# Variable Coordination Modes Realized with a Dihydroxyalkyldiphosphane as a Hemilabile Ligand: A Combined $^{103}$Rh-NMR and Density-Functional Study

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Cationic rhodium complexes of (*R*,*R*)-1,4-bis(diphenylphosphanyl)butane-2,3-diol and cyclic diolefins exhibit temperature-dependent $^{31}$P- and $^{103}$Rh-NMR spectra which are best explained by a hemilabile coordination of one of the hydroxy groups to the rhodium center. A complex with this ligand bound in tridentate fashion is in equilibrium with a species with the common square-planar ligand arrangement. The $^{103}$Rh-NMR shift of the fivefold coordinated complex is found almost 500 ppm downfield from that of a fourfold coordinated species. This effect is characteristic for an increase in coordination number. At gradient-corrected levels of density-functional theory, a corresponding species with an oxygen-rhodium contact has been located, together with other isomers. The computed trends in energies and $^{103}$Rh chemical shifts are consistent with the experimental findings.

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**Introduction.** – The advent of high-field NMR spectrometry together with the development of the reverse detection methods have facilitated acquisition of NMR data of the so-called low-$\gamma$ nuclei, such as $^{57}$Fe, $^{103}$Rh, or $^{187}$Os. Therefore, an increasing body of data has been collected during the last years, and, although the factors determining the observed chemical shifts are not yet fully understood, several systematic studies, particularly on the $^{103}$Rh nucleus [1], have documented the importance of both geometrical factors, *i.e.*, bond angles and atomic distances in the coordination sphere, as well as electronic effects.

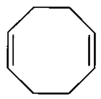
Much of the interest in such metal NMR shifts is motivated by a desire to elucidate the coordination chemistry and reactivity of the central ions which are important for catalytic applications. Rhodium complexes with phosphane ligands are widely used in homogeneously catalyzed reactions and have, therefore, attracted special attention.

The idea to tailor catalysts with special properties for specific purposes initiated the synthesis of ligands with additional functional groups, *e.g.*, (*R*,*R*)-1,4-bis(diphenylphosphanyl)butane-2,3-diol, 'dppb{OH}$_2$' [2]. Its rhodium complex **1** (nbd = norbornadiene) showed an interesting structural feature, namely an increase in the dppb{OH}$_2$ hapticity from 2 to 3 due to an additional contact between Rh and one of the OH groups, as evidenced by the structure in the solid and by low-temperature $^{31}$P-NMR spectra in solution [2].

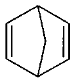
$[Rh(nbd)(dppb\{OH\}_2)]BF_4$ **1**

$[Rh(cod)(dppb\{OH\}_2)]BF_4$ **2**

We now report a systematic $^{103}$Rh- and $^{31}$-P-NMR study, calling special attention to effects of solvent, temperature, and variation in the diene (by including the cod (cod = cycloocta-1,5-diene) complex **2**). Our experimental results are complemented by density-functional-theory (DFT) calculations of the energy and chemical shifts for suitable model compounds; such calculations have recently been validated [3] and applied to rhodium compounds [1i–j]. $^{103}$Rh-NMR Spectroscopy is a particularly well-suited probe of the coordination geometry about Rh in solution.



cod



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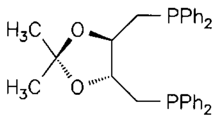

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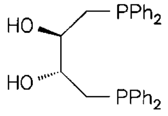
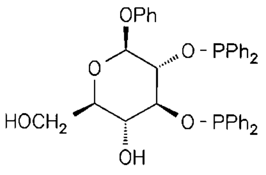
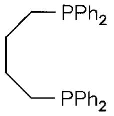


dppb{OH}$_2$



Ph–β–glup–OH



dppb

**Results.** – *NMR Spectroscopy.* Complex cations [Rh(P∩P)/(diene)]$^+$, where (P∩P) denotes a diphosphane forming a seven-membered rhodium chelate, are well-known and exhibit characteristic $^{103}$Rh-NMR shifts (*Table 1*). Clearly, the $\delta$($^{103}$Rh) values of **1** and **2** stand out, consistent with the ability of dppb{OH}$_2$ to act as tridentate ligand.

Table 1. *$^{103}$Rh-NMR Chemical Shifts δ of the Complexes* **1** *and* **2** (first entry) *and of Some Related Compounds [Rh (diene) (P∩P)]BF$_4$*[a]). Solutions in CD$_3$OD at ambient temperature.

| P∩P | δ [ppm] | |
|---|---|---|
| | Diene = nbd | Diene = cod |
| dppb{OH}$_2$ | 228 | −57 |
| diop | −204 | −233 |
| dppb | −210 | −262 |
| Ph–β-glup–OH | −296 | −305 |

[a]) *W. Baumann*, *D. Heller*, unpublished results.

The temperature and solvent dependence of the NMR spectra of **1** and **2** afford further information. In $^{31}$P-NMR spectra at ambient temperature, averaged signals recorded for **1** as well as for **2** indicate apparent $C_2$ symmetry of the corresponding cation. At low temperature in $CD_3OD$, two resonances separated by more than 40 ppm were recorded [2]. Solutions in chlorinated hydrocarbons exhibited an additional *doublet* characteristic for a species with $C_2$ symmetry (*Fig. 1*, *Table 2*). This behavior is the same for both the norbornadiene and the cyclooctadiene complex.

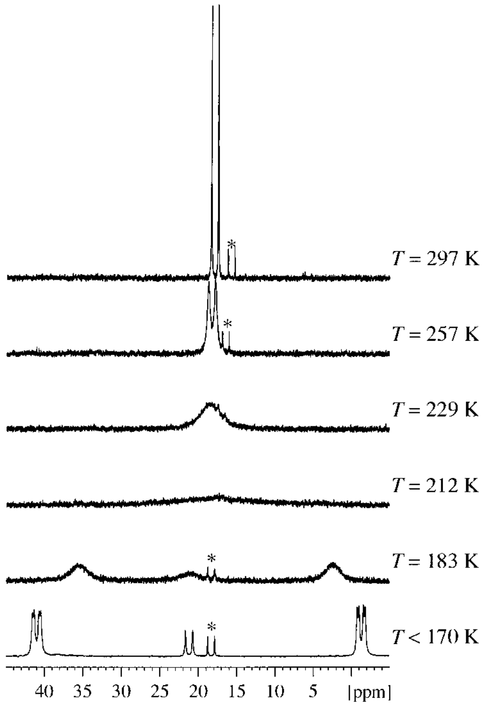


Fig. 1. *$^{31}$P-NMR Spectra of [Rh(nbd)(dppb[OH]$_2$)]BF$_4$* (**1**) *in $CD_2Cl_2$* (lowest trace in $CD_2Cl_2$/$CHCl_2F$/MeOH, exact temperature not determined). * denotes residual **2** (**1** is prepared from **2**).

Obviously, there are at least two different but interconverting species present in solution. The $^{103}$Rh-NMR shifts of both cyclooctadiene species were determined (see *Fig. 2* and *Table 3*); the signal of the symmetric species is found 474 ppm upfield from that of the asymmetric one. Assuming a temperature coefficient for the rhodium shift of 1 ppm K$^{-1}$ [1c] [4], one would expect to find the resonance of the symmetric form at room temperature at *ca.* $-330$ ppm, *i.e.*, in the region characteristic for other such complexes (*Table 1*). Unfortunately, temperatures below 180 K, where the symmetric norbornadiene species still exhibits a very broad phosphorus resonance, were not attainable with our triple-resonance probehead, thus no $^{103}$Rh correlation signal was obtained. The $^{103}$Rh-NMR shift for the unsymmetric species is, however, found again shifted to lower field (*Table 3* and *Fig. 3*).

The significantly low-field shift of the asymmetric form must be attributed to a drastic change of the coordination sphere about the Rh-atom, possibly due to incline of

Table 2. *$^{31}$P-NMR Chemical Shifts δ and Scalar Coupling Constants $^{1}$J ($^{31}$P,$^{103}$Rh)* ([Hz], in italics) *of Complexes* **1** *and* **2** *as Function of Solvent and Temperature*

| | | $[Rh(nbd)(dppb\{OH\}_2)]BF_4$ (**1**) | | $[Rh(cod)(dppb\{OH\}_2)]BF_4$ (**2**) | |
|---|---|---|---|---|---|
| Solvent | Temp. [K] | symmetric | asymmetric | symmetric | asymmetric |
| $CD_3OD$ | 186 | [a]) | 45.1[b]), *139*<br>– 2.3[b]), *129* | 18 (br.) | 33.8 (br.)<br>1.3 (br.) |
| | 297 | 18.0[c]), *141* | | 15.4, *137* | |
| $CD_2Cl_2$ | 257 | 18.3, *143* | | 16.5, *141* | |
| | 297 | 17.9, *145* | | 15.7, *142* | |
| $CDCl_3$ | 297 | | | 15.1, *140* | |
| | 307 | 18.3, *143* | | 15.4, *141* | |
| $CD_2Cl_2/CHCl_2F/CH_3OH$ | 180 | 21 (br.) | 39 (br.)<br>– 1 (br.) | 17.7, *145* | [a]) |
| $CD_3OD/CD_2Cl_2$ | 185 | | | 17.9, *145* | 32.9 (br.)<br>0.4 (br.) |
| | 301 | | | 15.5, *140* | |

[a]) Not detected due to low concentration. [b]) $T = 183$ K. [c]) $T = 315$ K.

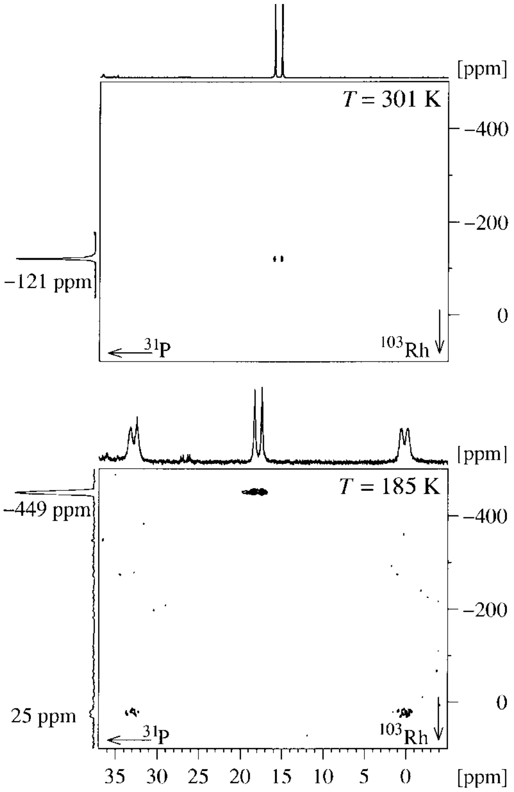


Fig. 2. *$^{31}$P,$^{103}$Rh{$^{1}$H} HMQC Spectra of $[Rh(cod)(dppb\{OH\}_2)]BF_4$* (**2**) *in a $CD_3OD/CD_2Cl_2$ mixture*

Table 3. *$^{103}$Rh-NMR Chemical Shifts δ of Complexes* **1** *and* **2** *as Function of Solvent and Temperature*

<table>
<tr><th></th><th></th><th colspan="2">[Rh(nbd)(dppb{OH}$_2$)]BF$_4$<br>(<b>1</b>)</th><th colspan="2">[Rh(cod)(dppb{OH}$_2$)]BF$_4$<br>(<b>2</b>)</th></tr>
<tr><th>Solvent</th><th>Temp. [K]</th><th>symmetric</th><th>asymmetric</th><th>symmetric</th><th>asymmetric</th></tr>
<tr><td>$CD_3OD$</td><td>186</td><td>[a])</td><td>226[b])</td><td>[d])</td><td>24</td></tr>
<tr><td></td><td>297</td><td colspan="2">228[c])</td><td colspan="2">– 57</td></tr>
<tr><td>$CD_2Cl_2$</td><td>257</td><td colspan="2">57</td><td colspan="2">– 279</td></tr>
<tr><td></td><td>297</td><td colspan="2">73</td><td colspan="2">– 216</td></tr>
<tr><td>$CDCl_3$</td><td>297</td><td colspan="2"></td><td colspan="2">– 129</td></tr>
<tr><td></td><td>307</td><td colspan="2">179</td><td colspan="2">– 117</td></tr>
<tr><td>$CD_2Cl_2/CHCl_2F/CH_3OH$</td><td>180</td><td>[d])</td><td>206</td><td>– 455</td><td>[a])</td></tr>
<tr><td>$CD_3OD/CD_2Cl_2$</td><td>185</td><td></td><td></td><td>– 449</td><td>25</td></tr>
<tr><td></td><td>301</td><td colspan="2"></td><td colspan="2">– 121</td></tr>
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[a]) Not detected due to low concentration. [b]) $T = 183$ K. [c]) $T = 315$ K. [d]) Not detected due to strong line broadening.

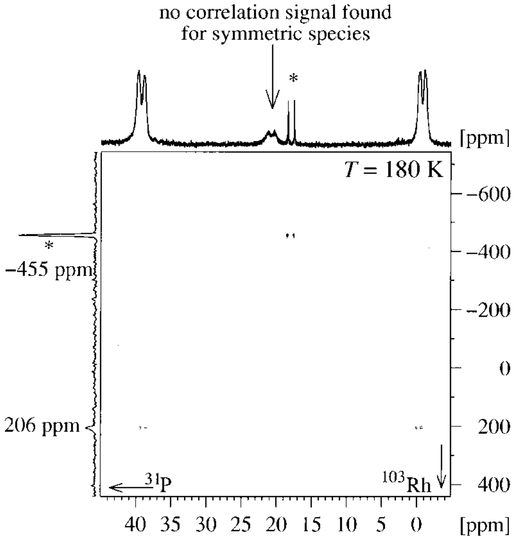

Fig. 3. *$^{31}$P,$^{103}$Rh{$^1$H} HMQC Spectrum of [Rh(nbd)(dppb{OH}$_2$)]BF$_4$* (**1**) *in a $CD_2Cl_2/CHCl_2F$/MeOH mixture.* * denotes residual **2** (**1** is prepared from **2**).

one of the OH groups to the metal (*Fig. 4*), as was found in the crystalline norbornadiene complex [2]. The transition from a square-planar to a square-pyramidal (or trigonal-bipyramidal) coordination sphere reduces the ligand field splitting which is, according to *Ramsey*'s theory [5], connected with a low-field shift of the nuclear resonance due to increased paramagnetic contributions. Consequently, the observation of a low-field shift provides strong evidence for O–Rh interaction, not only in the solid state, but also in solution.

*Elsevier* and co-workers described a similar phenomenon for the complexes $[(Ar_2P-C_2H_4-PAr_2)_2Rh]X$ (Ar = pentafluorophenyl) [1c]. For $X = PF_6^-$ a shift

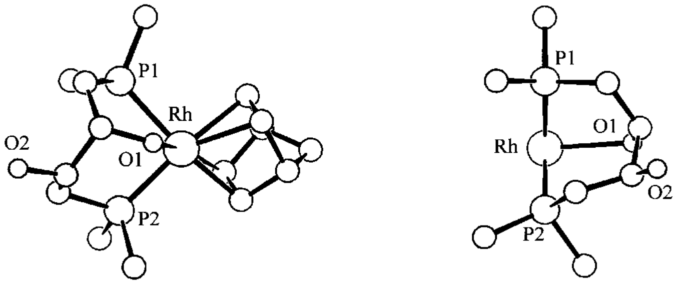

Fig. 4. *Molecular structure of complex* **1** (X-ray crystallography [2], Ph groups and $BF_4$ anion omitted). *Left:* The atoms P–Rh–P are aligned parallel to the paper plane. *Right:* Conformation of the seven-membered chelate, atoms P–Rh–P aligned perpendicular to the paper plane (diene ligand omitted).

$\delta(^{103}Rh)$ of $-672$ ppm was found, but for the chloride ($X = Cl^-$) 163 ppm was reported. Therefore, the expected ionic structure with a square-planar ligand arrangement was assumed for the hexafluorophosphate, but a covalent structure with coordination number 5 or even a dinuclear bis(μ-chloro)complex with coordination number 6 was discussed for the chloride because of its large low-field shift. More recently, *Lindner et al.* reported a similar phenomenon, *i.e.*, four- and five-coordinate neutral $Rh^I$ complexes where the $^{103}$Rh-NMR resonance of the latter is shifted *ca.* 700 ppm downfield [6]. For truly ionic structures of $Rh^I$ complexes, the influence of the anion on the $^{103}$Rh-NMR shift is only few ppm [1c].

*DFT Calculations.* To complement the NMR findings, we have performed DFT calculations for norbornadiene and the cyclooctadiene model complexes in which the phenyl groups at phosphorus have been replaced by hydrogen atoms (see *Experimental*).

For the norbornadiene model complex, four conformations were optimized (*Fig. 5*). Three of them (**1B**, **1C** and **1D**) do not show any O–Rh interaction, but **1A** exhibits this contact with an atomic distance somewhat larger than that found in the crystalline state (*Table 4*). Despite the fairly long Rh ··· O distance, topological analysis of the B3LYP/II′ electron density reveals the presence of a bond critical point (bcp) between both atoms, indicative of a bonding interaction[1]).

Conformers **1A** and **1B** do not exhibit molecular symmetry (point group $C_1$) and have chemically inequivalent P-atoms. Conformers **1C** and **1D** have been optimized with a twofold axis ($C_2$) imposed and have, thus, equivalent P-atoms. The latter two may be regarded as models for the symmetric species[2]). The computed energetic separation of the conformers in the gas phase is notable (25 kJ $mol^{-1}$), but may change in solution, particularly in protic solvents (see discussion of solvent dependence below).

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[1]) At this Rh ··· O bcp, the computed values for $\rho$ and $-\nabla^2\rho$, 0.03 and 0.15 a.u., respectively, are somewhat smaller than the corresponding values at the Rh ··· P bcps, 0.09 and 0.16 a.u., respectively (averaged values).

[2]) An analytical calculation of the harmonic vibrational frequencies of **1D** reveals one imaginary mode concerning the OH groups, *i.e.*, **1D** does not represent a local minimum. In the true minimum structure, however, the dppb backbone is not expected to deviate substantially from $C_2$ symmetry (formation of an intramolecular H-bond, as in **1B**, is most likely) and the $^{103}$Rh chemical shift should be very similar. Detailed work on the conformational behavior of seven-membered chelates is in progress (*R. Kadyrov*; for details, see [21]).

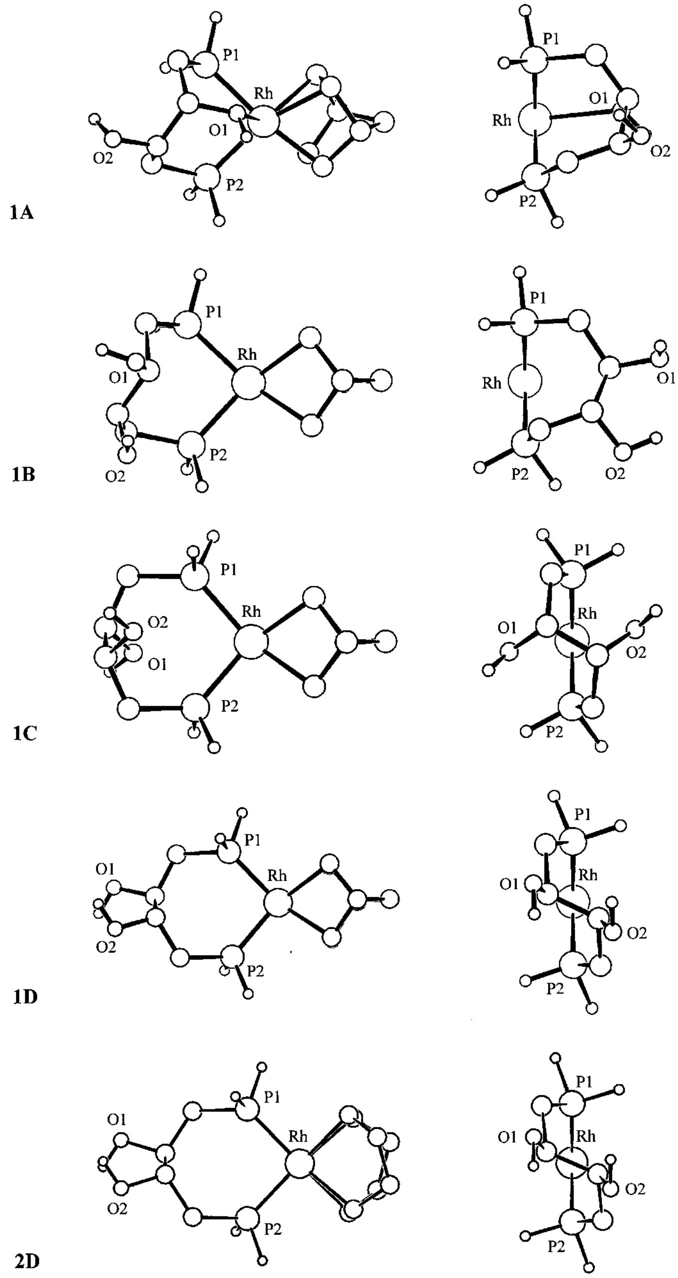

Fig. 5. *DFT-Optimized structures of the model complex cations* $[Rh(diene)(H_2P-CH_2-CH_2OH-CH_2OH-CH_2-PH_2)]^+$. Orientations of the molecules and fragments are the same as in *Fig. 4*.

Table 4. *Comparison of Experimental and Calculated Data* (relative energies[a]) [kJ mol$^{-1}$] for the nbd complexes, $^{103}$Rh-NMR chemical shifts[b]), atomic distances[a]) [Å], and bond angles[a]) [°])

| Compound | $E_{rel}$ | $\delta(^{103}Rh)$ | $d$(Rh–P1) | $d$(Rh–P(2)) | $d$(Rh–O(1)) | $d$(Rh–O(2)) | ∠(P(1)–Rh–P(2)) |
|---|---|---|---|---|---|---|---|
| **1** (X-Ray [2]) | – | – | 2.376 | 2.284 | 2.397 | 5.146 | 93.6 |
| **1A** (DFT) | 0 | 13 | 2.354 | 2.306 | 2.541 | 5.280 | 89.2 |
| **1B** (DFT) | – 9.6 | – 389 | 2.324 | 2.325 | 4.862 | 4.715 | 91.0 |
| **1C** (DFT) | – 1.0 | – 145 | 2.341 | 2.341 | 3.633 | 3.633 | 98.8 |
| **1D** (DFT) | 15.5 | – 404 | 2.322 | 2.322 | 5.500 | 5.500 | 95.6 |
| **2D** (DFT) | – | – 532 | 2.314 | 2.314 | 5.583 | 5.583 | 92.5 |

[a]) BP86/ECP1 level. [b]) GIAO-B3LYP/II′ level.

The computed $^{103}$Rh chemical shifts (*Table 4*) emphasize the influence of the coordination sphere. The most shielded Rh-atom is found for **1D** where the metallacycle adopts a twisted-boat conformation (*Fig. 5*). Changing this to the boat arrangement **1B** leads to a slight downfield shift of only 15 ppm. A stronger effect (259 ppm) results if the OH groups move from an equatorial (**1D**) to an axial position (**1C**). If now the O–Rh rhodium interaction occurs (**1A**), a further downfield shift of 158 ppm results. To separate electronic effects (coordination number) from geometrical ones (distortion of the coordination geometry) [1i–j], an additional calculation was performed on a molecule of structure **1A** where the coordinated OH group was replaced by a non-coordinated H-atom, leaving all other geometrical parameters unchanged. The resulting $^{103}$Rh-NMR shift (– 148 ppm, remarkably close to that of **1C**) is 161 ppm up-field compared to **1A**, which is a measure of the 'pure electronic' effect of the coordinated OH group. The difference with respect to the value computed for **1B** (relaxed geometry, no OH coordination) is 241 ppm and can be taken as an estimate for the 'purely geometric' effect due to the distortion of the phosphane and diene ligands.

Although quantitative agreement between the model-calculated and the experimental values could not be expected, the agreement is remarkable and, what is most important, the observed trends are reproduced, also for the cyclooctadiene complex. A calculation for its $C_2$-symmetric form **2D** shows that its $^{103}$Rh shift appears 128 ppm high-field shifted compared to the analogous norbornadiene complex **1D** (*Tables 3* and *4*). This tendency is known [1b–d] and also found for similar complexes (*Table 1*).

**Discussion.** – Taking all observations into account, the behavior of complexes **1** and **2** is best explained by an equilibrium between (at least) two species, one of them featuring the interaction of one of the OH groups with the Rh center. Since there are two OH groups, this interaction may alternate, and could involve several non-coordinated intermediates. One of these may be analogous to **1C**, as it has the OH groups in a similar (axial) position as **1A**, but it should be pointed out that the nature of the apparently symmetric forms in solution cannot be established unambiguously at this point. It is less probable that the structures are represented by **1C**, for the experimentally determined $^{103}$Rh-NMR shift difference is much larger than that calculated for the two model complexes.

In contrast, the calculated shift difference between the symmetric form **1D** and the asymmetric form **1A** (417 ppm) is close to the observed value of 474 ppm for the respective cyclooctadiene complexes. Besides $C_2$-symmetric structures corresponding to the model species **1D** and **2D** (which are not energetic minima), one can imagine rapidly interconverting asymmetric species without Rh–O contacts, such as **1B** and its enantiomer. Such a rapid equilibrium would also account for the observation of a symmetric species with an almost identical $^{103}$Rh-NMR shift, provided it occurs much faster (too fast to be frozen out at the NMR time scale) than the reversible formation of the unsymmetric species with Rh–O contact.

The position of the equilibria is, of course, solvent-dependent; measurements at low temperature show that, in the protic solvent MeOH, exclusively the asymmetric, five-coordinate species is present. Addition of aprotic solvents like $CH_2Cl_2$ shifts the equilibrium to the side of the species without O···R interaction. This was also deducible from the pronounced solvent dependence of the averaged $^{103}$Rh-NMR shift found in the region of fast exchange (*Table 3*), which moves to low field in protic methanol (coordinated OH group preferred) and to high field in aprotic chlorinated hydrocarbons (free OH groups preferred). Obviously, one free hydroxy function is stabilized by *inter*molecular H-bonds in MeOH, whereas, in chlorinated hydrocarbons, an *intra*molecular H-bond is formed instead, and oxygen coordination to rhodium is no longer favored.

In summary, $^{103}$Rh-NMR is a sensitive tool to probe changes in the coordination sphere of Rh complexes. The DFT results support our interpretation that the OH groups of the dppb{OH}$_2$ moiety can act as 'hemilabile ligands'. This ability may be the key to the peculiarities observed when the dppb{OH}$_2$ ligand is used in enantioselective, Rh-catalyzed hydrogenation reactions [2].

**Experimental.** – The preparation and characterization of the Rh complexes are described in [2]. A *Bruker ARX 400* NMR spectrometer ($B_o = 9.4$ T), equipped with a commercial triple-resonance probe (doubly-tuned $^1$H/$^{31}$P coil with a surrounding broadband coil) was used, $\pi/2$ pulse widths for $^{31}$P and $^{103}$Rh were 13.9 and 29.5 μs, resp. Chemical shifts $\delta$ are given in ppm relative to external $H_3PO_4$ ($^{31}$P) or $\Xi = 3.16$ MHz ($^{103}$Rh) [7], positive signs indicating low-field shifts. $^{103}$Rh-NMR Shifts were determined by inverse detected (four-pulse HMQC) triple-resonance experiments $^{31}$P, $^{103}$Rh{$^1$H} [8]; each determination was carried out at least twice with variation of the $^{103}$Rh frequency and the $t_1$ increment to ensure that the signals in the $F_1$ dimension were not folded. Temperatures were measured with the MeOH thermometer.

*Computational Details.* Geometries have been fully optimized with the *Gaussian* series of programs [9] employing the gradient-corrected density functionals of *Becke* (1988) [10] and *Perdew* (1986) [11] for exchange and correlation, resp., together with a quasi-relativistic effective core potential and the corresponding [6s5p3d] valence basis set for Rh [12], and standard 6-31G* basis [13] on the ligands (designated BP86/ECP1). Magnetic-shielding tensors have been computed with the GIAO (gauge-including atomic orbitals)-DFT method as implemented [14] in the Gaussian 94 program, employing *Becke*'s three-parameter exchange DFT/*Hartree-Fock* hybrid functional [15] and the correlation functional of *Lee et al.* [16], a fine integration grid (finegrid option), together with basis II, *i.e.*, a well-tempered [16s10p9d] basis [17] on Rh (contracted from the 22s14p12d set and augmented with two d shells of the well-tempered series) and the recommended IGLO basis II [18] for the ligands (which is essentially of polarized triple-zeta quality) except H, for which the IGLO basis DZ [18] has been used. This level is designated GIAO-B3LYP/II′. Exper. $^{103}$Rh chemical shifts of a number of Rh complexes have been well reproduced using this particular combination of theoretical methods [1i][3][19]. Theoretical relative $^{103}$Rh chemical shifts (referenced to the usual standard frequency of $\Xi = 3.16$ MHz [7]) have been calculated as $\delta = \sigma_{\text{standard}} - \sigma_{\text{calc}}$; employing the $\sigma_{\text{standard}}$ value from [3], –878 ppm. This value has been obtained from $\sigma_{\text{calc}}$. *vs.* $\delta_{\text{exper}}$. linear regressions employing BP86/ECP1 geometries. Topological analysis of the total electron density has been performed with the MORPHY program [20].

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