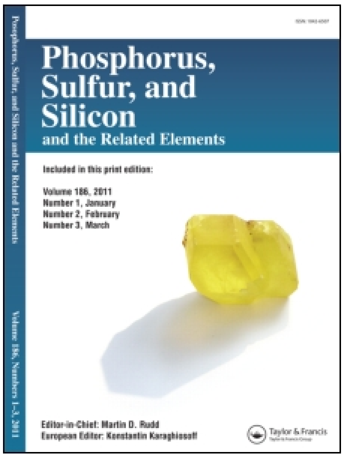

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Chirality Recognition of Selenium Compounds by NMR Spectroscopy in the Presence of a Chiral Dirhodium Complex

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To cite this Article Duddeck, Helmut , Malik, Shahid , Moeller, S. , Gáti, Tamás , Tóth, Gábor and Rozwadowski, Zbigniew(2005) 'Chirality Recognition of Selenium Compounds by NMR Spectroscopy in the Presence of a Chiral Dirhodium Complex', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 993 — 1000

To link to this Article: DOI: 10.1080/10426500590905905

URL: http://dx.doi.org/10.1080/10426500590905905

Phosphorus, Sulfur, and Silicon, 180:993–1000, 2005

ISSN: 1042-6507 print / 1563-5325 online
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*Diastereomeric adducts of chiral soft-base selenium ligands with the enantiopure dirhodium complex **Rh*** allows stereodifferentiation by NMR spectroscopy of various nuclei (dirhodium method). The individual adduct species can be identified by low-temperature NMR spectroscopy.*

Keywords ^{1}H, ^{31}P and ^{77}Se NMR; dirhodium complex; phenylselenenylalkanes; phosphine selenides; variable-temperature NMR

INTRODUCTION

Selenium-containing compounds play an increasing role in modern organic chemistry. Consequently, a substantial number of reviews and monographs were published at the end of the seventies and during the eighties.[1–8] Nowadays, this field is a well-established methodology for functional group transformation, and stereoselectivity and stereospecifity play an ever increasing role.[9,10] In parallel, selenium-77 has attracted a wide NMR spectroscopic interest. A number of reviews and data collections have appeared since the 1980s.[11–17]

Received January 16, 2004; accepted October 8, 2004.

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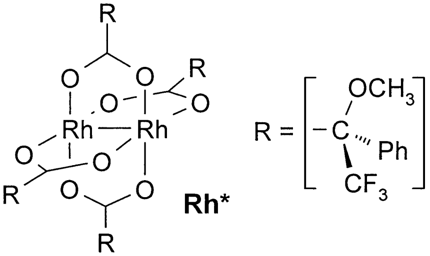
On the other hand, only very few experimental methods exist by which enantiomers of chiral selenium-containing compounds devoid of any other polar functions can be discriminated. We have recently shown that the enantiopure dirhodium complex $Rh_2^{(II)}$[(*R*)-(+)-MTPA$_4$] (**Rh***, MTPA–H ≡ Mosher's acid; see Scheme 1)[18–24] is an excellent chiral solvating agent which—as a soft Lewis acid—is particularly suitable for soft Lewis basic functionalities (dirhodium method). Thereby, it is complementary to the classical chiral lanthanide shift reagents which are hard Lewis acids and, consequently, often fail in forming adducts strong enough for chirality recognition. In an early orienting experiment, we were able to show that chiral selenohydrocarbons can be resolved easily, indeed.[25]

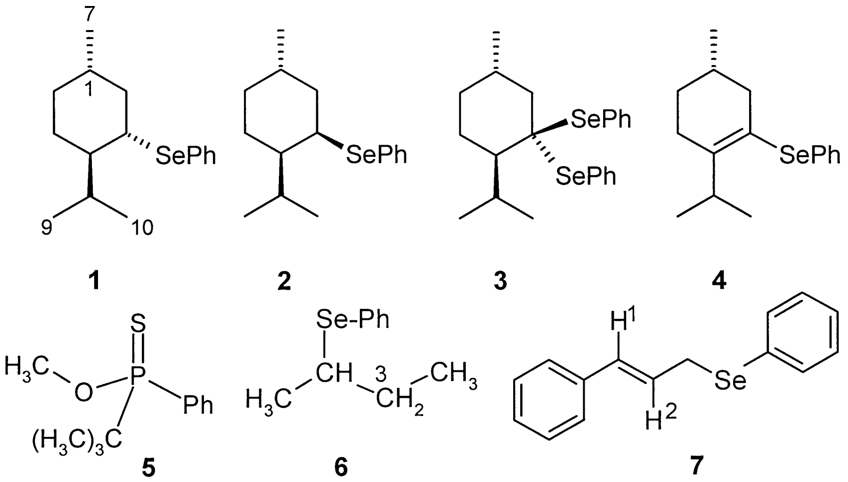


SCHEME 1 Structure of the dirhodium complex **Rh***.

RESULTS AND DISCUSSION

Differentiation of Enantiomers

Although diorganyl selenides are nonpolar compounds, they can easily form kinetically instable adducts with **Rh*** (for the structure of these adducts see below) because the selenium atom is a soft Lewis base and a good donor. This is exemplified by the results of a series of phenylselenenylmenthane derivatives **1–4** (see Scheme 2).[26] In each case, several pairs of separated signals [$\Delta\nu = \nu$ (1*R*-enantiomer) − ν(1*S*-enantiomer)] were detected which can be attributed to either the 1*R*- or the 1*S*-enantiomer so that integration of the ^{1}H and/or the ^{31}P signals provides the composition of the non-racemic mixture (Figure 1). However, the random scattering of the signs of the $\Delta\nu$-values (Table I) shows that there is no chance to extend this method into a rule for determining absolute configurations for this class of compounds. The reason is the lability of the adducts and their conformational flexibility (see below).



SCHEME 2 Selenium-containing compounds discussed.

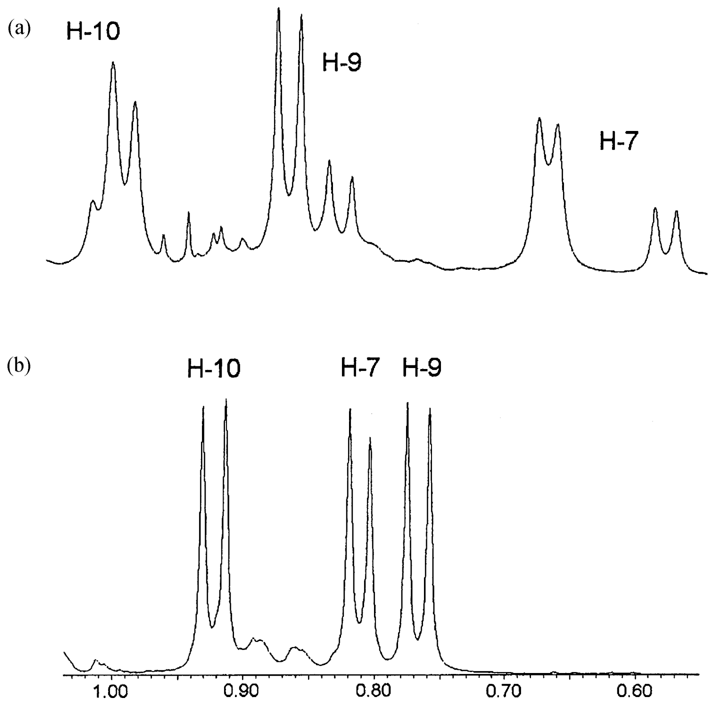


FIGURE 1 Section of the 400 MHz ^{1}H NMR spectrum of **1** in the absence (b) and in the presence (a) of an equimolar amount of **Rh***.

TABLE I Diastereomeric Dispersions of the Methyl Signals of Nonracemic of Mixtures 1–4: $\delta\nu = \nu$ (1R-Enantiomer) $- \nu$ (1S-Enantiomer)

$\Delta\nu(^1H)$	**1**	**2**	**3**	**4**
H-7	+35.4	−3.1	−35.6	−7.3
H-9	+15.4	−31.2	−15.0	−6.4
H-10	−7.8	0	∼ −1	∼ −1

Phosphine selenide (P=Se) is another low-polarity functionality which can be resolved successfully by the the dirhodium method.[27] An example is shown for compound **5** in Figure 2: Each sort of NMR-active nuclei shows dispersion effects.

Adduct Species

The dirhodium complex **Rh*** offers two axial rhodium positions for donor ligands (L) to dock (Scheme 3):

$$[\text{Rh-Rh}] + \text{L} \rightleftharpoons \underset{(1{:}1\text{-adduct})}{\text{L} \rightarrow [\text{Rh-Rh}]} \underset{-\text{L}}{\overset{+\text{L}}{\rightleftharpoons}} \underset{(2{:}1\text{-adduct})}{\text{L} \rightarrow [\text{Rh-Rh}] \leftarrow \text{L}}$$

SCHEME 3 Adduct formation equilibria; for clarity reasons, the dirhodium complex **Rh*** is represented by [Rh-Rh] in this scheme.

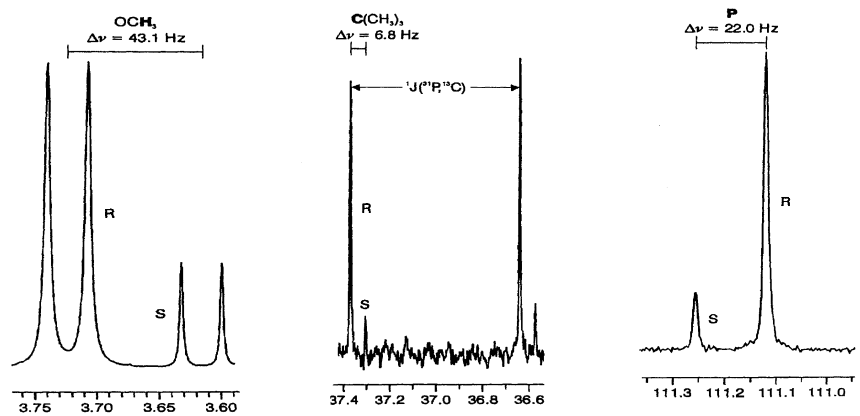


FIGURE 2 ^{1}H (left), ^{13}C (middle) and ^{31}P NMR signals (right) of the methoxy group in a nonracemic mixture of the phosphine selenide **5**.

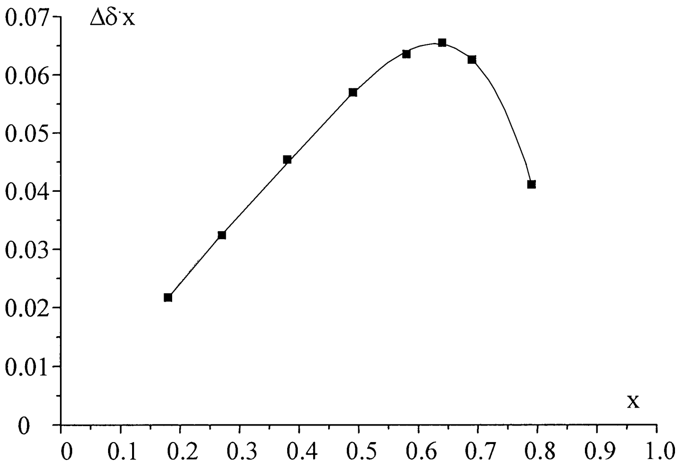


FIGURE 3 Job plot for H-3 in the **Rh***-adduct of **6**; mol fractions x of **6** *vs.* the product of ^{1}H signal shift $\Delta\delta$ and x.

A Job plot (Figure 3) prepared for 2-phenylselenenylbutane (**6**) reveals a maximum of the curve at a molar fraction of ca 0.66 for **6** indicating the predominance of 2:1-adducts (Scheme 3).[28] The same result was obtained by low-temperature ^{1}H NMR spectroscopy of the related selenide **7** (Figure 4):[29] Each of the olefinic proton signals separates into two; in each case, for each proton the left signal belongs to the free ligand **7** and the right one to the ligand **7** in the 2:1-adduct.

The dynamics of adduct formation and ligand exchange is exemplified in Figure 5.[29] At an equimolar amount of **7** and **Rh*** (left) two ^{77}Se signals can be identified at 213 K, one at $\delta = 308$ for the 2:1- and one at $\delta = 300$ for the 1:1-adduct. At room temperature (300 K) no signal is visible due to coalescence. On the other hand, two ^{77}Se signals at $\delta = 335$ (free **7**) and at 308 (2:1-adduct) appear under ligand excess conditions (5:1, right); again coalescing signals at 300 K. Finally, when the optimal ratio for 2:1-adducts is reached (middle), its signal is observed at all temperatures because any ligand exchange takes place among identical species. Analogous results can be deduced from ^{1}H NMR signals as well.[29]

There is another experimental parameter showing the composition of the adducts species frozen at 213 K. The ^{1}H chemical shift of the methoxy group in the Mosher acid residues of the complex **Rh*** is sensitive to the number of ligands attached. This chemical shift behavior is more or less independent of the nature of the ligand. Figure 6 shows the signals for the chiral selenoether **6**.[27] Note the dispersion of the signal of the 2:1-adduct ($\delta \approx 2.83$–2.89; resolution-enhanced in the

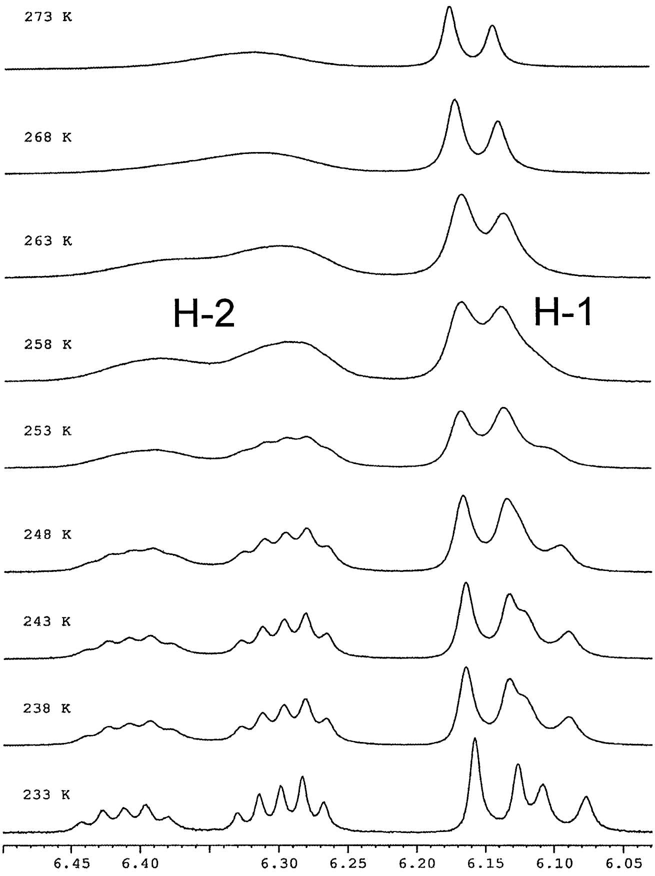


FIGURE 4 Temperature-dependent ^{1}H NMR spectra of the olefinic H-1 and H-2 of the selenide **7**; molar ratio **Rh***: **7** = 1 : 5 (excess of selenide).

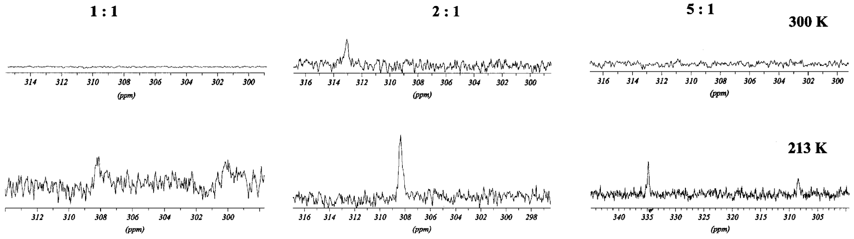


FIGURE 5 ^{77}Se NMR signals at various ratios of **7** to **Rh***, as indicated; top: at 300 K, bottom: at 213 K; in $CDCl_3$.

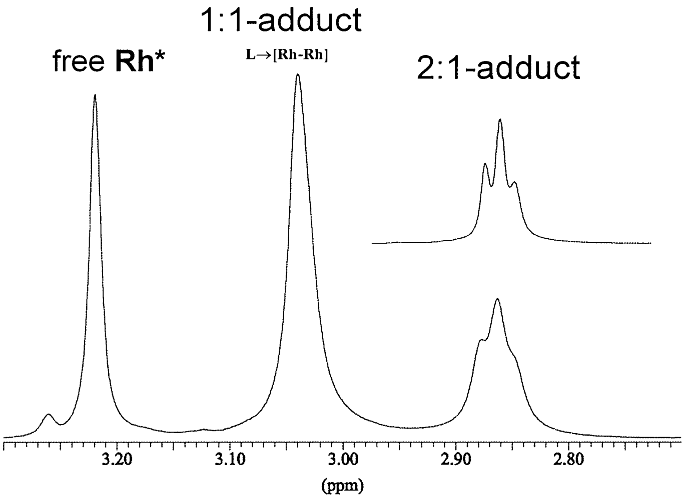


FIGURE 6 ^{1}H NMR signals at a molar ratio 1.5:1 of **6** to **Rh***, at 213 K in $CDCl_3$.

upper trace) which is due to the existence of several diastereomeric adducts: (*R*)-**6**/(*R*)-**6**, (*S*)-**6**/(*S*)-**6**, (*S*)-**6**/(*R*)-**6**, and (*R*)-**6**/(*S*)-**6**.

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