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REGULAR ARTICLE

Chemical reactivity of second-row transition metal clusters from Hückel-type calculations

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Abstract Chemical reactivity of mixed transition metal clusters of the second-row is investigated by extended Hückel molecular orbital calculations including a parametrized core repulsion term. Using atomization energies and charge or Fukui indices for bond and site attacks, respectively, it is found that reactivity is enhanced in mixed clusters in comparison with pure ones in agreement with available experimental results.

Keywords Technetium–ruthenium and rhodium–palladium clusters · Chemical reactivity

1 Introductory remarks on mixed transition-metal clusters

1.1 Reactivity problems

In many instances, second-row transition metal clusters (from Tc to Pd) present an enhanced chemical reactivity when one or more atoms of the cluster are replaced by another one from the same row. This is the case when for catalytic purposes palladium clusters are partially doped with rhodium. It is also the case when an unavoidable Tc–Ru transmutation occurs in technetium clusters found in platinoid alloys of spent fuels from nuclear reactors. The first case is a positive effect which is monitored industrially for catalytic gas exhaust systems. The second one turns out to have luckless consequences on the stability of spent fuels coming from nuclear reactors, as far as platinoid clusters are considered.

More generally speaking, the study of the reactivity or the inertness of metal clusters is nowadays a very active and interdisciplinary field of research ranging from atomic, molecular to solid state physics both experimentally and theoretically. Because chemical reactivity is very much influenced by the interplay of different atoms, we have tried to clarify its consequences on the electronic picture of mixed (Pd–Rh and Tc–Ru) compounds by quantum chemical computations.

1.2 Methodology considerations

The numerical results obtained through quantum chemical calculations, using ab initio methods implemented now in efficient computer programs, are rather impressive. This concerns isolated small molecules, those considered in Astrochemistry (e.g., the HCN/HNC pair) as well as in reaction systems involved in Organic Chemistry, or in Biochemistry (e.g., precursors of polypeptides and nucleic acids). Accurate studies for molecules containing only one metal can be easily performed even for elements of the second row, but the case of compounds where several metals are linked together is much more complicated for theoretical as well as practical reasons.

As indicated by some ab initio calculations for simple polyatomic clusters formed from a single transition element (e.g., Pd) [1–5], the main difficulty for a self-consistent treatment originates from the existence of almost

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degenerated states close to the expected ground state (with possibly different multiplicities). The situation is even worse when we consider mixed clusters (e.g., Pd–Rh species) because of the increased intricacy of their electronic energy spectrum and the possibility of many isomers. If we regard the finite metal clusters as precursors of ordinary metallic conductors, we can speak of an adiabaticity drawback in the construction of the ground state potential energy surface, a well-known difficulty in Dynamics calculations by the Car–Parrinello method. According to a suggestion of Prof. O. Salvetti we decided to perform extended-Hückel-type calculations (EXTHUC) instead of attempting to have chemical information on these compounds by resorting to the DFT methodology, as done for compounds with formally d [14] transition metals [6–9]. In fact, DFT does not eliminate the quasi-degeneracy problem above-mentioned, in spite of the semi-empirical character of its functionals. The number of electrons assigned to the orbital energy levels is the main ingredient of the EXTHUC theory, which in its iterative form with respect to charge distribution may be considered as a pre-density functional theory [10]. Our basic idea was the possibility of simulating ab initio treatments using appropriate EXTHUC parameters for transition metals.

2 The EXTHUC approach

Given the lack of precise data on the nature and the mechanisms of reactions occurring between metal clusters and molecules, we have identified the chemical processes in question to simple atom and bond attacks, intelligible in terms of standard chemical descriptors (i.e., atomic charges, spin densities, Fukui indices and energy differences). The purpose of this paper was to evaluate these quantities conveniently.

Our calculations method can be summarized as follows:

1. The extended Hückel method (EXTHUC) in the primitive form developed by Wolfsberg and Helmholz for the study of transition metal anions [11] has been chosen as the starting point of our theoretical approach for clusters. The molecular orbitals are computed in a non-iterative way from a Hamiltonian matrix whose diagonal elements for *s*, *p*, *d* basis functions are extracted from spectroscopic Slater–Condon parameters for atoms [12], and the off-diagonal elements evaluated by means of the standard formula:

$$H_{pq} = K\left(H_{pp} + H_{qq}\right)S_{pq} \tag{1}$$

Overlap integrals, S_{pq}, have been calculated from single-zeta Slater integrals with optimized exponents for the second-row transition metals [13] and Coulomb matrix elements H_{pp}'s have been taken not from the corresponding usual electronegativities because of their lack of accuracy in the series Tc, Ru, Rh, but from the survey of Alvarez [14], those for Ru being interpolated between the two distinct sets given by that author. Actually, EXTHUC is a tight-binding treatment with overlap [15] generating the usual band model of solids when the size of the compounds considered increases to infinity [16].

A rather large set of K parameters going from the value $K = 1.75$ chosen by Hoffmann for Organic Chemistry [17] to much greater values for inorganic compounds are found in the literature. In the present case, our choice $K = 3$ has a computational advantage: it leads to a clear-cut distribution of the occupied molecular orbitals in two families, those having a dominant *s*-character, which can be associated to the skeleton of the cluster, and those having a dominant *d*-character, which mimic the *d*-band of solids in the case of finite-size system. The orbital energies e_d forming an almost closed shell are distributed around the H_{dd} matrix elements in a rather small interval, whereas the energies of the former look like the eigenvalues of the topological graph formed by a network including n equivalent vertices [18]. Taking a common value γ for each matrix element H_{pq} of the chemical formula, we find a lowest eigenvalue e_i equal to $(n-1)\gamma$ and $(n-1)$ highest eigenvalues equal to $-\gamma$. Therefore, it is possible to isolate the pseudo d-band of the cluster by taking a not too small K value; but changing K and possibly overlaps S_{pq} do not imply a concomitant variation of the cluster binding energy because the core repulsion terms included in the treatment has to be readjusted accordingly.

2. The total one-electron energy spectrum is computed as a sum of occupied orbital energies:

$$E_1 = \sum_i v_i e_i \tag{2}$$

using occupation numbers v_i, the value of which were fixed according to the *Aufbau* recipe described in [19]. For the *d*-dominant orbitals, v_d is fixed to the average population of the five *d*-orbitals of the isolated atom in its chemical significant $d^q s$ [1] valence states, i.e., $v_d = q/q5.5$ for a pure cluster P_n and $(nq + nq')/5(n + n')$ for a mixed cluster $P_nQ_{n'}$. The total number of remaining electrons, exactly equal to the number of atomic centers, is distributed among the *s*-dominant orbitals with the double occupancy or an equidistribution for those located below or above the *d*-block.

3. In the usual EXTHUC method, the calculation of atomization energies (binding energies) is computed by subtracting atomic energies from the sum of molecular orbital energies. Separating the sum of the $(4d^q 5\ s)$ matrix elements H_{pp} from their molecular counterpart, we get a provisional estimate ΔE_0 of the atomization energy. It is later improved by adding a repulsion component E_{rep} to the

electronic energy E_{elec} in order to generate better potential energy curves. To do so we have used a Born–Mayer repulsion term of the form:

$$E_{\mathrm{c}} = \sum_{k'} \sum_{k \neq k'} \alpha_{\mathrm{PQ}} \mathrm{e}^{-\beta_{\mathrm{PQ}}(r_{k,k'} - d_{\mathrm{PQ}})} \qquad (3)$$

with two bond parameters α_{PQ} and β_{PQ} The values of α_{PQ} and β_{PQ} are chosen in such a way that total energies are in agreement with ab initio reference data. We make the assumption of a balance between electronic and repulsive components of the forces acting on atoms at equilibrium geometry. This is achieved in our program by computing as usual first derivatives of the energy with atomic displacement along the sides x, y, z of a cube taken as Cartesian coordinates. In principle the α_{PQ} parameters are specific energy prefactors corresponding to a pair of atoms P, Q located at centers k and k', while exponentials including the β_{PQ} parameters describe the repulsive trend of the ion–core interaction in terms of metal–metal distances $r_{k,k'}$through the formula $\beta_{\mathrm{PQ}}\left(r_{k,k'} - d_{\mathrm{PQ}}\right)$. The d_{PQ} constants are generally identified to the bulk interatomic distance [20, 21] whereas the $r_{kk'}$ distances correspond to the equilibrium bond lengths we have selected. Slightly different EXTHUC approaches of metal clusters may be found in the earlier literature, for instance that of [22, 23].

Fitting α and β parameters on given atomization values is straightforward for tetrahedral pure clusters because we can identify the six pairs of nuclear centers k, k' to the six equivalent bonds. So we can distribute the two components of the total energy E_{elec} and E_{rep} in equal parts between the six bonds and determine α and β by considering one bond only. First we compute β by taking the ratio between the Hellmann–Feynman first derivative of E_{elec} and E_{rep} itself. Starting with this value, we get α by assuming that E_{rep} balances the deviation of our primitive atomization energy ΔE_0 from the reference data for tetramers. As theoretical references energies are not available for Tc and Ru, we have extrapolated them from our study of Rh_4 using the ratio between our estimate and ab initio atomization energy.

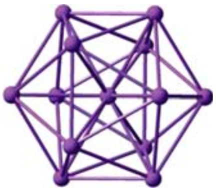
Parameters β_{PQ} are kept constant independently of the size of the cluster, but the α_{PQ} have been readjusted for larger compounds in such a way the electronic and repulsive forces on atoms at equilibrium are still vanishing.

The input data of the present study for pure clusters are gathered in Table 1 (EXTHUC parameters) and Table 2 (repulsion potential). The data for mixed clusters were obtained using a geometric-mean rule between different atoms for the α_{PQ}'s and an arithmetic mean rule for β_{PQ} and $d_{\mathrm{PQ.}}$ As regards equilibrium bond lengths, their values were fixed to the arithmetic average of the P–P and Q–Q bonds for pure compounds of the same size.

Table 1 EXTHUC parameters (H_{PP} in au, exponent ζ)

	K	H_{PP}	ζ
Tc			
5s–5s	3	−0.370	1.85
5p–5p		−0.198	1.85
4d–4d		−0.471	3.00
Ru			
5s–5s	3	−0.331	1.75
5p–5p		−0.184	1.75
4d–4d		−0.467	3.20
Rh			
5s–5s	3	−0.297	1.75
5p–5p		−0.168	1.75
4d–4d		−0.459	3.55
Pd			
5s–5s	3	−0.269	1.80
5p–5p		−0.138	1.80
4d–4d		−0.442	3.60

Table 2 Geometry and core repulsion parameters for second-row transition metal clusters

	Symmetry	α	β	$r^{a}_{kk'}$
	T_d	Tc 0.054	0.697	4.8545
		Ru 0.055	0.526	4.7500
		Rh 0.045	0.618	4.8150
		Pd 0.060	0.522	5.0758
	O_h	Tc 0.038	0.697	4.9468
		Ru 0.031	0.526	4.9210
		Rh 0.030	0.618	4.9210
		Pd 0.041	0.522	5.1280
	I_h	Tc 0.022	0.697	5.0415
		Ru 0.017	0.526	4.9330
		Rh 0.017	0.618	5.1695
		Pd 0.023	0.522	5.0153

[a] Equilibrium bond lengths to be compared to the following bulk values

$d_{\mathrm{Tc–Tc}} = 5.11$; $d_{\mathrm{Ru–Ru}} = 5.01$; $d_{\mathrm{Rh–Rh}} = 5.08$; $d_{\mathrm{Pd–Pd}} = 5.20$

3 Results

The atomization energy Δa_p of the process $P_n \rightarrow nP$ concerning a pure cluster is its binding energy with respect to its atomic constituents. Since this quantity is connected to the magnitude of the energy stored in the cluster, we have expressed it in atomization energy per atom $\delta p = \Delta a_p/n$ with the intention of investigating this reaction for clusters of different size and to consider clusters $P_{n'}Q_{n''}(n + n'' = n)$.

Because atomization energies increase in absolute value with n, expressing these quantities per bond: $\delta_{p\text{–}p} = \Delta a_p/m$, instead of atom could be thought more appropriate. Fortunately, both partitions are completely equivalent for algebraic reasons in the case of a tetrahedron ($n = 4$, $m = 6$) and numerical reasons in the case of an octahedron ($n = 6$, $m = 12$), but only approximately in the case of an icosahedron with in addition an atom P at the center ($n = 12 + 1$, $m = 30 + 12$). Let us note however, that both concepts give different information: the atomization energy per atom may be tentatively connected to bulk properties, whereas the atomization energy per bond allows an insight into the chemical reactivity.

To compare mixed clusters to their parent pure species, it is convenient to express the atomization energies Δa_{PQ} of the former with respect to the approximate values $\Delta A'_{PQ}/n$ they should have if an additive rule in terms of pure clusters were valid. Using atomization energies per atom for clusters of the same size n, we have:

$$\Delta A'_{PQ} = n'\delta_P + n''\delta_Q$$

hence, an energy increment per mixed bond equal to:

$$\varepsilon_{PQ} = \left(\Delta A_{PQ} - \Delta A'_{PQ}\right)\Big/m'$$

where m' is the number of mixed bonds P–Q in the cluster considered. The almost constant value of ε_{PQ} in each series of compounds $P_{n'}Q_{n''}$ justifies the interpretation of $\varepsilon_{PQ} < 0$ as an excess energy per bond, in addition to the fact that an analysis in terms of atomization energy per bond δ_{PP}, δ_{QQ} for pure clusters would give the same results. A survey of the results obtained in this way is given in Table 3.

4 Comments and conclusions

For pure clusters, atomization energies reported above correspond to molecules whose size ($n = 4$, 6, 13) and geometry (symmetry point group: T_d, O_h, I_h) were chosen both for convenience reasons and a possible relationship with bulk properties accessible to experiment. The general tendency exhibited by these values is a regular increase with the size of the cluster and a decrease when going from the left to the right of the second row of transition metals. In spite of evident reserves from the physical and chemical points of view, the theoretical trend to a decrease of atomization energy per atom from Tc to Pd is consistent with the enthalpies for bulk varying regularly from 7.06 kcal/mol for Tc to 3.92 kcal/mol for Pd, and the overall agreement of theory with experiment is encouraging for the present EXTHUC method. The results concerning mixed Pd–Rh and Tc–Ru clusters are illustrated in Fig. 1. It is seen that the insertion of a foreign atom, for instance Rh or Ru, introduces a negative almost constant energy increment per heteronuclear bond with respect to its mean value for pure clusters. This may be interpreted as an additional storage of chemically available energy, which we correlate to a rise of reactivity due to the heteronuclear bonds. The values reported for the Pd–Rh increment are not only consistent with the well-known characteristics of palladium catalysers including rhodium impurities, but also they suggest a better efficiency of very small mixed clusters probably because of a lowering of the energy barrier

Table 3 Additivity parameters δ_P (in brackets) and increments $\varepsilon_{P\text{–}Q}$ for atomization energies in tetramers ($m' = 3,4,3$), hexamers ($m' = 4$) and tridecamers ($m' = 5{+}1$, face substitutions)

	$-\Delta A$	$-\varepsilon_{Tc\text{–}Ru}$		$-\Delta A$	$-\varepsilon_{Pd\text{–}Rh}$
Tc_4	0.6672 (0.1668)	–	Pd_4	0.2960 (0.0740)	–
Tc_3Ru	0.6675	0.0026	Pd_3Rh	0.3827	0.0072
Tc_2Ru_2	0.6627	0.0026	Pd_2Rh_2	0.4548	0.0071
$TcRu_3$	0.6528	0.0025	$PdRh_3$	0.5128	0.0070
Ru_4	0.6378 (0.1595)	–	Rh_4	0.5568 (0.1392)	–
Tc_6	1.0744 (0.1791)	–	Pd_6	0.5111 (0.0852)	–
Tc_5Ru	1.0962	0.0020	Pd_5Rh	0.6046	0.0060
$TcRu_5$	1.1335	0.0019	$PdRh_5$	0.8823	0.0056
Ru_6	1.1315 (0.1886)	–	Rh_6	0.9295 (0.1549)	–
Tc_{13}	3.4558 (0.2658)	–	Pd_{13}	1.8375 (0.1413)	–
$Tc_{12}Ru$	3.4614	0.0019	$Pd_{12}Rh$	1.9380	0.0045
$Ru_{12}Tc$	3.4027	0.0024	$Rh_{12}Pd$	2.7500	0.0048
Ru_{13}	3.3825 (0.2602)	–	Rh_{13}	2.7945 (0.2150)	–

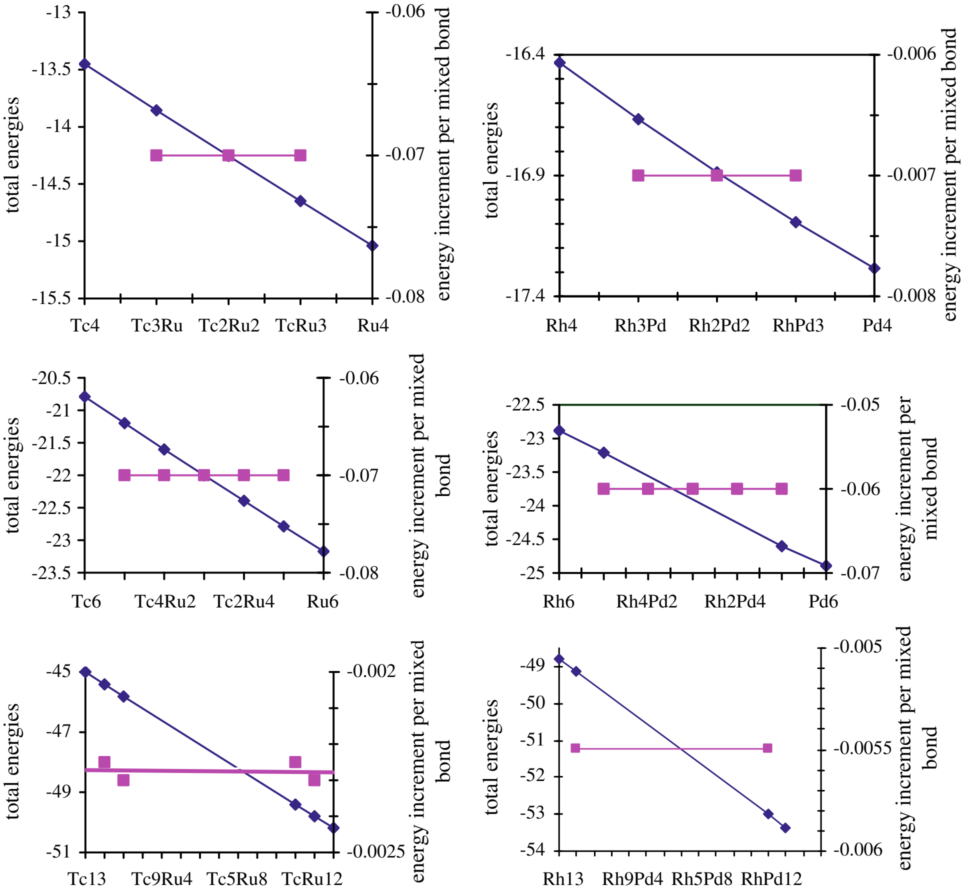


Fig. 1 Effect of atom mixing in atomization energy in the Tc–Pd series

for the formation of adducts on the Pd–Rh bonds. The negative Tc–Ru increment indicates that the mixed bonds act as a reservoir of energy, and so we are entitled to predict a particular affinity of the Tc–Ru bonds to chemical reagents involved in addition reactions.

In principle, the preceding conclusions are valid only for bond attacks. Moreover, they are consistent with those suggested for site-reactivity descriptors derived from a more conventional Mulliken population analysis. Charge distributions may be used for probing the reactivity of different sites with respect of cationic and anionic attacks, while spin densities are invoked for radicalic attacks. The latter can be identified to a common set of condensed Fukui indices [24] for the possible three types of reagents if, as it is presently the case, they are generated by HOMO-SOMO-LUMO eigenvectors belonging to the same energy level. These quantities are given in Table 4 for the Tc–Ru tetrahedral clusters.

Table 4 Mulliken charges and Fukui indices of mixed Tc–Ru tetramers

		Mulliken charges	Fukui indices*
Tc_4	Tc	0	0.250
Tc_3Ru	Tc	−0.260	0.260
	Ru	+0.780	0.219
Tc_2Ru_2	Tc	−0.521	0.270
	Ru	+0.521	0.230
$TcRu_3$	Tc	−0.763	0.279
	Ru	+0.289	0.240
Ru_4	Ru	0	0.250

Actually, the combined effect of the delocalization of the electron cloud between equivalent centers (as in pure clusters) and the changes of the nuclear charges of some atoms is responsible for the variations observed. Tetrahedral and icosahedral systems show similar charge and spin distributions.

Whatever the descriptor used for chemical reactivity is, namely, energy increment per heteronuclear bond corresponding to bond attack or charges and Fukui indices corresponding to atom attack, similar trends are observed. This tendency does not depend of the size of the cluster considered and we can state as a general rule that the inclusion of foreign atoms in clusters of a given transition metal enhances the reactivity of the cluster independently the type of attack (site or bond) is. In the particular case of technetium, its unavoidable decay may cause an enhanced reactivity of technetium sites towards chemical reagents located in the vicinity of the cluster. In the terminology of

Radiochemistry, we would have so to say an inverse Szilard–Chalmers effect that is formation of a chemical bond instead of an extant bond through nuclear transmutations. This fact could have environmental consequences.

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