Electronic Structure and Bonding Energetics of a Complex Undergoing Intramolecular Disproportionation: Ab Initio Two-Configuration SCF and CI Investigation on $O_3ReReCl_2(H_2PCH_2PH_2)_2$

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Ab initio SCF, two-configuration SCF (TCSCF), and CI calculations have been carried out on $O_3ReReCl_2(H_2PCH_2PH_2)_2$ (1), a model for $O_3ReReCl_2(dmpm)_2$, a recently characterized complex undergoing intramolecular disproportionation. Calculations show that the formal oxidation states Re(VI)–Re(II) do not correspond to the real distribution of the valence d electrons. The electronic constraints associated with the pentagonal pyramid conformation of the $ReCl_2(dmpm)_2$ unit induce an important charge transfer toward the trioxorhenium fragment eventually leading to a d^2–d^4 distribution of the metal electrons, which corresponds to metal oxidation states V (in the trioxorhenium unit) and III. The electronic structure of the trioxorhenium group in **1** is then markedly different from that of the monometallic species $(L)ReO_3$, where L is a σ-donor ligand. In fact, the metal–metal bond in **1** is strongly polarized and can be interpreted in terms of a σ donation from $[ReO_3]^-$ to $[ReCl_2(H_2PCH_2PH_2)_2]^+$. The energy of the unsupported metal–metal bond has been computed by considering a dissociation into neutral or into ionic fragments. Correlation of the σ electron pair and conformational relaxation of the isolated fragments are requisite to obtain a reliable value of the bonding energy. The energy of the homolytic dissociation products in their computed equilibrium conformation, namely planar ReO_3 and octahedral $ReCl_2(H_2PCH_2PH_2)_2$, happens to be higher than the energy of **1** by 78 kJ·mol^{-1}.

Introduction

One of the current trends of organometallic chemistry is the development of systematic routes for the synthesis of heterobi- or polymetallic complexes displaying in the same molecule a variety of sites for potential catalytic activity.[1] In a similar way, the chemical activity of *homobinuclear* complexes can be given enlarged potentialities if the symmetry connecting most of the time the two metal fragments is broken, giving rise to two atoms of the same metal in different environments and oxidation states. In contrast to the wide field of heterobimetallics, the domain of dimetal complexes undergoing such intramolecular disproportionation remains at the present time extremely scattered.[2-7] All those complexes were obtained from symmetric dimers exhibiting a multiple metal–metal bond, and all of them *except for the title molecule* retain M–M formal bond orders varying from 3 to 4. Theoretical investigations have been focused up to now on models of the Mo(IV)–Mo(0) complex characterized by Chisholm and co-workers, $(iPrO)_4MoMo(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[6] SCF-Xα-SW calculations carried out by Bursten and Schneider[8] show that in spite of the formal d^2–d^6 charge distribution, the metal valence electrons are shared so as to generate a triple metal–metal bond in the reported molecule and, possibly, a quadruple metal–metal bond if alkoxides are replaced by weaker π donors permitting the δ charge transfer to occur. CASSCF calculations carried out in our group on a model of the same complex[9] indicate that the triple bond is established between highly charged fragments (±0.90 e). The combination of the multiple d–d coupling with the electrostatic attraction results in a binding energy between the two fragments of 560 kJ·mol^{-1}, largely higher than the stabilization energies of 250–350 kJ·mol^{-1} currently attributed to Mo–Mo triple bonds.[10] The dirhenium(VI,II) complex $O_3ReReCl_2(dmpm)_2$ (dmpm = $Me_2PCH_2PMe_2$) recently characterized by Ara and colleagues[7] (Figure 1) provides another enticing opportunity to investigate the bonding energetics of disproportionated species: this complex presents an unsupported Re–Re bond which is formally single in spite of a very short bond

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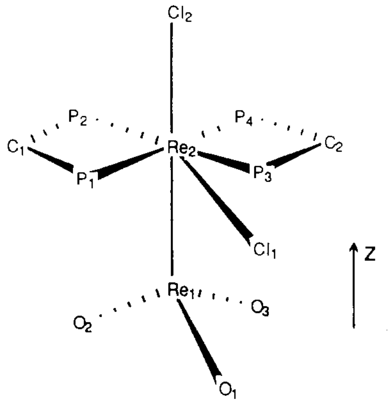

Figure 1. View of the $O_3ReReCl_2(H_2PCH_2PH_2)_2$ molecule.

length (2.4705 Å). It has been also noticed[7] that the difference in coordination numbers (4 and 7) appears unprecedented in the field of metal–metal-bonded dimetallics. Finally, the trioxorhenium fragment has been characterized in a series of complexes with a single donor atom (O,[11] Cl[12]) or ligand (CH_3,[13] alkyl, or aryl substituents,[13,14] N(mesityl)$_2$,[15] or more complex monoanionic ligands[16]). It is of interest to know whether the $ReCl_2(dmpm)_2$ fragment also acts as a σ donor toward the trioxorhenium or if another bonding mechanism is at work.

Computational Strategy

Two-configuration SCF (TCSCF) calculations have been carried out on a model of the complex of Ara et al. where the dmpm ligands have been replaced by $H_2PCH_2PH_2$ groups (**1**). The reference space is composed of the metal–metal $\sigma^2\sigma^{*0}$ and $\sigma^0\sigma^{*2}$ configurations accounting for a proper dissociation of the Re–Re bond. The calculations were performed by means of the ASTERIX program system[17] modified for core potential integral evaluation.[18] We employed the relativistic effective core potentials of Christiansen et al.[19] for the Re atoms, leaving the 5s and 5p shells out of the core. The 15 remaining electrons are described with an optimal 6s,5p,5d basis set contracted into 4s,4p,4d and including diffuse functions. The core potentials of Hay and Wadt[20] have been used for P and Cl atoms. The outer s and p shells were described with reoptimized 5s,5p basis sets contracted into 3s,3p sets. All-electron basis sets were used for the other atoms, namely the 10s,5p basis set optimized by Huzinaga for oxygen,[21] increased with one s diffuse function and one p diffuse function (exp 0.0752 and 0.0515, respectively) and contracted to 6s,4p according to Dunning's procedure,[22] the 9s,5p basis set optimized by Huzinaga for carbon[23] and contracted to 3s,2p, and a 4s basis set contracted into double-ζ for hydrogen.[21] This resulted in a molecular basis set composed of 248 contracted Gaussians for **1**, generating as much as 162 949 570 two-electron integrals above the rejection threshold of 10^{-7} hartrees due to the modest symmetry (C_s) of the molecule. The calculation on **1** was carried out using the geometry experimentally determined for $O_3ReReCl_2(dmpm)_2$ and assuming P–H distances of 1.417 Å collinear to the directions of the P–C bonds. The correlation of the electron pair involved in the metal–metal coupling was then completed by a two-reference configuration interaction expansion accounting for all possible excitations of those two electrons in the complete virtual space.[24] In order to investigate the bond energy between the ReO_3 and the $ReCl_2(H_2PCH_2PH_2)_2$ moieties, SCF, TCSCF, and CI calculations were carried out on both fragments in different electronic configurations and geometries. Assuming first that no geometrical relaxation did occur in the isolated fragments, two dissociation processes were considered yielding (i) $[ReO_3]^-$ and $[ReCl_2(H_2PCH_2PH_2)_2]^+$ both in a closed-shell singlet state and (ii) neutral fragments both in their $^2A'$ ground state. To be consistent with the calculation performed on **1**, the energy of the fragments was determined at the TCSCF and CI levels for $[ReO_3]^-$ and at the SCF level for the cation and for the neutral species.

In a second series of calculations, a geometry optimization at the SCF level was carried out on each dissociation fragment, successively considered in its ionic and in its neutral state of lowest energy.[26] A TCSCF + CI treatment was finally carried out at the optimal geometry of $[ReO_3]^-$.

Results and Discussion

Electronic Structure of 1. The total energy computed for **1** at the SCF level amounts −518.190 696 hartrees. Correlating the electron pair responsible for the metal–metal bond improves the energy value to −518.227 510 hartrees. A Mulliken analysis of the correlated wave function (Table I) exhibits an important charge transfer *from the $ReCl_2(H_2PCH_2PH_2)_2$ moiety to the trioxorhenium fragment.* The net fragment charge amounts ±0.785 e. Except for the population of the d_{z^2} orbitals of both metal atoms, the orbital charge distribution is not drastically modified with respect to that obtained for separate $[ReO_3]^-$ and $[ReCl_2(H_2PCH_2PH_2)_2]^+$ ions.[27] The electronic structure of the metal in the unrelaxed $[ReO_3]^-$ ion is characterized by a very high population of the 6s + 6p shell (1.89 e, mainly concentrated on the 6s orbital). Three molecular orbitals of $[ReO_3]^-$ receive an important contribution from the metal 6s orbital. Two of them are involved in metal–oxygen bonding, illustrating once again the trend, analyzed in many complexes of transition metals, to promote electron density into the outer sp shell of the metal in order to increase the potentialities for covalent bonding.[28] The last orbital to benefit from a large 6s contribution is the HOMO of $[ReO_3]^-$, which can be described as an almost pure metal hybrid orbital with s + d_{z^2} character. The nature of the HOMO also accounts for the high population of the metal d_{z^2} orbital in $[ReO_3]^-$ (1.560 e). The other two by two near-degenerate d orbitals of the anion receive some population (0.635 and 0.718 e) from their interaction with the oxo ligands. If d electrons only are considered, the electronic structure of $[ReO_3]^-$ appears in

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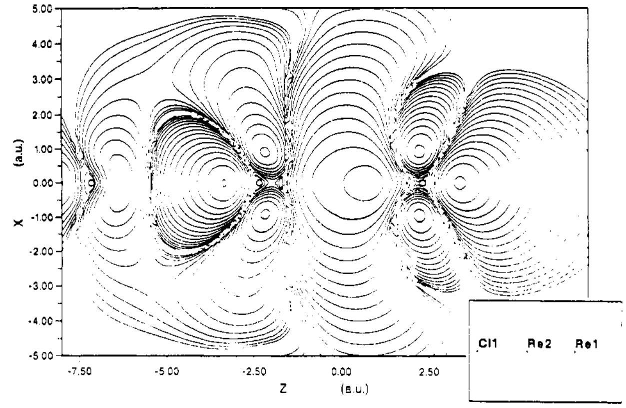

Figure 2. Electron density generated by the Re–Re σ-bonding orbital of the TCSCF wave function in the plane containing the Re–Re axis and perpendicular to the σ_h mirror plane. The outermost contour line corresponds to 2×10^{-5} e·Å^{-3}. The density is doubled at every subsequent contour.

Table I. Mulliken Analysis of the Wave Function Computed for $O_3ReReCl_2(H_2PCH_2PH_2)_2$ (**1**) and for the Isolated, Unrelaxed, Ionic or Neutral Moieties ReO_3 (**2**) and $ReCl_2(H_2PCH_2PH_2)_2$ (**3**)

	molecule 1		ionic fragments		neutral fragments	
	2	**3**	$[2]^-$	$[3]^+$	**2**	**3**
			Net Charges			
fragment	−0.785	+0.785	−1.0	+1.0	0.0	0.0
metal	+0.717	−0.190	+0.806	−0.100	+1.149	−0.020
			Metal Orbital Populations			
6s	1.584	0.335	1.460	0.490	1.053	0.518
Σ6p	0.530	0.884	0.455	0.776	0.518	0.695
d_{xy}	0.783	0.751	0.718	0.771	0.776	0.610
d_{xz}	0.697	1.815	0.643	1.908	0.833	1.833
d_{yz}	0.760	1.889	0.639	1.930	0.828	1.906
$d_{x^2-y^2}$	0.796	0.773	0.718	0.792	0.775	0.654
d_{z^2}	1.133	0.743	1.560	0.432	1.067	0.803

agreement with the formal assignment of the metal as Re(V), d^2 *in the anion.* The presence of an occupied metal orbital with s + d_{z^2} character enables the trioxorhenium ion to act as a σ donor. As a matter of fact, the orbital populations of the ReO_3 moiety in the dimetal system **1** agree with the interpretation of the bonding as a σ donation *from the Re(V) atom of* $[ReO_3]^-$ *to the Re(III) atom of* $[ReCl_2(H_2PCH_2PH_2)_2]^+$. The d_{z^2} population of Re(V) decreases from 1.560 e in $[ReO_3]^-$ to 1.133 e in **1** to the benefit of the d_{z^2} orbital of the facing metal (Table I).[1] The populations of all other valence orbitals of Re(V) have slightly *increased*, which suggests a tightening of the metal–oxo bonds.

The density distribution generated by the Re–Re σ-bonding orbital obtained from the TCSCF calculation (Figure 2) confirms the interpretation of the bonding in terms of a σ donation or, at least, of a strongly polarized σ bond. The bonding maximum of density located on the Re–Re axis at 0.82 Å only from Re(V) clearly belongs to the atomic basin of this metal.[29] In spite of the pure σ-bonding character of the orbital, the disk-shaped region of bonding density extends very far apart from the metal–metal axis, conspicuously exhibiting the contribution of the diffuse 6s orbital of rhenium to the bonding hybrid.

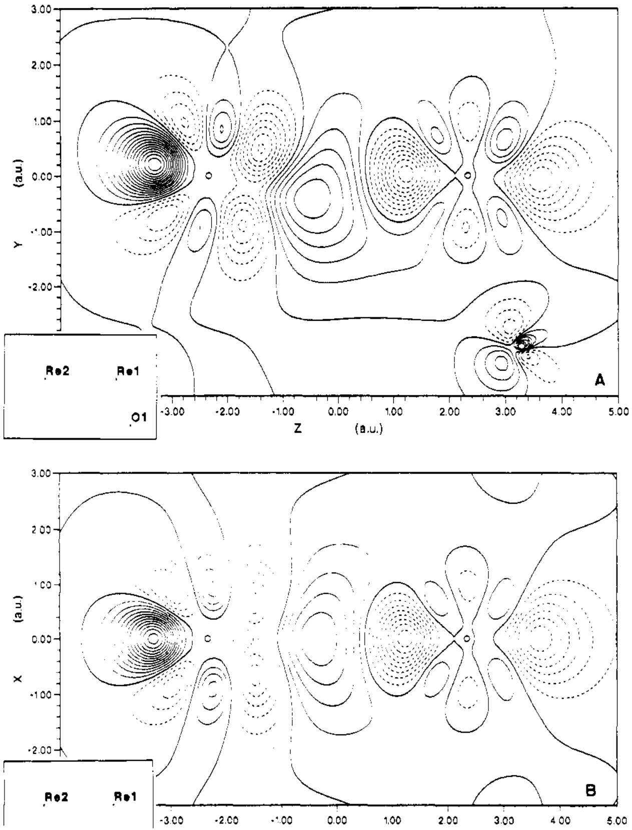

Figure 3. Plot of the electron deformation density in **1** with respect to the *ionic* fragments $[ReO_3]^-$ and $[ReCl_2(H_2PCH_2PH_2)_2]^+$: (A) σ_h mirror plane containing the two metal atoms, one oxygen, and one chlorine; (B) plane perpendicular to σ_h containing the two metals. Solid lines represent positive density, negative contours are dashed, and zero contours are bold. Contour interval: 0.05 e·Å^{-3}.

Deformation Density Maps. The electron deformation density distribution, computed as

$$\Delta\rho = \rho_{(1)} - (\rho_{[ReO_3]^-} + \rho_{[ReCl_2(H_2PCH_2PH_2)_2]^+})$$

has been represented in Figure 3 in two perpendicular planes containing the Re–Re axis. Those maps first illustrate the information obtained from the population analysis of the trioxorhenium fragment: slight density accumulations in the regions of the d_{xz}, d_{yz} orbitals and a diffuse sphere of 6s density compensate for the large depopulation of the d_{z^2} orbital, *thus globally maintaining in the molecule the charge separation of the ionic fragments.* The most important information conveyed by the maps is the presence around the center of the Re–Re axis of a large, disk-shaped region of density accumulation characteristic of a relatively strong metal–metal bond.[30] This accumulation cannot be attributed to an artifact possibly generated by the reference to a superposition of ionic fragments. Central peaks similar in location and height are also characterized in the distribution computed with respect to a superposition of *neutral* fragments in their doublet ground state, as displayed in Figure 4. It should be noted that the bond accumulation characterized around the Re–Re axis is surprisingly similar in shape and height to the peaks generated by some *quadruple* metal–metal bonds of chromium and molybdenum.[9,31] No doubt that the interpretation is quite different in the present case: the Re–Re coupling is a pure σ single bond, and the isotropic extension of the density accumulation in the x and y directions, classically interpreted as the signature of a triple or quadruple metal–metal bond, results in the present case from the prominent role of the diffuse 6s orbitals of rhenium in the bonding MO.

Interpretation of the Bonding. The strongly dipolar character of **1** revealed by the Mulliken population analysis has induced us to rationalize the bonding in **1** as an interaction between two charged fragments. An obvious alternative is to consider the Re–Re bonding as a covalent coupling between two neutral

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(29) According to the Mulliken population analysis, 73% of the σ-bonding electron density should be attributed to the trioxorhenium fragment.

(30) One should however keep in mind that the present map is computed with respect to a superposition of molecular fragments, which tends to magnify the region of bonding density, if compared to a standard promolecule composed of neutral, spherical atoms. See for instance: Hall, M. B. In *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, M. B., Eds.; Plenum: New York, 1982, pp 205–220.

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fragments exhibiting each a σ hybrid populated with one electron. But how can we explain then the massive charge transfer toward the trioxorhenium fragment and the strongly polarized character of the σ-bonding orbital?

The answer lies in the organization of the coordination sphere around the Re(III) atom: five ligands in the equatorial plane and two ligands, including $[ReO_3]^-$, in axial positions (Figure 1). The accommodation in the xy plane of five σ-donor ligands requires both the d_{xy} and the $d_{x^2-y^2}$ orbitals to be unoccupied in order to generate in this plane a torus of low electron density, i.e. an acceptor zone with cylindrical symmetry. The directionality constraints therefore vanish, and the five ligands are accommodated in the equatorial plane so as to minimize the electronic and steric repulsions. Let us consider now the d_{z^2} orbital, which is destabilized (i) by an antibonding interaction with the equatorial ligands acting through its toroidal component and (ii) by the presence of two ligands in axial positions. The d_{z^2} orbital eventually remains unoccupied, and no more than two orbitals, d_{xz} and d_{yz}, are then left to accommodate without penalty the metal valence electrons (Table I). The heptacoordinated rhenium atom is then forced into the oxidation state III.[32] The electron pair that cannot be either accommodated by the heptacoordinated metal, or equally shared between the two moieties, is then transferred to the σ hybrid of the trioxorhenium unit. It should be noticed that the description of the trioxorhenium fragment in terms of a σ donor is quite unusual, since most complexes characterized with ReO_3 are $(L)ReO_3$ species, where L unambiguously represents a *σ-donor* ligand.[11-16] Ab initio SCF calculations carried out on methyltrioxorhenium and on the recently characterized cyclopentadienyltrioxorhenium[33] both predict the ligand, either σ or π donor, and the trioxorhenium unit to be neutral radicals rather than ionic fragments.[34]

Bonding Energetics. The Re–Re bond in **1** is unsupported, which provides a rare opportunity to investigate the bond energy. The energies computed at the SCF, TCSCF, and CI levels for **1** and for the fragments ReO_3 (**2**) and $ReCl_2(H_2PCH_2PH_2)_2$ (**3**), either unrelaxed or in their optimized geometry, are reported in Table II. In the following discussion and in the energy diagram of Figure 5, it is implicit that the σ electron pair is either correlated through TCSCF and CI treatments (in **1** and in $[\mathbf{2}]^-$) or shared between the two neutral fragments considered each in their doublet ground state and then appropriately described at the open-shell SCF level of approximation.

Let us first consider the dissociation into two metal fragments, either neutral or ionic, without allowing for any change in the geometry of the fragments with respect to their conformation characterized in **1**. Two conclusions emerge from Figure 5: (i) the homolytic and the ionic dissociation processes are comparable in energy, with a slight advantage (59 kJ·mol^{-1}) for the homolytic path and (ii) the computed dissociation energy is not less than 500 kJ·mol^{-1} (560 kJ·mol^{-1} for the ionic dissociation path). How can be interpreted such a huge bonding energy? If ionic fragments are considered, it appears obvious that the most important stabilization factor is by far the electrostatic interaction.[35] If we now start from the neutral fragments, the bond energy of 500.5 kJ·mol^{-1} is much too large to be considered as an exclusive consequence of the overlap between the σ hybrids. It should be remembered that the SOMO of fragment **3** is strongly destabilized by antibonding interactions with both the equatorial ligands and the axial chlorine atom.[32] A major part of the stabilization energy should therefore be attributed to the substantial charge transfer that goes along with the bond formation, drastically reducing the contribution of the destabilized SOMO.

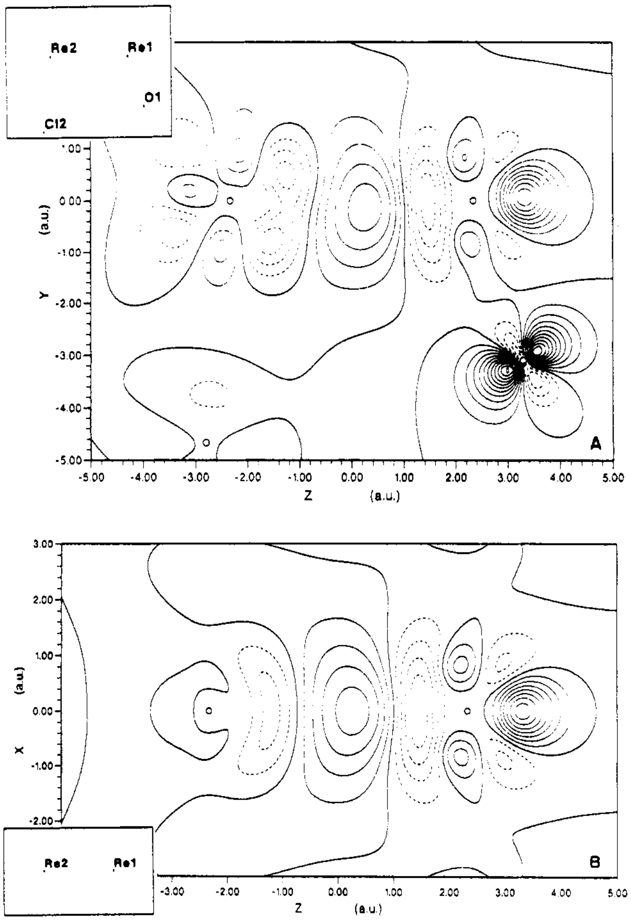

Figure 4. Plot of the electron deformation density in **1** with respect to the *neutral* fragments. Planes and contours are as in Figure 3.

Optimizing the geometry of the fragments completely modifies the bonding energetics. The conformation of minimal energy for $[ReO_3]^-$ is computed to be planar D_{3h}, with a Re–O bond length of 1.726 Å. When the pair correlation energy is accounted for, the stabilization with respect to the pyramidal geometry of the unrelaxed fragment amounts 86 kJ·mol^{-1}. The planar D_{3h} conformation which minimizes the electrostatic repulsion between the oxygen atoms is also preferred by the neutral fragment with an optimal distance of 1.699 Å and a stabilization of 53 kJ·mol^{-1}. The most drastic change in conformation and in energy affects the $ReCl_2(H_2PCH_2PH_2)_2$ fragment. It is clear that the pentagonal pyramid structure is disadvantaged even for the cation because of (i) the steric and electronic crowding in the equatorial plane and (ii) the relatively large electrostatic repulsion between the axial and the equatorial chlorine ligands. In the hypothetical free fragment, the coordination sphere will obviously reorganize in a quasi-octahedral conformation with both chlorine ligands in axial positions. Because of the near-degeneracy of the d_{xz} and

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(32) In the unrelaxed *neutral* $ReCl_2(H_2PCH_2PH_2)_2$ fragment, the σ donation from both the equatorial ligands and the axial chlorine atom destabilizes the singly occupied metal σ orbital, which is pushed much higher in energy than the SOMO of the trioxorhenium fragment, thus accounting for the polar character of the metal–metal bond. An electronically less demanding conformation would tilt both chlorine atoms by 45° to make them coincide with the directions of the metal d_{xz} orbital, whereas the equatorial diphosphine ligands adopt a symmetric conformation with the carbon atoms along the y axis. Three orbitals, namely d_{yz}, $d_{x^2-y^2}$, and d_{z^2} are then available to accommodate the metal d electrons, giving more flexibility to the electronic structure. In the experimentally characterized complex, however, this conformation cannot be competitive because of the repulsive contacts between the chlorine atoms and the methyl substituents of the dmpm units.

(33) Hermann, W. A.; Taillefer, M.; de Méric de Bellefon, C.; Behm, J. *Inorg. Chem.* **1991**, *30*, 3247–3248.

(34) (a) Szyperski, T.; Schwerdtfeger, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1228–1231. (b) Wiest, R.; Bénard, M. Unpublished data.

(35) The electrostatic attraction of the ionic fragments has been evaluated according to Morokuma's energy decomposition procedure.[36] It amounts 1144 kJ·mol^{-1}, compensated in part by the exchange repulsion that develops between the two fragments.

(36) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236–1244. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325–340.

Table II. Closed-Shell or Open-Shell SCF, TCSCF, and CI Energies (hartrees) Obtained for **1** and for the Fragments ReO_3 (**2**) and $ReCl_2(H_2PCH_2PH_2)_2$ (**3**)[a]

molecule	level of computation	geometry	sym	state	energy (hartrees)
1	SCF(CS)	exptl	C_s	$^1A'$	–518.190 696
	TCSCF[b]	exptl	C_s	$^1A'$	–518.204 568
	CI[c]	exptl	C_s	$^1A'$	–518.227 510
[**2**]$^-$	SCF(CS)	unrelaxed	C_s	$^1A'$	–302.801 387
	TCSCF[b]	unrelaxed	C_s	$^1A'$	–302.811 157
	CI[c]	unrelaxed	C_s	$^1A'$	–302.815 988
[**3**]$^+$	SCF(CS)	unrelaxed	C_s	$^1A'$	–215.198 243
[**2**]$^-$ + [**3**]$^+$	pair correl included	unrelaxed			–518.014 231
bond energy					0.213 279
2	SCF(OS)	unrelaxed	C_s	$^2A'$	–302.684 226
3	SCF(OS)	unrelaxed	C_s	$^2A'$	–215.352 682
2 + **3**		unrelaxed			–518.036 908
bond energy					0.190 602
[**2**]$^-$	SCF(CS)	optimized	D_{3h}	$^1A'_1$	–302.836 085
	TCSCF[b]	optimized	D_{3h}	$^1A'_1$	–302.841 233
	CI[c]	optimized	D_{3h}	$^1A'_1$	–302.848 920
[**3**]$^+$	SCF(OS)	optimized	D_{2h}	$^3B_{1g}$	–215.314 700
[**2**]$^-$ + [**3**]$^+$	pair correl included	optimized			–518.163 620
bond energy					0.063 890
2	SCF(OS)	optimized	D_{3h}	$^2A'_1$	–302.704 483
3	SCF(OS)	optimized	D_{2h}	$^2B_{3g}$	–215.493 366
2 + **3**		optimized			–518.197 849
bond energy					0.029 661

[a] Fragments **2** and **3** are considered in unrelaxed and optimized geometries, in the lowest energy states of their neutral and ionic forms. The Re–Re bond energy is given with respect to dissociation into neutral or ionic fragments, either unrelaxed or optimized. [b] The reference configurations in **1** are $\sigma^2\sigma^{*0}$ and $\sigma^0\sigma^{*2}$, σ designating the Re–Re bonding orbital. In $[ReO_3]^-$, the HOMO, with $5d_{z^2}$ + 6s character, correlates with an unoccupied orbital located in the same region of space. [c] Starting from the TCSCF orbital, all excitations of the two σ electrons with respect to the above-mentioned reference configurations are included.

d_{yz} levels, the octahedral structure of **3** has been computed and optimized in the $^3B_{1g}$ state with d_{xz} and d_{yz} occupied each with one electron. The stabilization with respect to the unrelaxed form amounts 306 kJ·mol^{-1}, with an important decrease of the Re–Cl bond length (2.427 Å compared to 2.483 Å for the equatorial Re–Cl bond and 2.553 Å for the axial Re–Cl bond in **1**) and an elongation of the Re–P bond length (2.524 Å vs an average Re–P distance of 2.439 Å in **1**).

Since an octahedral complex has three orbitals available to accommodate the valence d electrons (d_{xz}, d_{yz}, and $d_{x^2-y^2}$), this conformation should be still better suited to the neutral d^5 fragment. As a matter of fact, the stabilization with respect to the pentagonal pyramid reaches 369 kJ·mol^{-1} with equilibrium distances Re–Cl = 2.543 Å and Re–P = 2.481 Å.

Eventually, the Re–Re bond energy computed with respect to neutral fragments in their optimal structures does not exceed 78 kJ·mol^{-1} (Table II). Incidentally, neglecting the correlation energy of the σ-bonding electron pair would have reversed the conclusions concerning the relative stability of **1** with respect to its fragments.[37]

The result of the present calculations, summarized in Figure 5, should not be regarded as a tentative reaction path. If a *real* dissociation is to be considered, a straightforward correspondence can be established between the occupied orbitals of **1** and those of the ionic fragments [**2**]$^-$ + [**3**]$^+$. A concerted relaxation of the fragments retaining the C_s symmetry should therefore lead to the ionic species *without an energy barrier*. From a standard orbital analysis, no barrier is required either for the homolytic dissociation into neutral fragments. However, the charge transfer and the geometrical reorganization are important and a more thorough investigation of the reaction path should be necessary. Such calculations are clearly beyond the scope of the present study.

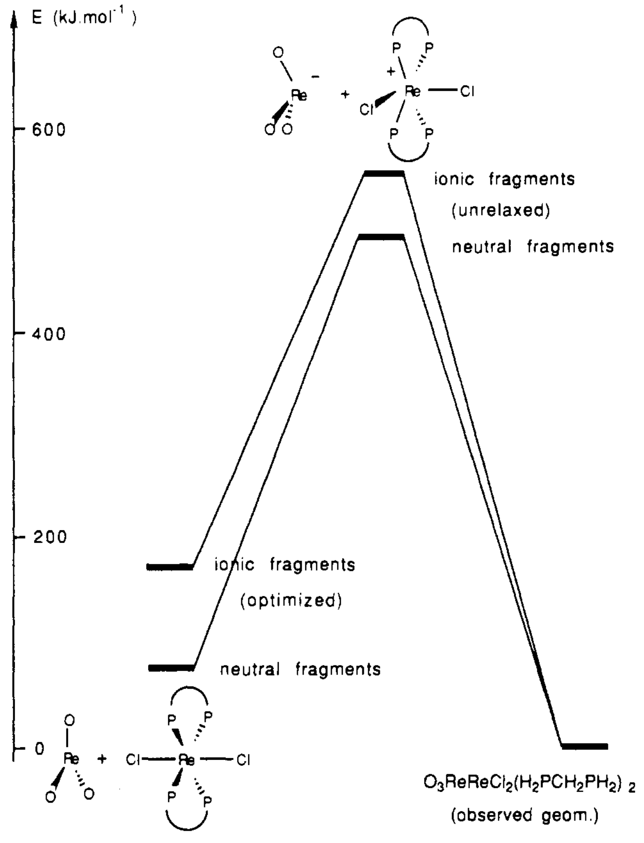

Figure 5. Relative energy (kJ·mol^{-1}) of the isolated fragments, either ionic or neutral, in their optimal geometry (left-hand side) and in their unrelaxed conformation (center) with respect to molecule **1** in its observed geometry (right-hand side).

Summary and Conclusion

Ab initio calculations have shown that the electronic structure of **1** is conditioned by the conformation of pentagonal pyramid of the $ReCl_2(dmpm)_2$ moiety. No more than two orbitals (d_{xz} and d_{yz}) are left to accommodate without penalty the valence d electrons, so that a d^4 electronic configuration is imposed on the corresponding rhenium atom. The consequences are (i) an important charge transfer toward a $5d_{z^2}$/6s hybrid orbital of the trioxorhenium fragment and (ii) a strongly polarized metal–metal bond that can be interpreted as a σ donation *from the trioxorhenium fragment to the $ReCl_2(dmpm)_2$ unit.* Calculation of the bond energy with respect to *unrelaxed* fragments, either ionic or neutral, yields very high energy values that can be interpreted either in terms of electrostatic interaction between the charged fragments or, if neutral species are considered, in terms of the stabilization associated with the charge transfer from the d^5 $ReCl_2(dmpm)_2$ unit to the trioxorhenium fragment. Conformational relaxation of the isolated fragments leads to considerable stabilization, especially for $ReCl_2(H_2PCH_2PH_2)_2$, either neutral or cationic, which adopts an octahedral structure with the chlorine atoms in axial positions. The bond energy computed with respect to fragments in their optimized geometry amounts to 78 kJ·mol^{-1} for the homolytic dissociation and 168 kJ·mol^{-1} for the separation into $[ReO_3]^-$ and $[ReCl_2(H_2PCH_2PH_2)_2]^+$.

Acknowledgment. All calculations have been carried out on the CRAY-2 computer of the CCVR (Palaiseau, France) through a grant of computer time from the Conseil Scientifique de Centre de Calcul Vectoriel de la Recherche.

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(37) A relatively large CI calculation (1 million configurations) was carried out on **1** to check by correlating 38 valence electrons that no other major nondynamic correlation effect was susceptible to qualitatively influence the results. The respective coefficients of the $\sigma^2\sigma^{*0}$ and $\sigma^0\sigma^{*2}$ configurations are 0.916 and –0.056. No other configuration has a coefficient higher than 0.05, thus ensuring the reliability of the TCSCF + CI description. It is expected however that the computed bond energy should be slightly increased by a more extended account of *dynamic* correlation and by optimizing the geometry of **1**.