$F_1 = -Y$) of a given polyhedron, the X value remains unchanged. Examples have been shown in Charts VII and VIII.

Polyhedral Holes and Condensed Polyhedra. It is possible to invoke the concept of "polyhedral holes" in place of face-sharing "fused (or condensed) polyhedra". Rule 6 applies to both concepts.[46] One example is the truncated ν_2 (frequency two, meaning that each edge corresponds to two metal–metal bonds) trigonal bipyramid (*49*), shown in Chart XVI, which has two octahedral holes and three trigonal-bipyramidal holes. If each octahedral hole contributes $X = 1$ (rule 4) and each trigonal-bipyramidal hole contributes $X = 2$ (rule 4), with three "hidden edges" (inner triangle of the center layer), $X = -3$ (rule 7), a net X value of 5 can be calculated. The predicted electron count is thus 166e as is indeed observed in the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ anions.[47] We note that the interlayer metal–metal distances are longer than the intralayer metal–metal bonds, in accord with the use of the X value of 2 for each of the three trigonal-bipyramidal holes. We predict that an electron count of 160e is more appropriate for a similar structure with more or less equal inter- and intralayer metal–metal distances.

Cage Size. It is evident from eq 5b that for a given number of vertices (V), as the number of faces (F) decreases, the cage size increases and hence the number of electrons (N) that can be "stored" in the cage increases. The cage may reach a size big enough to completely "encapsulate" a metal atom of approximately the same size for 12-vertex polyhedra or above. Notable examples include the icosahedron, cuboctahedron or twinned cuboctahedron, bicapped pentagonal prism, etc. Besides, the cage size must be more or less spherical (and of the right dimension) to completely incorporate atoms such as carbide, nitride, sulfide, or metal atoms. Two examples of the nonspherical cage are those within the dodecadeltahedron (which is ellipsoidal) and within the pentagonal bipyramid (which is disklike).

Conclusion

In summary, we have developed in this paper a new topological electron-counting theory based on Euler's theorem and the effective atomic number rule. Each polyhedron (of given numbers of vertices and faces), be it simple, capped, or condensed (via vertex, edge, or face sharing), is characterized by a parameter X, which can be determined from a set of simple rules. This simple scheme can also be used to predict the electron counts as well as to correlate the structures of a wide range of metal clusters of varying nuclearity (cf. following paper), thereby enabling one to achieve a better understanding of the interrelationships between the various cluster geometries.

Acknowledgment. I am indebted to Drs. N. J. A. Sloane and F. R. K. Chung of Bell Laboratories (Murray Hill, NJ) for many useful discussions concerning properties of polyhedra and to Kelly Keating (Bell Labs) for helpful comments. I am also grateful to Prof. J. Lauher for suggesting the alternative interpretation of X (as the number of "false" metal–metal bonds), to Prof. D. M. P. Mingos for many helpful suggestions concerning the manuscript, and to Drs. G. Longoni, S. Martinengo, A. Ceriotti, A. Fumagalli, L. Garlaschelli, M. C. Malatesta, D. Strumolo, and A. Albinati for numerous stimulating discussions during my 1-month visit at the Instituto di Chimica Generale dell'Universitã, Milan, Italy, in 1982.

(46) After submission of the present paper, an extension of the SEP theory to fused or condensed polyhedra has appeared: (a) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 706. (b) Mingos, D. M. P. *J. Organomet. Chem.* **1983**, *251*, C13.
(47) Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1978**, *No. 167*, 93.

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Applications of Topological Electron-Counting Theory to Polyhedral Metal Clusters[1]

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Received June 16, 1983

The simple topological electron-counting theory developed in the previous paper is applied to a wide range of transition-metal and post-transition-metal clusters of varying nuclearity. The results are in excellent agreement with experimental observations. This simple electron-counting scheme provides an alternative to the skeletal electron pair theory in that it can be used to correlate the known as well as to predict the yet unknown polyhedral structures of a general nature. The theory also provides a better understanding of the interrelationships between different cluster geometries.

Introduction

The last decade or two has witnessed a dramatic increase in interest in metal cluster chemistry. Principles underlying the stereochemistry and bonding of metal cluster compounds are generally well established through synthetic, structural, spectroscopic, and theoretical studies.[2] On the one hand, simple electron-counting schemes such as the effective atomic number (EAN) and the skeletal electron pair (SEP)[3,4] rules, which result from these systematic studies, are extremely useful in correlating the structures of a vast number of clusters to their electron counts. On the other hand, more insight can be gained through more elaborate treatments such as graph theory,[5] perturbed spherical shell theory,[6] isolobal concept,[3,4,7,8] and the extended Hückel molecular orbital (EHMO),[7-11] Fenske–Hall approximate Hartree–Fock,[12,13] and SCF–Xα–SW calculations[14-16] (in the order of increasing calculational complexity).

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(1) Part 1: Teo, B. K. *Inorg. Chem.*, preceding paper in this issue.
(2) For reviews, see: (a) Chini, P. *Gazz. Chim. Ital.* **1979**, *109*, 225. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (c) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (d) Johnson, B. F. G., Ed. "Transition Metal Clusters"; Wiley-Interscience: Chichester, England, 1980. (e) Benfield, R. E.; Johnson, B. F. G. *Top. Stereochem.* **1981**, *12*, 253. (f) Trogler, W. C.; Manning, M. C. *Coord. Chem. Rev.* **1981**, *38*, 89. (g) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1982.
(3) (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792; *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559, 563. (b) Wade, K. "Electron Deficient Compounds"; Nelson: London, 1971. (c) Wade, K. *Chem. Br.* **1975**, *11*, 177. (d) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
(4) (a) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. (b) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802. (c) Mason, R.; Mingos, D. M. P. *MTP Int. Rev. Sci.: Phys. Chem. Ser. Two* **1975**, *11*, 121. (d) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210.
(5) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.

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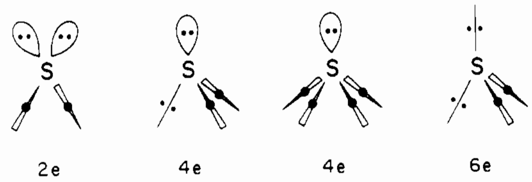
Chart I

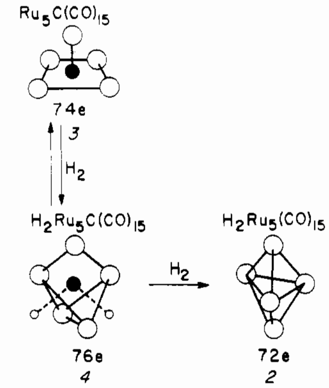


Generally speaking, the structures of transition-metal clusters exhibit a higher degree of complexity and variation than do the main-group element counterparts such as borane and related clusters.[17] While many metal clusters conform to the EAN rule, many others follow the SEP rule. Yet others may adopt structures that cannot be rationalized with either EAN or SEP schemes. In the preceding paper, a new topological electron-counting approach based on Euler's theorem for polyhedra and the effective atomic number rule for transition-metal complexes was developed. In this paper, we will describe application of this electron-counting scheme to a wide variety of metal clusters (containing 4–20 metal atoms), including those that violate either the EAN and/or the SEP rule. As we shall see, this new electron-counting scheme, which requires no theoretical calculations, can provide substantial new insight into the electronic requirements and the interrelationship of various polyhedral cluster structures.

General Remarks

Applications of the topological electron-counting theory to polyhedral structures allow us to predict the number of electrons required for a wide range of transition-metal carbonyl clusters and post-transition-metal naked clusters. Some of the results are tabulated in Table I. While Table I is more or less self-explanatory, the following clarifications may be helpful.

Chart II



First, the *total electron count*, N, is determined in the usual way by adding up the valence electrons contributed by the metal atoms and the electrons donated to the metals by the ligands. Thus, a cobalt atom has nine valence electrons, a carbonyl ligand (terminal or doubly or triply bridging) is a two-electron donor, a nitride is a five-electron donor, etc. Special attention should be paid to the difference between *surface* and *bulk* ligands. For example, as shown in Chart I, a doubly bridging sulfur atom (with two lone pairs) is a two-electron (2e) donor, a triply or quadruply bridging sulfur (with one lone pair) is a 4e donor, and an encapsulated sulfur is a 6e donor.

Second, though capping the different faces of a polyhedron may give rise to different X values, the resulting electron count remains unchanged. For example, capping the triangular vs. the square face of a trigonal prism gives rise to $X = 0$ and 1, respectively, yet both are 102e systems. The reason is that though capping an n-gonal face causes an increase in X by $n - 3$, the total number of faces increases by the same quantity and hence N remains unchanged (cf. eq 5b of the preceding paper). This observation is analogous to Mingos' capping principle[19] that the number of polyhedral skeletal MOs are unchanged by capping.

Applications

We shall now discuss some of the known polyhedral geometries listed in Table I and their electron counts. The electron counts for many yet-unknown geometries are also predicted in Table I.

Tetravertex Metal Clusters. The simplest tetravertex polyhedron of high symmetry is a tetrahedron (*1*). Many metal clusters possess a completely bonding tetrahedral geometry, with or without bridging ligands. The former is exemplified by $Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4$[20] and $Fe_4S_4(NO)_4$,[21] and the latter by $Ir_4(CO)_{12}$[22] and $Co_4(CO)_{12}$.[23] A *tetrahedron* (*1*) has four vertices, four triangular faces, and an X value of zero (rule 3); the predicted electron count is 60 (cf. Table I), as is indeed observed.

Pentavertex Metal Clusters. The three commonly observed polyhedral geometries for pentametal clusters are the trigonal bipyramid (*2*), square pyramid (*3*), and hinged butterfly (*4*), as tabulated in Table I. For *trigonal bipyramids* (*2*), the EAN

(6) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563.
(7) (a) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148. (b) Hoffmann, R. *Science (Washington, D.C)* **1981**, *211*, 995. (c) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (d) Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *Ibid.* **1978**, *100*, 6088.
(8) (a) Halpern, J. *Discuss. Faraday Soc.* **1968**, *46*, 7. (b) Ellis, J. E. *J. Chem. Educ.* **1976**, *53*, 2. (c) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318. (d) Mingos, D. M. P. *Trans. Am. Crystallogr. Assoc.* **1980**, *16*, 17. (e) Albright, T. A. *Ibid.* **1980**, *16*, 35.
(9) (a) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (b) Lauher, J. W. *Ibid.* **1979**, *101*, 2604. (c) Lauher, J. W. *J. Organomet. Chem.* **1981**, *213*, 25.
(10) Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1980**, *197*, 233.
(11) (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1974**, 133; **1976**, 1163. Mingos, D. M. P.; Forsyth, M. I. *Ibid.* **1977**, 610. (b) Evans, D. G.: Mingos, D. M. P. *Organometallics* **1983**, 2, 435 and references cited therein. See also ref 23 of this reference.
(12) (a) Hall, M. B.; Fenski, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Kostic, N. M.; Fenske, R. F. *Ibid.* **1983**, *22*, 666. (c) Rives, A. B.; You, X.-Z.; Fenske, R. F. *Ibid.* **1982**, *21*, 2286.
(13) (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *J. Organomet. Chem.* **1974**, *70*, 413. (b) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103. (c) Teo, B. K. Ph.D. Thesis, University of Wisconsin (Madison), 1973.
(14) (a) Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1982**, *21*, 3458. (b) Sherwood, D. E., Jr.; Hall, M. B. *Organometallics* **1982**, *1*, 1519. (c) Chesky, P. T.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 4419.
(15) (a) Cotton, F. A.; Stanley, G. G. *Chem. Phys. Lett.* **1978**, *58*, 450. (b) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1980**, *19*, 132.
(16) (a) Yang, Y. C.; Johnson, K. H.; Salahub, D. R.; Kaspar, J.; Messmer, R. P. *Phys. Rev. B: Condens. Matter* **1981**, *24*, 5673 and references cited therein. (b) Messmer, R. P.; Knudson, S. K.; Johnson, K. H.; Diamond, J. B.; Yang, C. Y. *Phys. Rev. B: Solid State* **1976**, *13*, 1396 and references cited therein. (c) Salahub, D. R.; Messmer, R. P. *Ibid.* **1977**, *16*, 2526 and references therein. (d) For reviews, see: Messmer, R. P. *Surf. Sci.* **1981**, *106*, 225. Johnson, K. H. *CRC Crit. Rev. Solid State Mater. Sci.* **1978**, *7*, 101. For more recent reviews, see: Case, D. A. *Annul Rev. Phys. Chem.* **1982**, *33*, 151. (e) For $X\alpha$ methodology, see: Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1; "The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1974; Vol. 4. Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.
(17) Lipscomb, W. N. "Boron Hydrides"; W. A. Benjamin: New York, 1963.
(18) Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.
(19) See ref 23 in ref 11b of this paper.
(20) Neuman, M. A.; Trinh, T.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3383.
(21) Gall, R. S.; Chu, C. T. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 4019.
(22) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.
(23) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

rule predicts $N = 72$; our simple rules (rule 4) predict $N = 72, 76$. Indeed, the majority of the trigonal-bipyramidal metal carbonyl clusters known to date are 76e systems, for example, $[Ni_5(CO)_{12}]^{2-}$,[24] $[Rh_5(CO)_{15}]^{-}$,[25] $[Rh_5(CO)_{14}I]^{2-}$,[26] $[Ni_3M_2(CO)_{16}]^{2-}$[27] (M = Cr, Mo, or W), $[RuIr_4(CO)_{15}]^{2-}$,[28] and $[PtRh_4(CO)_{14}]^{2-}$[29]—with elongated trigonal-bipyramidal geometry (axial–equatorial > equatorial–equatorial metal–metal distances). Only a few pentametal clusters such as $Os_5(CO)_{16}$,[30] $[Os_5(CO)_{15}]^{2-}$,[31] and $[PtRh_4(CO)_{12}]^{2-}$[29] are known to be 72e systems with more or less regular trigonal-bipyramidal structures. Post-transition-metal clusters are all 72e systems.[32]

For *square pyramids* (*3*) rule 3 gives $X = 0$ and the electron count is predicted to be $N = 74$ as is observed in, for example, $Ru_5C(CO)_{15}$.[33] For the hinged-butterfly C_{2v} geometry (*4*) with two triangular and two puckered square faces ($F = 4$), $X = 0$ and $N = 76$e as is observed in $Ru_5C(CO)_{16}$ or $H_2Ru_5C(CO)_{15}$.[34]

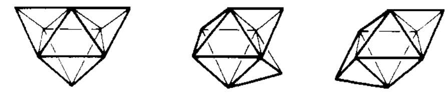
Note that in going from trigonal-bipyramidal to square-antiprismatic to hinged-butterfly geometries, the electron count generally increases (from 72 to 74 to 76e) as the number of faces decreases from 6 to 5 to 4. This feature is quite common in polyhedral metal clusters as is evident in Table I. These polyhedral structures can also interconvert as illustrated in Chart II for $H_2Ru_5(CO)_{15}$ (trigonal bipyramid, 72e), $Ru_5C(CO)_{15}$ (square pyramid, 74e), and $H_2Ru_5C(CO)_{15}$ (hinged butterfly, 76e) as reported by Johnson, Lewis, and co-workers.[35]

Hexavertex Metal Clusters. Hexametal polyhedral clusters can adopt one of the following structures: *bicapped tetrahedron* (*5*), *octahedron* (*6*), *trigonal antiprism* (*7*), *capped square pyramid* (*8*), *edge-sharing bitetrahedron* (*9*), *pentagonal pyramid* (*10*), or *trigonal prism* (*11*). The corresponding electron counts are 84, 86 (or less commonly, 84 and 90), 86, 86, 86, 88, and 90e (or less commonly, 86e). The pentagonal pyramid is a yet-unknown geometry in metal cluster chemistry.

The bicapped tetrahedron *5a* has $X = 0$ (rules 2 and 3) and $N = 84$ as is indeed observed in $Os_6(CO)_{18}$[36] and $Os_4H_2(CO)_{12}(AuPPh_3)_2$.[37a] The bicapped tetrahedron can also be considered as a capped trigonal bipyramid (*5b*), and $X = 0$ or 2 or $N = 84$ or 88e is predicted. The observed electron count in $Ni_3Os_3(CO)_9Cp_3$[37b] is 87e.

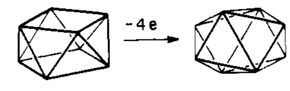
The majority of *octahedral* metal clusters are 86e systems, as predicted. Examples include $Rh_6(CO)_{16}$[38] and $[Fe_6C(CO)_{16}]^{2-}$.[39] An octahedron can be formed by capping the

Chart III



17a *17b* *17c*

Chart IV



21 *19*

square face of a square pyramid; thus rule 2 predicts $X = 1$. Alternatively, it can be considered as a special trigonal antiprism with twelve edges of equal length; rule 5 again predicts $X = 1$. A third route to an octahedron is to demand all 12 edges of a tetragonal bipyramid be equal; rule 4 predicts $X = 1$ or 3. The latter, however, is less common because there are only two octahedral clusters, $Ni_6(\eta^5\text{-}C_5H_5)_6$[40] and $[Fe_6S_8(PEt_3)_6]^{2+}$[41] known to have 90 electrons ($X = 3$). In this context, they are more appropriately considered as "exceptions" in that they have four extra electrons in the energetically low-lying molecular orbitals that may be substantially *metal–ligand antibonding* in character. Early-transition-metal clusters often have less electron counts. One typical example is $[Mo_6Cl_{14}]^{2-}$,[42] an octahedral cluster with 84e ($X = 0$). This case ($X = 0$) should again be considered as an "exception".

A trigonal-antiprismatic cluster is predicted to have $X = 1$ and $N = 86$e; one example is the $[Ni_6(CO)_{12}]^{2-}$ dianion.[43]

The capped (△) square pyramid *8* (cf. Chart VIII in the preceding paper) has $X = 0$ (rules 2 and 3) and $N = 86$e as is observed in $Os_6H_2(CO)_{18}$.[44a]

The edge-sharing bitetrahedral geometry *9* with $X = 1$ is predicted to have $N = 86$e. The observed electron count in $Os_4H_2(CO)_{12}(AuPPh_3)_2$[44b] is 84e.

The trigonal prisms have $X = 0$ (rule 1) and $N = 90$e as observed in, for exam[illegible] the $[Rh_6C(CO)_{15}]^{2-}$ dianion[45] and the $[Co_6N(CO)_{15}]^{-}$ [illegible]anion.[46] One exception is the $[Pt_6(CO)_{12}]^{2-}$ dianion,[illegible] which has 86e. As we shall see later in this paper, the platinum carbonyl clusters often exhibit electron counts lower than expected (cf. footnotes *b* and *c* of Table I) due in part to the tendency to form a 16- rather than 18-electron count for platinum.

Heptavertex Metal Clusters. There are fewer examples of heptametal polyhedral clusters. The two known geometries are (1) a tricapped tetrahedron (*12a*) with 10 faces and 96-electron count as exemplified by $Au_3Ru_4(CO)_{12}(PPh_3)_3H$[47] and $Au_3CoRu_3(CO)_{12}(PPh_3)_3$[48] and (2) capped octahedron

(24) Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 5034.
(25) Fumagalli, A.; Koetzle, T. F.; Takusagawa, F.; Chini, P.; Martinengo, S.; Heaton, B. T. *J. Am. Chem. Soc.* **1980**, *102*, 1740.
(26) Martinengo, S.; Ciani, G.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 1059.
(27) Ruff, J. K.; White, R. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 2159.
(28) Fumagalli, A.; Koetzle, T. F.; Takusagawa, F. *J. Organomet. Chem.* **1981**, *213*, 365.
(29) Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Brückner, S. "13th Meeting of the Italian Association of Inorganic Chemistry", Camerino, Italy, 1980; Proc. A11.
(30) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 271.
(31) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 920. Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* **1972**, *11*, 838.
(32) Edwards, P. A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903.
(33) Farrar, D. H.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1981**, 415.
(34) Johnson, B. F. G. *Philos, Trans. R. Soc. London, Ser. A* **1982**, *No. 308*, 5.
(35) See ref 34.
(36) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.
(37) (a) Johnson, B. F. G., et al. *Polyhedron* **1982**, *1*, 105. (b) Sappa, E.; Lanfranchi, M.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Chem. Commun.* **1981**, 995.
(38) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963**, *85*, 1202.
(39) Churchill, M. R.; Wormald, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2410.
(40) Paquette, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6621.
(41) Cecconi, F.; Ghilardi, C. A.; Middolini, S. *J. Chem. Soc., Chem. Commun.* **1981**, 640.
(42) Schäfer, H.; Schnering, H. G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281.
(43) Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616.
(44) (a) McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 883. (b) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *Polyhedron* **1982**, *1*, 105.
(45) Albano, V. G.; Braga, D.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1981**, 717.
(46) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095.
(47) Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 773.
(48) Bruce, M. I.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1141.

Table I. Electron Counting in Transition-Metal Cluster Systems

		predicted				obsd	
no.	polyhedron	V	F	X	N	N	example
1	**tetrahedron**	4	4	0	60	60	$Ir_4(CO)_{12}$,[22] $Co_4(CO)_{12}$[23]
2	**trigonal bipyramid (hexadeltahedron)**	5	6	0	72	72	$Os_5(CO)_{16}$,[30] Sn_5^{2-}, Pb_5^{2-}[32]
				2	76	76	$[Ni_5(CO)_{12}]^{2-}$,[24] $[Rh_5(CO)_{14}I]^{2-}$[26]
3	square pyramid	5	5	0	74	74	$Ru_5C(CO)_{15}$[33]
4	hinged butterfly^a	5	4	0	76	76	$Ru_5C(CO)_{16}$, $H_2Ru_5C(CO)_{15}$[34]
5a	bicapped tetrahedron	6	8	0	84	84	$Os_6(CO)_{18}$,[36] $Os_4H_2(CO)_{12}(AuPPh_3)_2$[37a]
5b	capped trigonal bipyramid	6	8	2	88	87	$Ni_3Os_3(CO)_9Cp_3$[37b]
6	**octahedron**	6	8	1	86	86	$Rh_6(CO)_{16}$,[38] $[Fe_6C(CO)_{16}]^{2-}$[39]
				3	90	90	$Ni_6(\eta^5\text{-}C_5H_5)_6$,[40] $Fe_6S_8(PEt_3)_6^{2+}$[41]
				0	84	84	$[Mo_6Cl_{14}]^{2-}$[42]
7	trigonal antiprism	6	8	1	86	86	$[Ni_6(CO)_{12}]^{2-}$[43]
8	capped square pyramid	6	7	0	86	86	$Os_6H_2(CO)_{18}$[44a]
9	edge-sharing bitetrahedron	6	8	1	86	84	$Os_4H_2(CO)_{12}(AuPPh_3)_2$[44b]
10	pentagonal pyramid	6	6	0	88		
11	trigonal prism	6	5	0	90	90	$[Rh_6C(CO)_{15}]^{2-}$,[45] $[Co_6N(CO)_{15}]^{-}$[46]
						$86^{b,c}$	$[Pt_6(CO)_{12}]^{2-}$[18]
12a	tricapped tetrahedron	7	10	0	96	96	$Au_3Ru_4(CO)_{12}(PPh_3)_3H$,[47] $Au_3CoRu_3(CO)_{12}(PPh_3)_3$[48]
12b	bicapped trigonal bipyramid	7	10	2	100		
13	bicapped square pyramid	7	9	0	98		
14	capped octahedron	7	10	1	98	98	$[Rh_7(CO)_{16}]^{3-}$[49]
15	**pentagonal bipyramid (decadeltahedron)**	7	10	2	100		
16a	capped (Δ) trigonal prism	7	7	0	102		
16b	capped (□) trigonal prism	7	8	1	102		
17	bicapped octahedron	8	12	1	110	110	$[Os_8(CO)_{12}]^{2-}$,[50] $[Re_8C(CO)_{24}]^{2-}$[51]
18	fused octahedron and trigonal bipyramid	8	12	1	110	110	$Cu_2Ru_6C(CO)_{16}(NCCH_3)_2$[52]
19	**triangular dodecahedron (dodecadeltahedron)**	8	12	1	110		
				3	114		
20a	bicapped (Δ^2) trigonal prism	8	9	0	114	114	$Cu_2Rh_6C(CO)_{15}(NCCH_3)_2$[53]
20b	bicapped (Δ,□) trigonal prism	8	10	1	114		
20c	bicapped ($\square^2$) trigonal prism	8	11	1	112		
				2	114		
				3	116		
21	square antiprism	8	10	1	114	114	$[Co_8C(CO)_{18}]^{2-}$[54]
				3	118	118	$[Ni_8C(CO)_{16}]^{2-}$,[55] Bi_8^{2+}[56]
22	square-face-sharing bi(trigonal prism)	8	8	0	116	116	$[Co_6Ni_2C_2(CO)_{16}]^{2-}$[57]
23	cube (hexahedron)	8	6	0	120	120	$Ni_8(PPh)_6(CO)_8$[58]
24	cuneane	8	6	0	120	120	$Co_8S_2(N\text{-}t\text{-}Bu)_4(NO)_8$[59]
25	tricapped octahedron	9	14	1	122		
26	face-sharing bioctahedron	9	14	2	124	122	$[Rh_9(CO)_{19}]^{3-}$[60]
27a	tricapped (Δ^2,□) trigonal prism	9	12	1	126		
27b	tricapped (Δ,$\square^2$) trigonal prism	9	13	2	126		
27c	**tricapped ($\square^3$) trigonal prism**	9	14	2	124		
				3	126		
				4	128	128	Ge_9^{2-}[63]
28a	capped (Δ) square antiprism	9	12	1	126		
				3	130		
28b	capped (□) square antiprism	9	13	2	126		
				4	130	130	$[Rh_9P(CO)_{21}]^{2-}$,[65] $[Ni_9C(CO)_{17}]^{2-}$,[66] Sn_9^{4-},[67] Ge_9^{4-}[63]
29	face-sharing octahedron and trigonal prism	9	11	1	128	128	$[Ni_9(CO)_{18}]^{2-}$[61]
30	tricapped ($\square^3$) trigonal prism with elongated interlayer edges	9	11	2	130	130	Bi_9^{5+}[64]
				3	132		
				4	134		
31	($3^8 5^2$) decahedron	9	10	1	130		
32	triangular-face-sharing bi(trigonal prism)	9	8	0	132	$128^{b,c}$	$[Pt_9(CO)_{18}]^{2-}$[62]
33	capped cube	9	9	1	132	132	
34	($3^5 5^3$) octahedron	9	8	1	134		
35	ν_2 tetrahedron (tetracapped octahedron)	10	16	1	134	134	$[Os_{10}C(CO)_{24}]^{2-}$[68]
36	**bicapped ($\square^2$) square antiprism**	10	16	3	138		
				5	142	142	$[Rh_{10}S(CO)_{22}]^{2-}$,[69] $[Rh_{10}P(CO)_{22}]^{3-}$[70]
37	edge-sharing bioctahedron	10	16	3	138	138	$[Ru_{10}C_2(CO)_{24}]^{2-}$[71]
38	bicapped cube	10	12	2	144		
39	pentagonal antiprism	10	12	3	146		
40	pentagonal prism	10	7	0	150		
41a	face-to-face fused trioctahedron	11	18	2^d	148	148	$[Rh_{11}(CO)_{23}]^{3-}$[72]
41b	face-to-face fused trioctahedron without central bond	11	18	3^d	150		
42	tricapped ($\square^3$) cube with two face diagonals	11	17	3	152		
43	capped (□) square-face-sharing trigonal prism and square antiprism	11	16	2	152		
				3	154	154	$[Co_{11}C_2(CO)_{22}]^{3-}$[73]
				4	156		
44a	**octadecahedron**	11	18	5	154		
44b	convex (expanded) **octadecahedron**	11	18	6	156		
45	tricapped cube	11	15	3	156		
46	capped pentagonal antiprism	11	16	5	158		
47	capped pentagonal prism	11	11	2	162		
48	hexacapped octahedron	12	20	1	158	160	$[Fe_6Pd_6(CO)_{24}H]^{3-}$[74]

Table I (*Continued*)

no.	polyhedron	predicted V	predicted F	predicted X	predicted N	obsd N	obsd example
49	truncated ν_2 trigonal bipyramid (hcp)	12	20	2	160		
				5	166	166	$[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$[75]
50	face-sharing trioctahedron	12	20	3	162	158 + n	$[Rh_{12}(CO)_{25}H_n]$[76]
51	face-sharing bi(square antiprism)	12	18	2	164	166	$[Rh_{12}C_2(CO)_{24}]^{2-}$[78]
				6	172	167	$[Rh_{12}C_2(CO)_{24}]^{3-}$[78]
						168	$[Rh_{12}C_2(CO)_{24}]^{4-}$[78]
52	capped (□) fused trigonal prism–square antiprism–trigonal bipyramid	12	18	1	162		
				3	166	166	$Rh_{12}C_2(CO)_{25}$[79]
				5	170		
53	**icosahedron**	12	20	7	170	170	$[Rh_{12}Sb(CO)_{27}]^{3-}$[80]
						162	$[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$[81]
54	cuboctahedron (ccp)	12	14	1	170		
55	twinned cuboctahedron (hcp)	12	14	1	170	170	$[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$[82]
56	hexagonal antiprism	12	14	1	170		
				3	174		
57	bicapped pentagonal prism	12	15	4	174		
58	triangular-face-sharing tri(trigonal prism)	12	11	0	174	$170^{b,c}$	$[Pt_{12}(CO)_{24}]^{2-}$[77]
59	hexagonal prism	12	8	0	180		
60	3-connected ν_3 truncated tetrahedron (($3^4 6^4$) octahedron)	12	8	0	180		
61	($4^4 5^4$) octahedron	12	8	0	180		
62	pentacapped cube	13	21	5	180	180	$[Rh_{14}(CO)_{25}]^{4-}$[83]
63	octacapped octahedron (face-centered cube)	14	24	1	182		
64	ν_2 trigonal bipyramid	14	24	2	184		
				5	190		
65	hexacapped cube	14	24	6	192		
66	rhombic dodecahedron (body-centerd cube)	14	"24"	>6	>192	198	$[Rh_{15}(CO)_{30}]^{3-}$[84]
67	tetracapped (□^{2},⬠^{2}) pentagonal prism	14	21	6	198	200^e	$[Rh_{15}C_2(CO)_{28}]^{-}$[85]
68	triangular-face-sharing tetra(trigonal prism)	15	14	0	216	$212^{b,c}$	$[Pt_{15}(CO)_{30}]^{2-}$[86]
69	bicapped pentagonal-face-sharing bi(pentagonal prism)	17	20	4	244	238^c	$[Pt_{19}(CO)_{22}]^{4-}$[87]
70	pentagonal dodecahedron	20	12	0	300		

^{a} With two triangular and two puckered square faces. ^{b} Platinum clusters with the general formula $[Pt_3(CO)_6]_m^{2-}$ (formed by a stack of m nearly eclipsed platinum triangles) are 4e short ($42m + 2$) of the electron count predicted for triangular-face-sharing trigonal prisms ($42m + 6$). ^{c} Platinum carbonyl clusters are often 4–6e under the required electron count possibly due to its tendency to form a 16-electron configuration. ^{d} $X = 3 - 1 = 2$ for three octahedra fused face-to-face. If the hidden edge connecting atoms 1 and 2 in Chart XXII is lengthened, $X = 3$. ^{e} Two edges are lengthened to 3.332 (2) Å while others range from 2.734 (3) to 3.024 (3) Å.

(*14*) with 10 faces and 98-electron count as exemplified by the $[Ru_7(CO)_{16}]^{3-}$ trianion,[49] both as predicted. The yet-unknown polyhedral geometries of pentagonal bipyramid (*15*) and capped (Δ or □) trigonal prism (*16*) are predicted to have electron counts of 100 and 102e, respectively.

Octavertex Metal Clusters. To the best of our knowledge, there are seven known polyhedral geometries for octametal clusters. The most compact cluster is the bicapped octahedra (*17a–c*) shown in Chart III. Since capping triangular faces does not increase the X value (rule 2), the X value remains the same as that of an octahedron ($X = 1$, rule 4); with 12 faces, N is predicted to be 110e as observed in, for example, the $[Os_8(CO)_{22}]^{2-}$ dianion[50] and the $[Re_8C(CO)_{24}]^{2-}$ dianion,[51] both with structure *17a*.

A recently reported cluster, $Cu_2Ru_6C(CO)_{16}(NCCH_3)_2$,[52] has an interesting polyhedral structure of a fused octahedron and trigonal bipyramid (*18*; cf. Chart XIII in the preceding paper), which has an electron count of 110e, as predicted (cf. Table I). Adding (formally) four electrons to $Cu_2Ru_6C(CO)_{16}(NCCH_3)_2$ gives rise to $Cu_2Rh_6C(CO)_{15}(NCCH_3)_2$,[53] which has a bicapped (Δ^2) trigonal prismatic structure (*20a*) with, as predicted, 114 electrons.

For *square antiprisms* (*21*, cf. Chart IV), rule 5 predicts $X = 1$ or 3, which corresponds to $N = 114$ or 118 for square antiprisms. Examples include $[Co_8C(CO)_{18}]^{2-}$,[54] which is a 114e system, and $[Ni_8C(CO)_{16}]^{2-}$[55] and Bi_8^{2+},[56] which are 118e systems.

The eight-vertex triangular dodecahedron or dodecadeltahedron (*19*) is rather interesting. As demonstrated in Chart XIII of the preceding paper, it can be derived from either a bicapped octahedron (*17b*) or a fused octahedron and trigonal bipyramid (*18*), giving rise to $X = 1$. It can also be formed by removing two electron pairs ($Y = -2$) from a square antiprism (*21*), one from each of the two square faces, thereby forming two new metal–metal bonding interactions (Chart IV), giving rise to $X = 1$ or 3. With 8 vertices and 12 faces, a triangular-dodecahedral metal cluster is predicted to have 110 or 114 electrons. No such structres are known in metal cluster chemistry. It is, however, interesting to note that the $[Ni_8C(CO)_{16}]^{2-}$ dianion[55] is a square-antiprismatic metal cluster with 118e. Removal of four electrons from the 118e system results in the 114e tetragonally distorted square antiprism as observed in the $[Co_8C(CO)_{18}]^{2-}$ dianion.[54] It can, in principle, also lead to a 114e triangular dodecahedron. The fact that the triangular dodecahedron is yet unknown in metal cluster geometry (in contrast to boranes) may be due to the size and shape of

(49) Albano, V. G.; Bellon, P. L.; Ciani, G. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1024.
(50) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 60.
(51) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 705.
(52) Bradley, J. S.; Pruett, R. L.; Hill, E.; Ausell, G. B.; Leonowicz, M. E.; Modrick, M. A. *Organometallics* **1982**, *1*, 74.
(53) Albano, V. G.; Braga, D.; Martinengo, S.; Chini, P.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1980**, 52.
(54) Albano, V. G.; Chini, P.; Ciani, G.; Martinengo, S.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1978**, 463.
(55) Longoni, G.; Ceriotti, A.; Della Pergola, R.; Manassero, M.; Perego, M.; Piro, G.; Sansoni, M. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *No. 308*, 47.
(56) Krebs, B.; Hucke, M.; Brendel, C. S. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 445.

Chart V

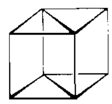


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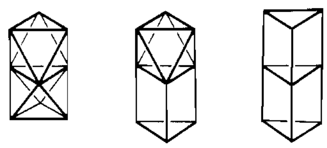
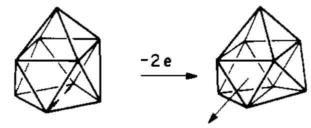
Chart VI



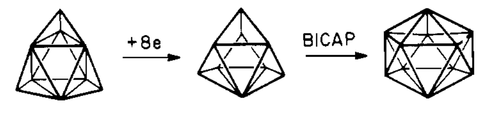
26 *29* *32*

Chart VII



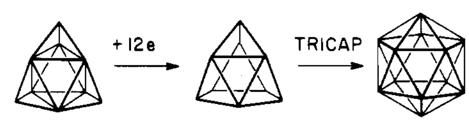
28b *27c*

Chart VIII



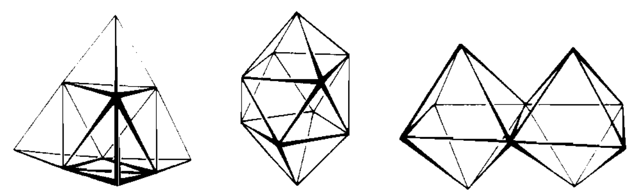
25 *31* *44*

Chart IX



25 *34* *53*

Chart X



35 *36* *37*

the cavity. Thus a possible candidate, e.g. $Cu_2Ru_6C(CO)_{16}(NCCH_3)_2$,[52] instead adopts a different geometry based on a face-sharing octahedron and trigonal bipyramid.

From Table I we see that bicapped trigonal prisms are predicted (rule 2) to be 114 e systems as is indeed observed in $Cu_2Rh_6C(CO)_{15}(NCCH_3)_2$[53] with two triangular caps (*20a*). The bicapped trigonal prisms with two square caps (*20c*), however, can also be formed by removing two electrons from one of the square diagonals of a square antiprism *21* as illustrated in Chart XIII of the preceding paper. Hence *20c* should take on X values of 1, 2, and 3 (cf. eq 6 of the preceding paper), leading to electron counts of 112, 114, and 116e.

The square-face-sharing bi(trigonal prism) (*22*; cf. Chart V) can also be viewed as a distorted cube (*23*) with two face diagonals. In both cases, $X = 0$ (rules 1 and 6 in the former case; rule 7 in the latter) and with 8 faces, $N = 116$e as is indeed observed for the $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ dianion.[57]

The *cube* (*23*) and the *cuneane* (*24*) polyhedra are rather interesting. Despite their drastically different symmetries, both cube and cuneane share the common geometrical characteristic that each vertex has a degree of three (3-connected), giving rise to $X = 0$ (rule 1). Since each has six faces, we expect an electron count of 120e for both the cube and the cuneane. This is indeed observed in $Ni_8(PPh)_6(CO)_8$[58] and $Co_8S_2(N\text{-}t\text{-}Bu)_4(NO)_8$,[59] respectively. Note that cuneane can be formed by rotating one edge of a cube by 90°, thereby transforming four of the square faces into two trigonal and two pentagonal faces.

It should be noted that the electron counts for the known octametal polyhedral clusters span the range of 110–120e with the bicapped octahedron having the smallest cage and the cube having the largest cage size.

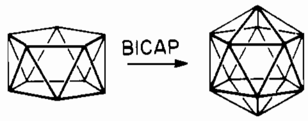
Nonavertex Metal Clusters. The face-sharing bioctahedral nonametal cluster (*26*; Chart VI) has a face count of 14 and an X value of 2 (two octahedra, rules 4 and 6), giving rise to the predicted electron count of 124e. The observed value in the $[Rh_9(CO)_{19}]^{3-}$ trianion[60] is 122e (two electrons less than expected). The closely related face-sharing octahedron and trigonal prism (*29*; Chart VI), with 11 faces and $X = 1$, is predicted to have $N = 128$e as is indeed observed in the $[Ni_9(CO)_{18}]^{2-}$ dianion.[61] Yet another related polyhedron is the triangular-face-sharing bi(trigonal prism) (*32*; Chart VI), which has $F = 8$ and $X = 0$ and is therefore predicted to have 132 electrons. The observed value in the $[Pt_9(CO)_{18}]^{2-}$ dianion[62] is 128 (four electrons less than expected). Once again, the platinum carbonyl clusters exhibit a tendency to have 4 or 6 electrons less than expected.

There are three types of tricapped trigonal prisms, depending upon the location of the capping atoms (*27a–c* in Table I). For the nine-vertex tricapped (□^{3}) trigonal prism, *27c*, which is the only one known to date, rule 2 predicts $X = 3$ for capping the three square faces of the trigonal prism *11*. A second route (cf. Chart VII) to a tricapped trigonal prism (a deltahedron) is to remove one electron pair ($Y = -1$) from the square face of a monocapped (□) square antiprism (*28b*), thereby forming a new metal–metal bond and buckling the square face to form two triangle faces ($F_2 - F_1 = 1$). Again $X_2 = X_1 = 2$ or 4 remains unchanged (cf. eq 6 of the preceding paper). Thus the expected X value for the tricapped trigonal prism is 2, 3, and 4; eq 5b of the preceding paper gives electron counts of 124, 126, and 128e, respectively. The Ge_9^{2-} dianion[63] is an example of the 128e system. Elongation along the C_3 axis gives rise to polyhedron *30*, reducing the number of faces to 11 (8 triangular and 3 rhombic square faces) and leads to $N = 130$, 132, or 134e. The Bi_9^{5+} pentacation[64] is an example of a 130e system.

Similarly, there are two types of capped square antiprisms (*28a,b* in Table I); only *28b* shown in Chart VII has been observed in, for example, $[Rh_9P(CO)_{21}]^{2-}$[65] and $[Ni_9C(CO)_{17}]^{2-}$,[66] as well as in the post-transition-metal clusters Sn_9^{4-}[67] and Ge_9^{4-}.[63] With 13 faces and $X = 2$ or 4 (a square antiprism gives rise to $X = 1$ or 3, capping the square face gives rise to $X = 1$), *28b* is predicted to have $N = 126$ or 130e. The observed value in the above-mentioned examples is 130e.

(57) Longoni, G.; Ceriotti, A.; Della Pergola, R.; Manassero, M.; Sansoni, M., unpublished results.
(58) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
(59) Chu, C. T. W. Ph.D. Thesis, University of Wisconsin (Madison), 1977.
(60) Martinengo, S.; Fumagalli, A.; Bonfichi, R.; Ciani, G.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 825.
(61) Dahl, L. F., et al., private communication.
(62) See ref 18.
(63) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.
(64) Friedman, R. M.; Corbett, J. D. *Inorg. Chem.* **1973**, *12*, 1134.
(65) Vidal, J. L.; Walker, W. E.; Pruett, R. L.; Schoening, R. C. *Inorg. Chem.* **1979**, *18*, 129.
(66) See ref 55.
(67) Corbett, J. D.; Edwards, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 3313.

Chart XI



39 *53*

Cleavage of only four metal–metal bonds in the tricapped octahedron *25* (Chart VIII) with $X = 1$ via addition of four electron pairs ($Y = 4$) gives rise to the ($3^8 5^2$) decahedron *31* ($F_2 - F_1 = 10 - 14 = -4$) with $X = 1$ and $N = 130$e. No examples are known.

Similarly, the nonavertex ($3^5 5^3$) octahedron (*34*) shown in Chart IX can be visualized as being formed by adding six electron pairs ($Y = 6$) to a tricapped octahedron (*25*), which has an X value of 1, resulting in cleavage of six metal–metal bonds. Once again, the $X = 1$ (eq 6 of the preceding paper) value remains unchanged since $F_2 - F_1 = 8 - 14 = -6$. With eight faces (five triangles and three pentagons), eq 5 of the preceding paper predicts $N = 134$e for the yet-unknown polyhedron *34*.

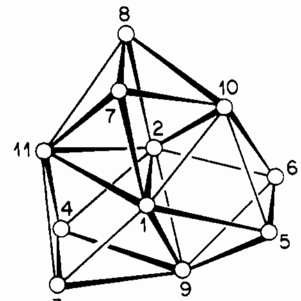
Finally, the monocapped cube (*33*) is predicted to have an electron count of 132e since $X = 1$ (rule 2, capping a square face) and $F = 9$. No examples are yet available.

Decavertex Metal Clusters. Three recently synthesized and structurally characterized *decametal* clusters with different electron counts and drastically different geometries (Chart X) also conform to the rules set forth in the preceding paper. The $[Os_{10}C(CO)_{24}]^{2-}$ dianion,[68] which has a carbide, has the two-frequency (ν_2) tetrahedral structure *35* (i.e., a tetrahedron with edges formed by three atoms linked by two metal–metal bonds). This structure can also be viewed as a tetracapped octahedron (or, equivalently, that it has an octahedral hole), and hence we expect $X = 1$. With 16 (small) triangular faces on the surface, eq 5b of the preceding paper predicts $N = 134$e, as is indeed observed. $[Rh_{10}S(CO)_{22}]^{2-}$[69] or $[Rh_{10}P(CO)_{22}]^{3-}$,[70] with a central sulfide or phosphide atom, has been shown to adopt the bicapped-square-antiprismatic structure *36*. A square antiprism is expected to have $X = 1$ or 3, and capping the two square faces ($X = 1$ for each capping) increases the X value to either 3 or 5. With 16 exposed triangular faces, eq 5b of the preceding paper predicts an electron count of 138 or 142. The latter was actually observed for both clusters. Finally, the $[Ru_{10}C_2(CO)_{24}]^{2-}$ anion,[71] with two carbides, adopts the edge-sharing bioctahedral geometry *37*. Since each octahedron contributes $X = 1$ and edge-sharing further increases the X value by 1, the total X value equals 3. With 16 exposed triangular faces, $N = 138$, as is indeed observed.

Three other yet-unknown polyhedral structures are also tabulated in Table I: the bicapped cube (*38*), with $F = 12$ and $X = 2$, is expected to be a 144e cluster; the pentagonal antiprism (*39*, in Chart XI), with $F = 12$ and $X = 3$, is predicted to have 146 electrons; finally the pentagonal prism (*40* in Chart I of the preceding paper), with $F = 7$ and $X = 0$, is likely to have 150 electrons.

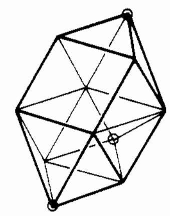
Undecavertex Metal Clusters. One of the most interesting undecametal polyhedral clusters is the $[Rh_{11}(CO)_{23}]^{3-}$ trianion[72] shown in Chart XII. It can be described as a face-to-face

Chart XII



41a

Chart XIII



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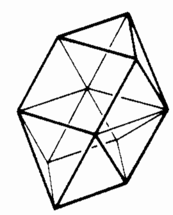

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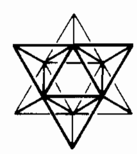
Chart XIV



48

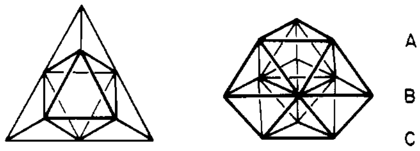
fused trioctahedron (*41a*) with 18 "exposed" faces. The net X value is 2 since three octahedra give rise to a total X value of 3 (rule 4) and one "hidden" edge within the polyhedron contributes an X value of -1 (rule 7). We therefore predict an electron count of 148e for *41a*, which is gratifyingly observed. If the "hidden" edge is lengthened by adding two electrons to *41a*, the yet-unknown polyhedron of face-to-face trioctahedron without the central edge (*41b*) with a 150-electron count is expected.

Tricapping ($\square^3$, indicated by open circles) a cube with two face diagonals (*22* in Chart V) produces the polyhedron *42* shown in Chart XIII with 17 faces and X of 3 (tricapping, rule 2). This yet-unknown polyhedron is predicted to have 152 electrons (cf. Table I). The related structure *43* is also shown in Chart XIII; it has one less edge as well as one less face than *42* and hence $X = 3$ (rule 7) and $N = 154$e. The polyhedron *43* can also be considered as a monocapped ($\square$) trigonal prism (top half) sharing a square face with a square antiprism (bottom half); the shared square face, of course, is just the plane that divides the cube in the first description into two equal halves. The X value for this latter description is 2 or 4 (capping a square face of the trigonal prism contributes $X = 1$ and the square antiprism has $X = 1$ or 3); the predicted N value is therefore 152 or 156e. The observed N value of 154e in the $[Co_{11}C_2(CO)_{21}]^{3-}$ trianion[73] better fits the first description.

The 11-vertex octadecahedron (*44*), a deltahedron with 18 faces, can be formed by capping the two pentagonal faces of the 9-vertex ($3^8 5^2$) decahedron (*31*) as illustrated in Chart VIII. The X value for *44* is 5 (X for *31* is 1, and capping each pentagonal face increases X by 2). The predicted electron count is 154e. This polyhedral skeleton, however, is yet un-

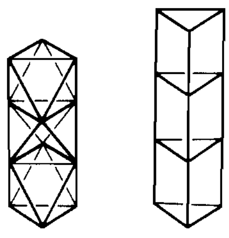
(68) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2099.
(69) Ciani, G.; Garlaschelli, L.; Sironi, A.; Martinengo, S. *J. Chem. Soc., Chem. Commun.* **1981**, 563.
(70) Vidal, J. L.; Walker, W. E.; Schoening, R. C. *Inorg. Chem.* **1981**, *20*, 238.
(71) Hayward, C. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7347.
(72) Fumagalli, A.; Martinengo, S.; Ciani, G.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1983**, 453.
(73) Albano, V. G.; Braga, D.; Ciani, G.; Martinengo, S. *J. Organomet. Chem.* **1981**, *213*, 293.

Chart XV



49

Chart XVI



50 *58*

known in metal cluster chemistry.

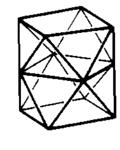
The yet to be discovered undecametal polyhedral clusters are, for example, the tricapped cube and the capped pentagonal antiprism and prism; the predicted electron counts are 156, 158, and 162e, respectively (cf. Table I).

Dodecavertex Metal Clusters. Dodecametal clusters exhibit intriguing polyhedral skeletal variation. The hexacapped octahedral (*48*) cluster[74] $[Fe_6Pd_6(CO)_{24}H]^{3-}$, shown in Chart XIV, has 160 electrons, in reasonable agreement with the predicted value of 158e based on $F = 20$ and $X = 1$ (cf. Table I).

The truncated ν_2 (frequency two, meaning that each edge corresponds to two metal–metal bonds) trigonal bipyramid (*49*), shown in Chart XV, has two octahedral holes and three trigonal-bipyramidal holes. If each octahedral hole contributes $X = 1$ (rule 4) and each trigonal-bipyramidal hole contributes $X = 2$ (rule 4), with three "hidden edges" (inner triangle of the center layer), $X = -3$ (rule 7), and a net X value of 5 can be calculated. The predicted electron count is thus 166e as is indeed observed in the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ anions.[75] We note that the interlayer metal–metal distances are longer than the intralayer metal–metal bonds, in accord with the use of the X value of 2 for each of the three trigonal-bipyramidal holes. We predict that an electron count of 160e is more appropriate for a similar structure with more or less equal inter- and intralayer metal–metal distances. It is interesting to note that the layer stacking arrangement in *49* corresponds to the hexagonal close-packed (hcp) structure. Polyhedron *49* therefore represents the most compact 12-vertex polyhedron.

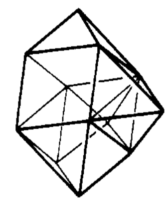
The face-sharing trioctahedral structure (*50*), which can also be described as a stack of four staggered triangles of metal atoms, is shown in Chart XVI and observed in $[Rh_{12}(CO)_{25}H_n]$,[76] where n is still undetermined. With 20 faces and $X = 3$ (three octahedra of $X = 1$ each), we predict $N = 162$. The observed value is $158 + n$, where $n > 0$. We predict that $n = 4$ and that face-sharing trioctahedral clusters of general formula $[Rh_{12}(CO)_{25}H_{4-n}]^{n-}$ should exist. The related triangular-face-sharing tri(trigonal prismatic) structure (*58* in Chart XVI) is observed in $[Pt_{12}(CO)_{24}]^{2-}$[77] (which can also be described as a stack of four eclipsed (though somewhat twisted) metal triangles); with 11 faces and $X = 0$, $N = 174$e is predicted. The observed value in $[Pt_{12}(CO)_{24}]^{2-}$ is 170e, again 4e below the expected value.

Chart XVII



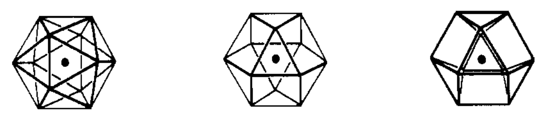
51

Chart XVIII



52

Chart XIX



53 *54* *55*

The square-face-sharing bi(square antiprism) *51*, shown in Chart XVII, has 18 faces and $X = 2$ or 6 (each square antiprism contributes $X = 1$ or 3); the predicted electron count is 164 or 172e. The observed values in the $[Rh_{12}C_2(CO)_{24}]^{n-}$ anions,[78] where $n = 2$, 3, and 4, are 166, 167, and 168e, respectively, well within the predicted range.

The structure of the $Rh_{12}C_2(CO)_{25}$ cluster[79] (*52*, Chart XVIII) can be described as a square-face-capped fused trigonal prism–square antiprism–trigonal bipyramid. The X value is 1 (square cap) + $\{^1_3$ (square antiprism) + $\{^0_2$ (trigonal bipyramid) − 1 (one hidden edge) or a net of 1, 3, or 5. Another way of describing *52* is to "fuse" polyhedron *43* with a trigonal bipyramid; in this case, $X = 3$ (for *43*) + $\{^0_2$ (for trigonal bipyramid) = $\{^3_5$. The predicted N value is 162, 166, or 170e. The observed electron count in $Rh_{12}C_2(CO)_{25}$ is 166e.

The *icosahedron 53* (Chart XIX) can be considered as a bicapped pentagonal antiprism (*39*, Chart XI). Rule 5 predicts $X = 3$ for the pentagonal antiprism *39*. Capping the two pentagonal faces further increases the X value to 7 (rule 2; $X = 2$ for each capping). Hence, for a dodecametal cluster of icosahedral geometry (20 triangular faces), one expects an electron count of 170 as is indeed observed in the $[Rh_{12}Sb(CO)_{27}]^{3-}$ trianion[80] (though with three very long (3.3 Å) Rh–Rh bonds). An 162e icosahedral cluster, which is 8 electrons below the expected value, was reported for the $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ trication.[81] As with the platinum carbonyl clusters, gold phosphine clusters also have the tendency to have electron counts 4 or 6 electrons under the expected values.

As discussed in the preceding paper, both the cuboctahedron (ccp) *54* and the twinned cuboctahedron (hcp) *55* (Chart XIX) can be formed by structural perturbation of the icosahedron *53*. With $V = 12$, $F = 14$, and $X = 1$, both are predicted to have 170 electrons. A twinned cuboctahedron was observed for the 170e systems $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$.[82] The reason that

(74) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242.
(75) Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1978**, *No. 167*, 93.
(76) Martinengo, S., private communication.
(77) Lower, L. D. Ph.D. Thesis, University of Wisconsin (Madison), 1978.
(78) Martinengo, S., private communication.
(79) Albano, V. G.; Chini, P.; Martinengo, S.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1974**, 299.
(80) Vidal, J. L.; Troup, J. M. *J. Organomet. Chem.* **1981**, *213*, 351.
(81) Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 201.

Chart XX

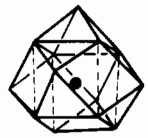


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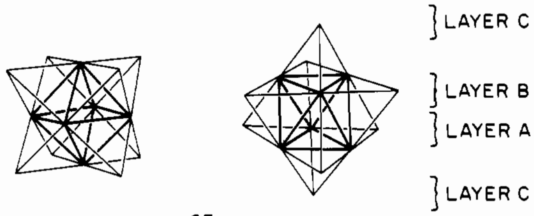
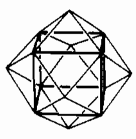
Chart XXI

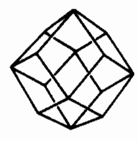


63

Chart XXII



65



66

the icosahedron, the cuboctahedron, and the twinned cuboctahedron all require 170 electrons is that their bonding requirements are quite similar despite their distinctive symmetries.

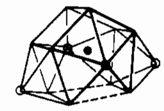
Note that the cuboctahedron (*54*) has an A, B, C pattern, corresponding to the cubic close-packed (ccp) structure, whereas the twinned cuboctahedron (*55*) has an A, B, A pattern, corresponding to the hexagonal close-packed (hcp) structure as shown in Chart XIX. Of all the polyhedra described so far, the icosahedron, cuboctahedron, and twinned cuboctahedron have a cavity large enough to completely encapsulate a metal atom. Note that the encapsulated metal atom is *not* considered part of the polyhedral network. It is considered merely as an electron contributor in the total electron count. Note also that a cuboctahedron is formed by truncating either a cube or an octahedron of frequency two (ν_2).

Also included in Table I are the yet unknown hexagonal antiprism (*56*), bicapped pentagonal prism (*57*), hexagonal prism (*59*), 3-connected ν_3 truncated tetrahedron (or ($3^4 6^4$) octahedron) (*60*), and ($4^4 5^4$) octahedron (*61*; cf. Chart I in the preceding paper), predicted to have electron counts of 170 (or 174), 174, 180, 180, and 180e, respectively.

Tridecavertex Metal Clusters. There is only one known 13-vertex tridecametal polyhedral cluster: the pentacapped cube (*62*) shown in Chart XX. With 21 faces and $X = 5$ (capping 5 square faces), the predicted electron count is 180e as is indeed observed in the $[Rh_{14}(CO)_{25}]^{4-}$ tetraanion.[83] Other tridecametal polyhedral clusters are, of course, possible by either capping or fusing lower polyhedra.

Tetradecavertex Metal Clusters. The 14-vertex polyhedra octacapped octahedron (or face-centered cube) *63* (Chart XXI), hexacapped cube *65* (Chart XXII), and rhombic dodecahedron (or body-centered cube; central atom not shown) *66* (Chart XXII) are interrelated in that the expansion of the inner octahedron in *63* and the concomitant shrinkage of the outer cube result in *65*. Similarly, slight expansion of the inner

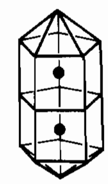
Chart XXIII



67

—— 2.87(av)
----- 3.33

Chart XXIV



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cube in *65* will produce *66*. Our rules readily apply to *63* and *65*, predicting $X = 1$ for *63* which has an octahedral cavity, and $X = 6$ for *65*, which has the six square faces of the inner cube ($X = 0$) capped. Adding Y electron pairs (where Y is a small number) to *65* produces *66*. Assuming that the 12 rhombic faces in *66* can be approximated by 24 triangular faces, the X value for *66* is then $6 + Y$. As tabulated in Table I, the predicted electron counts for *63*, *65*, and *66* are 182, 192, and $(192 + 2Y)$e, respectively. The observed value for the structurally known rhombic dodecahedral cluster[84] $[Rh_{15}(CO)_{30}]^{3-}$ is 198e, from which a Y value of 3 can be deduced.

The tetracapped ($\square^2$,⬠^{2}) pentagonal prism (*67*, Chart XXIII), with 21 faces and $X = 6$ (cappings, rule 2), is predicted to have an electron count of 198e. The observed value in the $[Rh_{15}C_2(CO)_{28}]^-$ monoanion[85] is 200e. The latter, though, has two long metal–metal bonds, making one of the square faces of the pentagonal prism into a rectangular face. This may account for the two extra electrons.

Also included in Table I is the yet-unknown 14-vertex ν_2 trigonal bipyramid (*64*), which can be formed by bicapping (Δ^2) polyhedron *49*. The X value of 2 or 5 remains unchanged; with 24 faces, the electron count of 184 or 190e is expected.

Pentadecavertex Metal Clusters. Only one polyhedron is known for 15-vertex polyhedral metal clusters; the triangular-face-sharing tetra(trigonal prism) (*68*) formed by a stack of five eclipsed (though slightly twisted) metal triangles. With 14 faces and $X = 0$, *68* is predicted to have an electron count of 216e. The observed value in the $[Pt_{15}(CO)_{30}]^{2-}$ dianion[86] is 212e, again four electrons below the predicted value.

Higher Clusters. Metal clusters of higher nuclearities are less common than metal clusters of lower nuclearities. Nevertheless, tremendous progress has been made in recent years. A few examples of structurally characterized large clusters are $[Pt_{19}(CO)_{22}]^{4-}$[87] and $[Pt_{38}(CO)_{44}H_2]^{2-}$[88] as well as $[Rh_{17}(CO)_{30}]^{3-}$[89] and $[Rh_{22}(CO)_{37}]^{4-}$.[90] For these high-nuclearity clusters, electron counting becomes an increasingly difficult problem. Many simple rules are no longer applicable

(82) Ciani, G.; Sironi, A.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1981**, 519.
(83) Martinengo, S.; Ciani, G.; Sironi, A.; Chini, P. *J. Am. Chem. Soc.* **1978**, *100*, 7096.
(84) Vidal, J. L.; Kapicak, L. A.; Troup, J. M. *J. Organomet. Chem.* **1981**, *215*, C11.
(85) Albano, V. G.; Sansoni, M.; Chini, P.; Martinengo, S.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1976**, 970.
(86) See ref 18.
(87) Washecheck, D. M.; Wucherer, E. J.; Dahl, L. F.; Ceriotti, A.; Longoni, G.; Manassero, M.; Sansoni, M.; Chini, P. *J. Am. Chem. Soc.* **1979**, *101*, 6110.
(88) Ceriotti, A.; Washecheck, D.; Dahl, L. F.; Longoni, G.; Chini, P., private communication.
(89) Ciani, G.; Magni, A.; Sironi, A.; Martinengo, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1280.
(90) Martinengo, S.; Ciani, G.; Sironi, A. *J. Am. Chem. Soc.* **1980**, *102*, 7564.

for metal clusters containing, e.g., more than 13 metal atoms. Our rules are no exception. Nevertheless, we include in Table I a 17- and a 20-vertex polyhedra of high symmetry. The 17-vertex bicapped ($\mathcal{O}^2$) face-sharing bi(pentagonal prism) (*69*, Chart XXIV), with 20 faces and $X = 4$, is expected to have 244 electrons. The observed value in the $[Pt_{19}(CO)_{22}]^{4-}$ tetraanion,[87] with two encapsulated platinums in the pentagonal-prismatic holes, is 238e, six electrons below the predicted value, again a characteristic of platinum carbonyl clusters.

The 20-vertex pentagonal dodecahedron (*70*), with 12 pentagonal faces and $X = 0$ (3-connected, rule 1; cf. Chart I in the preceding paper), is predicted to have an electron count of 300e. This polyhedral structure is yet unknown in metal cluster chemistry though the corresponding polyhedron in organic chemistry—the dodecahedrane[91] $C_{20}H_{20}$—has been synthesized recently.

A new approach to electron counting for high nuclearity metal clusters has been developed by Teo.[92]

Conclusion

It is shown in this paper that the topological electron-counting theory, developed in the preceding paper, can be applied to a wide variety of transition-metal or post-transition-metal clusters. This theory encompasses polyhedra that follow, as well as those that violate, the effective atomic number and/or the skeletal electron pair rule. As is evident from Table I, the agreement between the predicted and the observed electron counts (N) is generally very good. The only major exceptions are the platinum carbonyl or gold phosphine clusters of high nuclearity, which often have electron counts of four or six electrons under the predicted value. For example, the series of $[Pt_3(CO)_6]_m^{2-}$ clusters, which have structures formed by stacking m nearly eclipsed platinum triangles (polyhedra *11*, *32*, *58*, *68*), all have electron counts of $42m + 2$, four electrons below the expected value of $42m + 6$.[93] Another example is the $[Pt_{19}(CO)_{22}]^{4-}$ tetraanion, which has 238 electrons (six electrons short) rather than the expected value of 244e. A similar situation is also found for gold phosphine clusters. For example, the $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ trication[81] is 8e below the expected electron count of 170e for an icosahedral cluster. This phenomenon may be related to the fact that platinum or gold has a tendency to form 16e rather than 18e complexes.

Acknowledgment. We are indebted to Drs. N. J. A. Sloane of AT&T Bell Laboratories (Murray Hill, NJ) for numerous stimulating discussions concerning properties of polyhedra and to Prof. J. Lauher, Prof. D. M. P. Mingos, and Kelly Keating for many helpful comments. B.K.T. is grateful to Drs. S. Martinengo, A. Ceriotti, A. Fumagalli, L. Garlaschelli, M. C. Malatesta, D. Strumolo, and A. Albinati for numerous stimulating discussions during his 1-month visit at the Instituto di Chimica Generale dell'Università, Milan, Italy, in 1982.

(91) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503.
(92) Teo, B. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1362.
(93) For discussions on this and related subjects, see, for example: (a) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. (b) Evans, J. *J. Chem. Soc., Dalton Trans.* **1980**, 1005. (c) Briant, C. E.; Evans, D. G.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1144. (d) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *240*, 321.

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Steric and Electronic Control of the Arbuzov Reaction in Transition-Metal Halides: A ^{1}H and ^{31}P NMR Study of the Reaction of $[CpCo(L\frown L)X]^+$ Complexes ($L\frown L$ = N, P, As Chelate Ligands; X^- = Cl^-, Br^-, I^-, CN^-) with $P(OCH_3)_3$

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Received June 21, 1983

Synthesis of a series of complexes, $[CpCo(L\frown L)X]^+$ ($L\frown L$ = N, P, As chelate ligands; X^- = Cl^-, Br^-, I^-, CN^-), was undertaken with the goal of characterizing the Michaelis–Arbuzov reaction between these complexes and $P(OCH_3)_3$. ^{1}H and ^{31}P NMR results provide support for the previously postulated two-step mechanism involving an initial equilibrium reaction $[CpCo(L\frown L)X]^+ + P(OCH_3)_3 \rightleftarrows \{CpCo(L\frown L)[P(OCH_3)_3]\}^{2+} + X^-$ followed by alkylation of X^- to produce an organometal–phosphonate complex, $\{CpCo(L\frown L)[P(OCH_3)_3]\}^{2+} + X^- \rightarrow \{CpCo(L\frown L)[P(O)(OCH_3)_2]\}^+ + CH_3X$. Several of the intermediate phosphite dications were synthesized and characterized. They enable the above reactions to be qualitatively separated. The initial reaction was quenched by sterically bulky chelate ligands. The rate of the overall reaction parallels the electron donor power of the attacking nucleophile ($CN^- > I^- > Br^- > Cl^-$) and also depends on the donor atoms of $L\frown L$ (N > P). Chelate dissociation occurs when $L\frown L$ = As. The results for $[CpCo(L\frown L)X]^+$ and other transition metal–halide complexes are discussed in terms of why the Arbuzov reaction takes place in some of these complexes but not with others.

Introduction

Some transition-metal complexes possessing a substitutionally labile nucleophilic ligand are known to react with alkyl phosphites and yield a final product containing a coordinated phosphonate ligand rather than coordinated phosphite.[1–8]

$$L_nM{-}X + P(OCH_3)_3 \rightarrow L_nM{-}P(O)(OCH_3)_2 + CH_3X \quad (1)$$

Equation 1 is formally analogous to the Michaelis–Arbuzov reaction (hereinafter referred to as the Arbuzov reaction)

(1) Haines, R. J.; DuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28* 405.
(2) Clemens, J.; Neukomm, H.; Werner, H. *Helv. Chim. Acta* **1974**, *57*, 2000.
(3) Trogler, W. C.; Epps, L. A.; Marzilli, L. G. *Inorg. Chem.* **1975**, *14*, 2748. Trogler, W. C.; Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 3699. Toscano, M. L.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 421.
(4) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 179.
(5) Towle, D. K.; Landon, S. J.; Brill, T. B.; Tulip, T. H. *Organometallics* **1982**, *1*, 295.
(6) Landon, S. J.; Brill, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6571.
(7) Labinger, J. A. *J. Organomet. Chem.* **1977**, *136*, C31.

