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Fluxional Processes in Asymmetric Hydroformylation Catalysts $[\mathrm{HRhL}^\frown\mathrm{L(CO)_2}]$ Containing C_2-Symmetric Diphosphite Ligands

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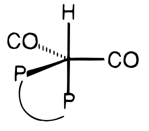
Solution structures of hydridorhodium diphosphite dicarbonyl complexes $[\mathrm{HRhL}^\frown\mathrm{L_{1-9}(CO)_2}]$ have been studied. Diphosphites $\mathrm{L}^\frown\mathrm{L_1}$ to $\mathrm{L}^\frown\mathrm{L_9}$ are based on C_2 symmetric (2*R*,3*R*)-butane-2,3-diol, (2*R*,3*R*)-diethyl tartrate, (2*R*,4*R*)-pentane-2,4-diol, and (2*S*,5*S*)-hexane-2,5-diol backbones substituted with 1,1′-biphenyl-2,2-diyl- or (*S*)-(−)-1,1′-binaphthyl-2,2′-diylphosphoroxy derivatives. Variable-temperature (293−163 K) ^{31}P and ^{1}H NMR spectroscopy revealed fluxional behavior in the trigonal bipyramidal $\mathrm{HRhL}^\frown\mathrm{L(CO)_2}$ complexes of $\mathrm{L}^\frown\mathrm{L_{1-9}}$ which could be frozen out at low temperatures. Depending on the length of the bridge between the two phosphorus atoms in the diphosphite ligands, equatorial−axial or bis-equatorial coordination takes place. Enthalpies of activation ($\Delta H^{\ddagger}$) varying between 36.7 and 62.5 kJ mol^{-1} have been calculated for the phosphorus exchange observed in these hydridorhodium diphosphite dicarbonyl complexes. The enthalpies of activation increase with larger steric bulkiness of the coordinated diphosphite ligands.

Introduction

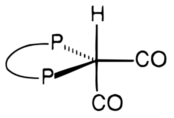
In the last two decades, much research has been directed toward the development of selective rhodium hydroformylation catalysts modified with phosphite ligands.[1] In spite of the encouraging results often reported on catalysis, little attention has been paid to the solution structures of these catalysts. In the early 1970s, Muetterties and Meakin[2] were the first to report on the chemical and dynamic solution properties of $\mathrm{HRh(PR_3)_4}$ and $\mathrm{HRh(CO)_{\mathit{x}}(PR_3)_{4-\mathit{x}}}$ species (R = $\mathrm{(OCH_2)_3C}$-*n*-Pr, R = $\mathrm{OCH_2CH_3}$ and R = O-*i*-Pr), the putative intermediates in the hydroformylation reaction. These complexes, containing monophosphite ligands, showed fluxional behavior on the NMR time scale, which is very common for five-coordinate transition metal complexes.[3]

Brown[4] and Casey[5] reported on solution structures of selective rhodium hydroformylation catalysts modified with mono- and diphosphine ligands. Nowadays, it is generally assumed that both (di)phosphine and (di)phosphite ligands form trigonal bipyramidal hydridorhodium complexes which are the active catalysts in the hydroformylation reaction.

Only recently, detailed analysis has been performed on the solution structures of these catalysts containing diphosphite ligands.[6] We reported the solution structures of enantioselective hydridorhodium diphosphite dicarbonyl hydroformylation catalysts: $[\mathrm{HRhL}^\frown\mathrm{L(CO)_2}]$. From diphosphite ligands ($\mathrm{L}^\frown\mathrm{L}$), based on chiral butane-2,3-diol, pentane-2,4-diol, and hexane-2,5-diol backbones, it appeared that either structure **a** or structure **b** is stabilized depending on the length and the flexibility of the bridge between the two phosphorus atoms.[6b]



structure **a**



structure **b**

Generally, short-bridged diphosphites forming seven-membered rings coordinate in an equatorial−axial fashion to rhodium giving rise to phosphorus−rhodium−phosphorus bite angles close to 90° (structure **a**).[6b,c] In contrast, diphosphites forming flexible eight- or nine-

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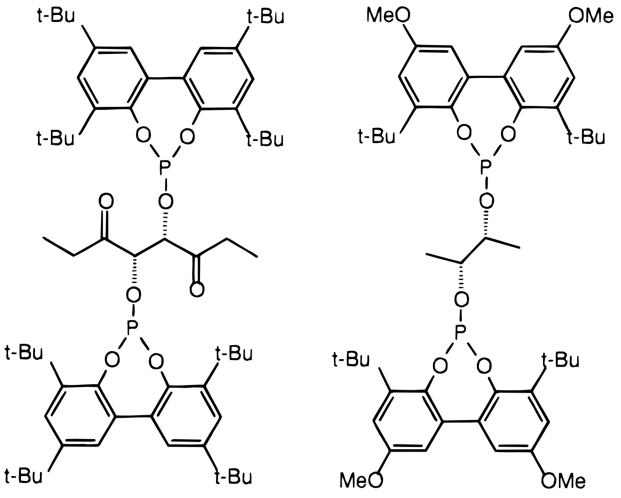
membered chelate rings coordinate bis-equatorially since the phosphorus−rhodium−phosphorus bite angles may now reach values close to 120° (structure **b**).[6b,c] These larger bidentate ligands show preferential bis-equatorial coordination because of lesser steric congestion in the equatorial plane of the trigonal bipyramidal (TBP) rhodium complexes, as already described by Brown and Kent.[4] It was shown that the highest enantioselectivity in asymmetric hydroformylation was observed for bis-equatorially coordinating diphosphite ligands.[6c,e] Distorted trigonal bipyramidal rhodium hydroformylation catalysts, containing phosphorus−rhodium−phosphorus bite angles deviating from 120°, have been reported recently by van Rooy[7] and Kranenburg.[8] The development of bidentate phosphorus ligands with specific structural requirements has led to highly (enantio)selective hydroformylation catalysts.[6−9]

Preliminary spectroscopic studies have shown that the fluxionality observed in HRhL⌒L(CO)$_2$ complexes could be completely frozen out in the low-temperature region.[6c] In an extension of our work to develop highly enantioselective hydroformylation catalysts, we report the detailed dynamics and a plausible one-step mechanism which may explain the fluxional behavior observed in trigonal bipyramidal HRhL⌒L(CO)$_2$ complexes.

Results and Discussion

NMR and IR Spectroscopy. The synthesis of C_2-symmetric diphosphites (L⌒L$_{1-9}$) as well as the corresponding HRhL⌒L(CO)$_2$ complexes have been previously described elsewhere.[6] The proton-decoupled phosphorus NMR spectrum of HRhL⌒L$_1$(CO)$_2$ shows only one doublet (δ = 155.1, $^1J_{\rm RhP}$ = 218 Hz, benzene-d_6) in the phosphite region. According to C_2 symmetry, the phosphorus atoms are equivalent in free ligand L⌒L$_1$. However, irrespective of the coordination mode to rhodium, the complexes HRhL⌒L(CO)$_2$ have C_1 symmetry. Only one doublet is observed in the ^{31}P NMR spectrum, which means that either the chemical shifts of both phosphorus atoms accidentally coincide or that they exchange rapidly on the NMR time scale. The ^{1}H NMR spectrum shows a double triplet (dt) structure in the hydride region. The double triplet is caused by coupling with two degenerate phosphorus nuclei and an additional coupling with rhodium (δ = −9.80 ppm, $^2J_{\rm HP}$ = 80.4 Hz, $^1J_{\rm HRh}$ = 6.0 Hz). Small *cis* phosphorus−hydride coupling constants up to 30 Hz have been reported in HRhL⌒L(CO)$_2$ complexes with bis-equatorially coordinating diphosphine[4,5,8] and diphosphite ligands.[9,10] In contrast, relatively large phosphorus−hydride coupling constants have been reported for HRh[P(OCH$_2$)$_3$CC$_3$H$_7$]$_4$ and HRh[PO(CH$_2$H$_5$)$_3$]$_4$ complexes in the slow exchange region.[2b,c] A *trans* relationship (structure **a**) is responsible for large phosphorus−hydride coupling constants (*i.e.*, $^2J_{\rm P_{ax}H}$ = 152 and 179 Hz, respectively). The intermediate phosphorus−hydride coupling constant ($^2J_{\rm PH}$ = 80.4 Hz) found in HRh(L⌒L$_1$)(CO)$_2$ suggests a time-averaged *cis,trans* relationship between the phosphorus and the hydride nucleus, and an average coupling constant is observed.



(2R,3R)-**L⌒L$_1$** *(2R,3R)*-**L⌒L$_2$**

HRhL⌒L(CO)$_2$ complexes containing equatorially−axially coordinating ligands: L⌒L$_1$ and L⌒L$_2$

The proton-coupled ^{31}P NMR spectrum of HRh(L⌒L$_1$)(CO)$_2$ shows a double double doublet structure which is caused by the time-averaged phosphorus coupling with rhodium ($|^1J_{\rm RhP}|$ = 213.8 Hz) and with the hydride ($|^2J_{\rm PH}|$ = 80.4 Hz). The smallest coupling constant ($|^3J_{\rm PH}|$ = 12.5 Hz) arises from the proton bonded to the chiral carbon atom of the (2*R*,3*R*)-diethyl tartrate backbone. A slight broadening is caused by a very small phosphorus−proton $^4J_{\rm PH}$ coupling constant.

Variable-temperature (293−163 K) ^{31}P and ^{1}H NMR experiments in toluene-d_8 showed considerable line broadening, which is indicative of a fluxional process. The fluxional behavior was completely frozen out in the low-temperature range (213−163 K). The slow exchange ^{31}P{^{1}H} NMR spectrum shows two phosphorus chemical shifts (δ = 167.3 and 156.1 ppm) with different phosphorus−rhodium coupling constants ($^1J_{\rm RhP}$ = 247.9 and 162.8 Hz).

Since line broadening occurred due to the increased viscosity of toluene at this temperature, low-limit spectra (193−163 K) were recorded in a mixture of acetone-d_6 and THF-d_8 (ratio 1:1). The ^{31}P−^{1}H spectrum recorded at 163 K is shown in Figure 1A. The fluxionality had been halted completely, and now it gave two phosphorus chemical shifts (δ = 167.4 and 156.9 ppm) with different phosphorus−rhodium coupling constants ($^1J_{\rm RhP}$ = 238.0 and 154.0 Hz, respectively). The calculated spectrum is given in Figure 1B and agrees very well with the observed spectrum.

It has to be noted that the observed room-temperature phosphorus chemical shift is not the exact average of the no-exchange chemical shifts. This is probably due to the different deuterated solvents used in the variable-temperature experiments. Since typical rhodium−

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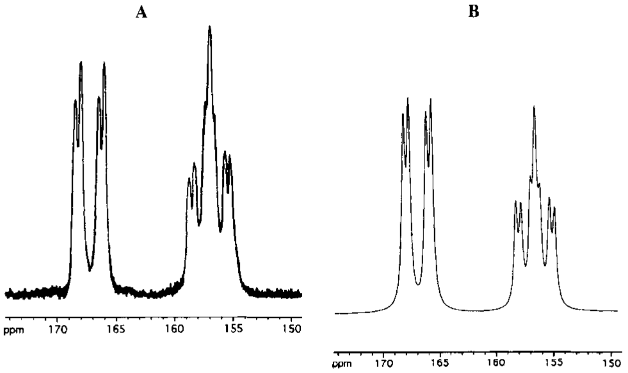

Figure 1. (A) 121.5 MHz $^{31}P-^{1}H$ NMR spectrum (phosphite region) of $HRhL^\frown L_1(CO)_2$ in acetone-d_6:THF (1:1, 163 K). (B) Calculated 121.5 MHz $^{31}P-^{1}H$ NMR spectrum (phosphite region) of $HRhL^\frown L_1(CO)_2$.

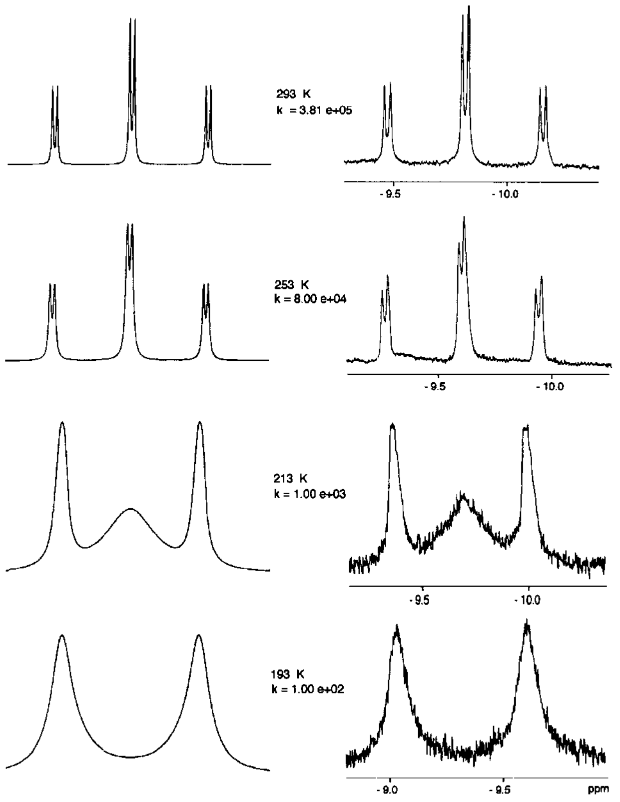

Figure 2. Calculated and observed variable-temperature ^{1}H (300 MHz) NMR spectra for $HRhL^\frown L_1(CO)_2$ (hydride region).

equatorial phosphorus coupling constants are in the range of 220−246 Hz,[6,7] we conclude that the coupling constant ($^{1}J_{RhP}$) of 238.0 Hz corresponds to an equatorially coordinated phosphorus atom (P_{eq}). The expected small *cis* $^{2}J_{P_{eq}H}$ coupling constant could not be resolved at low temperature. In contrast, the other phosphorus atom shows a large $^{2}J_{P_{ax}H}$ coupling constant of ∼190 Hz, which is indicative of a *trans* relationship between the hydride and the axially coordinated phosphorus atom[6c] (Figure 2, lower trace).

The two phosphorus atoms have a $^{2}J_{P_{eq}P_{ax}}$ coupling constant of 58 Hz with one another. This value is very similar to the low-temperature coupling constant of 63 Hz reported by Meakin[2c] in $HRh[P(OCH_2)_3CC_3H_7]_4$. Takaya[11] reported the first example of a trigonal bipyramidal hydridorhodium complex with an equatorially−axially coordinating phosphine−phosphite ligand (T = 298 K, $CDCl_3$, $^{1}J_{RhPhosphine(eq)} = 119$ Hz, $^{2}J_{Phosphine(eq)H} = 21$ Hz and $^{1}J_{RhPhosphite(ax)} = 183$ Hz, $^{2}J_{Phosphite(ax)H} = 159$ Hz). From these results, it can be concluded that axially coordinating phosphites exhibit somewhat smaller phosphorus−rhodium coupling constants ($^{1}J_{RhP_{ax}}$) but much larger phosphorus−hydride coupling constants ($^{2}J_{P_{ax}H}$) in comparison with equatorially coordinating phosphites. During *in situ* formation of $HRhL^\frown L_1(CO)_2$, hydrolysis of the diphosphite ligand ($L^\frown L_1$) sometimes occurred as a side reaction, which gave rise to phosphonate resonances in the NMR spectra (between 0 and 10 ppm, $^{1}J_{PH} = 1598$ Hz, benzene-d_6). Infrared experiments have been carried out on both the hydride and deuteride complexes in solution to find out whether competing rhodium species were present. Two absorptions, with different intensities observed at 2036 and 1990 cm^{-1}, are ascribed to combined terminal rhodium−carbonyl vibrations in the $HRhL^\frown L_1(CO)_2$ complex. The rhodium−hydride vibration could not be observed in the IR spectrum. Most likely, this band is hidden under one of the two rhodium carbonyl vibrations. Additional absorptions were found at 2080, 2050, and 1860 cm^{-1} that became more intense when the corresponding ^{31}P and ^{1}H NMR spectra showed more catalyst decomposition. A plausible explanation may be that under atmospheric conditions dissociation of carbon monoxide results in the formation of carbonyl-bridged rhodium clusters (*vide infra*). For example, infrared spectroscopic studies on rhodium carbonyl clusters of $Rh_4(CO)_{12}$ have indeed showed absorptions in this region.[12] The corresponding deuterated complex gave major terminal rhodium−carbonyl vibrations at nearly the same wavenumbers: *i.e.*, 2035 and 1994 cm^{-1}. These results are fully in agreement with two *cis*-positioned carbonyl ligands, as depicted in structure **a**.

Table 1. NMR Spectroscopic Data for $HRhL^\frown L_1(CO)_2$ and $HRhL^\frown L_2(CO)_2$ at 293 K

ligand[a]	$\lvert\delta\ ^{31}P\rvert$[b,c]	$\delta\ ^{1}H$[b,c]	$\lvert ^{1}J_{RhP}\rvert$[d]	$\lvert ^{1}J_{PH}\rvert$[d]	$^{1}J_{RhH}$[d]
$L^\frown L_1$	155.1	−9.80	218	80	6.0
$L^\frown L_2$	154.2	−10.05	209	96	7.2

[a] $HRhL^\frown L(CO)_2$ complexes prepared in toluene-d_8 starting from 0.0194 mmol of $Rh(acac)(CO)_2$, 40 °C, 8 h under 15−20 bar of syngas. [b] $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR spectra recorded under atmospheric conditions. [c] Chemical shifts (δ) in ppm. [d] Coupling constants in hertz.

Similar spectroscopic studies have been carried out with $HRhL^\frown L_2(CO)_2$.[6c] An average rhodium−phosphorus coupling constant of $|^{1}J_{RhP}| = 209$ Hz ($\delta = 154.20$ ppm, THF-d_8:toluene-d_8 = 1:1) was observed, indicating a fast fluxional equatorial−axial exchange of $L^\frown L_2$. In contrast, with $HRhL^\frown L_1(CO)_2$ it appeared that the exchange could not be halted on the NMR time scale at low temperature. As a consequence, the observed spectra were not completely resolved and appeared as broadened resonances in the ^{31}P and ^{1}H spectra. However, approximate NMR and IR data could be abstracted and are given in Tables 1−3. The relatively large average hydride−phosphorus coupling constant of 209 Hz suggests a *trans* coordination of one of the phosphorus atoms. Furthermore, the nearly identical infrared absorptions found for both the hydride and the deuterido

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Table 2. NMR Spectroscopic Data for $\mathrm{HRhL^{\frown}L_1(CO)_2}$ and $\mathrm{HRhL^{\frown}L_2(CO)_2}$ at Low *T*

ligand[a]	δ $^{31}P_{eq}$[b,c]	δ $^{31}P_{ax}$[b,c]	δ ^{1}H[b,c]	$^{1}J_{RhP_{eq}}$[d]	$^{1}J_{RhP_{ax}}$[d]	$^{1}J_{P_{eq}H}$[d]	$^{1}J_{P_{ax}H}$[d]	T[e]
$\mathrm{L^{\frown}L_1}$	167.4	156.9	−9.35	238.0	154.0	<3.0	190	163
$\mathrm{L^{\frown}L_2}$	n.r.[f]	n.r.[f]	−9.80	n.r.[f]	n.r.[f]	<3.0	211	193

[a] $\mathrm{HRhL^{\frown}L(CO)_2}$ complexes prepared in toluene-d_8 starting from 0.0194 mmol of $\mathrm{Rh(acac)(CO)_2}$, 40 °C, 8 h under 15−20 bar of syngas. [b] $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H NMR spectra recorded under atmospheric conditions. [c] Chemical shifts (δ) in ppm. [d] Coupling constants in hertz. [e] Temperature in Kelvin. [f] Not resolved.

Table 3. Infrared Spectroscopic Data of $\mathrm{DRhL^{\frown}L(CO)_2}$ Complexes

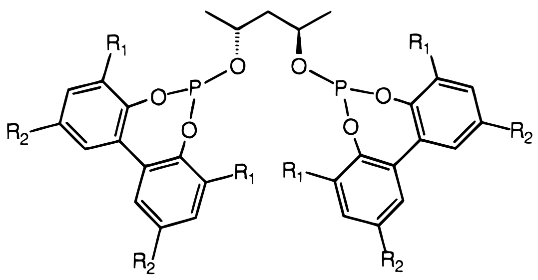
$\mathrm{DRhL^{\frown}L(CO)_2}$[a]	D-Rh-CO[b]
$\mathrm{L^{\frown}L_1}$	2035, 1994
$\mathrm{L^{\frown}L_2}$	2029, 1988
$\mathrm{L^{\frown}L_5}$	2081, 2008
$\mathrm{L^{\frown}L_6}$	2079, 2003
$\mathrm{L^{\frown}L_8}$	2054, 2005
$\mathrm{L^{\frown}L_9}$	2052, 2004

[a] $\mathrm{DRhL^{\frown}L(CO)_2}$ complexes prepared in toluene-d_8 starting from 0.0194 mmol of $\mathrm{Rh(acac)(CO)_2}$, 40 °C, 8 h under 15−20 bar of $\mathrm{D_2/CO}$. [b] IR spectra recorded under atmospheric conditions at room temperature, wavenumbers in cm^{-1}.

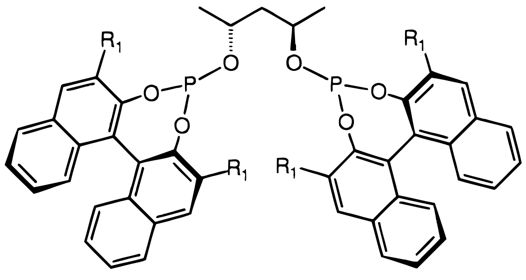
complex are in accord with an equatorial−axial coordination of ligand $\mathrm{L^{\frown}L_2}$.

The $\mathrm{HRhL^{\frown}L(CO)_2}$ complex of $\mathrm{L^{\frown}L_2}$ showed an additional chemical shift in the ^{31}P NMR spectrum (δ = 154.9 ppm, $^{1}J_{RhP}$ = 336 Hz). This orange side product was characterized as the carbonyl-bridged dimeric rhodium species $\mathrm{Rh_2(L^{\frown}L_2)_2(CO)_2}$ (IR RhCO = 1818 cm^{-1}, mass spectroscopy FAB^{+} = m/z 1986). Orange crystals of comparable carbonyl-bridged dimeric rhodium complexes containing four monodentate triphenylphosphine ligands or triisopropyl phosphite ligands have been reported.[2d,4,13] Rhodium−rhodium-bonded carbonyl-bridged dimers containing bidentate phosphine ligands have been reported by James.[14]

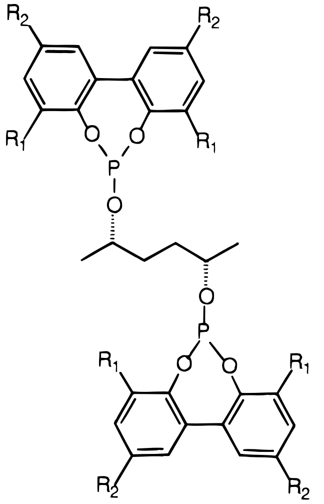
Diphosphites $\mathrm{L^{\frown}L_{3-9}}$, which form eight- or nine-membered chelate rings upon coordination to rhodium, have also been studied by NMR and IR spectroscopies.[6c,e] Solutions of $\mathrm{HRhL^{\frown}L_{3-9}(CO)_2}$ complexes in toluene are yellow, and the NMR and infrared spectra show considerably less decomposition compared to $\mathrm{HRhL^{\frown}L(CO)_2}$ complexes containing ligands $\mathrm{L^{\frown}L_1}$ and $\mathrm{L^{\frown}L_2}$. Infrared absorption of rhodium−carbonyl clusters were almost absent. These results suggest rather stable hydridorhodium diphosphite dicarbonyl complexes of $\mathrm{L^{\frown}L_{3-9}}$. Table 3 shows the IR resonances of the deuteride complexes of $\mathrm{L^{\frown}L_5}$, $\mathrm{L^{\frown}L_6}$, $\mathrm{L^{\frown}L_8}$, and $\mathrm{L^{\frown}L_9}$. In all cases, two rhodium−carbonyl bands with the same intensity, somewhat shifted compared to the hydride complexes,[6c] are observed, in agreement with deuterium and carbonyl ligands *trans* to one another in $\mathrm{DRhL^{\frown}L(CO)_2}$ complexes (structure **b**).



(2R,4R)-**L∩L₃** : R$_1$ = SiEt$_3$, R$_2$ = H
(2R,4R)-**L∩L₄** : R$_1$ = Si-t-BuMe$_2$ R$_2$ = H
(2R,4R)-**L∩L₅** : R$_1$ = t-Bu, R$_2$ = t-Bu
(2R,4R)-**L∩L₆** : R$_1$ = t-Bu, R$_2$ = OMe



(Sax,2R,4R,Sax)-**L∩L₇** : R$_1$ = SiMe$_3$



(2S,5S)-**L∩L₈**; R$_1$ = t-Bu, R$_2$ = t-Bu
(2S,5S)-**L∩L₉**; R$_1$ = t-Bu, R$_2$ = OMe

$\mathrm{HRhL^{\frown}L(CO)_2}$ complexes containing bis-equatorially coordinating ligands: $\mathrm{L^{\frown}L_{3-9}}$

At room temperature, ^{31}P NMR spectra showed doublets for $\mathrm{HRhL^{\frown}L(CO)_2}$ complexes of $\mathrm{L^{\frown}L_{3-9}}$ with rhodium−phosphorus coupling constants between 237 and 227 Hz. The observation of only one doublet suggests that phosphorus atoms accidentally coincide or rapidly exchange on the NMR time scale. Evidence for the latter process was again obtained from variable-temperature NMR experiments between 293 and 203 K. At temperatures between 293 and 253 K, line broadening occurred caused by a fluxional process. On further cooling to 223 K, a sharp double AB-system appeared, which is indicative of two chemically different phosphorus atoms P$_1$ and P$_2$ in the C_1-symmetric $\mathrm{HRhL^{\frown}L(CO)_2}$ complex (chemical shifts at 168.1 and 165.5 ppm). Since comparable variable-temperature

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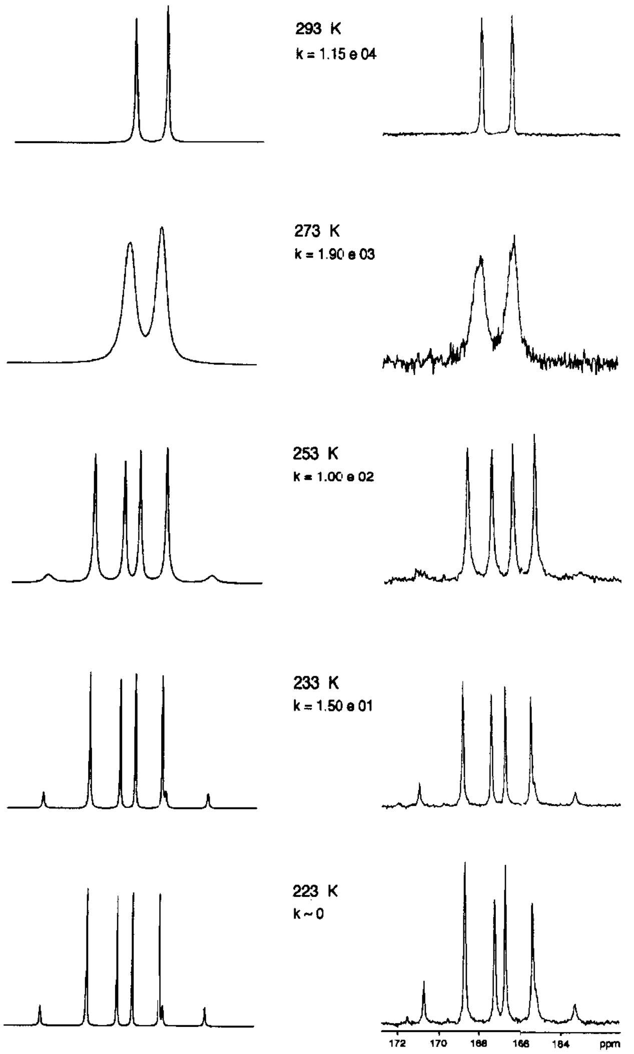

Figure 3. Calculated and observed variable-temperature $^{31}P\{^1H\}$ NMR spectra of HRhL⌒L$_4$(CO)$_2$.

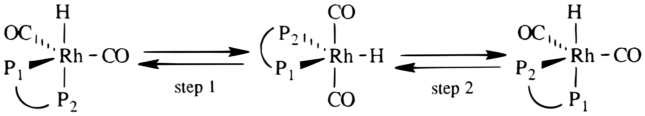

Figure 4. Berry-type rearrangements.

NMR spectra were found for HRhL⌒L(CO)$_2$ complexes of L⌒L$_{3-9}$, only those of L⌒L$_4$ are shown in Figure 3. From detailed NMR studies reported recently, it was concluded that diphosphites L⌒L$_{3-9}$ coordinate bis-equatorially to rhodium in HRhL⌒L(CO)$_2$ hydroformylation catalysts.[6c,e] All complexes reported in this article showed fluxional behavior on the NMR time scale, albeit with different exchange parameters depending on equatorial–axial or bis-equatorial ligand coordination.

Dynamic Processes in HRhL⌒L(CO)$_2$ Complexes of L⌒L$_{1-9}$. Ligand exchange in trigonal bipyramidal and square pyramidal hydridometal HML$_4$ complexes has been explained by so-called Berry-type rotations:[3] *i.e.*, in one step two axial ligands exchange positions with two equatorial ligands (Figure 4). However, it is rather unlikely that a Berry mechanism is operative in HRhL⌒L(CO)$_2$ complexes containing bidentate diphosphites since phosphorus exchange requires two successive Berry-type interconversions via a high-energy intermediate having a hydride ligand equatorially coordinated to rhodium.[15] In addition, it is not probable that phosphorus–rhodium–phosphorus bite angles can vary freely between 90° and 180° without considerable energy strain. Previous reports on solution structures of HRhL⌒L(CO)$_2$ complexes have demonstrated that stabilization of structure **a** *or* **b** is predominantly determined by the length of the bridge in the diphosphite ligand.[6b]

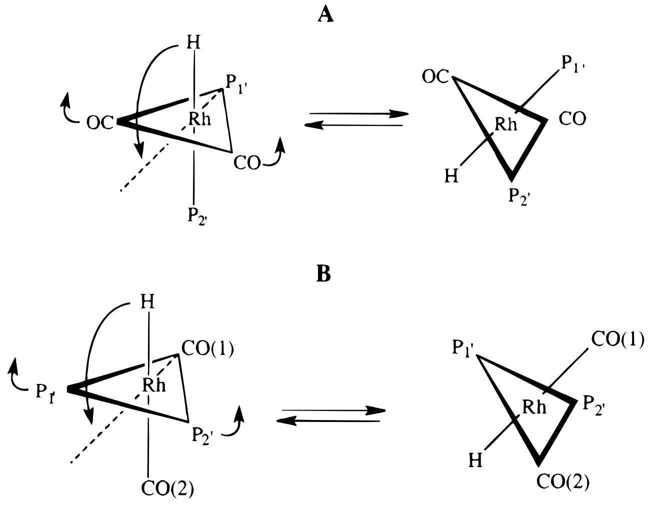

Figure 5. (A) Equatorial–axial phosphorus exchange. (B) Equatorial–equatorial phosphorus exchange.

Phosphorus exchange by phosphorus–rhodium bond cleavage, giving rise to monodentate-coordinated diphosphites, is rather unlikely since complexes containing monophosphite and monophosphine ligands retain rhodium–phosphorus coupling in variable-temperature NMR spectra.[3] In our opinion, the low-energy rearrangement mechanism, as postulated by Meakin[2a,b] for phosphorus exchange in HML$_{4-x}$(CO)$_x$ complexes (M = Rh, Ir and x = 1–4) containing monophosphites, is also applicable to HRhL⌒L(CO)$_2$ complexes containing flexible diphosphite ligands L⌒L$_{1-9}$.

Figure 5 shows a simultaneous bending motion of the hydride and the carbon monoxide ligands in hydridorhodium phosphite dicarbonyl complexes containing equatorially–axially coordinating phosphites (L⌒L$_1$ and L⌒L$_2$) and the motion of the hydride and phosphite functions for bis-equatorially coordinating diphosphites (L⌒L$_{3-9}$), respectively.

From the observed and calculated ^1H and ^{31}P NMR spectra, the rate constants (k) for the fluxional process have been determined for HRhL⌒L(CO)$_2$ complexes of L⌒L$_{1-2}$ and L⌒L$_{3-9}$, respectively. For example, the spectra shown in Figures 2 and 3 have been used to calculate exchange rate constants (k) at different temperatures (T). In Figure 6, the rate constants for phosphorus exchange are given as a function of the temperature for the HRhL⌒L$_1$(CO)$_2$. These Eyring plots were constructed for all HRhL⌒L(CO)$_2$ complexes of L⌒L$_{1-9}$.

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[15] To our knowledge, no examples exist for trigonal bipyramidal HML$_4$ complexes containing an equatorially coordinated hydride ligand. X-ray and infrared studies on HML$_4$ and HM(N)$_x$L$_{4-x}$ complexes always show the hydride in an axial position. For examples, see refs 4, 5, and (a) Frenz, B. A.; Ibers, J. A. *The Hydride Series*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol. I, Chapter III. (b) Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 725. (c) LaPlaca, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1963**, *85*, 3501. (d) Bor, G.; Sbrignadello, G.; Noack, K. *Helv. Chim. Acta* **1975**, *58*, 815.

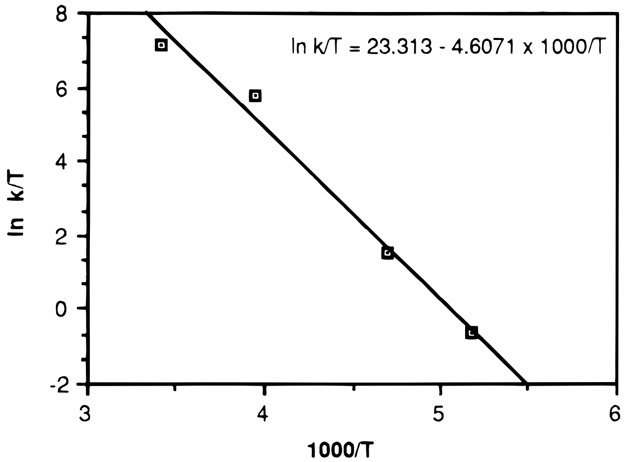

Figure 6. Eyring plot: data obtained from variable-temperature 300 MHz ^{1}H NMR (hydride region) of $HRhL^{\frown}L_1(CO)_2$.

Table 4. Thermodynamic Data Obtained from VT ^{1}H and ^{31}P NMR Spectroscopy (293−193 K)

ligand	$\Delta G^\ddagger_{293K}$ (kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})
$L^{\frown}L_1$	39.4 ± 4.7	38.3 ± 3.5	−3.7 ± 0.6
$L^{\frown}L_2$	33.5 ± 3.1	35.3 ± 2.6	+5.9 ± 0.7
$L^{\frown}L_3$	51.7 ± 6.5	54.7 ± 4.7	+10.1 ± 1.5
$L^{\frown}L_4$	49.1 ± 5.8	62.4 ± 5.2	+45.5 ± 6.6
$L^{\frown}L_5$	46.6 ± 7.1	38.6 ± 4.3	−27.7 ± 5.2
$L^{\frown}L_6$	45.4 ± 8.8	36.7 ± 5.0	−29.7 ± 7.1
$L^{\frown}L_7$	48.2 ± 4.6	51.0 ± 3.5	+9.5 ± 1.1
$L^{\frown}L_8$	44.3 ± 2.1	32.1 ± 1.1	−41.8 ± 2.5
$L^{\frown}L_9$	45.0 ± 5.2	35.5 ± 3.0	−32.5 ± 4.7

From the Eyring equation[16] and the Eyring plots, the enthalpies of activation ($\Delta H^\ddagger$) and the entropies of activation ($\Delta S^\ddagger$) were calculated for phosphorus exchange in $HRhL^{\frown}L(CO)_2$ complexes of $L^{\frown}L_{1-9}$. From the equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, Gibbs free energies ($\Delta G^\ddagger$) of activation have been calculated for the fluxional phosphorus exchange. The data are given in Table 4.

A striking conclusion is that the phosphorus exchange of equatorially−axially coordinating phosphites shows a much lower energy barrier than bis-equatorially coordinating diphosphites. According to the Meakin mechanism, the former require movement of two carbonyl functions instead of the bisphosphite function in the case of the latter. Since motion of two carbonyl ligands is expected to be easier than that of a bridged diphosphite ligand, the lower $\Delta G^\ddagger$ for equatorially−axially coordinated complexes is in support of the Meakin mechanism.

It is reasonable to assume that the calculated enthalpies of activation ($\Delta H^\ddagger$) reflect the energy barriers for the rhodium−phosphorus bending modes during the rearrangement mechanism. Equatorially−axially coordinated diphosphites $L^{\frown}L_1$ and $L^{\frown}L_2$ show rearrangement energy barriers in the range reported by Meakin[2a,b] and Verkade[2c] for hydridorhodium complexes containing monophosphite ligands. As expected for bis-equatorial coordinating diphosphite ligands $L^{\frown}L_{3-9}$, the trend shows decreasing barriers with decreasing bulkiness at the *ortho* substituents of the biaryl moieties of the ligands. The highest enthalpies of activation ($\Delta H^\ddagger$ = 54.7 and 62.4 kJ mol^{-1}) are found for $L^{\frown}L_3$ and $L^{\frown}L_4$ bearing the relatively large *ortho* substituents $Si(CH_2CH_3)_3$ and Si(*tert*-Bu)$(CH_3)_2$, respectively. Ligands $L^{\frown}L_5$ and $L^{\frown}L_6$ with $C(CH_3)_3$ substituents at the *ortho* positions and $C(CH_3)_3$ or OCH_3 groups at the *para* positions showed lower enthalpies of activation ($\Delta H^\ddagger$ = 38.6 and 36.7 kJ mol^{-1}) compared to $L^{\frown}L_3$ and $L^{\frown}L_4$, which reflects the decrease in the steric bulkiness of the *ortho* substituents. It seems obvious that the enthalpy of activation is predominantly determined by the steric hindrance of the *ortho* substituents. This is in accord with the results obtained for ligand $L^{\frown}L_7$. The energy barrier of 51.0 kJ mol^{-1} exceeds those reported for ligands having the less steric $C(CH_3)_3$ substituents at the *ortho* positions, as is the case in ligands $L^{\frown}L_5$, $L^{\frown}L_6$, $L^{\frown}L_8$, and $L^{\frown}L_9$. However, the results calculated for $L^{\frown}L_7$ should be interpreted with care since the influence of the rigid bis(naphthyl) groups on the exchange process is unknown. The lowest energy barriers ($\Delta H^\ddagger$ = 35.5 and 32.1 kJ mol^{-1}) are found for ligands $L^{\frown}L_8$ and $L^{\frown}L_9$ which form nine-membered rings upon coordination to rhodium. The larger rings formed probably give rise to the formation of more flexible $HRhL^{\frown}L(CO)_2$ complexes and facilitate the phosphorus disposition during the exchange process.

The entropies of activation are relatively small ($\Delta S^\ddagger$ between 45.5 and −41.8 J K^{-1} mol^{-1}), which is indicative of intramolecular rearrangement processes. However, it has to be noted that small inaccuracies in the temperature can cause a wide variation in the intercept ln *k*/*T* and concomitantly the magnitude of $\Delta S^\ddagger$ and $\Delta G^\ddagger$ by using the Gibbs free energy relation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. Additionally, fitting of the observed and calculated ^{1}H and ^{31}P NMR spectra can cause errors in the rate constants (*k*). For relatively large molecules with considerable steric congestion, it is not easy to predict whether entropies increase or decrease from moving away from the low-energy equilibrium state.

The most flexible complexes derived from equatorially−axially coordinating phosphites $L^{\frown}L_{1-2}$ induce relatively low enantioselectivity in the hydroformylation of styrene (20% and 34%, respectively).[6a,c] Higher enantioselectivity is found for the more rigid bis-equatorially coordinating diphosphites $L^{\frown}L_{3-7}$ based on 2,4-pentanediol (up to 87%).[6c,e] However, when the flexibility increases again, as in the case of ligands based on the longer bridge 2,5-hexanediol, low enantioselectivities are found again.[6c]

Conclusion

Depending on the length of the bridge between the phosphorus atoms in the bidentate diphosphites, equatorial−axial or bis-equatorial ligand coordination takes place in hydridorhodium diphosphite dicarbonyl complexes. Seven-membered chelate rings give rise to equatorial−axial coordination, while eight- and nine-membered rings preferably coordinate bis-equatorially to rhodium. $HRhL^{\frown}L(CO)_2$ complexes of ligands $L^{\frown}L_{1-9}$ show fluxional behavior on the NMR time scale which, in most cases, could be completely frozen out in the low-temperature region (233−193 K). Enthalpies of activation have been calculated for the fluxional processes ($\Delta H^\ddagger$ = 62.4−32.1 kJ mol^{-1}). It appeared that the energy barrier lowered with a decrease in steric bulkiness of the *ortho* substituent of the ligand. Further-

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[16] (a) The assumption is used that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are constant over the temperature range (293−193 K) employed. (b) Eyring equation: $kT^{-1} = k_B h^{-1} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$ with $k_B = 1.3807 \times 10^{-23}$ J K^{-1} and $h = 6.63 \times 10^{-34}$ J s.

more, it can be concluded that on going from eight- to nine-membered chelate ring sizes, lower energy barriers for ligand exchange are found in $HRhL\frown L(CO)_2$ complexes. This probably results from less steric congestion in flexible nine-membered bis-equatorial chelate rings. The rearrangement mechanism, proposed by Meakin for monodentate ligands, may also explain the fluxionality found in $HRhL\frown L(CO)_2$ complexes containing equatorially−axially and bis-equatorially coordinated diphosphites; it is believed that the phosphorus atoms can easily exchange without changing the phosphorus−rhodium−phosphorus bite angles appreciably.

Experimental Section

General. NMR spectra were obtained on a Bruker AMX 300 spectrometer. TMS and H_3PO_4 were used as a standard for, respectively, ^1H and ^{31}P NMR. Hydridorhodium diphosphite dicarbonyl [$HRhL\frown L(CO)_2$] complexes were prepared in a laboratory-made stainless steel autoclave (200 mL), as reported elsewhere.[6] Syngas 3.0 (H_2:CO = 1:1) was purchased from Praxair. The corresponding deuterido complexes were prepared by using a mixture of D_2 and CO. Deuterated solvents were purchased from Janssen Chimica and Aldrich Chemical Co. without further purifications. NMR samples were flushed with nitrogen before measuring. For the low-temperature NMR experiments, toluene was evaporated with a stream of nitrogen and replaced by a mixture of acetone-d_6:THF-d_8 (ratio 1:1). Infrared (IR) spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Mass spectroscopy (FD) was carried out using a JEOL JMS SX/SX102A four-sector mass spectrometer coupled to a JEOL MS-MP7000 data system. For the chemical-exchange calculations, an NMR simulation program has been applied (geNMR version 3.4, 1992, *IvorySoft*, Dr. P. H. M. Budzelaar). The program uses standard Liouville representations of quantum mechanics to evaluate dynamic spectra, as described by Binsch.[17]

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