Research Article

Magnetic Resonance in Chemistry

Received: 22 August 2009 Accepted: 4 December 2009 Published online in Wiley Interscience: 11 January 2010

(www.interscience.com) DOI 10.1002/mrc.2562

Experimental verification of diverging mechanisms in the binding of ether, thioether, and sulfone ligands to a dirhodium tetracarboxylate

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Complexation of the oxygen atom in 2-butylphenylethers and sulfur in 2-butylphenylthioethers to a rhodium atom in dirhodium tetracarboxylate $Rh^{(II)}{}_2[(R)\text{-}(+)\text{-MTPA}]_4$ is compared. Oxygen atoms complex via electrostatic attraction exclusively leading to an increase in α effects on C-2 complexation shifts in the sequence $OCH_3 > F > Br > NO_2$. However, that trend is opposite in thioethers. This can be rationalized by an additional highest occupied molecular orbital (HOMO)–LUMO interaction and the response of this interaction upon complex formation shifts. Thereby, an experimental evidence was found for the existence of the HOMO–LUMO binding mechanism which has been proposed previously based on theoretical considerations and indirect spectroscopic evidence. Sulfones hardly bind to $Rh^{(II)}{}_2[(R)\text{-}(+)\text{-MTPA}]_4$. Diastereomeric dispersion effects at ^{13}C and ^{1}H signals can be observed for all compounds indicating that enantiodifferentiation is easy in all classes of functionalities.

Keywords: ethers; thioethers; sulfones; dirhodium complex; ^{1}H NMR; ^{13}C NMR; complexation; chiral differentiation

Introduction

Dirhodium complexes as well as their adducts have been in the focus of interest for many years.[1–3] During the last decade, we have shown that the enantiomers of many chiral ligands, particularly those of soft Lewis bases, can be differentiated easily by adding an equimolar amount of the dirhodium complex $Rh^{(II)}{}_2[(R)\text{-}(+)\text{-MTPA}]_4$ (**Rh***, MTPA-H = methoxytrifluoromethylphenylacetic acid ≡ Mosher's acid; see Scheme 1)[4] to their $CDCl_3$ solution and monitoring the diastereomeric dispersion $\Delta\nu$ of their ^{1}H (or ^{13}C) NMR signals at room temperature (dirhodium method).[5] In addition, the complexation site in the ligand molecules can be identified from inductive effects on chemical shifts $\Delta\delta$. Recently, we investigated ether ligands where oxygen atoms are attached to aromatic ring systems and, to our surprise, found that the most significant complexation shifts are observed at aromatic atoms beyond the *ipso*-carbon bound to oxygen.[6] This, however, is not compatible with the above explanation; rather, it reminds of resonance effects.

In order to gain further insight into the complexation mechanisms of chalcogen ligands, we extended our study to structurally analogous thioethers (**2**) and sulfones (**3**). Although ethers (**1**) are hard ligands, thioethers are soft representing a different ligand category in the dirhodium experiment when compared with the ethers.[5]

In the present study, we provide experimental evidence of the existence of orbital interaction when sulfur atoms are binding sites.

Results and Discussion

The complete and unambiguous NMR signal assignment of the free ligands **2a–2e** and **3a–3e** (Scheme 2) is straightforward by applying routine NMR methods, such as DEPT, COSY, HMQC, and HMBC techniques. The assignment strategies were analogous to those reported for the ethers **1a–1e**.[7] ^{13}C and ^{1}H chemical shifts are listed in Table 1. ^{13}C and ^{1}H complexation shifts $\Delta\delta$ and diamagnetic dispersion effects $\Delta\nu$ provoked by adduct formation in the presence of an equimolar amount of **Rh*** are collected in Table 2; NMR data of **1e**, which have not been reported before,[7] are given in the Section on Experimental.

Binding sites and adduct formation

The complexation site of the ligand molecule in the adduct with the dirhodium complex **Rh*** can be identified by the deshieldings of nearby ^{1}H and, particularly, ^{13}C nuclei (complexation shifts $\Delta\delta$).[5] In a qualitative interpretation of positive $\Delta\delta$-values, one can assume that an increase of the electron-acceptor properties of the binding atom takes place (inductive effect).[5]

Recently, we investigated ether ligands where oxygen atoms are attached to aromatic ring systems and found significant complexation shifts at aromatic atoms beyond the *ipso*-carbon bound to oxygen.[6] Therefore, we wanted to study this phenomenon, namely, the fact that complexation shifts seem to be entirely different if aliphatic or aromatic carbons are involved. Araliphatic ethers[7] and thioethers (compounds **1** and **2**, respectively, in Scheme 2) were chosen as candidates.

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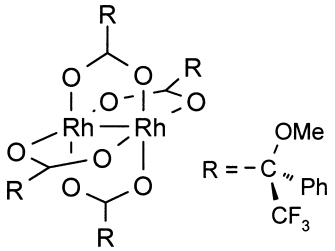
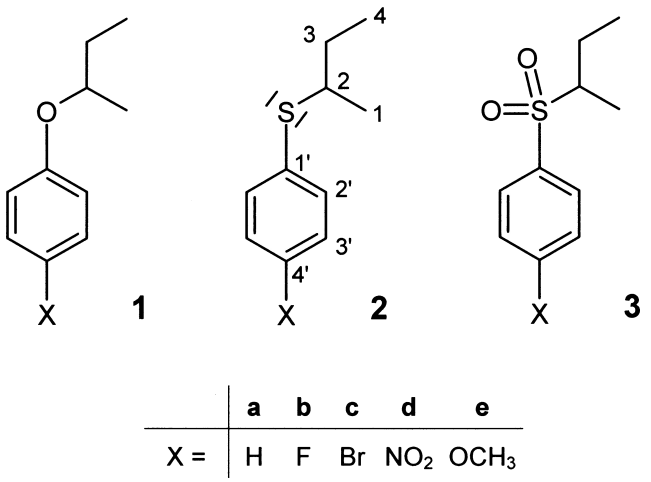


Scheme 1. Structure of the dirhodium complex **Rh***.



	a	b	c	d	e
X =	H	F	Br	NO_2	OCH_3

Scheme 2. Structures of 2-butylphenylethers (**1**) as well as their thioether (**2**) and sulfone (**3**) analogs.

Table 1. ^{13}C and ^{1}H chemical shifts δ of the thioethers **2a**–**2e**, in ppm; solvent $CDCl_3$

	2a	2b[a]	2c	2d	2e
C-1	20.5	20.5	20.4	20.2	20.5
C-2	44.8	45.9	45.0	43.2	46.2
C-3	29.4	29.4	29.4	29.3	29.3
C-4	11.4	11.4	11.4	11.4	11.4
C-1′	135.5	130.1	134.8	145.1	125.2
C-2′/6′	128.7	135.0	133.3	127.7	135.5
C-3′/5′	131.8	115.8	131.8	123.9	114.2
C-4′	126.5	162.2	120.6	147.3	159.3
O**C**H_3	–	–	–	–	55.2
H-1	1.27	1.23	1.26	1.38	1.21
H-2	3.15	3.04	3.13	3.40	2.96
H-3[b]	1.53/1.66	1.50/1.60	1.52/1.64	1.65/1.75	1.47/1.60
H-4	1.00	1.00	1.00	1.05	0.99
H-2′/6′	7.39	7.40	7.24	7.36	7.38
H-3′/5′	7.27	6.99	7.40	8.12	6.83
H-4′	7.20	–	–	–	–
O**C**$\mathbf{H_3}$	–	–	–	–	3.79

[a] Coupling constants involving ^{19}F: $^{3}J(^{19}F,^{1}H) = 8.9$ Hz (H-3′/5′); $^{4}J(^{19}F,^{1}H) = 8.7$ Hz (H-2′/6′); $^{1}J(^{19}F,^{13}C) = 247.1$ Hz (C-4′); $^{2}J(^{19}F,^{13}C) = 21.7$ Hz (C-3′/5′); $^{3}J(^{19}F,^{13}C) = 8.1$ Hz (C-2′/6′); $^{4}J(^{19}F,^{13}C) = 3.4$ Hz (C-1′); $^{6}J(^{19}F,^{13}C) = 1.0$ Hz (C-2).
[b] Diastereotopic protons; no stereochemical assignment.

Ethers form rather weak adducts with **Rh*** [7,8] and the binding energy is expected to be based primarily on electrostatic interaction. Orbital [highest occupied molecular orbital (HOMO)–LUMO] interaction does not contribute significantly if oxygen, as a second-row element, is involved; the HOMO–LUMO gap is too large.[9]

We had found that the inductive effect of the ether oxygen on aliphatic α carbons is enhanced when it is complexed to the rhodium atom ($\Delta\delta > 0$). This is in accordance with the original interpretation (see above). However, deshielding complexation shifts $\Delta\delta$ at the aromatic *ipso*-carbons (also α-positioned) were minute, whereas *ortho*- and *para*-carbon signals were influenced by the resonance effect of oxygen.[7]

This latter effect can be modulated by remote substituents at the benzene ring; the modulation of this resonance correlates linearly with the magnitude of the inductive effect exerted on the aliphatic α carbon atoms.[7] On the other hand, the ^{13}C chemical shift modulation at the *ortho*-carbons (C-2′/6′) follows the resonance effect (σ_R)[10] of the *para*-positioned substituent X: the larger σ_R, the larger $\Delta\delta$(C-2′/6′)[7]; the *p*-OCH_3 analog **1e**, introduced in the present study, fits nicely into that correlation with a negative slope (Fig. 1; filled squares).

Analogously, the correlation of complexation shifts $\Delta\delta$ at the α-positioned carbons C-2 of **1a**–**1e** shows a negative slope as well when plotted *versus* inductive effect parameters (σ_I) (Fig. 2; filled squares).

As shown in the Figs 1 and 2, the corresponding correlations are opposite for the thioethers **2** (open squares) and, generally, larger $\Delta\delta$-values are observed. This is an evidence for a significant divergence in adduct formation mechanisms: exclusive dipole attraction for oxygen ligands and an additional HOMO–LUMO interaction in the case of thioether ligands.

*Phenylethers **1a–1e***

Calculated electrostatic charges at C-2 (density functional with B3LYP 6-31G* basis set; Table 3) are parallel to the $\Delta\delta$(C-2)-values supporting the dominance of the electrostatic nature in the binding process and confirming our earlier interpretation.[7]

*Phenylthioethers **2a–2e***

As shown by Deubel,[9] electrostatic attraction plays an important role for soft-base ligands but HOMO–LUMO interaction may be significant too. Apparently, the latter mechanism overrules the first in the thioethers producing correlations with positive slopes (Figs 1 and 2; open squares).

A semiquantitative rationalization for this opposite behavior of complexation shifts at C-2 in correlation with the Hammett parameters of X is offered in the following. First of all, the HOMOs are totally different; in contrast to ethers (Fig. 3, left) those of the thioethers are essential the free electron pairs at sulfur (Fig. 3, right).[11] Interestingly, this difference is accompanied by a change in calculated conformations: while the O–C-2 bond is nearly coplanar with respect to the aromatic ring [**1a**: torsion angle ϕ(C-2/O/C-*ipso*/C-2′) = 2°], the corresponding angle of **2a** is ϕ(C-2/S/C-*ipso*/C-2′) = 73.5° so that the free electron pair at sulfur is situated nearly within the σ-plane of the benzene ring. Thereby, the thioether-HOMO is easily accessible for adduct formation with a rhodium atom of **Rh***.

It is well known[12] that σ_p, the paramagnetic contribution to the nuclear shielding, dominates the chemical shift of heavier atoms; it is governed, along with some other structural effects, by the mean

Table 2. ^{13}C and ^{1}H complexation shifts $\Delta\delta$ (in ppm) and diastereomeric dispersions $\Delta\nu$ (in HZ; integers) of the thioethers **2a**–**2e**, in ppm; solvent: $CDCl_3$

	2a	2b	2c	2d	2e
C-1	−2.5/11	−2.5/10	−2.6/15	−2.5/10	−2.5/11
C-2	3.4/7	2.6/3	3.1/6	4.4/4	2.3/5
C-3	−1.8/4	−1.7/4	−1.8/3	−1.8/4	−1.7/6
C-4	−0.3/11	−0.3/10	−0.5/13	−0.7/13	−0.3/11
C-1′	−6.1/0	−5.4/0	−6.1/0	−6.0/4	−5.3/5
C-2′/6′	0.1-/1	1.2/2	−1.4/5	5.5/2	0.3/4
C-3′/5′	2.3/3	0.1/1	3.5/1	−0.3/1	0.1/2
C-4′	2.6/0	1.2/0[a]	3.1/0	0.1/0	1.3/0
O**C**H$_3$	–	–	–	–	0.2/1
H-1	0.2/4	0.2/4	0.2/7	0.1/9	0.2/4
H-2	0.6/1	0.7/1	0.6/0	0.6/1	0.7/0
H-3[b]	0.4/0	0.4/1	0.4/0	0.3/1	0.4/1
H-4	0/5	0/5	0/5	0/8	0/4
H-2′/6′	0.4/0	0.4/2	0.4/1	0.4/0	0.3/2
H-3′/5′	n.d.[c]	−0.1/6	−0.1/0	−0.2/2	−0.1/7
H-4′	0.1/1	–	–	–	–
O**CH$_3$**	–	–	–	–	−0.1/3

[a] $^{1}J(^{19}F,^{13}C) = 249.9$ Hz (C-4′), change by complexation: $\Delta J(^{19}F, ^{13}C) = +2.8$ Hz; no significant changes in ^{19}F couplings to other nuclei.
[b] No stereochemical assignment for the diastereotopic protons; values are averaged.
[c] 'n.d.', not detectable.

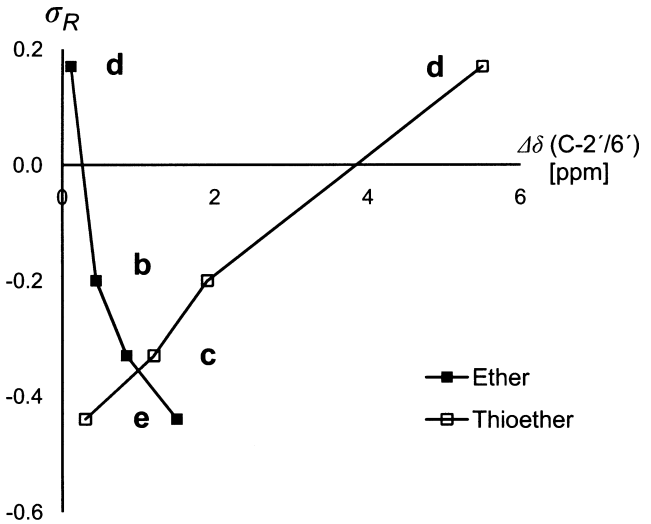


Figure 1. Complexation shifts $\Delta\delta$ at the *ortho*-carbons C-2′/C-6′ of **1a** to **2e** plotted *versus* resonance effect parameters of X (σ_R). The letters **b** to **e** mark the substituents X (see Scheme 2): **b,** X = F; **c,** X = Br; **d,** X = NO_2; **e**, X = OCH_3.

excitation energy $\langle E\rangle$ and the spatial dimension of the p-orbital in the valence shell (2p for ^{13}C):

$$\sigma_p \sim \langle E\rangle^{-1} r_{2p}{}^{-3} \quad (1)$$

The effect of the mean excitation energy $\langle E\rangle$ is dominated by the energetically smallest, i.e. the HOMO(n_S)–LUMO($\pi^*_{arom.}$) transition (Scheme 3). By adduct formation with **Rh***, the HOMO(n_S) of sulfur interacts with the LUMO(σ^*_{Rh-Rh}) of the Rh–Rh bond

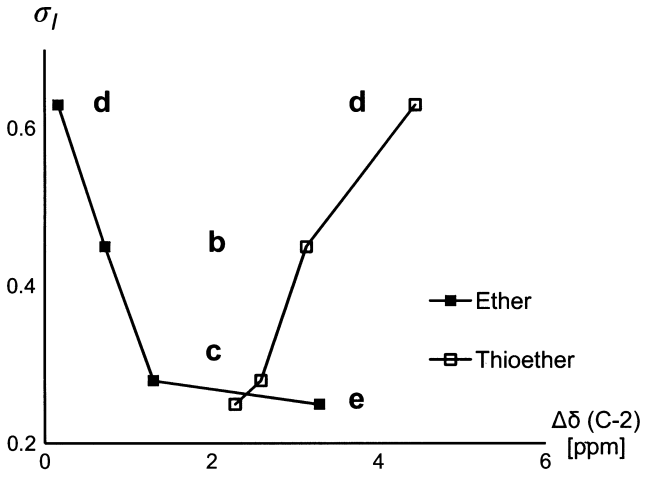


Figure 2. Complexation shifts $\Delta\delta$ at the α-positioned carbons C-2 of **1a**–**2e** plotted *versus* the inductive effect parameters of X (σ_I). The letters **b** to **e** mark the substituents X (see Scheme 2): **b**, X = F; **c**, X = Br; **d**, X = NO_2; **e**, X = OCH_3.

Table 3. Complexation shifts $\Delta\delta$(C-2) and calculated[a] electrostatic and Mulliken charges at C-2 for the *para*-substituted phenylethers **1b**–**1e**

X =	NO_2	Br	F	OCH_3
Electrostatic charge	0.423	0.547	0.576	0.575[b]
Charge (Mulliken)	0.060	0.142	0.142	0.146[b]
$\Delta\delta$(C-2), in ppm	0.16	0.72	1.30	3.29

[a] Calculated density functionals with B3LYP 6-31G* basis set.
[b] Averaged value for *cisoid* and *transoid* conformations; the energy difference for the two conformations is minute.

in the complex **Rh***, so that its energy is lowered. Thereby, the HOMO(n_S)–LUMO($\pi^*_{arom.}$) transition energy is increased. This transition energy change becomes even larger if the HOMO energy is higher and closer to the LUMO(σ^*_{Rh-Rh}) energy. As can be seen in Table 4, there is a sequence in the calculated HOMO energies of the thioethers **2** predicting the strongest effect for **2e** (X = OCH_3) and the weakest for **2d** (X = NO_2). So, according to Eqn (1) the smallest complexation shift is expected for **2e** and the largest for **2d**. The group electronegativity of the sulfur atom is changed correspondingly which, in turn, affects the α-positioned aliphatic carbon (C-2) in the same direction. This trend is, indeed, observed as shown in Fig. 2.

*Phenyl sulfones **3a–3e***

All ^{13}C and ^{1}H NMR data of the sulfones are listed in Section on Experimental. Complexation effects are more or less negligible in the sulfones and so is the modulation by X. This shows that the oxygen atoms, the only possible binding sites, are too hard for any effective association to rhodium.

Enantiodifferentiation by ^{13}C and ^{1}H signal dispersions ($\Delta\nu$)

As can be seen from the $\Delta\nu$ data in Table 2, some ^{1}H and ^{13}C signal splittings of compounds **2** due to the formation of diastereomeric adducts with **Rh*** can be recognized. Among the ^{1}H NMR signals, those of the terminal methyl groups (H-1 and H-4) display the

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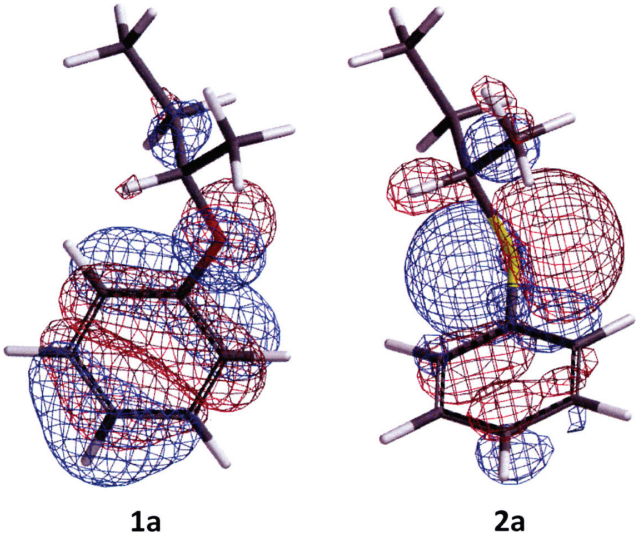
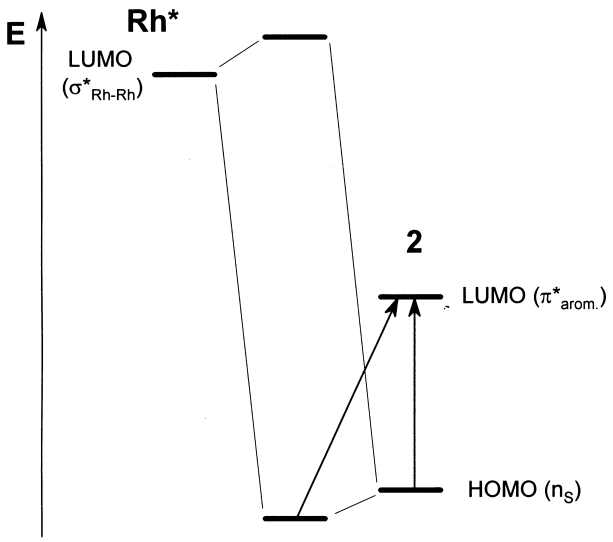


Figure 3. Highest occupied molecular orbitals (HOMO) of the ether **1a** (left) and the thioether **2a** (right); calculated density functionals at the B3LYP 6-31G* level.[11].



Scheme 3. Schematic representation of the HOMO–LUMO interaction between a thioether **2** and the dirhodium complex **Rh***.

most pronounced dispersions that can easily be integrated and used for chiral differentiation (Fig. 4).

Slight signal dispersions are even observed for the sulfones (see Section on Experimental), although their affinity to rhodium is very low.

Experimental

Spectroscopy

All NMR measurements were performed in analogy to those described for the corresponding ethers **1**; details of the one- and two-dimensional NMR experiments (DEPT90 and DEPT135, gradient-selected COSY, HMQC, and HMBC spectra) can be found in Ref. [7]

^{1}H (400.1 MHz) and ^{13}C (100.6 MHz) NMR measurements were recorded at room temperature on a Bruker Avance DPX-400 spectrometer. Samples were *ca* 0.01–0.025 mmol in $CDCl_3$. The chemical shift reference is internal tetramethylsilane ($\delta = 0$ ppm).

In the standard dirhodium experiment, **Rh*** and equimolar amounts of the ligands **2a–3d**, respectively, were dissolved in 0.7 ml $CDCl_3$; quantities of 10–25 mg of **Rh*** (*ca* 0.01–0.025 mmol concentration) were employed. If necessary, the dissolution process was accelerated by exposing the NMR sample tubes to an ultrasonic bath for a couple of minutes. In earlier reports on soft-base ligands, the use of acetone-d_6 for increasing the solubility of **Rh*** has been recommended.[5] This auxiliary, however, has been avoided in this study because acetone-d_6 may be a competitor to hard-base ligands in the adduct formation.

Note that $\Delta\nu$-values are B_0 dependent and have no signs here because racemates have been investigated. In this work, all dispersion values $\Delta\nu$ are given as integers in Hz as determined at $B_0 = 9.4$ T corresponding to 400 MHz ^{1}H and 100.6 MHz ^{13}C.

Infrared (IR) spectra were recorded on a Bruker Vector 22 and mass spectra on a Micromass LCT.

Table 4. Calculated HOMO energies (*E*, in kJ/mol) and complexation shifts $\Delta\delta$(C-2, in ppm) for *para*-substituted phenylthioethers (**2**)

X =	H (**2a**)	NO_2 (**2d**)	Br (**2c**)	F (**2b**)	OCH_3[a] (**2e**)
E(HOMO)	−572.0	−36.9[b]	−21.3[b]	+11.7[b]	+13.0[b]
$\Delta\delta$(C-2)		+1.0[c]	−0.3[c]	−0.8[c]	−1.1[c]

[a] Average of values for the *cisoid* and *transoid* conformers.
[b] Relative to the energy of the parent compound with X = H (**2a**); calculated density functionals with B3LYP 6-31G* basis set.
[c] These values refer to the corresponding value of the parent compound with X = H (**2a**).

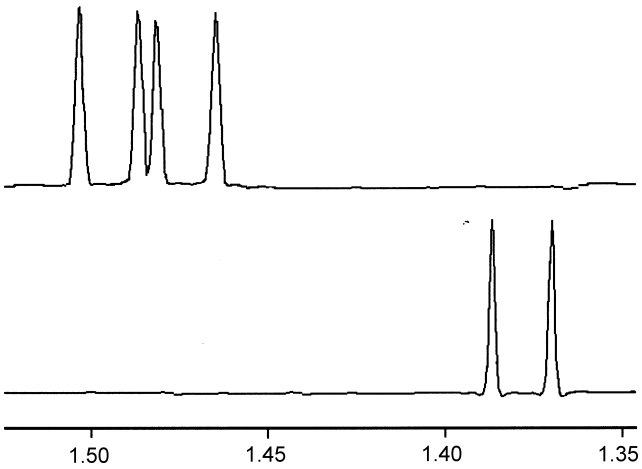


Figure 4. ^{1}H NMR signals of the terminal methyl groups H-1 of thioether **2d**; bottom: free ligand, top: in the presence of an equimolar amount of **Rh***; the dispersion $\Delta\nu$ is 9 Hz (at 9.4 T; 400 MHz ^{1}H).

Substances

The syntheses of **Rh***[4] and the ethers **1a–1d**[7] have been described by us earlier. Ether **1e** and some of the thioethers and sulfones, namely, **1e**,[13] **2a**,[14] **2d**,[15] **2e**,[16] and **3a**,[17] have been described in the literature; all others are new. In nearly all cases, complete spectral datasets were not documented properly; therefore, we collect them in the following (for atom numberings see Scheme 2).

4-Methoxy-1(1-methylpropyloxy)benzene (1e)

The preparation of **1e** followed the procedure described for **1a–1d**[7] except that 2-butyl-*p*-toluenesulfonate was used instead of 2-bromobutane. The resulting ether **1e** was obtained as a colorless oil; yield 61%. ^{13}C NMR ($CDCl_3$): δ = 9.8 (CH_3, C-4, 19.3 (CH_3, C-1), 29.2 (CH_2, C-3), 55.7 (CH, C-2), 76.2 (CH_3, O**C**H_3), 114.6 (CH, C-3′/5′), 117.4 (CH, C-2′/6′), 152.2 (C, C-1′), 153.8 ppm (C, C-4′); ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, 3H, H-4), 1.26 (d, 3H, H-1), 1.65 (m, 2H, H-3), 3.76 (s, 1H, OC**H$_3$**), 4.16 (ddq, 1H, H-2), 6.80 (m, 2H, H-3′/5′), 6.85 ppm (m, 2H, H-2′/6′); IR (liquid) $\tilde{\nu}$: 3048, 2978, 2927, 1576, 1487, 1377, 1221, 1080, 83 cm^{-1}. High-resolution mass spectrometry ESI-negative calculated for $C_{11}H_{15}O_2$: 179.1072 $[M-H]^-$ found: 179.1043 $[M-H]^-$.

General procedure for the synthesis of the thioethers 2a–2e

Racemic thioethers **2a**–**2e** were prepared by nucleophilic substitution reaction of *rac.*-2-butyl toluenesulfonate (obtained previously from toluenesulfochloride and 2-butanol in chloroform and pyridine at 0 °C) and the respective commercially available thiophenoles.[18]

In a solution of 7.0 ml of the respective thiophenol in 6 ml acetone, 1.06 g K_2CO_3 (7.6 mmol) was suspended, and then 1.76 g *rac.*-2-butyl toluenesulfonate (7.7 mmol) was added. The mixture was refluxed for 24 h, and acetone was evaporated under reduced pressure. The residue was dissolved in 10 ml water and extracted twice with 10 ml toluene. The combined organic phases were washed twice with 10 ml aqueous sodium hydroxide (10%), dried over Mg_2SO_4 followed by evaporation of toluene under reduced pressure. The obtained raw product was a slightly yellow liquid that was chromatographed on silica gel with a petrol ether/acetone mixture (10 : 1) as eluent. It should be noted that purification by chromatography on silical gel may lead to considerable loses, probably due to a acid-catalyzed thiophenol elimination.

The phenyl thioethers are slightly yellow, highly viscous liquids.

(1-Methylpropyl)thiobenzene (2a)

Yield: 58%. For NMR data, see Tables 1 and 2; IR (liquid) $\tilde{\nu}$: 3056, 2963, 2924, 1584, 1479, 1438, 1025, 740, 691 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 166 (38, M^+), 110 (100, M^+-C_4H_8), 77 (10, $C_6H_5^+$), 65 (13).

4-Fluoro-1(1-methylpropylthio)benzene (2b)

Yield: 65%. For NMR data, see Tables 1 and 2; IR (liquid) $\tilde{\nu}$: 3050, 2964, 1589, 1488, 1219, 828 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 184 (30, M^+), 128 (100, M^+-C_4H_8), 57 (20).

4-Bromo-4(1-methylpropylthio)benzene (2c)

Yield: 54%. For NMR data, see Tables 1 and 2; IR (liquid) $\tilde{\nu}$: 3050, 2964, 2924, 1472, 1384, 1091, 1069, 1008, 810 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 244/266 (42/41, M^+), 188/190 (98/100, M^+-C_4H_8), 109 (68 $C_6H_4S^+$), 57 (59).

4-Nitro-1(1-methylpropylthio)benzene (2d)

Yield: 62%. For NMR data, see Tables 1 and 2; IR (liquid) $\tilde{\nu}$: 3048, 2966, 2927, 1576, 1507, 1477, 1332, 1080, 837, 741 cm^{-1}; (70 eV, rel. int. %) *m/z* 211 (98, M^+), 155 (100, M^+-C_4H_8), 109 (57, $C_6H_5NO_2^+$), 69 (54).

4-Methoxy-1(1-methylpropylthio)benzene (2e)

Yield: 58%. For NMR data, see Tables 1 and 2; IR (liquid) $\tilde{\nu}$: 3060, 2960, 1570, 1325, 1283, 826 cm^{-1}; (70 eV, rel. int. %) *m/z* 196 (88, M^+), 140 (100, M^+-C_4H_8), 109 (52), 69 (32).

General procedure for the synthesis of the sulfones 3a–3e

The thioethers **2a–2e** (0.25 g, 1.48 mmol) were dissolved in 30 ml dichloromethane. Then, 0.59 g $KMnO_4$ (3.73 mmol) and 0.30 g $CuSO_4$ (1.85 mmol) were added and the mixture refluxed for 24 h. After cooling to room temperature, the purple solution was filtered over celite 535 (pH ≥8.5, Merck) and the solid washed with dichloromethane. The combined, nearly colorless organic phases were evaporated under reduced pressure to afford yellow, highly viscous liquids.[19]

(1-Methylpropyl)sulfonylbenzene (3a)

Yield: 74%. ^{13}C ($CDCl_3$) δ = 11.0 (CH_3, C-4); 12.5 (CH_3, C-1); 22.4 (CH_2, C-3); 61.4 (CH, C-2); 128.9 (CH, C-2′/6′); 129.0 (CH, C-3′/5′); 133.4 (C, C-4′); 137.4 ppm (C, C-1′); $\Delta\delta$ = 0.0 (C-1), 0.1 (C-2, C-3, C-4), −0.1 (C-1′), 0.5 (C-2′/6′), 0.1 ppm (C-3′/5′, C-4′); $\Delta\nu$ = 1 (C-1, C-2, C-3, C-4, C-1′, C-3′/5′), 0 Hz (C-2′/6′, C-4′); ^{1}H ($CDCl_3$) δ = 0.96 (t, 3H, H-4); 1.27 (d, 3H, H-1); 1.44 and 2.01 (ddq, 2H, H-3a/3b); 2.96 (tq, 1H, H-2); 7.56 (m, 2H, H-3′/5′); 7.65 (m, 1H, H-4′); 7.88 ppm (m, 2H, H-2′/6′); $\Delta\delta$ = 0.0 ppm (all protons); $\Delta\nu$ = 1 (H-1), 0 Hz (H-2 to H-4′); IR (liquid) $\tilde{\nu}$: 3023, 2934, 2912, 1584, 1336, 1287, 1151, 1020, 688 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 198 (83, M^+), 142 (100, M^+-C_4H_8), 57 (42).

4-Fluoro-1(1-methylpropylsulfonyl)benzene (3b)

Yield: 76%. ^{13}C ($CDCl_3$) δ = 11.1 (CH_3, C-4); 12.6 (CH_3, C-1); 22.6 (CH_2, C-3); 61.8 (C, C-2, $^6J_{FC}$ = 1.3 Hz); 116.4 (CH, C-3′/5′, $^2J_{FC}$ = 22.4 Hz); 131.8 (CH, C-2′/6′, $^3J_{FC}$ = 8.0 Hz); 133.5 (C, C-1′, $^4J_{FC}$ = 3.7 Hz), 165.8 ppm (C, C-4′, $^1J_{FC}$ = 247.1 Hz); $\Delta\delta$ = −0.1 (C-1, C-2′/6′), 0.0 (C-2, C-3, C-3′/5′, C-4′), −0.1 (C-4), −0.3 ppm (C-1′); $\Delta\nu$ = 2 (C-1), 0 (C-2, C-2′/6′, C-3′/5′), −0.1 (C-1′), 1 Hz (C-3, C-4,); ^{1}H ($CDCl_3$) δ = 0.99 (t, 3H, H-4); 1.27 (d, 3H, H-1); 1.44 and 2.02 (ddq, 2H, H-3a/3b); 2.94 (tq, 1H, H-2); 7.23 (m, 2H, H-3′/5′, $^3J_{FH}$ = 8.5 Hz), 7.89 ppm (m, 2H, H-2′/6′, $^4J_{FH}$ = 8.8 Hz); $\Delta\delta$ = 0.0 (H-1, H-3, H-4, H-2′/6′), 0.1 ppm (H-2), not detected (H-3′/5′); $\Delta\nu$ = 2 (H-1, H-2, H-3), 1 Hz (H-4, H-2′/6′), not detected (H-3′/5′); IR (liquid) $\tilde{\nu}$: 3025, 2935, 1578, 1321, 1235, 1212, 1117, 1068, 827, 802 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 216 (64, M^+), 160 (100, M^+-C_4H_8), 149 (54), 57 (38).

4-Bromo-1(1-methylpropylsulfonyl)benzene (3c)

Yield: 73%. ^{13}C ($CDCl_3$) δ = 11.1 (CH_3, C-4); 12.6 (CH_3, C-1); 22.5 (CH_2, C-3); 61.7 (CH, C-2); 128.9 (C, C-4′); 130.6 (CH, C-3′/5′); 132.4 (CH, C-2′/6′); 136.5 ppm (C, C-1′); $\Delta\delta$ = −0.1 (C-1), 0.0 (C-2), 0.0 (C-3), −0.1 (C-4), −0.3 (C-1′), 0.0 (C-2′/6′), 0.0 (C-3′/5′), 0.1 ppm (C-4′); $\Delta\nu$ = 2 (C-1), 1 (C-2), 1 (C-3), 1 (C-4), 0 (C-1′), 0 (C-2′/6′), 0 (C-3′/5′), 0 Hz (C-4′); ^{1}H ($CDCl_3$) δ = 0.99 (t, 3H, H-4); 1.27 (d, 3H, H-1); 1.43 and 2.00 (ddq, 2H, H-3a/3b); 2.94 (tq, 1H, H-2); 7.70 (m, 2H, H-2′/6′); 7.74 ppm (m, 2H, H-3′/5′); $\Delta\delta$ = 0.0 (H-1, H-3, H-4, H-3′/5′), 0.1 ppm (H-2); $\Delta\nu$ = 2 (H-1, H-2, H-3), 1 Hz (H-4, H-2′/6′, H-3′/5′); IR (liquid) $\tilde{\nu}$: 3030, 2962, 1510, 1331, 1250, 846, 763, 705 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 278/276 (87/85, M^+), 222/200 (98/100, M^+-C_4H_8), 141 (48 $C_6H_4S^+$), 57 (24).

4-Nitro-1(1-methylpropylsulfonyl)benzene (3d)

Yield: 82%. ^{13}C ($CDCl_3$), $\delta = 11.0$ (CH_3, C-4); 12.5 (CH_3, C-1); 22.5 (CH_2, C-3); 61.7 (CH, C-2); 124.2 (CH, C-3′/5′); 130.5 (CH, C-2′/6′); 143.4 (C, C-1′); 150.9 ppm (C, C-4′). $\Delta\delta = -0.2$ (C-1), 0.0 (C-2), 0.0 (C-3), −0.1 (C-4), −0.4 (C-1′), 0.1 (C-2′/6′), 0.0 (C-3′/5′), 0.0 ppm (C-4′); $\Delta\nu = 4$ (C-1), 2 (C-2), 2 (C-3), 2 (C-4), 0 (C-1′), 0 (C-2′/6′), 0 (C-3′/5′), 1 Hz (C-4′); ^{1}H ($CDCl_3$) $\delta = 1.01$ (t, 3H, H-4); 1.30 (d, 3H, H-1); 1.47 and 2.01 (ddq, 2H, H-3a/3b); 3.02 (tq, 1H, H-2); 8.09 (m, 2H, H-2′/6′); 8.41 ppm (m, 2H, H-3′/5′); $\Delta\delta = 0.0$ (H-1,H-3, H-4, H-2′/6′), 0.1 ppm (H-2, H-3′/5′); $\Delta\nu = 2$ (H-1, H-3, H-4), 3 (H-2), 1 Hz (H-2′/6′, H-3′/5); IR (liquid) $\tilde{\nu}$: 3068, 2924, 1522, 1348, 1291, 1131, 1085, 854, 759, 737, 705 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 244 (20, M^+), 188 (40, M^+-C_4H_8), 57 (100).

4-Methoxy-1(1-methylpropylsulfonyl)benzene (3e)

Yield: 67%. ^{13}C ($CDCl_3$), $\delta = 11.2$ (CH_3, C-4); 12.6 (CH_3, C-1); 22.6 (CH_2, C-3); 55.6 (CH_3, O**C**H_3); 61.7 (CH, C-2); 114.2 (CH, C-3′/5′); 128.8 (C, C-1′); 131.1 (CH, C-2′/6′); 163.6 ppm (C, C-4′).; $\Delta\delta = -0.1$ (C-1), 0.1 (C-2), 0.0 (C-3), −0.1 (C-4), −0.1 (C-1′), 0.1 (C-2′/6′), 0.1 (C-3′/5′), 0.1 (C-4′) (C-4′), 0.2 ppm (OCH_3); $\Delta\nu = 2$ (C-1), 1 (C-2), 1 (C-3), 1 (C-4), 0 (C-1′), 0 (C-2′/6′), 0 (C-3′/5′), 0 (C-4′), 1 Hz (OCH_3); ^{1}H ($CDCl_3$) $\delta = 0.97$ (t, 3H, H-4); 1.26 (d, 3H, H-1); 1.40 and 2.02 (ddq, 2H, H-3a/3b); 2.91 (tq, 1H, H-2); 3.89 (s, 3H, OC**H$_3$**); 7.02 (m, 2H, H-3′/5′), 7.79 ppm (m, 2H, H-2′/6′); $\Delta\delta = 0$ (H-1, H-3, H-4, H-2′/6′), 0.1 (H-2), −0.1 ppm (H-3′/5′); $\Delta\nu = 2$ (H-1, H-3), 0 Hz (H-2, H-4, H-2′/6′, H-3′/5′); IR (liquid) $\tilde{\nu}$: 3035, 2972, 1594, 1292, 1257, 1132, 1088, 833, 804 cm^{-1}; EI-MS (70 eV, rel. int. %) *m/z* 242 (78, M^+), 186 (100, M^+-C_4H_8), 141 (37), 57 (21).

Calculations

All molecular calculations were calculated by density functional methods (B3LYP 6-31G* level) using the SPARTAN '08 package, version 1.0.0., Wavefunction Inc., Irvine, CA.[11]

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (grant Du 98/34).

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