

# Self-Assembly of Cobaloximes and Rhodoximes with 3-Aminophenylboronic Acid: A Molecular Triangle and a Polymer

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The reactions of methylaquacobaloxime and ethylaquacobaloxime with 3-aminophenylboronic acid in water produce supramolecular triangles **3a** and **3b** respectively, through the reaction of boron with the oxime oxygens of the alkylcobaloxime and the coordination of pyridine to cobalt. The reaction is reversible and strongly pH dependent. The complexes **3a** and **3b** precipitate immediately from the solution at pH 7, but dissolve quickly at both acidic (below 4) and basic (above 9) pH values. The aggregates are re-formed by readjusting the pH to neutrality and the precipitation-dissolution cycle may be repeated several times without an apparent decrease in yield. The complexes were fully characterised by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The X-ray structure shows that the neutral chiral supramolecule **3a** is a triangle of cobalt atoms

with an approximate C<sub>3</sub> symmetry. The side of the triangle is about 9.5 Å. The ring closure is ensured by the torsion angles around the B–C and C–NH<sub>2</sub> bonds, which vary in the range 25–30° and 97–109°, respectively. The reaction of methylaquarhodoxime with 3-aminophenylboronic acid in water at pH 7 results in the displacement of H<sub>2</sub>O by 3-aminophenylboronic acid only. The polymeric form **4** precipitates from CD<sub>3</sub>OD in the NMR tube with time. The X-ray structure shows that **4** is a polymeric species with a zig-zag chain arrangement, with Rh...Rh distances of 9.2 Å. The chain arrangement is characterized by torsion angles around the B–C and C–NH<sub>2</sub> bonds of 61° and 92°, respectively. (© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

## Introduction

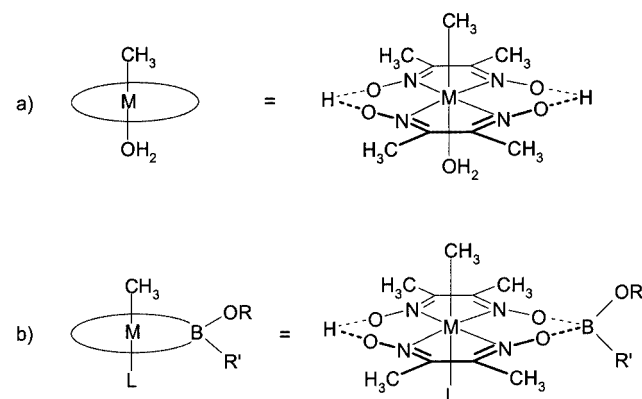
Use of the metal-ligand interaction to form inorganic supramolecules from mononuclear building blocks is a rapidly developing field in supramolecular chemistry.<sup>[1]</sup> Transition metal-directed self-assembly has been used to construct a large variety of molecular polygons and polyhedra, but molecular triangles with metal ions in vertex positions are still relatively rare, mainly due to the impossibility of generating the required 60° angle in a metal fragment of common coordination number. The majority of molecular triangles with metal ions at the corners are based on the square-planar geometry of Pt<sup>II</sup> and Pd<sup>II</sup> complexes<sup>[2]</sup> and display right-angled vertices. The closure of the triangle is made possible by ligands with appropriate coordinate vectors or by rather flexible ligands. The latter approach often results in low yields, owing to the formation of equilibrium mixtures, in which larger species, typically squares, are also present.<sup>[1]</sup> We report here the selective formation, in high yield, of neutral supramolecular triangles by reaction of octahedral organoaquacobaloximes with 3-aminophenylboronic

acid. Furthermore, we show that changing the metal atom from Co to Rh causes a dramatic change in the structure and an inorganic polymer is formed.

## Results and Discussion

### Synthesis

Alkylaquabis(dimethylglyoximates) of Co<sup>III</sup> (alkylaquacobaloximes, Scheme 1) have already been shown to be suit-

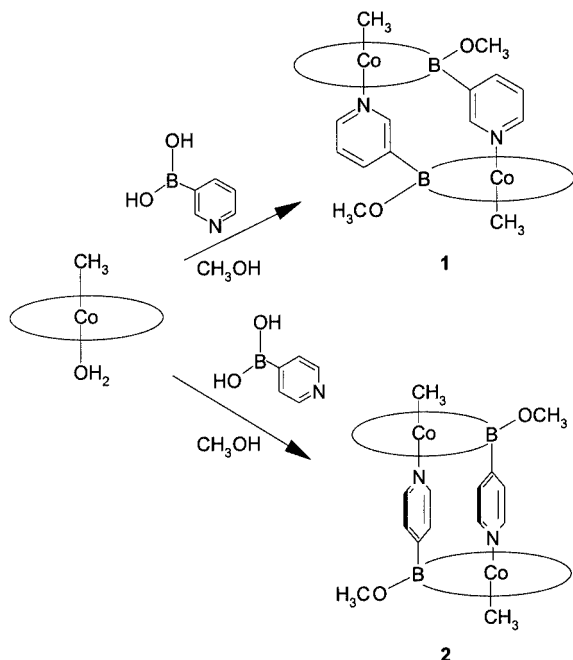


Scheme 1. Structural (right) and schematic (left) representation of a) alkylaquabis(dimethylglyoximate) (M = Co, Rh); b) monoborylated alkylbis(dimethylglyoximate)

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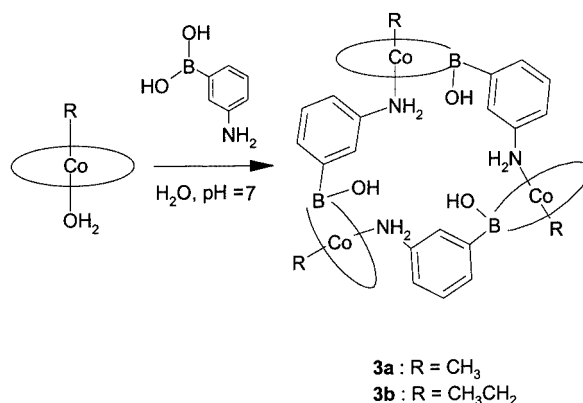
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able for self-assembly with functionalized arylboronic acids, such as 3- and 4-PyB(OH)<sub>2</sub>.<sup>[3]</sup> In fact, similar to *cis*-diols,<sup>[4]</sup> the oxime bridges are very reactive towards boronic acids and the axial water ligand can easily be replaced by the pyridinyl group. The reaction of methylaquacobaloxime with 3-pyB(OH)<sub>2</sub> gives cyclic dimer **1**, with coplanar pyridinyl moieties, whereas the reaction with 4-pyB(OH)<sub>2</sub> gives cyclic dimer **2**, with parallel pyridinyl rings (Scheme 2). The reactions are strongly pH dependent, because the formation of the dinuclear species **1** and **2** requires the neutral (or zwitterionic) form of the boronic acid.<sup>[3b]</sup>



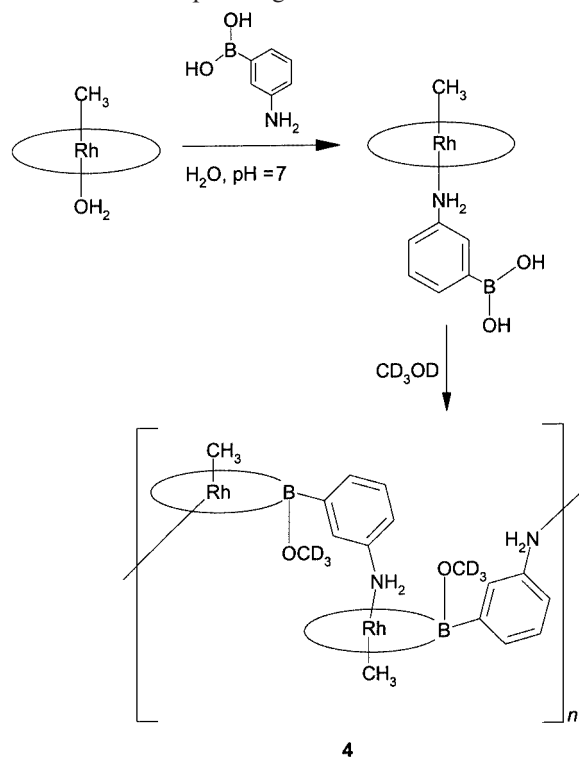
Scheme 2

The macroscopic *pK<sub>a</sub>* values for the first and the second deprotonation of the 3-aminophenylboronic acid, determined by spectrophotometric titration, are 9.14 and 4.56, respectively. These values suggest, by analogy with the reactions with pyridinylboronic acids, that self-assembly should occur within this pH range. Indeed, when the pH of an aqueous solution of organoquacobaloxime containing 3-aminophenylboronic acid is slightly less than an equimolar amount is adjusted to about 7, complexes **3a** and **3b** precipitate immediately from the solution (Scheme 3). Further acidification of the solution to below pH 4 results in the dissolution of the precipitate. The aggregate is re-formed by restoring the pH of the solution back to neutrality and is redissolved at alkaline pH values (above pH 9). The precipitation/dissolution cycle may be repeated at least twenty times without an apparent decrease in yield. The same trimer **3a** can be synthesized in methanol, without esterification of the B(OH) groups, provided the reagent concentration is sufficiently high to induce an immediate precipitation. If the precipitation occurs after a longer time, or if the precipitate is left in contact with the solution, the <sup>1</sup>H NMR spectrum shows a mixture of several products.



Scheme 3

The reaction of [CH<sub>3</sub>Rh(DH)<sub>2</sub>H<sub>2</sub>O] with 3-aminophenylboronic acid in water at pH 7 (Scheme 4) results in the displacement of H<sub>2</sub>O by 3-aminophenylboronic acid only, as suggested by an incomplete X-ray structural analysis and by the <sup>1</sup>H NMR spectrum in CD<sub>3</sub>OD. The polymeric form **4** precipitates from CD<sub>3</sub>OD in the NMR tube with time (Scheme 3). A <sup>1</sup>H NMR study in D<sub>2</sub>O of a solution containing [CH<sub>3</sub>Rh(DH)<sub>2</sub>H<sub>2</sub>O] and 3-aminophenylboronic acid in equimolar amounts does not give any evidence of a condensation reaction between the oxime bridge and the boronic acid in the pH range 9.5–0.6.



Scheme 4

#### X-ray Structure Determination of **3a**

The structure of one enantiomer of the racemic crystal of **3a** is depicted in Figure 1. The molecule has an approx-

imate  $C_3$  symmetry, with the threefold axis perpendicular to the plane of the cobalt atoms. Each B–OH group makes an intramolecular H-bond with the amino group coordinated to Co (Figure 1), with relatively short  $\text{NH}\cdots\text{O}$  distances in the range 2.95(1)–3.04(1) Å. The conformational freedom of B and the torsion around the Co–NH<sub>2</sub> bond are thereby “frozen”, so that the structure is essentially defined by the values of the torsion angles around the B–C and C–NH<sub>2</sub> bonds, which have very similar values in the three independent units. The torsion angles HO–B–C–C <sub>$\alpha$</sub>  and Co–NH<sub>2</sub>–C–C <sub>$\alpha$</sub>  (where C <sub>$\alpha$</sub>  = C40, C46, and C52, Figure 1) vary in the ranges 25–30° and 97–109°, respectively. The mean plane of the three carbon atoms of the methyl groups, each from one bis(dimethylglyoximate) moiety, is nearly parallel to that of the Co triangle [at an interplanar distance of 1.35(1) Å]. The Co plane is 1.76 Å from the approximately parallel mean plane of the O atoms of the boron OH groups. Therefore, one side of **3a** is hydrophilic (OH groups), while the other side is hydrophobic. A water molecule (O2W) is H-bonded to the three boron OH groups at distances in the range 2.82(1)–2.85(1) Å (Figure 1) and lies approximately at the mid-point of the three hydroxyl O atoms. It is interesting to note that the trimer/OW2 aggregates are held together by a network of H-bonds between the (OH)<sub>3</sub>···OW2 grouping of one aggregate and that of the neighbouring aggregate, related by a crystallographic twofold axis along  $z$  (at  $x = 1/2$ ,  $y = 1/4$ ). Figure 2 shows the H-bond network, with O···O distances in the

range 2.82–3.02 Å. Two distributions of the H atoms with half occupancy, related by the twofold axis, are represented. Each O atom has a distorted tetrahedral arrangement with four O···O H-bonds around OW2 and with two O···O, one NH···OH, and one O–B bond around each O atom of the boron (OH) groups.

### Characterization of **3a** and **3b** by NMR Spectroscopy

The <sup>1</sup>H NMR spectrum of **3a** in CDCl<sub>3</sub> is in agreement with the trimeric structure of Figure 1. Four signals are observed for the equatorial methyl groups of each cobaloxime moiety, due to the loss of equivalence caused by the self-assembly process. One signal is shifted considerably upfield ( $\delta = 1.39$  ppm) in comparison with the usual range found for alkylcobaloximes.<sup>[5]</sup> This signal has been assigned to the protons on C18, C21 and C31, which lie above the plane of the phenyl rings and in the cone of their magnetic shielding. The protons of the NH<sub>2</sub> groups are diastereotopic and give rise to two doublets, one of which is in the aromatic part of the spectrum and the other in the range  $\delta = 3.0$ –3.5 ppm. The protons on B(OH) and the oximic protons give rise to two singlets at  $\delta = 4.48$  and 18.0 ppm, respectively. In the spectrum of complex **3b**, the methylene protons of the ethyl groups are diastereotopic and give rise to the AB part of an ABM<sub>3</sub> pattern. All the other signals are almost superimposable onto those of **3a**. The strong similarity of the spectra suggests a trimeric structure also for **3b**.

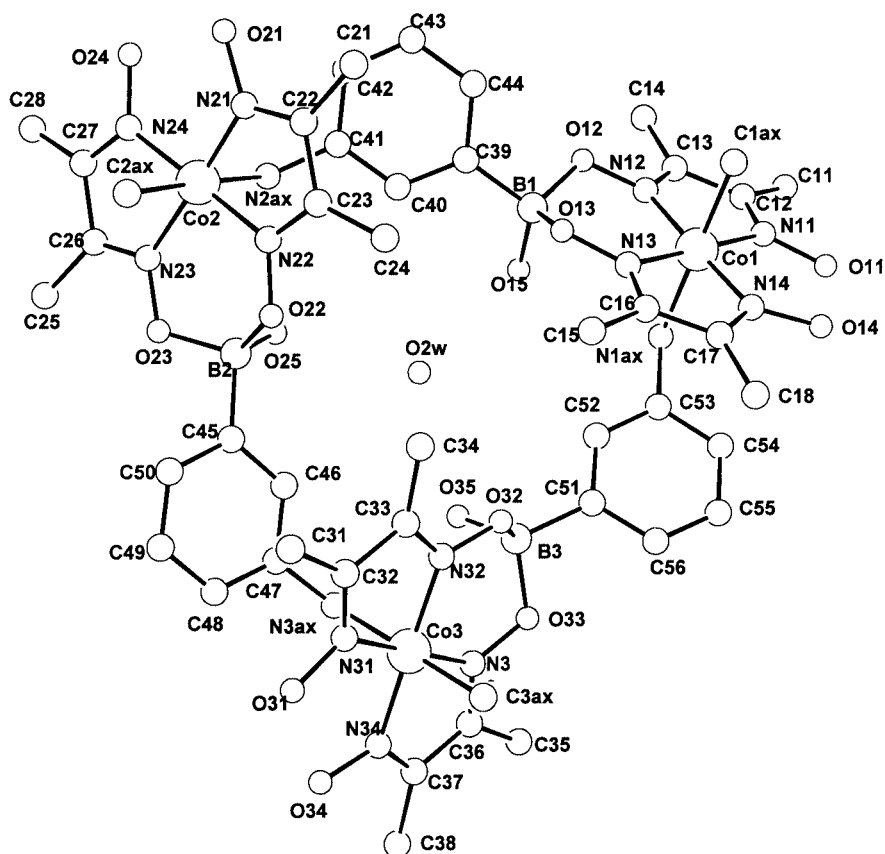


Figure 1. Molecular structure of one enantiomer of **3a**, with the labelling scheme for the atoms

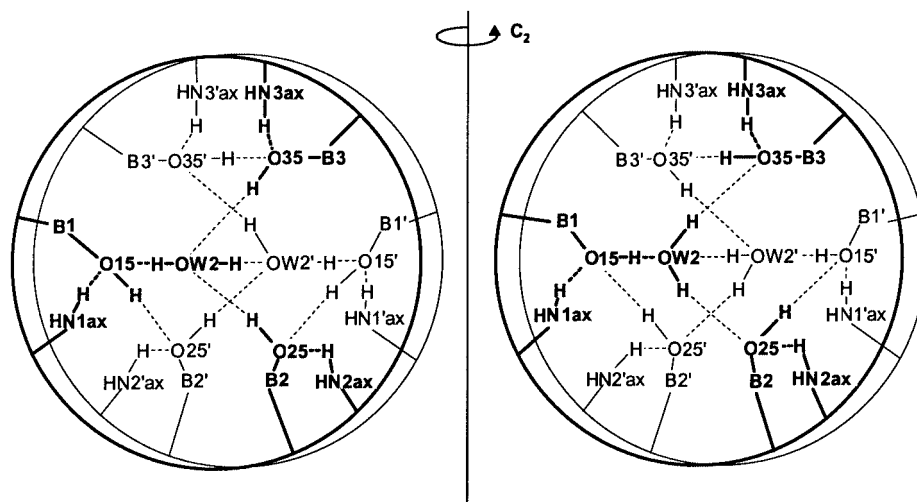


Figure 2. Two H-bond distributions, with half occupancy H atoms, in the network involving OW2 and boron OH groups; the superimposition of the two schemes has  $C_2$  symmetry

The spectra show little variation with concentration (except for the  $\text{NH}_2$  protons) in the range  $2 \times 10^{-2}$  to  $1 \times 10^{-3}$  M or with temperature in the range  $-60$  to  $+50$  °C. Therefore, the trimers are very stable in  $\text{CDCl}_3$  solution and do not coexist in equilibrium with other species, even if a model inspection suggests that a tetranuclear square species is sterically allowed.

#### X-ray Structure Determination of 4

The structure of **4** is shown in Figure 3. In spite of the increase of about 0.1 Å in the coordination distances of rhodoximes with respect to those of the analogous cobaloximes, the local geometry of each unit is very similar to that of the unit in **3a**. An intramolecular H-bond between the coordinated amino group and the axially directed  $\text{OCD}_3$  group, arising from the esterification of  $\text{B}(\text{OH})$  in  $\text{CD}_3\text{OD}$  [ $\text{NH}\cdots\text{OCD}_3$  distance of 2.88(1) Å], is still present. Conformational changes, essentially due to a significant variation in the B–C and C– $\text{NH}_2$  torsion angles with respect to **3a**, lead to the chain arrangement shown in Figure 3, with a Rh $\cdots$ Rh distance of 9.159(4) Å. The O5–B1–C9–C10 and Rh–N5–C11–C12 torsion angles are 61(1) and 92(1)°, respectively. The polymer **4** is too insoluble in non-coordinating solvents to be studied by  $^1\text{H}$  NMR spectroscopy.

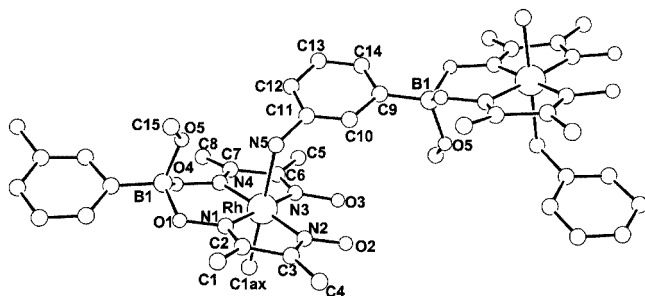


Figure 3. The chain arrangement of the polymeric species **4** with the labelling scheme for the atoms

#### Conclusion

The neutral trimers **3a** and **3b** are one of the few examples of triangular supramolecular structures based on an octahedral metal centre,<sup>[6]</sup> and show some novel elements. The fast assembly/disassembly process is reversible and “triggered” by a pH variation.<sup>[7]</sup> Furthermore, the 3-aminophenylboronic acid does not connect the cobaloxime units through two direct metal-ligand interactions, as occurs in most of the reported triangles.<sup>[1,2]</sup> The connection is created, on one side, by the reaction of the  $\text{B}(\text{OH})_2$  group with the oxime bridge at the periphery of the equatorial ligand and, on the other side, by the coordination of the amino group to cobalt. The chirality of **3** is a consequence of this way of binding. A further consequence of the use of the asymmetric linker is the complete diastereoselectivity in the formation of **3** and **4**. The  $^1\text{H}$  NMR spectra of **3** do not show epimerization even at elevated temperatures ( $\text{CDCl}_3$ , 50 °C).

Methyloquacobaloxime and methyloquarhodoxime give very different products under similar conditions. As both the geometry and the coordination properties of the complexes are very similar, we believe that the relevant point is the esterification of the OH groups in **4**, due to their prolonged contact with deuterated methanol. This hypothesis is supported by evidence that complex **3a** can be recovered from methanol, without esterification of the  $\text{B}(\text{OH})$  groups, but decomposes if left in contact with the solvent for a longer time. Probably, esterification reduces the stabilization arising from the H-bonds between the water molecule (OW2) and the three boron OH groups in the cyclic form **3** (Figure 2). The steric hindrance of  $\text{OCH}_3$  could contribute to prevent the cyclization in **4**.

#### Experimental Section

**General Remarks:** NMR spectra were recorded on a Jeol EX-400 spectrometer ( $^1\text{H}$  at 400 MHz and  $^{13}\text{C}$  at 100.4 MHz) with TMS



as internal standard.  $[\text{CH}_3\text{Co}(\text{DH})_2\text{H}_2\text{O}]$ ,  $[\text{CH}_3\text{CH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}]^{[8]}$  and  $[\text{CH}_3\text{Rh}(\text{DH})_2\text{H}_2\text{O}]^{[9]}$  were prepared according to literature procedures. All other reagents were reagent grade and used without further purification.

**Synthesis of 3a and 3b:** The appropriate alkylaquacobaloxime (0.40 mmol) was dissolved in an aqueous alkaline solution (10 mL) with a pH of about 11 and 3-aminophenylboronic acid (0.37 mmol) was added. After filtration, the pH of the solution was lowered to about 7.0 with concentrated  $\text{HClO}_4$ . A highly insoluble yellow precipitate formed immediately, which was filtered and washed with water. X-ray quality crystals of **3a** were obtained by slow diffusion of a solution of the complex into  $\text{CH}_2\text{Cl}_2$  in *n*-heptane.

**3a:** Yield: 70 mg (40%).  $\text{C}_{45}\text{H}_{75}\text{B}_3\text{Co}_3\text{N}_{15}\text{O}_{18}$  (1323, with  $3\text{H}_2\text{O}$ ): calcd: C 40.8, H 5.71, N 15.8; found C 40.4, H 5.51, N 15.2.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 0.64 (s, 9 H, axial  $\text{CH}_3$ ), 1.39 (s, 9 H, eq.  $\text{CH}_3$ ), 1.90 (s, 9 H, eq.  $\text{CH}_3$ ), 2.13 (s, 9 H, eq.  $\text{CH}_3$ ), 2.27 (s, 9 H, eq.  $\text{CH}_3$ ), 3.26 (d,  $^2J_{\text{H-H}}$  = 8.3 Hz, 3 H,  $\text{NH}_2$ ), 4.48 (s, 3 H, BOH), 6.67 (d,  $^3J_{\text{H-H}}$  = 7.8 Hz, 3 H, ar. H), 6.88 (d,  $^2J_{\text{H-H}}$  = 8.3 Hz, 3 H,  $\text{NH}_2$ ), 7.04 (m, 3 H, ar. H), 7.09 (s, 3 H, ar. H), 7.35 (d,  $^3J_{\text{H-H}}$  = 7.1 Hz, 3 H, ar. H), 18.01 (s, 3 H, OHO) ppm.  $^{13}\text{C}$  NMR (100.4 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 11.46, 12.18, 13.10, 14.60 (equatorial  $\text{CH}_3$ ), 118.74, 124.36, 126.49, 129.44, 137.38 (aromatic carbons), 148.77, 149.62, 154.27, 156.69 (C=N).

**3b:** Yield: 90 mg (50%).  $\text{C}_{48}\text{H}_{81}\text{B}_3\text{Co}_3\text{N}_{15}\text{O}_{18}$  (1365, with  $3\text{H}_2\text{O}$ ): calcd: C 42.2, H 5.98, N 15.4; found C 41.0, H 5.60, N 15.0.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 0.24 (t,  $^3J_{\text{H-H}}$  = 7.6 Hz, 9 H,  $\text{CH}_3$  of ethyl), 1.37 (s, 9 H, eq.  $\text{CH}_3$ ), 1.57 (m,  $^2J_{\text{H-H}}$  = 7.6 Hz, 6 H,  $\text{CH}_2$  of ethyl), 1.87 (s, 9 H, eq.  $\text{CH}_3$ ), 2.09 (s, 9 H, eq.  $\text{CH}_3$ ), 2.26 (s, 9 H, eq.  $\text{CH}_3$ ), 3.38 (d,  $^2J_{\text{H-H}}$  = 8.3 Hz, 3 H,  $\text{NH}_2$ ), 4.47 (s, 3 H, BOH), 6.66 (d,  $^3J_{\text{H-H}}$  = 7.6 Hz, 3 H, ar. H), 6.73 (d,  $^2J_{\text{H-H}}$  = 8.3 Hz, 3 H,  $\text{NH}_2$ ), 7.03 (m, 3 H, ar. H), 7.09 (s, 3 H, ar. H), 7.32 (d,  $^3J_{\text{H-H}}$  = 7.1 Hz, 3 H, ar. H), 17.87 (s, 3 H, OHO) ppm.  $^{13}\text{C}$  NMR (100.4 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 15.83 (axial  $\text{CH}_3$ ), 25.63 (axial  $\text{CH}_2$ ), 11.47, 12.24, 13.20, 14.77 (equatorial  $\text{CH}_3$ ), 118.75, 124.46, 126.56, 129.31, 137.60 (aromatic carbons), 148.80, 149.73, 154.42, 156.86 (C=N).

**Synthesis of 4:** Methylaquarhodoxime (0.10 mmol) was dissolved in an aqueous alkaline solution (3 mL) with a pH of about 11 and 3-aminophenylboronic acid (0.12 mmol) was added. The pH of the solution was lowered to about 7.0 with concentrated  $\text{HClO}_4$  and the solution left to stand. After some days yellow needle crystals were collected. Both an incomplete X-ray structure (due to the very low resolution) and the  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{OD}$  strongly suggested that the yellow product was a rhodoxime with coordinated aminophenylboronic acid. After some days, X-ray quality crystals of **4** were collected from the  $\text{CD}_3\text{OD}$  solution in the NMR tube. Yield: 10 mg (20%)  $[\text{C}_{16}\text{H}_{25}\text{N}_5\text{BO}_5\text{Rh} + 1\text{H}_2\text{O}]_n$ ; calcd. C 38.5, H 5.45, N 14.0; found C 37.8, H 5.10, N 13.9. The polymer **4** is too insoluble in non-coordinating solvents to be studied by  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectroscopy.

**Equilibrium Studies:** The deprotonation constants of the 3-aminophenylboronic acid were determined by spectrophotometric titration as previously described.<sup>[3b]</sup>

**Structure Determination of 3a and 4:** Single crystals, suitable for X-ray data collection, were obtained as reported above. X-ray diffraction data for **3a** and **4** were collected at room temperature with a Nonius DIP 1030 H System, using graphite-monochromated  $\text{Mo-K}_\alpha$  radiation. For all compounds a total of 36 frames were collected, using the Xpress program,<sup>[10]</sup> over a half of reciprocal space, with a rotation of  $5^\circ$  about the  $\omega$  axis. A Mac Science Image Plate (diameter = 300 mm) was used and the crystal-to-plate distance

was fixed at 90 mm. The determination of unit-cell parameters, integration of reflection intensities and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite.<sup>[11]</sup> Reflections, which were measured on previous and later frames, were used to scale the frames onto each other, a procedure that partially eliminated absorption effects, taking into account also any crystal decay. The structures were solved by direct methods,<sup>[12]</sup> followed by Fourier syntheses, and refined by full-matrix least-squares (on  $F^2$ ) cycles.<sup>[13]</sup> Compounds **3a** and **4** co-crystallized with water molecules and 0.5 molecules of  $\text{CH}_2\text{Cl}_2$  in the case of **3a**, and 1.5 molecules of  $\text{CD}_3\text{OD}$  in the case of **4**. All solvent molecules were refined isotropically. The H atoms were not refined but were included at calculated positions in the final refinements. The solvent H atoms and the disordered hydrogen of the B–OH were not included. A suite of programs<sup>[14]</sup> was also used for the geometrical and final calculations. Crystal and refinement data are given in Table 1. CCDC-175792 (**3a**) and CCDC-175793 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

Table 1. Crystallographic data for **3a** and **4**

	3a	4
Formula	$\text{C}_{45.5}\text{H}_{66}\text{ClO}_3\text{N}_{15}\text{O}_{19.5}$	$\text{C}_{17.5}\text{H}_{29.5}\text{BN}_5\text{O}_9\text{Rh}$
Mol. wt.	1379.8	567.7
System	Orthorhombic	Orthorhombic
Space group	Ibca	$P2_12_12_1$
<i>a</i> , Å	28.829(3)	11.468(2)
<i>b</i> , Å	29.662(4)	14.503(3)
<i>c</i> , Å	33.896(4)	16.216(4)
<i>V</i> , Å <sup>3</sup>	28985(5)	2691(1)
<i>Z</i>	16	4
$\rho_{\text{calc}}$ , g·cm <sup>−3</sup>	1.27	1.40
<i>T</i> , K	293	293
$\mu$ (Mo- $K_\alpha$ ), mm <sup>−1</sup>	0.785	0.683
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )] <sup>[a]</sup>	0.084	0.071
<i>wR</i> 2 (all data) <sup>[b]</sup>	0.262	0.192

$$R1 = \|F_0\| - \|F_c\|/\|F_0\|. \quad [b] \quad wR2 = [w(|F_0|^2 - |F_c|^2)^2/w|F_0|^2]^{1/2}.$$

## Acknowledgments

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