Regio- and Stereoselective Ring-Opening Reactions of Chiral Substituted Spiro[2.4]hepta-4,6-dienes: A New, Simple, and Versatile Approach to the Synthesis of Optically Active Bidentate Cyclopentadienyl−Phosphine Ligands. X-ray Crystal Structure of (*S*)-[Rh(η^2-C_2H_4)(η^5-$C_5H_4CH_2CHPhPPh_2$-κP)]

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Summary: The ring-opening reaction of (S)-1-phenylspiro-[2,4]hepta-4,6-diene with $LiPPh_2$ proceeds with full regio- and stereoselectivity, taking place at phenyl-substituted carbon and with complete inversion of the configuration at the stereogenic center, yielding (S)-[Li-($C_5H_4CH_2CHPhPPh_2$)]. Optically active complexes of rhenium, rhodium, zirconium, and iron with this new chiral bidentate ligand have been prepared; additionally, the X-ray crystal structure of (S)-[Rh(η^2-C_2H_4)(η^5-C_5H_4-$CH_2CHPhPPh_2$-κP)] is reported.

Ligands possessing both a cyclopentadienyl and a heteroatom connected by an appropriate spacer are receiving considerable interest in synthesis and catalysis, as they lead to increased rigidity in a metal complex through additional intramolecular coordination of the heteroatom, avoiding free rotation of the cyclopentadienyl group.[1] For example, half-sandwich complexes of group 4 metals containing linked cyclopentadienyl−amido ligands (the so-called "constrained geometry catalysts", CGC) have already found technological applications.[2] Among the possible heteroatoms, phosphorus has been receiving growing interest in view of the general importance of phosphine ligands in organometallic chemistry and homogeneous catalysis. Available data clearly suggest that the cyclopentadienyl−phosphino ligand, as a (5 + 2)-electron ligand, forms a fairly stable chelate ring with early and late transition metals.[3] Additionally, the introduction of chirality into these systems, in which the phosphorus is coordinated to the metal, may assist in controlling the stereochemistry of reactions taking place at the metal center and therefore could eventually increase the stereoselection in catalytic reactions, particularly if the stereogenic center is in close proximity to the metal. Although recent reports based on such compounds have appeared in the literature,[4] general and simple synthetic procedures for obtaining these hybrid ligands and their metal complexes in optically active form remain relatively undeveloped.

In this communication we describe a new simple general pathway to obtain chiral cyclopentadienyl−phosphine bidentate ligands containing stereogenic centers on the side chain. We have adapted the method first described by Kauffmann, based on opening reactions of spiro[2.4]hepta-4,6-dienes.[5] Traditionally, such substances have been synthesized by bis-alkylation of freshly cracked cyclopentadiene with the corresponding dibromoalkane in the presence of sodium amide or sodium hydride.[6] However, a more convenient approach to introduce chirality into these spiroannulated precursors is the use of the corresponding bis-mesylates or -tosylates as alkylating reagents. Our investigations started with the utilization of (*R*)-1-phenyl-1,2-ethanediol ((*R*)-**1**), which is easily converted into the bis(methane-

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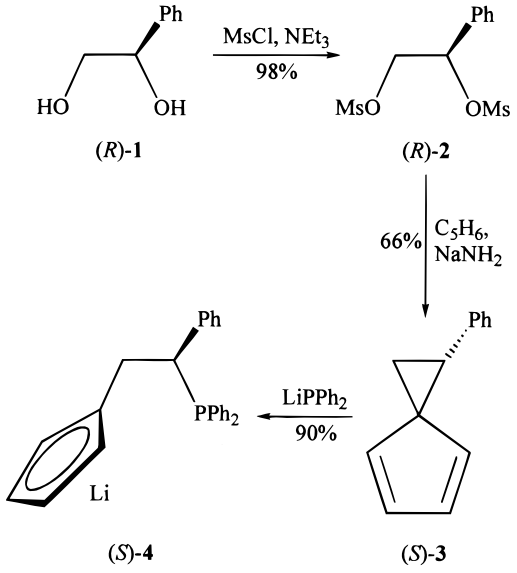
Scheme 1



sulfonate) ester (*R*)-**2** in quantitative yield by reaction with methanesulfonyl chloride (Scheme 1; for experimental details and analytical data see the Supporting Information).

Displacement of the methanesulfonate groups in the intermediate (*R*)-**2** by cyclopentadiene/sodium amide formed the spiroannulated diene (*S*)-**3**.[7] The formation of the spiro compound involves first a mesylate displacement by $Na(C_5H_5)$, followed by a fast deprotonation of the substituted cyclopentadienyl ring, and finally a second mesylate displacement, producing intramolecular cyclization. As a result, both carbons in (*R*)-**2** undergo an S_N2 pathway with complete inversion of configuration at the stereogenic center, as has been shown by Halterman in many examples.[8]

The ring-opening reaction of (*S*)-**3** with $LiPPh_2$ proceeds with complete regiospecificity by attack of the nucleophile at the substituted carbon atom of the cyclopropane ring, bringing the stereogenic center close to the phosphorus atom. Interestingly, this regioselectivity is the opposite to that found for the nucleophilic opening of phenyl epoxide and phenyl episulfide with lithium phosphides, yielding respectively β-hydroxyphosphines and β-mercaptophosphines.[9] Substituted cyclopropanes with electron-withdrawing groups on the other hand are ring-opened at the most substituted bond of the ring.[10] As far as we know, the only precedent for a similar opening reaction of a chiral (but racemic) susbstituted spiro[2.4]hepta-4,6-diene was reported by Rieger in order to synthesize unsymmetrical *ansa*-indenyl and -fluorenyl ligands with chiral ethylene bridges. The regioselectivity found there in the reaction between spiro[(2-phenylcyclopropane)-1,1′-indene] and NaCp was the same as that reported here, with the phenyl group located in a position α to the incoming Cp group.[11] The ring-opening reaction of (*S*)-**3** with $LiPPh_2$ proceeds with complete inversion of the configuration at the stereogenic center, as is demonstrated by characterization of the metal complexes synthesized from the lithium salt (*S*)-**4** (vide infra).

This synthetic pathway has the following advantages.

(i) The chiral precursors are easily available in multigram quantities, particularly after Jacobsen's recent spectacular report on an inexpensive, hydrolytic, kinetic resolution of terminal epoxides which produces optically active monosubstituted 1,2-ethanediols.[12]

(ii) The lithium salt (*S*)-**4** obtained from the opening reaction either can be used directly without further purification to synthesize organometallic complexes.

(iii) The method has been extended by us to chiral, C_2-symmetric 1,2-disubstituted spiro[2.4]hepta-4,6-dienes leading to ligands with stereogenic centers in both positions of the side chain.[13]

(iv) The method can be combined with other ways to introduce chirality into the ligands. For example, the simple opening reaction of the spiroannulated indene derivative reported by Rieger[11] should lead to diastereomeric ligands combining both planar-indenyl-based chirality as well as central chirality on the side chain. Alternatively, opening reactions with chiral nucleophiles might produce ligands combining chirality on the spacer and also chiral information directly attached to the heteroatom.

(v) According to Kauffmann's protocol,[5] the length of the spacer between the cyclopentadienyl ring and the phosphorus could be also modified just by changing the length of the diol precursor. The scope of nucleophiles that can be used in the opening reaction also shows high variability.

The lithium salt (*S*)-**4** was reacted with some metal halide precursors to produce optically active transition-metal complexes. The reaction of 1 equiv of (*S*)-**4** with $[Re(CO)_5Br]$ led to the 18-electron tricarbonylrhenium complex (*S*)-**5** (Scheme 2). The ^{31}P NMR spectrum of the crude product showed only a single resonance at -0.6 ppm, proving the regioselectivity of the opening reaction of (*S*)-**3**. To determine the enantiomeric purity of complex (*S*)-**5**, it was first treated with an excess of BH_3·THF, to protect the phosphorus atom against eventual oxidation and also to increase the polarity of the resulting adduct, (*S*)-**5**·BH_3. The compound (*S*)-**5**·BH_3 was then found to be 97% enantiomerically pure by HPLC.[14] As the diol precursor also had an ee of 97%, the pathway represented in Scheme 1 is fully stereospecific.

(7) To the best of our knowledge, compound **3** in optically active form has not been reported before in the literature. For syntheses of racemic **3**, see for example: (a) Johnson, C. R.; Lockard, J. P.; Kennedy, E. R. *J. Org. Chem.* **1980**, *45*, 264. (b) Reference 6b.

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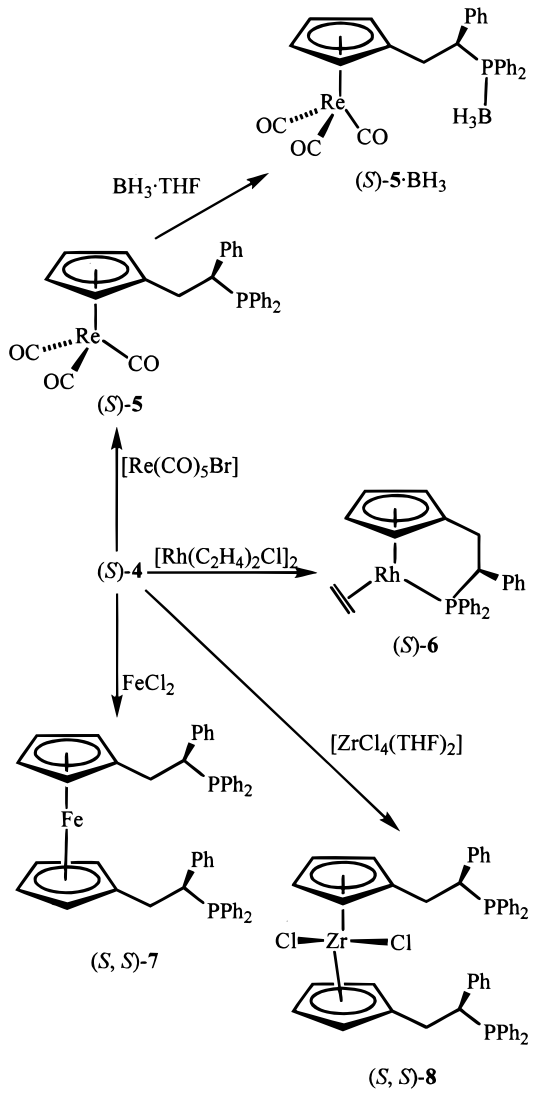
(14) Racemic **5**·BH_3 prepared from racemic 1-phenyl-1,2-ethanediol (**1**) was resolved using the column (*S,S*)-Whelk-01 (4 × 250 mm), 99/1 *n*-heptane/2-propanol as eluent, flow 1 mL/min: t_1 = 10.7 min (*S* enantiomer), t_2 = 11.9 min (*R* enantiomer). The optically active compound (*S*)-**5**·BH_3 was run under the same conditions and was found to be 98.7% *S* enantiomer, 1.3% *R* enantiomer; ee = 97%.

Scheme 2



The reaction of 1 equiv of (*S*)-**4** with $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ led to (*S*)-**6.** The intramolecular coordination of the phosphorus atom in (*S*)-**6** was confirmed by the large coupling constant between phosphorus and rhodium observed in the ^{31}P NMR spectrum ($^1J_{P-Rh} = 217$ Hz). The absolute configuration of (*S*)-**6** could be determined by an X-ray crystal structure analysis and was found to be *S* (Figure 1).[15] This agrees with our expectation, as the opening reaction of (*S*)-**3** normally should proceed again via an S_N2 mechanism, with a backside attack of the nucleophile and with inversion of configuration.

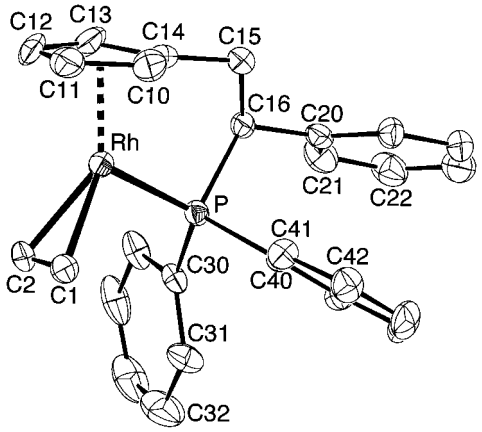


Figure 1. Molecular structure and crystallographic numbering scheme for (*S*)-**6** (PLATON representation). Ellipsoids are scaled to enclose 30% probability.

It is also possible to synthesize sandwich complexes bearing two cyclopentadienyl−phosphine ligands. Reaction of 2 equiv of (*S*)-**4** with $FeCl_2$ or $[ZrCl_4(THF)_2]$ led to the corresponding ferrocene and zirconocene derivatives (*S*,*S*)-**7** and (*S*,*S*)-**8**, both obtained as single enantiomers bearing homochiral ligands, as is shown by their ^{31}P NMR spectra, in which only a single resonance was found. This is another evidence of the stereoselectivity in the opening reaction of (*S*)-**3**. If epimerization took place, the reaction of 2 equiv of the resulting racemic lithium salt with $FeCl_2$ or $[ZrCl_4(THF)_2]$ would yield a mixture of diastereomers and two signals in the ^{31}P NMR spectra would be expected. For example, it has been reported by Erker and co-workers that the reaction of 2 equiv of the related racemic lithium salts $Li[C_5H_4\text{-}CR^1R^2PAr_2]$ with $ZrCl_4$ led to the corresponding zirconocenes as 1:1 diastereomeric mixtures.[4e] The sandwich complexes (*S*,*S*)-**7** and (*S*,*S*)-**8** might be used themselves as chiral C_2 symmetric ligands through coordination of the two phosphine functionalities.[4k,16]

We are currently investigating the application of the optically active complexes presented in this paper for new stereospecific or asymmetric catalytic reactions. We are also concentrating on other transition metals as well as on the synthesis of new ligands containing chiral information not only in the side chain but also at the phosphorus and/or in the cyclopentadienyl ring (planar chiral ligands).

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Supporting Information Available: Text giving experimental procedures, analytical data, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Compound (*S*)-**6**, $C_{27}H_{26}PRh$, crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 9.745(13)$ Å, $b = 14.590(4)$ Å, $c = 15.777(6)$ Å; $V = 2244(3)$ Å^3, and $Z = 4$. Data collection was carried out with a Nonius CAD4 diffractometer at 243 K. Least-squares refinement[17] on F^2 converged at R1 = 0.0446 and wR2 = 0.1147, with an enantiomorph polarity parameter of −0.03(7).[18] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-###. Copies of the data can be obtained free of charge on application to The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. +1223/336-033; E-mail, teched@chemcrys.cam.ac.uk).

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