14

$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$

B.O. $= \frac{1}{2}[8-6]$

$= \frac{1}{2} \times 2 = 1$

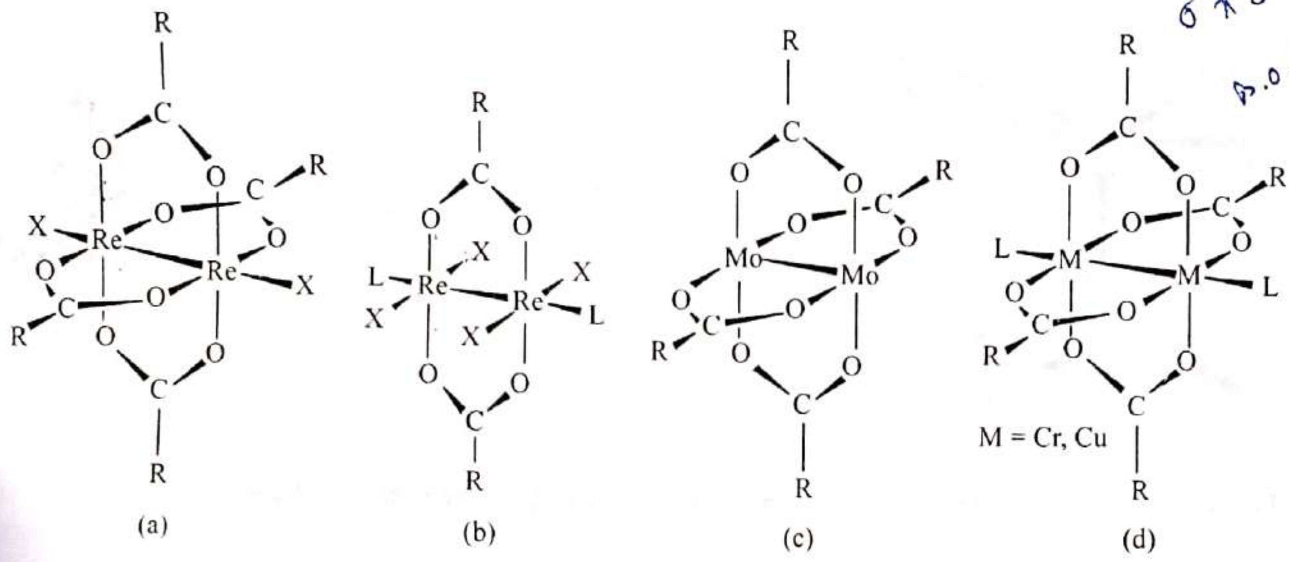

Fig. 13.12 Molecular structures of some carboxylate complexes containing metal-metal bonding: (a) Re—Re = 220 pm, X = Cl, Br, I; (b) Re—Re = 220 pm, X = Br, Cl, L = H_2O; (c) Mo—Mo = 210 pm; (d) Cr—Cr = 236 pm, Cu—Cu = 264 pm, L = H_2O. Re—Re bond lenghts are averages; individual values are known to greater accuracy.

the $\sigma^2\pi^4\delta^2$ bonding model.[56] Experimentally determined electron densities[57] are consistent with the quadruple bond picture.

Pauling[58] has provided an alternative, valence bond treatment of the quadruple bond involving *spd* hybrid orbitals and four equivalent bent bonds. His model also explains the experimental facts described above and provides a good estimate of the bond length.

The strength of the quadruple bond in dirhenium and dimolybdenum compounds has been a matter of considerable difference of opinion. Early estimates of the bond energy ranged from as low as 300 kJmol^{-1} (weaker than a C—C single bond) to as high as 1500 kJ mol^{-1} (stronger than any other known bond). Recent studies indicate that for 3*d* elements the bond energy lies in the 40–100 kJ mol^{-1} range, while for 4*d* and 5*d* elements values fall between 250 and 450 kJ mol^{-1}.[59] The relative weakness of these quadruple bonds may seem paradoxical, but we should recognize that comparing them with multiple bonds between small atoms which utilize *p* orbitals is not valid because *p* orbitals provide superior overlap and lead to inherently stronger bonds.

The $[Re_2Cl_8]^{2-}$, with its quadruple bond, is an example of a complex with all of its bonding molecular orbitals filled (Fig. 13.13c). Both δ and δ* orbitals are nearly nonbonding, however, and it would be expected that electrons could be added to the δ* level or removed from the δ level without too much loss in stability. In keeping with this expectation, $Re_2Cl_4(PMe_2Ph)_4$ ($\sigma^2\pi^4\delta^2\delta^{*2}$, Fig. 13.13e) and $[Re_2Cl_4(PMe_2Ph_4]^+$ ($\sigma^2\pi^4\delta^2\delta^{*1}$, Fig. 13.13d) which have occupied antibonding orbitals have been synthesized. In addition, $[Mo_2(SO_4)_4]^{3-}$ ($\sigma^2\pi^4\delta^1$, Fig. 13.13b) and $[Mo_2(HPO_4)_4)^{2-}$ ($\sigma^2\pi^4$. Fig. 13.13a) which have less than full occupation of the δ bonding orbitals have been prepared. The characterization of $W_2Cl_4(OR)_4(R)_2$ (R = Me,Et) with a W=W double bond completed a series of ditungsten compounds with bond orders of 4, 3, 2, and 1.[60]

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[56] Hall, M. B. *Polyhedron*, **1987**, *6*, 679–684. Ziegler, T.; Tschinke, V.; Becke, A. *Ibid.* 685–693. Bursten, B. E.; Clark, D. L. *Ibid.* 695–704.

[57] Hino, K.; Saito, Y.; Benard, M. *Acta Crystallogr., Sect. B.* **1981**, *37*, 2164–2170.

[58] Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3799–3801.

[59] Ziegler, T.; Tschinke, V. Becke, A. *Polyhedron* **1987**, *6*, 685–693.

[60] Anderson. L. B. Cotton, F. A : DeMarco. D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R A. *J. Am them Soc*, **1981.**, *103*, 5078–5086.

Re_2^{+4}

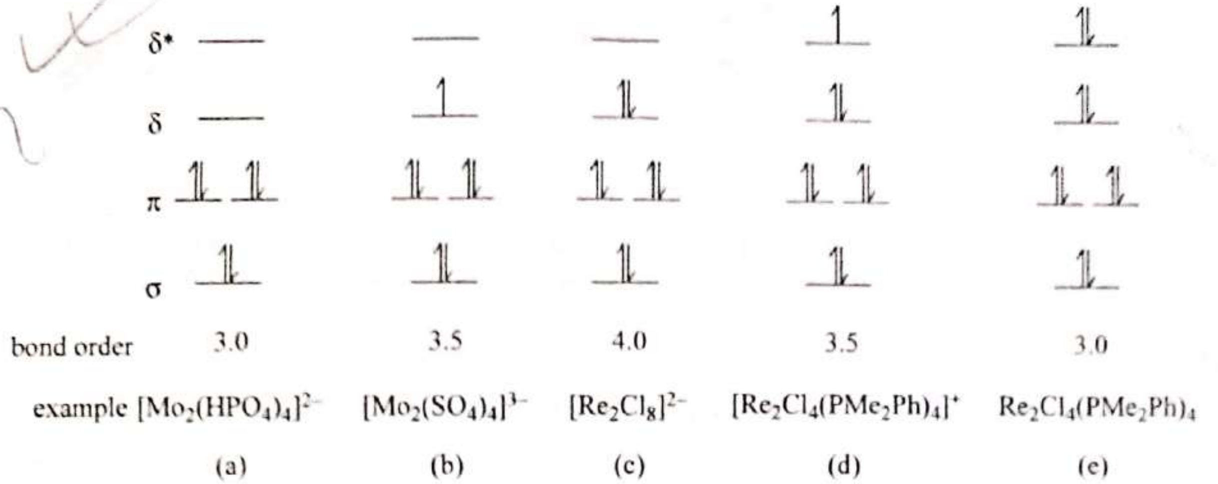

Fig. 13.13 Qualitative molecular orbital diagram for dinuclear rhenium and molybdenum complexes. All of the bonding molecular orbitals are filled for $[Re_2Cl_8]^{2-}$ (c) and a bond order of 4 results for one σ, two π, and one δ bond. When electrons are added to the δ* level, the bond order is reduced as shown for (d) and (e). Removing electrons for the δ bond also leads to lower bond order as shown by (a) and (b) [Taken in part from Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35. Reproduced with permission.]

There are two metals, Cu(II) and Cr(II), in the first transition series which form acetate complexes similar in structure to the rhenium and molybdenum carboxylate complexes (Fig. 13.13d). Like their Re and Mo analogues, the Cu and Cr complexes are diamagnetic, indicating that spins are paired. They differ significantly from the complexes of the heavier metals, however. The Cu—Cu distance in the Cu(II) (d^9) complex is 264 pm, which is actually somewhat longer than the Cu—Cu distance in metallic copper (256 pm). It appears that the Cu—Cu bond in copper(II) acetate is only a weak single bond resulting from pairing the odd electron on each copper atom.

The chromium(II) acetate molecule was long thought to have the same metal–metal bond length as the copper compound and thus have a similar weak bond. However, its structure was redetermined and the Cr—Cr distance was found to be 236.2 pm, which is considerably shorter than that found in metallic chromium (249.8 pm).[61] In fact, the Cr—Cr bond has been estimated to be about 45 kJ mol^{-1}, which makes it stronger than the Cu—Cu bond.[62] All of this evidence and orbital symmetry suitability might suggest that the Cr—Cr bond in chromium acetate is a quadruple bond. Still, not everyone is willing to go that far. The problem is that this "quadruple" bond is estimated to be only about as strong as a typical Cr—Cr single bond.[63] It appears that most participants in the debate have chosen to view the bond as a very weak quadruple bond. Aside from this controversy, the chief interest in dichromium compounds has been in the wide range of bond lengths they display (185–254 pm). Some of these are the shortest metal–metal bonds known and have been dubbed "super-short" bonds. The variation in bond length, which is dependent upon the nature of the substituent ligands, is in sharp contrast to the relative uniformity in the length of quadruple bonds in the heavier congeners (Mo—Mo = 204–218 pm; W—W = 216–230 pm).

Among the more interesting metal–metal multiple bonded complexes are the hexaalkoxo dinuclear tungsten and molybdenum complexes, $[M_2(OR)_6]$ (M = Mo, W):[64]

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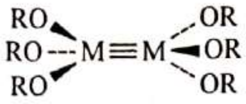
[61] Cotton, F A.; DeBoer, B. G.; LaPrade., M. D., Pipal, J. R; Ucko, D. A. *J. Am. Chem. Soc.* **1970**, *92*, 2926–2927

[62] Cannon. R. D. *Inorg. Chem.* **1981**, *20*, 2341–2342.

[63] Hall, M. B. *Polyhedron* **1987**, *6*, 679–684.

[64] Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 574–586



These complexes are chemically like polynuclear metal carbonyl complexes (class I) but are included here instead of in Chapter 18 because they do not possess metal–carbon bonds. A rich chemistry has been developed in which alkoxides function as stabilizing ligands for 12-electron clusters.[65] The alkoxide group, RO, has two filled *p* orbitals capable of donating π electron density to the metal centers. Even so, because these *p* orbitals are ligand centered, the complexes are looked upon as coordinatively unsaturated and containing formal metal–metal triple bonds ($\sigma^2\pi^4$) The M≡M bonds are somewhat analogous to carbon–carbon triple bonds For example, the metal–metal bond can undergo addition reactions.

$$\mathrm{(RO)_3W{\equiv}W(OR)_3 + 2X_2 \longrightarrow (X)_2(RO)_3W - W(OR)_3(X)_2} \quad (\mathrm{X = Cl, Br, I}) \tag{13.55}$$

$$(i\text{-PrO})_3\mathrm{Mo{\equiv}Mo}(\mathrm{O}\text{-}i\text{-Pr})_3 + i\text{-PrOO-}i\text{-Pr} \longrightarrow (i\text{-PrO})_4\mathrm{Mo{=}Mo}(\mathrm{O}\text{-}i\text{-Pr})_4 \tag{13.56}$$

It is also possible to prepare $(t\text{-BuO})_3\mathrm{W{\equiv}CR}$ (R = Me, Et Ph) compounds in which the isolobality of CR and $\mathrm{W(OR)_3}$ is apparent:[66]

$$(t\text{-BuO})_3\mathrm{W{\equiv}W}(\mathrm{O}\text{-}t\text{-Bu})_3 + \mathrm{RC{\equiv}CR} \longrightarrow 2(t\text{-BuO})_3\mathrm{W{\equiv}CR} \tag{13.57}$$

It has been shown that $\mathrm{W_2}(\mathrm{O}\text{-}i\text{-Pr})_6$ dimerizes, existing in equilibrium with $\mathrm{W_4}(\mathrm{O}\text{-}i\text{-Pr})_{12}$, a molecule which may be thought of as an analogue of cyclo–butadiene (Fig. 13.14).[67]

The tetramer has been shown to be fluxional such that the tungsten–tungsten double and single bonds migrate about the $\mathrm{W_4}$ ring. At the same time, the two isopropoxide groups attached to each wingtip tungsten undergo proximal/distal exchange (Fig. 13.14). All of this motion taken together has come to be known as "The Bloomington Shuffle" after the city in which it was discovered.[68]

Trinuclear Clusters

The best-known examples of noncarbonyl clusters containing three metal atoms are the rhenium trihalides $[(\mathrm{ReCl_3})_3]$ and their derivatives. The basic structural unit is shown in Fig. 13.15a. Each rhenium atom is bonded to the other two rhenium atoms directly by metal–metal bonds and indirectly by a bridging halogen ligand. In addition, each rhenium atom in the triangular array is coordinated by two more halide ligands above and below the plane defined by the three rhenium atoms. Each Re(III) has a d^4 configuration which would lead to a paramagnetic complex if only metal–metal single bonds were present. The complexes are diamagnetic, however, which implies that each Re atom is doubly bonded to its rhenium neighbors.

In the solid state the halides retain this basic unit, but further bridging between rhenium atoms by chloro ligands results in a polymeric structure (Fig. 13.15b). Likewise, dissolving the halides in solutions of the hydrohalic acids leads to formation of dodecahalotrirhenate(III) ions. $[\mathrm{Re_3X_{12}}]^{3-}$ (Fig. 13.15c), in which additional halide ligands have coordinated to the empty positions present in the $\mathrm{Re_3X_9}$, units. Other ligands (such as $\mathrm{R_3P}$, $\mathrm{Me_2SO}$, or MeCN) can also coordinate to these positions. The $\mathrm{Re_3}$ cluster is persistent in many chemical transformations. The bond length is 240–250 pm, which is indicative of strong bonding although weaker than in $[\mathrm{Re_2X_8}]^{2-}$.

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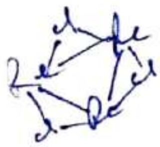
[65] Chisholm, M. H. *Angew. Chem. Int. Ed. Engl.* **1986,** *25*, 21–30. Chisholm, M H ; Clark. D. L.; Hampden-Smith, M. J.; Hoffman, D. H. *Angew. Chem. Int. Ed. Engl.* **1989,** *28*, 432–444 Chisholm, M. H. *Acc. Chem. Res.* **1990,** *28*, 419–425.

[66] McCullough, L. G.; Schrock, R. R.; DeWan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985,** *107*, 5987–5998.

[67] Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J Am. Chem. Soc.* **1989,** *111*, 574–586.

[8] Is it possible that this name was proposed the same year that the Chicago Bears choreographed the "Superbowl Shuffle"?



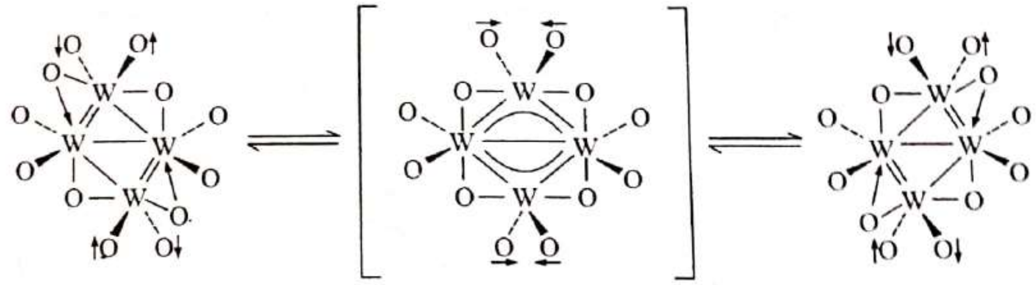


Fig. 13.14 Dynamic intramolecular rearrangement of $W_4(O\text{-}i\text{-}Pr)_{12}$. [From Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989,** *111*, 574–586. Reproduced with permission.]

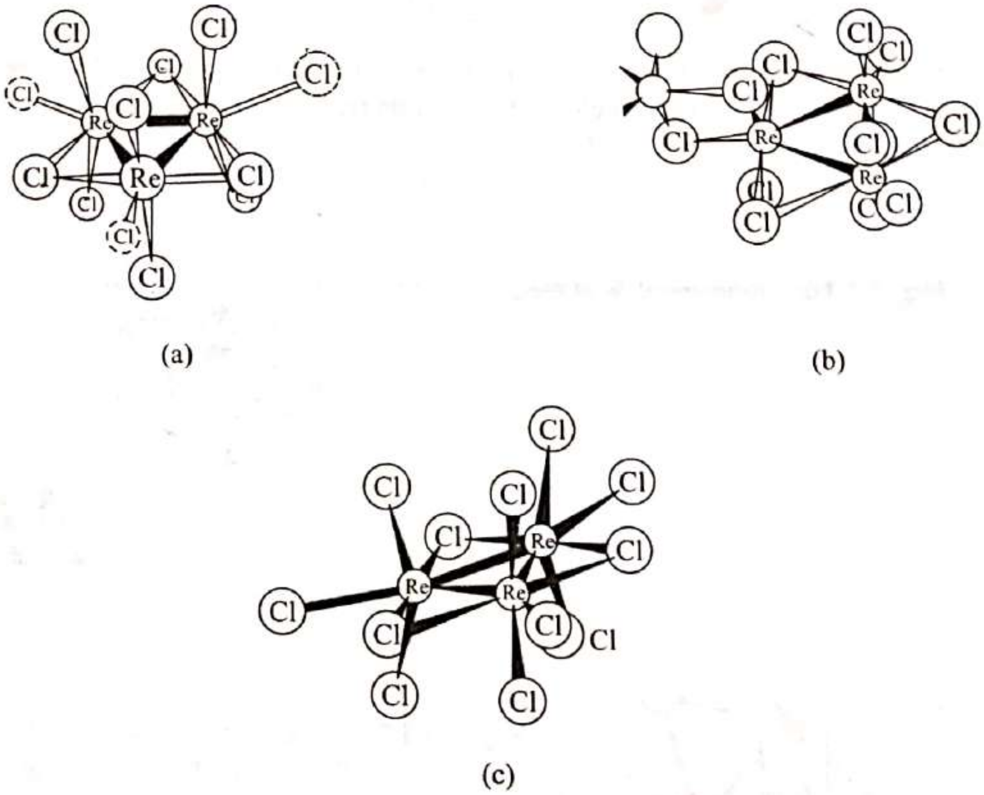


Fig. 13.15 Rhenium(III) clusters: (a) The structural unit present in a Re(III) trinuclear cluster. The positions marked ○ are empty in the trihalides in the gas phase but have coordinating groups in other situations. [From penfold, B. R. In *Perspectives in Structural Chemistry*; Dunitz, J. D.; Ibers, J. A., Eds.; Wiley: New York, 1968; Vol. 2, p 71. Reproduced with permission.] (b) The structure of solid $(ReCl_3)_3$. [From Cotton, F. A.; Mague, J. T. *Inorg. Chem.* **1964,** *3*, 1402. Reproduced with permission.] (c) The $[Re_3Cl_{12}]^{3-}$ anion. [From Bertrand, J. A.; Cotton, F. A.; Dollase, W. A. *Inorg. Chem.* **1963,** *2*, 1166. Reproduced with permission.]

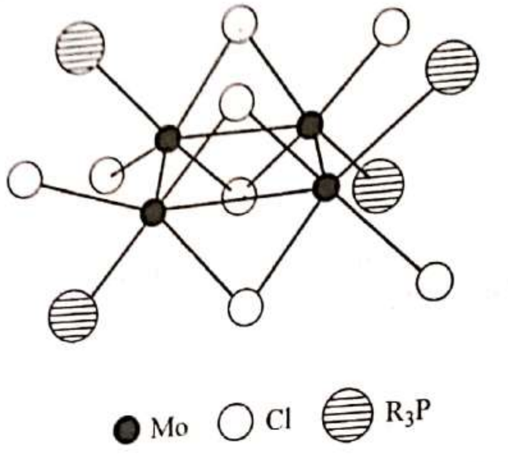
Tetranuclear Clusters

Although common among carbonyl clusters, far fewer examples of tetranuclear clusters are found among the halides and oxides. One example noted previously is $W_4(OR)_{12}$ which forms by dimerization of $W_2(OR)_6$.

The tetrameric $W_4(OR)_{16}$ has also been synthesized. Whereas $W_2(OR)_6$ and $W_4(OR)_{12}$ may be viewed as unsaturated, $W_4(OR)_{16}$ is saturated, containing W—W single bonds (Fig. 13.16).[69]

Quadruply bonded dinuclear compounds also can dimerize to give tetrameric molecules:

$$2K_4Mo_2Cl_8 \xrightarrow{R_3P} \quad + KCl \qquad (13.58)$$



The resulting four-membered ring is not square, and it appears from bond length measurements that there are alternating single and triple Mo—Mo bonds.[70] Tetranuclear cluster units (rhomboidal Mo_4), connected by oxygen atoms and forming infinite chains, are found in $Ba_{1.14}Mo_8O_{16}$.[71]

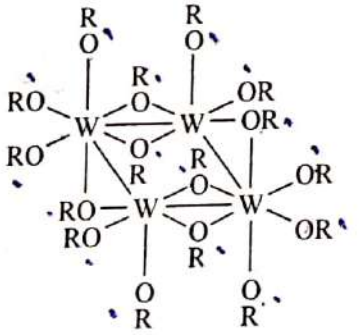
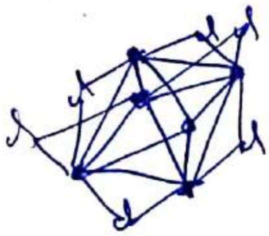
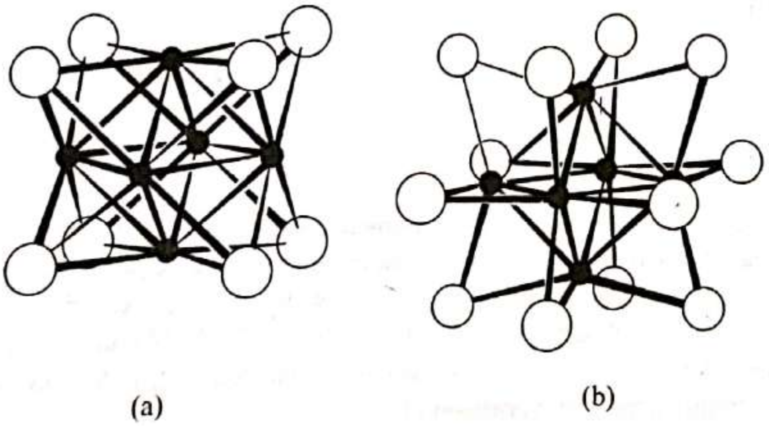


Fig. 13.16 Structure of $W_4(OR)_{16}$.





(a) (b)

Fig. 13.17 The structure of the $Mo_6Cl_8^{4+}$ ion; ● = Mo, ○ = Cl. (b) The structure of the $M_6X_{12}^{2+}$ ions; ● = Nb, Ta; ○ = Cl, Br. [From Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240. Reproduced with permission.]

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[69] Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C.; Leonelli, J; Foing, K. *J. Am. Chem. Soc.* **1981**, *103*, 6093–6099.

[70] McCarley, R. E.; Ryan. I. R.; Torardi. C. C. In *Reactivity of Metal–Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series 155; American Chemical Society: Washington, DC. 1981; p 41.

[71] McCarley, R. E. In *Inorganic Chemistry Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 273.