Heteroatom Chemistry
Volume 9, Number 5, 1998

Chiral Recognition of Selenides and Iodides by ^{1}H NMR Spectroscopy in the Presence of a Chiral Dirhodium Complex

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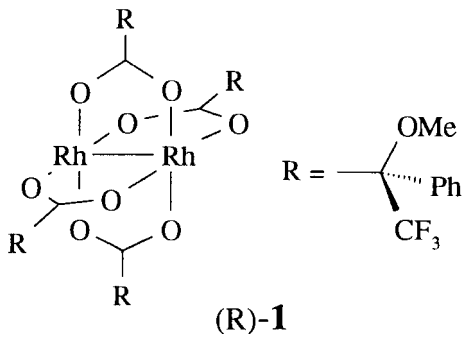
Received 15 October 1997

ABSTRACT: *Chiral recognition of aryl alkyl selenides and alkyl iodides can be achieved by ^{1}H NMR spectroscopy in the presence of dirhodium tetra-(R)- or tetra-(S)-α-methoxy-α-(trifluoromethyl)-phenylacetate [$Rh_2(MTPA)_4$,* **1***]. Generally, these classes of compounds are weak donors and fail when using the classical chiral lanthanoid shift reagent. Alkyl bromides do not show similar effects.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:471–474, 1998

RESULTS AND DISCUSSION

Parallel to the rapid development of stereoselective organic syntheses, chiral recognition is becoming increasingly important. Among these techniques, spectroscopic and chromatographic methods are most prominent [1]. NMR spectroscopy, in particular ^{1}H NMR, is well established because it often gives good results when spectra are recorded in the presence of a chiral lanthanoid shift reagent (CLSR) [2]. However, this method requires a substrate with a sufficiently basic functional group such as OH, NR_2, C = O, and others. If these are absent, complexation between substrate and CLSR molecules is too weak for chiral recognition. Thus, there is a considerable demand for certain classes of compounds to have an alternative procedure. Recently, we have shown that (R)-**1** (Scheme 1) and its enantiomer (S)-**1** (dirhodium complexes with four MTPA, i.e., Mosher's acid [3], residues) are very suitable for chiral recognition in various classes of compounds that form complexes with CLSR being too weak for chiral recognition by ^{1}H NMR spectroscopy. Among those functional groups are olefins [4], epoxides [5], and nitriles [6]. This article reports that our method can even be extended to selenides and iodides.

Organoselenium chemistry plays an increasing role in modern stereo- and regioselective organic chemistry [7], and, in parallel, ^{77}Se NMR spectroscopy has been developed into a routine method [8]. Therefore, it is useful to have an independent technique to monitor the composition of mixtures of enantiomers of aryl alkyl selenides. Therefore, we



(R)-**1**

SCHEME 1

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 CCC 1042-7163/98/050471-04

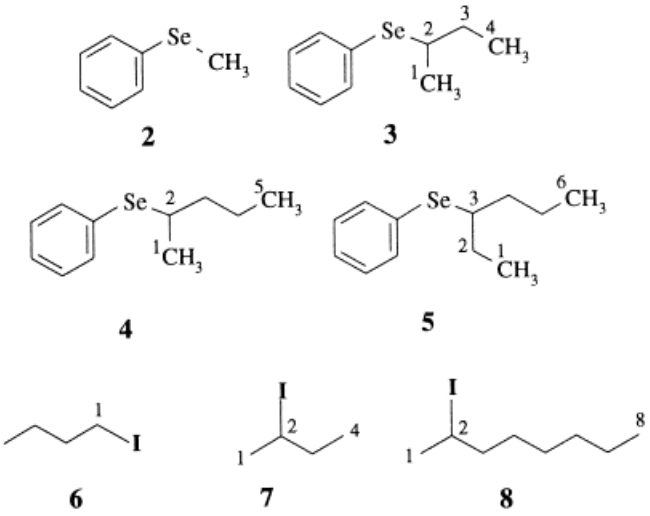
tested the ability of our $Rh_2(MTPA)_4$ reagent (**1**) for a representative class of selenides (**2–5**) and extended our study to some readily available alkyl iodides (**6–8**) (Scheme 2).

As an example, Figure 1 shows the two methyl signals of the iodide **7;** the lower trace is the ^{1}H NMR spectra in the absence and the upper trace in the presence of a twofold molar amount of (R)-**1**.

As can be seen from Table 1, the ^{1}H signal shifts due to complexation ($\Delta\delta$) are very moderate or even nearly absent. Values of up to 0.7 ppm for the selenides and 0.15 ppm for the iodides are observed. Such low shifts have been recognized earlier for some other functional groups as well [4–6], and they are helpful in that there is generally no major problem in identifying substrate ^{1}H signals after addition of a one- or even a twofold molar ratio of **1**. The signal shifts fade away quickly with an increasing number of bonds from the heteroatom that is considered to be the binding site at the equatorial positions of the dirhodium complex, that is, in the direction of the Rh–Rh bond (see Figure 2), the usual binding mode of weak ligands [9]. Although the selenides appear to be slightly better, both the selenides and the iodides are weak donors in a kinetically labile, fast-exchanging equilibrium of $Rh_2(MTPA)_4$ (**1**) and the substrate molecules **S**.

$$Rh_2(MTPA)_4 + \mathbf{S} \rightleftarrows Rh_2(MTPA)_4 \cdots \mathbf{S}$$

Therefore, the strongest $\Delta\delta$ values were achieved when using a molar ratio of 2:1 for **1** vs. the substrate, that is, by shifting the equilibrium to the right-hand side. Further addition of **1** did not provide any improvement.



SCHEME 2

In accordance with our earlier findings [4–6], signal dispersions ($\Delta\nu$) due to diastereotopic interaction within the $Rh_2(MTPA)_4 \cdots$ **S** complex appear preferentially in the periphery of the molecule, even over wide distances (e.g., H-8 in **8**); they are small if not negligible at the binding sites. This may be explained by the model displayed in Figure 2. The chiral information of complex **1** is oriented primarily in the outer sphere of the molecule (indicated by asterisks), that is, at the positions of the chiral residues of the MTPA ligands. Therefore, it is reasonable to assume that those hydrogen atoms farther away from the heteroatom in X (Se or I) are more exposed to chiral steric and/or anisotropic interaction than those that are closer.

It should be noted that the selenium atom is indeed the binding site and not the phenyl group. We exposed 2-phenylbutane to the same conditions but found no signal shifts ($\Delta\delta$) nor dispersions ($\Delta\nu$) at all.

In order to explore the limits of the method, we subjected some alkyl bromides (2-bromobutane, 2-bromopentane, and 1-bromo-2-phenylpropane) to the same experiment, without, however, finding any significant signal shifts ($\Delta\delta$) or signal dispersions ($\Delta\nu$). Thus, we suspect that it is the polarizability of the halogen atom, not its nucleophilicity, that is responsible for its ability to complex to the rhodium atom.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra have been recorded at 400 MHz (Bruker AM-400) under routine conditions. $CDCl_3$ has been used as the solvent. Spectral resolution was ca 0.1 Hz per data point.

The synthesis of dirhodium tetra-(R)- and tetra-(S)-α-methoxy-α-(trifluoromethyl)-phenylacetate [$Rh_2(MTPA)_4$, **1**] has been described before [4]. The selenides **2** and **3** have been prepared according to known procedures [10]. The syntheses of **4** and **5** were performed in analogy to **2** and **3** [10].

2-Phenylselenenylpentane **4**

Yellow liquid. ^{1}H NMR ($CDCl_3$), see Table 1. ^{13}C NMR ($CDCl_3$) δ 134.8 (2 CH), 129.5 (C), 128.8 (2 CH), 127.2 (CH), 39.7 (CH_2), 39.5 (CH), 22.1 (CH_3), 21.0 (CH_2), and 13.8 (CH_3). IR (film) 2956, 1580, 1476, 1436, 1020, 736, and 692 cm^{-1}. MS *m/z* (rel. intensity) 228 (24, M^+), 158 (100, $PhSeH^+$), 78 (39).

3-Phenylselenenylhexane **5**

Yellow liquid. ^{1}H NMR ($CDCl_3$), see Table 1. ^{13}C NMR ($CDCl_3$) δ 134.8 (2 CH), 129.5 (C), 128.8 (2 CH), 127.1

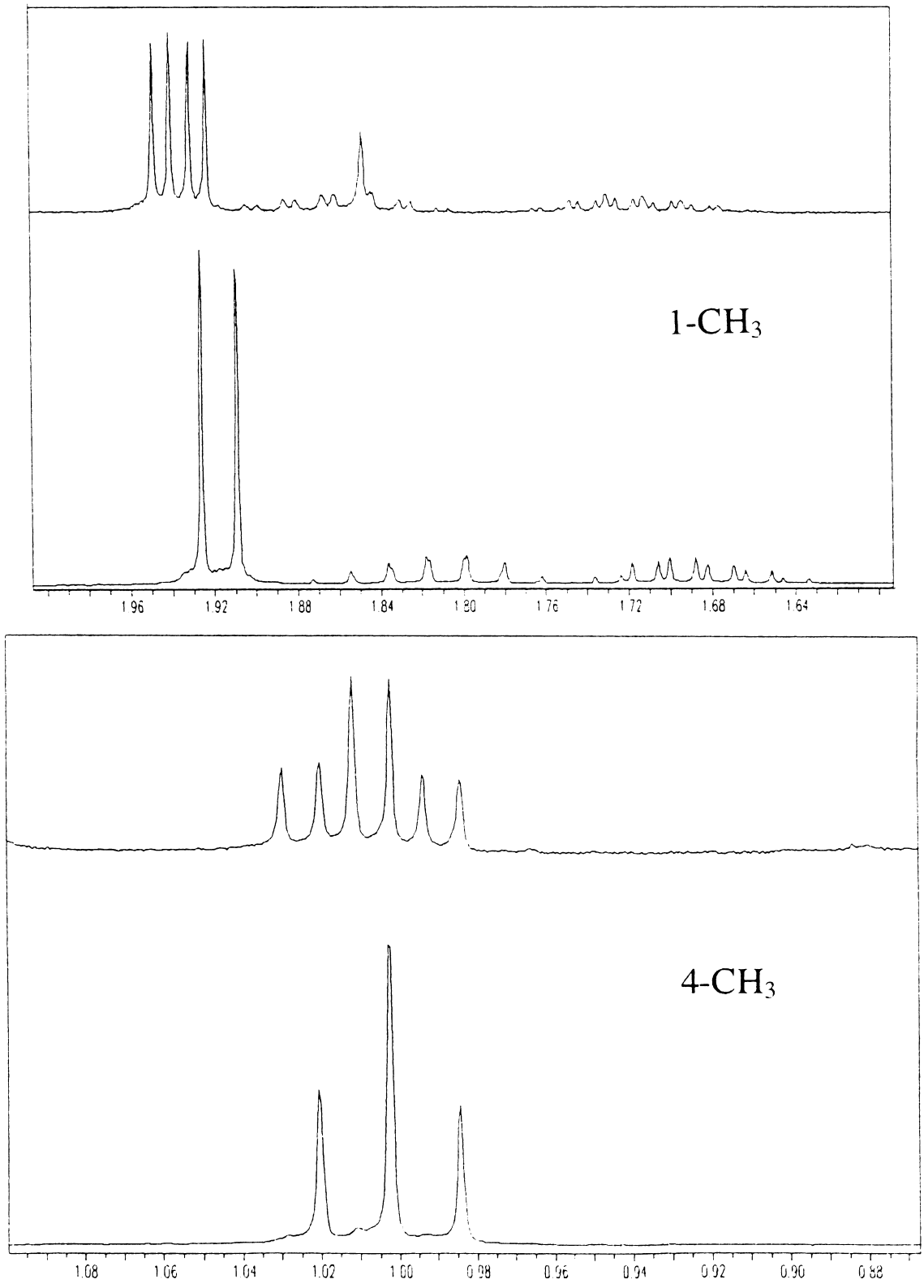


FIGURE 1 Methyl ^{1}H NMR signals of **7** in the absence (*lower traces*) and the presence (*upper traces*) of (R)-**1**.

TABLE 1 ^{1}H NMR Spectral Data of the Selenides **2–6** and the Iodides **7–9**[a]

		^{1}H Chemical Shifts		$\Delta\delta$	$\Delta\nu$
	H–	*Free*	*Complexed*	(*ppm*)	(*Hz*)
2	1	2.35	2.74	0.39	
3	1	1.39	1.50	0.11	—
	2	3.24	3.86	0.62	1.0
	3a	1.70	2.04	0.34	—
	3b	1.61	1.82	0.21	1.0
	4	0.99	0.99	0.00	3.3
4	1	1.40	1.52	0.12	4.5
	2	3.30	3.90	0.60	—
	3	ca 1.56	1.92	ca 0.40	—
	4a	ca 1.56	1.70	ca 0.30	—
	4b	ca 1.56	1.44	ca −0.10	—
	5	0.89	0.83	−0.06	2.2
5	1	1.00	0.97	−0.03	—
	2	1.64	2.03	0.39	—
	3	3.13	3.83	0.70	—
	4	1.64	1.78	0.14	—
	5	1.47	1.50	0.03	—
	6	0.89	0.81	−0.08	7.2
6	1	3.20	3.32	0.12	
	2	1.80	1.83	0.03	
	3	1.42	1.42	0.00	
	4	0.92	0.91	−0.01	
7	1	1.92	1.94	0.02	3.0
	2	4.17	4.32	0.15	1.4
	3a	1.81	1.87	0.06	2.3
	3b	1.69	1.72	0.03	2.0
	4	1.00	1.01	0.01	4.0
8	1	1.85	1.93	0.08	1.0
	2	4.12	4.25	0.13	[b]
	3	1.77	1.86	0.09	[b]
	4	1.54	1.62	0.08	[b]
	5	1.40	1.48	0.08	[b]
	6/7	1.29	[b]	[b]	[b]
	8	0.95	1.02	0.07	0.8

[a]Recorded at 400 MHz, in $CDCl_3$; ratio of **1** : substrate was 2 : 1.
[b]Not observable due to signal overlap and signal complexity.

(CH), 48.4 (CH), 37.1 (CH_2), 28.2 (CH_2), 20.9 (CH_2), 13.9 (CH_3), and 12.0 (CH_3). IR (film) 2956, 2928, 1580, 1476, 1436, 1020, 736, and 692 cm^{-1}. MS *m/z* (rel. intensity) 242 (21, M^+), 158 (100, $PhSeH^+$), 156 (51), 85 (17), 78 (39), 77 (20).

The iodides **6–8** have been purchased commercially (**6** and **7** from Aldrich, **8** from Lancaster) and have been used without further purification. 2-Bromobutane and 2-bromopentane are commercial compounds (Aldrich). 1-Bromo-2-phenylpropane has been prepared from the corresponding alcohol with PBr_3.

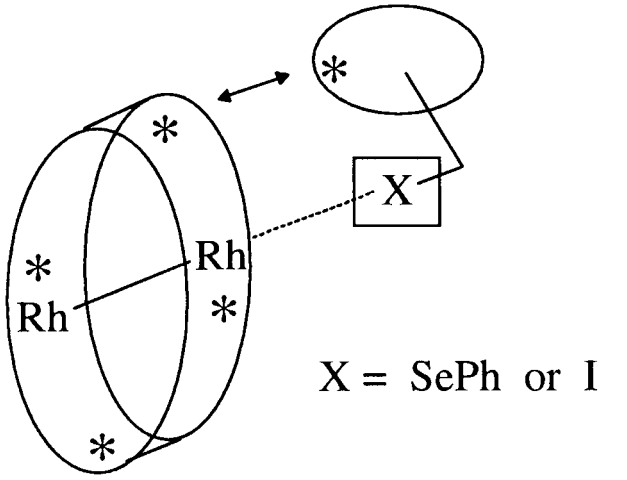


FIGURE 2 Schematic representation of the $Rh_2(MTPA)_4 \cdots$ substrate complex.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. One of the authors (S. H.) thanks the Deutscher Akademischer Austauschdienst for a fellowship at Hannover University.

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