Diphosphine and Dithiolate Rhodium Complexes: Characterization of the Species under Hydroformylation Conditions

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The solution structures of the dominant species present during the styrene hydroformylation using rhodium precursors [Rh(μ-OMe)(cod)]$_2$ (**1**) and the dithiolate-bridged complex [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ (**9**) in the presence of BDPP [(2S,4S)-bis(diphenylphosphine)pentane] have been determined. The high-pressure spectroscopic studies have revealed that the mononuclear complex [HRh(BDPP)(CO)$_2$] (**7**) is the predominant species during the hydroformylation process, but the dimeric species [Rh(BDPP)(CO)$_2$]$_2$ (**8**) is also present and in equilibrium with **7**. Equilibrium constants were measured by ^{31}P NMR spectroscopy (at [Rh] = 0.0138–0.0157 grat·L^{-1}, 5–50 bar of H$_2$, 5 bar of CO, 298–343 K, the molar ratio of **7:8** ranges from 1 to 20). Kinetic measurements have shown that the half-life of the species at ambient temperature is on the order of magnitude of 1 min. Variable-temperature ^{31}P and ^{1}H NMR spectra (293–193 K) revealed fluxional behavior in complex **7** where the bidentate diphosphine BDPP adopts equatorial–axial coordination to rhodium in the trigonal-bipyramidal complex [HRh(BDPP)(CO)$_2$] (bite angle ≈90°). A low free energy of activation ($\Delta G^{\ddagger}_{193K}$ = 44 kJ·mol^{-1} and $\Delta G^{\ddagger}_{293K}$ = 44 kJ·mol^{-1}) for phosphorus exchange has been measured for the fluxional process observed in complex **7**.

Introduction

Hydroformylation is one of the most extensively studied homogeneous catalytic processes.[1] Improvement of rates and selectivities as well as mechanistic aspects receive a great deal of attention.[2]

The asymmetric hydroformylation represents a potentially powerful synthetic tool for the synthesis of a large number of pharmacologically important compounds and different chiral building blocks.[3,4] Recently, hydroformylation catalyst precursors based on [Rh-

(acac)(CO)$_2$] modified with chiral phosphine–phosphite[5] or diphosphites[6] and [Rh(cod)(diphosphinites)][7] have provided ee's between 50% and 96% in the hydroformylation of styrene and other olefins, as well as excellent chemo- and regioselectivity in some cases.

The solution structures of selective rhodium catalysts modified with phosphorus ligands have been reported,[8,9] and selectivity has recently been shown to depend on the structure of the modified diphosphines and diphosphites.[9,10] It was shown that bidentate phosphorus ligands form trigonal-bipyramidal hydridorhodium com-

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(1) See for reviews: (a) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (b) Tolman, C. A.; Faller, York and London, 1983; Chapter 2, pp 88–89. (c) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17. (d) Frohhning, C. D.; Kohlpaintner, Ch. W. In *Applied Homogeneous Catalysis with Organometallic Compounds;* Cornils, B., Herrmann, W. A., Eds.; Springer-Verlag: New York, 1996; p 29–90.
(2) (a) Van Leeuwen, P. W. N. M In *Surface Science and Catalysis*; Moulijn, J. A., Ed.; Vol. 79. (b) Van Leeuwen, P. W. N. M.; Van Santen, R. A. Elsevier: Amsterdam, 1993; Chapter 6.2 and references therein. (c) Horiuchi, T.; Shirekawa, E.; Nozaki, K.; Takaya, H. *Organometallics* **1997**, *16*, 2981.
(3) Gladiali, S.; Bayón, J. C.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1453.
(4) Agbossou, F.; Carpentier J. F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485.

(5) (a) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033. (b) Horiuchi, T.; Ohta, T.; Shirakawa, E.; Nozaki, K.; Takaya, H.; *J. Org. Chem.* **1997**, *62*, 4285 and references therein.
(6) (a) Buisman, G. J. H.; Vos, E. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans* **1995**, 409. (b) Babin, J. E.; Whiteker, G. T. WO 93/03839, US 911.518, 1992. (c) Buisman, J. H.; Van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929. (d) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L. *J. Organomet. Chem.* **1995**, *494*, C15.
(7) RajanBabu, T. V.; Ayers, T. A. *Tetrahedron Lett.* **1994**, *35*, 4295.
(8) Brown, J. M.; Kent, A. *J. Chem. Soc., Perkins Trans. 1* **1987**, 1597.
(9) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A., Jr.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.
(10) (a) van Leeuwen, P. W. N. M.; Buisman, G. J. H.; van Rooy, A.; Kamer, P. C. J. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 61. (b) Buisman, G. J. H.; van Leeuwen, P. W. N. M.; Kamer, P. C. J. *Organometallics*, in press.

plexes, the putative catalysts in the hydroformylation reaction, determining the stereoselectivity of the reaction.[3,4]

Several studies related to asymmetric hydroformylation of olefins using dithiolate-bridged rhodium(I) complexes have been reported.[11] Chiral dithiolate-bridged rhodium(I) complexes have been used in combination with diphosphines such as dppp, DIOP, and BDPP in styrene hydroformylation. The system $[Rh_2(\mu\text{-BCOS})(cod)_2]_2$/BDPP provided the best results, giving ee's up to 55% and regioselectivity of 96% in 2-phenylpropanal.[11d]

Through this study using dithiolate-bridged rhodium precursors in combination with diphosphines, it has been found that, interestingly, catalytic precursors based on available rhodium systems such as $[Rh(\mu\text{-OMe})(cod)]_2$ or $[Rh(acac)(CO)_2]$ using the structurally simple diphosphine BDPP provided a regioselectivity in 2-phenylpropanal of 95% with an ee up to 60%. The ee obtained depends heavily on the excess of diphosphine, the appropiate P/Rh ratio being 4 in this case.[12]

In this context, important questions are what the active species is in the catalytic system $[Rh(\mu\text{-OMe})(cod)]_2$/BDPP and what the role of the chiral dithiolate ligand is in the above-mentioned dithiolate−diphosphine systems. Furthermore, the participation of the dithiolate-bridged rhodium complexes in the catalytic cycle remains a matter of controversy.

Recently, we have studied[13] the reactivity of tetracarbonylrhodium complexes $[Rh_2(\mu\text{-dithiolate})(CO)_4]$ (dithiolate = $-S(CH_2)_4S-$, BCOS) with achiral diphosphines such as dppe and dppp. In this work, we propose that the reaction of dinuclear dithiolate-bridged Rh(I) complexes with a stoichiometric amount of diphosphine yields a mixture of a dinuclear complex which maintains the dithiolate ligand bridging the two rhodium atoms, $[Rh_2(\mu\text{-BCOS})(dppp)_2]$, and the unexpected ionic complexes $[Rh(dppp)_2]^+[Rh(dithiolate)(CO)_2]^-$ and $[Rh(CO)(dppp)_2]^+[Rh(dithiolate)(CO)_2]^-$. In the presence of an excess of diphosphine, only the ionic complexes incorporating the dithiolate in the anionic fragment are observed. Since, a H_2/CO pressure is present during the hydroformylation process, a further study should be made under hydroformylation conditions.

Characterization of reaction intermediates during the rhodium-catalyzed hydroformylation has only been scarcely performed. This is probably due to the difficulties that arise when an autoclave spectroscopy system has to be developed that enables the study of the real working catalyst. Today, high-pressure NMR (HP-NMR)[14] and high-pressure IR (HPIR)[15] are regularly applied techniques to identify organometallic compounds under high pressure.

In the present paper, we report the results of the study, by means HPNMR and HPIR spectroscopy, of the
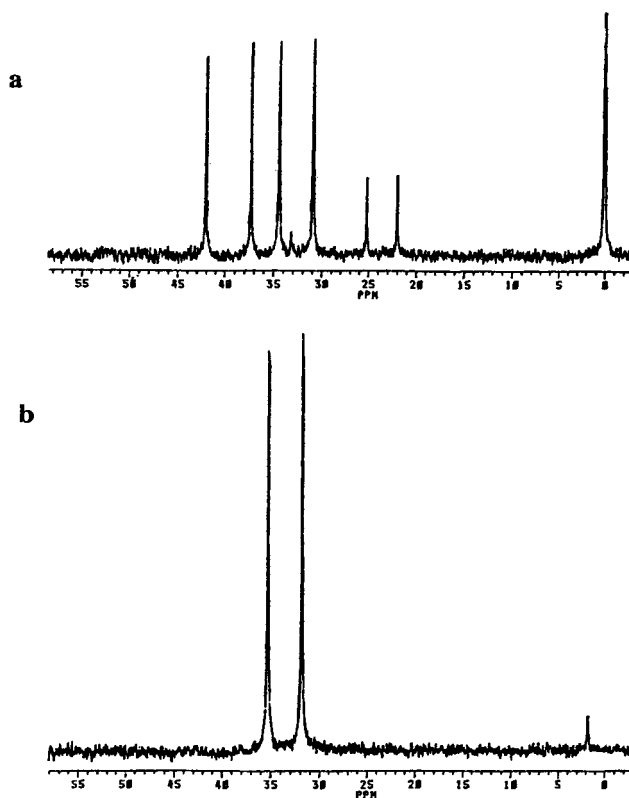
(11) (a) Aaliti, A.; Masdeu, A. M.; Riuz, A.; Claver, C. *J. Organomet. Chem.* **1995**, *489*, 101. (b) Masdeu, A. M.; Orejón, A.; Ruiz, A.; Castillón, S.; Claver, C. *J. Mol. Catal.* **1994**, *94*, 149. (c) Masdeu-Bultó, A. M.; Orejón, A.; Castillón, S.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1885. (d) Castellanos-Páez, A.; Castillón, S.; Claver, C. *J. Organomet. Chem.* **1997**, *539*, 1.
(12) Masdeu-Bultó, A. M.; Orejón, A.; Castellanos, A.; Castillón, S.; Claver, C. *Tetrahedron: Asymmetry* **1996**, *7*, 1829.
(13) Castellanos-Páez, A.; Thayaparan, J.; Castillón, S.; Claver, C. *J. Organomet. Chem.*, in press.
(14) See for example: (a) Elsevier, C. J. *J. Mol. Catal.* **1994**, *92*, 285. (b) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (c) Horvath, I. *Organometallics* **1986**, *5*, 2333. (d) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1597.

Figure 1. $^{31}P\{^1H\}$ NMR spectra for the reaction of complex **1** with (a) BDPP, (b) BDPP under 10 bar of H_2.

species present for the precursor system $[Rh(\mu\text{-OMe})(cod)]_2$/BDPP under hydroformylation conditions. In the same way, to obtain information about the role of the chiral dithiolate bridge, we have studied the system $[Rh_2(\mu\text{-BCOS})(cod)_2]_2$/BDPP.

Results and Discussion

Solution Structure of the Species Formed during the Reaction of $[Rh(\mu\text{-OMe})(cod)]_2$ with (−)-BDPP under Hydroformylation Conditions. Initially, we studied the reactivity of the complex $[Rh(\mu\text{-OMe})(cod)]_2$ (**1**) with (−)-BDPP (toluene-d_8) under hydroformylation conditions. To know the intermediate species formed during the hydroformylation process, we did a spectroscopic study of the solutions resulting from the successive addition of (a) an excess of BDPP (BDPP/Rh = 2) to a solution of $[Rh(\mu\text{-OMe})(cod)]_2$ in toluene-d_8 at room temperature under nitrogen atmosphere, (b) 10 bar of H_2, and (c) 10 bar of CO (20 bar of H_2/CO).

The $^{31}P\{^1H\}$ NMR spectrum of solution a (Figure 1a), shows three doublets at δ 39.7 ($^1J_{Rh-P}$ = 192 Hz), 32.8 ($^1J_{Rh-P}$ = 141 Hz), and 23.7 ($^1J_{Rh-P}$ = 130 Hz) in a ratio of 20:16:1 (Table 1). The resonance of the free diphosphine is at δ 0 ppm. The ^1H NMR spectrum shows a broad signal in the hydride region (δ − 12 ppm).

The doublet at 39.7 ppm ($^1J_{Rh-P}$ = 192 Hz) must be attributed to the dinuclear rhodium complex **2** that maintains the methoxy bridge and contains one diphos-

(15) (a) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835. (b) Rigby, W.; Whyman, R. W.; Wilding, K. J. *Phys. Sci. E, Instrum.* **1970**, *3*, 572. (c) Tinker, H. B.; Morris, D. E. *Rev. Sci. Instrum.* **1972**, *7*, 1024. (d) Walker, W. E.; Cosby, L. A.; Martin, S. T. U.S. Patent 3 886 364, 1975 (to Union Carbide Corp).

Table 1. $^{31}P\{^1H\}$ and ^1H NMR Data of the Species Formed in the Reaction of [Rh(μ-OMe)(cod)]$_2$ /4BDPP with H$_2$/CO^a

complex	$^{31}P\{^1H\}$		^1H			P(bar)	
	δ	$^1J_{\text{Rh-P}}$ (Hz)	δ^b	$^1J_{\text{H-Rh}}$	$^2J_{\text{H-P}}$	H$_2$	CO
2	39.7	192					
3	23.7	130					
4	32.8	141	-12^c	8	16	10	
5^{d,e}	56.6, 37.6	157, 138					
7	29.8	112	-8.8	11	57	10	10
8	24.4	145.7^f				10	10

^{a} Room temperature. ^{b} Hydride region. ^{c} Broad signal. ^{d} Simulated spectrum based on an AB$_2$X system. ^{e} $^2J_{\text{P-P}} = 100$ Hz. ^{f} Obtained from the simulated spectrum. Additional J values measured were $^2J_{\text{P,P}} = 45.7$ Hz, $^3J_{\text{P,P''}} = 5$ Hz, $^2J_{\text{P',Rh}} = 8$ Hz.

Scheme 1

P-P= BDPP
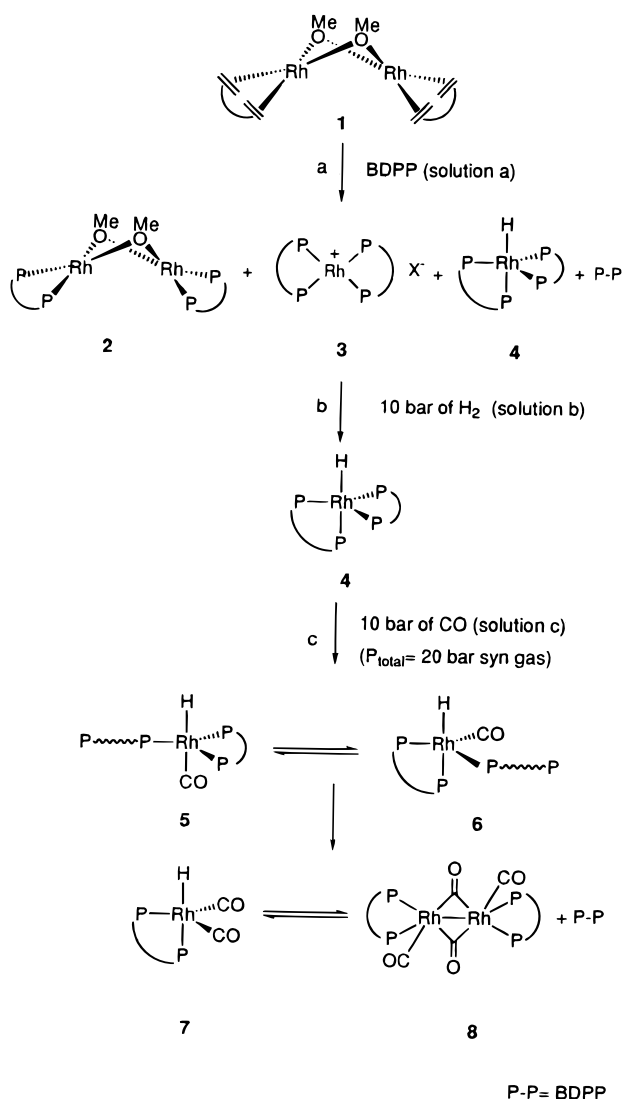
phine coordinated to each rhodium (Scheme 1). Similar compounds have been previously reported, [Rh(μ-Cl)-(dppp)]$_2$ and [Rh(μ-Cl)(diop)]$_2$, which show very similar rhodium–phosphorus coupling constants ($^1J_{\text{Rh-P}} = 184$ and 191 Hz respectively).[16] The doublet at 23.7 ppm ($^1J_{\text{Rh-P}} = 130$ Hz) is attributed to a square-planar rhodium complex **3** with two BDPPs coordinating to the metal (Scheme 1). The cation [Rh(dppp)$_2$]$^+$ ($^1J_{\text{Rh-P}} =$

132 Hz),[13] where the anion is Cl$^-$ or BF$_4^-$, has been previously reported by Sanger[17] and James.[18]

Concerning the doublet at 32.7 ppm ($^1J_{\text{Rh-P}} = 141$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum, this is the only signal that remains after the solution was pressurized with 10 bar of H$_2$ at 60 °C for 1 h (solution b; Figure 1b, Table 1). This signal could be attributed to the mononuclear rhodium complex **4** (Scheme 1), in view of the coincidence of the spectroscopic data with the previously reported compounds [HRh(L−L)$_2$], where L−L = dppe ($^1J_{\text{Rh-P}} = 142.5$ Hz), dppp ($^1J_{\text{Rh-P}} = 141.8$ Hz), and diop ($^1J_{\text{Rh-P}} = 146$ Hz).[18]

At −60 °C, the ^1H NMR spectrum shows a broad quintet of doublets at −12 ppm ($^1J_{\text{Rh-H}} = 8$ Hz, $^2J_{\text{P-H}} = 16$ Hz). This pattern is due to the coupling of the hydride with four equivalent phosphorus atoms (cf. [HRh(dppp)$_2$], $^1J_{\text{Rh-H}} = 8$ Hz and $^2J_{\text{P-H}} = 20.8$ Hz).[18]

This compound could have a tbp geometry containing a hydride in an axial position or a tetrahedral geometry with a hydride coordinated to one face.[19] The presence of only one doublet in the $^{31}P\{^1H\}$ NMR spectrum with a coupling constant $^1J_{\text{Rh-P}}$ of 141 Hz (an average between Rh−P$_{\text{ax}}$ and Rh−P$_{\text{eq}}$)[18,20] led Meakin to suggest a fluxional behavior in the tetrahedral structure involving a movement of the hydride over the edges of a tetrahedron.[19]

In the first step (solution a), the hydride formation is ascribed to decomposition of the methoxy group (μ-OMe) of [Rh(μ-OMe)(cod)]$_2$ to hydride and formaldehyde.[21] The $^{31}P\{^1H\}$ NMR spectrum of **4** was unchanged after 72 h under these conditions.

Subsequently, 10 bar of CO was added to the solution ($P_{\text{total}} = 20$ bar H$_2$/CO) at room temperature (solution c). After a few minutes at 60 °C, the solution changed from orange to yellow and the $^{31}P\{^1H\}$ NMR spectrum showed a set of signals centered at 37.6 and 56.6 ppm, which will be discussed below, and a single doublet at 32.7 ppm assigned to complex **4**. After that, the signal at 32.7 decreased until it had completely disappeared while a new doublet appeared at 29.8 ppm (Figure 2a).

After 2 h, two doublets were observed in the $^{31}P\{^1H\}$ NMR spectrum, the doublet at 29.8 ppm ($^1J_{\text{Rh-P}} = 112$ Hz) and a new one at 24.4 ppm ($^1J_{\text{Rh-P}} = 154$ Hz) (Figure 2b). The ^1H NMR spectrum of this solution revealed a double triplet in the hydride region ($\delta = -8.8$ ppm, $^1J_{\text{H-Rh}} = 11$, $^2J_{\text{H-P}} = 57$ Hz) (Table 1), indicative of the coupling of a hydride with the rhodium and with two degenerate phosphorus nuclei (see Figure 5).

Small cis phosphorus−hydride coupling constants (between 1 and 16 Hz) are reported in HRh(L−L)(CO)$_2$ complexes with bis-equatorially coordinating diphosphine[9,14c] ligands. In contrast, relatively large phosphorus−hydride coupling constants[19,22] are found for fluxional complexes containing trans P−Rh−H configurations. The trans relationship is responsible for

(16) Slack, D. A.; Greveling, I.; Baird, M. *Inorg. Chem.* **1979**, *18*, 3125.

(17) Sanger, A. *J. Chem. Soc., Dalton Trans.* **1977**, 120.
(18) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180.
(19) Meakin, P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 5271.
(20) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660.
(21) (a) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. *J. Organomet. Chem.* **1986**, *316*, 343. (b) Fernández, M. J.; Esteruelas, M. A.; Jiménez, M. S.; Oro, L. *Organometallics* **1986**, *5*, 1519.
(22) Hyde, E. M.; Swain, J. R.; Verkade, J. G.; Meakin, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1169.

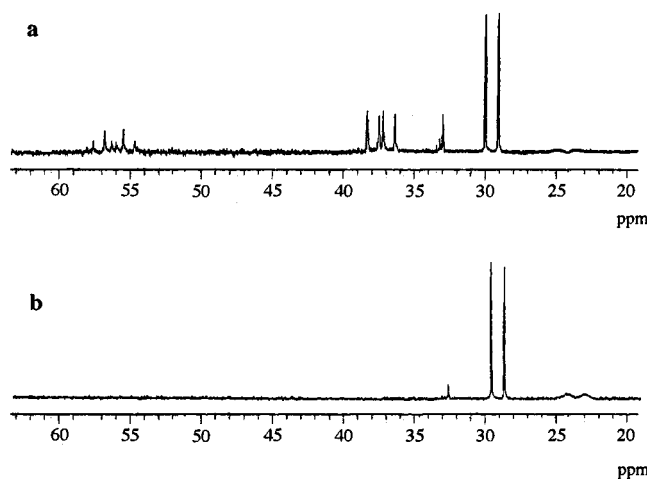**Figure 2.** $^{31}P\{^1H\}$ NMR spectra for the reaction of complex **1** with (a) BDPP under 10 bar of H_2 and 10 bar of CO at 60 °C after 5 min, (b) BDPP under 10 bar of H_2 and 10 bar of CO at 60 °C after 2 h.

the large phosphorus−hydride coupling constant (90−120 Hz) observed for those complexes in the slow exchange limit.[6a,9,14c] In the present case, the intermediate phosphorus−hydride coupling constant ($^2J_{H-P} =$ 57 Hz) observed suggests a time-averaged cis, trans relationship between the phosphorus and hydride nuclei. A fast equatorial−axial exchange of the phosphorus atoms results in an averaged coupling constant ($|J_{Rh-P}| = 112$ Hz). It was impossible to observe the distinct P_{ax}−H and P_{eq}−H coupling constants, not even when the slow exchange limit was reached at −80 °C.

From these results the doublet at 29.8 ppm is assigned to the mononuclear rhodium complex **7** (Scheme 1) in which one diphosphine has been displaced by two CO moieties from **4**. Complex **7** has a tbp geometry in which BDPP is equatorially−axially coordinated to the rhodium center.

The amplified spectrum of the signal at 24.4 ppm (Figure 3a, Table 1) exhibits a complex pattern consistent with an AA′A″A‴XX′ spin system. This type of signal has been previously assigned to carbonyl diphosphine dimers [Rh(CO)$_2$(diphosphine)]$_2$ (diphosphine = dppe, dppp, diop)[23] and [Rh$_2$(CO)$_{8-x}$L$_x$] ($x = 0-2$, L = phosphite)[24] which have a Rh−Rh bond and two CO groups bridging the metal atoms. The existence of only one doublet evidences that the four phosphorus atoms are chemically equivalent on the NMR time scale at ambient temperature in a structure such as **8** (Scheme 1). The AA′A″A‴XX′ spin system has been simulated (Figure 3b), obtaining the following coupling constants $^2J_{P-P} = 46$ Hz, $^4J_{P-P} = 5$ Hz, $^1J_{P-Rh} = 145.7$ Hz, and $^3J_{P-Rh} = 8$ Hz (Table 1). At −80 °C, the dimer shows a pair of doublets, each with a minor amount of fine splitting.

At room temperature, carbonyl site exchange between terminal and bridging positions will cause the pairs of phosphorus atoms to become chemically equivalent, and this notion is corroborated by the ^{13}C NMR spectrum that shows a single broad resonance at 221 ppm for the
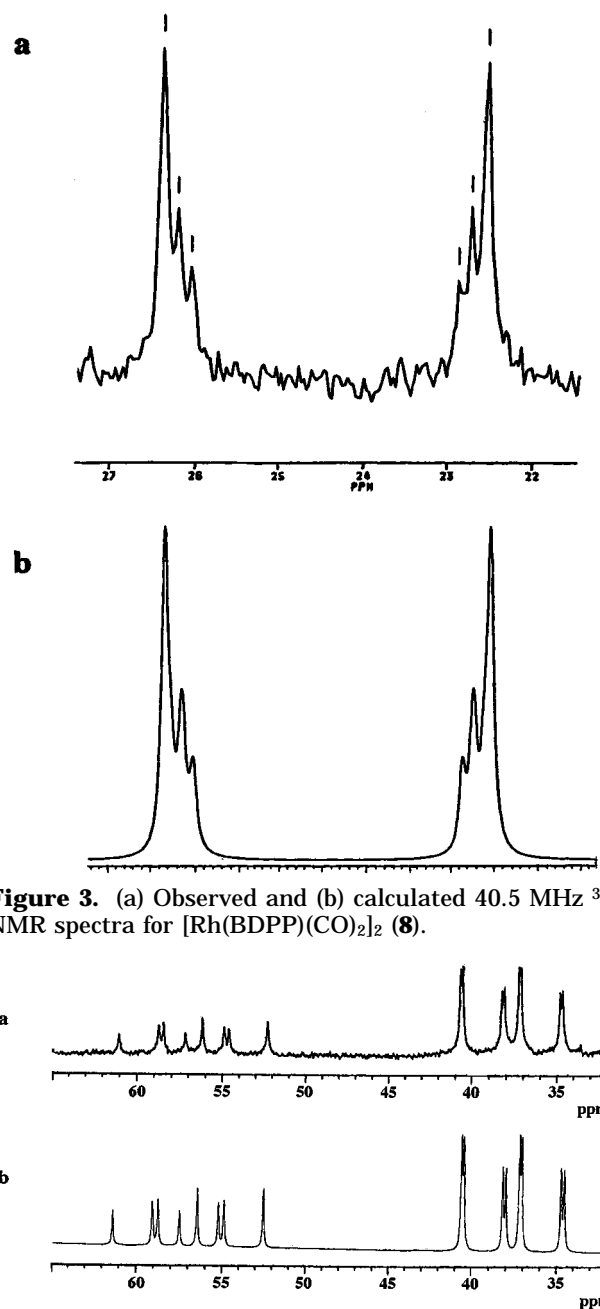
(23) James, B. R.; Mahajan, D.; Rettig, S. J.; Williams, G. M. *Organometallics* **1983**, *2*, 1452.
(24) Brown, D. T.; Eguchi, T.; Heaton, B. T.; Iggo, J. A.; Whyman, R. *J. Chem. Soc., Dalton Trans.* **1981**, 677.

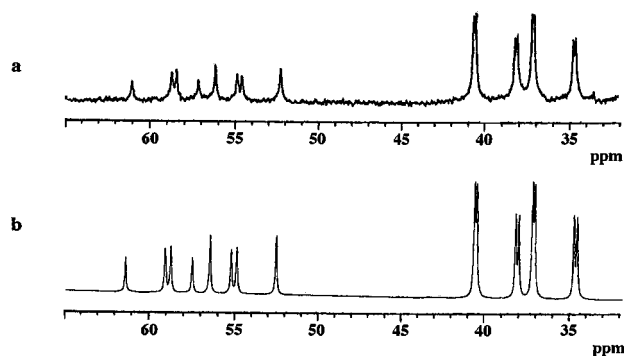**Figure 3.** (a) Observed and (b) calculated 40.5 MHz ^{31}P NMR spectra for [Rh(BDPP)(CO)$_2$]$_2$ (**8**).

Figure 4. (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectra of complex **5** (or **6**).

carbonyl ligands, indicating that the four carbon monoxide ligands are equivalent. At −80 °C, two broad signals are observed at 245 and 195 ppm.

To obtain information about the possible equilibrium between **7** and **8**, the solution containing these complexes was pressurized to 50 bar of H_2. A new multiplet between 37 and 56 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum after 2 h at 80 °C (Figure 4a), together with the doublets corresponding to **7** and **8**. This pattern of signals was previously observed when 10 bar of CO was added to the solution containing **4** (see Figure 2a; Scheme 1, solution c). This spectrum has a 16-line multiplet component that originates from a four-spin ($^1/_2$) system which could be simulated by using an AB$_2$X (i.e., P_A2P_BRh) model (Figure 4b).

Hughes et al.[25] have described complexes exhibiting similar patterns in the $^{31}P\{^1H\}$ NMR spectroscopy, such

Table 2. FT-IR Selected Data of the Species Formed in the Reaction of [Rh(μ-OMe)(cod)]$_2$ with BDPP + H$_2$/CO[a]

		ν_{CO} (cm^{-1})	
run	t (min)	terminal	bridge
1	1	1988, 1965, 1944	1765, 1744, 1718
2	30	1965	1765, 1744, 1718
3	30[b]	1988, 1944	

[a] After the HPNMR study at room conditions. [b] Spectrum resulting from the subtraction of spectrum 2 from spectrum 1.

as [HRhCO(L−L)(PR)], [HRhCO(L−L)$_{1.5}$]$_2$, [HRhCO(L−L)(L−L)$_m$] where R = Ph$_3$ and EtPh$_2$, m = monodentate, and L−L = diphosphine. These types of complexes have an approximate tbp geometry and contain three phosphine ligands coordinated to the metal.

Since the system has rhodium−phosphorus coupling constants of 157 and 138 Hz and a phosphorus−phosphorus coupling constant of 100 Hz, we conclude that the phosphorus atoms are in equatorial positions (**5**). An AB$_2$X multiplet, however, could also arise from a fluxional structure (**6**) in which P$_B$ and P$_C$ rapidly equilibrate.[25]

In the hydride region, the ^{1}H NMR spectrum shows the doublet triplet corresponding to **7** at −8.8 ppm ($^1J_{H-Rh}$ = 11, $^2J_{H-P}$ = 57 Hz) and a broad quadruplet at −10.2 ppm corresponding to the new species **5**. The coupling constant ($^2J_{H-P}$ = 16 Hz) of this new species indicates that the hydride is coupled with three equivalent phosphorus atoms in equatorial positions. The expected small H−Rh coupling constant could not be resolved.

In summary, the multiplet observed between 37 and 56 ppm is attributed to the complex [HRh(CO)(BDPP)(BDPP)$_m$] (where m signifies that the diphosphine is coordinated as a monodentate ligand) with structure **5** or a fluxional structure **6**. Consequently, complex **7** should be formed from a ligand exchange of CO with **4** via the intermediate species **5** (Scheme 1).

The FT-IR spectrum of the final solution under atmospheric conditions (after depressurized) shows several strong absorptions in the terminal carbonyl (1988, 1965, and 1944 cm^{-1}) and bridging carbonyl (1744, 1727, and 1718 cm^{-1}) regions (Table 2). After 30 min at these conditions, the solution changed from yellow to orange and the FT-IR spectrum only showed the 1965, 1744, and 1718 cm^{-1} carbonyl absorptions assigned to carbonyl dimeric species **8**. The subtraction of the second spectrum from the first showed only the terminal CO absorptions at 1988 and 1944 cm^{-1} assigned to mononuclear complex **7** (Table 3).

Solution Structure of the Species Formed during the Reaction of [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ with (−)-BDPP under Hydroformylation Conditions. It has been reported that dithiolate-bridged rhodium complexes are precursors in the olefin hydroformylation reaction.[11] Since studies providing information about the actual involvement of the dithiolates in the catalytic reaction have not been carried out, we considered it of interest to study a dithiolate−diphosphine system under hydroformylation conditions.

We tried to identify the species formed in the case of the dithiolate-bridged rhodium complex [Rh$_2$(μ-BCOS)-

Table 3. ^{31}P{^{1}H} and ^{13}C NMR Data of the Species Formed for the Reaction of [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ (9) with BDPP and H$_2$/^{13}CO

		^{13}C			^{31}P{^{1}H}		
complex	T	δ	$^1J_{C-Rh}$	$^2J_{C-P}$	δ	$^1J_{Rh-P}$	$^2J_{P-C}$
7	20	199[a]	69	8.5	30.1	112	9
	−80	199[b]					
8	20	221[b]			24.4	145.7[b]	
	−80	245, 195[b]				181, 188[c]	
10[d]	20	202	28		26.1	123	
	−80	202	34		26.1	123	

[a] Doublet triplet. [b] Obtained from the simulated spectrum. [c] $^1J_{Rh-P_{ax}}$ and $^1J_{Rh-P_{rad}}$.

(cod)$_2$]$_2$ (**9**) using the same procedure followed for [Rh-(μ-OMe)(cod)]$_2$/BDPP. We carried out a spectroscopic study of the solutions obtained by sucessive addition of (d) 4 bar of ^{13}CO to a suspension of [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ and an excess of BDPP (BDPP/Rh = 2) in toluene-d_8, (e) 4 bar of H$_2$ (total pressure = 8 bar of H$_2$/^{13}CO).

Since the mixture of [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ and BDPP forms a yellow suspension in toluene-d_8, we decided to synthesize the tetracarbonyl complex [Rh$_2$(μ-BCOS)-(CO)$_4$], which is very soluble in common solvents.[11d] Thus, after the addition of 4 bar of ^{13}CO, the suspension gradually changed from yellow to orange until complete dissolution was obtained at 60 °C (solution d). The ^{31}P-{^{1}H} NMR spectrum showed only a doublet at 26.0 ppm ($^1J_{Rh-P}$ = 122 Hz) and the signal of free BDPP at 0 ppm. Since the BDPP$_{free}$/BDPP$_{coord}$ ratio was 3, we concluded that only one diphosphine is coordinated to two rhodium atoms.

The HPIR of a similar solution of 10 bar of CO showed two absorptions in the terminal carbonyl region (1991-(s) and 1952(s) cm^{-1}), which could be attributed to a cis relationship in a dinuclear complex of the type [Rh$_2$(μ-BCOS)(μ-BDPP)(CO)$_2$] (**10**). The doublet observed at 26.0 ppm in the ^{31}P (^{1}H) NMR spectrum corresponds to two phosphorus atoms in equivalent environments, although a more complicated signal could be expected in the proposed species due to the chirality of the BCOS dithiolate bridge. In the ^{13}C NMR spectrum, a signal corresponding to the coordinated carbon monoxide with $^1J_{C-Rh}$ = 28 Hz is observed. A $^2J_{P-C}$ coupling constant, which should be expected for this signal, is not observed.
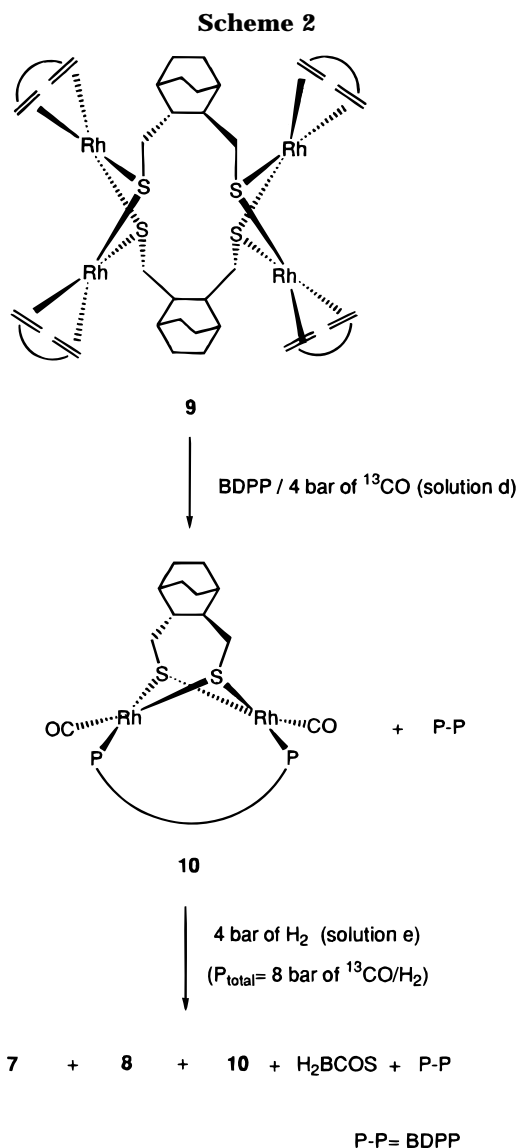
Kalck et al. have reported the X-ray structure of a related bis(thiolate) diphosphine-bridged rhodium complex [Rh$_2$(μ-t-BuS)$_2${(μ-Ph$_2$PCH$_2$)$_2$Zr(η-C$_5$H$_5$)$_2$}(CO)$_2$][26] and the preparation of [Rh$_2$(μ-t-BuS)$_2${(μ-diphospine)$_2$}-(CO)$_2$], diphosphine = dppp, dppb.[27] Only in the case of [Rh$_2$(μ-t-BuS)$_2${(μ-Ph$_2$PCH$_2$)$_2$Zr(η-C$_5$H$_5$)$_2$}(CO)$_2$] was a $^2J_{P-C}$ = 12 Hz observed.

Although species **10** is proposed as a dinuclear *cis*-dicarbonyl species containing a bridging BDPP, according to previous reactivity studies,[13,26,27] the difference of the infrared carbonyl frequencies ($\Delta\nu$ = 30 cm^{-1}) indicates that a *cis*-dicarbonyl structure where both COs were coordinated to the same rhodium center cannot be excluded. The ^{13}C NMR spectrum recorded in order to have more information about this species does not allow one to obtain the required data to complete the

(25) Hughes, O. R.; Young, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6636.

(26) Choukroun, R.; Gervais D.; Jaud, J.; Kalck, Ph.; Senocq, F. *Organometallics* **1986**, *5*, 67.

(27) Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, Ph.; Choukroun, R.; Gervais, D. *J. Mol. Catal.* **1986**, 35, 213.

Scheme 2

9

BDPP / 4 bar of ^{13}CO (solution d)

10

4 bar of H$_2$ (solution e)

(P$_{total}$= 8 bar of ^{13}CO/H$_2$)

7   +   **8**   +   **10** + H$_2$BCOS + P-P

P-P= BDPP

characterization of the species. Attempts to isolate this species adding a stoichiometric amount of diphosphine (BDPP/Rh = 1/2) after bubbling CO to a solution of the complex **9** were unsuccessful as insoluble polymeric products were obtained upon precipitation.

According to the previously reported styrene hydroformylation data,[12] it is important to note that a BDPP/Rh ratio (at the concentrations used) of 2 is required to obtain an optimal ee of 55% when the [Rh(μ-OMe)-(COD)]$_2$ complex is used as the precursor while the tetranuclear rhodium BCOS precursor (**9**) provides the same ee at a BDPP/Rh ratio of 1.[11c,12] In the dithiolate system, rhodium occurs in part as a rhodium dithiolate, which explains why the optimal enantioselectivities are obtained at different BDPP/Rh ratios in the two systems.

Subsequently, 4 bar of H$_2$ was added to solution e at room temperature. After 2 h at 60 °C, the solution changed from orange to yellow and the ^{31}P{^{1}H} NMR spectrum showed a doublet of triplets at 30.1 ppm ($^1J_{Rh-P}$ = 112 and $^2J_{P-P}$ = 9 Hz), a doublet at 26.1 ppm ($^1J_{Rh-P}$ = 123 Hz), and a very broad doublet at 24.4 ppm ($^1J_{Rh-P}$ = 154 Hz) (Table 3).

The double of triplets at 30.1 and the doublet at 24.4 ppm agree with species **7** and **8**, respectively (Schemes

Table 4.   Equilibrium Constants of the Equilibrium between Complexes 7, 8, and H$_2$ (eq 3)

T (K)	$1/T (\times 10^3)$	K_e	ln K_e
298	3.356	0.67	−4.0
308	3.247	0.79	−0.23
323	3.096	1.07	0.07
343	2.915	1.77	0.57

Table 5.   Asymmetric Hydroformylation of Styrene Using the in Situ HPIR Autoclave

entry	precursor	t (h)	BDPP/Rh	%C$_{ald}$	%2-PP/3-PP	%ee[a]	IR (cm^{-1})
1[b]	**1**	7	2	100	95/5	45(R)	1988, 1944
2[b]	**9**	24	2	97	94/6	40(R)	1988, 1944
3[c]	**1**	7	2	86	94/6	45(R)	
4[d]	**9**	24	2	99	94/6	43(R)	

[a] Determined by GC, absolute configuration in parentheses. [b] The catalyst was prepared from the corresponding precursor under hydroformylation conditions, 9 bar of syn gas and 65 °C during 16 h. Styrene/precursor = 200 (molar). Solvent: 2-methyltetrahydrofuran (15 mL), CO/H$_2$ = 1; T = 65 °C; P = 10 bar. [c] Reference 12. [d] Reference 11d.

1 and 2), and the signal at 26.1 ppm corresponds to the remaining species **10**. The phosphorus-to-carbon coupling constant ($^2J_{P-C}$ = 9 Hz) evidences the presence of two equivalent CO molecules coordinated to rhodium in complex **7**-^{13}CO. The broad doublet at 24.4 ppm might suggest the existence of phosphorus-to-carbon couplings in complex **8**-^{13}CO. The coupling constants could not be resolved for **10**-^{13}CO.

The ^{13}C NMR showed a complex signal at 199 ppm that appears as a doublet of triplets ($^1J_{C-Rh}$ = 69 Hz, $^1J_{C-P}$ = 8.5 Hz) (Table 3). At −80 °C, the signal was very broad and the coupling constants could not be resolved.

The ^{1}H NMR spectrum shows only a double triplet structure in the hydride region (−8.8 ppm, $^1J_{H-Rh}$ = 11 Hz, $^2J_{H-P}$ = 57 Hz) (see Figure 5) characteristic of **7**. A more detailed study of the fluxional process in complex **7** is presented in the next section.

The FT-IR spectrum of the final solution under atmospheric conditions shows several absorptions in the terminal carbonyl (1940, 1921, and 1899 cm^{-1}) and bridging carbonyl (1724 and 1705 cm^{-1}) regions (Table 5). The 1921, 1724, and 1718 cm^{-1} carbonyl absorptions are assigned to the carbonyl dimeric species **8**-^{13}CO. The terminal CO absorptions at 1940 and 1899 cm^{-1} could be assigned to the mononuclear complex **7**-^{13}CO.

In summary, the displacement of the dithiolate ligand is clearly evidenced in complexes **7** and **8** under these conditions. In part, the dithiolate is observed as **10**, in which one diphosphine bridges the two metal centers.

For comparison purposes, a similar study with the simple diphosphine dppp and precursor **9** has been carried out. After 1 h under hydroformylation conditions (10 bar of H$_2$/CO = 1, 60 °C, dppp/Rh = 2), the ^{31}P{^{1}H} NMR spectrum showed two doublets at 14.6 ($^1J_{Rh-P}$ = 113 Hz) and 8.9 ppm ($^1J_{Rh-P}$ = 154 Hz). These doublets can be assigned to [RhH(dppp)(CO)$_2$] (**11**) and [Rh$_2$(dppp)$_2$(CO)$_4$] (**12**), analogous to **7** and **8**, respectively. Complex **12** has been previously synthesized by James et al,[23] and the X-ray determination of its structure revealed the existence of a Rh−Rh bond. No signals corresponding to species similar to **10** were observed. Recently,[13] we reported a study concerning the reactivity of tetracarbonyl dithiolate-bridged rhod-

Scheme 3

Berry-Type Rearrangements

Scheme 4

Equatorial-Axial Phosphorus Exchange
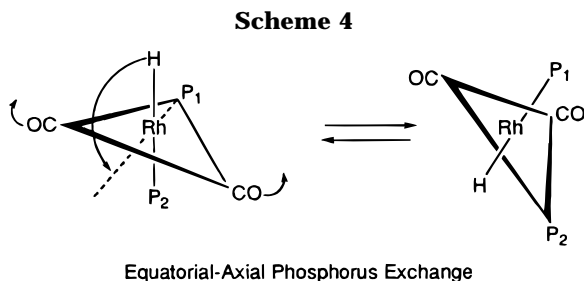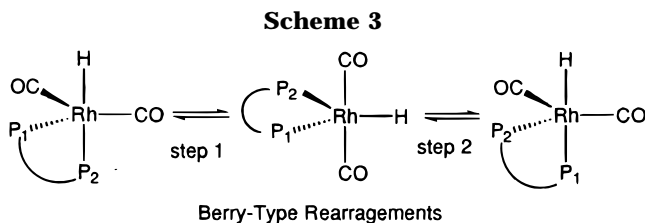
ium(I) complexes toward dppe and dppp where the related mononuclear cations [Rh(dppp)$_2$(CO)]$^+$ and [Rh-(dppp)$_2$]$^+$ were observed under CO atmosphere.

The FT-IR spectrum of the final solution under atmospheric conditions also shows several absorptions in the terminal carbonyl (1988, 1978, 1962, 1945, and 1922 cm^{-1}) and bridging carbonyl (1766, 1745, and 1725 cm^{-1}) regions. The absorptions at 1962, 1765, and 1725 cm^{-1} are assigned to carbonyl dimeric species such as **12**. The subtraction of the second spectrum from the first showed only the terminal CO absorptions at 1988 and 1945 cm^{-1} assigned to the mononuclear complex **11**.

Fluxional Processes in [HRh(BDPP)(CO)$_2$] (7). Equatorial–axial ligand exchanged in tbp and square-pyramidal HML$_4$ complexes has been explained by so-called Berry[28]-type and turnstile rotations.[19] In both mechanisms, two axial nuclei exchange positions with two of the equatorial nuclei in one step. As proposed by Meakin,[19] such a rearrangement in HRhPP(CO)$_2$ complexes for equatorial–axial phosphorus exchange seems very unlikely because it requires two successive Berry-type interconversions (Scheme 3) via a high-energy intermediate containing an equatorially coordinated hydride ligand.

Furthermore, this mechanism requires rather flexible diphosphine ligands because the bite angle varies between 90° and 120°. A rearragement mechanism for phosphorus exchange in HM(CO)$_x$P$_{4-x}$ complexes (M = e.g., Rh, Ir; P = monophosphine, monophosphite), which is less energy demanding than the Berry-type rotations, has been reported.[28] A simple hydride motion inter-converts the equatorial (P$_1$) and the axial (P$_2$) phosphorus atoms (Scheme 4). A simultaneous bending motion of the hydride and the carbon monoxide ligands now places the hydrogen axially to P$_1$, thus exchanging both phosphorus nuclei.

Previous reports[5,6a,10,29,30] on solution structures of related chelated phosphorus ligand HRhPP(CO)$_2$ complexes revealed that variation of the bite angle lead to formation of either structure **a** or structure **b**. The bite angle concept is one of the most important contributions to the understanding the behavior of Rh–chelate phosphorus ligand systems in the hydroformylation reac-

a　　　　　　　　b
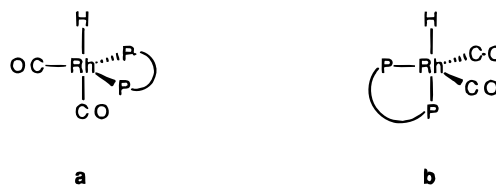
tion.[9] Few examples in the literature show the presence of hydride tbp intermediates with structure **a** or **b** depending on the bite angle of the phosphorus ligand. Therefore, the phosphine–phosphite BINAPHOS ligand provides intermediates with structure **b** in which the phosphine moiety is located at the equatorial site and the phosphite moiety at the axial site,[5] and bulky diphosphites are established to form hydridorhodium complexes with both phosphorus atoms coordinating to the equatorial sites (structure **a**).[6a,d]

The variable-temperature NMR study reported here demonstrates that the diphosphine BDPP leads to formation of structure **b**. From the observed and calculated variable-temperature NMR spectra (Figure 5), the rate constants (k) have been determined at different temperatures. The rate constants (ln k/T) for the rearrangement mechanism are presented as a function of the temperature (Eyring plot, Figure 6). From eq 1 and the Eyring plot the enthalpy of activation ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$) have been calculated for the exchange process ($\Delta H^{\ddagger}$ = 44.37 kJ·mol^{-1} and $\Delta S^{\ddagger}$ = 0.405 J·K^{-1}mol^{-1}). The small value

$$k \cdot T^{-1} = k_{\mathrm{B}} \cdot h^{-1}(e^{\Delta S^{\ddagger}/R})(e^{-\Delta H^{\ddagger}/RT}) \qquad (1)$$

with k_{B} = 1.3807 × 10^{-23} J·K^{-1} and h = 6.63 ×

$$10^{-34} \text{ J·s}$$

calculated for the entropy of activation is characteristic of an intramolecular rearrangement process and makes $\Delta G^{\ddagger}$ relatively insensitive to temperature changes (eq 2, e.g., $\Delta G^{\ddagger}_{193K}$ = 44 kJ·mol^{-1} and $\Delta G^{\ddagger}_{293K}$ = 44 kJ·mol^{-1}). The energy barrier to rearrangement is very

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (2)$$

similar to values reported by Meakin[19,31] and Verkade[22] (30.5–43.9 kJ·mol^{-1}) for hydridorhodium complexes containing monophosphine and monophosphite ligands.

Calculation of Equilibrium Constants of Dimer–Monomer Equilibria. Since the pioneering work of Wilkinson, it has been known that complexes of type **7** and **8** are in equilibrium,[20,32,33] the position of which depends on the hydrogen concentration and the ligands. This equilibrium is of great importance to the overall kinetics observed during hydroformylation. When rhodium would reside mainly in the dimeric state under fast equilibration, a first-order dependence in hydrogen

(28) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(29) (a) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719. (b) Buisman, G. J. H.; van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1997**, *16*, 5681.

(30) Pottier, Y.; Mortreux, V.; Petit, F. *J. Organomet. Chem.* **1989**, *370*, 333.

(31) (a) Meakin, P.; Jesson, J. P.; Tebbe, F. N.; Mutterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 1797. (b) Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835.

(32) Brown, C. K.; Wilkinson, G. *Tetrahedron Lett.* **1969**, *22*, 1725.

(33) Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A,* **1970**, 2753.

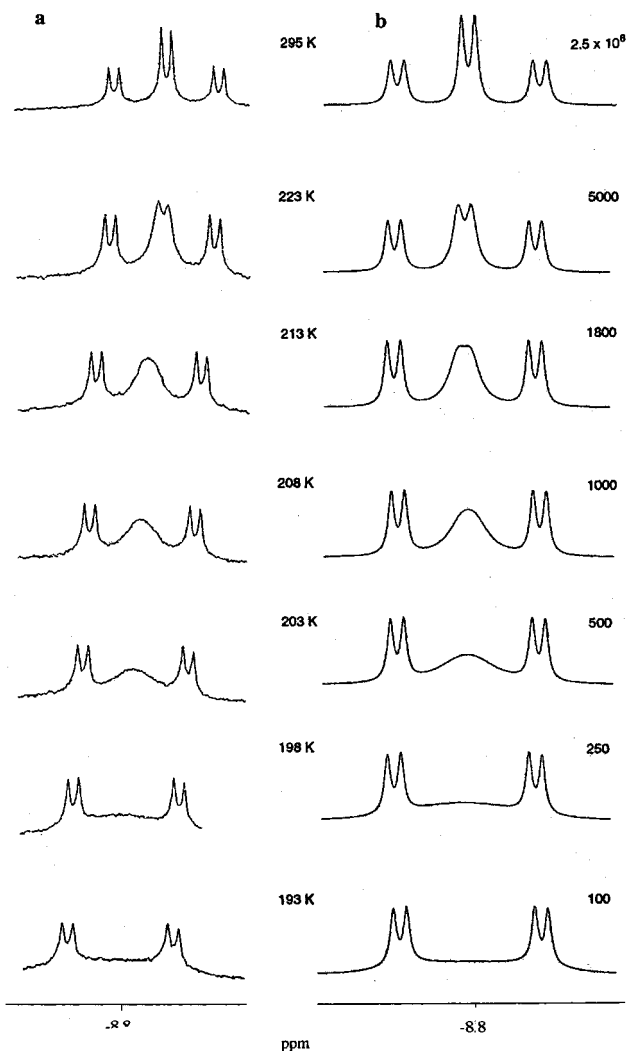**Figure 5.** (a) Observed and (b) calculated VT 300 MHz ^{1}H NMR spectra for [HRhBDPP(CO)$_2$] (**7**) with an eq–ax coordinating diphosphine (hydride region).

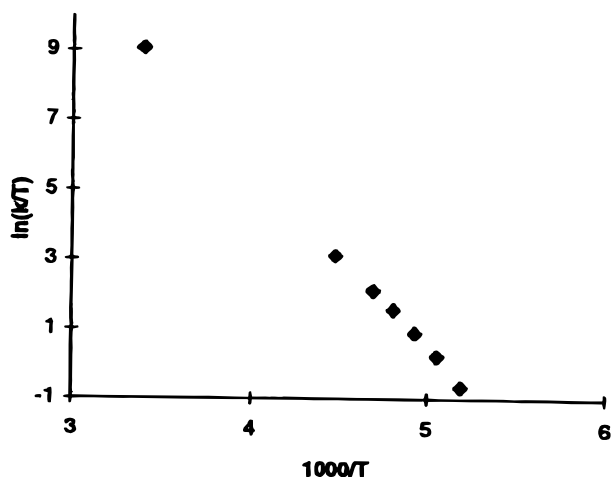**Figure 6.** Eyring Plot: phosphorus exchange rate constants obtained from VT 300 MHz ^{1}H NMR spectra (hydride region) in HRh(BDPP)(CO)$_2$ (**7**).
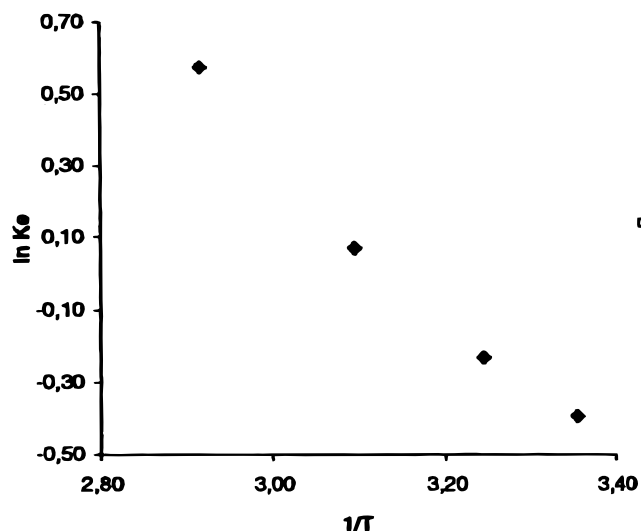
Figure 7. Dependency of the ln K_e versus $1/T$ of the equilibrium reaction between complexes **7** and **8**. Conditions: complexes **7** and **8** were formed in situ in the HPNMR tube from a solution of **1** and BDPP at $P = 10$ bar of H$_2$/CO, 1:1, and $T = 60$ °C. After that an additional H$_2$ pressure (5–45 bar) was added to the corresponding solution, the equilibrium constants were calculated from the ^{31}P{^{1}H} NMR spectra.

were observed under certain conditions using BDPP, we have measured the equilibrium constants in toluene by means of ^{31}P NMR spectroscopy.

The data were collected in the temperature range 298–343 K, and the pressure was varied from 5 to 50 bar of H$_2$ at 5 bar of CO (Table 4). The total rhodium concentrations amounted to 0.0138–0.0157 grat·L^{-1}. Hydrogen concentrations were calculated using Henry's law; the concentrations at 1 bar (0.1 MPa) were taken from the literature[34] and amounted to 0.0037, 0.0039, 0.0043, and 0.0047 M at 298, 308, 323, and 343 K. As expected, the concentration of hydride **7** increases with H$_2$ pressure while the dimer concentration decreases. At ambient temperatures and slightly above, the equilibrium constant is roughly 1, provided that the hydrogen concentration used in the calculation is that mentioned above. As can be seen from Figure 7, the calculated equilibrium constant for eq 3 increases with temperature. In part, this change is also due to the

$$\mathbf{8} + H_2 \rightleftharpoons (2)\ \mathbf{7} \qquad (3)$$

$$K_e = \frac{[\mathbf{7}]^2}{[\mathbf{8}][H_2]}$$

higher concentration of dihydrogen at higher temperatures. The approximate thermodymanic data for this process are $\Delta H = 18$ kJ·mol^{-1} and $\Delta S = 60$ J·mol^{-1}·K^{-1}. These data should be used with some caution, since they were obtained from integration of NMR spectra and other species not observed might be involved. The effects of temperature, pressure, and concentration remains, however, pertinent to hydroformylation.

These data show that with BDPP as the ligand, at room temperature, relatively high catalyst concentra-

pressure would be measured. Many people have reported a positive order in dihydrogen pressure for the hydroformylation reaction and, as we will see in the following, the dimer–monomer equilibrium remains, however, pertinent to such systems. As both species

(34) *Solubilities of Inorganic and Organic Compounds*, Part 1.; Stephen, H., Stephen, T., Eds.; Pergamon Press: Oxford, 1963; Vol. 1.

tions, and partial pressures of H_2 below 5 bar, rhodium will be predominantly present as the dimer (**8**). More monomer will be formed when the pressure of H_2 is raised, and hence, the rate of hydroformylation will increase with pressure, regardless of the mechanism of the actual rhodium hydride catalyst. Preliminary data show that other phosphines show the same behavior and that the equilibrium constants do not differ significantly. Many authors have reported on the formation of dimeric species,[23,30,32,33,35-37] but so far, no quantitative data have been reported.

Having found that the monomer–dimer equilibrium may disturb the outcome of kinetic studies, we also asked the question whether the rate at which the equilibrium is established might influence kinetic data. We knew that the reaction was too slow to be studied by an NMR exchange method and too fast to be studied by conventional kinetics recording NMR spectra. Therefore, we turned to IR spectroscopy using the equipment described previously.[15a] First, the reaction mixture was equilibrated at 5 bar of H_2 and 5 bar of CO at 298 and 323 K. The H_2 pressure was raised quickly to 25 bar at 298 K and 15 bar at 323 K, and the intensity of the absorption of the dimer **8** at 1744 cm^{-1} was recorded. The signal assumes the new equilibrium value with half-lives of 100 s at 298 K and 10 s at 323 K. Since the reaction is second order in hydride concentration, the kinetics are complex and, again, other species may occur that are not observed with this technique. Therefore, these preliminary data do not allow a detailed analysis, but one can see that in many cases the monomer–dimer equilibrium may have rates on the same order of magnitude of the hydroformylation reaction. Hence, both the position of the equilibrium and the rate of this process should be considered in hydroformylation studies.

Asymmetric Hydroformylation of Styrene: HPIR Autoclave. After the detection by NMR and IR spectroscopic studies of the dominating species of complexes **1** and **9** under hydroformylation conditions, we studied the hydroformylation reaction in the presence of the substrate in an in situ HPIR autoclave at 10 atm and 65 °C and (−)-BDPP/Rh = 2 to gain information on possible intermediates during the process.

The experimental and literature hydroformylation results are summarized in Table 5. First, the active catalyst was prepared overnight from the starting rhodium precursors **1** and **9** under typical hydroformylation conditions (65 °C, 9 bar of syngas, 16 h), and then the IR spectrum was recorded. In both cases, the IR spectrum revealed the carbonyl absorptions at 1988 and 1944 cm^{-1} (Table 5) assigned to the mononuclear hydrido complex **7**, but a small quantity of complex **8** was also observed, as concluded from the presence of the weak carbonyl absorptions at 1745 and 1724 cm^{-1}. After the induction time, the substrate (0.5 mL) was added by means of the separately pressurized reservoir and the final pressure was set to 10 bar of syngas. The hydroformylation reaction was monitored for 7 h for catalyst precursor **1** and 24 h for precursor **9** (Table 5).

The absorptions corresponding to complex **7** (1988 and 1944 cm^{-1}) are retained throughout the reaction in both cases. These results suggest that complex **7** is the predominant species during the catalytic cycle but complexes **8** (system **1**/BDPP) or complexes **8** and **10** (system **9**/BDPP) could be present in small quantities (≤3%). The enantiomeric excesses were determined by GC, and they were 45% (*R*) when **1** was the catalyst precursor and 40% (R) when the catalyst was **9** (Table 5).

Conclusions

HPNMR and HPIR spectroscopic studies revealed that when the diphosphine BDPP is added to the dinuclear catalytic precursors **1** and **9** under hydroformylation conditions, mononuclear species **7** and the dimeric complex **8** are principally formed. The reaction of the dithiolate-bridged rhodium complex **9** with BDPP under CO pressure leads to complex **10**, which is stable at high pressure and temperature. This complex retains the dinuclear structure with bridging dithiolate ligands.

We propose that the predominant species for the catalytic reaction is **7**. Variable-temperature ^{31}P and ^{1}H NMR spectroscopic studies revealed that the diphosphine BDPP is equatorially–axially coordinated. Species **7** and **8** are in equilibrium, and we have found that the concentration of the hydride species **7** strongly depends on the reaction parameters. Since many hydroformylation studies are conducted at temperatures below 353 K and high catalyst concentrations, this equilibrium should be taken into account to explain the dependence of the rate on the dihydrogen concentration.

Experimental Section

General Methods. All operations were performed under an atmosphere of nitrogen or argon by using standard Schlenck techniques or a nitrogen box. Solvents were dried and distilled prior to use.

The chiral diphosphine (−)-BDPP was purchased from Strem Chemicals, and [Rh(μ-OMe)(cod)]$_2$[38] and [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$[11d] were prepared according to literature procedures.

^{1}H NMR (300 or 100 MHz, referenced to TMS) and ^{31}P{^{1}H} NMR spectra (121.5 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker AMX-300 or AC 100 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer (at 75.5 MHz). Assigments in complex NMR spectra were aided by simulation with Fortran Program LAME (LAOCOON) or geNMR 3.5M software. IR spectra were obtained on a Nicolet 510 FT-IR.

Gas chromatography was performed on a Carlo Erba GC 6000 Vega series or an Interscience Mega 2 series apparatus (split/splitless injector, J&W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa of He, FID detector).

The in situ HPIR experiments[15a] were performed in an SS 316 55 mL autoclave equipped with IRTRAN windows (700 cm^{-1}, ϕ = 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) can be added by means of a separately pressurized reservoir. The rhodium complexes [Rh(μ-OMe)(cod)]$_2$ (10 mg, 0.02 mmol) or [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ (25 mg, 0.02 mmol) and BDPP (70 mg, 0.16 mmol) were dissolved in 15 mL of toluene. The autoclave was closed and flushed several times with CO/H_2. After pressurizing and heating of the mixture, the autoclave was placed in

(35) Chan, A. C. S.; Shieh, H.-S.; Hill, J. R. *J. Chem. Soc., Chem. Commun.* **1983**, 688.

(36) Morris, D. E.; Tinker, H. B. CHEMTECH **1972**, 554.

(37) Yagupsky, M.; Brown, C. K.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A*, **1970**, 937.

(38) Usón, R.; Oro, L. A.; Cabeza, J. *Inorg. Synth.* **1985**, *23*, 126.

the infrared spectrometer and, while the samples were stirred, the infrared spectra were recorded. Hydroformylation studies were performed in methyltetrahydrofuran using the same equipment, and the substrate was charged to the reservoir and added to the reaction mixture by overpressure. Upon addition, the reaction started, as evidenced by a pressure drop and an increase of the temperature, and the infrared spectra were recorded. The final solution was analyzed by GC. The pressure-jump HPIR experiments were carried out as follows: complexes **7** and **8** were formed in situ in the autoclave from a solution of **1** (50 mg, 0.1 mmol) and BDPP (100 mg, 0.22 mmol) in 15 mL of toluene at 10 bar of $H_2/CO = 1$ and $T = 50$ °C. After that, additional H_2 pressure (20 bar at 298 K or 10 bar at 223 K) was added to the corresponding solution. Data points were collected every 60 s at 298 K and every 3 s at 233 K. Smooth curves of the absorptions of the dimer at 1744 cm^{-1} were obtained, showing the decay of the dimer concentration.

The in situ HPNMR experiments[14a] were carried out in a sapphire tube ($\phi = 10$ mm). The rhodium complexes [Rh(μ-OMe)(cod)]$_2$ (5 mg, 0.01 mmol) and [Rh$_2$(μ-BCOS)(cod)$_2$]$_2$ (6.2 mg, 0.01 mmol) and BDPP (18 mg, 0.04 mmol or 9 mg, 0.02 mmol) were dissolved in toluene-d_8 (1.5 mL) in the nitrogen box, and the sapphire tube was closed. After pressurizing the mixture with H_2/CO, the tube was placed in the NMR spectrometer and the spectra were recorded.