Inter- and Intramolecular Hydrogen Bonds with Transition Metal Atoms in Metallocenes of the Iron Subgroup

Galina Orlova[†] and Steve Scheiner*[,‡]

Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901

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The intramolecular M···HO bond in α-metallocenylcarbinols (M = Fe, Ru, Os) and the intermolecular Os···HOH bond in the water complex with osmocene have been studied by extended Hückel (EH) and density functional theory (DFT) methods at the BLYP and B3PW91 levels. There is no evidence that Fe will form such a H-bond. M···HO bonds involve the d-orbitals of the more basic Ru and Os atoms, but otherwise appear to be conventional H-bonds. The approximate intramolecular M···H bond energies are 5.0 and 4.1 kcal/mol for Os and Ru, respectively, as compared to 11.7 kcal/mol for the intermolecular Os···HOH bond. The intermolecular M···H−O bond appears to be of linear type with elongation of the H−O distance. There are steric requirements that accompany these H-bonds. The M−ring distances must be long enough in the intramolecular complexes to permit the carbinal to correctly approach the metal; bulky substituents on the cyclopentadienyl rings inhibit intermolecular bonding.

Introduction

The nature of interactions between a transition metal center (M) and an R−H fragment, as well as the structure of the resulting M···H−R complexes, has been of interest to experimental and theoretical chemists for some time. This type of interaction plays an important role in homogeneous catalysis, for example. It has been shown that in the case of coordinatively and electronically unsaturated complexes of transition metals, and when R = C or H, an agostic interaction occurs.[1−4] This sort of agostic interaction consists of σ-donation from an R−H bonding orbital to a low-lying unoccupied d-AO of the transition metal, along with back donation from a π-AO of the metal atom to an antibonding MO of the R−H bond. This simple but effective model has been used successfully in the explanation of activation of inert aliphatic C−H bonds by transition-metal compounds[1−3] and for H_2−M bonding in η^2-H_2 molecular complexes.[5−7] Further application of molecular orbital theory to M···H−R bonding leads to the supposition that electron-rich transition metal atoms of the groups VI−VIII of neutral inorganic and organometallic compounds (for example, sandwich and half-sandwich) can also form M···H−R hydrogen bonds with proton donors by means of interaction between occupied d-orbitals and the H−R bond. This assumption required two decades before it was experimentally confirmed. Epstein et al. have reviewed a long series of unsuccessful attempts to detect M···H−R bonding in metallocene−proton donor systems.[8]

Recent IR and NMR investigations by the Epstein group[8−14] have turned to various transition metal complexes of the IVth period and the VIIth group. It would appear that in ferrocenes[9,10] and half-sandwich carbonyls of Mn and Re,[11] for example, a hydrogen atom is situated close to the metal center. This location has been attributed to steric factors since the intramolecular M···H interactions disappear when steric obstacles are removed. In one case, an intermolecular Fe···H bond was observed for the system trifluoroacetic acid−ferrocene only at low temperature (−60 °C).[13]

In contrast, stable intra- and intermolecular M···H−R bonds were noted in complexes of electron-rich transition metals of the VIIIth group of the Vth and VIth periods in metallocenes of Ru and Os, and in half-

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[†] Permanent address: Institute of Physical & Organic Chemistry, Rostov University, Rostov on Don, Russia 344090. E-mail: orlova@ipoc.rnd.runnet.ru.

[‡] E-mail: scheiner@chem.siu.edu.

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sandwich carbonyls of Rh and Ir. These M···H bonds persist even when the steric obstacles for displacement of the H atom from the transition metal atom are absent. In these complexes, the M···H bond coexists with more conventional H-bonds involving the π-electron density of cyclopentadienyl rings (H-π) and with the lone pairs of oxygens of the CO groups (H-p). The simultaneous presence of various types of H-bonding in a single sort of complex provides an opportunity for comparative analysis in the substituted metallocenes. M···H bonds manifest spectral characteristics typical of H-bonds: correlation with basicity, temperature dependence, and isotopic ratio. The enthalpy of formation of intermolecular M···H bonds appears to be in the 4−6 kcal/mol range;[9] it increases down the group and to the right in the period.[9,10,12] The formation constant is very small compared to the more conventional H-π and H-p bonds, an observation that has been tentatively explained in terms of steric factors.[12]

Certain aspects of intra- and intermolecular M···H bonds remain unresolved. There is little information available about the energetic and geometrical parameters of intra- and intermolecular M···H bonds. It is also important to learn more about the interplay between electronic and steric factors as contributors to the presence (or absence) of M···H bonds in metallocenes. This communication examines the intramolecular M···H bond in α-metallocenylcarbinols (M = Fe, Ru, Os) and the intermolecular M···H bond in the aqua complex of osmocene by means of theoretical calculations.

Extended Hückel Study of Intramolecular M···H Bond

The major purpose of this section is to define the sort of interaction between orbitals of metallocene and those of the H−O group that might provide the putative intramolecular M···H bonding in α-metallocenylcarbinols. Approximate molecular orbital (MO) calculations of the extended Huckel (EH) type were applied to the dicyclopentadienyl sandwich in which a CH_2OH group is placed on one of the rings. The EH method has been used successfully by Hoffmann et al.[18ab] for studying intramolecular interactions in cationic substituted metallocenes and various types of H-bonding in transition metal complexes. It is stressed that it is not our intent here to derive quantitative data, but rather to understand the underlying interactions. The CACAO program[36] was used, and the average C−C, C−M, C−O, and C−H bond lengths and angles were taken from experimental data[14] and from ref 18a.

Two principal configurations **1** and **2** might be considered for the α-metallocenylcarbinol. Structure **1** contains a potential M···H bond, whereas in **2** the M···H interaction is eliminated by internal rotation of the H atom around the C−O bond. The Walsh diagram in Figure 1 illustrates the energy changes of important orbitals upon internal rotation **1** → **2** for Os and Ru. (The values for the latter are in parentheses.) It is well-known that EH describes many internal rotations satisfactorily, so these distortions should be handled reasonably well by the calculations. The total energy increase, upon rotation **1** → **2**, by 7.0 (3.4) kcal/mol is mainly attributable to a rise in the energies of MOs 35 and 36 (37). The collective contribution that these MOs make to the entire increase is about 60%. Thus, the calculation suggests that the α-metallocenylcarbinol is stabilized by the M···H interaction, which is connected with these MOs, and that this stabilization is larger for the more basic Os.

A piece of supporting evidence arises from the Mulliken overlap populations between the metal atom and H. This quantity is equal to 0.05 for Ru and 0.08 for Os, in the range of values suggestive of a genuine attractive interaction. In contrast to the behavior of Ru and Os, the **1** → **2** rotation for α-ferrocenylcarbinol lowers the total energy. This result is consistent with IR and X-ray indications of an absence of an intramolecular Fe···H interaction in the substituted ferrocenes.[9,10,14]

Examination of the MOs of M···H bonding structure **1** reveals that the primary interactions involve s−p antibonding combination of H−O with two of three occupied d-orbitals of the metallocene core (z^2, x^2-y^2, xy) which are not directly involved in bonding with the cyclopentadienyl rings. These d-orbitals of the metallocene core combine to form three combinations which interact with the s- and p-orbitals of the OH group, forming two weakly bonding orbitals 35 and 36 (37). (The third orbital avoids overlap with H−O.) It is important to note that the indicated MOs are similar to the three-centered MOs which provide the conventional X−H−O bridged hydrogen bond. Indeed, experimentally M···H demonstrates the same properties men-

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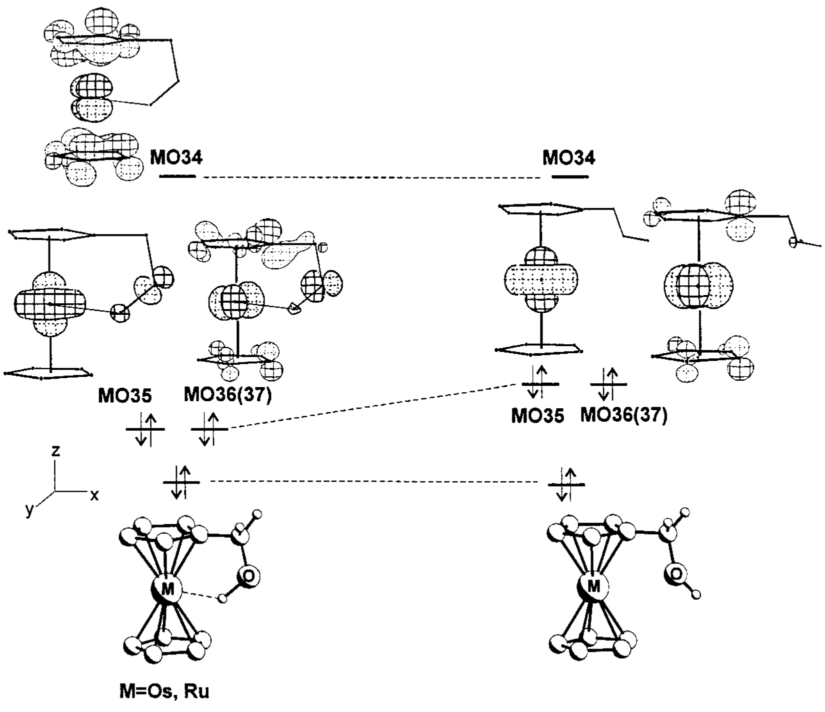

Figure 1. Walsh diagram of internal rotation around the C−O bond for α-metallocenylcarbinols, including contour drawings of MOs 35 and 36 for Os, 36 and 37 for Ru.

tioned above as X−H. One might expect elongation of the H−O bond upon M···H bonding as a result of electron donation to antibonding MOs of H−O.

DFT Study of Intra- and Intermolecular M···H Bonds

1. Method. Since the EH calculations are too approximate to be considered conclusive, it is important to raise the level of theory. However, computational study of the metallocenes is not an easily tractable problem, as it typically requires a high level of theory. At the CCSD(T) level, a triple-ζ basis set yields an adequate iron−ring distance (Fe−Cp) of 1.66 Å[19] (the experimental length is 1.65−1.66 Å[20]). In fact, reasonable reproduction of this M−Cp distance can be used as one test of the suitability of a particular type of calculation for the metallocenes. For example, SCF methods overestimate R(Fe−Cp) (~1.9 Å), while MP2 values are too short (~1.59 Å).[19] Other metallocenes, such as ruthenocene and osmocene, have not yet been investigated by ab initio methods to our knowledge.

DFT methods, especially with nonlocal corrections[21] (DFTNL), have shown some promise in regard to calculations of ferrocene[22] and borylferrocenes.[23] Calculations by Fan and Ziegler[22] yield a Fe−Cp distance of 1.648 Å, quite close to experiment. Other calculations[23] indicate little difference between double-ζ and triple-ζ basis sets with respect to geometries and energies of substituted ferrocenes, suggesting that DFTNL with basis sets of double-ζ quality can be constructively applied to metallocenes.

In this spirit, the present article applies DFT calculations, via the GAUSSIAN 94 program,[24] using Becke's 1988 (B)[25] and Becke's three-parameter functional (B3)[26] with correction for exchange, in conjunction with Lee, Yang, and Parr (LYP)[27] and Perdew and Wang's (PW91)[28] nonlocal correction to correlation. The basis set used is of the pseudopotential variety,[29] with the standard LANL2DZ[24] contraction.

2. Results and Discussion. Calculated results for conformers **1**, **2**, and **4** of α-metallocenylcarbinols of Ru and Os are presented in Figure 2. Structures **1** and **2** are identical to those in Figure 1; **4** differs from **2** only in terms of rotation of the CH_2OH group. The geometries and energies shown were obtained with the BLYP and B3PW91 (latter in parentheses) procedures. Energies are relative to structure **1**, which is the most stable of those considered.

It is first important to note that the BLYP and B3PW91 results do not differ by much. With either variant of DFT, structure **2** represents a transition state[30] on the potential energy surface (PES), rather than a minimum. The eigenvector corresponding to the imaginary frequency represents a rotation of the carbinol group around the C−C bond, leading to structure **4**. The latter geometry is higher in energy than **1** by around 1.5 kcal/mol for either metallocene and with both BLYP and B3PW91. Geometry **2** differs from **1** primarily in the breakage of the H-bond in the latter. The energy of **2** relative to **1** may hence be considered as an estimate of the M···H bonding energy. The energy of the intramolecular Os···H bond is 4.3−5.0 kcal/mol, 0.5−1.0 kcal/mol higher than the equivalent quantity in the Ru analogue. This computed pattern is consistent with the experimental observation of a stronger interaction with the larger and more basic transition metal.

The DFT geometries are not unreasonable. For structure **4**, where the influence of the carbinol substituent is minimal, R(Os−Cp) is calculated by B3PW91 to be 1.861 and 1.857 Å for the unsubstituted and substituted cyclopentadienyl rings, respectively, in quite decent agreement with an experiment value of 1.855 Å

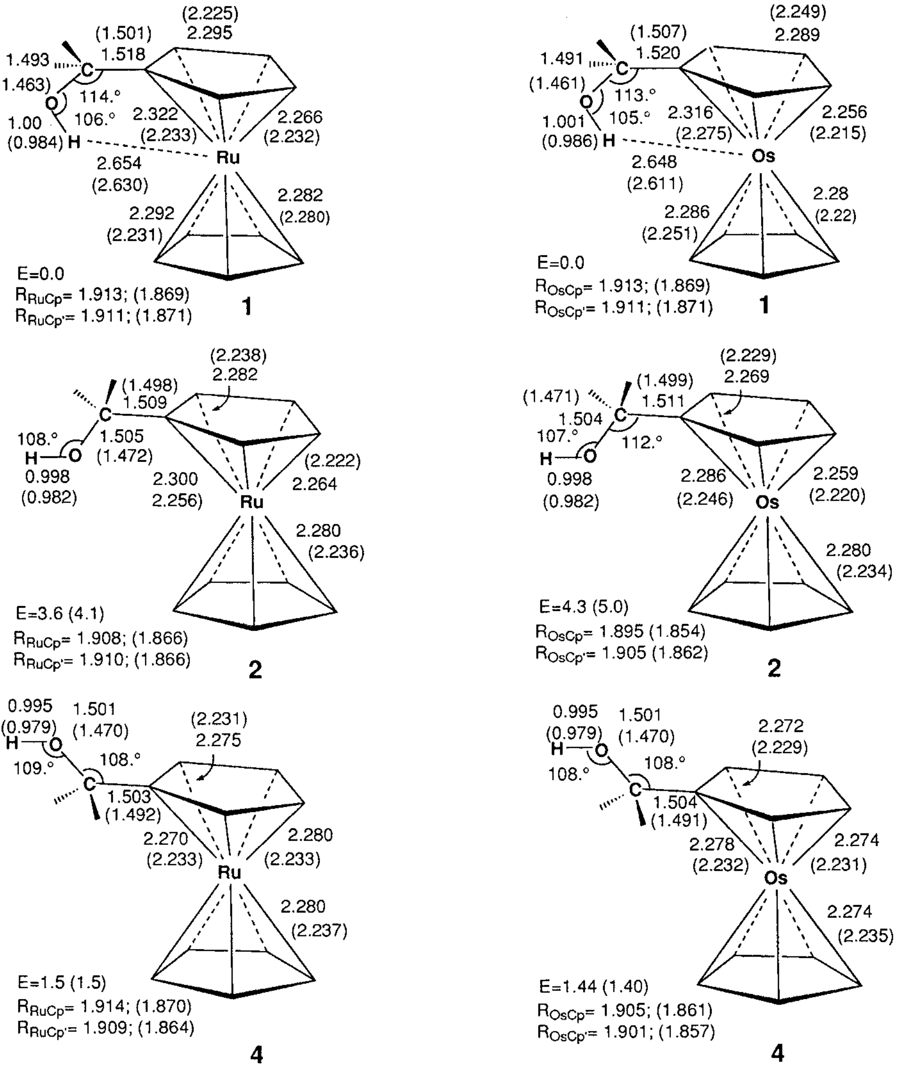

Figure 2. Geometries (in Å and deg) and relative energies (kcal/mol) of **1**, **2**, and **4** computed by the BLYP and B3PW91 (values in parentheses) methods. Ru complexes shown on the left, Os on the right. Cp and Cp′ refer to unsubstituted and substituted Cp rings, respectively.

for unsubstituted osmocene.[31] The BLYP distances are exaggerated by some 0.04 Å. Turning to the ruthenium system, the B3PW91 Ru–Cp distance is 1.870 Å, significantly longer than the experimental value of 1.816 Å for ruthenocene[32] and longer in fact than even *R*(Os–Cp). The valence and dihedral angles of both metallocenes calculated by BLYP and B3PW91 are similar. The rings in structures **1**, **2**, and **4** are staggered by about 11°. They are nearly parallel, with relative angles of inclination less than 4°, in all cases. The putative M···H bond is characterized by a distance separating these two atoms of 2.65 Å for the BLYP procedure and slightly shorter with B3PW91. In either case, *R(*M···H) is shorter for Os than for Ru. Another indication of the stronger interaction of Os relates to the stretching of the covalent OH bond. This bond lengthens by 0.005 Å on going from **4** to **1** for the Ru complex, but by 0.006–0.007 Å for Os.

The charges and overlap populations obey trends typical of conventional H-bonding. Data computed by the Mulliken procedure are shown in Figure 3 for structures **1** and **4** of the Os complexes. The formation of the H-bond upon transition from **4** to **1** raises the atomic charge on the bridging hydrogen by 0.038. At the same time, the proton-accepting metal atom increases its negative charge by 0.041. The enhanced density on this atom arises in part by draining density from the Cp rings; the unsubstituted ring loses 0.050 in cumulative density. The weakening of the OH bond is signaled by a drop in the relevant overlap population by 0.015, equal in magnitude to the H···M overlap population in **1**. It is well-known, of course, that Mulliken (or any other) type of charge partitioning is sensitive to basis set and may sometimes provide misleading atomic charges, especially for transition metal complexes. Nonetheless, the Mulliken procedure

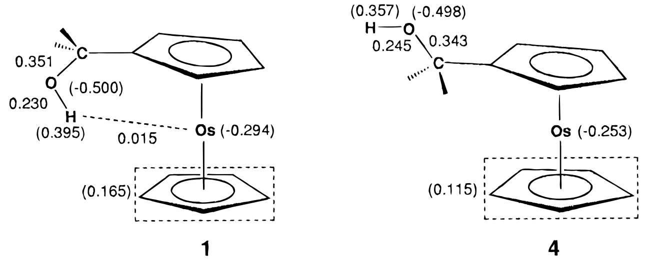

Figure 3. B3PW91 Mulliken overlap populations and atomic charges (in parentheses) for **1** and **4** structures of Os complexes. Group charge shown for indicated Cp ring.

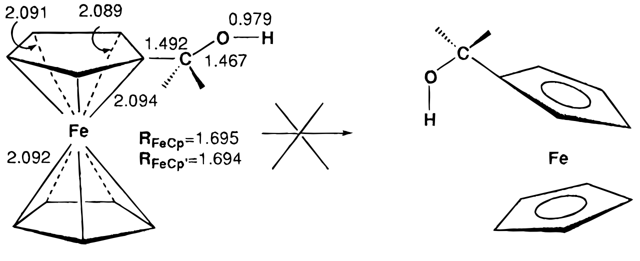

Figure 4. B3PW91 geometries (in Å and deg) for α-ferrocenylcarbinol.

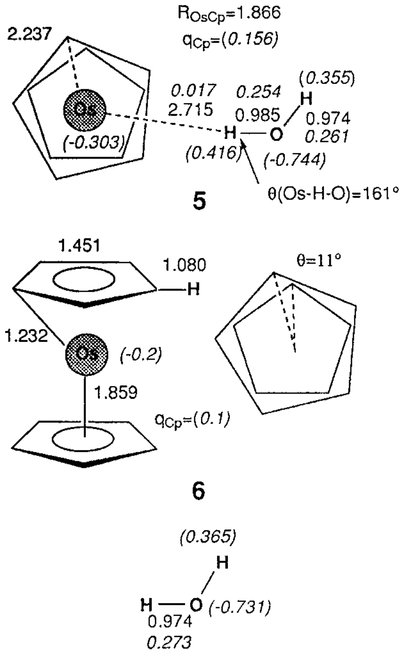

Figure 5. B3PW91 geometries (in Å and deg), Mulliken charges (italic values in parentheses), and overlap populations (italic) for **5**−**7**.

is usually valid if one is concerned chiefly with trends in the data, rather than with absolute charges.[33]

As it seems reasonably clear that a H-bond exists in the Ru and Os complexes, we turn our attention now to possible reasons for the absence of such an interaction with Fe. The appropriate α-ferrocenylcarbinols were optimized using the B3PW91 method. As illustrated on the left of Figure 4, the Fe−Cp separation in conformer **4** is 1.695 Å, 0.035 Å longer than the experimental distance in ferrocene. There was no minimum found that corresponds to structure **1**. As indicated on the right side of Figure 4, forcing the OH group closer to Fe pries the rings apart and causes the energy of the system to rise.

One last issue considered is the possibility of an intermolecular M···H bond, free of the restraints that arise when both the proton donor and acceptor are located on the same molecule. Figure 5 illustrates the result when a water molecule **7** is allowed to approach osmocene **6**. The two rings in the latter molecule are staggered by 11°, with a R(Os−Cp) distance of 1.859 Å. Upon forming complex **5**, the two rings remain parallel, but stretch away from one another by 0.007 Å.

Turning to the specifics of the M···H interaction, the Os···HO bond is of linear type. (The linearity of intermolecular M···H−O bonds was assumed in the review in ref 8b.) The bridging hydrogen of water is located 2.715 Å away from the Os center. The OH bond in water stretches by 0.011 Å when the H-bond is formed, as compared to only 0.006 Å in the intramolecular case. The lengthening of HO bond upon M···HO bonding is an important characteristic with respect to the processes of protonation and deprotonation of transition metal complexes in low polar media. It has been shown[8b] that proton transfer in the M···HOR (R = $COCF_3$) molecular complexes leads to the more stable ionic-type complex.

$$\mathrm{M + HOR \rightarrow M{\cdots}H{-}OR \rightarrow (MH)^{+}{\cdots}OR^{-}} \qquad (1)$$

One may suppose that initial polarization of the H−O bond in the molecular complex is an important factor in the subsequent proton transfer. This sort of H−O bond stretch was noted also in the intermolecular complex of water and half-sandwich hydride (Cp)(NO)(CO)(H)Re···H-OH (**8**) calculated in our recent work[34b] by the DFT B3PW91/LANL2DZ method. The H−O bond in **8** stretched by 0.006 Å, even more than the analogous lengthening of 0.004 Å upon NO···HO bonding in the isomeric (Cp)(CO)(H)ReNO···H−OH. Interestingly, the computed Re···H distance in **8** is the same (2.715 Å) as the Os···H distance in **5**.

Since the H-bond in this case is intermolecular, one may uambiguously compute the interaction energy of the complex, relative to the sum of the two isolated subsystems. The H-bond energy, computed in this way (without BSSE correction) is 11.7 kcal/mol. This value compares with experimental estimates for osmocene−alcohol systems in the range 4.2−5.2 kcal/mol.[12] One would of course expect significant differences since the latter value pertains to enthalpies of a somewhat different series of systems, measured in solution, as compared to the calculated energy in the gas phase. At any rate, the overestimate of the H-bond energy by DFT is no surprise, as it was observed in our previous study of related systems.[34] The H···Re bond energy was computed to be 10.9 kcal/mol[34b] in **8**. These results obtained for the Os and Re intermolecular M···H complexes show that the M···H bonding strengthens as the metal atom becomes more basic.

An analysis of the Mulliken charges and overlap populations shows that the interacting molecules are polarized by one another. The negative charge on Os and the positive charges on the rings both increase, as do the positive charge on H_{Os} and the negative charge on the water oxygen atom. The Mulliken overlap population of the Os···H bond is 0.017, slightly greater than that observed in the intramolecular analogue.

Conclusions

Both, the intra- and intermolecular M···H interactions in metallocenes appear in most respects to be conventional H-bonds with M = Ru or Os. Geometric and electronic perturbations are consistent with patterns typically seen in H-bonds. The bridging hydrogen interacts with the occupied d-orbitals of the metal atom. There are indications that the H-bond is stronger for the larger and more basic Os atom. Fe is apparently too weak a base to form a similar sort of H-bond, or steric restraints of the Cp rings may prevent its formation. These intramolecular H-bonds can be compared to an intermolecular interaction, where intramolecular geometrical restraints are relaxed and the proton donor is an entirely separate molecule. Again, the osmocene forms a strong H-bond of linear type with a separate water molecule, similar to that observed when the proton donor is attached to one of the Cp rings. The O−H bond stretches significantly upon intermolecular M···H−O interaction, contributing to a subsequent ionization of H−O.

There are certain steric requirements for such a H-bond to form. If the M−Cp distance is too short, at least one of the Cp rings will have to incline so as to permit a M···H interaction, destabilizing the system. If intermolecular, it is most favorable if the proton donor can approach the metal along a plane that is parallel to the Cp rings. The latter conclusion agrees with IR data[12] for an intermolecular Ru···H bond, where a decrease in the intensity of the ν(M···HO) band is observed on going from ruthenocene to permethylated ruthenocene, even though the electron-donating ability of Ru is greater in the latter system. The authors[12] hypothesize that the methyl groups impose a steric hindrance for interaction between the proton donor and metal center. This hindrance was later confirmed by molecular mechanics calculations of Os···H bonding complexes of osmocene and decamethylosmocene.[35]

Comparative analysis of BLYP and B3PW91 reveals that both methods reflect the same general trends and yield similar relative energies. B3PW91 geometries are in better agreement with experimental. Ferrocene and osmocene geometries are described by B3PW91 with particularly good accuracy. The unexpectedly large difference between the DFT and experimental Ru−Cp distance may warrant further scrutiny.

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