$P\bar{1}$. Successful refinement of the structure confirms this choice of space group. Least-squares refinement and difference-Fourier syntheses revealed all remaining non-hydrogen atoms. At this stage, the non-hydrogen atoms were assigned anisotropic temperature factors and the cyclopentadienyl and phenyl H atoms were calculated geometrically (r_{C-H} = 0.95 Å)[27] and given isotropic temperature factors held invariant at $1.25U_{iso}$ of the C atoms to which they were attached. After several cycles of least-squares refinement of these parameters and a secondary extinction parameter,[28] an inner-data difference Fourier map revealed the methyl H atoms which were also included in the least-squares (U invariant). The structure was refined until all shift/error ratios were less than 0.2, the final residuals being $R_F = 0.020$ and $R_{wF} = 0.028$ for 323 variables. The final value for the extinction parameter was $1.4\ (2) \times 10^{-6}$. Refinement throughout was by least-squares analysis, minimizing the function $\sum w(F_o| - |F_c|)^2$. In the early stages the least-squares analysis was by full-matrix using unit weights ($w = 1$). For the final cycles it was block-diagonal (Gauss–Siedel) with the weighting scheme $w = 1/[(\sigma(F))^2 + pF^2]$. The parameter p was varied to give minimum variation of the averaged $\sum w(|F_o| - |F_c|)^2$ with F_o and $(\sin \theta)/\lambda$; the best fit was obtained with $p = 5 \times 10^{-5}$. The biggest features in a final difference map were areas of negative electon density ($|\rho_{max}|$ = 0.36 (6) e Å^{-3}) around the Mo atoms. Neutral scattering factors with anomalous dispersion corrections for the non-hydrogen atoms were used.[29] Computer programs[30] were run on a PDP-8e computer.

Thermal motion corrections were calculated for the more precise bond lengths in Table III. Those involving the central core of the molecule [Mo(1), Mo(2), P, S, C(21)] were calculated from a rigid-body model of these atoms alone.[31] The remainder were based on a riding model.[32] The uncorrected bond lengths are cited in the discussion to be consistant with previously reported structures. The magnitude of some corrections (up to 7 esd's for the Mo–Mo distance) should be regarded as a warning when comparing bond lengths from different structure determinations. Corrections to angles are small (typically ≤1 esd) and are not reported.

Temperature factors, additional bond lengths and angles, and least-squares planes have been deposited as Tables SI, SII, and SIII, respectively.

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Registry No. 1, M = Mo, R = H, 56200-27-2; 1, M = Mo, R = CH_3, 69140-73-4; 1, M = W, R = H, 62853-03-6; 4, 19172-47-5; 5, M = Mo, R = H, 86392-82-7; 5, M = Mo, R = CH_3, 86392-83-8; 5, M = W, R = H, 86392-84-9; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Temperature factors, additional bond lengths and angles, least-squares planes, and a listing of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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Electron Counting in Cluster Species. The Significance of the Structure and Isomerism of the Iron–Molybdenum–Sulfur Cluster Compound (Dicyclopentadienyldimolybdenum)diron Octacarbonyl Disulfide, $(\eta^5\text{-}C_5H_5)_2Mo_2Fe_2(CO)_8S_2$, a Hexanuclear Species in Which Two Mo_2FeS Tetrahedra Share a Common Mo–Mo Edge

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The published structures of two isomers of the mixed-metal complex $(\eta^5\text{-}C_5H_5)_2(CO)_2Mo_2Fe_2(CO)_6S_2$, when viewed as Mo_2FeS tetrahedra sharing common Mo–Mo edges, are related in a particularly simple fashion. These clusters belong to a family of edge-sharing bitetrahedral electron-precise clusters of which several examples are already known. The skeletal electron requirements and scope for isomerism of mixed transition-metal–main-group element clusters of these types and their relationship to electron-deficient octahedral clusters are noted.

Recent elucidation of the structure of the mixed metal cluster compound $Cp_2Mo_2Fe_2(CO)_6(\mu_3\text{-}S)_2(\mu\text{-}CO)_2$ (1)[1] (Cp ≡ $\eta^5\text{-}C_5H_5$) showed this compound to have a planar arrangement of its four metal atoms. Tetranuclear transition-metal clusters with 62 valence shell electrons (VSE's) usually have butterfly-shaped structures,[2-4] as had already

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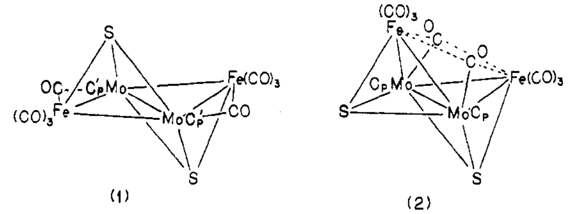

Figure 1. Schematic drawing of the two isomers of $Cp_2Mo_2Fe_2(CO)_8S_2$ from ref 1 and 5.

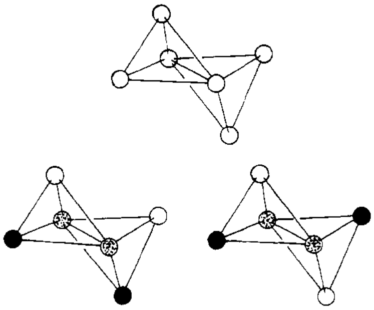

Figure 2. A metal butterfly and planar four-metal "cluster" as isomers of a $M'_2M''_2X_2$ bitetrahedral heteroatom cluster. The open circles refer to Fe, the dotted circles to Mo, and the closed circles to S.

been found for an isomer of 1, compound 2[5] (Figure 1), so this result may be construed as casting doubt on the value of electron-counting methods of predicting or rationalizing cluster structures.

We suggest that although compound 1 provides a salutary reminder that more than one plausible structure may need to be considered for a particular formula or electron count, a simple rationale for its structure, and for the different metal arrangements in 1 and 2, is available if these isomers are considered as *hexanuclear* rather than tetranuclear clusters, i.e., if the sulfur atoms they contain are considered as additional skeletal atoms. Viewed thus, compounds 1 and 2 consists of two tetrahedral, tetranuclear Mo_2FeS clusters sharing a common edge, the Mo–Mo bond. As fused clusters, the important difference between them is that, whereas in 1 the Fe–S vectors are opposed, in 2 they are parallel—hence the difference between their Mo_2Fe_2 shapes (Figure 2). This type of isomerism, although new in transition-metal chemistry, is already known in boron cluster chemistry. The two known isomers of the octadecaborane, $B_{18}H_{22}$, effectively consist of *nido*-decaborane(14)-type units sharing a common edge, differing in the relative orientations of the two fragments.[6,7] Hence, the discovery of 1 and 2 provides yet another nice example of the underlying unity between main-group and transition-metal clusters.

Our bonding rationale is as follows. Of the 66 VSE's of the metal *and* sulfur atoms, four can be allocated to the two sulfur atoms, giving each the lone pair of electrons they are assumed to have in the usual metal VSE count.[3] Of the remaining 62 metal VSE's, we assign two to each metal–metal bond (of which there are five) and two to each metal–sulfur bond (of which there are six). This completes the valence shell requirements of the sulfur atoms and involves each iron atom in three skeletal bonds (leaving it six spare valence shell AO's) and each molybdenum atom in five skeletal bonds (leaving it four spare valence shell AO's). The remaining 40 VSE's are precisely the number needed to fill these spare metal AO's, whether for metal–ligand bonding or as nonbonding electrons. Compounds 1 and 2 are thus systems in which each of the 11 skeletal bonds—one Mo–Mo, four Mo–Fe, two Fe–S, and four Mo–S—can be regarded as a two-center electron pair bond and so are examples of electron-precise clusters.

It is worth noting that if 1 or 2 is treated as a borane-type cluster in which each skeletal atom uses three AO's for skeletal bonding, then the $Mo_2Fe_2S_2$ skeleton, formally held together by seven skeletal bond pairs (two electrons from each $Fe(CO)_3$ unit, one from each Cp(OC)Mo unit, and four from each sulfur atom, would be expected to have an octahedral structure with each skeletal atom bonded to its four neighbors by bonds of order ca. 0.6. That the preferred structures are adopted instead can be attributed to various factors: the better use made of the available electrons, the preference of sulfur to cap triangular rather than tetragonal faces, and the capacity of molybdenum to use more than three AO's for cluster bonding—in its halide and oxide cluster chemistry, molybdenum generally uses four AO's for cluster bonding.[2,8]

An electron count that suggests an octahedral structure if a cluster is of the borane type must clearly in the future be recognized as compatible with a bitetrahedral structure like that of 1 or 2. Interestingly, both types of structure are already known in osmium cluster chemistry. The anion $Os_8(CO)_{22}{}^{2-}$[9] is an eight-atom, 110-VSE system that adopts the expected bicapped octahedral structure (treated as a borane-type cluster, it is an eight-atom, seven skeletal bond pair system). Its octahedral Os_6 core contains 86 VSE's (each capping $Os(CO)_3$ unit formally contributes two VSE's). Its protonated derivative, $HOs_8(CO)_{22}{}^{-}$,[10] however, contains an Os_6 core consisting of two tetrahedra (one bicapped) sharing a common edge, for which a network of two-center bonds can be drawn to account for all the metal atom connectivities, giving each metal atom a share in 18 electrons. That this localized bond network is probably an oversimplification of the electronic structure is indicated by the shortness of the Os···Os bond that is shared between the two tetrahedra (the Mo···Mo bonds in compounds 1 and 2 are also shorter than expected for normal single bonds).[1,5]

That alternative, electron-precise structures (fused tetrahedra) may be available and preferred when electron-deficient structures are possible is of course not new elsewhere in cluster chemistry. Compounds of the formula $R_4C_4B_6R'_6$, formed by pyrolysis of trialkylboranes R'_3B, have been shown[11] to adopt classically bonded adamantane-like structures (in which each boron atom incidentally uses only three valence shell AO's) instead of the alternative *nido*-carborane structures like that of $B_{10}H_{14}$ that would be compatible with the molecular formula.

It should be stressed that electron-precise fused tetrahedral structures of the types of compounds 1 and 2 will not be realistic alternatives for *all* species for which an

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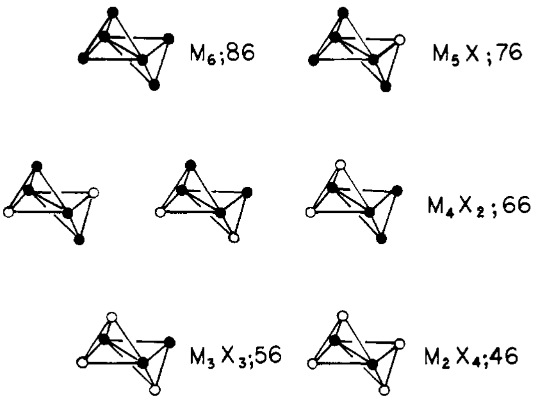

Figure 3. Valence shell electron counts for electron-precise hexanuclear clusters with structures in which two tetrahedra share one edge. Each transition metal (●) obeys the 18-electron rule and each main-group element, X (○), obeys the octet rule.

electron count otherwise suggests a $B_6H_6^{2-}$-type octahedral structure. The atoms shared between the two tetrahedra must have the capacity to form *five* skeletal bonds, so if these are all two-center electron pair bonds, it is unrealistic to expect the shared atoms to be p-block elements or even transition metals from the extreme right-hand side of the d block. The range of possible candidates for edge-shared bitetrahedral structures, incorporating either exclusively transition metals or both main-group and transition elements is illustrated in Figure 3, together with the number of VSE's required to make each of the 11 edges a two-center bond.[12,13] It is only for M_4X_2 systems, containing four transition-metal atoms M and two main-group atoms X in the skeleton, that isomerism can occur of the type displayed by compounds 1 and 2, though a third isomer is possible for these systems in which all four metal atoms are in one tetrahedron, and other types of isomerism are possible in mixed-metal systems.

The bonding in clusters of these structural types in which the main-group atoms are the carbon atoms of acetylene residues has been discussed by Hoffman and co-workers,[14] who considered unsaturated systems like $(Cp(OC)Nb)_2(RCCR)_2$ (which with 44 VSE's formally contains a Nb═Nb double bond)[15] and predicted the stability of saturated 46 VSE systems. Further known examples of such M_2C_4 systems include the iron species $(OC)_2Fe(RCCR)_2Fe(CO)_2$ (44 VSE's)[16] and mixed-metal clusters $Cp(OC)M(RCCR)_2Co(CO)_2$ (M = Mo, W) (46 VSE's)[17] while related derivatives $Cp(OC)M(RCCR)_2M(CO)Cp$ (M = Cr, Mo) have been invoked as likely intermediates in the sequential linking of acetylene residues at dichromium or dimolybdenum centers.[18] Tetrametalladicarba clusters of formulae $[Cp(OC)MCr(CO)Cp][RCW(CO)_2Cp][RCCr(CO)_2Cp]$ (where M = Cr or W), with bitetrahedral structures capable of showing the type of isomerism that compounds 1 and 2 show, appear to be involved in reactions between $[Cr_2(CO)_4Cp_2]$ and the carbyne complex $[W(\equiv CR)(CO)_2Cp]$.[19] A bitetrahedral Pd_4Hg_2 cluster, $Pd_4(CO)_4(PEt_3)_4Hg_2Br_2$, with isomer 2 geometry, is of interest as an 82-VSE six-atom member of the family of compounds discussed here.[20] Presumably, the two wing-tip palladium atoms of its Pd_4 butterfly are 16-electron species.

To return to compounds 1 and 2, we suggest that these provide a helpful reminder of the need to consider *all* the skeletal atoms, non-metal as well as metal, in cluster electron-counting and structure predictions and also of the need to consider electron-precise or fused clusters as well as more delocalized bonding schemes. The only slight difference between 1 and 2, as far as the bonding is concerned, lies in the positions of the unique pair of carbonyl ligands. These are μ-bridging between molybdenum and iron atoms in 1, semi-μ_3-bridging in 2. Although this difference may make the iron atoms in 1 very slightly more positively charged, there will be little difference between these compounds as far as the actual metal oxidation states are concerned.

In conclusion, we urge that molecular formulas and the number of VSE's they imply should continue to be regarded as useful guides to possible cluster shapes, while recognizing that further novel structures compatible with particular skeletal atom and electron numbers may remain to be discovered. To paraphrase Shakespeare,[21] there are more shapes in the heaven and earth of cluster chemistry than are dreamt of in our current electron-counting philosophy.

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