High-Pressure Infrared Studies of Rhodium Complexes Containing Thiolate Bridge Ligands under Hydroformylation Conditions

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In situ high-pressure IR spectroscopy studies of the rhodium catalyst systems $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PR_3$ (R = Ph, OPh), $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$, $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2/PPh_3$, $[Rh_2\{\mu\text{-}XANTOSS\}(COD)_2]_2/PPh_3$, and $[Rh(acac)(CO)_2]/PR_3$ (R = Ph, OPh) revealed the presence of mononuclear rhodium hydride species under hydroformylation conditions (80 °C, 5−30 bar). The activities and selectivities, obtained during the hydroformylation of 1-hexene using these systems as catalyst precursors, can be fully accounted for by the mononuclear species observed. Deuterioformylation experiments using dinuclear $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PR_3$ systems lent no support to a dinuclear mechanism.

Introduction

Rhodium-catalyzed hydroformylation has received a great deal of attention in recent years both from academia and industry.[1] Despite this fact, there are very few studies which aim to observe intermediates under reaction conditions. The two most appropriate techniques, high-pressure NMR and IR spectroscopy, both have shortcomings and the crucial intermediates may still escape from direct observation.

Nowadays, high-pressure NMR[1i,j,n,o,2] spectroscopy is used on a routine basis for identifying organometallic compounds under high pressure. However, in order for the signal-to-noise ratios to be satisfactory, high concentrations (10−100 mM) are required. At these high concentrations metal/ligand and monomer/dimer equilibria deviate considerably from the equilibria in catalytic experiments (0.1−1 mM). Furthermore, the gas volume above the solution is often too small and mass transport is too slow to allow a fast catalytic reaction to be monitored for a longer period of time. Infrared spectroscopy is a better alternative.[1a,b,d−f,j,k,3]

Two techniques are available: transmission and reflectance spectroscopy.[1b] Transmission spectroscopy gives the highest signal-to-noise ratio and the highest resolution, but reflectance spectroscopy is a real in situ technique. One drawback of the transmission cells, which are usually connected to the autoclave via a pump and tubing, is that during transport to the cell the catalyst consumes the gases dissolved and the actual spectrum is not representative of the contents of the autoclave. A new transmission cell has been described that avoids this problem.[1k,4] Rhodium carbonyl complexes have strong absorptions for the CO stretching vibrations. Hence, low concentrations that approach real catalyst conditions can be used. Mechanistic aspects of the hydroformylation reaction using high-pressure IR (HPIR) have been only studied for mononuclear complexes containing triarylphosphines,[1b] monophosphites,[1a,f] and diphosphites.[1i,j,k]

Kalck et al. described the advantages of using dinuclear bridged rhodium thiolate complexes as catalyst precursors in the hydroformylation reaction.[5] A catalytic cycle, based on spectroscopic evidence and theoretical calculations, in which the dinuclear framework is retained for all steps has been proposed for $[Rh_2(\mu\text{-}SR)_2$-

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$(CO)_2(PR_3)_2$] precursors. Kinetic studies and an investigation of catalyst crossover reactions provided evidence that mononuclear species were present in a mixture of the two complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2(P(OMe)_3)_2]$, in which R = ^{t}Bu and Ph.[6] More recently, Angelici et al.[7] described how rhodium thiolate catalysts were immobilized by tethering them onto silica which remained active for several cycles. The selectivity and activity were markedly affected by the phosphine donor. It was suggested that under the reaction conditions mononuclear thiolate species were formed.

Stanley et al. reported dinuclear species of a different type, for the complex $[Rh_2(ndb)_2(et,ph\text{-}P4)](BF_4)_2$ (nbd = norbornadiene; et,phP4 = $(Et_2PCH_2CH_2)P(Ph)CH_2P(Ph)CH_2CH_2PEt_2$) with a binucleating tetraphosphine as a ligand. They proposed a catalytic cycle involving a dinuclear species based on *"in situ"* NMR studies and IR spectroscopic studies.[8]

In recent years we have used precursor systems with thiolate or dithiolate bridging ligands to hydroformylate alkenes.[9] We have also published one study on the role of the dithiolate ligand under hydroformylation conditions.[1o] In the present work, we report the results of the study by HPIR spectroscopy of different systems containing a thiolate or dithiolate bridge ligand, $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PR_3$ (R = Ph, OPh),[9a] $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PR_3$ (R = Ph, OPh, O-*o*-tBu),[9c] $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2/PPh_3$,[9c] and $[Rh_2\{\mu\text{-XANTOSS}\}(COD)_2]_2/PPh_3$[10] (XANTOSS = 9,9-dimethylxanthene-4,5-dithiolate) under hydroformylation conditions in order to obtain information about the species involved in the catalytic reaction. For comparative purposes we also studied the system $[Rh(acac)(CO)_2]$/phosphorus ligands, which is known to give mononuclear active species $[RhH(CO)_n(PR_3)_{4-n}]$ (n = 0−3) under hydroformylation conditions.[11]

Experimental Section

General Methods. All operations were performed under an atmosphere of nitrogen or argon by using standard Schlenk techniques. Solvents were dried and distilled before use.

$[Rh(acac)(CO)_2]$ was acquired from Johnson Matthey, and neutral Al_2O_3, PPh_3, and $P(OPh)_3$ were obtained from Aldrich. The complexes $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$,[12] $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]$,[9b] $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2$,[9b] and $[Rh_2\{\mu\text{-XANTOSS}\}(COD)_2]_2$[10] were prepared according to established methods. Oct-1-ene and hex-1-ene were acquired from Aldrich and were percolated over neutral alumina before use in order to remove peroxides.

Gas chromatography analyses were performed on a Hewlett-Packard 5890A gas chromatograph using an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m length × 0.2 mm i.d.) to separate the aldehydes.

IR spectra were recorded on a Nicolet 510 FTIR spectrophotometer with a resolution of 2 cm^{-1}. The GC-MS experiments were recorded on a Hewlett-Packard 5890II gas chromatograph equipped with a Hewlett-Packard 5971 mass spectrometer.

Standard Hydroformylation Experiments. A solution of the substrate, the catalyst precursor, and the phosphorus compound were placed in the evacuated autoclave. The gas mixture was introduced and the system heated. When thermal equilibrium was reached, the gas mixture was adjusted to the desired pressure. After the reaction, the autoclave was cooled to room temperature and depressurized. Samples were analyzed by gas chromatography.

The "in Situ" HPIR Experiments.[1k] The HPIR spectra were performed in an SS 316 55 mL autoclave equipped with ZnS windows (700 cm^{-1}, i.d. 10 mm, optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device. Liquid or dissolved reagents (up to 1 mL) were added from a separately pressurized reservoir. Rhodium complexes $[Rh_2(\mu\text{-}SR)_2(COD)_2]$ (0.04 mmol) and the corresponding phosphorus ligand were dissolved in 15 mL of 2-methyltetrahydrofuran. The autoclave was closed and flushed several times with the corresponding gas. After the autoclave was pressurized and the mixture was heated, the autoclave was placed in the infrared spectrometer and, while the sample was stirred, the infrared spectra were recorded. Hydroformylation studies were performed using the same equipment, and the substrate was taken from the reservoir and added to the reaction mixture by overpressure. Once this addition was made, the reaction started, as was evidenced by a pressure drop, and the spectra were recorded. The final solution was analyzed by GC.

Results and Discussion

HPIR Study of the $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PPh_3$ System under Hydroformylation Conditions. We studied the reactivity of the thiolate system $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PPh_3$ (**1**/PPh_3) under hydroformylation conditions. It had previously been reported that it is an efficient catalyst precursor for the hydroformylation of several olefins.[9a] The complex was recovered unchanged after the catalytic reaction.[12a] We studied the infrared spectra of system **1** under the reaction conditions that have previously been described as the most suitable for "thiolate" hydroformylation catalysts (5−7 bar, 60−80 °C). The in situ HPIR study involves three steps: (a) the addition of 2.5 bar of CO to **1**, (b) the addition of the phosphorus ligand, and (c) the addition of 2.5 bar of H_2. The reactions are carried out in 2-methyltetrahydrofuran, which due to

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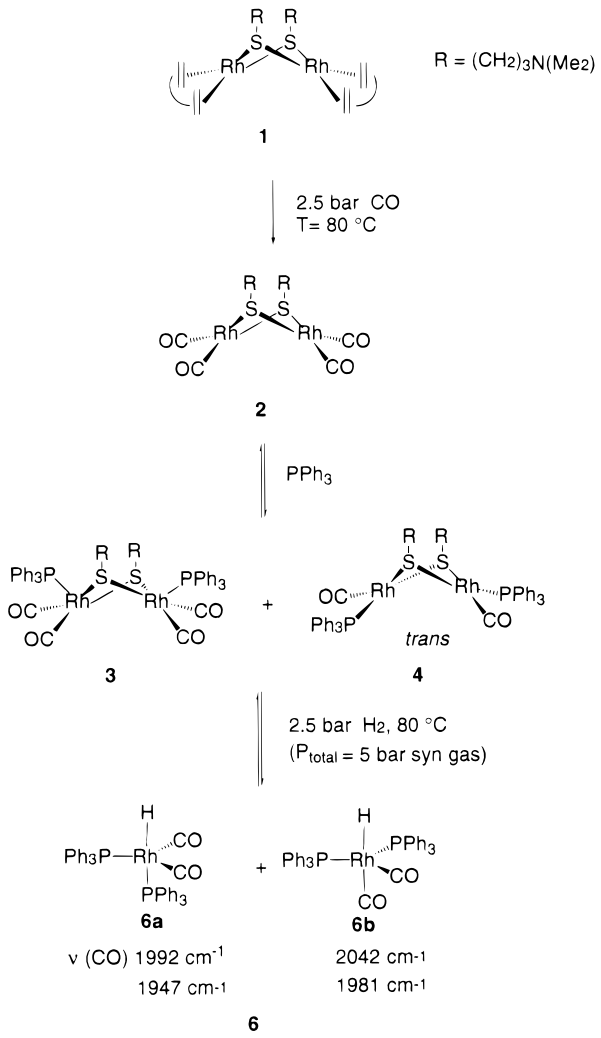
Scheme 1



the low polarity gives higher quality spectra and narrower lines than tetrahydrofuran, the solvent used previously in the catalytic studies.

Solution a: 2.5 bar of CO. The HPIR spectrum at 80 °C of solution a shows three ν(CO) frequencies at 2072 (m), 2053 (s), and 2004 (s) cm^{-1} attributed to the dinuclear rhodium complex $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_4]$ (**2**).[9a] This complex retains the thiolate bridge and contains two terminal CO ligands coordinated to each rhodium (Scheme 1). This species was the only one detected even under 15 bar of CO pressure and after 8 h of reaction.

Solution b: 2.5 bar of CO, Addition of PPh_3. Subsequently, different excesses of PPh_3 (PPh_3/Rh = 2, 5) were added to the solution at 80 °C. The HPIR spectrum showed ν(CO) frequencies at 2054 (s), 1989 (s), 1977 (s), and 1965 (s) cm^{-1} (Figure 1a and Table 1, entry 1). By comparison with data in the literature the first three signals were attributed to the pentacoordinated compound[13] $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_4(PPh_3)_2]$ (**3**) (Scheme 1). The signal at 1965 (s) cm^{-1} was attributed to the *trans*-dicarbonyl dinuclear mixed complex $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_2(PPh_3)_2]$ (**4**)[9a] (Scheme 1). It has been established that the decarbonylation of compound **3**, to give species **4**, is a reversible process.[13]

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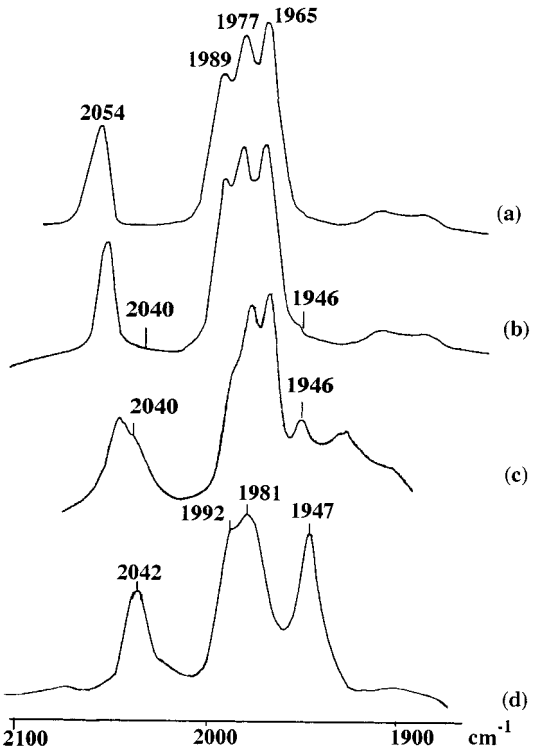


Figure 1. HPIR spectra: (a) reaction of **1** with CO and PPh_3; (b) reaction of **1** with CO, PPh_3, and H_2 after 2 h; (c) reaction of **1** with CO, PPh_3, and H_2 after 18 h; (d) reaction of **5** with CO, PPh_3, and H_2.

Table 1. HPIR Results of Catalyst Precursors $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(COD)_2]$ (1) and $[Rh(acac)(CO)_2]$ (5) with PPh_3[a]

		P (bar)		
entry no.	precursor	CO	H_2	IR (cm^{-1})
1	**1**	2.5		2054 (s),[b] 1989 (s),[b] 1977 (s),[b] 1965 (s)[c]
2	**1**	2.5	2.5	2054 (m),[b] 2040 (w),[d] 1989 (s),[b] 1977 (s),[b] 1965 (s),[c] 1946 (w)[d]
3	**5**	5	5	2042 (m),[d] 1992 (s),[d] 1981 (s),[d] 1947 (s)[d]

[a] Reaction conditions and abbreviations: 2-methyltetrahydrofuran (15 mL), 0.5 mmol catalyst precursor, s = strong, m = medium, w = weak, PPh_3/Rh = 2 and 5, T = 80 °C. [b] $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(CO)_4(PPh_3)_2]$ (**3**). [c] *trans*-$[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(CO)_2(PPh_3)_2]$ (**4**). [d] $[RhH(CO)_2(PPh_3)_2]$ (**6**).

The spectrum was unchanged after 18 h of reaction, even after the pressure was raised to 10 bar and the PPh_3 was added before the CO gas pressure was introduced.

Solution c: 2.5 bar of CO, PPh_3, and 2.5 bar of H_2. When the solution was pressurized with 2.5 bar of H_2 at 80 °C (5 bar of CO/H_2), new weak absorptions appeared at 2040 and 1946 cm^{-1} (Table 1, entry 2; Figure 1b). The intensities of these bands increased with time, and after 18 h the signals had become relatively strong (Figure 1c). Since these new absorptions appear only under H_2 pressure, the most likely new species contains a hydride ligand.

The System $[Rh(acac)(CO)_2]/PPh_3$ under Syngas Conditions. To identify the new signals at 2040 and 1946 cm^{-1} in the previous system containing dithiolate **1**, we performed the same set of experiments for the system $[Rh(acac)(CO)_2]/PPh_3$ (**5**/PPh_3). This system is

Table 2. Results of Hydroformylation of 1-Hexene with Catalyst Precursors 1, 10, 11, 17, and 5[a]

entry no.	precursor	*t* (h)	*P* (bar)	ligand	P/Rh	conversn (%)[b]	*n* (%)[c]	TOF (h^{-1})
1	**1**	3	5	PPh_3	2	70	77	47
2	**1**	4	5	PPh_3	5	95	81	47
3	**5**	0.25	5	PPh_3	2	90	77	720
4	**5**	0.25	5	PPh_3	5	91	82	827
5	**1**	3	5	$P(OPh)_3$	2	70	81	47
6	**1**	3	5	$P(OPh)_3$	5	26	84	17
7	**5**	0.3	5	$P(OPh)_3$	5	52	85	347
8	**5**	0.5	5	$P(OPh)_3$	2	83	81	339
9[d]	**5**	0.5	5	$P(OPh)_3$	5	83	83	1510
10[e]	**10**	6	30	PPh_3	2	96	73	8
11[e]	**5**	0.05	30	PPh_3	2	74	74	740
12[e]	**11**	19	5	PPh_3	2	96	72	3
13[f]	**18**	3	5	PPh_3	1	77	77	51
14[f]	**5**	0.75	5	PPh_3	1	86	79	115

[a] Reaction conditions: 1-hexene (10 mmol), complex (0.05 mmol), toluene (15 mL), 80 °C, $CO/H_2 = 1$. Precursors: **1**, $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(COD)_2]$; **5**, $[Rh(acac)(CO)_2]$; **10**, $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]$; **11**, $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2$; **18**, $[Rh_2(\mu\text{-SANTOSS})(COD)_2]_2$. [b] Conversion to aldehyde measured by GC integral ratio without internal standard. [c] Percentage of linear product. [d] Substrate/Rh = 1000. [e] Conditions: 1-hexene (10 mmol), complex (0.2 mmol). [f] Conditions: 1-hexene (10 mmol), complex (0.1 mmol), 65 °C. TOF = mol of aldehyde [mol of catalyst]$^{-1}$ h^{-1}.

known to give mononuclear active species $[RhH(CO)_n(PR_3)_{4-n}]$ ($n = 0-3$) under hydroformylation conditions.[11]

The solution obtained by adding an excess of PPh_3 (P/Rh = 5) to a solution of $[Rh(acac)(CO)_2]$ in 2-methyltetrahydrofuran at 80 °C at 10 bar of syngas was studied spectroscopically. The HPIR spectrum shows four absorptions at 2042 (m), 1992 (s), 1981 (s), and 1947 (s) cm^{-1} (Figure 1d) which are attributed to the compound $[RhH(CO)_2(PPh_3)_2]$ (**6**). This compound exists as two trigonal-bipyramidal isomers in equilibrium (**6a**, which contains an equatorial and an apical phosphine ligand, and **6b**, which contains two equatorial phosphines) (Table 1, entry 3).[1c] The bands at 1992 and 1947 cm^{-1} are attributed to the conformer containing the hydride trans to PPh_3, **6a** (Scheme 1), and the absorptions at 2042 (m) and 1981 (s) cm^{-1} are attributed to the geometry containing the hydride trans to the CO ligand, **6b** (Scheme 1).[1o,14] Thus, we conclude that the signals at 2040 and 1946 cm^{-1} in the HPIR of the system $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PPh_3$ under hydroformylation conditions are due to the isomers **6a**,**b** of the complex $[RhH(CO)_2(PPh_3)_2]$. The absorptions expected at 1992 and 1981 cm^{-1} for the complex $[RhH(CO)_2(PPh_3)_2]$ in the HPIR overlap with the signals at 1989 and 1979 cm^{-1} of the compound $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_4(PPh_3)_2]$ (**3**).

Thus, the HPIR experiments show that system **1** under hydroformylation conditions generates dinuclear thiolate-bridged carbonyl phosphine (**3** and **4**) and mononuclear rhodium(I) hydride (**6**) species.

To determine which of these species are the active ones in hydroformylation, comparative catalytic activity studies with precursors **1** and $[Rh(acac)(CO)_2]/PPh_3$ were performed under the same conditions. Table 2 shows the results of 1-hexene hydroformylation with the catalyst precursor $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$ (**1**) and $[Rh(acac)(CO)_2]$ (**5**) (entries 1−4).

We assume that, the conditions being the same, the regioselectivities observed are indicative of the nature of the active species in the catalytic process. Therefore, the fact that experiments 1−2 and 3−4 (Table 2) provide the same regioselectivity may indicate that these systems involve the same active species.

The argument that the selectivities of two systems are similar remains circumstantial evidence to prove that the catalyst is the same. Also, because the selectivity depends on the concentrations of the rhodium and free ligand, the latter is influenced by the nonactive rhodium species involved in metal−ligand equilibria.

This result shows that mononuclear species can be formed from the dinuclear compound $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$ in the presence of PPh_3 and that they might participate in catalysis. However, the presence of mononuclear hydrides is indicated more clearly by the HPIR study. The lower activity observed for the complex $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$ may be due to the low concentration of the mononuclear hydrido species, as detected by HPIR.

In summary, the HPIR study in combination with the results of the hydroformylation experiments using the systems $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PPh_3$ and $[Rh(acac)(CO)_2]/PPh_3$ allow us to conclude that mononuclear hydrido species are responsible for the catalytic activity in the first of these two systems.

The System $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$/$P(OPh)_3$ under Syngas Conditions. In the presence of phosphites, complex **1** was also shown to lead to active hydroformylation catalysts.[9a] Rhodium phosphite complexes are well-known catalysts for the hydroformylation reaction, and some of them are extremely active.[1k] Therefore, the suspicion arises that the activity of the dimeric rhodium thiolate complexes might be caused by the formation of traces of mononuclear rhodium hydride species. Thus, a sequence of reactions similar to the ones described above was carried out and the IR spectra were recorded in situ in the high-pressure IR cell. First, complex **1** was treated with 2.5 bar of CO gas (solution a, not shown), (b) triphenyl phosphite was added, and (c) hydrogen was added.

Solution b: 2.5 bar of CO Pressure and $P(OPh)_3$. The addition of 2.5 bar of CO to a solution of 2-methyltetrahydrofuran containing $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$ and $P(OPh)_3$ (P/Rh = 5) showed a strong band at 1994 cm^{-1}, which was attributed to the complex *trans*-$[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_2(P(OPh)_3)_2]$ (**7**)[9a] (Scheme 2; Table 3, entry 4; Figure 2a). We also

(14) van der Veen, L. A.; Boelen, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.

Scheme 2

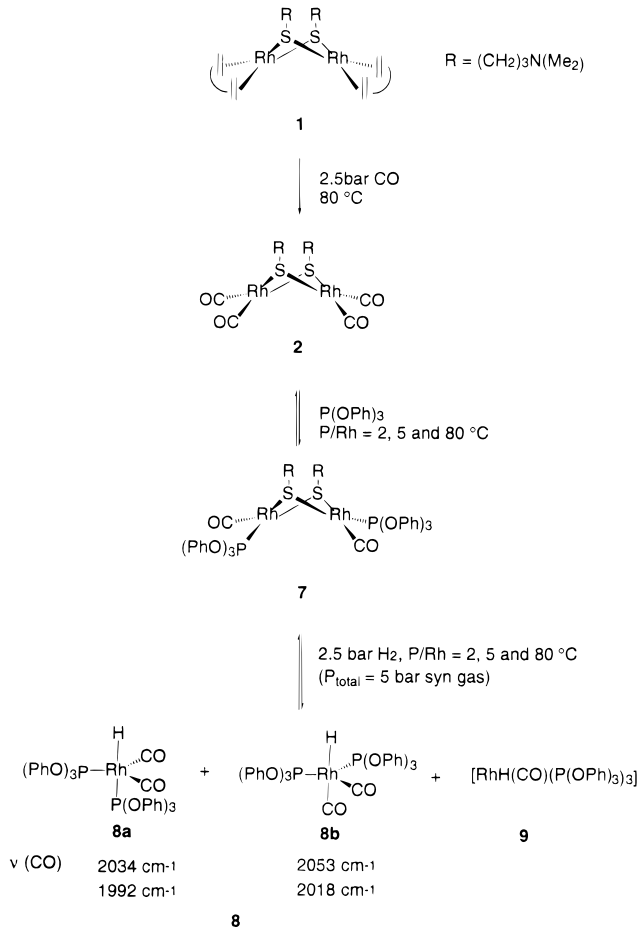


Table 3. HPIR Results of Catalyst Precursors $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(COD)_2]$ (1) and $[Rh(acac)(CO)_2]$ (5) with $P(OPh)_3$[a]

		P (bar)		
entry no.	precursor	CO	H_2	IR (cm^{-1})
4	**1**	2.5		2072 (m),[b] 2054 (m),[b] 2004 (m),[b] 1994 (s)[c]
5	**1**	2.5	2.5	2070 (w),[e] 2054 (m),[b,d] 2034 (w),[d] 2018 (m),[d] 2004 (m),[b] 1994 (s)[c]
6	**5**	5	5	2070 (m),[e] 2053 (w),[d] 2034 (m),[d] 2018 (m),[d] 1992 (m)[d]

[a] Reaction conditions and abbreviations: 2-methyltetrahydrofuran (15 mL), 0.5 mmol of catalyst precursor, s = strong, m = medium, w = weak, $P(OPh)_3/Rh = 2$ and 5, $T = 80$ °C. [b] $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(CO)_4]$ (**2**). [c] *trans*-$[Rh_2\{\mu\text{-}S(CH_2)_3N(Me)_2\}_2(CO)_2(P(OPh)_3)_2]$ (**7**). [d] $[RhH(CO)_2(P(OPh)_3)_2]$ (**8**). [e] $[RhH(CO)(P(OPh)_3)_3]$ (**9**).

observed weak absorptions that were attributed to the tetracarbonyl species $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(CO)_4]$ (**2**).

Solution c: 2.5 bar of CO, $P(OPh)_3$, and 2.5 bar of H_2. When this solution was pressurized with 2.5 bar of H_2 at 80 °C (5 bar of CO/H_2), new signals appeared at 2070, 2034, and 2018 cm^{-1} and the intensity of the band at 2054 cm^{-1} increased (Table 3, entry 5; Figure 2b). The new absorptions appeared immediately and increased with time.

The formation of the species leading to these new absorptions depends on pressure, temperature, and the ratio of phosphite to rhodium. Thus, if we raise the pressure of CO/H_2 to 19 bar, these new absorptions increase immediately. At 50 °C these species appear after 2 h of reaction, and at 40 °C they appear after 3 h. When the temperature is kept at 50 °C by applying P/Rh = 2, these new species do not appear until after 4 h.

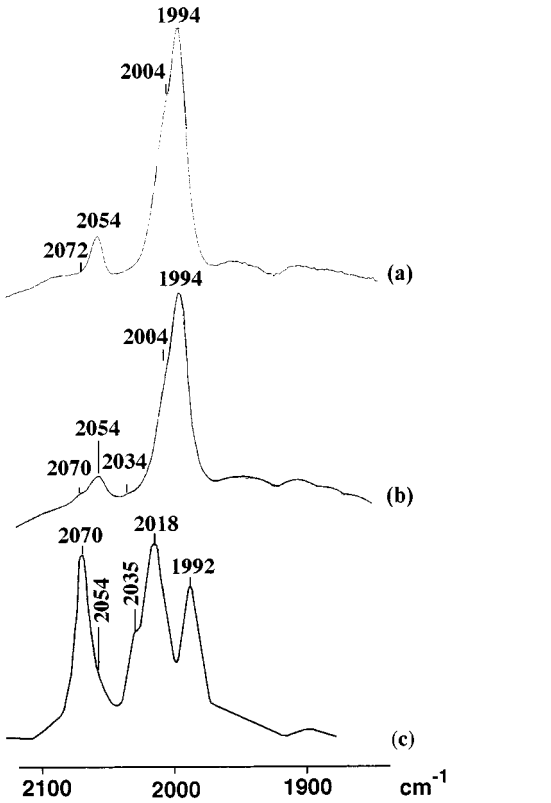


Figure 2. HPIR spectra: (a) reaction of **1** with CO and $P(OPh)_3$; (b) reaction of **1** with CO, $P(OPh)_3$, and H_2; (c) reaction of **5** with CO, $P(OPh)_3$, and H_2.

The System $[Rh(acac)(CO)_2]/P(OPh)_3$ under Syngas Conditions. As in the previous PPh_3 study, to compare the system with a conventional rhodium system which provides mononuclear species, the spectroscopy study of $[Rh(acac)(CO)_2]/P(OPh)_3$ (P/Rh = 5) in methyltetrahydrofuran was carried out at 80 °C under 10 bar of syngas.

The HPIR spectrum showed five signals at 2070, 2053, 2034, 2018, and 1992 cm^{-1} (Table 3, entry 6, Figure 2c). The absorptions at 2034 and 1992 cm^{-1} are attributed to the trigonal-bipyramidal geometry of the compound $[RhH(CO)_2(P)_2]$ (**8a**), which has the phosphorus ligands in equatorial and axial positions, and the signals at 2053 and 2018 cm^{-1} are attributed to the hydride complex in which the phosphorus ligands are in equatorial−equatorial positions, **8b**[1a,11,15] (Scheme 2). The absorption at 2070 cm^{-1} corresponds to ν(CO) of the compound $[RhH(CO)(P)_3]$ (**9**)[16] (Scheme 2).

Comparing the frequencies for the catalytic system $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/P(OPh)_3$ (Table 3, entry 5) and the precursor $[Rh(acac)(CO)_2]/P(OPh)_3$ (Table 3, entry 6) clearly shows that mononuclear hydrido pentacoordinate species are present in the solution of the dinuclear thiolate precursor (2070, 2034, 2018, and 2054 cm^{-1}).

(15) (a) Trzeciak, A. M.; Ziółkowski, J. J. *J. Mol. Catal.* **1983**, *19*, 41. (b) Buisman, G. J. H. Ph.D. Thesis, University of Amsterdam, 1995.
(16) Trzeciak, A. M. *J. Organomet. Chem.* **1990**, *390*, 105.

The assignment of these frequencies to mononuclear species is in agreement with the observation that their concentration increases when the pressure increases but decreases when the ratio P/Rh or the temperature decreases.

Hydroformylation results confirm the spectroscopic observations in HPIR, since the regioselectivities (Table 2, entries 5−6 and 7−8) obtained with the systems $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/P(OPh)_3$ and $[Rh(acac)(CO)_2]/P(OPh)_3$ are the same. This suggests that the mononuclear species are the same. Since the HPIR study shows that the mononuclear species is present only in a low concentration under hydroformylation conditions, a catalytic experiment with a similarly low precursor concentration $[Rh(acac)(CO)_2]/P(OPh)_3$ was carried out using a high ratio of substrate to precursor (entry 9). The considerable activity of this system shows that the mononuclear species observed in HPIR can fully account for the activity of the catalyst precursor $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$.

HPIR Study of Dinuclear or Tetranuclear Bridged Rhodium Dithiolate Systems with PPh_3 under Hydroformylation Conditions. A priori, complexes containing bridging alkanedithiolates could be more resistant to bridge cleavage than the corresponding monothiolates because of their chelating properties. Thus, we considered it of interest to study dithiolate−phosphine systems under hydroformylation conditions.

The systems studied are known to have different activities in 1-hexene hydroformylation, and their activity heavily depends on the ring size of the bridging dithiolate ligand. Thus, the catalyst precursor $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$ (**10**) shows significant activity only at 30 bar and 80 °C and with the ligand-to-metal ratio P/Rh = 2, whereas the precursors $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2/PPh_3$ (**11**) and $[Rh_2(\mu\text{-XANTOSS})(COD)_2]_2/PPh_3$ (**18**) are active at 5 bar, 80 °C, and P/Rh = 2 and at 5 bar, 65 °C, and P/Rh = 1, respectively.[9c,10]

HPIR Study of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$ and $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2/PPh_3$ under Hydroformylation Conditions. To obtain information about the species present during the hydroformylation reaction, we measured the HPIR spectra of the solutions, which were prepared as follows: (a) addition of CO, (b) addition of PPh_3, and (c) addition of H_2.

Solution a: Addition of CO. To obtain solutions similar to the ones used in the catalytic experiments, 15 bar of CO was added to the solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]$ and 2.5 bar of CO to the solution of $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2$ in 2-methyltetrahydrofuran at 80 °C. The HPIR spectra of the solutions show three frequencies attributed to the dinuclear tetracarbonylrhodium complexes $[Rh_2\{\mu\text{-}S(CH_2)_nS\}(CO)_4]$[9c] ($n = 2$, **12**; $n = 4$, **13**) (Table 4, entries 7 and 11, respectively).

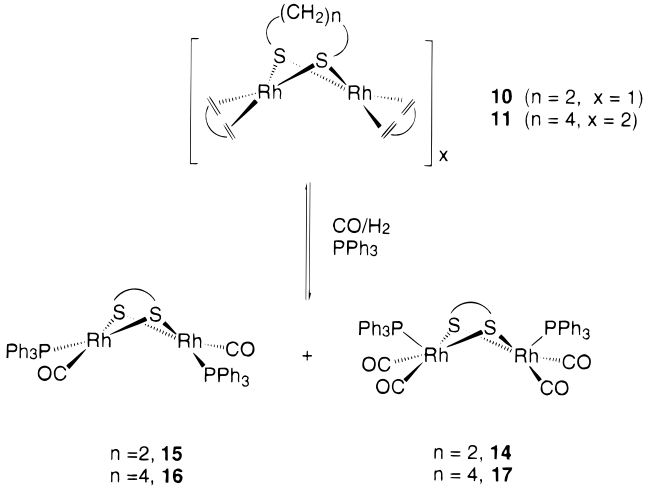
Solution b: Addition of PPh_3. Subsequently, an excess of PPh_3 (P/Rh = 2) was added at 80 °C. In the case of the compound $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]$ the HPIR showed new ν(CO) frequencies at 2057, 1996, and 1982 cm^{-1}, which were attributed to the pentacoordinated compound $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4](PPh_3)_2]$ (**14**), and a strong band at 1966 cm^{-1} corresponding to the *trans*-dicarbonyl dinuclear mixed complex $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ (**15**)[9c] (Table 4, entry 8; Scheme 3). Analogous species were detected for the compound $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2$. In this case the HPIR shows a new ν(CO) frequency at 1964 cm^{-1}, which is attributed to complex **16**,[9c] and three peaks at 2050, 1988, and 1974 cm^{-1} corresponding to the pentacoordinated complex **17** (Table 4, entry 12; Scheme 3).

Table 4. HPIR Results of Catalyst Precursors $[Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2]$ (10) and $[Rh_2(\mu\text{-}S(CH_2)_4S)(COD)_2]_2$ (11)[a]

		P (bar)		
entry no.	precursor	CO	H_2	IR (cm^{-1})
7[b]	**10**	15		2072 (m),[c] 2059 (s),[c] 2018 (s)[c]
8	**10**	15		2072 (w),[c] 2057 (m),[c,d] 2018 (w),[c] 1996 (m),[d] 1982 (m),[d] 1966 (s)[e]
9	**10**	15	15	2072 (w),[c] 2057 (m),[c,d] 2018 (w),[c] 1996 (m),[d] 1982 (m),[d] 1966 (s)[e]
11[b]	**11**	2.5		2073 (w),[f] 2050 (s),[f] 2007 (w)[f]
12	**11**	2.5		2050 (m),[h] 1988 (m),[h] 1974 (s),[h] 1964 (s)[g]
13	**11**	2.5	2.5	2050 (m),[h] 1988 (m),[h] 1974 (s),[h] 1964 (s)[g]

[a] Reaction conditions: 2-methyltetrahydrofuran (15 mL), 0.2 mmol catalyst precursor. s = strong, m = medium, w = weak. $PPh_3/Rh = 2$ and T = 80 °C. [b] Experiments without PPh_3. [c] $[Rh_2(\mu\text{-}S(CH_2)_2S)(CO)_4]$ (**12**). [d] $[Rh_2(\mu\text{-}S(CH_2)_2S)(CO)_4(P)_2]$ (**14**). [e] $[Rh_2(\mu\text{-}S(CH_2)_2S)(CO)_2(P)_2]$ (**15**). [f] $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$ (**13**). [g] $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_2(P)_2]$ (**16**). [h] $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4(P)_2]$ (**17**).

Scheme 3

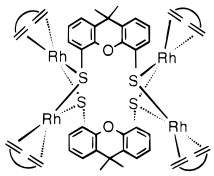


Solution c: Addition of H_2. When the solutions of the compounds $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]$ and $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2$ were pressurized with 15 bar of H_2 (total pressure 30 bar of CO/H_2) and 2.5 bar of H_2 (total pressure 5 bar of CO/H_2), respectively (Table 4, entries 9 and 13), the HPIR spectra showed no change, not even after 48 h of reaction time (Scheme 3).

For the compound $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$ a similar series of experiments was carried out using a high ratio of H_2 to CO ($H_2/CO = 8$, total pressure 30 bar). After 2 h, the spectra showed a weak absorption at 2048 cm^{-1} that can be attributed to the mononuclear hydride species **6b**.

These HPIR experiments show that under hydroformylation conditions only dinuclear species are detected and that, if mononuclear species are present, their concentration is below the HPIR detection limit. Thus, while there is not definite proof of the nature of

Scheme 4



18

CO/H_2 = 5 bar
PPh_3/Rh = 1
T= 65 °C

$[Rh_2(\mu\text{-XANTOSS})(CO)_4]_2$ + $[RhH(CO)_2(PPh_3)_2]$ + $[Rh_2(\mu\text{-XANTOSS})(CO)_2(PPh_3)_2]_2$

19 **6** **20**

the active species, the hydroformylation results give some clue about what might be going on. The regioselectivities for the systems $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$ and $[Rh(acac)(CO)_2]/PPh_3$ are the same (Table 2, entries 10 and 11) and are typical of a Rh/PPh_3 catalyst. The activities obtained using precursors **10** and **11** are extremely low (entries 10−12). The activity of the dithiolate systems is lower than that of the thiolate systems $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]$/phosphorus ligand (and precursor **5**) and may be attributed to the high stability toward cleavage of the dithiolate systems, which gives the active mononuclear hydrido species. In complexes **10** and **11** the dithiolates act as bridging ligands, forming five- and six-membered rings with the metal, which lead to more stable complexes.[9b] Their activities amount to only 1% of those of the active hydride species. Since the detection limit under the present conditions is 5%, hydride formation cannot be proven for these systems.

When the pressure is released, the dinuclear compounds $[Rh_2(\mu\text{-thiolate})_2(CO)_4(PPh_3)_2]$ are re-formed in solution.[5c,9c,12a]

HPIR Study of the $[Rh_2(\mu\text{-XANTOSS})(COD)_2]_2/PPh_3$ Catalytic System under Hydroformylation Conditions. This system is very active for the hydroformylation of 1-hexene under very mild conditions (5 bar of CO/H_2 and 65 °C).

The addition of 2.5 bar of CO to a solution of $[Rh_2(\mu\text{-XANTOSS})(COD)_2]_2$ (**18**) (Scheme 4) gives an HPIR spectra which shows six signals assigned to the compound $[Rh_2(\mu\text{-XANTOSS})(CO)_4]_2$ **(19)**.[10]

The subsequent addition of PPh_3 (P/Rh = 1) to the solution at 65 °C showed three new peaks at 1992 (s), 1982 (s), and 1970 (m) cm^{-1}, which are attributed to the complex $[Rh_2(\mu\text{-XANTOSS})(CO)_2(PPh_3)_2]_2$ (**20**).

When the solution was pressurized with 2.5 bar of H_2 at 65 °C (total pressure 5 bar of CO/H_2), the HPIR spectrum immediately showed new, strong signals at 2040 and 1947 cm^{-1} characteristic of the mononuclear species $[RhH(CO)_2(PPh_3)_2]$. The regioselectivity obtained in the corresponding hydroformylation experiment is the same as that for $[Rh(acac)(CO)_2]$ (Table 2, entries 13 and 14). This is in agreement with the presence of the mononuclear pentacoordinate rhodium species. The catalyst precursor $[Rh_2(\mu\text{-XANTOSS})(COD)_2]_2/PPh_3$ is more active than the precursor systems $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(COD)_2]/PPh_3$ and $[Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2]_2/PPh_3$ (Table 2, entries 10, 12, and 13). This reflects the propensity of these systems to give mononuclear active species such as the ones found in the HPIR study. Apparently, the geometry enforced by the XANTOSS backbone leads to bridged thiolate complexes that are only moderately stable with respect to mononuclear hydrido carbonyls.

Deuterioformylation Experiments. In an attempt to find out the role that dinuclear rhodium thiolate species play, we conducted a series of experiments using D_2 and mixtures of D_2 and H_2 in hydroformylation reactions. Inspection of the mechanisms proposed for dirhodium thiolate complexes[5c] and monohydride rhodium species[17] reveals that the incorporation of D_2/H_2 during the hydroformylation reaction may be different for the two mechanisms. In the generally accepted mechanism for rhodium hydride catalysts[18] the two hydrogen atoms built into the aldehyde product stem from two different dihydrogen molecules (Figure 3). Therefore, in a mixture of H_2 and D_2 (1/1) a statistical mixture of un-, mono-, and dideuterated products forms, which may be disturbed by kinetic isotope effects (an isotope effect was observed for the bulky rhodium phosphite catalyst).[1f] Another provision to be made is that the addition of hydride to alkene is irreversible, which is the case if the temperature is sufficiently low.[19] Indeed, a reaction carried out using 1-octene (**5**: 2 PPh_3, $H_2/D_2/CO$ (1/1/1), at 50 °C, 5 bar total pressure) gave a statistical mixture of deuterated products.

The mechanism proposed for dinuclear thiolate-bridged complexes[5c] is a special case (Figure 4). In this mechanism, dihydrogen is added to the dimer and both hydrogens are incorporated in the same product molecule, provided that no H/D exchange occurs between the dihydrido complex and free dihydrogen. Thus, hydroformylation using a mixture of H_2 and D_2 (1/1) may lead to products containing either two added hydrogen atoms or two added deuterium atoms.

The experiments were carried out using the thiolate-bridged rhodium complex **1**[9a] for 3 h at 5 bar of syngas, 50 °C, and a $P(OPh)_3/Rh$ ratio of 2. Under these mild conditions the dimers should be the active species. The HPIR study indeed showed that the mononuclear species only reached the detection limit after 4 h of reaction.

The crude mixture resulting from the hydroformylation experiments using $[Rh_2\{\mu\text{-}S(CH_2)_3N(Me_2)\}_2(COD)_2]/PPh_3$ (P/Rh = 2) as the catalyst precursor were analyzed by GC-MS, either directly, using the aldehydes, or indirectly, using the alcohols obtained by reduction with $LiAlH_4$. The results were the same for both methods. The following experiments were performed: (1) pressurization of the system with 5 bar of CO/D_2 (1/1) and subsequent addition of 1-octene and (2) pressurization of the system with 5 bar of $CO/H_2/D_2$ (1/1/1) followed by addition of 1-octene. The GC-MS trace in experiment

(17) (a) O'Connor, C.; Yagupsky, G.; Evans, D.; Wilkinson, G. *J. Chem. Soc. D* **1968**, 420. (b) Evans, D.; Yaguspsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660. (c) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133. (d) Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2753.

(18) van Leeuwen, P. W. N. M.; van Koten, G. In *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, 2nd ed.; van Santen, R. A., Moulijn, J. A., van Leeuwen, P. W. N. M., Eds.; Elsevier: Amsterdam, 1995; Chapter 6.

(19) (a) Uccello-Baretta, G.; Lazzaroni, R.; Settambolo, R.; Salvadori, P. *J. Organomet. Chem.* **1991**, *417*, 111. (b) Casey, C. P.; Petrovich, L. M. *J. Am. Chem. Soc.* **1995**, *117*, 6007. (c) Horiuchi, T. E.; Shirakawa, E. K.; Nozaki, K. H.; Takaya, H. *Organometallics* **1997**, *16*, 2981.

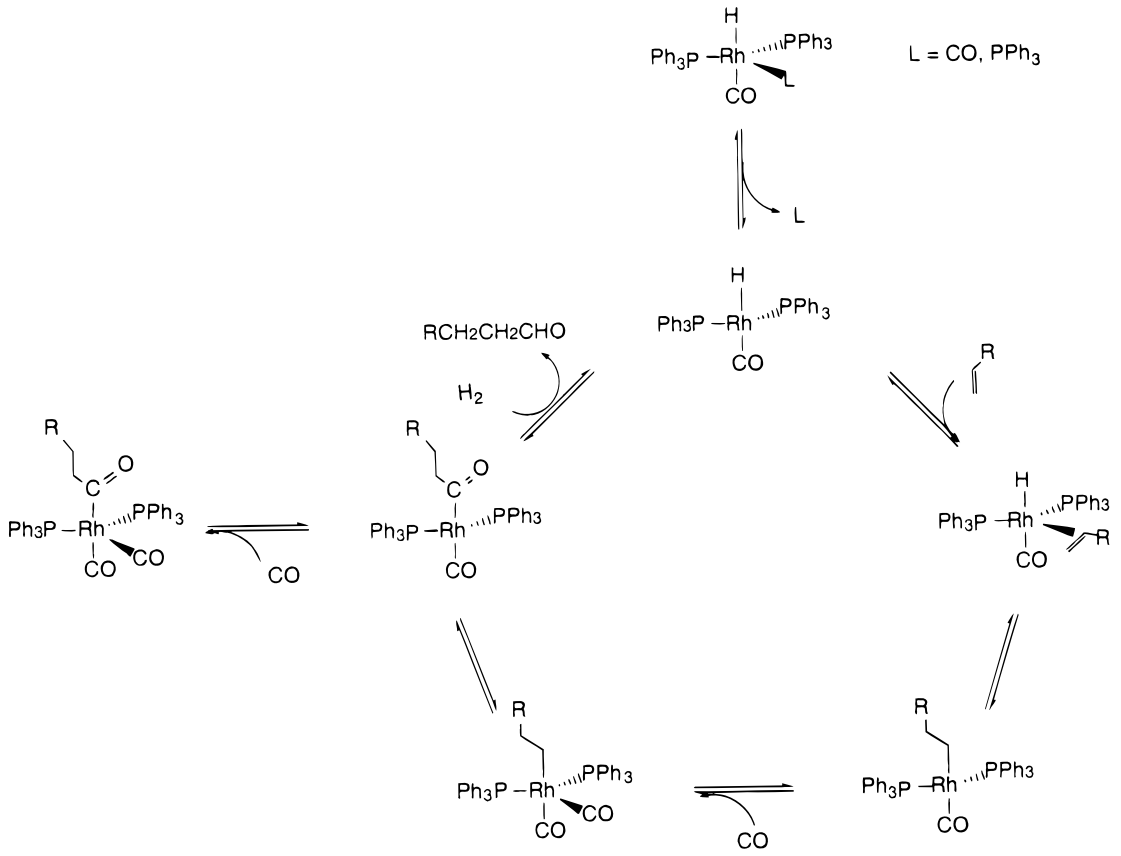


Figure 3. Presently accepted mechanism of hydroformylation catalyzed by $[RhH(CO)_2(PPh_3)_2]$.

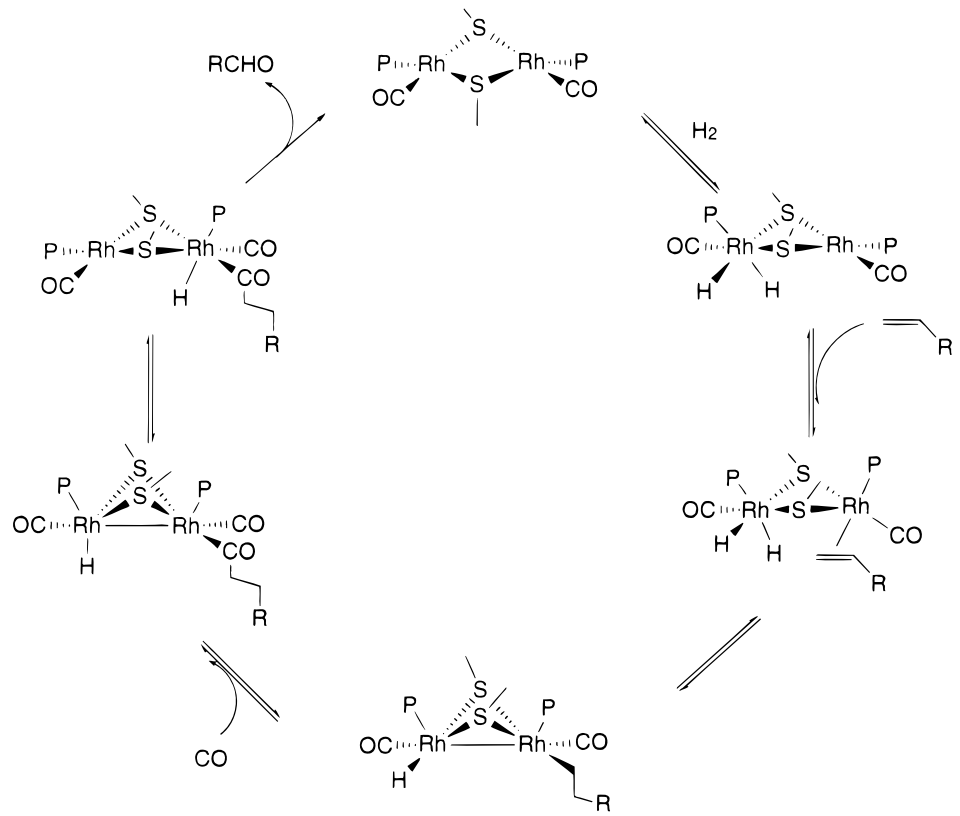


Figure 4. Catalytic cycle of hydroformylation proposed for dinuclear thiolate complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$.

1 shows only one peak M, for the dideuterated compound, and no signals were observed at M − 1 or M + 1, which indicates that no isomerization has taken place. For experiment 2, we obtained a statistical distribution of approximately 1/2/1 for M − 1, M, and M + 1, corresponding to the peaks of alcohol, monodeuterio alcohol, and dideuterio alcohol. This result is in accordance with the presence of a mononuclear rhodium

hydride catalyst. If the reaction mechanism involved dinuclear species,[5c] only dideuterated alcohols or dihydrogenated alcohols would be expected. In a separate experiment we tried to observe the putative dihydrido−dirhodium intermediate. The dinuclear $[Rh_2(\mu\text{-}SC_3H_7)_2(CO)_4]$, which is similar to complex **2**, was studied using HP NMR spectroscopy under pressures as high as 50 bar of H_2, but no change was detected in the ^1H or the ^{31}P spectra in a temperature range of 25−80 °C.[20]

In summary, the deuterioformylation experiments indicate that mononuclear species formed under hydroformylation conditions are most probably responsible for the activity of the catalyst, thus supporting the outcome of the HPIR spectroscopy and hydroformylation experiments.

Conclusions

HPIR spectroscopic studies and hydroformylation experiments revealed that, when phosphorus ligands PPh_3 and $P(OPh)_3$ are added to the thiolate compounds **1** under hydroformylation conditions, mononuclear species are formed, which are responsible for the hydroformylation activity.

HPIR spectroscopic studies of the more stable dithiolate compounds indicate that their behavior under hydroformylation conditions depends on their stability toward syngas. Thus, complexes **10** and **11** are more resistant to the dithiolate cleavage than is compound **18**. In all cases the activity and selectivity observed correlates with the concentration of monomeric rhodium hydride species. For **10** and **11** no hydride was observed under the conditions applied, but the activitiy of these systems was correspondingly low.

Acknowledgment. We thank the Ministerio de Educación y Ciencia and the Generalitat de Catalunya for financial support (Grant No. QFN-95-4725-C03-2; CICYT-CIRIT). We thank Oscar Pamies and Wim G. J. de Lange for their valuable assistance.

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(20) Diéguez, M.; Mhammedi, S.; Bayón J. C.; van Leeuwen, P. W. N. M. Unpublished results.