Table III. Edge Bond Orders in D_{2d} Polyhedral Clusters Implied by Localized 2- and 2-Center Bond Schemes

edge type[a]	skel coord nos. of linked atoms	edge bond orders ($\bar{n}$)[b] and lengths (l, pm)				
		B_8Cl_8		$B_8H_8^{2-}$		$B_8H_8^{4-}$
		$\bar{n}$	l	$\bar{n}$	l	$\bar{n}$
a	4-4	$^2/_3$	168	$^5/_6$	158	1
b	4-5	$^1/_2$	175	$^1/_3$	178	$^5/_6$
c	4-5	$^1/_3$	178	$^5/_6$	174	$^1/_3$
d	5-5	$^1/_3$	200	$^1/_3$	193	$^1/_3$

[a] See Figure 1. [b] Deduced by giving equal weight to each of the contributing canonical forms.

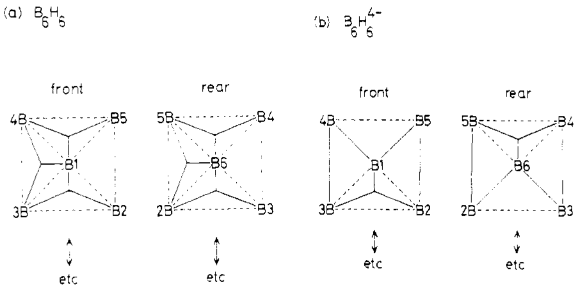

Figure 6. Localized bond arrangements for hypothetical octahedral species B_6H_6 and $B_6H_6^{4-}$.

of their relative bond orders on going from B_8Cl_8 to $B_8H_8^{2-}$, a reversal matched by their relative lengths. This localized bond treatment thus provides an alternative rationale to the MO treatment outlined above, in which the differences in bond lengths between B_8Cl_8 and $B_8H_8^{2-}$ were seen to correlate directly with the edge-bonding or -antibonding character of the HOMO of $B_8H_8^{2-}$.

Similar arguments to the above can be used to allocate nine 3-center bonds to the skeleton of B_9Cl_9, or three 2-center and seven 3-center bonds to the skeleton of $B_9H_9^{2-}$, allowing the differences between these tricapped trigonal-prismatic structures to be rationalized. These arguments will be elaborated in a systematic study of the complete range of known closo systems, to be published elsewhere.

A corollary of the condition that each vertex atom should be involved in three skeletal bonds is that, as the skeletal coordination number of an atom increases, so must the number of 3-center bonds it forms. This implies that the atoms of high coordination number will be more positively charged and those of low coordination number will be more negatively charged than the average, since the electron density on an atom will decrease as the proportion of 3-center bonds it forms increases. This correlation between electron density and coordination number in closo species is a familiar feature of borane-type clusters that also emerges from MO treatments.

One disadvantage of localized bond schemes is the progressive increase in edge bond order they imply for sequences $B_nH_n < B_nH_n^{2-} < B_nH_n^{4-}$ and the n, $(n + 1)$, and $(n + 2)$ electron pairs available respectively are all given a bonding role, whereas the MO argument outlined above suggests the bond order peak will be reached for the species $B_nH_n^{2-}$, since the extra two skeletal electrons in species $B_nH_n^{4-}$ (or their isoelectronic analogues) would have to be accommodated in antibonding MO's.

A more serious disadvantage is illustrated in Figure 6, which shows the apparently plausible bond arrangements that can be drawn for hypothetical octahedral clusters of formulas B_6H_6 and $B_6H_6^{4-}$, which would have six and eight electron pairs, respectively, available for skeletal bonding. Resonance between canonical forms such as these would provide apparently satisfactory bonding descriptions of these species, neither of which, however, would be expected to have regular octahedral structures (see Table I). These localized bond schemes, and the similar plausible localized bond networks that can be drawn for other hypothetical deltahedral clusters B_nH_n or $B_nH_n^{4-}$ (or isoelectronic analogues), cannot therefore be taken as reliable indicators of which structures may exist. (In many cases, localized bond schemes of known closo anions $B_nH_n^{2-}$ appear less plausible than those that can be drawn for hypothetical species B_nH_n or $B_nH_n^{4-}$.)

One further unsatisfactory feature of localized bond schemes is worthy of comment. This is that closo → nido reductive cage opening is predicted to occur as the number of skeletal bond pairs is increased from $(n + 2)$ to $(n + 3)$, whereas such changes normally occur when the number of skeletal bond pairs increases from $(n + 1)$ to $(n + 2)$. This follows from a consideration of hypothetical species $B_nH_n^{6-}$, for which the equations of balance require nine 2-center and $(n - 6)$ 3-center skeletal bonds. Since a 2-center bond can account for the bonding of only one polyhedral edge, while a 3-center bond can account for the bonding of at most the three edges surrounding the face it occupies, these skeletal bonds can account for the bonding of a maximum of $9 + 3(n - 6)$, i.e., $3(n - 3)$ polyhedral edges. The bonding capacity of these bond networks is thus insufficient to account for all of the $3(n - 2)$ polyhedral edges of a closo n-vertex polyhedron. The implication is that closo geometries are inappropriate for clusters $B_nH_n^{6-}$ or isoelectronic species. Adding a pair of electrons to a species $B_nH_n^{4-}$ would be expected to lead to reductive cluster opening of the closo → nido type that actually normally accompanies the conversion of $B_nH_n^{2-}$ into $B_nH_n^{4-}$.

Conclusion. The arguments elaborated above illustrate that the degeneracies of the HOMO and LUMO of closo, n-atom, $(n + 1)$-bond-pair clusters provide a better guide to the possible shapes of related clusters with two more or two fewer electrons than do localized bond schemes. These latter do, however, have value in deducing the electron distribution and approximate bond orders in clusters of known structure.

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Department of Chemistry
Durham University Science Laboratories
Durham DH1 3LE, England

Marion E. O'Neill
Kenneth Wade*

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Steric Effects in Metal Cluster Compounds

Sir:

The qualitative discussion of the role of steric effects in influencing the stereochemistries, stabilities, and catalytic properties of mononuclear transition-metal complexes, particularly of tertiary phosphines, has been greatly assisted by the cone-angle concept introduced by Tolman.[1] The current interest in the chemical properties of transition-metal cluster compounds raises similar problems regarding the relative importance of steric and electronic effects. Some progress has been made toward understanding the electronic factors responsible for the adoption of particular metal polyhedral geometries,[2] but the discussion of steric effects has been limited by the absence of a simple procedure for assessing the relative

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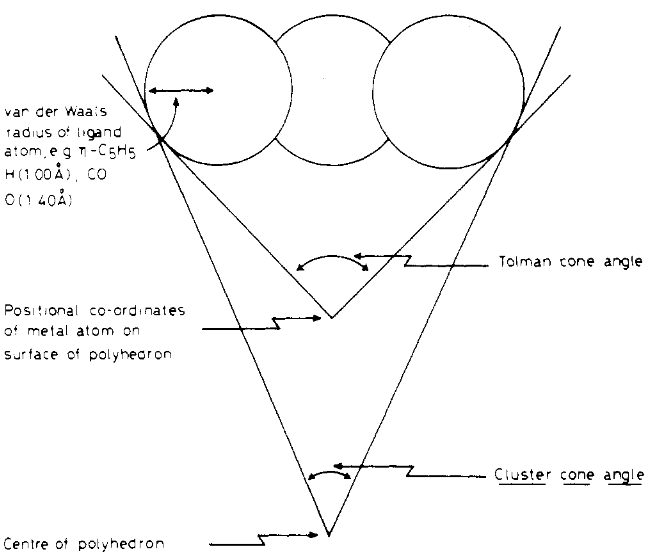

Figure 1. Definition of cluster cone angle and comparison with the Tolman cone angle.

Table I. Cluster Cone Angles for Some Common Metal-Ligand Fragments (deg)

	tetrahedron	octahedron	icosahedron
ideal cone angle	109.5	90.0	63.9
		$M(\eta\text{-}C_5H_5)^a$	
M-M = 2.50 Å	97	92	82
M-M = 2.90 Å	90	85	75
		$M(CO)_3{}^b$	
M-M = 2.50 Å	114	108	96
M-M = 2.90 Å	108	102	90
		$M(CO)_2{}^b$	
M-M = 2.50 Å	68 (99, 36)^c	64 (94, 34)	57 (83, 30)
M-M = 2.90 Å	64 (94, 33)	60 (89, 31)	54 (78, 28)
		$M(CO)^b$	
M-M = 2.50 Å	36	34	30
M-M = 2.90 Å	33	31	28
		MCl^d	
M-M = 2.50 Å	55	51	44
M-M = 2.90 Å	50	47	40

[a] C-C = 1.42 Å, C-H = 1.08 Å, M-C = 2.21 Å (M-M = 2.50 Å), 2.29 Å (M-M = 2.90 Å), van der Waals radius of hydrogen = 1.00 Å. [b] C-O = 1.18 Å, M-C = 1.82 Å (M-M = 2.50 Å), 1.95 Å (M-M = 2.90 Å), C-M-C = 90°, van der Waals radius of O = 1.40 Å. [c] For the anisotropic $M(CO)_2$ fragment the values in parentheses refer to the extreme cone angles in the plane of the fragment and perpendicular to it. The latter have been assumed to be equal to the cone angle of M(CO). A mean value has also been estimated. [d] M-Cl = 2.40 Å (M-M = 2.50 Å), 2.50 Å (M-M = 2.90 Å), van der Waals radius Cl = 1.80 Å.

magnitudes of such effects. The importance of such steric effects in the context of the synthesis of high-nuclearity clusters became apparent to us as a result of our recent successful synthesis of the first example of an icosahedral gold-tertiary phosphine cation.[3] The isolation of such a species required the utilization of dimethylphenylphosphine, which has a smaller cone angle than the more commonly used triphenylphosphine. In this communication I propose an extension of Tolman's cone-angle concept that provides a simple, yet seemingly effective, method for discussing in a semiquantitative fashion the relative importance of steric effects in cluster compounds.

In a cluster compound that has metal-metal bond lengths that lie in the normal range, the total number of ligands that can be accommodated around the metal polyhedron will be influenced primarily by the cone angle that they subtend at the center of the polyhedron, rather than that which is subtended at a vertex metal atom. The latter may be more relevant when the metal atoms are separated by long distances, however. Therefore, it is useful to define a *cluster cone angle* such as that illustrated in Figure 1 in terms of the origin of the polyhedron. The relationship between the cluster cone angle and the conventional Tolman cone angle is also shown in the figure.[3] The cluster cone angle has been calculated for some common ligands in a manner analogous to that developed by Tolman[1] using van der Waals radii, and the results are summarized in Table I. Since the cluster cone angle depends on the cluster metal-metal bond length and the polyhedral type, the table includes typical values for tetrahedral, octahedral, and icosahedral clusters with metal-metal bond lengths appropriate to first- (M-M = 2.50 Å) and third-row (M-M = 2.90 Å) transition metals. These crude estimates of the relative steric constraints introduced by some common ligands found in cluster chemistry give rise to some reasonably accurate descriptions of limiting cluster stoichiometries.

The table lists the computed cluster cone angles for the commonly occurring $M(CO)_3$, $M(CO)_2$, and M(CO) fragments, from which it can be seen that the steric effects of the carbonyl ligands are approximately additive. Consequently the cluster cone angles given in the table for M(CO) fragments may be used to calculate the maximum number of ligands, n_{max}, that can be accommodated around the cluster according to the formula

$$n_{max} = \frac{\text{ideal polyhedral cone angle} \times \text{no. of metal atoms}}{\text{M(CO) cone angle}}$$

Typical n_{max} values for binary carbonyls of first-row transition metals are 12.2 (tetrahedron), 15.8 (octahedron), and 25.3 (icosahedron). These calculated values reproduce the experimentally established limiting stoichiometries reasonably well since the highest carbonyl ratios are found in the following tetrahedral and octahedral cluster compounds and ions:[4] $Co_4(CO)_{12}$, $Fe_4(CO)_{13}{}^{2-}$, $Co_6(CO)_{16}$, and $Fe_6C(CO)_{16}{}^{2-}$. The steric saturation in $Fe_4(CO)_{13}{}^{2-}$ has been noted by other workers, who have attributed the butterfly metal polyhedral geometry in $Fe_4(CO)_{13}H^-$ to steric effects.[5]

The corresponding values of n_{max} for M-M = 2.90 Å are only slightly larger, viz., 13.2 (tetrahedron), 17.2 (octahedron), and 27.8 (icosahedron), and reproduce the larger limiting stoichiometries observed for second- and third-row transition-metal cluster compounds, viz., $Os_4H_2(CO)_{13}$, $Ru_6C(CO)_{17}$, $Ru_6H(CO)_{18}{}^-$, $Os_6(CO)_{18}{}^{2-}$, and $Rh_{13}H_3(CO)_{24}{}^{2-}$ (anticuboctahedral).[4] The steric unsaturation in $M_4(CO)_{12}$ third-row transition-metal cluster compounds is also indicated by the occurrence of the hydrido complexes $Os_4H_4(CO)_{12}$, $Re_4H_4(CO)_{12}$, and $Re_4H_6(CO)_{12}{}^{2-}$ and the observation of alternative carbonyl conformations in the first two examples.[4]

From the arguments developed above it is apparent that steric effects will only exert a significant influence on the stereochemistries of binary metal carbonyl cluster compounds when the total number of carbonyl ligands exceeds n_{max}. In such situations the carbonyls could adopt the spherical polyhedra described by Johnson[6] in order to minimize the ligand

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nonbonded repulsions. In all other situations electronic effects should predominate and the carbonyls will adopt polyhedra that maximize the metal–carbonyl and metal–metal bonding interactions.

The calculated cluster cone angles for the $M(\eta\text{-}C_5H_5)$ fragment in clusters of the first-row transition metals suggest that an octahedral $M_6(\eta\text{-}C_5H_5)_6$ cluster is sterically saturated since there is a good match between the cluster cone angle (92°) and the ideal cone angle for an octahedron (90°), but a tetrahedral $M_4(\eta\text{-}C_5H_5)_4$ cluster is sterically unsaturated since the cluster cone angle (97°) is significantly smaller than the ideal cone angle for a tetrahedron (109.5°). Therefore, in the latter case it should be possible to incorporate additional small ligands such as CO and H into the cluster coordination sphere. These conclusions are supported by recent structural analyses on $Ni_6(\eta\text{-}C_5H_5)_6$ and $Ni_6(\eta\text{-}C_5H_5)_6^+$ by Dahl et al.[7] and the occurrence of compounds such as $Fe_4(CO)_4(\eta\text{-}C_5H_5)_4$, $Ni_4H_3(\eta\text{-}C_5H_5)_4$, and $Co_4H_4(\eta\text{-}C_5H_5)_4$.[4] The fact that the computed cone angle of $M(\eta\text{-}C_5H_5)$ is smaller than that for $M(CO)_3$ accounts for the fact that, although $Ni_6(\eta\text{-}C_5H_5)_6$ is known, the corresponding $M_6(CO)_{18}$ complexes have not been isolated for the first-row transition elements. The calculated cluster cone angles given in the table also suggest that icosahedral $M_{12}(\eta\text{-}C_5H_5)_{12}$ will be sterically very strained unless the metal–metal bond lengths greatly exceed 2.90 Å.

The development of this cluster cone-angle concept to other ligands of interest in the context of cluster chemistry, e.g., tertiary phosphines, phosphites, isocyanides, etc., is currently under investigation and will be discussed in detail in a subsequent publication. Although these computed cluster cone angles serve as a basis for a detailed discussion of cluster stoichiometries and stereochemistries, the more general qualitative point that emerges from such an analysis is that the successful synthesis of high-nuclearity clusters requires due consideration not only of the relevant electronic factors but also of the steric requirements of the ligands on the periphery of the cluster.

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Inorganic Chemistry Laboratory
University of Oxford
Oxford OX1 3QR, United Kingdom
D. M. P. Mingos

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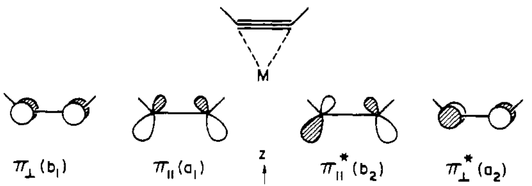
Structural and Theoretical Evidence for Participation of the Second Acetylene π Orbital in Transition-Metal Alkyne Complexes

Sir:

In transition-metal–olefin complexes there is no ambiguity about the role of the olefin π and π* orbitals in bonding—the classic Dewar–Chatt–Duncanson model[1,2] is a fine approximate description of what happens. An alkyne presents to a metal two π orbitals—$\pi_\perp$, **1a**, and $\pi_\parallel$, **1b**—as well as two π* orbitals, $\pi_\parallel^*$, **1c**, and $\pi_\perp^*$, **1d**. The "first" π system, $\pi_\parallel$ and $\pi_\parallel^*$, clearly acts in a manner analogous to olefin π and π*. It has been suggested that the "second" acetylene π system, $\pi_\perp$, may play an important role in bonding in some mononuclear transition-metal complexes.[3-7] There is no doubt that the $\pi_\perp$ system *can* participate in metal–alkyne interactions whenever a vacant metal d orbital of the same symmetry is present. But to what extent does it do so? Unfortunately the second π system's effect is often masked by the primary $\pi_\parallel$ and $\pi_\parallel^*$ interactions, making it difficult to isolate the $\pi_\perp$ contribution.



1a **1b** **1c** **1d**

Very recently structures of three diphenylacetylene complexes of Mo(II) have been determined, $(\eta^5\text{-}C_5H_5)_2Mo(PhC{\equiv}CPh)$ (**2**),[8,4c] $Mo(CN\text{-}t\text{-}Bu)_2(S\text{-}t\text{-}Bu)_2(PhC{\equiv}CPh)$ (**3**),[9] and Mo(*meso*-tetra-*p*-tolylporphyrin)(PhC≡CPh) (**4**).[4c] Although these diamagnetic molecules have the same d^4 electron count, they exhibit significant differences in the Mo–acetylene interaction. The Mo–C(acetylene) distance decreases significantly on going from **2** to **3** to **4**, while the C–C distance is slightly elongated in the same order (Table I). We wish to report here that this geometrical trend is accounted for only when the $\pi_\perp$ contribution is taken into account.

To probe the effect, we carried out extended Hückel calculations on some simplified models, $(\eta^5\text{-}C_5H_5)_2Mo(HC{\equiv}CH)$, $Mo(CNH)_2(SH)_2(HC{\equiv}CH)$, and Mo(porphyrin)(HC≡CH).[10] In each case the acetylene geometry was fixed: $h(Mo\text{–}C_2H_2) = 1.95$ Å, $r(C\text{–}C) = 1.28$ Å, $\theta(C\text{–}C\text{–}H) = 150°$. A framework for the analysis of metal–acetylene interactions is found in the conceptual construction of each complex from a metal fragment and an acetylene. We have sketched the four π orbitals of acetylene in **1a**–**d**. The frontier orbitals of each metal fragment are reasonably well-known[11] and are shown in Figure 1.

For $(\eta^5\text{-}C_5H_5)_2Mo$ the two low-lying d orbitals ($1a_1$ and b_2) and the spd-hybridized $2a_1$ lie in the *yz* plane. At higher energy there are two d orbitals (b_1 and a_2) perpendicular to the plane. An ML_4 fragment such as $Mo(CNH)_2(SH)_2$ has five frontier orbitals—three t_{2g}-like d_π orbitals (b_2, a_2, a_1) and two hybrids above them.[11b] Of those the highest hybrid combination, a_1, is omitted from Figure 1. The t_{2g} set is split substantially by the asymmetry of the ligand set—in particular a_1 is destabilized by interaction with occupied S p_π orbitals, while b_2 and a_2 are kept low by interaction with acceptor orbitals of the isocyanides. Mo(porphyrin), in which the Mo atom is moved out of the porphyrin plane by 0.63 Å, carries four low-lying d orbitals.[11c] The $x^2 - y^2$ is strongly pushed up by N lone pairs and is not shown in Figure 1.

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