Chemical Applications of Topology and Group Theory. II. Metal Complexes of Planar Unsaturated Carbon Systems[1]

R. B. King[2]

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30061. *Received June 23, 1969*

Abstract: The geometries of minimum diameter planar networks of linked sp^2 carbon atoms are considered. Empirical data suggest that those with diameters less than about 2.1 carbon–carbon bond lengths can entirely bond to a single metal atom whereas those with larger diameters bond either partially to a single metal atom or entirely to two metal atoms. The π-electronic structures of such planar networks of linked sp^2 carbon atoms all have a lowest lying σ-bonding molecular orbital followed by one or, more commonly, two orthogonal, higher lying but generally bonding or nonbonding π molecular orbitals. The possible coordination polyhedra for metal complexes with one or two such orthogonally double π-donor ligands or with one single π-donor ligand are considered using the techniques developed in the first paper of this series[1] and compared with the geometries found in some known complexes.

The first paper of this series[1] generated possible polyhedra for coordination numbers from four through nine, inclusive, from basic mathematical and geometrical principles. By examining the 32 possible sp^3d^n hybrids some conclusions could be drawn concerning the favored coordination polyhedra for different coordination numbers in various types of complexes. In this treatment only forward σ bonding between the ligands and the central metal atom was considered. For this reason, this treatment is not directly applicable to complexes with π-donor ligands such as π-cyclopentadienyl which also engage in forward π bonding as well as forward σ bonding with metal atoms.

This second paper of the series extends this treatment to metal complexes of planar unsaturated carbon systems, a class of ligands which forms not only forward σ bonds but also forward π bonds (and occasionally forward bonds of even higher nodality) to metal atoms. However, before modifying the treatment of the first paper to include complexes containing π-donor ligands, an examination is made of possible π-donor ligands and the symmetries of their filled bonding molecular orbitals which can overlap with empty metal hybrid orbitals of appropriate symmetry.

Generation of Possible Planar Unsaturated Carbon Ligands

Consider a planar network of linked sp^2 carbon atoms. The connectivity of a carbon atom in such a network is defined as the number of other carbon atoms to which it is directly bonded and can only be 1, 2, or 3 for a network for sp^2 carbon atoms. The parameter c_n of a network, N_1, of sp^2 carbon atoms is defined as the number of carbon atoms with connectivity n.

For a planar network of sp^2 carbon atoms, the following relationships must be satisfied. (1) $\Sigma_n nc_n = 2b$ where b is an integer equal to the number of carbon–carbon bonds in the network. This relationship also implies that $\Sigma_n nc_n$ is an even number. (2) $c_1 \leq c_2 + 2c_3$ if $c_2 + c_3 > 1$. If this relationship is not satisfied, there will be insufficient bonds to hold the network together. (3) $c_3 \leq -2 + \Sigma_n c_n$. If this relationship is not satisfied, there will be two π bonds between adjacent carbon atoms which is inconsistent with the assumption of sp^2 hybridization. The two orthogonal π-electron systems of sp carbon networks are best treated separately; such networks of sp (rather than sp^2) carbon atoms will not be treated in the present paper. (4) In order to prevent excessive angular strain the number of carbon–carbon bonds in the network cannot exceed the number of carbon atoms if there are three-membered rings present.

The diameter, d, of a planar network of sp^2 carbon atoms is defined as the maximum distance between two carbon atoms in the network assuming equal carbon–carbon bond lengths and measuring the diameter in units of this carbon–carbon bond length. A minimum diameter is desirable for most efficient bonding of an entire planar network of sp^2 carbon atoms to a single metal atom. If the diameter of the network is too large, the overlap of the metal hybrid orbitals with the network molecular orbitals will be poor, resulting in either only a portion of the network being bonded to the metal atom or the network being bonded to more than one metal atom.

In this treatment the planar networks of sp^2 carbon atoms will be assumed to have standard geometry. In standard geometry the carbon–carbon bond distances are equal and the carbon–carbon bond angles are 120° unless some other angle is necessary to satisfy the following conditions: (1) rings must be regular polygons; (2) bonds exocyclic to rings (such as in fulvene) must bisect the exterior angles of the ring; (3) carbon atoms in a chain of six or more (*e.g.*, heptatrienyl) carbon atoms must be at the vertices of a regular polygon with n vertices where n is the number of carbon atoms in the chain. This condition is used to minimize the diameter of the planar network while still avoiding steric interference between the hydrogen atoms on the carbon atoms at each end of the chain. This "doubling back" of long carbon chains also reduces the nodality of their molecular orbitals. The diameters of networks will also be minimized by using the cisoid rather than the transoid configuration of any dienoid four-carbon portions of the network.

Table I summarizes the possible c_1, c_2, and c_3 values

(1) Part I of this series: R. B. King, *J. Am. Chem. Soc.*, 91, 7211 (1969).

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

Table I. Potential Planar Unsaturated Carbon Networks[a]

Network[b]	c_1	c_2	c_3	$c_2 + c_2 + c_3$	b	d	Bonding orbitals σ	Bonding orbitals π	Bonding orbitals δ	Nonbonding orbitals	Antibonding orbitals π	Antibonding orbitals δ	Antibonding orbitals ϕ	Antibonding orbitals Other
Ethylene (1)	2	0	0	2	1	1.000	1	0	0	0	1	0	0	0
Cyclopropenyl (2)	2	3	0	3	3	1.000	1	0	0	0	2	0	0	0
Allyl (3)	2	1	0	3	2	1.732	1	0	0	1(π)	0	1	0	0
Cyclobutadiene (4)	0	4	0	4	4	1.414	1	0	0	2(π)	0	1	0	0
Methylenecyclopropene (5)	1	2	1	4	4	1.932	1	1	0	0	1	0	0	1
Butadiene (6)	2	2	0	4	3	2.000	1	1	0	0	0	1	1	0
Trimethylenemethane (7)	3	0	1	4	3	1.732	1	0	0	2(π)	0	0	1	0
Cyclopentadienyl (8)	0	5	0	5	5	1.613	1	2($\perp$)	0	0	0	2 (45°)	0	0
Methylenecyclobutenyl (9)	1	3	1	5	5	2.414	1	1	0	1(π)	0	1	1	0
Dimethylenecyclopropenyl (10)	2	1	2	5	5	2.732	1	1	0	1(π)	0	2	0	0
Pentadienyl (11)	2	3	0	5	4	1.732	1	1	0	1(π)	0	2	0	0
2-Methylenebutadiene (12)	3	1	1	5	4	2.646	1	1	0	1(π)	0	1	1	0
Benzene (13)	0	6	0	6	6	2.000	1	2($\perp$)	0	0	0	2	1	0
Fulvene (14)	1	4	1	6	6	2.540	1	2($\perp$)	0	0	0	1	0	2
1,2-Dimethylenecyclobutene (15)	2	2	2	6	6	2.414	1	2($\perp$)	0	0	0	2	1	0
Trimethylenecyclopropane (16)	3	0	3	6	6	2.732	1	2($\perp$)	0	0	0	1	0	2
Hexatriene (17)	2	4	0	6	5	2.000	1	2($\perp$)	0	0	0	2	1	0
Methylenepentadienyl (18)	3	2	1	6	5	2.646	1	1	0	2(π,δ)	0	2	0	0
Diallylene (19)	4	0	2	6	5	2.646	1	1	0	2(π,δ)	0	1	1	0
Bicyclo[2.2.0]hexatriene (20)	0	4	2	6	7	2.361	1	2($\perp$)	0	0	0	2	1	0
Cycloheptatrienyl (21)	0	7	0	7	7	2.076	1	2($\perp$)	0	0	0	2	2	0
Benzyl (22)	1	5	1	7	7	3.000								
Dimethylenecyclopentenyl (23)	2	3	2	7	7	2.589	1	2($\perp$)	0	1(δ)	0	1	2	0
Trimethylenecyclobutyl (24)	3	1	3	7	7	3.414								
Heptatrienyl (25)	2	5	0	7	6	2.076	1	2($\perp$)	0	1(δ)	0	1	2	0
Trivinylmethyl (26)	3	3	1	7	6	3.000	1	2($\perp$)	0	1	0	2	0	1
Methylenediallylene (27)	4	1	2	7	6	2.732								
Bicyclo[2.2.0]heptatrienyl (28)	0	5	2	7	8	2.589	1	2($\perp$)	0	1(δ)	0	1	2	0
Cyclooctatetraene (29)	0	8	0	8	8	2.414	1	2($\perp$)	0	2(δ)	0	0	2	1(γ)
Methylenecycloheptatriene (30)	1	6	1	8	8	3.188								
Dimethylenecyclohexadiene (31)	2	4	2	8	8	3.000								
Trimethylenecyclopentene (32)	3	2	3	8	8	3.515	1	2($\perp$)	1	0	0	0	0	4
Tetramethylenecyclobutane (33)	4	0	4	8	8	3.414	1	2($\perp$)	1	0	0	0	0	4
Octatetraene (34)	2	6	0	8	7	2.414	1	2($\perp$)	1	0	0	1	2	1(γ)
Methyleneheptatriene (35)	3	4	1	8	7	3.188	1	2($\perp$)	0	2(δ)	0	0	2	1
Dimethylenehexadiene (36)	4	2	2	8	7	3.000	1	2($\perp$)	1	0	0	1	2	1(γ)
Trimethylenepentenyl (37)	5	0	3	8	7	3.464								
Pentalene (38)	0	6	2	8	9	3.080								
Benzocyclobutadiene (39)	0	6	2	8	9	3.162	1	2($\perp$)	1	0	0	1	2	1(γ)

[a] For a given set of c_1, c_2, and c_3 values, only the minimum diameter network (see text) is given. [b] Numbers in parentheses correspond to geometries shown in Figure 1.

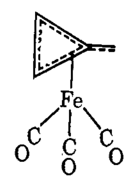
for planar networks containing up to eight sp^2 carbon atoms. In some cases more than one network is possible for a given combination of c_1, c_2, and c_3 values. In these cases the minimum diameter network is listed in Table I and is the one used for further treatment. For a given number of planar sp^2 carbon atoms, the minimum diameter network is the regular polygon; this appears to relate to the tendency of planar C_nH_n rings (*e.g.*, cyclopentadienyl) to form complexes with transition metals.

Among the planar sp^2 carbon networks shown in Table I, the following have been shown to bond entirely to a single transition metal: (1) ethylene (d = 1.000);[3] (2) cyclopropenyl (d = 1.000), *e.g.*, $[(C_6H_5)_3C_3NiBr]_2$[4] and $C_5H_5Mo(CO)_2C_3(C_6H_5)_3$;[5] (3) allyl ($d$ = 1.732);[6] (4) cyclobutadiene (d = 1.414), *e.g.*, $C_4H_4Fe(CO)_3$;[7] (5) butadiene (d = 2.000);[8] (6) trimethylenemethane (d = 1.732), *e.g.*, $C_4H_6Fe(CO)_3$;[9] (7) cyclopentadienyl (d = 1.613);[10] (8) pentadienyl (d = 1.732) in cyclohexadienyl and cycloheptadienyl complexes, *e.g.*, $C_6H_7Mn(CO)_3$;[11] (9) benzene (d = 2.000);[12] (10) hexatriene (d = 2.000) in metal complexes of conjugated trienes such as cycloheptatriene and 1,3,5-cyclooctatriene;[13] (11) cycloheptatrienyl (d = 2.076).[13] In special circumstances (*e.g.*, $(C_8H_8)_3Ti_2$[14] and $(C_8H_8)_2U$[15]) cyclooctatetraene (d = 2.414) can also bond entirely to a single transition metal, but more commonly either a part (four or six carbon atoms) of the cyclooctatetraene ring bonds to a single metal atom or an entire cyclooctatetraene ring bonds to two metal atoms. Other planar networks in Table I, including

(3) R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 77 (1962).
(4) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964).
(5) R. G. Hayter, *J. Organometal. Chem.*, **13**, P1 (1968).
(6) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).
(7) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965); J. D. Fitzpatrick, L. Watts, S. F. Emerson, and R. Pettit, *ibid.*, **87**, 3254 (1965).
(8) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).
(9) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).
(10) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1958); F. A. Cotton and G. Wilkinson, *Progr. Inorg. Chem.*, **1**, 1 (1959); J. M. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).
(11) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961).
(12) H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid-Metal Complexes," The Ronald Press Co., New York, N. Y., 1966.
(13) M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 353 (1966).
(14) H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 898 (1966); H. Dietrich and H. Dierks, *ibid.*, **5**, 899 (1966).
(15) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

some with $d > \sim 2.1$, may either bond partially to a single transition metal (*e.g.*, butadiene,[16] hexatriene,[17] cycloheptatrienyl,[18] benzyl,[19] cyclooctatetraene,[20] and benzocyclobutadiene[21]) or may bond entirely to two transition metals (*e.g.*, butadiene,[16] fulvene,[22] hexatriene,[23] diallylene,[24] cycloheptatrienyl,[25] and cyclooctatetraene[26]).

This examination of the planar networks of sp^2 carbon atoms which form metal complexes suggests that in order for a planar network to bond entirely to a single metal atom, its diameter must be less than ~ 2.1. The only planar network of sp^2 carbon atoms with $d < 2.1$ which has not yet been shown to bond entirely to a single metal atom is methylenecyclopropene ($d = 1.932$). The unavailability of suitable organic intermediates probably accounts for the absence of methylenecyclopropene complexes in the literature; reaction of 1,2-dichloro-3-methylenecyclopropane with $Fe_2(CO)_9$ under mild conditions might yield methylenecyclopropenetricarbonyliron, $C_4H_4Fe(CO)_3$ (I).



I

Table I also lists the molecular orbitals for the most important planar sp^2 carbon networks which were obtained from the results of Hückel calculations published in various tables.[27] Table I classifies the molecular orbitals according to their bonding, nonbonding, or antibonding character and according to their symmetry. All of the bonding and nonbonding molecular orbitals as well as some of the antibonding molecular orbitals could readily be classified as σ, π, δ, ϕ, or γ orbitals on the basis of having zero, one, two, three, or four symmetrically situated nodal planes passing through a common center point. The nodality of some of the highest energy antibonding molecular orbitals, especially those of the most complex and least symmetrical systems, could not be so readily ascertained, but the high energies of these orbitals make them unimportant for this discussion.

Examination of Table I indicates that the majority of the planar sp^2 carbon networks have a lowest lying σ-bonding molecular orbital followed by two higher lying but still bonding or nonbonding orthogonal π orbitals. Such networks will be called "orthogonal double π-donor ligands." They can donate three electron pairs to a metal atom by forming one forward σ bond and two orthogonal forward π bonds. This composite "triple bond" has cylindrical symmetry like the similar carbon–carbon triple bond in acetylene. Because of the cylindrical symmetry of the bond between a metal atom and an orthogonal double π-donor ligand, treatment of metal complexes of this type is simpler than treatment of metal complexes with single π-donor ligands (*e.g.*, π-allyl) where the metal–ligand π bond does not have cylindrical symmetry.

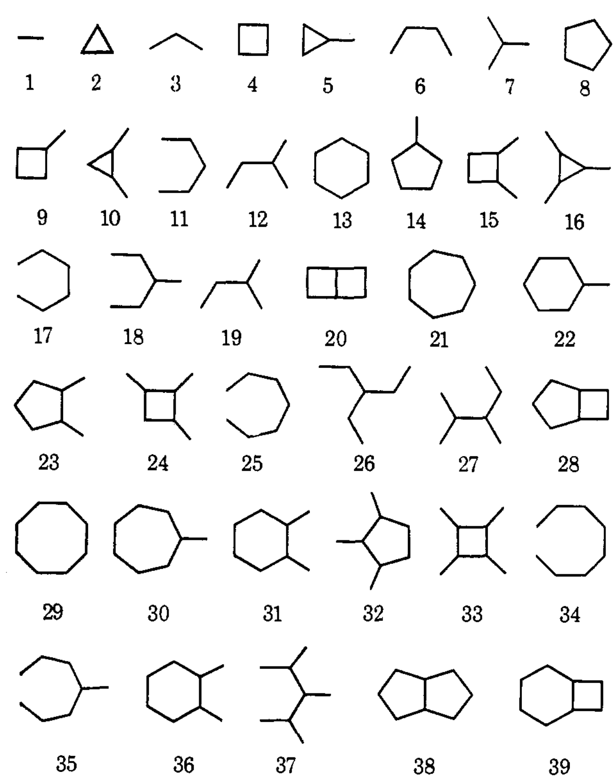


Figure 1. Geometries of networks considered in Table I.

Polyhedra and Hybridization Schemes for Complexes of Orthogonally Double π-Donor Ligands

Table II summarizes the coordination polyhedra for complexes containing orthogonally double π-donor ligands. The polyhedra listed in Table II are those formed from vertices located at the positions of the σ-donor ligands and at the "center" of the orthogonally double π-donor ligand; the center of the orthogonally double π-donor ligand is defined as the intersection of the nodal planes of the two orthogonal π orbitals and the plane of the carbon atoms. These σ-bonding coordination polyhedra thus do not contain the vectors of the two orthogonal π orbitals; thus a nine-coordinate complex with one orthogonally double π-donor ligand will have a σ-bonding coordination polyhedron with only seven vertices. The position of the orthogonally double π donor ligand is specified in Table II when ambiguity would otherwise result. Possible sp^{3}d^n hybridizations for the different coordination polyhedra and different locations of the orthogonally double π-donor ligand were obtained by conventional group theo-

(16) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1156 (1962).
(17) H. D. Murdoch and E. Weiss, *ibid.*, **46**, 1588 (1963).
(18) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 785 (1964).
(19) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966); F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 5418 (1968).
(20) B. Dickens and W. N. Lipscomb, *ibid.*, **83**, 4862 (1961).
(21) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).
(22) E. Weiss, W. Hübel, and R. Merényi, *Ber.*, **95**, 1155 (1962); J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Cryst.*, **19**, 85 (1965).
(23) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Am. Chem. Soc.*, **86**, 3590 (1964).
(24) A. Nakamura and N. Hagihara, *J. Organometal. Chem.*, **3**, 480 (1965).
(25) F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, **91**, 847 (1969).
(26) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960); F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 2026 (1968).
(27) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, Oxford, 1965; C. A. Coulson and A. Streitwieser, Jr., "A Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965.

Table II. Possible Coordination Polyhedra for Complexes Containing Orthogonally Double π-Donor Ligands

σ-Bonding polyhedron	No. of elements *v*	*e*	*f*	Location of double π donor[a]	Point group[b]	Other parameters *s*	*p*	*l*	*x*
I. Complexes with One Orthogonally Double π-Donor Ligand									
(A) Coordination no. four[c]									
Linear	2	1	1		C_{4v}[d]	8	1	1	1
(B) Coordination no. five[c]									
Trigonal planar	3	3	2		C_{2v}	4	3	2	1
(C) Coordination no. six[c]									
Square planar	4	4	2		C_{2v}	4	3	2	2
Tetrahedron	4	6	4		C_{3v}	6	2	3	2
(D) Coordination no. seven[c]									
Square pyramid	5	8	5	Apical	C_{4v}	8	1	3	1
Square pyramid	5	8	5	Basal	C_s	2	7	3	6
Trigonal bipyramid	5	9	6	Apical	C_{3v}	6	2	3	2
Trigonal bipyramid	5	9	6	Equatorial	C_{2v}	4	2	3	2
(E) Coordination no. eight[c]									
Trigonal prism	6	9	5		C_s	2	5	3	3
Irregular hexahedron	6	10	6	Anywhere	C_1	1	5	3	5
Pentagonal pyramid	6	10	6	Apical	C_{5v}	10	1	3	1
Pentagonal pyramid	6	10	6	Basal	C_s	2	5	3	3
Diagonally deficient cube	6	11	7	*e*	C_s	2	2	3	2
Diagonally deficient cube	6	11	7	*f*	C_s	2	5	3	3
Octahedron	6	12	8		C_{4v}	8	3	4	1
(F) Coordination no. nine[c]									
Tetragonal base–trigonal base	7	11	6	On refl plane	C_s	2	0	3	0
Tetragonal base–trigonal base	7	11	6	Off refl plane	C_1	1	1	3	1
3-Capped trigonal prism	7	12	7	Apical	C_{3v}	6	1	3	1
3-Capped trigonal prism	7	12	7	On refl plane	C_s	2	1	3	1
3-Capped trigonal prism	7	12	7	Off refl plane	C_1	1	1	3	1
4-Capped trigonal prism	7	13	8	On refl plane	C_s	2	1	3	1
4-Capped trigonal prism	7	13	8	Off refl plane	C_1	1	1	3	1
Skewed tetragonal base–trigonal base	7	14	9	On refl plane	C_s	2	1	3	1
Skewed tetragonal base–trigonal base	7	14	9	Off refl plane	C_1	1	1	3	1
Pentagonal bipyramid	7	15	10	Apical	C_{5v}	10	1	4	1
Pentagonal bipyramid	7	15	10	Equatorial	C_{2v}	4	0	4	0
II. Complexes with Two Orthogonally Double π-Donor Ligands									
(A) Coordination no. six[c]									
Linear	2	1	1		D_{4v}[d]	16	1	1	1
(B) Coordination no. seven[c]									
Trigonal planar	3	3	2		C_{2v}	4	2	2	2
(C) Coordination no. eight[c]									
Square planar	4	4	2	*cis*	C_{2v}	4	0	2	0
Square planar	4	4	2	*trans*	D_{2h}	8	0	2	0
Tetrahedron	4	6	4		C_{2v}	4	2	3	2
(D) Coordination no. nine[c]									
Square pyramid	5	8	5	Both basal: *cis*	C_s	2	0	3	0
Square pyramid	5	8	5	Both basal: *trans*	C_{2v}	4	1	3	1
Square pyramid	5	8	5	Basal and Apical	C_s	2	1	3	1
Trigonal bipyramid	5	9	6	Both apical	D_{3h}	12	1	3	1
Trigonal bipyramid	5	9	6	Both equatorial	C_{2v}	4	1	3	1
Trigonal bipyramid	5	9	6	Apical, equatorial	C_s	2	1	3	1

[a] In cases of polyhedra with nonequivalent vertices, this column indicates the location of the vertex corresponding to the σ bond to the orthogonally double π-donor ligand. [b] The vertex or vertices where the orthogonally double π-donor ligand(s) are located are considered nonequivalent to the other vertices where purely σ-donor ligands are located in determining the point group of the polyhedron. [c] In determining the coordination number both the forward σ bonds and the forward π bonds are considered. [d] To avoid the awkward $C_{\infty v}$ and $D_{\infty h}$ point groups, the π vectors of the orthogonally double π-donor ligands are considered to impart fourfold rotational symmetry to the system. [e] Here the orthogonally double π-donor ligand is considered to be in one of the four coplanar coordination positions also coplanar with the metal atom in the diagonally deficient cube. [f] Here the orthogonally double π-donor ligand is considered to be in one of the two remaining coordination positions of the diagonally deficient cube.

retical methods[28] which involved the determination of irreducible representations for both Γ_σ and Γ_π followed by finding the sp^3d^n hybrids corresponding to these irreducible representations. As in the first paper[1] the number of different sp^3d^n combinations corresponding to any spatial orientation of a given polyhedron with a given location of the orthogonally double π donor is called its permutivity, *p*. Similarly the number of different sp^3d^n combinations corresponding to a specific spatial orientation of a given polyhedron with a given location of the orthogonally double π donor is called its flexibility, *x*. Other symbols, definitions, and portions of the procedure correspond to those used in the first paper.[1]

Table III lists possible polyhedra for the 32 possible sp^3d^n hybrids in complexes with one orthogonally double π-donor ligand. These polyhedra include those listed in Table II as well as a few less symmetrical ones such as the C_s trigonal pyramid and C_{2v} rectan-

(28) For a general discussion of the pertinent group theoretical techniques, see F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963.

Table III. Coordination Polyhedra in Complexes with One Orthogonally Double π-Donor Ligand Corresponding to Various Possible Combination of d Orbitals[a]

Coord no.	Forward bonding d orbitals xy	yz	zx	$x^2 - y^2$	z^2	Possible σ-bonding polyhedra[b]
4	0	0	0	0	0	Linear (1)
5	0	0	0	0	1	
5	0	0	0	1	0	
5	0	0	1	0	0	Planar triangle (1)
5	0	1	0	0	0	Planar triangle (1)
5	1	0	0	0	0	Planar triangle (1)
6	0	0	0	1	1	
6	0	0	1	0	1	Planar square (2), C_s-trigonal pyramid (6)[c]
6	1	0	0	0	1	
6	0	0	1	1	0	Planar square (2), C_s-trigonal pyramid (6)[c]
6	0	1	0	0	1	Planar square (2), C_s-trigonal pyramid (6)[c]
6	0	1	0	1	0	C_s-Trigonal pyramid (6)[c]
6	1	0	0	1	0	Tetrahedron (2)
6	0	1	1	0	0	Tetrahedron (2), C_s-trigonal pyramid (6)[c]
6	1	0	1	0	0	Tetrahedron (2), C_s-trigonal pyramid (6)[c]
6	1	1	0	0	0	Tetrahedron (2), C_s-trigonal pyramid (6)[c]
7	1	0	0	1	1	Apically substituted trigonal bipyramid (2)[c]
7	0	1	0	1	1	Apically substituted trigonal bipyramid (2)[c]
7	0	0	1	1	1	Apically substituted trigonal bipyramid (2)[c]
7	1	0	1	0	1	Basally substituted square pyramid (6)
7	1	1	0	0	1	Basally substituted square pyramid (6)
7	0	1	1	0	1	Equatorially substituted trigonal bipyramid (2), apically substituted trigonal bipyramid (2)[c]
7	1	0	1	1	0	Basally substituted square pyramid (6)
7	1	1	0	1	0	Basally substituted square pyramid (6)
7	0	1	1	1	0	Apically substituted square pyramid (1), equatorially substituted trigonal bipyramid (2)
7	1	1	1	0	0	Apically substituted rectangular pyramid (1)
8	1	1	1	1	0	Apically substituted pentagonal pyramid (1)[d]
8	1	1	1	0	1	. . .[d]
8	1	1	0	1	1	Octahedron (1)[d]
8	1	0	1	1	1	Octahedron (1)[d]
8	0	1	1	1	1	Octahedron (1)[d]
9	1	1	1	1	1	Possibilities with $p = 1$ listed in Table II

[a] All of the hybrids listed in this table also utilize the one s and the three p orbitals. [b] The flexibility values of the polyhedra are given in parentheses. [c] The basally substituted square pyramid can also use this hybridization. [d] The trigonal prism, 6,10,6-polyhedron, and 6,11,7-polyhedron can also use these hybridizations.

gular pyramid formed by squeezing the C_{3v} tetrahedron and the C_{4v} square pyramid, respectively.

In the cases of complexes with two orthogonally double π-donor ligands (Table IV) only eight distinct sp^3d^n hybrids need to be considered since the minimum coordination number is six requiring at least the sp^3d^2-[yz,zx] orbitals to be used; it is therefore only necessary to consider the eight possible combinations of utilization or nonutilization of the d[xy], d[$x^2 - y^2$], and d[z^2] orbitals in the hybrids.

Table IV. Coordination Polyhedra in Complexes with Two Orthogonally Double π-Donor Ligands Corresponding to Various Combinations of d Orbitals[a]

Coord no.	d orbitals used for forward bonding xy	$x^2 - y^2$	z^2	Possible σ-bonding polyhedra
6	0	0	0	Linear
7	0	0	1	Trigonal planar
7	0	1	0	Trigonal planar
7	1	0	0	
8	0	1	1	
8	1	0	1	Tetrahedral
8	1	1	0	Tetrahedral
9	1	1	1	Polyhedra with $p = 1$ in Table II

[a] All of the hybrids listed in this table also utilize the one s, three p, and two d[yz,zx] orbitals.

It is reasonable to suppose that polyhedra with maximum symmetry and minimum nonzero flexibility are favored in complexes containing orthogonally double π donors as well as in complexes containing just conventional σ donors. However, the larger size of the bonding portion of the orthogonally double π-donor ligand acts as an impediment to the approximation of a sphere, thereby decreasing the special stability of triangulated polyhedra.

In the cases of complexes with one orthogonally double π-donor ligand, there is only one possible polyhedron for coordination numbers four (*e.g.*, C_5H_5NiNO) and five (*e.g.*, $C_5H_5Co(CO)_2$). For coordination number six the C_{3v} tetrahedron (as found in $C_5H_5Mn(CO)_3$[29]) appears to be favored over the less symmetrical C_{2v} planar square and C_s trigonal pyramid (isosceles triangular base). For coordination number seven the apically substituted square pyramid has maximum symmetry and minimum flexibility; the seven-coordinate derivatives $C_5H_5M(CO)_4$ (M = V[30] and Nb[31]) utilize this polyhedron. For coordination number eight it is difficult to decide between the apically substituted pentagonal pyramid and the octahedron; the apically substituted pentagonal pyramid has the dis-

(29) I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, 23A, 273 (1967).
(30) J. B. Wilford, A. Whitla, and H. M. Powell, *J. Organometal. Chem.*, 8, 495 (1967).
(31) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 87, 2576 (1965).

Table V. Possible Coordination Polyhedra for Complexes Containing One Single π-Donor Ligand

σ-Bonding polyhedron	No. of elements v	e	f	Location of π donor[a]	Point group[b]	Other parameters s	p	l	x
(A) Coordination no. four[c]									
Trigonal planar	3	3	2	⊥	C_{2v}	4	−1[f]	2	−1[f]
Trigonal planar	3	3	2	∥	C_{2v}	4	1	2	1
(B) Coordination no. five[c]									
Square planar	4	4	2	⊥	C_{2v}	4	2	2	2
Square planar	4	4	2	∥	C_{2v}	4	−1[f]	2	−1[f]
Tetrahedron	4	6	4		C_{3v}	6	4	3	4
(C) Coordination no. six[c]									
Square pyramid	5	8	5	Apical	C_{4v}	8	2	3	2
Square pyramid	5	8	5	Basal ⊥	C_s	2	7	3	6
Square pyramid	5	8	5	Basal ∥	C_s	2	3	3	3
Trigonal bipyramid	5	9	6	Apical	C_{3v}	6	4	3	4
Trigonal bipyramid	5	9	6	Equatorial ⊥	C_{2v}	4	2	3	2
Trigonal bipyramid	5	9	6	Equatorial ∥	C_{2v}	4	2	3	2
(D) Coordination no. seven[c]									
Trigonal prism	6	9	5	⊥	C_s	2	3	3	2
Trigonal prism	6	9	5	∥	C_s	2	7	3	6
Irregular hexahedron	6	10	6	Anywhere	C_1	1	10	3	10
Diagonally deficient cube	6	11	7	⊥[d]	C_s	2	7	3	6
Diagonally deficient cube	6	11	7	∥[d]	C_s	2	3	3	1
Diagonally deficient cube	6	11	7	⊥[e]	C_s	2	3	3	3
Diagonally deficient cube	6	11	7	∥[e]	C_s	2	7	3	6
Octahedron	6	12	8		C_{4v}	8	3	4	2
(E) Coordination no. eight[c]									
Tetragonal base–trigonal base	7	11	6	On plane ⊥	C_s	2	0	3	0
Tetragonal base–trigonal base	7	11	6	On plane ∥	C_s	2	5	3	3
Tetragonal base–trigonal base	7	11	6	Off plane	C_1	1	5	3	5
3-Capped trigonal prism	7	12	7	Apical	C_{3v}	6	4	3	4
3-Capped trigonal prism	7	12	7	Other ⊥	C_s	2	5	3	3
3-Capped trigonal prism	7	12	7	Other ∥	C_s	2	2	3	2
4-Capped trigonal prism	7	13	8	Apical ⊥[g]	C_{2v}	4	2	3	2
4-Capped trigonal prism	7	13	8	Apical ∥[g]	C_{2v}	4	0	3	0
4-Capped trigonal prism	7	13	8	On plane ⊥	C_s	2	5	3	3
4-Capped trigonal prism	7	13	8	On plane ∥	C_s	2	2	3	2
4-Capped trigonal prism	7	13	8	Off plane	C_1	1	5	3	5
Skewed tetragonal base–trigonal base	7	14	9	On plane ⊥	C_s	2	5	3	3
Skewed tetragonal base–trigonal base	7	14	9	On plane ∥	C_s	2	2	3	2
Skewed tetragonal base–trigonal base	7	14	9	Off plane	C_1	1	5	3	5
Pentagonal bipyramid	7	15	10	Apical	C_{5v}	10	3	4	2
Pentagonal bipyramid	7	15	10	Equatorial ⊥	C_{2v}	4	3	4	1
Pentagonal bipyramid	7	15	10	Equatorial ∥	C_{2v}	4	0	4	0
(F) Coordination no. nine[c]									
Cube	8	12	6		C_{4v}	8	0	3	0
"Distorted cube"	8	13	7	⊥	C_s	2	1	3	1
"Distorted cube"	8	13	7	∥	C_s	2	0	3	0
8,14,8-Polyhedron	8	14	8	On plane ⊥	C_s	2	1	3	1
8,14,8-Polyhedron	8	14	8	On plane ∥	C_s	2	0	3	0
3,3-Bicapped trigonal prism	8	15	9	Anywhere	Various		0	3	0
Square antiprism	8	16	10	⊥	C_s	2	0	4	0
Square antiprism	8	16	10	∥	C_s	2	1	4	1
4,4-Bicapped trigonal prism	8	17	11	On plane ⊥	C_s	2	0	4	0
4,4-Bicapped trigonal prism	8	17	11	On plane ∥	C_s	2	1	4	1
4,4-Bicapped trigonal prism	8	17	11	Off plane	C_1	1	1	4	1
"Dodecahedron"	8	18	12	⊥	C_s	2	1	4	1
"Dodecahedron"	8	18	12	∥	C_s	2	0	4	0

[a] In case of polyhedra with nonequivalent vertices this column indicates the location of the vertex corresponding to the σ bond to the single π-donor ligand. In cases where ambiguity would otherwise result, the orientation of the forward π bond of the π donor to the metal atom is specified as parallel (∥) or perpendicular (⊥) to the reflection plane. [b] The vertex where the single π-donor ligand is located is considered nonequivalent to the other vertices where purely σ-donor ligands are located. [c] In determining the coordination number, both the forward σ bonds and the forward π bonds are considered. [d] Here the single π-donor ligand is considered to be in one of the four coplanar coordination positions also copolanar with the metal atom in the diagonally deficient cube. [e] Here the single π-donor ligand is considered to be in one of the two remaining coordination positions of the diagonally deficient cube. [f] A −1 value for the permutivity or flexibility for a polyhedron is defined to mean that two p orbitals at most can be used for the hybrid. [g] Position relative to reflection plane through three (rather than one) ligand positions.

advantage of a pentagonal face but the advantage of equal distances from the central metal atom to the five solely σ-donor ligands and greater relative distance between these ligands and the orthogonally double π-donor ligand. The complexes $C_5H_5Mo(CO)_2X_3$ are presumably eight-coordinate;[32] however, their structures have not yet been determined. For coordination number nine with one orthogonally double π-donor ligand, the apically substituted pentagonal bipyramid has the highest symmetry and hence is favored; this polyhedron is found in the zirconium complex $C_5H_5Zr(CH_3COCHCOCH_3)_3$.[33]

(32) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc., A*, 1606 (1966); M. L. H. Green and W. E. Lindsell, *ibid.*, 686 (1967).

Table VI. Examples of the Conversion of Polyhedra with One Orthogonally Double π-Donor Ligand to Equivalent Polyhedra with Only σ-Donor Ligands

Coord no.	d orbitals used for forward bonding[a] xy	yz	zx	$x^2 - y^2$	z^2	Polyhedron with one orthogonally double π-donor ligand	Equivalent polyhedron with only σ-donor ligands
4	0	0	0	0	0	Linear	Tetrahedron
5	1	0	0	0	0	Planar triangle	Twisted wedge
6	1	1	0	0	0	Tetrahedron	Trigonal prism or trigonal antiprism
7	0	1	1	1	0	Apically substituted square pyramid	7,11,6-Polyhedron

[a] The sp^3 orbitals are also included in the forward bonding hybrid.

In the cases of complexes with two orthogonally double π-donor ligands, there is only one possible polyhedron for coordination numbers six (*e.g.*, $(C_5H_5)_2Fe$) and seven (*e.g.*, $(C_5H_5)_2ReH$). The only eight-coordinate polyhedron with nonzero permutivity is the tetrahedron; complexes of the type $(C_5H_5)_2MX_2$ therefore must be based on this polyhedron and have canted cyclopentadienyl rings in accord with actual observations.[34] All of the nine-coordinate polyhedra except one have unit permutivity; the decision between the several alternatives is not clear. The proton nmr spectrum[35] of the nine-coordinate derivative $(C_5H_5)_2TaH_3$ shows two of the protons bonded to the tantalum to be of one type and the remaining proton bonded to the tantalum to be of another type. This excludes the most symmetrical D_{3h} doubly apically substituted trigonal bipyramid with parallel rings which would require equivalence of the three hydrogen atoms in $(C_5H_5)_2TaH_3$. The C_5H_5 rings are thus canted in the nine-coordinate $(C_5H_5)_2TaH_3$ as in the eight-coordinate complexes $(C_5H_5)_2MX_2$.

Polyhedra of the type $(C_5H_5)_3M$ with three orthogonally double π-donor ligands have zero permutivity; hence tris-π-cyclopentadienyl derivatives are not possible for metals using only s, p, and d orbitals.

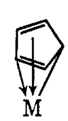
Polyhedra and Hybridization Schemes for Complexes of Single π-Donor Ligands

The bond between a transition metal and a single π-donor ligand (*e.g.*, π-allyl) has symmetry properties like the carbon–carbon double bond in ethylene and other olefins. It thus does not possess the cylindrical symmetry of the bond between a transition metal and an orthogonally double π-donor ligand. This lack of cylindrical symmetry increases the number of possible coordination polyhedra for complexes with one single π-donor ligand since there are many pairs of coordination polyhedra differing in only whether the forward π bond is perpendicular ($\perp$) or parallel ($\|$) to a reflection plane. Thus whereas 26 polyhedra are considered for four-coordinate to nine-coordinate complexes either with no π donor ligands of any type or with one orthogonally double π donor ligand, the number of polyhedra considered for four-coordinate to nine-coordinate complexes with one single π donor ligand rises to 50 (Table V). Complexes with two or more single π-donor ligands (*e.g.*, $(C_3H_5)_2Fe(CO)_2$, $(C_3H_5)_3Rh$, and $(C_3H_5)_4Zr$) are not considered in this paper, since the number of possible coordination polyhedra becomes inconveniently large owing to complexities arising from different relative orientations of the metal–ligand π bonds to the different single π-donor ligands. In such relatively complex cases it may be more convenient to reduce the system of σ-donor and π-donor ligands to an equivalent system containing just σ-donor ligands which can then be treated by the techniques discussed in the first paper of this series.[1]

(33) M. Elder, J. G. Evans, and W. A. G. Graham, *J. Am. Chem. Soc.*, 91, 1245 (1969).
(34) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).
(35) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *ibid.*, 4854 (1961).

Conversion of Systems with π-Donor Ligands to Equivalent Polyhedra with Only σ-Donor Ligands

A polyhedron with single π-donor and/or orthogonally double π-donor ligands may be converted to a polyhedron with only σ-donor ligands but similar sp^3d^n hybridization by substituting two σ-donor ligands at the ends of each single π-donor ligand and a triangle of three σ-donor ligands in the plane of each orthogonally double π-donor ligand. In the cases of π-cyclopentadienyl derivatives, this process corresponds to a representation of the metal–π-cyclopentadienyl bond in the localized form II. Similarly in the cases of π-allyl derivatives, this process corresponds to a representation of the metal–π-allyl bond in the localized form III. Table VI gives some of the more important examples of the conversion of systems with orthogonally double π-donor ligands to equivalent polyhedra with only σ-donor ligands. This process appears potentially useful for the conversion of systems with more complex combinations of π-donor ligands than those treated specifically in this paper to equivalent σ-bonding polyhedra which can then be treated by the techniques of the first paper.[1]



II

III

Acknowledgment. I am indebted to the Petroleum Research Fund for partial support of this work under Grant 2838-A1,3.