Structures of \( d^4 \) MH\( _3 \)X: a Computational Study of the Influence of the Metal and the Ligands

POBLADOR BAHAMONDE, Amalia Isabel, RAYNAUD, Christophe, EISENSTEIN, Odile

Abstract

Density functional theory (DFT, PBE0, and range separated DFT, RSH + MP2) and coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) calculations have been used to probe the structural preference of \( d^4 \) MH\( _3 \)Xq (M = Ru, Os, Rh\(^+\), Ir\(^+\), and Re\(^-\); X = H, F, CH\(_3\), CF\(_3\), SiH\(_3\), and SiF\(_3\)) and of MX\(_4\) (M = Ru; X = H, F, CH\(_3\), CF\(_3\), SiH\(_3\), and SiF\(_3\)). Landis et al. have shown that complexes in which the metal is sd\( ^3 \) hybridized have tetrahedral and non-tetrahedral structures with shapes of an umbrella or a 4-legged piano stool. In this article, the influence of the metal and ligands on the energies of the three isomeric structures of \( d^4 \) MH\(_3\)X and MX\(_4\) is established and rationalized. Fluoride and alkyl ligands stabilize the tetrahedral relative to non-tetrahedral structures while hydride and silyl ligands stabilize the non-tetrahedral structures. For given ligands and charge, 4d metal favors more the non-tetrahedral structures than 5d metals. A positive charge increases the preference for the non-tetrahedral structures while a negative charge increases the preference for the tetrahedral structure. The factors that [...]
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Amalia I. Poblador-Bahamonde, Christophe Raynaud,* and Odile Eisenstein*

Institut Charles Gerhardt, Université Montpellier 2, CNRS UMR 5253, cc 1501, Place Eugène Bataillon, 34095 Montpellier, France

Supporting Information

ABSTRACT: Density functional theory (DFT, PBE0, and range separated DFT, RSH + MP2) and coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) calculations have been used to probe the structural preference of $d^4$ MH$_3$X ($M =$ Ru, Os, Rh$^+$, Ir$^+$, and Re$^+$; X = H, F, CH$_3$, CF$_3$, SiH$_3$, and SiF$_3$) and of MX$_4$ ($M =$ Ru, X = H, F, CH$_3$, CF$_3$, SiH$_3$, and SiF$_3$). Landis et al. have shown that complexes in which the metal is sd$^3$ hybridized have tetrahedral and non-tetrahedral structures with shapes of an umbrella or a 4-legged piano stool. In this article, the influence of the metal and ligands on the energies of the three isomeric structures of $d^4$ MH$_3$X and MX$_4$ is established and rationalized. Fluoride and alkyl ligands stabilize the tetrahedral relative to non-tetrahedral structures while hydride and silyl ligands stabilize the non-tetrahedral structures. For given ligands and charge, $4d$ metal favors more the non-tetrahedral structures than $5d$ metals. A positive charge increases the preference for the non-tetrahedral structures while a negative charge increases the preference for the tetrahedral structure. The factors that determine these energy patterns are discussed by means of a molecular orbital analysis, based on Extended Hückel (EHT) calculations, and by means of Natural Bond Orbital (NBO) analyses of charges and resonance structures (NRT analysis). These analyses show the presence of through-space interactions in the non-tetrahedral structures that can be sufficiently stabilizing, for specific metals and ligands, to stabilize the non-tetrahedral structures relative to the tetrahedral isomer.

INTRODUCTION

Unsaturated transition metal complexes are a model of reactive intermediates, and their structures and electronic properties can provide useful information on how they could react. These species are often very reactive and hard to characterize by experimental means. Therefore, structure and bonding analyses and computational studies have been useful to establish the structures of these complexes. The structure of unsaturated species does not always follow the rules that apply for saturated systems. For instance, it has been found that the structure of unsaturated species cannot be always predicted by the valence shell electron pair repulsion (VSEPR) theory or by a simple ionic model. WMe$_6$ and WH$_6$ are notable cases for the failure of the VSEPR rule. For instance, WCl$_6$ is octahedral while WMe$_6$ and WH$_6$ are not. Analysis of the metal–ligand bonding within such complexes shows that the electron delocalization between the $\pi$-donor ligand and the formally empty metal $d$ orbital increases the electron density at the metal which, in turn, becomes less unsaturated. Therefore, the structures of polyhydride or polyalkyl complexes are considered as informative of the fundamental structural preferences associated with the metal coordination number and the number of $d$ electrons. Unfortunately, few systems of this type have been characterized experimentally, a clear consequence of the poor stability of highly unsaturated species. For this reason, computational studies have been widely used.

Landis et al. have shown that valence bond concepts can be used for describing the shape of a variety of hydride and alkyl systems. A primary feature of their studies is that the valence empty ($n+1)p$ orbitals of a $nd$ metal do not contribute to the metal–ligand bonds, which are constructed from the ($n+1)s$ and available $nd$ orbitals. Consequently, the shape of the hydride complex, where the metal has $\lambda$ nonbonding electron pairs, is determined by the optimal spatial distribution of the $sd^{\omega}$ ($\omega = 5 - \lambda$) hybrid set, that is, the spatial distribution that minimizes the interactions between the hybrid orbitals. In general, there is more than one optimal spatial distribution for a given $sd^{\omega}$ set and quantum calculations are used to determine the relative energies of these isomeric structures.$^{7a,8,9}$ Similar results were obtained using the orbitally ranked symmetry
analysis method (ORSAM) since for low coordinated complexes the metal orbital uses also the \((n + 1)s\) and \(nd\) orbitals and the ranking of the structures is also done by quantum calculations. In these studies, only hydride complexes were calculated but other ligands were not explicitly considered. Likewise the influence of the metal was not explored.

Well-defined experimental species are rather limited since the only known complexes of this type are the homoleptic neutral \([MH_3X]^+\) (\(M = \text{Re}, \text{Os}\) and \(\text{Ir}\)), and anionic \([\text{ReH}_3X]^−\) \((X = \text{H}, \text{F}, \text{CF}_3, \text{CH}_3, \text{SiF}_3, \text{and SiH}_3)\), cationic \(\text{Ru}(\text{C}_6\text{H}_{11})_4\), \(\text{Ru}(\text{o-Tolyl})_4\), \(\text{Ru}(\text{Mesityl})_4\), \(\text{Os}(\text{C}_6\text{H}_{11})_4\), \(\text{Os}(\text{o-Tolyl})_4\), and \(\text{Ir}(\text{Mesityl})_4\) are stable and have a tetrahedral coordination at the metal. However, the bonding analysis of Landis and the ORSAM analysis of Hall predict that other isomers with non-tetrahedral structures should be possible, and calculations for \(\text{RuH}_4\) and \(\text{OsH}_4\) have shown that non-tetrahedral structures could even be preferred or at least competitive, but no rationale for these results is available.

We were intrigued by these results, and we wanted to explore whether other isomers with non-tetrahedral structures could even be preferred or at least competitive, but no rationale for these results is available.

Two methods (1 and 2) were used to obtain the geometries and energies at the DFT level. Additional methods were used to increase the accuracy of the relative energies of the isomers, methods 3 and 4. The validity of the DFT method was established with method 5.

Method 1. The geometry optimizations were performed at the DFT level of theory with Gaussian 09 using the B3PW91 functional. The metal centers were described with the Stuttgart/Dresden (SDD) quasi-relativistic effective core potentials (RECP) and the associated basis sets. The 6-31G(d,p) basis set were used for the other atoms.

Method 2. The geometries obtained with the method 1 were used as initial input for optimization with the PBE0 functional and triple-c-zeta quality basis sets on all atoms, de2-TZVPP, with the corresponding RECP for the metal. With rare exceptions, the optimized structures obtained with method 2, and method 1 are similar. Bond lengths only differ by about 0.01 \(\text{Å}\), and bond angles differ by less than 5°. The structures and energies obtained with method 2 are used for describing the results in this Article. All stationary points were fully characterized by analytical frequency calculations as either a minimum or a transition state. Intrinsic reaction coordinate (IRC) calculations followed by geometry optimizations were used to associate a transition state to the corresponding two minima. The energies reported in this article do not include the ZPE correction, but it has been verified that the ZPE correction does not modify significantly the relative energies of the isomers. The optimized geometries for all stationary points and the ZPE corrected energies are given in the Supporting Information.

Method 3. Single-point short-range (sr-) DFT/long-range (lr-) ab initio calculations on the DFT (PBE0/de2-TZVPP) geometries were carried out for all structures using the Molpro 2010.1 program.

Method 4. Single-point coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) calculations on the DFT (PBE0/de2-TZVPP) optimized geometries were carried out for \(\text{ML}_4\) (\(M = \text{Ru} \) and \(\text{Os}\); \(X = \text{H}, \text{F}, \text{CF}_3, \text{CH}_3, \text{SiF}_3, \text{and SiH}_3\)) using the Orca 2.9 program. In this case, all atoms were described with de2-QZVPP basis sets with the corresponding RECP for the metal.

Method 5. Single-point MR-CI and MR-ACPF-2a calculations on the DFT (PBE0/de2-TZVPP) optimized geometries were carried out for \(\text{RuH}_4\) using the Orca 2.9 program. In this case, all atoms were described with a de2-QZVPP basis sets with the corresponding RECP for the metal. Resolution of the identity (RI) approximation was used for the integral transformation with de2-QZVPP/C auxiliary basis sets. For these MRCl and MR-ACPF-2a calculations, the reference space was built from full valence CASSCF orbitals (12 electrons, 10 orbitals) using a selection threshold (Tpre) set to 10^-6. The selection of the excited configurations from the reference space was done with a selection threshold (Tsel) of 10^-7. The effect of the rejected configurations was estimated using second order perturbation theory.

Analysis of the Results. The Extended Hückel (EHT) calculations were carried out with the Yahnep program. The Ru 4d, 5s, and 5p orbitals are \(-14.9, -10.4,\) and \(-6.87\) eV, respectively. The energy of the "normal" hydrogen 1s orbital is \(-13.6\) eV. A better electron-donating ligand than "normal" hydrogen is characterized by \(H_2\) higher than \(-13.6\) eV and a poorer electron-donating ligand is characterized by \(H_2\) lower than \(-13.6\) eV. Ligands of variable electron-donating power were represented by varying the \(H_2\) value of the four hydrogen atoms between \(-15.6\) and \(-12.6\) eV. The Natural Bond Orbital (NBO) charges and the Natural Resonance Theory (NRT) analysis were obtained using the NBO methodology with the NBO 5.0 program.

In d^4 \(\text{ML}_4\) species, where two d orbitals are used to host the four metal electrons, the \((n + 1)s\) and three \(nd\) metal orbitals are available to form the four metal–ligand bonds. This leads to sd hybridization at the metal, and the shape of the complex is determined by the optimal spatial distribution of these four sd hybrids. The neutral polyhydride complex, \(d^4 \text{ML}_4\), is an ideal model system in that the H–M–H angles are very close to those that minimize the overlap between the metal hybrid orbitals at the metal which are 71° and 109°. It results that the structures can be constructed by placing the metal at a center of a cube and the four ligands at four vertices such that no ligands are trans (Figure 1). This gives three possible structures, which have the shape of a tetrahedron, \(T_d\), an umbrella, \(C_{3v}\), and a 4-legged-piano stool, \(C_{4v}\), as shown in the top part of Figure 2. In \(T_d\), all coordination sites are equivalent and all bond angles are 109°. In \(C_{3v}\), there are three basal hydrides, \(H_a\), and one apical hydride, \(H_b\) with \(H_a−M−H_a\) and \(H_b−M−H_b\) angles of 71° and 109°, respectively. In \(C_{4v}\), the four hydrides are equivalent, and the cis H–M–H angle is equal to 71°. Changing the metal and

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**Figure 1.** Dispositions of ligands for sd^1 hybridization in idealized d^4 ML4 (M in blue at the center of the cube and L in black).
the ligands lead to different angles, which influence the opening of the umbrella and the height of the piano stool.

When one of the three hydrogen atoms is replaced by an X ligand, tetrahedral, umbrella, and 4-legged piano stool isomeric structures are still found (Figure 2 bottom). Only the umbrella complex has nonequivalent sites. The presence of X gives rise to two isomers, namely, umb, where X is at the apical site and umbb, where X is at the basal site.

Validation of the Use of Single Reference Methods for d4 MH3X. The geometries of MH3X were optimized at a DFT level and the energetics were obtained with methods 2, 3, and 4. DFT (PBE0 and RSH+MP2), and CCSD(T), respectively. However, the use of single reference (SR) methods for the description of unsaturated species could be questionable. Even with truncation of excitations at the double and triple level, single reference methods, such as CCSD(T), recover a large portion of the dynamic correlation energy, but may fail when a significant amount of nondynamical correlation energy is present. In contrast, multireference methods, such as MRCI or MR-ACPF, recover both dynamical and nondynamical correlation energies.

To check the validity of the SR calculations for d4 MH3X, single points MRCI and MR-ACPF-2a calculations were carried out for the three isomers of RuH4 (td, umb, and pst). For these MRCI and MR-ACPF-2a calculations, the reference space was built from full valence CASCCF orbitals (12 electrons, 10 orbitals) and the effect of the rejected configurations was estimated using second order perturbation theory (Table 1).

All calculations show that the umb and pst isomers are lower in energy than the td isomer. Furthermore, all methods give a similar energetic pattern. Umb and pst are lower than td by 9.1 to 12.9 and 9.4 to 14.7 kcal mol\(^{-1}\), using the PBE0, RSH+MP2, and CCSD(T) methods, respectively. There is a marginal tendency for pst to have a lower energy than umb. It is also worth noting that the range separated hybrid RSH+MP2 calculations and the single reference coupled cluster calculations give values that are close. This overall good agreement between the single reference and multireference methods suggests that these unsaturated metal species do not contain a significant amount of nondynamical correlation energy. This indicates that a single reference method can be used for the computational study of d4 MH3X.

In addition, several diagnostics have been suggested to evaluate the SR/MR character for molecular systems. The T1 and D1 diagnostics\(^{33}\) (the Frobenius norm and matrix 2-norm of coupled cluster amplitudes for single excitations respectively) are arguably the most widely used diagnostics for SR coupled cluster calculations. Alternatively, the weight (\(C_0^2\)) of the leading configuration state function in a MRCI can be used to determine the multireference character. The T1 and D1 diagnostics were tested primarily on small organic molecules, and it was suggested that any T1 diagnostic larger than 0.02 and any D1 diagnostic larger than 0.05 invalidate the use of SR methods. However, a recent study of Jiang et al. pointed out that the criteria established for organic molecules (T1 < 0.02 and D1 < 0.05) are no longer valid for molecular systems with transition metals.\(^{34}\) On the basis of a statistical analysis of a set of 225 species, these authors proposed T1 < 0.05 and D1 < 0.15 as amplitude criteria for the validation of SR-based methods in the case of d-block energetics. The T1 and D1 diagnostics of the single reference CCSD(T) calculations are reported in Table 2 for the three isomers of RuH4 (td, umb, and pst); the weight of the leading configuration (\(C_0^2\)) from the multireference MRCI or MR-ACPF-2a calculations is also indicated. For the three isomers of RuH4, both T1 and D1 diagnostics from SR CCSD(T) calculations are less than the values suggested by Jiang et al. as acceptable limits. In addition, the weight of the leading configuration is higher than 0.80 for the MRCI and MR-ACPF-2a calculations. This confirms that these unsaturated molecular systems do not contain any substantial MR character. Single references methods are thus validated for the calculations of RuH4. This validation applies to all d4 MH3X and MX4 studied in this article (T1 and D1 diagnostics given in the Supporting Information for RuH4 and OsH4X).

RuH4X. (a). RuH4. The DFT calculations show that RuH4 has td, umb, and pst minima. The umb and pst isomers have similar energies and both species are more stable than the tetrahedral structure by about 9 kcal mol\(^{-1}\). These results differ from those obtained by Landis. Molecular mechanic (MM) calculations including hybridization and resonance in a valence bond (VB) approach (Hypervalent-VALBOND (HV-VB) MM

![Figure 2. Possible structures for d4 MH4 (top) and d4 MH3X (bottom) with labeling.](image-url)
DFT calculations using a different ECP and a different functional for the metal \(^7\text{a,8}\) from the one used in this work give \(\text{td}\) and \(\text{pst}\) as the only minima, with \(\text{pst}\) being 8.6 kcal mol\(^{-1}\) lower in energy relative to \(\text{td}\). The Hartree–Fock and MP2 calculations by Hall et al. show several minima with relative energies that depend on the computational method used.\(^9\)

The essential structural features of the three isomers of RuH\(_4\) are shown in Figure 3. The Ru–H bond is 1.55 Å in \(\text{td}\), in kcal mol\(^{-1}\) relative to the \(\text{td}\) structure, using method 2.

The apical Ru–H\(_b\) bond of 1.51 Å is slightly shorter than the basal Ru–H\(_a\) bond of 1.54 Å. The H\(_b\)–Ru–H\(_a\) and the H\(_b\)–Ru–H\(_b\) angles of 64° and 102°, respectively, are close to the corresponding ideal values of 71° and 109° predicted for a sd\(^2\) hybridized metal. The acute H\(_b\)–Ru–H\(_a\) angle leads to a nonbonded H\(_a\)···H\(_b\) distance of 1.62 Å, which is less than the sum of the van der Waals (vdW) radii of the two hydrogens (1.20 Å).\(^3\) In \(\text{pst}\), the Ru–H bond of 1.53 Å and the angles of 67° and 103° for cis H–Ru–H and trans H–Ru–H angles, respectively, are similar to the ideal values of 71° and 109°. In \(\text{ pst}\), the shorter nonbonded H···H distance is 1.69 Å, which is less than the sum of the vdw radii of the two hydrogens although slightly longer than in \(\text{umb}\). Therefore, both \(\text{umb}\) and \(\text{pst}\) have short nonbonded H···H distances that are not present in the \(\text{td}\) structure wherein the H···H nonbonded distance is 2.54 Å.

The transition states between these minima were searched using method 2 to evaluate the depth of the associated wells on the potential energy surface and the possibility of exchange between the three minima (Figure 3). A transition state of \(8.7\) kcal mol\(^{-1}\) above \(\text{td}\) was located between \(\text{td}\) and \(\text{umb}\) and another transition state between \(\text{umb}\) and \(\text{pst}\) with an energy of 2.9 kcal mol\(^{-1}\) above \(\text{umb}\). No transition state was identified between \(\text{td}\) and \(\text{pst}\). The tetrahedral structure is thus separated from the other minima by a significant barrier, but there is a low energy barrier between \(\text{umb}\) and \(\text{pst}\). The structural features of the two transition states are shown in Figure 3. The transition state between \(\text{td}\) and \(\text{umb}\) isomers inverts the configuration at the metal as it inverts the umbrella. At the transition state, the ruthenium atom is in the equatorial plane formed by the three H\(_b\) hydrogens and the Ru–H\(_a\) bond is perpendicular to the equatorial plane; this inversion at the metal occurs without significant change in the Ru–H bond distances. The transformation of \(\text{umb}\) to \(\text{pst}\) is a concerted swinging motion of two H\(_b\) relative to the plane defined by Ru–H\(_a\) and the third Ru–H\(_b\) bonds. At the transition state, Ru–H\(_a\) and two Ru–H\(_b\) bonds are coplanar. This transformation also occurs without significant change of the Ru–H bond distances.

(b). RuH\(_3\)X (X = H, F, CH\(_3\), CF\(_3\), SiH\(_3\), and SiF\(_3\)). The structures of RuH\(_3\)X (X = H, F, CH\(_3\), CF\(_3\), SiH\(_3\), and SiF\(_3\)) were determined at the DFT level with method 2. The results are shown in Figure 4 as a histogram in which the energies of the non-tetrahedral structures are plotted relative to the \(\text{td}\) structure, which is a minimum for all X groups. Figure 4 shows that X influences the relative energies of the various minima and also the number of minima. For instance, RuH\(_3\)F has only two minima, \(\text{td}\) and \(\text{umb}\), while the four minima shown in Figure 2 are obtained for all other X.

Single point calculations with method 3, RSH+MP2, and method 4, CCSD(T), are shown in Figure 5. These calculations show energetic patterns similar to that obtained with method 2. Methods 3 and 4 stabilize more the non-tetrahedral structures relative to the tetrahedral references than method 2. In the case where method 2 gives a non-tetrahedral structure less stable than \(\text{td}\), the difference in energy between \(\text{td}\) and non-tetrahedral structures is decreased. In the case where method 2 gives a non-tetrahedral structure more stable than \(\text{td}\), the difference in energy is increased.

In RuH\(_3\)F, the isomers \(\text{td}\) and \(\text{umb}\) are isoenergetic. The Ru–H bond lengths and the angles between the Ru–H bonds are similar to that of RuH\(_4\) in the corresponding isomers. The Ru–F is longer at the basal site of \(\text{umb}\), than in \(\text{td}\) (1.85 and 1.80 Å, respectively).

Figure 3. DFT optimized structures of minima and transition states of interconversion between minima for RuH\(_4\). The distances are in Å and the angles in degrees. The DFT energies are given in kcal mol\(^{-1}\) relative to the \(\text{td}\) structure, using method 2.

Figure 4. DFT energies, in kcal mol\(^{-1}\), for RuH\(_3\)X (X = F, CF\(_3\), CH\(_3\), H, SiF\(_3\), and SiH\(_3\)) complexes, relative to the tetrahedral isomer, \(\text{td}\). The energies are in blue for the umbrella with apical X, \(\text{umb}\), in red for the umbrella with basal X, \(\text{umb}\), and in green for the 4-legged piano-stool structure, \(\text{pst}\). Light green is used to indicate structures with hydride bridging Ru–Si.

RuH₃X complexes are similar. The structural features of the RuH₄, some structural aspects need to be mentioned. The RuH₃SiH₃ and RuH₃SiF₃ also have the four minima like were obtained by Landis et al. with \( \text{umb} \) and \( \text{pst} \) being 3.5 and 5.2 kcal mol\(^{-1} \) above the \( \text{td} \). The structures of \( \text{td}, \text{umb}, \) and \( \text{pst} \) are similar to those found for RuH₄. An energy barrier of 10.9 kcal mol\(^{-1} \) relative to \( \text{td} \) separates \( \text{td} \) and \( \text{umb}, \) and an energy barrier of 5.8 kcal mol\(^{-1} \) relative to \( \text{umb} \) separates \( \text{umb} \) and \( \text{pst} \).

The DFT energies for OsH₃X (X = H, F, CH₃, CF₃, SiH₃, and SiF₃). Three minima were located for OsH₄ (Figure 6). In contrast to the preference for non-tetrahedral structures found for RuH₄, the three isomers of OsH₄ are isoenergetic. Similar results have been obtained by Landis et al. with \( \text{umb} \) and \( \text{pst} \) being 3.5 and 5.2 kcal mol\(^{-1} \) above the \( \text{td} \). The structures of \( \text{td}, \text{umb}, \) and \( \text{pst} \) are similar to those found for RuH₄. An energy barrier of 10.9 kcal mol\(^{-1} \) relative to \( \text{td} \) separates \( \text{td} \) and \( \text{umb}, \) and an energy barrier of 5.8 kcal mol\(^{-1} \) relative to \( \text{umb} \) separates \( \text{umb} \) and \( \text{pst} \).

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[IrH₄]⁺ have a preference for non-tetrahedral geometries. The preference for the non-tetrahedral relative to the tetrahedral structures is stronger for the cationic than for the neutral species; for [RhH₄]⁺ the preference for non-tetrahedral structure increases by over 25 kcal mol⁻¹ relative to RuH₄. For [IrH₄]⁺, the preference for the non-tetrahedral structure is more marked than for OsH₄ but less so than for RhH₄⁺. The influence of the total charge and the nature of metal on the preferential structures of d⁴ [MH₄]q (q = −1, 0, and 1) is thus important. Consequently, going from the left to the right of the periodic table increases the preference for non-tetrahedral geometries but going down a column decreases this preference.

The geometries of the minima for [ReH₄]⁻, [RhH₄]⁺, and [IrH₄]⁺ are similar to those previously found for RuH₄. The H–M–H angle shows a pattern that parallels the preference for the non-tetrahedral structures. In the umb isomer of [ReH₄]⁻, the H₁– M–H₂ and the H₃–M–H₄ angles are larger than in the neutral systems. A similar pattern is seen in the pst isomer. The opposite trend is found in the cationic systems. For [IrH₄]⁺, the minima are those of the type shown in Figure 2. In the case of [RhH₄]⁺, the pst isomer is a highly fluxional structure where the decrease of a cis H–Rh–H angle from 63 to 38° occurs with essentially no energy cost. No umb type structure was located as minimum. Overall, the structures of isoelectronic d⁴ MH₄ are thus sensitive to the total charge; a negative charge opens the umbrella and flattens the 4-legged piano stool and a positive charge closes the umbrella and raises the height of the 4-legged piano stool. Going down a column of the periodic table also opens the umbrella and flattens the 4-legged piano stool.

The histograms for the relative energies of the isomers for [ReH₃X]⁻, [RhH₃X]⁺, and [IrH₃X]⁺ are shown in the Supporting Information. The pattern of energies can be understood from the pattern obtained for the ruthenium and osmium complexes. For [ReH₃F]⁻ the tetrahedral structure is the only minimum. For X = CH₃, CF₃, and SiH₃, the tetrahedral structures are more stable than the non-tetrahedral structures, and, in the case of [ReH₃SiF₃]⁻, pst and td are isoenergetic. For [IrH₃F]⁺, the umbrella structure with equatorial F is marginally more stable than td, but the umbrella structure with apical F is significantly less stable than td. In the case of [RhH₃X]⁺, non-tetrahedral structures are more stable than td for X = H, SiF₃, and SiH₃. For X = CF₃ and CH₃, structures of different natures than found for...
all other metal complexes are found to be more stable than tetrahedral structure. No comparison can be done with the other cases, and this was not explored further.

RuX₄. The diamagnetic homoleptic Ru(C₆H₁₁)₄₁¹ Ru(o-Tolyl)₄₁² Ru(Mesityl)₄₁³ Os(C₆H₁₁)₄₁¹ Os(o-Tolyl)₄₁⁴ and Ir(Mesityl)₄₁₅, which are the only 12-electron d⁴ MR₄ complexes to have been synthesized and fully characterized, are remarkably stable. They are colored as expected from the presence of low-lying empty metal d orbitals. In all cases, X-ray diffraction studies show that these complexes have a tetrahedral structure in the solid state. The NMR study of the tetracresityl complex of ruthenium shows a fluxional behavior attributed to the rotation of the ligand about the Ru–C bond.¹³ To better compare with the experimental structures, RuX₄ complexes were calculated for X = F, CH₃, CF₃, SiH₃, and SiF₃. The optimization of RuF₄ and Ru(CF₃)₄ yields only tetrahedral isomers. Two minima are found for Ru(CH₃)₄ with the td structure being 32.2 kcal mol⁻¹ below the pst structure. A preference for non-tetrahedral isomers is obtained with the silyl substituted complexes. For Ru(SiH₃)₄ and Ru(SiF₃)₄ the umb isomer is 12.6 kcal mol⁻¹ and 17.1 kcal mol⁻¹ more stable than the td isomer, respectively. In addition, structures with a pst shape in which the SiH₃ and SiF₃ ligands have hydrides or fluoride bridging the Ru–Si bond are also located as minima lower than the td isomer (−29.8 and −23.5 kcal mol⁻¹ for Ru(SiH₃)₄ and Ru(SiF₃)₄, respectively), but they will not be considered. These calculations on homoleptic complexes show that non-tetrahedral geometries are possible even with ligands more bulky than H. Furthermore, the energy trend obtained for RuHₓX (Figure 4) is also present for RuX₄. Fluorine is the ligand that most disfavors the non-tetrahedral geometry in the RuHₓX series; consequently RuF₄ has only a tetrahedral structure. The CH₃ ligand disfavors slightly less the non-tetrahedral structures; consequently a non-tetrahedral structure is found as a high-lying secondary minimum. Finally, SiH₃ and SiF₃ ligands, which most favor non-tetrahedral structures in the RuHₓX series, lead to homoleptic complexes with preference for non-tetrahedral structures. The only exception to this trend is the case of Ru(CF₃)₄ whose tetrahedral structure cannot be predicted from the influence of a single CF₃ ligand on the structural preference of RuF₄(CF₃). Clearly, the structures of the alkyl and aryl complexes that have been synthesized do not display the diversity of possible structures for d⁴ RuX₄.

■ DISCUSSION

The bonding analysis of Landis and Weinhold⁸ as well as the ORSAM analysis of Hall¹⁰ show that d⁴ MH₃X and MX₄ have several structures. In this analysis, the metal uses the (n + 1)s and the nd orbitals, which are not occupied by the electrons of the metal lone pairs to establish the covalent metal–ligand bond. For an sd³ hybridization that applies to d⁴ tetraordinated complexes, the tetrahedral structure is one of the possible structures. The non-tetrahedral structures have umbrella and 4-legged piano stool shapes. However, the valence-bond analysis of Landis and Weinhold⁸ and the ORSAM model of Hall¹⁰ do not provide any information on the relative energies of the various isomeric forms. The DFT and ab initio calculations show that the metal and the ligands influence significantly the relative energies of the several isomers. In MH₃X, the non-tetrahedral structures have nonbonded distances between proximate atoms that are relatively short. This is the case in particular for MH₄ wherein the nonbonding H···H distances in the non-tetrahedral geometries are shorter than the sum of the vdW distances. The increased steric hindrance resulting from the replacement of the hydrogens in RuH₄ by relatively bulky alkyls and aryl ligands could have been the reason for all experimentally known systems to be tetrahedral. However, the calculations show that CH₃ and SiH₃ ligands lead to opposite structural preference, the former ligand increasing the preference for the tetrahedral structure and the latter for the non-tetrahedral structures. These trends apply to RuHₓX and RuX₄ showing that the steric effects of groups larger than hydrides do not determine the structural preferences. Calculations show that the metal also plays an important role on the structural preference. Going from the left to the right of the periodic table, that is, from anionic to cationic isoelectronic complexes increases the preference for the non-tetrahedral structures while going down a column of the periodic table increases the preference for the tetrahedral structures. Factors that also play a role are, among others, the relative electronegativity of the metal and the electron-donating/electron-withdrawing ability of the ligands. To understand better these factors, a molecular orbital analysis, based on EHT calculations, has been carried out for RuH₄ and a NBO charge analysis complemented by a NRT analysis based on the calculated DFT densities have been carried out for RuH₄ and OsH₄.

(a) Molecular Orbital Analysis. The EHT total energies of the td, umb, and pst structures for RuH₄ give a preference for a non-tetrahedral structure. Increasing the electron-withdrawing ability of the ligand by lowering the hydrogen H₂ Coulombic integral gives a preference for a tetrahedral structure. This modeling of ligands reproduces the results of the DFT calculations. For instance (i) F and CH₃ are more electron-withdrawing than H and SiH₃ and thus favor the tetrahedral structure, (ii) Os 5d orbitals are higher in energy than Ru 4d orbitals and thus ligands appear to be more electron-withdrawing relative to Os than Ru. Likewise, in a cationic complex where the metal is more electron-attracting, all ligands appear more electron-donating. The reverse is true for anionic complexes.

A Walsh diagram is used to gain further insight into why EHT calculations reproduce qualitatively the structural preference obtained with higher-level calculations. Only the occupied molecular orbitals of RuH₄ are necessary in this analysis (Figure 9). The Cᵥ or Cᵥ group notations are used for labeling the molecular orbitals for the three structural forms. The td structure has two nonbonding d orbitals of e symmetry to host four electrons. The four Ru–H bonds are represented by two molecular orbitals of a₁ symmetry and two orbitals of e symmetry. Only the molecular orbitals of a₁ symmetry have a contribution on the hydrogen located on the z axis. In umb, all molecular orbitals of e symmetry have the same energy as in td because they have no contribution on the hydrogen on the z axis. The only molecular orbitals, which have different energies for td and umb, are the molecular orbitals of a₁ symmetry. They are constructed in a similar manner in td and umb. The lower one, 1a₁, is the in-phase combination of the metal 5s orbital and the 1s orbital of the four hydrogens. The higher orbital of a₁ symmetry, 2a₁, is mostly made of the in-phase combination of a d₁ with the four hydrogens. The contribution of the 5p orbitals has been found to be negligible in all molecular orbitals even if permitted by symmetry; it will not be mentioned further. The key point of the analysis is that, in 2a₁, the coefficient of the hydrogen on the z axis has the sign opposite to that of the other three hydrogens, which are in-phase with the torus part of d₁.
The energy of 1a₁ is thus lower in umb than in td because the in-phase relationship between all hydrogens stabilizes the orbital when the hydrogen atoms are closer (umb vs td). In contrast, the energy of 2a₁ is higher in umb than in td because the out-of-phase relationship between the apical and basal hydrogens raises the energy of this molecular orbital when the distances between the nonbonded hydrogens are shorter and the overlap increases. Two antagonist effects are thus at work and umb is more stable than td if the energy lowering of 1a₁ is more important than the energy rise of 2a₁. The 1a₁ orbital is more located on the hydrogens than on the metal because the energy level H₂ of the hydrogen is orbital is always lower than the energy level H₅ of the 5s of the metal. In contrast, the 2a₁ orbital is more located on the metal when the energy of the hydrogen is orbital is higher than that of the metal d orbital, and it is more located on the hydrogen atoms when it is lower. Therefore, the energy rise of the 2a₁ orbital upon going from td to umb is small in the first case and large in the second case. Consequently, electron-donating ligands favor umb and electron-withdrawing ligands favor td.

A similar reasoning applies to the comparison between td and pst. In pst, the four nonbonding metal electrons are hosted in 2a₁ (dₓ²−ᵧ²) and b₂ (dₓz) orbitals (Figure 9). The four Ru−H bonding orbitals are described by an 1a₁ orbital made mostly from the metal s orbital, two orbitals of e symmetry made mostly from the metal dₓz and dᵧz orbitals, and a b₁ orbital made from dₓz. The contribution of the 5p orbitals has been found to be negligible even if permitted by symmetry, as already noted above. The 1a₁ orbital favors the pst structure because of the in-phase relationship between all hydrogens. The b₂ orbital disfavors the pst structure because of the out-of-phase relationship between the hydrogens. The two degenerate orbitals of e symmetry have essentially no influence on the structural preference because of the long distance between the two trans hydrogens. The influence of the energy level H₂ of the hydrogens on the variation of energy of the 1a₁ and b₁ orbitals between td and pst is similar to that obtained for the case of td vs umb. Electron-donating ligands favor pst and electron-withdrawing ligands favor td.

(b). NBO Charge Analysis. The NBO charges for RuH₄ and OsH₄ are shown in Figure 10. For these two species in which the metal is formally at a high oxidation state, M⁴⁺, the NBO charge at the metal is negative indicating, as currently recognized, that the calculated charge has no relation with formal oxidation state. The negative charge is small for the td complex but increases to a maximum value of −0.3 for the non-tetrahedral species. Accordingly, the charge on the hydrogens is very small and positive in RuH₄. In the non-tetrahedral structures, the hydrogens carry a positive charge; the largest positive charge is carried by the apical hydrogen of umb. The results are qualitatively similar for OsH₄, but the electronic density on the metal is smaller for Os than for Ru and the charge is even marginally positively charge in td. The charge distribution in the Ru and Os complexes does not give a rationale for the stronger energetic preference for non-tetrahedral structures in the case of Ru. However, the charge distribution indicates that electron-donor ligands are beneficial for the non-tetrahedral structures.

(c). NRT Analysis. A natural resonance (NRT) analysis of the DFT density was carried out for the three isomers, td, umb, and pst of RuH₄ and OsH₄. This analysis is aimed at determining the valence structures that describe the total electron density of these complexes in the various isomeric forms. This analysis has led met with criticism but has been found to be qualitatively useful for understanding electronic structures. The results are shown in Figure 11. In the td isomer, the dominant structure has four covalent M−H bonds and two lone pairs at the metal. This valence structure accounts for 97% of the density for RuH₄ and 98% for OsH₄. For the umb isomer, the same structure accounts for only 80% of the total density for RuH₄ and 90% for OsH₄. The remaining part of the electron density is represented by structures with two covalent M−H bonds, three lone pairs at the metal, and a proton and a hydride characterizing an ionic interaction between the metal fragment and the hydrogen atoms. The structure with a proton at the apical site has higher weight (12% for RuH₄ and 6% for OsH₄) than that with a hydride at the apical site (7% for RuH₄ and 3% for OsH₄). The structure with the proton and the hydride at the basal sites has the smallest weight 1%. For the pst isomer, the main structure is that with four M−H bonds and two lone pairs at the metal (79% of the total electron density for RuH₄ and 89% for OsH₄). The remaining part of the electron density is represented by a valence structure with two covalent M−H bonds, three lone pairs at the metal, and a proton and a hydride on cis hydrogen.
The electron densities of umb isomers. The same isomers in the case of RuH4. The same diagram and the NRT analyses provide a consistent interpretation of the e... interactions are complemented by the well-known through space interaction between a hydride and a nearby silyl group, originating from the ability of silicon to become hypervalent. This interaction, which has been known as SISHA40 or IHI,41 is magnified when the silyl group is substituted by halide. This accounts for the preference for non-tetrahedral structures for RuH4(SiH3) and RuH4(SiF3). The fact that Ru(SiH3)4 and Ru(SiF3)4 also prefer non-tetrahedral structures show that interactions different from SISHA and IHI are at work.

CONCLUSIONS

DFT (PBE0 and range separated DFT, RSH+MP2) and CCSD(T) calculations have been used to determine the preferred structures of MH3X (M = Ru, Os, Rh+, Ir+, and Re+; X = H, F, CH3, CF3, SiH3, and SiF3) and MX4 (M = Ru; X = H, F, CH3, CF3, SiH3, and SiF3). Tetrahedral and non-tetrahedral structures are found as possible minima. The non-tetrahedral structures show that interactions different from SISHA and IHI are at work.
favor the non-tetrahedral structures. The factors that determine these energy patterns have been discussed by means of a molecular orbital analysis based on EHT calculations and NBO charge analysis supplemented by an NRT analysis. All analyses show that electron-donating ligands favor the non-tetrahedral structures. Furthermore, the EHT and the NRT analyses suggest the presence of possible weak attractive interactions between atoms that are closer in umb and pst than in td. These weak attractive interactions are magnified when the ligands are good electron donor to the metal center.

## ASSOCIATED CONTENT

* ASSOCIATED CONTENT

### Supporting Information

List of coordinates of all calculated structures with energies E and ZPE corrected energies (E + ZPE). Histograms of energies (methods 2 and 3) for [ReH\(_2\)X\(_3\)], [RhH\(_2\)X\(_3\)], and [IrH\(_2\)X\(_3\)]. Potential energy surfaces for the transformations between the isomers of RuH\(_2\)X. NBO charges and NRT analysis for RuH\(_2\)X (X = F, CH\(_3\), and SiH\(_3\)). This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: odile.eisenstein@univ-montp2.fr (O.E.), christophe.raynaud@univ-montp2.fr (C.R.).

### Notes

The authors declare no competing financial interest.

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(39) The percentages shown in Figure 11 include the contribution of equivalent hydrogens.