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Preparation of carbonyl phosphine rhodium complexes with dithiolate bridges. Application as catalyst precursors in the hydroformylation of 1-hexene

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Abstract

The reactivity of $[Rh_2(\mu\text{-}S(CH_2)_nS)(CO)_4]$ ($n = 2$, 3 or 4) have been investigated and mixed carbonyl phosphine complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(CO)_2(PR_3)_2]_x$ (R = C_6H_5, C_6H_{11}, O-2-^{t}BuC$_6$H$_4$; $n = 2$, 3 and 4; $x = 1$ or 2) have been prepared and studied by IR, ^{31}P-{^{1}H} NMR and FAB mass spectrometry. Dinuclear complexes $[Rh_2(\mu\text{-}S(CH_2)_2S)(CO)_2(PR_3)_2]$ (R = C_6H_5, C_6H_{11}, O-2-^{t}BuC$_6$H$_4$) and tetranuclear $[\{Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2\{P(O\text{-}2\text{-}^tBuC_6H_4)_3\}_2\}_2]$ formulations are proposed on the basis of FAB mass spectrometry.

The complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 or 4; COD = 1,5-cyclooctadiene) have been used as catalyst precursors for 1-hexene hydroformylation. The influence of different dithiolates and phosphines on the catalytic activity and the selectivity have been explored.

Keywords: Rhodium; Hydroformylation; Dithiolate bridges; Catalysis

1. Introduction

It is well known that dinuclear bridged thiolate [1–3], fluorothiolate [4–6] and aminothiolate [7,8] rhodium complexes $[\{Rh(\mu\text{-}SR)(L)(L')\}_2]$ (L = L' = COD or L = CO, L' = PR_3), are active catalyst precursors in the hydroformylation of alkenes at low conditions of pressure and temperature (5 bar, 80°C). In general, carbonyl phosphine complexes $[\{Rh(\mu\text{-}SR)(CO)(PR_3)\}_2]$ are used as catalyst precursors [1–3], or the catalytic systems are prepared in situ by adding phosphorus ligands to $[\{Rh(\mu\text{-}SR)(COD)\}_2]$ under hydroformylation reaction conditions [7,8].

Reaction of diolefin thiolate-bridged complexes with CO gave the corresponding tetracarbonyls $[\{Rh(\mu\text{-thiolate})(CO)_2\}_2]$ which are inactive in hydroformylation under mild conditions [2]. The reactivity towards tertiary phosphines has also been studied, and in most cases dinuclear complexes $[\{Rh(\mu\text{-}SR)(CO)(PR_3)\}_2]$ are obtained [3,6,8], although mononuclear species have also been observed [5].

The different reports do not allow a definitive conclusion concerning the mono- or di-nuclearity of the species during the catalytic cycle, although kinetics studies provide evidence for the presence of mononuclear species in the case of hydroformylation of alkenes catalysed by $[\{Rh(\mu\text{-}SR)(CO)(PR_3)\}_2]$ [9]. In other cases evidence of mono- or di-nuclear species has been claimed, depending on the nature of the initial precursor system and on the reaction conditions. For instance, in the case of aminothiolate-bridge precursors using PPh_3 as auxiliary ligand, the dinuclear mixed $[\{Rh(\mu\text{-}S(CH_2)_3NH_3)(CO)(PR_3)\}_2]$ is recovered at the end of the catalytic reaction [7], but for the same precursor system using tris(2-*t*-butylphenyl)phosphite as auxiliary ligand, mononuclear species have been isolated at the end of the reaction [8].

Continuing our study of the preparation and reactivity of rhodium(I) complexes with sulphur ligands, and with the aim of exploring the influence of a more rigid structure on catalytic activity, we prepared dithiolate-bridged dinuclear complexes. We have recently reported [10] the synthesis and characterisation of $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 or 4) and the corresponding tetracarbonyls $[Rh_2(\mu\text{-}S(CH_2)_nS$

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$(CO)_4$]. The X-ray structures of $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$ or 3) confirm the dinuclearity, but for $n = 3$ or 4, evidence for the simultaneous formation of tetranuclear complexes have also been observed. For the carbonyl complexes the IR carbonyl frequencies suggest the formation of tetracarbonyl dinuclear complexes.

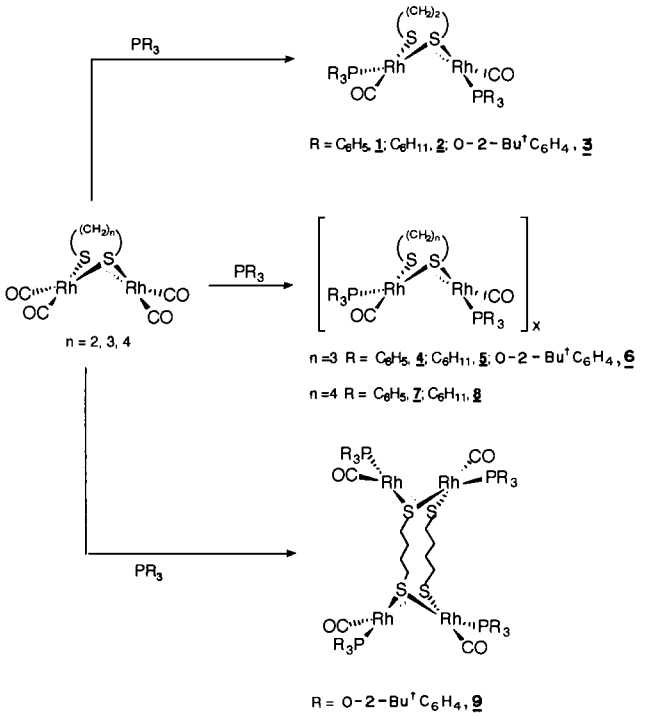
In the present work we report the study of the reactivity of the carbonyl complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(CO)_4]$ ($n = 2$, 3 or 4) with phosphines and the catalytic activity of the $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 or 4) as a catalyst precursors for 1-hexene hydroformylation.

2. Results and discussion

2.1. Preparation of $[\{Rh_2(\mu\text{-dithiolate})(CO)_2(PR_3)_2\}_x]$ ($x = 1$ or 2) complexes

The reactions of the tetracarbonylated dithiolate-bridged rhodium complexes $[Rh_2(\mu\text{-}S(CH_2)_n)S)(CO)_4]$ ($n = 2$, 3 or 4) [10] with PR_3 ($R = C_6H_5$, C_6H_{11}, or O-2-$^tBuC_6H_4$) have been studied and mixed carbonyl phosphorus ligand complexes $[\{Rh_2(\mu\text{-}S(CH_2)_nS)(CO)_2(PR_3)_2\}_x]$ have been obtained (Scheme 1).

For $n = 2$, the addition of the stoichiometric amount of phosphine to a dichloromethane solution of the tetracarbonyl affords brown, moderately air-stable products for which the C, H and S analyses correspond to the stoichiometry $[\{Rh_2(\mu\text{-}S(CH_2)_2S)(CO)_2(PR_3)_2\}_x]$, ($R = C_6H_6$ **1**, $R = C_6H_{11}$ **2** or R = O-2-$^tBuC_6H_4$ **3**). Complex **1** has been described recently [11] and suggested to be dinuclear because of the X-ray structure of the dinuclear complex obtained through oxidative addition of $HgCl_2$ to the corresponding dicarbonylbis(triphenylphosphine) dithiolate-bridged rhodium(I) complex.



Scheme 1.

Table 1
IR ν(CO) stretching frequencies and $^{31}P\text{-}\{^1H\}$ NMR data for **1** to **9** complexes

Complex	IR ν(CO) cm^{-1} CH_2Cl_2)	$^{31}P\text{-}\{^1H\}$	
		δ (ppm)	^1J(P–Rh) (Hz)
1	1964(s)	38.8(d)	158
2	1941(s)	36.8(d)	118
3	1996(s)	119.5(d)	266
4	1964(s)	38.3(d)	152
5	1948(s)	36.8(d)	119
6	1996(s)	116.3(d)	263
7	1966(s)	38.7(d)	161
		36.9(d)	156
8	1942(s)	36.8(d)	118
9	1996(s)	116.6(d)	274
		120.5(d)	256

In order to obtain more information about the nuclearity of the complexes described in this work, complexes **2** and **3** were examined by FAB mass spectrometry. Molecular ions were observed (at $m/z = 914$ and 1311, respectively) as expected for dinuclear species.

The Fourier transform IR spectra of the complexes in dichloromethane solution show only one stretching ν(CO) frequency, attributed to *trans* dicarbonyl dinuclear mixed complexes [12] (Table 1). The $^{31}P\text{-}\{^1H\}$ NMR spectra of the $CDCl_3$ solution of the complexes **1**, **2** and **3** show the presence of a doublet at δ(ppm) = 38.8(d) (^1J(Rh–P) = 158 Hz) for **1**, δ(ppm) = 36.8(d) (^1J(Rh–P) = 118 Hz) for **2** and at δ(ppm) = 119.5(d) (^1J(Rh–P) = 266 Hz) for **3** indicating that the phosphines are equivalent.

The reaction of the $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$, with PPh_3 gives $[\{Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_2(PPh_3)_2\}_x]$ **4**. The IR spectrum in dichloromethane shows one ν(CO) frequency (1964 cm^{-1}, Table 1) indicating a *trans* disposition of the carbonyl groups. The $^{31}P\text{-}\{^1H\}$ NMR data, δ(ppm) = 38.3(d) (^1J(Rh–P) = 152 Hz) confirms the preparation of a compound of the same type as **1**, **2** and **3**. The elemental analysis is consistent with the formulation $[\{Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_2(PPh_3)_2\}_x]$. Attempts to determine its nuclearity by FAB mass spectrometry were unsuccessful.

Reaction of dichloromethane solutions of $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$ with tricyclohexylphosphine and tris(2-^{t}butylphenyl) phosphite resulted in the formation of $[\{Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_2(PR_3)_2\}_x]$ in solution ($R = C_6H_{11}$ **5**, or R = O-2-$^tBuC_6H_4$ **6**) as the IR and

^{31}P-{^{1}H} NMR data indicated (Table 1). Unfortunately, it was not possible to isolate pure compounds in the solid state.

In the preparation of $[Rh_2(\mu\text{-}S(CH_2)_3S)(COD)_2]$, the starting material for the syntheses of the corresponding carbonyl $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$, two different products were obtained, and the ^{1}H NMR data suggest that both products are in equilibrium in solution [10]. One of the complexes was characterised by X-ray diffraction as a dinuclear species and the FAB mass spectrometry data indicates that the second one could be tetranuclear [10]. Probably, the presence of species of different nuclearity and different reactivity towards PR_3 in solution could be the reason why we did not obtain pure products with $P(C_6H_{11})_3$ and $P(O\text{-}2\text{-}^{t}BuC_6H_4)_3$. Attempts to separate the possible mixture of complexes, or to obtain X-ray crystal structure data, were unsuccessful.

In the case of the tetracarbonyl complex with $n = 4$, reaction with PR_3 resulted in moderately air-stable compounds (**7** for $R = C_6H_5$, **8** for $R = C_6H_{11}$, and **9** for $R = O\text{-}2\text{-}^{t}BuC_6H_4$) for which elemental analysis, ν(CO) stretching frequencies and the ^{31}P-{^{1}H} NMR spectra (Table 1) correspond to the formulation *trans*-$[\{Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2(PR_3)_2\}]_x$ stoichiometry. In the case of complexes **7** and **9**, the ^{31}P-{^{1}H} NMR spectra show the expected doublet, and another signal that can be attributed to the presence of *cis* and *trans* isomers.

In order to obtain information about the nuclearity, the FAB mass spectra of $[\{Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2(PR_3)_2\}_x]$ were examined. In the case of the complex with $P(O\text{-}2\text{-}^{t}BuC_6H_4)_3$ (**9**) the spectrum shows a peak at $m/z = 1720$ corresponding to the loss of two phosphite molecules from a tetranuclear species. This confirms the formation of the tetranuclear complex. For **7** and **8** FAB mass spectrometry was inconclusive.

2.2. Catalytic activity

In this work $[Rh_2(\mu\text{-dithiolate})(COD)_2]$ were used as catalyst precursors for the hydroformylation of 1-hexene. We have focused on the influence of the different dithiolate ligands and the effect of PR_3 on the catalytic activity and selectivity. Two different systems were used, complexes $[Rh_2(\mu\text{-dithiolate})(COD)_2]$ in hydroformylation conditions, and complexes $[Rh_2(\mu\text{-dithiolate})(COD)_2]/PR_3$, where phosphines or phosphites with different properties were used. In general phosphorus donors are present in the hydroformylation catalytic systems [1–3,7,8]. In the absence of phosphorus donors inactive species are formed [2] or side reactions are generally observed [13].

The results obtained in 1-hexene hydroformylation with the different precursor systems using $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, **10**; 3, **11**; and 4, **12**) are shown in Table 2. Catalytic hydroformylation was achieved in most of the cases. In a few experiments formation of by-products were observed to some degree ($\leq 10\%$). Analytical chromatographic data exclude the presence of olefin isomerization or hydrogenation products.

At 5 bar pressure and 80°C catalysts precursors **10** and **11** were not active in 1-hexene hydroformylation (entries 1 and 2). At 30 bar, with $[Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2]$ in the absence of phosphorus donors, 76% aldehyde conversion was obtained and no side reactions were observed but the selectivity was practically zero, $n/iso = 1/1$ (entry 3). At 70 bar, 10% of a by-product was observed (entries 4).

Table 2
Hydroformylation of 1-hexene using the $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]/PR_3$ $n = 2$ (**10**), 3 (**11**) and 4 (**12**) systems as catalyst precursors [a]

Entry	Catal. precursor	PR_3	P/Rh	Solvent	P(bar)	% Conv [b]	% n [c]	% iso [d]	% by-product
1 [e]	**10**	PPh_3	1	D	5	–			
2 [e]	**11**	PPh_3	1	D	5	–			
3	**10**	–	–	T	30	76	52	48	–
4	**10**	–	–	T	70	56	56	44	10
5	**10**	PPh_3	2	T	30	96	73	26	–
6	**10**	PPh_3	2	T	70	97	74	27	–
7	**10**	PPh_3	4	T	30	94	75	25	–
8	**10**	PPh_3	4	T	70	98	73	27	–
9	**10**	PPh_3	2	D	30	94	74	26	–
10 [e]	**10**	PPh_3	2	D	30	64	74	26	–
11	**10**	$P(O\text{-}o^{t}BuPh)_3$	2	D	30	36	65	35	–
12	**10**	$P(OPh)_3$	2	D	30	90	77	26	–
13 [f]	**12**	PPh_3	1	D	5	84	69	31	7
14 [e,g]	**12**	PPh_3	2	D	5	96	72	28	–

[a] Reaction conditions: 1-hexene (20 mmol), complex (0.1 mmol), solvent (15 ml) (T: toluene, D: 1,2-dichloroethane), $CO/H_2 = 1$. Catalyst/substrate ratio = 1/100. [b] aldehyde conversion measured by chromatography integral ratio without addition of internal standard. [c] 1-heptanal (% $n = 100(n/(n + iso))$. [d] 2-methyl-hexanal (% iso = 100(iso/(n + iso)). [e] 1/200 reaction time 5 h. [f] 11 h. [g] 19 h.

When PPh_3 was added (P/Rh = 2) at 30 bar, 96% of conversion to aldehydes was achieved and the selectivity, as expected, increased to 73% in 1-heptanal (entry 5).

Practically no difference in conversion or selectivity was observed, when the pressure was increased to 70 bar (entry 6), or when the excess of phosphorus donor was P/Rh = 4 (entries 5 and 7, 6 and 8). The same results were obtained when toluene or 1,2-dichloroethane were used as solvents (entries 5 and 9). Changing the catalyst substrate ratio from 1/100 to 1/200 decreases the activity (entries 9 and 10).

Recently, bulky phosphites such as P(O-2-^{t}BuC$_6$H$_4$)$_3$ have been shown to be efficient auxiliaries in the hydroformylation reaction of internal or cyclic olefins [8,14]. In the present work we also used this phosphite in the hydroformylation of 1-hexene, but low conversion and selectivity were obtained (entry 11). However, $P(OPh)_3$ yielded results similar to those obtained with PPh_3 (entries 9 and 12). Since this phosphite has similar electronic properties to those of P(O-2-^{t}BuC$_6$H$_4$)$_3$ [15], the low activity in entry 11 may be attributed to steric effects.

In the case of [Rh$_2$(μ-S(CH$_2$)$_4$S)(COD)$_2$] (**12**) the catalytic activity in the hydroformylation of 1-hexene was obtained even under mild conditions. At 5 bar, when the ratio PPh_3/Rh = 1,84% of aldehyde conversion was obtained although 7% of undesired products were also observed (entry 13). However at the same pressure, using PPh_3/Rh = 2, practically total conversion in aldehydes was achieved (entry 14) and no by-products were observed. For [Rh$_2$(μ-S(CH$_2$)$_2$S)(COD)$_2$], **10**, 30 bar was required to achieve the same conversion (entry 5).

The reaction time was optimised. In most cases, the conversion was practically complete at 5 h and regioselectivity was maintained.

IR spectra were recorded on the resultant solutions resulting from experiments 1–3, 6, 13 and 14. The ν(CO) frequencies obtained are summarised in Table 3. In experiments 1 and 2, performed with **10** and **11** at 5 bar, the observed ν(CO) bands are not consistent with the formation of the corresponding mixed carbonyl phosphine complexes **1** and **4**. Probably, CO-bridged of inactive species are formed during the catalytic cycle (ν(CO) = 1827 cm^{-1}). At 30 bar in absence of PPh_3 (entry 3), the ν(CO) frequencies correspond to the tetracarbonyl complex [Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_4$] [10]. With PPh_3 in P/Rh = 2 at 70 bar was used (entry 6), the formation of the [Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_2$(PPh$_3$)$_2$] (**1**) was observed, as indicated by the presence of ν(CO) at 1963 cm^{-1}, but other signals corresponding to different species were also detected.

For [Rh$_2$(μ-S(CH$_2$)$_4$S)(COD)$_2$] at 5 bar, when PPh_3/Rh = 1 (entry 13), formation of complex **7** was observed by IR analysis (ν(CO) = 1967 cm^{-1}) and the tetracarbonyl species [Rh$_2$(μ-S(CH$_2$)$_4$S)(CO)$_4$] was also present as shown by ν(CO) bands corresponding to the tetracarbonyl complex (ν(CO) = 2075(s), 2059(s), 2007(s) cm^{-1}) [10]. Other unidentified species showing ν(CO) at 2091(sh) and 1979(sh) cm^{-1} were also present. When enough PPh_3 was added to compete with CO pressure (P/R = 2), the formation of the mixed complex CO/PPh_3, **7**, was detected by IR (entry 14). In this case only one ν(CO) band appeared at 1967 cm^{-1}, corresponding to the value 1966 cm^{-1} for complex **7**, (Table 1).

Table 3
IR ν(CO) streaching frequencies for solutions after catalytic hydroformylation

Entry	IR ν(CO) (cm^{-1})
1	2065(m), 1980(s), 1827(s)
2	1980(s), 1827(s)
3	2077(s), 2059(s), 2014(s)
6	1963(s), 1950(sh), 1877(sh), 1864(s)
13	2091(sh), 2075(m), 2055(s), 2007(s), 1979(sh), 1967(s)
14	1967(s)
Complexes	
[Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_4$] [10]	2077(s), 2059(s), 2014(s)
[Rh$_2$(μ-S(CH$_2$)$_4$S)(CO)$_4$] [10]	2075(s), 2059(s), 2007(s)

3. Experimental details

Elemental analyses were carried out with a Carlo-Erba microanalyzer. IR spectra were recorded on a Nicolet 5ZDX-FT instrument, ^{31}P NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer using external 85% H_3PO_4 as reference. FAB mass spectrometry was performed on a VG Autospect in a nitrobenzyl alcohol matrix. Gas chromatography analyses were performed in a Hewlett-Packard 5890A in a Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm). All syntheses of rhodium complexes were carried out under di-nitrogen using standard Schlenk techniques. Solvents were distilled and deoxygenated before use. Complexes [Rh$_2$(μ-S(CH$_2$)$_n$S)(CO)$_4$] (n = 2, 3 or 4) were prepared according to literature methods [10]. Phosphorus reactants were of commercial origin and used without further purification. Tris(2-^{t}butylphenyl)phosphite was prepared as previously described [14].

3.1. Preparation of [Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_2$(PR$_3$)$_2$] (R = C$_6$H$_5$ (1), C$_6$H$_{11}$ (2), or O-2-^{t}BuC$_6$H$_4$ (3)

To a solution of [Rh$_2$(μ-S(CH$_2$)$_2$S)(CO)$_4$] (50 mg, 0.122 mmol) in dichloromethane (5 ml) was added 10% excess of the corresponding PR_3 (0.268 mmol). The resulting solution was stirred for 20 minutes, filtered

and the filtrate reduced to 0.5 ml under vacuum. Addition of 5 ml of methanol precipitated a solid, collected by filtration, washed with cold methanol and dried under vacuum. Complex **1** (dark brown), 74% yield. Anal. found.: C 54.5, H 4.1, S 7.8; calc. for $Rh_2C_{40}H_{34}O_2P_2S_2$: C 54.7, H 3.9, S 7.3%. Complex **2** (brown), 69% yield. Anal. found.: C 51.6, H 7.4, S 7.2; Calc. for $Rh_2C_{40}H_{70}O_2P_2S_2$: C 52.5, H 7.7, S 7.0%. Complex **3** (brown), 70% yield. Anal. found.: C 58.9, H 6.3, S 4.9; Calc. for $Rh_2C_{64}H_{82}O_8P_2S_2$: C 58.6, H 6.3, S 4.9%.

3.2. Preparation of $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_2(PR_3)_2]$ ($R = C_6H_5$ (4))

To a solution of $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$ (50 mg, 0.118 mmol) in dichloromethane (5 ml) was added a slight excess (10%) of PPh_3 (0.260 mmol). The resulting solution was stirred for 20 minutes, filtered, and the filtrate reduced to 0.5 ml under vacuum. Addition of 5 ml of methanol precipitated a red-brown solid, **4**, collected by filtration, washed with cold methanol, and dried under vacuum. 70% yield. Anal. Found.: C 54.6, H 4.1, S 7.5; Calc. for $Rh_2C_{41}H_{36}O_2P_2S_2$: C 55.2, H 4.0, S 7.2%.

3.3. Reaction of $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$ toward PR_3 $R = C_6H_{11}$ and O-2-$^tBuC_6H_4$

To a solution of $[Rh_2(\mu\text{-}S(CH_2)_3S)(CO)_4]$ (50 mg, 0.118 mmol) in dichloromethane (5 ml) was added the stoichiometric amount and a slight excess (10%) of the corresponding PR_3 (0.260 mmol). The resulting solution was stirred for 20 minutes and filtered off. IR and $^{31}P\{^1H\}$ NMR analyses indicate the formation of the complexes **5** and **6** in solution (Table 1).

3.4. Preparation of $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2(PR_3)_2]$ ($R = C_6H_5$ (7), C_6H_{11} (8), or O-2-$^tBuC_6H_4$ (9))

To a solution of $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$ (50 mg, 0.114 mmol) in dichloromethane (5 ml) was added a slight excess (10%) of the corresponding PR_3 (0.250 mmol). The resulting solution was stirred for 20 minutes, filtered and the filtrate reduced to 0.5 ml under vacuum. Addition of 5 ml of methanol precipitated a solid, collected by filtration, washed with cold methanol and dried under vacuum. Complex **7** (light brown), 68% yield. Anal. found.: C 54.8, H 4.1, S 7.1; calculated for $Rh_2C_{42}H_{38}O_2P_2S_2$: C 55.5, H 4.2, S 7.1%. Complex **8** (light brown), 54% yield. Anal. found.: C 52.8, H 7.8, S 7.0; calculated for $Rh_2C_{42}H_{74}O_2P_2S_2$: C 53.5, H 8.3, S 6.8%. Complex **9** (light brown), 57% yield. Anal. found.: C 59.8, H 6.6, S 4.2; calc. for $Rh_2C_{66}H_{86}O_8P_2S_2$: C 60.9, H 6.4, S 4.8%.

3.5. Catalysis

Hydroformylation experiments were carried out in a autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. The inside of the autoclave cap is Teflon-covered to avoid direct contact of solution with stainless steel. Constant temperature was maintained by circulation of water through a double jacket.

3.6. Standard catalysis experiment

A solution of the substrate (20 mmol), the catalyst precursor (0.1 mmol) and the phosphorus compound in 15 ml of solvent was introduced into the evacuated autoclave. The gas mixture was introduced and system was heated. When thermal equilibrium had been reached, the gas mixture was introduced until desired pressure. After the given reaction time, the autoclave was cooled to room temperature and depressurised. Analyses of samples were performed by FT-IR spectroscopy and by gas chromatography.

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