nuclei. At the beginning and end of the 3d transition series, the calculated[5] equilibrium internuclear distances R_e are shorter than the nearest-neighbor distance in the bulk, especially at the right-hand end of the series, e.g., for Fe_2, Co_2, and Ni_2, $R_e = R_{bulk} - (0\text{–}4\ \text{Å})$. The binding in these systems is accordingly attributed to the overlap of the d orbitals since at these short distances core penetration cancels out most of the energy gain from the strong overlap of the 4s orbitals. On the other hand, in the middle of the series the half-filled, high-spin atomic d shell gives rise to repulsion like a closed shell, and Cr_2 for example is thought to have a large R_e value with only a single bond of s-electron character—it is just too expensive in energy to flip the d-electron spins to make additional bonds. Accordingly, the theoretical interpretation of the common occurrence of Cr_2L_n complexes (low spin) with short Cr–Cr bonds is that in going from Cr_2 to Cr_2L_n the difference is that ligands (L) can move the metal s- (p-) electron density out into the metal–ligand bonds: the attractive d-electron force between the metal centers is then sufficient to overcome the spin-correlation energy and the Cr–Cr bond contracts dramatically with respect to high-spin Cr_2.

While the spin-correlation energy seriously complicates a full theoretical treatment of the M_2 systems (especially the estimation of binding energies), this is less of a problem in bi- and polynuclear metal compounds where the spins may be saturated by the extra bonds and low-spin states are common. Hence in choosing a homonuclear metal reference system to which some M_nL_m complex may be related, one must pay attention to the spin states of the two systems since the spin-correlation energy can be an important factor providing an effective repulsive interaction. In the homonuclear diatomic molecules one can say that relative to the bulk metal the repulsive s- (p-) electron forces can be substantially alleviated as the s-electron density "spills out" into empty space, and in systems of small spin multiplicity one *expects* contraction of the bond under the influence of the attractive d-electron force. I thus believe that the competition between attractive d-electron forces and repulsive s- (p-) electron forces is the principal factor governing the stereochemistry of metal–metal bonds. This principle can be generalized to the statement that metal–metal bond length variation in bi- and polynuclear transition-metal compounds should be a reflection of the ability of the ligands to remove the s- (p-) electron density from the vicinity of the metal atom (so as to reduce core penetration at the metal atom sites), leaving d-electron bonds that are much like those found in the bulk metal and metal diatomics: implicit in this view is that the d-electron density is not changed too much by ligation, i.e., that the d electrons only play a relatively minor role in ligand bonding, and this seems consistent with ESR measurements on transition-metal complexes. Other things being equal, one thus expects ligands that are Lewis acids to be associated with shorter metal–metal bonds than are basic ligands.

An illustration of these remarks can be found in the structural systematics of transition-metal carbonyls containing two or more metal atoms. In the conventional synergic bonding mechanism, the carbonyl 5σ orbitals donate electron density to the metal unit, while electron density is pushed off the cluster through hybridization between the metal $d\pi$ orbitals and the carbonyl 2π levels. The carbonyl 5σ orbital is a sp-hybrid orbital, and so this bonding mechanism implies that the sp-electron density at each metal atom is enhanced as carbonyl ligands are brought up to the metal cluster, but there is no compensating increase in d-electron density. Hence we may expect metal carbonyls to have longer metal–metal bond lengths than in the corresponding homonuclear metal systems, although this comparison may be upset by the spin-correlation energy balance in the middle of the transition-metal series (it ought to be valid for the group 8 metals where polynuclear metal carbonyls are found[7]). The carbonyl shell round the metal unit can also be thought of as a layer of dielectric (insulating) material, and so in comparison with a metal cluster embedded in bulk metal, it is reasonable to presume that the metal cluster sp electrons are more confined in metal cluster carbonyls than in the bulk metals: one thus also expects metal–metal bond lengths in cluster carbonyls to be greater than in the bulk metals. Consideration of the fragmentary structural data on M_2 systems, the structural systematics of the bulk metals, and the data for metal carbonyls shows these expectations to be borne out in practice.[6] Moreover the exceptional structures of the "two-dimensional" cluster carbonyls $M_3(CO)_6^{2-}$ (M = Ni, Pt)[7] and oligomers of this planar fragment can also be simply understood from this point of view: in these systems the metal sp electrons are *not* confined by ligands above and below the molecular plane, and so just as I have argued for the homonuclear metal dimers, some of the repulsive sp force between metal atoms can be relieved by the sp-electron density spilling out into the vacuum. As a result the M–M bonds in the $M_3(CO)_6$ unit are significantly shorter than in the bulk metals, and this remains true in the oligomers $[M_3(CO)_6]_n^{2-}$, n, > 1, in which interfragment M–M bonds are significantly longer than in the bulk metals.[6,7]

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References and Notes

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Additions and Corrections

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Ronald F. Ziolo* and Jan M. Troup: Threefold Configuration Tellurium(IV). Crystal Structure of Trimethyltelluronium Tetraphenylborate.

Page 2271. The superscript "1" should not appear behind Ronald F. Ziolo's name. His corresponding address is: Xerox Corp., Webster Research Center, Webster, NY 14580.—Ronald F. Ziolo