3724 *Inorg. Chem.* **1997,** *36,* 3724−3729

1,2-Diamidolenes, -Diphosphidolenes, and -Dithiolenes as Riders on Sawhorses (L_6M_2 Units). A Theoretical Interpretation of the Stereochemistries, Residual Bonding Capabilities, and Contrasts to the Behavior of 1,2-Dioxolenes

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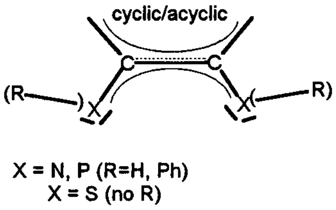
Received October 2, 1996[⊗]

This paper analyzes from the theoretical viewpoint (ehmo calculations with the graphic interface of CACAO) the bonding capabilities of conjugated π-ligands containing the unit XCCX (X = S, NR, PR) when they ride on binuclear fragments of the type L_6M_2 (*sawhorse*). The stereochemistries are monitored for a number of structures retrieved from the Cambridge Database. In the starting prototype, *e.g.* the complex $[(CO)_2(PPh_3)Ru\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}Ru(PPh_3)(CO)_2]$ with 34 valence electrons, the *rider* donates 4 electron pairs to two d^7 metals and a single M−M bond is featured. In spite of the predicted electron similarities between diamidolenes and dioxolenes, no case has been reported of a catecholate ligand adapting to the same *riding* mode and therefore being able to donate a total of 4 lone pairs to the metals. The different behavior is largely ascribed to poor interactions of b_1 symmetry when the donor atoms of the rider are of higher electronegativity. Stronger donors, such as phosphorus and sulfur, still support the riding mode but elongate understandably the M−M bond. In presence of d^6 metal atoms, the *riding* ligand bends over one of the metals and also donates the electrons of the C=C π-bond itself. Alternatively, an extra ligand (terminal or bridging) can be added to the primary framework M_2L_6. In all of the latter cases, the various factors affecting the nature of the M−M bond are theoretically interpreted.

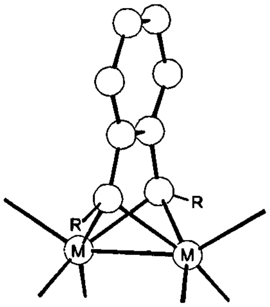
Introduction

Dianionic, conjugated π-ligands characterized by the unit XCCX (X = S, NR, PR), **I**, are often observed to ride a binuclear fragment of the type L_6M_2 (*sawhorse*). In these bifunctional ligands, the carbons linked to the heteroatoms are sp^2 hybridized, hence characterized by a more or less delocalized π system. In principle, the donor capabilities of these ligands are spread over a wide range (from 2 to 10 electrons) depending on the overall stereochemistry of the complex. In fact, not only the *in-plane* electron pair of each heteroatom is used for dative bonding but also the orthogonal p_π pair, if sufficiently localized. Also, the C−C π bond in between the heteroatoms may occasionaly become a source of electrons for donation to the metals.

A typical example in which a diamidolene ligand *rides* on a *sawhorse* is given by the compound $[(CO)_2(PPh_3)Ru\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}Ru(PPh_3)(CO)_2]$, reported by some of us and schematized in **II**.[2] The four Ru−N bonds themselves suggest that the dianionic *rider* behaves as the donor of eight electrons, hence the 34 electron count of the complex. A single metal−metal bond is predictable according to the effective atomic number rule,[3] which is consistent with the separation of 2.559(1) Å between two formal d^7 metals.



I



II

A search in the Cambridge Structural Database[4] shows several other examples where the riding ligand sits upright on the *sawhorse*. Interestingly, the Ru−Ru separation elongates by ca. 0.2 Å in a system with the framework **II**, where nitrogens are substituted by phosphorus donors (PPh[5] groups in place of the NH ones[2]). Analogously, for the bimetallic substrate $Fe_2(CO)_6$, a riding diamidolene $N(H)C(H){=}C(H)N(^tBu)^{2-}$ [6] forces the Fe−Fe separation to be ca. 0.12 Å shorter than in the case of a riding dithiolene $SC(H){=}C(H)S^{2-}$ [7] (2.38 *vs* 2.50 Å).

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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(2) Garcia-Granda, S.; Obeso-Rosete, R,; Rubio-Gonzalez, J. M.; Anillo, A. *Acta Crystallogr. Sect, C* **1990**, *46*, 2043. Anillo, A.; Obeso-Rosete, R.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 2019.

(3) See for instance: Mingos, D. M. P.; Wales, D. J. In *Introduction to Cluster Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1990.

(4) Cambridge Structural Database System, version 5.11; Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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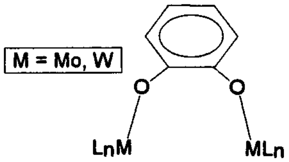
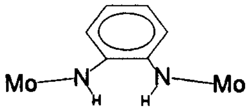
S0020-1669(96)01206-2 CCC: $14.00

In spite of the often invoked similarity between diamidolenes and dioxolenes in terms of redox behavior and electronic properties, we are not aware of any bimetallic species in which a catecholate rides the sawhorse in the fashion shown in **II**. When the latter ligand acts as a bridge,[8] each oxygen atom donates at most one electron pair to a single metal atom (see **III**).

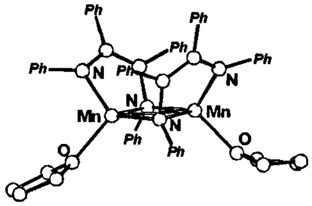


III



IV

Diamidolene (**IV**) and dithiolene ligands themselves are also found to donate single lone pairs to separate metals in dimers such as (HB(pz)$_3$)(NO)IMo[μ-N(H)$_2$C$_6$H$_4$N(H)]MoI(NO)(HB-(pz)$_3$),[9] HB(pz)$_3$ = tris(3,5-dimethylpyrazolyl)borato, and (CO)$_5$Mn[μ-SC(C$_6$H$_4$F)=C(C$_6$H$_4$F)S]Mn(CO)$_5$.[10]



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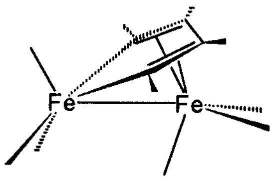


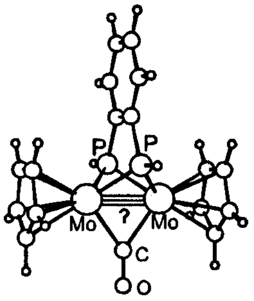
VI

Interestingly, in the bis(tetrahydrofuran−Mn) dimer,[11] shown in **V**, any diamidolene ligand still acts as a bridge but only *via* one of the nitrogen atoms, the second heteroatom being terminally linked. In this manner, each ligand donates a total of six electrons. In none of the cases above is the supporting bimetallic unit of the *sawhorse* type.

In this paper, we start to illustrate the bonding capabilities of the conjugated XCCX ligands when donating 8 electrons to a *sawhorse* unit. The theoretical arguments help to understand why the M−M bond strength decreases in going from the donors of the first row (nitrogen) to those of the second row (phosphorus, sulfur) and why dioxolenes do not adapt to the same bonding mode.

Then, we examine the cases of metals with electron counts lower than the d^7. The riding π-conjugated molecule is forced to bend toward one of the metals so that the electrons of the C=C bond in between the heteroatoms are also involved and the ligand becomes formally a 10-electron donor. The new arrangement compares with that of ferroles, **VI**, in which a butadienyl dianion is bent over one metal and becomes the donor of 8 electrons (two σ lone pairs and two π-bonding electron pairs). A MO analysis of the latter system was presented in a pioneering theoretical paper by Thorn and Hoffmann.[12]

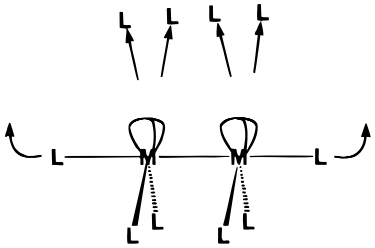
Finally, we point out some examples indicating that, for the proper electron count, the L$_6$M$_2$ framework accepts one extra ligand either at the terminal or bridging position. The single M−M bond may or may not exist in the M$_2$L$_7$ skeleton. If it does, its MO underpinnings are somewhat different than before and need to be addressed in some details. As a unique case, the compound CpMo[μ-PhP(C$_6$H$_4$)PPh][μ-CO)MoCp,[13] **VII**, is formally reducible to the latter species but two formal Mo(II) ions suggest a triple Mo≡Mo bond. A detailed analysis of M≡M triple bonding in triply bridged environments will be presented by some of us elsewhere.[14]



VII

Results and Discussion

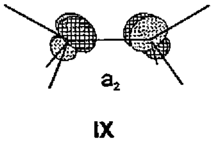
L$_6$M$_2$(μ-XCCX) Dimers for M = d^7. In order to understand the bonding interactions between the *sawhorse* and the *riding* bifunctional ligand, one can start from a classic binuclear complex of the type M$_2$L$_{10}$ (M = Mn, Re; L = CO). In the latter, the local octahedral geometry of one metal is completed by the other metal (or better to say the facing L$_5$M fragment). If two *cis*, mutually eclipsing, equatorial donors are simultaneously removed from the two metals, pairs of empty σ-hybrids are developed, as shown in **VIII**.



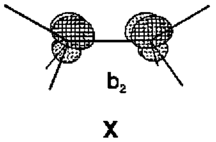
VIII

Intuitively, the tilting of each terminal L$_3$M fragment, as indicated by the circular arrows, reorients the direction of all of the hybrids toward the midsection of the *sawhorse*, where the donor atoms of the *riding* ligand **I** are located (see **III**).

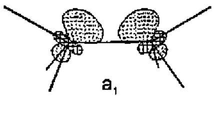
In the C_{2v} symmetry, the combinations of the four hybrids, which behave as a$_2$, b$_2$, a$_1$, and b$_1$, are depicted in **IX**−**XII** as CACAO drawings.[15]



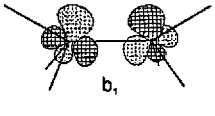
IX



X



XI



XII

All of these are the potential acceptors of the electron pairs donated by the bridging ligand. Their energetics are somewhat

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(8) De Learie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1988**, *27*, 3842. Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 2123.

(9) Al Obaidi, N. J.; Mc Whinnie, L. W.; Harmor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1988**, 269.

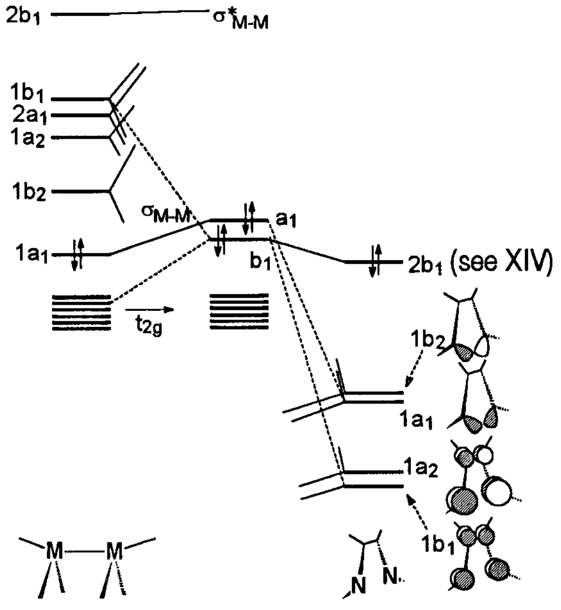
(10) Lindner, E.; Butz, I. P.; Hiller, W.; Fawzi, R.; Hoeme, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 996. Lindner, E.; Butz, I. P.; Hoeme, S.; Hiller, W.; Fawzi, R. *J. Organomet.Chem* **1983**, *259*, 99.

(11) Walther, D.; Ritter, U.; Kempe, R.; Sieler, J.; Undeutsch, B. *Chem. Ber.* **1992**, *125*, 1529.

(12) Thorn, D. L.; Hoffmann, R. *Inorg. Chem* **1978**, *17*, 126.

different as the *in-phase* combinations are lower than the out-of-phase ones ($b_2 < a_2$ and $a_1 < b_1$) and so are the levels noded in the plane of the drawing (**IX** and **X**) *vs* the unnoded ones.

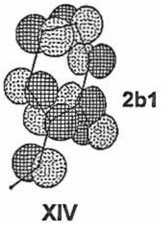
From another viewpoint, the d^7-d^7 bimetallic fragment is formed by two classic pyramidal L_3M units[16] somewhat reoriented with respect to the potentially common C_3 axis. Thus, **IX**−**XII** originate from the degenerate and orthogonal d_π local orbitals lying above the "t_{2g}" sets. In addition, the L_3M σ hybrids (d, s, and p in character) form *in-phase* (filled $1a_1$) and *out-of-phase* (empty $2b_1$) combinations. The MO scheme is outlined in **XIII**, where the L_6M_2 levels **IX**−**XII** are those comprised between $1a_1$ and $2b_1$, at the left side of the diagram. Notice that only 12 metal-based FMOs are reported, as the remaining 6 combinations are already involved in bonding/antibonding interactions with the terminal ligands.



XIII

The L_6M_2 FMOs $1a_1$ and $2b_1$ can be already considered the M−M σ and σ^* MOs of the dimer. Due to the σ/d_π rehybridization, the main lobes of the latter point downward, *i.e.* opposite to those in **XI** ($2a_1$) and **XII** ($1b_1$). Also for this reason, the σ and σ^* levels should not be involved in any major interaction with the orbitals of the *rider* although this is not totally the case (*vide infra*).

Two of the four M−L bonds are due to the interaction of σ *lone pairs* of the *rider* ($1a_1$ and $1b_2$) with the metal combinations **XI** and **X**, respectively. The other bonds stem from interactions of the type a_2 and b_1 which involve the ligand π system and the corresponding metal levels **IX** and **XII**. While the interactions of the type b_2, a_2, and a_1 appear to be sufficiently strong (the electron fractions conveyed into the metals are 0.62, 0.315, and 0.25, respectively and the OP values range in between 0.23 and 0.11), the overall interaction of the type b_1 appears weaker.

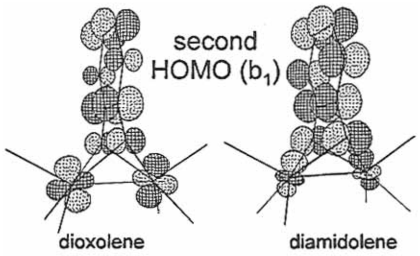


XIV

The *rider* has at least two filled π combinations of b_1 symmetry for the donation into the level **XII**. Although the ligand's HOMO (**XIV**) lies in a better energy position, its donor capabilities are poor because of the nodal properties (π^* at the CN linkages). Since the lower $1b_1$ spans the whole NCCN π bonding region, it overlaps better. For diamidolene, the relatively small 0.09 value of the $\langle 1b_1|1b_1\rangle$ OP is still 3 times larger than that involving the ligand's HOMO ($\langle 1b_1|2b_1\rangle$). By comparison, the analogous $2b_1$ HOMO of diphosphidolenes becomes the most efficient donor while that of catecholates does not even make a positive OP with **XII**. Indeed, the interplay of the b_1 interactions is even more complicated and requires further comments.

As shown by the dotted lines in **XIII**, a b_1 combination of metal FMOs, within the bulk of "t_{2g}" levels, is somewhat repulsive toward the ligand's HOMO. For catecholates, this effect is larger because the HOMO lies deeper (*ca.* 0.5 eV) on account of the electronegativity of the oxygen atoms. At the same time, the donor capabilities of $2b_1$ are low because the weight of the oxygen p_π orbitals (9%) is significantly smaller than that of the carbon ones (22%).[17] As a comparison, the corresponding percentages in the diamidolene ligand (see **XIV**) are 19 and 12 for the nitrogen and carbon atoms, respectively.

For the complexes containing catecholate and diamidolene ligands, the direct comparison of the second HOMO b_1, in any case delocalized through the metals and the *rider* (see **XV**), excludes a mere nonbonding character for the latter. Also, it is immediately evident that, in the case of catecholate, the metal lobes are significantly redirected by the mixing with the lower t_{2g} component.



XV

The C−X π^* character of the combination **XIV** (X = O, N) imposes, at one time, M−X bonding and M−C antibonding relations with respect to the metal acceptor FMO $1b_1$ (**XII**). For M−X bonding distances of 2.17 Å, the p_π orbitals of the X atoms are well off the bisecting plane containing the metal lobes so their overlap cannot be large. Conversely, even if the adjacent C atoms are further apart (2.63 Å), their antibonding relationship with the metals is not negligible (the corresponding M−C OP values are negative (ca. −0.08 for both the catecholate and diamidolene cases). Ultimately, the overall $\langle 1b_1|2b_1\rangle$ metal−ligand OP is vanishing because of the contrasting effects.

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(13) Kyba, E. P.; Mather, J. D.; Kassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371.

(14) Mealli, C. Work in progress.

(15) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

(16) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital interactions in Chemistry*; Wiley: New York, 1985.

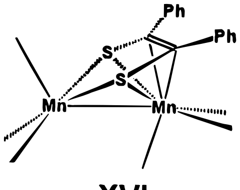
(17) The concentration of the electrons at the carbon atoms linked to oxygen was already pointed out as responsible for the unique attack of an O_2 molecule on the series of cationic complexes $[(\text{triphos})M(\text{catecholate})]^+$ (M = Co, Rh, Ir; triphos = $CH_3(CH_2PPh_2)_3$). Theoretical arguments suggested that the nucleophilic carbon atom in close proximity to an acidic metal favors the polarization of O_2 and its concerted addition across the M···C pair of atoms. See: (a) Barbaro, P.; Bianchini, C.; Mealli, C.; Meli, A. *J. Am. Chem. Soc.* **1991**, *113*, 3181. (b) Barbaro, P.; Bianchini, C.; Linn, K.; Mealli, C.; Meli, A.; Vizza, F. *Inorg. Chim. Acta.* **1992**, *198*−*200*, 31.

As mentioned, the situation changes for diphosphidolene and dithiolene ligands where the larger diffuseness of the heteroatoms p_π orbitals forces the $\langle 1b_1|2b_1\rangle$ OP to become the largest of the b_1 symmetry. By comparison of the given series of *riders*, the contribution of the b_1 type interactions to the overall bonding is smaller and the more contracted and the more electronegative are the heteroatoms. Perhaps significantly, no complex of the type **II** which carries a catecholate as a *rider* has been reported as yet.

Additional theoretical information comes from Walsh diagrams (not reported) constructed by increasing the separation between the *rider* and the *sawhorse*. Not only the HOMO of the complexes (a_1) stabilizes (see the comments below) but also the second HOMO (b_1) stabilizes, in a parallel way. For diamidolene, each frontier MOs (b_1 and a_1) stabilizes progressively by *ca.* 0.4−0.5 eV in the range of Ru−N distances 2.08−2.35 Å. Nonetheless, a minimum of the total energy is found at *ca.* 2.20 Å (close to the experimental value[2] of 2.17(1) Å) thus suggesting that, at this geometry, competing bonding/antibonding effects are properly balanced. The energy gains are much less evident for catecholates, and eventually the energy minimum (at the long Ru−O separations of 2.33 Å) is barely different from the sum of the energies for the separated fragments. By contrast, if the donors are phosphorus or sulfur atoms, the effects are very much enhanced for both the b_1 and a_1 frontier MOs, in particular for the latter. Consistently with the experimental cases presented in the Introduction,[5−7] a deep total energy minimum (3 eV) is observed for elongating the Ru−P distances from 2.2 to *ca.* 2.4 Å (the latter value is slightly longer than the experimental distance[5] of 2.35 Å).

Also the Ru−Ru linkage is optimized *ca.* 0.2 Å longer in the diphosphidolene with respect to the corresponding diamidolene case.[2] To be sure that the result is not biased at the ehmo level, the Ru−Ru separation was fixed at 2.62 Å and, significantly, the corresponding value of the Ru−Ru OP is larger for the diamidolene than for the diphosphidolene *rider* (0.29 *vs* 0.18). The electronic factors which underlie the trend are those already outlined. When the *rider* is raised over the *sawhorse*, the large repulsion between the P σ lone pairs and the Ru−Ru σ bonding level (see **XIII**) is dramatically reduced. Moreover, the stabilization of the frontier MO b_1 confirms that whereas its antibonding component vanishes at the long separation, the bonding Ru−P components remain sufficiently large due to the diffuseness of the phosphorus p_π orbitals. As an important consequence, a larger electron density into the metal FMO $1b_1$ weakens the metal−metal linkage because of the antibonding character of the level **XII** itself. Moreover, even a small mixing of the major M−M σ^* level ($2b_1$) into the metal ligand bonding interaction contributes to elongate significantly the M−M bond itself.

$L_6M_2(\mu$-XCCX) Dimers with M < d^7. At this point, we address systems of the type $L_6M_2(\mu$-XCCX) with two electron less than the ones considered above [*e.g.*: Mn(I) *vs* Fe(I) or Ru(I)]. An interesting example is provided by the species $(CO)_6Mn_2[\mu$-S(Ph)C=C(Ph)S],[18] schematically represented in **XVI**.

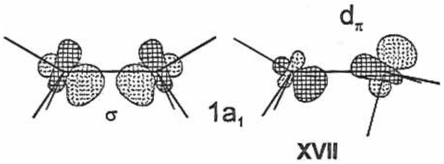


XVI

Now, the *riding* ligand appears rotated about the X···X vector so that the C=C π bond, linked to the heteroatoms, becomes η^2 coordinated to one of the metals. In this manner, the whole bridge becomes the donor of 10 electrons. Notice that, in order to avoid any hindrance with the *rider*, the three terminal ligands at the rightmost metal atom have an inverted configuration. The *sawhorse* shape is lost, but in view of the cylindric symmetry of the frontier L_3M hybrids for a d^6 metal center, the overall bonding capabilities of L_6M_2 should not be dramatically affected.

Before we proceed, it is worth pointing out that the complex **XVI** closely resembles the ferrole, **VI**, with the basic difference that the butadienyl ligand carries only four π-electrons. A theoretical analysis of ferroles[12] pointed out that a dimer complex with the $C_4H_4^{2-}$ ligand in the upright position has a small HOMO (a_1)−LUMO (b_1) gap; hence, it is subject to second-order Jahn−Teller effects.[19] For an upright XCCX unit, we have shown that the interaction of the empty metal $1b_1$ level (see **XII**) with the filled ligand π level **XIV**, noded in the middle of the C−X vectors, cannot be large. This interaction is null in ferroles where the analog of **XIV** is empty, being the π^* LUMO of $C_4H_4^{2-}$. The bending of the *rider* toward one of the metals (seen as a JT deformation) allows the interaction of this LUMO with the filled combination of metal d_π/σ hybrids. The latter is essentially the level $1a_1$ of L_6M_2 which, for two d^7 metals as in **VI**, corresponds to the main M−M σ-bonding level (see diagram **XIII**). By rotation of one L_3M fragment with respect to the *sawhorse*, the corresponding metal atom acquires enhanced d_π features (compare the two situations in **XVII**). In the ferrole, $1a_1$ is used for back-donation into the LUMO of $C_4H_4^{2-}$ and up to three electron pairs end up to formally populate the butadienyl π system.

A similar picture applies to the Mn(I) dimer **XVI**. In this case the two electrons involved belong to the ligand (the filled $2b_1$ level **XIV**), whereas, for d^6 metals, the combination $1a_1$ (or the one derived from it after the symmetry is lowered from C_{2v} to C_s) must be considered empty. Still a major question needs to be addressed. Is there still a direct M−M σ bond, if the M−M overlap in $1a_1$ is evidently diminished (see **XVII**) and the $1a_1$ level itself is devoted to metal−ligand bonding?



XVII

Indeed, the local metal environments are now quite different. The η^2 coordination of the C=C bond allows the rightmost metal atom (d^6) to achieve a stable pseudo-octahedral geometry whereas the other metal (also d^6) is best approximated to a square pyramid. To simplify the picture, the leftmost metal atom is assigned an empty σ hybrid which appears as that depicted in **XVII** (right side drawing) but belongs more to the FMO descending from $2b_1$ (σ^*_{M-M} in **XIII**). Eventually, the direct M−M interaction is best described as a dative bond from one low-lying, filled, and properly oriented t_{2g} orbital of the octahedral metal atom into the σ-hybrid at the square pyramid. The interpretation is confirmed by a FMO analysis, by the sufficiently large[20] Mn−Mn ROP (*ca.* 0.1), and by the fact that one low MO (formerly belonging to the t_{2g} block in **XII**) assumes the aspect of an M−M σ-bonding level. The picture

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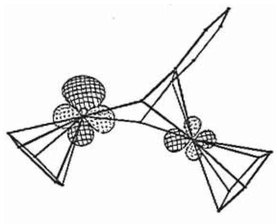
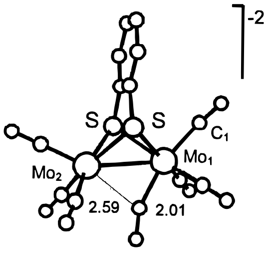
applies to ferroles as well with the difference that the Fe atom, η^4 coordinated to the butadienyl dianion, has a d^8 configuration, is saturated in the pseudo-five-coordinated environment and uses one low *xz*-type nonbonding orbital in the dative M−M bonding.

Addition of an Extra Ligand to the L_6M_2(*μ*-XCCX) Framework. The qualitative picture, illustrated at the end of the previous section, assigns acidic character to the square-pyramidal metal atom which is not dihapto coordinated to the C=C linkage. This can be saturated by a *lone pair* of the other metal (M−M bond) or, perhaps better, by a strong two electron donor with the loss of the direct M−M linkage. A significant example is provided by the characterized complex Cp*Ru(*μ*-SC_6H_4S)Cp*P$(OCH_3)_3$, Cp* = C_5Me_5, obtainable *via* the nucleophilic attack of trimethoxyphosphine to the precursor containing a Ru−Ru linkage.[21] The structure of the latter precursor is undetermined but is likely of the type **XVI** with the dithiocatecholate ligand bent over one metal atom. We have used a model with two Cp ligands, both displaced opposite to the SCCS *rider* (*syn* conformation). The opening of the dihedral angle RuSSRu evidentiates the formation of a low, empty *σ*-hybrid at the less coordinated Ru atom (see **XVIII**). Significantly, the phosphine ligand in the final product gets positioned just on the same side as the *rider*.



XVIII

In actuality, the experimental structure contains two Cp* ligands. In view of their hindrance and the required Ru−Ru bond, the *anti* conformation is most reasonable in the precursor. The *syn* conformer seems attainable only if the M−M linkage breaks up. Thus, the overall mechanism for the attack of a two electron donor may be rather complex and should account not only for the relative weights of Ru−P bond formation *vs* Ru−Ru bond breaking but also for the role played by the M−η^2-C=C linkage. Does the SCCS unit always donate 10 electrons to the metals or does it shift to the *upright* position thus allowing the M−P and the M−M bonds to coexist at some point? The latter situation is indeed substantiated by the dianionic complex $[(CO)_7Mo_2(\mu\text{-}SC_6H_4S)]^{2-}$ [22] shown in **XIX**.



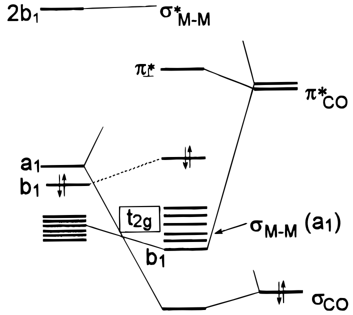
XIX

Here, a seventh CO terminal ligand completes the octahedron at the rightmost d^6 metal atom (the carbonyl in question shows an incipient bridging character indicated by the angle Mo_1−C−O of 164°). In turn, the latter metal uses one t_{2g} *lone pair* to saturate the empty *σ* hybrid which forms at the facing square pyramidal center. In spite of the same electron counting as in the above Cp_2Ru_2 derivative, the addition of a seventh ligand into the L_6M_2 framework favors the cleavage of the M−η^2-C_2 linkage rather than that of the M−M bond itself.

In contrast to the MO scheme **XIII** and to the leftmost drawing in **XVII**, the *ca.* 15° upward rotation of the $(CO)_3Mo$ fragment, at the right side, strongly reduces the M−M bonding character from the FMO $1a_1$. Also, for a d^6−d^6 configuration the latter level is empty and localized at the atom Mo_1. Eventually, it becomes the acceptor of the *σ* lone pair of the seventh CO ligand. On the other side, the residual acidity of the atom Mo_2 is formally saturated by one lower t_{2g} *lone pair* located at the atom Mo_1 itself. Thus the level $2b_1$ (see **XIII**) maintains a specific M−M *σ** character even though the direct interaction is weak in view of the long Mo−Mo separation of ca. 2.98 Å.

The situation just described seems to be critically affected by the nature and the energetics of the metal orbitals themselves. In fact, in the Cr_2 analog of **XIX** [with the dianion $S(C_6Cl_4)S^{2-}$ as *rider*][22] the seventh CO ligand is symmetrically bridging (average Cr−C_{bridge} = 2.09 Å). The shorter M−M separation 2.66 Å is perhaps indicative of stronger Cr−Cr *vs* Mo−Mo bonding, but it mainly reflects the different atomic radii.

The overall bonding picture can be interestingly compared with that of the classic diiron enneacarbonyl, $(CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_3$, for which the existence of a direct Fe−Fe bond has been the subject of some controversy. The point has been previously addressed also by one of us in terms of both qualitative and more quantitative (*ab-initio*) computational approaches.[24] By consideration of the central levels of diagram **XIII** [corresponding to the generic unit $L_3M(\mu\text{-}XCCX)ML_3$], their interactions with the frontier MOs of the bridging CO are easily interpreted (see **XX**).



XX

Thus the former M−M bonding level a_1 (empty for the d^6−d^6 dimer) interacts strongly with the carbonyl lone pair (a_1 in **XXI**). Also, it is evident that a low *out-of-phase* combination of *in-plane* t_{2g} levels back-donates electrons into the *in-plane* *π** level of the CO bridge (b_1 in **XXI**).

Concerning the direct metal−metal interactions, while the high-lying MO $2b_1$ maintains a clear-cut *σ** character, the corresponding *σ* MO of a_1 symmetry is found within the bulk of "t_{2g}" levels in analogy to what proposed for $Fe_2(CO)_9$.[24] Formally, the metal−metal bonding is possible because another filled "t_{2g}" level with *σ** character (b_1 in **XXI**) becomes devoted to metal−bridge bonding thus reducing the direct metal−metal repulsion.

The symmetric arrangement of $Cr_2(CO)_7$ skeleton implies a covalent nature of the metal−metal bond, while in the asym-

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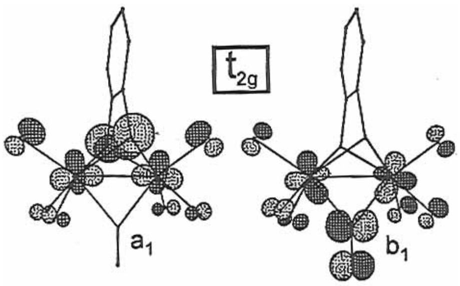
(20) On the basis of some previous experiences with direct M−M bonding by using the ehmo method, positive OP values, even lower than 0.1, are already indicative of a good interaction (see ref 24).

(21) Hornig, A.; Englert, U.; Kolle, U. *J. Organomet. Chem.* **1994**, *464*, C25.

(22) Zhuang, B.; Huang, L.; He, L.; Lu, J. *Inorg. Chim. Acta* **1989**, *160*, 229.

(23) Sellmann, D.; Wille, M.; Knoch, F. *Inorg. Chem.* **1993**, *32*, 2534.



XXI

metric $Mo_2(CO)_7$ derivative we admit a dative bond from the octahedrally saturated center to the square pyramidal one. The point deserves further comments. An appropriate modeling of the interconversion between the two possible tautomers (for both Mo and Cr species) indicates that the relative energetics are quite flat (fluctuations in the order of 4 kcal/mol). Accordingly, the ehmo method is inadequate to predict the most stable structure of a given metal species whereas the calculated redistribution of metal charges for the increasing asymmetry of the CO bridge is significant. Perhaps counterintuitively, the five-coordinate metal atom (Mo_2 in **XIX**) becomes electron richer than the octahedral analog (by 0.1 electrons for the model with terminal CO). While the residual acidity of the unsaturated d^6 metal is mainly directional, three inert "t_{2g}" lone pairs are localized at it. By contrast, the octahedral metal uses one "t_{2g}" lone pair for the dative bonding. The simple considerations on electron counting and on the role of metal orbitals in clusters, presented elsewhere,[25] help to clarify these points.

For polymetallic species, a system of two equations provides the number of expected M−M bonds (m) and the total number of metal lone pairs (n). This is based on the simple idea that, after discarding the metal orbitals used for M−L bonding, only the M−M bonding and the metal nonbonding levels can be doubly occupied. For dimers with (**XXII**) or without (**XXIII**) the bridging carbonyl, the equations involve the total number of metal orbitals ($9V$) for V metal atoms (=2), the total number of M−L bonds ($L = 12$ and $L = 11$ for the CO bridged and unbridged dimers, respectively) and the total valence electron count ($T = 34$).

$$2m + n = 9V - L = 18 - 12 = 6$$
$$2m + 2n = T - 2L = 34 - 24 = 10$$

XXII

$$2m + n = 9V - L = 18 - 11 = 7$$
$$2m + 2n = T - 2L = 34 - 22 = 12$$

XXIII

Obviously, the solutions of **XXII** are $m = 1$ and $n = 4$, while those of **XXIII** are $m = 1$ and $n = 5$. The result is a guideline to interpret the MO results. Consistently with the EAN rule,[3] there is always a single M−M bond while an extra *lone pair* is expected for the asymmetric dimer. If one starts from the diagram **XX** (only four of the six t_{2g} levels can be considered lone pairs), the visual analysis itself suggests that, on increasing the asymmetry, one "t_{2g}" orbital of the octahedral metal is used to saturate the empty σ hybrid of the five-coordinated center whereas another t_{2g} member localizes more at the latter center. Given the greater diffuseness of the molybdenum d orbitals (and more in general of the elements of the 2nd and 3rd transition rows), a direct M−M interaction is more feasible and need not to be subtly mediated by the metal−carbonyl bridge bonding, a situation which is apparently even more controversial than the existence of the M−M linkage itself.[24]

Computational Details

All the MO calculations were of the extended Hückel type[26] (ehmo) using a weighted-modified Wolfsberg−Helmholz formula.[27] The literature STO parameters were used for Ru,[28] Fe,[29] Mo,[29] Cr,[29] and Mn,[30] and the standard ones, for the main group elements. The 3D drawings and correlation and/or interaction diagrams were performed with the program CACAO.[15] In general, the structural models were constructed to approximate at the very best the geometries of the reported crystal structures. In particular, the model of the *sawhorse* + *rider* complexes, used to build up the interaction diagram **XIII** and the related arguments, does basically reproduce the structure of $[(CO)_2(PPh_3)Ru\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}Ru(PPh_3)(CO)_2]^2$ with H atoms in place of Ph groups. The CACAO input files are available from the authors on request.

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