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Rhodium(I) fluorothiolate complexes as hydroformylation catalyst precursors. Crystal structure of two polymorphs of *trans*-[Rh(SC_6F_5)(CO)(PPh_3)$_2$]

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Abstract

The perfluorothiolate dinuclear compounds [Rh(μ-SC_6F_5)(COD)]$_2$ **1** and [Rh(μ-SC_6F_5)(CO)$_2$]$_2$ **2** react with PPh_3 to give monomeric and dimeric complexes, the particular product depending upon the PR_3/Rh ratio and reaction conditions. Reaction of **2** with 2 moles of PPh_3 renders *cis*-**7** and *trans*-[Rh(μ-SC_6F_5)((CO)(PPh_3)]$_2$ **8**, while with 4 moles of PPh_3 *trans*[Rh(SC_6F_5)(CO)(PPh_3)$_2$]**10a** is obtained. This latter product can otherwise be prepared by Cl metathesis from *trans*-[RhCl(CO(PPh_3)$_2$] in toluene. This same reaction in dichloromethane however yields the *cis* isomer **10b**. When a larger excess of PPh_3 is used, a mixture of compounds **11a** and **11b** is formed. An X-ray crystal structure study shows *trans*[Rh(SC_6F_5)(CO)(PPh_3)$_2$] to exit as two polymorphs. **11a** crystallises in the space group $P2_1/n$ of the monoclinic system with $a = 12.489(1)$, $b = 15.430(5)$, $c = 19.719(1)$ Å, $\alpha = \gamma = 90$, $\beta = 92.84(1)°$, and **11b** is triclinic, space group $P\bar{1}$ with $a = 9.764(2)$, $b = 12.197(6)$, $c = 17.880$ Å, $\alpha = 100.18(5)$, $\beta = 101.92(2)$, $\gamma = 113.61(2)°$. Both PPh_3 ligands are mutually *trans* and the difference in ν(CO) stretching frequencies, 1989 and 1939 cm^{-1}, can be explained in terms of o-phenyl H...CO interactions in the latter. The [Rh(μ-SC_6F_5)(COD)]$_2$ *1* and [Rh(μ-SC_6F_5)(CO)$_2$]$_2$ *2*/nPPh_3 systems have been studied as catalyst precursors for the hydroformylation of 1-heptene in toluene at 30 bar and 343 K. Selectivity towards the linear aldehyde is enhanced when dimeric complexes are used. © 1997 Elsevier Science S.A.

Keywords: Rhodium; Thiolate; X-ray diffraction; Hydroformylation

1. Introduction

Complexes containing thiolate ligands are of great interest due to their importance in catalytic processes [1–9], the role they play in carbon–sulphur bond formation, especially as intermediates in desulphurization processes, and because of their involvement in a large number of biological systems [10–16]. With thiolate ligands $(RS)^-$, manipulation of steric and electronic properties of these pseudohalide groups is possible by varying the basicity and/or bulkiness of the R substituents [17]. It has been shown that, depending on the basicity of R, thiolates stabilise monomers as well as polymeric compounds [18]. Dimeric homo- and hetero-metallic species are formed either by bridging sulphur atoms or using assisted thiolate ligands with another donor group [19].

Thiolates also allow the formation of unsaturated metal centres through intramolecular ligand–metal interactions [20,21].

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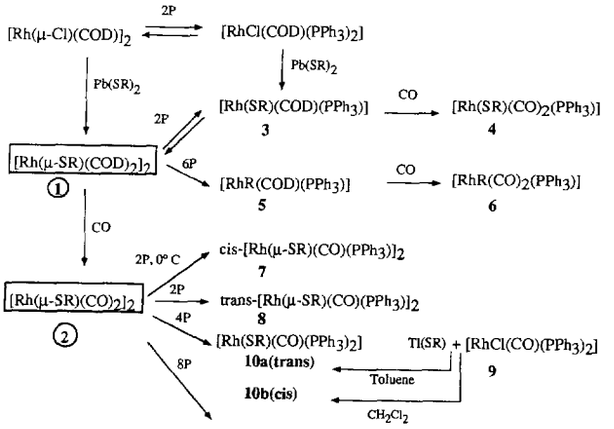
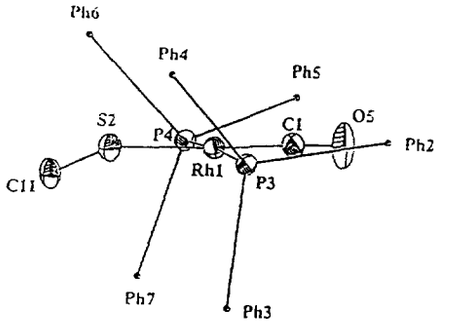
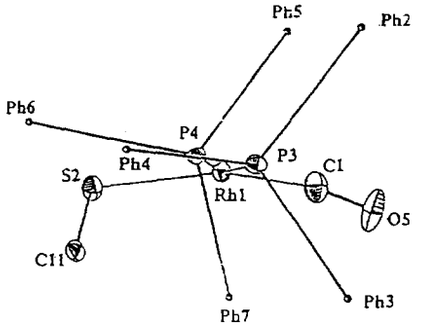




11a



11b

Scheme 1. P = PPh_3, R = C_6F_5, Phn (centroids of Cn1-Cn6 phenyl rings).

The reactivity of dinuclear [22,23] and mononuclear [13,24,25] thiolate rhodium complexes has been extensively studied in recent years to more fully understand their role in catalytic reactions such as hydroformylation of olefins [26–30]. The study of these reactions continues to be of great interest not only from a mechanistic point of view but also from the point of view of finding reaction conditions which would allow overall yields and selectivity of the desired products to be improved upon [31–35].

As part of our research programme on perfluorinated thiolate complexes, we describe here the catalytic performance of dimeric and monomeric '$Rh(SC_6F_5)$' complexes in the presence of varying amounts of PPh_3, and in which other reaction parameters such as temperature, pressure, solvent, etcetera were kept constant, in order to further extend the discussion to dimeric complexes immobilised on phosphinated silica.

The complexes studied, together with related thiolate-phosphine compounds relevant to our discussion of intermediates in the hydroformylation reaction are summarised in Scheme 1.

2. Experimental

All manipulations were carried out under dry oxygen-free nitrogen atmosphere using Schlenk-tube techniques. Solvents were dried and degassed using standard techniques.

Complexes were characterised by infrared spectroscopy over the 4000–400 cm^{-1} range as KBr pellets or in a solution cell using a Nicolet ZDX Fourier Transform IR spectrophotometer. Data are expressed in wavenumbers (cm^{-1}) along with relative intensities (s, strong; m, medium; w, weak). The ^{1}H, ^{31}P NMR spectra were recorded on a Varian Unity FT-300 or a Varian Gemini FT-200 spectrometer. The chemical shifts were measured relative to the residual deuterated solvents (^{1}H), and H_3PO_4 $\delta = 0$ (^{31}P). Complexes were studied in C_6D_6 at room temperature. Mass spectra were obtained on a VG AutoSpec mass spectrometer, FAB positive, using a matrix of nitrobenzyl alcohol.

Elemental analyses were determined by SIDI, UAM Cantoblanco, Madrid, Spain.

2.1. Single-crystal X-ray structure analysis

A mixture of yellow (**11a**) and orange (**11b**) crystals suitable for X-ray diffraction studies was obtained from a toluene solution at 263 K. The crystals were separated under a microscope with a needle. Crystallographic data for both compounds are listed in Table 1.

Intensity data for **11a** and **11b** were collected with graphite monochromated Cu $K\alpha$ radiation on an Enraf-Nonius CAD4 and Seifert XRD 3000S diffractometer, respectively, using an $\omega/2\theta$ scan technique. No crystal decomposition was observed. Data were corrected for Lorentz and polarisation effects and absorption corrections were applied using the data of the corresponding Ψ scan [36]. **11a** was solved by Patterson methods and subsequent difference Fourier techniques DIRDIF [37]. **11b** was solved by direct methods using SIR92 [38]. In both cases refinement was performed by weighted least-squares techniques using SHELX93 [39]. All non-hydrogen atoms were refined in the anisotropic mode and hydrogen atoms were refined isotropically with a thermal parameter amounting to 1.2 times the value of the

Table 1
X-ray crystal data and structure refinement for **11a**, and **11b**

	11a	**11b**
Formula	$C_{43}H_{30}F_5OP_2RhS$	$C_{43}H_{30}F_5OP_2RhS$
F_w	854.58	854.58
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Crystal size, mm	0.15×0.18×0.20	0.20×0.15×0.50
a, Å	12.489(1)	9.764(2)
b, Å	15.430(5)	12.197(6)
c, Å	19.719(1)	17.880(4)
α, deg	90	100.18(5)
β, deg	92.84(1)	101.92(2)
γ, deg	90	113.61(2)
V, A^3	3795.3(1)	1827.3(1)
Z	4	2
D_{calc}, Mg/m^{-3}	1.496	1.553
$F(000)$	1728	864
Absorption coefficient, mm^{-1}	5.450	5.660
Transmission coefficient	0.923–1.000	0.932–1.000
θ range, deg	2–60	2–60
Wavelenghth, Å	1.5418	1.5418
Temperature, K	293 (2)	293(2)
Index ranges	$0 \le h \le 14$, $0 \le k \le 17$, $-22 \le l \le 22$	$0 \le h \le 10$, $-12 \le k \le 12$, $-19 \le l \le 19$
Reflections collected	5621	5435
Independent reflections	5472 [R(int) = 0.001]	5321 [R(int) = 0.008]
Refinement method	Full-matrix l. s. on F^2	Full-matrix l. s. on F^2
Data/restraints/parameters	5472/0/478	5321/0/478
Goodness-of-fit on F^2	1.017	1.053
Final R indices [$I > 2s(I)$]	$R_1 = 0.065$, $wR_2 = 0.178$	$R_1 = 0.0643$, $wR_2 = 0.171$
R indices (all data)	$R_1 = 0.087$, $wR_2 = 0.207$	$R_1 = 0.078$, $wR_2 = 0.184$
Largest diff peak and hole	1.032 and −1.086 e $Å^{-3}$	1.177 and −1.563 e $Å^{-3}$

equivalent isotropic thermal parameter of their carrier atoms. The maximum and minimum electron densities of the final difference synthesis (Table 1) are, in both cases, located near the Rh atoms. Tables of atomic parameters, bond distances and angles, drawings and structure factor tables have been deposited at the Cambridge Crystallographic Data Centre.

2.2. Catalytic activity

Catalytic activity measurements were carried out in a 300 cm^3 stainless steel autoclave (Magnedrive Autoclave Engineers). The reactor, once evacuated, was charged by suction with a mixture of catalyst, 50 ml of toluene and 2.5 ml of 1-heptene from a Schlenk tube kept under nitrogen. Carbon monoxide was then introduced (5 bar) and the mixture was warmed to 373 K. Subsequently, the CO pressure was raised to 15 bar and the H_2 pressure to 30 bar. During the experiment an equimolar mixture of $CO:H_2$ was fed to the reactor. The reaction mixture was magnetically stirred at 750 r.p.m. Analysis of the solutions, removed periodically from the reactor was carried out by gas–liquid chromatography, using a 20 meter column of 16% Carbowax 20M on a Chromosorb WAW-DMCS 80/100 support, in the case of the aldehydes, and 20% β,β'-oxypropionitrile on Chromosorb P 80/100 for the isomerised olefins. Konik KNK300-HRGC and Shimadzu GC-R1A chromatographs, were used.

2.3. Preparation of compounds

Complexes $[Rh(\mu\text{-}Cl)(COD)]_2$ [40], $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ **1** [41], $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ **2** [42], *trans*-$[RhCl(CO)(PPh_3)_2]$ **9** [43], and $TlSC_6F_5$ [44] were prepared according to published methods. All other reagents were supplied commercially. Solvents were dried and distilled under nitrogen prior to use.

2.3.1. *cis-[Rh(μ-SC$_6$F$_5$)(CO)(PPh$_3$)]$_2$ 7*

Toluene (5 ml), cooled to 268 K, was added to a mixture of $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ **2**, (0.1476 g, 0.21 mmol) and PPh_3 (0.1118 g, 0.42 mmol). An immediate evolution of gas was observed. The mixture was magnetically stirred for 15 min and then warmed to room temperature. The orange solution was cooled to yield an orange crystalline solid. The solid was filtered off, washed with hexane and dried under vacuum.

Calc. for $C_{50}H_{30}F_{10}S_2P_2O_2Rh_2$: C, 50.7; H, 2.6; S, 5.4. Found: C, 51.0; H, 2.7; S, 5.3%. IR: ν(CO): 1994, 1977 cm^{-1}. Mass spectrum: (m/z) 1184 (M^+), 1128 (M^+–2CO), 985 (M^+–SR), 957(M^+–SR–CO).

2.3.2. *trans-[Rh(μ-SC$_6$F$_5$)(CO)(PPh$_3$)]$_2$ 8*

To a mixture of $[Rh(\mu\text{-}SC_6F_5)CO)_2]_2$ **2**, (0.0452 g, 0.063 mmol) and PPh_3 (0.033 g, 0.12 mmol), toluene (3 ml) was added at room temperature. CO was evolved vigorously. The solution was magnetically stirred for one hour, then ethanol (20 ml) was added. The orange solution was cooled to produce an orange crystalline product. The solid was filtered off, washed with ethanol and dried under vacuum.

Calc. for $C_{50}H_{30}F_{10}S_2P_2O_2Rh_2.C_7H_8$: C, 53.6; H, 3.0; S, 5.0. Found: C, 53.4; H, 3.0; S, 4.9%. IR: ν(CO): 1984 cm^{-1}. Mass spectrum: (m/z) 1184 (M^+), 1128 (M^+–2CO), 985 (M^+–SR), 957 (M^+–SR–CO).

2.3.3. *trans-[Rh(SC$_6$F$_5$)(CO)(PPh$_3$)$_2$] **10a***

To a mixture of $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ **2**, (0.1295 g, 0.180 mmol) and PPh_3 (0.1890 g, 0.72 mmol), toluene (3 ml) was added at room temperature, which was followed by a vigorous evolution of CO. The solution was magnetically stirred for one hour, then ethanol (20 ml) was added. The yellow solution was cooled from which a crystalline lemon yellow compound was obtained. The solid was filtered off, washed with ethanol and dried under vacuum.

Calc. for $C_{43}H_{30}F_5SP_2ORh$: C, 60.4; H, 3.5; S, 3.7. Found: C, 60.5; H, 3.3; S, 3.5%. ^{31}P NMR: $\delta = 28.0$ d, J(P–Rh) = 135 Hz. IR: ν(CO): 1989 cm^{-1}. Mass spectrum: (m/z) 854 (M^+), 826 (M^+–CO), 655 (M^+–SR), 627 (M^+–CO–SR), 364 (M^+–CO–SR–PPh_3).

10a can be prepared like **10b** (see below) using toluene as solvent

2.3.4. *cis-[Rh(SC$_6$F$_5$)(CO)(PPh$_3$)$_2$] **10b***

A mixture of trans-$[RhCl(CO)(PPh_3)_2]$ **9**, (0.0273 g, 0.039 mmol) and $Tl(SC_6F_5)$ (0.0160 g, 0.039 mmol) and dichloromethane (5 ml) was stirred for two hours at room temperature. The TlCl precipitate was filtered off and the solution evaporated to dryness under vacuum.

Calc. for $C_{43}H_{30}F_5SP_2ORh$: C, 60.4; H, 3.5; S, 3.7. Found: C, 60.5; H, 3.2; S, 3.7%. IR: ν(CO): 1977 cm^{-1}. Mass spectrum: (m/z) 854 (M^+), 826 (M^+–CO), 655 (M^+–SR), 627 (M^+–CO–SR), 365 (M^+–CO–SR–PPh_3).

*2.3.5. trans-[Rh(SC$_6$F$_5$)(CO)(PPh$_3$)$_2$] **11a**, **11b***

A mixture of [Rh(μ-SC$_6$F$_5$)(CO)$_2$]$_2$ **2**, (0.0587 g, 0.081 mmol), PPh$_3$ (0.171 g, 0.651 mmol) and toluene (5 ml) was magnetically stirred at room temperature for two days, ethanol was then added (10 ml) and the solution cooled to render a mixture of microcrystalline yellow and orange solids. This mixture was filtered off, washed with ethanol and dried under vacuum. A second crop of crystals containing both species was obtained from the mother liquors.

Calc. for C$_{43}$H$_{30}$F$_5$SP$_2$ORh: C, 60.4; H, 3.5; S, 3.8. Found: C, 60.5; H, 3.3; S, 3.5%. ^{31}P NMR: δ = 28.0 d, J(P–Rh) = 132 Hz. IR: ν(CO): 1989, 1939 cm^{-1}. Mass spectrum: (m/z) 854 (M$^+$), 826 (M$^+$–CO), 655 (M$^+$–SR), 627 (M$^+$–CO–SR), 365 (M$^+$–CO–SR–PPh$_3$).

3. Results and discussion

3.1. Rhodium complexes

The reactivity of dimeric complexes containing halides or (SR)$^-$ bridges towards nucleophiles and particularly mono and diphosphines has been extensively investigated. A variety of products can be isolated depending upon the reaction conditions, PR$_3$/Rh ratios and the nature of the SR groups. Compounds [Rh(SR)(COD)]$_2$, (R = C$_6$F$_5$, C$_6$H$_4$F, C$_6$HF$_4$, CF$_3$) when reacted with phosphines, render monomeric species [Rh(SR)(COD)(PPh$_3$)] [24,25]. Treatment of **1** with PPh$_3$ (P/Rh = 1) in toluene at room temperature affords the monomeric complex **3** [42] which is in equilibrium with the dimeric species, a feature found in analogous chlorinated systems [45]. When P/Rh is 6 and the reaction is carried out in toluene at room temperature, **3** is obtained in 45% yield while a mixture of crystalline compounds is produced at reflux. Separation and full characterisation of all the components of this mixture has not been possible although the desulphurated complex **5** has been identified. Sulphur abstraction with subsequent formation of SPPh$_3$ and the pentafluorophenyl complex takes place [23].

It has been previously reported that dimeric tetracarbonyl thiolate species, when reacted with phosphines, can produce pentacoordinated complexes in which the bridges are retained, although they are known to easily evolve to tetracoordinated species with the formation of [Rh(μ-SR)(CO)(PPh$_3$)]$_2$ [46–49]. With fluorinated thiolates (R = C$_6$H$_4$F, CF$_3$), the reaction with PPh$_3$ produces dimeric species [Rh(μ-SR)(CO)(PPh$_3$)]$_2$ and with R = C$_6$HF$_4$ yields the monomeric complex *trans*-[Rh(SC$_6$HF$_4$)(CO)$_2$(PPh$_3$)] [22]. It is not possible to establish a straightforward correlation between SR-group electronegativity and this behaviour.

Two possible mechanisms have been postulated to rationalise the formation of *trans* monometallic compounds from their parent bridged dimers [51]:

(1) Bridge splitting and isomerization (postulated as being the more likely) and (2) Substitution and bridge splitting (Possibly due to the σ-donor, π-acceptor nature of both thiolate and phosphine).

These two mechanisms are summarised below:

(1) *Bridge splitting and isomerization*:

$$[Rh(\mu-SR)(CO)_2]_2 + 2PPh_3 \rightarrow \quad 2\ cis-[Rh(SR)(CO)_2(PPh_3)]$$
$$\downarrow +2PPh_3$$
$$2\ cis-[Rh(SR)(CO)(PPh_3)_2] + 2CO$$
$$\downarrow \text{isomerization}$$
$$2\ trans-[Rh(SR)(CO)(PPh_3)_2]$$
$$\uparrow +2PPh_3$$

(2) *Substitution and bridge splitting*:

$$[Rh(\mu-SR)(CO)_2]_2 + 2PPh_3 \rightarrow [Rh(\mu-SR)(CO)(PPh_3)]_2 + 2CO$$

We have observed a similar outcome from the reaction of **2** (R = C$_6$F$_5$) with PPh$_3$ (1:2 molar ratio) which rendered *trans*-[Rh(SC$_6$F$_5$)(CO)(PPh$_3$)$_2$] **10a** [50], and which was fully characterised by FAB mass spectrometry, ^{1}H, ^{31}P NMR and elemental analysis. This compound was also prepared by reacting *trans*-[RhCl(CO)(PPh$_3$)$_2$] **9** with Tl(SC$_6$F$_5$) in toluene. However, when the reaction was performed in dichloromethane **10b** was formed. The ^{31}P NMR of both compounds are identical which can indicate a rapid equilibrium between them, although they differ in their ν(CO) in KBr which appear at 1989 and 1977 cm^{-1} for **10a** and **10b**, respectively. By warming a toluene solution of **10b** conversion into **10a** takes place.

The possibility of an O$_2$ adduct has been discarded since **10b** was recovered unreacted after bubbling dry oxygen through a solution in CH$_2$Cl$_2$. A *cis*-arrangement to, *cis*-[Rh(SC$_6$F$_5$)(CO)(PPh$_3$)$_2$] can be proposed similar to that for *cis*-[RhCl(CO)(PPh$_3$)$_2$] reported previously in the literature [52].

When the ratio P/Rh is 1, complex **7** is formed when the reaction is performed at 273 K whereas compound **8** is isolated when the reaction is carried out at room temperature. $[Rh(\mu\text{-}SR)(CO)(PPh_3)]_2$ **7** shows two ν(CO) frequencies at 1994 and 1977 cm^{-1} which are attributed to CO groups in a *cis* disposition. Similarly, compound $[Rh(SR)(CO)_2(PPh_3)]$ **4** shows two ν(CO) absorptions almost at the same frequencies. The presence of these species would agree with the above mechanism 1. Compound **8** shows a single ν(CO) frequency at 1984 cm^{-1} which could be attributed to a dimer containing CO and PPh_3 ligands in a *trans* disposition. **7** and **8** show two doublets in the ^{31}P NMR spectra at exactly the same frequency (36.5d, 36.7d) and with the same magnetic coupling constants (J(P–Rh) = 160 Hz). Both these doublets are present in a ratio of 70:30 at room temperature which may be explained by a *cis–trans* isomerization under these conditions.

Addition of a larger proportion of PPh_3 (P/Rh = 8), renders a mixture of yellow and orange compounds, **11a** and **11b**. These compounds can be separated from a toluene solution of the mixture by precipitation with hexane, with **11b** being the more insoluble product. Incidentally, by allowing the solution of **11b** to stand, almost quantitative conversion to **11a** occurs. The ν(CO) frequencies are 1989 (**11a**) and 1939 (**11b**) cm^{-1}. In order to confirm the nature and nuclearity of these compounds an X-ray structure analysis was undertaken, which showed the existence of two polymorphs of *trans*-$[Rh(SR)(CO)(PPh_3)_2]$. The structure of the compounds and reason for the difference between the ν(CO) will be discussed below. Although **10a** and **11a** seem to be the same compound, the nomenclature outlined in the reaction path is maintained.

We have obtained a reasonable number of different complexes by reacting compounds **1** and **2** with phosphine ligands only. One should keep in mind, however, that under hydroformylation conditions each of these species are also bound to come into contact with other competing ligands such as alkene, hydride and excess CO and thus the identity of the 'truly active' catalyst becomes more uncertain.

3.2. Crystal structure analysis of *trans*-$[Rh(SC_6F_5)(CO)(PPh_3)_2]$, 11a and 11b

trans-$[Rh(SC_6F_5)(CO)(PPh_3)_2]$ **11**, can be obtained as two polymorphous species. **11a** crystallises in the space group $P2_1/n$ of the monoclinic system and **11b** in the space group $P\bar{1}$ of the triclinic system. Figs. 1 and 2 show a perspective view of **11a** and **11b** respectively and define the atomic numbering scheme.

In both compounds the Rh atom has a coordination geometry which deviates from the ideal square planar. Both molecules display the same mutual arrangement of ligands around the central Rh atom, the phosphines being *trans* to each other, although there are some conformational differences. Some selected distances and angles are depicted in Table 2. The Rh–P, Rh–C and C–O distances are within the normal ranges [53,54].

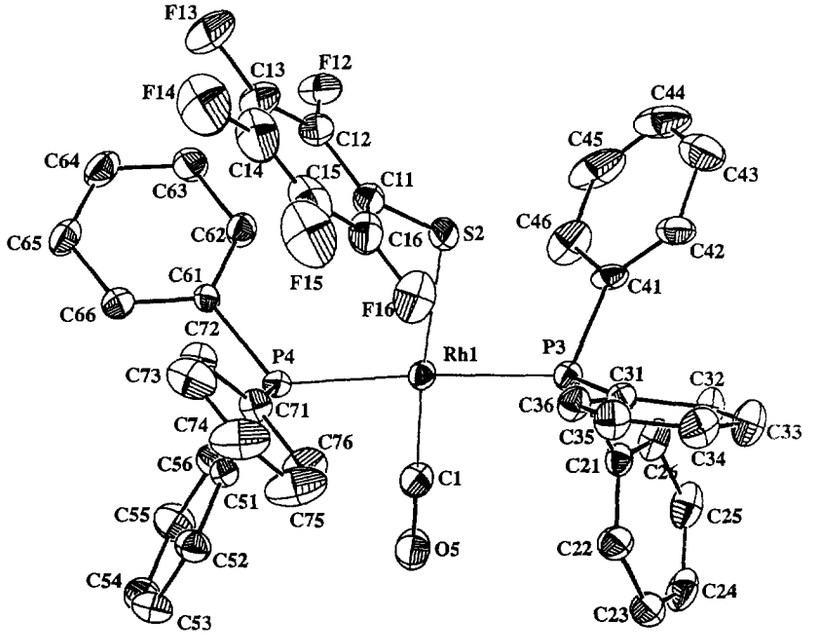


Fig. 1. Molecular structure and atomic numbering scheme for *trans*-$[Rh(SC_6F_5)(CO)(PPh_3)_2]$ **11a**. Hydrogen atoms have been omitted for clarity.

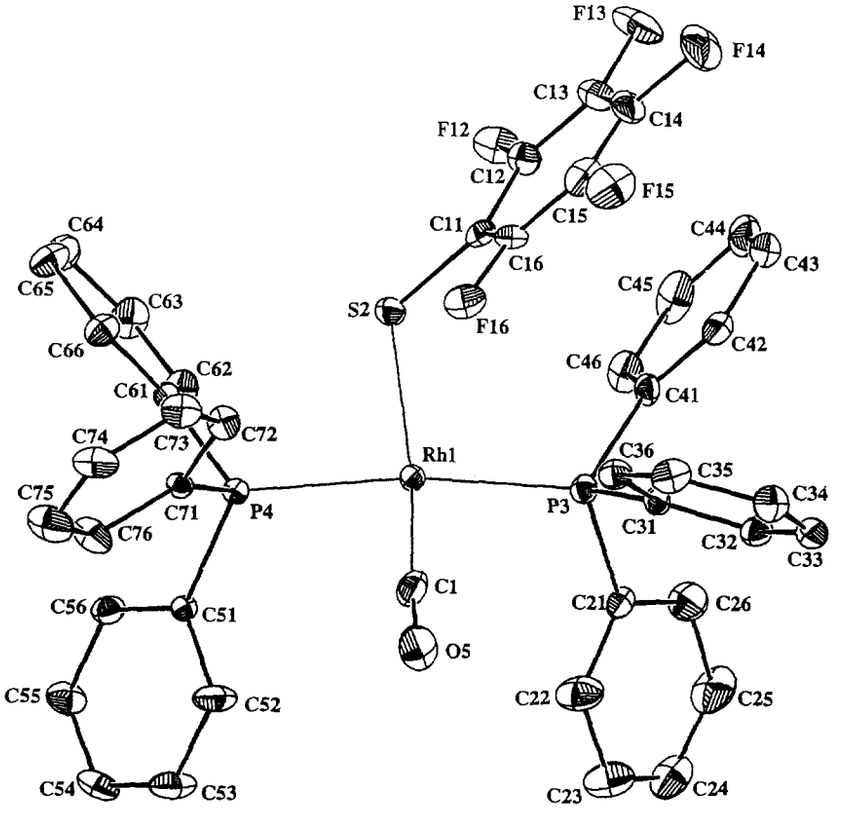


Fig. 2. Molecular structure and atomic numbering scheme for *trans*-[Rh(SC_6F_5)(CO)(PPh_3)$_2$] **11b**. Hydrogen atoms have been omitted for clarity.

The Rh–S distances are shorter than those for other reported Rh–SC_6F_5 mononuclear complexes [55] although the number of SR groups attached to Rh is greater and the ancillary ligands are different. The angles between the CO and adjacent phosphine ligands are almost identical in both molecules: **11a** [P3–Rh1–C1, 90.3(3)°; P4–Rh1–C1, 88.0(3)°], **11b** [P3–Rh1–C1, 90.8(3)°; P4–Rh1–C1, 87.4(3)°]. The most remarkable difference is in the mutual orientation of SC_6F_5 and phosphines, which probably causes a different orientation of the PPh_3 phenyl rings or vice-versa. The angle S2–Rh1–P4 in **11a** is 98.2(1)° due to the mutual conformation of C61–C66 phenyl ring and SC_6F_5 while in **11b** an almost identical value, 98.5(1)°, exits between the atoms S2–Rh1–P3. P4–Rh–P3 deviates 5.3(1)° from 180° in **11a** and 11.8(1)° in **11b**. S2–Rh1–C1 deviates 6.6(3)° and 17.8(3)°, respectively.

Table 2
Selected bond distances (Å) and angles (°) with standard deviations for complexes **11a** and **11b**

	11a	**11b**
Rh1–P3	2.322(2)	2.337(2)
Rh1–P4	2.319(2)	2.336(2)
Rh1–S2	2.393(2)	2.373(2)
S2–C11	1.77(1)	1.75(1)
Rh1–C1	1.79(1)	1.80(1)
C1–O5	1.16(1)	1.17(1)
H22–C1/H56–C1	3.07/3.44	
H22–C1/H52–C1		2.49/2.52
H22–O5/H56–O5	3.04/3.7	
H22–O5/H52–O5		2.52/2.58
P3–Rh1–S2	83.8(1)	98.5(1)
P4–Rh1–S2	98.2(1)	86.4(1)
P3–Rh1–C1	90.3(3)	90.8(3)
P4–Rh1–C1	88.0(3)	87.4(3)
P4–Rh1–P3	174.7(1)	168.2(1)
S2–Rh1–C1	173.4(3)	162.2(3)
Rh1–S2–C11	115.1(3)	109.9(3)

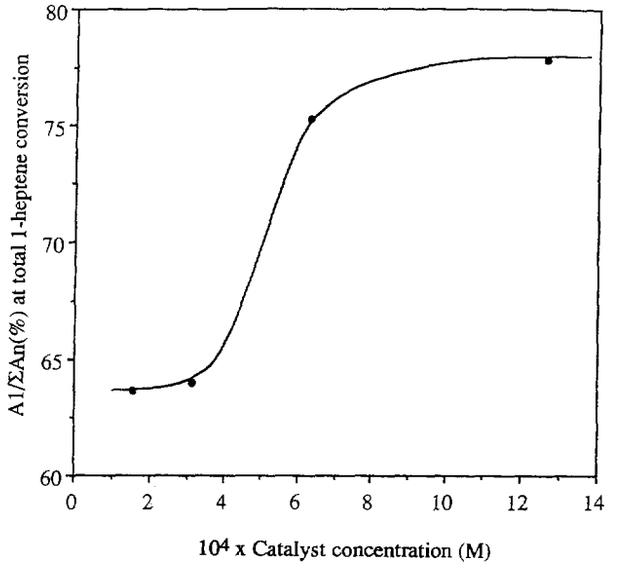


Fig. 3. Effect of catalyst concentration. Catalyst: [Rh(μ-SC_6F_5)(COD)]$_2$ **1**. Molar ratio P/Rh = 2. An = Aldehyde (n = 1, 2, 3). Temperature = 343 K; P_T = 30 bar (CO/H_2 = 1/1).

There is a correlation between the S2–Rh1–C11 angle and the S2–Rh1 bond distance (115.1(3)°, 2.393(2) Å in **11a** and 109.9(3)°, 2.373(2) Å in **11b**) which could be accounted for a pπ–dπ S–Rh interaction in the latter [56].

The dihedral angles between the C_6F_5 and phenyl rings indicate that the former is almost parallel to C71–C77 in **11a** and C41–C46 in **11b** respectively, the corresponding values being 6.4(4)° and 1.45(3)°. The angles between the phenyl rings nearest to CO (C51–C56 and C21–C26) are 48.1(3)° in **11a** and 87.4(4)° in **11b**.

A striking difference between **11a** and **11b** is the carbonyl stretching frequency at 1989 an 1939 cm^{-1} respectively in KBr. The Rh1–S2, Rh1–C1 and C1–O5 distances are very similar although the orientation of SC_6F_5 is different. This prompted us to analyse the possibility of an intramolecular interaction between the CO and o-phenyl H atoms of the closest phenyl rings. The H22–C1, H22–O5, H56–C1 and H56–O5 distances are all greater than 3 Å in **11a**. In **11b** H22–C1 = 2.49, H22–O5 = 2.66, H52–C1 = 2.52, H52–O5 = 2.58 Å. This interaction in the solid state could explain the decrease in ν(CO) due to the electronic interaction of H and π^* of the CO. This intramolecular CH...OC–M interaction could account for the stabilisation of the polymorphous forms and has been reported previously for Mn complexes [57] and for planar Rh (I) complexes wherein CH...Cl interactions [58–60], were observed.

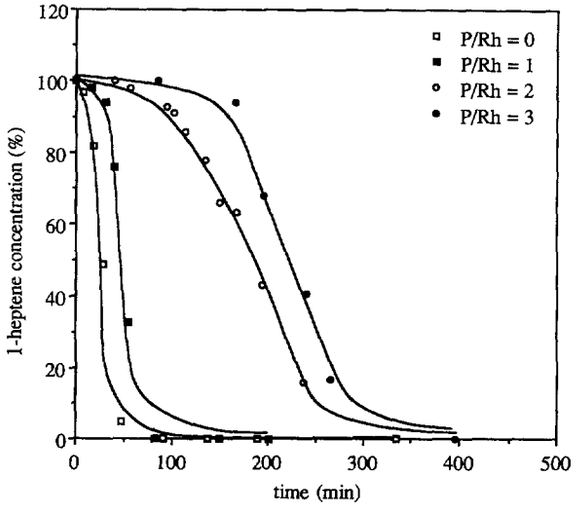


Fig. 4. Effect of P/Rh molar ratio on induction time and 1-heptene conversion rate. Catalyst: [Rh(μ-SC_6F_5)(COD)]$_2$ **1**. Catalyst concentration = 6.29×10^{-4} M. Temperature = 343 K; P_T = 30 bar (CO/H_2 = 1/1).

Table 3
Hydroformylation of 1-heptene. Effect of the PPh_3/Rh molar ratio at total 1-heptene conversion. [Rh(μ-SC_6F_5)(COD)]$_2$ **1**. (**1**, **1/P**, **1/2P**, **1/3P**), [Rh(μ-SC_6F_5)(CO)$_2$]$_2$ **2** (**2**, **2/P**, **2/2P**), [Rh(SC_6F_5)(CO)(PPh_3)$_2$], **10a**, [Rh(SC_6F_5)(CO)(PPh_3)$_2$], **10b**

Compound	PPh_3/Rh (molar ratio)	1–H %	2–H %	3–H %	A4 %	A3 %	A2 %	A1 %	A1/ΣA*n* %
1	0	0	0	0	4	12	44	40	40
2		0	3	1	4	10	40	42	44
1/P	1	0	0	0	2	9	36	53	53
2/P		0	0	0	4	9	37	50	50
1/2P	2	0	3	0	0	0	24	73	75
2/2P		0	1	0	0	0	24	75	76
10a		0	1	0	2	6	39	52	52
10b		0	5	1	0	2	26	66	70
1/3P	3	0	2	0	0	0	21	77	78

Catalyst concentration = 6.29×10^{-4} M. n-H = n-heptene (n = 1, 2, 3). Al = n-Octanal; A2 = Methylheptanaldehyde; A3 = Ethylhexanaldehyde; A4 = Propylpentanaldehyde. T = 343 K; P_T = 30 bar (CO/H_2 = 1/1)

3.3. Hydroformylation

Dimeric thiolate Rh complexes have been widely studied as hydroformylation catalysts [61–66]. The nature of the R moiety has been found to have a profound effect on the catalytic behaviour of these species.

It has been established that the performance of catalytic precursors with R groups which exert a + I inductive effect, e.g., Bu^t, is better than that shown by complexes with an electron withdrawing effect, e.g., C_6F_5, C_6F_4H, C_6H_4F [28]. When a large excess of free phosphine or phosphite is added to the complexes [Rh(μ-SR)(CO)$_2$]$_2$, selectivity towards linear aldehydes is not enhanced [67] and activity decreases. In the very well studied catalyst [Rh(H)(CO)(PPh_3)$_3$], addition of PPh_3 decreases activity but increases selectivity towards linear aldehydes [31]. The reaction is affected by so many factors such as nuclearity of complexes, SR, ancillary ligands, solvent, total pressure, catalyst concentration and even evaluation of data that extrapolation of results or tendencies to find the optimum conditions is extremely difficult.

We have undertaken a detailed study of several of these variables to be able afterwards to make accurate comparisons with immobilised Rh thiolate species. We have studied the hydroformylation of 1-heptene at 30 bar ($CO:H_2$ = 1) and 343 K using toluene as solvent.

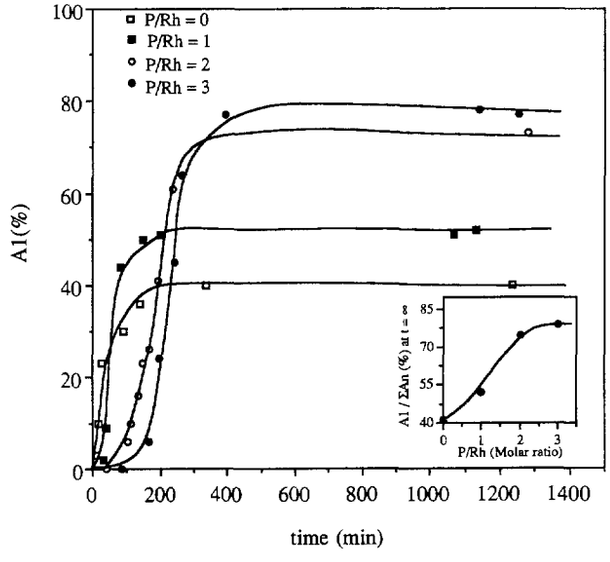


Fig. 5. Effect of P/Rh molar ratio on A1 selectivity. Catalyst: [Rh(μ-SC_6F_5)(COD)]$_2$ **1**. Catalyst concentration = 6.29×10^{-4} M. Temperature = 343 K; P_T = 30 bar (CO/H_2 = 1/1).

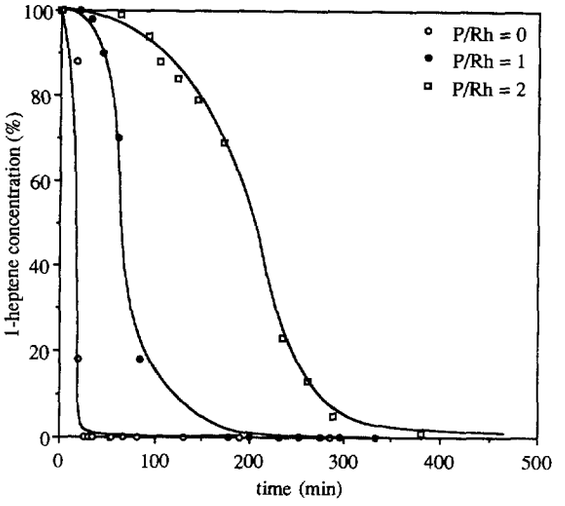


Fig. 6. Effect of P/Rh molar ratio on induction time and 1-heptene conversion rate. Catalyst: $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ **2**. Catalyst concentration = 6.29×10^{-4} M. Temperature = 343 K; P_T = 30 bar (CO/H_2 = 1/1).

The tested species can be named for simplicity in tables and figures as: **1**, **1/P**, **1/2P**, **1/3P**, **2**, **2/P**, **2/2P**, and **10** depending on the addition of 1, 2, 3 PPh_3/Rh to complexes **1**, **2**, and **10**:

$[Rh(\mu - SC_6F_5)(COD)]_2(P/Rh = 0,1,2,3) \rightarrow$ **1,1/P,1/2P,1/3P**

$[Rh(\mu - SC_6F_5)(CO)_2]_2(P/Rh = 0,1,2) \rightarrow$ **2,2/P,2/2P**

$[Rh(SC_6F_5)(CO)(PPh_3)_2]$ (intrinsic P/Rh = 2) → **10a**, **10b** (**10a** prepared by reacting **2** with $4PPh_3$ and **10b** from $[RhCl(CO)(PPh_3)_2]$ and $Tl(SC_6F_5)$).

Using the catalyst **1/2P** we have studied the effect of the catalyst concentration at: 1.55, 3.13, 6.29 and 12.63 10^{-4} mol L^{-1} which represents a molar ratio alkene/catalyst: 2082, 1029, 511 and 255 respectively. The analyses of products after partial conversion of the olefin, show, as expected a marked increase in activity with increasing concentration. For example, at ca. 200 minutes 1-heptene conversion was 48, 43, 57 and 95.6%, respectively. Isomerisation to 2-heptene occurs to some extent. It is only at low catalyst concentration (3.13×10^{-4} M) that isomerization to 3-heptene takes place. When the reaction is completed ($t = \infty$) the difference in selectivity towards A1 (n-octanal) shifts from 63 to 73% when the concentration is varied from 1.55 to 6×10^{-4} and only to 77% the concentration is much higher (12.63×10^{-4} M).Fig. 3

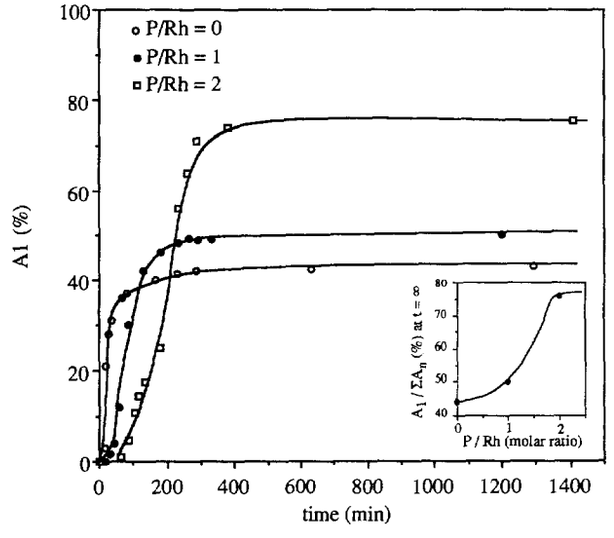


Fig. 7. Effect of P/Rh molar ratio on A1 selectivity. Catalyst: $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ **2**. Catalyst concentration = 6.29×10^{-4} M. Temperature = 343 K; P_T = 30 bar (CO/H_2 = 1/1).

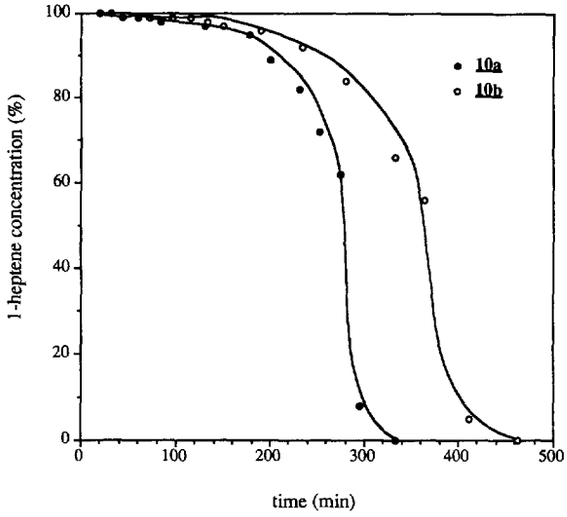


Fig. 8. 1-heptene conversion rate. Catalysts: $[Rh(SC_6F_5)(CO)(PPh_3)_2]$ **10a**, **10b**. Catalyst concentration = 6.29×10^{-4} M. Temperatures = 343 K; P_T = 30 bar ($CO/H_2 = 1/1$).

Considering the equilibrium: $[Rh(\mu\text{-SR})(COD)]_2$ **1** + $2PPh_3 \leftrightharpoons$ $2[Rh(SR)(COD)(PPh_3)]$ **3**, an increase in the concentration of **1** would imply an increase in the ratio dimer/monomer which, as indicated from the results shown above, should lead to a better selectivity of the dimer towards A1, although this equilibrium may not be necessarily postulated under hydroformylation conditions. 6×10^{-4} M was chosen as the optimal concentration for the rest of the tests. Addition of increasing amounts of PPh_3 to compound **1** (**1**, **1/P**, **1/2P**, **1/3P**) lowers the catalytic activity as shown in Fig. 4 and increases the induction periods. However the selectivity towards the linear aldehyde, A1/ΣAn %, increases dramatically from 40 to 78%. (Table 3, Fig. 5).

The difference in selectivity is not remarkable (from 75 to 78%) when P/Rh is increased from 2 to 3.

The study was extended to the complex $[Rh(\mu\text{-SR})(CO)_2]_2$ **2**, in which addition of PPh_3, P/Rh = 0, 1, 2 was performed. The results are shown in Table 3 and Figs. 6 and 7.

The same trend as in the former catalyst series is observed.

A comparison of the results at $t = \infty$ shows no large differences in selectivity between both series (precursors **1** and **2**) although with precursor **2** the reaction is remarkably faster with **2/2P** having converted approximately 74% 1-heptene after 200 minutes, while the corresponding conversion for **1/2P** was only 57%. $[Rh(SR)(CO)(PPh_3)_2]$ **10a**

Table 4
Some selected carbonyl stretching frequencies of catalyst precursors in hydroformylation reaction conditions

Compound	Scheme N°	ν(CO) cm^{-1} [a]	Hydroformylation [b]
$[Rh(\mu\text{-SR})(COD)]_2$	**1**		**1/P** I: 2090w, 2075vs, 2050w, 2026vs, 2012m F: 2076vs, 2050vw, 2022vw, 2000 vw, 1968w **1/2P** F: 2077vs, 2020vw, 1996w, 1968w **2** I: 2093w, 2075vs, 2028vs F: 2075, 2040, 1989 **2/P** I: 2074s, 2051w, 2014s, 1987s
$[Rh(\mu\text{-SR})(CO)_2]_2$	**2**	2093, 2076, 2040	F: 2071w, 2050m, 2020vs, 2001vs, 1978vs **2/2P** I: 2073m, 1995vs, 1982vs F: 2050w, 2020m, 1995s, 1975vs
cis-$[Rh(SR)(CO)_2(PPh_3)]$	**4**	1993, 1977	
cis-$[Rh(R)(CO)_2(PPh_3)]$	**6**	2077, 2014	
2 + $2PPh_3$ 0°C	**7**	1994, 1977	
2 + $2PPh_3$ r.t.	**8**	1984	
2 + $4PPh_3$	**10a**	1989	
9 + Tl(SR)	**10b**	1978	I: 2073vs, 2035w, 2011m, 1995vs, 1985m F: 2074m, 2035w, 2011m, 1995vs, 1985vs
trans-$[RhCl(CO)(PPh_3)_2]$	**9**	1965	

[a] KBr pellets, R = C_6F_5, P = PPh_3, [b] Solvent: toluene, I: initial, under 5 bar of CO at 298 K, F: final, at the end of the hydroformylation reaction ($t = \infty$).

and **10b** gave slightly different results. **10a** gave a faster conversion and showed poorer selectivity towards A1 than **10b** (Table 3, Fig. 8).

The optimum performance is attained with dimeric complex **2** and both dimers are better catalysts than the monomers.

Table 4 shows the carbonyl stretching frequencies of the compounds studied, as the solid precursor (KBr pellets) and in solution at the initial state of the catalytic reaction under 5 bar of CO at 295 K and at the end of the hydroformylation reaction ($t = \infty$). A mixture of dimeric and monomeric species can be envisaged although it is not possible to extract conclusions about the nature of the active species. Peaks at about 1800 cm^{-1} that would justify bridge carbonyl groups should be taken with care because are present in the solvent spectra.

From kinetic studies on alkene hydroformylation with $[Rh(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ as catalyst, it has been postulated that monomeric compounds are the active species in this reaction. The rate equation is first order with respect to the alkene concentration and half order with respect to rhodium dimer suggesting dissociation of the dimer into monomeric species [68].

On the basis of these results we can conclude that addition of PPh_3 to the thiolate dimeric complexes induces an increase in A1 selectivity with concomitant decrease in activity. However both parameters are enhanced by using dimeric precursors instead of monomeric analogues with the same phosphine content. Finally, it should be borne in mind that comparisons and correlations have to be done with caution when some parameters are changed.

Acknowledgements

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