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CH Activation by a Heavy Metal Cation: Production of H₂ from the Reaction of Acetylene with C₄H₄-Os(+) in Gas phase

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Abstract: While first-row transition metal cations, notably Fe(+), catalyze the gas-phase conversion of acetylene to benzene, a distinct path is chosen in systems with Os, Ir, and Rh cations. Rather than losing the metal cation M(+) from the benzene–M(+) complex, as is observed for the Fe(+) system, the heavy metal ions activate CH bonds. The landmark system C₄H₄-Os(+) reacts with acetylene to produce C₆H₄-Os(+) and dihydrogen. Following our work on isomers of the form C_{2n}H_{2n}-Fe(+), we show by DFT modeling that the CH bonds of the metalla-7-cycle structure, C₆H₆-Os(+), are activated and define the gas-phase reaction path by which H₂ is produced. The landmark structures on the network of reaction paths can be used as a basis for the discussion of reactions in which a single Os atom on an inert surface can assist reactions of hydrocarbons.

Keywords: heavy metals; gas-phase catalysis; CH activation; DFT modeling of organometallics



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1. Introduction

The computational modeling of metal-intermediated catalysis is generally difficult, owing to the structural complexity of the solid structures and surfaces involved in most processes. Some simplification is achieved for systems in which a metal cluster or even a single metal atom is isolated on an inert support [1–5], and further simplification is found in more unusual gas-phase processes involving homogeneous clusters M_n(+k) [6–8]. The limiting case (n = 1) offers the modeler the easiest task, but complications remain: the charge and the spin states of the metal atom can favor distinct structures and reaction paths.

The experimental studies of single-metal ion catalysis are well established [9–11]. The single-metal Fe(+1)-catalyzed transformation of acetylene into benzene is of particular interest. The experimental investigation of the gas-phase, metal-assisted activation of hydrocarbons has employed mass spectrometry (MS) and infrared spectroscopy (IR). MS does not reveal molecular structures but only fragmented masses and associated empirical formulas. IR provides bonding information, but this must be interpreted within a structural model. Computational modeling can fill in gaps, defining equilibrium structures, reaction paths, and transition state geometries. Accordingly, these experimental investigations are often accompanied or supplemented by computational modeling [12]. Recent studies show that several 5d transition metal cations activate small hydrocarbons, producing dihydrogen [13–15]. Of these heavy metals, tantalum, tungsten, osmium, iridium, platinum we have chosen to study Osmium, as a congener of the extensively studied iron.

In this report we extend our theoretical investigations to osmium cation reactions with acetylene, which, compared to the modeling of Iron cation systems [16,17], seems to be largely neglected. We hope the structures and energetics we report here can guide the interpretation of the future experimental data on gas-phase systems and single-atom catalytic processes involving a single atom on a surface.

The Fe(+) structures we already reported [16] included some that were not studied previously [17]. These are the Fe analogies to **6**, **7A** and **7B**, **8**, **12**, **13**, **S1** and **S2**. Species **6**, **7**, and **8** are eta-1, eta-2, and eta-3 complexes of Fe(+) with the C_4H_4 ring. Eta-2 coordination can connect adjacent C atoms (**7A**) or nonadjacent C atoms (**7B**). Species **11** may be what Chretien and Salahub [17] call $Fe(c-C_4H_4)(C_2H_2)$ cation; in that species Fe participates in a ferro-cyclopentyl ring and a three-membered ferro-cyclopropenyl ring, according to these authors. Structure **12** is called chair and structure **13** is called saddle for easy reference and visualization.

The species studied here include the Os(+) analogs of the $C_{2n}H_{2n}$ -Fe(+) structures from reference [16]; that is, **2–15** as shown in Figure 1.

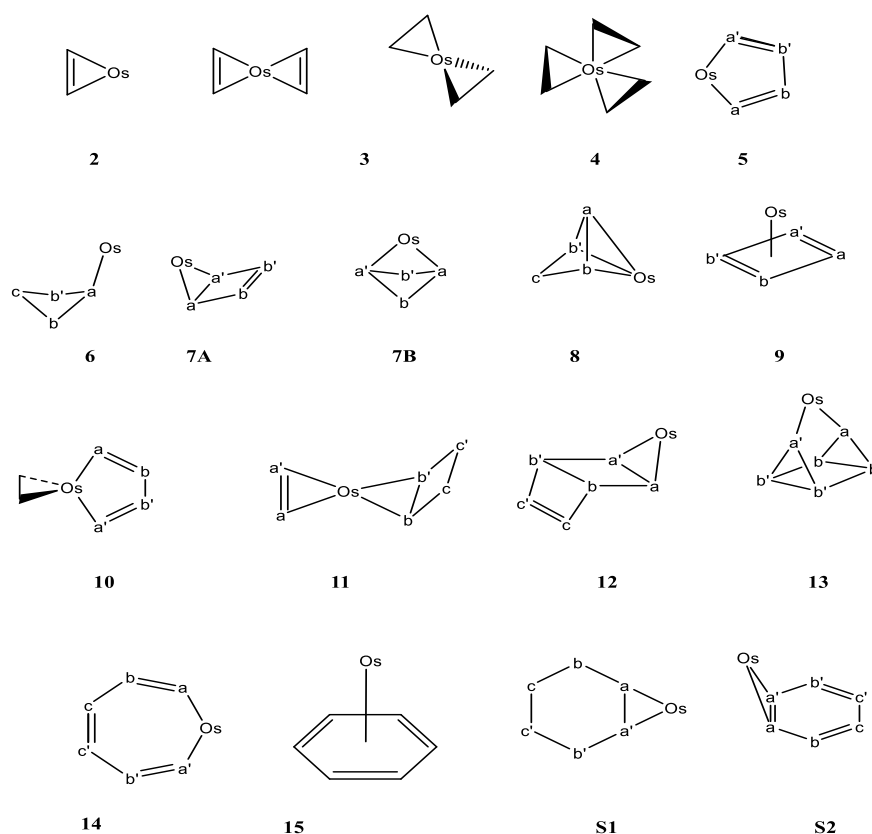


Figure 1. Some of the structures described in this work.

2. Computational Methods

In our work on Fe(+) catalyzed transformation of acetylene into benzene [16] we evaluated the relative performance of Density Functional and Complete Active Space Self-Consistent Field (CASSCF) Hamiltonians. Some states required a multi-configurational wave function for even and qualitatively correct representation. Remarkably, density functional theory (DFT) with the ω B97XD [18] range- and dispersion-corrected functional, and the aug-cc-pTZV basis [19], offered a surprisingly coherent account of structures and energetics. In view of the effectiveness of density functional theory for FeC_6H_6 cation, and its relatively modest demands on computational resources, we chose an analogous model for the study of the OsC_6H_6 cations. Owing to the presence of the heavy metal osmium, we chose the def2-tzvp basis [20,21] which incorporated a pseudopotential representing the 60-electron inner core of the metal; this basis treats all electrons of C and H. For some preliminary calculations we used the pseudopotential, MWB60, and its associated basis functions [21] for Os and def2-tzvp for C and H. All computations were accomplished with Gaussian 09 [22] and Gaussian 16 [23]. Full coordinates for structures along the Os dehydrogenation pathways are available from C.T.

3. Results

3.1. Energetics and Structures for Fe(+)C₆H₆ Species

Figure 2 displays the Gibbs energies, which are reported in the Gaussian output from computations including a vibrational analysis:

$$E(\text{Gibbs}) = E_D + Z + 5RT/2 - TS \quad (1)$$

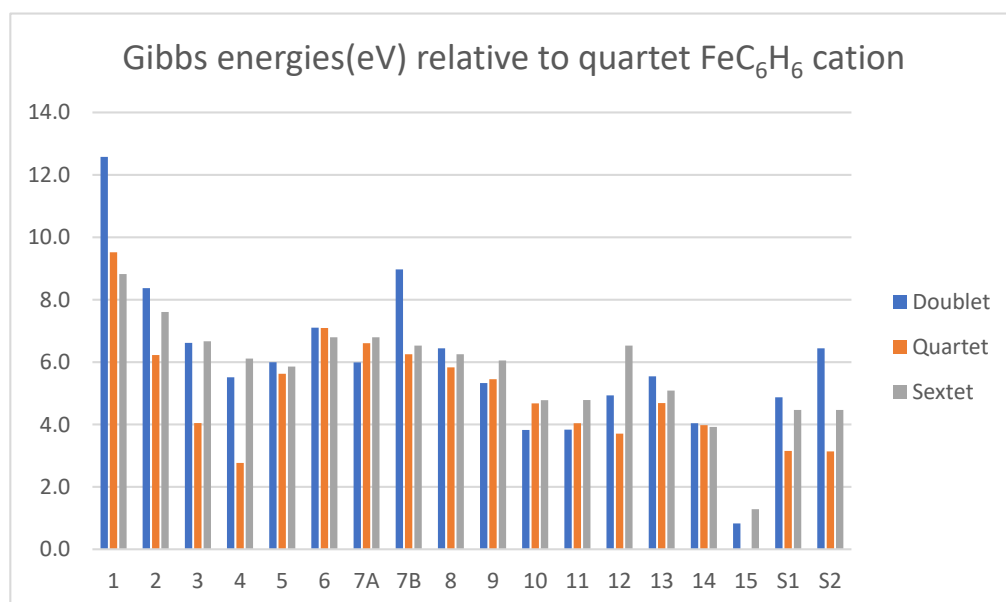


Figure 2. Gibbs Energy profile for landmark structures for the C_{2n}H_{2n}-Fe(+) system.

The Gibbs energy is composed of (a) the electronic energy E_D computed in the ω B97XD/def2-tzvp model; (b) Z which is the zero-point vibrational energy; (c) a thermal correction representing the integral of the ideal gas constant-pressure heat capacity, $C_p = 5R/2$, integrated from lower bound 0 to the standard temperature T ; and (d) the entropy term. S is composed of several parts, including a vibrational portion which can be evaluated by use of the vibrational partition function, a spin multiplicity contribution of form $k \ln(W)$ for which W is the spin multiplicity, and a translational portion which can be evaluated by the Sackur Tetrode equation, applicable for an ideal gas composed of particles of mass m . All these terms are computed within the Gaussian software [22,23].

Figure 2 shows that the Fe cation has a sextet ground state, as Hund's rule implies. The addition of acetylene to the Fe cation stabilizes the system, but acetylene adducts 2–4 (that is Fe(HCCH)_n for $n = 1, 2$, and 3) all favor quartet spin. Each addition of an acetylene stabilizes the quartet relative the doublet. The incremental stabilization of the quartet declines as successive acetylenes are added. The sextet is always much more unstable than the quartet (by about 1.4, 2.6, and 3.4 eV for $n = 1, 2$, and 3) in the series of iron-acetylene adducts. The quartet of species 4 lies at 2.8 eV relative to the reference energy for the quartet, Fe-benzene. The question then is how, in view of the high energies of species 5–9, reaching 6 eV or more, could the Fe(HCCH)₃ cationic system rearrange to form Fe(+)-benzene? We must assume that a substantial portion of the original energy (>8 eV relative to Fe-benzene) is retained in the gas phase cluster.

We did not trace out a full reaction path network for the Fe system, but we can identify some possible landmarks (relative minima in Gibbs energy). If the reaction branches from the quartet of the species 3 cation with an unbound acetylene at 4.0 eV, then the quartets of species 10–14 are within relatively easy reach. We note that all spin states of species 14 are higher in energy than the quartet of species S1. The quartet and sextet of S2 return upon the reoptimization to the C_{2v} structure of S1.

3.2. Energetics and Structures for Os(+)C₆H₆ Species

The corresponding Gibbs energy profile for Os(+) species is shown in Figure 3. Once again the sextet is the most stable state of Os(+). As acetylenes are added, the system is stabilized; in this case the doublets are favored. Doublets of species **5**, **7A**, and **9** are energetically accessible for Os(+) systems, in contrast to the case for Fe(+) systems. Note that, for each system, species **6** seems to be highly energetic and thus unlikely to be populated. In further contrast to the Fe(+) systems, the doublets of Os(+) species **10–14** are all available. The structures **10**, **11**, and **13** have particularly stable doublets. The Os(+)-benzene ground-state doublet **15** can be formed with ease from species **13**.

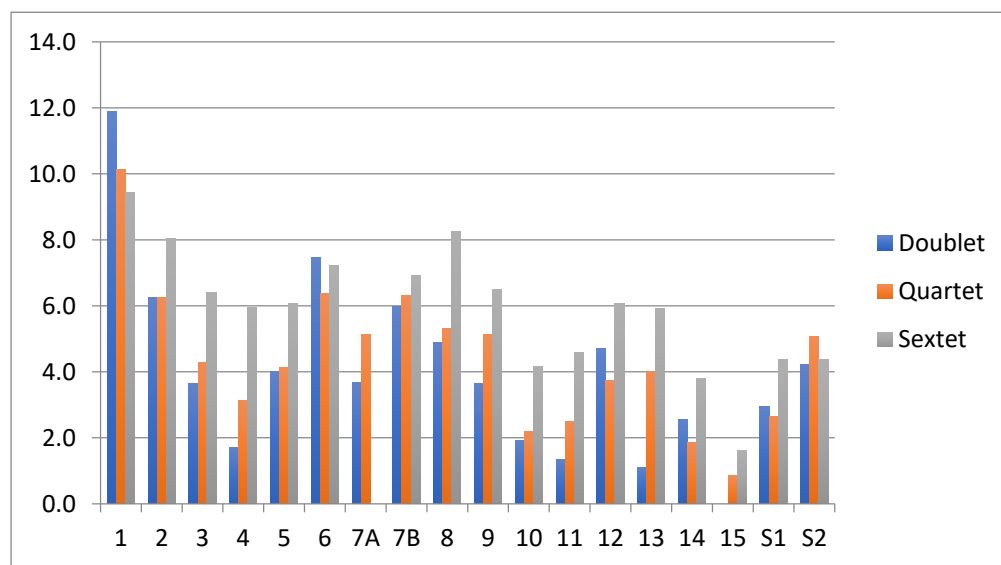


Figure 3. Gibbs energy profile for OsC₆H₆ cation (eV).

If we examine the quartet multiplicity system, which for structure **3** lies only about 0.5 eV higher in energy than the doublet, the passage to the quartets for **5**, **10**, **11**, **12**, **13** and especially **14** (for which the quartet is the ground state) are within energetic reach. From **14** only a modest energy investment is needed to liberate H₂ and achieve the ground state quartet of **S1**. We remind the reader, that barring rapid collisional cooling, all the original energy in the system remains in the OsC₆H₆(+) cluster. If H₂ departs the reaction zone, quartet OsC₆H₄(+) remains, as observed [5].

3.3. Comparison of MC₆H₆ Cation Energetics for M = Fe and Os

There are significant differences between the Fe(+) and Os(+) energy profiles:

- A decline is found for both systems in BE as acetylenes are added. However, successive binding energies (BE) of acetylenes are about 50% greater for Os(+) than Fe(+). **This favors the production of C–O binding in the Os system.**
- The quartet is the ground state of the benzene-Fe(+) complex, consistent with other computational results [20]. The doublet is preferred for the benzene-Os(+) complex.
- The energy requirement for expelling benzene and sextet Os(+) from the ground-state, doublet benzene-Os(+) is 3.67 eV, while producing a sextet Fe(+) from the ground-state quartet, benzene-Fe(+), requires 3.08 eV. **This inhibits the benzene production for Os(+) relative to Fe(+).**
- Species doublet **14** and doublets **S1** and **S2** are relatively high in energy for the Fe(+) system, but more accessible in the Os(+) system. **This favors H₂ production for the heavy metal cation.**
- The energy requirement for producing H₂ from **14** leaving C₆H₄-Os(+) is substantial (0.78 eV) but the elimination product at 2.5 eV is lower in energy than the free benzene and separate Os(+), by 3.3 eV.

3.4. Reaction Paths for Extrusion of H_2 from OsC_6H_6 Cation

It is observed that $Os(+)$ activates the CH bond of acetylene, producing H_2 and leaving an OsC_6H_4 cation residue [5]. Neither the pathway for H_2 production nor the structure of the residue has yet been defined, so we explored steps in the reaction. We begin with the seven-membered ring (Species 14 of Figure 1) and the complex of Os with benzene (Species 15 of Figure 1). We introduce a new naming scheme, X_n , with labels $X = B$ for bicyclic and $X = C$ for monocyclic species, and with n coding the number of H atoms attached to Os. For $n = 1, 2, 3$, the number of attached H atoms are 0, 1, and 2. Further descriptors are attached as needed.

3.4.1. Overview of the Reaction Network for the H_2 Extrusion from OsC_6H_6 Doublet Cation

To provide an overview of the multiple reaction paths, the reaction network is sketched on a globe (Figure 4). We begin with the species **B1c**, the C_{6v} complex of $Os(+)$ with benzene) and **C1** (1-Osmacyclohept-2,4,6-triene), located on a slice of the sphere, defining a plane perpendicular to the poles and circumscribed by the “Arctic Circle”. These OsC_6H_6 (+) species have each of the six H atoms attached to its own C atom. They appear on the first of four planar slices of the sphere, the “Arctic Circle”. The second slice, the “Tropic of Cancer”, contains **C2** and **B2** *cis* and *trans*; these species have a single H atom attached to osmium. Reaction paths connecting **C1** with **C2** and also **B1c** with **B2** *cis* and *trans* species are shown by the curved lines. These paths pass through transition states each marked by an asterisk. It is also possible to interconvert **C1** with **B1c**, and **C2** with **B2** *cis* and *trans*; such paths are marked by straight lines passing through transition states marked by X. Similarly, we find **C3** and **B3** structures with two H atoms connected to osmium on the “Tropic of Capricorn” with analogous reaction paths. Finally, at the “Antarctic Circle” we find species, **C4** and **B4**, which have the formula $OsC_6H_4(+)$; the H_2 is extruded.

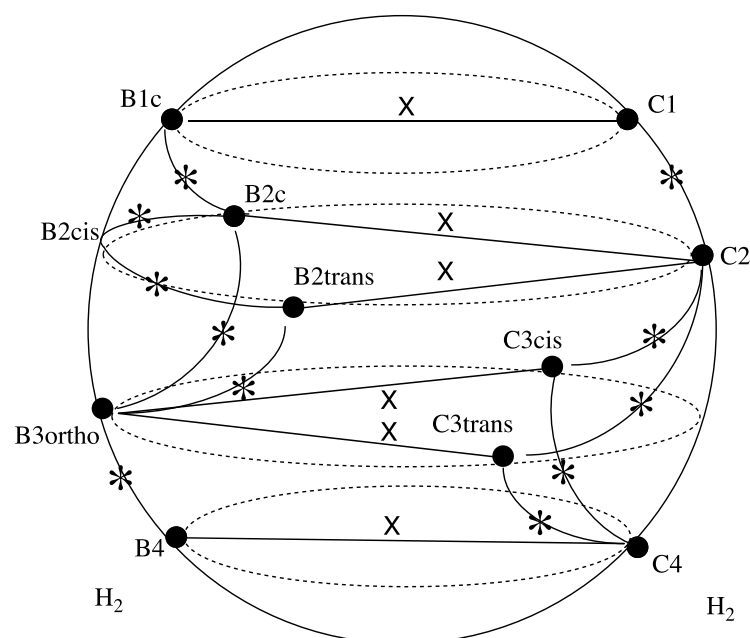
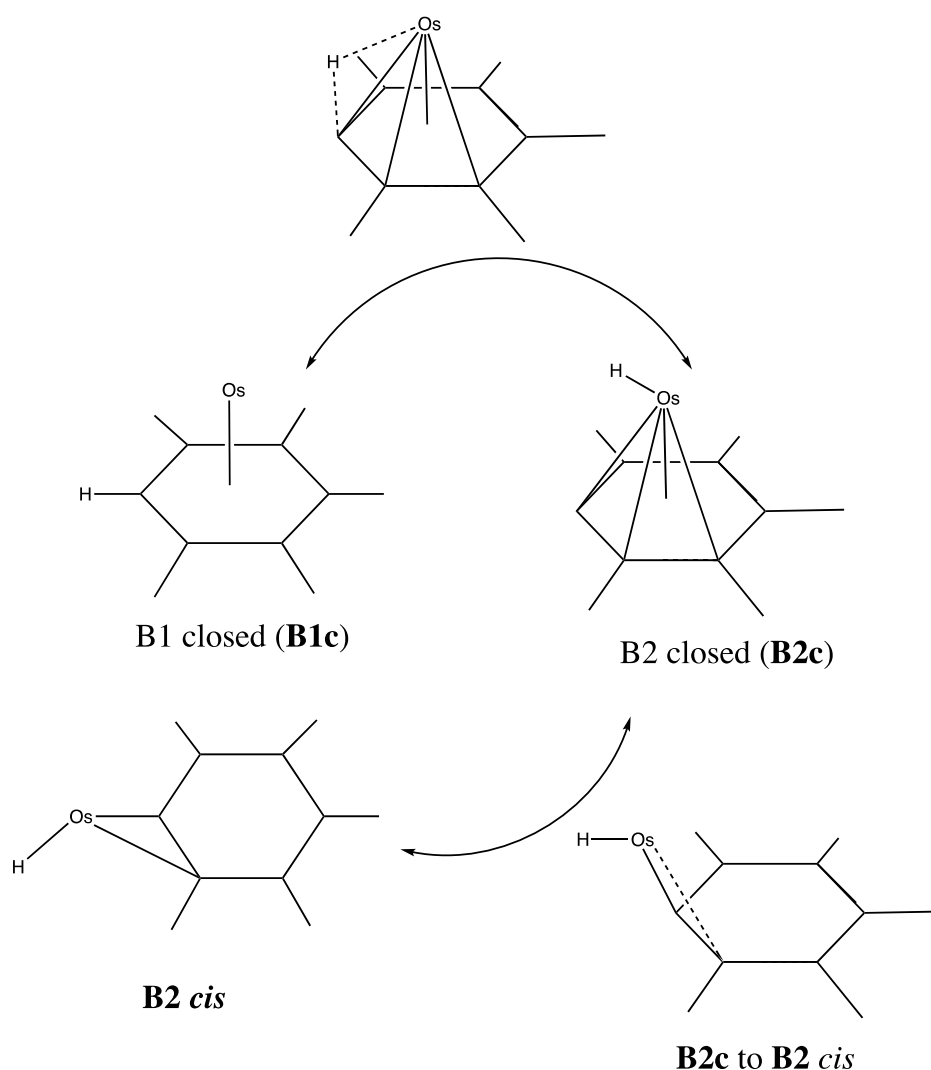


Figure 4. Reaction path network for osmium-catalyzed production of H_2 from OsC_6H_6 cation. A sphere (outlined by the solid circle) is sliced to define four planes intersecting the sphere as shown by dotted lines. These planes contain species labeled $X = B$ and C with indices 1, 2, 3, and 4 in sequence from top to bottom. The number of H atoms attached to Os are 0, 1, and 2 for X_1 , X_2 , and X_3 ; X_4 refers to OsC_6H_4 cation. Interconversions of bicyclic species (BB paths) appear on the left; interconversions of monocyclic species (CC paths) appear on the right. Transition states are each marked with an asterisk *. Interconversions of monocyclic and bicyclic species follow BC paths with transition states marked by X.

3.4.2. Is the C_{6v} Complex of Os with Benzene OsC_6H_6 (+) a Sink?

We explore the reaction paths beginning with the lowest energy structure for the OsC_6H_6 cation, which is the C_{6v} complex of Os with benzene with a doublet spin state. We call this “B1 closed” or **B1c** (Figure 5). Is there a path from this species allowing the production of H_2 ? Table 1 contains Gibbs energy values in Hartrees and relative Gibbs energies in eV for species that we identify as we progressing through the B-path. The first step must be a H transfer from C to Os. We find a transition state at 2.645 eV for that H transfer. An intrinsic reaction coordinate passing through that transition state from **B1c** leads to an $HOs-C_6H_5$ cation at 1.361 eV. The protonated osmium atom is coordinated (η^3) to the C_6H_5 ring in this structure, which we call “B2 closed” or **B2c**. This species can pass to the **B2 cis** lying at 1.734 eV through a transition state at 2.285 eV. A conversion to **B2 trans** (at 2.380 eV) requires a passage through a TS at 2.039 eV.



Transformation between B1 and B2 through TS B1 to B2

Figure 5. Structures for rearrangements of the most stable OsC_6H_6 cation species, the doublet complex of an Os atom with a phenyl ring.

Table 1. Energetics (ω B97XD/def2-tzvp) for landmarks along the B path for H transfer to polycyclic Os species from the most stable species, the C_{6v} complex of Os cation with benzene, $OsC_6H_6^+$. This is called **B1 closed**. Species labels and Gibbs energies (G) in Hartrees are reported along with relative Gibbs energies, $G-G_0$, in electron volts (eV). The Gibbs energy for **B1 closed** is the reference point (0).

Species	G	G- G_0 (eV)	Barriers (eV)	See
B1 closed	−322.593606	0		Figure 5
B1 closed to B2 closed	−322.496390	2.645	2.645:1.284	
B2 closed	−322.543587	1.361		
B2 closed to B2 cis	−322.509613	2.285	0.924: 0.551	
B2 cis	−322.5298548	1.734		Figure 6
B2 cis to B2 trans	−322.512661	2.202	0.468:0.592	
B2 trans	−322.534412	1.610		
B3 ortho	−322.533566	1.633		
B2 trans to B3 ortho	−322. 526011	1.839	0.229:0.206	
B2 cis to B3 ortho	−322.522966	1.922	0.188:0.289:	
B3 cis	−322.521829	1.953		
B3 cis to B3 trans	−322.505038	2.410	0.457:0.820	
B3 trans	−322.535153	1.590		
B3 ortho to B3 trans	−322.524222	1.887	0.254:0.297	
B3 ortho to B3' ortho	−322.532158	1.687	0.054:0.054	Figure 7
H_2 + B4	−322.500601	2.530		Figure 11

B2 cis and trans to B3 ortho and B3 trans

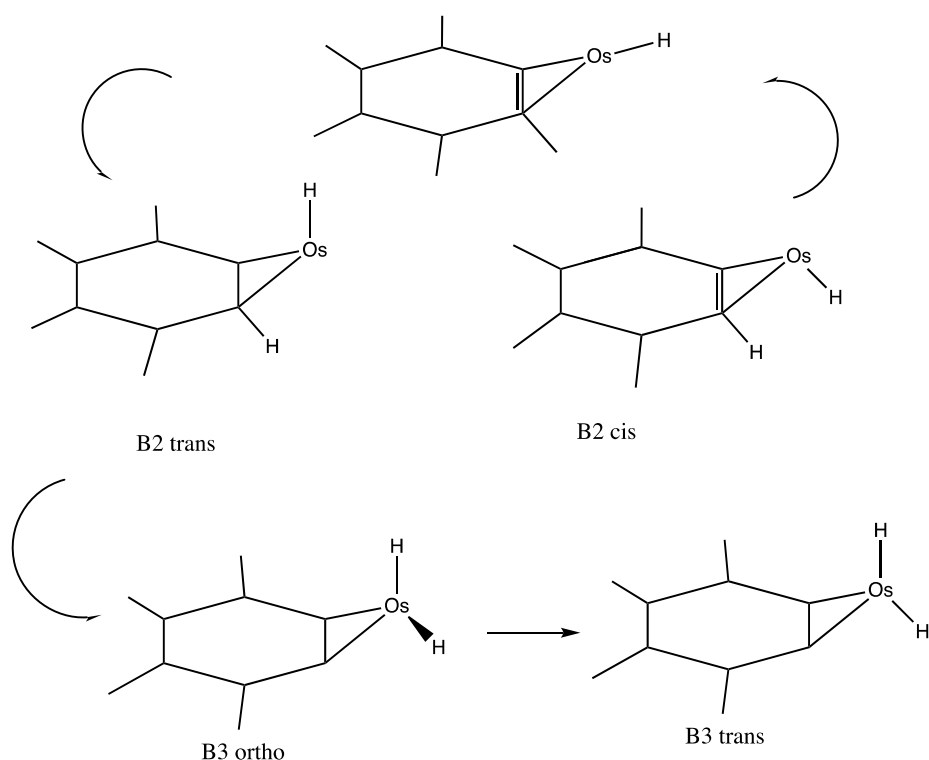


Figure 6. Landmarks for the second proton transfer to Os for the bicyclic scaffold (the Bicyclic Path B) which passes to **B3 ortho**. The barrier to conversion to **B3 trans** is 0.254 eV.

Transition state between mirror isomers of ortho B3

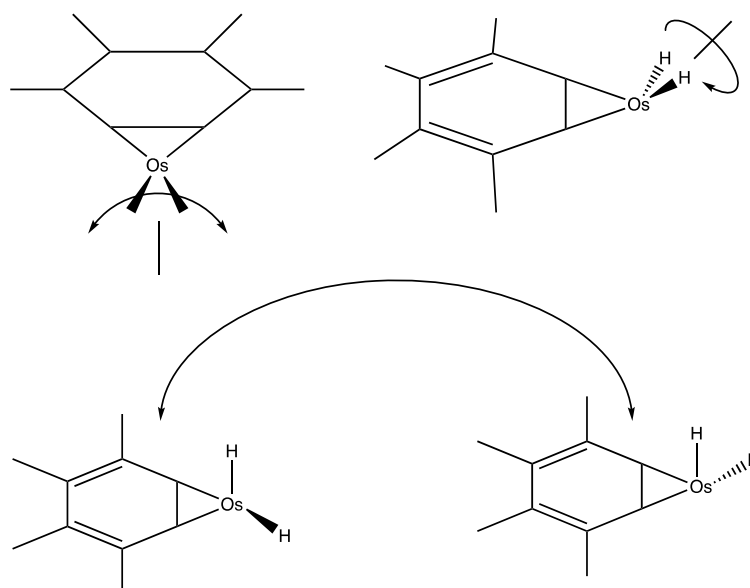


Figure 7. Interconversion of **B3** *ortho* (lower left) and **B3'** *ortho* (lower right). Two views of the TS appear at top.

3.4.3. Continuation of the B Path toward H₂ Extrusion

The second H transfer passes over a small barrier to produce a structure we call “ortho”, **B3**, with the two Os–H bonds, perpendicular and parallel to the molecule’s C₆H₄ hydrocarbon plane, respectively. (See Figure 6.) The *cis* and *trans* isomers of bicyclic H₂OsC₆H₄ are very close in energy to the ortho form; they can be easily interconverted.

B2 *cis* and **B2** *trans* can be interconverted by the clockwise or anticlockwise twist of the torsion angle C–C–Os–H around an Os–C bond. The lower energy path (with a TS at 2.039 eV) breaks an Os–C bond entirely and detaches the Os atom from the phenyl ring, while the higher energy path (with a TS at 2.202 eV) only weakens the Os–C bond to the hydrogenated alpha C so that the bicyclic nature of the structure is preserved and the Os atom stays above the phenyl plane.

B2 *trans*, lying at 1.610 eV, need only surmount a small barrier of 0.121 eV to arrive at **B3** *ortho* lying at 1.633 eV. (See Table 1.) Similarly, **B2** *cis* lies at 1.734 eV encounters a modest barrier, 0.188 eV on its way to **B3** *ortho*. **B3** *ortho* at 1.633 eV can find its way to **B3** *trans* at 1.590 eV by surmounting a modest barrier of 0.254 eV.

B3 *ortho* can easily interconvert to an equivalent form **B3'** *ortho*. These isomers are separated by a very low barrier (0.054 eV). See Figure 7.

Loss of H₂ from **B3** *ortho* to produce **B4** is endothermic by 0.893 eV (Table 1). The energy to affect the extrusion is available only if the original Os(+):3HCCH cluster is not rapidly cooled in the course of reaction. This is evidently the case for the experimental observation of a very low-pressure gas-phase system [5].

3.4.4. Overview of the C Reaction Path for H₂ Extrusion from 1-Osma-cyclohepta 2,4,6-triene (C1)

An alternative path for hydrogen extrusion may be traced from monocyclic 1-Osma-cyclohepta 2,4,6-triene (Species 14 in Figure 1 above). We call this structure **C1**. Gibbs energies in Hartrees and the relative energies in eV are collected in Table 2. **C1** lies at 1.518 eV relative to the C_{6v} cationic complex of Os with benzene. The first H transfer to Os shown in Figure 9 generates species **C2** at 1.236 eV, after passing through a TS at 2.243 eV; that is, over a barrier of 0.725 eV.

Table 2. Energetics (ω B97XD/def2-tzvp) for landmarks along the C path for H transfer to polycyclic Os species from the most stable C species of OsC_6H_6 cation. Species labels and Gibbs energies (G) in Hartrees are reported along with relative Gibbs energies in electron volts (eV). The energy reference point is the energy of the C_{6v} complex of the Os cation with benzene, OsC_6H_6^+ (see Table 1).

Species	G	G-G ₀ (eV)	See
C1	−322.537790	1.518	Figure 9
C1 to C2	−322.511164	2.243	
C2	−322.548169	1.236	Figure 8
C2 to C3 cis	−322.488162	2.869	
C3 cis	−322.521893	1.951	
C2 to C3 trans	−322.483549	2.994	
C3 trans	−322.512357	2.210	
C3 cis	−322.521893	1.951	Figure 11
C3 cis to C3 trans	−322.510759	2.259	
H₂ + C4	−322.475475	3.214	

Path for the First H transfer (C path)

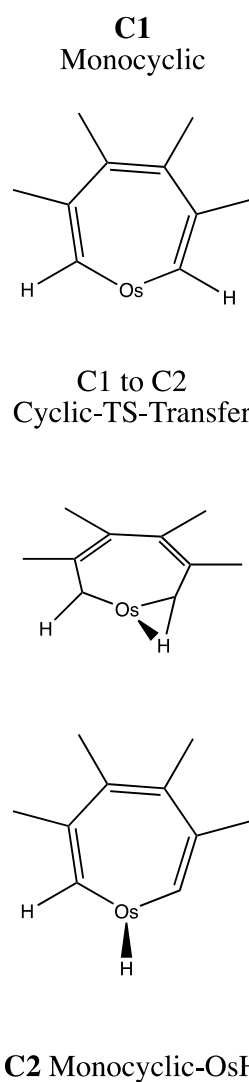
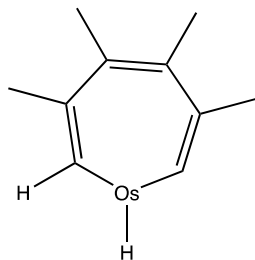


Figure 8. Landmarks for the second proton transfer to Os for the cyclic scaffold (the Cyclic Path C, steps **C2 to C3**) which may branch to “cis” and “trans” pathways, to cis- $\text{H}_2\text{OsC}_6\text{H}_4$ or trans- $\text{H}_2\text{OsC}_6\text{H}_4$.

Path for the Second H transfer (monocyclic)

C2

Monocycle-OsH

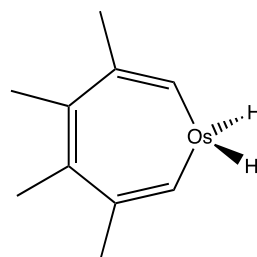
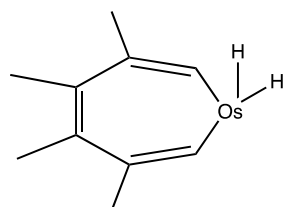
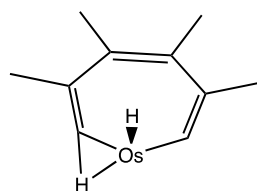
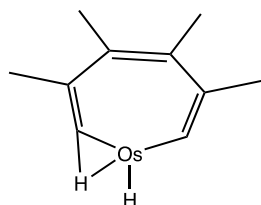


TS C2 to cis-C3

TS C2 to trans-C3

“cis” TS

“trans” TS



“cis” Product

“trans” product

cis-C3

trans-C3

Figure 9. Landmarks for the first proton transfer to Os, which can take place on the cyclic scaffold (the Cyclic Path C, steps C1 to C2).

3.4.5. Second H Transfer (C Path)

The second H transfer for the C species is shown in Figure 8. The destination C3 (monocyclic $\text{H}_2\text{OsC}_6\text{H}_4$) can exist in *cis* and *trans* forms, which lie 0.715 and 0.974 eV above C2, respectively (See Table 2). The barriers opposing the passage of C2 to C3 *cis* and *trans* are large: 1.633 and 1.758 eV, respectively. Although C2 seems accessible, from B2 (see below) it would not be feasible to advance further along the C path.

3.4.6. Can Crossover from C to B Paths Occur?

Figure 10 shows the passage from C2 to B2 *cis* and *trans*. The barriers are 1.063 and 1.144 eV, respectively (Table 3). This reinforces the notion that C2 may be a trap, from which the system must only retreat.

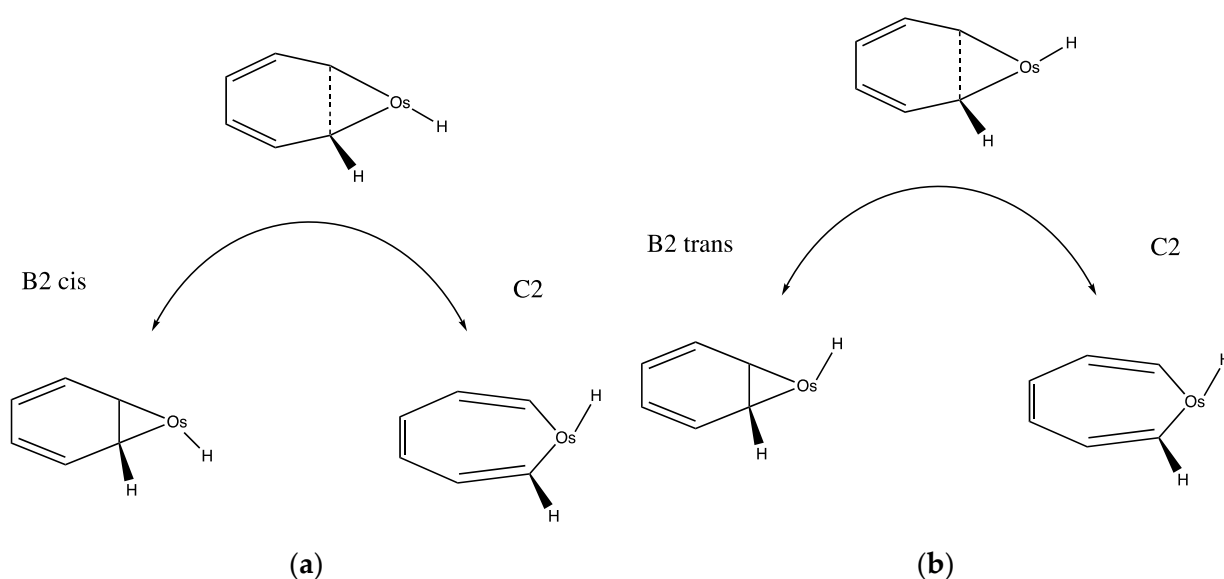


Figure 10. Transformation (a) between *cis* B2 and C2 and (b) between *trans* B2 and C2.

Table 3. Energetics for C–B crossover.

Species	G	G–G ₀ (eV)	See
B2 <i>trans</i> to C2 TS	–322.506130	2.380	Figure 10
B2 <i>cis</i> to C2 TS	–322.509119	2.298	
H ₂ + C4 to H ₂ + B4	–322.466052	3.470	

B3 trans which lies at 1.590 eV is 0.363 eV more stable than **B3 cis**. The barrier impeding passage from **B3 trans** to **C3 trans** is estimated as 1.364 eV, so the crossover to the C path seems quite unlikely.

We explored the possibility of the interconversion of the residues B4 and C4 (Table 3). We found that the barrier for the passage of C4 (at 3.214 eV) to B4 (at 2.530 eV) was modest, only 0.256 eV. However, the reverse path would have to surmount a barrier of 0.960 eV. Therefore, we see no opportunity for the crossover to the C path from the B path at this stage.

3.4.7. Extrusion of H₂ from OsC₆H₆ (+)

If in fact **C3 cis** and **trans** species were to be formed, the endothermicity for H₂ extrusion (Figure 11) would be 1.263 eV for **C3 cis** and 1.004 eV for **C3 trans** (Table 2).

The passage from **B3 ortho** to **B4** and H₂ (Table 1), and also the passage from **C3 cis** to **C4** and H₂, (Table 2) do not admit a description of transition states. The potential energy curve for the production of H₂ from **B3 ortho** is smoothly uphill with no hint of a transition state. The dissociation from **C3 cis** is likewise uphill without a transition state. Overcoming the energy cost requires that the reactive cluster is not rapidly cooled. This need may well be met in a low-pressure gas, but this is less likely in a condensed phase.

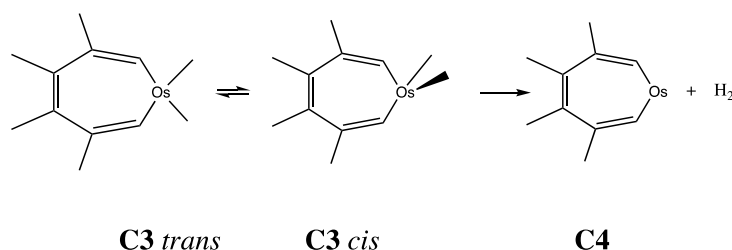
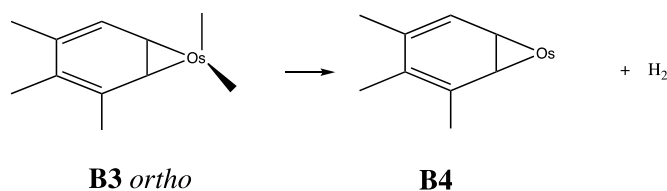
Dissociation from **C3 cis** to **C4** : H₂Dissociation from **B3 ortho** to **B4** : H₂

Figure 11. Landmarks for the extrusion of H₂ from cationic H₂OsC₆H₄ *cis* and *trans* **C3** and from **B4**.

4. Discussion

We located landmarks on the reaction paths producing H₂ from OsC₆H₆ cationic species. While we must assume that the reactive cluster has abundant energy to affect the extrusion of dihydrogen, the potential surface must still favor a particular flow. We distinguished the **B** paths (in which the reacting species are bicyclic 6.1.0 rings) from the **C** paths (in which the species are monocyclic seven-membered rings) and also allowed the possibility of crossover. Figures 12 and 13 show what we consider to be the most significant of the many possible passages from **B1c** to H₂ and a residue, either **B4** or **C4**.

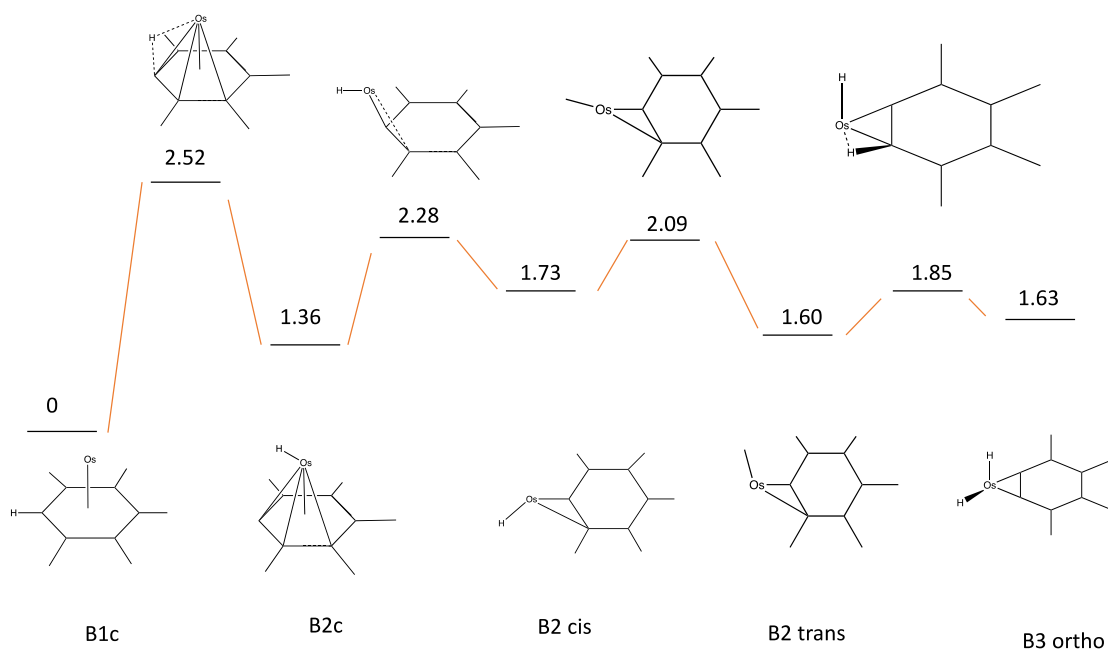


Figure 12. Landmarks in the B path for the production of H₂.

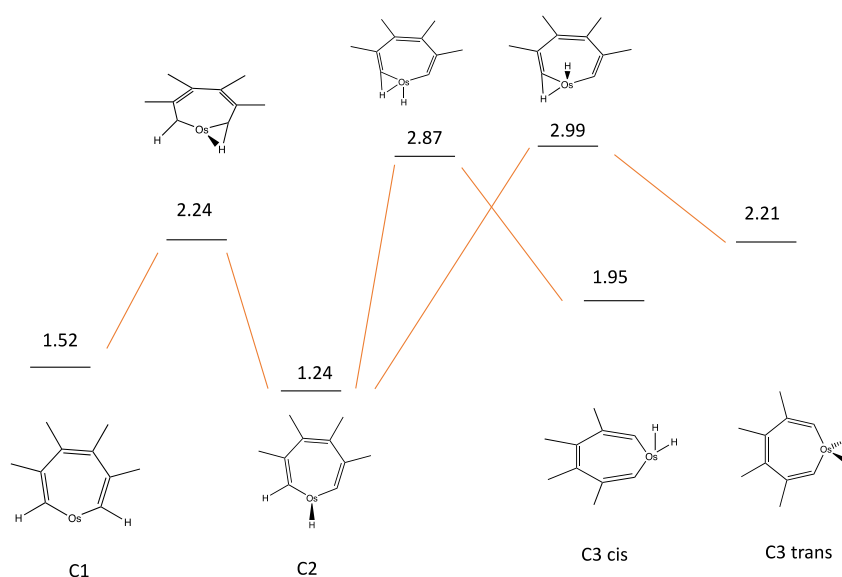


Figure 13. Landmarks in the C path for the production of H_2 .

Figure 12 shows the possible evolution from **B1c**. We had little choice in the first step but to produce **B2c** and then **B2 cis**, even though the passage was endothermic by 1.734 eV and surmounted a barrier of 2.52 eV. **B2 cis** can interconvert easily to the slightly more stable **B2 trans** at 1.610 eV, facing a barrier of 0.355 eV.

B2 cis or **trans** could form **B3 ortho** by overcoming the small barriers of 0.188 eV or 0.105 eV. Then, **B3 ortho** can generate **B4** and H_2 at a cost of 0.897 eV.

B2 cis or **trans** could cross over to the much more stable **C2** (1.236 eV), opposed by perhaps surmountable barriers of 0.555 eV or 0.688 eV, respectively. Figure 13 shows that from there it is uphill to **C3 cis** or **trans** at 1.951 or 2.21 eV, over high barriers of 0.918 or 0.784 eV. The production of **C4** and H_2 requires 1.263 eV from **C3 cis** or 1.004 eV from **C3 trans**.

We conclude then that a likely reaction path is **B1c** to **B2c** to **B2 cis**; followed by the possible isomerization to **B2 trans** and production of **B3 ortho**. If **C1** is populated the system could find its way to **C2**, which could then convert to **B2** and continue along the path already described.

How can we discern any features of the paths actually followed? **C2** and **B2 trans** may be the longest-lived intermediate species for the systems with a single H transfer, and **C3 cis** and **B3 ortho** among systems for systems with a second H transfer would have very different IR spectra. Likewise, the residues from H_2 extrusion, **C4** and **B4**, would have very different IR spectra. While the experimental challenges would be considerable, distinguishing some aspects of the reaction net may be possible.

5. Conclusions

Using density functional methods, we have evaluated the energies and structures of species evolving from the benzene complex of the osmium cation, $OsC_6H_6^+$, and an isomeric seven-membered unsaturated ring, tracing reaction paths that lead to the evolution of hydrogen gas. The experimental facts [5], based on gas-phase observations of species produced from clusters of acetylene with osmium, revealed no direct structural information. A more detailed examination of the mass spectrometry data may offer proof of such smaller clusters such as those suggested by our density functional modeling.

This work deals with the evolution of dihydrogen from acetylene by the simplest possible process involving single-heavy-atom catalysis. The details of the structure of intermediate species presented here may find their counterparts in single-atom catalysis, involving graphene and solid-state surfaces, adding depth to the description of practical conversion processes.

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