crystallization from CH_2Cl_2–C_5H_{12}, a yield of 1.90 g (80%) of product, mp 175–177 °C, was obtained with IR bands at 2023, 1933, and 1905 cm^{-1}. Anal. Calcd for $C_{34}H_{34}MoN_2O_4P_2$: C, 58.97; H, 4.95; N, 4.05; P, 8.95; mol wt 692.5. Found: C, 59.12; H, 5.20; N, 4.02; P, 9.06; mol wt 691.

$L_{IIs}W(CO)_4$. This compound was prepared analogously from $W(CO)_6$ (3.5 mmol) and L_{IIs} (3.5 mmol) in 25 mL of diglyme for 2 h at a bath temperature of 155–160 °C. The yellow product, mp 203–205 °C, was recrystallized from CH_2Cl_2–C_5H_{12} in 37% yield. The CO stretching frequencies are 2017, 1916, and 1897 cm^{-1}. Anal. Calcd for $C_{34}H_{34}N_2O_4P_2W$: C, 52.33; H, 4.39; N, 3.59; P, 7.94. Found: C, 51.45; H, 4.51; N, 3.43; P, 7.70.

$L_{IIs}Cr(CO)_4$. $(C_7H_8)Cr(CO)_4$ (1.05 g, 4.1 mmol) and 2.05 g (4.2 mmol) of L_{IIs} were stirred for several days under N_2 in 25 mL of benzene. After removal of the solvent, the oily residue was dissolved in CH_2Cl_2 and greenish yellow crystals precipitated upon addition of CH_3OH. The product, mp 122–124 °C, with CO stretches at 2020, 1920, and 1903 cm^{-1}, was formed in 37% yield. Anal. Calcd for $C_{34}H_{34}CrN_2O_4P_2$: C, 62.96; H, 5.28; N, 4.32; P, 9.55. Found: C, 62.31; H, 5.56; N, 4.09; P, 9.74.

$L_{IIs}[Cr(CO)_5]_2$. $Cr(CO)_6$ (1.76 g, 8.0 mmol) and L_{IIs} (1.92 g, 4.0 mmol) were heated in 25 mL of diglyme at an oil bath temperature of 155–160 °C for 2 h. Excess $Cr(CO)_6$ was removed by filtration, and the filtrate was concentrated by rotary evaporation. The resulting oil was dissolved in CH_2Cl_2 and an off-white precipitate, mp 126–127 °C, formed on addition of CH_3OH, in 38% yield. The compound has IR stretches at 2068, 1983, and 1940 cm^{-1}. Anal. Calcd for $C_{40}H_{34}Cr_2N_2O_{10}P_2$: C, 55.31, H, 3.95; N, 3.22; P, 7.13. Found: C, 54.86; H, 4.14; N, 3.00; P, 7.42.

$L_{IIs}[Mo(CO)_5]_2$. $[Et_4N][Mo(CO)_5I]$ (1.0 g, 2.0 mmol) and 0.5 g (1.0 mmol) of L_{IIs} were stirred under N_2 at rt in 20 mL of $CHCl_3$ for 24 h. The mixture was evaporated to dryness, and the residue dissolved in CH_2Cl_2 and reprecipitated with CH_3OH. After being washed with H_2O, the white crystals, mp 135–137 °C, with IR bands at 2073, 1990, and 1943 cm^{-1}, represented an 80% yield. Anal. Calcd for $C_{40}H_{34}Mo_2N_2O_{10}P_2$: C, 50.23; H, 3.58; N, 2.93; P, 6.48. Found: C, 49.86; H, 3.76; N, 3.00; P, 6.58.

$L_{IIs}[W(CO)_5]_2$. The compound was prepared as above from 0.5 g (1.0 mmol) of L_{IIs} and 0.84 g (2.0 mmol) of $(C_6H_5NH_2)W(CO)_5$ in 25 mL of C_6H_6. Yellow crystals, mp 147–149 °C, were recrystallized from CH_2Cl_2–CH_3OH in 68% yield. The compound has IR bands at 2072, 1980, and 1933 cm^{-1}. Anal. Calcd for $C_{40}H_{34}N_2O_{10}P_2W_2$: C, 42.43; H, 3.03; N, 2.47; P, 5.47. Found: C, 42.30; H, 3.30; N, 2.40; P, 5.61.

$L_{IV}[Cr(CO)_4]_2$. L_{IV} (0.85 g, 1.0 mmol) and 0.5 g (2.2 mmol) of $Cr(CO)_6$ were heated in 10 mL of diglyme for 2 h in an oil bath at 170–175 °C. After removal of the solvent, the crude product was washed several times with CH_2Cl_2–acetone solution. The yellow compound (55%), dec pt >180 °C, is only sparingly soluble in organic solvents. It has CO stretches at 2011, 1928, and 1893 cm^{-1}. Anal. Calcd for $C_{62}H_{52}Cr_2N_2O_8P_4$: C, 63.06; H, 4.44; N, 2.37; P, 10.49. Found: C, 62.55; H, 4.65; N, 2.28; P, 10.27.

$L_{IV}[Mo(CO)_4]_2$. The reaction between $Mo(CO)_6$ and L_{IV} was carried out in 10 mL of toluene at an oil bath temperature of 120 °C. The resulting white crystals, dec pt >250 °C, with IR bands at 2025, 1935, 1907, and 1896 (sh) cm^{-1}, are insoluble in CH_2Cl_2, EtOH, C_6H_6, and acetone. The yield was 70%. Anal. Calcd for $C_{62}H_{52}Mo_2N_2O_8P_4$: C, 58.64; H, 4.13; N, 2.21; P, 9.76. Found: C, 58.40; H, 4.27; N, 2.15; P, 9.77.

$L_{IV}[W(CO)_4]_2$. The yellow compound, dec pt >250 °C, was prepared in 62% yield from $W(CO)_6$ and L_{IV} in diglyme at a bath temperature of 180 °C for 3 h. It is also only sparingly soluble in organic solvents. The CO stretches are at 2018, 1919, and 1895 cm^{-1}. Anal. Calcd for $C_{62}H_{52}N_2O_8P_4W_2$: C, 51.55; H, 3.63; N, 1.94; P, 8.58. Found: C, 51.03; H, 3.82; N, 1.86; P, 8.75.

$L_{IV}Cr(CO)_4$. L_{IV} (2.3 g, 2.7 mmol) and 0.7 g (2.7 mmol) of $C_7H_8Cr(CO)_4$ were stirred under N_2 in 40 mL of C_6H_6 for 24 h at room temperature. After concentration via rotary evaporation, the residue was dissolved in CH_2Cl_2 and reprecipitated by the addition of CH_3OH. The slightly greenish powder, mp 105–108 °C, after recrystallization from CH_2Cl_2–CH_3OH, weighed 1.76 g (64%). The IR CO bands are at 2006, 1913, and 1887 cm^{-1}. Anal. Calcd for $C_{58}H_{52}CrN_2O_4P_4$: C, 68.50; H, 5.15; N, 2.75; P, 12.18. Found: C, 67.97; H, 5.20; N, 2.51; P, 11.70.

$L_{IV}[Cr(CO)_4][Mo(CO)_4]$. $C_7H_8Mo(CO)_4$ (0.3 g, 1 mmol) and 1.0 g (1.0 mmol) of L_{IV} $Cr(CO)_4$ were stirred under N_2 in 50 mL of C_6H_6 for 72 h. The greenish white precipitate which formed was recrystallized from acetone. The yield was 40%. Anal. Calcd for $C_{62}H_{52}CrMoN_2O_8P_4$: C, 60.79; H, 4.28; N, 2.29; P, 10.11. Found: C, 60.42; H, 4.26; N, 2.26; P, 10.50.

$L_{IV}[W(CO)_5]_4$. L_{IV} (0.85, 1.0 mmol) and 2.5 g (6.0 mmol) of $PhNH_2W(CO)_5$ were stirred in 30 mL of benzene. The solution was concentrated by rotary evaporation, and a ^{31}P NMR spectrum was taken of the crude reaction mixture (a supersaturated solution). Yellow crystals, with CO stretching frequencies of 2073, 1980, and 1935 cm^{-1}, formed in 72% yield. Anal. Calcd for $C_{74}H_{52}N_2O_{20}P_4W_4$: C, 41.37; H, 2.44; N, 1.30; P, 5.77. Found: C, 41.89; H, 2.71; N, 1.84; P, 5.95.

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Registry No. L_I, 43133-27-3; L_{IIs}, 43133-28-4; L_{IIu}, 43133-29-5; L_{IV}, 43133-31-9; $L_ICr(CO)_5$, 73926-17-7; $L_IMo(CO)_5$, 73926-18-8; $L_IW(CO)_5$, 73940-54-2; $L_{IIu}Cr(CO)_4$, 73926-19-9; $L_{IIu}Mo(CO)_4$, 73926-20-2; $L_{IIu}W(CO)_4$, 73940-55-3; $L_{IIu}[W(CO)_5]_2$, 73940-56-4; $L_{IIs}Cr(CO)_4$, 73926-21-3; $L_{IIs}Mo(CO)_4$, 58904-31-7; $L_{IIs}W(CO)_4$, 73926-22-4; $L_{IIs}[Cr(CO)_5]_2$, 73926-23-5; $L_{IIs}[Mo(CO)_5]_2$, 73926-24-6; $L_{IIs}[W(CO)_5]_2$, 73926-25-7; $L_{IV}[Cr(CO)_4]_2$, 73926-26-8; $L_{IV}[Mo(CO)_4]_2$, 73926-27-9; $L_{IV}[W(CO)_4]_2$, 73940-57-5; $L_{IV}Cr(CO)_4$, 73926-29-1; $L_{IV}Mo(CO)_4$, 54340-53-3; $L_{IV}[Cr(CO)_4][Mo(CO)_4]$, 73926-28-0; $L_{IV}[W(CO)_5]_4$, 73926-30-4; $[Et_4N][Cr(CO)_5I]$, 14780-98-4; $[Et_4N][Mo(CO)_5I]$, 14781-00-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $PhNH_2W(CO)_5$, 16969-72-5; $(C_7H_8)Cr(CO)_4$, 12146-36-0; $(C_7H_8)Mo(CO)_4$, 12146-37-1.

Correspondence

Alternative Bonding Models for an Unusual Metallocarborane Containing a Wedging B–H Group

Sir:

The skeletal geometries of many seemingly disparate polyhedral cagelike molecules may be rationalized and predicted by a set of simple, empirical electron-counting rules.[1] In this regard, a commonly accepted rationalization[2] (supposedly[2b,c] based on Mingos' capping principle[3]) for the peculiar skeletal geometry of $CpCoFeMe_4C_4B_8H_8$[4] (Cp = η^5-C_5H_5, Me = CH_3) (Figure 1) is that the double-face-capping (wedging) BH vertex *suggested* by the molecular structure determination[2a] is a direct result of a hyperdeficiency[5] of two

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[1] (a) Mingos, D. M. P. *Nature Phys. Sci.* **1972**, *236*, 99. (b) Grimes, R. N. *Ann. N. Y. Acad. Sci.* **1974**, *239*, 180. (c) Wade, K. *Chem. Brit.* **1975**, *11*, 177. (d) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (e) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1976**, 2606.

[2] (a) Maxwell, W. M; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 3490. (b) Grimes, R. N. *Acc. Chem. Res.* **1978**, *11*, 420. (c) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3255.

[3] Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

[4] See Figure 1 for a drawing of the molecular structure and atom numbering scheme for $CpCoFeMe_4C_4B_8H_8$.

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skeletal electrons. This skeletal electron (henceforth abbreviated SE) hyperdeficiency obtains from the following considerations: quoting from ref 2a, "Insertion of a (η^5-C_5H_5)Co unit (a two-electron donor) into the $[(CH_3)_2C_2B_4H_4]_2FeH_2$ precursor, with concomitant loss of the two "extra" hydrogens, increases the number of framework atoms (*n*) without increasing the number of framework electrons."

However, despite its superficial reasonableness there are several difficulties with the above approach. The basis of the capping principle is Mingos' qualitative perturbation theoretical analysis (complemented by EHMO calculations)[3] which states that a capped polyhedron has the same number of skeletal[6] bonding orbitals as the parent uncapped polyhedron because the interaction of the frontier orbitals of a face-capping MH fragment (or isolobal BH, $M(CO)_3$, etc., fragments)[7] with those of the central polyhedron results in the stabilization of only those skeletal bonding orbitals of the central polyhedron which are of σ and π symmetry with respect to the capping axis[7]—the frontier orbitals of the capping fragment being destabilized. Hence, no new skeletal bonding orbitals are introduced. The frontier orbital orientational sense of the capping fragment in this analysis[7] clearly does not lend itself to a rationalization of *double* face capping, especially by a first-row-atom vertex such as boron, which uses only four orbitals for chemical bonding.

Moreover, if, as suggested by King and Rouvray,[8] the common iron atom in $CpCoFeMe_4C_4B_8H_8$ contributes two SE's to each fused polyhedron,[9] then the SE count for this species is *not* hyperdeficient—containing 34 SE's (respectively obtaining 2, 3, 2, and 4 SE's from each BH, CH, CpCo, and Fe vertex), which is precisely the amount required[1] for a "normal" skeletal geometry consisting of a seven-vertex pentagonal-bipyramidal (PB) FeC_2B_4 cage (16 = 2*n* + 2 SE's) fused at the iron atom to an eight-vertex dodecahedral (DD) $FeCoC_2B_4$ cage (18 = 2*n* + 2 SE's). Evidently the skeletal geometry exhibited by $CpCoFeMe_4C_4B_8H_8$ cannot be immediately explained in terms of simple skeletal electron-counting rules. This correspondence is thus an attempt to provide alternative rationalizations for the unusual skeletal structure of $CpCoFeMe_4C_4B_8H_8$, which presented particular difficulties in an earlier paper,[8] in lieu of more rigorous theoretical calculations. Perhaps this correspondence might lead to such calculations, which are needed to substantiate or vitiate the alternative viewpoints presented herein.

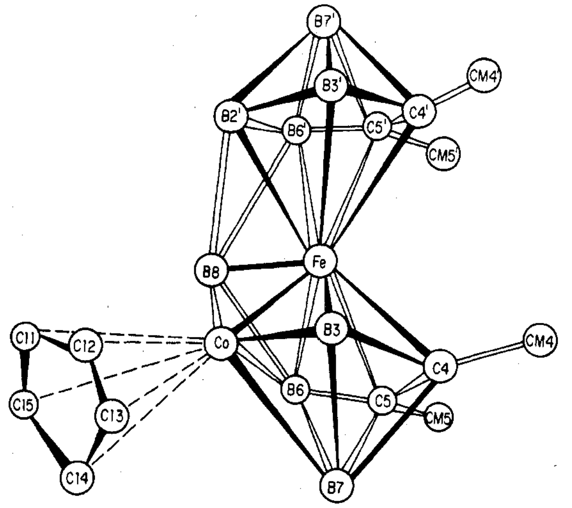

Figure 1. Molecular structure and numbering system for $CpCoFeMe_4C_4B_8H_8$. The hydrogen atoms are omitted for clarity.

$CpCoFeMe_4C_4B_8H_8$ contains two PB's fused at the iron atom as well as a singular wedging BH group joined to the iron atom and apparently (vide infra) face capping both PB's.[4] Each skeletal atom can be considered to provide three orbitals for skeletal bonding (the common iron atom providing three orbitals for skeletal bonding in each fused polyhedron). With the local *z* direction for each skeletal atom pointing toward the centroids of their respective polyhedra, these three orbitals may be partitioned into a "unique internal"[8] or "radial"[1c] orbital of sp_z hybridization and a degenerate pair of "tangential"[1c] or "twin internal"[8] orbitals composed of the p_x and p_y orbitals for boron and carbon and of p_xd_{xz} and p_yd_{yz} hybrids for the transition metals.[3] If one treats the "extra" wedging HB(8)[4] vertex separately and first considers the bonding in the portion of the molecule in which the iron atom serves as a vertex common to two PB's, then, in the manner described previously,[8] in each PB, the global mutual overlap of the seven radial orbitals (the topology of which is represented by a K_7 graph) and the pairwise surface overlap of the 14 twin internal orbitals (the topology of which is represented by seven isolated K_2 graphs) generate 8 = *n* + 1 skeletal bonding orbitals for a total of 16 such orbitals in the two PB's. These are then filled with 32 SE's (respectively obtaining 2, 2, 3, and 4 SE's from each BH, CpCo, MeC, and Fe), leaving six electrons on the CpCo unit to fill its three nonbonding orbitals and four electrons on the iron to fill two of its three nonbonding orbitals.

The unique HB(8) vertex is, of course, still a source of the three orbitals and two electrons just as if it were a bona fide vertex of one of the two fused PB polyhedra. However, to accommodate the double face capping, the orbitals must now be reoriented such that the radial sp hybrid is directed toward the iron atom. The pairwise overlap of this radial sp hybrid with the remaining empty, originally nonbonding[6] orbital of the iron is represented by a K_2 graph and generates yet another

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(5) This term[2] describes a skeletal electron count of less than 2*n* + 2 for an *n* atom "electron deficient" cluster.

(6) N.B. Terms such as skeletal and nonbonding are used throughout this paper within the semantic context of the *operational* partitioning of fragment orbitals in Wade's scheme[1] and not necessarily in an absolute sense; cf. footnote 9, ref 1b.

(7) The frontier orbitals of these isolobal framents are composed of one "radial"[1c] or "unique internal"[8] orbital of σ symmetry with respect to the capping axis (defined as passing through the capping atom and the centroid of the parent polyhedron) and a degenerate pair of "tangential"[1c] or "twin internal"[8] orbitals of π symmetry with respect to the capping axis.[3]

(8) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.

(9) One may start from the well-established viewpoint[10] that six electrons are shared between a metal vertex and each of its polyhedral fragments. Since a neutral quasi *closo*[11]-$R_2C_2B_xH_x$ fragment can be considered as a formal four-electron donor ligand, it follows that a *commo*-M vertex (M = transition metal) formally contributes two electrons for skeletal bonding in *each* fused polyhedron. It may be further taken that a *commo*-M vertex uses three of its nine valence orbitals for skeletal bonding in each fused polyhedron. This leaves three nonbonding[6] orbitals on the metal with which to accommodate up to 6 − *y* electrons and *y* additional electrons formally supplied by *y* metal-bound[12] hydrogens. This is completely equivalent to the viewpoint of Grimes[12b] in which the $(Me_2C_2B_4H_4)_2FeH_2$ precursor is formally viewed as two nido pentagonal-pyramidal $(Me_2C_2B_4H_4)^{2-}$ moieties fused to an $[Fe^{II}H_2]^{4+}$ unit. The loss of the two metal-bound hydrogens as $\cdot H^0$ from the $[Fe^{II}H_2]^{4+}$ unit would result in a formal $[Fe^{IV}]^{4+}$ unit. Thus, the loss of metal-bound hydrogens will have no effect on the skeletal electron count.[13]

(10) Jones, C. J.; Evans, W. J. Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 543.

(11) Muetterties, E. L. "Boron Hydride Chemistry"; Academic Press: New York, 1975; p 10.

(12) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 263. (b) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 4818.

(13) A further problem with the original rationalization is that it would also imply that the paramagnetic formal d^5 Fe(III) species $(Me_2C_2B_4H_4)Fe^-$ (formed by the formal loss from $(Me_2C_2B_4H_4)_2FeH^-$ of the metal-bound hydrogen as $\cdot H^0$)[14] is hyperdeficient one SE when, in fact, by bookkeeping, the formal electron deficiency is only with respect to a nominal filled-shell d^6 electronic configuration of the iron.[15]

(14) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343.

(15) Nishimura, E. K. *J. Chem. Soc., Chem. Commun.* **1978**, 858.

bonding orbital. This is filled with the two electrons from HB(8) in the form of a boron–iron dative bond, the precedent for which may be found in the "borine" substituted metal carbonyls.[16] The two remaining p orbitals on the unique HB(8) can then interact with the surfaces of each of the two PB moieties. The topology of these surface capping interactions are such that one of the seven pairwise K_2 interactions in each PB (vide supra) is now represented by a K_3 graph. However, this has no effect on the number of skeletal bonding orbitals inasmuch as any complete graph, K_n, has but only one positive eigenvalue and hence generates only one bonding orbital.[8]

We have thus reconciled the singular double-face-capping structure of $CpCoFeMe_4C_4B_8H_8$ with its nominal 34 SE's. However, because of the borderline distances involved (vide infra), an interesting possibility is that B(8) is *not* directly involved in a covalent bonding interaction with B(2′)/B(6′) such that $CpCoFeMe_4C_4B_8H_8$ might be regarded as $(Me_2C_2B_4H_4)$-*commo*-Fe-$(CpCoMe_2C_2B_4H_4)$, consisting of a PB FeC_2B_4 moiety fused at the iron atom to a capped-pentagonal-bipyramidal (CPB) $FeCoC_2B_4$ moiety. In that event, the PB moiety has the appropriate number of SE pairs ($8 = n + 1$) for its idealized closo geometry whereas the CPB moiety is distorted from the idealized DD appropriate[1] for its $9 = n + 1$ SE pairs. With eight-vertex polyhedra, however, the geometrical distortions needed to send one idealized geometry into alternative forms are small.[17] In fact, for the $FeCoC_2B_4$ moiety, the idealized CPB and DD geometries are related by a minimal diamond–square–diamond (dsd) motion[18] involving the Fe, Co, B(8), and B(3) atoms.[4] For rationalization of this distortion of the $FeCoC_2B_4$ moiety from the usually favored[1,17] DD form, it is noted that the iron atom is, prima facie, an extremely electron-deficient[19] formal 16-electron Fe(IV) vertex[9] while the cobalt atom is, prima facie, a formal 18-electron Co(III) vertex—the likes of which are known to be fairly readily oxidized.[20] This suggests an intramolecular electron transfer from cobalt to iron concomitant with the formation of a hyperpolyhedral metal–metal bond[15,21] (diamagnetism, Fe–Co = 2.48 Å[2a]) such that a stable filled-shell electronic configuration is attained by both metals.

The distortion of the $FeCoC_2B_4$ moiety toward an idealized CPB geometry can thus be viewed as being necessary to accommodate the hyperpolyhedral iron–cobalt bond involving the metal atoms located at otherwise nonadjacent vertices of the polyhedron. In terms of the King/Rouvray graph-theoretical approach,[8] this minimal dsd distortion may be represented by a permutation of the pairwise K_2 polyhedral surface bonding topology, rather than a deltahedral partitioning via a "casting out" of a tetrahedron such that the number of skeletal bonding orbitals, per se, remains unaffected—the metal–metal bond being an extra or hyperpolyhedral K_2 graph.

Implicit in the above rationalization is the assumption that the HB(8) vertex uses its three frontier orbitals for bonding in the $FeCoC_2B_4$ moiety exclusively—the radial sp hybrid of HB(8) being directed toward the centroid of the $FeCoC_2B_4$ CPB polyhedron—thereby precluding a covalent face-capping interaction with the PB FeC_2B_4 moiety. The following considerations give strong support to this viewpoint: (1) while the B(8)–B(6)/Fe/Co distances[2a] in the CPB $FeCoC_2B_4$ moiety are normal for bonded distances in metallocarboranes, the B(8)–B(2′)/B(6′) distances (average = 2.14 Å)[2a] are exceptionally long[22] —being 0.4 Å longer (average) than the remaining B–B distances; (2) the comparatively short B(2′)–B(6′) distance (1.68 Å)[2a] is much more consistent with skeletal four-coordination than with the skeletal five-coordination if B(2′)/B(6′) were to be covalently bonded to B(8);[23] (3) skeletal models show that the dsd distortion from a DD toward a CPB (vide supra) serves to force the B(8) vertex of the $FeCoC_2B_4$ moiety toward the B(2′)–B(6′) edge of the fused PB FeC_2B_4 moiety; (4) the dihedral angle between the planes defined by the equatorial rings of the PB's in $CpCoFeMe_4C_4B_8H_8$ is 9.35°[12a] such that the two pairs of eclipsed MeC groups are moved *toward* each other and are well within the sum of their van der Waals radii.[12a] In the $(Me_2C_2B_4H_4)_2FeH_2$ precursor, a similar ring tilt is observed.[12a] These observations clearly run counter to expectations based on steric considerations unless there are nonbonded steric interactions on the side of the molecule opposite the MeC groups. That such interactions exist between two wedged metal-bond hydrogens in the $(Me_2C_2B_4H_4)_2FeH_2$ precursor was suggested by Pipal and Grimes.[12a] Considering that the B(8)–B(2′)/B(6′) distances are already exceptionally long for covalent bonding interactions whereas the MeC···MeC repulsions would seem to favor shorter B(8)–B(2′)/B(6′) contacts, we suggest that such nonbonded steric interactions are also operative between B(8) and B(2′)/B(6′) in $CpCoFeMe_4C_4B_8H_8$.[24] This viewpoint is further supported by the fact that in the cobaltocenium-substituted derivative of $(Me_2C_2B_3H_5)$-*commo*-$Co(Me_2C_2B_4H_4)^-$, the dihedral angle between the equatorial rings is 6.5° such that the eclipsed MeC groups are moved *away* from each other.[26] A similar effect is observed in $(Me_2C_2B_9H_9)_2Ni$.[27]

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(16) Schmid, G.; Petz, W.; Nöth, H. *Inorg. Chim. Acta* **1970**, *4*, 423.

(17) (a) Muetterties, E. L.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7520. (b) Klanberg, F.; Eaton, D. R.; Guggenberger, L. J.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1271. (c) Muetterties, E. L.; Hoel, E. L.; Salentine, C. G.; Hawthorne, M. F. *Ibid.* **1975**, *14*, 950. (d) Pipal, J. R.; Grimes, R. N. *Ibid.* **1979**, *18*, 257. (e) Bowser, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 4623; Evans, J. *J. Chem. Soc., Dalton Trans.* **1978**, 18.

(18) Lipscomb, W. N. *Science (Washington, D. C.)* **1966**, *153*, 373.

(19) No stable metalloheteroboranes containing iron atoms in the formal +4 oxidation state are known.

(20) Inter alia: (a) Dustin, D. F.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 1380. (b) Brennan, D. E.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3399.

(21) This term[15] relates to the fact that such a metal–metal bond, real or formal, presents a pairwise interaction above and beyond that ostensibly required[1,6,8] for polyhedral skeletal bonding per se and distinguishes it from the metal–metal bonds found, e.g., between the Co atoms in $Cp_2Co_2C_2B_6H_8$ (Hoel, E. L.; Strouse, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 1388). As such, the electron pair involved is not included in the nominal skeletal[6] electron count.

(22) B–B distances which are considered as being unambiguously indicative of covalent bonding interactions in boranes and heteroboranes normally range from 1.7 to 1.9 Å (footnote 26, ref 2a). The B–B distances in excess of 2.0 Å and considered as being indicative of covalent bonding interactions in the following references are significantly shorter than the average B(8)–B(2′)/B(6′) distance of 2.14 Å in $CpCoFeMe_4C_4B_8H_8$. Nearly all of these long B–B bonds occur between high-coordinate borons bonded to one or more carbon atoms (which presumably withdraw electron density) or occur in fluxional, thermally unstable or thermally interconvertible species such that the long bonds have been, or may be, attributed to a perturbation toward some rearrangement pathway. (a) Green, M.; Spencer, J. L.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1974**, 571. (b) Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2270. (c) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1974**, *13*, 1411. (d) Friesen, G. D.; Little, J. L.; Huffman, J. C.; Todd, L. J. *Ibid.* **1979**, *18*, 755. (e) Grimes, R. N.; Zalkin, A.; Robinson, W. T. *Ibid.* **1976**, *15*, 2274. (f) Callahan, K. P.; Strouse, C. E.; Sims, A. L.; Hawthorne, M. F. *Ibid.* **1974**, *13*, 1393. (g) Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Ibid.* **1973**, *12*, 2262. (h) Tsai, C.; Streib, W. E. *J. Chem. Soc.* **1966**, *88*, 4513. (i) Maxwell, W. M.; Weiss, R.; Sinn, E.; Grimes, R. N. *Ibid.* **1977**, *99*, 4016.

(23) Brown, L. D.; Lipscomb, W. N. *Inorg. Chem.* **1977**, *16*, 2989.

(24) Significantly, while the average B(8)–B(2′)/B(6′) distance is 0.4 Å longer than that of the remaining B–B bonding distances in $CpCoFeMe_4C_4B_8H_8$, it is only 0.26 Å shorter than the intramolecular nonbonded B···B contacts found in the fused species $B_{20}H_{16}(NCCH_3)_2$ (2.40 Å)[25] and only 0.10 Å shorter than that regarded as nonbonding in isomer V of $Cp_2Fe_2Me_4C_4B_8H_8$ (2.241 Å),[22i] while nonbonded B···B contacts as short as 2.0 Å have been deemed as being possible.[25]

(25) Enemark, J. H.; Friedman, L. B.; Lipscomb, W. N. *Inorg. Chem.* **1966**, *5*, 2165.

(26) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447.

(27) Churchill, M. R.; Gold, K. *J. Am. Chem. Soc.* **1970**, *92*, 1180.

In summary, we believe the original rationalization of the structure of $CpCoFeMe_4C_4B_8H_8$ to contain several inconsistencies. At this stage, a rationalization of the peculiar skeletal geometry exhibited by $CpCoFeMe_4C_4B_8H_8$ requires two alternative bonding models, since it is impossible, from crystallographic data alone, to unambiguously distinguish between true covalent bonding interactions involving B(8) and B(2′)/B(6′) and an apparent or pseudo double face capping caused by geometric and steric constraints.

Registry No. $CpCoFeMe_4C_4B_8H_8$, 58814-74-7.

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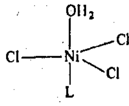
Interpretation of Volumes of Activation and the Effect of Bond Length Changes of the Nonexchanging Ligands

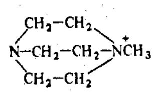
Sir:

In a recent letter to this journal,[1] it has been suggested that the use of volumes of activation to determine reaction mechanisms may be considerably complicated by important changes in the metal–ligand bond lengths of the nonexchanging ligands on going from reactant to transition state. The author tries to make two major points.

(a) For a dissociative reaction, as one ligand is lost, there is compression of the remaining bonds with reduction of the volume of the primary coordination sphere and collapse of the solvent onto this primary solvation sphere. In terms of a potential energy function $U(r)$, the equilibrium bond length is simply the distance at which the energy is minimum, i.e., when $\partial U/\partial r = 0$. If one adopts a classical function where both attractive and repulsive forces are simply proportional to the number of ligands, then the bond length must be independent of the number of ligands.[2] The contributions to the potential which give rise to changes in the equilibrium radius as the number of ligands is changed are clearly those that depend on the geometry of the complex. The most important of these are ligand–ligand repulsive (and attractive) forces.[3] The crystal field effect also comes into this category, but for the purposes of this qualitative discussion, we shall restrict interest to d^0, d^5, and d^{10} ions where this effect is absent. Quantum mechanical calculations on ion–water clusters of the form $M(H_2O)_n^{\pm}$ (M = Li, Na, K, F, Cl; n = 1, 10) also predict such contractions. With Na^+ (effective ionic radius 1.02 Å[4]) as an example, the metal–oxygen bond length contracts from 2.35 to 2.32 Å on going from n = 6 to 5.[5] This would give rise to a volume contraction of about 3 $cm^3\ mol^{-1}$. We have no quantum mechanical calculations for a 2+ ion of similar size, e.g., Ca^{2+} (1.00 Å), but from considerations of a classical potential function, we might expect ligand–ligand interactions to be a smaller contribution to the overall energy, and hence the volume reduction would be less than 3 $cm^3\ mol^{-1}$. Since the transition state for a dissociative D reaction occurs before the reactive intermediate, this "negative contribution" to the volume of activation due to bond contraction would be less than that given above. Finally, it is accepted that water-exchange reactions generally proceed via interchange mechanisms.[6] For an I_d mechanism, the transition state consists of five strong metal–water bonds and two weak ones,[7] and thus we would expect the "negative contribution" to be less than that for a D mechanism. It would thus seem this contribution cannot be much larger than the accuracy to which ΔV^* can be measured (±1 $cm^3\ mol^{-1}$). It was suggested[1] that evidence for this contraction could be obtained by comparing the Ni(II)–water bond length in complex I of 2.10 Å with the "normal radius sum of 2.16 Å". Pauling[8] is cited for this sum.



I



L

The correct value for the Ni(II)–water bond length in $Ni(H_2O)_6^{2+}$ is in fact 2.05 Å.[9] It seems superfluous to add how inadvisable it is to try to compare small differences in bond lengths in complexes whose overall charges differ by two and where the attached ligands are so different. *We conclude that bond contraction does occur going from six- to five-coordinate but, at least for an ion like Ca^{2+}, the effect on ΔV^* must be very small indeed.*

(b) It is stated that across the first transition series, earlier members with few t_{2g} electrons should be more susceptible to contraction.[1] We do not dispute this.[10] However, from this

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[1] Langford, C. H. *Inorg. Chem.* **1979**, *18*, 3288.

[2] In general, the potential function can be written in the form $U(r) = -nU_{att}(r) + nU_{rep}(r)$, where n is the number of ligands and $U_{att}(r)$ and $U_{rep}(r)$ are the attractive and repulsive contributions. The equilibrium bond length occurs when $U'_{att}(r) = U'_{rep}(r)$, where the prime denotes the first differential with respect to r. If $U_{att}(r)$ and $U_{rep}(r)$ do not depend on n (i.e., there are no interactions that depend on the geometrical arrangement of ligands), then the equilibrium bond length will not depend on n.

[3] See for example: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 62.

[4] In this work, we use the recent, extensive compilation of: Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1970**, *26*, 1076. This tabulation contains results for most metal ions in all common oxidation states, coordination numbers, and both high and low spin (where relevant).

[5] Kistenmacher, H.; Popkie, H.; Clementi, E. J. *Chem. Phys.* **1974**, *61*, 799.

[6] Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. *ACS Monogr.* **1978**, *No. 174*, Chapter 1.

[7] Meyer, F. K.; Newman, K. E.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 5588.

[8] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960.

[9] We have found 11 accurate determinations of the Ni(II)–O bond length in $Ni(H_2O)_6^{2+}$, 6 in solution and 5 in the solid state. With one exception, ref 9g (2.15 Å), all other values lie between 2.04 and 2.06 Å (mean value 2.053; standard deviation 0.007 Å). The solid-state values were the averaged bond lengths since the octahedron is frequently slightly distorted due to crystal-packing effects. (a) Grimes, N. W.; Kay, H. F.; Webb, M. W. *Acta Crystallogr.* **1963**, *16*, 823. (b) O'Connor, B. H.; Dale, D. H. *Ibid.* **1966**, *21*, 705. (c) Gallezot, P.; Weigel, D.; Prettre, M. *Ibid.* **1967**, *22*, 705. (d) Baggio, S.; Becka, L. N. *Acta Crystallogr., Sect. B* **1969**, *25*, 1150. (e) Bol, W.; Gerrits, G. J. A.; van Panthaleon Van Eck, C. L. *J. Appl. Crystallogr.* **1970**, *3*, 486. (f) Bigoli, F.; Braibanti, A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Acta Crystallogr., Sect. B* **1971**, *27*, 1427. (g) Shapovalov, I. M.; Radchenko, I.; Lesoristskaya, M. K. *Zh. Strukt. Khim.* **1972**, *13*, 140. (h) Ohtaki, H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 701. (i) Camini, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *Discuss. Faraday Soc.* **1977**, *64*, 62. (j) Sandrom, D. R.; Dodgen, H. W.; Lytle, F. W. *J. Chem. Phys.* **1977**, *67*, 473.

[10] We do, however, wish to make several points about Table II of ref 1. We presume the units should be pm not nm. The ionic radii used are those of Pauling[8] and date "in part" from 1926. They do not show the well-established nonmonotonous variation along the first-row transition-metal series which is caused by crystal field effects. With the radii of Shannon and Prewitt,[4] a trend similar to that reported in ref 1 is observed, but Ti and V do not continue the trend. The value for V is low and for Ti somewhat larger. This is readily explained when it is realized that d^3 and d^8 ions show most crystal field contraction which is why the values of V and Ni are low whereas the value for Cr is large since we are subtracting the radius of a d^3 ion. Much of the trend observed is thus simply due to crystal field effects. A better procedure would have been to compare 2+ and 3+ ions of similar d electron configuration. With regard to metal–ligand vibrations, the frequencies of the d^{10} ions are closely similar to those of the d^5 ions (see ref 8 of ref 1). It is again clear that much of the trend is simply a crystal field effect. Similar but less extensive data for 3+ ions and d^0 to d^5 ions also support this.

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