

**The Weak Metal–Water Bond
in Diphenylborylated Organoaquacobaloximes
and Rhodoximes Leads to the Formation
of an Unusual Dinuclear Rh(III) Complex***

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The synthesis and characterization of a series of $\text{RM}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ complexes ($\text{M} = \text{Co}$ and Rh) and the X-ray structure of the dinuclear $[\textit{n}\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$ (**1**) obtained by recrystallization of $\textit{n}\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ in non coordinating solvent are reported.

The crystals of (**1**) are built up by neutral centrosymmetric dinuclear $[\textit{n}\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$ units and CH_2Cl_2 crystallization molecules in the ratio 1:1. The Rh ion of one $\textit{n}\text{-PrRh}(\text{DH})(\text{DBPh}_2)$ unit achieves hexacoordination by coordination of one of the oxime O atoms of the other unit. The formation of the dimer by recrystallization of $\textit{n}\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ in non coordinating solvent may be ascribed to the concomitant effect of the weak metal–water bond in the monomeric aqua complex, the strong tendency of Rh to achieving hexacoordination in such organo derivatives, and the ease of losing a BPh_2 bridge of the diphenylborylated organorhodoximes.

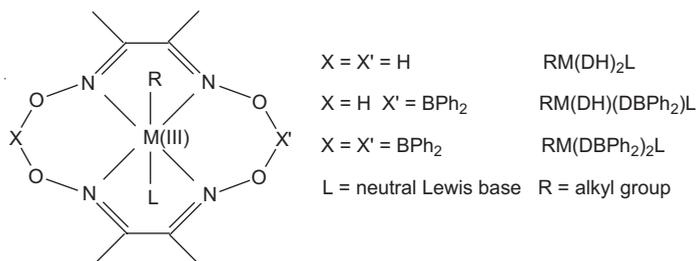
Key words: organorhodoximes, organocobaloximes, borylated, aqua-derivatives, dinuclear, synthesis, structure.

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

In order to study the electronic and the steric influence of the macrocyclic equatorial ligands on the axial fragment, particularly on the Co–C bond, in simple vitamin B₁₂ models such as cobaloximes, we have recently reported a series of Co(III) and Rh(III) organometallic complexes containing modified bis(dimethylglyoximato) ligands, in which either one or both of the H atoms of the oxime bridge have been replaced by diphenylboryl, BPh₂, groups (Scheme 1).¹



Scheme 1.

These ligands should provoke significant changes in the electronic density at the metal centre with respect to the parent (DH)₂ derivatives, as well as allow the study of the steric / electronic interactions between the axial ligands and the boron side phenyl groups, in a way similar to that carried out on octahedral Fe(II) derivatives having the (DBPh₂)₂ equatorial ligand.² When L = N-MeIm or py both mono and diborylated derivatives have been isolated and the complexes can be formulated as RM(III)(DH)_{2-n}(DBPh₂)_nL, with *n* = 1 or 2, M = Co or Rh.¹ The diborylated Rh derivatives are less stable in solution than the Co ones; the difference has been explained in terms of the strain imposed on the equatorial coordination angles by the BPh₂ ring closure, which is significantly larger in Rh than in Co derivatives.^{1b}

With the aim of investigating the influence of the neutral L ligand on the stability of this class of compounds, we have studied those having L = H₂O. Aquaderivatives were chosen for two reasons: i) the small bulk of H₂O ii) the weak coordinating ability of H₂O to the metal centre, as it has been shown by the substitution of water by methanol when CH₃Co(DBPh₂)₂(H₂O) was recrystallized from the latter solvent.^{1c}

We report here the synthesis and the characterization of a series of RM(DBPh₂)₂(H₂O) complexes (M = Co and Rh) and the X-ray structure of the dinuclear [*n*-PrRh(DH)(DBPh)₂]₂ obtained by recrystallization of *n*-PrRh(DBPh₂)₂(H₂O) in non coordinating solvent.

EXPERIMENTAL

Syntheses

$\text{RCo}(\text{DH})_2(\text{H}_2\text{O})$,³ $\text{RRh}(\text{DH})_2(\text{H}_2\text{O})$,⁴ $\text{MeCo}(\text{DBPh}_2)_2(\text{H}_2\text{O})$,^{1c} and $\text{MeRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ ^{1b} have been synthesized as previously described. Solvent and reagents were commercially purchased and were used without further purification. ^1H and ^{13}C spectra were recorded on a Jeol EX-400 (^1H at 400 MHz and ^{13}C at 100.4 MHz) from CDCl_3 solutions with TMS as internal standard.

$\text{RM}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ ($M = \text{Co}$, $R = \text{Me}$, Et , $n\text{-Pr}$, $n\text{-Bu}$, $\text{trans-}\beta\text{-Sty}$, Ph ; $M = \text{Rh}$, $R = \text{Me}$, Et , $n\text{-Pr}$, $i\text{-Pr}$)

0.1 g of the corresponding $\text{RM}(\text{DH})_2(\text{H}_2\text{O})$ was suspended in about 50 ml of CH_2Cl_2 saturated with water; then acetone was added until dissolution. Diphenylborinic anhydride in molar ratio 3:1 with complex was added to the solution, which was heated for one day at 30–32 °C for the alkyl cobalt derivatives and at 40 °C for the remaining complexes. Partial evaporation of the solvent afforded the products, which are red for $M = \text{Co}$ and yellow for $M = \text{Rh}$. All the complexes were recrystallized from $\text{CH}_2\text{Cl}_2/i\text{-PrOH}$. ^1H NMR spectra and elemental analyses are reported in Table I.

$[\text{n-PrRh}(\text{DH})(\text{DBPh}_2)]_2$

$[\text{n-PrRh}(\text{DH})(\text{DBPh}_2)]_2$ was obtained by recrystallization of $n\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ from $\text{CH}_2\text{Cl}_2/n\text{-heptane}$ and was characterized by the X-ray structural analysis.

$\text{MeCo}[(\text{DH})(\text{DBPh}_2)]\text{BPh}_2(\text{OH}) \cdot \text{CH}_2\text{Cl}_2$

0.1 g of $\text{MeCo}(\text{DH})_2 \cdot \text{H}_2\text{O}$ (0.3 mmol) was dissolved in 100 ml of anhydrous CH_2Cl_2 and treated with 0.4 g of diphenylborinic anhydride (1.2 mmol). The solution was refluxed for two days. Partial evaporation of the solvent afforded the product as orange powder. NMR spectra shows the presence of CH_2Cl_2 in a ratio about 1:1 with the complex.

^1H NMR (CDCl_3) δ/ppm : 1.1 (s, 3H, CH_3 ax), 2.33 (s, 6H, $\text{CH}_3\text{C}=\text{NOH}$), 2.54 (s, 6H, $\text{CH}_3\text{C}=\text{NOBPh}_2$), 7.0–8.3 (m, 20H, aromatic H). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3) δ/ppm : 13.3 ($\text{CH}_3\text{C}=\text{NOH}$), 13.6 ($\text{CH}_3\text{C}=\text{NOBPh}_2$), 157.2 ($\text{CH}_3\text{C}=\text{NOH}$), 157.5 ($\text{CH}_3\text{C}=\text{NOBPh}_2$).

Anal. Calcd. for $\text{C}_{34}\text{H}_{39}\text{N}_4\text{O}_5\text{B}_2\text{Cl}_2\text{Co}$ ($M_r = 735.1$): C, 55.5; H, 5.3; N, 7.6%; found: C, 55.6; H, 5.2; N, 7.4%.

Data Collection and Refinement of $[\text{n-PrRh}(\text{DH})(\text{DBPh}_2)]_2$

Small yellow crystals of $0.07 \times 0.07 \times 0.10$ mm, suitable for X-ray structural investigations, were obtained by slow diffusion of $n\text{-heptane}$ into solutions of $n\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ in dichloromethane. Unit-cell constants were determined from the geometric parameters of 25 well-centered reflections with θ values in the range 11–15. X-ray intensities were recorded on an Enraf-Nonius CAD4 diffractometer using monochromatized $\text{Mo-K}\alpha$ radiation. A total of 5351 unique reflections were collected in the range $4 < 2\theta < 52^\circ$ using the ω - 2θ scan technique. Lorentz polarization were applied. No absorption correction was applied because of the small size of the crystal. Only 1658 reflections having $I > 2\sigma(I)$ were considered observed and used in the structure analysis. The small number of collected reflections is due to the small

TABLE I

¹H NMR spectra and elemental analyses of complexes RM(DBPh₂)₂(H₂O)

Complex	¹ H NMR (CDCl ₃) δ/ppm	Calculated	Found
EtCo(DBPh ₂) ₂ (H ₂ O)	012 (t, 3H, CH ₃ ax), 1.85 (m, 2H, H of αC), 2.53 (s, 12H, CH ₃ eq), 7.00–7.50 (m, 20 H, aromatic H)	C ₃₄ H ₃₉ N ₄ O ₅ B ₂ Co (<i>M_r</i> = 664.2): C, 61.5; H, 5.9; N, 8.4%	C, 61.1; H, 5.8; N, 8.1%
<i>n</i> -PrCo(DBPh ₂) ₂ (H ₂ O)	0.71 (t, 3H, CH ₃ ax), 0.89 (m, 2H, H of βC), 1.66 (m, 2H, H of αC), 2.54 (s, 12H, CH ₃ eq), 7.00–7.50 (m, 20 H, aromatic H)	C ₃₅ H ₄₁ N ₄ O ₅ B ₂ Co (<i>M_r</i> = 678.3): C, 62.0; H, 6.1; N, 8.3%	C, 61.6; H, 6.4; N, 7.8%
<i>n</i> -BuCo(DBPh ₂) ₂ (H ₂ O)	0.8 (t, 3H, CH ₃ ax), 1.7 (m, 2H, H of αC), 2.52 (s, 12H, CH ₃ eq), 7.–7.5 (m, 20 H, aromatic H)	C ₃₆ H ₄₃ N ₄ O ₅ B ₂ Co (<i>M_r</i> = 692.3): C, 62.5; H, 6.3; N, 8.1%	C, 61.8; H, 6.5; N, 7.7%
<i>Trans</i> -β-StyCo(DBPh ₂) ₂ - (H ₂ O)	2.47 (s, 12H, CH ₃ eq), 6.28 (d, 1H, H of αC), 6.38 (d, 1H, H of βC), 7.0–7.6 (m, 25 H, aromatic H)	C ₄₀ H ₄₁ N ₄ O ₅ B ₂ Co (<i>M_r</i> = 738.3): C, 65.1; H, 5.6; N, 7.6%	C, 64.1; H, 5.5; N, 7.6%
PhCo(DBPh ₂) ₂ (H ₂ O)	2.42 (s, 12H, CH ₃ eq), 6.9–7.63 (m, 25 H, aromatic H)	C ₃₈ H ₃₉ N ₄ O ₅ B ₂ Co (<i>M_r</i> = 712.3): C, 64.1; H, 5.5; N, 7.9%	C, 64.0; H, 5.5; N, 7.8%
EtRh(DBPh ₂) ₂ (H ₂ O)	0.50 (t, 3H, CH ₃ ax), 1.42 (q, 2H, H of αC), 2.49 (s, 12H, CH ₃ eq), 7.0–7.5 (m, 20 H, aromatic H)	C ₃₄ H ₃₉ N ₄ O ₅ B ₂ Rh (<i>M_r</i> = 708.2): C, 57.7; H, 5.5; N, 7.9%	C, 57.2; H, 5.5; N, 8.0%
<i>n</i> -PrRh(DBPh ₂) ₂ (H ₂ O)	76 (t, 3H, CH ₃ ax), 1.06 (m, 2H, H of αC), 1.26 (m, 2H, H of βC), 2.50 (s, 12H, CH ₃ eq), 7.00–7.51 (m, 20H, aromatic H)	C ₃₅ H ₄₁ N ₄ O ₅ B ₂ Rh (<i>M_r</i> = 722.3): C, 58.2; H, 5.7; N, 7.7%	C, 57.5; H, 5.8; N, 7.8%
<i>i</i> -PrRh(DBPh ₂) ₂ (H ₂ O)	0.73 (t, 3H, CH ₃ ax), 2.49 (s, 12H, CH ₃ eq), 7.0–7.8 (m, 20H, aromatic H)	C ₃₅ H ₄₁ N ₄ O ₅ B ₂ Rh (<i>M_r</i> = 722.3): C, 58.2; H, 5.7; N, 7.7%	C, 57.3; H, 5.4; N, 7.8%

dimension of the used crystal. Unfortunately, attempts to obtain larger crystals failed. The structure was solved by the Patterson and Fourier methods and refined by the full-matrix least-squares technique, for all non-hydrogen atoms. Because of the small number of reflections, only Rh and Cl of the CH_2Cl_2 crystallization molecule were refined anisotropically and the remaining non H atoms were refined isotropically. Hydrogen atoms were not refined but included at calculated positions in the final refinement. In the last cycle, 166 variable parameters were refined and the final conventional R factor was 0.092.

The difference Fourier map revealed no chemically significant residual electron density. All calculations were carried out using SHELX program package.⁵ Crystal data and refinement details are reported in Table II. Selected bond lengths and angles are reported in Table III. Complete tables of atomic parameters and bond lengths and angles are included as Supporting Information.

TABLE II
Crystal data and structure refinement for 1

Identification code	[<i>n</i> -PrRh(DH)(DBPh ₂) ₂]	
Empirical formula	C ₂₃ H ₂₈ BN ₄ O ₄ Rh · 0.85 CH ₂ Cl ₂	
Formula weight	610.40	
Temperature	293(2) K	
Wavelength	0.71100 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 11.006(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 15.953(5) Å	$\beta = 108.21(2)^\circ$
	<i>c</i> = 16.410(5) Å	$\gamma = 90^\circ$
Volume	2737.0(14) Å ³	
Density (calculated)	1.512 Mg/m ³	
Absorption coefficient	0.856 mm ⁻¹	
<i>F</i> (000)	1266	
Crystal size	0.07 x 0.07 x 0.1 mm	
Theta range for data collection	2.10 to 25.98°	
Index ranges	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 19, -20 ≤ <i>l</i> ≤ 19	
Reflections collected (unique)	5351	
Independent reflections	1658 [<i>I</i> > 2σ(<i>I</i>)]	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	5351 / 2 / 166	
Goodness-of-fit on <i>F</i> ²	1.121	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.092, <i>wR</i> 2 = 0.1898	
<i>R</i> indices [<i>I</i> > 3σ(<i>I</i>)]	<i>R</i> 1 = 0.065	
Largest diff. peak and hole	1.011 and -1.005 e Å ⁻³	
<i>R</i> 1 = $S \sum F_o - F_c / S \sum F_o $	<i>wR</i> 2 = $[S w(F_o^2 - F_c^2)^2 / S w(F_o^2)^2]^{1/2}$	

TABLE III
Selected bond lengths /Å and angles /° for **1**

Bond lengths /Å			
Rh–N(1)	1.954(13)	O(1)–N(1)	1.40(2)
Rh–N(2)	1.984(13)	O(1)–B(1)	1.51(2)
Rh–N(3)	1.964(13)	O(2)–N(3)	1.34(2)
Rh–N(4)	1.968(13)	O(2)–B(1)	1.54(2)
Rh–C(21)	2.099(16)	O(3)–N(2)	1.39(2)
Rh–O(4)#1	2.297(11)	O(4)–N(4)	1.38(2)
Bond angles /°			
N(1)–Rh–N(2)	76.8(5)	N(1)–O(1)–B(1)	116.1(13)
N(1)–Rh–N(3)	98.4(6)	N(3)–O(2)–B(1)	114.4(12)
N(1)–Rh–N(4)	176.1(6)	N(4)–O(4)–Rh#1	106.4(8)
N(1)–Rh–C(21)	86.7(6)	C(2)–N(1)–O(1)	116.9(13)
N(1)–Rh–O(4)#1	96.8(5)	C(2)–N(1)–Rh	122.3(11)
N(2)–Rh–N(3)	172.1(5)	O(1)–N(1)–Rh	120.3(10)
N(2)–Rh–N(4)	105.7(5)	C(3)–N(2)–O(3)	119.8(13)
N(2)–Rh–C(21)	88.1(6)	C(3)–N(2)–Rh	117.3(11)
N(2)–Rh–O(4)#1	91.0(4)	O(3)–N(2)–Rh	122.8(9)
N(3)–Rh–N(4)	78.8(6)	C(6)–N(3)–O(2)	120.0(13)
N(3)–Rh–C(21)	85.4(6)	C(6)–N(3)–Rh	114.7(11)
N(3)–Rh–O(4)#1	95.8(5)	O(2)–N(3)–Rh	123.0(10)
N(4)–Rh–C(21)	90.3(6)	C(7)–N(4)–O(4)	122.9(14)
N(4)–Rh–O(4)#1	86.3(5)	C(7)–N(4)–Rh	118.6(12)
C(21)–Rh–O(4)#1	176.0(5)	O(4)–N(4)–Rh	118.5(9)

Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y-1, -z+1$.

RESULTS

Studies in Solution

As it was previously reported for the methyl derivatives of both Co and Rh,^{1b, 1c} only the diborylated derivatives were isolated when the neutral axial base was water, even if the synthesis was carried out in the presence of a less than equimolar amount of diphenylborinic anhydride. Furthermore, ¹H NMR spectra provided no evidence of the formation of monoborylated derivatives in solution.

It is interesting to note that authentic RCo(DBPh₂)₂(H₂O) and RRh(DBPh₂)₂(H₂O) were obtained by reacting the corresponding aquacobaloximes and aquarhodoximes with diphenylborinic anhydride in CH₂Cl₂/ace-

tone mixtures saturated with water. Non coordinating solvent without water addition led to species containing one BPh_2 bridge in the equatorial ligand and a molecule of $\text{B(Ph)}_2(\text{OH})$ (probably arising from the dissociation of diphenylborinic anhydride) coordinated *trans* to R. In the case of methylcobaloxime the complex $\text{CH}_3\text{Co}[(\text{DH})(\text{DBPh}_2)]\text{BPh}_2(\text{OH}) \cdot \text{CH}_2\text{Cl}_2$ was isolated and characterized by ^1H and ^{13}C NMR spectroscopy. Both the CH_3 protons and the CH_3 and $\text{C}=\text{N}$ carbons of the equatorial ligand gave two well separated signals; one of which, at higher frequency, was assigned to the nuclei on the boron bridge side and the other, at lower frequency, to the nuclei on the hydrogen bond side. Integration of the aromatic protons confirms the presence of $\text{B(Ph)}_2(\text{OH})$. Unfortunately, the crystals are not stable enough to allow structural characterization. The analogous Rh compound has not been isolated but its formation in CDCl_3 solutions has been previously reported.^{1b}

If the aquacomplexes were recrystallised from methanol, the axial water was replaced by a molecule of the solvent.

All the attempts to obtain single crystals of the octahedral aquacomplexes failed; when $n\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ was recrystallized from $\text{CH}_2\text{Cl}_2/n\text{-heptane}$, single crystals of the dimer $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$ (1) were recovered.

X-ray Structure of $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$

The crystals of (1) are built up by neutral centrosymmetric dinuclear $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$ units (Figure 1) and CH_2Cl_2 crystallization molecules in the ratio 1:1. The Rh ion of one $n\text{-PrRh}(\text{DH})(\text{DBPh}_2)$ unit achieves hexacoordination by coordination of one of the oxime O atoms of the other unit. The distorted octahedral coordination is characterized by Rh–N equatorial distances in the range 1.95(1) to 1.98(1) Å (Table II). The Rh–C axial distance is 2.10(2) Å, close to the value of 2.079(2) reported for $\text{EtRh}(\text{DH})_2\text{py}$,⁶ and the *n*-propyl ligand assumes a zig-zag conformation with a torsion angle N4-Rh-C21-C22 of $-42.8(16)^\circ$ (Figure 1). The long Rh–O4' distance of 2.297(11) Å is not far from the Cu–O' distances reported for similar dimeric species $[\text{Cu}(\text{dioximato})]_2$, which vary from 2.242(3) to 2.301(3) Å.⁷ The four equatorial N donors are coplanar within ± 0.03 Å and the Rh atom is displaced by 0.07 Å out of their mean plane towards the axial O4' donor. The Rh, N4, O4, Rh', N4', O4' ring has an approximate chair conformation (Figure 1), with N4 and N4' displaced by ± 0.8 Å out of the plane of the other four atoms. The Rh...Rh distance is 4.004(5) Å, not far from those reported⁷ for dimeric Cu analogues, where it ranges from 3.825(1) to 3.909 Å. The N1, C2, C3, N2 ring is nearly coplanar with the four N donor plane [$5.0(7)^\circ$] but makes a dihedral angle of $20(2)^\circ$ with the N3, C6, C7, N4 ring, which in

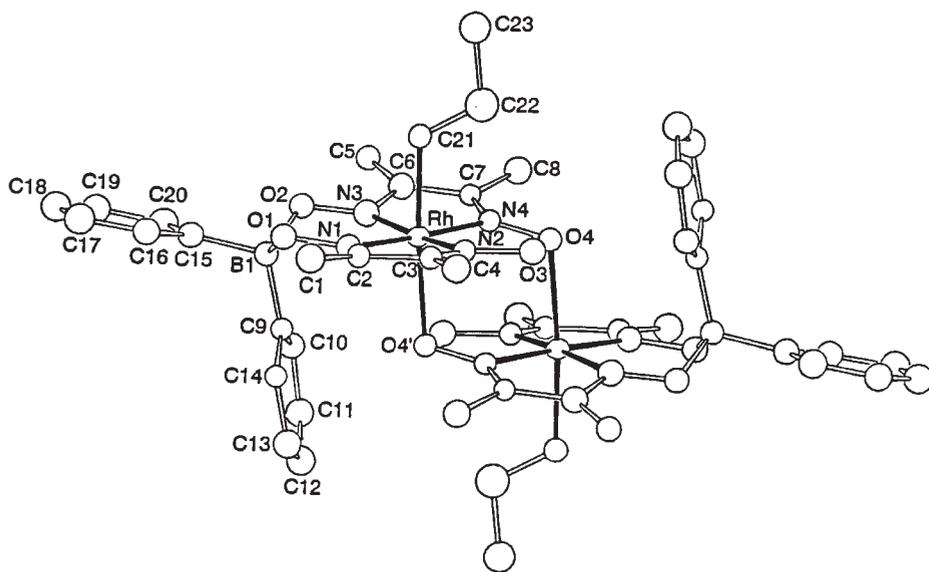


Figure 1. ORTEP drawing with a numbering scheme for the non hydrogen atoms of $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)]_2$.

turn make an interplanar angle of $15(3)^\circ$ with that of the equatorial donors. Thus, the $\text{Rh}(\text{DH})(\text{DBPh}_2)$ unit adopts a strongly asymmetric umbrella shape bending towards the alkyl ligand. The $\text{O3} \cdots \text{O4}$ distance of the oxime bridge of $2.88(2) \text{ \AA}$ is about 0.2 \AA longer than those found in $\text{RRh}(\text{DH})_2\text{py}$ complexes⁶ and 0.3 \AA longer than the $\text{O1} \cdots \text{O2}$ distance of $2.56(2) \text{ \AA}$ on the side of B bridge. These figures are similar to those found in the monomeric $\text{MeRh}(\text{DH})(\text{DBPh}_2)(\text{N-MeIm})$, where they are $2.729(5)$ and $2.577(5) \text{ \AA}$, respectively.^{1b} As a consequence, the N1-Rh-N3 and N2-Rh-N4 coordination angles have significantly different values of $98.4(6)$ and $105.7(5)^\circ$, respectively. Since in $\text{RRh}(\text{DH})_2\text{L}$ ⁶ those angles are nearly equal and average $104.0(1)^\circ$, it is confirmed that the B ring closure requires a significant squeeze of the corresponding N-Rh-N angle.

DISCUSSION

Dimers similar to **1** have been isolated and structurally characterized previously for $\text{Cu}(\text{II})(\text{DH})_2$ complexes⁷ but not for $\text{Rh}(\text{III})$ or $\text{Co}(\text{III})$, although the formation of $[\text{MeCo}(\text{DH})_2]_2$ species has been proposed to explain the temperature dependence of ^1H NMR spectra in non coordinating solvent.⁸ In the present case, the formation of the dimer starting from *n*-

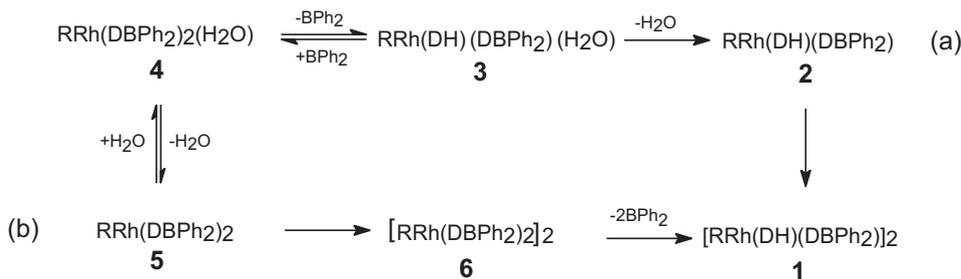
$\text{PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ in non coordinating solvent may be ascribed to the concomitant effect of the ease of losing the BPh_2 bridge in Rh derivatives, the weak metal–water bond in the monomeric aqua complex, and the strong tendency of Rh to achieving hexacoordination in such organo derivatives.

In fact, although the second boryl bridge is quite stable in the Rh aqua derivatives (monoborylated derivatives have not been observed yet), probably owing to the scarce steric bulk of the water molecule, in the N-MeIm derivative the boryl bridge closure requires a significant squeeze of the corresponding N–Rh–N angles, which possibly destabilizes the complexes with $n = 2$ with respect to those with $n = 1$.^{1b} A similar distortion is observed in **(1)** and may account for the dissociation of one boryl bridge.

Weak bonding of water in these complexes is suggested by its easy replacement both by $\text{B}(\text{Ph})_2(\text{OH})$ and by CH_3OH . The recent finding that the $\text{Co}-\text{H}_2\text{O}$ bond is longer in $\text{CH}_3\text{Co}(\text{DBF}_2)_2(\text{H}_2\text{O})$ than in the parent methylcobaloxime supports the hypothesis that the insertion of boryl bridges weakens the binding of the axial water.⁹

The tendency to maintaining hexacoordination has been shown to be particularly enhanced in alkylrhodoximes even when compared to alkylcobaloximes, whose stable pentacoordinate species have not been reported so far.¹⁰

On the basis of the above considerations, two alternative paths (Scheme 2) leading to the formation of the dimeric species **1**, starting from the parent $\text{RRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ complex in non coordinating solvent can be proposed.



Scheme 2.

In the first hypothesis (Scheme 2a), the diborylated aqua complex loses one BPh_2 group, giving species **3**. In **3** the weakly bound H_2O is lost, giving the pentacoordinated species **2** which easily dimerizes in the absence of coordinating ligands owing to the strong tendency of Rh to achieve hexacoordination.

In the alternative path (Scheme 2b), the diborylated aqua complex loses the axial water and then dimerizes to maintain hexacoordination, forming dimer **6**, similar to that of Figure 1, but highly crowded owing to the presence of two BPh₂ bridges. This crowding causes dissociation of one boryl bridge in both of the equatorial ligands. The second path appears to be more plausible because of the weak binding of the axial water and the relative stability of the second boryl bridge in the aquaderivatives.

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SAŽETAK

Slaba veza između metala i molekule vode u organoakvakobaloksimima i rodoksimima s difenilborilnim ogrankom dovodi do stvaranja neuobičajenog dinuklearnog kompleksa Rh(III)

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U radu se izvješćuje o pripravi i potankom opisu niza kompleksa opće formule $\text{RM}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ ($\text{M} = \text{Co}$ ili Rh) i o molekulskoj i kristalnoj strukturi dinuklearnog $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)_2]$ (**1**) pridobivenog rekristalizacijom $n\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ iz nekoordinirajućeg otapala. Kristali spoja (**1**) izgrađeni su od neutralnih dinuklearnih jedinaka $[n\text{-PrRh}(\text{DH})(\text{DBPh}_2)_2]$ koje posjeduju kristalografsku simetriju centra inverzije i molekule kristalizacijskog metilen-klorida u omjeru 1:1. Atom rodija jedne jedinke $n\text{-PrRh}(\text{DH})(\text{DBPh}_2)_2$ postiže koordinacijski broj 6 koordiniranjem jednog od oksimskih atoma kisika druge jedinke. Nastajanje dimera rekristalizacijom $n\text{-PrRh}(\text{DBPh}_2)_2(\text{H}_2\text{O})$ iz nekoordinirajućeg otapala može se opisati istodobnim učinkom slabe veze ostvarene između atoma metala i molekule vode u monomernom akvakompleksu, jakom težnjom Rh za postizanjem koordinacijskog broja 6 u takovim organskim derivatima i lakoćom kojom difenilborilni most napušta organorodoksime.