Can μ_4-Alkyne and μ_3-Alkenyl Ligands Be Considered as Six- and Five-Electron Donors, Respectively?

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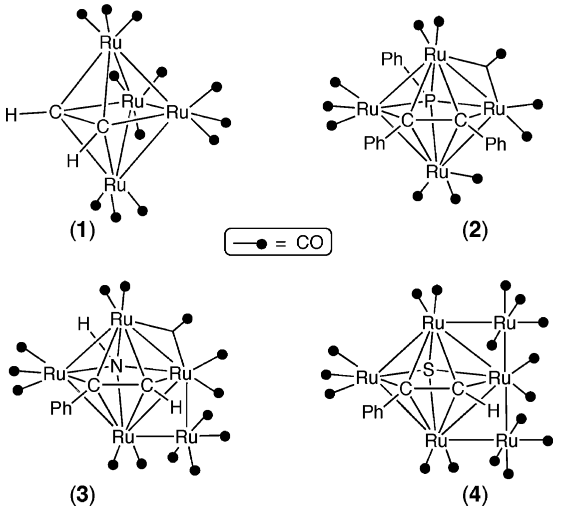
Summary: EHMO calculations have revealed that alkynes bridging four metal atoms are four-electron-donor ligands and that alkenyl groups bridging three metal atoms are three-electron-donor ligands. Therefore, the answer to the title question is "no". The clusters that contain these ligands have large HOMO−LUMO gaps, despite being electronically unsaturated (according to the EAN rules). These are the conclusions of the present contribution, which tries to shed light on the hitherto existing controversy about the number of electrons that these ligands contribute to the metal clusters that hold them.

Introduction

Transition-metal cluster complexes having quadruply bridging alkyne ligands are familiar to cluster chemists. In fact, searching the Cambridge Structural Database, we have found that, to date, there exist more than 160 X-ray structures of polynuclear compounds that contain these particular ligands.[1] Their nuclearity varies from 4 to 10, but most of them are tetranuclear. Ruthenium is the most represented metal, followed by cobalt and osmium. Although most compounds are homometallic, a considerable number of heterometallic clusters of this type are also known (ca. one-third).[1] The examples shown in Chart 1 correspond to the cluster compounds $[Ru_4(\mu_4\text{-}HCCH)(CO)_{12}]$ (**1**),[2] $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}PhCCPh)(\mu\text{-}CO)(CO)_{10}]$ (**2**),[3] $[Ru_5(\mu_4\text{-}NH)(\mu_4\text{-}PhCCH)(\mu\text{-}CO)(CO)_{13}]$ (**3**),[4] and $[Ru_6(\mu_4\text{-}S)(\mu_4\text{-}PhCCH)(CO)_{17}]$ (**4**).[5]

These complexes have always been accompanied by some controversy related to the number of electrons contributed by the alkyne ligand to the total electron count of their complexes. Many authors treat these ligands as four-electron donors in their cluster electron counts,[2,4−6] but other authors think that these ligands contribute six electrons to their clusters.[7] According to the EAN rules, the assumption that μ_4-alkyne ligands are four-electron donors results in the great majority of the known examples of clusters having these ligands being electronically deficient by at least two electrons, regardless of their nuclearity. For example, assuming that μ_4-alkyne ligands are four-electron donors, the electron counts for compounds **1**−**4** are 60, 62, 76, and 90 electrons, respectively. However, the EAN rules predict electron counts of 62, 64, 78, and 92 electrons, respectively, for these complexes.

Chart 1



It is also remarkable that these clusters generally obey the requirements of the polyhedral skeletal electron pair theory[8] and that a careful inspection of their molecular structures shows no evidence of metal−metal bond-localized unsaturations. In addition, their stability is considerable, since they generally require high temperatures to react with other compounds, and this is unexpected for unsaturated compounds.

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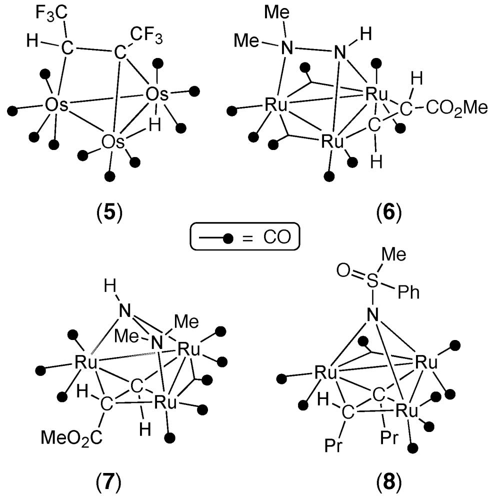
Chart 2



Therefore, it may be wrong to consider μ_4-alkyne ligands as four-electron donors in their clusters. But, can these ligands be considered as six-electron donors? A positive answer would imply the overlap of empty metal orbitals with the filled orbital responsible for the σ-component of the alkyne ligand C−C bond. However, in these clusters, the alkyne C−C distances are in the range 1.40−1.47 Å, which roughly corresponds to a single bond order.

In relation with this, bridging alkenyl ligands have always been considered as three-electron donors. It is curious that, with the exception of the closed (three M−M bonds) clusters $[Os_3(\mu\text{-}H)(\mu_3\text{-}CF_3CCHCF_3)(CO)_{10}]$[9] (compound **5** in Chart 2) and $[Ru_2W(\mu\text{-}NPh)(\mu_3\text{-}CF_3CCHCF_3)(C_5Me_5)(CO)_7]$,[10] most trinuclear clusters containing μ_3-alkenyl ligands are open (two M−M bonds) derivatives[11−13] (see, for example, compounds $[Ru_3(\mu_3\text{-}Me_2NNH)(\mu_3\text{-}CHCHCO_2Me)(\mu\text{-}CO)(CO)_7]$ (**7**)[11] and $[Ru_3\{\mu_3\text{-}NS(O)PhMe\}(\mu_3\text{-}CPrCHPr)(\mu\text{-}CO)(CO)_7]$ (**8**)[12] in Chart 2).

It should be noted that the way by which the μ_3-alkenyl ligand coordinates to the closed clusters is different from that observed in the open derivatives.

The cluster $[Ru_3(\mu_3\text{-}Me_2NNH)(\mu\text{-}CHCHCO_2Me)(\mu\text{-}CO)_2(CO)_6]$ (**6**), which has an edge-bridging alkenyl ligand and is an isomer of **7**, is a 48-electron closed derivative.[11] According to DFT calculations, complex **7** is thermodynamically more stable than **6**[11] and this is unexpected if **7** is coordinatively unsaturated. There is no doubt that the edge-bridging alkenyl ligand of complex **6** contributes three electrons to the cluster, but the same alkenyl ligand (this time in a face-capping position) should contribute five electrons to the open cluster **7**, if **7** obeys the EAN rules (50 electrons). Curiously, the alkenyl C−C distance of the face-capped compound **7**, 1.444(6) Å, is only slightly longer than that of the edge-bridged derivative **6**, 1.36(1) Å.[11] A question similar to that exposed above arises: can μ_3-alkenyl ligands behave as five-electron donors when the carbon atoms of the alkenyl moiety are still bonded to each other? As above, a positive answer would imply the overlap of empty metal orbitals with the filled orbital responsible for the σ component of the alkenyl ligand C−C bond.

To shed some light on this controversial situation, we decided to perform molecular orbital calculations on cluster complexes containing μ_4-alkyne and μ_3-alkenyl ligands. The present contribution describes the results of these calculations.

Results and Discussion

Molecular orbital calculations were performed on two representative cluster complexes: namely, complex **1** (as an example of a cluster having a μ_4-alkyne ligand) and $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$, a simplified model of complex **7** (as an example of a cluster having a μ_3-alkenyl ligand). The calculations were carried out at the extended Hückel level,[14] using the fragment molecular orbital (FMO) approach. The characteristics of the bonding between the organic (alkyne or alkenyl) fragment and the corresponding metallic cluster fragment were elucidated by analyzing the overlaps between their FMOs. This allowed us to identify the FMOs of the organic fragment that are involved in the bonding of this fragment with the cluster metallic core.

For complex **1**, four overlaps between FMOs of the alkyne and FMOs of the tetrametallic fragment account for 77% of the bonding between these two fragments (Figure 1). Many other minor overlaps (with individual contributions <3%) are responsible for the remaining 23%.

The overlaps between FMO7 and FMO8 of the alkyne fragment with FMO3 and FMO2, respectively, of the metallic fragment account for the two σ-type interactions between the C atoms of the alkyne fragment and the Ru atoms of the butterfly hinge of **1**. The overlap between the metallic FMO4 and the organic FMO6 implies electronic donation from the bonding π orbitals of the C−C bond to the wingtip metals, and the FMO1 to FMO9 overlap implies electronic retrodonation from the metals to the empty antibonding π orbitals of the C−C bond. These two overlaps imply a considerable reduction of the C−C bond order, since they practically destroy the π components of the C−C bond. However, the σ component of the alkyne C−C bond is negligibly affected by the attachment of this fragment to the metallic core, because the overlaps of its FMO5, which is mainly responsible for the σ component of the C−C bond, with metallic orbitals are negligible (they account for less than 3% of the total bonding). Therefore, as FMO6 and FMO7 are the only filled alkyne orbitals involved in the bonding of this ligand with the tetrametallic fragment, *the alkyne ligand of complex **1** is a four-electron donor*.

For the trinuclear face-capped alkenyl complex $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$, three overlaps between alkenyl FMOs and trimetallic FMOs account for 86% of the bonding between these two fragments

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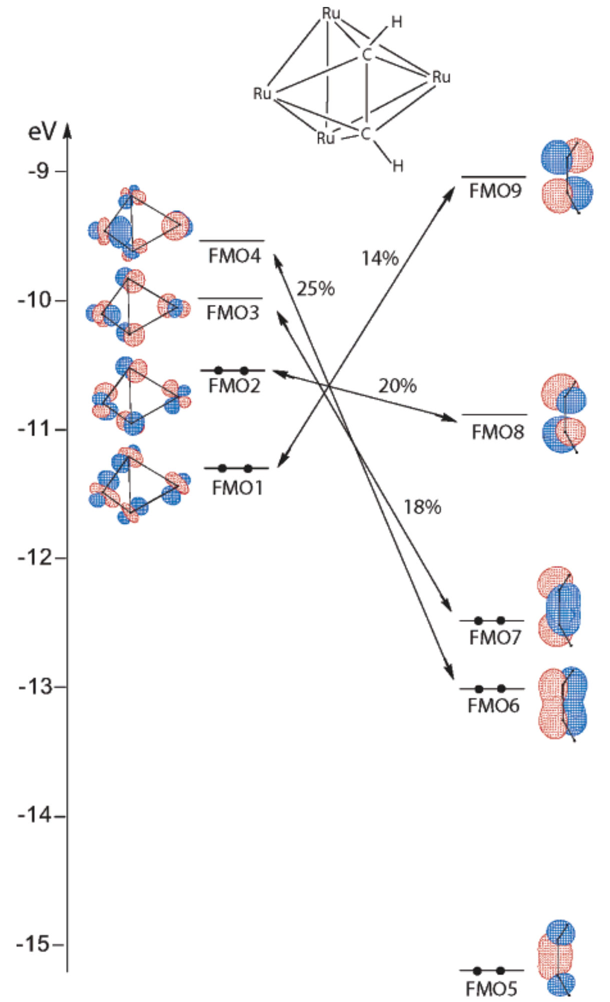

Figure 1. Diagram showing the most important overlaps between FMOs of the tetraruthenium (left) and alkyne (right) fragments of compound **1** (the arrows connect the overlapping orbitals). The percentages indicate the contribution of the corresponding overlap to the bonding between the two fragments. For clarity, CO ligands are not represented.

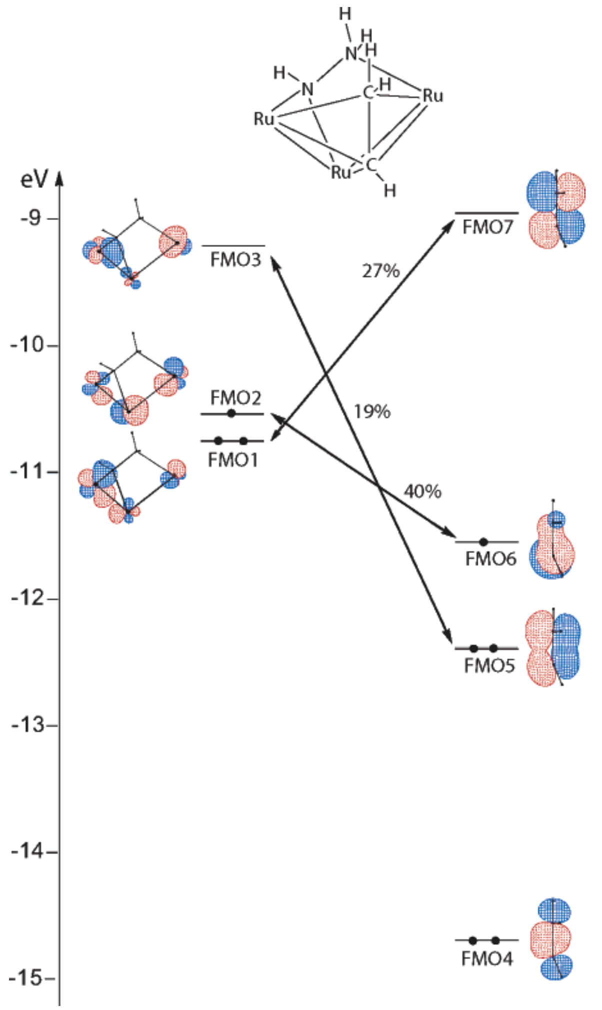

Figure 2. Diagram showing the most important overlaps between FMOs of the triruthenium (left) and alkenyl (right) fragments of $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$ (the arrows connect the overlapping orbitals). The percentages indicate the contribution of the corresponding overlap to the bonding between the two fragments. For clarity, CO ligands are not represented.

(Figure 2). Other minor overlaps (with individual contributions <4%) are responsible for the remaining 14%. The overlap between the alkenyl FMO6 and the metallic FMO2 is responsible for the σ-type interaction between the alkenyl fragment and one of the Ru atoms attached to the amido NH moiety of the hydrazido ligand. The overlap between the metallic FMO3 and the alkenyl FMO5 implies electronic donation from a bonding π orbital of the C−C bond to the two remaining Ru atoms, and the FMO1 to FMO7 overlap implies electronic retrodonation from the metals to the empty antibonding π orbital of the C−C bond. These two overlaps practically destroy the π component of the C−C bond. Interestingly, the σ component of the alkenyl C−C bond remains intact after the attachment of this fragment to the metallic core, because the overlaps of the alkenyl FMO4, which is mainly responsible for the σ component of the alkenyl C−C bond, with metallic FMOs are negligible (they account for less than 1% of the total bonding). Therefore, as FMO5 and FMO6 are the only electron-containing orbitals of the alkenyl fragment involved in the bonding with the trimetallic fragment, the cluster $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$ contains a *three-electron-donor alkenyl ligand*.

The bonding situations in these μ_4-alkyne and μ_3-alkenyl cluster complexes are in fact comparable. The organic fragment of these compounds can be viewed as a C=C moiety that is σ-bonded to four groups (two M and two R in the μ_4-alkyne derivatives, and one M and three R in the μ_3-alkenyl derivatives) and π-bonded to two metal atoms. Therefore, the previous questions can be reformulated as, can an alkene be considered as a four-electron donor when it is π-bonded to two metal atoms? As shown above, the answer is "no". The fact that accounts for this answer is that the energy gaps between the orbital responsible for the σ component of the ligand C−C bond and the empty metallic orbitals of proper symmetry are too large for effective overlaps.

Therefore, as far as the EAN rules are concerned, the cluster compounds that are the subject of this work are unsaturated. Generally, unsaturated compounds have a small HOMO−LUMO gap, but this is not the case for compounds **1** and $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$, whose computed HOMO−LUMO gaps are 1.79

eV (41.3 kcal/mol) for the former and 2.28 eV (52.6 kcal/mol) for the latter. Therefore, it is not so rare that unsaturated compounds have a large HOMO−LUMO gap. In addition, the remaining gaps between molecular orbitals of the frontier region (HOMO − 1 and HOMO, LUMO and LUMO + 1, etc.) are very small. This implies that other electron counts would result in less stable structures. These facts account for the high stability of the cluster types studied in this work, which, as commented upon in the Introduction, contrasts with the instability of most unsaturated compounds.

As far as we are aware, only one previous theoretical study on cluster complexes having a μ_4-alkyne ligand has been published. It reports EHMO calculations on $[Ru_4(\mu_4\text{-}\eta^2\text{-}CH_2CHCCH)(CO)_{12}]$, a cluster in which the bridging ligand is an enyne coordinated through the alkyne carbon atoms. A large HOMO−LUMO gap is mentioned (the value is not given). Although the authors assume that the enyne ligand is a four-electron donor, they do not specifically study the number of electrons contributed by this ligand to the cluster electron count.[15]

It has also been reported that the EHMO-computed HOMO−LUMO gap of the alkenyl cluster $[Ru_3\{\mu_3\text{-}NS(O)H_2\}(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$, a simplified model of complex **8** (Chart 2), is large (2.01 eV), but the authors of that work do not mention which FMOs of the alkenyl fragment are involved in the bonding of this ligand with the metal atoms.[16]

Concluding Remarks

EHMO calculations have demonstrated that μ_4-alkyne and μ_3-alkenyl ligands of polynuclear carbonyl cluster complexes are four- and three-electron donors, respectively. With this ligand electron assignment, most of these clusters do not obey the EAN rules, resulting in electronic unsaturation. However, they have large HOMO−LUMO gaps, in agreement with their experimental stability.

Although the EAN rules are frequently used in cluster chemistry to predict the number of CO ligands or the hapticity of a particular ligand in a cluster complex, the data reported in the present work suggest that, for carbonyl clusters containing μ_4-alkyne and/or μ_3-alkenyl ligands, the use of the EAN rules should be discouraged.

Computational Details

Molecular orbital calculations were performed at the extended Hückel level,[14] using the CACAO program package.[17] The standard CACAO parameters were used for all atoms. The input structural parameters for complex **1** were taken from its X-ray structure.[2] The input structural parameters for the model compound $[Ru_3(\mu_3\text{-}H_2NNH)(\mu_3\text{-}CHCH_2)(\mu\text{-}CO)(CO)_7]$ were based on those of the X-ray-characterized cluster $[Ru_3(\mu_3\text{-}Me_2NNH)(\mu_3\text{-}CHCHCO_2Me)(\mu\text{-}CO)(CO)_7]$ (**7**),[11] which was conveniently modified by replacing its methyl and methoxycarbonyl groups with hydrogen atoms.

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