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Electron counting and bonding analysis in triruthenium clusters containing sulfoximido ligands: true or false electron-deficient systems?

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Abstract

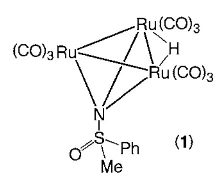
Triruthenium clusters containing a methylphenylsulfoximido cap or bridge, $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)MePh]$ (**1**), $Ru_3(CO)_{10}(\mu_2\text{-}H)[\mu_3\text{-}NS(O)MePh]$ (**2**), $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}CPhCHBu)[\mu_3\text{-}NS(O)MePh]$ (**3**), $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PhCCCCHPh)[\mu_2\text{-}NS(O)MePh]$ (**4**), and $Ru_3(CO)_7(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhCCCCHPh)[\mu_3\text{-}NS(O)MePh]$ (**5**) have been examined by EHT and DFT calculations in order to analyze the bonding present in the clusters and to establish the electron counting. They clearly show that a μ_3-sulfoximido group is not a $3e^-$ ligand as one may be led to think at first sight, but rather acts as a three-orbital/$5e^-$ system, i.e. should be considered as isolobal to an $N–R^-$ ligand. Because of some delocalization of its π-type orbitals on the sulfur and oxygen atoms, it is expected to bind slightly less strongly to metal atoms than classical imido ligands. Once in a μ_2 coordination mode, the sulfoximido ligand retains a lone pair on its pyramidalized N atom and becomes a two-orbital/$3e^-$ ligand. It follows that clusters **1**, **2**, **4** and **5** are electron-precise, whereas cluster **3** is electron deficient with respect to the $18e^-$ rule but obeys the polyhedral skeletal electron pair electron-counting rules. Consistently, all the calculated clusters exhibit large HOMO–LUMO gaps and no trace of electron deficiency can be found in their electronic structures.

Keywords: Bonding analysis; DFT and EHT calculations; Electron counting; Ruthenium clusters; Sulfoximido ligands

1. Introduction

Ruthenium clusters with optically active ligands have found considerable interest as potential catalysts for enantioselective reactions [1]. We therefore introduced the chiral methylphenylsulfoximido ligand into the trinuclear ruthenium system by reaction of $Ru_3(CO)_{12}$ with MePhS(O)NH. The only high-yield product of this reaction, $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)MePh]$ (**1**, Eq. (1)), which we isolated in both enantiomeric forms and characterized by single-crystal X-ray crystallography, was considered to be an electron-deficient $46e^-$ cluster (taking into account the sulfoximido cap as a $3e^-$ ligand [2].

$$Ru_3(CO)_{12} + MePhS(O)NH \rightarrow Ru_3(CO)_9H[NS(\mathbf{O})MePh] + 3CO$$
(**1**)



(1)

Although a normal electron count of $48e^-$ could not be ruled out for **1** (considering the μ_3-sulfoximido cap as a $5e^-$ donor, which would imply an $N^-–S^+$ formalism), several arguments were in favor of the electron-deficiency of **1**: capping N–R ligands act as $4e^-$ donors, and no $5e^-\text{-}\mu_3\text{-}N^-–R^+$ cap has been reported so far [3]. The sulfur–nitrogen bond in **1** (1.566 Å) [2] can be

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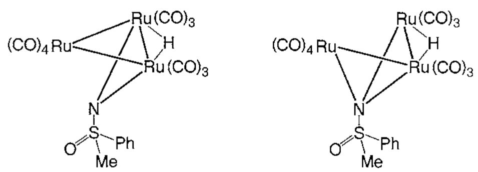
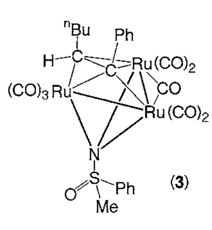
interpreted as an N=S double bond in comparison with methionylsulfoximine (1.529 Å) [4], which would leave 3e$^-$ on the nitrogen atom of the N=S(O)MePh fragment, in accordance with an electron count of 46e$^-$ for the cluster. In addition, apart from the slightly longer Ru–Ru bond carrying the μ_2-hydrido bridge (2.831 Å), the Ru–Ru bonds in **1** are distinctly shorter (2.674 and 2.683 Å) [2] than the average ruthenium–ruthenium distance in $Ru_3(CO)_{12}$ (2.854 Å) [5], which we interpreted in terms of two missing electrons in **1** with respect to the 18e$^-$ rule (48e$^-$ for the Ru_3 system). The most striking argument for the electron deficiency of **1** came from its reactivity: **1** was found to absorb carbon monoxide to give the addition product $Ru_3(CO)_{10}$-H[NS(O)MePh] (**2**, Eq. (2)) which we considered to have the normal electron count of 48e$^-$ [2].

$$\underset{(\mathbf{1})}{Ru_3(CO)_9H[NS(O)MePh]} + CO \rightarrow \underset{(\mathbf{2})}{Ru_3(CO)_{10}H[NS(O)MePh]}$$



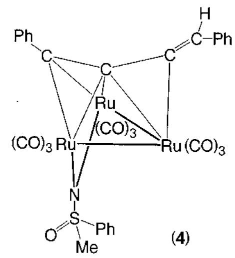
(2)

Cluster **2** was isolated and fully characterized by spectroscopic (IR, NMR and MS) and micro-analytical data, but, since no suitable crystals could be obtained, its structure is not known. We suggested **2** to contain a closed Ru_3 skeleton and a bridging 3e$^-$-sulfoximido ligand in addition to the hydrido bridge, $Ru_3(CO)_{10}(\mu_2$-H)[μ_2-N=S(O)MePh], but an alternative structure containing an open Ru_3 triangle and a capping 5e$^-$-sulfoximido ligand in addition to the hydrido bridge, $Ru_3(CO)_{10}(\mu_2$-H)[μ_3-NS(O)MePh], must also be considered.



(3)

The reactivity of cluster **1** towards alkynes turned out to be very interesting. Whereas terminal alkynes RC≡CH give the expected vinyl 48e$^-$ complexes of the type $Ru_3(CO)_{10}(\mu_2$-η^2-CH=CHR)[μ_3-NS(O)MePh] with a closed Ru_3 skeleton [6], internal alkynes react with opening of the Ru_3 framework. With PhC + CBu, the cluster $Ru_3(CO)_8(\mu_3$-η^2-CPhCHBu)[μ_3-NS(O)MePh] (**3**) is obtained [6], whereas PhC≡C-p-C_6H_4–NO_2 reacts with carbon–carbon coupling to give the clusters $Ru_3(CO)_9(\mu_3$-η^2-PhCCCCHPh)[μ_2-NS(O)MePh] (**4**) and $Ru_3(CO)_7(\mu_2$ - CO)(μ_3 - η^2 - PhCCCCHPh)[μ_3 - NS(O)-MePh] (**5**) [7]. Counting the NS(O)MePh ligand as a 3e$^-$ donor, **3** was considered as a 46e$^-$ cluster (the ligand PhC=CHBu being a 3e$^-$ donor), **4** as a 50e$^-$ cluster (the ligand PhC=C=C=CHPh being a 5e$^-$ donor), and **5** as a 48e$^-$ cluster (the ligand PhC + C–C=CHPh being a 5e$^-$ donor). As an open Ru_3 cluster requires 50e$^-$ with respect to the 18e$^-$ rule, **4** should be electron precise, **5** (short of 2e$^-$) and **3** (short of 4e$^-$) should be electron deficient [6,7].



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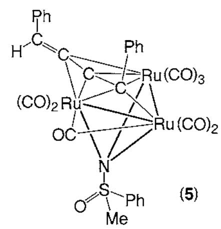


(5)

The number of electron-deficient Ru_3 clusters is still extremely limited. The clusters $Ru_3(CO)_5H_2(P^tBu_2)_2$-($Ph_2PCH_2PPh_2$) [8], $Ru_3(CO)_9H(PPh_2)$ [9], $Ru_3(CO)_7$-(PhCCPh)($Ph_2PCH_2PPh_2$) [10], $Ru_3(CO)_7H(C_{12}H_{10})$ [11], $Ru_3(CO)_{10}H_2$ [12] and $Ru_3(CO)_9H_2(PPh_3)$ [12] are 46e$^-$ systems, whereas the clusters $Ru_3(CO)_6H_2(PCy_3)_3$ [13,14] and $[Ru_3(CO)_7H(PCy_3)_2]^-$ [15] have a formal electron count of only 44e$^-$. Given this situation and the electron-donating capacity of a sulfoximido ligand being somewhat doubtful, we decided to establish the electron counting of our triruthenium sulfoximido clusters on a solid theoretical basis, in order to find out which of these Ru_3 clusters are truly electron deficient and which are not.

2. Computational details

2.1. EHMO calculations

All the calculations were carried out within the standard extended Hückel formalism [16] using the modified Wolfsberg–Helmholz formula [17]. The CACAO package developed by Mealli and Proserpio was used [18]. Standard atomic parameters were taken for

H, C, O, N and S [16,17]. The exponents ζ and the valence shell ionization potential (H_{ii} in electron-volts) used for Ru are the standard CACAO parameters [17], i.e. respectively: 2.078, -8.60 for 5s, 2.043, -5.10 for 5p. The H_{ii} value considered for 4d was -12.20. A linear combination of two Slater-type orbitals ($\zeta_1 = 5.378$, $c_1 = 0.5450$; $\zeta_2 = 2.303$, $c_2 = 0.6261$) was used to represent the atomic 4d orbitals. The following bond distances (Å) and angle (°) were considered: Ru–Ru = 2.750; Ru–N = 2.120; Ru–C = 1.900; C–O = 1.150; N–S = 1.556; S–H = 1.335; S–O = 1.449; NSO = NSH = 109 = HSH = 109.5.

2.2. DFT calculations

DFT calculations were carried out on the models using the Amsterdam Density Functional (ADF) program [19] developed by Baerends and coworkers [20] using the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization [21]. The atom electronic configurations were described by a triple-ζ Slater-type orbital (STO) basis set for H 1s, C 2s and 2p, N 2s and 2p, O 2s and 2p, S 3s and 3p, augmented with a 3d single-ζ polarization for C, N, O and S atoms and with a 2p single-ζ polarization for the H atom. A triple-ζ STO basis set was used for Ru 4d and 5s, augmented with a single-ζ 5p polarization function for Ru. A frozen-core approximation was used to treat the core shells up to 1s for C, N and O, up to 2p for S and up to 4p for Ru 20a. The geometries were optimized using the analytical gradient method implemented by Verluis and Ziegler [22].

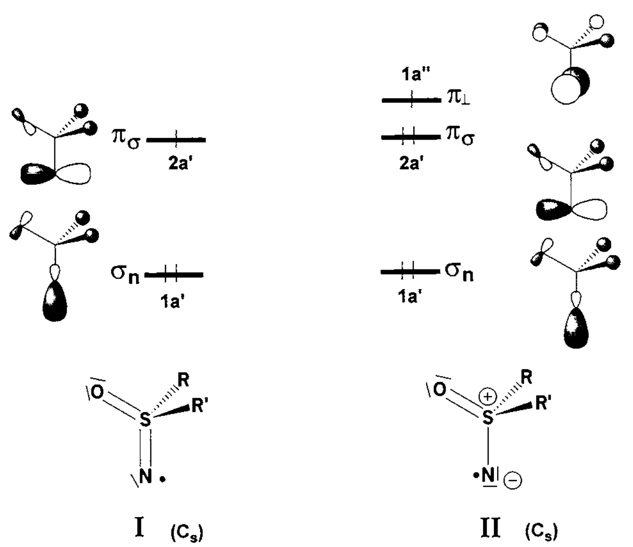


Fig. 1. The two orbital situations which are a priori possible for the sulfoximido ligand: in **I** it is is a two-orbital/3e$^-$ ligand (the π_{NS} and π^*_{NS} orbitals are not used for metal–ligand bonding); in **II** it is a three-orbital/5e$^-$ ligand.

3. Results and discussion

3.1. Orbital description of the problem

The question about how many electrons are given by the sulfoximide ligand to the triruthenium unit raises another important question. What is the number and the nature of the sulfoximide frontier orbitals (FOs) in which these electrons are located? Considering the sulfimido ligand as a 3e$^-$ donor implies the existence of an S=N double bond. This means that the nitrogen atom uses two of its four AOs (or combinations thereof) for bonding with the sulfur. Consequently, there are two non-bonding AOs (or combinations thereof) which are left for forming the FO set of the sulfimido ligand.

Such a situation, with one σ-type orbital (σ_n) and one π in-plane orbital (π_σ) is sketched in **I** (Fig. 1). It is similar to that of a vinylidene (C=CR$_2$) ligand, for example, which has one electron less in the FO set. On the other hand, considering the sulfimido ligand as a 5e$^-$ donor implies the existence of an S–N single bond. This means that the nitrogen atom uses only one combination of its four AOs for bonding with the sulfur. Therefore, three non-bonding AOs (or combinations thereof) are left for forming the FO set. Such a situation, with one σ-type orbital (σ_n) and two nearly degenerate π-type orbitals ($\pi_\perp$ and π_σ) is sketched in **II** (Fig. 1). It is similar to that of a carbyne (C–R) ligand for example, which has two electrons less in the FO set. The existence of two nearly degenerate π-type FOs in **II** provides the ligand with axial (conical) bonding abilities, which is not the case for **I**.

Assuming that the sulfoximide ligand binds to the metal atoms in making localized 2e$^-$/two-center bonds implies that it uses for bonding as many FOs as it makes N–Ru bonds. With only two FOs left on the ligand in the case of **I**, a localized bonding in a μ_3 coordination mode is forbidden. Only situation **II** allows the formation of three localized Ru–N bonds. However, situation **I**, associated with delocalized electron-deficient bonding, cannot be completely ruled out in the case of the μ_3 coordination mode of sulfoximido in **I**. In fact, such a delocalization, which is favored by the hypervalent nature of sulfur, occurs in compound 1, as shown by DFT calculations (vide infra).

Finally, it should be noted that there are ligands whose FO sets correspond to a situation intermediate between **I** and **II**. In these systems, such as N=NR$_2$ (hydrazido), or P=NR$_2$, the existence of a weak double bond induces a low-lying π* MO that can, to some extent, be involved in the bonding with the metal [23]. The possibility of the sulfoximido ligand being a member of this family of close to conical (but definitely non-conical) ligands cannot be ruled out either.

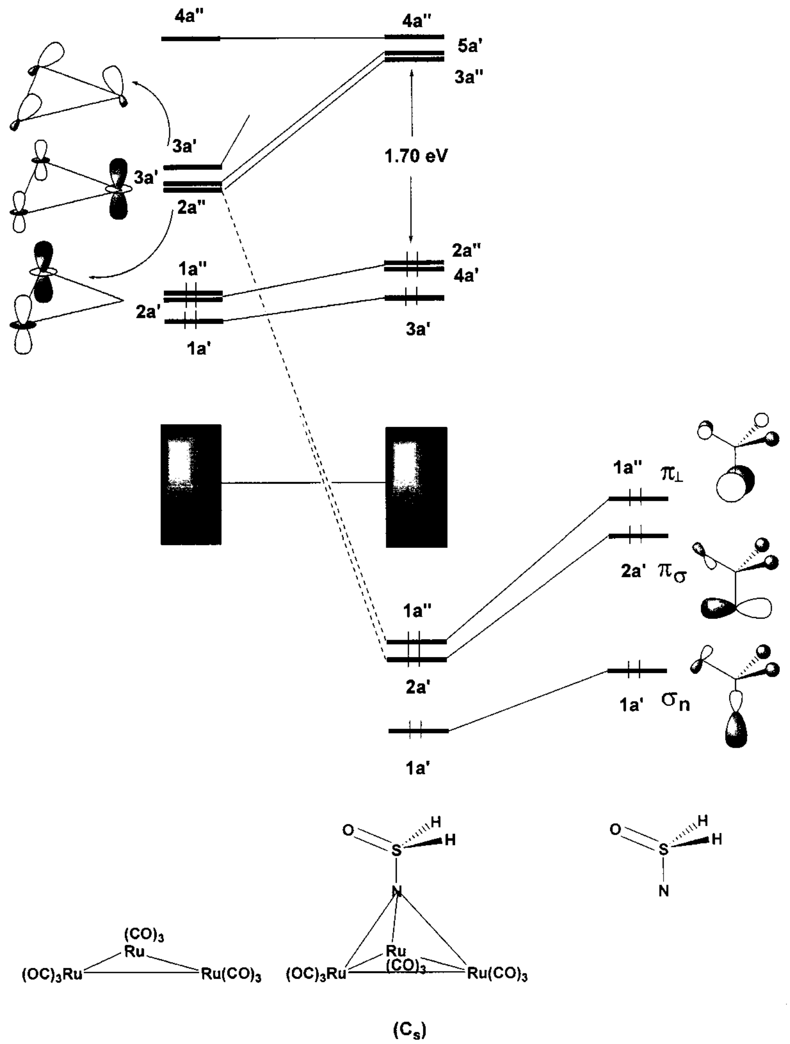


Fig. 2. EHT MO diagram of the C_s model $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$, based on the interaction of the $Ru_3(CO)_9$ and $[NS(O)H_2]^-$ fragments.

3.2. EHT analysis of the electronic structure of cluster *1*

We first investigate the C_s model $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$, which is derived from **1** by deprotonation and substitution of the Ph and Me groups of the sulfoximido ligand by H atoms. The MO diagram of this model is shown in Fig. 2, based on the interaction of the $Ru_3(CO)_9$ and $[NS(O)H_2]^-$ fragments (fragment charges are formal).

The C_{3v} $Ru_3(CO)_9$ fragment exhibits the well known set of three accepting FOs of a $42e^-$ M_3L_n unit prepared for receiving a $6e^-$ μ_3-ligand [24,25]. Calculations indicate that there is a one-to-one interaction between these three orbitals and the three highest occupied orbitals of $[NS(O)H_2]^-$. The other $2e^-$/two-orbital bonding interactions are much weaker and can be neglected. Clearly, this is the situation **II** that applies to the sulfoximide ligand. The $\pi_\perp$ and π_σ FOs of the $[NS(O)H_2]^-$ fragment are very close in energy: they have nearly the same localization on N (87% and 94% respectively). After interaction, they have similar occupations ($1.61e^-$ and $1.60e^-$ respectively). The $3p_\pi$ sulfur participation to $\pi_\perp$ (as well as to π_σ) is negligible. These AOs are mainly involved in the various S–O and S–H σ-type and π-type interactions. The conical nature of the $[NS(O)H_2]^-$ FO set is exemplified by almost equal Ru–N and Ru–Ru overlap populations ($1 \times 0.355 + 2 \times 0.353$ and $1 \times 0.238 + 2 \times 0.239$ respectively). These values compare well with those obtained for the related $48e^-$ C_{3v} model $\{Ru_3(CO)_9[\mu_3\text{-}NH]\}^{2-}$ (0.361 and 0.241 respectively) in which the conical NH^{2-} fragment acts as a $6e^-$ donor. In this latter model, the occupation of the degenerate π-type FOs is 1.60. Clearly, in the $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ model, the $[NS(O)H_2]^-$ ligand act as a three-orbital $6e^-$ ligand leading to a cluster $48e^-$ count.

Calculations were also made on the real cluster **1**, assuming the experimental X-ray structure of C_1 symmetry. The results are very similar to those obtained for the simplified model $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$, as exemplified for example by the Ru–N overlap populations (0.350, 0.349 and 0.345) or by the S–N and S–O overlap populations (0.787 and 0.676 respectively), which compare well with the corresponding values in $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ (0.787 and 0.682 respectively). Neither in **1** nor in $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ is there a low-lying LUMO, which would have been the indicative of some cluster electron deficiency.

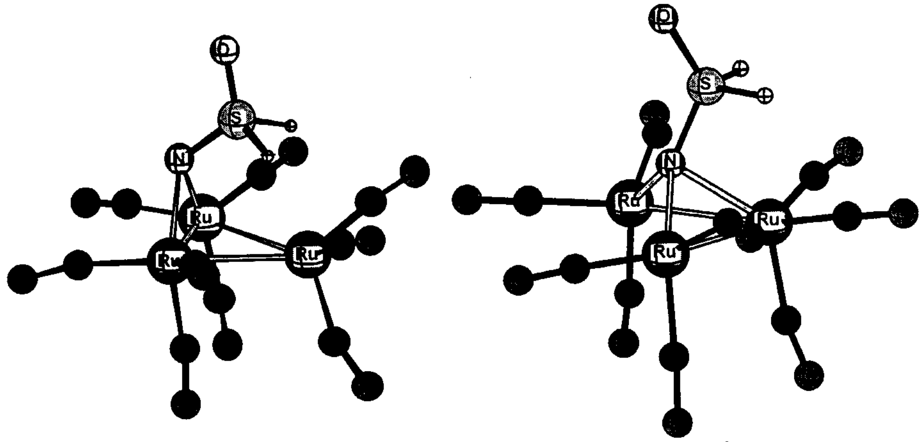
3.3. DFT analysis of the electronic structure of cluster 1

In order to put the qualitative EHT results on firm grounds, we have undertaken DFT (see Section 2). The major results are given in Table 1. The geometrical data corresponding to the optimized structures of the $\{Ru_3(CO)_9[\mu_3\text{-}NH]\}^{2-}$ (C_{3v}), $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ (C_s) and $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2]$ (C_s) models, as well as on **1** (C_1), clearly indicate similar types of bonding within the Ru_3N pyramid. A comparison of the Ru–N distances in $\{Ru_3(CO)_9[\mu_3\text{-}NH]\}^{2-}$ and $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ suggest that the NH ligand is somewhat more strongly bound to the metal triangle than the $NS(O)H_2$ ligand. This results in stronger Ru–Ru bonds in the latter. The DFT fragment MO population analysis confirms that $NS(O)H_2$ is a weaker ligand than NH. Indeed, the FO populations (and especially the π-type ones) of the $NS(O)H_2$ ligand are larger than those of the NH ligand (Table 1). This difference was not so clearly evidenced at the EHT level (see Section 3.2). Clearly, the π-type FOs in the sulfoximido ligand are also somewhat involved in the bonding within the ligand, but this delocalization effect is not very important, supporting situation **II** of Fig. 1. In fact, at the DFT level, both nearly degenerate π-type sulfoximido FOs exhibit some sulfur contribution associated with N–S π-bonding character. As a result, their occupation strengthens the N–S bond, leading to a rather short N–S distance. Because these π-type $NS(O)H_2$ FOs have less nitrogen localization than those of an NR ligand, they interact to a lesser extent with the metal triangle, inducing longer N–Ru and shorter Ru–Ru bonds in the former case.

Going from $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^-$ to $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2]$ results in some shortening of the Ru–N distances and lengthening of the Ru–Ru and N–S distances, indicating stronger meta-sulfoximine interaction in the case of the protonated species. This is also supported by the fragment analysis data (Table 1). The geometry of the real compound **1** was also optimized assuming no symmetry element. The geometrical

Table 1
Major DFT results computed for $\{Ru_3(CO)_9[\mu_3\text{-}NH]\}^{2-}$, $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^{-1}$, $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^{-3}$ and $\{Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2\}$. The experimental bond distances of compound **1** are given in square brackets

Compounds	$\{Ru_3(CO)_9[\mu_3\text{-}NH]\}^{2-}$	$\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^n$			$\{Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2\}$
	(C_{3v})	$n=-1$ (C_s)	$n=-3$ (C_s)	$n=-3$ (C_s)	(C_s)
			Isomer A	Isomer B	
HOMO/LUMO gap (eV)	2.55	2.27	1.27	0.83	2.35
	2.758	2.733	2.697	3.618	2.821 [2.831]
		2.724	2.956	2.873	2.749 [2.673]
		2.724	2.956	2.873	2.749 [3.683]
Ru–Ru (Å)	2.078	2.176	3.347	2.177	2.138 [2.120]
		2.134	2.208	2.226	2.128 [2.105]
		2.134	2.208	2.226	2.128 [2.110]
Ru–H (Å)					[1.632]
					[1.749]
N–S (Å)		1.559	1.565	1.558	1.562 [1.565]
S–O (Å)		1.483	1.522	1.508	1.472 [1.448]
S–H (Å)		1.395	1.416	1.411	1.392
N–H (Å)	1.020				
Mulliken atomic net charges					
Ru	0.64	0.46	0.43	0.41	0.59
		0.67	0.50	0.61	0.75
		0.67	0.50	0.61	0.75
N	−0.84	−0.65	−0.48	−0.66	−0.71
S		0.46	0.45	0.49	0.55
$NS(O)H_2$ and NH FMO occupations					
π	1.44	1.68	1.59	1.81	1.66
π_σ	1.44	1.75	1.79	1.76	1.73
σ_n	1.70	1.77	1.82	1.81	1.76



A B

Fig. 3. Optimized geometries of the two isomers found for the $\{Ru_3(CO)_9[NS(O)H_2]\}^{3-}$ model.

data are close to those obtained for $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2]$. The optimized Ru–Ru distances in **1** are in a reasonable agreement with the experimental values. Overall, there is a good agreement between the computed and the X-ray data.

As found with the EHT calculations, the DFT HOMO–LUMO gaps of $\{Ru_3(CO)_9[\mu_3\text{-}NS(O)H_2]\}^{-}$ and $Ru_3(CO)_9(\mu_2\text{-}H)[\mu_3\text{-}NS(O)H_2]$ are large. No significant energy gap is found between either the LUMO or the LUMO(+ 1), which would suggest that these species could accept two supplementary electrons without any significant structural change. We have checked this hypothesis in optimizing the geometry of the electron-rich $\{Ru_3(CO)_9[NS(O)H_2]\}^{3-}$ model under the C_s symmetry constraint. Two different isomers (named **A** and **B**), both of C_s symmetry, were found. They are displayed in Fig. 3 and their major metrical data are given in Table 1. **A** is the most stable (by 0.20 eV). It exhibits a μ_2 coordination mode of the sulfoximido ligand, associated with a pyramidalization (sp^3 hybridization) of the nitrogen atom, which minimizes the repulsions between the nitrogen and ruthenium lone pairs. This result shows clearly that **1** cannot accept two supplementary electrons without bond breaking. In this $\{Ru_3(CO)_9[\mu_2\text{-}NS(O)H_2]\}^{3-}$ isomer, the sulfoximide ligand uses one combination of its three FOs to localize a lone pair, and two combinations for making two Ru–N bonds. Counting it as neutral, it is a $3e^-$ donor to the $48e^-$ Ru_3 cluster. Isomer **B** exhibits a μ_3 coordination mode of the sulfoximido ligand, associated with an open Ru_3 triangle. In **B**, the sulfoximido ligand provides $5e^-$ to the $50e^-$ electron-precise Ru_3 cluster (Fig. 3).

3.4. MO analysis and electron counting in clusters 2–5

Owing to the good agreement between EHT and DFT calculations, calculations on clusters **3**–**5** have been carried out at the EHT level, assuming experimental molecular X-ray structures. Since no X-ray structure is available for **2**, this compound was not calculated. However, in the light of the calculations described above, it appears obvious that both structures proposed for **2** are electron precise. In the structure containing the closed Ru_3 triangle (left side), the μ_2 sulfoximide is a $3e^-$ donor, giving rise to the expected cluster $48e^-$ count. In the structure containing the open Ru_3 triangle (right side), the μ_3 sulfoximide is a $5e^-$ donor, giving rise to the expected cluster $50e^-$ count. Owing to the DFT-optimized isomers **A** and **B** of the related $\{Ru_3(CO)_9[NS(O)H_2]\}^{3-}$ model, both structures proposed for **2** appear reasonable. Since **A** was calculated to be the most stable isomer of $\{Ru_3(CO)_9[NS(O)H_2]\}^{3-}$, we tentatively ascribe to **2** the structure that exhibits an η^2-coordinated $NS(O)H_2$ ligand associated with a closed metal triangle.

EHT calculations on compound **3** indicate clearly that, in the same manner as in **1**, the μ_3 sulfoximido ligand act as a $5e^-$ donor to the Ru_3 system. The computed HOMO–LUMO gap is large (2.01 Å). This is the only significant gap in the frontier MO region, indicating that there is no other electron count that can stabilize the structure of **3**. Assuming that the CPhCHBu retains a σ C–C bonding electron pair, it is expected to behave as a $3e^-$ donor ligand. This leads to the $48e^-$ count for the open Ru_3 triangle, suggesting electron deficiency, a result apparently at variance with the EHT results. The obtaining of the expected $50e^-$ count would require one to consider the delocalization of the σ C–C bonding pair on the metal atoms. A better explanation for the stability of **3** is perhaps obtained within the framework of the polyhedral skeletal electron pair (PSEP) theory [26], which takes better account of the hypercoordination mode of the C(Ph) atom. One should first note that one of the (HBu)C–Ru contacts is

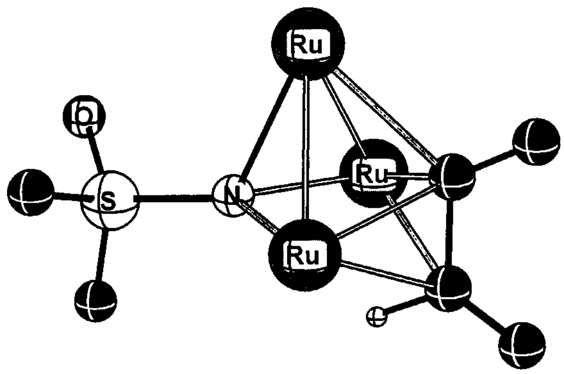


Fig. 4. A view of the core of **3** showing the distorted NRuCRu 'square' capped by a ruthenium atom. The (HBu)C carbene group bridges the Ru–C(Ph) edge of the NRuCRu 'square' and is weakly bonded to the other Ru atom.

particularly long (2.50 Å). Consistently, the corresponding computed overlap population is small (0.068). Neglecting this weak bonding contact, the core of **3** can be seen as a distorted NRuCRu 'square' capped by a ruthenium atom, as shown in Fig. 4. The (HBu)C group bridges one (Ph)C–Ru edge of this capped 'square pyramid'. The PSEP theory predicts a count of seven skeletal electron pairs for such an architecture. Assuming that the (HBu)C bridging ligand provides the cluster core with $2e^-$, the capped 'square pyramid' does obey the PSEP rules. The efficiency of this PSEP description of **3** is that it implicitly delocalizes the electrons over the whole cluster cage.

On the other hand, there is no need to consider delocalization of the C–C σ bonding pairs in **4** to obtain the expected $50e^-$ count for the open Ru_3 triangle, assuming that the μ_2-NS(O)MePh ligand, which exhibits a pyramidalized N atom [7], is a $3e^-$ donor and the PhCCCCHPh ligand a $5e^-$ donor. This is supported by EHT calculations in which no electron deficiency can be traced (HOMO–LUMO gap: 1.68 eV). A similar situation occurs with **5**, which, with a μ_3-NS(O)MePh $5e^-$ donor ligand, can be described as a $50e^-$ species. Consistently, a large HOMO–LUMO gap is also computed for this species (1.91 eV). One can note that going from **4** to **5** corresponds to the formal removal of a $2e^-$ CO ligand. Consequently, in order to maintain the $50e^-$ count of the Ru_3 open triangle, the μ_2 ($3e^-$) sulfoximide ligands is changed into a μ_3 ($5e^-$) ligand. Interestingly, the PhCCCCHPh ligand acts as a $5e^-$ donor in both complexes, but its connectivity with respect to the metal atoms is different: There are six Ru–C bonding contacts in **4** and seven in **5**.

4. Conclusion

Calculations indicate clearly that, despite its rather short N–S bond, a μ_3-sulfoximido ligand is a three-orbital/$5e^-$ ligand, i.e. should be described by situation **II** of Fig. 1. Because of some delocalization of its π-type FOs on the sulfur and oxygen atoms, it is expected to bind less strongly to metal atoms than classical imido ligands, resulting in slightly shorter metal–metal bonds. Once in a μ_2 coordination mode, a sulfoximido retains a lone pair on its pyramidalized N atom and becomes a two-orbital/$3e^-$ ligand. It follows that clusters **1**, **2**, **4** and **5** are electron-precise, with the Ru atoms following the $18e^-$ rule. Consistently, they exhibit large HOMO–LUMO gaps. Compound **3** is electron-deficient with respect to the $18e^-$ rule if the C–C σ bonding pair is not included. However, the electron count of this species can be rationalized within the PSEP formalism and no particular indication of electron deficiency can be found in its electronic structure, except for the existence of the weak (HBu)C–Ru bond (2.50 Å).

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