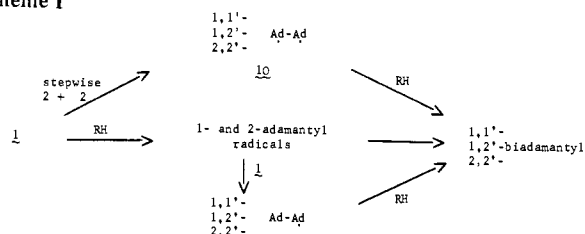Scheme I

tadiene, the same four products are accompanied by 13% **2**. The structure of **2** was verified by a comparison of spectra with those obtained by McKervey.[12,23] In addition, 5% of another product, whose spectra were consistent with a vinylcyclobutane, was isolated. Although the detailed structure of this compound awaits further work, it appears to be the result of a [2 + 2] cycloaddition of **1** to butadiene.

It seems clear from the formation of **2** that adamantene is produced by the pyrolysis of **9**. Formation of the $C_{20}H_{28}$ fraction is less diagnostic, as it is difficult to resolve fully the question of the composition of this mixture. At least isolation of this material is consistent with the intermediacy of adamantene. Most intriguing is the isolation of the biadamantyls. What is the mechanism of their formation? Control experiments show that they are not secondary products formed by pyrolysis of the $C_{20}H_{28}$ fraction and do not interconvert under the reaction conditions. Three possible routes suggest themselves (Scheme I). Were adamantene to dimerize in a stepwise fashion, a set of 1,4 diradicals **10** would be produced that might abstract hydrogen to form the biadamantyls. However, we know of no precedent for such a process. If adamantene abstracts hydrogen to give the 1- and 2-adamantyl radicals, either subsequent dimerization or addition to adamantene would yield the biadamantyls.[25]

No source of biadamantyls not involving adamantene, probably a powerful hydrogen abstractor, is apparent. If this surmise is correct, why haven't biadamantyls been formed in all the previously reported reactions thought to involve adamantene? If adamantene is an intermediate in all these reactions, the difference in behavior may be due to the disparate environments or even to the possibility that adamantenes of different spin states, singlet or triplet, are involved.

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David J. Martella, Maitland Jones, Jr.*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Paul v. R. Schleyer

Institut für Organische Chemie
Universität Erlangen-Nürnberg
8520 Erlangen, Federal Republic of Germany

Ab Initio Studies of the Metal–Metal Bond in $Re_2Cl_8^{2-}$

Sir:

Since the discovery[1,2] of the "quadruple" metal–metal bond in $Re_2Cl_8^{2-}$, numerous experimental[3-6] and theoretical[7-9] studies have been carried out to understand the bonding and electronic spectra of this species and related complexes. In this preliminary communication we report the results of ab initio calculations on the lowest electronic states of $Re_2Cl_8^{2-}$ and $Re_2Cl_8^{3-}$. These calculations have been made possible by the development of ab initio effective core potentials[10] (ECP's) which enable one to replace all but the outer valence electrons with a local potential which reproduces the energies and shapes of the valence orbitals. Calculations using ECP's yield results which are generally in good agreement with all-electron calculations. In addition, the dominant relativistic effects in heavy atoms such as Re can be included[11] in the ECP's. Although an assessment of the overall reliability of core potential calculations will await results of many more calculations, recent studies of Au, Hg and Xe compounds[12] yielded potential energy curves, excitation energies, and ionization potentials that compared well with experimental data.

Ab initio studies by Benard and Veillard[13] of multiple bonds in Cr dimers have shown that a proper description requires a *multi-configuration* wavefunction, in contrast to the traditional *single-configuration* Hartree–Fock wavefunction.[14] These effects of electron correlation can account for as much as 100–200 kcal/mol of the bond energy in Cr and Mo dimers,[13,15] and for ~90 kcal/mol of the triple bond in N_2.[16] The starting point for the present calculations on $Re_2Cl_8^{2-}$ is a generalized valence bond (GVB) description[16,17] of the eight electrons in the Re–Re bond while the remaining Cl-like orbitals are described in terms of doubly-occupied molecular orbitals. Instead of representing the overall wavefunction by the single configuration $(\ldots (\sigma)^2(\pi_x)^2(\pi_y)^2(\delta_{xy})^2)$ each of the pairs in the Re–Re bond is represented by a two-configuration function (e.g., $c_1(\sigma)^2 - c_2(\sigma^*)^2$ instead of $(\sigma)^2$, where $\sigma(\sigma^*)$ is the bonding (antibonding) combination of metal $5d_{z^2}$-like orbitals). This allows proper dissociation into $ReCl_4^-$ fragments (when $c_1 = c_2$ for all four pairs). Alternatively each pair can be cast into a GVB representation (e.g., $\sigma_a(1)\bar{\sigma}_b(2) + \sigma_b(1)\bar{\sigma}_a(2)$ for the σ pair) where the overlap of the GVB orbitals $\langle \sigma_a | \sigma_b \rangle = S_\sigma = (c_1 - c_2)/(c_1 + c_2)$ can be taken to be a measure of the bond order. A single contracted Gaussian function was used to represent the 3s and 3p functions on each

Table I. Analysis of the Four Pairs Describing the Eight 5d Electrons in $Re_2Cl_8^{2-}$

Pair	Overlap ("bond order")	2-Configuration representation[a]
σ	0.65	$0.98\ (\sigma)^2 - 0.21\ (\sigma^*)^2$
π_x	0.51	$0.95\ (\pi_x)^2 - 0.31\ (\pi_x^*)^2$
π_y	0.51	$0.95\ (\pi_y)^2 - 0.31\ (\pi_y^*)^2$
δ_{xy}	0.11	$0.78\ (\delta)^2 - 0.63\ (\delta^*)^2$
Total	1.78	

[a] The σ, σ^*, π, π^*, δ, and δ^* orbitals refer to a_{1g}, a_{2u}, e_u, e_g, b_{1g}, and b_{2u} symmetry orbitals, respectively.

Table II. Calculated Excitation Energies for the Lowest States of $Re_2Cl_8^{2-}$ and $Re_2Cl_8^{3-}$

State	Main confign	Excitation energy, eV			
		GVB	CI-1[a]	CI-2[b]	Exptl
		$Re_2Cl_8^{2-}$			
$^1A_{1g}$	$(\delta)^2, (\delta^*)^2$	0.00	0.00	0.00	
$^3A_{2u}$	$(\delta)^1(\delta^*)^1$	0.08	0.26	0.35	
$1\,^1A_{2u}$	$(\delta)^1(\delta^*)^1$		3.34	2.87	1.76–1.94
		$Re_2Cl_8^{3-}$			
$^2B_{2u}$	$(\delta)^2(\delta^*)^1$		0.00	0.00	
$^2B_{1g}$	$(\delta)^1(\delta^*)^2$		0.95	0.93	

[a] GVB-CI: involves eight valence orbitals and includes 64 spin functions in the CI calculation on the ground state. [b] (1 + 2)-CI: involves eight valence plus 28 virtual orbitals and includes 402 energy-selected spin eigenfunctions.

Cl, while a more flexible basis comprised of two contracted functions was used to describe each of the 5d, 6s, and 6p orbitals of Re.[18]

The results of the 4-pair, 16-configuration GVB calculation on the ground $^1A_{1g}$ state of $Re_2Cl_8^{2-}$ are summarized in Table I. The eight orbitals involved in the Re–Re bond (σ, σ^*, π_x, π_x^*, π_y, π_y^*, δ_{xy}, δ_{xy}^*) are almost exclusively 5d in character and are comprised of the z^2, xz, yz, and xy 5d components expected from the interaction of two $(5d)^4$ ML_4 fragments. The major admixtures into these 5d-like orbitals are metal 6s (13%) in σ and Cl 3p (5 and 9%) in π and δ, respectively. A $Re^{+1.22}Cl^{-0.55}$ charge distribution is obtained from the Mulliken population analysis. The effect of the second configuration in each pair becomes progressively more important in the σ, π, and δ pairs. As a result the overlap decreases in the order $S_\sigma\ (0.65) > S_{\pi_x} = S_{\pi_y}\ (0.51) > S_\delta\ (0.11)$. The resulting total bond order of 1.8 is markedly smaller, as usual, than the formal bond order of four.[19] (For comparison, the overlaps in the N_2^- triple bond[16] are $S_\sigma = 0.89$ and $S_\pi = 0.69$ for a total bond order of 2.3.) The nearly equal weights of the bonding $(\delta)^2$ and antibonding (δ^*) configurations indicate an extremely weak δ-bond between the $5d_{xy}$ orbitals on each metal atom. In such a situation one expects a very low-lying triplet state, and indeed GVB calculations on the $^3A_{2u}$ state arising from the $\delta \rightarrow \delta^*$ excitation place it at 0.08 eV *above* the $^1A_{1g}$ state. The necessity of a multiconfiguration approach is dramatically illustrated by a comparison of the energies of the main configuration for the $^1A_{1g}$ and $^3A_{2u}$ states which predicts the triplet state to be 3.5 eV *below* the singlet state (in contradiction with the observed diamagnetism of the complex[1]).

To obtain more quantitative estimates of the excitation energies, CI calculations (Table II) were carried out, where additional single and double excitations were generated which were not included in the GVB wavefunction. The more accurate (1 + 2)-CI results (Table II) place the $^3A_{2u}$ state at 0.35 eV (2800 cm^{-1}). The singlet–triplet splitting suggests that the

δ orbitals account for only 0.2 eV of the binding in the ground state.

The corresponding δ–δ^* $^1A_{2u}$ state is found to lie at 2.87 eV (23 000 cm^{-1}). Experimentally[2,3] a z-polarized absorption band at 14 000 cm^{-1} has been assigned in $Re_2Cl_8^{-2}$ to the dipole allowed $^1A_{1g}$–$^1A_{2u}$ transition, which implies the calculations overestimate the excitation energy by $\sim$1 eV. There appear to be no experimental studies in the long-wavelength region, 2000–3000 cm^{-1}, to confirm the presence of a $^3A_{2u}$ state, however. The most recent theoretical studies of metal–metal bonds have been of the Xα-scattered wave type,[9] which in the case of $Re_2Cl_8^{2-}$ predict a $\delta \rightarrow \delta^*$ transition energy of 4488 cm^{-1} to an excited state which corresponds to a mixture of singlet and triplet spin multiplicities.

Similar calculations (Table II) on $Re_2Cl_8^{3-}$ predict an excitation energy of 0.93 eV (7500 cm^{-1}) for the $^2B_{2u}$–$^2B_{1g}$ ($\delta \rightarrow \delta^*$) transition. Although experimental evidence is lacking, this value is comparable with the observed excitation energy (5900 cm^{-1}) in the isoelectronic $Tc_2Cl_8^{3-}$ species[20] for the $\delta \rightarrow \delta^*$ band.

Results for the higher electronic states of $Re_2Cl_8^{2-}$ as well as the effects of spin-orbit coupling[21] and of point charges about the cluster will be presented in a forthcoming paper, where the reliability of ECP calculations will be discussed at greater length.

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P. Jeffrey Hay

Theoretical Division
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545
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