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Journal of Organometallic Chemistry 551 (1998) 375–381

Journal of Organometallic Chemistry

Reactivity of tetracarbonyl dithiolate-bridged rhodium(I) complexes with diphosphines [1]

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Received 19 July 1997; received in revised form 2 September 1997

Abstract

The reactivity of the complexes [Rh_2(μ-dithiolate)$(CO)_4$] {dithiolate = $S(CH_2)_4S$ (**1**) (1,4-butanedithiol), BCOS (**2**) ((+)-*trans*-2,3-bis(mercaptomethyl)-bicyclo[2.2.2]octane)} with diphosphines has been studied. Addition of the diphosphine to a solution of the μ-dithiolate dirhodium(I) complex [Rh_2(μ-dithiolate)$(CO)_4$] unexpectedly resulted in the novel ionic species $[Rh(CO)(diphosphine)_2]^+$ $[Rh(dithiolate)(CO)_2]^-$ (diphosphine = dppp) and $[Rh(diphosphine)_2]^+$ $[Rh(dithiolate)(CO)_2]^-$ (diphosphine = dppe, dppp). The solution structures of the CO/diphosphine complexes were studied by IR and ^{31}P NMR. © 1998 Elsevier Science S.A.

Keywords: Rhodium complexes; Chiral thiolate; Diphosphines; Ionic complexes

1. Introduction

It is well known that diphosphine rhodium complexes form active catalysts for olefin hydroformylation [1–6]. The activity and selectivity of these catalysts depend on the steric and electronic properties of the diphosphine ligands. Thus, it has been observed that the addition of diphosphine ligands to the $HRh(CO)(PPh_3)_3$ precursor provides higher linear-to-branched ratios in the hydroformylation of 1-hexene to heptanal [1–3]. It was suggested that a dinuclear catalyst complex, observed by ^{31}P NMR [2], with three phosphines coordinated to rhodium $[HRh(CO)(P–P)(P–P)_m]$ (m = monodentate), was responsible for the catalytic activity.

Casey et al. [4] have recently observed a correlation between the size of the natural bite angle of chelating diphosphines and the regioselectivity for formation of straight-chain aldehydes in the rhodium-catalyzed hydroformylation of 1-hexene. Van Leeuwen et al. [6] have studied a homologous series of diphosphines based on rigid heterocyclic aromatics and have observed that in the hydroformylation of 1-hexene, the regioselectivity into the *n*-aldehyde increased in proportion to the increase in the bite angle.

On the other hand, dinuclear rhodium complexes containing thiolate bridge ligands have proved to be efficient catalysts under mild conditions in olefin hydroformylation in the presence of phosphines [7] and diphosphines [8–11]. Kalck et al. have reported the X-ray structure of some thiolate-bridged diphosphine rhodium complexes in which the diphosphine acts as a bridging ligand between the two metal atoms, such as {$Rh_2(\mu\text{-}^tBuS)_2[\mu\text{-}(Ph_2PCH_2)_2Zr(\eta\text{-}C_5H_5)_2](CO)_2$} (**3**) [8], {$Rh_2(\mu\text{-}^tBuS)_2(\mu\text{-dppb})(CO)_2$} (**4a**) [9], and {$Rh_2(\mu\text{-}^tBuS)_2[\mu$-bis(diphenylphosphino)-ferrocene]$(CO)_2$} (**4b**) (Fig. 1) [9].

Recently, asymmetric hydroformylation of styrene has been performed using dinuclear dithiolate-bridged rhodium complexes with different chiral diphosphines as auxiliary ligands [12–14]. Systems based on the dinuclear achiral dithiolate-bridged complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 and 4) shown to be active hydroformylation catalysts in the presence of (+)-(2*R*,3*R*)- or (−)-BDPP {(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane} [12].

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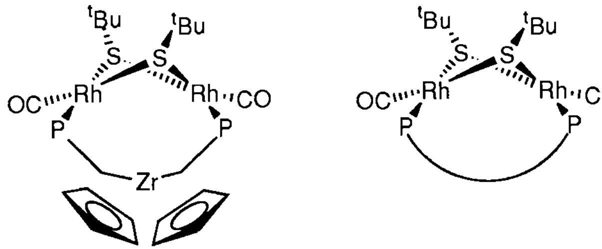
[1] Dedicated to Peter M. Maitlis on the occasion of his 65th birthday.



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4a P-P= dppb
4b P-P= dppr

Fig. 1.

Table 1
$^{31}P\{^1H\}$ NMR data of the resulting solution of the reaction of $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$ with diphosphines[a]

Diphosphine	δ[b]	$^1J_{Rh-P}$	$^2J_{P-P}$	T (°C)
dppe	58.1(d)	133.1		25, −60
dppp	23.8(d)	126.7		25
	−15.6(dt)	85.1	46	−60
	−12.0(dt)	116.7	46	

[a] Measured in ppm (upfield negative) from 85% H_3PO_4.
[b] Chloroform as a solvent, diphosphine/Rh = 4; d: doublet, dt: doublet of triplets. When dppb was used, only a complex mixture of species was observed in the $^{31}P\{^1H\}$ NMR spectrum.

Likewise, different chiral dithiolate-bridged complexes such as $[Rh_2(\mu\text{-}(-)\text{-}(DIOS)(COD)_2]_2$ (DIOS = 2,3-*O*-isopropylidene-1,4-dithiolato-L-threitol) [13] and $[Rh_2(\mu\text{-}(+)\text{-}(BCOS)(COD)_2]_2$ (BCOS = (+)-*trans*-2,3-*bis*(mercaptomethyl)-bicyclo[2.2.2]octane) [14] have been used in combination with chiral diphosphines such as DIOP {(2*S*,3*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane)} and BDPP in styrene hydroformylation, and show that the system $[Rh_2(\mu\text{-}(+)\text{-}(BCOS)(COD)_2]_2$/BDPP [14] provides the best results, obtaining up to 55% of enantiomeric excess.

In a comparative study, when the achiral diphosphine dppp, structurally related with BDPP, was used with the rhodium precursor $[Rh_2(\mu\text{-}(+)\text{-}(BCOS)(COD)_2]_2$, an ee of 10% in (*S*)-2-phenylpropanal was obtained.

The effect of the presence of chiral thiolates, albeit small in some instances, seems to indicate that complexes containing thiolates are involved in catalysis. The participation of the dithiolate-bridged rhodium complexes in the catalytic cycle remains a matter of controversy, and additional evidence is required. In the present paper, we report the results of the reactivity of $[Rh_2(\mu\text{-dithiolate})(CO)_4]$ (dithiolate = $-S(CH_2)_4S-$ [15], BCOS [14]) complexes towards dppp and related diphosphines. These results shed some light on the behaviour of these systems.

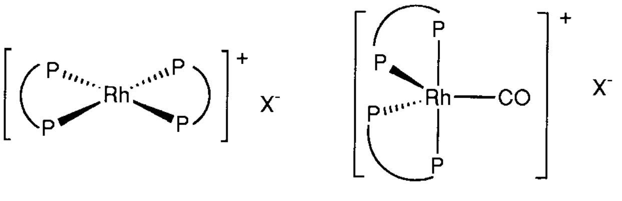
2. Results and discussion

It is generally accepted that carbonyl–phosphine complexes are the catalytic precursors in hydroformylation processes. Therefore, the reaction of $[Rh_2(\mu\text{-dithiolate})(CO)_4]$ (dithiolate = –S(CH2)$_4$S–, BCOS) towards diphosphines was carried out under CO atmosphere. Firstly, a stoichiometric amount of the diphosphines dppe, dppp and dppb (diphosphine/Rh = 1) was added to solutions of the $[Rh_2(\mu\text{-dithiolate})(CO)_4]$ (dithiolate = $-S(CH_2)_4S-$, BCOS) complexes in dichloromethane under CO atmosphere. The solutions changed from red to lemon-yellow, and the addition of methanol caused brown solids to precipitate, which were not soluble in common solvents. Since pure complexes could not be isolated, a spectroscopic study of the reactivity was made.

*Reactivity of $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$ (**1**) with dppe, dppp and dppb.* When the diphosphines were added to a solution of the dinuclear rhodium complex **1** (diphosphine/Rh = 2) in chloroform under CO atmosphere, a lemon-yellow solution was obtained in all cases. The $^{31}P\{^1H\}$ NMR spectra at room temperature show a doublet at δ 58.1 ($^1J_{Rh-P} = 133.1$ Hz) (diphosphine = dppe), and a doublet at δ 23.8 ($^1J_{Rh-P} = 126.7$ Hz) (PP-PP = dppp), (Table 1) which are attributed to the species $[Rh(dppe)_2]^+$, respectively, their NMR data are in agreement with previously reported compounds **5a** and **5b** (Fig. 2) [16,17]. These NMR results excluded the formation of dinuclear structures as **4**. The $^{31}P\{^1H\}$ NMR spectrum for dppb indicates the presence of a complex mixture, which has also been observed in other studies [16,17].

At −60°C, the $^{31}P\{^1H\}$ NMR spectrum of the solutions containing $[Rh(dppe)_2]^+$ remains unchanged. However, at this temperature, the spectrum of the solution containing dppp showed a doublet of doublet of triplets at δ 15.6 ($^1J_{Rh-P} = 85.1$ Hz, $^2J_{P-P} = 46$ Hz) and −12.0 ($^1J_{Rh-P} = 116.7$ Hz, $^2J_{P-P} = 46$ Hz) (Table 1). This pattern had previously been assigned to the $[Rh(CO)(dppp)_2]^+$ cation (**6**) (Fig. 2) [16,17].

*Reactivity of $[Rh_2(\mu\text{-}BCOS)(CO)_4]$ (**2**) with dppp.* Since the highest enantioselectivity in the hydroformylation, reaction of styrene [12–14] was obtained using the diphosphine BDPP (ee as high as 55%), we decided to



5a P-P= dppe
5b P-P= dppp

X= BF_4^-

6a P-P= dppp, X= BF_4^-
6b P-P= dppp, X= Cl^-

Fig. 2.

conduct the following study with the achiral, structurally related diphosphine dppp. As it has been described above for complex **1**, pure compounds were not isolated in the reaction of complex **2** with different diphosphines.

To study the effect of the excess of diphosphine dppp/Rh = 1/2, 1, 2, 4, 8 ratios were used in the reaction of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (**2**) with dppp.

2.1. NMR study

When dppp was added to a solution of the complex **2** in dichloromethane-d_2 (dppp/Rh = 1/2) the $^{31}P\{^1H\}$ NMR spectrum showed a complicated mixture of species. However, when a stoichiometric amount of dppp (dppp/Rh = 1) was added under CO atmosphere, the $^{31}P\{^1H\}$ NMR spectrum at room temperature in dichloromethane-d_2 shows a doublet at δ 8.0 ($^1J_{Rh-P} = 131.5$ Hz) and two doublets of doublets at δ 10.0 ($^1J_{Rh-P} = 109.3$, $^2J_{P-P} = 43$ Hz) and δ 22.0 ($^1J_{Rh-P} = 116.6$, $^2J_{P-P} = 43$ Hz) (Fig. 3a; Table 2). The doublet at δ 8.0 corresponds to the species $[Rh(dppp)_2]^+$ (**5b**) (Fig. 2; Scheme 1), which has previously been reported [16,17]. In our case, this cation (**5b**) could be included in a new ionic species such as $[Rh(dppp)_2]^+X^-$ (**7**). The two doublets of doublets could be attributed to dinuclear species containing dppp (**8**) (Scheme 1), where the two phosphorus atoms are non-equivalent due to the chirality of the BCOS dithiolate-bridge.

At low temperature (−60°C), the spectrum showed that the two doublets of doublets attributed to the dinuclear complex **8** were unchanged (Fig. 3b), while the doublet corresponding to the species $[Rh(dppp)_2]^+$ (**5b**) (δ 8.0 ppm) disappeared, and two new doublets of

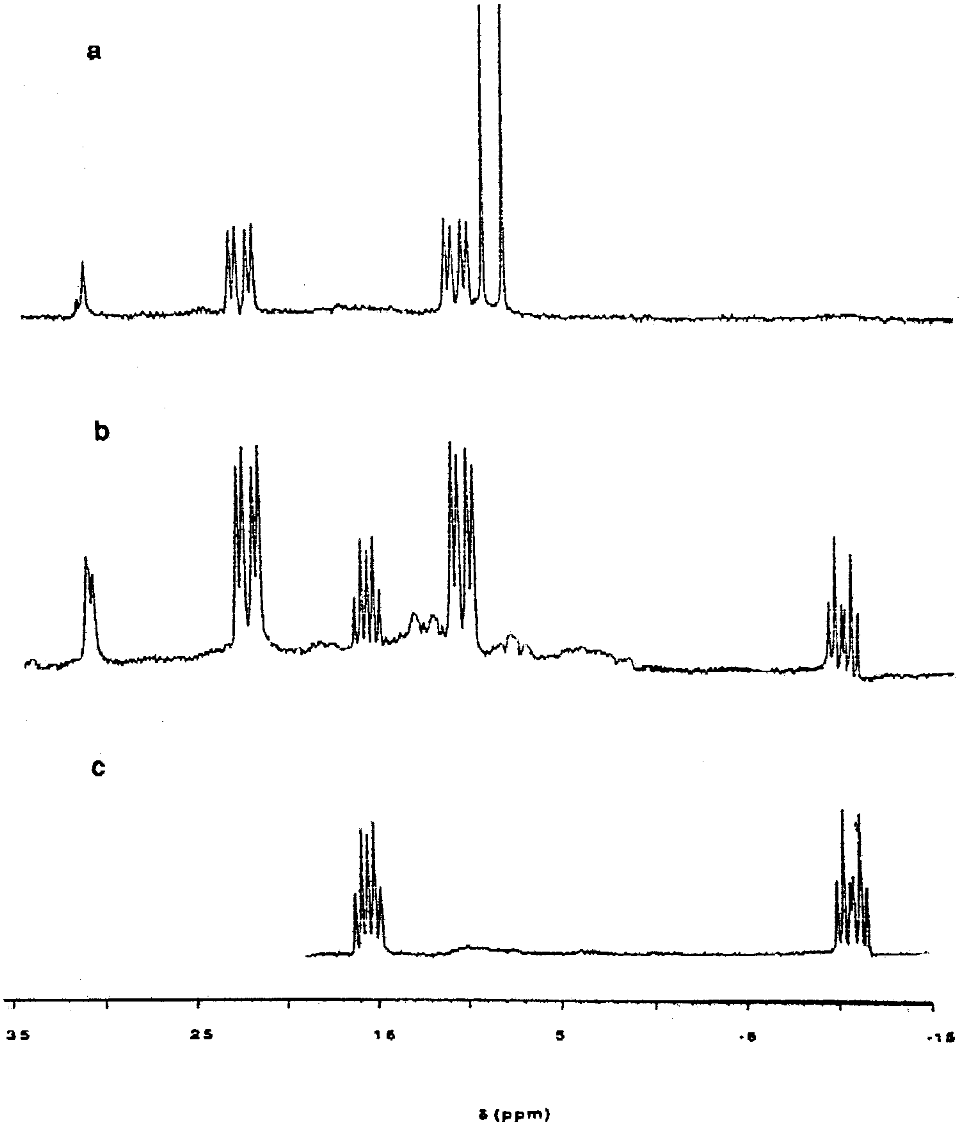


Fig. 3. $^{31}P\{^1H\}$ NMR spectra of the reaction of **2** with CO/dppp. (a) CO/2dppp, room temperature; (b) CO/2dppp, −60°C; (c) CO/4dppp, −60°C.

Table 2
$^{31}P\{^1H\}$ NMR data of the resulting solution of the reaction of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ with dppp[a]

dppp/Rh	T (°C)	δ[b]	$^1J_{Rh-P}$	$^2J_{P-P}$
2	25	8.0(d)	131.5	–
		10(dd)	109.3	43
		22(dd)	116.6	43
2	−60	10(dd)	109.3	43
		22(dd)	116.6	43
		−10.3(dt)	115	46
		15.6(dt)	87	46
4	25	8.0(d)	131.5	–
		−10.0(b)	–	–
		15.0(b)	–	–
4	−60	−10.3(dt)	115	46
		15.6(dt)	87	46

[a] Measured in ppm (upfield negative) from 85% H_3PO_4.

[b] Dichloromethane as a solvent. d = doublet, dd = doublet of doublets, dt = doublet of triplets, b = broad signal.

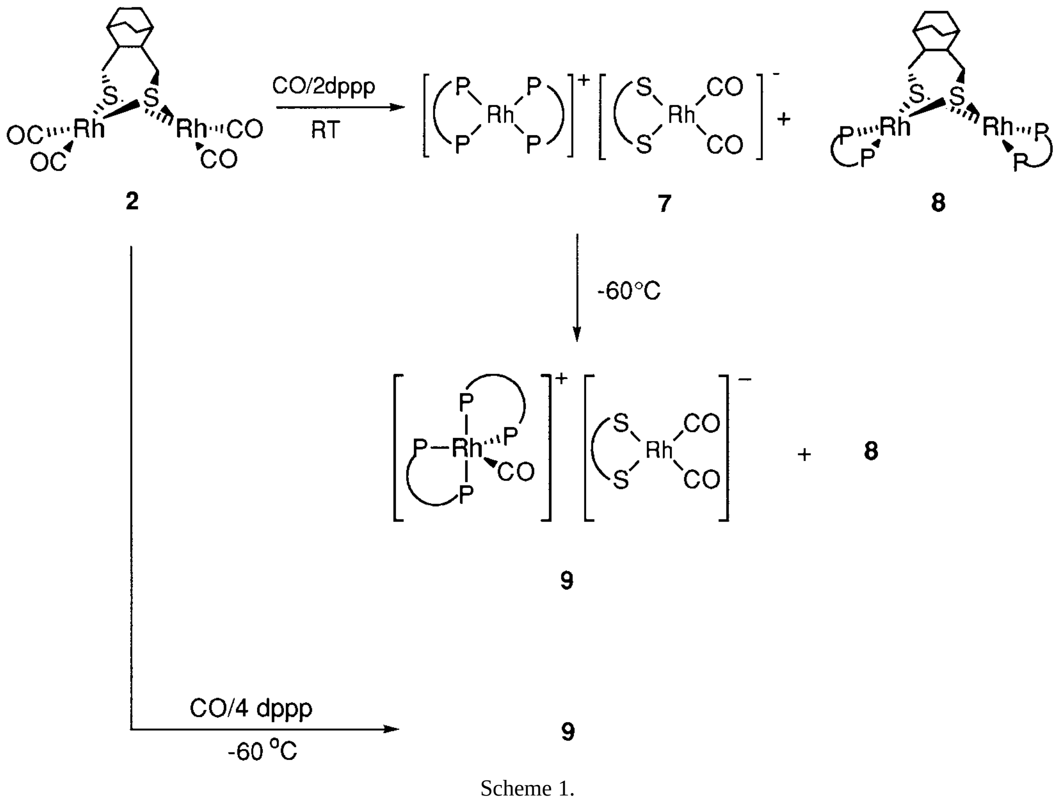
triplets at δ −10.3 ($^1J_{Rh-P} = 115$ Hz, $^2J_{P-P} = 46$ Hz) and 15.6 ($^1J_{Rh-P} = 87$ Hz, $^2J_{P-P} = 46$ Hz), corresponding to a A_2B_2X spin system, were observed (Fig. 3b; Table 2).

This last system is the only one observed at low temperature when dppp/Rh = 2 (4 mol of dppp per mol of **2**) (Fig. 3c), and it has been attributed to the pentacoordinate carbonyl diphosphine complex $[Rh(CO)(dppp)_2]^+Y^-$ (**9**) (Scheme 1). Although at room temperature, broad signals indicate fluxional behaviour, at −60°C, a sharper pattern is observed (Fig. 3c). Similar spectroscopic data have been found for $[Rh(CO)(dppp)_2]BF_4$ (**6a**) and $[Rh(CO)(dppp)_2]Cl$ (**6b**) (Fig. 2) [16,17], confirming the proposed structure for cation in complex **9**.

When the same reaction was carried out in the presence of **2** and a **4** and 8-fold excess of diphosphine per rhodium, similar results were obtained.

Thus, the presence of cationic species similar to compounds **5** and **6** is well evidenced, while the nature of the anion in these compounds remains to be determined. As only one species was formed when dppp/Rh = 2, this species was isolated. The microanalysis matches the stoichiometry $[Rh_2(BCOS)(dppp)_2(CO)_3]$ (**9**) (Scheme 1). The FAB spectrum shows a m/z ion of 927 that corresponds to the $[Rh(dppp)_2]^+$ cation. The FAB spectrum corresponding to the anion shows a fragment of m/z 331 which can be attributed to the loss of one CO molecule to give $[Rh(BCOS)(CO)]^-$. The conductivity data (for formula $[Rh_2(BCOS)(dppp)_2(CO)_3]$, $\Lambda = 234\ \Omega^{-1}\ cm^2\ mol^{-1}$ in acetone) indicated that the complex is a 1:1 electrolyte.

When the isolated complex was dissolved in dichloromethane-d_2, the $^{31}P\{^1H\}$ NMR spectrum showed two well resolved doublets of triplets at 18.5 ($^1J_{Rh-P} = 122$ Hz, $^2J_{P-P} = 30$ Hz) and −8.9 ppm ($^1J_{Rh-P} = 85$ Hz, $^2J_{P-P} = 30$ Hz) at room temperature. Even at low



Scheme 1.

Table 3
Selected FT-IR data of the resulting solution of the reaction of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ with dppp[a]

dppp/Rh	Atmosphere[b]	ν_{CO} (cm^{-1})
2	CO	1950, 1992, 2020
4	CO	1950, 1992, 2020
4	N_2	1716, 1992, 2020

[a] Dichloromethane as a solvent, 25°C.

[b] The different spectra were recorded under the specified atmosphere, bubbling the corresponding gas through the solution.

temperature (−60°C), the same pattern of signals was observed. However, when this solution was placed under CO atmosphere, the pattern of signals corresponding to the cation **9** was also observed, δ −10.3 ($^1J_{Rh-P}$ = 115 Hz, $^2J_{P-P}$ = 46 Hz) and 15.6 ($^1J_{Rh-P}$ = 87 Hz, $^2J_{P-P}$ = 46 Hz), being the only signals present after 1 h. A similar behaviour was reported by James and Mahajan [17] for the ionic complex $[Rh(CO)(dppp)_2]BF_4$ (**6a**) in a study at different temperatures.

2.2. IR study

IR experiments were carried out on the complexes in solution to find out whether other rhodium species were formed, and to try to characterize the nature of the anion in the complex **9**. The reaction of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (**2**) with 4 mol of dppp (dppp/Rh = 2) was monitored by FT-IR spectroscopy (Fig. 4).

The IR spectrum under CO atmosphere revealed three terminal carbonyl bands at 1950, 1992 and 2020 cm^{-1} (Fig. 4a; Table 3). The band at 1950 cm^{-1} can be attributed to the pentacoordinated diphosphine complex, since it has been reported that the compound $[Rh(CO)(dppp)_2]BF_4$ (**6a**) [17] presents a carbonyl band at 1930 cm^{-1}. The other bands at 1992 and 2020 cm^{-1} could be attributed to a *cis* dicarbonyl complex in a square planar environment as in the proposed $[Rh(BCOS)(CO)_2]^-$.

When the CO atmosphere in the solution is replaced by nitrogen, only the bands at 1990 and 2020 cm^{-1} appeared (Fig. 4b), indicating that the $[Rh(CO)(dppp)_2]^+$ (**6**) cation readily loses CO in solution to generate $[Rh(dppp)_2]^+$ (**5b**) [17], as evidenced by the absence of the CO band at 1950 cm^{-1}. After 1 h under nitrogen atmosphere, the band at 1950 cm^{-1} completely disappeared, and a strong bridge carbonyl band at 1716 cm^{-1} was observed together with the bands at 1992 and 2020

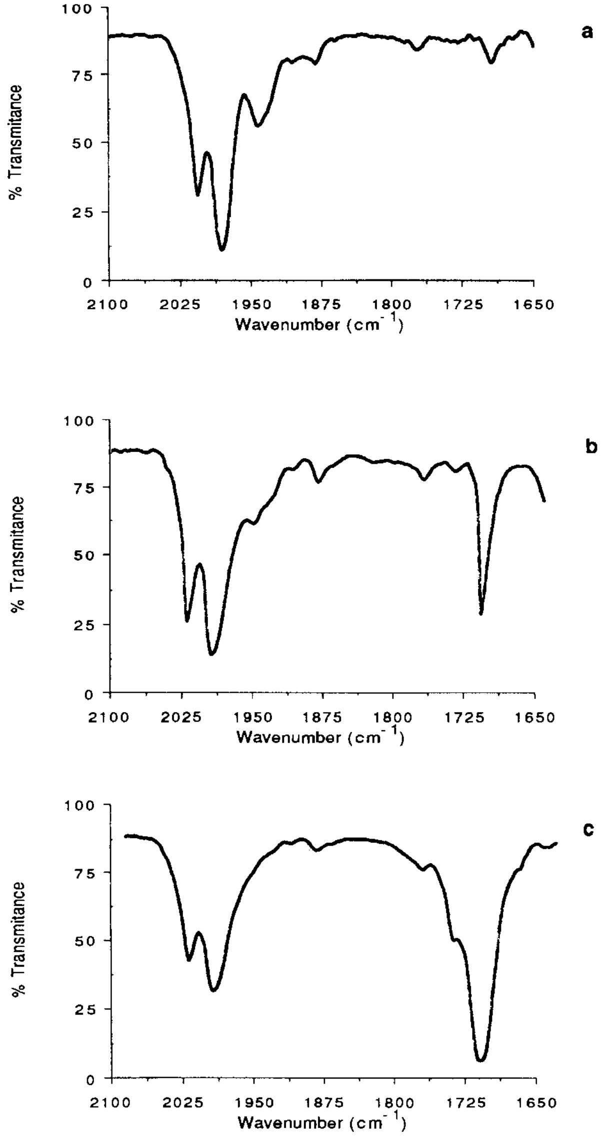


Fig. 4. Carbonyl region of FT-IR spectra of the reaction of **2** with CO/4dppp at room temperature. (a) atm. of CO; (b) atm. of N_2; (c) atm. of N_2 after 1 h.

Table 4
Selected spectroscopic data of the mixed CO/diphosphine rhodium complexes[a]

Complex	Formula	$^{31}P\{^1H\}$ NMR			FT-IR
		δ	$^1J_{Rh-P}$	J_{P-P}	ν_{CO} (cm^{-1})
7	$[Rh(dppp)_2][Rh(BCOS)(CO)_2]$	8.0	131.5	–	1992, 2020
8	$[Rh_2(\mu\text{-BCOS})(dppp)_2]$	10.0	109.3	43	–
		22.0	116.6	43	
9[b]	$[Rh(dppp)_2(CO)][Rh(BCOS)(CO)_2]$	−10.3	115	46	1950, 1992, 2020
		15.6	87	46	

[a] T = 25°C.

[b] T = −60°C. When complex **9** was isolated and dissolved in dichloromethane-d_2 at room temperature, two doublets of triplets at 18.5 ($^1J_{Rh-P}$ = 122 Hz, $^2J_{P-P}$ = 30 Hz) and −8.9 ppm ($^1J_{Rh-P}$ = 85 Hz, $^2J_{P-P}$ = 30 Hz) were observed (see Ref. [17]).

cm^{-1} (Fig. 4c). This result indicates that other CO-bridged species are formed.

The IR spectrum when 2 mol of dppp were added to a solution of **2** (dppp/Rh = 1) was similar to the spectra mentioned above carried out under nitrogen. This indirectly showed the absence of coordinated CO in the compound **8**.

The species present during the reaction of the complex **2** with the dppp are shown in Scheme 1, and their spectroscopic data are summarized in Table 4.

3. Conclusion

The reaction of the dinuclear dithiolate-bridged Rh(I) complexes with a stoichiometric amount of diphosphine yields a mixture of a dinuclear complex that maintains the dithiolate ligand bridging the two rhodium atoms $[Rh_2(\mu\text{-dithiolate})(dppp)_2]$, and the unexpected ionic complexes, $[Rh(CO)(diphosphine)_2]^+$ $[Rh(dithiolate)(CO)_2]^-$ (diphosphine = dppp) and $[Rh(diphosphine)_2]^+$ $[Rh(dithiolate)(CO)_2]^-$ (diphosphine = dppe, dppp). In the presence of an excess of diphosphine, the dithiolate bridge is broken, and only the ionic complexes incorporating the dithiolate in the anionic fragment are obtained. Further studies under hydroformylation conditions are in progress.

4. Experimental

4.1. General procedure

The dithiolate-bridged Rh(I) complexes $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$ [15] and $[Rh_2(\mu\text{-BCOS})(CO)_4)]$ [12] were synthesized as described in the literature. All rhodium complexes were prepared using standard Schlenk techniques under a nitrogen or CO atmosphere. Solvents were distilled and deoxygenated before use. The diphosphines, dppe, dppp and dppb, were of commercial origin and used without further purification.

Proton and ^{13}C NMR spectra were measured on a Varian 300 MHz spectrophotometer, and chemical shifts are quoted in ppm downfield with $SiMe_4$ as the internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on the same equipment, using 85% H_3PO_4 as the external reference.

Fast atom bombardment (FAB) mass spectrometry was performed on a VG autospect in a nitrobenzylalcohol matrix. Infrared spectra were recorded on a Nicolet 5ZDX FT-IR spectrophotometer. Microanalyses were carried out on a Carbo Erba microanalyzer.

4.2. NMR experiments

In a typical experiment, the diphosphine (diphosphine/Rh = 1, 2, 4 or 8) was added to a solution of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (**2**) (5 mg, 9.7 mmol) in dichloromethane-d_2 (1 ml) under CO atmosphere. The resulting solution was stirred for 15 min under CO atmosphere. After this, the solution was transferred to a NMR tube and the $^{31}P\{^1H\}$ NMR experiment was done.

4.3. IR experiments

In a typical experiment, the diphosphine (diphosphine/Rh = 1 or 2) was added to a solution of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (5 mg, 9.7 mmol) in dichloromethane (5 ml) under CO atmosphere. The resulting solution was stirred for 15 min under CO atmosphere, and a sample was taken ($\sim$ 0.5 ml) for the FT-IR experiment at room temperature. After that, the same solution was stirred for 15 min under N_2 atmosphere and a sample was taken ($\sim$ 0.5 ml) for the FT-IR experiment at room temperature.

4.3.1. *$[Rh(CO)(dppp)_2][Rh(BCOS)(CO)_2]$ (**9**)*

A stoichiometric amount of dppp (263.6 mg, 0.64 mmol) was added to a solution of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (82 mg, 0.16 mmol) in dichloromethane (5 ml) under CO atmosphere. The resulting solution was stirred for 15 min under N_2 atmosphere and reduced to 0.5 ml under vacuum. Adding 5 ml of diethyl ether caused the precipitation of a brown solid that was collected by filtration, washed with cold ether and dried in vacuo obtaining 158 mg (77% yield). Anal. Found: C, 60.88; H, 5.28; S, 5.01. Calcd. for $Rh_2C_{67}H_{68}O_3P_4S_2$: C, 61.19; H, 5.18; S, 4.87. NMR (CD_2Cl_2): $^{31}P\{^1H\}$ δ 8.0 (d, $^1J_{P-Rh}$ = Hz), (d, J_{P-Rh} = 131.5 Hz). FT-IR (CH_2Cl_2): ν_{CO} 1950 (s), 1992, 2020 cm^{-1}. FAB mass spectra: m/z 927 $[Rh(dppp)_2]^+$; m/z 515 $[Rh(dppp)]^+$; m/z 331 $[Rh(BCOS)(CO)]^-$. Electrolyte (1:1) in acetone (conductivity 234 Ω^{-1} cm^2 mol^{-1}).

Acknowledgements

This work was supported in part by the Commission of the European Communities (Contract No. CI1*-CT93-0329). Authors thank Dr. Mariano Laguna for FAB mass spectra and Prof. Piet van Leeuwen for helpful discussions. A.C.-P. thanks DGAPA-UNAM (México) for a grant.

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