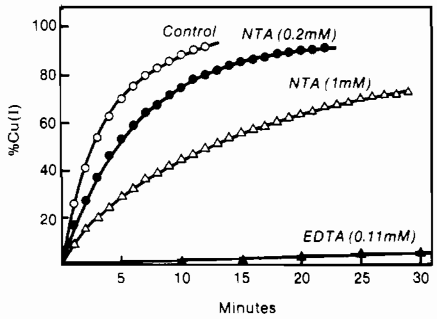

Figure 7. Reduction of Cu(II) by HEPES in the presence of batho as influenced by additional ligands stabilizing Cu(II). Initial conditions: [Cu] = 0.1 mM, [batho] = 2 mM, [NaCl] = 1.0 M, [HEPES] = 0.2 M, pH 7.0, 25 ± 1 °C. Stabilizing ligands are at the concentrations indicated.

energy of activation was found to be 24.3 kcal/mol.

For both HEPES and DMEA, the pH profile was measured (Figure 6). For low pH values ($pH < pK_a$) the rate decreased linearly with decreasing pH. For high pH values ($pH > pK_a$), there was only weak, if any, pH dependency (pK of HEPES = 7.48;[2] pK of DMEA = 9.29[10]).

The influence of ligands, which stabilize the Cu(II), is shown in Figure 7. Nitrilotriacetate (NTA) and ethylenediaminetetracetate (EDTA) were investigated. Increasing ligand concentration and incresing stability for Cu(II) inhibit the reduction (stability constants for Cu(II) with NTA, $\log K_1 = 12.4$ and $\log K_2 = 4.5$, and with EDTA, $\log K = 18.7$[10]).

Discussion

The results demonstrate that HEPES is oxidized by Cu(II) in the presence of ligands that stabilize Cu(I). The similar behavior of HEPES and DMEA suggests the oxidation of the alcoholic groups of both components with participation of nitrogen in ligand formation (Figure 1). The enhancement of the rate in the case of HEPES and DMEA compared with ethanol or glycerol can be explained on the basis of the formation of a weak ternary complex with the Cu(II)–batho system. Similar ternary complexes with the Cu(II)–2,9 dimethyl-1,10-phenanthroline system are known.[11,12] The direct interactions of Cu(II) with several N,N-disubstituted ethanolamines have been characterized. The first stability constant for complex formation with DMEA is $K_1 = 5 \times 10^4$.[13] The assumption that the Cu(II)–batho system forms a ternary complex with HEPES or DMEA as an intermediate in the reaction is strongly supported by the pH dependency of the reaction (Figure 6). Only the deprotonated species are able to reduce the Cu(II). This model is supported by the finding that the reaction is inhibited with NTA or EDTA.

Because the reaction is second order with respect to Cu(II), it appears that a pair of electrons must be transferred from the HEPES to two molecules of $Cu^{II}(batho)_2$. We therefore propose the following mechanism:

$$2Cu^{II}(batho)_2 + HEPES \overset{K}{\rightleftharpoons} [Cu^{II}(batho)_x]_2\text{–}HEPES \rightarrow 2Cu^{I}(batho)_2 + \text{oxidation products}$$

An estimated value for these interactions from kinetic data is $10^2 < K < 10^4\ mol^{-1}$. Direct data for the complexation of Cu(II) by 2,9-dimethyl-1,10-phenanthroline are available:[10] $\log K_1 = 6.1$, $\log K_2 = 4.9$. It has been suggested that similar constants are obtained for the Cu(II)–batho system. Under conditions chosen in this work, Cu(II) is present as a bis complex.[8,9]

In agreement with the proposed mechanism, tris(phenanthroline)iron(III) does not oxidize HEPES, even though it is a stronger oxidizing agent than the Cu(II)–batho complex ($E° = 1.1$ V[14]). As is well-known, Fe(III), unlike Cu(II), has a very low affinity for saturated amines.

We found that 1 equiv of HEPES is able to reduce 6 equiv of copper. This might be an explanation for the complex kinetics of this reaction in the later stages. Intermediates formed during the reaction could reduce the Cu(II) at a faster rate than HEPES itself. The fact that methanol, 2-propanol and Tris do not undergo a redox reaction may have to do with their lack of a specific structure or intermediate required for the reactivity.

In studies involving trace metals, especially Cu(II), HEPES should be used with caution as a buffer. There are weak but significant interactions between the metal and HEPES which may introduce experimental artifacts. If Cu(II) is present together with ligands that stabilize Cu(I), HEPES should never be used due to the reduction of Cu(II).

Acknowledgment. This work was supported in part by the National Institute of Arthritis, Diabetes, Digestive and Kidney Diseases, USPHS Grant AM12386. We thank Dr. Harvey Schugar for his wise and helpful advice.

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Notes

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Hyper-Closo Metallaboranes

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Greenwood, Kennedy, and co-workers have recently isolated and structurally characterized a wide variety of new phosphinometallaborane complexes.[1,2] Two complexes prepared via the cage-closure reactions (1) and (2) have been termed iso-closo

$$nido\text{-}(PMe_3)_2(CO)Ir(B_8H_{10}Cl) \xrightarrow[-H_2,\ CO]{135\ °C} H(PMe_3)_2Ir(B_8H_7Cl) \qquad (1)$$

$$nido\text{-}H(PPh_3)(Ph_2\overline{PC_6H_4)Ir(B}_9H_{12}) \xrightarrow[-2H_2]{85\ °C} H(PPh_3)(Ph_2\overline{PC_6H_4)Ir(B}_9H_8) \qquad (2)$$

metallaboranes, as their observed closed, polyhedral structures are not those normally found for nine- and ten-vertex closo metallaboranes. Greenwood et al. thus regard these complexes as simply different closo isomers. We suggest, on the basis of electron-counting arguments and by reference to known structural analogues, that these complexes contain two skeletal electrons

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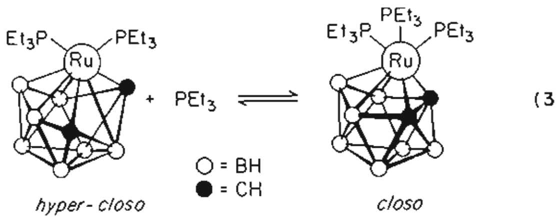
fewer than their closo counterparts and are thus best regarded as hyper-closo metallaboranes.

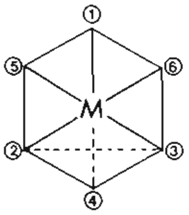
Note first that, in both eq 1 and 2, *four* electrons are lost as gaseous products in the thermolysis of the nido precursors (i.e., $N + 2 \rightarrow N$ skeletal electron pairs). In addition, the observed products contain two skeletal electrons *less* than the corresponding iridacarborane analogues, such as $H(PPh_3)_2Ir(C_2B_7H_9)$,[3] or the nickelaborane anion[4] $[(\eta\text{-}C_5H_5)Ni(B_9H_9)]^-$, both of which exhibit the normal closo bicapped-square-antiprismatic geometry. It is particularly important to note that the formal oxidation state of the metal (i.e., Ir^V in $HL_2Ir(B_nH_n)$ vs. Ir^{III} in $HL_2Ir(C_2B_nH_{n+2})$) does not necessarily change the number of skeletal electrons contributed by the metal vertex.[5]

Mason[7] and others[8-12] previously showed that N-vertex clusters possessing less than the $N + 1$ skeletal electron pairs needed for a closo geometry may adopt capped-closo structures, with one vertex capping a trigonal face for each "missing" skeletal electron pair. It was later demonstrated[3,13,14] that alternative distortions may also occur, and we used the term hyper-closo to include all *distorted* N-vertex polyhedra with less than $N + 1$ skeletal electron pairs.[15] Of particular relevance to this note is the equilibrium shown in (3), which demonstrates the two-electron relationship between these closo and hyper-closo structures.[3]



(3)

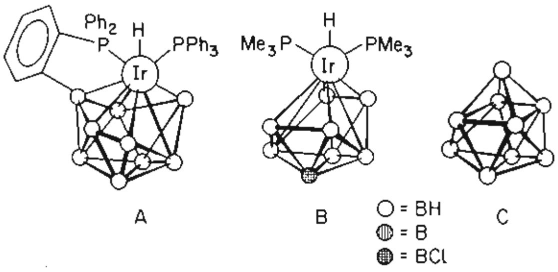
Table I. Comparison of Metal–Borane Bonding in Ten-Vertex Closo and Hyper-Closo Metallaboranes

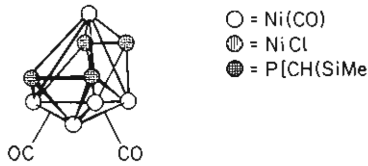


bond	bond distance, Å		
	IrB_9[a]	RuC_2B_7[b]	RhC_2B_7[c]
M–B(1)	2.16	2.02	2.10[d]
M–B(2)	2.19	2.19[d]	2.36[d]
M–B(3)	2.15	2.10[d]	2.21
B(2)–B(3)	>2.95	2.69[d]	1.79[d]
M–B(4)	2.39	2.49	3.50
M–B(5)	2.46	2.47	2.38
M–B(6)	2.38	2.34	2.32

[a] *hyper-closo*-$H(PPh_3)(Ph_2PC_6H_4)Ir(B_9H_8)$; ref 19. [b] *hyper-closo*-$[(o\text{-}CH_2{=}CHCH_2C_6H_4)PPh_2]Ru[(CMe)_2B_7H_7]$; ref 14. [c] *closo*-$H(PEt_3)_2Rh(C_2B_7H_9)$; ref 22. [d] Distances involve a CR vertex.

The structures of the two Greenwood–Kennedy metallaboranes are shown as A and B. The ten-vertex structure,[19] A, is very similar to that observed previously for $(Cp_2Fe)_2(C_2B_6H_8)$ and $L_2Ru[(CMe)_2B_7H_7]$,[13] where $L_2 = (o\text{-}CH_2{=}CHCH_2C_6H_4)PPh_2$, and differs from the closo structure in the bonding of the M-B(2)-B(4)-B(3) face (see Table I). The nine-vertex structure,[20] B, contains two modified bonding faces relative to the closo tricapped trigonal prism, C. An analogous structure has recently been determined by Olmstead and Power[21] for the nickel carbonyl cluster $Ni_5(CO)_6(Cl)(PR)_4$, where $R = CH(SiMe_3)_2$.





Although the skeletal electron count for this cluster is complicated by the presence of localized P–P multiple bonding and the odd-electron [NiCl] vertex, both of these features will limit the number of bonding skeletal electron pairs to less than the 10 required for a closo geometry, thus giving rise to the observed hyper-closo structure.

In summary, it appears that the combination of the electron-deficient metallaborane ligands with heavy-transition-metal vertices capable of existing in high formal oxidation states is favorable for the formation of stable hyper-closo structures. In view of a possible correlation of hyper-closo cage geometry with

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(5) According to Wade's rules, the number of skeletal electrons, E, contributed by a metal vertex is determined by using the equation $E = V + X - 12$ where V is the number of valence-shell metal electrons and X is the number of electrons contributed by the exopolyhedral ligands. This equation assumes that the metal center is electronically saturated and contributes three orbitals to cluster bonding (Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66). Greenwood, Kennedy, et al. have recently rationalized their observed "iso-closo" structures by considering a four-orbital contribution for the unsaturated metal vertex (Bould, J.; Crook, J. E.; Elrington, M.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Woolins, J. D. Abstracts, 2nd International Conference on the Chemistry of the Platinum Group Metals, Edinburgh, Scotland, July 1–6, 1984; No. A24). While the hyper-closo distortions do increase the hapticity of the borane ligand, the number of metal skeletal bonding orbitals need not be increased. Consider, for example, the closo iridacarborane complex $H(PPh_3)_2Ir(2,4\text{-}C_2B_8H_{10})$,[6] in which three metal skeletal bonding orbitals interact with the η^6-carborane ligand.

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(15) Examples of N-vertex/$2N$ skeletal-electron polyhedra that exhibit undistorted closo geometries include $[(\eta\text{-}C_5H_5)Co]_4B_4H_4$ ($N = 8$),[16] $(PPh_3)_2RuCl_2Ru(PPh_3)[B_{10}H_8(OMe)_2]$[17] ($N = 11$), and $Cl(PPh_3)Rh(1,7\text{-}C_2B_9H_{11})$[18] ($N = 12$).

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increased cage reactivity,[3] further synthetic, structural, and theoretical results in this area[23] should lead to a more fundamental understanding of heteroborane chemistry.

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Registry No. $H(PMe_3)_2Ir(B_8H_7Cl)$, 82447-28-7; $H(PMe_3)(Ph_2PC_6H_4)Ir(B_9H_8)$, 83251-41-6.

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(23) The preparation and characterization of 10-vertex, 20-skeletal-electron *hyper-closo*-(mes)$Fe(B_9H_9)$, where mes = η^6-mesitylene, have recently been reported: Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Inorg. Chem.* **1984**, *23*, 3992.

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Structure and Bonding in Some Recently Isolated Metallaboranes

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Dr. Baker's note[1] emphasizes that there are interesting points regarding the interpretation of the electronic structures of a number of recently reported polyhedral boron-containing cluster compounds. It thereby underlines the need for continued synthetic and further definitive structural work in this area, for the definitive correlation of solid-state and solution structures, for the development of minimum-presumption molecular orbital theories to account for the molecular and proposed electronic structures, and subsequently for the development of definitive experimentation that can be used to assess directly, rather than by inference or intuition, the applicability of any suitable theoretical approaches that may be developed.

A proportion of our work at Leeds is directed at the further exploration of some of these areas, particularly in non-carbon-containing metallaborane clusters, but it is by no means complete. Meanwhile we do not think it unreasonable to entertain the possibility that the metal-to-borane bonding in some of these new structural types may deviate from the assumption, implicit in simple electron-counting rules, that a metal cluster vertex contributes three orbitals with a quasi-conical symmetry to the cluster bonding scheme.[2–5] As a reviewer has emphasized, and we thank him for this, this idea is hardly new or heretical; Wade specifically addressed it 9 years ago in his 1976 electron-counting paper,[6] and it has been repeatedly invoked since then (see, for example, ref 7).

One of these deviations is that the metal may, in simple terms, contribute four (or more) principal valence orbitals to the cluster bonding, rather than three.[2–5,8–12] This possibility is not normally available to boron, since in most known compounds one of the four $\{s + p^3\}$-type hybrid orbitals is involved in exopolyhedral bonding, although isolated exceptions are recognized, for example in $[(CO)_{12}HFe_4BH_2]$[13] (and also, of course, in fused "macropolyhedral" clusters such as $B_{18}H_{22}$, but in these the formal boron orbital contribution will still remain $\leqslant 3$ to each of the individual subclusters). A four-orbital interaction may be expected to lead to cluster geometries and electronic configurations not found for simple boranes and carboranes, and it may further be expected that some of these structures would be characterized by higher metal-to-borane connectivities. Both of these features are characteristic of a number of the structures Dr. Baker mentions,[1] and for compounds that we have isolated,[6,10,14,15] we have sometimes chosen to use the descriptor "isocloso" when these have closed deltahedral structures. It should be emphasized that these particular "isocloso" structures approximate closely to high symmetries (C_{2v} for 9-vertex; C_{3v} for 10-vertex) and are *not* merely distortions either of regular closo symmetries (D_{3h} for 9-vertex; D_{4d} for 10-vertex) or of "capped closo" geometries; one simple generalization mentioned by a second reviewer (whom we also thank) is that the "isocloso" clusters would have the same formal electron count as a closo cluster, but that the metal vertex in the "isocloso" cluster would contribute four orbitals rather than three to the cluster bonding scheme.

It should also be emphasized that an assessment of these four-orbital and related bonding hypotheses, and the assessment of additional related chemistry such as solution equilibration etc.,[1] is often rendered difficult by a number of complicating features. These include the propensity of metals such as ruthenium, rhodium, and iridium to form sixteen- (and sometimes fourteen-) electron metal centers as well as eighteen-electron ones, the ability of clusters in certain circumstances to exist with geometries inappropriate for (more unambiguous) formal Wadian electron counts (e.g. B_8H_{12}, B_9Cl_9, $[(C_5H_5)_4Co_4B_4H_4]$, $[(C_5H_5)_4Ni_4B_4H_4]$, etc.),[16] and the fact that the effective energetic differences between formal valency states [e.g. iridium(III) vs. iridium(V), or ruthenium(II) vs. ruthenium(IV)] may not be all that great in these types of bonding environment.[17–20] These and other factors, of which some are mentioned by Dr. Baker[1] and which include, for example, changes in the π-acidity of the other ligands on the metal atoms,[21] introduce great flexibility in structural behavior, and simple electron-counting theory is often inappropriate in the absence of other evidence: it is therefore important that each structure is assessed on its merits, rather than by a rigid application of "rules" developed for simpler systems.[3,19,22]

In this context we find that a blanket use of the descriptor "hypercloso", for closed structures that appear not to conform to perceived "rules", is not universally helpful. Additional difficulties

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