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Journal of Organometallic Chemistry 505 (1995) 135–138

Journal of Organometallic Chemistry

Preliminary communication

New organo-cobalt complexes derived from cobaloximes with one or two diphenylboron moieties in the oxime bridges

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Received 17 May 1995

Abstract

The reaction between methylcobaloxime $[CH_3Co(DH)_2L]$ and diphenylborinic anhydride affords derivatives containing either one or two diphenylboron bridges, depending on the ratio of complex: diphenylborinic anhydride. The crystal structures of $[CH_3Co(DH)(DBPh_2)(N\text{-MeIm})]$ (**Ib**) and $[CH_3Co(DBPh_2)_2CH_3OH]$ (**IId**) show that in **Ib** the axial phenyl of the BPh_2 moiety faces the axial Me, while in **IId** the axial phenyls are "trans". The preferred conformations of these complexes in solution, as inferred from NMR spectra, are analogous to those found in the solid state.

Keywords: Cobalt; Cobaloximes; X-ray structures; Boron-substituted; Preparations

Octahedral Co^{III} bis(dimethylglyoximate) complexes (cobaloximes) (Scheme 1, a) [1] are of interest both as simple models of the vitamin B_{12} system (cobalamins) [2] and as a class of compounds, with a large variety of derivatives with different R and L ligands [3]. Closely related systems with modified oxime bridges have been also suggested (Scheme 1, b–d) [1,4]. Although these systems model the Co coordination in cobalamins, the essentially planar equatorial ligands do not allow the exploration of the influence of steric interactions between the equatorial side chains and the axial ligands that occur in B_{12} coenzyme. A relatively simple way of introducing steric crowding in cobaloximes is replacement of the oxime bridge protons by diphenylboron moieties (Scheme 1 e, f). The equatorial $DBPh_2$ group may "protect" one of the metal axial sites with its phenyl groups, allowing the exploitation of repulsive or

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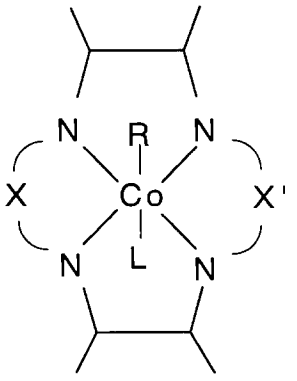

R = alkyl group L = neutral ligand

a) X = X' = O··H-O $RCo(DH)_2L$

b) X = X' = O-BF_2-O $RCo(DBF_2)_2L$

c) X = O··H-O, X' = CH_2-CH_2-CH_2 RCo[(DO)(DOH)pn]L

d) X = O··H-O, X' = CH_2-CHPy-CH_2 RCo[(DO)(DOH)pnPy]L

e) X = O··H-O, X' = O-BPh_2-O $RCo(DH)(DBPh_2)L$

f) X = X' = O-BPh_2-O $RCo(DBPh_2)_2L$

Scheme 1.

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SSDI 0022-328X(95)05858-3

attractive forces between the axial ligand and the Ph group of the equatorial macrocycle. Similar complexes were isolated many years ago for Ni^{II} [5] and Co^{III} [6], and, more recently, for Fe^{II} [7]. The last were studied thoroughly, and their conformation in solution, as inferred from ^1H NMR spectra has been proved to be strongly dependent on the relative bulk of the axial ligands. The magnetic anisotropy of the axially oriented BPh_2 phenyl group causes a remarkable shielding of the axial ligand facing it [7].

Here we report the synthesis and characterization of the first organobis(dimethylglyoximate) Co^{III} complexes containing either one or two diphenylboron groups replacing the oxime bridge protons. They have been synthesized by reaction of the organocobaloximes with diphenylborinic anhydride. The product contains one or two diphenylboron bridges, depending on the ratio of complex: diphenylborinic anhydride. The complexes $[CH_3Co(DH)(DBPh_2)L]$ (**Ia**, L = Py; **Ib**, L = *N*-MeIm) were isolated by adding an equimolar amount of diphenylborinic anhydride to the corresponding cobaloximes with an excess of the nitrogen base. The complexes $[CH_3Co(DBPh_2)_2L]$ (**IIa**, L = Py; **IIb**, L = *N*-MeIm) were prepared by reaction of the cobaloximes with an excess of diphenylborinic anhydride. Surprisingly, when the starting material was $[CH_3Co(DH)_2H_2O]$ the reaction product was always $[CH_3Co(DBPh_2)_2H_2O]$ (**IIc**), as shown by the NMR spectra (see below). The recrystallization of this compound from CH_2Cl_2 CH_3OH in order to obtain X-ray-quality crystals led to the isolation of $[CH_3Co(DBPh_2)_2CH_3OH]$ (**IId**) [1]. All the compounds were characterized by microanalysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and, in the cases of **Ib** and **IId**, by single crystal diffraction studies.

The ORTEP drawings of **Ib** and **IId** are shown together with the atom numbering schemes in Figs. 1 and 2, respectively [2].

[1] *Compounds* ***Ia*** *and* ***Ib****:* Diphenylborinic anhydride (0.15g, 0.43 mmol) was added to a solution of an equimolar amount of $[CH_3Co(DH)_2H_2O]$ (0.17g, 0.53 mmol) and Py or *N*-MeIm (about 0.1 ml) in CH_2Cl_2 (100 ml) and the mixture was stirred for two days at room temperature in the dark. Addition of methanol (10 ml) and partial evaporation of the solvent yielded a yellow precipitate, which was isolated by filtration and washed with methanol. The products were recrystallized by slow diffusion from CH_2Cl_2 /heptane. Calc. for $C_{26}H_{31}BCoN_5O_4$; 57.1 C, 5.71 H, 12.8 N. Found for **Ia**: 56.1 C, 5.6 H, 12.4 N. ^1H NMR($CDCl_3$, 400 MHz): δ 0.19 (s, 3H, CH_3 ax.), 2.14 (s, 6H, CH_3C=NOH), 2.38 (s, 6H, CH_3C=NOBPh$_2$), 7.07, 7.18 (m, 1 H each, *para* H of phenyls), 7.16, 7.28 (m, 2H each, *meta H* of phenyls), 7.27, 7.69 (m, 2H each, *ortho H* of phenyls), 7.34 (m, 2H, *meta H* of Py), 7.72 (m, 1H, *para H* of Py), 8.76 (m, 2H, *ortho H* of Py). $^{13}C\{^1H\}$ ($CDCl_3$, 100.4 MHz): δ 12.1 (CH_3C=NOH), 13.1 (CH_3C=NOBPh$_2$), 125.2, 126.0 (*para C* of phenyls), 125.3 (*meta C* of Py), 127.2 127.2 (*meta C* of phenyls), 131.4, 131.8 (*ortho C* of phenyls), 137.6 (*para C* of Py), 149.8 (*ortho C* of Py), 148.4 (CH_3C=NOH), 155.8 (CH_3C=NOBPh$_2$). Calc. for $C_{25}H_{32}BCoN_6O_4$: 54.6 C, 5.9 H, 15.3 N. Found for **Ib**: 54.4C, 5.8 H, 14.4 N. ^1H NMR($CDCl_3$, 400 MHz): δ 0.16 (s, 3H, CH_3 ax.), 2.15 (s, 6H, CH_3C=NOH), 2.39 (s, 6H, CH_3C=NOBPh$_2$), 3.58 (s, 3H, CH_3 of *N*-MeIm), 6.72 (s, 1H, *H5* of *N*-MeIm), 7.02 (s, 1H, *H4* of *N*-MeIm), 7.44(s, 1H, *H2* of *N*-MeIm) 7.06, 7.13 (m, 1 H each, *para H* of phenyls), 7.16 and 7.23 (m, 2H each, *meta H* of phenyls), 7.29, 7.61 (m, 2H each, *ortho H* of phenyls). $^{13}C\{^1H\}$ ($CDCl_3$, 100.4 MHz): δ 12.0 (CH_3C=NOH), 13.0 (CH_3C=NOBPh$_2$), 34.4 (CH_3 of *N*-MeIm), 121.1 (*C5* of *N*-MeIm), 128.2 (*C4* of *N*-MeIm), 137.8 (*C2* of *N*-MeIm), 125.1, 125.7 (*para C* of phenyls), 127.1, 127.1 (*meta C* of phenyls), 131.5, 131.7 (*ortho C* of phenyls), 147.6 (CH_3C=NOH), 154.9 (CH_3C=NOBPh$_2$). *Compounds* **IIa** *and* **IIb**: These compounds were prepared similarly, but a four-fold excess of diphenylborinic anhydride was added and the mixture was heated under reflux at 40 °C for two days. Calc. for $C_{38}H_{40}B_2CoN_5O_4$; 64.2 C, 5.7 H, 9.8 N. Found for **IIa**: 63.6 C, 5.5 H, 9.7 N. ^1H NMR($CDCl_3$, 400 MHz): δ 0.47 (s, 3H, CH_3 ax.), 2.49 (s, 12H, CH_3C=NOBPh$_2$), 6.98 (m, 2H, *meta H* of Py), 7.08, obs (m, 2H each, *para H* of phenyls), 6.93, 7.15 (m, 8H, *meta H* of phenyls), 7.12, 7.29 (m, 4H each, *ortho H* of phenyls), 7.51 (m, 1H, *para H* of Py), 7.70 (m, 2H, *ortho H* of Py). $^{13}C\{^1H\}$ ($CDCl_3$, 100.4 MHz): δ 13.4 (CH_3C=NOBPh$_2$), 125.0 (*meta C* of Py), 125.7, 125.8 (*para C* of phenyls), 126.9, 127.2 (*meta C* of phenyls), 131.5, 131.8 (*ortho C* of phenyls), 137.2 (*para C* of Py), 147.7 (*ortho C* of Py), 155.1 (CH_3C–NOBPh$_2$). Calc. for $C_{37}H_{41}B_2CoN_6O_4$: 62.2 C, 5.8 H, 11.8 N. Found for **IIb**: 61.7 C, 5.8 H, 11.6 N. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.39 (s, 3H, CH_3 ax.), 2.45 (s, 12H, CH_3C=NOBPh$_2$), 3.27 (s, 3H, CH_3 of *N*-MeIm), 6.06 (s, 1H, *H5* of *N*-MeIm), 6.40 (s, 1H, *H4* of *N*-MeIm), 6.45 (s, 1H, *H2* of *N*-MeIm) 7.08, obs (m, 2H each, *para H* of phenyls), 7.03, 7.16 (m, 4H each, *meta H* of phenyls), 7.22, 7.30 (m, 4H each, *ortho H* of phenyls). $^{13}C\{^1H\}$ ($CDCl_3$, 100.4 MHz): δ 13.2 (CH_3C=NOBPh$_2$), 34.6 (CH_3 of *N*-MeIm), 120.6 (*C5* of *N*-MeIm), 126.4 (*C4* of *N*-MeIm), 137.4 (*C2* of *N*-MeIm), 125.5, 125.7 (*para C* of phenyls), 126.7, 127.1 (*meta C* of phenyls), 131.8, 131.8 (*ortho C* of phenyls), 154.3 (CH_3C=NOBPh$_2$). *Compounds* **IIc** *and* **IId**: 0.26 g (0.8 mmol) of $[CH_3Co(DH)_2H_2O]$ were suspended in CH_2Cl_2 saturated with water and acetone was added until dissolution. After addition of 0.57 g (1.6 mmol) of diphenylborinic anhydride, the solution was heated under reflux at 40 °C for two days. Evaporation of the solvent afforded red crystals, which rapidly lose cristallinity in air. Calc. for $C_{33}H_{37}B_2CoN_4O_5$; 61.0 C, 5.7 H, 8.6 N. Found for **IIc**: 60.1 C, 5.7 H, 8.4 N. ^1H NMR($CDCl_3$, 400 MHz): δ 0.88 (s, 3H, CH_3 ax.), 2.54 (s, 12H, CH_3C=NOBPh$_2$), 7.02, 7.16 (m, 2H each, *para H* of phenyls), 7.12, 7.23 (m, 4H each, *meta H* of phenyls), 7.13–7.16, 7.50 (m, 4H each, *ortho H* of phenyls), $^{13}C\{^1H\}$ ($CDCl_3$, 100.4 MHz): δ 13.6 (CH_3C=NOBPh$_2$), 126.3, 126.4 (*para C* of phenyls), 127.2, 128.1 (*meta C* of phenyls), 131.1, 131.7 (*ortho C* of phenyls), 156.7 (CH_3C=NOBPh$_2$). Recrystallization of **IIc** from CH_2Cl_2 /methanol yielded red crystals of **IId**, which was characterized by X-ray diffractometry.

[2] X-ray diffraction data were collected on a CAD4 Enraf-Nonius diffractometer operating with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 296 °K in 2θ range 4–56°. Compound **Ib**: $C_{34}H_{39}B_2CoN_4O_5$, Mr = 664.27, monoclinic $P2_1/n$, a = 8.650(1), b = 16.243(3), c = 19.015(4) Å, β = 94.63(1)°, V = 1663.5(10) Å^3, unique observed reflections $I > 3\ \sigma\ (I) = 1498$, R = 6.4, R_w = 6.5. Compound **IId**: $C_{25}H_{32}BCoN_6O_4$, Mr = 550.32, monoclinic $P2_1/n$, a = 8.339(1), b = 11.509(1), c = 17.462(2) Å, β = 96.97(1)°, V = 2663.0(8) Å^3, unique observed reflections $I > 3\ \sigma\ (I) = 1266$, R = 6.1, R_w = 6.2. The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. Non-H atoms were refined isotropically except the Co atoms and the C/O disordered axial site in **Ib** that were treated anisotropically. Tables of thermal parameters, atom coordinates, bond lengths and angles for **Ib** and **IId** have been deposited at the Cambridge Crystallographic Data Centre.

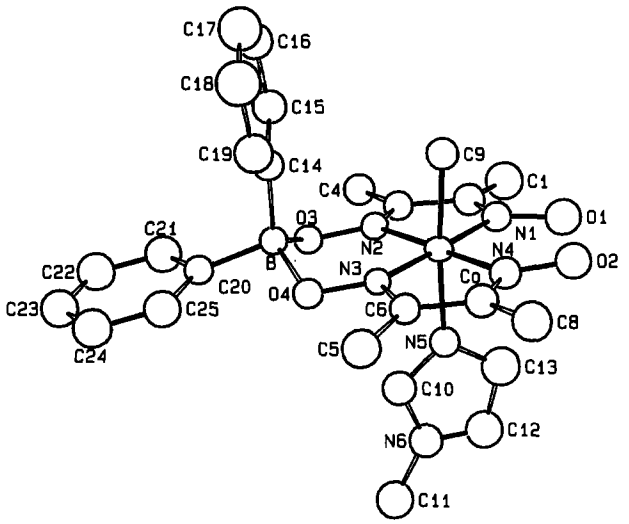

Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of molecule **Ib**.

In **Ib** the axial phenyl group of the BPh_2 moiety is on the side of the Me ligand. The orientation of *N*-MeIm is such that its plane bisects the equatorial six-membered ring. However the *N*-MeIm has two orientations rotated around the Co–N5 bond by 180° with occupancy factors of 0.7 and 0.3, respectively. Only the orientation with higher occupancy is shown in Fig. 1. Owing to the location on a crystallographic symmetry centre of molecules of **IId**, the axial ligands are superimposed. For sake of clarity, only one of the two orientations of the molecules of **IId** is shown. The "trans" conformation of the axial phenyl groups in **IId** is apparent in Fig. 2. The mean equatorial coordination Co–N distances are 1.863(5) Å in **IId** whereas they are 1.869(8) Å on the side of BPh_2 group and 1.878(8) Å on the side of the oxime bridge in **Ib**. Since the Co–N(eq) distances in more than one hundred cobaloximes average 1.8901(9) Å [1], the substitution of the oxime proton by BPh_2 appears to provoke a small but significant shortening of the Co–N bond. In contrast, in Costa's models where the oxime bridge is substituted by a propylene group (Scheme 1, c), the Co–N equatorial distances involving the imine N (average 1.912 (8) Å) are significantly longer than that involving the oxime N (average 1.880(9) Å)[1]. This trend probably reflects the different electronic charge put on the cobalt by the equatorial ligands. The O–O distance between the oxygens bound by a BPh_2 (2.519(6) Å in **IId** and 2.510(10) Å in **Ib**) is slightly longer than that between the oxygens bound by a hydrogen bond (2.469(12) Å in **Ib** and an average value of 2.487(2) in cobaloximes [1]). The C–Co–N axial fragment in **Ib** has Co–N and Co–C distances of 2.014(9) and 1.995(12) Å. The latter is similar to the Co–Me bond lengths reported in several cobaloximes having trans N-donor ligands (1.985(3)–2.006(8) Å)[8], and is similar to that of 2.019(3) reported in $[CH_3Co(DH)_2Im]$ [9]. A comparison of analogous coordination bond angles does not show significant differences. The disorder observed in **IId** prevents useful comment on the axial bond lengths.

For **Ia** and **Ib**, the NMR spectra show that the axial methyl protons are about 0.6 ppm to higher field and the trans axial ligand protons are just slightly deshielded with respect to the corresponding cobaloximes [10]. As with the corresponding Fe^{II} complexes [7], this can be attributed to the magnetic anisotropy of the phenyls and indicates that the preferred orientation in solution has the axially oriented phenyl facing the axial methyl. The equatorial methyl protons, as well as the CH_3 and the C=N carbons, give rise to two well-separated signals. One, at almost the same frequency as in the parent cobaloxime, is assigned to the nuclei on the side of the hydrogen bridge, and one, very close to the frequency observed for **IIa** and **IIb**, is attributed to the nuclei on the side of the boron side.

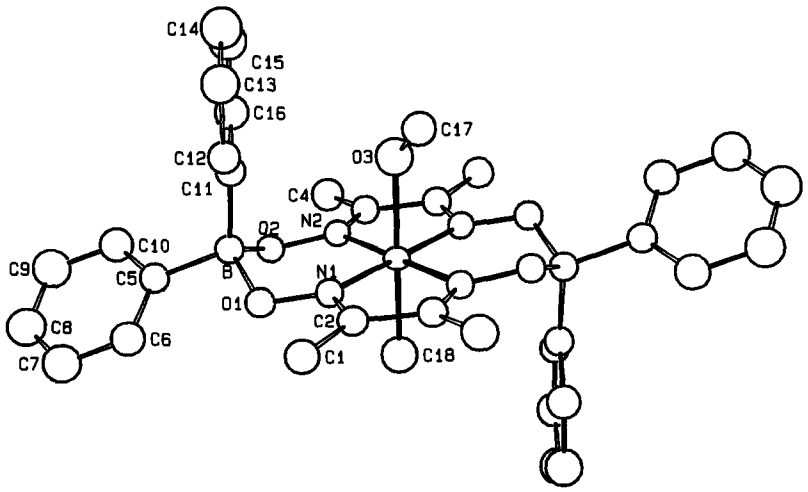

Fig. 2. ORTEP drawing (50% probability thermal ellipsoids) and labelling scheme for non-hydrogen atoms of molecule **IId**.

In **IIa** and **IIb** the axial methyl protons resonate at frequencies intermediate between those in the complexes **Ia** and **Ib** and the parent cobaloximes, whereas the py and *N*-MeIm protons are shielded, both with respect to **Ia** and **Ib** and to the parent cobaloximes. This can be explained through the aromatic magnetic anisotropy if in the main conformation in solution one BPh_2 axial phenyl faces the methyl group and the other faces L. The effects, even if weaker, are analogous to those observed for compounds $[Fe^{II}(DBPh_2)_2]$ [7].

The protons of the phenyl rings always give rise to two patterns which are almost of types AA'MM'X and the corresponding ^{13}C spectra show two groups of signals for all the complexes. The presence of just two kinds of phenyl for **IIa, IIb**, and **IIc** suggests that a fast interconversion on NMR time scale occurs, as already shown for the analogous Fe^{II} derivatives [7]. Extension of the synthesis and the solid state and solution investigations to other derivatives with different R and L are in progress.

Acknowledgements

We are grateful to CNR (Rome) and to MURST (Rome) for financial support.

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