

Strong Homonuclear Metal-Metal Bonds

F. A. COTTON

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received December 31, 1968

The deliberate study of compounds with metal-to-metal (M-M) bonds began only about a decade ago. Prior to that there were a few compounds known which contain M-M bonds, but they had been made by accident, were considered (if at all) as curiosities, and aroused little (if any) active interest. Today there is a great deal of activity in the field, and it has become evident that M-M bonding is widespread, important, and interesting. This Account presents a brief review with emphasis on the aspects to which recent work in the author's own laboratory has contributed; no effort is made to give a comprehensive overview.

General Remarks

In order to place in context the specific, detailed observations which form the main subject of this article, a few prefatory, general remarks are appropriate. More complete accounts of certain points may be found in several review articles.¹⁻⁶ In this Account we shall be concerned entirely with transition metals, and the word *metal* will be used throughout with that restriction understood.

Occurrence of M-M Bonds. M-M bonds are found only where metal atoms are in low formal oxidation states. There is, of course, the obvious but by no means trivial case of the elements themselves. Aside from these (and alloys), there are two broad classes of substances containing low-valent metal atoms: (1) the halides and chalcogenides of the metals in their lower oxidation states; (2) polynuclear metal carbonyls and related compounds.

Several factors favor M-M bond formation by metal atoms in low oxidation states. First, we may consider a thermochemical cycle for the reaction of M(s) with X₂ (one of the halogens) to form a compound M_mX_x. The step M(s) → M(g) is very endothermic (100-175 kcal/g-atom for Zr, Nb, Mo, Tc, Ru, and Rh, and 150-200 kcal/g-atom for Hf, Ta, W, Re, Os, Ir, and Pt). In a compound where *x/m* is small, not enough energy can be released by M-X bond formation to match the energy expended in vaporizing M(s) and dissociating X₂. Hence, stability can only be achieved by formation of other bonds, namely M-M bonds. This viewpoint has been stressed by Schäfer and Schnering.¹ Second, in compounds involving higher formal oxidation states there are many polar M-X bonds. The effective nuclear

charge for valence shell orbitals of the metal is therefore high, and the orbitals are much contracted. Such contracted orbitals cannot overlap effectively to form M-M bonds. The orbital size factor has been emphasized by Sheldon.⁷ Third, if the metal atom is closely surrounded by many nonmetal atoms, as it will be in a compound in which it has a high oxidation number, steric factors will militate against the close approach of metal atoms to one another.

Low formal oxidation state constitutes a *necessary* but not *sufficient* condition for M-M bond formation. For metal atoms of the first transition series, the oxidation numbers +3 and even +2 do not, except in rare cases,⁸ allow M-M bond formation. As a general rule only when the metals are formally zerovalent or nearly so, as in polynuclear carbonyls, do these light metals form M-M bonds. It now seems clear, empirically, that the tendency to M-M bond formation is great only in the second and third transition series, except for carbonyl compounds, where the very lowest oxidation numbers (≤0) are found. This is presumably because in oxidation states such as +3 and +2 the valence shell orbitals, particularly the d orbitals, project far enough beyond the core only for these heavy atoms. In the lighter metal atoms, even in oxidation state +2, the d orbitals are too contracted to allow sufficient M-M overlap.

Present information (which could be misleading due to its incompleteness) suggests that the M-M bonding tendency, in compounds other than the carbonyl types, is greatest among those second and third transition series metals lying to the left, *viz.*, Nb and Ta, Mo and W, Tc and Re, and that it diminishes among the heavy transition metals further to the right. While it is not obvious from thermochemical data (which are fragmentary) that this trend should exist, other considerations suggest it. First, there is the orbital size factor. The 4d and 5d orbitals contract steadily with increasing atomic number. Second, the accumulation of electrons in the d orbitals eventually reaches a point where these orbitals are so fully occupied in the lower oxidation states that valence states of high multiplicity are unattainable. The carbonyl type compounds are exempt from both these limitations. The effect of orbital contraction is largely offset by the extremely low formal oxidation state, while the great π acidity of CO and related ligands effectively removes electrons from the M-M antibonding orbitals.

(7) J. C. Sheldon, *Australian J. Chem.*, **17**, 1191 (1964).

(8) One such case is the [(CH₃NC)₅Co-Co(CNCH₃)₅]¹⁴⁺ ion, where Co-Co = 2.74 Å (F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964)).

(1) H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

(2) J. Lewis and R. S. Nyholm, *Sci. Progr.*, **52**, 557 (1964).

(3) J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

(4) F. A. Cotton, *Quart. Rev. (London)*, **20**, 389 (1966).

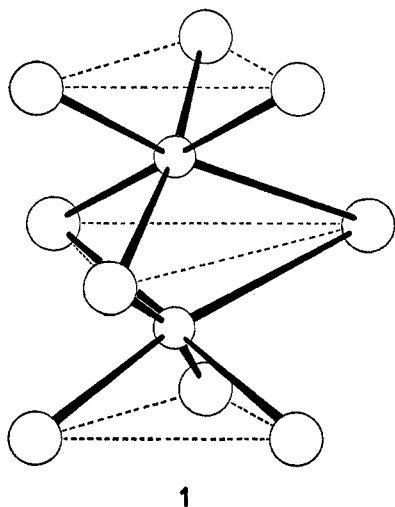
(5) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

(6) B. R. Penfold in "Perspectives in Structural Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1968, p 71.

Influence of Formal Oxidation Number. For any particular metal it is possible empirically to locate a transitional region within the entire range of its known formal oxidation states in which M-M bonding gains ascendancy. To illustrate this the structures of some rhenium and molybdenum compounds in various oxidation states may be surveyed.

Rhenium compounds containing the metal in formal oxidation states from +7 to -1 are known.^{9a} Many of those in the lowest states (+2 to -1) involve ligands which form multiple, nonpolar bonds to the metal, thereby stabilizing these low oxidation states without the necessity of M-M bond formation. In the highest oxidation states (+7, +6, +5), following the generalizations above, no M-M bonding occurs. It is interesting that although rhenium(V) chloride is dimeric, consisting of two ReCl_6 octahedra sharing an edge, the structure¹⁰ shows the distortional features⁵ of a repulsive $\text{M} \cdots \text{M}$ interaction and the $\text{Re} \cdots \text{Re}$ distance is long, 3.74 Å; magnetic data are consistent with the absence of an M-M bond.

The threshold for M-M bond formation occurs for rhenium at an oxidation number of about +4. ReCl_4 has a polymeric structure¹¹ in which ReCl_6 octahedra share alternatively faces and vertices and the geometry across the shared faces has the compressed features characteristic⁵ of M-M bonding ($\text{Re-Re} = 2.73$ Å). Similarly in the Re_2Cl_9^- ion, which consists of two ReCl_6 octahedra sharing a face (the *bioctahedron* structure (1) with D_{3h} symmetry) the distortions due to



compression⁵ and the short Re-Re distance of ~ 2.71 Å demonstrate the existence of an M-M bond.¹²

Another Re(IV) compound with M-M bonding is

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966: (a) p 962; (b) 932.

(10) K. Mucker, G. S. Smith, and Q. Johnson, *Acta Cryst.*, **B24**, 874 (1968).

(11) M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Am. Chem. Soc.*, **89**, 2759 (1967).

(12) P. F. Stokely, Ph.D. Thesis, Massachusetts Institute of Technology, 1969.

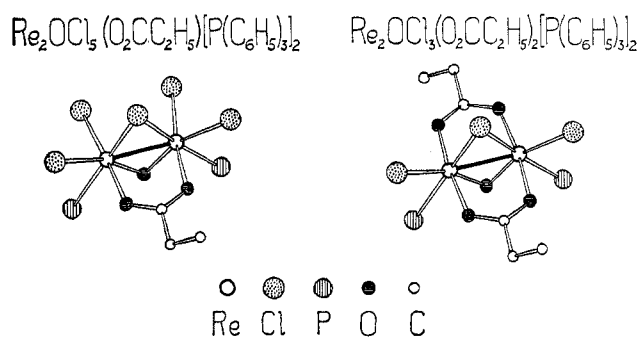


Figure 1. The nearly homologous structures of two compounds of rhenium with the formal oxidation numbers 4+ (left) and 3.5+ (right). The Re-Re distances differ by only ~ 0.01 Å.

$\text{Re}_2\text{OCl}_5(\text{O}_2\text{CC}_2\text{H}_5)_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ whose structure¹³ is shown at the left of Figure 1. Here there are two octahedra sharing an edge, and again there are compressional distortions⁵ and a short Re-Re distance (2.52 Å) which attest to the existence of M-M bonding. It is important to note, however, that, judging by the Re-Re distances, the M-M bonding here is much stronger than in ReCl_4 or Re_2Cl_9^- . Moreover, there are numerous Re(IV) compounds, *e.g.*, the well-known ReCl_6^{2-} ion, which lack M-M bonding entirely. Thus, when we say that for rhenium an oxidation state of IV constitutes the threshold for M-M bonding, we mean only that this is where it begins to be *possible* and *significant*, but not *mandatory*. Nor is the strength of the bonding, as gauged by Re-Re distances, a direct and single-valued function of oxidation number. It is obviously also a function of other features of the molecular structure such as the identities and arrangement of bridging ligands.

Presumably constraints of the latter kind are responsible for the fact that in $\text{Re}_2\text{OCl}_3(\text{O}_2\text{CC}_2\text{H}_5)_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$, which contains Re(3.5) in a structure¹⁴ very similar to that of the Re(IV) compound just described (see Figure 1), the Re-Re distance (2.51 Å) is not significantly shorter, despite the decrease in oxidation number.

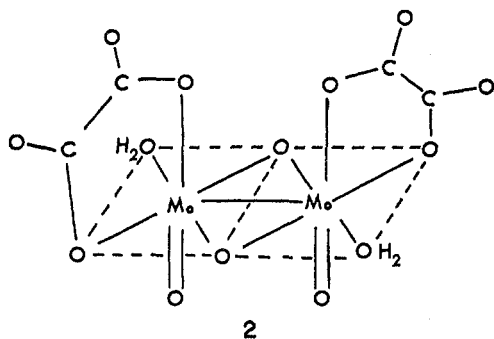
It is only with oxidation number III that rhenium demonstrates the ability to form very strong M-M bonds, as in compounds such as Re_3Cl_9 and $\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ to be discussed later. Even in this low oxidation state it is not mandatory that M-M bonds be formed, and mononuclear Re(III) complexes are known.

Turning now to molybdenum, which forms compounds ranging in oxidation number^{9b} from +6 to -2, we find behavior similar to that of rhenium, but more complex. With molybdenum the influence of the nature of the bridging ligands is shown clearly by the fact that with oxygen and chlorine the threshold of M-M bonding is reached at different oxidation states. Structural evidence for Mo-Mo bonding in the $\text{Mo} \left\langle \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \right\rangle \text{Mo}$ system is found¹⁵ for Mo(V) in the anion shown as 2 whereas

(13) F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, **7**, 1784 (1968).

(14) F. A. Cotton, R. Eiss, and B. R. Foxman, *ibid.*, **8**, 950 (1969).

(15) F. A. Cotton and S. M. Morehouse, *ibid.*, **4**, 1377 (1965).



both structural¹⁶ and magnetic¹⁷ evidence show that there is no Mo-Mo bond in $\text{Mo}_2\text{Cl}_{10}$. MoO_2 has a rutile-like structure but is distorted by the presence of Mo-Mo bonds (2.51 Å).¹⁸ Another Mo(IV) compound with oxygen, $\text{Zn}_2\text{Mo}_3\text{O}_8$, also contains distinct Mo-Mo bonds.¹⁹ In MoCl_4 , on the other hand, there is no Mo-Mo bonding,²⁰ the shortest Mo-Mo distance being 3.50 Å. Even in one form (β) of MoCl_3 there is no Mo-Mo bonding,²⁰ but in another (α) there is evidence²⁰ for it (Mo-Mo = 2.76 Å), though it does not appear to be very strong. It is with $\text{Mo}^{2.5+}$ and, especially, Mo^{2+} that a powerful tendency to M-M bond formation in chloro complexes is seen, as will be described later. Thus, with oxygen bridges Mo-Mo bonding comes into play in much higher oxidation states than in halides. This is probably in the main a steric effect.

Types of Compounds with M-M Bonds. When M-M bond formation is sufficiently favored by the factors discussed above that it may become strong and/or extensive, compounds of several structural types can be formed.

Suppose we have a metal atom with several suitable orbitals and several electrons, say n of each, available for M-M bond formation. The general possibilities are the following. (1) A group of metal atoms may associate so that each one forms a single bond to each of n others. If the number of available orbitals is greater than the number of electrons, an even larger number of bonds of fractional order may be formed. *Metal atom clusters* of polygonal or polyhedral form are thus produced. (2) Pairs of metal atoms may form multiple bonds of order n . (3) The intermediate situation may arise, *i.e.*, formation of small clusters with multiple M-M bonds. For example, instead of n single bonds, there might be $n/2$ double bonds.

Metal Atom Clusters. Of the above possibilities, metal atom cluster compounds with M-M bonds of low order were the first to be recognized.^{1,4,6} Examples of polyhedral clusters are the $\text{Mo}_6\text{Cl}_8^{4+}$ and the $\text{M}_6\text{X}_{12}^{2+}$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$) species depicted in Figures

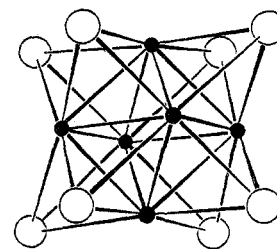


Figure 2. The structure of the $\text{Mo}_6\text{Cl}_8^{4+}$ ion (filled circles are Mo atoms; open circles are Cl atoms).

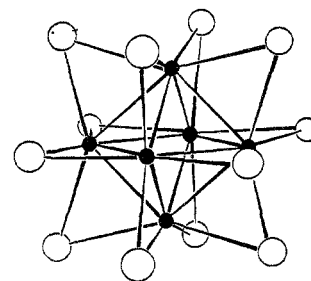


Figure 3. The M_6X_{12} structure (filled circles are metal atoms; open circles halogen (X) atoms).

2 and 3. In $\text{Mo}_6\text{Cl}_8^{4+}$ the Mo-Mo bonds are single while the Nb-Nb and Ta-Ta bonds are of order $2/3$. In the recently characterized $\text{Nb}_6\text{I}_8^{3+}$ (isostructural²¹ with $\text{Mo}_6\text{Cl}_8^{4+}$) the Nb-Nb bond order is only 0.58.

Polygonal (*i.e.*, triangular) clusters with approximately single bonds (seven electrons for three M-M bonds) are found in the niobium halides of the $\beta\text{-Nb}_3\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) type.²² These have the structure shown in Figure 4. Because of the extensive bridging by halogen atoms in this structure, the Nb-Nb distance is distinctly sensitive to the size of the bridging atoms. Thus, it increases in the order 2.81, 2.88, and 3.00 Å in the Cl, Br, and I compounds. The relative weakness of the Nb-Nb bonding doubtless makes it relatively easy to stretch the M-M bonds.

The type of triangular cluster (Figure 5) formed by the rhenium halides and many of their derivatives is an example of possibility 3 above. Each rhenium atom uses five orbitals in forming bonds to halogen and other ligand atoms. There remain then four valence shell orbitals populated by four electrons. In the triangular cluster each rhenium atom forms two double bonds,²³ one to each of its two neighbors. It is interesting to note that, in this kind of a trinuclear cluster where the bridging is less extensive and the M-M bonds are inherently stronger, the change from Cl to I in the basic Re_3X_3 unit does not cause any appreciable increase in the Re-Re distances.²⁴

(16) D. E. Sands and A. Zalkin, *Acta Cryst.*, **12**, 723 (1959).

(17) W. Klemm and H. Steinberg, *Z. Anorg. Allgem. Chem.*, **227**, 193 (1936).

(18) B. G. Brandt and A. C. Skapski, *Acta Chem. Scand.*, **21**, 661 (1967).

(19) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

(20) H. Schafer, H. G. v. Schnering, J. Tillack, F. Kuhnen, H. Wöhrle, and H. Bauman, *Z. Anorg. Allgem. Chem.*, **353**, 281 (1967).

(21) L. R. Bateman, J. F. Blount, and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1082 (1966).

(22) A. Simon and H. G. von Schnering, *J. Less-Common Metals*, **11**, 31 (1966).

(23) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964); J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965); S. F. A. Kettle, *Theoret. Chim. Acta*, **3**, 282 (1965).

(24) M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7**, 1563 (1968).

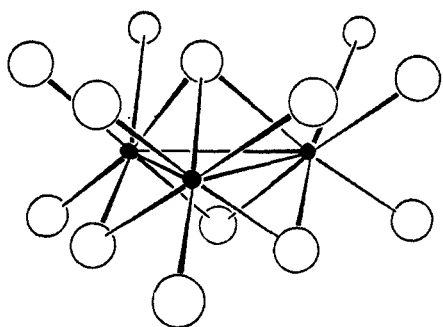


Figure 4. The structure of the Nb_3X_8 compounds (filled circles are Nb atoms; open circles are halogen atoms).

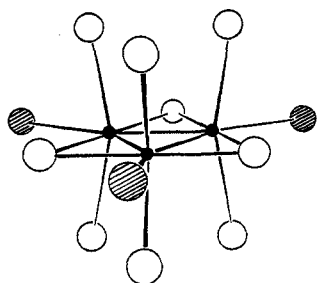


Figure 5. The $Re_3X_6L_3$ -type cluster (filled circles are Re atoms; open circles are X atoms; hatched circles are L groups).

Two-Center Multiple Bonds

We turn now to compounds of the second structural type mentioned above, namely those containing pairs of metal atoms united by multiple M-M bonds.

Quadruple Bonds. The strongest M-M bonds—and quite possibly the strongest of *all* known chemical bonds—are those which occur in several dinuclear complexes of rhenium, molybdenum, and technetium. In any event, these bonds have the highest order (or multiplicity) known: they are quadruple bonds, made up of one σ , two π , and one δ component, with a total of eight electrons binding two atoms together.

The existence of a quadruple bond was first recognized in the $Re_2Cl_8^{2-}$ ion, whose structure²⁵ is shown in Figure 6. The description of the Re-Re bond as quadruple²⁶ arose from the need to explain the two most striking features of this structure:²⁵ (1) the exceptional shortness of the Re-Re distance, *viz.*, 2.24 Å compared to 2.75 Å in the metal and 2.40–2.50 Å in the Re_3X_9 species; (2) the eclipsed rotational configuration. The first feature suggests an extremely strong and therefore multiple bond, while the second demands that at least one component of this multiple bond must have a rotational dependence which favors the eclipsed configuration strongly enough to overcome the tendency of repulsive forces to stabilize a staggered configuration.

It was shown²⁶ that after allowance for Re-Cl bonds and net charge, each Re atom remains with four d (or predominantly d) orbitals and four electrons. One of these orbitals has σ character, two of them form a de-

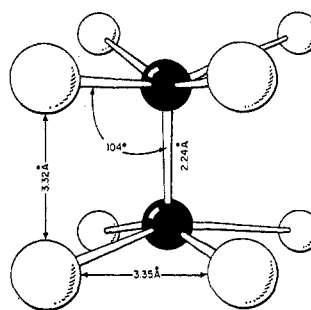


Figure 6. The structure of the $Re_2Cl_8^{2-}$ ion.

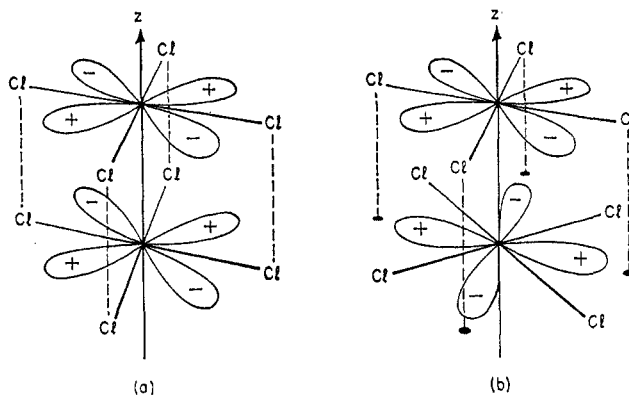


Figure 7. A sketch showing how δ overlap depends on rotational angle: (a) eclipsed configuration having maximum overlap; (b) staggered configuration having zero overlap.

generate pair with π character, and the fourth has δ character with respect to the common fourfold axis of the $ReCl_4$ groups. It is therefore possible for two such groups to interact forming one σ , two π , and one δ bonding orbitals (and, of course, antibonding orbitals corresponding to each). These four bonding orbitals are then occupied by the four pairs of electrons, and the quadruple bond is formed. The δ component restructures rotation in just such a way as to favor the eclipsed configuration: the δ overlap is maximal for this configuration and goes to zero for the staggered configuration, as shown in Figure 7.

In addition to the bonding (σ , π^2 , δ) and antibonding (σ^* , π^{*2} , δ^*) orbitals just mentioned, there are two approximately nonbonding orbitals of σ type, $\sigma_n(1)$, $\sigma_n(2)$, with maximum amplitude along the fourfold axis but projecting away from the two rhenium atoms. A simple energy level diagram for $Re_2Cl_8^{2-}$ based on semiquantitative MO theory²⁷ (omitting, for clarity, all MO's concerned predominantly with Re-Cl bonding) is given in Figure 8. The computations leading to this diagram provided a rough estimate of Re-Re bond strength, *viz.*, 300–400 kcal/mol.

While the fact that even one quadruple bond exists is of some interest, an isolated case could scarcely be regarded as having importance. Therefore, following the recognition of this one example, efforts were directed

(25) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(26) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(27) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 924 (1967). In the diagram which appears in this reference the g and u character of the π and π^* orbitals is incorrectly stated. The necessary correction has been made on the diagram as reproduced here.

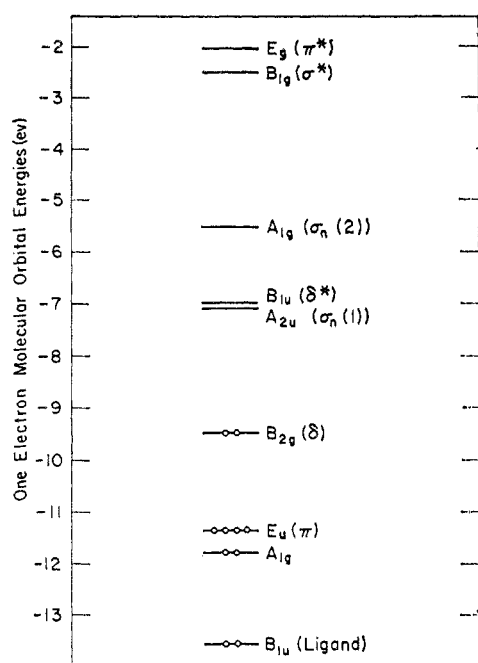
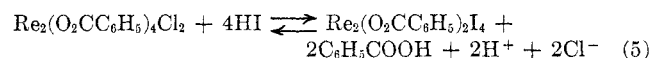
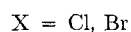
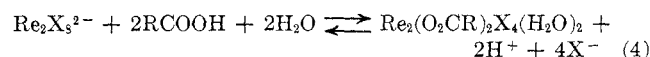
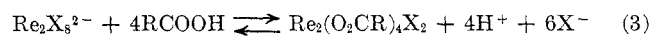
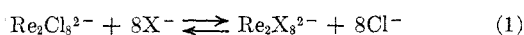


Figure 8. A partial MO diagram for $\text{Re}_2\text{Cl}_8^{2-}$, showing mainly the orbitals involved in Re-Re bonding.

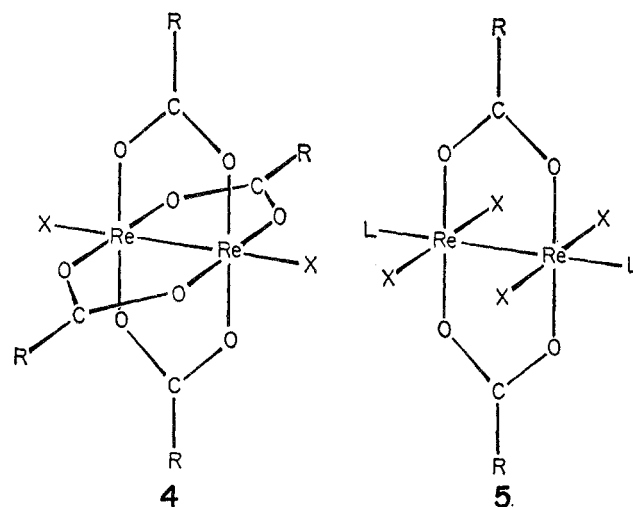
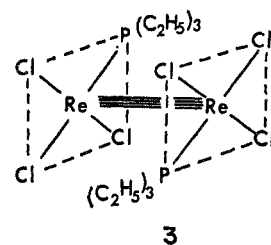
to determining the generality of this and related forms of exceedingly strong M-M bonding. These efforts have been rewarded by the discovery of a number of additional examples, and it now seems likely that the discovery of still others may be expected.

With rhenium it has been found that a variety²⁸⁻³² of metatheses and substitutions can be carried out (eq 1-5).



In all of these reactions, the quadruply bonded Re_2 group remains intact. The $\text{Re}_2\text{Br}_8^{2-}$ ion is isostructural³³ with $\text{Re}_2\text{Cl}_8^{2-}$, and the compound $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$ has structure³⁰ **3**. The $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ and $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4(\text{H}_2\text{O})_2$ compounds have structures^{34,35} **4**

and **5**, respectively. In all of these compounds the configuration is eclipsed and the Re-Re distance is in the range 2.22-2.24 Å.



The compound $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_2\text{I}_4$ is of particular interest. Despite the fact that it contains large iodide ions as ligands, it has the shortest Re-Re distance yet observed, 2.198 Å. Unlike the previously known $\text{Re}_2(\text{O}_2\text{CR})_2\text{X}_4(\text{H}_2\text{O})_2$ compounds, this one contains no water molecules or other ligands in the end positions and the iodide ions are swept back so that the coordination polyhedron about each rhenium atom is approximately a trigonal bipyramid, as shown in Figure 9. Thus, despite the inherent size of the iodine atoms, the structure as a whole allows for minimizing such repulsive forces as might tend to impede close approach of the metal atoms.³⁶

It is perhaps not too surprising that the quadruply bonded Re_2 unit persists through many ligand replacement reactions. A more subtle question concerns the ability of the strongly linked duo of metal atoms to persist through redox reactions. This is actually only one aspect of the more general question of how far one may deviate from the exact filling of the set of bonding orbitals in Figure 8 by eight electrons and still retain the tight diatomic unit. Upon the answer to this ques-

(28) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(29) F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

(30) F. A. Cotton and B. M. Foxman, *ibid.*, **7**, 2135 (1968).

(31) W. K. Bratton and F. A. Cotton, unpublished studies.

(32) A. S. Kotelnikova and V. G. Tronev, *Zh. Neorgan. Khim.*, **3**, 1008 (1958).

(33) P. A. Koz'min, V. G. Kuznetsov, and Z. V. Popova, *Zh. Strukt. Khim.*, **6**, 651 (1965).

(34) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

(35) P. A. Koz'min, M. D. Surzhkaya, and V. G. Kuznetsov, *Zh. Strukt. Khim.*, **8**, 1107 (1967).

(36) It is quite possible that the Re-Re bond becomes shorter not only due to a lessening of nonbonded repulsions but also because the presence of fewer ligands allows the formation of hybrid orbitals suitable for optimizing M-M overlap. A similar and probably related effect⁶ is seen in $\text{Re}_3\text{X}_9\text{L}_2$ compounds where bonds to the Re atom lacking an L are shorter than that between the other two.

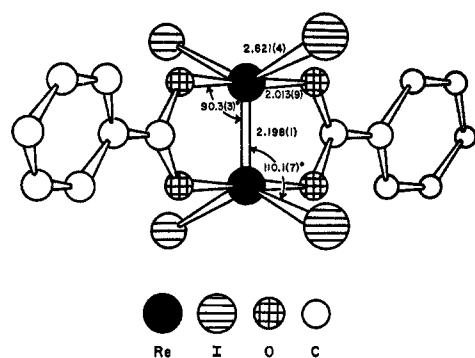


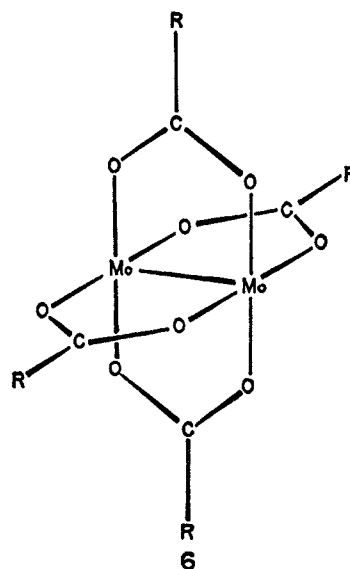
Figure 9. The structure of the $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_2\text{I}_4$ molecule.

tion depends the prospect for the formation of such units by other metals.

The energy level diagram for $\text{Re}_2\text{Cl}_8^{2-}$ would suggest that it might be possible to add one or two electrons to $\text{Re}_2\text{X}_8^{2-}$ species without disrupting them structurally, provided the added electrons could enter one or both of the σ nonbonding orbitals.³⁷ It has been found that the $\text{Re}_2\text{X}_8^{2-}$ species undergo polarographic reduction to $\text{Re}_2\text{X}_8^{3-}$ and $\text{Re}_2\text{X}_8^{4-}$ species.³⁸ With $\text{X} = \text{Cl}$ and NCS the waves appear to be reversible, which would suggest but not prove that the reductions occur without great structural reorganization. However, the reductions occur at rather negative potentials, and none of the reduced species has yet been isolated, so that their structures can be determined.

There is, however, a technetium species,³⁹ $\text{Tc}_2\text{Cl}_8^{3-}$, which has been characterized structurally.⁴⁰ It has an eclipsed structure entirely analogous to the $\text{Re}_2\text{Cl}_8^{2-}$ structure, with a strikingly short Tc-Tc distance of 2.13 Å.

Other examples of eight-electron quadruple bonds (compounds isoelectronic to those of rhenium) are provided by molybdenum(II) which has given promise of being the second most prolific former of strong M-M bonds. The first such Mo(II) compounds to be discovered⁴¹ were the diamagnetic dinuclear carboxylates, $\text{Mo}_2(\text{O}_2\text{CR})_4$. The acetate was found to have a structure⁴² of type **6** with the exceedingly short Mo-Mo bond length of 2.11 Å. Since Mo(II) is isoelectronic with



Re(III) it is no great extrapolation to formulate the bonding in $\text{Mo}_2(\text{O}_2\text{CR})_4$ in strict analogy to that in $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$, namely with a quadruple Mo-Mo bond.

With the analogy between $\text{Mo}_2(\text{O}_2\text{CR})_4$ and $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ in mind, it is natural to wonder if $\text{Mo}_2(\text{O}_2\text{CR})_4$ can undergo ligand exchange to produce compounds analogous to other Re(III) compounds with strong Re-Re bonds, *e.g.*, $\text{Mo}_2\text{Cl}_8^{4-}$ by analogy to $\text{Re}_2\text{Cl}_8^{2-}$. It has recently been demonstrated⁴³ that the $\text{Mo}_2\text{Cl}_8^{4-}$ ion can be obtained by treatment of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with cold HCl and that this ion is isostructural with $\text{Re}_2\text{Cl}_8^{2-}$ having an eclipsed configuration and a very short (2.14 Å) Mo-Mo bond.

It is interesting to note that both the $\text{Mo}_2\text{Cl}_8^{4-}$ ion and the cluster species $\text{Mo}_6\text{Cl}_8^{4+}$ contain Mo(II) and that their structures have a certain similarity. As Figure 10 shows, each one consists of a cubic set of eight Cl atoms. In $\text{Mo}_2\text{Cl}_8^{4-}$, this cube embraces a quadruply bonded pair of Mo(II) atoms, each of which is coordinated by a square set of four chlorine atoms; in $\text{Mo}_6\text{Cl}_8^{4+}$ the cube embraces six Mo(II) atoms, each again coordinated by a square set of Cl atoms, but now each Mo forms four single bonds, one to each of four nearest Mo neighbors. These two species perfectly illustrate the dichotomy of extremes described earlier, in which a metal atom with n orbitals and n electrons available for M-M bonding might form one bond of order n to another similar metal atom or, alternatively, belong to a cluster in which it would form single bonds to n other similar metal atoms. Mo(II) actually forms compounds of both kinds.

A number of compounds besides those containing $\text{Mo}_2\text{Cl}_8^{4-}$ can be obtained by treatment of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with mineral acids depending on reaction conditions, and the task of definitively characterizing these products is still in progress.

One other type of compound, *viz.*, $\text{M}^I_3\text{Mo}_2\text{Cl}_8$ ($\text{M}^I = \text{Rb}, \text{Cs}$), which has already been structurally

(37) The exact distribution of the $\sigma_n(1)$, $\sigma_n(2)$, and δ^* orbitals shown in Figure 8 is not to be taken literally, even for $\text{Re}_2\text{Cl}_8^{2-}$. The ordering of these orbitals among themselves is definitely subject to variation for different molecules. The main features of the diagram, *e.g.*, (1) that the δ orbital is the highest lying bonding orbital, (2) that the δ^* orbital is the lowest lying antibonding orbital, and (3) that the two σ_n orbitals and the δ^* orbital lie near the middle of the large energy gap between the strongly bonding orbitals (σ , π) and the strongly antibonding orbitals (σ^* , π^*), are rather certain to be correct and are all that need concern us in the present discussion.

(38) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 1257 (1967).

(39) J. D. Eakins, D. G. Humphreys, and E. D. Mellish, *J. Chem. Soc.*, 6012 (1963).

(40) F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(41) E. Bannister and G. Wilkinson, *Chem. Ind. (London)*, 319 (1960); T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

(42) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(43) J. V. Brenneke and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

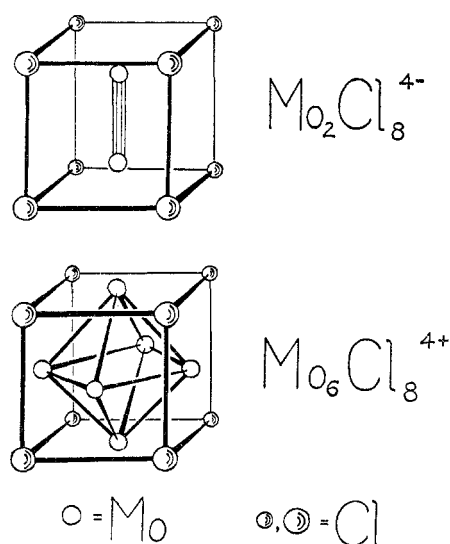


Figure 10. A structural comparison of the two M-M bonded Mo(II) chloro complexes.

characterized, is so novel as to deserve brief mention. Despite the "Mo₂Cl₈" stoichiometry, this compound is structurally unlike the Mo₂Cl₈⁴⁻ ion; evidently the loss of just one electron by the latter leads to structural instability. These compounds have crystal structures⁴⁴ quite analogous to those of several compounds containing M₂Cl₈³⁻ ions which have the bioctahedron structure **1**, the difference being that one-third of the Cl atoms are missing randomly from the crystallographic positions corresponding to bridging Cl atoms of the bioctahedron structure. Presumably the structure consists of Mo₂Cl₈³⁻ units each of which is an Mo₂Cl₈ unit defective in one bridging chlorine atom, with the vacant position disordered from molecule to molecule along each threefold axis of the crystal. The Mo-Mo distance in this compound of Mo^{2.5+} is 2.38 Å, indicative of moderately strong M-M bonding, but less strong than in Mo₂Cl₈⁴⁻.

Triple Bonds. It might be thought, from consideration of Figure 8, that oxidation of Re₂X₈²⁻ or one of the related molecules containing Re^{III}₂ could be carried out by removing one or perhaps both of the electrons from the δ orbital which is the least stable, filled orbital. Since the δ bond is the weakest of the four components of the quadruple bond, even the loss of both δ electrons could leave a very strong triple bond. However, loss of the δ interaction would make the M-M bond inherently axially symmetric, thereby permitting non-bonded repulsions or other secondary forces to determine the rotational configuration. Thus, in hypothetical species such as Re₂Cl₈ or Mo₂Cl₈²⁻ we would expect M-M bond lengths only a little longer than those in Re₂Cl₈²⁻ and Mo₂Cl₈⁴⁻ and staggered configurations (D_{3d} symmetry).

Thus far, however, the hypothetical species just mentioned remain exactly that—hypothetical. Oxida-

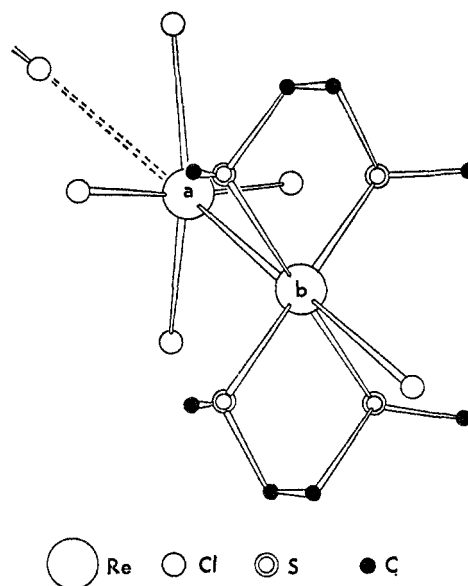


Figure 11. The structure of ReCl₄Re(DTH)₂Cl. The molecules form infinite linear chains ···Re_a-Re_b-Cl···Re_a-Re_b-Cl···.

tion⁴⁵ of Re₂Cl₈²⁻ and Re₂Br₈²⁻, carried out with Cl₂ and Br₂, respectively, proceeds with gross structural reorganization, giving as products the Re₂X₉⁻ ions. Re₂Cl₉⁻ has been shown¹² to have a bioctahedron structure with a relatively long Re-Re bond (~2.71 Å). Rhenium(IV) chloride itself is also built up of Re₂Cl₉ units strung together by sharing of terminal Cl atoms.¹¹ The reason our simple expectations as to the structural effects of removing two electrons from Re₂Cl₈²⁻ have not been realized is probably that the change from oxidation number III to IV markedly lessens the capacity of rhenium to form M-M bonds. A rearrangement from the Re₂X₈²⁻ type structure, in which the strong M-M bond is essential, to the bioctahedron structure, in which a lesser degree of M-M bonding is tolerable, therefore occurs. These changes with rhenium may be compared with the Mo₂Cl₈⁴⁻ to Mo₂Cl₈³⁻ structural change.

There is, however, one compound in which the structural consequences of losing the δ interaction but retaining an unbridged triple bond are clearly displayed. This is the compound ReCl₄Re(DTH)₂Cl (DTH = CH₃-SCH₂CH₂SCH₃), whose structure⁴⁶ is shown in Figure 11. This molecule may best be considered to contain rhenium atoms in the two formal oxidation states III (Re_a) and II (Re_b), with the result (explained in more detail elsewhere^{5,46}) that the δ interaction in the eclipsed configuration of the molecule is not strong enough to stabilize that configuration. The molecule therefore goes over to the staggered configuration, as Figure 11 shows; as shown in Figure 7, the δ component of M-M bonding must then be *entirely* absent. The loss of this contribution to the Re-Re bond should lead to an increase in the distance and this is observed, the distance here being 2.293 ± 0.002 Å as compared to distances

(45) F. Bonati and F. A. Cotton, *ibid.*, **6**, 1353 (1967).

(44) M. J. Bennett, J. V. Brenic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).

(46) M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc. (London)*, **A303**, 175 (1968).

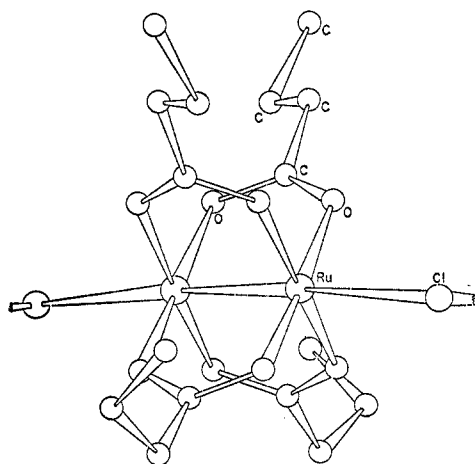


Figure 12. The structure of $\text{Ru}_2(\text{O}_2\text{CC}_3\text{H}_7)_4\text{Cl}$.

in the 2.198–2.247 Å range for Re–Re quadruple bonds. The relatively small increase is not unexpected because (a) the bonding component lost is a relatively weak one, and (b) bond length is, in general, relatively insensitive to bond order in the region of high bond orders.

In conclusion, two compounds formed by metals further to the right of the transition group may be discussed. One of these is a compound of ruthenium, $\text{Ru}_2(\text{O}_2\text{CC}_3\text{H}_7)_4\text{Cl}$,⁴⁷ which has the structure⁴⁸ shown in Figure 12. It consists of $\text{Ru}_2(\text{O}_2\text{CC}_3\text{H}_7)_4^+$ units, isostructural with $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds (6), connected into infinite chains by long, weak bonds to bridging Cl^- ions. The Ru–Ru distance is very short, *viz.*, 2.281 Å, showing that a strong M–M bond exists. The $\text{Ru}_2(\text{O}_2\text{CR})_4^+$ unit has three more electrons than $\text{Mo}_2(\text{O}_2\text{CR})_4$ and it has three unpaired electrons.⁴⁷ All of the above facts may be accommodated by the energy level diagram⁴⁸ shown in Figure 13. The three unpaired electrons occupy the two nonbonding σ orbitals and the δ^* orbital. The four M–M bonding orbitals are fully occupied.

There are several reasons why the Ru–Ru distance, though short enough to indicate that there is strong M–M bonding, is significantly longer than that in the quadruply bonded $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The combination of a higher nuclear charge and a higher oxidation number for the Ru atoms must cause contraction of their d

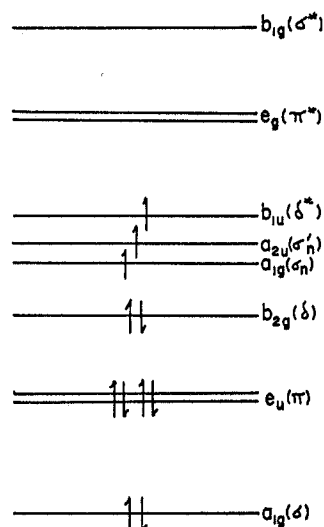


Figure 13. A qualitative energy level diagram for the M–M bonding in $\text{Cl}\cdots\text{Ru}_2(\text{O}_2\text{CR})_4\cdots\text{Cl}$.

orbitals, thus reducing their inherent capacity to form M–M bonds relative to that of the Mo atoms in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Second, the presence of an electron in the δ^* orbital, which is definitely antibonding, and of electrons in the normally nonbonding σ_n orbitals, one or both of which may, in fact, have some M–M antibonding character, should weaken the Ru–Ru interaction. Because of the tendency of the set of bridging carboxylate groups to enforce an eclipsed configuration it is not possible to say whether the net δ interaction is very large here or not.

In the case of the $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2$ ($\text{L} = e.g., \text{H}_2\text{O}$) species,⁴⁹ which also contain an $\text{M}_2(\text{O}_2\text{CR})_4$ unit of type 6, the M–M distance is still longer (~ 2.4 Å), but nevertheless short enough to imply that there is appreciable M–M bonding. For these diamagnetic species, which have six more electrons than do the $\text{Mo}_2(\text{O}_2\text{CR})_4$ molecules, we presume that the $\sigma_n(1)$, $\sigma_n(2)$, and δ^* orbitals are entirely filled. The δ bonding must therefore be completely cancelled; an eclipsed structure is preserved by the rigidity of the carboxylate bridges.

The work from my own laboratory which is described here was supported primarily by the U. S. Atomic Energy Commission. I am grateful to this agency for steady support of our work in this field from the beginning. The names of my many able coworkers are cited at appropriate places in the text.

(47) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).

(48) M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).

(49) M. A. Porai-Koshits and A. S. Antschishkina, *Dokl. Akad. Nauk SSSR (Eng. Transl.)*, **146**, 902 (1962).