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Catalytic activity of some fluorothiolate derivatives of rhodium(I). Crystal structure of $[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$

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Abstract

The thiolato-bridged dinuclear compounds $[Rh(\mu\text{-}L)(CO)_2]_2$, L = SC_6F_5 (**1**), p-SC_6HF_4 (**2**) and p-SC_6H_4F (**3**) have been obtained from the corresponding chloride-bridged species by reactions with the lead thiolates $Pb(L)_2$. Compound **3** crystallizes in the space group $P2_1/a$ with $a = 17.2722(6)$, $b = 8.9804(2)$, $c = 25.1874(12)$ Å, $\beta = 102.741(3)°$, $Z = 8$. The values of the dihedral angles, 115.3(1) and 114.3(1)°, between the two coordination planes S–Rh–S, for both molecules, point to a "bent" geometry with intermetallic Rh–Rh distances of 3.076(2) and 3.070(2) Å, which are consistent with assumed absence of metal–metal bonding.

The $[Rh(\mu\text{-}L)(CO)_2]_2/nPPh_3$ systems involving **1** to **3** or the corresponding complex with L = SCF_3 (**4**) have been studied as catalyst precursors for the hydroformylation of 1-hexene in dichloroethane at 5 bar and 30 °C. The extent of aldehyde conversion ranges from 5 to 94%, with selectivities towards linear relative to branched aldehydes in the range 3 to 3.5.

Introduction

In recent years dinuclear rhodium complexes have received considerable attention in respect of their catalytic activity. It has been shown that dinuclear rhodium complexes with thiolate [1], azolate [2], or aminothiolate [3] bridged ligands are active precursors for the hydroformylation of olefins under mild conditions of pressure (5 bar) and temperature (80 ° C).

A potential advantage of these dinuclear species is the ease of making changes in the bridging ligands. Variation of the substituents at the thiolate bridge ligands could give information about the influence of functionalized groups in the catalytic process.

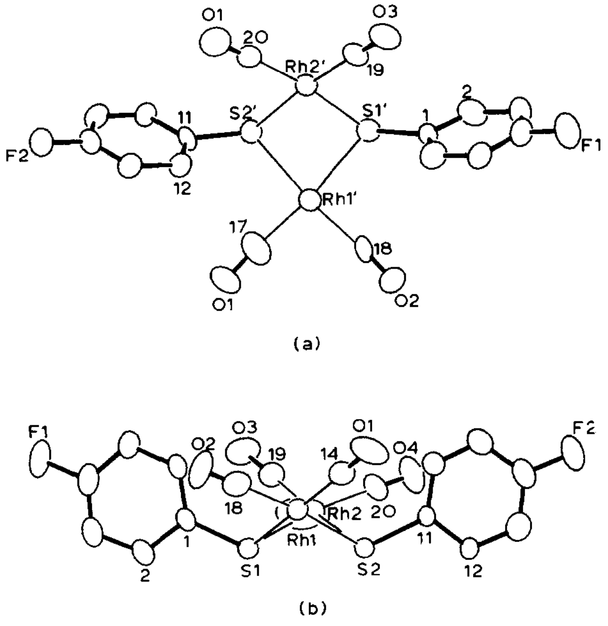
In continuation of our interest in the chemistry of fluorinated thiolato-metal compounds [4], we describe here a new method of synthesis of the dinuclear rhodium complexes $[Rh(\mu\text{-}L)(CO)_2]_2$, L = SC_6F_5 (**1**), $p\text{-}SC_6HF_4$ (**2**) and $p\text{-}SC_6H_4F$ (**3**). The crystal structure of $[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$ has been determined by an X-ray diffraction study. The $[Rh(\mu\text{-}L)(CO)_2]_2/nPPh_3$ systems involving **1** to **3** or the previously reported $[Rh(\mu\text{-}SCF_3)(CO)_2]_2$ (**4**) [5] have been used as catalyst precursor in the hydroformylation of 1-hexene at 5 bar and 80 ° C.

Results and discussion

Treatment of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with $Pb(L)_2$ (L = SC_6F_5, $p\text{-}SC_6HF_4$ or $p\text{-}SC_6H_4F$) afforded compounds **1** to **3**. These stable crystalline solids have been made previously [6a–6c] by other procedures but our method gives higher yields (> 90%).

Molecular structure of 3

Two independent molecules of the complexes are present in the crystal as shown in Fig. 1 [7]. This is consistent with the IR spectrum of this compound which shows six bands, at 2072s, 2064s, 2055s, 2042s, 2031s, and 2017 cm^{-1} [6c].



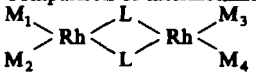
(a)

(b)

Fig. 1. View of $[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$.

Table 1

Comparison of intermetallic distances and dihedral angles [a]



Compound [b]	L	M_1	M_2	M_3	M_4	Rh–Rh (Å)	π^π(°) [c]	π^ω(°) [d]	π^ω(°) [d]
CPMPRH	S	P	C	P	C	3.061(1)	114.9	5.8	2.3
TPCHRH	S	X1	X2	C	C	3.119(2)	113.6	0.7	3.0
PMPCRH	Cl	C	P	C	P	3.167(1)	124.8	6.1	4.2
DIWRIK10	Cl	P	X1	P	X2	3.172(4)	120.5	11.9	19.4
FATHOX	Cl	X2	P	X1	P	3.134(1)	123.0	15.0	19.6
$[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ [e]	S	X1	X2	X3	X4	2.95	118.4	9.2	11.6
$[Rh(\mu\text{-}SC_6HF_4)(COD)]_2$ [f]	S	X1	X2	X4	X4	2.960(4)	117.8	11.6	10.6
Molecule **a** [g]	S	C	C	C	C	3.076(2)	115.3(1)	5.6(5)	5.3(7)
Molecule **b** [g]	S	C	C	C	C	3.070(2)	114.3(1)	7.5(5)	5.8(5)

[a] X are the midpoints of carbon–carbon double bonds. [b] The names of the compounds correspond to the codes given in the CSDB [9]. [c] π=L–Rh–L plane. [d] ω = Mi–Rh–Mj plane. [e] Reference 12. [f] Reference 6c. [g] This work.

The coordination around each rhodium atom is approximately square-planar. The intermetallic distances of 3.076(2) and 3.070(2)Å are too large to indicate interaction between the metal atoms [8].

The coordination planes through the rhodium and sulphur atoms are folded along the S–S vector at dihedral angles of 115.3(1) and 114.3(1)° in molecules **a** and **b**, respectively. The observed rhodium–rhodium distances as well as the values of the dihedral angles agree well with those listed for other in the Cambridge Structural Data Base [7]. Such dihedral angles are significantly larger in some sulphur compounds (see Table 1) than in di-μ-chloride complexes, and this may indicate that the Rh_2S_2 is more compact than the Rh_2Cl_2 core [10].

The Rh–S [range 2.350(4)–2.377(4) Å] and S–S [3.005(6)–2.987(5) Å] distances in **3** are in good agreement with those observed previously [6c,10–12]. The S atoms have a tetrahedral geometry.

The C–C bond distances in the aromatic rings fall in the ranges 1.325(35)–1.439(25) and 1.319(35)–1.401(28)Å, for molecules **a** and **b**, respectively.

The fluorinated phenyl rings of the thiolato bridges are in a *syn, endo* configuration with respect to the four membered $[RhS]_2$ core, and the mean planes of the phenyl rings are approximately perpendicular to the Rh–Rh vector.

Hydroformylation

It has been reported that $[Rh(\mu\text{-}SC_6F_5)(COD)]_2/PPh_3$ and the [Rh(μ-SC6F5)(COD)]$_2$/diphosphine systems prepared in situ are catalyst precursors for hydroformylation of olefins at 50 Kg/cm^2 and 80 ° C, although the selectivities for linear relative to branched aldehydes (n/iso) were low [13].

In the present work precursor systems for the hydroformylation reaction were prepared by addition of triphenylphosphine (Rh/PPh_3 molar ratio = 1/1, 1/2, 1/4) to 1,1-dichloroethane solutions of the $[Rh(\mu\text{-}L)(CO)_2]_2$ complexes $L = SC_6F_5$, SC_6HF_4, SC_6H_4F, SCF_3 [5,6c]. Mild conditions, namely 5 bar and 80 ° C, were used. The results are summarized in Table 2.

When the Rh/PPh_3 molar ratio was 1/1 or 1/2 hydroformylation was observed in all experiments; only linear and branched aldehydes were obtained, no hydro-

Table 2

Hydroformylation results [a]

Exp.	Complex	Rh/PPh_3	Induction period (h)	% Conversion aldehyde	%h	n/iso	ν(CO)
1	$[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$	1/1	6	81	76	3.2	1974
2	$[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$	1/2	5	82	78	3.5	1979
3	$[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$	1/4	–	6	76	3.2	1979
4	$[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$	1/2	8	18	75	3.0	1980 1825
5	$[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$	1/4	–	5	76	3.3	1979 1827
6	$[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$	1/2	0	94	77	3.2	1978
7	$[Rh(\mu\text{-}SCF_3)(CO)_2]_2$	1/2	11	35	76	3.2	1979

[a] Reaction conditions: 0.1 mmol of complex; [1-hexene]/[complex] = 400, CO/H_2 = 1/1. Total pressure = 5 bar, temperature = 80 ° C, solvent = 15 mL 1,2-dichloroethane. ν(CO) in 1,2-dichloroethane solution recorded at the end of the reaction. Reaction time: 20 h.

genation or isomerization products being detected. However, long induction periods were necessary in the case of the $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ and $[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$ complexes. The best results were obtained with the $[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$ complex, 94% conversion into aldehydes being achieved along with 77 selectivity towards linear aldehyde.

The presence of excess of PPh_3 ligand (Rh/PPh_3 molar ratio = 1/4) in the case of $[Rh(\mu\text{-}S_6F_5)(CO)_2]_2$ and $[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$ strongly lowers the catalytic activity, although the selectivity towards linear aldehyde is essentially maintained. It was reported previously [13] that when the related $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2 + nPPh_3$ ($n = 2, 4$) systems were used as catalyst precursors the selectivity towards linear aldehyde was not increased when the $nPPh_3/Rh$ molar ratio changed from 1 to 2. It is noteworthy that a different effect was previously observed in the case of the $[RhH(CO)(PPh_3)_3]$ catalyst with which the presence of an excess of the ligand produced a strong decrease in the activity but an increases in the selectivity [14]. Different behaviour again was recently observed with the related dinuclear $(Rh(\mu\text{-}S(CH_2)_3N(CH_3)_2)(COD)]_2/PR_3$ system when used as catalyst precursor under the same hydroformylation conditions (5 bar, 80 ° C), in this case, when different excesses of PPh_3 were used (molar ratio $Rh/PPh_3 = 1/1, 1/2, 1/5, 1/10$) the selectivity increased without a significant decline in activity [3b].

The precursor systems described in this work are less active than the related μ-thiolate bridged ligand complexes [1]. The difference in behaviour could be attributed to the presence of the fluorine substituents in the thiolato bridging ligands.

Studies on reactivity of the tetracarbonyl rhodium complexes $[Rh(\mu\text{-}L)(CO)_2]_2$ towards PPh_3 have been carried out previously in our laboratory [6c]. When $L = SC_6H_4F$ and SCF_3, $Rh/P = 1/2$ molar ratio, the dinuclear $[Rh(\mu\text{-}L)(PPh_3)(CO)]_2$ complexes were obtained. The IR spectra show two $\nu(CO)$ frequencies in accord with a *cis*-disposition.

In contrast, under the same conditions, treatment of $[Rh(\mu\text{-}SC_6HF_4)(CO)_2]_2$ with triphenylphosphine leads to formation of the mononuclear $[Rh(SC_6HF_4)(PPh_3)(CO)_2]$ complex. However the IR spectra recorded at the end of the hydroformylation reaction show a single frequency in the $\nu(CO)$ region, indicating of that other species had been formed under the hydroformylation conditions. Furthermore, when low conversions were obtained (experiments 3, 4, 5, in Table 2), $\gamma(CO)$ frequencies were observed at 1827–1825 cm^{-1}, probably attributable to the presence of inactive dimeric species with briging carbonyl groups [15].

Experimental

Solution and refinement

Suitable red single crystals of $[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$ were grown by solvent diffusion of ethanol into a concentrated solution of **3** in toluene at 0 ° C.

Table 3 outlines the procedures used to solve and refine the molecular structure. Weighting schemes were chosen empirically using functions of the type $w = K/f(F_o) \cdot g(\sin \theta/\lambda)$, with K chosen to ensure that $\langle w \Delta^2 F \rangle = 1$ and to give no trends in $\langle w \Delta^2 f \rangle$ vs. $\langle F_o \rangle$ and $\langle \sin \theta/\lambda \rangle$.

Fractional atomic coordinates for non-hydrogen atoms are listed in Table 4. Relevant geometrical parameters are given in Table 5. Additional material available

Table 3

Crystal data and details of data collection

Crystal data	
Formula	$C_{16}H_8Rh_2S_2F_2O_4$
Crystal habit	Prism of rectangular base
Crystal size (mm)	$0.17 \times 0.28 \times 0.10$
Symmetry	Monoclinic, $P2_1/a$
Unit cell determination:	Least-squares fit from 96 reflections ($\theta < 45°$)
Unit cell dimensions	$a = 17.2722(6)$, $b = 8.9804(2)$, $c = 25.1874(12)$ Å $\beta = 102.741(3)°$
Packing: V(A^3), Z	3810.7(2), 8
Dc(g·cm^{-3}), M, F(000)	1.995, 572.2, 2208
μ(cm^{-1})	167.37
Experimental data	
Technique	Four circle diffractometer Bisecting geometry Graphite oriented monochromator: Cu-K_α $\omega/2\theta$ scans, scan width: 1.5° Detector apertures $1.0 \times 1.0°$
Total measurements	Up to 65° in θ
Speed	1 min/reflec.
Number of reflections:	
Measured	6485
Independent	6485
Observed	5037 [$3\sigma(I)$ criterion]
Standard reflexions:	2 reflections every 90 minutes Variation: no
Max-min transmission factors:	1.355-0.589 [16]
R values befor and after absorption correction	0.167-0.097
Solution and refinement	
Solution	Patterson function and DIRDIF
Refinement	L.S. on Fobs with 2 blocks
Parameters:	
Number of variables	469
Degrees of freedom	4568
Ratio of freedom	10.7
H atoms	Difference synthesis
Final shift/error	0.08
Max. thermal value	$U_{22}[F(2)] = 0.20(2)$Å^2
Final ΔF peaks	1.15 e.Å^{-3}
Extinction correction	No
Final R and R_w	0.079-0.109
Computer and programs	VAX 11/750 XRAY76 System [17] DIRDIF [18]
Scattering factors	Int. Tables for X-Ray Crystallography [19]

from the authors comprises the H-atom parameters, anisotropic thermal parameters for non-hydrogen atoms, and structure factors.

Starting materials. $RhCl_3 \cdot nH_2O$, C_6F_5SH, p-C_6HF_4SH, p-C_6H_4FSH, and AgF were supplied by the Aldrich Chemical Co.

All manipulations were carried out under dry oxygen-free nitrogen by standard vacumm and Schlenk-tube techniques. $[Rh(\mu\text{-}Cl)(CO)_2]_2$ [20], $[Rh(\mu\text{-}SCF_3)(CO)_2]_2$

Table 4

Final atomic coordinates

Atom	*x*	*y*	*z*
Rh(1)	0.33526(7)	0.38229(14)	0.98935(5)
Rh(2)	0.34074(7)	0.04666(13)	1.01295(5)
S(1)	02600(2)	0.1861(5)	0.9423(2)
C(1)	0.2815(9)	0.1536(18)	0.8772(6)
C(2)	0.2194(11)	0.1376(23)	0.8338(7)
C(3)	0.2310(14)	0.1144(26)	0.7811(8)
C(4)	0.3049(14)	0.1005(23)	0.7757(8)
C(5)	0.3688(12)	0.1156(27)	0.8172(8)
C(6)	0.3556(11)	0.1440(25)	0.8683(7)
S(2)	0.3019(2)	0.2454(5)	1,0619(1)
C(11)	0.3695(8)	0.2657(17)	1.1263(5)
C(12)	0.3384(10)	0.2673(23)	1.1713(6)
C(13)	0.3865(14)	0.2789(27)	1.2222(8)
C(14)	0.4684(14)	0.2941(24)	1.2270(8)
C(15)	0.5001(11)	0.2965(25)	1.1808(8)
C(16)	0.4506(10)	0.2806(22)	1.1308(7)
F(1)	0.3186(10)	0.0732(22)	0.7249(5)
F(2)	0.5185(9)	0.3069(18)	1.2769(5)
C(17)	0.4026(11)	0.5191(22)	1.0319(8)
O(1)	0.4459(9)	0.6049(19)	1.0563(8)
C(18)	0.3504(11)	0.4647(26)	0.9262(8)
O(2)	0.3557(12)	0.5256(20)	0.8859(7)
C(19)	0.3784(11)	−0.0889(19)	0.9704(8)
O(3)	0.4032(10)	−0.1740(19)	0.9423(8)
C(20)	0.3962(10)	−0.0420(21)	1.0761(8)
O(4)	0.4303(11)	−0.0995(20)	1.1155(6)
Rh(1′)	0.26963(7)	0.03018(14)	0.52194(5)
Rh(2′)	0.42648(7)	0.13104(14)	0.49449(5)
S(1′)	0.4018(2)	−0.0059(5)	0.5692(2)
C(1′)	0.4290(8)	0.1023(21)	0.6292(6)
C(2′)	0.4875(12)	0.0463(24)	0.6711(9)
C(3′)	0.5159(14)	0.1267(37)	0.7179(8)
C(4′)	0.4876(13)	0.2643(29)	0.7221(8)
C(5′)	0.4299(13)	0.3342(26)	0.6817(9)
C(6′)	0.4024(12)	0.2464(18)	0.6355(8)
S(2′)	0.3298(2)	−0.0393(5)	0.4498(2)
C(11′)	0.2824(8)	0.0361(17)	0.3854(6)
C(12′)	0.2424(11)	0.1610(22)	0.3808(7)
C(13′)	0.2101(12)	0.2236(23)	0.3280(8)
C(14′)	0.2208(11)	0.1406(31)	0.2835(8)
C(15′)	0.2584(12)	0.0109(27)	0.2879(7)
C(16′)	0.2906(12)	−0.0469(27)	0.3391(7)
F(1′)	0.5179(9)	0.3463(21)	0.7673(6)
F(2′)	0.1906(7)	0.1978(23)	0.2320(5)
C(17′)	0.1696(12)	0.0595(28)	0.4787(9)
O(1′)	0.1086(9)	0.0727(24)	0.4522(8)
C(18′)	0.2326(10)	0.0640(21)	0.5841(7)
O(2′)	0.2076(9)	0.0860(22)	0.6207(6)
C(19′)	0.4973(11)	0.2668(23)	0.5366(8)
O(3′)	0.5401(8)	0.3461(18)	0.5623(7)
C(20′)	0.4310(10)	0.2335(25)	0.4305(8)
O(4′)	0.4313(9)	0.2978(19)	0.3910(7)

Table 5

Selected geometrical parameters

(a) *Bond distances(Å) and angles(°)*

	(a)	(b)		(a)	(b)
Rh(1)-Rh(2)	3.076(2)	3.070(2)	S(1)-C(1)	1.772(17)	1.783(17)
Rh(1)-S(1)	2.353(4)	2.350(4)	S(2)-C(11)	1.780(14)	1.787(13)
Rh(1)-S(2)	2.367(5)	2.377(4)	F(1)-C(4)	1.360(26)	1.374(25)
Rh(1)-C(17)	1.847(19)	1.860(18)	F(2)-C(14)	1.386(24)	1.365(22)
Rh(1)-C(18)	1.843(18)	1.826(22)	C(17)-O(1)	1.122(23)	1.152(24)
Rh(2)-S(1)	2.364(5)	2.363(4)	C(18)-O(2)	1.118(25)	1.174(28)
Rh(2)-S(2)	2.360(4)	2.350(4)	C(19)-O(3)	1.123(24)	1.185(28)
Rh(2)-C(19)	1.880(18)	1.846(18)	C(20)-O(4)	1.150(27)	1.158(24)
Rh(2)-C(20)	1.873(21)	1.834(20)			
S(1)-Rh(1)-S(2)	79.1(2)	78.4(1)	C(20)-Rh(2)-S(1)	171.8(6)	170.1(6)
S(1)-Rh(1)-C(18)	94.2(5)	91.9(7)	Rh(1)-S(1)-Rh(2)	81.4(1)	81.3(1)
C(17)-Rh(1)-C(18)	91.3(9)	92.5(9)	Rh(1)-S(1)-C(1)	113.6(6)	112.5(6)
C(17)-Rh(1)-S(2)	95.5(7)	97.2(6)	Rh(2)-S(1)-C(1)	109.5(6)	113.4(6)
C(17)-Rh(1)-S(1)	174.4(7)	172.7(6)	Rh(1)-S(2)-Rh(2)	81.2(1)	81.0(1)
C(18)-Rh(1)-S(2)	171.6(6)	170.3(7)	Rh(1)-S(2)-C(11)	114.0(5)	115.1(5)
S(1)-Rh(2)-S(2)	79.0(2)	78.7(1)	Rh(2)-S(2)-C(11)	108.8(5)	110.4(5)
S(1)-Rh(2)-C(19)	95.6(6)	97.9(6)	O(1)-C(17)-Rh(1)	177.9(23)	177.0(18)
C(19)-Rh(2)-C(20)	91.3(9)	91.9(8)	O(2)-C(18)-Rh(1)	177.5(16)	174.9(20)
C(20)-Rh(2)-S(2)	93.9(6)	91.7(6)	O(3)-C(19)-Rh(2)	178.9(18)	178.6(17)
C(19)-Rh(2)-S(2)	173.4(6)	172.0(6)	O(4)-C(20)-Rh(2)	177.9(17)	179.0(18)

(b) *Planes [deviations(Å) in brackets]*

		(a)	(b)
i: S(2),C(17),C(18),S(1)	[Rh(1)	0.032(1)	0.051(1)]
ii: S(1),C(19),C(20),S(2)	[Rh(2)	0.074(1)	−0.048(1)]
iii: C(1) ··· C(6)	[F(1)	0.040(16)	−0.023(20)]
iv: C(11) ··· C(16)	[F(2)	−0.036(15)	−0.017(16)]

Planes	Angles(°)	
	(a)	(b)
i–ii	113.9(4)	110.9(3)
iii–iv	154.4(7)	169.9(7)

[5], [AgSCF$_3$] [21] and Pb(SC$_6$F$_5$)$_2$ [22] were prepared by published methods. The lead derivatives Pb(SC$_6$HF$_4$)$_2$ and Pb(SC$_6$H$_4$F)$_2$ were obtained by reaction between equimolar quantities of the corresponding thiol and lead acetate in water. Solvents were dried and distilled under nitrogen prior to use. All other materials were used as commercially supplied.

A typical procedure for preparation of [Rh(μ-L)(CO)$_2$]$_2$ (L = C$_6$F$_5$ (**1**), *p*-C$_6$HF$_4$ (**2**) or *p*-SC$_6$H$_4$F (**3**)) was as follows: A solution of [Rh(μ-Cl)(CO)$_2$]$_2$ (0.60 g, 1.5 mmol) in acetone (30 mL) was added under nitrogen, at room temperature to one of Pb(SC$_6$F$_5$)$_2$ in acetone (30 mL) or to a suspension of Pb(SC$_6$HF$_4$)$_2$ or Pb(SC$_6$H$_4$F)$_2$ (1.60 mmol) in acetone (30 mL). The mixture was heated under reflux (17 h for **1** and 24 h for **2** and **3**) until the suspended lead thiolate had been consumed. The solution was then cooled to room temperature and the precipitated PbCl$_2$ was filtered off and washed repeatedly with acetone. The filtrate and washings were combined and the solvent was taken off under vacum. The solid residue was purified by chromatography on a column of silica-gel, with chloroform as eluent. The yellow-orange (**1**, **2**) or red (**3**) fraction was collected (60 mL), concentrated under vacuum (20 mL) and cooled to give yellow (**1**, **2**) or red (**3**) crystals. These were dried under vacuum.

Compound **1**: Yield: 1.01 g (92%). Anal. Found: C, 26.76; F, 26.58. $C_{16}F_{10}O_4Rh_2S_2$ calcd.: C, 26.83; F, 26.53%.

Compound **2**: Yield: 0.99 g (94%). Anal. Found: C, 28.09; H, 0.44; F, 22.24. $C_{16}H_2F_8O_4Rh_2S_2$ calcd.: C, 28.25; H, 0.30; F, 22.35%.

Compound **3**: Yield: 0.81 g (92%). Anal. Found: C, 33.37; H, 1.29; F, 6.53. $C_{16}H_8F_2O_4Rh_2S_2$ calcd.: C, 33.59; H, 1.41; F, 6.64%.

Hydroformylation experiments were carried out in a 150 mL stainless steel autoclave equipped with a magnetic stirrer and glass inlet. The temperature was kept constant at 80 ° C by circulating water through a double jacket. The mixture of syngas ($H_2/CO = 1$) was introduced at constant pressure of 5 bar from a gas tank. The fall of pressure in the reservoir was monitored with a transducer connected to an electronic measuring recorder. The dichloroethane solution of the rhodium complexes containing the required of the relevant phosphine and the 1-hexene were introduced into the evacuated autoclave. This was heated and when the system had reached thermal equilibrium the syngas was introduced at 5 bar and the stirring started. After each run the solution was analyzed by IR spectroscopy with a Nicolet 5ZDX-FT spectrometer and by GLC with a Hewlett-Packard 5840A chromatograph equipped with an 6mX1/8" column of OV-17 on Chromosorb WHP.

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