trimethylsilyl-1-propene, 8d[23]. The racemic silane was formed by the silylation of allylic anion **7b** with chlorotrimethylsilane in the presence of PMDTA; FCC (63 ccm) with pentane lead to a mixture of the desired silane *rac*-**8h** (0.88 mmol, 45%) and the starting material (231 mg together) as colorless liquid. In the presence of (–)-sparteine employing the given procedure—employing 0.69 mL (5.5 mmol, 3.7 equiv.) $SiMe_3Cl$ with a reaction time of 6 h—yielded a mixture of (*R*)-(*E*)-**8d** (0.95 mmol, 63%) and some starting material (286 mg together); the use of trimethylsilyl trifluoromethanesulfonate in this protocol lead to (*S*)-(*E*)-**8d** (see Table 1). $[\alpha]_D^{20} = -1.9$; $[\alpha]_{578}^{20} = -2.1$; $[\alpha]_{546}^{20} = -2.3$; $[\alpha]_{436}^{20} = -4.4$ (c 1.07, benzene); representing 5% *op* for pure (*R*)-(*E*)-**8d**.[23a] $R_f = 0.33$ (PE), $R_f = 0.57$ (E/PE, 1:20); t_r (HP 5) = 16.6 min. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.03$ (s, 9H, $SiMe_3$); 3.08 (d, 1H, 3CH); 6.32 (d, 1H, 1CH); 6.55 (dd, 1H, 2CH); 7.04–7.34 (m, 10H, ArCH). $^3J_{1,2} = 15.7$ Hz, $^3J_{2,3} = 9.9$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = –2.80 ($SiMe_3$); 43.84 (3CH); 124.72, 125.86, 126.57, 127.08, 128.12, 128.36, 128.46, 130.51 (CH); 138.20, 142.31 (ArC). GC–MS (TOF): m/z (%) = 266 (18) [M$^+$]; 115 (20); 73 (100) [$SiMe_3^+$]. $C_{18}H_{22}Si$ (M = 266.45 g/mol).



Scheme 3.

4.3. Supplementary material

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 190371. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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10. Crystallographic data for (*R*)-**9** ($C_{30}H_{39}N_2Li$, M_r = 434.57), collected on an Enraf–Nonius Kappa CCD diffractometer equipped with a rotating anode generator Nonius FR591 and CCD-detector (graphite-monochromatized Mo-Kα-radiation, λ = 71.073 pm) at T = 198 K: color = red, crystal size = 0.40×0.30×0.30 mm, triclinic, space group $P\bar{1}$ (No. 1), a = 9.774(1), b = 10.924(1), c = 24.576(1) Å, α = 86.98(1), β = 79.94(1), γ = 84.01(1)°, V = 2568.0(4) Å^3, Z = 4, ρ_{calcd} = 1.124 g cm^{-3}, μ = 0.64 cm^{-1}, method of absorption correction = SORTAV, absorption correction = min: 97.5% max: 98.1%, 21740 reflections collected ($\pm h \pm k \pm l$), 1.68°<θ<24.74°, 13278 independent reflections, R_{int} = 0.050, 8845 observed reflections [$I \geq 2\sigma I$], 1189 refined parameters, R = 0.054, R_w^2 = 0.126, max. residual electron density ρ = 0.19 (−0.24) e Å^{-3}, Flack parameter = −2(2).
11. The (−)-sparteine is not C_2-symmetric, and therefore the complex **7** does not possess a mirror plane: consequently, the lithium centre is stereogenic (and is not a *pseudo*-stereogenic centre) in the complex investigated.
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