# Fluorosulfur Containing Pincer Potential Ligands, 1,3-(CH<sub>2</sub>SR<sub>f</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and 1,2,4,5-(CH<sub>2</sub>SR<sub>f</sub>)<sub>4</sub>C<sub>6</sub>H<sub>2</sub>. X-Ray Structure of 1,3-(CH<sub>2</sub>SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>

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Abstract: The fluorosulfur containing pincer ligands 1,3- $(CH_2SR_f)_2C_6H_4$  [ $R_f = C_6F_5$  (1) and 4-HC\_6F\_4 (2)] and 1,2,4,5- $(CH_2SR_f)_4C_6H_2$  [ $R_f = C_6F_5$  (3) and 4-HC\_6F\_4 (4)] have been prepared by treatment of 1,3- $(CH_2Br)_2C_6H_4$  or 1,2,4,5- $(CH_2Br)_4C_6H_2$  with the corresponding lead thiolate Pb(SR<sub>f</sub>)<sub>2</sub>.

Key words: fluorine, sulfur, fluorinated pincer ligands

There is a growing interest in new materials bearing fluorosulfur moieties since they are expected to display interesting and useful properties relevant to several fields. Thus, the presence of fluorine in biologically active compounds can impart a profound influence on their biological activity. This influence has led to the development of several potent agricultural and therapeutic agents<sup>1</sup> as exemplified in pheromone chemistry, fluorinated retinoids, pyrethroids and enzyme inhibitors.<sup>2–6</sup>

On the other hand, an increasing number of academic and industrial groups are working on the design of ligands and homogeneous catalysts containing perfluoroalkyl or -aryl groups and their application in fluorous biphase systems (FBS) catalysis.<sup>7</sup> As a consequence, organofluorine chemistry has seen a flurry of research activity recently and a growing emphasis has been placed on the development and evaluation of new fluorinating reagents,<sup>8</sup> enantioselective synthesis of fluorocarbonyl compounds,<sup>8,9</sup> and the synthesis of fluorinated transition metal complexes.<sup>10</sup>

Pincer ligands of several types have been a continuous topic of research in organometallic chemistry and catalysis in recent years.<sup>11</sup> The exploration of metal complexes with these ligands has shown them suitable for novel applications in the activation of small molecules and bonds otherwise difficult to activate (e.g. C–H, C–Cl, C–F).<sup>12</sup> These ligands have also rendered iridium species active for selective dehydrogenation of *n*-alkanes to  $\alpha$ -olefins<sup>13</sup> and helped palladium complexes in opening a potential new field in the research of the C–C coupling reactions.<sup>14</sup> Thus, following our current interest in transition metal complexes with fluorinated thiolates and sulfides,<sup>15</sup> and the synthesis of new compounds able to complex in a pin-

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Art Id.1437-210X,E;2003,0,10,1565,1568,ftx,en;M00503SS.pdf. © Georg Thieme Verlag Stuttgart · New York cer like fashion,<sup>16</sup> we turned our efforts towards the synthesis of fluorine based thioether pincer ligands.

In this paper we describe the synthesis and characterization of pincer dithioether and tetrathioether ligands with fluorinated substituents 1,3-(CH<sub>2</sub>SR<sub>f</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> [R<sub>f</sub> = C<sub>6</sub>F<sub>5</sub> (1) and 4-HC<sub>6</sub>F<sub>4</sub> (2)] and 1,2,4,5-(CH<sub>2</sub>SR<sub>f</sub>)<sub>4</sub>C<sub>6</sub>H<sub>2</sub> [R<sub>f</sub> = C<sub>6</sub>F<sub>5</sub> (3) and 4-HC<sub>6</sub>F<sub>4</sub> (4)]. The structure of 1 was corroborated with a single crystal X-ray analysis.

The reactions between metal thiolates and hydrocarbon halides have been used frequently to provide the corresponding thioether compounds.<sup>17</sup> We have used lead polyfluoroaryl thiolates for the introduction of the polyfluoroarylthiolate moiety through their metathesis reactions with the appropriate bromide species.

Thus lead polyfluoroarylthiolates,  $Pb(SR_f)_2$ , react with 1,3-  $(CH_2Br)_2C_6H_4$  to give the dithioether compounds 1,3-  $(CH_2SR_f)_2C_6H_4$  [ $R_f = C_6F_5$  (1) and 4-HC\_6F\_4 (2)] (Equation 1) or with 1,2,4,5- $(CH_2Br)_4C_6H_2$  to give the tetrathioether compounds 1,2,4,5- $(CH_2SR_f)_4C_6H_2$  [ $R_f = C_6F_5$  (3) and 4-HC\_6F\_4 (4)] (Equation 2).



Equation 1



Equation 2

In all reactions, stoichiometric quantities of the corresponding bromomethyl-substituted benzene and lead polyfluoroarylthiolate were suspended in toluene and the

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stirred mixture set to reflux for 24 hours. After this time, PbBr<sub>2</sub> was separated by filtration, the solvent was evaporated under vacuum and the residue purified by chromatography to afford microcrystalline white powders.

In the FAB-mass spectra all compounds show the signals corresponding to the molecular ion  $[M]^+$  and the ion due to the loss of a proton  $[M - H]^+$ , which are of significant intensities for the dithioether compounds **1** and **2** and of low intensities for the tetrathioether compounds **3** and **4**. Compounds **1** and **2** show peaks that correspond to the loss of one SR<sub>f</sub> group,  $[C_6H_4(CH_2SR_f)(CH_2)]^+$  (high intensities), and to the loss of two SR<sub>f</sub> groups  $[C_6H_4(CH_2)_2]^+$  (intensities higher than 15%). Compounds **3** and **4** exhibit identifiable peaks with fragments corresponding to successive loss of one, two, and three SR<sub>f</sub> groups,  $[C_6H_2(CH_2SR_f)_3(CH_2)]^+$ ,  $[C_6H_2(CH_2SR_f)_2(CH_2)_2]^+$  and  $[C_6H_2(CH_2SR_f)(CH_2)_3]^+$  (several intensities) (Table 1).

**Table 1**Molecular and Fragmentation Peaks for Compounds 1,3- $(CH_2SR_f)_2C_6H_4$  and 1,2,4,5- $(CH_2SR_f)_4C_6H_2$ 

Product	FAB-MS, $m/z$ (%)
$1,3-(CH_2SC_6F_5)_2C_6H_4$ (1)	502 (33), 501 (34), 303 (100), 104 (35)
$1,3-[CH_2S(4-HC_6F_4)]_2C_6H_4(2)$	466 (25), 465 (18), 285 (92), 104 (16)
$1,2,4,5\text{-}[(CH_2SC_6F_5)]_4C_6H_2(\textbf{3})$	926 (2), 925 (4), 727 (32), 528 (6), 329 (15)
$\begin{array}{l} 1,2,4,5\text{-}[CH_2S(4\text{-}HC_6F_4)]_4C_6H_2\\ \textbf{(4)}\end{array}$	854 (4), 853 (5), 673 (25), 492 (2), 311 (9)

The IR spectra of these compounds exhibit the characteristic absorptions of SR<sub>f</sub> groups. The <sup>1</sup>H and <sup>19</sup>F NMR spectra are more illustrative. <sup>1</sup>H NMR spectra of **1** and **2** show a multiplet at low field corresponding to the aromatic protons of the  $C_6H_4$  skeleton and a single signal for the CH<sub>2</sub> groups. In addition, the <sup>1</sup>H NMR spectrum of **2** presents a triplet of triplets in the aromatic region attributed to the *para* hydrogen of the 4-HC<sub>6</sub>F<sub>4</sub> moieties. The <sup>1</sup>H NMR spectra of the tetrathioether compounds **3** or **4** exhibit two signals (singlets), which reveal the presence of the aromatic protons in the  $C_6H_2$  skeleton and the aliphatic CH<sub>2</sub> protons. The <sup>1</sup>H NMR spectrum of the compound **4**  shows an additional triplet of triplets in the aromatic region that corresponds to the *para* hydrogen of the 4-HC<sub>6</sub>F<sub>4</sub> rings. The <sup>19</sup>F NMR spectra of compounds **1** and **3** exhibit three different resonances for the *ortho*, *para* and *meta* fluorine atoms,<sup>18</sup> while compounds **2** and **4** show two resonances corresponding to the *ortho* and *meta* fluorine atoms. The <sup>1</sup>H and <sup>19</sup>F chemical shifts of compounds **1** to **4** and relevant coupling constants are collected in Table 2.

Compound 1 was recrystallized by slow evaporation from a mixture hexane– $CH_2Cl_2$  (4:1), which afforded single crystals which were analyzed by X-ray diffraction crystallography.<sup>19</sup> The corresponding structure is shown in Figures 1 and 2. Selected bond lengths and angles are collected in Table 3. The solid-state structure corresponds to the results found from <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy in solution.

In summary, we have synthesized four new fluorosulfur compounds. These molecules can be used as potentially tridentate and hexadentate pincer ligands with transition metals.



**Figure 1** ORTEP diagram of  $1,3-(CH_2SC_6F_5)_2C_6H_4$  (1)



Figure 2 ORTEP diagram of 1. View along the planes of the aryl rings

**Table 2** <sup>1</sup>H and <sup>19</sup>F NMR Chemical Shifts  $\delta$ , of 1,3-(CH<sub>2</sub>SR<sub>f</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and 1,2,4,5-(CH<sub>2</sub>SR<sub>f</sub>)<sub>4</sub>C<sub>6</sub>H<sub>2</sub>

Product	<sup>1</sup> H NMR	<sup>19</sup> F NMR
$\overline{1,3-(CH_2SC_6F_5)_2C_6H_4(1)}$	7.12 (m, 4 H, C <sub>6</sub> H <sub>4</sub> ), 4.00 (s, 4 H, 2 CH <sub>2</sub> )	-132.86 (m, 4 $F_o$ , 2 $C_6F_5$ ), -152.62 (t, 2 $F_p$ , 2 $C_6F_5$ , ${}^3J_{FF}$ = 20.7 Hz), -161.56 (m, 4 $F_m$ , 2 $C_6F_5$ )
$1,3-[CH_2S(4-HC_6F_4)]_2C_6H_4$ (2)	7.14 (m, 4 H, C <sub>6</sub> H <sub>4</sub> ), 7.00 (tt, 2 H, 2 C <sub>6</sub> F <sub>4</sub> H, ${}^{3}J_{\rm HF} = 9.6$ Hz, ${}^{4}J_{\rm HF} = 7.2$ Hz), 4.06 (s, 4 H, 2 CH <sub>2</sub> )	-134.04 (m, 4 $F_o$ , 2 $C_6F_4H$ ), -138.78 (m, 4 $F_m$ , 2 $C_6F_4H$ )
$1,2,4,5-(CH_2SC_6F_5)_4C_6H_2$ (3)	6.86 (s, 2 H, C <sub>6</sub> H <sub>2</sub> ), 4.20 (s, 8 H, 4 CH <sub>2</sub> )	-133.26 (m, 8 $F_o$ , 4 $C_6F_5$ ), -151.80 (t, 4 $F_p$ , 4 $C_6F_5$ , ${}^3J_{FF} = 20.7$ Hz), -161.25 (m, 8 $F_m$ , 4 $C_6F_5$ )
$1,2,4,5\text{-}[CH_2S(4\text{-}HC_6F_4)]_4C_6H_2 \text{ (4)}$	7.06 (tt, 4 H , 4 C <sub>6</sub> F <sub>4</sub> H, ${}^{3}J_{\text{HF}} = 9.6$ Hz, ${}^{4}J_{\text{HF}} = 7.2$ Hz), 6.88 (s, 2 H, C <sub>6</sub> H <sub>2</sub> ), 4.22 (s, 8 H, 4 CH <sub>2</sub> )	$-133.91 \text{ (m, 8 } F_o, 4 C_6 F_4 \text{H}), -138.22 \text{ (m, 8 } F_m, 4 C_6 F_4 \text{H})$

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Table 3	Selected Bond Lengths (A) and Angles (°) for 1	1,3
(CH <sub>2</sub> SC <sub>6</sub> H	$_{5})_{2}C_{6}H_{4}(1)$	

Atoms	Bond Lenghts (Å)	Atoms	Bond An- gles (°)
S(1)-C(9)	1.751(3)	C(9)-S(1)-C(7)	100.34(15)
S(1)-C(7)	1.813(3)	C(15)-S(2)-C(8)	102.37(17)
S(2)-C(15)	1.748(4)	C(6)-C(1)-C(7)	119.2(4)
S(2)-C(8)	1.778(3)	C(2)-C(1)-C(7)	120.9(4)
F(1)-C(10)	1.340(3)	C(3)-C(2)-C(1)	121.4(4)
F(2)-C(11)	1.356(4)	C(2)-C(3)-C(4)	119.1(4)
F(3)-C(12)	1.330(4)	C(2)-C(3)-C(8)	120.3(4)
F(4)-C(13)	1.348(4)	C(4)-C(3)-C(8)	120.6(4)
F(5)-C(14)	1.339(4)	C(5)-C(4)-C(3)	119.0(4)
C(1)-C(6)	1.376(4)	C(4)-C(5)-C(6)	122.0(4)
C(1)-C(2)	1.376(4)	C(5)-C(6)-C(1)	118.6(4)
C(1)-C(7)	1.497(4)	C(1)-C(7)-S(1)	111.5(2)
C(2)-C(3)	1.367(4)	C(3)-C(8)-S(2)	108.6(2)
C(3)-C(4)	1.391(4)	C(14)-C(9)-S(1)	122.0(3)
C(3)-C(8)	1.502(4)	C(10)-C(9)-S(1)	123.0(3)
		C(16)-C(15)-S(2)	122.0(4)
		C(20)-C(15)-S(2)	122.5(5)

All reactions were carried out under argon using conventional Schlenk glassware; solvents were dried using established procedures and distilled under argon immediately prior to use. TLC (Merck,  $5 \times 7.5$  cm<sup>2</sup> Kieselgel 60 F<sub>254</sub>) was used to monitor the progress of the reaction under study with hexane-CH<sub>2</sub>Cl<sub>2</sub> (4:1) as eluent. IR spectra were recorded on a Magna-Nicolet 750 FT-IR spectrometer as KBr pellets. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded with a Varian Mercury-VX spectrometer operating at 300 MHz and with a Varian Unity spectrometer operating at 376 MHz respectively. Chemical shifts are relative to TMS  $\delta = 0$  (<sup>1</sup>H) and CFCl<sub>3</sub>  $\delta = 0$  (<sup>19</sup>F) using CDCl<sub>3</sub> as solvent. Positive ion FAB mass spectra were recorded on a Jeol JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 KV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 KeV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two [poly(ethylene glycol) or CsI] reference ions. Elemental analyses were determined by Galbraith Laboratories Inc., USA. The starting materials, pentafluorothiophenol, 2,3,5,6-tetrafluorothiophenol, 1,3-di(bromomethyl)benzene and 1,2,4,5-tetrakis(bromomethyl)benzene were obtained from Aldrich Chemical Co. and used without further purification. Pb(SR<sub>f</sub>)<sub>2</sub> (R<sub>f</sub> = C<sub>6</sub>F<sub>5</sub>, 4-HC<sub>6</sub>F<sub>4</sub>) were prepared according to published procedures.<sup>18,20</sup> In all reactions stoichiometric quantities of reactants were used.

#### 1,3-(CH<sub>2</sub>SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (1); Typical Procedure

To a mixture of 1,3-di(bromomethyl)benzene (0.98 g, 3.7 mmol) in toluene (100 mL) was added  $Pb(SC_6F_5)_2$  (2.24 g, 3.7 mmol). The stirred mixture was maintained under reflux for 24 h. After this

time, PbBr<sub>2</sub> was filtered off, the solvent was removed under vacuum and the residue purified by column chromatography (silica gel, hexane–CH<sub>2</sub>Cl<sub>2</sub>, 4:1). Compound **1** was obtained as microcrystalline white powder (1.58 g, 85%); mp 52 °C.

IR (KBr): 1522, 1482, 1105, 979, 863 cm<sup>-1</sup> (SC<sub>6</sub>F<sub>5</sub>).

Anal. Calcd for  $C_{20}H_8F_{10}S_2$ : C, 47.82; H, 1.61. Found: C, 47.54; H, 1.61.

# $1,3\text{-}[CH_2S(4\text{-}HC_6F_4)]_2C_6H_4\ (2)$

White microcrystalline powder; yield: 83%; mp 75 °C.

IR (KBr): 1488, 1434, 1175, 912 cm<sup>-1</sup> (4-HC<sub>6</sub>F<sub>4</sub>S).

Anal. Calcd for  $C_{20}H_{10}F_8S_2$ : C, 51.50; H, 2.16. Found: C, 50.44; H, 2.16.

### 1,2,4,5-(CH<sub>2</sub>SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>C<sub>6</sub>H<sub>2</sub> (3)

White microcrystalline powder; yield: 94%; mp 176 °C.

IR (KBr): 1518, 1483, 1096, 977, 859 cm<sup>-1</sup> (SC<sub>6</sub>F<sub>5</sub>).

Anal. Calcd for  $C_{34}H_{10}F_{20}S_4$ : C, 44.06; H, 1.09. Found: C, 43.69; H, 1.06.

### $1,2,4,5-[CH_2S(4-HC_6F_4)]_4C_6H_2$ (4)

White microcrystalline powder; yield: 88%; mp 159 °C.

IR (KBr): 1489, 1435, 1173, 917 cm<sup>-1</sup> (4-HC<sub>6</sub>F<sub>4</sub>S).

Anal. Calcd for  $C_{34}H_{14}F_{16}S_4$ : C, 47.78; H, 1.65. Found: C, 47.41; H, 1.52.

### X-ray Crystal Data for 1

The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer. Single crystals of 1 were obtained from hexane– $CH_2Cl_2$  (4:1) as colorless needles,  $C_{20}H_8F_{10}S_2$  (502.39); Monoclinic P21/n (No. 14) with a = 19.218(3), b = 4.7630(10), c = 21.118(3) Å,  $\beta = 91.579(4)^{\circ}$ , V = 1932.3(6) Å<sup>3</sup>, Z = 4,  $D = 1.727 \text{ g/cm}^3$ , absorption coefficient 0.376 mm<sup>-1</sup> was performed at 293(2) K using graphite monochromated MoKa radiation  $(\lambda = 0.71073 \text{ Å})$ , limiting indices  $-22 \le h \le 22, -5 \le k \le 5, -25 \le l \le 1$ 25, θ-range for data collection 1.93 to 24.99°, reflections collected 22860, independent reflections 22871 ( $R_{int} = 0.1183$ ). Completeness to  $\theta = 24.99^{\circ}$  100.0%, data/restrains/parameters = 22871/0/ 290. The structure was solved by direct methods and refined by fullmatrix least-squares on F<sup>2</sup> using SHELXL-97 program system.<sup>21</sup> All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms was calculated as a riding model. The weighting scheme was  $w = 1/[s^2(F_o^2) + (0.0001P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Goodness-of-fit on F<sup>2</sup> 0.721; final R indices [I >  $2\sigma(I)$ ], R1 = 0.0724, wR2 = 0.0942; R indices (all data) R1 = 0.2415, wR2 = 0.1347.

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