

RECP calculations for reactions of H₂ with Pt, Os, Ir, and Re – a systematic comparison

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Summary. Relativistic effective core potential calculations have been carried out for the reactions of Pt, Os, Ir, and Re with H₂. The calculations demonstrate the importance of a singly occupied 6s orbital for forming a strong bond. Pt and Ir have low-lying states with such occupancy, whereas Os and Re only attains this through a rather costly excitation. In consequence, the reaction barriers are considerably smaller for Pt and Ir than for Os and Re.

Key words: RECP – Platinum – Osmium – Iridium – Rhenium – Hydrogen

1 Introduction

The study of transition-metal chemistry and its role in catalytic processes, both homogeneous and heterogeneous, is one of the most active areas in modern chemistry. The development of powerful experimental techniques, in particular spectroscopic methods, has been a prerequisite for the advance in this field. This development has also raised many questions challenging theory at the atomic and molecular level, and theoretical aspects of the field are receiving a rapidly increasing attention.

Today, methods for quantitative quantum chemical calculations on molecules containing light elements are well established, while the situation is somewhat more complicated for transition metal compounds due to their size and the problem with *d*-orbitals. The theoretical study of heterogeneous catalysis on metal surfaces presents a number of additional challenges. The “infinite” extent of the metal surface places these systems beyond the reach of the ordinary methods of quantum chemistry, and some model approximation must be employed if such systems are to be studied at all with present day resources. One approach is the cluster approximation in which the metal is represented by a finite cluster of atoms, usually 5–50. Cluster models have been applied in a number of theoretical studies of catalytic processes, and have provided very useful insight into these reactions. However, even minimal model systems consisting of one metal atom and the reacting molecule may yield useful information in model calculations, as

demonstrated by comparison of early work on such models with later cluster results. Also, some of the most interesting and useful catalysts today incorporate third row transition metal atoms. For a reliable treatment of such atoms relativistic effects must be accounted for, as indicated by several studies [1, 2]. Unfortunately, prohibitively large computational resources are required for even an approximate treatment of relativistic effects in many-electron systems, and again some model approximation must be made. Today the most promising approach is based on relativistic effective core potentials (RECPs) [2]. This method has been applied to various compounds containing third row transition metal atoms [3–7], and offers an attractive possibility for studying heterogeneous as well as homogeneous catalysis.

Reactions between transition metals from the third row and hydrogen molecules:



with $M \in \{\text{Re, Os, Ir, Pt}\}$ may be viewed as models for the important reductive elimination and oxidative addition reactions which are involved in many metal-catalyzed processes. These reactions between the bare metal and hydrogen are interesting as an approach to understanding homogeneous catalysis and may also provide insight into the process of chemisorption on metal surfaces.

The hydrogen addition reaction has been extensively studied for the first and second row transition metal atoms by Blomberg and coworkers [8, 9]. For the third row transition metals there exist studies by Balasubramanian et al. [3–5] on MH_2 with $M = \text{Pt, Ir}$ and Re , and by Low and Goddard [7] on PtH_2 . These calculations are, however, carried out using RECPs that are not strictly comparable from one element to another, and the basis sets employed lack f -functions. Preliminary calculations show that f -functions are required for Pt to yield reasonable atomic excitation energies between states that have a different electronic occupation in the d -shell. The inclusion of f -functions stabilizes the d^{10} configurations and destabilizes d^8s^2 configurations with respect to the ground state (d^9s^1); quantitatively by 5.7 and 10.2 kcal/mol for $^1S(d^{10})$ and $^3F(d^8s^2)$, respectively. For the molecule, the reaction energy decreases by 6 kcal/mol upon removal of the f -functions. This is an entirely molecular effect, since both the molecular energy minimum and the energy reference state correspond to a d^9s^1 configuration. These findings concerning the importance of f -function are in line with an earlier study on the PtH molecule [10]. For Re, the f -functions appear to affect the atomic spectrum only. Again, the effect is largest for energy differences between states which differ in the d -shell occupation. The reaction energy changes with less than 2 kcal/mol (6A_1) upon adding f -functions. The corresponding figure for the 4B_1 potential energy surface is only 1 kcal/mol. Another weakness of the earlier mentioned studies is that they are conducted using RECPs without any representation of the nodes of the orbitals. This might lead to spurious results. In the present investigation, the reactions of H_2 with Pt, Ir, Os, and Re have been studied within a consistent procedural framework. The RECPs as well as the basis sets have been developed in similar manner for all the metal atoms. Double zeta basis sets have been used for the valence electrons except for d -orbitals where a triple zeta description was employed, and f -functions are included in order to provide a reasonable description of the correlation energy. The states for the atoms are calculated and compared with available experimental information. A potential energy curve for the lowest state of each symmetry is calculated for each of the reactions.

2 Methods

In this work we use basis sets of Gaussian type functions. The hydrogen atoms are treated at the all-electron level using medium-sized basis sets. The hydrogen atom basis contains 5s-functions contracted to 3 [11] and augmented with one *p*-function with exponent 0.8. The RECP procedure used in this work has been described in detail previously [2]. For all metal atoms a primitive 19s14p11d5f basis was energy optimized in non-relativistic restricted Hartree–Fock calculations [12]. This (uncontracted) basis set was used in atomic reference calculations based on the relativistic no-pair Douglas–Kroll approximation [13]. These results were in turn used to calibrate the RECPs. The RECP parameters were determined using a truncated 8s6p8d basis, where the inner exponents were optimized to fit the atomic orbitals. In all calculations the 5s, 5p and 4d atomic orbitals were kept frozen in the atomic shapes, whereas the 6s and 5d atomic orbitals were considered valence. The local potential consisted of three terms and the coefficients in front of the projection operators were set equal to the absolute value of the *ab initio* core orbital energy.

For the molecular calculations a general contraction based on the atomic RECP calculations was used, leaving the two outer *s*- and *d*-functions free. One extra *d*-function with exponent 0.1 was added for polarization of the bonding region. Pilot calculations for the molecular cases showed that a proper description of 6p was essential for a reasonable treatment of *sp*-hybridization in the linear molecular and the transition states. With a general contraction the addition of two extra *p*-functions was insufficient to describe a 6p atomic, as was clearly indicated by the unrealistically high 6p-orbital energy obtained mainly due to the 5p orthogonality. To remedy this problem two additional *p*-functions were optimized at the non-relativistic level using an excited atomic state where the 6p atomic orbital was occupied. Using this new basis a calculation on the RECP level was carried out on the same atomic state to obtain the coefficients for the 6p function. The final *p*-basis was then constructed from two fully contracted functions describing the atomic 5p and 6p atomic orbitals and two uncontracted outer *p*-functions. The *f*-functions consisted of 3 primitive exponents found by optimizing the SDCI energy of the atoms in their ground states. These exponents were optimized as an even-tempered series with a ratio of $\sqrt{5}$ leaving only one degree of freedom for optimization.

CASSCF calculations were carried out for the metal atoms with an active space including all atomic valence space. Subsequent multireference SDCI calculations were carried out including the configurations having coefficients larger than 0.05 in the CASSCF wavefunction. With the attack on the H–H bond by the metal atom being of greatest interest in studies of catalytic processes, the reaction path was chosen as a symmetric C_{2v} approach of the metal to the bond center. Potential surfaces for some of the lowest states of the reactions between the metals and hydrogen were studied, and stationary points were determined at the MRCCI level including configurations with coefficients larger than 0.05 from an all-valence CAS calculation. In determining the geometries, the *f*-functions were excluded. The distance between the metal and the hydrogen molecule was taken as reaction coordinate, and the H₂ bond distance was optimized for every point. Finally the stationary points were recalculated with the *f*-functions included to obtain the energy differences.

The program package MOLECULE-SWEDEN [14] has been used for all calculations reported here.

3 Results

3.1 Atoms

The results for the RECP calculations on atoms are presented in Tables 1–4 together with experimental results [15]. To obtain the L–S values statistical averaging over the experimental j – j states has been carried out. For Pt two experimental values are given, with the first set derived by straightforward averaging. To obtain the other set we adjusted the 3D_2 – 1D_2 coupling by looking at deviations from the Lande interval rule and applying the approximate selection rule $\Delta l = 0, 1$ [16]. Supporting this rule is the fact that we apply hydrogen-like basis functions. For Pt this implies that spin-orbit coupling between $d^9 s^1$ and $d^8 s^2$ terms is neglected. Preliminary calculations treating the spin-orbit part perturbationally indicate that this approximation is valid. The 3D_3 and 3D_1 states are now unaffected by spin-orbit coupling and the Lande rule is applied to place 3D_2 . The J -averaging using this value for 3D_2 should be more comparable to our calculations. The spin-orbit stabilization energy is the difference between the actual value and the value predicted by the Lande rule. Assuming that 1D_2 is destabilized by the same amount of energy, we can adjust it to a more comparable value. Table 1 shows that the elimination of the 3D_2 – 1D_2 coupling changes the splitting dramatically; it falls from 32 to 12 kcal/mol, which is in fair agreement with our

Table 1. Low-lying terms of the platinum atom. Relative energies in kcal/mol. The E'_{exp} are corrected experimental values, see text. The experimental energies for the 5D term stem from the $j = 4$ component only, and are therefore too low

Term	Occupation	E_{CI}	E_{exp}	E'_{exp}
3D	$d^9 s^1$	0	0	0
1S	d^{10}	7	11	6
3F	$d^8 s^2$	14	15	10
1D	$d^9 s^1$	6	32	12
5D	$d^8 s^1 p^1$	87	80*	75*

Table 2. Low-lying terms of the iridium atom. Relative energies in kcal/mol

Term	Occupation	E_{CI}	E_{exp}
4F	$d^7 s^2/d^8 s^1$	0	0
2P	$d^8 s^1$	17	22
2F	$d^8 s^1$	19	26
4P	$d^8 s^1$	26	32
2G	$d^7 s^2$	29	34
4P	$d^7 s^2$	28	40
2D	$d^8 s^1$	15	48
2H	$d^7 s^2$	48	48
6D	$d^7 s^1 p^1$	72	76
6F	$d^7 s^1 p^1$	72	83

Table 3. Low-lying terms of the osmium atom. Relative energies in kcal/mol. For the ³P term, only the *j*-component with highest energy is experimentally assigned, and therefore only an upper limit can be inferred from experiment

Term	Occupation	E _{Cl}	E _{exp.}
⁵ D	<i>d</i> ⁶ <i>s</i> ²	0	0
⁵ F	<i>d</i> ⁷ <i>s</i> ¹	59	17
³ P	<i>d</i> ⁷ <i>s</i> ¹	30	52
³ F	<i>d</i> ⁷ <i>s</i> ¹	38	28
³ H	<i>d</i> ⁶ <i>s</i> ²	41	34
⁷ P	<i>d</i> ⁵ <i>s</i> ² <i>p</i> ¹	64	—
⁷ D	<i>d</i> ⁶ <i>s</i> ¹ <i>p</i> ¹	94	68

Table 4. Low-lying terms of the rhenium atom. Relative energies in kcal/mol

Term	Occupation	E _{Cl}	E _{exp.}
⁶ S	<i>d</i> ⁵ <i>s</i> ²	0	0
⁴ P	<i>d</i> ⁵ <i>s</i> ²	51	37
⁶ D	<i>d</i> ⁶ <i>s</i> ¹	44	41
⁴ G	<i>d</i> ⁵ <i>s</i> ²	55	45
⁸ P	<i>d</i> ⁵ <i>s</i> ¹ <i>p</i> ¹	54	61
² D	<i>d</i> ⁵ <i>s</i> ²	76	66

result of 6 kcal/mol. This treatment is not possible for the *d*⁸ *s*² terms. One can however predict that ³F must be stabilized by spin-orbit coupling since it is lowest in energy, expecting the value of our calculation to be too high. Our result is only 4 kcal/mol too high, and no conclusion should be made on this basis. It is still reasonable to expect a less dramatic perturbation of the ³F term, since the terms to which it couples are considerably higher in energy. The experimental L–S estimates arrived at through this procedure are quite close to those obtained in the calculations, suggesting that a straightforward statistical averaging may not provide data suitable for comparison with L–S coupled results.

For platinum the *d*⁸ *s*² states are approximately 10 kcal/mol higher than the *d*⁹ *s*¹ state – this will be reflected in the bonding picture for the platinum compounds. It is also worth noting that the *d*⁸ *s*¹ *p*¹ state is substantially above the other state. This is the excited state that is responsible for the *sp*-hybridization in the linear structure.

For iridium the agreement with experimental results is reasonable for all states, except ²D, taking the state averaging into consideration. We are, however, at a loss to explain the sizable discrepancy for the ²D state. The lowest quartet states show heavy mixing between the *d*⁷ *s*² and the *d*⁸ *s*¹ occupations. Again it is worth noting that the lowest doublets are 15–20 kcal above the quartets and that the *d*⁷ *s*¹ *p*¹ occupation is far above the two other possibilities. In previous calculations only the ⁴F and the ²F have been considered [4]. For osmium and rhenium the picture is quite similar. The agreement is reasonable except for two states for osmium

showing discrepancies that we are not able to explain. Again the states with p -occupation are far above the other states.

We want to emphasize at this point that these atomic results are of crucial importance in explaining the potential curves and the stationary points for each of the reactions.

3.2 PtH_2

The geometry and energy differences for the stationary points are displayed in Table 5, whereas the characters of the active orbitals for the separated system limits (SSLs) and the molecular energy minima are listed in Table 6. For all the Tables 6, 8, 10 and 12 we list the occupation of the active orbitals. This information is mainly qualitative – in order to keep the information compact, we have simplified to some extent. For instance, when the tables list an orbital as a singly occupied d -orbital, it may have some contamination of s -character and an occupation slightly different from unity.

The prominent state for platinum is the 1A_1 . The SSL for this state is the $d^{10} 1S$ state which is smoothly transferred into $d^9 s^1$ to allow bonding through sd -hybridization. This makes an angled structure preferable and a very strong binding is obtained. It is interesting to note that our results for the geometry are in excellent agreement with recent Dirac–Hartree–Fock (DHF) calculations by Dyal [17] which yield a Pt–H distance of 1.52 Å and a H–Pt–H angle of 88 degrees. Dyal's calculations show a decomposition energy of 35 kcal/mol, while our corresponding value is 50, but as our calculations are one-component, and his do not include correlation, agreement on this point is not to be expected.

For all other singlets studied by us the $^1D d^9 s^1$ state is the SSL state. Symmetry restrictions force all these states to have two open orbitals in the minimum geometry. One is an antibonding orbital in the B_1 representation which is primarily a d -orbital and the other is a pure d -orbital. The system tries to compensate for this by applying the p -orbital. This is seen from a population analysis which shows d - and sp -populations of approximately 8.5 and 1.5 electrons respectively. Both the antibonding character of the b_1 -orbital and the p -excitation force the energy up. The geometries are also reflecting this as the binding angles are larger compared with almost 90 degrees for the 1A_1 state. For the triplet states the pattern is almost the same; high energy in the minimum due to symmetry restrictions.

Table 5. Geometries and energies for PtH_2 . Distances in Ångströms, angles in Degrees, and relative energies in kcal/mol

State	Dissoc. E	Transition R	Transition ϕ	Transition E	Minimum R	Minimum ϕ	Minimum E
3A_1	0	1.52	124	+ 62	1.66	180	+ 9
3B_1	0	1.69	40	+ 46	1.60	132	– 8
3A_2	0	1.61	74	+ 23	1.61	135	– 1
3B_2	0	1.63	53	+ 22	1.63	129	+ 6
1A_1	7	–	–	–	1.52	86	– 50
1B_1	6	1.71	37	+ 53	1.60	133	– 1
1A_2	6	1.62	79	+ 30	1.61	137	+ 9
1B_2	6	1.61	50	+ 35	1.63	122	+ 22

Table 6. Occupation of active orbitals at the Separated System Limit (SSL) and minimum energy geometries for PtH₂. For the minima, σ and σ^* denotes the bonding orbitals in A_1 and B_1 symmetries, respectively. For the SSL, σ denotes the H₂ bonding orbital

State	Geometry	Irreducible representations			
		A_1	A_2	B_1	B_2
3A_1	SSL	$\sigma^2 d^2 d^1 s^1$	d^2	d^2	d^2
	Minimum	$\sigma^2(sd)^1 d^1$	d^2	$d^2 \sigma^{*2}$	d^2
3B_1	SSL	$\sigma^2 d^2 d^2 s^1$	d^2	d^1	d^2
	Minimum	$d^2 \sigma^2 d^1$	d^2	$\sigma^{*2} d^1$	d^2
3A_2	SSL	$\sigma^2 d^2 d^2 s^1$	d^1	d^2	d^2
	Minimum	$d^2 d^2 \sigma^2$	d^2	$\sigma^{*2} d^1$	d^1
3B_2	SSL	$\sigma^2 d^2 d^2 s^1$	d^2	d^2	d^1
	Minimum	$d^2 \sigma^2 d^2$	d^1	$\sigma^{*2} d^1$	d^2
1A_1	SSL	$\sigma^2 d^2 d^2$	d^2	d^2	d^2
	Minimum	$d^2 d^2 \sigma^2$	d^2	σ^{*2}	d^2
1B_1	SSL	$\sigma^2 d^2 d^2 s^1$	d^2	d^1	d^2
	Minimum	$d^2 \sigma^2 d^1$	d^2	$\sigma^{*2} d^1$	d^2
1A_2	SSL	$\sigma^2 d^2 d^2 s^1$	d^1	d^2	d^2
	Minimum	$d^2 d^2 \sigma^2$	d^2	$\sigma^{*2} d^1$	d^1
1B_2	SSL	$\sigma^2 d^2 d^2 s^1$	d^2	d^2	d^1
	Minimum	$d^2 d^2 \sigma^2$	d^1	$\sigma^{*2} d^1$	d^2

For all potential surfaces except the 1A_1 state there exist transition states with barriers in the region 20–50 kcal/mol. All these barriers are of the Woodward–Hoffman type, which is revealed from studying the electronic structure of the SSL and the molecular minima. The calculated reaction energy for the 1A_1 state is ca. 17 kcal/mol lower than obtained by Low and Goddard [7]. This is partly due to the applied f -functions and partly due to our modification of the atomic excitation energy, see the section above on atoms. In agreement with the results of Balasubramanian [3] we find 3A_1 linear and 1A_1 to have bent minimum geometry. For all other states Balasubramanian has calculated only the linear cases, and no potential curves are studied. We find, however, that for all other states the bent structures are the ground states.

3.3 IrH₂

Energies for transition states and minima as well as geometries are presented in Table 7, while orbital occupations are listed in Table 8. Both quartet and doublet states are calculated for all four symmetries. The ground state for iridium is assumed to be $d^7 s^2 {}^4F$. This state is, however, mixed with $d^8 s^1$ in our calculations. The lowest doublets are the 2D and 2P states, respectively 15 and 17 kcal/mol above the ground state. Both these states have a $d^8 s^1$ occupation. Accordingly one might expect both doublet and quartets to be easily accessible to sd -hybridization making strong bonds and low energy minima.

Table 7. Geometries and energies for IrH₂. Distances in Ångströms, angles in Degrees, and relative energies in kcal/mol

State	Dissoc. E	Transition R	Transition ϕ	Transition E	Minimum R	Minimum ϕ	Minimum E
⁴ A ₁	0	1.58	89	+ 10	1.66	136	- 7
⁴ A ₂	0	1.50	67	+ 32	1.65	145	- 13
⁴ B ₁	0	1.75	68	+ 20	1.66	145	- 12
⁴ B ₂	0	1.75	68	+ 17	1.66	136	- 7
² A ₁	15	-	-	-	1.53	89	- 41
² A ₂	15	-	-	-	1.69	69	- 34
² B ₁	15	1.57	33	+ 33	1.65	141	- 2
² B ₂	15	-	-	-	1.58	92	- 32

Table 8. Occupation of active orbitals at the Separated System Limit (SSL) and minimum energy geometries for IrH₂. For the minima, σ and σ^* denotes the bonding orbitals in A₁ and B₁ symmetries, respectively. For the SSL, σ denotes the H₂ bonding orbital

State	Geometry	Irreducible representations			
		A ₁	A ₂	B ₁	B ₂
⁴ A ₁	SSL	$\sigma^2 d^1 d^1 s^1$	d^2	d^2	d^2
	Minimum	$\sigma^2(\sigma d)^2 d^2$	d^1	$\sigma^2 d^1$	d^1
⁴ A ₂	SSL	$\sigma^2 d^2 d^1 s^1$	d^1	d^2	d^2
	Minimum	$d^2 \sigma^2 d^1$	d^2	$\sigma^2 d^1$	d^1
⁴ B ₁	SSL	$\sigma^2 d^2 d^2 s^1$	d^1	d^2	d^1
	Minimum	$\sigma^2 d^1 d^1$	d^2	$\sigma^2 d^1$	d^2
⁴ B ₂	SSL	$\sigma^2 d^2 d^1 s^1$	d^2	d^2	d^2
	Minimum	$s^2 \sigma^2 d^1$	d^1	$\sigma^2 d^1$	d^2
² A ₁	SSL	$\sigma^2 d^2 d^1 s^1$	$d^{1.5}$	d^2	$d^{1.5}$
	Minimum	$d^2 \sigma^2 d^1$	d^2	σ^2	d^2
² A ₂	SSL	$\sigma^2 d^2 s^1 d^1$	d^1	d^2	d^2
	Minimum	$d^2 d^2 \sigma^2$	d^1	σ^2	d^2
² B ₁	SSL	$\sigma^2 d^2 d^{1.5} s^1$	$d^{1.5}$	$d^{1.5}$	$d^{1.5}$
	Minimum	$\sigma^2 d^1 (s)^1$	d^2	$\sigma^2 d^1$	d^2
² B ₂	SSL	$\sigma^2 d^2 s^1 d^1$	d^2	d^2	d^1
	Minimum	$d^2 d^2 \sigma^2$	d^2	σ^2	d^1

The doublets dissociate into the ²D states at the SSL – these are 15 kcal/mol higher than the quartets. The ²B₁ state is forced to occupy an antibonding b₁-orbital and tries to compensate for this by using the p-orbital for binding. This results in transition state of 33 kcal/mol and a minimum almost at the same energy as the ground state at the SSL. For the other three doublet states we find minima 30 to 40 kcal/mol below the ⁴A₁ obtained from the atomic ground state. This should be compared to the ¹A₁ state for PtH₂ where the binding energy was 50 kcal/mol. The difference is almost equal to the atomic excitation energy.

For the quartets the SSL state is the Ir atom ground state. For these states we have a similar situation as for the 2B_1 state: Symmetry forces one antibonding b_1 -orbital to be occupied and introduces some p -character into the s -bond of this symmetry. All these states will therefore have high barriers in the transition states and very shallow minima in the minimum geometries. This situation is also revealed in the molecular angle in the minimum structure. For all the quartets and for the 2B_1 state the angles are much larger than 90 degrees reflecting a large degree of sp hybridization.

These results for Ir are in reasonable agreement with previous calculations by Balasubramanian and Dai [4].

3.4 OsH₂

Results for critical points of the most interesting potential curves for osmium are presented in Tables 9 and 10. The ground state of osmium is the 5D state with occupation $d^6 s^2$. The lowest calculated states with singly occupied s -orbital are the 5F and the 3F states, which are found to lie to 59 and 30 kcal/mol respectively above the ground state. This indicates that preparing the Os atom for sd -hybridization should require 30–60 kcal/mol. Again comparing with platinum one should not expect osmium to bind in any state, as is indeed the case. The lowest states are found at the same energy as the SSL without any binding energy. The two states with the lowest minima are the 5A_1 and 3B_1 states. For both states there are large barriers in both the entrance and exit channels.

Table 9. Geometries and energies for OsH₂. Distances in Ångströms, angles in Degrees, and relative energies in kcal/mol

State	Dissoc. E	Transition R	Transition ϕ	Transition E	Minimum R	Minimum ϕ	Minimum E
5A_1	0	1.58	37	+ 63	1.67	180	+ 1
3B_1	30	–	–	–	1.55	83	+ 4
3A_1	30	1.62	32	+ 55	1.59	106	+ 27

Table 10. Occupation of active orbitals at the Separated System Limit (SSL) and minimum energy geometries for OsH₂. For the minima, σ and σ^* denotes the bonding orbitals in A_1 and B_1 symmetries, respectively. For the SSL, σ denotes the H₂ bonding orbital

State	Geometry	Irreducible representations			
		A_1	A_2	B_1	B_2
5A_1	SSL	$\sigma^2 d^2 s^2 d^1$	d^1	d^1	d^1
	Minimum	$\sigma^2 (sd)^2 d^1$	d^1	$\sigma^{*2} d^1$	d^1
3A_1	SSL	$\sigma^2 s^2 d^2 d^1$	d^1	d^1	d^1
	Minimum	$\sigma^2 d^1 (sd)^1$	d^2	σ^{*2}	d^2
3B_1	SSL	$\sigma^2 s^2 d^{1.25} d^1$	$d^{1.25}$	$d^{1.25}$	$d^{1.25}$
	Minimum	$d^2 \sigma^2 (sd)^2$	d^1	σ^{*2}	d^1

Table 11. Geometries and energies for ReH_2 . Distances in Ångströms, angles in Degrees, and relative energies in kcal/mol

State	Dissoc. E	Transition R	Transition ϕ	Transition E	Minimum R	Minimum ϕ	Minimum E
6A_1	0	1.89	39	63	1.79	180	- 1
4A_1	55	1.80	73	86	1.80	180	+ 46
4B_1	51	-	-	-	1.66	123	+ 19
4B_2	51	1.65	39	59	1.67	117	+ 25

Table 12. Occupation of active orbitals at the Separated System Limit (SSL) and minimum energy geometries for ReH_2 . For the minima, σ and σ^* denotes the bonding orbitals in A_1 and B_1 symmetries, respectively. For the SSL, σ denotes the H_2 bonding orbital

State	Geometry	Irreducible representations			
		A_1	A_2	B_1	B_2
6A_1	SSL	$\sigma^2 s^2 d^1 d^1$	d^1	d^1	d^1
	Minimum	$\sigma^2 d^1 d^1$	d^1	$\sigma^{*2} d^1$	d^1
4A_1	SSL	$\sigma^2 s^2 d^1 d^1$	d^1	d^1	d^1
	Minimum	$\sigma^2 d^1 d^1$	d^1	$\sigma^{*2} d^1$	d^1
4B_1	SSL	$\sigma^2 s^2 d^1$	d^1	d^2	d^1
	Minimum	$(sd)^2 \sigma^2 d^1$	d^1	σ^{*2}	d^1
4B_2	SSL	$\sigma^2 s^2 d^2 d^1$	d^1	d^1	-
	Minimum	$\sigma^2 d^1 d^1$	d^2	σ^{*2}	d^1

3.5 ReH_2

The last system studied is the insertion of rhenium into the hydrogen bond (Tables 11 and 12). The lowest atomic state with a singly occupied s -orbital is the 6D state 44 kcal/mol above the ground state. The excitation of one s -electron into the $6p$ -orbital is also of interest and we found the most stable state with $6p$ occupation to be the 8P state with the occupation $d^5 s^1 p^1$.

The SSL for the 6A_1 potential energy surface is characterized by the 6S ($d^5 s^2$) atomic state of Re. At the molecular minimum energy a linear geometry is calculated with bond distances of 1.85 Å. The binding in this geometry takes place through an sp hybridization which incorporates an electron transfer from $6s$ to $6p$. This is only possible if two electrons are transferred from the A_1 to the B_1 irreducible representation of the C_{2v} symmetry group. Bonding through sd -hybridization is here prohibited from symmetry and the requirement of the very high multiplicity. The calculated transition barrier is 67 kcal/mol above the SSL while the molecular minimum is calculated to be 1 kcal/mol below the SSL. This is consistent with the discussions above. The binding is not much weaker than for the platinum case, but the atomic excitation energy make the system almost unstable.

The SSL for the 4A_1 state is the 4G atomic term of rhenium 55 kcal/mol above the 6S ground state, as the lower-lying 4P state is symmetrically inaccessible. For

the other quartets the 4P term describes the SSL. For symmetry reasons the 4A_1 has the same orbital occupation as the 6A_1 . The decoupling of the spins from a very stable sextet with a half-filled d -shell with all spins parallel appears to be rather costly and makes the reaction endothermic by almost 50 kcal/mol. For the two other quartets the binding take place with a sd -hybridization and this makes probably both the atomic excitation and the bonding favourable compared to the A_1 quartet. The 4B_1 state is given with no reaction barrier, but one should bear in mind that this is compared with a SSL involving the 4P state.

Comparing with previous studies by Balasubramanian and Dai [5] we find our reaction energies to be systematically higher. At the CASSCF level the agreement is very good, when dynamical correlation is included consistent differences between his results and ours are found. As f -functions are found to have negligible influence on the energetics of Re, the discrepancy probably stems from the use of different RECPs.

4 Discussion and conclusion

The calculated results for insertion of the metals into the H–H bond show a strong energetics dependence on the atomic spectra. This has been pointed out and discussed earlier for the lighter elements of the transition metals [18, 19]. It is imperative for efficient bonding to have a singly occupied s -orbital. For platinum the $d^9 s^1$ state is the ground state, whereas for all the other atoms the ground state has a doubly occupied s -orbital. For iridium, osmium and rhenium it is therefore necessary to move one electron from the s -orbital to either the $6p$ or the $5d$ orbital. In the first case this opens up for an sd -hybridization and in the second case an sp -hybridization is possible. For iridium there exists a low-lying $d^8 s^1$ term and both platinum and iridium have small barriers in the entrance channel for the M–H₂ reactions – 6 and 15 kcal/mol respectively – whereas they show a large barrier for reductive elimination – 50 and 41 kcal/mol. For osmium and rhenium there are no low-lying states with a singly occupied s -orbital, and accordingly we predict large barriers in the entrance channel, giving reactions that are either endothermic or only slightly exothermic. The barrier for elimination of H₂ is 56, 56, 62 and 62 kcal/mol for Pt, Ir, Os, and Re respectively. One may conclude from this that the bond energies are the same for all the metals within the accuracy of our calculations. This would mean that the relative position of the s - and d -orbital in the late third-row transition metal atoms is insignificant for making bonds to hydrogen.

For catalytic reactions both the addition and the elimination barriers are of importance. It should not be too difficult to make the addition reaction take place, which means a low barrier in the entrance channel. On the other hand, a too high barrier against elimination will prohibit the catalytic effects. This means that it is not necessarily the state with the lowest minimum that is of greatest interest in catalytic processes. Ligands may alter this situation and prepare the metals in a way that makes them even better catalysts.

When heterogeneous catalysis is studied, the embedding effects may totally change this situation in one way or the other. This modification of the entrance and exit barriers are a very interesting field that should be subject to further study with theoretical methods. Blomberg and coworkers [18] have in a recently published paper studied the activation to alkane C–H and C–C bonds. In that paper reaction energies for the insertion of the metals Ni, Co, Fe, Rh, and Pd into the H–H bond are also given. These results together with results from the present study are

Table 13. Reaction energies for the $M + H_2$, ($M = Fe, Co, Ni, Rh, Pd, Re, Os, Ir, Pt$) reactions, kcal/mol. Third-row results are from the present work; the results for the first- and second-row metals are taken from [18] and references therein

	Fe	Co	Ni
	0.7	- 2.6	- 8
		Rh	Pd
		- 31	- 6
Re	Os	Ir	Pt
- 1	+ 1	- 41	- 50

presented in Table 13. The presented figures reveal an increasing exothermicity when going down in the periodic table. Blomberg and coworkers point out in their paper that efficient hybridization requires orbitals of similar size, and the addition reaction therefore proceeds much easier for metal atoms in the second transition row than for those in the first row. This trend is even more pronounced for the third row transition metals compared with those in the first and second rows. This is as should be expected. Due to the strong relativistic effects in the third row there is a significant contraction of the s -orbital and a slight expansion of the d -orbital. These effects make the size of the d -orbital more comparable with the s -orbital for these atoms. Finally one should bear in mind that all these calculations are carried out without the inclusion of the spin-orbit interaction which is expected to be important for the third row transition metals. For the atoms spin-orbit coupling is without doubt very important, while the effect upon chemical properties like those studied together with geometries here remains less obvious. The agreement between our results for PtH_2 and those of Dyall [17] is quite encouraging in this respect.

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