

Double C–H Bond Activation of an NHC N-Methyl Group on Triruthenium and Triosmium Carbonyl Clusters: A DFT Mechanistic Study

Javier A. Cabeza*[†] and Enrique Pérez-Carreño[‡]

Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain, and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo, Spain

Received June 30, 2008

The mechanisms of two recently reported thermal transformations of NHC-triruthenium and -triosmium cluster complexes, which involve the unusual oxidative addition of two C–H bonds of an NHC N-methyl group, have been investigated by density functional theory calculations. The transformations of $[M_3(\text{Me}_2\text{Im})(\text{CO})_{11}]$ ($\text{Me}_2\text{Im} = 1,3\text{-dimethylimidazol-2-ylidene}$; $M = \text{Ru}$ (**1a**), Os (**1b**)) into the ligand-capped dihydrido derivatives $[M_3(\mu\text{-H})_2(\mu_3\text{-}\kappa^2\text{-MeImCH})(\text{CO})_9]$ ($M = \text{Ru}$ (**3a**), Os (**3b**)) are mechanistically very similar, but they differ in the energy barriers of key steps. For both metal systems ($M = \text{Ru}$, Os), the first step is a ligand rearrangement that moves the Me_2Im ligand from an equatorial (in **1a** and **1b**) to an axial coordination position. Both C–H activation steps are oxidative addition processes, and each one is preceded by a CO elimination step that provides a coordinatively unsaturated intermediate. The first C–H oxidative addition occurs via a transition state that implies an unusual interaction of an N-methyl hydrogen atom with two metal atoms simultaneously. This transition state directly leads to an intermediate that contains an edge-bridging hydride and an edge-bridging MeImCH_2 ligand, i.e., $[M_3(\mu\text{-H})(\mu\text{-}\kappa^2\text{-MeImCH}_2)(\text{CO})_{10}]$ ($M = \text{Ru}$ (**2a**), Os (**2b**)). The second C–H oxidative addition takes place via an interaction of the unbridged metal atom with a CH_2 hydrogen atom of the bridging MeImCH_2 ligand. This gives a face-capping MeImCH ligand and a terminal hydride that subsequently rearranges to an edge-bridging position to give **3a** or **3b**. The activation barriers of both CO elimination steps are higher for the osmium system than for the ruthenium system. For both metal systems, the slowest step is the first CO elimination.

Introduction

Ruthenium complexes containing N-heterocyclic carbene (NHC) ligands, and particularly 1,3-disubstituted imidazol-2-ylidenes, are among the most active catalysts for important organic reactions, such as olefin metathesis^{1–3} and various C–C bond forming processes.³ However, recent reports have shown that the N-R arms of some NHC-ruthenium complexes may get involved in intramolecular C–H,^{4–10} C–C,^{8,9} and/or C–N^{6,10} bond activation reactions. Some NHC ligand degradation processes have important implications in catalyst activation^{7a} and deactivation.^{1,11} In fact, a ruthenium complex with an N-alkyl-metalated NHC ligand has been shown to be a more

efficient catalyst than the nonmetalated precursor for a tandem oxidation/Wittig/reduction reaction that forms C–C bonds from alcohols.^{7a} On the contrary, the deactivation of the second and third generations of Grubbs alkene metathesis catalysts occurs via intramolecular C–H bond activation processes.¹ Therefore, the design of new NHC-ruthenium complexes, the study of their thermal intramolecular transformations, and the rationalization of the factors that control such processes are now relevant themes of research.

The current interest in combining ruthenium complexes with NHC ligands led our research group,^{4–6,12–14} and also other

* Corresponding author. E-mail: jac@fq.uniovi.es.

[†] Departamento de Química Orgánica e Inorgánica-IUQOEM.

[‡] Departamento de Química Física y Analítica.

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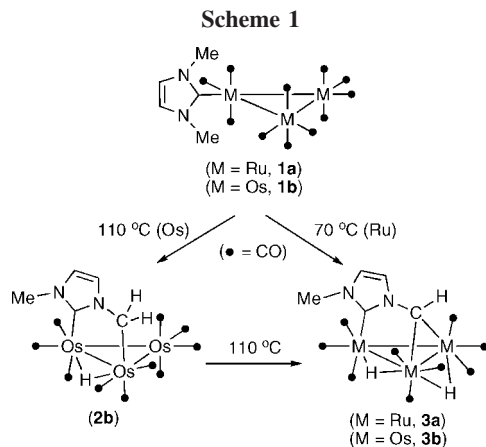
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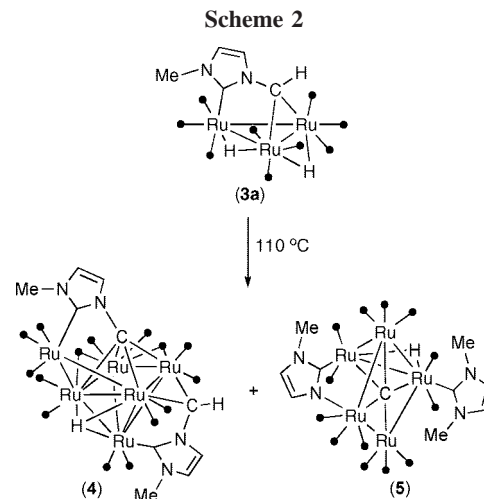
investigators,¹⁵ to study the incorporation of NHCs into ruthenium carbonyl clusters.¹⁶ Very recently, some osmium carbonyl clusters containing NHC ligands have also been synthesized.^{5,12,14,17}

Studying the thermal stability of the NHC trinuclear clusters $[M_3(\text{Me}_2\text{Im})(\text{CO})_{11}]$ ($\text{Me}_2\text{Im} = 1,3\text{-dimethylimidazol-2-ylidene}$; $M = \text{Ru}$ (**1a**), Os (**1b**)), we observed that the thermolysis of the triruthenium cluster **1a** in THF at reflux temperature leads to an unusual activation of two N-methyl C–H bonds of the Me_2Im ligand that ends in the ligand-capped dihydrido derivative $[\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-}\kappa^2\text{-MeImCH})(\text{CO})_9]$ (**3a**).^{4,5} No intermediates were observed in this transformation (Scheme 1). However, the triosmium cluster **1b** was stable in refluxing THF, but it also gave a ligand-capped dihydrido derivative, $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\kappa^2\text{-MeImCH})(\text{CO})_9]$ (**3b**), when it was heated in toluene at reflux temperature. In this case, the transient intermediate $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\kappa^2\text{-MeImCH}_2)(\text{CO})_{10}]$ (**2b**) could be observed and characterized (Scheme 1).⁵

Further heating of the ruthenium cluster **3a** in toluene at reflux temperature led to a separable mixture of $[\text{Ru}_6(\mu_3\text{-H})(\mu_5\text{-}\kappa^2\text{-MeImC})(\mu_3\text{-}\kappa^2\text{-MeImCH})(\mu\text{-CO})_2(\text{CO})_{13}]$ (**4**) and $[\text{Ru}_5(\mu_5\text{-C})(\mu\text{-H})(\mu\text{-}\kappa^2\text{-MeIm})(\text{Me}_2\text{Im})(\text{CO})_{13}]$ (**5**) (Scheme 2).⁶ While the bridging carbyne ligand of cluster **4** arises from the activation of three C–H bonds of an N-methyl NHC group, the formation of the carbide ligand of cluster **5** requires the additional activation of a C–N bond. The activation of all three C–H bonds of a mesityl methyl group of $[\text{Os}_4(\mu\text{-H})_4(\text{Mes}_2\text{Im})(\text{CO})_{11}]$ ($\text{Mes}_2\text{Im} = 1,3\text{-dimesitylimidazol-2-ylidene}$) has also been reported.^{17b}

Therefore, it seems that polynuclear ruthenium and osmium carbonyl clusters that contain NHC ligands have the necessary characteristics to become involved in reactions that imply the degradation of the N-arms of coordinated NHC ligands via multiple bond activation processes.

We now report a theoretical mechanistic study of the transformation of clusters **1a** and **1b** into **3a** and **3b**, respectively.



Although such a study was expected to be complicated and time-consuming due to the complex nature of the species and the multistep processes involved, we decided to carry it out because (a) it would provide data that could help explain why NHC-containing clusters are prone to become implicated in multiple intramolecular bond activation processes; (b) due to the polynuclear nature of the metallic species involved, this study could shed light on hitherto unknown aspects of the oxidative addition of C–H bonds to metal–metal bonded metal atoms; and (c) it would allow a comparison of the ruthenium and osmium systems. A few theoretical studies dealing with intramolecular bond activation reactions in NHC–ruthenium complexes have been reported,^{9,18} but they correspond to mononuclear systems in which a double C–H activation of a methyl group is not possible.

Computational Details

Density functional theory (DFT) calculations were carried out using Becke's three-parameter hybrid exchange–correlation functional¹⁹ and the B3LYP nonlocal gradient correction.²⁰ The LanL2DZ basis set, with relativistic effective core potentials, was used for the Os and Ru atoms.²¹ The basis set used for the remaining atoms was the 6-31G, with addition of (d,p)-polarization.²² It has been previously shown that the B3LYP/LanL2DZ/6-31G approximation used in this paper provides reasonable agreement with available experiments and higher-level methods in analogous systems.²³ No simplified model compounds were used for the calculations. Crystallographically determined structures provided initial geometries for the optimization of **1a** and **3a**. The optimized structures of all the ruthenium species (**1a**, **3a**, intermediates, and transition states) were used as initial geometries for the osmium species. Changing osmium for ruthenium and subsequent structure optimizations provided the final geometries of all the osmium species. All stationary points were confirmed as energy minima (reactants, products, and intermediates; all positive eigenvalues) or

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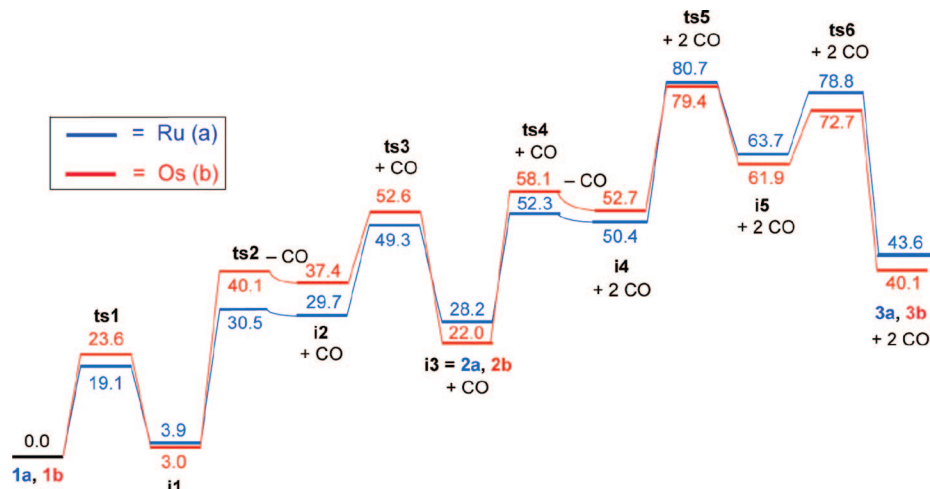


Figure 1. Relative energy profiles (kcal/mol) for the thermal transformation of **1a** into **3a** + 2 CO (blue trace) and that of **1b** into **3b** + 2 CO (red trace).

Table 1. Computed Distances (Å) between Selected Atoms of the Stationary Points Involved in the Transformation of **1a** into **3a**

atoms	1a	ts1a	i1a	ts2a	i2a	ts3a	i3a	ts4a	i4a	ts5a	i5a	ts6a	3a
C1–Ru1	2.155	2.137	2.216	2.209	2.198	2.149	2.139	2.129	2.129	2.107	2.105	2.113	2.112
C2–Ru2	6.271	5.212	5.761	5.881	5.140	4.178	3.787	2.677	2.503	2.193	2.248	2.200	2.131
C2–Ru3	6.015	4.894	4.307	4.034	3.484	2.421	2.200	2.229	2.177	2.099	2.081	2.101	2.152
H1–C2	1.091	1.088	1.085	1.086	1.091	1.452	2.771	2.904	2.850	2.764	2.751	2.791	2.798
H2–C2	1.091	1.091	1.092	1.092	1.092	1.088	1.092	1.110	1.152	2.125	2.739	2.373	2.674
H1–Ru1	3.735	3.610	3.142	3.202	3.065	1.997	1.786	1.786	1.771	1.775	1.822	1.763	1.786
H1–Ru3	5.852	4.135	3.365	3.160	2.495	1.737	1.801	1.802	1.830	1.838	1.793	1.824	1.807
H2–Ru2	7.326	6.094	6.329	6.594	5.506	4.443	3.694	2.177	1.945	1.618	1.610	1.613	1.814
H2–Ru3	7.077	5.894	4.715	4.548	3.833	2.727	2.774	2.924	2.879	3.494	3.393	2.699	1.804
C3–Ru3	1.967	1.967	1.951	3.054									
C4–Ru2	1.964	1.952	1.952	1.969	1.977	1.951	1.953	3.508					

transition states (one imaginary eigenvalue) by analytical calculation of frequencies. IRC calculations were used to verify that the transition states found were correct saddle points connecting the proposed minima. All energies given in this article are potential energies calculated in the gas phase. It was verified that the gas phase potential energy profiles are similar to the free energy profiles. Atomic NPA (natural population analysis) charges were derived from the natural bond order (NBO) analysis of the data.²⁴ All calculations were carried out without symmetry constraints utilizing the Gaussian03 package.²⁵

Results and Discussion

The Ruthenium System. The energy profile of the transformation of the triruthenium cluster **1a** into **3a** + 2 CO is displayed in Figure 1, in which the given energies are relative to that of the starting material and include the energy of none (starting material to **ts2a**), one (**i2a** to **ts4a**), or two (**i4a** to final product) CO molecules. Table 1 shows the evolution of a selection of interatomic distances as going from **1a** to **3a** through the corresponding intermediates and transition states.

The first step of the overall transformation is a ligand rearrangement on Ru1 that, through a trigonal twist rotation that involves two COs and the Me₂Im ligand (energy barrier = 19.1 kcal/mol), moves the Me₂Im ligand from an equatorial (in **1a**) to an axial coordination site (in **i1a**) (Figure 2). The

next step is the rate-limiting step (energy barrier = 30.5 kcal/mol) of the overall transformation of **1a** into **3a**. It is a CO elimination process in which an axial CO group of Ru3 is released (C3–Ru3 = 3.054 Å in **ts2a**) at the same time that the N-methyl H1 hydrogen atom becomes close to the Ru1 and Ru3 metal atoms (H1–Ru1 = 3.202 Å and H1–Ru3 = 3.160 Å in **ts2a**). The unsaturation of the Ru3 atom of intermediate **i2a** is alleviated by a hydrogen-bonding interac-

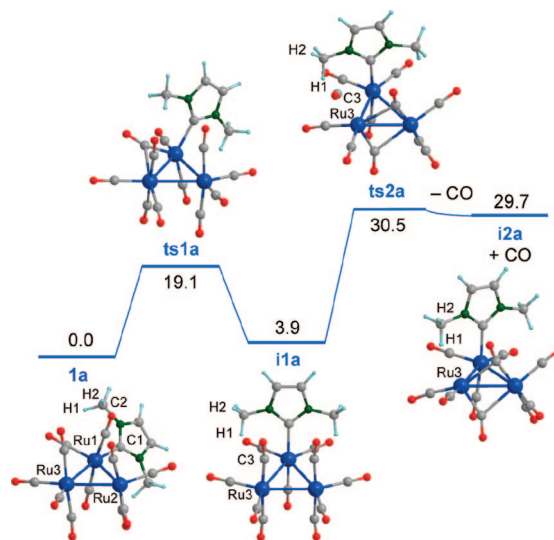


Figure 2. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation **1a** into **i2a** + CO.

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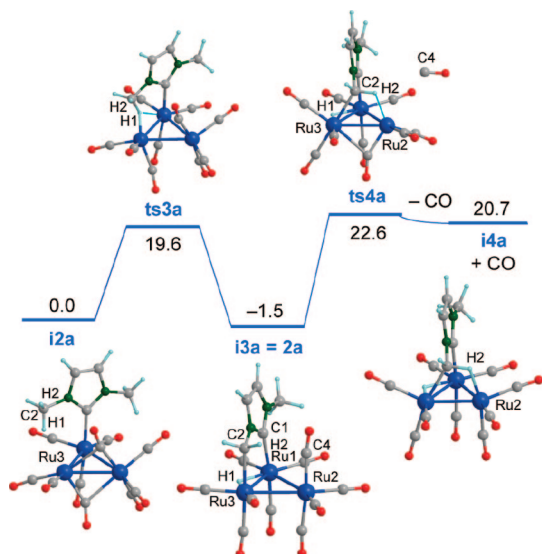


Figure 3. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation **i2a** into **i4a** + CO.

tion between Ru3 and H1 (2.495 Å) and also by the interaction of Ru3 with two semibridging CO ligands.

The coordinative unsaturation (EAN electron count = 46) and the opposite signs of the atomic charges of H1 (+0.226) and the ruthenium atoms Ru1 (−0.247) and Ru3 (−0.228) of **i2a** promote an easy (energy barrier = 19.6 kcal/mol) oxidative addition of the C2–H1 bond to Ru3, in such a way that, in the transition state **ts3a** (Figure 3), the H1 atom is at bonding distance from Ru1 and Ru3 (1.997 and 1.737 Å, respectively), while the C2 atom approaches the Ru3 atom (2.421 Å) and separates from H1 (1.452 Å). The so-formed intermediate **i3a** has the Ru1–Ru3 edge bridged by a hydride (H1–Ru1 = 1.786 Å, H1–Ru3 = 1.801 Å) and by an MeImCH₂ ligand (C1–Ru1 = 2.139 Å, C2–Ru3 = 2.200 Å). On going from **i2a** to **i3a**, the metal atoms Ru1 and Ru3 maintain their negative charge (−0.318 and −0.256, respectively, in **i3a**), but the charge of H1 changes from positive to negative (−0.126 in **i3a**). This step represents an unprecedented mechanistic proposal for an oxidative addition C–H activation process, shedding light on hitherto unknown aspects of the oxidative addition of C–H bonds to metal–metal bonded metal atoms.

Figure 3 shows that the next step is a new CO elimination process (energy barrier = 22.6 kcal/mol). A rotation about the C1–Ru1 bond of **i3a** provokes an emerging interaction of H2 with Ru2 (2.177 Å in **ts4a**) that is accompanied by the release of an axial CO ligand from Ru2 (C4–Ru2 = 3.054 Å in **ts4a**). The coordinative unsaturation of the Ru2 atom of intermediate **i4a**, which is attached to only three CO ligands, is alleviated by a strong interaction with the H2 atom (H2–Ru2 = 1.945 Å). Such an interaction is favored by the opposite signs of the atomic charges of these atoms (+0.203 for H2 and −0.240 for Ru2).

The H2⋯Ru2 interaction of intermediate **i4a** evolves toward the oxidative addition of the C2–H2 bond to the Ru2 atom, to give intermediate **i5a** (Figure 4), which has a CH fragment spanning the Ru2–Ru3 edge (C2–Ru2 = 2.248 Å, C2–Ru3 = 2.081 Å) and a terminal hydride ligand on Ru2 (H2–Ru2 = 1.610 Å). The transition state **ts5a** is 30.3 kcal/mol above **i4a**. The negative atomic charge of Ru2 in **i4a** (−0.240) is augmented in **i5a** (−0.404), while the positive atomic charge of H2 in **i4a** (+0.203) is considerably reduced in **i5a** (−0.012).

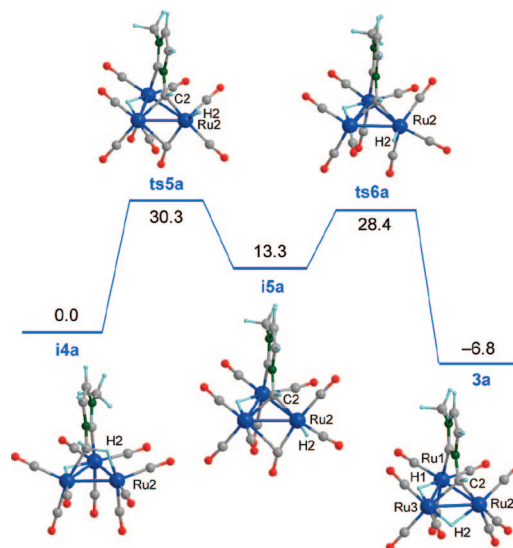


Figure 4. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation of **i4a** into **3a**.

In the last step, the terminal hydride ligand H2 of **i5a** moves to a bridging position, spanning the Ru2 and Ru3 metal atoms (Figure 4), through an accessible transition state (**ts6a** is 1.9 kcal/mol below **ts5a**). The final product, **3a**, is 6.8 kcal/mol more stable than intermediate **i4a**.

The dihydrido cluster **3a** reacts easily with carbon monoxide to give **1a**.⁴ This experimental fact agrees well with the theoretical energy profile shown in Figure 1, which indicates that such reaction is thermodynamically favored. However, considering the transformation of **1a** into **3a**, the relative energies shown in Figure 1 for the stationary points are not realistic from a synthetic point of view because some of them include the energy of one (**i2a** to **ts4a**) or two (**i4a** to **3a**) CO molecules and, experimentally, the transformation of **1a** into **3a** requires a continuous purge of the released CO with an inert gas.⁵ Therefore, it is more realistic to consider **1a**, **i2a**, and **i4a** as starting points of independent processes, with relative energies of 0.0 kcal/mol with respect to the species that contain the same number and type of atoms, as done in Figures 2–4.

The Osmium System. For comparison purposes, the energy profile of the transformation of the triosmium cluster **1b** into **3b** + 2 CO is shown in Figure 1, together with that of the ruthenium system. The optimized structures and relative energies of the stationary points involved in the transformation of **1b** into **i2b** + CO, **i2b** into **i4b** + CO, and **i4b** into **3b** are displayed in Figures 5–7, respectively. A selection of interatomic distances between atoms of the stationary points that connect **1b** to **3b** is given in Table 2.

Mechanistically, the reaction pathway of the osmium system is very similar to that of the ruthenium system. Therefore, only the differences between the two metal systems are discussed in the following paragraphs.

Although the key structural features (distances between the metal atoms and the C and H atoms of the metalated N-methyl group) of the stationary points involved in each metal system are very similar, some ruthenium intermediates (**i2a**, **i5a**) and transition states (**ts2a**, **ts4a**, **ts5a**) differ from the corresponding osmium ones in that the former contain one bridging CO ligand, whereas that ligand is terminal (**i2b**, **ts2b**, **ts4b**) or only incipiently bridging (**i5b**, **ts5b**) in the latter. Ruthenium carbonyl

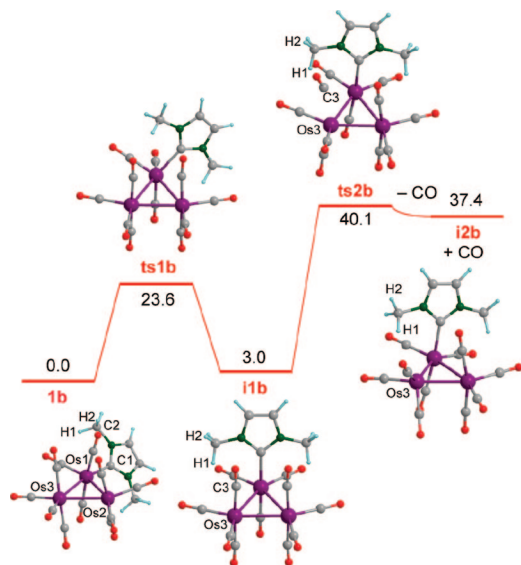


Figure 5. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation of **1b** into **i2b** + CO.

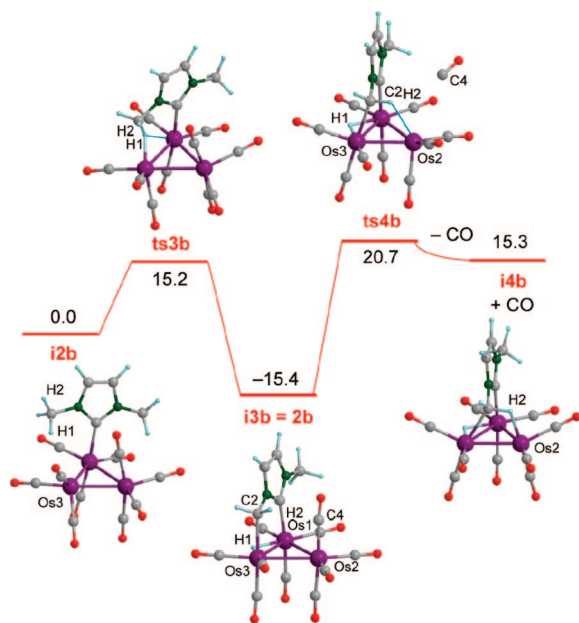


Figure 6. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation of **i2b** into **i4b** + CO.

cluster complexes have a greater propensity to contain bridging CO ligands than their analogous osmium clusters.²⁶

Experimentally, it has been observed that osmium carbonyl clusters have a lower tendency to undergo CO substitution reactions than analogous ruthenium carbonyl cluster complexes.²⁷ This empirical observation is also reflected by the present theoretical study. Thus, although the first CO elimination step is rate-limiting in the ruthenium and the osmium reactions studied in this work, the two steps that involve the elimination

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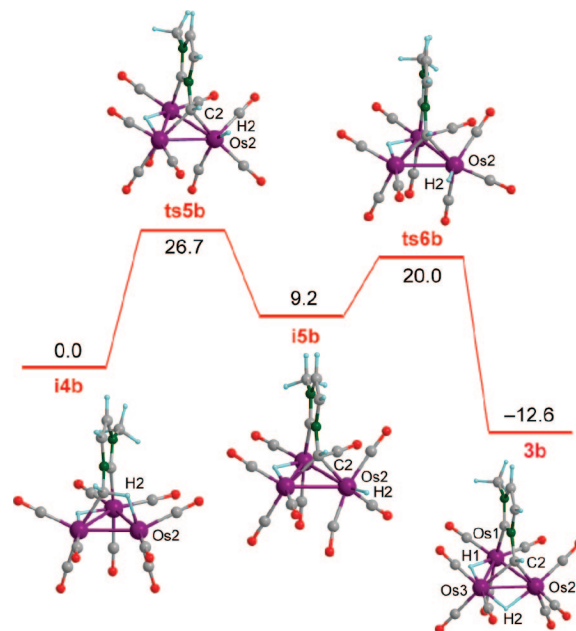


Figure 7. Optimized structures and relative energy profile (kcal/mol) of the stationary points involved in the transformation of **i4b** into **3b**.

of a CO ligand (whose transition states are **ts2** and **ts4**) have activation barriers that are 9.6 and 12.0 kcal/mol higher for the osmium system than for the ruthenium system, actually being the two most costly steps of the whole osmium system (40.1 and 36.1 kcal/mol, respectively). These facts account for the experimental observation that the osmium reaction needs a higher temperature to proceed than the ruthenium reaction.⁵

The osmium intermediate **i3b** lies 15.4 kcal/mol below its precedent intermediate **i2b** (Figure 6), and its transformation into **i4b** costs 36.1 kcal/mol, only 4.0 kcal/mol less than the highest energy barrier of the whole osmium reaction (**ts2b**, 40.1 kcal/mol). This energy value explains that **i3b** (**2b** in Scheme 1) was experimentally observed as a transient intermediate when the osmium reaction was carried out.⁵ In contrast, the ruthenium intermediate **i3a** was not experimentally observed because it lies only 1.5 kcal/mol below **i2a** (Figure 3) and its transformation into **i4a** costs only 24.1 kcal/mol (**ts4a**), 6.4 kcal/mol less than the energy barrier of the whole ruthenium reaction (**ts2a**).

Concluding Remarks. This theoretical work has shed light not only on why but also on how polynuclear carbonyl clusters that contain NHC ligands may undergo multiple intramolecular C–H activation processes that result in degradation of alkyl groups of the NHC N-arms.

There are several of factors that can contribute to facilitate intramolecular C–H bond activation processes in carbonyl metal clusters that contain NHC ligands. (a) Ligand C–H bonds and cluster metal atoms can be very close to each other. This is more difficult (depending on the nature of the NHC N-R group) in mononuclear complexes. (b) NHC-containing ruthenium and osmium carbonyls are electron-rich species because the metals are low-valent group-8 atoms and the NHC ligands are very basic. (c) The metal atoms of these clusters bear negative charges, whereas the hydrogen atoms of C–H bonds bear positive charges. This charge distribution facilitates the formation of C–H...M hydrogen-bonding interactions that may evolve toward C–H activation processes. (d) Ruthenium and osmium carbonyl clusters can undergo thermal decarbonylation processes that transform them into reactive unsaturated electron-

Table 2. Computed Distances (Å) between Selected Atoms of the Stationary Points Involved in the Transformation of **1b** into **3b**

atoms	1b	ts1b	i1b	ts2b	i2b	ts3b	i3b	ts4b	i4b	ts5b	i5b	ts6b	3b
C2–Os2	6.026	5.116	5.716	5.646	5.302	4.080	3.780	3.156	2.491	2.231	2.289	2.206	2.158
C2–Os3	6.245	5.191	4.229	4.272	3.866	2.488	2.214	2.224	2.198	2.107	2.091	2.126	2.170
H1–C2	1.090	1.086	1.085	1.084	1.089	1.361	2.756	2.864	2.873	2.775	2.835	2.820	2.859
H2–C2	1.091	1.091	1.092	1.092	1.779	1.087	1.093	1.096	1.161	2.099	2.772	2.395	2.711
H1–Os1	3.556	3.512	3.160	3.184	3.384	2.142	1.820	1.809	1.795	1.796	1.794	1.791	1.794
H1–Os3	5.986	4.365	3.303	3.326	2.921	1.763	1.820	1.820	1.852	1.865	1.840	1.842	1.850
H2–Os2	7.048	5.898	6.288	6.296	6.134	4.235	3.743	2.869	1.960	1.647	1.651	1.639	1.832
H2–Os3	7.331	6.109	4.637	4.822	4.686	2.769	2.799	2.838	2.938	3.346	3.729	2.834	1.840
C3–Os3	1.962	1.958	1.949	3.226									
C4–Os2	1.965	1.952	1.950	1.941	1.951	1.946	1.951	3.640					

rich species that, to alleviate their unsaturation, are prone to undergo an intramolecular oxidative addition of a C–H bond close to the unsaturated metal atom. (e) Although the overall reactions are endothermic, the release of CO gas makes them irreversible, driving the reactions to the end.

As it is very improbable, or impossible, to have more than one NHC C–H bond close to a single metal atom, multiple NHC C–H bond activation reactions have never been observed in mononuclear systems. However, the results reported herein explain why the activation of several NHC C–H bonds is not only possible but also easy, in metal cluster complexes, because different metal atoms can be close to different C–H bonds of the same molecule.

The way by which the first C–H activation step takes place in both studied systems (formation of **i3**) has no precedent. It implies an interaction of two metal atoms with an N-methyl hydrogen atom (**i2**, **ts3**) that evolves toward **i3**, which contains an edge-bridging hydride and an edge-bridging MeImCH₂ ligand. The second C–H activation step involves only one metal atom and, mechanistically, is similar to other C–H activation reactions that occur via oxidative addition in mononuclear complexes.²⁸ Therefore, the present work also contributes to gain new insights into how the oxidative addition of C–H bonds to metal–metal bonded metal atoms can take place.

Finally, the present work also explains why the osmium system requires higher temperature than the ruthenium system to proceed, because (a) each C–H activation step is preceded by the elimination of a CO ligand, (b) the C–H activation steps have lower energy barriers than the CO eliminations steps, and (c) the energy barriers of the latter processes are higher in osmium clusters than in ruthenium clusters.

Acknowledgment. This work has been supported by the European Union (FEDER grants) and the Spanish MEC (projects CTQ2007-60865 and MAT2006-1997).

Supporting Information Available: Complete ref 25, tables containing NPA atomic charges for selected atoms of all stationary points, and tables of atomic Cartesian coordinates for all optimized structures (intermediate species and transition states) reported in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM8006085

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