Total = 86e

Twelve of these electrons per rhodium (a total of 72) will be used for nonframework bonding leaving 14 for framework bonding. Thus there are seven bonding pairs in the framework corresponding to $2n + 2$ electrons and, as above a *closo* strcuture is predicted. It is worth noting that the 18-electron rule fails for $Rh_6(CO)_{16}$, while Wade's rules are entirely successful.

There are exceptions to Wade's rules, even among modest-sized clusters[42]. In some cases large transition metals cause geometrical distortion. In others, a kinetically favored structure may not be able to rearrange to a more thermodynamically favored one. In still other instances the assumption that transition metal atoms will use twelve electrons for external ligands is not valid. As with most rules, one should not expect predictions to be foolproof.

The bonding capabilities of transition metal clusters (no nonmetals in the framework), based on moleculear orbital calculations, has been nicely summarized by Lauher[43] (Table 18.7). Within this table we see three strcutures (tetrahedron, butterfly, and square plane) for tetranuclear metal clusters. The tetrahedron is a 60-electron cluster, while the butterfly and square plane clusters have 62 and 64 electrons, respectively. When we go from a tetrahedron to a butterfly, one of the edges of the tetrahedron is lengthened corresponding to bond breaking.

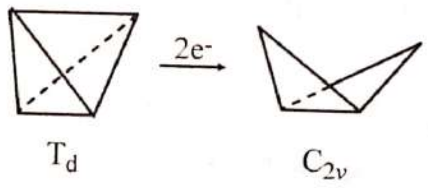


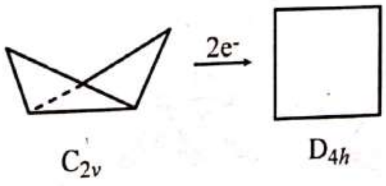
Table 18.7 Relationship between geometry, molecular orbitals, and cluster valence electrons[a]

Geometry	No. of metal atoms	Bonding molecular orbitals	Cluster electrons	Examples
Monomer	1	9	18	$Ni(CO)_4$
Dimer	2	17	34	$Fe_2(CO)_9$
Trimer	3	24	48	$Os_3(CO)_{12}$
Tetrahedron	4	30	60	$Rh_4(CO)_{12}$
Butterfly	4	31	62	$Re_4(CO)_{16}^{2-}$
Square plane	4	32	64	$Pt_4(O_2CMe)_8$
Trigonal bipyramid	5	36	72	$Os_5(CO)_{16}$
Square pyramid	5	37	74	$Fe_5(CO)_{15}C$
Bicapped tetrahedron	6	42	84	$Os_6(CO)_{18}$
Octahedron	6	43	86	$Ru_6(CO)_{17}C$
Capped square pyramid	6	43	86	$Os_6(CO)_{18}H_2$
Trigonal prism	6	45	90	$Rh_6(CO)_{15}C^{3-}$
Capped octahedron	7	49	98	$Rh_7(CO)_{16}^{3-}$

[a] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305–5315. All framework atoms are transition metals.

To do this, two additional electrons must be added to the tetrahedron to keep all electrons paired. In fact this is a general principle: Adding electrons to a *closo* complex opens the structure, converting it to one of lower symmetry. The butterfly structure results when an edge is removed from the tetrahedron.

If we add two electrons to the butterfly structure, another edge is lengthened (another bond broken) and we end up with a square plane.



Metal Clusters[53]

Compounds containing metal–metal bonds are as old as chemistry itself (calomel was known to the chemists of India as early as the twelth century). The dimeric nature of the mercurous ion was not confirmed until the turn of this century and in the next half-century discussions focused on the possibility that zinc and cadmium might possess similar species. It was only some 30–35 years ago that the study of other metal–metal bonds begain in earnest; yet this branch of inorganic chemistry has grown at a phenomenal rate.

Metal cluster compounds can be conveniently grouped into two classes: (I) polynuclear carbonyls, nitrosyls, and related compounds; and (II) halide and oxide complexes. The former group is included in Chapter 18. The second class will be discussed in this section.[54]

Why do we separate clusters into two classes rather than deal with them as a single group of compounds? It is primarily because they have unrelated chemistry. Metal atoms in class I have low formal oxidation states, −1 to +1, while those in class II are found in higher formal oxidation states, +2 to +3. The transition metals on the right side of the periodic table (late transition metals) typically form class I clusters, while those on the left-hand side (early seond and third row transition metals) tend to form class II clusters.

Clusters of metal atoms are more likely among metals that have large energies of atomization (hence very high melting and boiling points). Thus the most refractory metals (Zr, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Re, Os, Ir, and Pt) have the greatest tendency to form metal clusters.

A second factor which must be considered is the nature of the *d* orbitals. The size of the *d* orbitals is inversely related to the effective nuclear charge. Since effective orverlap of *d* orbitals appears necessary to stabilize metal clusters, excessive contraction of them will destabilize the cluster. Hence large charges resulting from very high oxidation states are unfavorable. For the first transition series, the *d* orbitals are relatively small, and even in moderately low oxidation states (+2 and +3) they apparaently do not extend sufficiently for good overlap.

Dinuclear Compounds

The best-studied binuclear species are $[Re_2X_8]^{2-}$ ions. they may be prepared by reduction (with H_2, H_3PO_2, or PhCOCl) of perrhenate in the presence of X^-:

$$2ReO_4^- \xrightarrow[H_3PO_2]{HX} [Re_2X_8]^{2-} \qquad X = Cl, Br, I, NCS \tag{13.50}$$

The most interesting aspect of these compounds is their strcuture (Fig. 13.10), which possesses two unusual features. The first is the extremely short Re—Re distance of 224 pm compared with an average Re—Re distance of 275 pm in rehenium metal and 248 pm in Re_3Cl_9. The second unexpected feature is the eclipsed configuration of the chlorine atoms. One might have supposed that since the short Re—Re bond requires that the chlorine atoms lie at distances (~330 pm) which are less than the sum of their van der Waals radii (~340–360 ppm), the staggered configuration would be preferred (the chlorine atoms would then form a square antipism rather than a cube). Cotton explained both phenomena by invoking a quadruple bond.[55]

Cotton's rationale was as follows. The z (i.e. z) axis of the ion is taken as the line joining the two rehenium atoms. Each rhenium atom is bonded to four chlorine atoms that are almost in a square planar array (the Re is 50 pm out of the plane of the four Cl atoms). We may take the Re—Cl bonds to involve approximate dsp^2 hybrids on each metal utilizing the $d_{x^2-y^2}$ orbital. The metal d_{z^2} and p_z orbitals lie along the bond axis and may be hybridized to form one orbital directed toward the other rhenium atom and a second orbital directed in the opposite direction. The former can overlap with the similar orbital on the second rhenium atom to form a σ bond (Fig. 13.11a), while the second hybrid orbital forms an approximately nonbonding orbital.

The d_{xz} and d_{yz} orbitals of each rhenium are directed obliquely toward their counterparts on the other rhenium and can overlap to form two π bonds (Fig. 13.11b), one in the xz plane and one in the yz plane. A fourth bond can now form by "sideways" overlap of the remaining two d orbitals, a d_{xy} on each rhenium, the result being a δ bond. Overlap of the d_{xy} orbitals can only occur if the chlorine atoms are eclipsed (Fig. 13.11c). If the chlorine atoms are staggered, the two d_{xy} orbitals will likewise be staggered with resulting zero overlap (Fig. 13.11d).

The Re—Cl bonds in the complex may be regarded as dative bonds between the Cl^- ligands and Re^{3+} (d^4) ions. The eight d electrons from the two metals will occupy the a bonding, two π bonding, and one δ bonding orbitals to form the quadruple bond; hence the complex is diamagnetic. The model successfully accounts for the strength of the bond, the short Re—Re distance, and the eclipsed configuration.

There have been many compounds discovered which resemble the $[Re_2X_8J]^{2-}$ ions in possessing extremely short M—M distances, eclipsed conformations and, presumably, quadruple metal–metal bonds. The isoelectronic molybdenum(II) species, $[Mo_2Cl_8]^{2-}$, is known and both Re(III) and Mo(II) form a large series of carboxylate complexes of formulas $Re_2(RCO_2)_2X_4$, $Re_2(RCO_2)_4X_2$, and $Mo_2(RCO_2)_4$:

$$ReCl_8^{2-} + 2MeCOOH \longrightarrow Re_2(MeCO_2)_2Cl_4 + 4Cl^- + 2H^+ \tag{13.51}$$

2

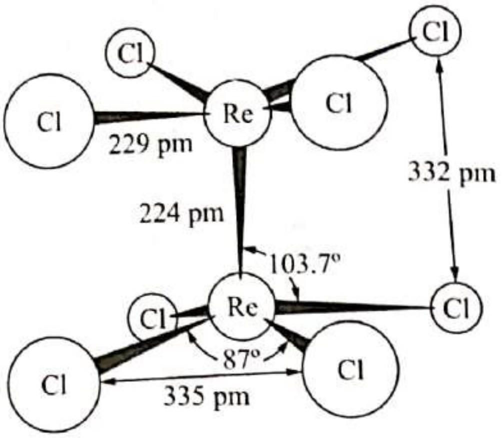
$$RE_2Cl_8^{2-} + 4MeCOOH \longrightarrow Re_2(MeCO_2)_4Cl_2 + 6Cl^- + 4H^+ \tag{13.52}$$

$$Re_2(MeCO_2)_4Cl_2 + 4PhCOOH \longrightarrow Re_2(PhCO_2)_4Cl_2 + 4MeCOOH \tag{13.53}$$

$$2Mo(CO)_6 + 4MeCOOH \longrightarrow Mo_2(MeCO_2)_4 + 12CO + 2H_2 \tag{13.54}$$

Structurally these complexes (Fig. 13.12) are clearly related to $[Re_2Cl_8]^{2-}$, the only difference being (for the rhenium complexes) the addition of ligands to overlap with the metal dp hybrid orbitals which were nonbonding in $[Re_2Cl_8]^{2-}$.

Although Cotton's molecular orbital scheme was largely qualitative, based on an approach involving a combination of atomic orbitals, a variety of theoretical studies have confirmed the essential correctness of



Re^{3+} (d^4)

Re-Cl bond dative bond

275) 3.10 (0.15
275
2350

Fig. 13.10 The structure of the octachlorodirhenate(III) ion, $Re_2Cl_8^{2-}$ [From Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330. Reproduced with permission.]

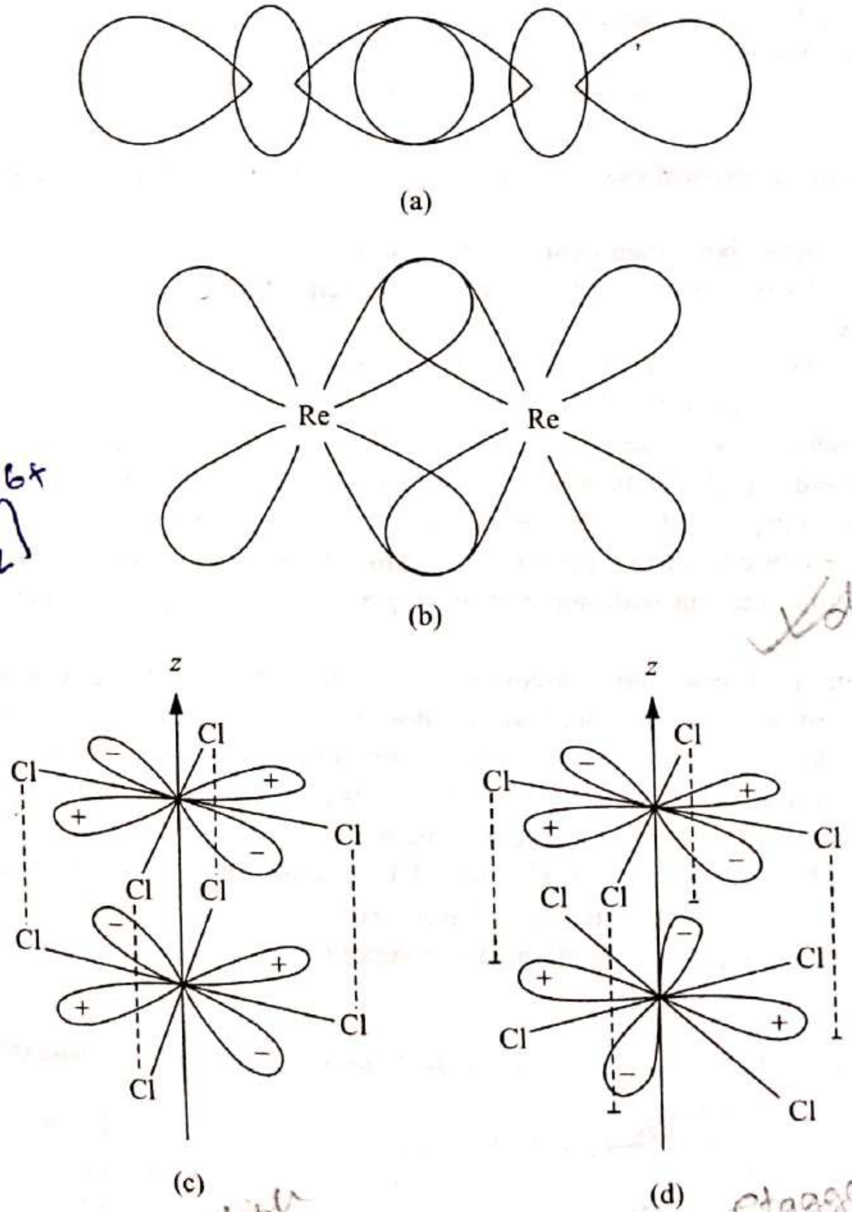


Fig. 13.11 Multiple bonding between rhenium atoms; (a) Formation of a σ bond from overlap of d_z^2 orbital of each rhenium atom. (b) Formation of a π bond from overlap of the d_{xz} orbital of each rhenium atom. A second π bond forms in the *yz* plane. (c) Positive overlap from d_{xy} orbitals to form a δ bond in the eclipsed conformation. (d) Zero overlap occuring in the staggered conformation. [In part from Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240. Reproduced with permission.]

$[Re_2]^{6+}$

diamagnetic complex Re_2Cl_8

Re-Re - quadruple bond

δ d_{xy}

π d_{xz}, d_{yz}

σ d_{z^2}

staggered form [illegible] zero overlap

eclipse

staggered