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Localization vs Delocalization of the Odd Electron in Nonsymmetric Rh_2^{5+} Complexes: An ab Initio SCF/CI Study of $[Rh_2(tcl)_4]^+$ and $[Rh_2(tcl)_4CO]^+$ (tcl = ω-Thiocaprolactamate)

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Ab initio MO/SCF and CI calculations are reported for the Rh_2^{4+} complexes $Rh_2(tcl)_4$ (**1**) and $Rh_2(tcl)_4CO$ (**2**) by using the polar (4,0) conformation of the bridging ligands characterized for the latter complex. The axial bonding of one CO molecule to the rhodium atom coordinated to the sulfur ends of the tcl ligands [$Rh(S_4)$] is shown to induce a disproportionation of the Rh(II)–Rh(II) core leading to dative bonds from both the CO ligand and the second rhodium atom to $Rh(S_4)$. The bonding along the metal–metal axis therefore corresponds to the scheme $Rh(I) \rightarrow Rh(III) \leftarrow CO$. The effects of this metal–metal bond polarization on the energy balance of the monoadducts are discussed. A qualitative interpretation of the visible spectra of **1** and **2** is given. The lowest d-metal and ligand ionization energies have been determined by using the ΔSCF/CI methodology. The semioccupied molecular orbital (SOMO) of $[Rh_2(tcl)_4]^+$ is a δ-type orbital ($\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ configuration). Concerning $[Rh_2(tcl)_4CO]^+$, the ΔSCF/CI calculations yielded very close energies for the $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ and for the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$ configurations. The lack of any symmetry constraint connecting the two rhodium atoms leads to a pair of localized descriptions for each doublet state of the Rh_2^{5+} complex. The trend of some nonsymmetric Rh_2^{5+} complexes to appear as true mixed-valent Rh(II)–Rh(III) complexes displaying a partial or complete localization of the spin density associated with the odd electron can be related to a large energy splitting between the descriptions localized on each metal and/or to a small metal–metal overlap in the SOMO. Such a localization of the spin density on the $Rh(S_4)$ atom of $Rh_2(tcl)_4CO$ can be predicted from the ab initio calculations. The role of the CO ligand appears most important in this localization process.

1. Introduction

Since the first report concerning the preparation of tetrakis(carboxylato) compounds of the type $Rh_2(O_2CR)_4L_2$,[3] dirhodium complexes have been extensively studied from the viewpoints of synthesis,[4-13] electrochemistry,[7-10,13] chemical reactivity,[11,12] cancer research,[14] spectroscopy,[7,15-18] and theoretical investigation.[18-20] All theoretical studies now agree with the existence of a single σ bond in the neutral complex, corresponding to the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ for the Rh_2^{4+} unit.[18-20] The relative ordering of the σ, π*, and δ* molecular orbitals seems however to be strongly dependent upon equatorial and axial coordination.[15] The nature of the Rh_2^{5+} cationic species has therefore been the subject of various investigations by means of electron spin resonance (ESR),[7,9,10,15] gas-phase photoelectron spectroscopy,[17,18] and quantum-mechanical calculations.[18-20] The theoretical works emphasized the importance of a balanced description of electron relaxation and correlation effects for the various doublet states of interest[20] and confirmed the close vicinity of the π* and δ* levels in dirhodium tetracarboxylates.[18,19b,20]

Most experimental and all theoretical studies presently available deal with complexes where the two rhodium atoms are equivalent by symmetry. Not surprisingly, all ESR studies have reported

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until recently an equal distribution of the odd-electron density over the two metal centers.[9] Recent progress in the synthesis has produced dirhodium complexes in which the two metal atoms are in a different coordination sphere.[9,11] In some cases, the difference comes from axial coordination only.[15a] ESR measurements on such complexes have shown that the different environments of the two metal atoms could significantly affect the distribution of the spin density in the ground state of the Rh_2^{5+} cation.[9,15a] The analysis of the hyperfine structure of the $\mathbf{g}_{\parallel}$ tensor has shown that the spin density could be either unequally distributed[15a] or even localized on one metal only, as in $Rh_2(ap)_4Cl$, where ap = 2-anilinopyridinate.[9]

The synthesis of a series of such nonsymmetric dirhodium complexes with ω-thiocaprolactamate (tcl = $\mathrm{NC(S)CH_2(CH_2)_3CH_2}$) as equatorial ligands has been recently reported.[10] The present study will focus on two of these complexes, namely $Rh_2(tcl)_4$ (**1**) and $Rh_2(tcl)_4CO$ (**2**). The crystal structure of **2** has shown that the environments of the two rhodium atoms are different in both the axial and the equatorial coordination sites. The four nitrogen donor atoms are distributed in the equatorial plane of the same rhodium atom, which will be referred to as $Rh(N_4)$. The second metal, $Rh(S_4)$, is surrounded by four sulfur atoms.[10] At variance with that of $Rh(N_4)$, for which the axial site remains vacant, the coordination sphere of $Rh(S_4)$ is completed by a carbonyl ligand. In complex **1** electrochemically generated under its cationic form, but not characterized yet,[10] both axial sites remain vacant and the polarity of the Rh–Rh bond is only due to the difference in the equatorial environments.

We report here ab initio calculations on the ground state and the lowest ionized states of **1** and **2**. Our goal is to address the problem of the polarity of the Rh–Rh bond. More specifically, we intend to discuss the following points: (i) modification of the electronic structure and metal–metal bonding of the dirhodium complexes induced by the respective differences in the equatorial and axial environments; (ii) respective influence of the equatorial environment and axial monoligation on the sequence of the highest d-metal MOs; (iii) possible origin of the localization of the odd electron observed in some polar dirhodium complexes.

2. Computational Details

In all calculations, the ω-thiocaprolactamate ion has been modeled by a $(S–CH–NH)^-$ molecule. The interatomic distances in **1** and **2**, including the Rh–Rh bond length of 2.495 Å, were taken from the crystal structure reported for **2**.[10] The S–Rh–Rh–N torsional angle of 21° was however not retained in our model systems, and the $(S–CH–NH)^-$ ligands were assumed to be planar, in order to take advantage from the C_{4v} symmetry point group. The z axis has been chosen collinear with the metal–metal bond.

The Gaussian basis set for rhodium was taken from the 15s,9p,8d set of Veillard and Dedieu,[21] incremented with an extra p function of exponent 0.15 and contracted to [6,4,4]. The basis set for sulfur is a 11s,7p basis set from Huzinaga,[22] incremented with one d polarization function of exponent 0.55 and contracted to [4,3,1]. For first-row atoms and hydrogen, 9s,5p and 4s basis sets were used respectively and contracted to [3,2] and [2].[22]

The calculations on the lowest ionized states of **1** and **2** have been carried out at the ΔSCF/CI[23] level. SCF calculations have been performed by using the ASTERIX system of programs.[24] The CI calculations were carried out with the program originally developed by Brooks and Schaefer[25] for single and double excitations from a single reference wave function, using the graphical unitary group approach.[26]

Table I. Net Charges and Valence Orbital Populations (Electrons) for $Rh(N_4)$ and $Rh(S_4)$ in the Complexes Modeling $Rh_2(tcl)_4$ (**1**) and $Rh_2(tcl)_4CO$ (**2**) (from the Mulliken Population Analysis of the SCF Wave Function)

	$Rh_2(tcl)_4$		$Rh_2(tcl)_4CO$	
	$Rh(N_4)$	$Rh(S_4)$	$Rh(N_4)$	$Rh(S_4)$
		Net Charge		
	+1.08	+0.38	+0.86	+0.38
		Orbital Populations		
$4d_{z^2}$	+1.05	+1.15	+1.41	+0.98
$4d_{x^2-y^2}$	+0.60	+0.87	+0.50	+1.04
$4d_{xy}$	+1.96	+1.99	+1.94	+1.99
$4d_{xz} + 4d_{yz}$	+4.00	+3.97	+3.98	+3.85
5s	+0.05	+0.15	+0.29	+0.13
$5p_z$	+0.04	+0.04	+0.03	+0.16
$5p_x + 5p_y$	+0.03	+0.36	−0.01	+0.46

3. The Ground State of $Rh_2(tcl)_4$ (1) and $Rh_2(tcl)_4CO$ (2)

At variance with complexes of the type Rh_2 (RNOCR′),[7] the dirhodium thioacetate $Rh_2(SOCCH_3)_4$,[27] and dirhodium complexes with lactamate ligands,[28] the tcl complexes prefer the (4,0) polar conformation to a (2,2) conformation with the four sulfur and nitrogen donor atoms equally distributed in the equatorial planes of the two rhodium atoms.[10] The SCF calculations carried out on both the (4,0) and the trans-(2,2) model isomers of **1** indicate that the electronic factors monitoring the equatorial coordination would favor a nonpolar conformation. The trans-(2,2) conformation is found more stable than the (4,0) isomer by about 10 kcal/mol. One could therefore assume that the polar conformation obtained in the originally synthesized $Rh_2(tcl)_4tclH$ arises as a consequence of steric crowding between the bulky rings of the "real" tcl ligands. Another possible explanation is the stabilization of the polar complex by axial monoligation. Preliminary calculations carried out at the SCF level indicate that the stabilization energy of a carbon monoxide molecule coordinated to a rhodium atom is larger by about 20 kcal/mol in the $Rh(S_4)$ than in the $Rh(N_4)$ environment. The difference in bond energies can be mainly attributed to an important variation in electrostatic repulsion between the positively charged carbon atom and either $Rh(S_4)$ (net charge +0.38e, as computed in the polar conformation of the $Rh_2(tcl)_4$ model system) or $Rh(N_4)$ (net charge +1.08e). Since these net charges are almost exactly averaged in the nonpolar (2,2) conformation (+0.73e), an intermediate Rh–CO bonding energy can be expected from axial coordination in the (2,2) conformation, yielding a decrease of about 10 kcal/mol in the stabilization energy per axial ligand. This rationalization and the possible role of steric hindrance are obviously not exclusive.

As previously mentioned, the Mulliken population analysis carried out on the SCF wave function obtained for **1** shows an important difference in charge between $Rh(S_4)$ (+0.38e) and $Rh(N_4)$ (+1.08e) (Table I). About half of this difference comes from a significant participation of the metal 5p orbitals in the bonding with sulfur. The $5p_x$ and $5p_y$ populations of $Rh(S_4)$ are 0.18e each, instead of 0.02e for $Rh(N_4)$. Most of the rest is due to an increase of 0.28e in the $d_{x^2-y^2}$ population of $Rh(S_4)$ with respect to $Rh(N_4)$ (Table I). These changes in metal orbital populations can be consistently interpreted in terms of a strong metal–sulfur interaction with some covalent character, at variance with the more dative Rh–N bond. The metal–metal σ bond in **1** appears little affected by the polarity of the Rh_2 core. The difference in the d_{z^2} orbital populations is 0.10e only, $Rh(S_4)$ still having the highest population. The σ-bonding orbital ($30a_1$) appears quite delocalized over the two metal atoms with balanced contributions of 44% from $Rh(N_4)$ and 42% from $Rh(S_4)$. The energy and the character of the σ-bonding orbital are nearly identical with those obtained for the symmetric (2,2) conformation.

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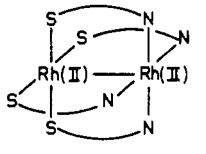
If we now turn to $Rh_2(tcl)_4CO$ (**2**), with the carbon monoxide coordinated to $Rh(S_4)$ as characterized in the crystal, the Rh_2 core appears deeply modified. The splitting of the metal net charges is reduced: 0.47e instead of 0.70e in **1**, $Rh(N_4)$ still having a higher positive charge (+0.86e). This global evaluation however conceals a much more polar distribution of the 4d orbital populations (Table I). But the major change involves the metal d_{z^2} orbitals. The incoming of the carbonyl lone pair gives rise to an electron transfer along the OC–Rh–Rh axis, pushing the electron density toward $Rh(N_4)$. This leads to a dramatic increase of the $4d_{z^2}$ population for this atom: 1.41e instead of 1.04e in **1**. As a consequence, the Rh–Rh σ-bonding orbital becomes highly localized on $Rh(N_4)$ (58% vs 21% only on $Rh(S_4)$). The correlative depopulation of the $4d_{z^2}$ orbital of $Rh(S_4)$ is not completely offset by the σ donation from the carbon lone pair, so that the orbital population drops to 0.98e (compared to 1.15e for $Rh(S_4)$ free of axial ligand) (Table I). Nevertheless, the σ transfer from CO to $Rh(S_4)$ amounts to 0.33e (vs 0.15e only for π back-donation), and the CO net charge is +0.18e. A *positive* net charge of this order of magnitude is not commonly found for CO, especially at short coordination distances, and corresponds to unusually strong σ-donation effects.[29,30] From this simple analysis of the orbital populations emerges a dual scheme for the Rh–Rh bonding in tcl complexes: (i) a strong covalent and practically symmetric σ bond between the metal atoms as in **1**; (ii) a mainly dative Rh–Rh σ bond resulting from a disproportionation as in **2**. This scheme leads to σ donations from both $Rh(N_4)$ and the axially coordinated ligand to $Rh(S_4)$. The formal oxidation numbers attributed to the metal atoms in **1** and **2** assume purely coordinative bonds in the equatorial planes. This is not quite exact since the Rh–S bond has a trend toward covalency more pronounced than the Rh–N interaction and this would in principle reduce the oxidation number of $Rh(S_4)$. It must be noticed that the covalent character of the Rh–S bond increases for complex **2** (see the $d_{x^2-y^2}$ and $p_{x,y}$ orbital populations of the $Rh(S_4)$ in Table I) and this effect tends to balance the disproportionation induced along the z axis by axial monoligation. This indirect effect could also contribute to orienting axial monoligation toward $Rh(S_4)$ rather than toward $Rh(N_4)$.



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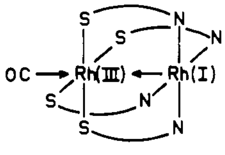

2

With regard to the effect of σ donation, the influence of π back-donation appears as a relatively small perturbation to the electron distribution in the metal atom. The overall $4d_{xz} + 4d_{yz}$ population of $Rh(S_4)$ is reduced from 3.97e to 3.85e. It is important to notice that, at variance with the σ interaction, π back-bonding has no sensible influence on the second metal atom: the overall π populations of $Rh(N_4)$ are 4.00e in $Rh_2(tcl)_4$ and 3.98e in the CO adduct. This comes from the π and π^* metal MOs being both doubly occupied, so that the metal π electrons can be considered as localized on each rhodium atom. The perturbation to the metal π population caused by axial monoligation therefore remains local and cannot induce a disproportionation of the dimetal unit, whatever may be the relative strength of the π back-donation with respect to the σ donation. In a similar way, the difference in environments of the rhodium atoms in the equatorial planes can also be considered as a local perturbation. As a matter of fact, it does not directly affect a molecular orbital delocalized over the metal atoms, since both $d_{x^2-y^2}$ metal orbital combinations are essentially unoccupied. At variance with the previous cases, the delocalized character of the σ bond makes it extremely sensitive to an asymmetric perturbation that may be easily transmitted to the second metal. As will be discussed in the next section, this perturbation, enhanced through the metal–metal σ bond, could be at the origin of the mixed-valent character of some Rh_2^{5+} complexes.[9] No generalization can be made however, since no more than three Rh_2^{5+} complexes have been reported to data that show an unequal distribution of the odd electron on the two metal centers.[9] More specifically, other work by Kadish has failed to indicate anything special about monoadducts in related systems. Additional experimental and theoretical work therefore seems necessary to refine the present model, delineate the possible influence of solvent interactions, and investigate the response of the metal–metal bond to a variation of the σ donativity of the axial ligand.

The trend toward Rh–Rh bond polarization could also depend upon the relative importance of σ donation and π back-donation. This problem has been extensively discussed in the literature.[29–31] The most recent and most general theoretical study due to Ziegler et al.[31] concludes that π back-donation is more important for the stability of $M(CO)_n$ systems than the σ interaction. However, the π back-donation is largest for the first-row elements, whereas σ donation is largest for second- and third-row atoms.[31] The decrease of π-acceptor interactions from the first to the second and third rows is attributed to 3d being closer in energy to π^*_{CO} than 4d and 5d.[30,31] The Rh–Rh bond polarization in $Rh_2(tcl)_4CO$ tends to further enhance this energy gap by localizing the high-energy π^* MO on $Rh(N_4)$ (77%) whereas the low-energy (π) MO has 65% weight on the CO-facing metal atom, $Rh(S_4)$ (Table IV). This localization of the π and π^* MOs is related to the variation of the nuclear charge shielding induced by the disproportionation process and discussed in section 4.3. In summary, the effects of the bond polarization on the stabilization of the complexes are as follows:

(i) The direct effect is an enhancement of the stabilization due to σ donation through a shift of the Rh–Rh σ population toward $Rh(N_4)$.

(ii) The polarization of the Rh–Rh σ bond causes a serious decrease of the metal–metal bond strength, in agreement with the long Rh–Rh distance of 2.495 Å found for **2**. The present SCF calculations show that the Rh–Rh total overlap populations computed for **1** and **2** at the same internuclear distance (2.495 Å) drop from +0.051 for **1** to −0.024 for the CO monoadduct **2**.

(iii) The final effect of the disproportionation of the Rh(II)–Rh(II) complex into Rh(I)–Rh(III)–CO is a deshielding of the Rh(III) nucleus leading to a stabilization of all atomic levels of $Rh(S_4)$ including 4d valence orbitals (see discussion in section 4.3). This stabilization of the $Rh(S_4)$ atomic levels increases the energy gap between the metal $4d_{xz,yz}$ and the carbonyl π^* orbitals, thus weakening the π-back-bonding interaction.

The polarization of the Rh–Rh σ bond will therefore depend on the balance between the enhancement of the σ donation and the weakening of both the metal–metal bond and the π back-bonding. One could therefore guess that the replacement of CO by a better π acceptor like CS should significantly reduce the trend toward metal–metal bond polarization. In a similar way, the replacement of the Rh_2^{4+} unit by a dicobalt system with comparable electronic structure should make a hypothetical CO monoadduct of this new complex much less sensitive to metal–metal bond polarization, due to the major role of π back-bonding in the stabilization of first-row metal carbonyl complexes.[31] Although some Co_2^{4+} complexes have been characterized,[32–34] only

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two of them correspond to the characteristic "lantern-type" pattern,[33,34] and their electronic structure could be different from the standard $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ MO scheme.[34,35]

4. The Lowest Ionized States of 1 and 2

1. Core- and d-Valence Hole States in Symmetric and Nonsymmetric Molecules. The calculation and interpretation of core ionization energies in symmetric molecules require special care because of the delocalization of the positive hole(s) over several atoms connected by the symmetry constraints.[36,37] The delocalization of the positive charge over *n* centers influences the SCF determination of the polarization energy of the valence shell by the core hole. It has been shown in this case that, at the symmetry-adapated Hartree–Fock level, only a fraction equivalent to $1/n$ of the polarization energy is recovered, the remaining part corresponding to correlation.[36,38] This effect has been discussed first for core holes in diatomic molecules and in solids.[39–41] It is however not confined to strictly core orbitals. Similar situations have been encountered upon ionization occurring in the *valence* shells of molecules characterized by weakly overlapping orbitals.[42] The outer d shells of transition-metal clusters and bi- or polynuclear complexes satisfy this condition, and not surprisingly, localization of the positive hole through symmetry-breaking MCSCF or CI expansions[36,43] was necessary to appropriately represent the d ionization states of Cu_2^+,[44] Ag_2,[45] Ni_2^+,[46] and other clusters or complexes.[47–49] The need for such localized solutions is implied by the difference in magnitude between the relaxation energy obtained for the outer d-valence ionization in the isolated metal atom and the relatively small stabilization expected from the d–d overlap in the cluster.[46,48c] *This does not mean that the localized representation of the ionized states implies a physical localization of the odd electron.* If we consider a symmetric system with two equivalent sites A and B, the same core ionized state can be represented by two wave functions ψ_A and ψ_B assocd. with identical energy values and respectively localizing the odd electron on A and B. One could however consider a resymmetrized wave function

$$\psi_{AB} = \alpha\psi_A + (1 - \alpha^2)^{1/2}\psi_B$$

with $\alpha = (1 - \alpha^2)^{1/2} = 1/2^{1/2}$.[50] It has been shown that the "symmetry-adapted" and "broken-symmetry" representations of the localized hole states were equivalent.[36] The problem of the *physical localization* of core holes on equivalent sites has been discussed by Schwarz et al.[38] and depends on the time interval necessary for the nonstationary localized state to hop from one site to another.[38]

Table II. Squares of the EHT/MO Coefficients for a Dirhodium System (d_{Rh-Rh} = 2.44 Å) with Different Values of the H_{ii} Parameters Assumed for Each Rhodium Atom[a]

ΔH_{ii}, eV	σ	π	δ
0.3	0.55/0.45	0.65/0.35	0.80/0.20
1.0	0.72/0.28	0.72/0.28	0.95/0.05

[a] Assuming an expansion of the type $\alpha\phi_{Rh_1} + (1 - \alpha^2)^{1/2}\phi_{Rh_2}$ for each atom, the values of $\alpha^2/(1 - \alpha^2)$ are reported for the σ-, π-, and δ-bonding orbitals and for ΔH_{ii} = 0.3 and 1 eV.

Table III. Ionization Energies (eV) Obtained from ΔSCF/CI Calculations on the Complexes Modeling $Rh_2(tcl)_4$ (**1**) and $Rh_2(tcl)_4CO$ (**2**)[a]

	$Rh_2(tcl)_4$ (**1**)		$Rh_2(tcl)_4CO$ (**2**)	
	SCF	CI	SCF	CI
closed-shell ground state	0	0	0	0
σ^1 $[Rh(N_4)]^+$	7.94		6.72	7.00
$[Rh(S_4)]^+$	7.80	8.27		
π^{*3} $[Rh(N_4)]^+$	7.47		6.65	6.74
$[Rh(S_4)]^+$	7.26	7.29	8.72	
δ^{*1} $[Rh(N_4)]^+$	7.24		6.53	6.69
$[Rh(S_4)]^+$	6.98	6.93	7.73	
tcl	7.29	7.13	7.37	7.42
tcl	7.72			

[a] Two solutions each corresponding to a localized representation of the positive hole either on $Rh(N_4)$ or on $Rh(S_4)$ have been characterized for most ionized states. The solution with lowest energy has been taken as a starting point for the ΔSCF/CI calculations. The origin of the energy scale is the energy computed for the ground state of the neutral molecule, namely −11 313.6936 hartrees (SCF) and −11 313.7838 hartrees (CI) for **1** and −11 426.3157 hartrees (SCF) and −11 426.4739 hartrees (CI) for **2**.

The problem of two sites A and B that are not equivalent has not been so extensively analyzed. One can however expect the following changes:

(i) Contrary to the symmetric situation, there is no more choice at the SCF level between "symmetry-adapted" and "broken-symmetry" representations of the core or d-metal hole states. The variational process will inevitably converge toward a solution localized either on center A or on center B, depending on the set of trial vectors.[52] These two localized solutions will now corre-

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(50) ψ_A and ψ_B being nonorthogonal, obtaining ψ_{AB} is not trivial and requires the use of sophisticated projection techniques.[51]

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spond to different values of the energy.

(ii) The localized solution associated with the lowest energy value can be expected to provide an energetically correct description of the relaxation. The most important correlation effects can be introduced through similar CI expansions carried out on the neutral molecule and on the localized wave function of lowest energy (ΔSCF/CI approximation[23]).

A resymmetrized wave function ψ_{AB} could in principle be obtained from the localized solutions ψ_A and ψ_B, the α coefficient increasing with the energy difference $\Delta E = E_B - E_A$. *This energy difference ΔE between the localized solutions obtained at the ΔSCF level could therefore be considered as a criterion for the physical localization of the odd electron.* Extended Hückel (EHT) calculations[53] carried out on a dirhodium molecule with different values of the 5d Coulombic parameter H_{ii} taken for each rhodium atom are reported in Table II. They show that low-overlap δ-type orbital combinations can already be considered as localized with $\Delta H_{ii} = 0.3$ eV. On the other hand, σ- and to some extent π-type orbital combinations characterized by a more important overlap require a separation larger than 1 eV between atomic energies to achieve a significant localization.

2. ΔSCF and ΔSCF/CI Results for the Ionized States of 1 and 2. Table III presents the lowest d-metal and ligand ionization energies computed for complexes **1** and **2** at the ΔSCF and ΔSCF/CI levels. The CI expansions carried out on the ground and ionized states included all single and double excitations generated from a unique reference state, upon a selected basis of molecular orbitals. These MO bases comprise the valence 5d and the virtual 6d shells of the metal atoms and, for complex **2**, the σ lone pair and the π and π* MOs of the carbonyl ligand.[54] The 6d metal MOs have been determined by using the hybridized atomic orbital procedure proposed by Illas et al.[55] At the ΔSCF level, two solutions have been obtained for the description of almost all ionized states and correspond to the localized representation of the positive hole either on $Rh(S_4)$ or on $Rh(N_4)$ (cf. the above discussion). Two exceptions must however be mentioned:

(i) The ionized state corresponding to the highest molecular orbital with tcl character was compelled to be delocalized because of the constraints associated with the C_{4v} point group.

(ii) The ionized state corresponding to the localization of the positive hole on the d_{z^2} orbital of $Rh(S_4)$ in $Rh_2(tcl)_4CO$ could not be characterized, the destabilization due to the inverse polarization of the Rh_2^{4+} core being probably larger than the relaxation energy of an ionized rhodium atom.

The sequences of the d-metal ionization energies at the CI level are the same for **1** and **2**, corresponding to the following order of the ionized states:

$$\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1} < \sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3} < \pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^1$$

In spite of this similarity, the photoelectron spectrum of the two complexes and the nature of their lowest ionized states can be predicted to be quite different. For $Rh_2(tcl)_4$, the ionizations arising from the δ* and from the π* MOs are relatively close in energy (respectively 6.93 and 7.29 eV (Table III)) but the σ orbital lies about 1 eV higher (8.27 eV). This large energy separation between the π^{*3} and σ^1 states appears at the CI level as a consequence of the pair correlation of the delocalized σ electrons in the closed-shell ground state. The ionized state associated with the lowest ligand orbital combination, which is the HOMO in the SCF ground-state wave function, appears at about the same energy level as the two lowest d-metal ionizations (Table III).

For $Rh_2(tcl)_4CO$, all three d-metal ionized states are now rather close in energy, particularly the δ^{*1} and the π^{*3} states. Due to the localization of the σ-electron density on $Rh(N_4)$ in the ground state of the neutral molecule (Table I), the relaxation energy of the σ^{*1} state increases and approaches the order of magnitude obtained for the globally nonbonding (π, π*) and (δ, δ*) electrons. For the same reason, the nondynamic correlation energy associated in the closed-shell ground state with the σ-electron pair tends to *decrease*[56] and so does the CI correction to the σ-ionization energy (0.28 eV instead of 0.47 eV for **1** (Table III)). At variance with the case of **1**, the three lowest d-metal ionized states appear clearly below the state arising from the ligand π ionization. It must be eventually noticed that the $\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^1$ state is computed to be the highest d-metal ionized state for both **1** and **2**, although it was assumed to be the ground state on the basis of ESR spectra[10] and of previous theoretical predictions involving dirhodium tetracarboxylates.[15c]

As discussed in section 4.1, two ΔSCF solutions have been characterized for most d-metal ionized states corresponding to a localization of the positive hole either on $Rh(N_4)$ or on $Rh(S_4)$. For $Rh_2(tcl)_4$ the energy splitting between the two localized solutions remains weak (0.15–0.25 eV) and consistently reflects the difference in charge between the two metal atoms: $Rh(S_4)$, which has the less positive net charge in the ground state of the neutral molecule, is most suited to localized the positive hole (Table III). According to the indications of Table II and on the assumption that the $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ doublet state is the ground state of the ionized molecule, such a small energy splitting could be sufficient to induce some *physical* localization of the positive hole on $Rh(S_4)$ in relation to the particularly weak δ–δ overlap.

Although the metal net charge ordering is the same for $Rh_2(tcl)_4CO$, a different situation is created by the disproportionation of the metal atoms induced by axial monoligation. If an ionization process localized on the π* or δ* orbital of $Rh(S_4)$ could be favored by the charge distribution, it however induces an important counterpolarization in the other orbitals of this Rh atom leading to an increase in their electron population. More specifically, this means an increase of the d_{z^2} population, destroying the stabilizing interaction with the σ lone pair of CO. An ionization process depopulating the $Rh(S_4)$ π* orbital would moreover weaken the back-donation interaction with CO. These destabilizing interactions result in a very large energy gap between the two localized solutions, especially for the π^{*3} state (2.07 eV) in favor of a positive hole localized on $Rh(N_4)$. The trend is consistent with the disproportionation scheme proposed for **2** and attributing the respective oxidation numbers 1 and 3 to $Rh(N_4)$ and $Rh(S_4)$. The removal of an electron from the d_{z^2} orbital of $Rh(S_4)$ would correspond to a complete reversal of this latter scheme, $Rh(S_4)$ being considered as a σ donor. Consistently, such a state could not be characterized at the ΔSCF level. The energies computed at the ΔSCF/CI level for the δ^{*1} and π^{*3} ionized states are separated by 0.05 eV only (Table III), and this gap is too small to allow for a reliable prediction concerning the nature of the ground state of the ionized molecule. It can be expected however from the ΔSCF energy gap obtained between the two localized descriptions of the same ionized state that the odd-electron spin density is physically concentrated on $Rh(N_4)$. (Note that the positive hole and the odd-electron spin density are localized on the *same* metal atom.)

We therefore expect $[Rh_2(tcl)_4CO]^+$ to behave as a mixed-valent Rh(II)–Rh(III) complex. No evidence concerning this point could be experimentally obtained from the ESR spectra of the related $Rh_2(tcl)_4tclH$ complex due to the lack of resolution of the *g* signal.[10] However, the complete localization of the odd electron could recently be evidenced for $[Rh_2(ap)_4]Cl$ (ap = 2-anilino-

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(54) The MO basis used for CI calculations represents 29 MOs for complex **1** and 39 MOs for **2**. The number of generated configurations for a given state is about 10 000 for **1** and about 17 500 for **2**. In all CI expansions, the weight of the reference configuration remains slightly higher than 90%.

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(56) The nondynamic correlation of the σ-electron pair in the closed-shell ground state mainly depends upon the exchange integral K_{σ,σ^*} associated with the double excitation from σ to σ*. The value of this exchange term is enhanced with the distribution of the σ and of the σ* density in the same region of space. K_{σ,σ^*} therefore decreases with the localization of the σ-electron density on one specific rhodium atom, inducing the localization of the σ* density on the other metal.

Table IV. SCF Orbital Energies (eV) for Metal 1s and 4d Levels in $Rh_2(tcl)_4$ (**1**) and $Rh_2(tcl)_4CO$ (**2**)

	$Rh_2(tcl)_4$			$Rh_2(tcl)_4CO$		
MO	$Rh(N_4)$	$Rh(S_4)$	energy	$Rh(N_4)$	$Rh(S_4)$	energy
1s	100	0	−22637.27	100	0	−22635.35
1s	0	100	−22636.16	0	100	−22637.87
σ	44	42	−10.02	58	21	−9.11
π	51	31	−13.66	10	65	−13.79
π^*	28	42	−11.68	77	10	−10.98
δ	11	69	−13.75	11	67	−14.33
δ^*	46	14	−11.81	53	8	−11.15
σ^*	50	43	+0.05	31	41	+1.41
$d_{x^2-y^2}$			+3.25			+2.32
$d_{x^2-y^2}$			+5.00			+5.94

pyridinate), another dirhodium complex displaying axial monoligation.[9] The experimental study could not decide however among the three factors that could be at the origin of the localization: (i) the effect of axial monoligation; (ii) the different equatorial coordination spheres surrounding the two rhodium atoms; (iii) the twist angle of the two equatorial planes.[9] It appears from the present study that axial monoligation is by far more important than differences in axial coordination to generate a polarization of the spin density in (Rh_2^{5+}) complexes. The splitting of the metal net charges caused by a polar distribution of the equatorial ligands could however be sufficient to cause some localization of the odd electron. The localization will in this case remain incomplete unless the metal–metal overlap in the open-shell MO comes close to zero (case of a $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ doublet ground state).

3. Comparison with Experimental Results. The ionization energies computed for $Rh_2(tcl)_4$ and for the CO adduct suffer from contradiction with experiment concerning an important point. All computed d-metal ionization energies *decrease* upon CO bonding by 1.27, 0.55, and 0.24 eV, respectively for the σ^1, π^{*3}, and δ^{*1} configurations. On the other hand, the reported half-wave potentials for oxidation increase in the order

$$Rh_2(tcl)_4 < Rh_2(tcl)_4tclH < Rh_2(tcl)_4CO$$

thus suggesting a lowering of the HOMO upon axial bonding.[10] A detailed analysis of the theoretical trends is therefore necessary to give a tentative explanation of the discrepancy. It must be noticed first that the tendency toward a decrease of the ionization energies of metal orbitals consistently appears at all levels of calculation, including Koopmans' theorem. The SCF energies for metal orbitals are displayed in Table IV. For localized orbitals such as π, π^*, δ, or δ^*, these MO energies can be correlated with the shielding of the nuclear charge due to valence electrons: the more shielded the nucleus, the higher the orbital energy. This difference in the valence-electron environments of $Rh(N_4)$ and $Rh(S_4)$ conversely affects the energy of the metal inner core orbitals. More accurately than the atomic net charges, which are strongly dependent upon space partitioning, the variation of these core orbital energies can therefore provide a measure for the relative shielding of the metal atoms. Table IV shows that $Rh(N_4)$ in **1** is less shielded than $Rh(S_4)$, having lower 1s orbital energy. This appears consistent with the localization of the odd electron on $Rh(S_4)$ in the lowest computed ionized states of **1** (Table III). Upon CO fixation, the disproportionation of the Rh(II)–Rh(II) complex into Rh(I)–Rh(III) deeply modifies the electron shielding in accordance with the change in formal oxidation number: $Rh(N_4)$, corresponding to Rh(I), becomes more shielded than $Rh(S_4)$, *but also more shielded than* $Rh(S_4)$ *in* **1**. The energy rise with respect to **1** is 0.81 eV for the 1s orbital, and this order of magnitude is retained for the π^* and δ^* orbitals (Table IV). Conversely, $Rh(S_4)$ in **2** becomes less shielded than $Rh(N_4)$ in **1**, and the 1s-, π-, and δ-orbital energies *decrease* accordingly. Concerning the σ orbital, delocalized in **1** but polarized in **2** on the most shielded atom, $Rh(N_4)$, the direct consequence of disproportionation is also a rise in energy. Moreover, the polarization of the σ orbital also weakens the metal–metal bond, reducing the stabilization due to the overlap of the d_{z^2} orbitals. Both effects operate in the same direction and lead to a considerable decrease of the ionization energy, 0.91 eV according to Koopmans' theorem approximation, 1.27 eV at the ΔSCF/CI level. This discussion is a reminder that the orbital energies are sensitive not only to direct changes in orbital interactions (as happens for the σ and σ^* MOs) but also to changes in the populations of the surrounding valence orbitals. As a consequence of such changes related to the Rh–Rh bond polarization, the highest occupied metal orbitals tend to be *destabilized* in the CO monoadduct.

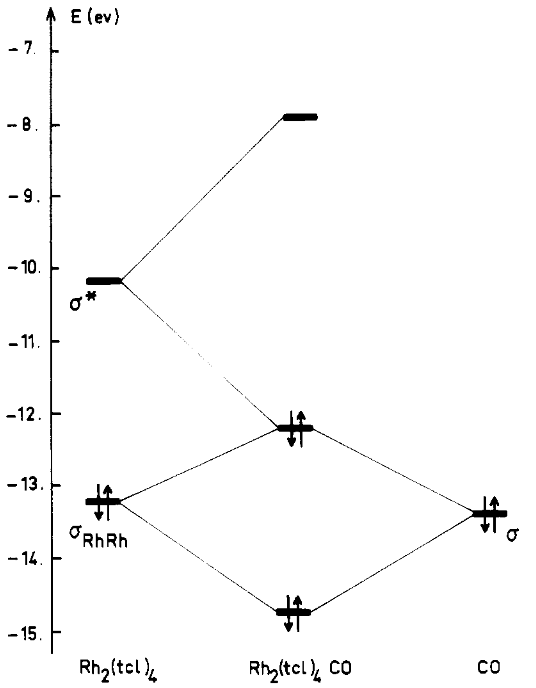

Figure 1. Orbital interaction diagram between the σ and σ^* MOs of $Rh_2(tcl)_4$ and the σ lone pair of the axial CO ligand (from extended Hückel calculations).

The opposite trend observed from half-wave potentials leads to questions about the possible role of the solvent ($C_2H_4Cl_2$ or CH_3CN) used for electrochemical studies. Since no definite conclusion can be drawn at the present stage of investigation, we intend to carry out in the near future experimental and theoretical investigations on the photoelectron spectra of $Rh_2(tcl)_4tclH$ and $Rh_2(tcl)_4CO$.

5. Qualitative Interpretation of the Visible Spectra of 1 and 2

The visible spectra of **1**, **2**, and the ionized form of **1** have been reported by Lifsey et al.[10] The absorptions of **1** and **2** are strikingly different: $Rh_2(tcl)_4$ has three peaks at 465, 500, and 610 nm with absorption intensity $\epsilon = 8 \times 10^2$ M^{-1} cm^{-1}, whereas $Rh_2(tcl)_4CO$ has only one peak at 500 nm ($\epsilon = 3 \times 10^2$ M^{-1} cm^{-1}). Although no characterization of the excited states has been carried out in the present work, a careful analysis of the energy levels arising from SCF and ΔSCF calculations should provide a qualitative interpretation of these differences. Let us first assume, in view of the reported ϵ values, that the observed peaks correspond to ligand field excitations. Three empty metal-orbital combinations could in principle accommodate an electron upon excitation from an occupied level: the σ^* orbital and both combinations of the $d_{x^2-y^2}$ rhodium orbitals. These latter MOs are however destabilized to high energies due to their interaction with the lone pairs of the bridging ligands (Table IV). *The direct consequence is the probable involvement of the* σ^* *orbital in all the reported peaks.* The changes in the σ^* orbital upon CO coordination will therefore represent a determining factor for the location of the ligand field peaks in **1** and **2**. An orbital energy diagram illustrating the interactions of the dimetal σ and σ^* MOs with the carbonyl σ lone pair has been obtained from extended Hückel calculations and is displayed in Figure 1. The dimetal σ-bonding combination at −13.2 eV strongly interacts with the CO lone pair at similar energy and gives rise to a stabilized combination with mainly CO character, at −14.75 eV. The other consequence of this interaction should be a strong destabilization of the dimetal σ orbital. This destabilization however remains moderate (−12.2 eV) *due to the interaction with the σ* orbital*, which gives rise to an orbital combination mainly localized on $Rh(N_4)$, as discussed above. The destabilization is finally transferred to the unoccupied σ* orbital (−7.8 eV instead of −10.2 eV in $Rh_2(tcl)_4$), which undergoes the inverse localization process. Although extended Hückel calculations tend to exaggerate the destabilization of the σ* MO, the same trend clearly appears from the energy of the σ* LUMO in SCF calculations (+0.05 eV in $Rh_2(tcl)_4$, +1.41 eV in $Rh_2(tcl)_4CO$; Table IV). Since the computed destabilization of the highest occupied metal levels, except for σ, is less than 0.6 eV (Table III), the energy rise of the σ* MO appears sufficient to explain the shift of the lowest peak to higher energies upon CO binding. A more detailed assignment of the peaks appears unwise at this level of theory. One could merely notice that the clustering of the three highest occupied metal levels within 0.3 eV in **2** (Table III) could explain the observation of a unique peak, whereas the characterization of three distinct peaks for **1** could be correlated with the more scattered distribution of the occupied levels (Table III). An interesting point is the marked distribution of the occupied levels (Table III). An interesting point is the marked decrease of the exctinction coefficient upon axial coordination. This can be interpreted in terms of the *opposite polariation* between the 4d component of the σ* MO on the one hand, polarized on $Rh(S_4)$,[57] and all three highest occupied levels on the other hand, polarized on $Rh(N_4)$ (Table III and IV). This opposite polarization will obviously reduce the spatial overlap between the mixing states and could therefore be at the origin of the observed collapse of the extinction coefficient.

6. Conclusions

The ab initio SCF/CI study of models for the $Rh_2(tcl)_4$ and $Rh_2(tcl)_4CO$ complexes and their cations stresses the importance of axial monoligation to their electronic structure. It appears that the strong σ bond with d_{z^2} density equally distributed over the two metal atoms is not significantly affected by the polar (4,0) distribution of the tcl ligands, in spite of an important charge polarization of the Rh(II)–Rh(II) core. This is due to the fact that the nonsymmetric perturbation effected by equatorial coordination remains local to each metal atom (i.e., the perturbation is not transmitted to the other metal through a delocalized M–M interaction). For the same reason, the π back-donation from $Rh(S_4)$ to CO in the monoadduct does not affect the other rhodium atom. On the other hand, the axial coordination of CO induces through the Rh–Rh σ bond a disproportionation of the dirhodium core leading ultimately to the Rh(I)→Rh(III)←CO bonding scheme. The polarization of the Rh–Rh bond greatly enhances the σ donation from CO to $Rh(S_4)$ but weakens both the Rh–Rh bond and the π back-donation to the axial ligand. The intensity of the response of the metal–metal σ bond to axial monoligation could result from the balance between these opposite effects. Another consequence of the localization of most of the d_{z^2} population on $Rh(N_4)$ in the CO monoadduct is the energy rise of the unoccupied σ* MO. This could explain the large differences in the positions and intensities of the bands observed in the visible spectra of **1** and **2**. These changes in the electronic structure of the neutral molecule could affect the ground state of the cation. The characterization at the ΔSCF/CI level of the lowest ionized states of $Rh_2(tcl)_4CO$ yielded practically identical energy values for the $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$ doublet states. Although the calculations cannot reliably decide between these two configurations in assigning the nature of the open-shell ground state, it appears that the spin density corresponding to the odd electron is most probably localized on $Rh(N_4)$, in agreement with the disproportionation scheme deduced from the ground-state wave function of the neutral complex. A similar localization is less probable for $[Rh_2(tcl)_4]^+$, although it is favored by the weak δ–δ overlap in the semioccupied MO of the complex. If such localization does occur, the spin density will be mainly concentrated on $Rh(S_4)$, the polarization being opposite to that predicted for the axially monoligated complex. One must finally keep in mind that the present ab initio study describes an isolated molecule. Bonding interactions with a polar solvent, which can be expected in view of the incomplete coordination sphere of these dirhodium complexes, could modify the reported results.

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(57) The large polarization of the 4d component of the σ* MO on $Rh(S_4)$ in $Rh_2(tcl)_4CO$ does not appear so clear-cut from the population analysis (41% weight on $Rh(S_4)$ but still 31% weight on $Rh(N_4)$; Table IV), due to an important contamination of the LUMO by the 5s orbital of $Rh(N_4)$.