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Geometry Optimization of a Ru(IV) Allyl Dicationic Complex: A DFT Failure?

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Abstract: Five pure and four hybrid DFT functionals associated with VDZP, VTZP, and VQZP basis sets are tested (Gaussian 03) for their performance on the geometry optimization of [Ru-(η^5-C$_5$H$_5$)(η^3-CH$_2$CHCHC$_6$H$_5$)(CH$_3$CN)$_2$]$^{2+}$. When the calculated geometries were compared with the X-ray structure determination for the analogous complex with permethylated cyclopentadienyl, it was found that in all cases the coordination mode of the η^3-allyl was very poorly described, despite the functional used. The Ru−C bond distance corresponding to the substituted allyl carbon was overestimated by 0.23−0.50 Å, depending on the functional and the basis set used. These results were reproduced by further testing carried out with the ADF program and larger basis sets. MP2 leads to an acceptable value for the same Ru−C distance, with an underestimation of 0.07 Å, suggesting that, at least in the case of the functionals tested, DFT does not provide an accurate description of a weak Ru−C interaction.

1. Introduction

Any survey covering the recent chemistry literature shows that DFT methods[1] have become a widely used tool in computational studies applied to all fields of chemistry and, in particular, to organotransition-metal chemistry.[2] A comparatively low computational cost, when compared to wave-function based methods, and the quality of the results obtained justify the number of published studies ranging from structural and thermochemical studies[3] to reaction modeling and mechanistic investigations.[2,4] Often the geometries calculated in the computational studies cannot be tested, owing to the absence of experimental results related to the transient nature of the species under study. On the other hand, it is well documented that when dealing with ground-state structures, an almost perfect agreement can be reached between calculated and experimental parameters.[2,5−8] The accuracy of DFT in transition-metal chemistry has been recently reviewed by Harvey.[9]

Among all functionals currently favored by chemists, the B3LYP emerges as one of the most popular, if not the most used functional, providing, in general, good geometries and reliable energies.[10] B3LYP is a hybrid functional including a 20% mixture of Hartree−Fock[11] exchange with DFT exchange-correlation, given by Becke's three-parameter functional[12] with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms.[13,14]

The nature of the functionals for exchange and correlation currently used, however, remains approximated, and constant effort is being made to develop new and more accurate functionals. As recently stated by Perdew et al.,[15] DFT users can play an important role in this task, by reporting relevant failures or "pathologic cases", thus helping the developers to understand weak points of the available functionals in order to improve them.

During our recent computational investigations on the role of the cyclopentadienyl Ru(IV) complex, [Ru(η^5-Cp)(η^3-CH$_2$-CHCHC$_6$H$_5$)(CH$_3$CN)$_2$]$^{2+}$ (Cp = C$_5$H$_5$), as a possible catalyst of organic reactions such as allylic alkylation[16] and Friedel−Crafts reaction,[17] we came across one of such "pathologic cases". In this work, we report the failure of B3LYP as well as other hybrid and pure DFT functionals, associated with currently used VDZP and VTZP basis sets, to describe

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correctly the coordination of the allyl ligand, $CH_2CHCHC_6H_5$, to ruthenium on the former complex. The calculated geometries are compared with the experimental X-ray structure of the analogous Cp^* complex, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2\text{-}CHCHC_6H_5)(CH_3CN)_2]^{2+}$ ($Cp^* = C_5Me_5$; $Me = CH_3$).[17]

2. Computational Details

The calculations were performed using the Gaussian 03 software package[18] or ADF (2005.01)[19−21] without symmetry constraints. Both pure and hybrid DFT functionals were tested in the geometry optimization of the complex studied. Along the text, the usual acronyms identify the combinations of exchange, pure or hybrid, with correlation functionals. The exchange functionals used included Becke's 1988 functional (B),[22] the exchange component of Perdew and Wang's 1991 functional (PW91)[23−27] and the 1996 functional of Perdew, Burke, and Ernzerhof (PBE).[28,29] These were combined with the following correlation functionals: Perdew 1981 local correlation functional with gradient corrections (P86),[30] the correlation functional of Lee, Yang, and Parr which includes both local and nonlocal terms (LYP),[13,14] Perdew and Wang's 1991 gradient-corrected correlation functional (PW91),[23−27] and the 1996 gradient-corrected correlation functional of Perdew, Burke, and Ernzerhof (PBE).[28,29] Three hybrid functionals, including a mixture of Hartree−Fock exchange with DFT exchange, were also tested, Becke's three-parameter functional (B3),[12] modified Perdew−Wang exchange (mPW1), as implemented by Adamo and Barone,[31] and the hybrid functional of Perdew, Burke, and Ernzerhof (PBE1).[29] Two wavefunction based methods were also used in the geometry optimizations: Hartree−Fock (HF)[11] and second-order Møller-Plesset correlation energy correction (MP2).[32−37] Three basis sets were used for Ru. Of these, two included effective core potentials (ECP), Los Alamos ECP with valence double-ζ (LanL2DZ),[38−41] here named I_M, and Stuttgart/Dresden ECP with valence triple-ζ (SDD),[42−44] labeled II_M. The third metal basis set tested is an all-electron basis, a standard 3-21G[45−50] (labeled III_M). In all three cases, I_M, II_M, and III_M, a f-polarization function was added for Ru.[51] The main group elements belonging to the ligands, C, H, and N, were described by Pople's split-valence basis, 4-31G(d) (basis I_L),[52−55] the same with diffuse functions added only to the three allylic carbon atoms, 4-31(+)G(d) (basis II_L), standard 6-311G(d,p) (basis III_L),[56−62] Ahlrichs' TZVP (basis IV_L),[63,64] and Dunning's correlation consistent cc-pVTZ (basis V_L)[65] and cc-pVQZ (basis VI_L).[66] Thus, for example, B3LYP/($II_M I_L$) stands for a B3LYP calculation using basis II_M for the metal (SDD plus f-polarization function) and I_L basis for C, H, and N, that is, 4-31G(d). Similarly, BP86/($III_M II_L$) means a BP86 calculation using III_M basis set for the metal (3-21G plus f-polarization) and II_L basis for C, H, and N, i.e., 4-31G(d) plus diffuse functions on the three allylic C atoms.

The calculations performed with the ADF program consisted of gradient corrected geometry optimizations,[67,68] without symmetry constraints, using the Local Density Approximation of the correlation energy (Vosko−Wilk−Nusair)[69] and the Generalized Gradient Approximation (Perdew−Wang[25] and Becke and Perdew exchange and correlation corrections).[22,30] Relativistic effects were treated
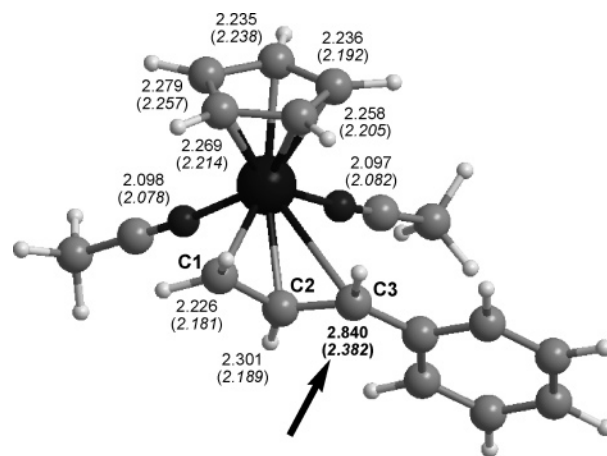

Figure 1. Optimized geometry of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2\text{-}CHCHC_6H_5)(CH_3CN)_2]^{2+}$ obtained at the B3LYP/($I_M I_L$) level, showing the calculated bond distances (Å) between the metal and all coordinating atoms, and experimental values taken from the X-ray structure of the analogous Cp^* complex (italics).

with the ZORA approximation.[70] TZ2P basis sets (triple ζ Slater-type orbitals, STO) were used to describe the valence shells of Ru (4p, 4d, 5s), C and N (2s and 2p), and H (1s), with a set of two polarization functions[71,72] added, and frozen core orbitals for Ru ([1−4]s, [2−3]p, 3d), C (1s), and N (1s).[73] The QZ4P is an all-electron basis set with quadruple ζ Slater-type orbitals, with four added polarization functions for Ru (one p and three f functions), C, N (two d and two f functions), and H (one s, two d, and two f functions).

3. Results and Discussion

During the course of our recent computational studies on the mechanism of the ruthenium catalyzed regioselective allylic alkylation reaction, several ruthenium cyclopentadienyl complexes, such as $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$ and $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHC_6H_5)(OCO_2\text{-}CH_3)]^+$, were checked as possible active species. While reasonable optimized geometries were obtained for the carbonate complex,[16] the geometry calculated for the bis-(acetonitrile) species at the B3LYP/($I_M I_L$) level (see Computational Details for basis set labels used throughout the text) led to an unexpected and very long Ru−C bond to one of the allylic carbon atoms. It is represented in Figure 1 as well as the relevant bond lengths around the metal (Ru−X) and the experimental values taken from the X-ray structure of the related Cp^* complex, $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2\text{-}CHCHC_6H_5)(CH_3CN)_2]^{2+}$.[17]

The molecule in Figure 1 represents a typical complex with pseudopiano stool geometry. The cyclopentadienyl ligand, Cp, is coordinated through its entire π-system, that is, in a η^5 mode, with the five carbon atoms bonded to the metal. The two acetonitrile ligands are coordinated end-on by the nitrogen atoms, while the allyl moiety completes the coordination sphere of the metal with its three carbon atoms binding the metal, in a formal η^3-allyl ligand.

The coordination of cyclopentadienyl and the two acetonitrile ligands is reasonably well described in the optimized geometry, with absolute deviations between the calculated and the experimental values for the Ru−X bond distances

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ranging between 0.003 and 0.055 Å, and this holds for all the computational approaches tested. However, this is not the case for the allyl coordination and especially not for the bond distance between the metal and the carbon adjacent to the phenyl ring (C3, marked with an arrow in Figure 1). The calculated Ru–C3 bond length is unacceptably overestimated by 0.458 Å, when compared with the experimental distance. In other words, the allyl coordination asymmetry is greatly enhanced in the calculated structure. This asymmetry is reflected by the difference between the Ru–C1 and Ru–C3 distances (terminal carbon atoms), which is 0.20 Å in the X-ray structure and rises to 0.61 Å in the calculated geometry. This result is difficult to understand since the method employed, B3LYP/($I_M I_L$), performed well in the optimization of analogous and isoelectronic Ru(IV) complexes, $[Ru(\eta^5-C_5H_5)(\eta^3-CH_2CHCHC_6H_5)LL']^{n+}$, such as the chloro acetonitrile molecule (L = Cl⁻, L′ = CH₃CN, n =1) with maximum (Δ) and mean (δ) absolute deviations for the distances around the metal of 0.14 and 0.05 Å, respectively.[74] Here, the comparison is also made to the experimental structure of the Cp* analogue. For the carbonate complex mentioned above (LL′ = CH₃OCO₂⁻, n = 1) the optimized geometry (Δ = 0.15 Å and δ = 0.07 Å) is also in good agreement with experimental data from the X-ray structure of the Cp* complex.[16] In addition, for these two complexes, the carbonate and the chloro acetonitrile molecules, the calculated Ru–C(allyl) distances are within 0.03–0.15 Å of the experimental values. On the other hand, the allyl coordination is also poorly described, at the B3LYP/($I_M I_L$) level, in the optimized geometry of the analogous dicationic bis(DMF) complex (DMF = dimethylformamide = Me₂-NCHO, complexed via the O-atom), although to a lesser extent than in the case of the bis(acetonitrile) molecule of Figure 1. In this case (L = L′ = DMF, n = 2) the Ru–C3 distance is overestimated by 0.390 Å, relative to that in the X-ray structure of the Cp* analogue,[17] while the coordination of the remaining ligands is well described by the calculations, with acceptable deviations (0.003–0.079 Å) for the Ru–X distances. These results suggest that the performance of B3LYP/($I_M I_L$) in the geometry optimization described is related to the charge on the cation, being much better for monocations than for dications. In the following discussion, we will focus only on the geometry optimization of the bis-(acetonitrile) complex, $[Ru(\eta^5-C_5H_5)(\eta^3-CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$, since this is the most puzzling case, and, in particular, on the problematic Ru–C3 distance.

Besides the limitations of the theory level, other reasons may be responsible for the mismatch between the calculated and the experimental Ru–C3 bond distance, e.g., solid-state packing effects and quality of the model. A close look at the X-ray structure seems to exclude the possibility that the presence of the counterions (PF₆⁻) leads to a distortion of the allyl coordination geometry. The closest contact of the anion to the allyl ligand, 3.161 Å, is observed between the allyl carbon C2 and fluorine atoms and is rather long. All of the C3–F distances are longer than 3.6 Å. The second aspect concerns the adequacy of cyclopentadienyl (Cp) as a model of pentamethylcyclopentadienyl (Cp*), and it might be asked whether the stereochemical constraints imposed by the

bulkier Cp*, or electronic effects associated with this ligand, affect the allyl coordination in a way that cannot be well reproduced by the calculations carried out with the simple model. Thus, the geometry of the real molecule, $[Ru(\eta^5-C_5-Me_5)(\eta^3-CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$, was also optimized at the same level of theory (B3LYP/($I_M I_L$)), in order to probe the quality of the model. The resulting geometry is very similar to the one obtained for the Cp model, with differences in the Ru–X bond lengths between 0.001 and 0.100 Å. In particular, the Ru–C3 distance in the Cp* complex (2.740 Å) is still 0.358 Å longer than the experimental one, although this value is slightly better than the one obtained with the Cp model (2.840 Å). This result demonstrates that the nature of the model used is not the main cause for the poor performance observed with B3LYP/($I_M I_L$).

The effect of allyl substituents on the calculated Ru–C(allyl) bonding distances was also analyzed by optimizing $Ru(\eta^5-C_5H_5)(\eta^3-CH_2CHCHR)(CH_3CN)_2]^{2+}$ complexes using same conditions (B3LYP/($I_M I_L$)) with R = H and R = Me. For R = H, the C_s molecule obtained had two equal bonds between the metal and the terminal carbon atoms (2.298 Å), reasonably close (within 0.1 Å) to the usual Ru–C(allyl) bond lengths.[74] With R = Me, the optimized Ru–C₁/₃ distances were 2.252 and 2.510 Å, revealing an asymmetric coordination of this ligand that is similar to that found when R = Ph (see above), with the longest Ru–C separation involving the substituted terminal carbon. This difference between the Ru–C1 and Ru–C3 bond lengths (0.26 Å) is, however, much less pronounced than for R = Ph (0.61 Å). This different behavior can hardly be explained solely by stereochemical factors, such as the size and shape of methyl and phenyl groups, specially taking into account that the "upright" conformation of phenyl minimizes repulsion with the closest acetonitrile ligand (see Figure 1).

The influence of the basis set on the optimized geometry of $[Ru(\eta^5-C_5H_5)(\eta^3-CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$ was tested through a series of calculations using the B3LYP functional and several basis sets. Three sets of basis (I_M, II_M, and III_M) were used to describe ruthenium, and another six (I_L, II_L, III_L, IV_L, V_L, and VI_L) for C, H, and N (see Computational Details). The Ru–C3 distances calculated with each basis set as well as the corresponding mean absolute deviation between the calculated and the experimental values of all Ru–X distances (δ) are summarized in Table 1. The basis sets selected are rather limited, but they include the typical basis set used in most computational studies recently published in all fields of chemistry. Besides, the option of using larger and better basis sets is not available for realistic medium sized systems and the computational capabilities of most users.

The results in Table 1 show a small dependence of the geometry obtained with the basis set used in the calculations. The Ru–C3 bond lengths differ at most by 0.075 Å, and the overall description of the coordination geometry of the entire complex is even more uniform, as reflected in the maximum difference of 0.018 Å for the δ values. However, a slight improvement occurs as better metal basis sets are used. Upon moving from I_M (LanL2DZ plus f-polarization) to II_M (SDD plus f-polarization), the Ru–C3 distance

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Table 1. Calculated Ru−C3 Bond Distances (Å) and Mean Absolute Deviations of All Ru−X Distances (δ, Å) between the Optimized Geometry of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$ and the Experimental One[a]

basis set	Ru−C3/Å	δ/Å
exp.[b]	2.382	
($I_M I_L$)	2.840 (0.458)	0.083
($II_M I_L$)	2.794 (0.412)	0.065
($III_M I_L$)	2.765 (0.383)	0.076
($II_M II_L$)	2.810 (0.428)	0.066
($II_M III_L$)	2.827 (0.445)	0.068
($II_M IV_L$)	2.833 (0.451)	0.071
($II_M V_L$)	2.840 (0.458)	0.070
($II_M VI_L$)	2.839 (0.457)	0.067

[a] The differences between each Ru−C3 value and the experimental one are given in parentheses (Å). [b] From the Cp* analogue.[17]

shortens 0.046 and δ becomes smaller. The use of an all-electron basis set for Ru (III_M = 3-21G*) leads to another decrease in the Ru−C3 distance (0.029 Å), though the overall description of the complex geometry is slightly worse than the one obtained with II_M (δ is 0.011 Å higher). The minor improvement obtained in the optimized Ru−C3 distance, going from II_M to III_M, is not compensated by the increase in computational cost due to the large all-electron basis set on the second row transition metal. Therefore, in the discussion below, the II_M basis set (SDD ECP with valence triple-ζ and an added f-polarization function) will be kept to describe the Ru atom, and different basis sets will be tested for the ligands. As the size of the basis set for C, H, and N increases, the quality of the calculated geometry decreases. The addition of diffuse functions to the basis sets of the three allylic carbons going from ($II_M I_L$) to ($II_M II_L$) leads to Ru−C3 distances larger by 0.016 Å, while valence triple-ζ basis sets (III_L, IV_L, and V_L) lengthen this distance another 0.017−0.030 Å. The Ru−C3 distance obtained with the quadruple-ζ basis set (VI_L) is pratically equal to the one produced by V_L (within 0.001 Å). This effect is diluted in the overall description of the molecule, and the δ values are less sensitive to the basis set used for the ligands, as shown by a maximum difference of 0.006 Å.

The $II_M I_L$ basis set (4-31G* for C, H, and N and the basis set described above for Ru) reveals the best compromise between accuracy and computational cost and was used for the following analysis of the effect of changing the functional and method within a wide range. The results are given in Table 2.

The results summarized in Table 2 clearly indicate the poor capability of all DFT functionals to describe the coordination geometry of the allyl ligand in the bis(acetonitrile) complex, overestimating the Ru−C3 bond length by amounts from 0.23 to 0.50 Å, though some differences worth noticing may be found. PW91 performs much better as a correlation functional than LYP or P86, both when pure DFT functionals (see the results obtained with BLYP, and BPW91 or PW91) and hybrid functionals are used (demonstrated by the results of B3LYP, B3PW91, and mPW1PW91). In fact, Adamo and Barone's hybrid functional resulting from modified Perdew−Wang exchange (mPW1PW91) yields one of the best results in Table 2, only surpassed by the hybrid functional of

Table 2. Calculated Ru−C3 Bond Distances (Å) and Mean Absolute Deviations for All Ru−X Distances (δ, Å) between the Experimental Structure[a] and the Optimized Geometry of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHC_6H_5)(CH_3CN)_2]^{2+}$, Obtained from HF, MP2, and Several DFT Functionals, with the ($II_M I_L$) Basis Set[b]

method	Ru−C3/Å	δ/Å
B3LYP	2.794 (0.412)	0.065
B3PW91	2.688 (0.306)	0.047
mPW1PW91	2.640 (0.258)	0.043
PBE1PBE	2.615 (0.233)	0.042
BP86	2.738 (0.356)	0.058
BLYP	2.884 (0.502)	0.088
BPW91	2.759 (0.377)	0.058
PW91	2.684 (0.302)	0.050
PBE	2.683 (0.301)	0.048
HF	2.978 (0.596)	0.123
MP2	2.314 (−0.068)	0.043

[a] From the Cp* analogue.[17] [b] The differences between each Ru−C3 value and the experimental one are given in parentheses (Å).

Perdew, Burke, and Ernzerhof (PBE1PBE). This observation refers to the calculated Ru−C3 distance as well as to the overall description of the geometry of the molecule, accounted by parameter δ. Another interesting point is the similarity in the performance of the two nonempirical functionals, PW91 and PBE,[15] with practically identical results for the Ru−C3 distance and similar δ values.

It can be added that the change in performance of the functional with the complexity of the basis set, observed for B3LYP (see discussion on the results of Table 1, above), applies to other functionals and basis sets, being thus quite general. For example, with the hybrid functional, mPW1PW91, the Ru−C3 bond length increases 0.008 Å going from the I_L to the II_L basis set, with the addition of diffuse functions for the three allylic carbon atoms.

Similar calculations (geometry optimization of the Ru complex) were carried out with the ADF program, testing two functionals (PW91 and BP98) with large Slater basis sets associated with that program. The results obtained with the basis set TZ2P showed a very long Ru−C3 bond (2.656 Å with PW91, 2.676 Å with BP86). Changing the basis set size from TZ2P to the larger QZ4P for C, H, and N and keeping TZ2P for Ru lead to an increase of 0.01 or 0.04 Å in the Ru−C3 distance with PW91 and BP86, respectively. On the other hand, when the metal basis set is also changed from QZ2P to QZ4P (QZ4P for all atoms), there is a small improvement on the calculated Ru−C3 distance that shortens 0.001 Å with PW91 (0.04 Å with BP86) relative to the previous values. They are still longer than the TZ2P bond lengths. Importantly, very long Ru−C3 distances (2.66−2.72 Å) were obtained in all ADF optimizations, in agreement with the other DFT calculations discussed above.

With respect to the wavefunction based methods, HF performs miserably, but the electronic energy corrected MP2 yields the best result shown in Table 2. More relevantly, this method provides the only result acceptable for a semiquantitative study of the case study complex, though MP2 underestimates the Ru−C3 bond length by 0.068 Å. The coordination of the η^3-allyl ligand is well reproduced by the MP2/($II_M I_L$) calculation with deviations of 0.002 and

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−0.049 Å for the other two carbon atoms, C1 and C2, respectively. However, as a value of δ (0.043 Å) equal to the one obtained with mPW1PW91 hints, the description of the coordination geometry of the nitriles and of the cyclopentadienyl is poorer with MP2 than with that hybrid functional. The two Ru−N distances are underestimated by 0.05 Å with MP2 and only by 0.02 Å and 0.03 Å with mPW1PW91. The maximum deviation on the Ru−C(Cp) bonds with the hybrid functional corresponds to an underestimation of 0.02 Å, while for MP2 it is 0.10 Å. In fact, MP2 is at its worst when describing the Ru−C(Cp) bonds, and the 0.10 Å underestimation corresponds to the maximum deviation between the optimized and the experimental Ru−X distances (Δ). For all the DFT functionals tested the worse optimized bond length (Δ) is the Ru−C3 distance.

Interestingly, for MP2, basis set convergence, in size, seems to be practically achieved with ($II_M I_L$). In fact, an optimization at the MP2/($II_M III_L$) level yielded a geometry similar to the one obtained at the MP2/($II_M I_L$) level, with the calculated Ru−C3 distance (2.301 Å) only 0.013 Å shorter than the one obtained with the smaller basis set (see Table 2). Unfortunately, our computational limitations prevent us from testing higher level wavefunction based methods or larger basis sets as well as preclude any mechanistic investigation even at the MP2/($II_M I_L$) level. In fact, the MP2 geometry optimization of [Ru(η^5-C_5H_5)(η^3-$CH_2CHCHC_6H_5$)(CH_3CN)$_2$]$^{2+}$ was about 30 times longer than the average of any of the DFT calculations.

The nature of the potential energy surface (PES) of [Ru(η^5-C_5H_5)(η^3-$CH_2CHCHC_6H_5$)(CH_3CN)$_2$]$^{2+}$ on the region corresponding to the elongation of the Ru−C3 bond was explored, in order to try to understand the results discussed above. A B3LYP/($II_M I_L$) calculation with the Ru−C3 distance fixed at the experimental value (2.38 Å) yielded a molecule only 3 kcal mol^{-1} less stable than the one obtained with the unconstrained calculation ($d_{Ru−C3}$ = 2.79 Å). This reflects a reasonably flat PES with respect to Ru−C3 stretching, indicating a weak interaction with probably a strong component of dispersion forces. It is well-known that DFT occasionally fails in the description of that sort of interactions,[9,75,76] and, in addition, a recent benchmark study[77] demonstrated that MP2 performs better than DFT in the description of weak interactions.

4. Summary

We report the failure of five pure and four hybrid DFT functionals, including some of the most commonly used by the chemistry community, in the description of the geometry of a Ru(IV) allyl complex, [Ru(η^5-C_5H_5)(η^3-$CH_2CHCHC_6H_5$)(CH_3CN)$_2$]$^{2+}$, especially with respect to the Ru−C bond distance for the substituted carbon atom of η^3-allyl ligand. MP2 was found to perform much better and yield a reasonable result, even with a poor basis set, probably due to a better account of a weak Ru−C interaction.

Supporting Information Available: Tables of atomic coordinates for all the optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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