

Structure of transition-metal cluster compounds: Use of an additional orbital resulting from the *f*, *g* character of *spd* bond orbitals*

(osmium complexes/ruthenium complexes/cobalt complexes/rhodium complexes/gold complexes)

LINUS PAULING

Linus Pauling Institute of Science and Medicine, 2700 Sand Hill Road, Menlo Park, California 94025

Contributed by Linus Pauling, September 19, 1977

ABSTRACT A general theory of the structure of complexes of the transition metals is developed on the basis of the enneacovalence of the metals and the requirements of the electroneutrality principle. An extra orbital may be provided through the small but not negligible amount of *f* and *g* character of *spd* bond orbitals, and an extra electron or electron pair may be accepted in this orbital for a single metal or a cluster to neutralize the positive electric charge resulting from the partial ionic character of the bonds with ligands, such as the carbonyl group. Examples of cluster compounds of cobalt, ruthenium, rhodium, osmium, and gold are discussed.

The composition and structure of a great many compounds of transition metals correspond well to the assumption that transition-metal atoms can use their set of nine hybrid sp^3d^5 bond orbitals in forming bonds (1-4). For example, cobalt has nine outer electrons and accordingly can form nine bonds, as in the molecule hydridotetracarbonylcobalt, $\text{HCo}(\text{CO})_4$, in which a single bond is formed with a hydrogen atom and double bonds are formed with each of the four carbon atoms. Another example is the enneahydridorhenate anion, $[\text{ReH}_9]^{2-}$, in which the rhenium atom, which has increased its number of valence electrons from 7 to 9 by transfer of 2 from an electropositive metal (potassium in K_2ReH_9), forms single bonds with each of 9 hydrogen atoms. A few complexes are known, however, for which the composition and structure indicate that an additional stable orbital, which can serve as a bond orbital, is present. The explanation of this deviation from the predictions of the simple hybrid-orbital theory of chemical bonds has not been obvious. I have now found that consideration of the *f*, and to some extent the *g*, character of *spd* bond orbitals leads to the conclusion that some transition-metal atoms or clusters of them are provided with an additional bond orbital by the release of some *spd* character through the contribution of a small amount of *f* and *g* character by the relatively unstable *f* and *g* orbitals.

Hybrid bond orbitals

In the simple theory of hybrid bond orbitals (5, 6) the bond strength *S*, equal to the value of the angular part of the wave function in the bond direction, is taken as a measure of the bond-forming power of the orbital. The values of *S* for the best hybrid *sp*, *spd*, and *spdf* bond orbitals are 2, 3, and 4, respectively. The carbon atom is usually described as forming bonds in the four tetrahedral directions by using a set of four best sp^3 bond orbitals, each with strength 2. It has been pointed out, however, that the bond orbitals have some *d* and *f* character,

estimated at about 4 and 2%, respectively, which increases the value of *S* to about 2.76, thus making the bonds significantly stronger (ref. 6, p. 126). The spectral term values for potassium, rubidium, and cesium correspond to 142, 142, and 152 kJ mole⁻¹ for the promotion energy of an electron from an sp^3d^5 orbital to the *4f* orbital. The observed energies of sublimation per bond for transition metals lie between about 120 and 280 kJ mole⁻¹. A simple calculation with the assumption that the bond energy of a metal-metal bond is proportional to *S*² and with consideration of the promotion energy leads to values of 1-4% of *f* character and about half as much *g* character. Spectral term values are not available for francium, but there is some indication that the promotion energy to *5f* for the heavy elements is smaller than that to *4f* for the lighter ones. It is possible that the amount of *f*, *g*, . . . character of the bond orbitals of a heavy enneacovalent transition metal is as great as 10%, which would permit it to be decaacovalent. For a lighter transition metal with, for example, only 2 or 3% of *f* and *g* character in the bond orbitals, the freed fractional orbitals, amounting to 0.18 or 0.27 per atom, might cooperate for an octahedral cluster M_6 or a tetrahedral cluster M_4 to permit occupancy by an unshared electron pair or even a singly bonded hydrogen atom. In addition, resonance to structures with no-bond character for a metal-metal bond in a cluster liberates an orbital on one of the metal atoms. These two mechanisms for producing an orbital in addition to those allowed by the sp^3d^5 structures presumably cooperate.

The centered cluster of 11 gold atoms

A number of compounds with composition $\text{Au}_{11}(\text{PR}_3)_7\text{X}_3$, $\text{R} = \text{C}_6\text{H}_5$, *p*- $\text{C}_6\text{H}_4\text{F}$, *p*- $\text{C}_6\text{H}_4\text{Cl}$, or *p*- $\text{C}_6\text{H}_4\text{CH}_3$ and $\text{X} = \text{I}$ or SCN , have been reported (7). X-ray investigations (7, 8) have shown that the Au_{11} cluster has one gold atom at its center. The discussion of the structure of this Au_{11} cluster requires discussion also of the structure of other compounds of gold. Many square planar complexes of quadriligated gold(III) are known. The theory of these square planar structures (5) allocates dsp^2 bond orbitals to them, with four unshared electron pairs in *d* orbitals and one *p* orbital not used. The formal charge on the gold atom is -1, and the single-bond covalent radius is about equal to the enneacovalent radius, 134 pm (1). In many square planar complexes, such as trichloro(triphenylphosphine)gold(III) (9), the gold atom may be described either as having formal charge 0 and forming a double bond with the phosphorus atom, which is then transargononic, or as having formal charge -1 and forming a single bond with this atom, which then has formal charge +1 and is argononic. There is evidence, mentioned below, that these two structures contribute in the approximate

* Publication No. 75 from the Linus Pauling Institute of Science and Medicine.

The costs of publication of this article were defrayed in part by the payment of page charges. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

ratio 2/1; that is, that the phosphorus atom has resultant charge of about $+1/3$. This structure is compatible with the observed bond lengths.

A neutral gold atom might thus form five bonds and have three unshared pairs, using the eight d^5sp^2 orbitals. In the cation $[\text{Au}_6\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3]^{2+}$ each of the gold atoms of the Au_6 octahedron has an attached phosphorus atom (10). The electric charge +2 corresponds to having formal charge 0 for the gold atoms and $+1/3$ for the phosphorus atoms; that is, there is resonance among the 15 structures in which there are four $\text{Au}=\text{PR}_3$ groups and two $\text{Au}-\text{P}^+\text{R}_3$ groups. With quinquivalent gold the number of bonding electron pairs resonating among the 12 gold-gold positions is 10, giving bond number 0.83. The observed bond lengths, 293–309 pm, are somewhat larger than expected for this bond number.

The central gold atom in a centered cluster would be expected to form as many bonds with the surrounding atoms as possible. The electroneutrality principle permits a minimum of 10 electrons for gold, formal charge +1. With the nine sp^3d^5 orbitals this Au^+ atom would have one unshared pair and eight bonding electrons, forming the cluster Au_9 . If one additional orbital were available, as discussed in the first section, it would have 10 bonding electrons, forming the cluster Au_{11} . In fact, these Au_9 and Au_{11} clusters are known. The $\text{Au}_{11}(\text{PR}_3)_7\text{X}_3$ compounds have 10 Au about the central Au at positions corresponding to the corners of a regular icosahedron with one triangular face condensed to a single corner. The average bond length for the 10 bonds to the central atom is 268 pm (7, 8). This is just equal to twice the enneavalent radius for gold, 134 pm, extrapolated from the sequence from W to Pt (1). (The single-bond metallic radius for gold is the same, 133.9 pm; ref. 6, p. 403.) There is accordingly no doubt that these bonds are single bonds. The complex ion $[\text{Au}_9\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3]^{3+}$ (11) has the eight peripheral gold atoms at the corners of a regular icosahedron that remain when two pairs of corners on opposite sides are deleted. The average value of the length of the eight bonds formed by the central atom, 271 pm, shows these bonds to be essentially single bonds. The peripheral bonds in the Au_9 and Au_{11} clusters have average bond length 281 and 298 pm, respectively, in rough agreement with the values calculated for quinquivalence, 275 and 286 pm.

Octahedral metal clusters with an extra orbital

Almost all complexes containing clusters of 2, 3, or 4 transition-metal atoms have structures that correspond to making use of the nine spd orbitals of each metal atom. Many complexes with an octahedral M_6 group, however, have one bond or two electrons more than expected from the simple theory. The compound $\text{Os}_6(\text{CO})_{18}$, in which the Os_6 is not octahedral but consists of three tetrahedra, the two outer ones sharing faces with the central one (12), has the normal number of electrons. Six of the carbonyl groups are attached to osmium atoms by single (dative) bonds, thus giving each osmium atom nine outer electrons, a total of 54. Thirty are used in the 6 single and 12 double bonds to carbonyl groups and the other 24 in the 12 osmium-osmium bonds. The molecule can accept two electrons, however, to form the anion $[\text{Os}_6(\text{CO})_{18}]^{2-}$, in which there is an Os_6 octahedron, with three carbonyl groups attached to each Os atom (13). The osmium-osmium bond lengths range from 281 to 289 pm, average 286 pm. This value is 10 pm larger than the single-bond value, as is often observed for bonds between iron, ruthenium, and osmium atoms (4). The nine spd orbitals per osmium atom are used in the osmium-osmium and osmium-carbon bonds, with none left over for the added pair of

electrons. I suggest that this pair occupies the additional $spd(f)$ orbital that is made available by the contribution of f (and to a smaller extent g) to all of the osmium bond orbitals. A contribution of 1.85% of f and g to each of the 54 bond orbitals would be enough to liberate one orbital for the cluster. There is also another mechanism for liberating an orbital for osmium and its congeners (4). Each Os has a singly bonded carbonyl attached, and resonance from $^+\text{O}=\text{C}-\text{Os}-\text{Os}-\text{C}=\text{O}^+$ to $^+\text{O}=\text{C}-\text{Os}^--\text{Os}=\text{C}=\text{O}$ occurs to the extent of about 30% per bond, as is indicated by the lengthening of the bond (4). The first osmium atom has an unoccupied orbital in the no-bond structure. This effect, combined with the f -orbital effect, would provide an orbital in the center of the octahedron for the added pair of electrons, which might be described as resonating among six orbitals, each provided for part of the time by one of the osmium atoms.

The ion $[\text{HOs}_6(\text{CO})_{18}]^-$, which is isoelectronic with $[\text{Os}_6(\text{CO})_{18}]^{2-}$, has a similar structure, with the hydrogen atom above one face of the Os_6 octahedron (13). The three edges of this face have length 297 pm, 11 pm greater than the average for the other nine, which is 286 pm, equal to the value for the deprotonated anion. The increase of these edges to a value corresponding to about 50% of no-bond character is the expected response to the need for these three osmium atoms to provide the orbitals among which the bond to the hydrogen atom can resonate.

The corresponding diprotonated molecule, $\text{H}_2\text{Os}_6(\text{CO})_{18}$, has a different kind of cluster, a tetrahedron sharing a face with a square pyramid (13). This cluster has only 11 edges, and accordingly can form 11 metal-metal bonds, the two bonds to the two hydrogen atoms, and the 30 bonds to the carbonyl group with use of only one extra orbital. The two hydrogen atoms probably are attached to the two osmium atoms of the pyramid that are not shared with the tetrahedron; this location is indicated by the length of the bond between these two atoms, 296.5 pm. The 10 other bond lengths lie between 280 and 289 pm, with an average of 284 pm.

The corresponding compounds of ruthenium, $[\text{HRu}_6(\text{CO})_{18}]^-$ and $[\text{H}_2\text{Ru}_6(\text{CO})_{18}]$, have structures different from those of the osmium compounds. The anion $[\text{HRu}_6(\text{CO})_{18}]^-$ has been shown by its infrared and nuclear magnetic resonance spectra and the x-ray studies of two crystalline modifications to have the hydrogen atom in the center of the Ru_6 octahedron (14). The octahedron is approximately regular, with $\text{Ru}-\text{Ru}$ bond length 287 pm. The hydrogen atom thus is attached to the six surrounding ruthenium atoms by a covalent bond resonating among the six positions, using the extra orbital of the Ru_6 group. The observed $\text{H}-\text{Ru}$ bond length 203 pm is a little less than the value 214 pm calculated from the single-bond value 167 pm and the correction $-60 \text{ pm} \log n$, with $n = 1/6$. This amount of strain is acceptable. $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ also has a structure (15) with an octahedral Ru_6 cluster, requiring an extra orbital. The octahedron is flattened, the edges of two opposite faces averaging 295 pm, with the others 286 pm. It is likely that the hydrogen atoms lie out from the centers of these two faces and are triply bridging.

There are a number of molecules known in which there is a carbon atom in the center of an M_6 octahedron. One of many examples that might be discussed is $\text{Ru}_6(\text{CO})_{17}\text{C}$ (16). With 24 orbitals required for the $\text{Ru}-\text{Ru}$ bonds, 28 for bonds to carbonyl carbon, and 4 for the other carbon atom, an extra orbital is needed. (Six dative bonds from carbonyl provide the electrons for the Ru_6 group.) The $\text{Ru}-\text{Ru}$ bond length 290 pm corresponds to $\text{Ru}-\text{C} = 205 \text{ pm}$, which is about 10 pm less than the expected value. Possibly the radius of a transition-metal atom

can be adjusted somewhat for some of its orbitals by changing their hybrid character.

For cobalt, rhodium, and iridium the neutral atoms have nine outer electrons and dative single bonds to carbonyl groups are not needed to give enneacovalence; correspondingly the lengthening of metal-metal bonds by resonance to the no-bond structures does not occur, and the observed bond lengths are almost always just twice the enneacovalent radius (4). Accordingly, for complexes of these metals an extra orbital would be provided only by the *f* and *g* character of the bond orbitals. An example is the anion $[\text{Co}_6(\text{CO})_{14}]^{4-}$ (17). In the Co_6 octahedron (Co—Co bond length 250 pm) each cobalt atom is doubly bonded to a radially directed terminal carbonyl and is also bonded to four of the eight other carbonyls that are directed out from the center of the faces of the octahedron. The bonds to these triply ligated carbonyls have bond number $\frac{2}{3}$; that is, each of these carbonyl groups forms two single bonds with cobalt, which resonate among the three adjacent cobalt atoms. The number of bond orbitals of each cobalt atom is thus $4 + 2 + 4 \times \frac{2}{3} = 8\frac{2}{3}$, leaving $\frac{1}{3}$ orbital per atom, which is 2 for the Co_6 cluster, for the two added electron pairs. Thus, for this cobalt cluster complex no extra orbital is used. The stability of this complex anion may be attributed to the partial ionic character of the Co—C bonds. With electronegativity values 1.9 for Co and 2.5 for C, the partial ionic character is 9% (ref. 6, p. 98), corresponding to transfer by the 28 bonds of 2.52 electrons from the Co_6 group to the carbonyl groups. The electronegativity of carbon is without doubt increased somewhat by its transfer of 0.44 electrons to its adjacent oxygen atom. Without this refinement, the resultant charges on the Co, C, and O atoms in the 4- anion are -0.25, +0.26, and -0.44, respectively, and with the electronegativity of carbon increased to 2.68 they are 0, +0.31, and -0.31, in each case in reasonable agreement with the electroneutrality principle.

For the rather similar complex ion $[\text{Co}_6(\text{CO})_{15}]^{2-}$ (18), with six doubly bonded and three bridging carbonyls on the Co_6 octahedron (as required to satisfy the enneacovalence of each cobalt atom), an extra orbital is needed for the added electron pair.

The need for added electrons to achieve electroneutrality is only about half as great for the heavier congeners of cobalt, rhodium and iridium, because they have a larger electronegativity, 2.2. If the electronegativity of rhodium were equal to that of carbon, the octahedral complex $\text{Rh}_6(\text{CO})_{15}$ would be expected to be stable. Instead, the complex $\text{Rh}_6(\text{CO})_{16}$, with one extra carbonyl, is found (19), with the transfer of charge resulting from the rather small partial ionic character of the rhodium-carbon bonds compensated by the reverse transfer from a dative $\text{Rh}^- - \text{CO}^+$ group. In this complex each rhodium atom has two nonbridging carbonyls attached and in addition forms two bonds with $n = \frac{2}{3}$ with two of the other four carbonyls, which are out from the centers of four nonadjacent faces of the Rh_6 octahedron. If we assume that each Rh atom uses four electrons and four orbitals in two double bonds to its two terminal carbonyls and $\frac{4}{3}$ to the bridging carbonyls, the cluster is left with 22 electrons and 22 orbitals, enough to form 11 Rh—Rh bonds, which resonate among 12 positions. This structure gives the bonds of the octahedron bond number $\frac{11}{12}$ and predicted bond length 274 pm, in reasonable agreement with the observed 277.6 pm. There is also resonance with the structures with one $\text{Rh}^- - \text{CO}^+$ group, an extra orbital, and 12 Rh—Rh bonds. These structures place a fraction of one electronic charge on the Rh_6 cluster equal to their contribution to the normal state of the molecule. A 60% contribution would cancel the positive charge given by the small (2%) ionic char-

acter of the rhodium-carbon bonds.

In counting electrons and orbitals in this molecule and others with a triligated carbonyl, the assignment of bond number $\frac{2}{3}$ to the three bonds formed with the metal atoms by this carbonyl, rather than $n = 1$, is made on the basis of the electroneutrality principle. The structure $\equiv\text{C}-\ddot{\text{O}}^-$, with consideration of the partial ionic character (22%) of the carbon-oxygen bond, places the charge -1.22 on the oxygen atom, which is not acceptable. The structures $=\text{C}=\ddot{\text{O}}$: (charge on oxygen, -0.44) and $-\text{C}=\ddot{\text{O}}^+$ (charge on oxygen, +0.36) are acceptable.

Discussion

The foregoing theory of the structure of the transition-metal cluster carbonyls differs from earlier theories largely in its emphasis on the enneacovalence of the metal atoms and on the electroneutrality principle. These considerations require that a terminal carbonyl group be attached to the metal atom by a double bond unless there is need for a dative single bond in order to bring the number of electrons on the metal atom up to its full complement of 9 or to achieve electroneutrality. It is a part of the theory that the structure $\text{M}=\text{C}=\ddot{\text{O}}$: includes the structures $\text{M}^- - \text{C}=\ddot{\text{O}}^+$ to the extent indicated by the value of the partial ionic character of the metal-carbon bonds.

The nature of earlier theories can be illustrated by the discussion of one of them (20), as applied to the molecule $\text{Rh}_6(\text{CO})_{16}$, which was described in the preceding paragraphs. The author states that "In $\text{Rh}_6(\text{CO})_{16}$, for example, 4 electron pairs can be allocated to the four metal-carbon bonds each metal atom is involved in (each metal has two terminal and two triply bridging carbonyl groups attached); 2 more pairs can be allocated to nonbonding orbitals on each metal atom; and 7 electron pairs remain for skeletal bonding." The suggested structure thus involves three single bonds from the metal atoms to each triply bridging carbonyl, which thus has the structure $\equiv\text{C}-\ddot{\text{O}}^-$. It is pointed out in the preceding section that this structure violates the electroneutrality principle and accordingly is unacceptable. Also, with this structure each of the 4 triply bridging carbonyls removes an electron from the Rh_6 cluster and each of the 12 terminal carbonyls adds an electron to the cluster. The formal charge of each rhodium atom thus becomes -1.33, and the actual charge would be reduced only to about -1.25 by the small amount of ionic character of the Rh—C bonds. Accordingly, the electroneutrality principle is again violated by the proposed structure. The structure places 12 unshared electron pairs and 7 Rh—Rh bonding pairs on the Rh_6 octahedron, corresponding to bond number $\frac{7}{12}$ and expected bond length 286 pm. The observed value, 278 pm, is so much smaller as to make it unlikely that there are only 7 bonding pairs. Indeed, the structure leaves 4 orbitals unused, so that 11 Rh—Rh bonds, rather than 7, could be formed. Also, the assumption that a single covalent bond holds each terminal carbonyl and three such bonds hold each triply ligated carbonyl would require the corresponding Rh—C distances to be equal, contrary to observation. The observed values, 186 and 217 pm, respectively, differ by 31 pm, which is almost exactly equal to the expected difference for bonds with bond number 2 and $\frac{2}{3}$. These several flaws and others like them require the rejection of this theory and others in which several unshared electron pairs are assigned to the transition metal atoms, except when required for electroneutrality.

The theory of enneacovalence and adherence to the electroneutrality principle account in a straightforward way for the composition and structure of most of the compounds of the transition metals. This theory occupies the place in transition-metal chemistry of the theory of the quadrivalence of carbon

in organic chemistry, with the increased complexity associated with the increase from quadrivalence to enneacovalence and from one stable bond angle, the tetrahedral angle 109.47° , to two, the best *spd* angles 73.15° and 133.62° (2, 3). Application of the theory should accelerate progress in the transition-metal field.

- Pauling, L. (1975) "Maximum-valence radii of transition metals," *Proc. Natl. Acad. Sci. USA* **72**, 3799–3801.
- Pauling, L. (1975) "Valence-bond theory of compounds of transition metals," *Proc. Natl. Acad. Sci. USA* **72**, 4200–4202.
- Pauling, L. (1976) "Correlation of nonorthogonality of best hybrid bond orbitals with bond strength of orthogonal orbitals," *Proc. Natl. Acad. Sci. USA* **73**, 274–275.
- Pauling, L. (1976) "Metal-metal bond lengths in complexes of transition metals," *Proc. Natl. Acad. Sci. USA* **73**, 4290–4293.
- Pauling, L. (1931) "The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules," *J. Am. Chem. Soc.* **53**, 1367–1400.
- Pauling, L. (1960) *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY), 3rd. ed.
- McPartlin, M., Mason, R. & Malatesta, L. (1969) "Novel cluster complexes of gold(0)-gold(1)," *J. Chem. Soc. Chem. Commun.*, 334–335.
- Albano, V. G., Bellon, P. L., Manassero, M. & Sansoni, M. (1970). "Intermetallic pattern in metal-atom clusters. Structural studies on $Au_{11}X_3(PR_3)_7$ species," *J. Chem. Soc. Chem. Commun.*, 1210–1211.
- Bandoli, G., Clementi, D. A., Marangoni, G. & Cattalini, L. (1973) "Ground-state *trans*-effect and molecular-structure of trichloro(triphenylphosphine)gold(III)," *J. Chem. Soc. Dalton Trans.*, 886–889.
- Bellon, P. L., Manassero, M., Naldini, L. & Sansoni, M. (1972) "Preparation and structure of the hexakis(tris-*p*-tolylphosphinegold) salt of tetraphenylborate and electronic structure of gold cluster compounds," *J. Chem. Soc. Chem. Commun.*, 1035–1036.
- Bellon, P. L., Cariati, F., Manassero, M., Naldini, L. & Sansoni, M. (1971) "Novel gold clusters. Preparation, properties, and x-ray structure determination of salts of octakis(triarylphosphine)-enneagold. $[Au_9L_8]X_3$," *J. Chem. Soc. Chem. Commun.*, 1423–1424.
- Mason, R., Thomas, K. M. & Mingos, D. M. P. (1973) "Stereochemistry of octadecacarbonylhexaosmium(0). A novel hexanuclear complex based on a bicapped tetrahedron of metal atoms," *J. Am. Chem. Soc.* **95**, 3802–3804.
- McPartlin, M., Eady, C. R., Johnson, B. F. G. & Lewis, J. (1976) "X-ray structures of the hexanuclear cluster complexes $[Os_6(CO)_{18}]^{2-}$, $[HOs_6(CO)_{18}]^-$, and $[H_2Os_6(CO)_{18}]$," *J. Chem. Soc. Chem. Commun.*, 883–885.
- Eady, C. R., Johnson, B. F. G., Lewis, J., Malatesta, M. C., Machin, P. & McPartlin, M. (1976) " $[HRu_6(CO)_{18}]^-$: A ruthenium atom having an interstitial H-ligand. X-ray crystal structures of two modifications," *J. Chem. Soc. Chem. Commun.*, 945–946.
- Churchill, M. R. & Wormald, J. (1971) "Crystal structure and molecular geometry of octadecarbonylhexaruthenium dihydride," *J. Am. Chem. Soc.* **93**, 5670–5677.
- Sirigu, A., Bianchi, M. & Benedetti, E. (1969) "The crystal structure of $Ru_6C(CO)_{17}$," *J. Chem. Soc. Chem. Commun.*, 596.
- Albano, V. G., Bellon, P. L., Chini, P. & Scatturin, V. (1969) "The crystal and molecular structure of the potassium salt of the hexanuclear carbonyl cobaltate $[Co_6(CO)_{14}]^{4-}$," *J. Organometal. Chem.* **16**, 461–470.
- Albano, V., Chini, P. & Scatturin, V. (1968) "Crystal and molecular structures of new cobalt carbonyl clusters," *J. Chem. Soc. Chem. Commun.*, 163–164.
- Cory, E. G., Dahl, L. F. & Beck, W. (1963) " $Rh_6(CO)_{16}$ and its identity with previously reported $Rh_4(CO)_{11}$," *J. Am. Chem. Soc.* **85**, 1201–1203.
- Wade, K. (1976) "Structural and bonding patterns in cluster chemistry," *Adv. Inorg. Chem. Radiochem.* **18**, 1–66.