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Molecular-orbital study of a quasi-linear Ru_2Mo trinuclear compound with a diamidolene ligand across each metal–metal linkage‡

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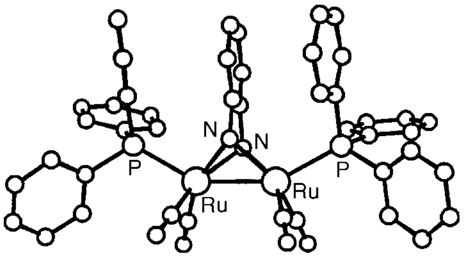
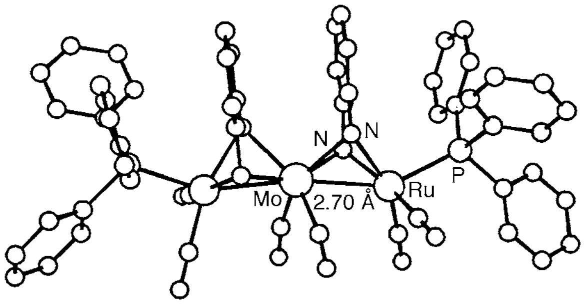
The electronic structure of the trinuclear compound $[(Ph_3P)(OC)_2Ru\{\mu\text{-}C_6H_4(NH)_2\}Mo(CO)_2\{\mu\text{-}C_6H_4(NH)_2\}\text{-}Ru(CO)_2(PPh_3)]$, with a diamidolene ligand riding upright over each of the quasi-collinear Ru−Mo linkages, has been investigated by means of the extended-Hückel method and a graphic interface. The ability of the dianionic riders to donate eight electrons to adjacent metals is interpreted, similarly for related Ru_2 dimers, in terms of perturbation theory. The molecule's distortion, from the highest possible C_{2v} to C_2 symmetry, was parametrized and the effects on the overall chemical bonding evaluated. The nature of the extended Ru−Mo−Ru linkage is addressed in some detail. The electronic redistribution over the ruthenium and molybdenum atoms is discussed in terms of their limiting oxidation states. Inferences are made as to the structure of a chromium analogue of the $MoRu_2$ compound, as yet unknown.

The bidentate diamide $[C_6H_4(NH)_2]^{2-}$ is able to donate four electron pairs when riding upright on binuclear fragments of the type L_6M_2 (sawhorse). Some of us[1] have previously reported the synthesis and the crystal structure of the dimeric species $[(Ph_3P)(OC)_2Ru\{\mu\text{-}C_6H_4(NH)_2\text{-}1,2\}Ru(CO)_2(PPh_3)]$ **1**. A derivative with a $\mu\text{-}Ph_2PCH_2PPh_2$ ligand in place of two carbonyls has also been characterized.[2] Similar compounds exist with conjugated diphosphidolene[3] and dithiolene[4] ligands and, usually, the replacement of N with the better donating S or P atoms results in an elongation of the M−M bond. By contrast, the 1,2-dioxolene anions (catecholates) do not seem to support the bridging co-ordination mode which implies the donation of four electron pairs to two metals. A theoretical study of these dimers has just been completed[5] to determine the electronic factors affecting the stereochemistry of the bridge and the strength of the M−M bond as well as to find a rationale for the different behaviour of dioxolenes.

During synthetic studies not only the mononuclear five-co-ordinated precursor $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ was treated with $[Ru(CO)_3(PPh_3)_3]$ to produce the dimer **1**, but also its reactivity toward $[M(CO)_6]$ (M = Cr, Mo or W) was tested.[6] In particular, a novel trinuclear species $[Ru_2Mo\{\mu\text{-}C_6H_4(NH)_2\}_2\text{-}(CO)_6(PPh_3)_2]$, **2**, was synthesized and characterized crystallographically. The overall molecule is significantly distorted from the highest possible C_{2v} symmetry and the three metals do not lie in a perfectly linear arrangement (Ru−Mo−Ru 167°). However, over each metal–metal linkage of *ca.* 2.70 Å one diamidolene ligand roughly maintains the same upright bridging mode as in the binuclear Ru_2 species **1** (a minor 10° tilting of the planar C_6N_2 skeleton about the N···N vector and toward the central Mo atom is observed).





To a first approximation, since the lateral moieties $(Ph_3P)(OC)_2Ru[(HN)_2C_6H_4)]$ are almost superimposable in compounds **1** and **2**, one could imagine the trimer as arising from the dimer upon replacement of one terminal unit $(Ph_3P)\text{-}(OC)_2Ru$ with the bulkier binuclear fragment $(Ph_3P)(OC)_2Ru\text{-}\{\mu\text{-}C_6H_4(NH)_2\}Mo(CO)_2$. As mentioned, such an assembly does not necessarily imply that the symmetry planes of the component fragments are maintained in the final complex. Ultimately, the trimer possesses at best a C_2 axis bisecting the central $(OC)_2Mo$ unit (other significant details of the stereochemistry will be illustrated subsequently). Quite interestingly, a search in the Cambridge Structural Database[7] shows only one other trinuclear species which is electronically and stereochemically comparable with **2**, namely the complex $[(OC)_3Fe(\mu\text{-}Bu^tS)_2\text{-}Mo(CO)_2(\mu\text{-}Bu^tS)_2Fe(CO)_3]$ **3**.[8] In the latter, two independent Bu^tS groups lie almost at the same positions as the nitrogen donors of the chelate diamidolene. Although the less constrained bridges seem to allow a larger molecular flexibility (in particular, the trimetallic unit is more bent with the angle

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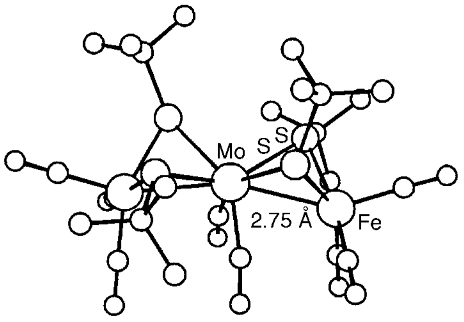
‡ *Non-SI units employed*: eV ≈ 1.60×10^{-19} J, cal = 4.184 J.



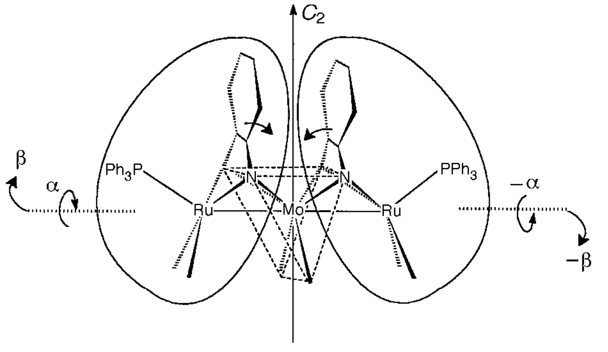
Fe–Mo–Fe being 160°), the two structures **2** and **3** are quite comparable. This is confirmed by very fine details such as the non-linearity of the two carbonyl ligands terminally bound to the central molybdenum atom. The *ca.* 10° bending of the angle Mo–C–O and the fact that both the C and O atoms lie in the same plane as the Mo–Ru vector suggest an incipient semi-bridging nature. In other words, each Ru or Fe atom appears to exert residual co-ordination ability toward one CO ligand which acts mainly as a two-electron donor toward molybdenum.

Intuitively, the deformational trends observed in these structures are meant to improve the strength of the overall metal–ligand and perhaps intermetal bonding. In this paper, we try to interpret for compound **2** how the relative orientation of the two bridging diamidolenes (between themselves and with respect to the L_3Ru and L_2Mo units) can influence the molecular orbital (MO) picture. From the latter we derive significant pieces of information on the nature of the intermetal bonding itself. In this task we exploit mainly the qualitative concepts of perturbation theory, as they can be developed from the results of extended-Hückel molecular orbital (EHMO) calculations[9] and interpreted with the graphic interface of the package CACAO.[10]

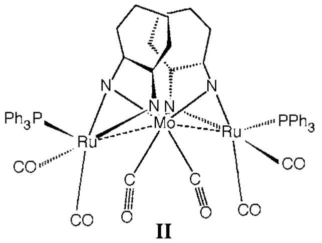
Results and Discussion

A model of the Ru_2Mo compound with the highest possible C_{2v} symmetry is shown in **I**. As mentioned it is related to the dimer **1**, since one terminal L_3M fragment of the latter is formally replaced by the bulkier fragment $Mo(CO)_2[\mu\text{-}C_6H_4(NH)_2]RuL_3$. In the starting geometry **I**, the Ru–Mo–Ru angle is 180° and the two L_3Ru fragments, as well as the two parallel diamidolene bridges, are mutually eclipsed whereas the $(OC)_2Mo$ plane bisects the two molecular halves. The co-ordination geometry at the Mo atom adapts to the trigonal prism highlighted by dashed lines in **I**.

We have found that it is possible to convert this geometry into that of the experimental C_2 molecule *via* a number of combined parametrizations. The most drastic ones are the screw motions α (in opposite directions and up to a maximum of 35°) of the two fragments $L_3Ru[\mu\text{–}C_6H_4(NH)_2]$ about the corresponding Mo–Ru axes which deviate from collinearity by *ca.* 13°. Moreover, since the vector (hence, the plane) Ru_2Mo reorients with respect to the fixed $(OC)_2Mo$ plane (the dihedral angle β ranges between 90 and 65°), the screw motion of the two Ru-centred fragments (of the type L_5M) is best described as that of two *anti*-propellers (working *via* combined α and β rotations). Finally, the *ca.* 10° bending of the planar bridges about the N · · · N axes and to the side of the central molybdenum atom is also mimicked. It is noteworthy that, upon the structural rearrangements, the co-ordination at the molybdenum changes from trigonal prismatic to pseudo-octahedral as highlighted in sketch **II**. Here, the plane of the drawing coincides approximately with the octahedral equatorial plane at the Mo atom: the latter is defined by the two CO ligands (slightly bent with angles Mo–C–O of *ca.* 170°) and two N atoms of different diamidolenes. The other two N donors are roughly axial as the angle N–Mo–N is not larger than 153°. It is also noteworthy that the Mo–Ru vectors, although non-collinear, pierce two opposite faces of the pseudo-octahedron at molybdenum (each face is defined by the two N atoms of the same chelate and by one CO ligand). The non-linearity of the Ru–Mo–Ru group is of importance to fix the nature of the intermetal bonding network (see below). By combining at subsequent steps all of the motions described above, the interconversion from the ideal (**I**) into the real system (**II**) can be monitored in terms of a global deformational co-ordinate. Indeed, it is strategically important to elucidate first the electronic structure of the most symmetric model (C_{2v}) with the various MOs subgrouped in a larger number of orthogonal classes. Subsequently, it becomes easier to follow the topological rearrangement and the mixing of the various orbitals when the symmetry is lowered to C_2.



I



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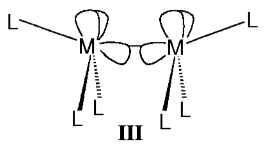
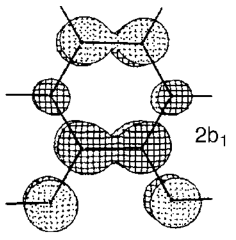


III

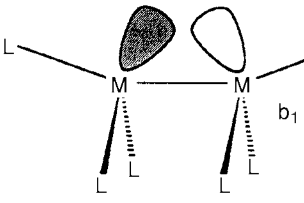
Before proceeding to the MO analysis, it is necessary to summarize some electronic features of the dimers of type **1**.[5] Their understanding is simplified by referring to the classic compounds M_2L_{10} (M = Mn or Re, L = CO) in which two square pyramids are glued together at their bases. Hence, two pairs of eclipsing equatorial carbon monoxides can be replaced by one bridging diamidolene, provided that the residual fragment L_6M_2 adapts to the sawhorse shown in **III**. The latter with C_{2v} symmetry is characterized by two sets of three hybrids at each metal atom (these are the typical frontier orbitals of L_3M fragments which lie above the t_{2g} set[11]).

The MO analysis[5] has shown that four of the latter hybrids (considered acceptors) are engaged in bonding–antibonding interactions with symmetry combinations (a_1, b_1, a_2 and b_2) of two σ and two π levels of the riding dianion. However, one of the four dative bonds, of type b_1, is critical. The π-conjugated bridge can barely use a low-lying π-bonding level as a donor ($1b_1$), whereas the involvement of the better energy-located highest occupied molecular orbital (HOMO) ($2b_1$, **IV**) is complicated by its nodal properties. In fact, the out-of-phase metal σ hybrids directed toward the diamidolene ligand (**V**) are bonding toward the lateral p_π orbitals of the nitrogen atoms and are, at the same time, antibonding toward the adjacent and central carbon orbitals.

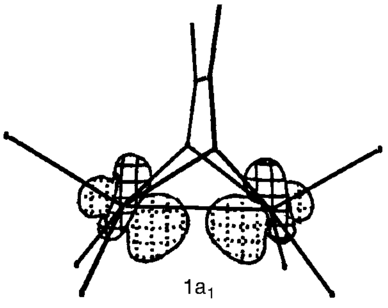
Ultimately, the co-operation of ligand $1b_1$ and $2b_1$ levels in



IV



V



VI

the donation of electrons guarantees the fourth bonding interaction between the metals and the bridge. The latter interaction is definitely improved in the presence of donors with diffuse orbitals (diphosphidolene or dithiolene ligands), whereas the contraction and the high electronegativity of the oxygen heteroatoms prevents catecholates from riding on sawhorses.[5]

Another point which stems from the MO analysis of the dimers[5] is that the two in-plane combinations of the metal hybrids **III**, not involved in bridge bonding, are responsible for the Ru−Ru single bond. The latter hybrids are typical of square-pyramidal metal fragments and, while their σ* combination (b$_1$) lies empty at high energy, the σ partner (1a$_1$, **VI**) is filled for the d^7–d^7 configuration.

The Ru$_2$Mo compound, where one L$_3$Ru fragment is replaced by the more complex unit L$_3$Ru[μ-C$_6$H$_4$(NH)$_2$]Mo(CO)$_2$, is also characterized by terminal square pyramids at the Ru. The corresponding σ hybrids can now interact with opportune molybdenum orbitals. Thus, it is important to specify these combinations and to ascertain their role.

One viewpoint considers ruthenium(II) species with acidic character localized at the empty σ hybrids. In this case the neutral molybdenum (d^6) could utilize two different lone pairs (filled t$_{2g}$ levels at the octahedral centre) to make dative bonds with the empty ruthenium σ hybrids (see below). The opposite viewpoint implies localization of electron density at the two Ru atoms. The ruthenium(0) species, fully saturated in a square-pyramidal environment, would be exceptionally strong σ nucleophiles, while the central molybdenum (Mo^{IV}) would be the acceptor of two additional metal lone pairs (beside the six from the ligands). The trigonal-prismatic co-ordination of Mo would suit better in this case, but it is clearly avoided.

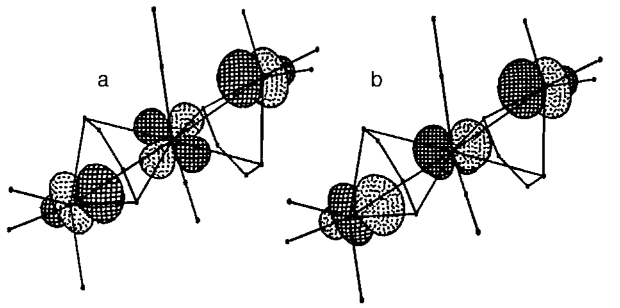
An intermediate hypothesis implies a double electron pairing between a molybdenum(II) species and the ruthenium(I) ones which also characterize the dimer **1**. Generally, a mononuclear, six-co-ordinated d^4 complex distorts from octahedral to keep diamagnetic, hence avoiding population of the triply degenerate t$_{2g}$ set with four electrons (Jahn–Teller effect).[11] Also the structure of the six-co-ordinated monomer [Mo{C$_6$H$_4$(NH)$_2$-1,2}(CO)$_2$(PPh$_3$)$_2$],[12] containing the same set of ligands as that of compound **2**, is significantly distorted. While the electronic effects in monomers[11] can hardly be extended to polynuclear species which present additional M−M interactions, it is true that neither of compounds **2** or **3** achieves a regular octahedral geometry at the central metal atom. In any case, it should not be forgotten that these structures are highly strained.

In assigning the most probable oxidation states of the metals, the trends in the ν(C≡O) data are also a good source of information. For example the IR wavenumbers of the CO ligands bound to molybdenum are larger for the d^4 monomer (1913 and 1826 cm^{-1})[13] than for compound **2** (1853 and 1795 cm^{-1}).[6] The latter data suggest a less electron-rich Mo atom in the monomer in spite of the strong basicity of the phosphine ligands and of the reduced efficiency of riding diamidolenes when they need to donate four electron pairs. Further support for a more electron-rich Mo atom in **2** comes from a comparison between the wavenumbers of the carbonyls bound to the Ru atoms in compound **2** (2022, 2008 and 1955 cm^{-1})[6] and in the dimer **1** (2002, 1968 and 1931 cm^{-1}).[1] The last values become even smaller for the dimeric derivative with dppm (1972 and *ca.* 1910 cm^{-1}),[2] thus confirming the idea of a higher basicity associated with the phosphines when bound to molybdenum. In conclusion, the experimental IR data suggest that the Ru atoms of **2** are more oxidized than the ruthenium(I) species present in the dimer. Significantly, the numerical EHMO results attribute to the Ru atoms a charge definitely more positive in **2** than in the dimer **1** (0.81 and 0.18, respectively).

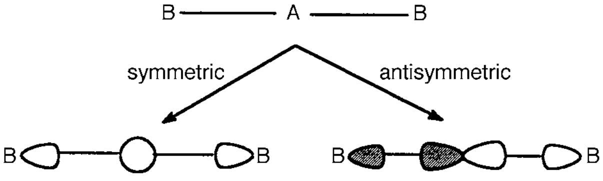
In the preceding paragraphs the possible distributions of the integer oxidation states at the metals have been illustrated. As is often the case in chemistry, limiting models of chemical bonding rarely depict the actual situation but serve as important reference points for the interpretation of the MO calculations. By anticipating here one of the conclusions, the Mo−Ru bonds are better described as weak dative bonds from two non-bonding levels at the central Mo atom (formally d^6) into empty acidic hybrids of the Ru atoms (also formally d^6).

The evolution of the MO levels during the interconversion from the ideal C_{2v} molecule into the experimental one (C_2) was followed in a Walsh diagram (not shown). The latter was constructed with the parameters defined in **I**. Not only the initially insufficient HOMO–LUMO (lowest unoccupied molecular orbital) gap of *ca.* 0.8 eV increases to >2.0 eV but also the total energy of the system is lowered by *ca.* 1.2 eV along the pathway: the gain is essentially due to some filled MOs centred at the molybdenum atom. This is not surprising as, in the starting trigonal-prismatic environment, the orbitals *xz* and *yz* (antibonding to the ligands) are destabilized with respect to orbital *xy* (non-bonding).[14] Thus for an electron count >d^2 rearrangement toward an octahedron is progressively favoured because also *xz* and *yz* become prevailingly non-bonding. In the present case, the distortion away from the trigonal prism at molybdenum (see **I**) reduces the importance of the Mo^{IV}/Ru^0 combination. Indeed, the pictorial MO analysis supports better the idea of centrifugal rather than centripetal electron flow, consistent with the combination Ru^{II}/Mo^0. The fragment molecular orbital analysis[15] of the interactions between the central (OC)$_2$Mo unit and the rest of the molecule (the overall model is close to the experimental C_2 structure) reveals significantly large overlap populations between the in- and out-of-phase combinations of the ruthenium σ hybrids and the molybdenum *xz* and *yz* types of orbitals. The drawings in **VII** present the latter interactions at the antibonding level (the LUMOs of the system). Importantly, the *xz* and *yz* orbitals of molybdenum (the *x* axis is across the page) lie *ca.* 2 eV deeper in energy than any ruthenium frontier σ hybrid (strongly destabilized by the *trans* axial ligand). According to perturbation theory,[16] the two bonding electron pairs are preferentially assigned to molybdenum (*i.e.* four of its six t$_{2g}$ electrons with the third electron pair occupying the non-bonding *xy* orbital).

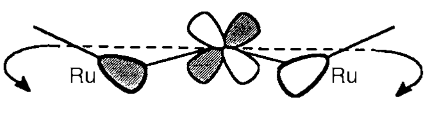
Looking at the right-hand part of **VII** (the central Mo atom lies deeper than the two Ru atoms), it is inferred that a number of structural factors improve the overlap between the two ruthenium σ hybrids (pointing toward the observer) and the upper lobes of the *xz* orbital. Essentially, there is a misalignment of the two *trans* phosphine ligands (the Ru−P and the Ru−Mo bonds form angles of *ca.* 148°) and a skewing of the



VII



VIII



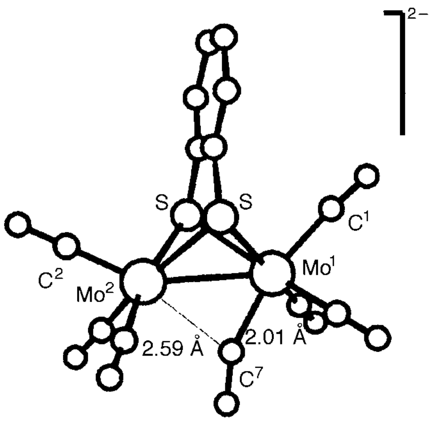
IX

RuL$_6$ octahedra (PRu···RuP torsion angle *ca.* 70°). Also important is the 13° bending of the Ru–Mo–Ru angle (in the MoFe$_2$ species **3** the bending is as much as 20°). Ultimately the distortive trends should favour the overall σ(Ru)–*xz*(Mo)–σ(Ru) interaction as the σ(Ru) lobes are pulled out of the *xz* nodal plane. In MO terms the A–B stick bonds of a linear AB$_2$ assembly ensue from interactions which are symmetric and asymmetric with respect to the orthogonal mirror plane (see **VIII**).

By assuming that the central Mo atom uses mainly the centrosymmetric d orbitals (given the six-co-ordination, its atomic orbital p_z is largely engaged with the ligands), the linearity of the extended Ru–Mo–Ru linkage could be consistent only with a three-centre two-electron model. Conversely, as shown in **IX** (the view is orthogonal to that in **VII**), the Ru–Mo–Ru bending (as well as the reorientation of the ruthenium σ hybrids) involves a second filled d orbital (*xz*) in what becomes an overall four-orbitals four-electron interaction. In conclusion, the structural details and the MO arguments offer jointly a rationale for the intermetal bonding and the preferential oxidation states of the metals.

As seen in structures **2**, **3** and **II**, the two CO ligands, terminally bound to molybdenum, are slightly bent so as to adapt to an incipient bridge-bonding mode in spite of the correspondingly long Ru–C separations of *ca.* 2.70 Å. The situation compares closely to that of the binuclear complex [(OC)$_3$Mo(μ-SC$_6$H$_4$S)Mo(CO)$_4$]$^{2-}$ [17] containing the dithiolate ligand as a rider between the fragments (OC)$_3$Mo and (OC)$_4$Mo (see **X**). One terminal CO ligand of the latter is also bent by *ca.* 10° and one Mo–C distance is significantly but not dramatically shorter than the other (2.01 and 2.59 Å, respectively). Interestingly, when the two Mo atoms are replaced by two Cr atoms the seventh CO ligand shifts to the fully bridging position, *e.g.* [(OC)$_3$Cr(μ-SC$_6$Cl$_4$CS)(μ-CO)Cr(CO)$_3$]$^{2-}$.[18]

Concerning the potential CrRu$_2$ analogue of MoRu$_2$ compound **2**, an alternative structure could be hypothesized. Each Ru–Cr bond could be bridged by one carbonyl ligand beside the diamidolene itself. While different strategies for the synthesis of the chromium derivative are still being elaborated,[19] a modelling of the interconversion between the two possible tautomers shows a very flat energy surface. The fluctuations are even smaller than those calculated for the dimeric tautomers (*ca.* 4 kcal mol^{-1}). Moreover, the small HOMO–LUMO gap of only a few tenths of an eV is by itself an indication of the instability of the alternative structure.



X

Simple considerations of electron counting, more than the always questionable quantitative response of the EHMO method, are helpful. One of us (C. M.) has previously proposed, for polynuclear compounds, a simple method which provides the number of M–M bonds (= *m*) and the number of free lone pairs at the metal atoms (= *n*).[20] A knowledge of the latter is important as their repulsion affects the strength of a given M–M linkage. For the CO-bridged and unbridged trinuclear compounds the values of *m* and *n* are calculated to be 2 and 7 and 2 and 5, respectively.§ While the number of M–M bonds is that predicted by the effective atomic number rule,[21] the seven lone pairs of the trimer with all-terminal CO ligands are consistent with the previous MO considerations. Recalling, that two of the three t_{2g} levels at the central metal atom were considered involved in dative, centrifugal M–M bonding, only the unused lone pair (*xy*) adds to the double set of t_{2g} nonbonding levels of the Ru atoms. Were the carbonyls bridging, one t_{2g} lone pair from each Ru atom would be involved in so-called back bonding to the carbonyl π* levels, hence the prediction of five metal lone pairs. In the interpretation of the overall MO picture these guidelines are certainly useful. Even though M–M repulsions are lessened in the CO-bridged system, the nature of the direct intermetal M–M bonding is significantly changed. The difficulty in separating the M–M and M–(μ-CO)–M characters of various MOs recalls the controversial situation observed in [Fe$_2$(CO)$_9$] where the through-bridge coupling seems to overwhelm any direct Fe–Fe interaction.[22] In this respect, the drawings of the low-lying LUMOs (**XI**) are highly indicative. The latter correlate, along the unbridged–bridged interconversion pathway, with the CrRu$_2$ antibonding levels **VII**. It is evident that an increasing in-phase coupling between the metal orbitals and the CO π* orbital stabilizes these empty levels in the bridged structure (hence the small HOMO–LUMO gap). Indeed, the overall CrRu$_2$ antibonding character of the LUMOs is subtly balanced by the Ru(μ-CO)Cr(μ-CO)Ru bridge-bonding character and, eventually, the lack of electrons in these levels may become a serious problem for the stability of the whole system.

In conclusion, qualitative considerations seem to favour the unbridged structure **2** also for the CrRu$_2$ trinuclear compound.

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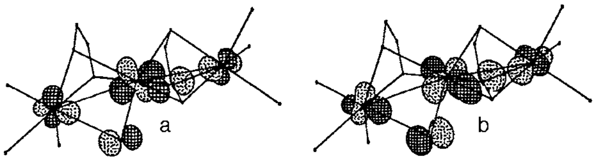
§ A system of two equations is written for the case with terminal CO groups (system A) and for the case with bridging CO groups (system B). The two sets of equations, to be solved for *m* and *n*, involve the total number of metal orbitals (9 × 3 = 27) available for the $V = 3$ metal atoms, the total number of metal–ligand bonds (L = 16 and 18, respectively) and the total valence electron count ($T = 50$ in each case): system A, $2m + n = 9V - L = 27 - 16 = 11$, $2m + 2n = T - 2L = 50 - 32 = 18$; system B, $2m + n = 9V - L = 27 - 18 = 9$, $2m + 2n = T - 2L = 50 - 36 = 14$.



XI

On the other hand, first-row transition metals are known to favour bridging CO because their d orbitals, too contracted, do not allow sufficient direct M−M interaction at long separations. Quantitatively, the EHMO response cannot be considered reliable and any definite answer to the question requires more sophisticated calculations or, much better, the synthesis and characterization of the species in question.

Computational Details

All the MO calculations were of the extended Hückel type[9,23] using a weighted-modified Wolfsberg–Helmholz formula.[24] The literature Slater atomic orbital parameters were used for Ru,[25] Mo,[26] and Cr,[26] and the standard ones for the main-group elements. The three-dimensional drawings and correlation and/or interaction diagrams were constructed with the program CACAO.[10] In general, the structural models were drawn to approximate, at the very best, the geometries of the reported crystal structures. The CACAO input files are available from one of the authors (C. M.) on request.

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