Organometallics 1991, *10*, 1213–1215 1213

Coupling of a η^5-Borole Complex via a B–O–B Link by Reaction of the B–Br Derivative with KOH. X-ray Structure of $\{1\text{-}[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co\}_2O$

Fung-E. Hong and T. P. Fehlner*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

A. L. Rheingold*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received August 24, 1990

Summary: The reaction of $[\eta^5\text{-}(1\text{-Br-}2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co$ with excess KOH leads to production of $\{1\text{-}[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co\}_2O$, (3) in good yield. The X-ray crystal structure of 3 has been determined: triclinic, $P\bar{1}$, $a = 16.114$ (4), $b = 16.978$ (4), $c = 22.738$ (6) Å, $\alpha = 80.50$ (2)°, $\beta = 75.63$ (2)°, $\gamma = 75.16$ (2)°, $V = 5791.0$ (25) Å^3, $Z = 4$, $R(F) = 9.71\%$. It shows that two individual borole complexes have been joined with a B–O–B link. The bond metrics displayed reflect both electronic and steric factors. The coupled product is stable with respect to hydrolysis to $[\eta^5\text{-}(1\text{-OH-}2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co$ in both acidic and basic solution.

Sandwich complexes linked via C–C bonds between the Cp rings have been the focus of considerable study.[1] Although not as well characterized in terms of properties, coupled polyhedral cages containing boron are also well known. Various bonds including direct, exo-polyhedral B–B, e.g., $1{:}1'\text{-}[B_4H_9]_2$[2] and C–C, e.g., 1:1′-(*closo*-1′,2′-$C_2B_{10}B_{11}$)-*closo*-1,2-$C_2B_{10}B_{11}$,[3,4] bonds as well as indirect coupling via another atom or group, e.g., Hg[5] or Au[6] have been used to link the cages. There have been a few examples of cages coupled by B–O–B bonds reported[7-10] and one containing coupled diborabenzene complexes is analogous to the principal compound dicussed here.[11] This is interesting because even though B–O–B linkages are ubiquitous in boron–oxygen chemistry, one would not immediately consider them as suitable candidates for coupling two molecular frameworks. Under normal conditions, the B–O bond, although very strong, is labile and readily cleaved by nucleophiles. This is one factor that lies behind the extremely complex chemistry exhibited by boron–oxygen systems.[12] However, of the known B–O–B linked cages, one[7] has been reported to be very resistant to cleavage even under vigorous conditions. Only two structural determinations of cages coupled with a B–O–B linkage are available, i.e., $[\mu\text{-}9,9'\text{-O-}\{5\text{-}(\eta^5\text{-}C_5H_5)\text{-}nido\text{-}5\text{-}RhB_9H_{12}\}_2$[8] and $6,6'\text{-}(B_{10}H_{13})_2O$[13]. One crystallographically characterized compound $8,8'\text{-O}(C_2B_9H_{10})_2Co$[14] does contain a B–O–B link between the carborane cages but the metal atom, bound to the open faces of both cages, provides the primary bond. Rational chemical routes to B–O–B linked systems are even fewer in number. In conjunction with a study of the reactivity of isolated B–H fragments,[15] we have uncovered an example of the straightforward formation of a bis-sandwich complex coupled by a B–O–B linkage and have structurally characterized it.

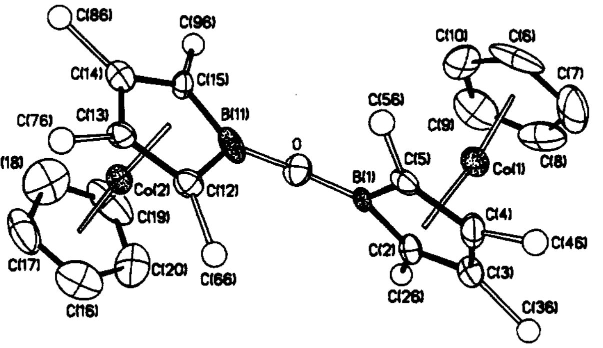


Figure 1. Molecular structure and labeling scheme for 3. Only ipso carbons of the phenyl groups are shown and hydrogen atoms are omitted for clarity. One of two crystallographically independent, but chemically similar, molecules is shown.

Results and Discussion

The hydrolysis of $[\eta^5\text{-}(1\text{-Br-}2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co$ (1) under basic conditions with $\leq$1 mol KOH per mol 1 leads to the formation of $[\eta^5\text{-}(1\text{-OH-}2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co$ (2).[15] However, if the reaction is carried out with a large excess of KOH, only minor amounts of 2 are observed, and the primary product produced has very different chromatographic behavior. The mass spectrum of this product suggested a dimeric species containing boron atoms, and the IR showed evidence of a B–O–B fragment.[16] Hence, the new compound was identified as $\{1\text{-}[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co\}_2O$ (3). The ratio of 3 to 2 reached a maximum of $\sim$9:1 for long

---

(1) See: Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 5031, and references therein.

(2) See: Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793, and references therein.

(3) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1643.

(4) A recent example of coupling via multiple bonding has been reported: Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4593.

(5) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886.

(6) Housecroft, C. E.; Rheingold, A. L.; Shongwe, M. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1630.

(7) Plešek, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1968**, *33*, 691.

(8) Kennedy, J. D. In *Boron Chemistry*; Heřmánek, S., Ed..; World Scientific: Singapore, 1987, 207. Ditzel, E. J.; Fontaine, X. L. R.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P.; Sisan, Z.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1692.

(9) Brown, M.; Fowkes, H.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P.; Nestor, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2597.

(10) Plešek, J.; Heřmánek, S.; Baše, K.; Todd, L. J.; Wright, W. F. *Collect. Czech. Chem. Commun.* **1976**, *41*, 3509.

(11) Herberich, G. E.; Hessner, B. *Chem. Ber.* **1982**, *115*, 3115.

(12) Hofmeister, H. K.; Van Waver, J. R. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1201.

(13) Greenwood, N. N.; McDonald, W. S.; Spalding, T. R. *J. Chem. Soc. Dalton Trans.* **1980**, 1251.

(14) Petřina, A.; Petříček, V.; Maly, K.; Šubrtová, V.; Linek, A.; Hummel, L. *Zeit. Kristal.* **1981**, *154*, 217.

(15) Hong, F.-E.; Eigenbrot, C. W.; Fehlner, T. P. *J. Am. Chem. Soc.* **1989**, *111*, 949.

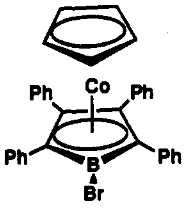
(16) The symmetric deformation frequency for $(Me_2B)_2O$ has been reported as 1405 cm^{-1}: Lanthier, G. F.; Graham, W. A. G. *Can. J. Chem.* **1969**, *47*, 569.

0276-7333/91/2310-1213$02.50/0

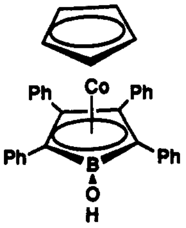
Table I. Crystallographic Parameters for $(C_{33}H_{25}BCo)_2O$

		(a) Crystal Parameters	
formula	$(C_{33}H_{25}BCo)_2O$	γ, deg	75.17 (2)
formula wt	998.61	V, Å^3	5791 (2)
space group	$P\bar{1}$	z	4
cyst syst	triclinic	cryst dimens, mm	0.45 × 0.20 × 0.20
a, Å	16.114 (4)	cryst color	deep red
b, Å	16.978 (4)	D(calc), g/cm^3	1.145
c, Å	22.738 (6)	μ(Mo Kα), cm^{-1}	6.11
α, deg	80.50 (2)	temp, °C	23 ± 1
β, deg	75.63 (2)	T(max)/T(min)	1.12
		(b) Data Collection	
diffractometer	Nicolet R3m/μ	no. of rflns collected	13059
monochromator	graphite	no. of indpt rflns	12447
scan technique	Wyckoff	R(merg), percent	1.38
radiation	Mo Kα (λ = 0.71073 Å)	no. of indpt rflns obsvd $F_o \geq 5\sigma(F_o)$	6251
2θ scan range, deg	4–42	std rflns	3 std/197 rflns
data collected	$\pm h$, $\pm k$, $+l$	var in stds, percent	<1
scan speed, deg/min	var 5–20		
		(c) Refinement	
$R(F)$, percent	9.71	$\Delta(\rho)$, eÅ^{-3}	1.24
$R(F_w)$, percent	9.84	N_o/N_v	9.40
Δ/σ (max)	0.029	GOF	1.726

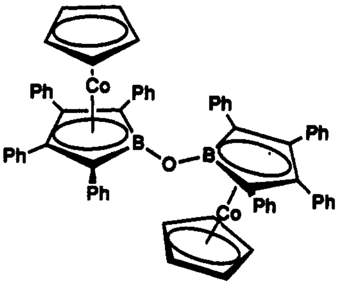
reaction times in the presence of excess KOH. Once formed, 3 was stable to hydrolysis to 2 under both acidic and basic conditions.



1



2



3

The identification of 3 was confirmed and the geometric parameters defined by an X-ray structure determination of a crystalline sample. The molecular structure of 3 is shown in Figure 1 and the crystallographic data are given in Table I. Selected bond distances and angles are listed in Table II. Compound 3 crystallizes with two independent, but chemically similar, molecules composing the asymmetric unit. The structural parameters of the individual borole cobalt complexes are very similar to those reported for $[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4BH)][\eta^5\text{-}(C_5H_5)]Co$ and need no further comment.[15] The B–O distances are in the range expected for a single, polar B–O bond[17] and are similar to those reported earlier (1.375 (8) Å for $[\mu\text{-}9,9'\text{-}O\text{-}\{5\text{-}(\eta^5\text{-}C_5H_5)\text{-}$*nido*$\text{-}5\text{-}RhB_9H_{12}\}_2$,[8] 1.395 (7) Å for $[\eta^6\text{-}C_5H_5BOMe][\eta^5\text{-}C_5H_5]Co$,[18] 1.358 (2) for $6,6'\text{-}(B_{10}H_{13})_2O$[13]). The B–O–B link is bent with an average B–O–B angle of 133° (130 (1) and 136 (1)°) which is larger than that reported for the coupled rhodaborane clusters (129.8 (5)°) but smaller than that reported for $6,6'\text{-}(B_{10}H_{13})_2O$ (139.1 (2)°).[13]

Table II. Selected Bond Distances and Angles for 1

	molecule A	molecule B
(a) Bond Distances (Å)		
Co(1)–CNT1[a]	1.662 (16)	1.665 (16)
Co(1)–CNT2	1.673 (16)	1.674 (16)
Co(2)–CNT3	1.657 (16)	1.661 (16)
Co(2)–CNT4	1.725 (16)	1.684 (16)
B(1)–O	1.412 (21)	1.412 (26)
B(11)–O	1.425 (24)	1.351 (23)
B(1)–C(5)	1.506 (20)	1.508 (27)
C(5)–C(4)	1.441 (26)	1.427 (26)
C(4)–C(3)	1.452 (23)	1.421 (20)
C(3)–C(2)	1.420 (22)	1.476 (26)
C(2)–B(1)	1.508 (27)	1.508 (23)
B(11)–C(12)	1.536 (22)	1.544 (28)
C(12)–C(13)	1.442 (25)	1.448 (23)
C(13)–C(14)	1.469 (23)	1.490 (23)
C(14)–C(15)	1.455 (22)	1.420 (27)
C(15)–B(11)	1.533 (30)	1.540 (22)
(b) Bond Angles (deg)		
CNT1–Co(1)–CNT2	172.1 (6)	173.4 (6)
CNT3–Co(2)–CNT4	174.7 (6)	174.9 (6)
B(1)–O–B(11)	130.2 (12)	135.6 (13)
O–B(1)–C(2)	124.4 (13)	128.9 (16)
O–B(1)–C(5)	129.5 (17)	124.6 (14)
B(1)–C(2)–C(3)	106.8 (12)	106.8 (13)
C(2)–C(3)–C(4)	110.9 (16)	107.6 (14)
C(3)–C(4)–C(5)	107.9 (13)	112.3 (16)
C(4)–C(5)–B(1)	107.9 (15)	106.4 (13)
C(2)–B(1)–C(5)	105.7 (14)	106.1 (17)
O–B(11)–C(12)	126.0 (19)	125.8 (14)
O–B(11)–C(15)	126.6 (14)	130.8 (17)
B(11)–C(12)–C(13)	107.0 (15)	108.2 (13)
C(12)–C(13)–C(14)	108.6 (13)	109.3 (15)
C(13)–C(14)–C(15)	111.6 (16)	108.4 (13)
C(14)–C(15)–B(11)	104.7 (13)	110.1 (15)
C(12)–B(11)–C(15)	106.8 (15)	103.2 (15)

[a] CNT1 = B(1), C(2)–C(5); CNT2 = C(6)–C(10); CNT3 = B(11), C(12)–C(15); CNT4 = C(16)–C(20).

Borole–metal complexes are well known[19] and the relationship of the geometric structure of borole complexes and

---

(17) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Oxford: London, 1975; p 851.

(18) Huttner, G.; Krieg, B.; Gartzke, W. *Chem. Ber.* 1980, *192*, 421.

(19) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, p 381.

Scheme I

3a 3b

other closely related compounds to the electronic structure at the boron atom can be understood on the basis of the elegant work of Herberich and co-workers,[20] as well as that of others.[18,21,22] That is, substituents on the boron atom of a coordinated borole that stabilize tricoordinate boron lengthen and weaken the metal-boron interaction thereby increasing the nonplanarity of the borole ring and reducing the cyclic conjugation. In **3**, assuming for the moment that there are no steric constraints, the B–O–B angle thus reports on the relative strength of the boron–cobalt interaction in the borole complex. That is, full η^5-coordination of the borole to cobalt should lead to B–O single bonds with free rotation and a bent B–O–B fragment as shown in limiting structure **3a** in Scheme I. On the other hand, an allene-like interaction between tricoordinate boron atoms concomitant with diene coordination of the C_4 fragment of the borole ring to the metal should lead to restricted rotation and a linear B–O–B geometry (structure **3b** in Scheme I). The large B–O–B angle (relative to an ether), the D_{2d}-like orientation of the trigonal planes containing the two boron atoms and the red color (relative to yellow $[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4BH)][\eta^5\text{-}(C_5H_5)]Co$) are compatible with O→B π-donation, i.e., structure **3b** is a significant contributor. It is interesting to note in this regard that, just as with the coupled cages and boroles, a significant range of B–O–B angles have been reported for non-ring structures. They range from 124° in $(HO)_3B\text{–}O\text{–}B(OH)_3$,[23] to 139° in B_2O_3,[24] to 153° in bis(4*H*-borepino[3,2-b:6,7-b′]dithienyl) ether.[25] The smallest B–O–B angles are associated with tetrahedral boron atoms, while the most open angle is associated with trigonal-planar boron atoms.

On the other hand, the B–O–B bond parameters can also be ascribed to bonding model **3a** perturbed by steric effects. The considerable steric bulk of the four phenyl substituents on the borole ring favors the observed structure with a twist of the borole rings about the B–O axes as well as a large B–O–B angle. Hence, as is usually the case, the true electronic structure is probably best represented by a combination of **3a** and **3b**.

The question of why compounds like **3** resist hydrolysis is related to the observed electronic and geometric structure. Hydrolysis may involve attack of $[OH]^-$ at boron followed by displacement of $[OR]^-$, where in the case of **3** R = $\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)Co$. For coupled closo cages, back-side attack is not possible and front-side attack is inhibited by the presence of the other cage. The uncoupled borole complex is readily attacked by nucleophiles at boron and, thus, inhibition must result strictly from some effect due to the other cage. From Figure 1, it is evident that the phenyl groups on the other complex shield boron from attack at the bottom of the ring. As noted above, this relative orientation of the two borole complexes is consistent with both electronic interactions of the boron atoms with the bridging oxygen atom plus cage–cage steric effects. Independent of the mechanistic source of stability, hydrolytically resistant B–O–B fragments can be considered as potentially useful coupling units for forming stable cluster oligomers or more complex extended structures. The fact that the B–O bond is one of the strongest bonds known adds further attractiveness to this type of use.

Experimental Section

All reactions and manipulations were carried out with standard Schlenk-ware under a dry nitrogen atmosphere.[26] Solvents were dried, degassed, and distilled before use. Silica gel (Kieselgel 60 PF_{254}, EM Science) made into a water slurry was used to prepare the 2-mm-thick, 20-cm-diameter discs on glass for centrifugal prep-TLC. The disks were baked before use. IR spectra were recorded in a CaF_2 cell on a Perkin-Elmer 1420 spectrophotometer. ^{11}B NMR spectra were obtained on a Nicolet NT 300 while ^1H spectra were obtained on a GN 300 spectrometer. ^{11}B shifts are reported with respect to $BF_3\cdot OEt_2$ ($\delta = 0$) and ^1H with respect to TMS ($\delta = 0$). The mass spectral data were recorded on a Finnigan MAT 8450 high-resolution mass spectrometer.

Synthesis of $\{1\text{-}[\eta^5\text{-}(2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co\}_2O$ (3). To a 20-mL Schlenk flask containing 0.03 mmol of $[\eta^5\text{-}(1\text{-}Br\text{-}2,3,4,5\text{-}Ph_4C_4B)][\eta^5\text{-}(C_5H_5)]Co$ in 6 mL of toluene was added a slurry of 0.6 g of KOH powder (10 mmol) in 6 mL of toluene and the mixture stirred at room temperature. Product formation was observed by TLC (**3** red, $R_f = 0.5$, 1:1 tol/hex, 0.9, CH_2Cl_2; **2** yellow, $R_f = 0.3$, CH_2Cl_2) and after 22 h the major species present was **3**. Centrifugal TLC with toluene yielded a red band. Partial removal of the toluene under vacuum followed by the addition of hexane and refrigeration led to the precipitation of **3** as well-formed red crystals. The overall yield was ≈30%. ^1H NMR (C_6D_6, 25 °C): δ 6.7–7.7 (m, 40 H, Ph), 4.49 (s, 10 H, Cp). ^{11}B NMR (C_6D_6, 25 °C): δ 20.2 (s, br). MS (CI, isobutane, *m*/*e* (rel intensity)) 996 (15), 997 (100), 998 (80), 999 (22). IR (CsF, toluene) ν 1730 (B–O), 1260 (B–O–B) cm^{-1}.

X-ray Crystallography. Crystallographic data are collected in Table I. A deep red crystal was used to collect 13059 reflections of which 12447 were independent and systematically present, and 6251 were considered observed ($5\sigma(F_o)$). No absorption correction was applied (low μ, well-shaped crystal). The structure was solved by direct methods. There are two independent, but chemically similar, molecules in the unit cell. At convergence, all non-hydrogen atoms, except those of the phenyl rings, were refined anisotropically, and hydrogen atoms only included on the Cp rings, calculated as idealized isotropic contributions. All calculations used and scattering factors are contained in the SHELXTL program library (5.1) (Nicolet XRD, Madison, WI).

Acknowledgment. We thank the National Science Foundation for the support of this work and Dr. J. D. Kennedy for a preprint and helpful comments.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for **3** (13 pages); a listing of structure factors for **3** (34 pages). Ordering information is given on any current masthead page.

---

[20] Herberich, G. E.; Ohst, H.; Mayer, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 969.

[21] Herberich, G. E.; Hessner, B.; Beswetherick, S.; Howard, J. A. K.; Woodward, P. *J. Organomet. Chem.* **1980**, *192*, 421.

[22] Siebert, W.; Full, R.; Edwin, J.; Kinberger, J.; Krüger, C. *J. Organomet. Chem.* **1977**, *131*, 1. Siebert, W.; Augustin, G.; Full, R.; Drüger, C.; Tsay, Y. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 262.

[23] Krogh-Moe, J. *Acta Crystallogr.* **1967**, *23*, 500.

[24] Strong, S. L.; Wells, A. F.; Kaplow, R. *Acta Crystallogr.* **1971**, *B27*, 1662.

[25] Value quoted in Jeffries and Parkanyi: Jeffries, A. T.; Parkanyi, C. *J. Phys. Chem.* **1976**, *80*, 287.

[26] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.