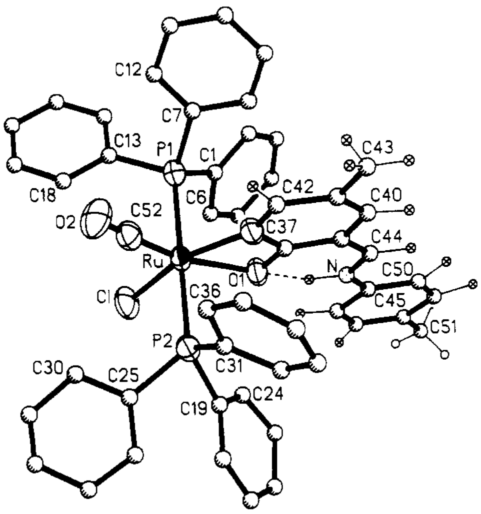

Figure 1. Perspective view of complex 3. Selected bond distances (Å) and angles (deg): Ru–Cl, 2.500 (2); Ru–P1, 2.386 (2); Ru–P2, 2.388 (2); Ru–O1, 2.235 (4); Ru–C37, 2.043 (6); Ru–C52, 1.800 (7); C52–O2, 1.157 (8); C38–O1, 1.314 (6); C44–N, 1.311 (8); N–H1N, 0.985 (11); O1···H1N, 1.753 (12); Cl–Ru–P1, 91.3 (1); Cl–Ru–P2, 89.2 (1); Cl–Ru–O1, 93.0 (1); Cl–Ru–C37, 156.9 (2); Cl–Ru–C52, 103.7 (2); P1–Ru–P2, 179.5 (1); P1–Ru–O1, 87.7 (1); P1–Ru–C37, 89.6 (2); P1–Ru–C52, 90.6 (2); P2–Ru–O1, 92.2 (1); P2–Ru–C37, 89.9 (2); P2–Ru–C52, 89.4 (2); O1–Ru–C37, 64.0 (2); O1–Ru–C52, 163.2 (2); C37–Ru–C52, 99.3 (3); N–H1N–O1, 143.8 (3). One PPh_3 ligand is disordered, each benzene ring appearing in two ways—of these only one set (C19–C36) is shown. The PPh_3 hydrogens are not shown for clarity.

ordinated (R) group in the ruthenium(IV) intermediate formed after oxidative addition is a stable ortho-metalated phenolato chelate ring. Reductive elimination therefore proceeds by the alternative route of H^+ elimination assisted by the azomethine nitrogen, which is thus obligatory for the reaction. The result is **2**. Base-promoted reductive H^+ elimination ($Ru^{IV}H + B \rightarrow Ru^{II} + HB^+$) from organometallic ruthenium(IV) hydride species has been documented elsewhere.[11]

The complex **3** can be deprotonated by base, and it forms multinuclear complexes with other metal ions such as copper(II), possibly via phenolato and azomethine nitrogen coordination. The reaction and properties of $Ru(p\text{-}XC_6H_4L)(CO)(PPh_3)_2Cl$ and cognate osmium complexes are under scrutiny.

Acknowledgment. We are grateful to the Department of Science and Technology, New Delhi, for establishing a National Single-Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Financial support received from the Council of Scientific and Industrial Research is also acknowledged.

Supplementary Material Available: Tables of positional parameters, thermal parameters, bond distances, and bond angles of 3 and a figure showing the nature of PPh_3 disorder (8 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

(10) (a) Doughty, D. H.; Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343–375. (b) Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521–3522. (c) Anton, A. B.; Avery, N. R.; Toby, B. H.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 684–694.

(11) (a) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705–706. (b) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984; pp 139–149.

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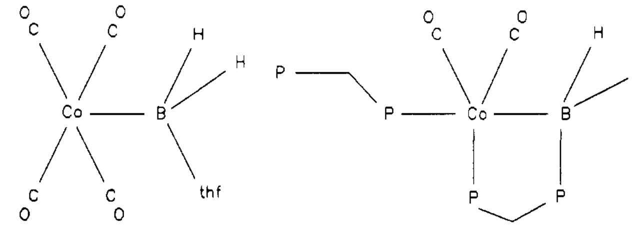
A Bridged Cobaltaborane Complex: First Structural Characterization of a Transition-Metal–BH_2 Bond

Transition-metal complexes containing $M\text{–}BH_2$ units have proved to be elusive, despite intensive research in transition-metal–borane chemistry.[1] The first such complex $[(CO)_4CoBH_2{\cdot}THF]$ (**1**) has recently been characterized by Fehlner and



1 2, PP = dppm

co-workers using spectroscopic methods at low temperature, but it decomposes rapidly at room temperature.[2] This paper reports a diphosphine-bridged derivative of **1**, that is stable at room temperature and has been characterized crystallographically.

The new complex $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$ (**2**), dppm = $Ph_2PCH_2PPh_2$, was prepared in one step but in low yield by reduction of cobalt(II) chloride or bromide with $NaBH_4$ in the presence of dppm and CO.[3] The major product of this reaction is $[Co_2(CO)_4(\mu\text{-dppm})_2]$ (**3**),[4] and the yellow complex **2** was separated from the black complex **3** by handpicking crystals.[3] Complex **2** is air-stable and was fully characterized by spectroscopic methods[5] and by an X-ray structure determination.[6] The structure of **2** is shown in Figure 1. It contains a distorted trigonal-bipyramidal (TBP) cobalt center with the monodentate dppm and boron ligands in axial positions and two carbonyls and a phosphorus donor of the μ-dppm ligand in equatorial positions. The major distortion probably arises from the steric interaction between the axial dppm ligand and the equatorially bonded ligands. This gives rise to the displacement of the equatorially bonded atoms away from P(4). Thus, the angles P(1)CoP(2) = 101.91 (3)°, BCoC(3) = 82.4 (2)°, and BCoC(4) = 75.5 (2)° are considerably distorted from the idealized 90° for a trigonal bipyramid.

(1) For example: (a) Fehlner, T. P. *New J. Chem.* **1988**, *12*, 307. (b) Housecroft, C. E. *Polyhedron* **1987**, *6*, 1935. (c) Coffy, T. J.; Medford, G.; Plotkin, J.; Long, G. J.; Huffman, J. C.; Shore, S. G. *Organometallics* **1989**, *8*, 2404. (d) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519; **1984**, *34*, 211.

(2) Basil, J. D.; Aradi, A. A.; Bhattacharyya, N. K.; Rath, N. P.; Eigenbrot, C.; Fehlner, T. P. *Inorg. Chem.* **1990**, *29*, 1260.

(3) A solution of $NaBH_4$ (0.12 g) in EtOH (15 mL) was added to a CO-saturated solution of $CoBr_2{\cdot}6H_2O$ (0.44 g) and dppm (1.00 g) in C_6H_6/EtOH (30 mL, 1:1) over 30 min. The mixture was stirred for 4 h, and then the solvents were removed and the product was washed with EtOH and recrystallized from CH_2Cl_2/EtOH. The large yellow crystals of **2** were separated by hand from black crystals of **3**.

(4) Elliot, D. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chim. Acta* **1988**, *142*, 195.

(5) Spectroscopic data (labeling defined in Figure 1) is as follows. IR: $\nu(CO)$ = 1925 (m), 1865 (s) cm^{-1}; $\nu(BH)$ = 2380 (w), 2310 (w) cm^{-1}. NMR in CD_2Cl_2: $\delta(^{31}P) = -33.0$ [d, $^2J(P^1P^3)$ = 28 Hz, P^1], 47.1 [br, P^3], 15.7 [d, $^2J(P^2P^4)$ = 155 Hz, P^2], 44.5 [d, $^2J(P^2P^4)$ = 155 Hz, P^4]; $\delta(^{11}B) = -25.9$ (br s). FAB-MS: found, m/z = 898, 884, 870, 841; calcd for $C_{52}H_{46}BCoO_2P_4$, m/z 896, 883 ($P - BH_2$), 868 ($P - CO$), 840 ($P - 2CO$). There was excellent agreement between the observed and calculated (for $P - 2CO + H$) envelope structures at m/z = 841, thus proving the presence of a single boron atom. EI-MS: confirms ^{11}B and ^{10}B at m/z = 11 and 10 in required ratio.

(6) Crystal data for $C_{52}H_{46}BCoO_2P_4{\cdot}0.5CH_2Cl_2$ (**2**): fw 937.2; monoclinic, space group $P2_1/c$; a = 19.520 (7), b = 10.943 (3), c = 24.625 (14) Å, β = 112.75 (4)°; V = 4850.7 Å^3; Z = 4; calculated density = 1.284 g cm^{-3}; ambient temperature; graphite-monochromated Mo Kα radiation; ω-scan technique from $0° \le 2\theta \le 48°$; octants measured $\pm h,k,l$, total reflections 8505; R = 0.054, R_w = 0.072; goodness of fit 1.657 for 583 variables and 5362 reflections with $I \ge 3\sigma(I)$. All calculations were carried out by using an AT&T 6386 WGS computer with a PC version of NRCVAX. NRCVAX: Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Data Bases*; Sheldrick, G. M., Kruger, C., Eds.; Clarendon Press: Oxford, England, 1985; p 167.

0020-1669/90/1329-5014$02.50/0

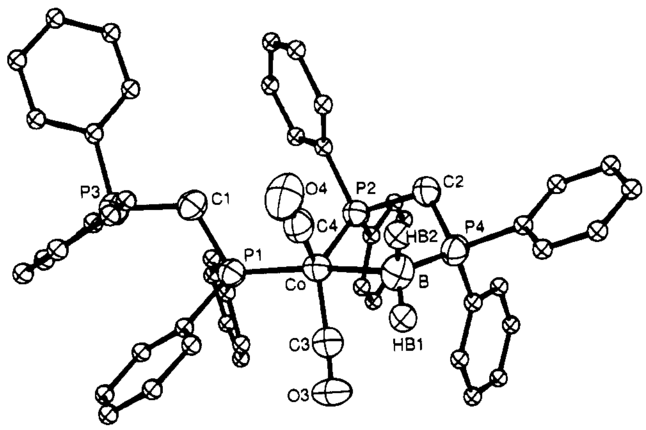


Figure 1. ORTEP diagram of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})(BH_2)]$ (**2**), showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: Co–B, 2.227 (6); Co–P(1), 2.193 (1); Co–P(2), 2.198 (1); Co–C(3), 1.745 (1); Co-C(4), 1.738 (1); P(4)–B, 1.912 (6); P(1)–Co–B, 164.3 (2); P(1)–Co–P(**2**), 101.91 (3); P(2)–Co–B, 93.1 (2); C(3)–Co–B, 82.4 (2); C(4)–Co–B, 75.5 (2); Co–B–P(4), 103.9 (3).

The other unusual feature of the structure of **2** is the long Co–B bond of 2.227 (6) Å. Most cobalt–boron bonds in cobaltaboranes fall in the range 2.00–2.15 Å.[7] The two hydrogen atoms on boron were located by difference Fourier techniques and were refined successfully, leading to approximately tetrahedral geometry around boron.

The detailed structure of **2** is significantly different from the square-pyramidal (SP) structure at cobalt deduced for **1** on the basis of spectroscopic data,[2] but it is well-known that the TBP and SP structures have similar energies. The long and presumably weak Co–B bond, now established for **2**, is probably a result of the weak nucleophilic character of $[Co(CO)_4]^-$, and the ease of decomposition or dissociation of unbridged complexes with Co–B bonds such as **1** and $[(CO)_4CoBH_3]^-$ can be rationalized on this basis.[2,8] Our molecular orbital calculations on the latter molecule, which may be considered a model for **2**, predict that the charges on the BH_3 and $Co(CO)_4$ fragments are −0.55 and −0.45 e, respectively, and the optimized Co–B bond distance is 2.43 Å.[9] The μ-dppm ligand may stabilize **2** not only by providing its well-known binucleating ability but also by providing steric shielding and by increasing the electron density on cobalt and hence giving greater covalency to the Co–B bond.[9] Complex **2** and related compounds with $M\text{–}BH_2$ bonds have great potential in synthesis if high-yield synthetic methods can be realized. Further work to this end is in progress.

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Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, anisotropic thermal parameters, and atomic distances and angles (10 pages); a listing of the observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

(7) See for example: (a) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *J. Organomet. Chem.* **1988**, *348*, C22. (b) Grimes, R. N., Ed. *Metal Interactions with Boron Clusters*; Plenum: New York, 1985.
(8) Parshall, G. W. *J. Am. Chem. Soc.* **1964**, *86*, 361.
(9) The Co–B bond in **2** is a 2c–2e bond, probably polarized in the sense $Co^{\delta-}\text{–}B^{\delta+}$. Evidence for this is seen in the low values of ν(CO) for **2**[5] compared to related Co(O) complexes such as $[Co_2(CO)_4(\mu\text{-dppm})_2]$.[4] In the extreme case, the Co–B bond could be considered as a donor-acceptor bond with $Co(CO)_2L_2^-$ as donor and BH_2L^+ as acceptor. In the MO calculations on the model compound $[(CO)_4Co\text{–}BH_3]$, the angles around the B and Co atoms were the tetrahedral and trigonal-bipyramidal angles, respectively, and distances were from literature values. The basis set for the ab initio calculation was STO-3G. An extended Huckel calculation gave good agreement on the charges on the fragments [−0.54 and −0.46 e on BH_3 and $Co(CO)_4$, respectively]: McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

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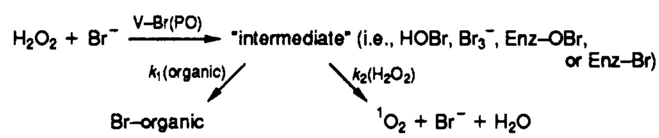
Chlorination Catalyzed by Vanadium Bromoperoxidase

Vanadium bromoperoxidase (V–Br(PO)) isolated from marine algae catalyzes the oxidation of bromide, which results in the bromination of certain organic compounds[1-3] or the production of singlet oxygen from the bromide-assisted disproportionation of hydrogen peroxide.[4]



The marine environment is a very rich source of halogenated natural products. Rhodophyta (red algae) produce the most diverse array of brominated and chlorinated compounds (e.g., terpenes, phenols, β-keto acids, etc.),[5,6] and phaeophyta (brown algae) produce large quantities (e.g., ca. 10^4 tons/year) of volatile brominated and chlorinated hydrocarbons (e.g., $CHBr_3$, $CHBr_2Cl$, etc.).[7] The biosynthesis of the brominated compounds is likely to be mediated by bromoperoxidase through electrophilic bromination by oxidized bromine species. By contrast, the origin of the marine chlorinated natural products has not been elucidated. It has been reported that chloride is neither a substrate nor an inhibitor of V–Br(PO),[8] whereas bromide and iodide are substrates and fluoride is an inhibitor of V–Br(PO).[9] In our investigations of the halide selectivity of V–Br(PO), we have reinvestigated the reactivity of V–Br(PO) with chloride. We report the first observation that vanadium bromoperoxidase *does* catalyze the oxidation of chloride by hydrogen peroxide *and* the chloride-assisted disproportionation of hydrogen peroxide.

(1) Vilter, H. *Phytochemistry* **1984**, *23*, 1387–1390.
(2) de Boer, E.; Plat, H.; Tromp, M. G. M.; Wever, R.; Franssen, M. C. R.; van der Plas, H. C.; Meijer, E. M.; Schoemaker, H. E. *Biotechnol. Bioengin.* **1987**, *30*, 607–610.
(3) Soedjak, H. S.; Butler, A. *Biochemistry* **1990**, *29*, 7974–7981.
(4) Everett, R. R.; Kanofsky, J. R.; Butler, A. *J. Biol. Chem.* **1990**, *265*, 4908–4914.
(5) See, for example: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251–280.
(6) Neidleman, S. L.; Geigert, J. *Biohalogenation: Principles, Basic Roles and Applications*; Ellis Horwood: New York, 1986 and references therein.
(7) Gschwend, P. M.; MacFarlane, J. K.; Newman, K. A. *Science* **1985**, *227*, 1033–1035.
(8) Wever, R.; Plat, H.; de Boer, E. *Biochim. Biophys. Acta* **1985**, *830*, 181–186.
(9) Everett, R. R.; Soedjak, H. S.; Butler, A. *J. Biol. Chem.* **1990**, *265*, 15671–15679.

